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Nickel and iridium pincer complexes with saturated frameworks - synthesis and reactivity

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Nickel and iridium pincer complexes with saturated frameworks – synthesis and reactivity

Abstract

As the tridentate chelate complexes referred to as pincer complexes have expanded their scope as homogeneous catalysts, there is an increased interest in electronic and steric fine-tuning of such complexes. One accessible variable in this aspect is the hybridisation of any coordinated carbon atoms. This thesis describes the synthesis of bis(phosphine) and bis(phosphinite) PCP pincer complexes with nickel and iridium. The studied pincer ligands have all-aliphatic backbones based on a linear alkyl or a cyclohexyl moiety. The presented families of new pincer complexes have been investigated with aspect to their coordination chemistry and stability. The reactivity of POCOP-supported nickel complexes towards carbon dioxide and carbon monoxide has been studied. Further, iridium pincer complexes with saturated frameworks have been evaluated as catalysts for alkane dehydrogenation reactions. The work also include indications of an unusual C(sp3)–C(sp3) reductive elimination at an iridium(III) centre, resulting in a net methyl migration from the metal to the ligand backbone.

Key words: PCP complexes, aliphatic pincer ligands, coordination, cyclometallation, iridium, nickel, organometallic synthesis, CO_2 activation, catalysis

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A doctoral thesis at a university in Sweden is produced as a monograph or as a collection of papers. In the latter case, the introductory part constitutes the formal thesis, which summarizes the accompanying papers. These have either already been published or are manuscripts at various stages (*accepted*, *submitted* or *in manuscript)*.

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“Dans ses écrits, un sage Italien
Dit que le mieux est l'ennemi du bien”

-Voltaire

Populärvetenskaplig sammanfattning

Enkla kolväten och koldioxid är kemiskt stabila föreningar med mycket låg reaktivitet. På grund av en god råvarutillgång finns ett stort intresse för aktivering och omvandling av dessa föreningar till mer förädlade eller användbara produkter. Reaktioner som bryter starka intramolekylära bindningar är vanligtvis svåra att genomföra på grund av en alltför hög energibarriär, men kan möjliggöras med katalys. Tillverkning av metallorganiska komplex och förståelse av hur dessa kan fungera som katalysatorer är således av stor relevans. En typ av sådana komplex är så kallade pincettkomplex som utgörs av en organisk molekyl, en *ligand*, som binder med tre atomer till ett metallcentrum på ett pincett- eller kniptångsliknande sätt. Denna tridentata koordination gör komplexet stabilt, ofta även vid de höga temperaturer som vanligtvis krävs vid industriella katalytiska processer.

Pincettkomplexen är kända i den vetenskapliga litteraturen sedan 1970-talet och utforskandet av deras reaktivitet och katalytiska förmåga är ständigt framåtskridande. Merparten av de tidigare studerade komplexen har ligander som är strukturellt uppbyggda av aromatiska kolväten. Valet av ligandtyp har dock visat sig ha en stor inverkan på den centrala metallatomens reaktivitet, eftersom det påverkar både hur elektronrikt metallcentrat blir och genom ligandens storlek och ordning i rymden även dess tillgänglighet.

Det arbete som presenteras i denna avhandling fokuserar på framställning av pincettkomplex med övergångsmetallerna nickel och iridium. Pincettliganderna som använts har en mättad kolvätestruktur, av antingen linjär eller cyklisk typ. Komplexen har undersökts med avseende på reaktivitet och katalytisk aktivitet.

List of papers

This thesis summarises and supplements the following papers, referred to by their Roman numerals I-VI.

I *Aliphatic pincer-type POCOP ligands and their complexation behaviour with iridium: Crystal structure of an iridium(III) phosphinite complex*

Jonasson, K. J.; Ahlsten, N.; Wendt, O. F. *Inorg Chim Acta* **2011**, *379*, 76.

II. *Synthesis and characterisation of new $PC_{sp3}P$-supported nickel complexes*

Jonasson, K. J.; Wendt, O. F. *J Organomet Chem* **2014**, *759*, 15.

III. *Synthesis and characterisation of a new family of $POC_{sp3}OP$ pincer complexes with nickel. Reactivity towards CO_2 and phenyl acetylene*

Jonasson, K. J.; Wendt, O. F. *Submitted for publication.*

IV. *Synthesis and Characterization of $POC_{sp3}OP$ Supported Ni(II) Hydroxo, Hydroxycarbonyl and Carbonate Complexes*

Jonasson, K. J.; Wendt, O. F. *Manuscript.*

V. *Catalytic dehydrogenation of cyclooctane and triethylamine by aliphatic iridium pincer complexes*

Polukeev, A. V.; Gritcenko, R.; Jonasson, K. J.; Wendt, O. F. *Submitted for publication.*

VI. *PC(sp^3)P Pincer Carbonyl Complexes with Iridium. Oxidative addition of Methyl Iodide and Subsequent Formation of a C(sp^3)–C(sp^3) Bond*

Jonasson, K. J.; Wendt, O. F. *Manuscript.*

VII. *Bis{μ-cis-1,3-bis[(di-tert-butylphosphanyl)oxy]cyclohexane-κ^2P:P'}bis[carbonylnickel(0)] including an unknown solvent molecule*

Jonasson, K. J.; Wendt, O. F. *Acta Cryst*. **2014**. E70, m176.

Papers not included in this thesis:

Kinetic and mechanistic investigation of the substitution reactions of four and five co-ordinated rhodium stibine complexes with a bulky phosphite

Hennion, C.; Jonasson, K. J.; Wendt, O. F.; Roodt, A. *Dalton Trans.* **2013**, *42*, 14134.

Pincer Complexes with Saturated Frameworks: Synthesis and Applications

Jonasson, K. J.; Wendt, O. F., Chapter 8 in *Pincer and Pincer-Type Complexes* by Szabó and Wendt (Eds.), Wiley-VCH, **2014**, in the press.

Contribution to papers I-VII:

I. Performed most of the experimental work, except the initial isolation and characterisation of complex **2** and the crystallographic work. Wrote most of the article.

II. Did all the experimental work, except some of the attempted cross-coupling experiments. Wrote most of the article.

III. Did all the experimental parts except the cyclic voltammetry measurements and some of the crystallographic work. Wrote most of the article.

IV. Performed the majority of the experimental work. Wrote the manuscript.

V. Did preparatory experimental work and assisted in writing the paper.

VI. Did all the experimental parts except some of the crystallographic work. Wrote most of the article.

VII. Performed the synthesis of the title compound. Wrote most of the article.

Abbreviations

Ac	Acetyl
Ad	Adamantyl
B.E.	β-elimination
COD	1,5-cyclooctadiene
COA	Cyclooctane
COE	Cyclooctene
DMA	Dimethylacetamide
DMAP	4-dimethylaminopyridine
DMF	Dimethylformamide
Et	Ethyl
eq	equivalent
h	hour(s)
HBcat	Catecholborane
^{i}Pr	*iso*-propyl
IR	Infra red
Me	Methyl
NHC	N-Heterocyclic carbene
NMR	Nuclear magnetic resonance
O.A.	Oxidative addition
O-TMEDA	Bis[2-(N,N-dimethylamino)ethyl] ether
Ph	Phenyl
R.E.	Reductive elimination
RT	Room temperature
RWGS	Reverse water-gas shift

^{t}Bu	*tert*-butyl
Tf	Trifluoromethanesulfonyl
TBA	2,2-dimethylbutane
TBE	3,3-dimethyl-1-butene
TFA	Trifluoroacetate
THF	Tetrahydrofuran
T.M.	Transmetallation
TMEDA	Tetramethylethylenediamine
TMS	Tetramethylsilane
TON	Turn over number
WGS	Water-gas shift
XRD	X-ray diffraction

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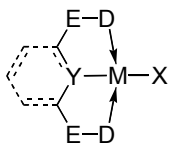
1. Pincer complexes with saturated frameworks

1.1 Introduction

Since the pioneering work by Shaw and co-workers in the late 70s,[1] the family of tridentate chelate complexes with transition metals currently known as pincer complexes, has grown tremendously in size and variation.[2] The common way to classify the various pincer ligands is based on the three atoms coordinated by the metal, here abbreviated DYD (Figure 1.1). D is a class of usually neutral two-electron donor atoms, with a spacer E, together referred to as the pincer arms. Atom Y is commonly carbon, but could also be silicon or any two-electron donor. These parameters can be tailored to control the reactivity of the pincer complex, by controlling the electronic properties as well as the steric environment around the metal centre.[3-5]



Y = C, N, O, Si
D = O, S, N, P or As
E = CH_2, O
M = transition or main group metals

Figure 1.1. Schematic representation of pincer complexes.

In their initial publications Shaw and co-workers introduced ligands of PCP type with both aromatic and aliphatic backbones (Figure 1.2),[1,6] but the former has almost completely dominated the literature since. This reflects the higher coordination stability of the planar and more rigid aromatic pincer backbone, along with a generally higher activation energy of the C(sp^3)–H bond relative the C(sp^2)–H bond that gives an overall more straightforward metallation process for the latter. The aromatic ligands are also usually relatively easy to synthesise from readily available starting materials, and due to the communication between the metal-centered *d*π orbitals and the π-system of the aromatic backbone, variation of the substituents in *para*-position allow for fine electronic tuning of the $PC_{Ar}P$ complexes.[7-10]

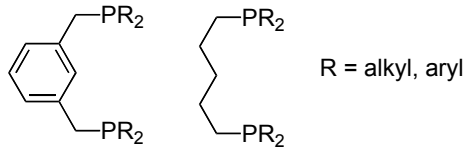


Figure 1.2. Shaw's original pincer ligands.

After the establishment of pincer complexes as potent catalysts for several chemical transformations,[11] the interest in steric and electronic tuning has increased. In this aspect the hybridisation of the coordinated central carbon is a highly relevant variable, since a more strongly σ-donating sp^3-hybridised PCP carbon will have a greater *trans*-influence on the ligand in the forth coordination site, than will an sp^2-hybridised $PC_{Ar}P$ carbon.[12] Thus, over the past decades a slowly growing collection of pincer ligands with saturated backbones have been reported, *cf.* Figure 1.3. Along with the straight alkyl chain featured already in Shaw's work, examples of cyclohexane-,[13-16] arylmethane-,[17] adamantane-,[18] dibenzobarrelene-,[19] cycloheptatriene-[20] and diarylmethane-based[21-22] scaffolds are known from the literature.

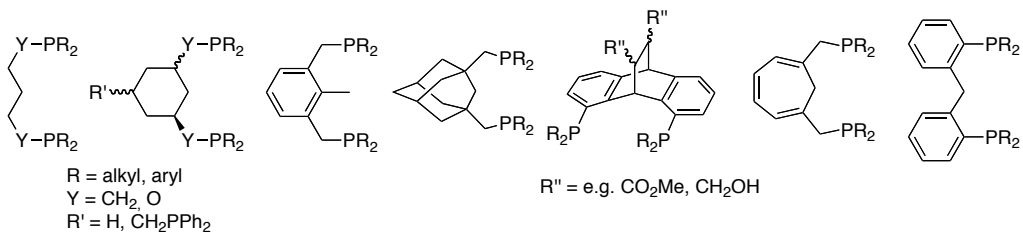
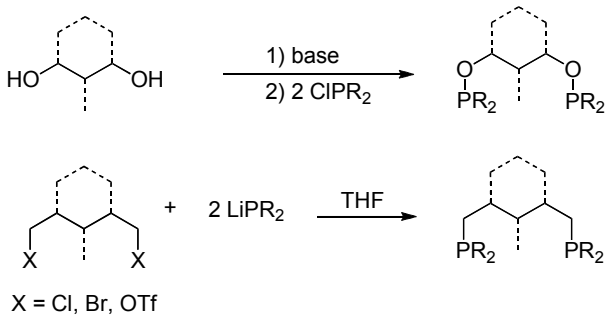


Figure 1.3. Examples of pincer ligands with an sp^3-hybridised central carbon atom.

1.2 Synthesis of the ligands

Generally, the phosphinite type of pincer ligands with saturated frameworks can be obtained by reacting a suitable diol with the chlorophosphine of choice in the presence of base (Scheme 1.1). A number of diols are commercially available and this is a straightforward reaction that often proceeds in high yield.[23-25] The synthesis of trialkylphoshine pincer ligands displays a bigger complexity and variety of reagents, but the highest yields are usually reported for the substitution reaction between an alkyl dihalide and the corresponding lithium phosphide.[13, 26-27]



Scheme 1.1. General synthesis of aliphatic POCOP and PCP ligands.

1.3 Complexation and coordination

The PCP pincer complex features an η^3-mer coordinated ligand with the P atoms in a *trans* arrangement, forming two fused five-membered chelate rings. The complexation of the ligand thus involves a cyclometallation, upon which a C–H bond is activated. This step is generally considered to be preceded by a simple *trans*-coordination of the phosphine arms, bringing the metal centre in the direct proximity of the C–H bond. Thereby the entropy of activation is reduced and the cyclometallation is facilitated. As already mentioned, activation of an sp^2-hybridised C_{Ar}–H bond is favoured relative its sp^3-hybridised counterpart, due to the higher *s*-character in the transition state of a concerted mechanism.[28-29] Further, the steric influences from the substituents on the phosphorus atoms play an important part in the cyclometallation; an increased tendency to metallate has been observed with more bulky substituents in the order Me < Ph < ^{t}Bu, suggesting a higher impact from steric than from electronic effects.[30] However, this is not established as a general trend, as certain cases demonstrate how replacing electron-releasing *tert*-butyl substituents with weakly electron withdrawing phenyl substituents on a $PC_{Ar}P$ ligand, allow for milder reaction conditions upon cyclometallation.[31]

1.4 The scope of this thesis

The aim of the work presented in this thesis was to develop new PCP complexes with saturated frameworks, utilising the late transition metals nickel and iridium. Further the reactivity of these complexes towards unreactive bonds and small molecules such as CO and CO_2 was studied, to evaluate their potential as catalysts for different homogeneous transformations.

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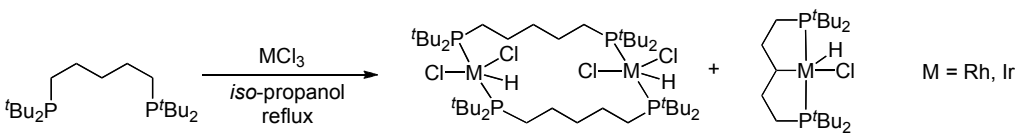
2. Complexation and coordination flexibility of aliphatic PCP complexes (paper I-III)

2.1 Acyclic PCP pincer ligands

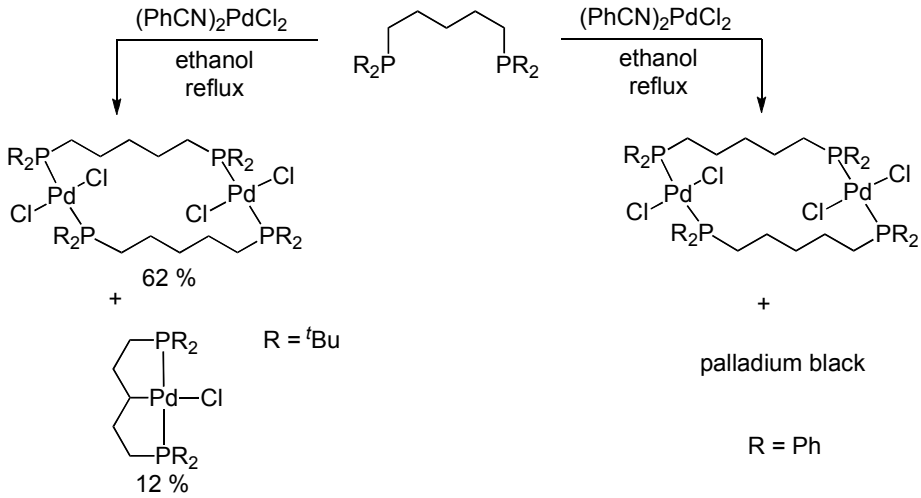
2.1.1. Cyclometallation vs. simple coordination

Already in the early work by Shaw the propensity of simple long-chain diphosphinoalkanes to form non-cyclometallated macrocyclic dimers was established. Complexation with both iridium[1] and rhodium[2] was reported to give this type of low-soluble side product (Scheme 2.1), however in the case of rhodium the dimeric species was successfully converted to the PCP coordinated complex upon treatment with 2-methylpyridine.



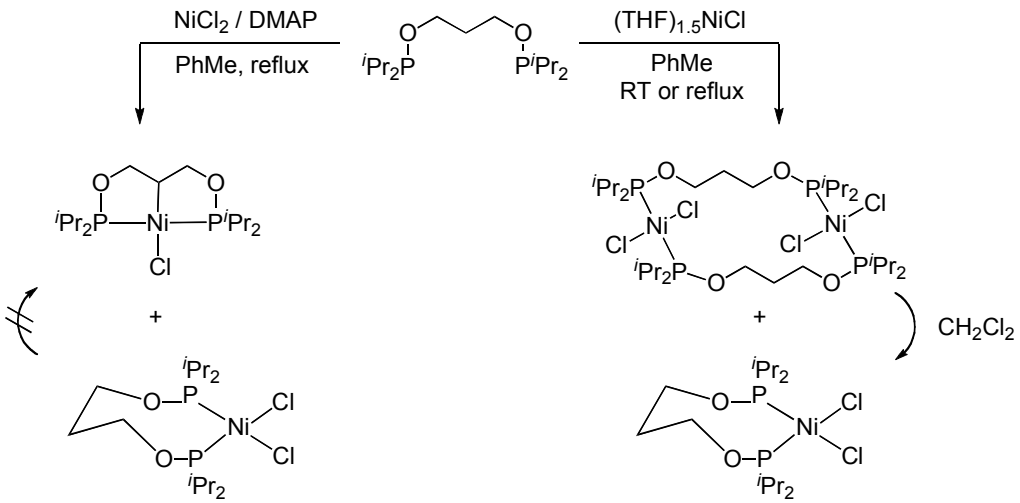
Scheme 2.1. Shaw's complexation of an acyclic PCP ligand with rhodium and iridium, achieving cyclometallation and formation of non-metallated dimers.

In the same fashion, Shaw obtained 16-atom cyclic dimers as the major species upon attempted cyclometallation of $R_2P(CH_2)_5PR_2$ with palladium (Scheme 2.2).[3] Similar results were obtained with platinum, although low solubility prohibited full characterisation. However, refluxing the dimeric platinum compound in trifluoroacetic acid, afforded a C_{sp3}–H activated PCP platinum TFA complex. It was later found by Trogler and co-workers that Shaw's 16-atom cyclic Pd dimer could be directly converted to the cyclometallated PCP complex upon heating to 260 °C.[4] The group of Zargarian has reported on the conversion of a similar nickel dimer to a $PC_{sp3}PNiBr$ complex upon heating to 110 °C in the presence of DMAP.[5]



Scheme 2.2. Shaw's synthesis of 16-atom cyclic dimers along with (attempted) cyclometallation to a $PC_{sp3}P$ palladium complex.

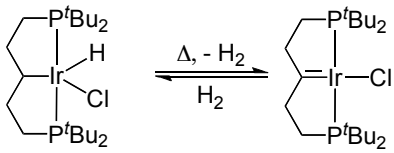
Zargarian and co-workers also reported a thorough study of the complexation behaviour of a corresponding bis(phosphinite) $POC_{sp3}OP$ ligand with nickel (Scheme 2.3). It was found that under all tested conditions a complex with a *cis*-dicoordinated 8-membered ring structure was formed, which could not be transformed into any other compound. In presence of DMAP, the target POCOP pincer complex was obtained in 33% yield.[6] In absence of DMAP a 16-membered cyclic dimer was formed and found to interconvert with the 8-membered monomer in solution. Subjecting this mixture to base at high temperatures, however, did not afford activation of the central C–H bond, suggesting that this process is thermodynamically allowed but its kinetics depend on the type of precursors used and intermediates formed under the reaction conditions.[7]



Scheme 2.3. Zargarian's study on the reactivity of aliphatic POCOP pincer ligands with nickel.

2.1.2. α- and β-hydrogen elimination of the ligand framework

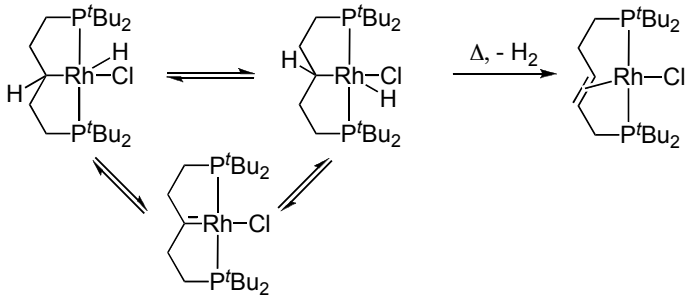
One weak point of the aliphatic pincer complexes is the presence of labile α- and β-hydrogen atoms in the backbone, which significantly reduce their coordination stability. Indeed the most powerful catalytic transformations utilising $PC_{sp3}P$ complexes as catalysts concerns complexes with bi- or tricyclic $PC_{sp3}P$ pincer scaffolds such as dibenzobarrelene[8] and adamantane[9] derivatives, lacking α- and/or β-hydrogens to avoid such plausible decomposition routes.



Scheme 2.4. Shaw's reversible α-elimination of an acyclic PCP iridium(III) complex.

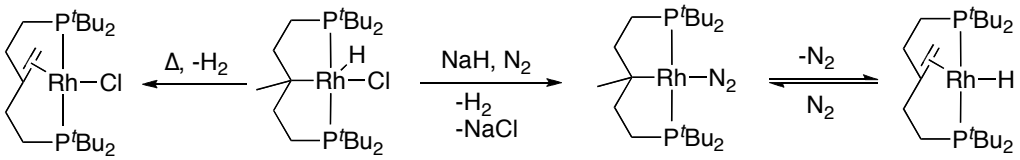
The studies of Shaw report on the release of H_2 upon thermolysis of a $PC_{sp3}P$ iridium(III) chloro hydride complex, forming the carbene complex through a presumed α-H elimination (Scheme 2.4).[1] The analogous rhodium complex instead undergoes β-elimination under the same conditions, forming an olefin chelate complex (Scheme 2.5).[10] Shaw and co-workers also suggest a reversible interconversion of the rhodium(III) chloro hydride complex via an α-elimination process, as based on an observed fluxionality on the NMR time scale.[2] Later, Gusev and Ozerov reported on a similar complexation behaviour for the analogous osmium and ruthenium complexes

in presence of base, affording the carbene complex in case of osmium and with ruthenium a mixture of the carbene and the olefin chelate complex.[11]



Scheme 2.5. Shaw's α- and β-elimination of an acyclic PCP rhodium(III) complex.

The group of Milstein found that introducing a methyl substituent on the coordinated carbon of the Rh(III) chloro hydride complex, resulted in selective β-elimination at elevated temperatues (Scheme 2.6). NaH reduction of the same complex under a N_2 atmosphere afforded a terminal nitrogen Rh(I) complex, which also induced a reversible β-elimination forming the hydride.[12]

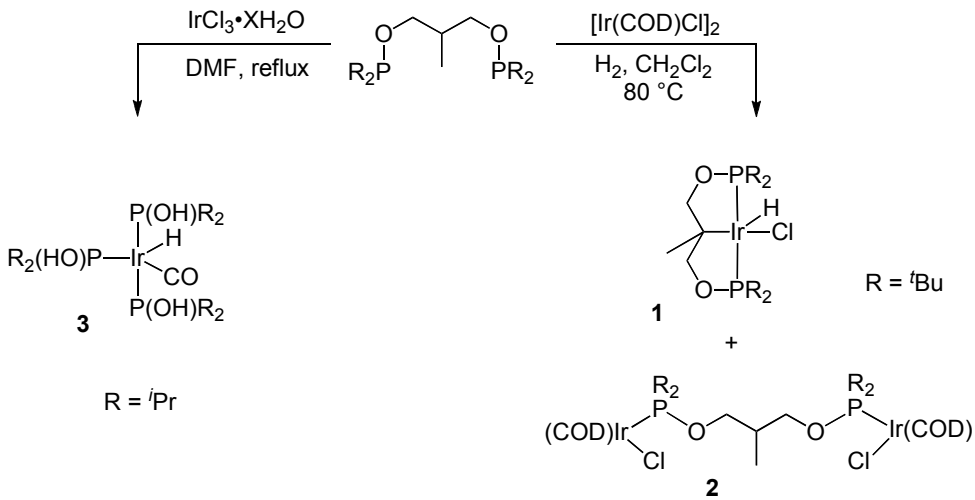


Scheme 2.6. Selective β-elimination of methyl substituted acyclic PCP rhodium complexes by Milstein.

2.1.3 Side products and decomposition in acyclic $POC_{sp3}OP$ pincer systems (Paper I)

As compared to the bis(phosphine) $PC_{sp3}P$ complexes, examples of bis(phosphinite) $POC_{sp3}OP$ complexes based on aliphatic backbones are less common and mainly involve first row transition metals.[13] To the best of our knowledge, the here presented complex **1** (Scheme 2.7) is the first reported $POC_{sp3}OP$ supported pincer complex with iridium.[14] The modest yield (24%) is partly ascribed to the formation of the binuclear linear complex **2**. The structure underlines both the lower propensity of acyclic pincer ligands to metallate, and also the difficulties in achieving complete substitution of the COD ligand, which is previously reported both at high temperatures[15-16] and in presence of H_2.[17] Altering the substituents on phosphorus from *tert*-butyl to *iso*-propyl groups, did not afford the *iso*-propyl analogue of **1** under the same reaction conditions, but instead a mixture of several uncharacterised ^{31}P-containing species, demonstrating

how a decreased sterical hindrance might open up for decompositions of the ligand backbone. This was further demonstrated by subjecting the *iso*-propyl substituted ligand to $IrCl_3$ in refluxing DMF, conditions previously used by Azerraf and Gelman,[8a,18] utilising DMF as a carbonyl source.[19] This protocol renders full decomposition of the ligand backbone and formation of $^{i}Pr_2P(OH)$ units coordinated to the metal in complex **3**. The route of this decomposition supposedly involves a breakage of the ligand C–O bond as a result of a phosphinite hydrolysis by residual water, an established reaction for metal coordinated phosphinites.[20] However, the ratio 1:3 between iridium and phosphorus, suggests that the decomposition can be induced on a mono-coordinated ligand or fragments of a ligand. The presence of a hydride ligand on iridium supports that a C–H activation of the pincer ligand has taken place, possibly followed by a β-elimination.



Scheme 2.7. Complexation behaviour of acyclic $POC_{sp3}OP$ ligands with iridium.

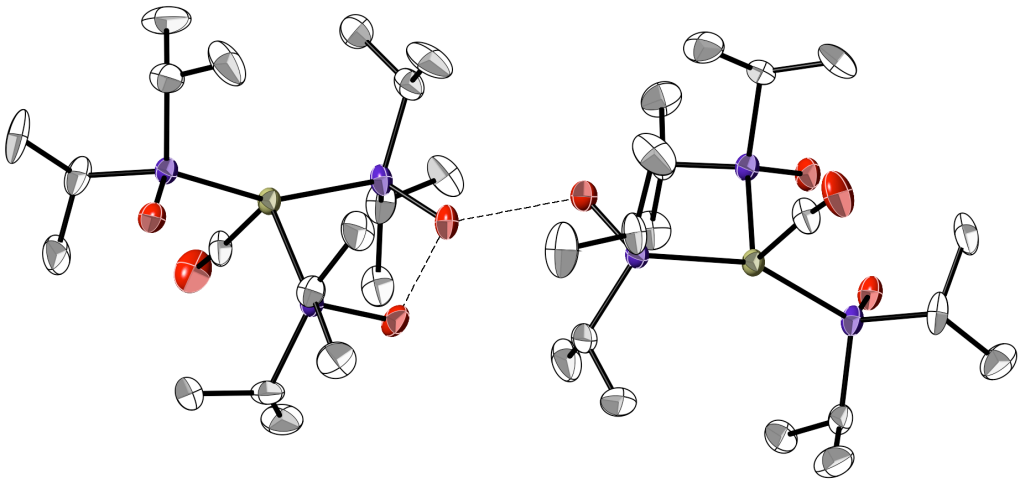
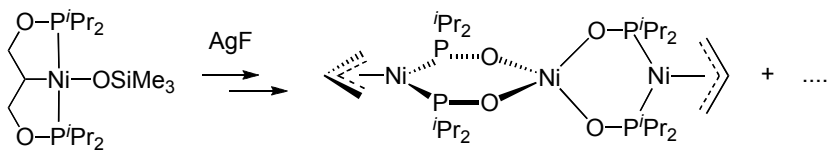
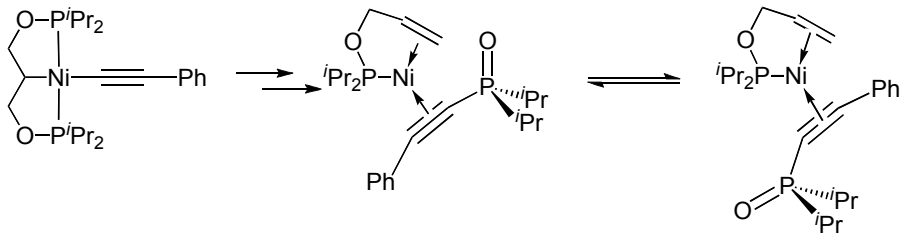


Figure 2.1. Molecular structure of complex **3**, confirming the assigned P(III)–OH moieties with the presence of inter- and intra-molecular hydrogen bonds.

Recent studies by the group of Zargarian also demonstrate the relatively general low stability of acyclic bis(phoshinite) pincer ligands, by identifying two new decomposition products from the attempted preparation of fluoro and phenylacetylide derivatives of a nickel complex (Scheme 2.8 and Scheme 2.9). In both cases the seemingly facile C–O bond rupture is the clear weak-point of the acyclic $POC_{sp3}OP$ ligands.[21]



Scheme 2.8. Zargarian's isolated decomposition products from attempted formation of a $POC_{sp3}OP$ nickel fluoride complex.

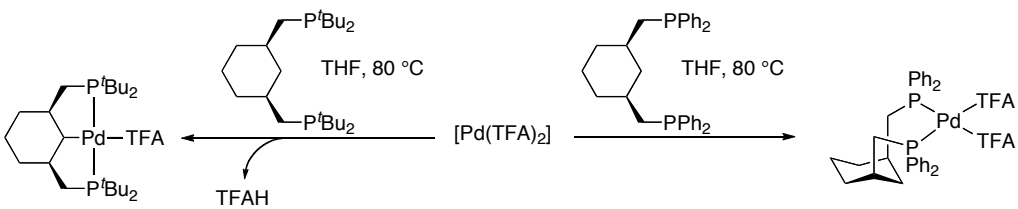


Scheme 2.9. Zargarian's isolated decomposition products from a $POC_{sp3}OP$ nickel phenylacetylide complex.

2.2 Cyclohexyl-based PCP ligands (Paper II and III)

2.2.1 Cyclometallation vs. simple coordination

In the early 00's Sjövall developed a group of *cis*-1,3-bis(substituted) cyclohexyl-based ligands to impose a higher rigidity of the pincer backbone whilst maintaining the electronic properties of an all-aliphatic structure. Initial cyclometallation attempts with a cyclohexyl-based $PC_{sp3}P$ ligand showed the same trend as reported by Shaw and co-workers for acyclic $PC_{sp3}P$ ligands concerning the influence from the phosphorus substituents,[22] giving cyclometallation only in the *tert*-butyl substituted case[23] and an 8-membered cyclic *cis*-coordinated complex with phenyl substituents (Scheme 2.10).[24] However, complexation with this type of ligand is generally straightforward and has been subsequently reported with rhodium,[25] ruthenium,[26] platinum[27] and iridium.[28]



Scheme 2.10. Coordination behaviour of Sjövall's cyclohexyl based bis(phosphine) ligands.

The chelate systems containing *cis*-substituted cyclohexane ligands adopt a chair conformation with a bisecting perpendicular pseudo-mirror plane.[22] As can be seen in Figure 2.2, the atoms P1, P2, C2, C7 and C8 are almost coplanar with the square plane around the metal, with atoms C1 and C3 both pointing away in the same direction. As a consequence the magnetic environment will be different on the two sides of the

square plane, resulting in dual resonances in the ^{1}H- and ^{13}C-NMR spectra for the *tert*-butyl substituents on phosphorus.

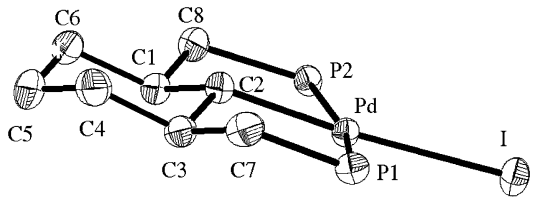
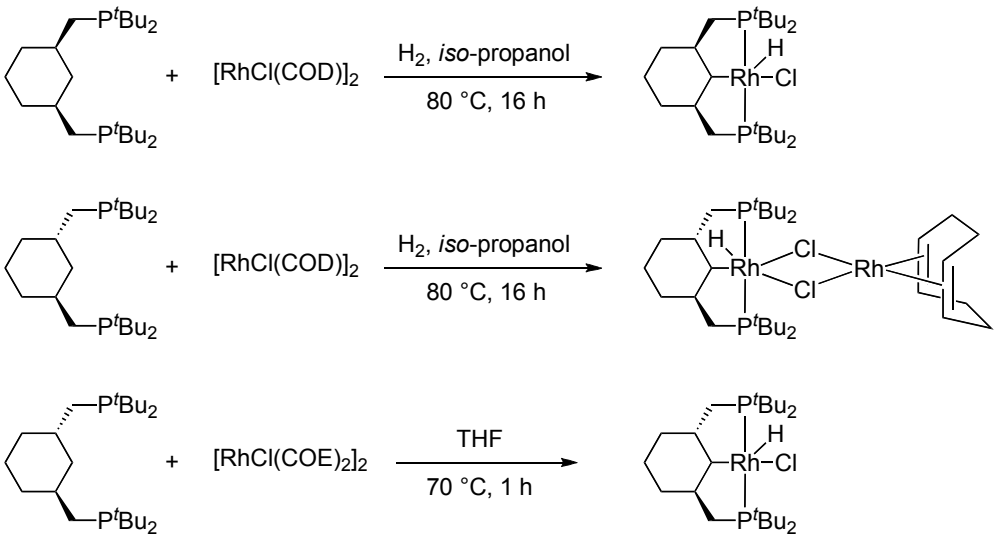


Figure 2.2. Conformation of a coordination complex with a *cis*-1,3-bis[(phosphinito)methyl]cyclohexane ligand. Reproduced from *ref*. 21 with permission from the Royal Society of Chemistry.

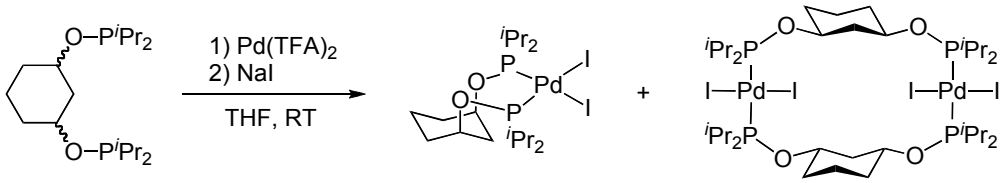
Gusev and co-workers have investigated the coordination behaviour of *cis*- and *trans*- substituted cyclohexyl-based bis(phosphine) ligands, achieving cyclometallation with Rh and Pd with both types of ligands. Although DFT calculations predicted a more strained system in the *trans* case (by 9-11 kcal/mol), structural characterisation confirmed almost identical, near ideal chair conformations adopted by the cyclohexyl ring in both the *cis*- and *trans*-complexes (Scheme 2.11).[17]



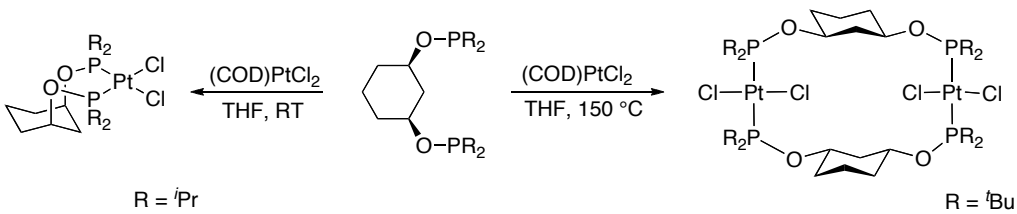
Scheme 2.11. Gusev's study on *cis* and *trans* isomers of a cyclohexyl-based PCP ligand with rhodium. Both isomers undergo cyclometallation with palladium as well.

As opposed to the aromatic systems, aliphatic phosphinites have consistently been much more reluctant to cyclometallate than the corresponding phosphines. Thus the cyclohexyl-based (bis)phosphinites has been found to resist all attempts of cyclometallation with palladium[29] and platinum[27] precursors, although the

corresponding bis(phosphine) ligands readily cyclometallate with both metals. The complexations exclusively generate 16-ring cyclic dimers and/or dicoordinated 8-membered rings (Scheme 2.12 and 2.13), that are resistant towards extensive heating and addition of base or AgOTf.

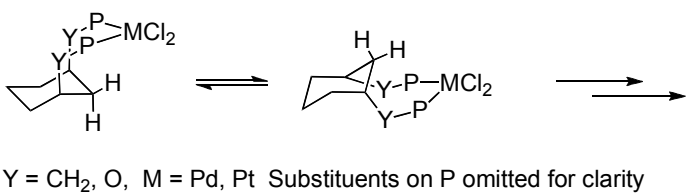


Scheme 2.12. Sjövall's cyclometallation attempts of a cyclohexyl-based $POC_{sp3}OP$ ligand with palladium.



Scheme 2.13. Olsson and Wendt's cyclometallation attempts of a cyclohexyl-based $POC_{sp3}OP$ ligand with platinum.

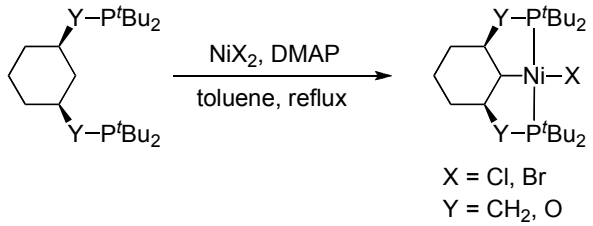
The 8-membered rings always display a diaxial conformation and previous work in our group has provided the possible explanation that the inability of the phosphinite ligands to cyclometallate is due to a kinetic barrier, possibly involving an axial–equatorial conformational change necessary for the C–H activation process. The shorter bond distances in the phosphinite can prevent a ring flip of the type shown in Scheme 2.14.[27]



Scheme 2.14. A ring flip from diaxial to diequatorial conformation, suggested to precede cyclometallation.

The work presented in this thesis involves the cyclometallation of *cis*-1,3-bis-(di-tert-butylphosphinito)cyclohexane with nickel, i.e. the first successful C_{sp3}–H bond activation and pincer complexation with this type of ligand (Scheme 2.15). The

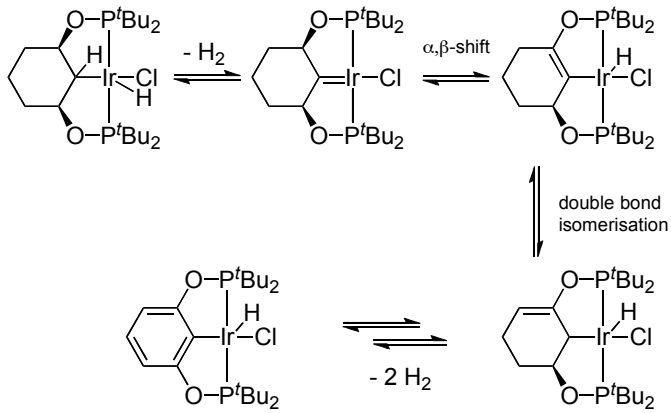
analogous bis(phosphine) complexes were obtained under the same reaction conditions, and the structural properties and reactivity of these compounds will be discussed in forthcoming chapters.



Scheme 2.15. Synthesis of new $PC_{sp3}P$ and $POC_{sp3}OP$ complexes with nickel.

2.2.2 Aromatisation

The cyclohexyl-based pincer complexes have proved to be more stable towards α- and β-hydrogen elimination reaction of the ligand backbone as compared to their acyclic counterparts. However, attempted cyclometallation of the *cis*-1,3-bis-(di-*tert*-butylphosphinito)cyclohexane ligand with iridium resulted in an acceptorless dehydrogenation and aromatisation of the cyclohexyl scaffold.[28] This unusual transformation has been suggested to proceed via consecutive α-eliminations and α,β-hydrogen shift reactions (Scheme 2.16).[30] Gusev and co-workers observed H-elimination from the corresponding bis(phosphine) complex on ruthenium, obtaining a mixture of carbenes and olefin chelate complexes,[26] so evidently these processes should be taken into account in the application of cyclohexyl-based pincer complexes.



Scheme 2.16. Suggested pathway for the dehydrogenation and aromatisation of a cyclohexyl pincer backbone.

2.3 Concluding remarks

The frequently reported formation of various side products in the complexation of all-aliphatic PCP ligands, e.g. in the form of 16-ring cyclic dimers, dicoordinated 8-membered ring systems and linear oligomers, underpin a higher backbone flexibility than in the aromatic PCP counterparts. The presence of easy abstractable α- and β-hydrogen atoms in the pincer backbone further impairs the coordination stability. The first all-aliphatic phosphinite complex with iridium was synthesised, although the acyclic $POC_{sp3}OP$ framework was disposed to form uncommon decomposition products. Cyclohexyl-based ligands of $PC_{sp3}P$ and $POC_{sp3}OP$ type has been found to readily cyclometallate with NiX_2 precursor, in a fashion that suffers from less byproduct formation than for their acyclic counterparts, showing the increased backbone rigidity imposed by the cyclic structure.

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3. Cyclohexyl-based PCP complexes with nickel. CO_2 activation and prospects in homogeneous catalysis (papers II-IV and VII)

3.1 Background

3.1.1 Cross-coupling Reactions Catalysed by Nickel Pincer Complexes

Transition metal-catalysed cross-coupling reactions are one of the most versatile and frequently used methods for the construction of new carbon-carbon bonds and are thus of great importance in organic synthesis.[1] Early in the development of coupling reactions, 1st row transition metals such as copper and nickel were identified as useful reagents and catalysts, but palladium-catalysed cross-couplings have dominated the field over the last decades, culminating in the 2010 Noble Prize in Chemistry to Ei-ichi Negishi, Akira Suzuki and Richard F. Heck for pioneering work in this area.[2-3] While the general catalytic cycle for cross-coupling reaction (Figure 3.1) commonly constitutes a Pd^0/Pd^{II} sequence, there has been a revived interest in developing nickel-based catalysts for various coupling reactions in recent years.[4-7] The reason for this, apart from the cheaper and more abundant metal source, is a generally higher stability towards β-hydrogen elimination of the key intermediate metal-alkyl species in case of nickel,[8] expanding the range of tolerable substrates. In addition, one-electron processes is more prevalent for nickel complexes, which opens up for new catalytic pathways that might not be accessible for the palladium systems.[9-10]

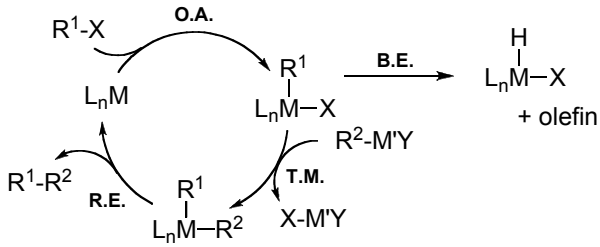
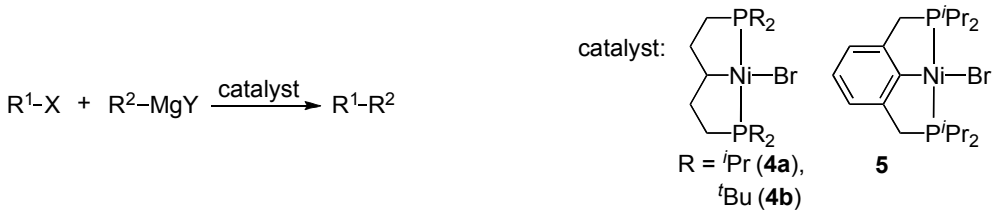


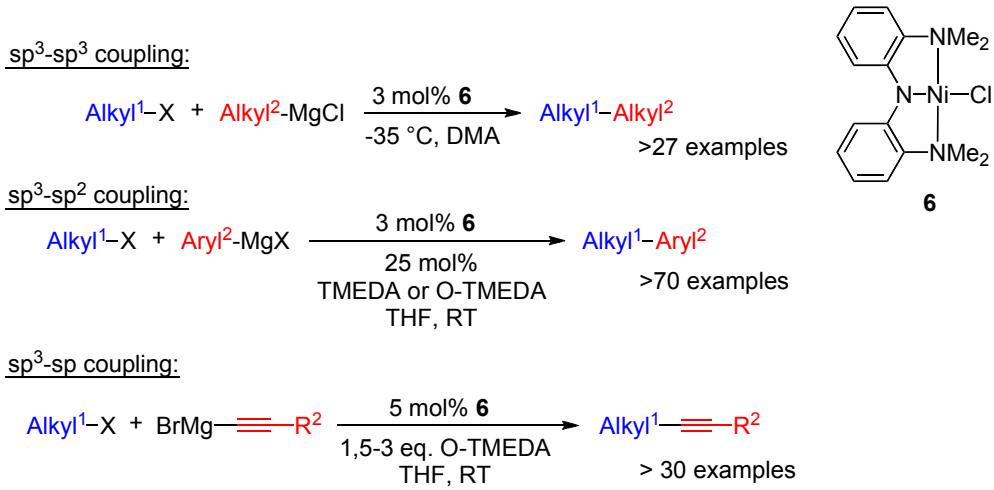
Figure 3.1. A general catalytic cycle for transition metal-catalysed C–C cross coupling reaction. O.A. = oxidative addition; B.E. = β-hydrogen elimination; T.M. = transmetallation; R.E. = reductive elimination.

In a study from 2008 Zargarian and co-workers explored the catalytic activity of nickel pincer complexes in Kumada-Corriu-Tamao coupling reactions, as a function of steric and electronic properties (Scheme 3.1). Refluxing MeMgCl and PhCl in THF in presence of **4a** (1 mol%) afforded toluene in 57% GC yield. By comparison, changing to complex **4b** with more bulky *tert*-butyl substituents resulted in a drop to 34% GC yield. Complex **5** was almost inactive under the same conditions, and thus the relative catalytic activity of these complexes correlates with the order of electron richness at the metal centres (**4a** > **4b** > **5**), as measured by the oxidation potentials from cyclic voltammetry data.[11] A later study by the same group reported on similarly low and variable yields for aromatically based bis(phosphinite) pincer complexes.[12]



Scheme 3.1. Schematic Kumada-Corriu-Tamao coupling and catalysts tested by Zargarian.

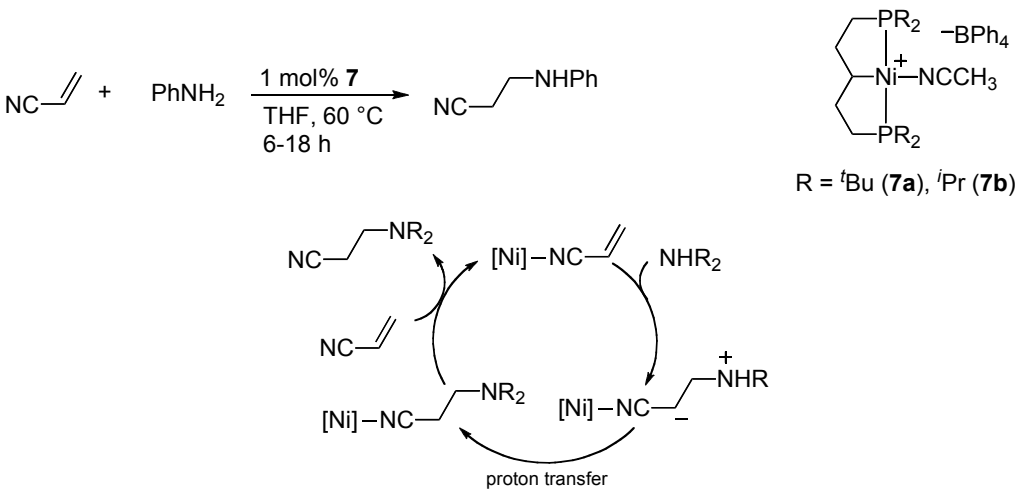
It is generally believed that oxidation of the metal is a critical step in nickel-catalysed cross-coupling reactions, and thus an electron-rich metal centre would be beneficial for catalysis. By introducing an NNN ligand with relatively hard amine donors, the group of Hu developed the "Nickamine" nickel pincer catalyst **6** for potential stabilisation of a Ni(IV) intermediate, if indeed such a species would be involved in a catalytic cycle.[13-14] The optimised conditions depicted in Scheme 3.2 allows for the coupling of even functionalised aryl Grignard reagents with a wide range of alkyl iodides and bromides, but going from primary to secondary alkyl halides drastically lowers the product yield.[15-17]



Scheme 3.2. Reactions of alkyl halides by the "Nickamine" catalyst **6** developed by Xile Hu.

Hu and co-workers have expanded their application of the nickamine catalyst to involve Sonogashira couplings[18] and alkylations of heterocycles.[19] Other important contributions to nickel pincer catalysed cross-couplings reactions come from the group of Inamoto, utilising bis(NHC)-based nickel pincer complexes in Kumada-Corriu-Tamao and Suzuki-Miyaura couplings.[20-22] PCP pincer complexes are less intensively studied, but examples include a naphtyl-based bis(phosphinite) nickel complexes reported by Morales-Morales for catalytic Suzuki-Miyaura couplings of aryl bromides with various substituents.[23]

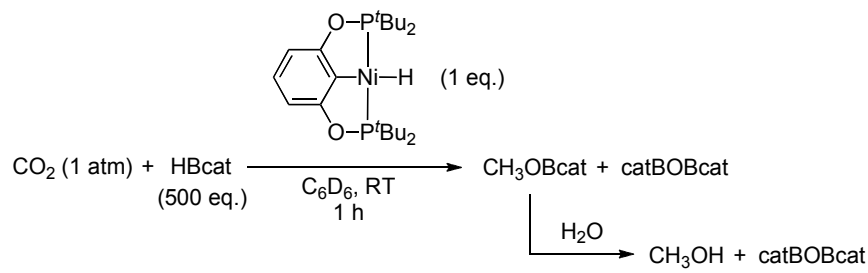
While the nickel pincer catalysed formation of carbon-carbon bonds is relatively well represented in the literature, formation of carbon-heteroatom bonds is much more uncommon. The group of Zargarian has reported on the catalytic amination of activated olefins using the all-aliphatic cationic Ni(II) PCP complexes **7a** and **7b**, postulating a "Lewis acid" mechanism where the Ni centre coordinates the nitrile group and thereby activates the olefin towards nucleophilic attack (Scheme 3.3). Aromatic analogues however, were found to be more efficient catalyst for the transformation.[24-26] Zargarian also utilised acyclic $POC_{sp3}OP$ nickel(III) complexes as catalysts for the Kharasch addition,[27] a reaction previously reported by van Koten and co-workers for aromatic NCN pincer complexes.[28-29]



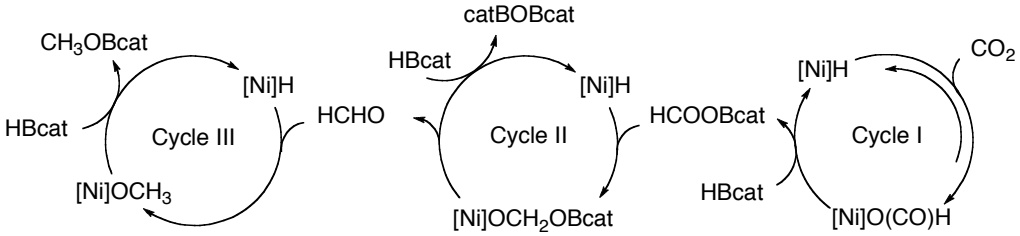
Scheme 3.3. Zargarian's catalytic amination of olefins with a cationic Ni^{II} complex.

3.1.2 Reduction of CO_2 to methanol derivatives

The utilisation of carbon dioxide as a C1 source for production of bulk or fine chemicals remains a major target in sustainable chemistry.[30-31] Transition metal-catalysed homogeneous hydrogenation of carbon dioxide typically gives either formic acid stabilised by a base,[32] or carbon monoxide via the reversed water gas shift reaction.[33] However, the conversion of carbon dioxide to its most reduced level in form of methane or methanol is even more desirable, especially for methanol due to the advantage of transporting a liquid rather than a gas. The group of Guan has reported on an efficient nickel pincer system for the catalytic hydroboration of carbon dioxide to methoxyboryl species using catecholborane (HBcat) (Scheme 3.4).[34-36] The suggested catalytic sequence involves three cycles, of which each cycle decreases the formal oxidation state of carbon by 2, and consumes 1 equivalent of HBcat to regenerate the active hydride species (Scheme 3.5).



Scheme 3.4. Catalytic reduction of CO_2 with HBcat by Guan and co-workers.

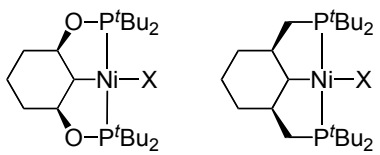


Scheme 3.5. Guan's proposed mechanism for nickel catalysed CO_2 reduction with HBCat.

3.2 Cyclohexyl-based pincer nickel complexes

3.2.1 Structural properties and prospects in cross-coupling catalysis (Paper II and III)

As mentioned in section 2.2.1, the work of this thesis involves the synthesis of the new cyclohexyl-based complexes **8** and **9** (Scheme 3.6). These compounds have been characterised in the solid state, as exemplified by the molecular structures of compounds **8b** and **9b** in Figure 2.4. Selected bond distances and angles for all four complexes are presented in Table 3.1. The Ni–X bond lengths are slightly shorter in the bis(phosphinite) complexes **8** than in the bis(phosphine) complexes **9**, indicating a lower *trans*-influence from the coordinated carbon in the former case, according to the expectations for a pincer scaffold possessing electron-withdrawing oxygen atoms. The Ni–X bond distances of complex **8-9** are in the upper range of what is previously reported for nickel complexes in the literature and generally longer (0.02-0.08 Å) than in comparable aryl based $PC_{sp2}P$[11, 37-38] and $POC_{sp2}OP$[27, 39] nickel complexes, underpinning the greater electron donation ability of a sp^3-hybridised carbon atom.



X = Cl (**8a**) X = Br (**8b**) X = Cl (**9a**) X = Br (**9b**)

Scheme 3.6. Novel cyclohexyl-based pincer nickel complexes.

The difference in electronic properties of the bis(phosphinite) relative bis(phosphine) pincer complexes were further elucidated by cyclic voltammetry experiments, where the measured oxidation potentials in going from Ni(II) to (III) lies

ca 0.33-0.35 V higher in the less donating bis(phosphinite) case (Figure 3.3). The same trend was previously observed by the group of Zargarian, comparing aryl-based PCP and POCOP Ni(II) bromide complexes.[26] The $E_{1/2}$ values of **8a** and **8b** compare to those reported by Zargarian for acyclic $POC_{sp3}OP$ Ni(II) complexes, although in their case the process is irreversible[27a] demonstrating a higher oxidative stability of the cyclohexyl based systems compared to the acyclic ones.

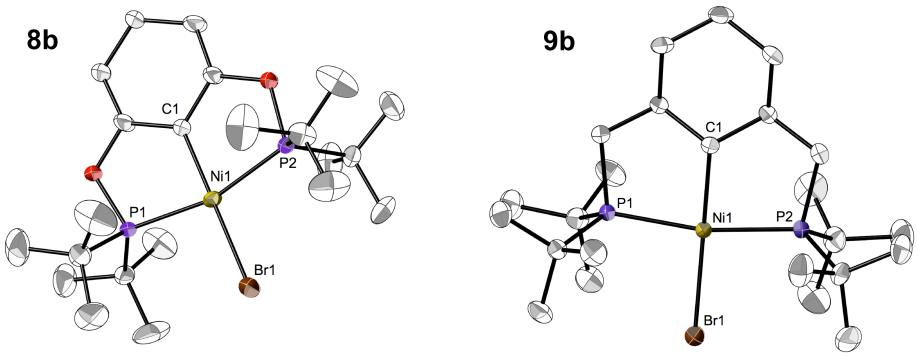


Figure 3.2. Molecular structures of compounds **8b** (left) and **9b** (right) at 30% probability level. Hydrogen atoms are omitted for clarity.

Table 3.1. Selected bond distances [Å] and angles [°] for compounds **8a**, **8b**, **9a** and **9b**.

	8a	**8b**	**9a**	**9b**
Ni–X	2.2357(10)	2.3764(4)	2.2497(14)	2.4303(4)
Ni–C1	1.939(3)	1.939(2)	1.990(4)	1.998(2)
Ni–P1	2.2019(9)	2.2163(7)	2.2346(11)	2.2402(7)
Ni–P2	2.1933(9)	2.2156(7)	2.2251(11)	2.2325(7)
C1–Ni–X	173.20(10)	179.44(8)	178.81(18)	169.48(7)
P–Ni–P	163.69(4)	163.50(3)	170.83(5)	168.48(3)

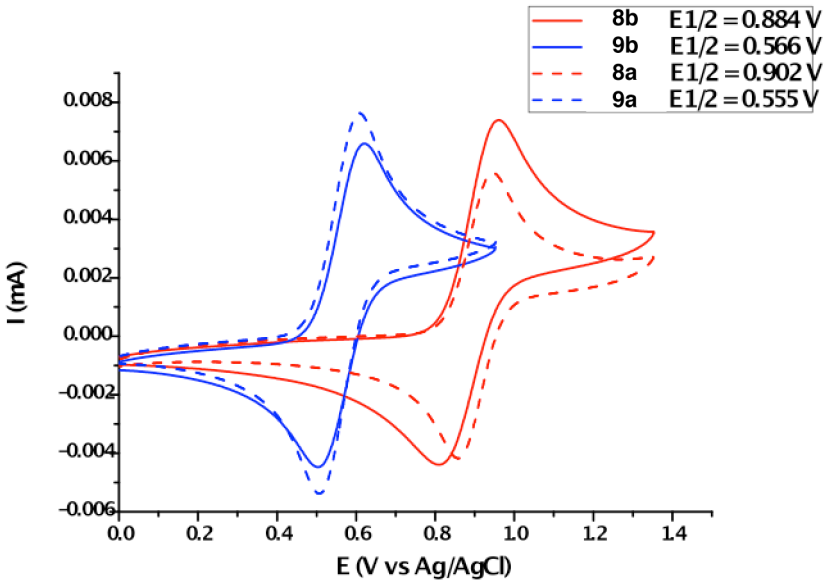
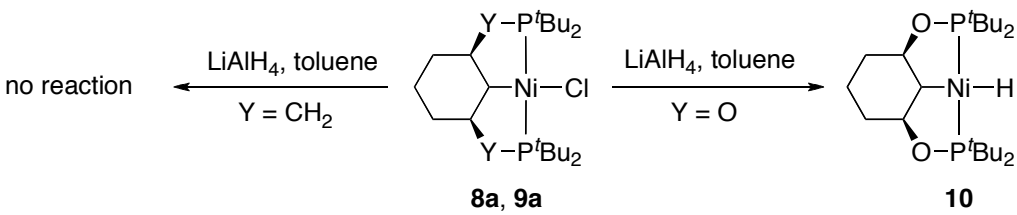


Figure 3.3. Cyclic voltammetry scans of 10^{-3} M solutions of compounds **8**-**9** at a Pt electrode in CH_2Cl_2 (0.1 M $(^nBu_4N)PF_6$ scan rate 0.1 V s^{-1}).

The $POC_{sp3}OP$ complexes **8a** and **8b** have a smaller P–Ni–P angle than their $PC_{sp3}P$ analogues **9a** and **9b**, reflecting on the shorter distances of the P–O and C–O bond than of the corresponding P–C and C–C bonds in the pincer arms. The more open coordination site in the POCOP complexes relative the PCP analogues is one possible explanation for their often observed higher reactivity, despite a more electron rich metal centre in the PCP case. One such example is presented in Scheme 3.7; complex **8a** is readily converted to the corresponding hydride complex **10**, while **9a** does not undergo the same transformation.

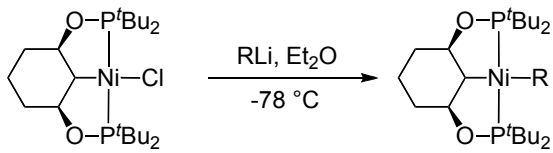


8a, **9a** **10**

Scheme 3.7. Reactivity of complexes **8a** and **9a** towards $LiAlH_4$. Synthesis of the cyclohexyl-based bis(phosphinite) nickel hydride complex **10**.

Compound **8a** can also be transformed to the corresponding methyl (**11**) and phenyl (**12**) complexes by reaction with the respective organolithium reagents

(Scheme 3.8). Complex **10-12** can be handled in air for a shorter period of time and they tolerate a temperature of 100 °C without significant signs of decomposition. Zargarian and co-workers have reported that the isolation of acyclic $^{i\text{Pr}}POC_{sp3}OP$-based hydride or alkyl nickel complexes has been unsuccessful due to a limited thermal stability.[40] They still postulated the $^{i\text{Pr}}POC_{sp3}OP$ nickel methyl complex as an *in situ* generated reactive intermediate in the Kumada-Corriu-Tamao cross coupling reaction, where the $^{i\text{Pr}}POC_{sp3}OP$ nickel chloride complex had comparable reactivities to the $^{i\text{Pr}}PC_{sp3}P$ counterpart.[11] Despite showing promising electronic properties and a relatively high rigidity, complexes **8** and **9** were found to be essentially inactive as catalysts for Kumada-Corriu-Tamao cross coupling reactions. Several primary and secondary alkyl halides were attempted for cross coupling with EtMgBr at varied reactions conditions, typically affording yields below 5% and never exceeding 20%. The main reason for this low activity is likely the sterical hindrance from the *tert*-butyl substituents. Complex **8a** has also been attempted as catalyst for the Buchwald-Hartwig amination reaction with unsatisfactory results.



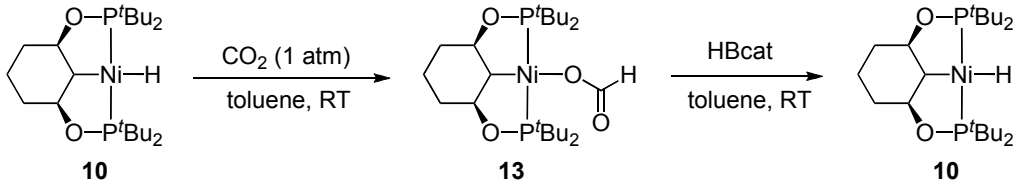
8a

Scheme 3.8. Synthesis of compounds **11** and **12**.

3.2.2 Insertion reactions with CO_2 and CO (Paper III, IV and VII)

3.2.2.1. Insertion into a Ni–H bond (Paper III)

The $POC_{sp3}OP$ nickel hydride complex **10** reacts analogously to Guan's $POC_{Ar}OP$ analogue when exposed to 1 atm CO_2, undergoing a quantitative and clean conversion to the corresponding formate (Scheme 3.9).[34-36] A stoichiometric reaction with catecholborane regenerates complex **10**, suggesting that this compound could complete the catalytic cycles for the reduction of CO_2 with catecholborane, as depicted in Scheme 3.2. However, following Guan's protocol for this catalytic process with **10**, no methanol could be detected. Plausibly the entering of cycle II, which is postulated as the highest kinetic barrier of the transformation, requires higher temperatures than the attempted ambient temperature, and further investigation of the catalytic capacity of complex **10** is suggested to follow up on these preliminary results.

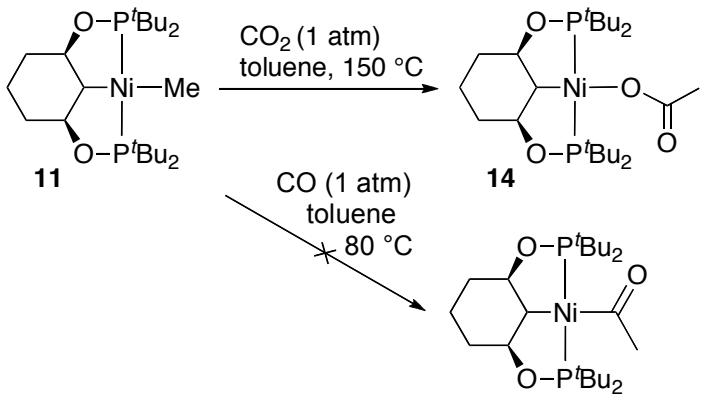


Scheme 3.9. Synthesis of the formate complex **13** and regeneration of **10** on addition of HBcat.

3.2.2.2. Insertion into a Ni–Me bond (Paper III)

Alongside the CO_2 insertion into the $POC_{sp3}OPNi–H$ bond, we wanted to study the reactivity of analogous Ni–Me bond for the same type of CO_2 insertion. The formation of a metal carboxylate in this fashion is a proposed key step in many transition-metal catalysed conversions of CO_2 into more valuable products, which is of general interest to the scientific community. The CO_2 insertion into group 10 transition metal-methyl and –hydroxide bonds is well exemplified for aromatically based PCP complexes, but no studies of PCP complexes with aliphatic backbones are reported to this date.

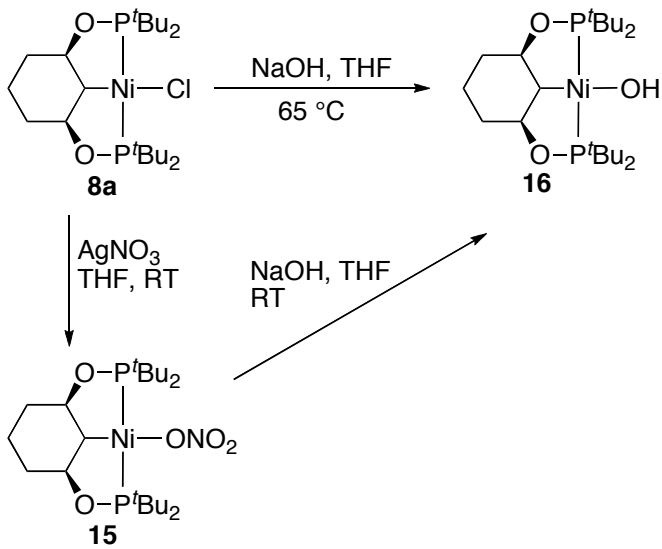
Complex **11** was found to have a reactivity similar to that reported for the analogous $PC_{Ar}P$ nickel methyl complex by Hazari and co-workers ($PC_{Ar}P$ = [2,6-$C_6H_3(CH_2P^tBu_2)_2]^-$),[41] in that it requires prolonged heating to 150°C in order to obtain the acetate complex **14** (Scheme 3.10) and that the barrier for insertion is substantially higher than for the corresponding hydrido complex. Reacting **11** with CO did not afford any conversion to the corresponding acyl complex, which is not so surprising since the migratory insertion of CO typically requires a pre-coordination to the metal centre. On the contrary, the insertion of CO_2 has been reported to proceed without initial coordination for both $PC_{Ar}PNi–Me$[41] and $PC_{Ar}PPd–Me$[42] complexes.



Scheme 3.10. Reactivity of complex **11** towards CO_2 and CO. Synthesis of complex **14**.

3.2.2.3. Insertion into a Ni–OH bond (Paper IV)

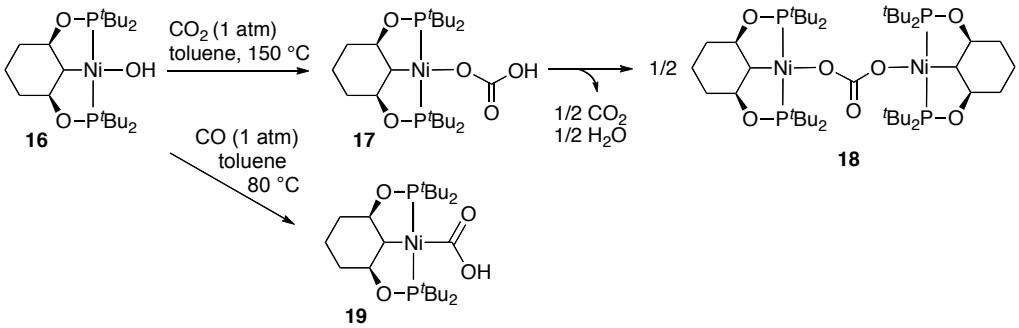
The synthesis of the hydroxo complex **16** was found not so straightforward. Following the protocol of Hazari and co-workers for their synthesis of a $PC_{Ar}PNi–OH$ complex from the corresponding chloride in reaction with sodium hydroxide was very sluggish and did not afford full conversion of **11** (Scheme 3.11). Their alternative and more efficient synthetic protocol, going via the $PC_{Ar}PNi–NH_2$ complex through reaction with sodium amide, was not accessible for the present system.[43] Also, reacting **8a** with KOH resulted in decomposition of the pincer structure to several uncharacterised phosphorus-containing fragments, similarly to the work by Guan and co-workers on $POC_{Ar}OPNiCl$ ($POC_{Ar}OP$ = $[2,6\text{-}C_6H_3(OPPh_2)_2]^-$).[44] Attempts to afford **16** from the hydride complex **10** in reaction with water was also unsuccessful. It was eventually found that the chloride complex **8a** could be readily converted to the corresponding nitrate complex **15**, which in turn underwent clean conversion to **16** in presence of sodium hydroxide, in accordance with published work on $PC_{Ar}P$ palladium complexes ($PC_{Ar}P$ = $[2,6\text{-}C_6H_3(CH_2P^tBu_2)_2]^-$).[45]



Scheme 3.11. Synthesis of complex **16** through a direct route or *via* complex **15**.

The hydroxide complex **16** readily inserts CO_2 to form the bicarbonate species **17** (Scheme 3.12). Upon concentration *in vacuo* this complex dimerises to form the bridged carbonate complex **18** under decarboxylation and water elimination. This reactivity was previously reported by Cámpora and co-workers for a similar aromatic $PC_{Ar}PNiOCOOH$ complex ($PC_{Ar}P$ = $[2,6\text{-}C_6H_3(CH_2P^iPr_2)_2]^-$). They suggest a reversibility of the initial CO_2 insertion, so that the dimerisation takes place through a CO_2 elimination from the bicarbonate complex to regenerate the (PCP)NiOH complex,

which then reacts with residual bicarbonate complex, forming a $\{(PCP)Ni\}_2\mu$-(CO_3) dimer.[46]



Scheme 3.12. Reactivity of complex **16** towards CO_2 and CO. Synthesis of the insertion products **17** and **19**. Subsequent conversion of the bicarbonate complex **17** to the bridged carbonate dimer **18**.

Carbon monoxide inserts into the Ni–OH bond of complex **16** to form the corresponding hydroxycarbonyl complex **19** (Scheme 3.12). The conversion proceeds at ambient temperature and 1 atm CO over a period of 3 days, and no formation of any bridged dimeric μ-CO_2-κ^2C,O species was indicated by means of ^{31}P-NMR spectroscopy under these conditions, as is reported for similar systems.[47-48] Supposedly the bulky *tert*-butyl substituents prevents the condensation reaction between the starting hydroxide compound and the hydroxycarbonyl compound formed in our system. Hydroxycarbonyl complexes have been proposed as intermediates in a number of transformations, such as CO_2 reductions and the water-gas shift reaction, and are structurally interesting as they constitute a non-classical metal-CO_2 coordination bearing a metal-carbon σ-bond instead of the typical metal-oxygen bond of a formate complex. However, reports on the isolation and characterisation of hydroxycarbonyl compounds are relatively scarce as they commonly have a low thermal stability, and are known to undergo CO_2 elimination to the corresponding hydride[48] and in a closed vessel even subsequent CO_2 insertion and isomerisation to the corresponding formate.[49] Concerning complex **19**, further studies of its stability and possible role as an intermediate are required.

The X-ray structure of **19** displays a crystal lattice where two molecules are oriented to form a pair with hydrogen bonds between two oxygen atoms (Figure 3.4). This resembles the structural features of previously reported hydroxycabonyl complexes with pincer ligands, such as (PNP)NiCOOH by Lee[48] (PNP = N[2-P^{i}Pr$_2$-4-Me-C_6H_3]$_2$) and ($PC_{Ar}P$)PdCOOH by Wendt[49] ($PC_{Ar}P$ = [2,6-C_6H_3($CH_2P^tBu_2$)$_2$]$^-$). The O–O distance of 2.681 Å is indicative of a fairly strong hydrogen bond, similar to what is previously reported for hydroxycarbonyl complexes.

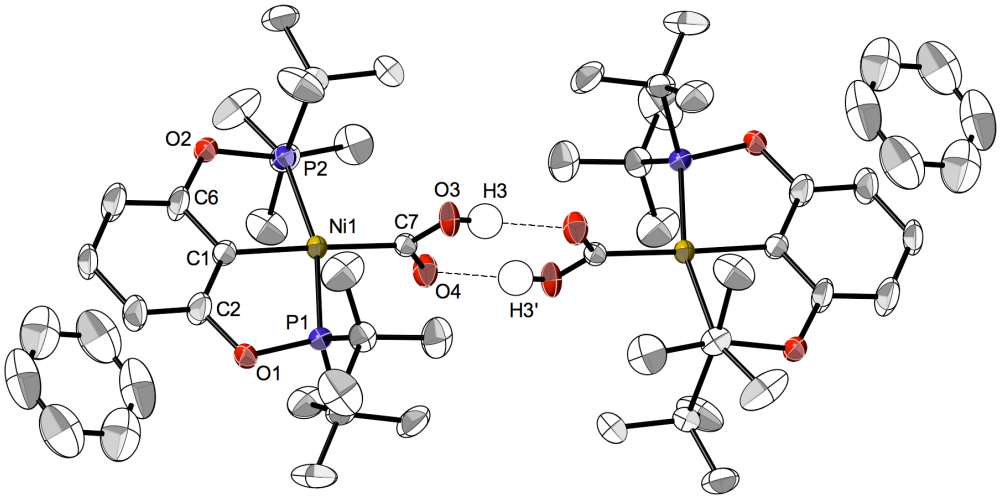
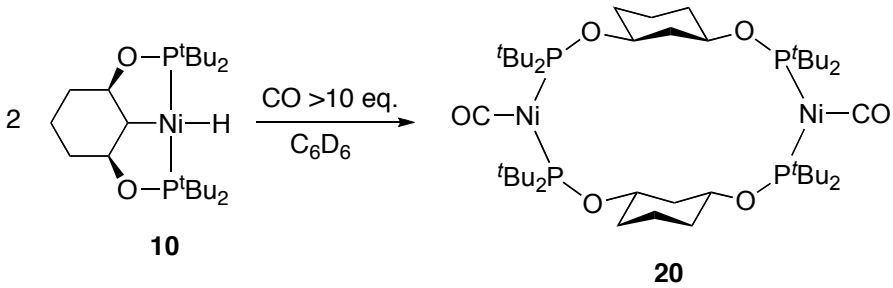


Figure 3.4. Molecular structure of complex **19** at 30% probability level. Hydrogen atoms are omitted for clarity.

3.2.2.4. Reactivity of a $POC_{sp3}OPNiH$ complex towards CO (Paper VII)

Under normal conditions, the hydride complex **10** shows no tendency to demetallate through a C–H bond forming reductive elimination of the pincer ligand. It withstands heating to 100 °C, even in presence of diphenylacetylene. However, treating a degassed solution of compound **10** with 1 atm CO results in formation of the dimeric nickel(0) species **20** (Scheme 3.13). This transformation is probably triggered by a pre-coordination of CO, giving an increased electrophilicity of the nickel centre due to the π-acidity of the ligating CO. Chen and co-workers have previously reported on a CO induced reductive elimination of the N–H bond of PNP-supported nickel(II) hydride complex (PNP = $[N(o\text{-}C_6H_4PR_2)_2]^-$, R = Ph, ^{i}Pr, Cy), affording a P,P'-coordinated dicarbonylic tetrahedral nickel(0) complex.[50] Examples of tricoordinate 16e nickel(0) complexes like **20** are relatively rare in the literature, and typically require the stabilisation by a bulky ligand.



10 **20**

Scheme 3.13. CO induced reductive elimination to form complex **20**.

3.2.3. Spectroscopical trends of the $POC_{sp3}OP$-based nickel complexes. (Papers III and IV)

The series of new $POC_{sp3}OP$-based nickel complexes included in this work show a direct correlation between the $^{13}C\{^1H\}$-NMR shift of the α-carbon and the σ-donating capacity of the ligand coordinated in *trans* position, suggesting an increased σ-donation in the order ONO_2 < OAc < OH < Cl < Br < Ph < Me < COOH < H. The $^{31}P\{^1H\}$-NMR signals of these $POC_{sp3}OP$ complexes are similarly correlated with the electronegativity of the ligating atom in the fourth coordination site. For complexes **17** and **18**, the expected tendency would be a slight shift downfield of the nickel bound α-carbon resonance for the stronger σ-donator CO_3^{2-} relative the less basic HCO_3^-, however in this case the difference of the ^{13}C resonances is insignificant (δ = 53.5 ppm in C_6D_6 for both compounds), and the ^{31}P-NMR shift is only slightly shifted upfield for complex **18** relative **17** (δ = 176.1 ppm and 178.2 ppm respectively in C_6D_6).

3.3. Concluding remarks

The first successful cyclometallation of a cyclohexyl-based bis(phosphinite) ligand has been accomplished with nickel. The analogous bis(phosphine) complexes are also reported, but although electrochemical analysis confirmed the electron rich nature of the metal centre in these compounds, and indicated a higher oxidative stability than in corresponding acyclic pincer complexes, they are found to be more or less unreactive as catalysts for various cross coupling reactions. The $PC_{sp3}P$ nickel halide complexes are remarkably inert towards hydride donors and base, but the $POC_{sp3}OP$ counterparts has allowed for the construction of a new family of $POC_{sp3}OP$-supported nickel(II) complexes, including the chloride, bromide, hydride, hydroxide, methyl and phenyl species. The isolation and full characterisation of these compounds underpins the relatively high stability imposed by the cyclohexyl-based framework in comparison to

the acyclic counterpart, of which methyl and hydride complexes have been postulated but never isolated or spectroscopically confirmed. With aspect to stoichiometric CO_2 insertion reactions, the cyclohexyl-based $POC_{sp3}OP$ essentially show comparable reactivity to similar aromatic $PC_{Ar}P$ and $POC_{Ar}OP$ complexes. Insertion of CO into a $POC_{sp3}OPNi–OH$ bond affords the structurally and catalytically interesting hydroxycarbonyl compound.

In view of the promising stability and electronic properties, yet very low catalytic activity for coupling reactions, of the here reported $POC_{sp3}OP$-supported nickel(II) complexes, a future expanded study should include the impact of steric hindrance. A series of cyclohexyl-based POCOP ligands could be obtained by varying the alkyl substituents on the phosphorus atoms and then cyclometallate with nickel to generate a new family of structurally varied complexes.

Considering the successful CO_2 insertion into the Ni–H bond of the $POC_{sp3}OP$ nickel hydride complex **10** to form a formate complex, continued efforts should be made to evaluate the capacity of **10** as a catalyst for CO_2 reduction to methanol derivatives, using boranes or other reducing agents.

3.4. References

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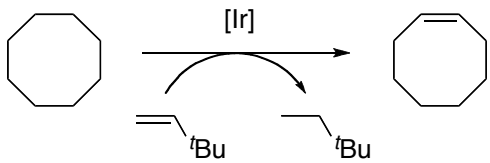
4. Iridium pincer complexes in dehydrogenation reactions (Paper V)

4.1 Background

Olefins are an utterly useful feedstock in the chemical industry, although far less naturally abundant than alkanes. The direct conversion of alkanes to alkenes via selective dehydrogenation is thus an important process, attracting interest for the manufacture of both fuels and fine chemicals.[1] Early examples of catalytic alkane transfer-hydrogenations by homogeneous complexes suffered from catalyst decomposition at the high temperatures required,[2-5] but a major breakthrough was achieved by Kaska, Jensen and co-workers who in 1996 reported that a PCP iridium pincer complex catalysed the transfer dehydrogenation reaction of cyclooctane (COA) to cyclooctane (COE) at 200 °C, using *tert*-butylethylene (TBE) as a hydrogen acceptor to form *tert*-butylethane (TBA) (Scheme 4.1).[6]



Scheme 4.1. Schematic drawing of the iridium catalysed COA/TBE transfer dehydrogenation.

Significant effort has since been made to develop selective dehydrogenation reactions under mild conditions, predominantly using iridium pincer catalysts,[7] and the range of substrates have expanded to include alcohols,[8-9] amine-boranes[10-11] and primary[12] and secondary amines.[13] The majority of the PCP ligands studied constitutes an aromatic backbone, e.g. benzene,[10-20] anthracene,[21] 7-6-7 fused rings[22] and metallocene[23-24] based systems (Figure 4.1).

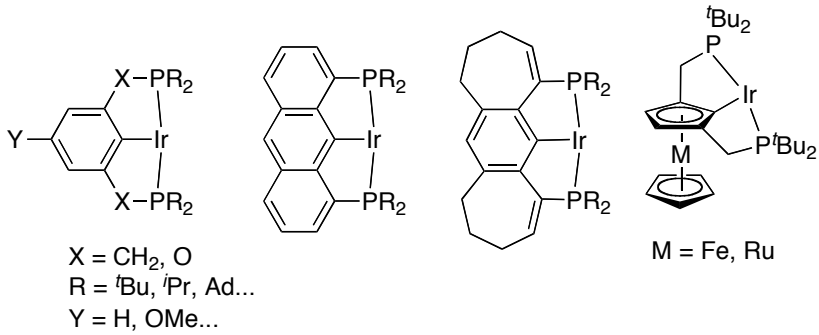


Figure 4.1. Aryl-based iridium pincer complexes used in alkane dehydrogenation reactions (14-electron species are depicted).

The mechanism of the COA/TBE transfer dehydrogenation as initially performed by Kaska and Jensen[6] has been thoroughly studied by Goldman and co-workers.[25] Insertion of TBE into an Ir–H bond of (PCP)IrH_2 (PCP = [2,6-$C_6H_3(CH_2P^tBu_2)_2]^-$) is followed by reductive C–H elimination of TBA giving a reactive 14-electron species that undergoes oxidative addition of a C–H bond of the alkane substrate. Subsequent β-hydride elimination generates the product olefin and completes the catalytic cycle (Figure 4.2). The transformation can also proceed via a direct loss of H_2 without the acceptor, although this is generally a slow process. The catalytic activity is significantly inhibited by olefins, either the dehydrogenated product or the sacrificial acceptor, through simple coordination and C–H activation to a vinyl hydride respectively.

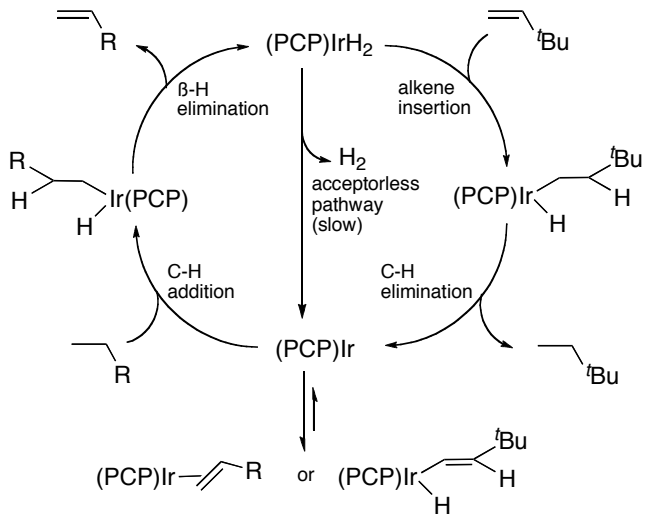


Figure 4.2. Proposed mechanism of *n*-Alkane/TBE transfer dehydrogenation (PCP = [2,6-$C_6H_3(CH_2P^tBu_2)_2]^-$).

A crucial and at certain conditions turnover-limiting step in the catalytic cycle is the C–H bond activation of the substrate. Introducing electron donating methoxy substituents in the *para*-position of benzyl-based PCP complexes, has been shown to give an increase in turnovers, due to a facilitated C–H activation at the more electron rich metal centre.[16, 27] The strong σ-donating ability of a sp^3-hybridised carbon atom in a PCP complex with saturated backbone is thus potentially beneficial for catalytic dehydrogenation reactions.

4.2 Aliphatic PCP iridium complexes as catalysts for dehydrogenation reactions. (Paper V)

In order to fill the gap in the scientific coverage of iridium pincer catalysed alkane dehydrogenation reactions, we wanted to explore the catalytic activity of our previously reported all-aliphatic complexes $POC_{sp3}OPIrHCl$ (**1**) ($POC_{sp3}OP$ = 1,3-bis-(di-*tert*-butylphosphinito)-2-methylpropane)[28] and $PC_{sp3}PIrHCl$ (**21**) ($PC_{sp3}P$ = *cis*-1,3-bis-[(di-*tert*-butylphosphino)methyl]cyclohexane)[29] (Figure 4.3).

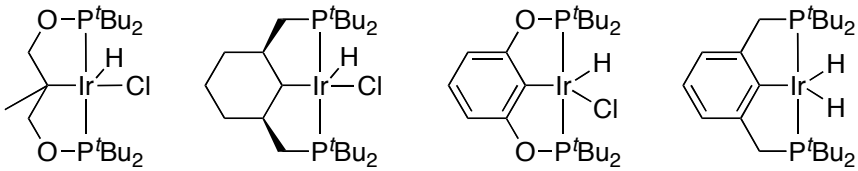


Figure 4.3. Pincer complexes tested in the transfer dehydrogenation experiments.

4.2.1. Dehydrogenation of cyclooctane

The COA/TBE transfer dehydrogenation (Scheme 4.1) has become an established test reaction to compare the catalytic activity for dehydrogenation reactions.[7] Since both the acceptor olefin (TBE) and the dehydrogenated product (COE) inhibit the reaction it is necessary to use the same ratio of catalyst, COA and TBE to be able to do a direct comparison. A lot of the reported literature data refers to the work of Brookhart[15], using COA/TBE/catalyst = 3030/3030/1, and thus these conditions were applied also in our study. NaO^{t}Bu (1.5 eq) was also added to generate the catalytically active 14-electron species from the hydrochloride complexes. The results of the attempted catalytic dehydrogenations along with relevant reference results are presented in Table 4.1. Application of complex **21** afforded a turnover of 50 (Entry 1), as compared to Brookhart's reported 1538 turnovers (Entry 3) using compound **22** as catalyst (Figure

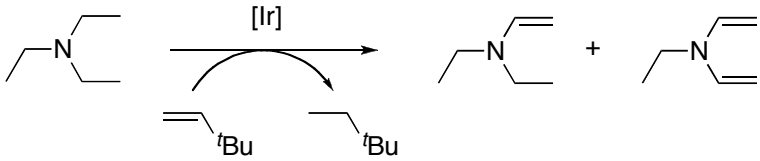
4.3). Successful reproduction of this result under the working conditions in our lab (Entry 4) serves as validation of the results for the other tested compounds. No dehydrogenation product was observed using **1** (Entry 2), probably due to the known low thermal stability of this compound that is probably lower still for the corresponding 14-electron complex. The same factor is likely to cause the low activity of **21**. Since presence of residual N_2 in the Ar atmosphere used in the above-described experiments could inhibit the catalytic activity through formation of relatively stable bridged N_2-dimers,[30] and this tendency could be stronger for a more electron rich $PC_{sp3}P$-supported metal centre, the catalysis was also carried out in vacuum. This however only gave a slight increase to 70 turnovers. Acceptorless dehydrogenation of COA by **21** gave 5 turnovers, as compared to 105 reported for complex **23** (Entry 5, Entry 6).

Table 4.1. Catalytic dehydrogenation reactions using different substrates and iridium catalysts

Entry	Catalyst	Substrate	Acceptor	T [°C]	TON	Reference
1	21	COA	TBE	200	50	Paper V
2	1	COA	TBE	200	0	Paper V
3	22	COA	TBE	200	1538	[15]
4	22	COA	TBE	200	1918	Paper V
5	21	COA	-	170	5	Paper V
6	23	COA	-	151	105	[31]
7	21	NEt_3 100 eq	TBE 200 eq	120	18.9	Paper V
8	21	NEt_3 10 eq	TBE 20 eq	120	4.3	Paper V
9	23	NEt_3 10 eq	TBE 10 eq	90	6.5	[32]
10	23	NEt_3 10 eq	TBE 30 eq	90	11.4	[32]

4.2.2. Dehydrogenation of triethylamine

Since the low thermal stability of the active species derived from **21** seemingly impairs the catalytic activity, we wanted to test it in a reaction that can proceed at lower temperatures, such as the transfer dehydrogenation of tertiary amines (Scheme 4.2). Using **21** as catalyst for NEt_3 dehydrogenation required a slightly higher reaction temperature than in the protocol reported by Goldman[32] and gave lower TONs at comparable conditions (Table 4.1, Entries 7-10). The reaction rendered a mixture of N,N-diethylvinylamine and N,N-divinylethylamine in approximately a 3:1 ratio.



Scheme 4.2. Schematic draw of the iridium catalysed NEt_3/TBE transfer dehydrogenation.

4.3. Concluding remarks

PCP pincer iridium complexes with aliphatic backbones have been tested for different alkane dehydrogenation reactions and the catalytic activity has proved to be relatively low compared to similar aromatic complexes. The main reason for this is the low thermal stability of the catalytically active species.

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5. Coordination behaviour and reactivity at a $PC_{sp3}P$-supported iridium centre (Paper VI)

5.1. Introduction

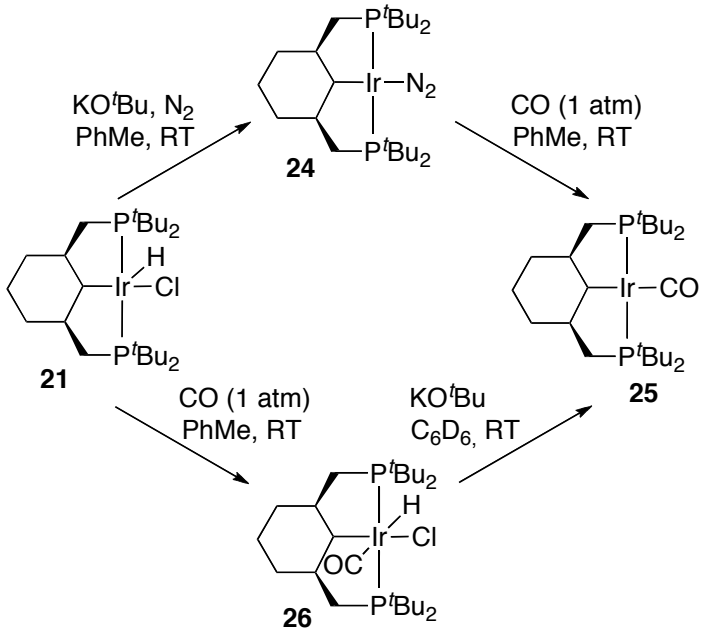
It is well documented that carbon monoxide can add coordinatively to both $PC_{sp2}P$-[1] and $PC_{sp3}P$-supported[2] iridium(III) complexes. Such iridium carbonyl complexes are suggested to be involved in catalytic transformations such as olefin hydroformylation reactions[3] and transfer dehydrogenations of ketones.[4-5] PCP iridium(I) carbonyl complexes are known for aromatically based pincer structures,[6-11] and has been reported to catalyse the decarbonylation of 2-naphtaldehyde[12] and the partial deoxygenation of diols[13] and glycerol.[14] There are however no $PC_{sp3}P$-supported iridium(I) carbonyl complexes reported to this date.

The nature of the coordinated PCP carbon is a pertinent variable, since the greater σ-donating ability of a C_{sp3}- compared to C_{sp2}-hybridised metallated carbon gives a stronger *trans* influence and a metal centre with higher nucleophilicity.[15] The electronic properties of the metal centre have a high influence on the propensity to perform e.g. oxidative additions and reductive eliminations - fundamental organometallic processes that are involved in many catalytic transformations and stoichiometric reactions for the making and breaking of covalent bonds.[16] This is exemplified by the work of Hartwig on $PC_{sp2}CP$ and $PC_{sp3}CP$ iridium(I) pincer complexes in reaction with NH_3, obtaining simple coordination in the first case but oxidative addition of an N–H bond in the latter.[17]

5.2. Carbonyl complexes of iridium(I) and iridium(III)

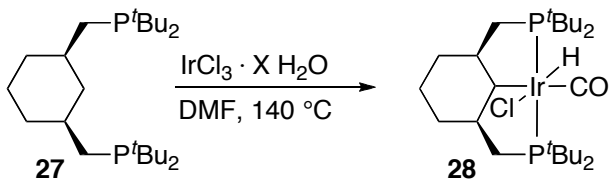
Complex **21** has been previously reported to form the terminal N_2-complex **24** under reductive conditions in presence of N_2 (Scheme 5.1).[18] Complex **24** readily undergoes substitution with the more strongly coordinating CO ligand to form the corresponding carbonyl complex **25**. The conversion is clean and rapid at room temperature, and is

accompanied by a colour change from orange to yellow, consistent with what could be expected for the more high-field CO ligand. The coordinatively unsaturated 16-electron complex **21** reacts according to the expectations to form the octahedral 18-electron complex **26**, maintaining the chloride ligand in *trans*-position to the PCP carbon. This complex can in turn be converted to complex **25** by addition of KO^{t}Bu (Scheme 5.1).



Scheme 5.1. Synthesis of complexes **24**, **25** and **26**.

Refluxing the cyclohexyl-based bis(phosphine) ligand **27** with $IrCl_3 \cdot H_2O$ in DMF afforded the structural isomer of **26** with the solvent acting as a carbonyl source (Scheme 5.2). Complex **28** features the carbonyl ligand located in a *trans*-position and the hydride and chloride both in *cis*-position to the metallated PCP carbon, as confirmed by the crystal structures.



Scheme 5.2. Synthesis of complex **28**.

Notably, the two isomers **26** and **28** have different orientations of their respective hydride ligands relative the hydrogen positioned on the α-carbon, as illustrated in the molecular structures in Figure 5.1. In complex **26** the hydride and α-hydrogen are located *anti* to each other, while in **28** they are *syn*. The *anti* configuration is the previously reported outcome for cyclohexyl-based $PC_{sp3}P$ complexes with iridium and is, thus, the expected for a concerted oxidative addition process via a C–H σ-complex.[18] Consequently, the hydride signal in the ^{1}H-NMR spectra displays a $^{2}J_{HH}$ coupling constant (J = 1.5 Hz) for complex **26** only, as shown in Figure 5.2, and no observable $^{2}J_{HH}$ coupling for *syn*-H in **28**. The more upfield shift for complex **28** compared to complex **26** (δ = -8.59 ppm and -18.7 ppm respectively in C_6D_6) is in agreement with the higher *trans*-influence from the carbonyl compared to the chloride ligand.

Spectroscopic and crystallographic characterisation of the new carbonyl complexes **25**, **26** and **28** agree well with what was previously reported for similar $PC_{sp2}P$ complexes[1,8], *i.e.* the Ir–CO bond lengths and the ν_{CO} stretching frequencies do not indicate any substantial electronic impact from the supposedly more strongly σ-donating $PC_{sp3}P$-ligand relative its $PC_{sp2}P$ counterpart.

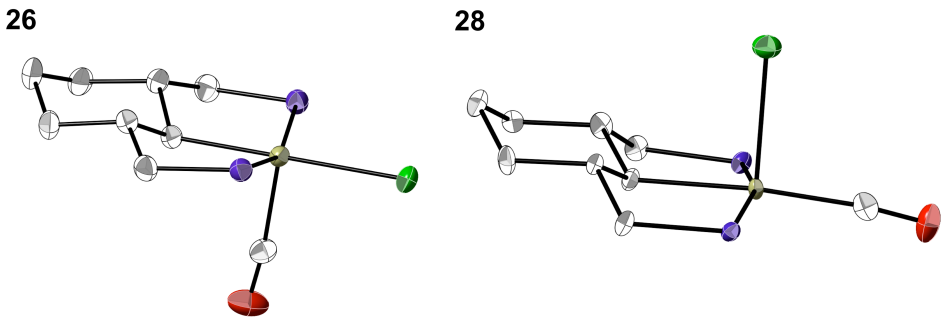


Figure 5.1. Side-views of the molecular structures of **26** and **28** at 30% probability level. Hydrogen atoms and substituents on phosphorus are omitted for clarity.

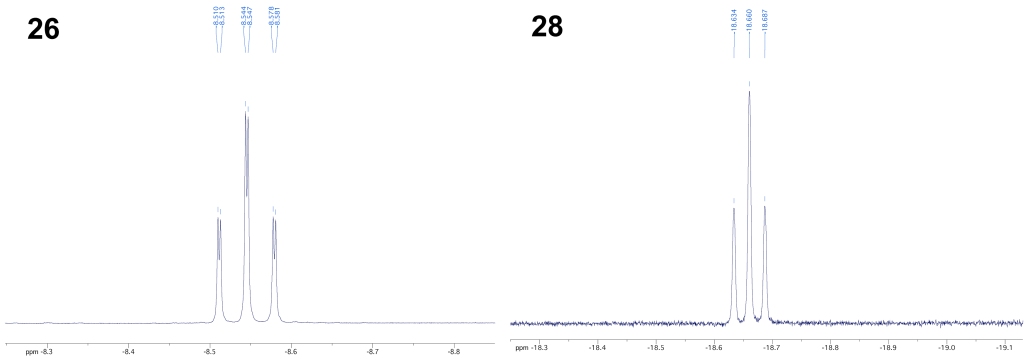
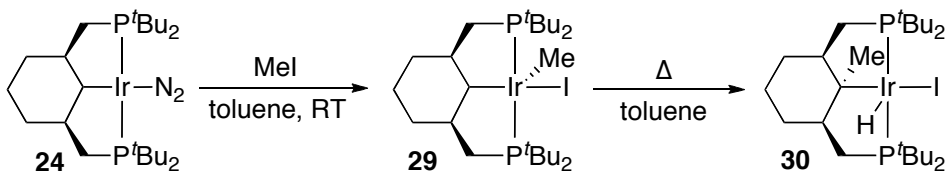


Figure 5.2. ^{1}H-NMR spectra of the hydride shifts of complexes **26** and **28**.

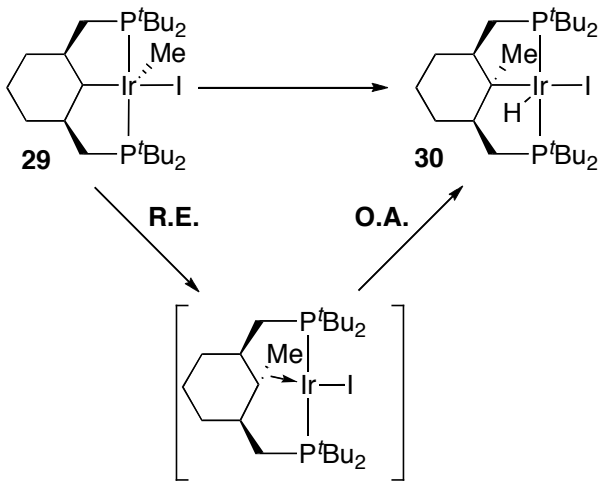
5.3. Oxidative addition of MeI and subsequent elimination of a C_{sp3}–C_{sp3} bond

Complex **24** reacts with methyl iodide to form the oxidatively added methyl iodide complex **29** in full conversion within 1 h (Scheme 5.3). The structure is confirmed by X-ray crystallography and NMR-spectroscopy. The NMR analysis displays a characteristic triplet at 2.15 ppm in the ^{1}H-NMR spectrum and a triplet at -27.8 ppm in the ^{13}C-NMR spectrum corresponding to the Ir–*CH*$_3$ moiety, in analogy with the previously reported aromatic counterpart.[20] The presence of a characteristic broadened triplet at 1.95 ppm corresponding to the α-proton of the cyclohexyl ring is further indicative of a PCP-coordinated structure. Upon handling a solution of **29** at room temperature, it is gradually converted to complex **30** over a period of days (Scheme 5.3). The transformation seemingly proceeds faster at elevated temperatures. The structure of **30** is the net result of a methyl migration from the metal to the metallated PCP carbon. The unambiguous presence of a hydride shift at -28.4 ppm in the ^{1}H-NMR spectrum of **30**, integrating 1:3 with the methyl protons at -1.02 ppm, argues for the suggested structure rather than a non-metallated η^2 C–C agostic species.



Scheme 5.3. Synthesis of complexes **29** and **30.**

The mechanism for this transformation is likely to proceed *via* a reductive elimination to generate a C_{sp3}–C_{sp3} coupled intermediate, followed by an oxidative addition of the remaining C–H bond in 2-position on the cyclohexyl backbone (Scheme 5.4). A similar result have been reported by Xu *et al.* upon the complexation of an acyclic $POC_{sp3}OP$ ligand with $Fe(Me)_2(PMe_3)_4$.[21] However, literature examples of C_{sp3}–C_{sp3} reductive eliminations at iridium centres are very limited.[20] Complex **29** adopts a distorted square pyramidal geometry around iridium, with the methyl ligand in an apical position *anti* to the α-hydrogen of the pincer ligand (Figure 5.3). **30** displays an unusual tilt of the cyclohexyl ring out of the coordination plane and a PCP carbon that is coordinated to the metal in an axial position. This geometry is indeed the expected outcome from two concerted elimination-addition reactions as shown in Scheme 5.4, and it further supports previous suggestions that reductive eliminations goes with configurational retention.[22] Figure 5.3 also visualises the interaction between the methyl carbon and the metal centre in compound **30**, as already confirmed by the negative ^{1}H-NMR shifts of the methyl protons. This interaction, with an interatomic distance of 2.45 Å, gives rise to bond angles around the α-carbon that strongly deviates from the ideal tetrahedral geometry.



Scheme 5.4. Proposed pathway for formation of **30**.

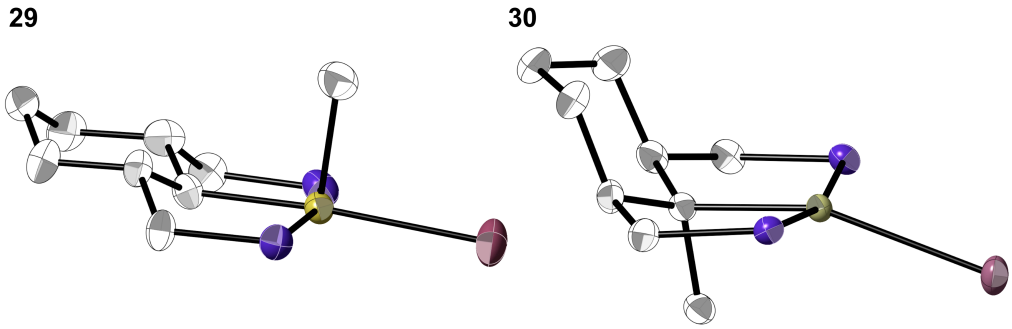


Figure 5.3. Side-views of the molecular structures of **29** and **30** at 30% probability level. Hydrogen atoms and substituents on phosphorus are omitted for clarity.

5.3. Concluding remarks

New cyclohexyl-based $PC_{sp3}P$ iridium(I) and iridium(III) carbonyl complexes have been synthesised and fully characterised. Spectroscopic and crystallographic data is comparable to analogous $PC_{sp2}P$ complexes with aromatic backbones. A $PC_{sp3}P$ iridium(I) terminal nitrogen complex undergoes facile oxidative addition of methyl iodide, although the product undergoes an unusual isomerisation resulting in a net methyl migration from the metal to the ligand backbone, supposedly through a reductive elimination-oxidative addition pathway. The possibility to run kinetic experiments of this reaction should be explored, to obtain further insight into the mechanism of this transformation. It would also be of interest to investigate the reactivity of the $PC_{sp3}P$ iridium(I) terminal nitrogen complex with *e.g.* phenyl iodide.

5.4 References

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Aliphatic pincer-type POCOP ligands and their complexation behaviour with iridium: Crystal structure of an iridium(III) phosphinite complex

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ABSTRACT

Reaction of 2 equivalents of 1,3-bis-(di-*tert*-butylphosphinito)-2-methyl-propane (**1a**) with $[Ir(COD)Cl]_2$ affords the first aliphatic diphosphinite PCP pincer complex with iridium, Ir(H){(t-Bu_2POCH_2)$_2$C(Me)}Cl (**2**). The poor yield of **2** is partly explained by the formation of a di-nuclear byproduct $[IrCl(COD)]_2(\mu_2$-{(t-Bu_2POCH_2)$_2$CH(Me)}) (**3**). Reaction of 1,3-bis-(di-*iso*-propylphosphinito)-2-methyl-propane (**1b**) under the same condition does not give any cyclometallation, and reaction with $IrCl_3{\cdot}H_2O$ in DMF leads to complete decomposition of the pincer ligand under the formation of Ir(H)(i-$Pr_2P(OH)$)$_3$(CO) (**4**), underpinning the comparatively low thermal stability of aliphatic phosphinite pincer systems.

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1. Introduction

Since the pioneering work of Shaw [1], aliphatic PCP pincer complexes of the late transition metals have drawn limited attention compared to their aromatic counterparts [2]. Nonetheless, more recent work has clearly shown that the hybridisation of the carbon coordinated to the metal highly influences the reactivity of the pincer complex [3–5].

Electronic and steric properties of the pincer complex can be further adjusted by varying the principal structure of the PCP ligand, and the replacement of phosphines for phosphinites acts in both these aspects. These phosphinite ligands (often denoted POCOP ligands) are generally more conveniently prepared than their PCP counterparts and with higher yields. Such POCOP complexes have been reported with aromatic backbones and have found applications in e.g. the palladium catalysed Heck reaction [6] and in iridium catalysed dehydrogenation reactions of ammonia borane [7] along with transfer dehydrogenation of alkanes [8] and primary amines [9].

Examples of POCOP complexes based on aliphatic backbones are less common and mainly involve first row transition metals [10,11]. Previous work in our group has shown that whereas a cyclohexyl based diphosphine $PC_{sp3}P$ ligand readily cyclometallates with palladium, platinum and iridium, the corresponding diphosphinite gives non-cyclometallated mono- or di-nuclear complexes with palladium and platinum [12]; with iridium the phosphinite ligand undergoes dehydrogenation upon coordination to the metal, resulting in a pincer complex with an aromatic backbone [13]. We therefore decided to investigate the cyclometallating properties of aliphatic phosphinite ligands lacking the possibility for aromatisation.

In this paper we report the synthesis of the first aliphatic diphosphinite PCP pincer complex with iridium, Ir(H){(t-Bu_2POCH_2)$_2$C(Me)}Cl (**2**). We also report the formation of the dinuclear compound **3**, again showing the decreased propensity for aliphatic phosphinites to cyclometallate. Finally, we report the product of a thermal decomposition of a phosphinite ligand involving cleavage of the C–O bond.

2. Experimental

2.1. General considerations

All compounds were prepared in an inert atmosphere of either nitrogen or argon, in a glove box or using high vacuum techniques. Non-chlorinated solvents were distilled from sodium/benzophenone ketyl and chlorinated solvents were distilled from CaH_2, using high vacuum techniques. Deuterated solvents and commercially available reagents were purchased from Sigma Aldrich and Acros Organics and used as received inside a glove box. Chemical shifts are given in ppm downfield from TMS (^{1}H- and ^{13}C NMR) using residual solvent peaks or H_3PO_4 (δ 0) as reference. Multiplicities are abbreviated as follows: (s) singlet, (d) doublet, (t) triplet, (m) multiplet, (v) virtual. Elemental analyses were performed by H.

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Table 1
Crystal data for compounds **2**–**4**.

	2	**3**	**4**
Formula	$C_{20}H_{44}ClIrO_2P_2$	$C_{36}H_{68}Cl_2Ir_2O_2P_2$	$C_{19}H_{46}IrO_4P_3$
fw	606.18	1050.21	623.70
Space group	$P2_1/c$	*Pnma*	$P2_1/n$
a (Å)	13.3180(4)	16.229(5)	9.0172(4)
b (Å)	12.3347(3)	13.514(5)	16.7256(7)
c (Å)	17.1377(4)	18.200(5)	17.5259(11)
β (°)	99.099(3)	90.00	90.00
V (Å^3)	2779.85(13)	3992(2)	2643.2(2)
Z	4	4	4
D_{calcd} (g cm^{-3})	1.539	1.762	1.557
μ (mm^{-1})	5.030	6.905	5.252
θ range (°)	2.39–32.99	2.51–25.02	2.32–33.01
Number of reflections collected	27382	21940	24436
Number of unique reflections	9493	3668	9174
$R(F)$ ($I > 2\sigma(I)$)[a]	0.0274	0.0315	0.0804
$wR_2(F^2)$ (all data)[b]	0.0634	0.0748	0.2416
S[c]	0.979	1.170	1.306
R_{int}	0.0332	0.0421	0.0628

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.
[b] $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|)^2]^{1/2}$.
[c] $S = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|)^2]^{1/2}$.

Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany. IR spectra were recorded on a Bruker Alpha spectrometer, with diamond ATR–FTIR detection.

2.2. Preparation of 1,3-bis-(di-tert-butylphosphinito)-2-methylpropane (**1a**)

To a solution of 2-methyl-1,3-propanediol (0.50 g, 5.55 mmol) in THF (10 mL) KH (470 mg, 11.2 mmol) was added and the reaction was left to stir at room temperature over night. ClP^tBu_2 (2.01 g, 11.1 mmol) was added and the mixture was stirred for an additional 20 h. The solvent was removed *in vacuo* and replaced with Et_2O. The resulting suspension was filtered through celite and concentrated in vacuo, giving **1a** as an essentially pure colourless oil that was used without further purification (Yield: 1.75 g, 84%). ^{1}H NMR (C_6D_6): δ 3.84–3.79 (m, 2H, OCH_2), 3.72–3.67 (m, 2H, OCH_2), 2.05 (oct, $^3J_{PH}$ = 6.4 Hz, 1H, $CH_3CH(CH_2)_2$), 1.13 (d, $^3J_{PH}$ = 11.2 Hz, 18H, 2 (CH_3)$_3$C), 1.12 (d, $^3J_{PH}$ = 11.1 Hz, 18H, 2 (CH_3)$_3$C), 0.94 (d, $^1J_{HH}$ = 6.9 Hz, 3H, CH_3CH). ^{13}C {^{1}H} NMR (C_6D_6) = δ 75.9 (d, J_{PC} = 20.9 Hz, CH_2O), 38.0 (t, J_{PC} = 7.5 Hz, CH_3CH), 35.4 (d, J_{PC} = 26.2 Hz, (CH_3)$_3$C), 35.2 (d, J_{PC} = 25.7 Hz, (CH_3)$_3$C), 27.7 (d, J_{PC} = 15.5 Hz, (CH_3)$_3$C), 27.6 (d, J_{PC} = 15.5 Hz, (CH_3)$_3$C), 14.6 (s, CH_3CH). ^{31}P {^{1}H} NMR (C_6D_6): δ 161.5 (s).

2.3. Preparation of 1,3-bis-(di-iso-propylphosphinito)-2-methylpropane (**1b**)

A hexane solution of *n*-BuLi (2.5 M, 1.60 mL, 4.00 mmol) was added to an ice-cooled and stirred solution of 2-methyl-1,3-propanediol (0.148 mL, 1.66 mmol) in THF (8 mL). After stirring for 2 h at room temperature, a solution of ClP^iPr_2 (0.557 mL, 3.33 mmol) in THF (1.5 mL) was added at 0 °C and the reaction was left to stir over night. The reaction was concentrated in vacuo, extracted with toluene (15 mL) and filtered through a pad of celite. Removal of solvent gave **1b** as an essentially pure pale yellow oil, that was used without further purification (Yield: 0.490 g, 91%). ^{1}H NMR (C_6D_6): δ 3.79–3.73 (m, 2H, OCH_2), 3.68–3.62 (m, 2H, OCH_2), 2.02 (oct, $^3J_{PH}$ = 6.4 Hz, 1H, $CH_3CH(CH_2)_2$), 1.69–1.59 (m, 4H, $CH(CH_3)_2$), 1.16–1.11 (m, 12H, 2 (CH_3)$_2$CH), 1.05–0.98 (m, 12H, 2 (CH_3)$_2$CH), 0.93 (d, $^1J_{HH}$ = 6.9 Hz, 3H, CH_3CH). ^{13}C {^{1}H} NMR (C_6D_6): δ 74.4 (d, J_{PC} = 19.5 Hz, 2 CH_2O), 37.9 (t, J_{PC} = 7.2 Hz, $CH_3CH(CH_2)_2$), 28.3 (d, J_{PC} = 17.9 Hz, 4 (CH_3)$_2$CH), 18.2 (d, J_{PC} = 5.0 Hz, (CH_3)$_2$CH), 18.0 (d, J_{PC} = 5.1 Hz, (CH_3)$_2$CH), 17.1 (d, J_{PC} = 1.4 Hz, (CH_3)$_2$CH), 17.0 (d, J_{PC} = 1.3 Hz, (CH_3)$_2$CH), 14.1 (s, CH_3CH). ^{31}P {^{1}H} NMR (C_6D_6): δ 152.4 (s).

2.4. Preparation of Ir(H){(t-Bu$_2$POCH$_2$)$_2$C(Me)}Cl (**2**) and [IrCl(COD)]$_2$(μ_2-{(t-Bu$_2$POCH$_2$)$_2$CH(Me)}) (**3**)

Inside a nitrogen atmosphere glovebox, [Ir(COD)Cl]$_2$ (79 mg, 0.12 mmol) was added to a solution of **1a** (90 mg, 0.24 mmol) in CH_2Cl_2 (1 mL) in a J. Young NMR tube. The tube was evacuated under high vacuum and H_2 was added at −196 °C. The reaction mixture was heated to 80 °C over night and after standing at RT for 24 h, orange–red crystals of **3** could be collected. (Yield: 0.011 g, 8.7%). ^{1}H NMR (C_6D_6): δ 5.35–5.27 (m, 4H C*H*=C*H*), 3.87–3.82 (m, 2H, OCH_2), 3.70–3.66 (m, 2H, OCH_2), 3.62–3.57 (m, 4H C*H*=C*H*), 2.21–2.12 (m, 4H, 2 CH=CH–CH_2), 2.04–1.98 (m, 4H, 2 CH=CH–CH_2), 1.94–1.90 (m, 1H, $CH_3CH(CH_2)_2$), 1.57–1.48 (m, 8H, 4 CH=CH–CH_2), 1.50 (s, 18 H, 2 (CH_3)$_3$C), 1.47 (s, 18 H, 2 (CH_3)$_3$C), 0.74 (d, $^1J_{HH}$ = 6.9 Hz, 3H, CH_3CH). ^{31}P {^{1}H} NMR (C_6D_6): δ 142.7 (s). *Anal.* Calcd. for $C_{36}H_{68}Cl_2Ir_2O_2P_2$: C, 41.17; H, 6.53. Found: C, 40.77; H, 6.80%.

The remaining reaction mixture was filtered through celite, concentrated in vacuo and re-dissolved in hexane, before a second filtration through celite. Reduction of solvent and cooling to −28 °C gave an orange precipitate of **2** (Yield: 35 mg, 24%). ^{1}H NMR (C_6D_6): δ 3.28–3.19 (m, 2H, OCH_2), 3.04–3.00 (m, 2H, OCH_2), 1.50 (vt, J_{HP} = 14.0 Hz, 18 H, 2 (CH_3)$_3$C), 1.29 (vt, J_{HP} = 13.5 Hz, 18 H, 2 (CH_3)$_3$C), 1.13 (s, 3H, $CH_3C(CH_2)_2$), −37.4 (t, J_{PH} = 13.4 Hz, 1H, Ir-*H*). ^{13}C {^{1}H} NMR (toluene-d8): δ 90.0 (vt, J_{PC} = 6.7 Hz, OCH_2), 46.6 (vt, J_{PC} = 24.1 Hz, $C(CH_3)_3$), 45.8 (vt, J_{PC} = 26.7 Hz, $C(CH_3)_3$), 39.0 (d, $^2J_{CH}$ = 5.5 Hz, Ir-*C*), 33.8 (vt, J_{PC} = 5.7 Hz, (CH_3)$_3$C), 33.4 (vt, J_{PC} = 6.2 Hz, (CH_3)$_3$C), 32.7 (s, CH_3C). ^{31}P {^{1}H} NMR (C_6D_6): δ 180.0 (d, J_{PH} = 13.4).

2.5. Preparation of Ir(H)(i-Pr$_2$P(OH))$_3$(CO) (**4**)

$IrCl_3 \cdot H_2O$ (0.01 g, 0.03 mmol) and **1b** (0.02 g, 0.062 mmol) was mixed in *N,N*-dimethylformamide (DMF, 0.6 mL) in a J. Young NMR-tube. The reaction was heated to 160 °C for 48 h, and upon cooling to RT **4** was obtained as an off-white, sparingly soluble material that was partly redissolved in methanol. Crystals for X-ray analysis was obtained upon standing over night. IR: υ_{CO} = 1722 cm^{-1}.

2.6. X-ray crystallography

Crystal data and details about data collection are given in Table 1. The intensity data sets of compounds **2**–**4** were collected at 293 K with an Oxford Diffraction Xcalibur 3 system using ω-scans and Mo Kα radiation (λ = 0.71073 Å) [14]. The data were extracted and integrated using Crysalis RED [15]. The structures were solved by direct methods and refined by full-matrix least-squares calculations on F^2 (all data) using SHELXTL 5.1 [16]. Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to parent sites, using a riding model. Complex **3** crystallises on a mirror plane and since this is not compatible with the C1-symmetry of the ligand, the methyl group in the aliphatic chain is disordered around the mirror plane. This was modelled with two methyl groups with an occupancy of one half. Constraining C10–C11 distances with SADI in SHELXL still gives unreasonably long values and the quantitative results from this structure should be treated with caution. The thermal ellipsoids of some atoms were constrained.

3. Results and discussion

Deprotonation of 2-methyl-1,3-propanediol and subsequent reaction with a chlorodialkylphosphine gave ligands **1a** and **1b**. These were characterised by NMR spectroscopy and used without further purification. Reaction of ligand **1a** in a closed vessel in dichloromethane with $[Ir(COD)Cl]_2$ at 80 °C gave the aliphatic iridium diphosphinite pincer complex **2**, along with a crystalline by-product, cf. Scheme 1. Compound **2** is the first aliphatic pincer phosphinite complex of iridium and it was characterised by NMR spectroscopy and X-ray diffraction. The ^{31}P NMR spectra exhibits a doublet at 180.0 ppm, due to coupling with the hydride, since the broadband proton decoupling does not reach into the hydride region; in ^{1}H NMR spectroscopy the hydride is observed as a triplet at −37.4 ppm. This is slightly downfield from values observed for similar complexes which lie between −41.4 and −44.7 ppm [1b,8b,13]. The *tert*-butyl methyl-protons are displayed as virtual triplets at 1.50 and 1.29 ppm showing the inequivalence of the two sides of the coordination plane (*vide infra*). The compound is quite sensitive and despite several attempts we were unable to obtain a satisfactory combustion analysis of the compound. Still, it is pure as judged by the NMR-spectra. The by-product was subjected to X-ray-analysis and was shown to be a di-nuclear COD complex, **3**. It was further characterised by NMR spectroscopy and elemental analysis. Compounds similar to **3** are known from the literature [17], although not with any acyclic pincer ligands. A slight increase in yield of **2** in favour of **3** has been observed by running the reaction under an atmosphere of hydrogen, which is likely to facilitate the dissociation of cyclooctadiene, although similar complexation reactions have also been reported to take place under an atmosphere of nitrogen or argon [1b,3]. It is clear, however, that with the current and similar systems removal of cyclooctadiene is not straightforward and we were not able to find conditions where **2** is the only product of this reaction. Another factor behind the low yield of **2** is believed to be a metal mediated ligand decomposition (*vide infra*), giving rise to a range of unassigned shifts in the ^{31}P {^{1}H} NMR spectra. This decomposition is more prominent at higher temperatures, but on the other hand the C_{sp3}-H activation of the cyclometallation was not observed below 80 °C. Perspective views of the molecular structures of compounds **2** and **3** are shown in Figs. 1 and 2, respectively, including selected bond angles and distances. As seen from Fig. 1, compound **2** exhibits a distorted square-pyramidal geometry with a hydride in the axial position. It co-crystallises with a molecule of benzene. The location of the hydride is supported by its high field chemical shift

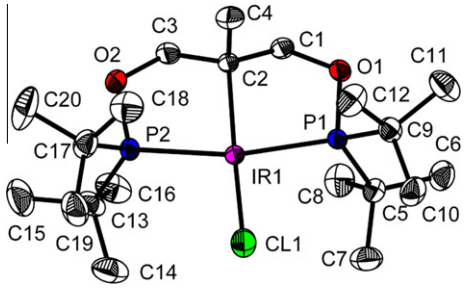


Fig. 1. DIAMOND [18] drawing of compound **2** at the 30% probability level. Hydrogen atoms and solvent benzene are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviation: Ir1–C2 2.108(3), Ir1–Cl1 2.413(1), Ir1–P1 2.2916(8), Ir1–P2 2.2844(9), P1–Ir1–P2 162.65(3).

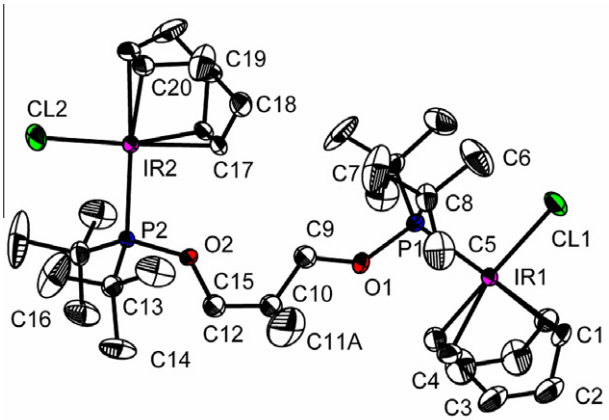
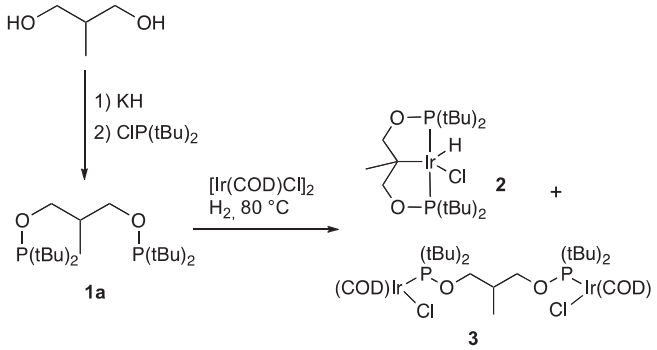
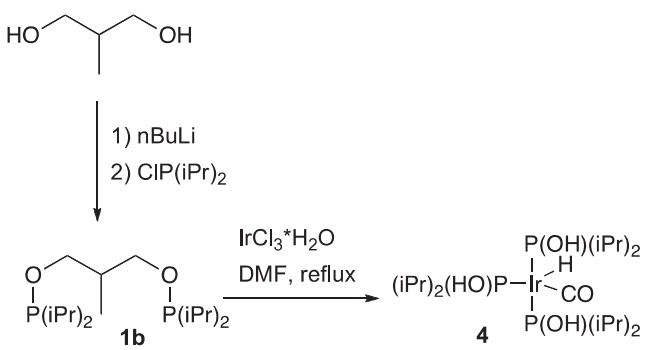


Fig. 2. DIAMOND drawing of compound **3** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviation: Ir1–C1 2.199(5), Ir1–C4 2.114(6), Ir1–P1 2.337(2), Ir1–Cl1 2.354(2), Cl1–Ir1–P1 95.44(7), C1–Ir1–C4 79.8(2).



Scheme 1.



Scheme 2.

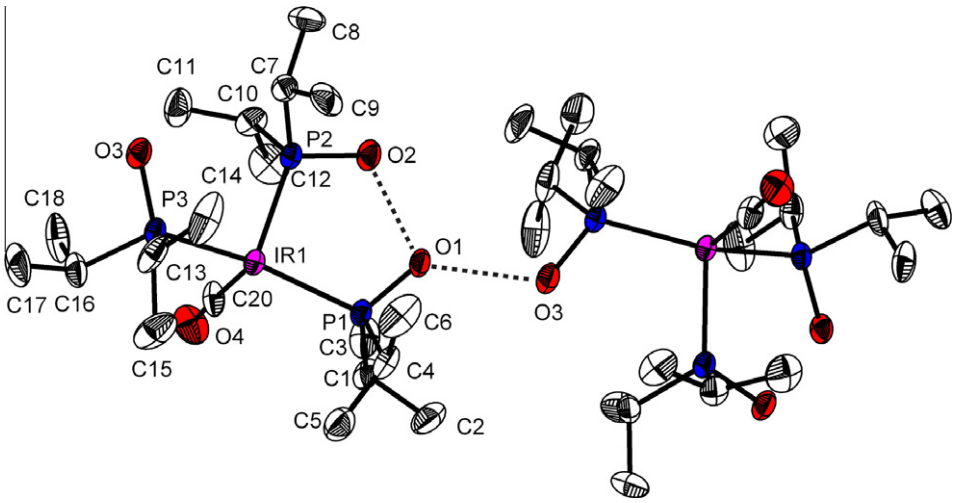


Fig. 3. DIAMOND drawing of compound **4** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviation: Ir1–C20 1.93(1), C20–O4 1.11(2), Ir1–P1 2.359(3), Ir1–P2 2.380(3), Ir1–P3 2.342(3), P1–O1 1.558(8), P2–O2 1.603(8), P3–O3 1.594(9), P1–Ir1–P3 155.9(1), P1–Ir1–P2 94.4(1), P2–Ir1–P3 100.3(1), P2–Ir1–C20 101.0(5), P1–Ir1–C20 97.9(4), P3–Ir1–C20 98.0(3).

and the fact that the angle Cl1–Ir1–C2 is 161° and bent towards the side where the methyl group C4 is residing; this indicates a transoid configuration of the hydride, highlighting the fact that the two sides of the coordination plane are inequivalent giving two sets of *tert*-butyl groups. The transoid configuration has previously been observed for the cyclohexyl PCP addition to iridium [13] and is expected as a result of a concerted oxidative addition process via a C–H σ-complex.

Reacting ligand **1b** under the same conditions as in Scheme 1 did not afford the ^{i}Pr-substituted analogue of **2**, but a range of uncharacterised, phosphorus containing compounds were obtained. Probably, the less bulky substituents on the phosphorus facilitate the ligand decomposition. The instability of the aliphatic diphosphinites is further illustrated by the reaction between **1b** and $IrCl_3{\cdot}H_2O$ in DMF, resulting in compound **4**, where the ligand backbone has been fully decomposed, forming *i*-$Pr_2P(OH)$ units (Scheme 2). These reaction conditions have been previously reported for cyclometallation of aliphatic PCP ligands with iridium, along with CO donation from the solvent [19]. However, in this case no formation of the analogous compounds Ir(CO){(*i*-$Pr_2POCH_2)_2C(Me)$}Cl_2 or Ir(H)(CO){(*i*-$Pr_2POCH_2)_2C(Me)$}Cl could be detected, by means of $^{31}P\{^{1}H\}$ NMR spectroscopy. Ligand **1a** seemingly reacts in the same fashion as **1b**, but due to low solubility of the so formed amorphous solid, characterisation by NMR spectroscopy was not achieved, nor was recrystallisation to obtain material suitable for X-ray crystallography. The same solubility behaviour is observed for **4**, and attempts to achieve useful NMR spectra failed. Thus, the compound was characterised by means of single crystal X-ray diffraction. The perspective view of the molecular structure is shown in Fig. 3, including selected bond angles and distances. We assign the structure as an iridium(I) hydride with three coordinated phosphinites. This assignment is based on a number of points. The P–O distances are in better agreement with a P(III)–O than a P(V)=O bond although one of the bonds is on the short side [20]. The trigonal bipyramidal structure (assuming the hydride occupies the fifth position) is typical for iridium(I) whereas iridium(III) often is square-pyramidal when five-coordinate. The strongest argument for our assignment, though, is the presence of an inter- and intramolecular network of hydrogen bonds in the sequence O2...O1...O3 with distances 2.488 and 2.581 Å, respectively. The low ν(C–O) also speaks in favour of an iridium(I) hydride formulation, since such a low stretching frequency requires an electron rich metal centre.

Based on the structure of **4** it also seems reasonable to believe that the thermal instability of ligands **1a** and **1b** reside in the C–O bond that is cleaved during the formation of **4**. It should be noted that this decomposition of the ligand is metal assisted; in the absence of metal, ligand **1a** is thermally stable in THF for several hours at 200 °C. This metal assistance is probably transmitted through the P-coordination, which polarises the C–O bond, making it more susceptible to attack by adventitious water.

4. Conclusions

Reaction of 2 equivalents of 1,3-bis-(di-*tert*-butylphosphinito)-2-methyl-propane (**1a**) with $[Ir(COD)Cl]_2$ affords the first aliphatic diphosphinite PCP pincer complex with iridium, Ir(H){(t-$Bu_2POCH_2)_2C(Me)$}Cl (**2**). The poor yield of **2** is partly explained by the formation of a di-nuclear byproduct $[IrCl(COD)]_2(\mu_2$-{(t-$Bu_2POCH_2)_2CH(Me)$}) (**3**). Reaction of 1,3-bis-(di-*iso*-propylphosphinito)-2-methyl-propane (**1b**) under the same condition does not give any cyclometallation, and reaction with $IrCl_3{\cdot}H_2O$ in DMF leads to complete decomposition of the pincer ligand under the formation of Ir(H)(*i*-$Pr_2P(OH))_3(CO)$ (**4**), underpinning the comparatively low thermal stability of aliphatic phosphinite pincer systems.

Acknowledgements

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Appendix A. Supplementary meterial

CCDC 814752–814754 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.09.034.

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Synthesis and characterisation of new $PC_{sp3}P$-supported nickel complexes

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ABSTRACT

The coordination behaviour of the aliphatic pincer ligand *cis*-1,3-bis-((di-*tert*-butylphosphino)methyl) cyclohexane with $NiCl_2$ and $NiBr_2$ was studied. Reflux in toluene afforded cyclometalated, tridentate $PC_{sp3}P$ pincer complexes, that were characterised by elemental analysis and NMR spectroscopy; the solid state structures were determined by X-ray diffraction showing an unusually long Ni–Br bond in the bromo complex. A preliminary account of their reactivity is reported and they were found to be unreactive towards base and hydride sources and to be poor catalysts in Kumada coupling reactions.

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1. Introduction

Over the last 30 years, pincer metal complexes have earned recognition as potent and versatile compounds in homogeneous catalysis [1]. However, replacement of precious metals with cheaper and more abundant first row transition metal alternatives remains one of the great challenges for the field [2]. One problem in this aspect might be the reluctance of 3d metals to undergo 2-electron oxidative addition and reductive elimination reactions. In combination with the weaker M–C bonds of the 3d metals this usually makes C–H activation and cyclometalation reactions more difficult. On the other hand, in the case of nickel complexes, 1-electron processes are more frequently occurring, opening up for catalytic pathways that may not be accessible for heavier analogues [3]. Recent advances of nickel pincer complexes in the literature involve various cross-coupling reactions [3,4], direct alkylations [5] alkene hydrogenations [6], hydroaminations [7], hydrosilylations [8] and reduction of carbon dioxide to methanol [9].

Amongst the published work on PCP pincer complexes, pincer ligands with aromatic backbones are in vast majority and this is also true for nickel complexes, although a number of aliphatic nickel pincer complexes have been reported [10,11]. In general, there are several known examples where the nature of the coordinating carbon alters the reactivity of a pincer complex, illustrating how a strongly σ-donating C_{sp3}-hybridised ligand can be a useful tool for electrochemical tuning [12], and this has opened up N–H oxidative addition pathways unavailable with traditional aromatic pincer ligands [13]. We have previously reported on the synthesis of the cyclohexyl-based $PC_{sp3}P$ ligand *cis*-1,3-bis-((di-*tert*-butylphosphino)methyl)cyclohexane (**1**), and we and others have shown its ability to cyclometalate with second and third row transition metals, such as palladium [14], platinum [15], rhodium [16] and iridium [17]. Here we report on the first complexation of this ligand with nickel, together with some reactivity data of these $PC_{sp3}P$-coordinated complexes.

2. Experimental section

2.1. General considerations

All manipulations were performed under a nitrogen or argon atmosphere using standard Schlenk or glovebox techniques, except where noted. Solvents were purified by vacuum distillation from sodium/benzophenone ketyl radical. The ligand *cis*-1,3-bis-((di-*tert*-butylphosphino)methyl)cyclohexane (**1**) was synthesized according to previously reported procedures [14]. All other chemicals where purchased from Acros, Alfa Aesar or Sigma Aldrich and used as received. ^{1}H, ^{13}C and ^{31}P NMR spectroscopy experiments were recorded on a Varian Unity INOVA 500 spectrometer, operating at

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499.76 MHz (^{1}H). Chemical shifts are given in ppm downfield from TMS, using residual solvent peaks (^{1}H and ^{13}C) or H_3PO_4 (^{31}P) as reference. Multiplicities are abbreviated as follows: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet, (v) virtual. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany. XRD-quality crystals of **2a** and **2b** were obtained through recrystallisation from pentane. Intensity data were collected with an Oxford Diffraction Excalibur 3 system, using ω-scans and Mo Kα ($\lambda = 0.71073$ Å) radiation [18]. The data were extracted and integrated using Crysalis RED [19]. The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL5.1 [20]. Molecular graphics were generated using CrystalMaker 8.3.5 [21]. All crystallographic data are available in CIF format (CCDC reference numbers 978220-21).

2.2. Preparation of trans-[NiCl{cis-1,3-bis-((di-tert-butylphosphino)methyl)}cyclo-hexane] (**2a**)

DMAP (15.2 mg, 0.125 mmol) was added to a stirred mixture of the *cis*-1,3-bis-[(di-*tert*-butylphosphino)methyl]cyclohexane ligand (50.0 mg, 0.125 mmol) and anhydrous $NiCl_2$ (48.5 mg, 0.374 mmol) in toluene (5 mL). The reaction mixture was heated to reflux for 24 h under a nitrogen atmosphere. The cooled suspension was concentrated *in vacuo*, dispersed in ethyl acetate and filtered in air through a pad of silica. Removal of the solvent afforded **2a** as a yellow crystalline powder. Yield: 36.9 mg (69% based on **1**). ^{1}H NMR (C_6D_6): δ 1.82–1.77 (m, Cy, 2H), 1.74–1.70 (m, Cy, 1H), 1.69–1.63 (m, PCH_2CH, 2H), 1.55–1.45 (m, Cy, 2H), 1.48 (vt, J = 13.0 Hz, ^{t}Bu, 18H), 1.45 (vt, J = 13.0 Hz, ^{t}Bu, 18H), 1.27 (t, J_{PH} = 11.0 Hz, *H*C–Ni), 1.29–1.24 (m, Cy, 1H), 1.11–1.03 (m, PCH_2CH, 2H), 0.82–0.74 (m, Cy, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ 53.3 (t, $^2J_{PC}$ = 11 Hz, HC–Ni), 49.5 (vt, J_{PC} = 21 Hz, *C*H), 35.7 (vt, J_{PC} = 19 Hz, CH*C*H_2CH_2), 35.2 (vt, J_{PC} = 11 Hz, *C*$(CH_3)_3$), 34.6 (vt, J_{PC} = 14 Hz, *C*$(CH_3)_3$), 32.3 (vt, J_{PC} = 18 Hz, P–*C*H_2), 30.4 (vt, J_{PC} = 5.0 Hz, C$(CH_3)_3$), 29.6 (vt, J_{PC} = 4.0 Hz, C$(CH_3)_3$), 27.2 (s, $CH_2CH_2CH_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 61.79 (s). Anal. Calcd for $C_{24}H_{49}ClNiP_2$ (493.74): C, 58.38; H, 10.00. Found: C, 58.24; H, 10.12.

2.3. Preparation of trans-[NiBr{cis-1,3-bis-((di-tert-butylphosphino)methyl)}-cyclohexane] (**2b**)

The compound was synthesized according to the same procedure and in the same scale as the corresponding chloride complex (**2a**). Yield: 42.9 mg (71% based on **1**). ^{1}H NMR (C_6D_6): δ 1.83–1.79 (m, Cy, 2H), 1.73–1.67 (m, Cy, 1H and m, PCH_2CH, 2H), 1.55–1.50 (m, Cy, 2H), 1.49 (vt, J = 12.5 Hz, ^{t}Bu, 18H), 1.46 (vt, J = 12.0 Hz, ^{t}Bu, 18H), 1.30–1.22 (m, Cy, 1H), 1.27 (t, J_{PH} = 11.0 Hz, *H*C–Ni), 1.11–1.05 (m, PCH_2CH, 2H), 0.81–0.73 (m, Cy, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ 56.3 (t, $^2J_{PC}$ = 11 Hz, HC–Ni), 49.3 (vt, J_{PC} = 26 Hz, *C*H), 35.7 (vt, J_{PC} = 19 Hz, CH*C*H_2CH_2), 35.5 (vt, J_{PC} = 11 Hz, *C*$(CH_3)_3$), 35.1 (vt, J_{PC} = 14 Hz, *C*$(CH_3)_3$), 32.8 (vt, J_{PC} = 18 Hz, P–*C*H_2), 30.7 (vt, J_{PC} = 4.7 Hz, C$(CH_3)_3$), 29.7 (vt, J_{PC} = 4.5 Hz, C$(CH_3)_3$), 27.2 (s, $CH_2CH_2CH_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 61.47 (s). Anal. Calcd for $C_{24}H_{49}BrNiP_2$ (493.74): C, 53.56; H, 9.18. Found: C, 53.44; H, 9.11.

2.4. General procedure for attempted Kumada coupling

RMgCl (0.27 mmol, 3 M THF solution) was added to a solution of RX (0.26 mmol) and the catalyst (3 mol%) in THF (0.5 mL). The mixture was heated to 120 °C for the desired time. A sample of the reaction was then withdrawn, quenched with 0.5 M HCl and diluted with THF. The organic phase was dried over $MgSO_4$ and filtered, and the resultant solution was analyzed by GC.

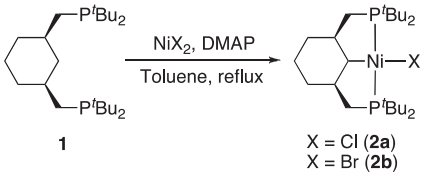
3. Results and discussion

The straightforward synthesis of pincer complexes **2a** and **2b** is illustrated in Scheme 1, following the synthetic protocol of Zargarian and coworkers for the non-cyclic 1,5-bis(phosphinito) pentane ligand [10b], but increasing the amount of NiX_2 from 2 to 3 equivalents.

The products were isolated in moderate to good yields, and no phosphorus containing species apart from the products could be observed in the crude reaction mixture by means of ^{31}P NMR spectroscopy. Thus, there is no indication that byproducts such as previously reported binuclear 16-atom ring chelate complexes or mononuclear complexes with *cis*-coordination to the P atoms are formed [22]. This however does not rule out the formation of such 16-atom cyclic dimers, since these compounds are known to be highly fluxional and sometimes low-soluble which makes them hard to detect by NMR spectroscopy. The somewhat limited yields could also be accounted for by formation of phosphorus containing nickel salts, but the solid residues formed during the reactions are highly insoluble and probably NMR silent, and any attempted characterization has been unsuccessful. The group of Zargarian has reported that nickelation of the 1,5-bis(phosphino)pentane ligand gives a byproduct with low solubility identified as a zwitterionic complex with an anionic tetrahedral nickel centre and a monocoordinated pincer ligand with one protonated non-coordinated phosphine. The protonation is suggested to take place by *in situ* generated HX, which supports their and our observation that addition of DMAP or other bases improves the yield for the complexation reaction [10a].

The ^{31}P{^{1}H} NMR spectra of **2a** and **2b** display a sharp singlet resonance that confirms the equivalence of the phosphorus nuclei in agreement with an expected *trans* geometry; this is also consistent with the appearance of the ^{t}Bu protons as virtual triplets in ^{1}H NMR spectra. The characteristic pattern of virtual triplets is also observed in the ^{13}C{^{1}H} NMR spectra, where all nuclei except the most remote methylene carbons of the cyclohexyl ring display coupling to phosphorus.

To confirm the cyclometalated structures, crystals of both complexes were subjected to an X-ray diffraction experiment. The details of the crystal structure solution and refinement are given in Table 1. The molecular structures, including selected bond distances and angles, of compound **2a** and **2b** are shown in Figs. 1 and 2, respectively. As expected from the NMR spectroscopy results, the *cis*-1,3-bis-((di-*tert*-butylphosphino)methyl)cyclohexane ligand is coordinated meridionally with the P atoms positioned *trans* to each other. The Ni atom adopts a distorted square planar geometry, with P(1)–Ni–P(2) angles around 170°. The cyclohexyl ring has a chair conformation and the three coordinated positions are all equatorially oriented in agreement with previous observations [14,15]. The Ni–Cl bond in **2a** is longer than in the analogous aromatic compounds [23], and very close to the reported bond length for a similar non-cyclic $^{tBu}PC_{sp3}P$ nickel complex [10a], underpinning the greater trans-influence from a sp^3-hybridized coordinated carbon compared to its sp^2-hybridized aromatic counterpart. However, the Ni–Br bond in **2b** (2.4303(4) Å) is significantly longer than Ni–Br



Scheme 1. Synthesis of **2a** and **2b**.

Table 1
Crystal data and collection and refinement details for compounds **2a** and **2b**.

	2a	**2b**
Formula	$C_{24}H_{49}ClNiP_2$	$C_{24}H_{49}BrNiP_2$
Fw	493.71	538.16
Space group	*Pna2₁*	*P2₁/c*
a/Å	22.9163(5)	11.4024(2)
b/Å	8.4324(3)	15.8824(3)
c/Å	14.4279(4)	15.6999(4)
α/deg	90	90
β/deg	90	98.245(2)
γ/deg	90	90
V/Å^3	2788.04	2813.83
Z	4	4
D_{calcd}/g cm^{-3}	1.176	1.270
μ/mm^{-1}	0.915	2.231
θ/range/deg	2.57–28.88	2.44–28.97
No. reflns collected	46,663	61,313
No. of unique reflns	6821	6895
$R(F)$ $(I > 2\sigma(I))$[a]	0.0563	0.0450
$wR2(F^2)$ (all data)[b]	0.1242	0.1005
S[c]	1.095	1.254
R_{int}	0.0975	0.0665

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.

[b] $wR2 = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|)^2]^{1/2}$.

[c] $S = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|)^2]^{1/2}$.

bonds in both aromatic (2.3290–2.3601 Å) [10d,24,25] and aliphatic (2.3712–2.3866 Å) [10a,10d] PCP nickel bromide complexes in literature. It approaches the bond length for the aromatic NCN nickel bromide complexes reported by van Koten and co-workers (NCN = C_6H_3-2,6-{$CH_2N(^iPr)Me$}$_2$ and C_6H_3-2,6-{$CH_2N(^tBu)Me$}$_2$, Ni–Br = 2.437(2) Å and 2.4459(30) Å) [26], and thus is one of the longest Ni(II)–Br distances reported to this date. The reason for this deviation is not obvious to us especially since the trans influence of the cyclohexyl ring in **2a** is no different from other sp^3-hybridized ligands. It can be noted that the position of the

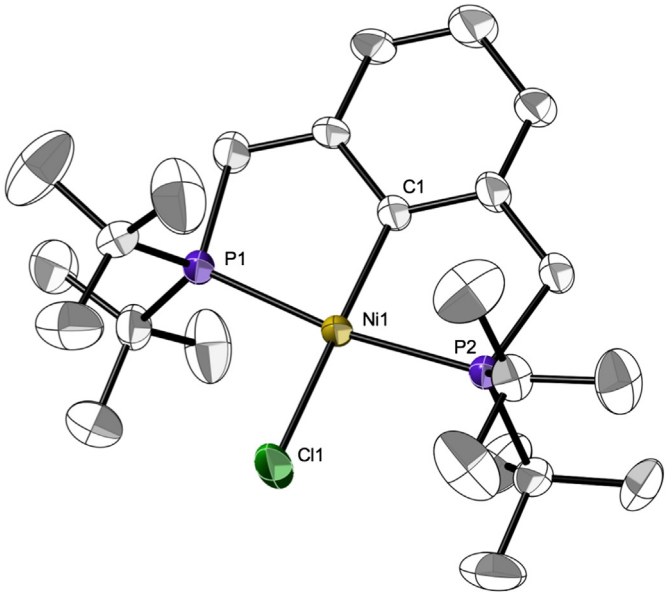


Fig. 1. Molecular structure of **2a** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.990(4), Ni1–P1 = 2.2346(11), Ni1–P2 = 2.2251(11), Ni1–Cl1 = 2.2497(14), C1–Ni1–Cl1 = 178.81(18), P1–Ni1–P2 = 170.83(5), P1–Ni1–C1 = 85.97(13), P2–Ni1–C1 = 85.06(13), P1–Ni1–Cl1 = 94.70(5), P2–Ni1–Cl1 = 94.46(5).

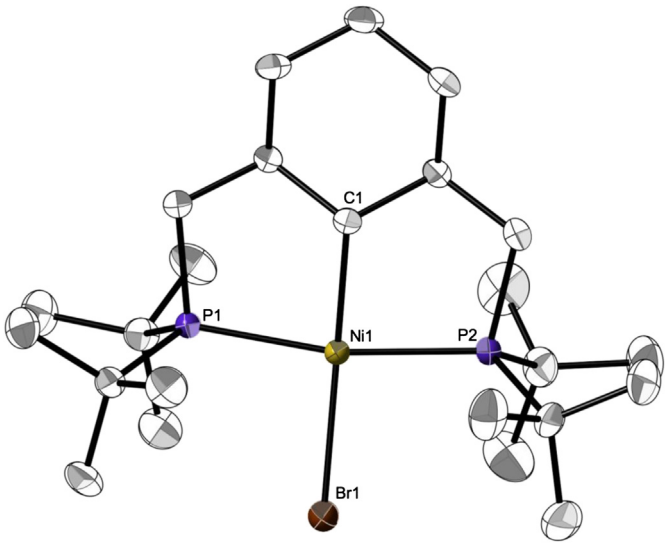


Fig. 2. Molecular structure of **2b** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.998(2), Ni1–P1 = 2.2402(7), Ni1–P2 = 2.2325(7), Ni1–Br1 = 2.4303(4), C1–Ni1–Br1 = 169.48(7), P1–Ni1–P2 = 168.42(3), P1–Ni1–C1 = 85.09(7), P2–Ni1–C1 = 85.15(7), P1–Ni1–Br1 = 95.476(19), P2–Ni1–Br1 = 95.26(2).

bromide deviates slightly from the coordination plane and it is also possible that the Ni–Cl distance is underestimated by the crystal structure due to libration [27].

The complexes showed no sign of decomposition upon exposure to air in solution, and could be stored under air as solids at room temperature or in pentane solution at −30 °C for several weeks. Initial studies confirm a low reactivity of these complexes; refluxing **2a** in toluene/ethanol (1:1) with $NaBH_4$ did not result in any conversion to the corresponding hydride, as is reported for the analogous aromatic nickel pincer complex [28], nor did treatment with $LiAlH_4$ in toluene that has been used for the synthesis of similar phosphinite pincer hydride complexes [9b]. Piers and co-workers have reported on the conversion of a $PC_{sp3}P$ nickel bromide complex to a rare nickel carbene complex through dehydrobromination with $KN(SiMe_3)_2$ [29], but under the same reaction conditions **2b** did not display any such reactivity. This rather unexpected lack of reactivity towards the strongly donating hydride and amide is more likely attributed to the bulky ^{t}Bu-substituents than to the electronic environment at the metal centre. **2a** and **2b** have also been tested as catalysts for Kumada coupling of alkyl and aryl halides with alkyl Grignard reagents, but the best GC yields were around 15%, for the coupling of EtMgCl and PhBr. Zargarian et al. have shown that the steric bulk of the phosphorus substituents strongly influences the reactivity in such reactions [10d], and a replacement of the ^{t}Bu-groups for less sterically demanding ^{i}Pr-groups is a topic for future investigations.

4. Conclusion

The complexation behaviour of the cyclohexyl-based $PC_{sp3}P$ ligand *cis*-1,3-bis-((di-*tert*-butylphosphino)methyl)cyclohexane towards $NiCl_2$ and $NiBr_2$ has been studied, giving two new $PC_{sp3}P$-supported nickel complexes. The bond distances found in the molecular structures indicate a high reactivity but they were found to be more or less unreactive in a number of standard reactions for these types of complexes.

Acknowledgements

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Synthesis and characterisation of a new family of $POC_{sp3}OP$ pincer complexes with nickel. Reactivity towards CO_2 and phenyl acetylene

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Abstract: A cyclohexyl based $POC_{sp3}OP$ pincer ligand ($POC_{sp3}OP$ = *cis*-1,3-Bis-(di-*tert*-butylphosphinito)-cyclohexyl) cyclometallates with nickel to generate a series of new $POC_{sp3}OP$ supported Ni(II) complexes, including the halide, hydride, methyl and phenyl species. *trans*-[NiCl{*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane}], ($POC_{sp3}OP$)NiCl (**1a**) and the analogous bromide complex (**1b**) were synthesized and fully characterised by NMR spectroscopy and X-ray crystallography. Cyclic voltammetry measurements of **1a** and **1b** alongside their bis(phosphine) analogues ($PC_{sp3}P$)NiCl (**2a**) and ($PC_{sp3}P$)NiCl (**2a**) ($PC_{sp3}P$ = *cis*-1,3-Bis-(di-*tert*-butylphosphino)cyclohexyl) indicate a reduced electron density at the metal centre upon introducing electron withdrawing oxygen atoms in the pincer arms. The methyl ($POC_{sp3}OP$)NiMe (**3**) and phenyl ($POC_{sp3}OP$)NiPh (**4**) complexes were formed from **1a** by reaction with the corresponding organolithium reagents. **1b** also reacts with $LiAlH_4$ to give the analogous hydride complex ($POC_{sp3}OP$)NiH (**5**). The methyl complex **3** reacts with phenyl acetylene to give the acetylide complex ($POC_{sp3}OP$)NiCCPh (**6**). The reactivity of compounds **3**-**5** towards CO_2 was studied. The hydride complex **5** and the methyl complex **3** both underwent CO_2 insertion to form the formate species ($POC_{sp3}OP$)NiOCOH (**7**) and acetate species ($POC_{sp3}OP$)NiOCOCH$_3$ (**8**), respectively, although with a higher barrier of insertion in the latter case. Compound **4** was unreactive towards CO_2 even at elevated temperatures. Complexes **3**-**8** were all characterized by NMR spectroscopy and X-ray crystallography.

Introduction

Transition metal complexes with PCP pincer ligands are known as powerful and versatile catalyst for various homogeneous transformations.[1] Among the first pincer complexes introduced by Shaw in the late 1970s, structures with aliphatic backbone were well represented,[2] but since then reports on the more structurally simple and robust aromatic counterparts have been in vast majority. However, with an increased request for fine electrochemical tuning of pincer complexes, the interest has risen in the strongly σ-donating anionic C(sp3)-hybridized pincer ligands.[3] The increased electron density at the metal centre can give the aliphatic pincer complexes a different reactivity compared to their aromatic counterparts. For example, Hartwig and co-workers illustrated this in their study of the reactivity of iridium PCP complexes towards NH_3, where an aliphatic ligand backbone gives N–H oxidative addition rather than simple coordination.[4] The presence of labile α- and β-hydrogen atoms in the backbone of aliphatic pincer complexes makes them less robust than their aryl-based counterparts, and recent literature examples include bi- or tricyclic $PC_{sp3}P$ pincer scaffolds such as dibenzobarrelene[5] and adamantane[6] derivatives, to avoid such plausible decomposition routes. However, a flexible coordination where a carbometallated spieces is in dynamic interplay with an α- or β-eliminated species might open up for new reactivities and mechanistic pathways for the aliphatic pincer complexes, motivating further investigations concerning the structures and properties of this type of complexes. Recent examples of novel reactivity and catalytic applications have included hydrogen exchange also on the ligand.[7]

Additional structural manipulation of the pincer ligand to change electrochemical and steric properties of the pincer complex can be accomplished by introducing electron withdrawing oxygen atoms in the pincer arms. These bis(phosphinite) or POCOP pincer complexes have been reported to have an increased catalytic activity relative the corresponding bis(phosphine) complexes in *e.g.* some transfer dehydrogenation reactions.[8]

We have previously reported on the coordination behaviour of cyclohexyl-based $POC_{sp3}OP$ ligands with Pd[9] and Pt,[10] where PCP-coordination through C–H bond activation was not observed, but instead a mixture of a binuclear 16-atom ring chelate complex and a mononuclear complex with *cis*-coordination was formed. In case of Ir, the conditions required for cyclometallation led to a coincident dehydrogenation and aromatisation of the cyclohexyl pincer backbone[11] underpinning the dynamic character of the ligand. Encouraged by the previous work of Zargarian on the

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Supporting information for this article is available on the WWW under http://www.XXXXXX/X or from the author.

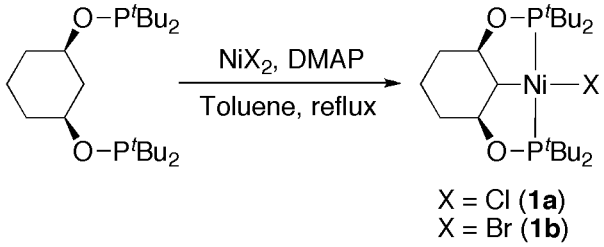
complexation of acyclic $POC_{sp3}OP$ pincer ligands with nickel,[12] we wanted to attempt cyclometallation of our similar cyclohexyl-based $POC_{sp3}OP$ ligand with this metal. Introducing earth-abundant 1st row metal alternatives in place of precious metal catalysts remains an important task in sustainable chemistry, and recent literature examples of catalysis by Ni pincer complexes involve various cross-coupling reactions,[13-14] direct alkylations,[15] alkene hydrogenations,[16] hydroaminations,[17] hydrosilylations[18] and reduction of carbon dioxide to methanol.[19]

We here report on the first successful cyclometallation of *cis*-1,3-bis-(di-*tert*-butylphosphinito)cyclohexane and present a series of new $POC_{sp3}OP$ supported Ni(II) complexes, including the halide, hydride, methyl and phenyl species. We further report on the reactivity of those compounds towards phenyl acetylene and CO_2. There is a major interest in transition metal mediated functionalization of CO_2, due to the potential utilization of this cheap and abundant green house gas as a synthetic C1 source.[20] Particularly crucial is the catalytic reduction of CO_2, where insertion into a metal-hydrogen bond in many cases is an essential step.[21] Another approach towards CO_2 activation is the insertion into a metal-carbon bond to form metal-carboxylates, which with their weaker metal-oxygen bond are more inclined to undergo further transformations. We[22] and others[23] have studied the CO_2 insertion mechanisms for group 10 aromatic PCP complexes, and the mechanism suggests that the insertion process is facilitated by increased electron density of the metal centre. To probe for electron richness we also report electrochemical studies of these and related nickel complexes.

Results and Discussion

The synthesis of the pincer complexes **1a** and **1b,** as illustrated in Scheme 1, follow the synthetic protocol of Zargarian and coworkers for their non-cyclic 1,5-bis(phosphinito)pentane ligand.[12] Complexes **1a** and **1b** are the first cyclometallated complexes with this ligand and indeed the first $POC_{sp3}OP$ nickel complexes with *tert*-butyl substitutents. Altering the NiX_2 equivalents between 1.5 and 3 had no impact on the product yields, which are typically ranging from 40-65%. Like we previously reported for the synthesis of the analogous diphosphine pincer complexes, monitoring the course of the complexation by means of ^{31}P-NMR spectroscopy did not reveal any phosphorus containing species apart from starting material and products. Thus, there is no sign of intermediates or byproducts such as binuclear 16-atom ring chelate complexes or mononuclear complexes with *cis*-coordination to the P atoms, which has been reported for similar systems.[24] The moderate yields are more likely originating from the formation of phosphorus containing nickel salts; the synthesis of **1a** goes via a purple suspension to a yellow solution with an orange/beige precipitate that is separated by filtration through silica (similar observations are made for **1b**, only the initially formed suspension is orange/brown and the solution slightly green before filtration through silica). The solid residue gradually turns green upon storage in air, but is at any stage highly insoluble and possibly NMR silent, and attempted characterization has been unsuccessful. Zargarian and coworkers have reported that nickelation of their 1,5-bis(phosphino)pentane ligand gives a byproduct with low solubility identified as a zwitterionic complex with an anionic tetrahedral nickel centre and a monocoordinated pincer ligand with one protonated non-coordinated phosphine. Supposedly, the protonating agent is HX generated *in situ*, which supports their and our observation that addition of DMAP or other bases improves the yield for these complexation reactions. We have previously found that for an aromatic pincer ligand, reaction with a nickel precursor gives the poorly soluble 16-atom ring chelate complex which could not be transformed to the cyclometallated product and it cannot be ruled out that such insoluble material is formed also here.[25] Exposing the reaction mixture to air before full conversion of the ligand resulted in oxidation of the ligand to the corresponding P(V) species *cis*-1,3-bis-(di-*tert*-butylphosphinate)cyclohexane (see supporting information for full characterization). Changing the reaction solvent in Scheme 1 to THF similarly resulted in formation of the oxidized ligand as the major phosphorus containing product, through a to us unknown mechanism, possibly involving residual H_2O in the solvent, despite using conventional drying procedures. This oxidation proceeds slowly even without presence of NiX_2, and hence there is no evident metal mediation. For non-cyclic $POC_{sp3}OP$ ligands a C–O cleavage reaction has been observed both for nickel and iridium complexes but the present system shows no tendency for such reactions.[26-27]

The $^{31}P\{^1H\}$ NMR spectra of the here reported pincer complexes display a singlet resonance that confirms the equivalence of the two phosphorus nuclei, in line with the expected *trans* geometry. This is consistent with the appearance of the ^{t}Bu protons as two (although sometimes slightly merged) virtual triplets in the ^{1}H NMR spectra. The characteristic pattern of virtual triplets is also observed in the $^{13}C\{^1H\}$ NMR spectra, where all nuclei except the most remote methylene carbon of the cyclohexyl ring display coupling to phosphorus. The cyclometallated structure is further supported by the identification of the proton on the α-carbon, presented as a broadened triplet around 1.5-2 ppm ($J_{PH} \approx 11$ Hz) in C_6D_6.



Scheme 1. Synthesis of ($POC_{sp3}OP$)NiCl (**1a**) and ($POC_{sp3}OP$)NiBr (**1b**).

X-ray quality crystals of **1a** and **1b** were obtained by slow evaporation of a yellow pentane solution at room temperature, and their molecular structures are given in Figures 1 and 2 respectively. These $POC_{sp3}OP$ complexes have a more narrow P–Ni–P angle than their $PC_{sp3}P$ counterparts;[28] in case of **1a** 163.69° as compared to 170.84° and for **1b** 163.50° as compared to 168.42°. This reflects on the shorter P–O and C–O distances compared to the corresponding P–C and C–C bonds in the $PC_{sp3}P$ analogue. The increased reactivity observed for POCOP relative PCP complexes (*vide infra*) is partly attributed to this more open coordination site, and is one possible explanation why

our recently reported ($PC_{sp3}P$)NiCl complex is unreactive towards hydride sources and base. The Ni–X bond lengths of **1a** and **1b** are slightly shorter than in their $PC_{sp3}P$ counterparts; 2.2357(10) Å (**1a**) and 2.3764(4) Å (**1b**) as compared to 2.2497(14) Å and 2.4303(4) Å respectively. This indicates a decreased *trans*-influence from the coordinated carbon, as implied by the electron withdrawing effect of the oxygen atoms in the pincer scaffold. However, the **1a** and **1b** Ni–X bond lengths are longer than for any reported ($POC_{Ar}OP$)Ni–Cl[29] or ($POC_{Ar}OP$)Ni–Br[30-31] complexes, and also slightly longer than those of the corresponding acyclic ($POC_{sp3}OP$)Ni–X complexes.[12] Crystal data and collection and refinement details for compounds **1a, 1b, 3** and **4** are presented in Table 1.

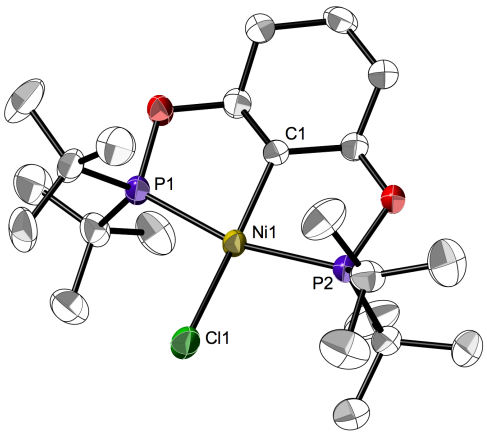
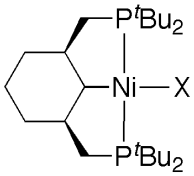


Figure 1. Molecular structure of **1a** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.939(3), Ni1–P1 = 2.2019(9), Ni1–P2 = 2.1933(9), Ni1–Cl1 = 2.2357(10), P1–O1 = 1.647(2), P2–O2 = 1.640(2), O1–C2 = 1.458(4), O2–C6 = 1.440(4), C1–Ni1–Cl1 = 173.20(10), P1–Ni1–P2 = 163.69(4), P1–Ni1–C1 = 81.71(9), P2–Ni1–C1 = 82.14(9), P1–Ni1–Cl1 = 98.71(4), P2–Ni1–Cl1 =97.60(4).



X = Cl (**2a**)
X = Br (**2b**)

Chart 1.

The redox properties of the $POC_{sp3}OP$ complexes **1a** and **1b**, alongside the recently reported $PC_{sp3}P$ analogues **2a** and **2b** (Chart 1)[28] were investigated by cyclic voltammetry. The four complexes show fully reversible oxidation processes from Ni(II) to (III) with a difference in oxidation potentials of ca 0.33-0.35 V between the $PC_{sp3}P$ and $POC_{sp3}OP$ complexes, in agreement with the less donating properties of the latter (Figure 3). The same trend was previously observed by the group of Zargarian, comparing aryl-based PCP and POCOP Ni(II) bromide complexes.[17] The $E_{1/2}$ values of **1a** and **1b** compare to those reported by Zargarian for acyclic $POC_{sp3}OP$ Ni(II) complexes, although in their case the process is irreversible.[30] This points to a higher oxidative stability of the cyclohexyl based systems compared to the acyclic ones. Scanning up to 2.4 V results in loss of reversibility for the first oxidation process, most likely due to the occurrence of a second oxidation, possibly from Ni(III) to Ni(IV) (Figure 4). This happens for both ligand frameworks but at a substantially higher potential than reported for the corresponding acyclic ligands.

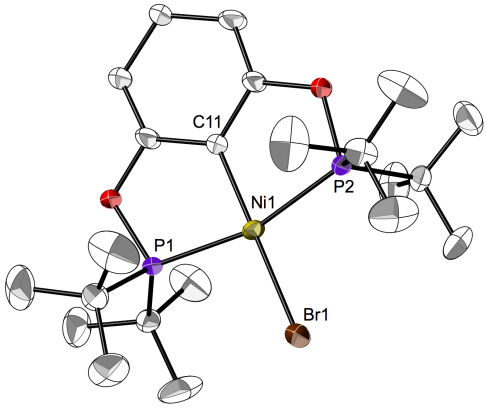


Figure 2. Molecular structure of **1b** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C11 = 1.939(2), Ni1–P1 = 2.2163(7), Ni1–P2 = 2.2156(7), Ni1–Br1 = 2.3764(4), C11–Ni1–Br = 179.44(8), P1–Ni1–P2 = 163.50(3), P1–Ni1–C11 = 81.79(7), P2–Ni1–C11 = 81.73(7), P1–Ni1–Br1 = 97.80(2), P2–Ni1–Br1 = 98.68(2).

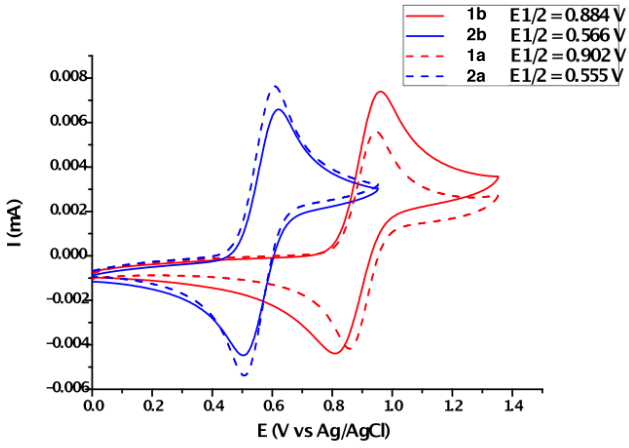


Figure 3. Cyclic voltammetry scans of 10^{-3} M solutions of compounds **1**-**2** at a Pt electrode in CH_2Cl_2 (0.1 M ($^nBu_4N$)PF_6 scan rate 0.1 V s^{-1}).

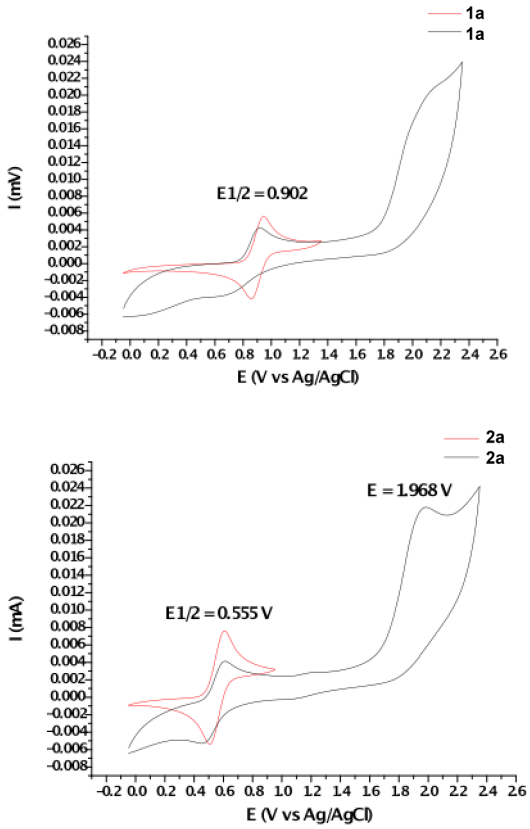
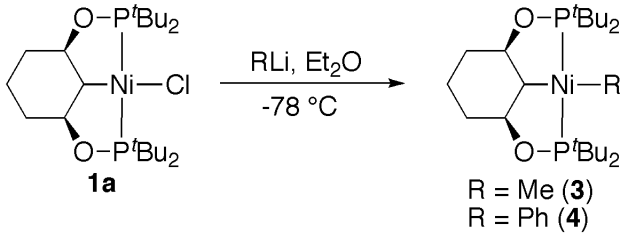


Figure 4. Cyclic voltammetry scans of 10^{-3} M solotions of compounds **1a** and **2a** at a Pt electrode in CH_2Cl_2 (0.1 M ($^nBu_4N$)PF_6 scan rate 0.1 V s^{-1}). Scanning up to 2.4 V makes the 1st oxidation irreversible (**1a**) or quasi-reversible (**2a**).

Complex **1a** undergoes reaction with methyl- or phenyllithium in diethyl ether, to give the corresponding nickel methyl (**3**) and phenyl compound (**4**) respectively (Scheme 2). The course of the reactions is clean, giving only trace amounts of remaining **1a** when using 2 eq. of the organolithium reagent. Reactions with Grignard reagents however are more sluggish and less clean, and isolation of **3** and **4** was not accomplished from such reaction mixtures, as opposed to the similar ($PC_{Ar}CP$)NiCl complex that readily reacts with MeMgCl or allylMgCl to form the methyl and allyl complex resplectively, in good yields.[23b] Accordingly, complexes **1a** and **1b** show similarly low catalytic activity for the Kumada cross coupling reaction as we previously reported for complexes **2a** and **2b**.[28] The Ni–Me moiety of **3** is characterised by high-field triplets in the ^{1}H (-0.24 ppm) and ^{13}C (-19.95 ppm) NMR spectra (C_6D_6). Compound **4** shows four unique shifts in the aromatic region, indicating that the phenyl substituent is not undergoing rapid rotation in solution and is not lying in the coordination plane. Complexes **3** and **4** are thermally stable and survive both aqueous work-up and exposure to air in the solid state for several days. Recrystallisation of compound **3** did not separate the traces of **1a**, and the elemental analysis was unsatisfactory. These are the first isolated nickel hydrocarbyl complexes with an aliphatic pincer phosphinite ligand.



Scheme 2. Synthesis of ($POC_{sp3}OP$)NiMe (**3**) and ($POC_{sp3}OP$)NiPh (**4**).

Both **3** and **4** gave X-ray quality crystals and a structure determination confirmed the molecular structures. As opposed to the observed trend for chloride and bromide complexes, the molecular structure of complex **3** reveals a slightly shorter Ni–Me bond distance than in the structurally similar ($PC_{Ar}P$)NiMe ($PC_{Ar}P$ = C_6H_3-2,6-($CH_2P^tBu_2$)$_2$);[24b] 2.016 Å compared to 2.026 (Figure 5). The expectedly stronger *trans* influence from a coordinated sp^3 hybridized carbon might be partly diminished by the presence of electron withdrawing oxygen atoms, though the bond is still slightly elongated; both complex **3** and **4** display similar or longer Ni–R bond lengths (R = Me, Ph) than for the acyclic (PCP)NiX complexes (PCP = $^iPr_2P(CH_2)_5P(^iPr)_2$) reported by Zargarian and co-workers[32] and the ($PC_{Ar}P$)NiX complexes ($PC_{Ar}P$ = C_6H_3-2,6-($CH_2P^iPr_2$)$_2$) reported by Cámpora and co-workers[33]. The molecular structure of **4** is given in Figure 6, showing a phenyl ring almost perpendicular to the coordination plane, as also suggested by the non-equivalent aromatic protons in the ^{1}H-NMR spectrum.

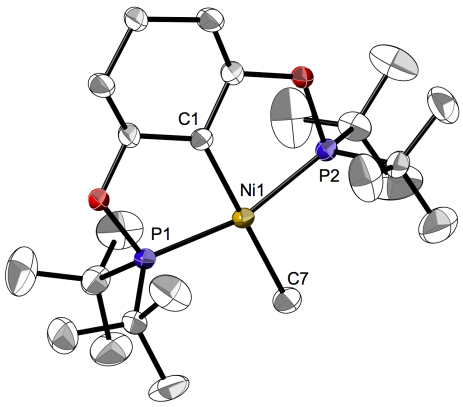


Figure 5. Molecular structure of **3** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.966(3), Ni1–P1 = 2.1854(8), Ni1–P2 = 2.1837(8), Ni1–C7 = 2.016(3), C1–Ni1–C7 = 176.71(15), P1–Ni1–P2 = 162.61(3), P1–Ni1–C1 = 81.39(8), P2–Ni1–C1 = 81.30(8), P1–Ni1–C7 = 98.48(9), P2–Ni1–C7 = 98.89(9).

Compound **1a** is readily converted to the nickel hydride complex by reduction with $LiAlH_4$ (Scheme 3), following the synthetic route used by Guan for the aromatic analogue.[18] The ^{1}H NMR spectrum of **5** reveals a typical hydride resonance as a triplet at -8.58 ppm (J_{HP} = 52.0 Hz). A concentrated hexane

solution of complex **5** afforded X-ray quality crystals upon storing at -28 °C under N_2 for several days. The structure of complex **5** was confirmed using X-ray crystallography and the hydride ligand could also be located in the Fourier map of the X-ray diffraction experiment 1.50 Å from the nickel centre (Figure 7). The Ni–C bond length (1.948(3) Å) is slightly shorter than in the methyl and phenyl complexes (1.966-1.970), and thus it is not reflecting the usually higher trans influence of the hydride. Compound **5** showed no tendency for decomposition through reductive elimination of the free ligand when stored in solution under N_2 at room temperature for several days. It is the first isolated nickel hydride with an aliphatic pincer phosphinite ligand. Crystal data and collection and refinement details for compounds **5-8** are presented in Table 2.

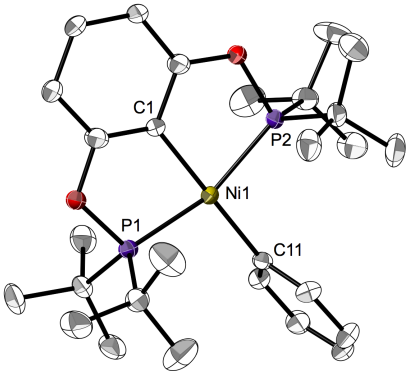
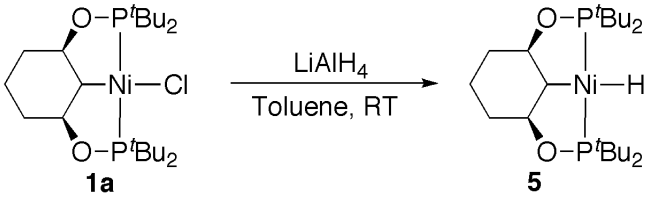


Figure 6. Molecular structure of **4** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.970(3), Ni1–P1 = 2.2049(10), Ni1–P2 = 2.1934(10), Ni1–C11 = 1.971(3), C1–Ni1–C11 = 173.81(16), P1–Ni1–P2 = 161.61(4), P1–Ni1–C1 = 81.04(10), P2–Ni1–C1 = 81.19(10), P1–Ni1–C11 = 100.65(10), P2–Ni1–C11 = 97.52(10).



Scheme 3. Synthesis of ($POC_{sp3}OP$)NiH (**5**).

The reactivity of ($POC_{sp3}OP$)NiMe (**3**) towards phenyl acetylene was investigated, showing a gradual conversion to the acetylide complex **6** over a period of 6 days, upon heating to 80 °C (Scheme 4). A coincident formation of CH_4 was observed by means of ^{1}H NMR spectroscopy (δ = 0.15 ppm in C_6D_6). Full conversion of **3** was not obtained upon prolonged reaction time, but no product was formed besides **6**, which could be obtained in pure form via crystallization from hexane. Thus the reactivity of **3** is substantially lower than that of the corresponding nickel complex with an acyclic $PC_{sp3}P$ ligand, which reacts already at room remperature.[32] The reaction is also somewhat slower than with a palladium methyl complex with an aromatic PCP ligand (PCP = C_6H_3-2,6-($CH_2P^tBu_2$)$_2$).[34] The lower reactivity is possibly of steric origin since the fastest reaction is observed for the nickel $PC_{sp3}P$ complex which bears ^{i}Pr substituents on the phosphorus. Reacting the hydride complex **5** with phenyl acetylene under the same conditions as in scheme 4, resulted in a mixture of several phosphorus containing species, as shown by $^{31}P\{^1H\}$ NMR, of which **6** is included but not predominant. This is in contrast to the results for (PCP)Pd and (POCOP)Pd complexes (POCOP = C_6H_3-2,6-(OP^tBu_2)$_2$), where the hydride complexes are highly reactive forming acetylide complexes in addition to small amounts of the β-phenylvinyl complex.[34, 35] The higher reactivity of the hydride is expected for the proposed σ-bond metathesis mechanism.[34] Also, in the present case a σ-bond metathesis mechanism is plausible but no H_2 formation was observed by ^{1}H-NMR, as would be expected for this pathway. However, it cannot be ruled out that any dihydrogen was present in the head-space. The composition did not change significantly over time and no isolation or characterisation was achieved for the compounds formed in addition to **6**; formation of the plausible β-phenylvinylic byproduct from 1,2-insertion into the Ni–H bond could for example not be supported by any clear olefinic proton shifts in the ^{1}H NMR spectrum.

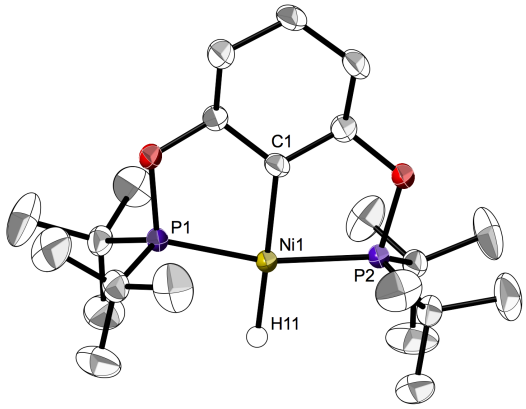
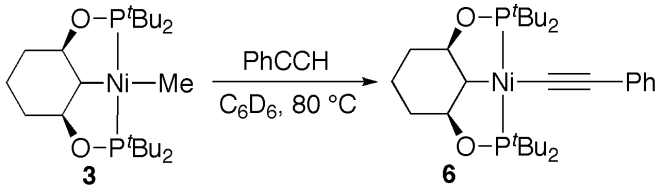


Figure 7. Molecular structure of **5** at the 30% probability level. Hydrogen atoms except the hydride are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.948(3), Ni1–P1 = 2.1405(9), Ni1–P2 = 2.1423(9), Ni1–H11 = 1.50(3), C1–Ni1–H11 = 175.5(12), P1–Ni1–P2 = 165.96(3), P1–Ni1–C1 = 82.82(9), P2–Ni1–C1 = 83.15(9), P1–Ni1–H11 = 95.8(12), P2–Ni1–H11 = 98.3(12).



Scheme 4. Synthesis of ($POC_{sp3}OP$)NiCCPh (**6**).

The molecular structure of compound **6** from an X-ray diffraction experiment is shown in figure 8, displaying a Ni–

C(alkyne) bond length (1.889(3) Å) that is significantly shorter than the Ni–C bond lengths in ($POC_{sp3}OP$)Ni–Me (**3**, 2.016(3) Å) and $POC_{sp3}OP$Ni–Ph (**4**, 1.971(3) Å), in consistency with the hybridization of the concerned carbon atoms. Like in the similar ($PC_{Ar}P$)NiCCP complex ($PC_{Ar}P$ = C_6H_3-2,6-($CH_2P^tBu_2$)$_2$) previously reported by Schmeier *et al.*,[23d] the phenyl acetylide ring is not coplanar with the coordination plane in complex **6**, but has a tilt of approximately 22°. The structure also shows some deviation from a linear geometry, with a C1–Ni1–C11 angle of 173.89°.

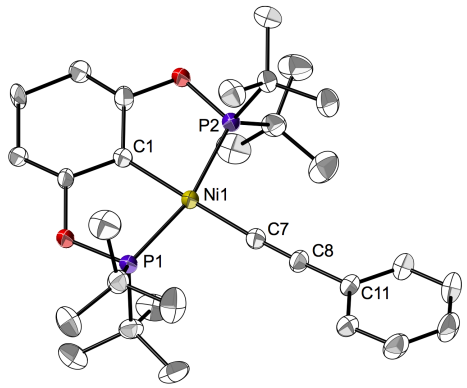
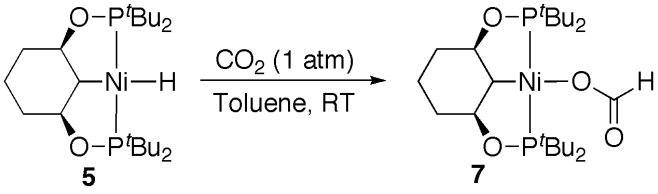


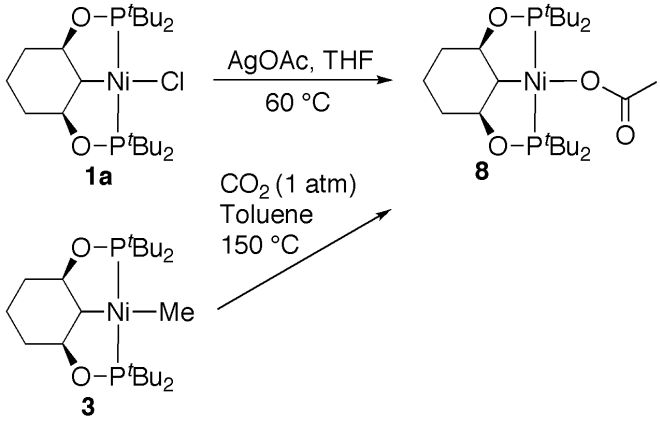
Figure 8. Molecular structure of **6** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.942(3), Ni1–P1 = 2.1779(10), Ni1–P2 = 2.1783(10), Ni1–C7 = 1.889(3), C7–C8 = 1.228(4), C8–C11 = 1.444(4), C1–Ni1–C7 = 177.74(16), P1–Ni1–P2 = 164.18(4), C7–C8–C11 = 176.1(4), P1–Ni1–C1 = 82.17(10), P2–Ni1–C1 = 82.01(10), P1–Ni1–C7 = 98.44(11), P2–Ni1–C7 = 97.37(11).

The formate complex **7** was obtained via direct CO_2 insertion intto the Ni–H bond (Scheme 5), analogously to the previously reported reaction with the corresponding ($POC_{Ar}OP$)NiH complex.[19] Full conversion of **5** was obtained at room temperature in less than 1h. The ^{1}H NMR spectrum featured a characteristic resonance for the formate proton at δ 8.50 ppm and ^{13}C NMR displays a singlet corresponding to the carbonyl at δ 167.7 ppm. Like the aromatic analogue, initial studies suggest that the formate **7** reacts stoichiometrically with 9-BBN to regenerate the hydride **5**. Thus **5** might be a plausible candidate for CO_2 reduction with boranes or similar reductants.



Scheme 5. Synthesis of ($POC_{sp3}OP$)NiOCOH (**7**).

The insertion of CO_2 into the Ni–Me bond of **3** required prolonged heating at 150 °C, thus showing the same trend of insertion barriers as reported for similar aromatic PCP nickel hydride and methyl complexes.[23b] 3 days of heating to 150 °C gave only partial conversion of **3** (~50%), and the course of the reaction was not clean (two uncharacterized doublets was observed with ^{31}P-NMR spectroscopy at 179.4 and 176.0 ppm respectively). Isolation of the acetate complex **8** in pure form was unsuccessful through this route, but it could be independently synthesized from the chloride complex **1a**, as depicted in Scheme 6, and thereby fully characterised. The insertion product was then identified by comparison. In the ^{1}H-NMR spectrum the acetate displays a characteristic singlet resonance at δ 2.03 ppm and in the ^{13}C-NMR spectrum a carbonyl shift at δ 175.3 ppm. The IR spectrum of **8** confirms an η^1-bound carboxylate ligand, by featuring two inequivalent stretching frequencies separated by more that 200 cm^{-1}.[36] Analogously, CO_2 insertion into the Ni–Ph bond was attempted for complex **3**, but no insertion product was observed even at elevated temperature, which is not surprising considering the low reactivity previously seen for group 10 complexes with sp^2-hybridized carbons. Both complex **3** and **4** were unreactive towards CO upon heating to 80 °C for several days. This is in keeping with previous result and the previously reported mechanism of CO_2 insertion into metal-hydrocarbyl bonds where there is no pre-coordination, as often required for CO insertion.[22-23] Overall the reactivity of the present nickel complexes is lower than the that of (PCP)Pd complexes and on par with aromatic (PCP)Ni complexes.



Scheme 5. Synthesis of ($POC_{sp3}OP$)NiOAc (**8**).

X-ray quality single crystals of the formate complex **7** was obtained from a concentrated hexane solution at -28 °C. The solid state structure confirms the binding of one oxygen atom to nickel (Figure 9); the minor difference in C–O bond distances (O3–C7 = 1.269(4) Å, O4–C7 = 1.225(4) Å) is indicative of some electron density delocalization, but in combination with the relatively long through-space Ni–O4 distance it argues against the possible η^2 coordination, in consistency with other reported crystallographically characterized nickel formate complexes [19a, 23b, 37]. Similarly, the molecular structure of **8** confirms the η^1 binding mode of the acetate (Fig. 10). Bond lengths and angles are very close to those reported for the formate complex **6**, and also in good agreement with the ($PC_{Ar}P$)NiOAc complex ($PC_{Ar}P$ = C_6H_3-2,6-(CH_2PPh_2)$_2$) previously reported by Zargarian and

Salah[31a], although a somewhat shorter Ni–O bond in their case might indicate a stronger Ni–OAc interaction.

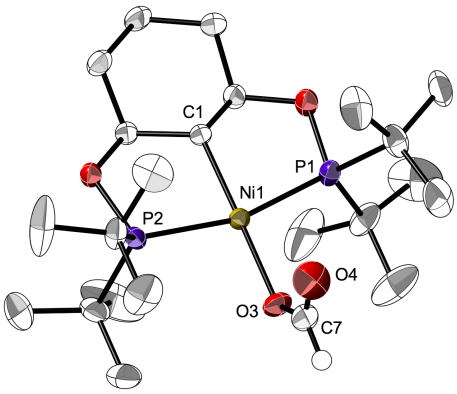


Figure 9. Molecular structure of **7** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.948(2), Ni1–P1 = 2.2208(7), Ni1–P2 = 2.2179(6), Ni1–O3 = 1.9455(17), O3–C7 = 1.269(4), O4–C7 = 1.225(4), C1–Ni1–O3 = 177.78(9), P1–Ni1–P2 = 163.01(2), Ni1–O3–C7 = 125.0(2), O3–C7–O4 = 127.6(3), P1–Ni1–C1 = 81.64(7), P2–Ni1–C1 = 81.49(7), P1–Ni1–O3 = 98.47(6), P2–Ni1–O3 = 98.33(6).

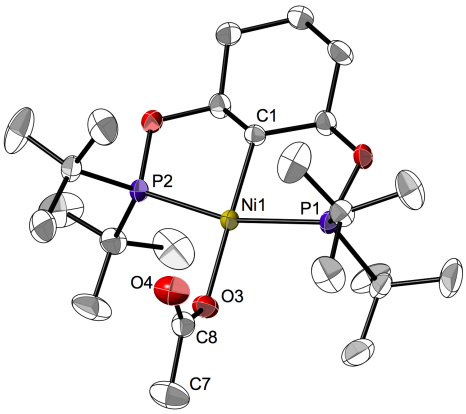


Figure 10. Molecular structure of **8** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.948(3), Ni1–P1 = 2.2198(7), Ni1–P2 = 2.2190(7), Ni1–O3 = 1.943(2), O3–C8 = 1.258(4), O4–C8 = 1.225(4), C8–C7 = 1.512(5), C1–Ni1–O3 = 176.37(11), P1–Ni1–P2 = 162.54(3), Ni1–O3–C8 = 125.5(2), O3–C8–O4 = 126.4(3), P1–Ni1–C1 = 81.91(9), P2–Ni1–C1 = 81.65(9), P1–Ni1–O3 = 98.60(7), P2–Ni1–O3 = 97.77(7).

Conclusion

We here report on the first metallation of a cyclohexyl-based $POC_{sp3}OP$ ligand; a new family of $POC_{sp3}OP$ supported Ni(II) complexes has been prepared with a variety of anionic ligands in the fourth coordination site, including halide, hydride, methyl and phenyl ligands. The current systems display similar oxidation properties (*i.e.* electron richness) as the corresponding acyclic aliphatic pincer systems. Yet, the rigidity of the cyclohexyl ring gives the hydrocarbyl and hydride complexes an unprecedented stability and allows for the first isolation of such complexes involving a ($POC_{sp3}OP$)Ni core. Also, the current system is completely unreactive towards C–O bond cleavage of the ligand, which is otherwise a major stibility issue of $POC_{sp3}OP$ complexes. Despite this increased stability the methyl complex reacts with phenyl acetylene to give a Ni(II) acetylide complex under the release of CH_4. A similar reaction occurs with the corresponding hydride complex, although in a much less clean fashion. The hydride and methyl species both react with CO_2 to generate Ni carboxylates, with a barrier of insertion much lower for the Ni–H than the Ni–Me bond.

Table 1. Crystal data and collection and refinement details for compounds **1a, 1b, 3 and 4.**

	1a	**1b**	**3**	**4**
formula	$C_{22}H_{45}ClNiO_2P_2$	$C_{22}H_{45}BrNiO_2P_2$	$C_{23}H_{48}NiO_2P_2$	$C_{28}H_{50}NiO_2P_2$
Fw	497.68	542.14	477.26	539.33
space group	$P2_1/c$	P-1	$P2_1/n$	P-1
a/Å	11.8903(16)	8.5911(3)	15.4508(6)	8.6401(5)
b/Å	16.265(3)	12.5206(5)	12.8395(3)	10.7568(6)
c/Å	14.820(2)	13.8206(5)	16.0043(8)	17.5095(10)
α/deg	90	98.560(3)	90	93.547(5)
β/deg	104.170(13)	96.924(3)	118.738(6)	97.484(5)
γ/deg	90	107.710(3)	90	110.584(6)
V/Å^3	2778.9(8)	1378.52(9)	2783.89(19)	1500.26(15)
Z	4	2	4	2
D_{calcd}/g cm^{-3}	1.190	1.306	1.139	1.194
μ/mm^{-1}	0.923	2.283	0.826	0.774
θ/ range/deg	2.50-28.84	2.52-28.85	2.54-28.76	2.46-28.78
No. reflns collected	35690	30253	46922	19608
No. unique reflns	6565	6563	6752	6971
$R(F)$ $(I>2\sigma(I))^a$	0.0584	0.0460	0.0567	0.0664
$wR2(F^2)$ (all data)^b	0.1458	0.1326	0.1602	0.1313
S^c	1.053	1.417	1.133	1.073
R_{int}	0.1199	0.0396	0.0694	0.0843

$^a R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $^b wR2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|)^2]^{1/2}$. $^c S = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|)^2]^{1/2}$.

Table 2. Crystal data and collection and refinement details for compounds **5**-**8**.

	5	**6**	**7**	**8**
formula	$C_{22}H_{46}NiO_2P_2$	$C_{30}H_{50}NiO_2P_2$	$C_{23}H_{46}NiO_4P_2$	$C_{24}H_{48}NiO_4P_2$
Fw	463.24	563.35	507.25	521.27
space group	$P2_1/c$	P-1	$P2_12_12_1$	$P2_12_12_1$
a/Å	16.945(3)	8.3539(4)	8.20020(10)	8.2348(2)
b/Å	10.8746(11)	12.7413(7)	16.0919(3)	16.1103(5)
c/Å	16.313(3)	15.9053(8)	21.2745(4)	21.6280(5)
α/deg	90	79.833(4)	90	90
β/deg	117.35(2)	76.137(4)	90	90
γ/deg	90	82.591(4)	90	90
V/Å^3	2670.2(7)	1611.17(14)	2807.31(8)	2869.30(13)
Z	4	2	4	4
D_{calcd}/g cm^{-3}	1.152	1.161	1.200	1.207
μ/mm^{-1}	0.859	0.724	0.828	0.812
θ/ range/deg	2.40-28.88	2.52-28.79	2.48-28.90	2.47-28.71
No. reflns collected	56538	35432	49618	37292
no. of unique reflns	6567	7737	6882	6886
R(*F*) (I>2σ(I))[a]	0.0597	0.0629	0.0398	0.0401
wR2(F^2) (all data)[b]	0.1573	0.1534	0.0987	0.1273
S[c]	1.145	0.991	1.054	0.863
R_{int}	0.1224	0.1037	0.0707	0.0588

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|)^2]^{1/2}$. [c] $S = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|)^2]^{1/2}$.

Experimental Section

General Comments. All manipulations were performed under a nitrogen or argon atmosphere using standard Schlenk or glovebox techniques, except where noted. Solvents were purified by vacuum distillation from sodium/benzophenone ketyl radical. The ligand *cis*-1,3-bis-(di-*tert*-butylphosphinito)cyclohexane was synthesized according to previously reported procedures.[10] All other chemicals where purchased from commercial suppliers and used as received. ^{1}H, ^{13}C and ^{31}P NMR experiments were recorded on a Varian Unity INOVA 500 spectrometer, operating at 499.76 MHz (^{1}H). For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0 ppm. Multiplicities are abbreviated as follows: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet, (br) broad, (v) virtual. IR sprectra were obtained on a Bruker ALPHA FT-IR. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

Crystallography. XRD-quality crystals of compounds **1a, 1b and 3**-**8** were obtained through recrystallization from benzene, toluene or hexane. Intensity data were collected with an Oxford Diffraction Excalibur 3 system, using w-scans and Mo Ka (λ = 0.71073 Å) radiation.[37] The data were extracted and integrated using Crysalis RED.[38] The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL5.1.[39] Molecular graphics were generated using CrystalMaker® 8.3.5.[40]

Synthesis and characterisation of compounds

***trans*-[NiCl{*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane}] (1a):** To a stirred mixture of the *cis*-1,3-bis-(di-*tert*-butylphosphinito)cyclohexane ligand (25.2 mg, 0.062 mmol) and anhydrous $NiCl_2$ (12.1 mg, 0.093 mmol) in toluene (5 mL) DMAP (7.6 mg, 0.062 mmol) was added. The mixture was heated to reflux for 24 h. The cooled down suspension was concentrated *in vacuo*, before being suspended in EtOAc and filtered through a pad of silica in air, giving **1a** as a yellow crystalline powder. Yield: 19.1 mg (62%). ^{1}H NMR ($CDCl_3$): δ 3.60 (dt, *J* = 3.5 Hz, *J* = 10.5 Hz, CH_2CHO, 2 H), 2.02-1.96 (m, CH_2CH_2CHO, 2 H and *H*C–Ni, 1 H), 1.78 (br d, *J* = 14.0 Hz, $CH_2CH_2CH_2$, 1 H), 1.48 (vt, *J* = 12.0 Hz, tBu, 18 H), 1.42 (vt, *J* = 12.0 Hz, tBu, 18 H), 1.2541.20 (m, $CH_2CH_2CH_2$, 1 H), 1.07 (dq, *J* = 4.0 Hz, *J* = 2.0 Hz, CH_2CH_2CHO, 2 H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 87.2 (vt, J_{PC} = 15 Hz, CH_2CHO, 2 C), 59.4 (t, J_{PC} = 14 Hz, HC–Ni, 1 C), 40.0 (vt, J_{PC} = 12 Hz, $C(CH_3)_3$, 2 C), 38.1 (vt, J_{PC} = 17 Hz, $C(CH_3)_3$, 2 C), 33.3 (vt, J_{PC} = 12 Hz, CH_2CH_2CHO, 2 C), 28.7 (vt, J_{PC} = 5.6 Hz, $C(CH_3)_3$, 6 C), 28.2 (vt, J_{PC} = 5.2 Hz, $C(CH_3)_3$, 6 C), 21.6 (s, $CH_2CH_2CH_2$, 1 C). ^{31}P{^{1}H} NMR (C_6D_6): δ 179.7 (s). Anal. Calcd for $C_{22}H_{45}ClNiO_2P_2$ (497.69): C, 53.09; H, 9.11. Found: C, 53.11; H, 9.10.

***trans*-[NiBr{*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane}] (1b):** Following the same procedure as for the analogous chloride (**1a**), a yellow powder was obtained. Yield: 21.8 mg (65%). ^{1}H NMR ($CDCl_3$): δ 3.51 (dt, *J* = 3.5 Hz, *J* = 10.0 Hz, CH_2CHO, 2 H), 2.03 (t, *J* = 11.0 Hz, *H*C–Ni, 1 H), 1.92-1.88 (m, CH_2CH_2CHO, 2 H), 1.53 (vt, *J* = 13 Hz, tBu, 18 H), 1.49 (vt, *J* = 13 Hz, tBu, 18 H), 1.39-1.32 (m, $CH_2CH_2CH_2$, 1 H), 1.00-0.89 (m, $CH_2CH_2CH_2$, 1 H and CH_2CH_2CHO, 2 H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 86.9 (vt, J_{PC} = 15 Hz, CH_2CHO, 2 C), 63.0 (t, J_{PC} = 14 Hz, HC–Ni, 1 C), 40.4 (vt, J_{PC} = 12 Hz, $C(CH_3)_3$, 2 C), 38.6 (vt, J_{PC} = 17 Hz, $C(CH_3)_3$, 2 C), 33.5 (vt, J_{PC} = 12 Hz, CH_2CH_2CHO, 2 C), 29.1 (vt, J_{PC} = 5.8 Hz, $C(CH_3)_3$, 6 C), 28.5 (vt, J_{PC} = 5.0 Hz, $C(CH_3)_3$, 6 C), 21.7 (s, $CH_2CH_2CH_2$, 1 C). ^{31}P{^{1}H} NMR (C_6D_6): δ 181.4 (s). Anal. Calcd for $C_{22}H_{45}ClBrO_2P_2$ (542.14): C, 48.74; H, 8.37. Found: C, 48.76; H, 8.39.

***trans*-[NiMe{*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane}] (3): 1a** (30.0 mg, 0.060 mmol) was dissolved in Et_2O (10 mL) and the solution was cooled down to -78 °C. MeLi (0.8 M in Et_2O, 0.15 mL, 0.12 mmol) was added dropwise via syringe and the reaction was left to reach room temperature over night. The reaction was quenched with water and the organic phase was dried with $MgSO_4$. Concentration in vacuo afforded **3** as an off-white crystalline solid. Yield: 22.6 mg (79%). ^{1}H NMR (C_6D_6): δ 3.55 (br t, *J* = 9.0 Hz, CH_2CHO, 2 H), 2.20-2.15 (m, CH_2CH_2CHO, 2 H), 1.65 (br s, $CH_2CH_2CH_2$, 1 H), 1.57 (t, *J* = 11.0 Hz, *H*C–Ni, 1 H), 1.39 (vt, *J* = 12.0 Hz, tBu, 18 H), 1.36 (vt, *J* = 12.0 Hz, tBu, 18 H), 1.10-1.06 (m, CH_2CH_2CHO, 2 H and $CH_2CH_2CH_2$, 1 H), -0.24 (t, *J* = 3.8 Hz, Ni–CH_3, 3 H). ^{13}C{^{1}H} NMR (C_6D_6): δ 85.4 (vt, J_{PC} = 18 Hz, CH_2CHO, 2 C), 67.6 (t, J_{PC} = 14 Hz, HC–Ni, 1 C), 39.5 (vt, J_{PC} = 12 Hz, $C(CH_3)_3$, 2 C), 37.6 (vt, J_{PC} = 12 Hz, $C(CH_3)_3$, 2 C), 33.6 (vt, J_{PC} = 12 Hz, CH_2CH_2CHO, 2 C), 28.6 (vt, J_{PC} = 5.2 Hz, $C(CH_3)_3$, 6 C), 28.1 (vt, J_{PC} = 6.0 Hz, $C(CH_3)_3$, 6 C), 22.4 (s, $CH_2CH_2CH_2$, 1C), -19.95 (t, J_{PC} = 19.4 Hz, Ni–CH_3, 1C). ^{31}P{^{1}H} NMR (C_6D_6): δ 187.0 (s)

***trans*-[NiPh{*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane}] (4):** Complex **1a** (28.0 mg, 0.056 mmol) was dissolved in Et_2O (5 mL) and cooled to -78 °C. Phenyl lithium (1.9 M in dibutylether) was added drop wise in twofold excess. The reaction mixture was allowed to reach room temperature and then stirred over night. The reaction was quenched with water and the product was extracted with additional Et_2O. Concentration *in vacuo* gave an off white solid residue that was recrystallized from toluene. Yield: 25.1 mg (83%). ^{1}H NMR (C_6D_6): δ 7.99 (d, *J* = 7.5 Hz, Ph, 1 H), 7.94 (d, *J* = 7.5 Hz, Ph, 1 H), 7.16-7.13 (m, Ph, 2 H), 6.96 (t, *J* = 7.0 Hz, Ph, 1 H), 3.60-3.55 (m, CH_2CHO, 2 H), 2.17-2.14 (m, CH_2CH_2CHO, 2 H), 1.71 (t, *J* = 11.0 Hz, *H*C–Ni, 1 H), 1.64 (br s, $CH_2CH_2CH_2$, 1 H), 1.32 (vt, *J* = 12.0 Hz, tBu, 18 H), 1.27 (vt, *J* = 12.0 Hz, tBu, 18 H), 1.08-1.04 (m, CH_2CH_2CHO, 2 H and $CH_2CH_2CH_2$, 1 H). ^{13}C{^{1}H} NMR (C_6D_6): δ 143.6 (d, J_{PC} = 1.6 Hz, Ph, 1 C), 143.4, (d, J_{PC} = 1.6 Hz, Ph, 1 C), 125.6 (vt, J_{PC} = 5.0 Hz, Ph, 1 C), 125.4 (vt, J_{PC} = 5.0 Hz, Ph, 1 C), 121.6 (vt, J_{PC} = 3.2 Hz, Ph, 1 C), 110.4 (s, Ph, 1 C), 85.3 (vt, J_{PC} = 15 Hz, CH_2CHO, 2 C), 67.5 (t, J_{PC} = 14 Hz, HC–Ni, 1 C), 40.4 (vt, J_{PC} = 13 Hz, $C(CH_3)_3$, 2 C), 38.5 (vt, J_{PC} = 19 Hz, $C(CH_3)_3$, 2 C), 34.1 (vt, J_{PC} = 12 Hz, CH_2CH_2CHO, 2 C), 29.1 (vt, J_{PC} = 6.6 Hz, $C(CH_3)_3$, 6 C), 28.7 (vt, J_{PC} = 5.6 Hz, $C(CH_3)_3$, 6 C), 22.6 (s, $CH_2CH_2CH_2$, 1 C). ^{31}P{^{1}H} NMR (C_6D_6): δ 184.3 (s). Anal. Calcd for $C_{28}H_{50}NiO_2P_2$ (539.34): C, 62.35; H, 9.34. Found: C, 62.48; H, 9.18.

***trans*-[NiH{*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane}] (5):** Under a stream of argon, $LiAlH_4$ (45.0 mg, 1.20 mmol) was added to a solution of **1a** (40.0 mg, 0.080 mmol) in toluene (3 mL). The suspension was stirred at room

temperature for 24 h. Filtration through a plug of celite rendered a pale yellow solution that was concentrated *in vacuo*. Recrystallisation from hexane afforded an off-white crystalline solid. Yield: 15.9 mg (43%). ^{1}H NMR (C_6D_6): δ 3.77-3.71 (m, CH_2CHO, 2 H), 2.28-2.24 (m, CH_2CH_2CHO, 2 H), 1.79 (dt, *J* = 2.0 Hz, *J* = 11.0 Hz, *H*C–Ni, 1 H), 1.73-1.68 (m, $CH_2CH_2CH_2$, 1 H), 1.37 (vt, *J* = 14.0 Hz, tBu, 18 H), 1.33 (vt, *J* = 13.0 Hz, tBu, 18 H), 1.22-1.18 (m, CH_2CH_2CHO, 2 H), 1.15-1.12 (m, $CH_2CH_2CH_2$, 1 H), -8.58 (t, *J* = 52.0 Hz, Ni–*H*, 1 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 86.7 (vt, J_{PC} = 17 Hz, CH_2CHO, 2 C), 71.6 (t, J_{PC} = 12 Hz, HC–Ni, 1 C), 38.7 (vt, J_{PC} = 16 Hz, $C(CH_3)_3$, 2 C), 36.6 (vt, J_{PC} = 21 Hz, $C(CH_3)_3$, 2 C), 34.4 (vt, J_{PC} = 12 Hz, CH_2CH_2CHO, 2 C), 28.9 (vt, J_{PC} = 6.6 Hz, $C(CH_3)_3$, 6 C), 28.7 (vt, J_{PC} = 7.0 Hz, $C(CH_3)_3$, 6 C), 23.2 (s, $CH_2CH_2CH_2$, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 210.9 (s).

Reaction of 3 with PhCCH. *trans*-[Ni(CCPh){*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane}] (6): A J. Young tube was charged with **3** (10.6 mg, 0.022 mmol) and C_6D_6. PhCCH (2.5 µL, 0.022 mmol) was added and the reaction was heated to 80 °C over a period of 6 days. The reaction mixture still contained ≈5% of compound **3**. Concentration *in vacuo* and recrystallization from hexane afforded the acetylide compound **6** as pale orange crystals. Yield: 7.9 mg (63%). ^{1}H NMR (C_6D_6): δ 7.46 (bd, J_{HH} = 7.5 Hz, Ar, 2 H), 7.16-7.12 (m, Ar, 1 H), 7.05-6.97 (m, Ar, 2 H), 3.64-3.61 (m, CH_2CHO, 2 H), 2.09-2.06 (m, CH_2CH_2CHO, 2 H), 1.89 (t, J_{PH} = 10.5 Hz, *H*C–Ni, 1 H), 1.53-1.49 (m, $CH_2CH_2CH_2$, 1 H), 1.47 (vt, *J* = 12.0 Hz, tBu, 18 H), 1.42 (vt, *J* = 12.0 Hz, tBu, 18 H), 1.03-0.93 (m, CH_2CH_2CHO, 2 H and $CH_2CH_2CH_2$, 1 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 130.5 (br s, C_{Ar}, 1 C), 130.0 (s, C_{Ar}, 2 C), 125.7 (s, C_{Ar}, 1 C), 125.3 (br s, *C*CPh, 1 C), 124.7 (s, C_{Ar}, 2 C), 116.5 (t, J_{PC} = 26.1 Hz, Ni–*C*CPh, 1 C), 87.0 (vt, J_{PC} = 18.3 Hz, CH_2CHO, 2 C), 68.1 (t, J_{PC} = 14.1 Hz, H*C*–Ni, 1 C), 40.3 (vt, J_{PC} = 14.2 Hz, $C(CH_3)_3$, 2 C), 38.2 (vt, J_{PC} = 20.0 Hz, $C(CH_3)_3$, 2 C), 33.8 (vt, J_{PC} = 12.2 Hz, CH_2CH_2CHO, 2 C), 28.8 (vt, J_{PC} = 6.2 Hz, $C(CH_3)_3$, 6 C), 28.5 (vt, J_{PC} = 5.8 Hz, $C(CH_3)_3$, 6 C), 22.3 (s, $CH_2CH_2CH_2$, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 194.3 (s). Anal. Calcd for $C_{30}H_{50}NiO_2P_2$ (563.36): C, 63.96; H, 8.95. Found: C, 63.92; H, 8.95.

Reaction of 5 with CO_2. *trans*-[Ni(OC(O)H){*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane}] (7): A degassed solution of **5** (40 mg, 0.086 mmol) in toluene (5 mL) was pressurised with CO_2 (1 atm). An immediate color change from off-white to yellow was observed, and the reaction mixture was stirred at room temperature for 40 min before being concentrated *in vacuo*. NMR analysis confirmed **7** as the sole product. ^{1}H NMR (C_6D_6): δ 8.50 (s, Ni–OCO*H*, 1 H), 3.51-3.42 (m, CH_2CHO, 2 H), 1.86-1.74 (m, CH_2CH_2CHO, 2 H and *H*C–Ni, 1 H), 1.49-1.42 (two overlapping vt, tBu, 36 H), 1.4-1.3 (m, $CH_2CH_2CH_2$, 1 H), 0.97-0.87 (m, CH_2CH_2CHO, 2 H and $CH_2CH_2CH_2$, 1 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 167.7 (s, Ni–*O*COH, 1 C), 87.4 (vt, J_{PC} = 19.0 Hz, CH_2CHO, 2 C), 54.7 (t, J_{PC} = 19.0 Hz, H*C*–Ni, 1 C), 39.7 (vt, J_{PC} = 13.6 Hz, $C(CH_3)_3$, 2 C), 37.9 (vt, J_{PC} = 21.0 Hz, $C(CH_3)_3$, 2 C), 33.5 (vt, J_{PC} = 14.5 Hz, CH_2CH_2CHO, 2 C), 28.1 (vt, J_{PC} = 8.2 Hz, $C(CH_3)_3$, 6 C), 27.8 (vt, J_{PC} = 8.0 Hz, $C(CH_3)_3$, 6 C), 21.6 (s, $CH_2CH_2CH_2$, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 193.0 (s).

***trans*-[Ni(OC(O)CH$_3$){*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane}] (8): 1a** (25 mg, 0.050 mmol) and AgOAc (14.8 mg, 0.089 mmol, 1.77 eq.) was mixed in THF (5 mL) and stirred at RT over night. The solvent was removed *in vacuo*, and the solid residues extracted with Et_2O and filtered through celite. Concentration *in vacuo* afforded **8** as a dark yellow crystalline solid. Yield: 22.0 mg (84%). ^{1}H NMR (C_6D_6): δ 3.47 (dt, *J* = 3.5 Hz, *J* = 11.0 Hz, CH_2CHO, 2 H), 2.03 (s, Ni–OCOC*H*$_3$, 3H), 1.87-1.83 (m, CH_2CH_2CHO, 2H) 1.75 (t, *J* = 11.0 Hz, *H*C–Ni, 1 H), 1.49-1.45 (two overlapping vt, tBu, 36 H), 1.38-1.32 (m, $CH_2CH_2CH_2$, 1 H), 0.98-0.89 (m, CH_2CH_2CHO, 2 H and $CH_2CH_2CH_2$, 1 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 175.3 (s, Ni–*O*COCH$_3$, 1C), 87.5 (vt, J_{PC} = 15.5 Hz, CH_2CHO, 2 C), 54.5 (t, J_{PC} = 17.0 Hz, H*C*–Ni, 1 C), 39.5 (vt, J_{PC} = 10.2 Hz, $C(CH_3)_3$, 2 C), 37.8 (vt, J_{PC} = 16.3 Hz, $C(CH_3)_3$, 2 C), 33.5 (vt, J_{PC} = 11.3 Hz, CH_2CH_2CHO, 2 C), 28.0 (vt, J_{PC} = 6.4 Hz, $C(CH_3)_3$, 6 C), 27.7 (vt, J_{PC} = 5.8 Hz, $C(CH_3)_3$, 6 C), 25.0 (s, Ni–OCO*C*H$_3$, 1C), 21.6 (s, $CH_2CH_2CH_2$, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): 178.8 δ (s). IR (ATR): $\nu_{as}(CO_2)$ = 1604 cm^{-1}, $\nu_s(CO_2)$ = 1373cm^{-1}. Anal. Calcd for $C_{24}H_{48}NiO_4P_2$ (521.28): C, 55.30; H, 9.28. Found: C, 55.48; H, 9.26.

Electrochemical studies. Cyclic voltammetry measurements on compounds **1-2** were carried out with a Biologic SP-150 potentiostat at 293 K, by using a three-electrode cell equipped with a platinum millielectrode of 0.126 cm^2 area, an Ag/Ag+ pseudo-reference electrode and a platinum wire counter electrode. Ferrocene was used as internal reference and the potential values were then re-adjusted with respect to the Ag/AgCl electrode. The electrolytic media involved a 0.1 mol/L solution of (^{n}Bu$_4$N)PF$_6$ in CH_2Cl_2. All experiments were performed at room temperature at 0.1 V s^{-1} at a concentration of the complexes of 10^{-3} M..

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Keywords: aliphatic pincer ligands • bis(phosphinite) POCOP complexes • nickel • cyclometallation • CO_2 insertion

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Synthesis and characterization of a new family of $POC_{sp3}OP$ Pincer complexes with nickel. Reactivity towards CO_2 and phenyl acetylene

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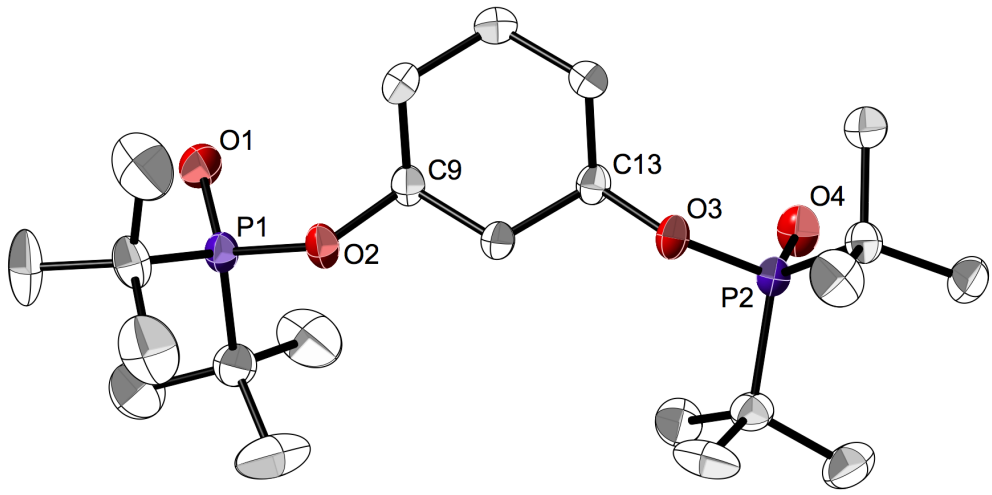
1. Characterisation of *cis*-1,3-bis-(di-*tert*-butylphosphinate)cyclohexane

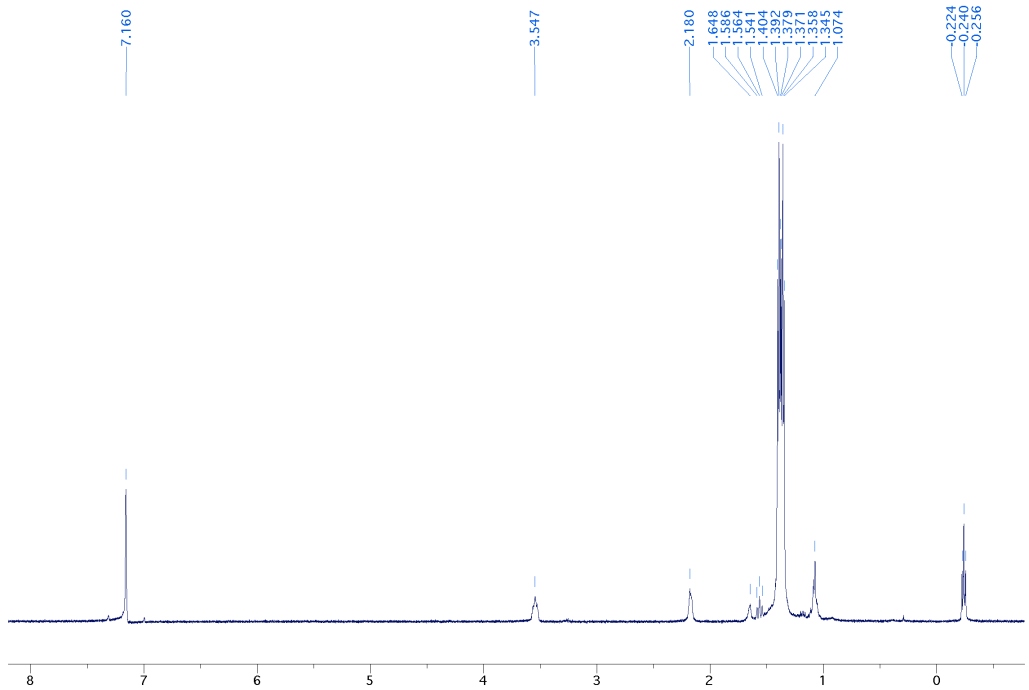
<u>*cis*-1,3-bis-(di-*tert*-butylphosphinate)cyclohexane</u>
cis-1,3-bis-(di-*tert*-butylphosphinito)cyclohexane (25.2 mg, 0.062 mmol) was dissolved in THF (5 mL) in air and the solution was stirred for 3h. Concentration in vacuo afforded *cis*-1,3-bis-(di-*tert*-butylphosphinate)cyclohexane as a white powder. X-ray quality crystals were obtained from a concentrated hexane solution upon cooling to -30 °C. Yield: 26.1 mg (96%) ^{1}H NMR (C_6D_6): δ 4.47-4.41 (m, CH_2CHO, 2 H), 2.93-2.91 (m, $OCHCH_2CHO$, 1 H), 1.97-1.95 (m, CH_2CH_2CHO, 2 H), 1.37-1.33 (m, $CH_2CH_2CH_2$, 1 H and $OCHCH_2CHO$, 1 H), 1.36 (vt, J_{PH} = 26.0 Hz, tBu, 36 H), 1.11-1,04 (m, CH_2CH_2CHO, 2 H), 0.88-0.80 (m, $CH_2CH_2CH_2$, 1 H). ^{13}C{^{1}H} NMR (C_6D_6): δ 72.6 (d, J_{PC} = 7.2 Hz, CH_2CHO, 2 C), 43.6 (d, J_{PC} = 1.8 Hz, $OCHCH_2CHO$, 1 C), 36.4 (d, J_{PC} = 3.6 Hz, $C(CH_3)_3$, 2 C), 35.7 (d, J_{PC} = 3.6 Hz, $C(CH_3)_3$, 2 C), 33.8 (d, J_{PC} = 2.4 Hz, CH_2CH_2CHO, 2 C), 26.7 (d, J_{PC} = 3.8 Hz, $C(CH_3)_3$, 12 C), 20.4 (s, $CH_2CH_2CH_2$, 1 C). ^{31}P{^{1}H} NMR (C_6D_6): δ 63.7 (s).



Molecular structure of *cis*-1,3-bis-(di-*tert*-butylphosphinate)cyclohexane at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: P1–O1 = 1.4622(16), P1–O2 = 1.5843(15), O2–C9 = 1.463(2), P2–O4 = 1.4692(16), P2–O3 = 1.5937(14), O3–C13 = 1.453(2), O1–P1–O2 = 115.12(9), P1–O2–C9 = 123.79(12), O3–P2–O4 = 114.81(9), C13–O3–P2 = 125.83(12).

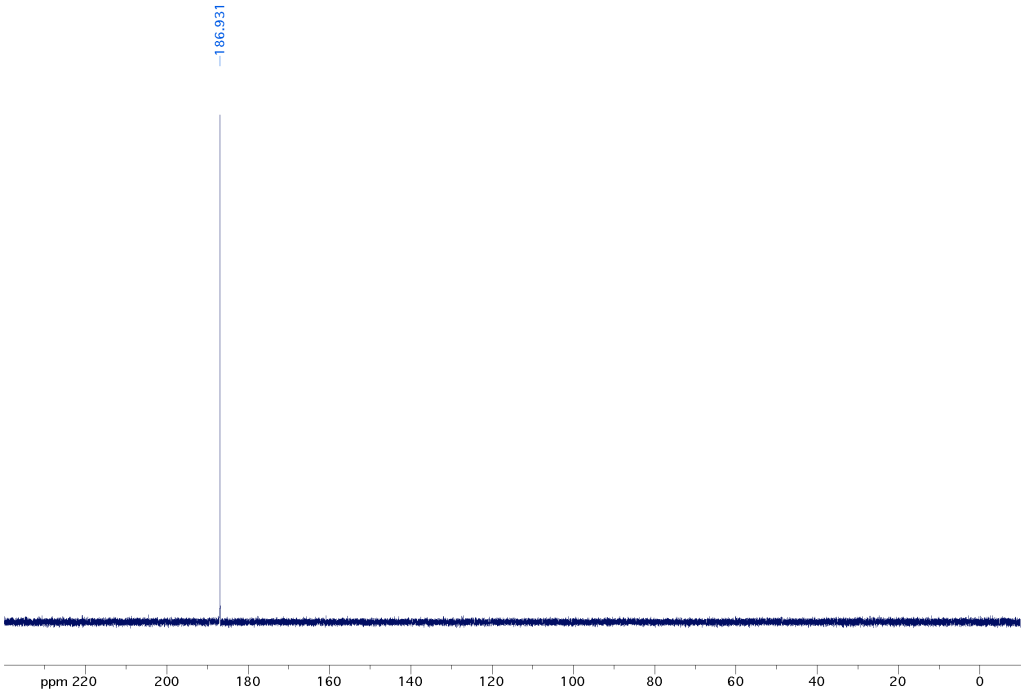
Crystal data and collection and refinement details:
$C_{22}H_{46}P_2O_4$, M = 436.53, triclinic, a = 8.5100(8), b = 11.8776(10), c = 13.9279(12) Å, α = 99.120(7), β = 105.357(8), γ = 97.834(7)°, V = 1316.7(2) Å^3, space group P-1 (No. 2), Z = 2, μ = 0.187 mm^{-1}, D_{calc} = 1.101 g cm^{-3}, θ range 2.52-33.12 deg, 13734 reflections measured, 8708 unique (R_{int} = 0.0303) which were used in all calculations. The final $wR(F^2)$ was 0.1739 and the S value 0,787 (all data). The $R(F)$ was 0.0731 (I>2σ(I)).

2. NMR-spectra

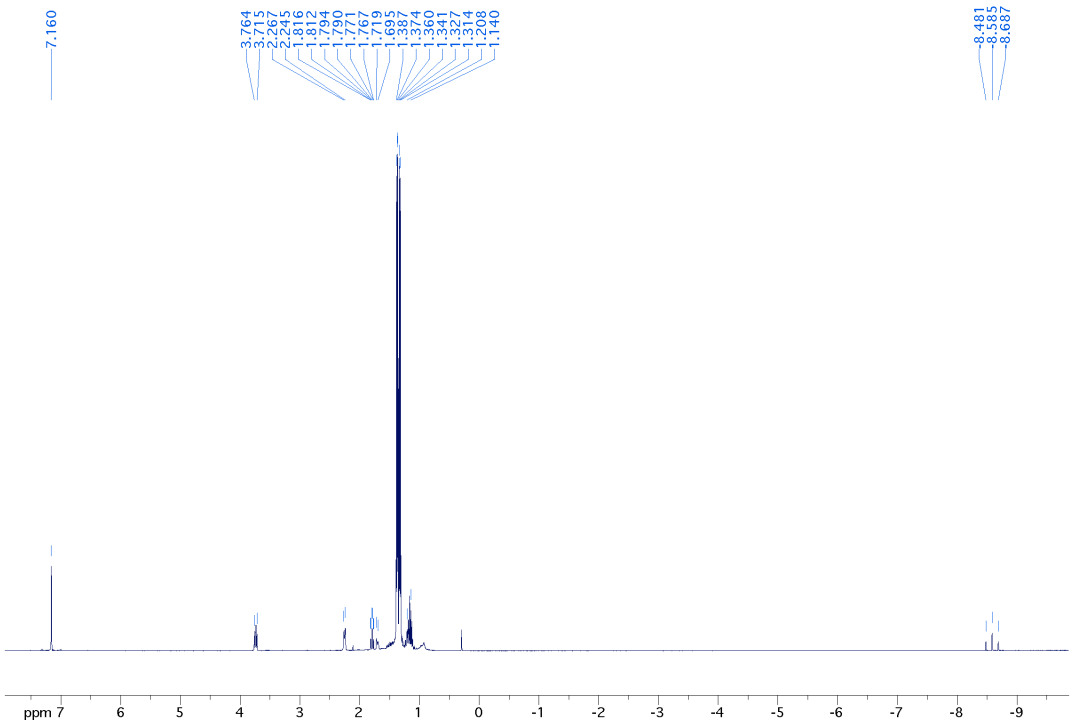


^{1}H-NMR (C_6D_6) of compound 3. The Ni–Me protons are displayed as a triplet at -0.24 ppm.

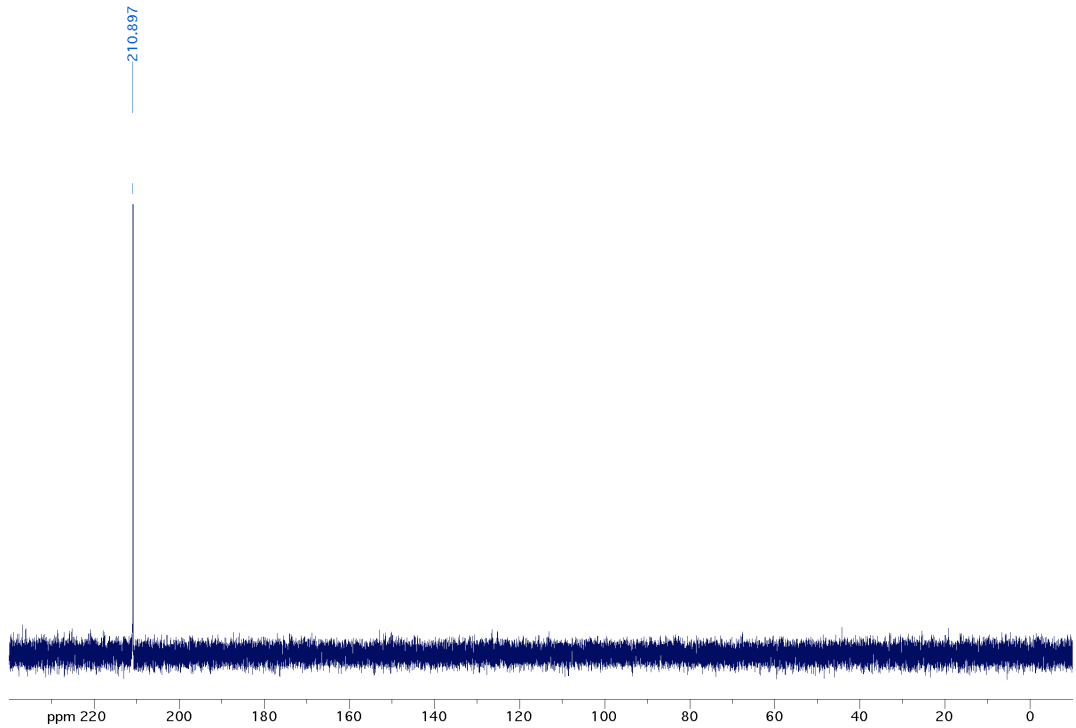
^{13}C-NMR (C_6D_6) of compound 3. The Ni–Me carbon are displayed as a triplet at -20 ppm. Trace amounts of 1a are notable, escpecially for its more intense shifts i.e. the CH_2CHO carbons at 87 ppm, the $C(CH_3)_3$ carbons around 28 ppm and the $CH_2CH_2CH_2$ carbon at 21 ppm. The singlet at 30 ppm corresponds to Apiezon brand H grease, and the singlet at 1 ppm is silicon grease.



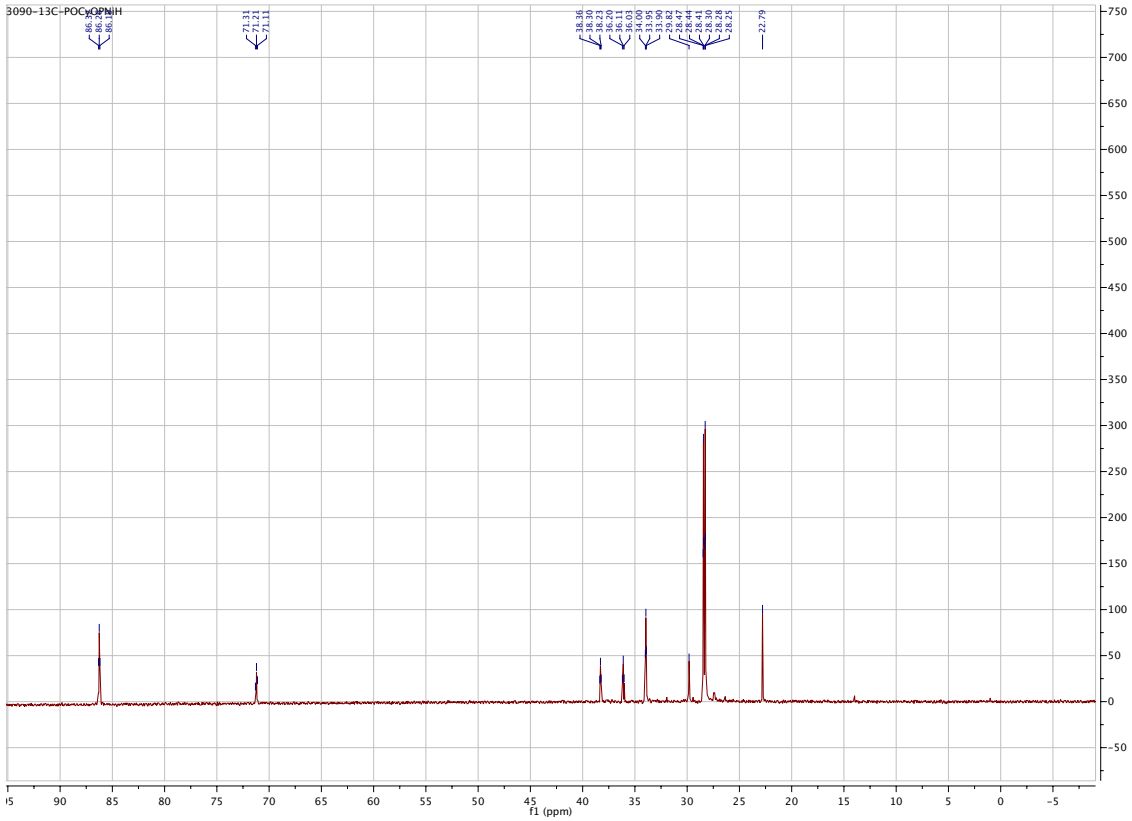
^{31}P-NMR (C_6D_6) of compound 3.



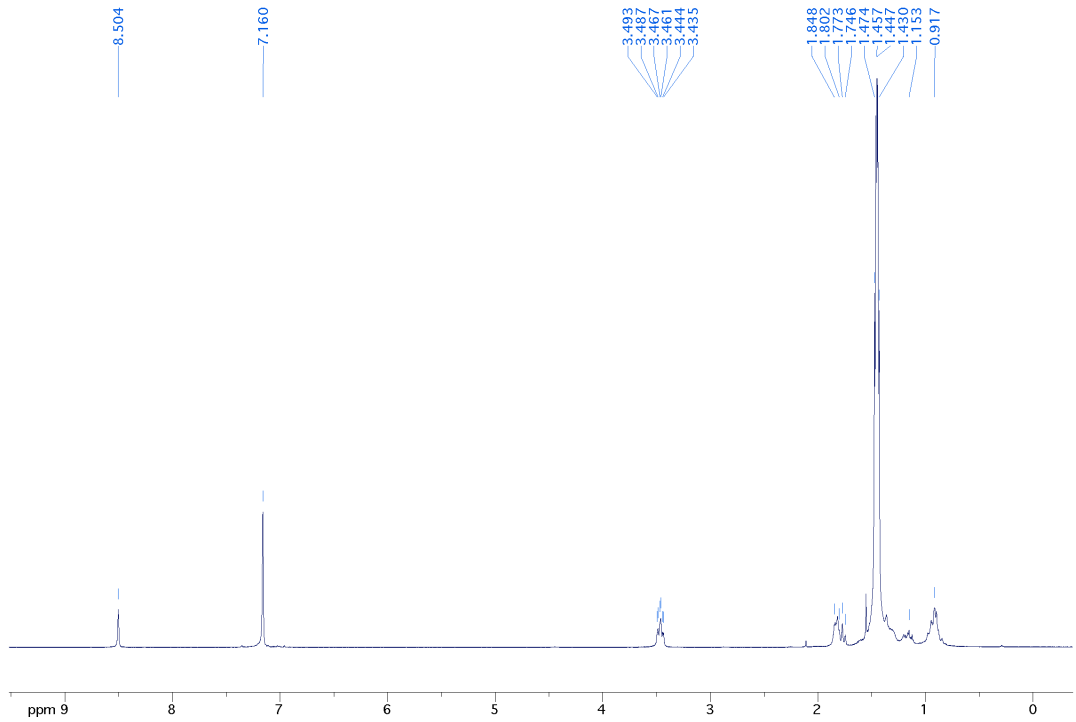
^{1}H-NMR (C_6D_6) of compound 5. The characteristic hydride shift appears at -8.6 ppm. The spectrum shows some silicon grease at 0.29 ppm and some Apiezon brand H grease at 0.90-0.98 ppm along with trace amounts of toluene at 2.11, 7.02 and 7.13 ppm.



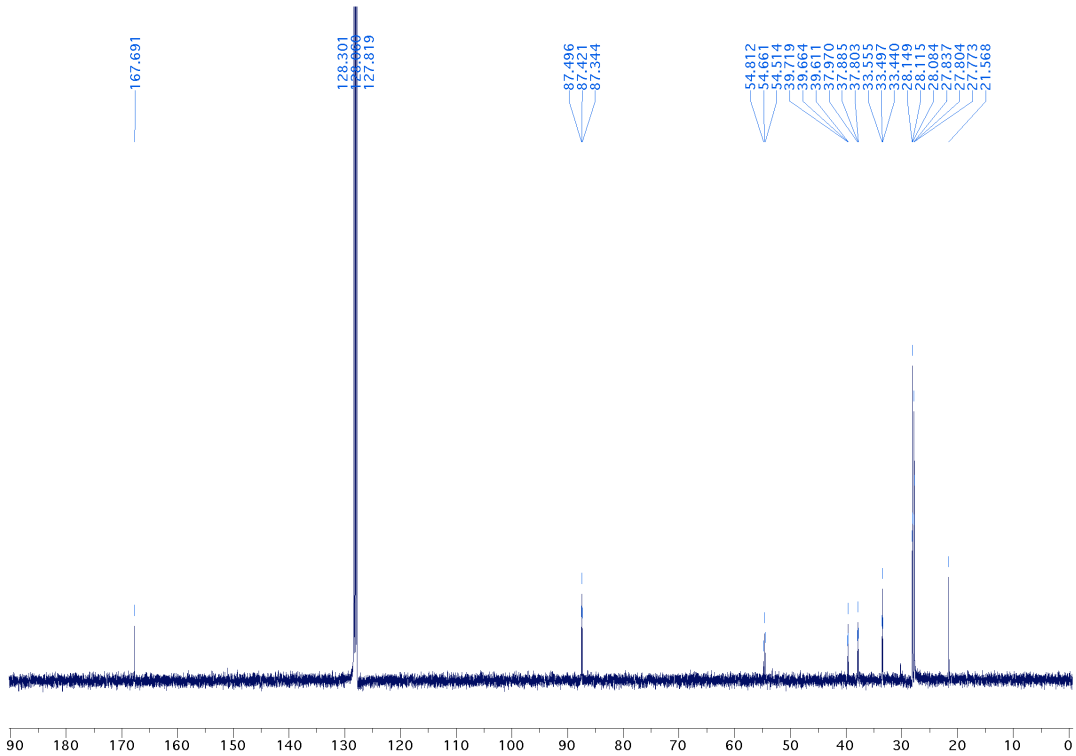
^{31}P-NMR (C_6D_6) of compound 5.



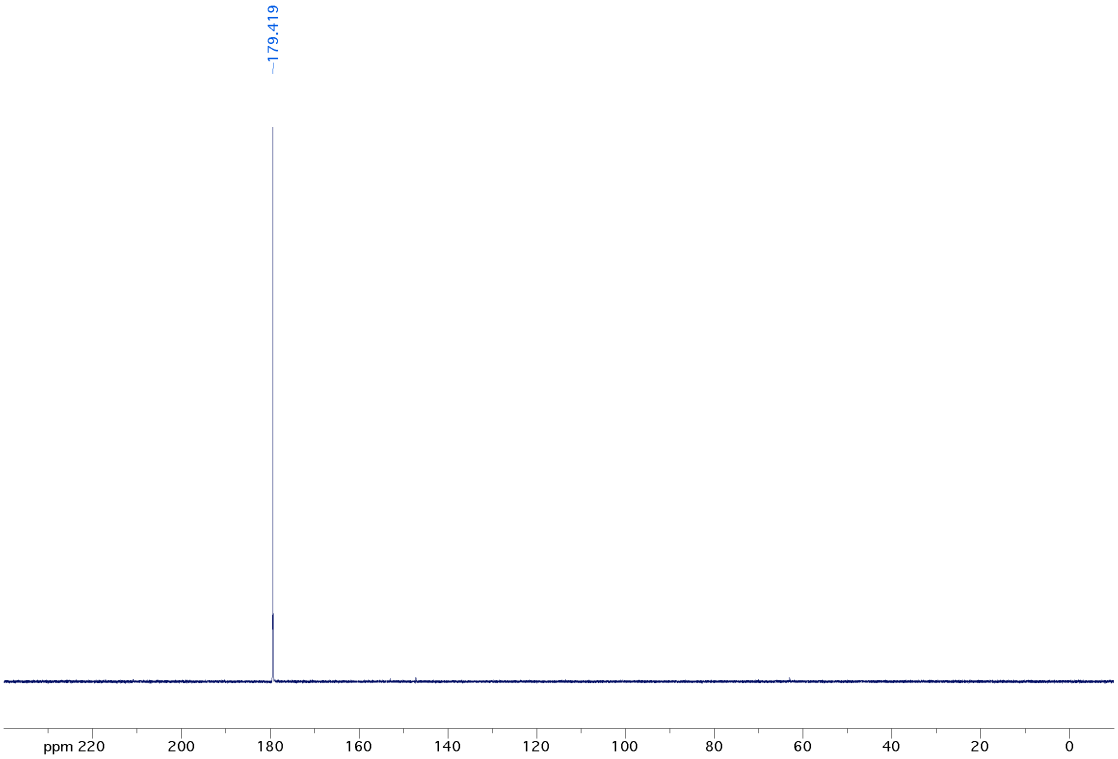
^{13}C-NMR (C_6D_6) of compound 5. The singlet at 30.2 ppm corresponds to Apiezon brand H grease.



^{1}H-NMR (C_6D_6) of compound 7. The singlet at 1.55 ppm refers to acetone contamination of the deuterated solvent. The spectrum suffers from some overlap, but the formate proton at 8.5 ppm and the CH_2CHO protons at 3.5 ppm are clearly distinguishable. The ^{t}Bu-protons are displayed as two slightly merged virtual triplets around 1.5 ppm.



^{13}C-NMR (C_6D_6) of compound 7. The low intense singlet at 30.2 ppm refers to acetone contamination of the deuterated solvent.



^{31}P-NMR (C_6D_6) of compound 7.

Synthesis and Characterization of $POC_{sp3}OP$ Supported Ni(II) Hydroxo, Hydroxycarbonyl and Carbonate Complexes

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Abstract

A nickel(II) hydroxo complex (**3**) supported by a cyclohexyl based $POC_{sp3}OP$ pincer ligand ($POC_{sp3}OP$ = *cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexyl) is reported. Complex **3** reacts with CO to form the corresponding hydroxycarbonyl complex, ($POC_{sp3}OP$)NiCOOH (**4**). Complex **3** is also reactive towards CO_2, forming a bicarbonate species (**5**) that under reduced pressure loses ½ eq. of H_2O and CO_2 to give a binuclear, bridged carbonate complex (**6**). All compounds were characterized in the solid state by X-ray diffraction.

Introduction

The chemical reactivity of late transition metal complexes containing metal-oxygen covalent bonds has attracted much interest over the last decades.[1] These bonds are generally weaker than their metal-carbon counterparts, and accordingly metal hydroxo and alkoxo complexes have been suggested as reactive intermediates in many catalytic processes,[2] and also to play an important part in several biological systems.[3] However, examples of mononuclear terminal hydroxo complexes of group 10 transition metals remain relatively few and typically require the steric stabilization that e.g. a tricoordinated PCP ligand with bulky phosphorus substituents constitutes,[4,5,6] in order to prevent formation of species with higher nuclearity such as bridged Ni(II)–(OH)–Ni(II)[7] or doubly bridged Ni(II)$(OH)_2$Ni(II) complexes.[8]

Investigating the reactivity of terminal hydroxo complexes towards CO_2 is relevant, partly from a biological perspective, where the metalloenzyme catalyzed hydration of CO_2 to carbonic acid takes place at a Zn–OH active site,[9] but also for synthetic applications in the development of transition metal mediated functionalisations of CO_2, e.g. in the synthesis of organic carbonates.[10] The potential utilization of cheap and abundant CO_2 as a synthetic C1 source remains a major target for making the chemical industry sustainable.[11]

CO_2 insertion into an M–X covalent bond commonly generates M–O(CO)X carboxylate species, but in enzyme chemistry Ni(II) is known to occasionally coordinate the CO_2 carbon. The carbon monoxide dehydrogenases (CODH's) catalyze the reversible reduction of CO_2 to CO at a nickel center via the formation of

a nickel-carbon bond.[11b,12] This process has been subject to biomimetic reactivity studies with Ni(II) pincer complexes, with hydroxycarbonyl species as proposed intermediates.[13] The process directly corresponds to the reverse water-gas shift reaction (RWGS), and accordingly hydroxycarbonyl species are suggested to play a crucial part as intermediates in the industrial organometallic catalysis of the forward reaction (WGS).[14]

Bicarbonate and hydroxycarbonyl complexes show a similarly low stability as the terminal hydroxo complexes, with a propensity of forming dimeric species, and it was not until recently that the first hydroxycarbonyl nickel complex was isolated and structurally characterized.[13]

Whereas the reactivity of group 10 $PC_{Ar}P$ hydroxo and alkoxo complexes towards CO and CO_2 is well documented, [4d, 5, 6b, 15] the chemistry of their $PC_{sp3}P$ counterparts has not been studied. Yet coordination of an sp^3-hybridised PCP carbon expectedly gives a higher electron density at a metal centre relative an sp^2-hybridised carbon, which might beneficial for insertion reactions into the M–OH bond. We have previously accomplished the first successful cyclometallation of a cyclohexyl-based $POC_{sp3}OP$ pincer ligand, affording tridentate chelate ($POC_{sp3}OP$)NiX complexes (X = Cl, Br).[16] We here report on the synthesis of the analogous hydroxo complex ($POC_{sp3}OP$)NiOH (**3**) via two alternative pathways. Reaction of **3** with CO or CO_2 gives insertion into the Ni–OH bond, affording the corresponding hydroxycarbonyl complex (**4**) and carbonate complex (**5**) respectively, that were both isolated and characterized by means of NMR spectroscopy and X-ray crystallography.

Experimental Section

General Comments. All manipulations were performed under a nitrogen or argon atmosphere using standard Schlenk or glovebox techniques, except if noted. Solvents were purified by vacuum distillation from sodium/benzophenone ketyl radical. The complex *trans*-[NiCl{*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane}] (**1**) was synthesized according to known procedures.[16] All other chemicals were purchased from commercial suppliers and used as received. ^1H, ^{13}C and ^{31}P NMR experiments were recorded on a Varian Unity INOVA 500 spectrometer, operating at 499.76 MHz (^1H). For ^1H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at $\delta = 0$ ppm.

Multiplicities are abbreviated as follows: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet, (br) broad, (v) virtual. IR spectra were obtained on a Bruker ALPHA FT-IR. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

Crystallography. XRD-quality crystals of compounds **2**-**6** were obtained through recrystallization from benzene or hexane. Intensity data were collected with an Oxford Diffraction Excalibur 3 system, using ω-scans and MoKα (λ = 0.71073 Å) radiation.[17] The data were extracted and integrated using Crysalis RED.[18] The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL5.1.[19] Molecular graphics were generated using CrystalMaker® 8.3.5.[20]

Preparation of *trans*-[NiONO$_2$\{*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane\}] (2). Complex **1** (40.0 mg, 0.080 mmol) and $AgNO_3$ (24.2 mg, 0.142 mmol) were dissolved in THF (5 mL) and the mixture was stirred over night at RT, whereafter the solvent was removed *in vacuo*. Extraction with Et_2O and evaporation of the solvent afforded **2** as a brick red, microcrystalline solid. Yield: 32.3 mg (77%). ^{1}H NMR (C_6D_6): δ 3.42 (dt, J = 3.5 Hz, J = 10.5 Hz, CH_2CHO, 2 H), 1.85 (t, J = 11.0 Hz, *H*C–Ni, 1 H), 1.77-1.72 (m, CH_2CH_2CHO, 2 H), 1.36 (vt, J = 13.5 Hz, tBu, 36 H), 1.37-1.35 (m, $CH_2CH_2CH_2$, 1 H), 0.92-0.79 (m, CH_2CH_2CHO, 2 H and $CH_2CH_2CH_2$, 1 H). ^{13}C{^{1}H} NMR (C_6D_6): δ 87.6 (vt, J_{PC} = 14.3 Hz, CH_2CHO, 2 C), 54.1 (t, J_{PC} = 14 Hz, HC–Ni, 1 C), 39.4 (vt, J_{PC} = 11.3 Hz, $C(CH_3)_3$, 2 C), 37.8 (vt, J_{PC} = 17.3 Hz, $C(CH_3)_3$, 2 C), 33.4 (vt, J_{PC} = 11.6 Hz, CH_2CH_2CHO, 2 C), 27.8 (vt, J_{PC} = 6.7 Hz, $C(CH_3)_3$, 6 C), 27.5 (vt, J_{PC} = 6.3 Hz, $C(CH_3)_3$, 6 C), 21.3 (s, $CH_2CH_2CH_2$, 1C). ^{31}P{^{1}H} NMR (C_6D_6): 180.3 δ (s). IR (ATR): $\nu_{as}(NO_2)$ = 1465 cm^{-1}, $\nu_s(NO_2)$ = 1287 cm^{-1}, ν(NO) = 1021 cm^{-1}. Anal. Calcd for $C_{22}H_{45}NNiO_5P_2$ (524.24): C, 50.40; H, 8.65; N, 2.67. Found: C, 50.60; H, 8.66; N, 2.64.

Preparation of *trans*-[NiOH\{*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane\}] (3). *Method I.* **1** (75.0 mg, 0.15 mmol) and NaOH (60.0 mg, 1.50 mmol) were dissolved in THF (5 mL) and the mixture was heated to 70 °C for a period of 14 days. The reaction was concentrated *in vacuo*, redissolved in pentane and filtered through celite. Storage at -30 °C afforded **3** as yellow crystals. Yield: 20.1 mg (28%).

Method II. **2** (78.6 mg, 0.15 mmol) and NaOH (60.0 mg, 1.50 mmol) were dissolved in THF (5 mL) and the reaction was stirred at RT for 24 h. The solvent was removed *in vacuo* and the solid residues dissolved in pentane and filtered through celite. Removal of the solvent afforded **3** as a yellow powder. Yield: 39.5 mg (55%). ^{1}H NMR (C_6D_6): δ 3.52-3.46 (m, CH_2CHO, 2 H), 1.96-1.93 (m, CH_2CH_2CHO, 2 H), 1.56 (t, J_{PH} =

11.5, *H*C–Ni, 1 H), 1.52 (vt, *J* = 13.0 Hz, tBu, 18 H), 1.48 (vt, *J* = 13.5 Hz, tBu, 18 H), 1.50-1.47 (m, $CH_2CH_2CH_2$, 1 H), 1.03-0.93 (m, CH_2CH_2CHO, 2 H and $CH_2CH_2CH_2$, 1 H), -2.71 (t, J_{PH} = 6.0, Ni–OH, 1 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 87.8(vt, J_{PC} = 17 Hz, CH_2CHO, 2 C), 54.6 (t, J_{PC} = 16 Hz, HC–Ni, 1 C), 39.3 (vt, J_{PC} = 10 Hz, $C(CH_3)_3$, 2 C), 37.3 (vt, J_{PC} = 16 Hz, $C(CH_3)_3$, 2 C), 33.7 (vt, J_{PC} = 12 Hz, CH_2CH_2CHO, 2 C), 28.4 (vt, J_{PC} = 7.2 Hz, $C(CH_3)_3$, 6 C), 28.0 (vt, J_{PC} = 4.4 Hz, $C(CH_3)_3$, 6 C), 22.1 (s, $CH_2CH_2CH_2$, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): 173.9 δ (s).

Reaction of 3 with CO. Formation of *trans*-[Ni(C(O)OH){*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane}] (4). Complex **3** was dissolved in C_6D_6 (0.6 mL) in a J. Young tube, and the tube was pressurized with approximately 2 atm CO. The sample was stored at RT for 3 days, until **4** was observed as the only significant compound by means of NMR-spectroscopy. Further storage at RT afforded fine, light yellow, X-ray quality crystals. ^1H NMR (C_6D_6): δ 9.08 (s, Ni–COO*H*, 1H), 3.55-3.50 (m, CH_2CHO, 2 H), 2.07-2.04 (m, CH_2CH_2CHO, 2 H), 1.65 (t, J_{PH} = 11.5 Hz, *H*C–Ni, 1H), 1.57-1.52 (m, $CH_2CH_2CH_2$, 1H), 1.40 (vt, *J* = 13.5 Hz, tBu, 18 H), 1.37 (vt, *J* = 13.5 Hz, tBu, 18 H), 1.09-0.90 (m, CH_2CH_2CHO, 2 H and $CH_2CH_2CH_2$, 1 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 227.9 (s, Ni–*C*OOH, 1 C), 85.8 (vt, J_{PC} = 14.2 Hz, CH_2CHO, 2 C), 68.6 (t, J_{PC} = 26.9 Hz, HC–Ni, 1 C), 40.4 (vt, J_{PC} = 15.8 Hz, $C(CH_3)_3$, 2 C), 38.5 (vt, J_{PC} = 20.7 Hz, $C(CH_3)_3$, 2 C), 33.9 (vt, J_{PC} = 12.1 Hz, CH_2CH_2CHO, 2 C), 28.6 (vt, J_{PC} = 5.5 Hz, $C(CH_3)_3$, 6 C), 28.3 (vt, J_{PC} = 5.3 Hz, $C(CH_3)_3$, 6 C), 22.4 (s, $CH_2CH_2CH_2$, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 193.4 (s).

Reaction of 3 with CO_2. Formation of *trans*-[Ni(OC(O)OH){*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane}] (5) and [{(*cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexane)Ni}$_2$(μ-CO_3)] (6). A degassed hexane solution (7 mL) of **3** (35 mg, 0.073 mmol) was treated with 1 atm CO_2, and a fine yellow precipitate appeared within seconds. After 4 h of stirring at RT the reaction mixture was treated with toluene (1.5 mL) to afford a clear solution. Slow evaporation of the solvents afforded **5** as yellow X-ray quality crystals. Running the reaction in C_6D_6 under 4 atm CO_2 gave **5** as the predominant species in solution within 3h, and full conversion of **3**. Removal of the C_6D_6 *in vacuo* afforded a solid residue that was fully soluble in hexane, and storage of a concentrated hexane solution at -30 °C for several days yielded X-ray quality crystals of **6**.

Complex **5**: ^1H NMR (C_6D_6): δ 12.4 (br s, Ni–OC(O)O*H*, 1H), 3.47-3.42 (m, CH_2CHO, 2 H), 1.81-1.77 (m, CH_2CH_2CHO, 2 H), 1.75 (t, J_{PH} = 11.0 Hz, *H*C–Ni, 1H), 1.48 (vt, *J* = 12.5 Hz, tBu, 36 H), 1.37-1.33 (m, $CH_2CH_2CH_2$, 1H), 0.93-087 (m, CH_2CH_2CHO, 2 H

and $CH_2CH_2CH_2$, 1 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.50 (br s, Ni–OCOOH, 1 C), 87.50 (vt, J_{PC} = 15.5 Hz, CH_2CHO, 2 C), 53.54 (t, J_{PC} = 29.4 Hz, HC–Ni, 1 C), 39.48 (vt, J_{PC} = 10.9 Hz, $C(CH_3)_3$, 2 C), 37.72 (vt, J_{PC} = 16.3 Hz, $C(CH_3)_3$, 2 C), 33.48 (vt, J_{PC} = 10.9 Hz, CH_2CH_2CHO, 2 C), 28.10 (vt, J_{PC} = 6.5 Hz, $C(CH_3)_3$, 6 C), 27.79 (vt, J_{PC} = 6.2 Hz, $C(CH_3)_3$, 6 C), 21.55 (s, $CH_2CH_2CH_2$, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 178.2 (s). IR (ATR): $\nu_{as}(CO_2)$ = 1615 cm^{-1}, $\nu_s(CO_2)$ = 1369cm^{-1}.

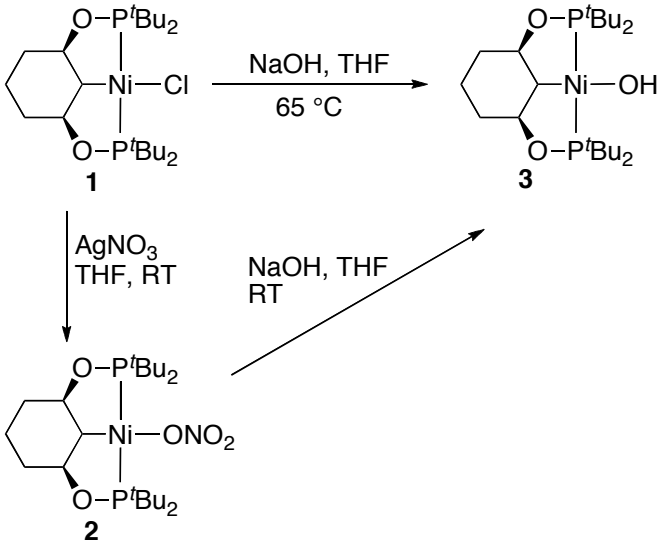
Complex **6**: ^1H NMR (C_6D_6): δ 3.50-3.45 (m, CH_2CHO, 4 H), 1.93-1.89 (m, CH_2CH_2CHO, 4 H), 1.65 (vt, *J* = 13.5 Hz, tBu, 36 H), 1.60 (vt, *J* = 13.0 Hz, tBu, 36 H), 1.65-1.58 (*H*C–Ni, 2H), 1.36-1.32 (m, $CH_2CH_2CH_2$, 2H), 1.02-0.90 (m, CH_2CH_2CHO, 4 H and $CH_2CH_2CH_2$, 2 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.50 (br s, μ-CO_3, 1 C), 85.79 (vt, J_{PC} = 13.6 Hz, CH_2CHO, 4 C), 53.5 (t, J_{PC} = 27.6 Hz, HC–Ni, 2 C), 39.46 (vt, J_{PC} = 9.9 Hz, $C(CH_3)_3$, 4 C), 37.77 (vt, J_{PC} = 15.2 Hz, $C(CH_3)_3$, 4 C), 33.66 (vt, J_{PC} = 11.6 Hz, CH_2CH_2CHO, 4 C), 29.14 (vt, J_{PC} = 6.4 Hz, $C(CH_3)_3$, 12 C), 28.61 (vt, J_{PC} = 6.2 Hz, $C(CH_3)_3$, 12 C), 21.81 (s, $CH_2CH_2CH_2$, 2 C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 176.1 (br s).

Results and discussion

Synthesis of the ($POC_{sp3}OP$)NiOH complex **3** from the chloride **1** was attempted according to the previously reported anion metathesis route used for making similar nickel hydroxide complexes.[4d,6a] However, like Hazari and coworkers, we found the reaction with NaOH to be quite slow, possibly due to the bulky *tert*-butyl substituents on the ligand framework (Scheme 1). Although **3** can be obtained by the direct route, we noted, analogously to previously published work on ($PC_{Ar}P$)Pd pincer complexes,[6a,21] that **1** is readily converted to the corresponding nitrate complex **2** in a reaction with $AgNO_3$, which in turn can undergo a straightforward reaction with NaOH to form **3** in shorter time and improved over-all yield. We also tried forming **3** from the analogous hydride complex ($POC_{sp3}OP$)NiH[16] in a reaction with H_2O, a transformation reported by Frech for their palladium pincer complexes with adamantyl core,[22] but for the current system this protocol was unsuccessful, giving no observed **3** and slow decomposition of the hydride complex to several uncharacterized ^{31}P containing species.

Thus, complex **2** was obtained in good yield upon stirring **1** with $AgNO_3$ at room temperature for 24 h and despite using a slight excess (1.77 eq.) of the silver reagent **1** did not show any tendency to oxidation to Ni(III). This has previously been reported

by Cámpora and coworkers for the formation of the structurally similar (PCP)NiONO$_2$ complex that gave the stable side product (PCP)Ni^{III}(ONO$_2$)$_2$ when exceeding a 1:1 ratio between (PCP)NiCl and AgNO$_3$ (PCP = C$_6$H$_3$-2,6-(CH$_2$P^{i}Pr$_2$)$_2$).[23] The ^{31}P NMR shift of **2** only shows a minor change relative the starting material **1** (δ = 180.3 ppm for **2** as compared to 179.7 ppm for **1**), but the ^{1}H NMR spectrum differs significantly as complex **2** displays a complete coalescence of the two characteristic virtual triplets corresponding to the 36 ^{t}Bu-protons. The FTIR data is clearly indicative of a η^1 coordinated nitrate ligand, and the observed bands are in good agreement with those reported by Campora.[23] The ^{1}H NMR spectrum of **3** displays a triplet resonance corresponding to the hydroxide proton at δ = -2.71 ppm (J_{HP} = 6.0 Hz), the high field shift underpinning the nucleophilicity of the ligand. However, the O–H vibration could not be observed in the IR-spectrum and neither was the OH proton located by X-ray diffraction of the single crystal. The compound was slightly contaminated with H grease (Apiezon) and was not subjected to elemental analysis; overall the NMR-spectroscopy characterization and X-ray structure are only compatible with the suggested structure of **3**.



Scheme 1

The molecular structures of complexes **2** and **3** are given in figure 1 and 2 respectively, along with crystal data and collection and refinement details for compounds **2-6** in Table 1**.** The complexes display the *cis*-1,3-bis-((di-*tert*-butylphosphinito)methyl)cyclohexane ligand coordinated in a meridional fashion with the P atoms positioned *trans* to each other. The Ni atom adopts a distorted square planar geometry with P(1)–Ni–P(2) angles around 165°. This is a slightly

more acute P–Ni–P angle than in our recently reported and structurally similar cyclohexyl-based bis(phosphine) $PC_{sp3}P$ nickel complexes.[24] The trend is due to the shorter P–O and C–O distances in a bis(phosphinite) complex than the corresponding P–C and C–C distances in an analogous bis(phosphine) complex, resulting in a more open coordination site in the $POC_{sp3}OP$ case. In both structures there is disorder in the cyclohexyl ring and in **2** this disorder can be resolved showing the presence of both chair conformations of the cyclohexyl ring in an approximate ratio of 57:43. This underpins the fluxional character of the ring flip in **2** as observed also in solution by the equivalence of the tBu groups. There is also disorder in the nitrate group that has two in-plane rotational positions. The Ni–OH bond of **3** is slightly longer than in the $PC_{sp3}P$-supported nickel hydroxo complexes reported by the groups of Piers[4e] and Zargarian;[25] 1.911(3) Å as compared to 1.9082(15) Å and 1.8793(14) Å respectively, indicating a relatively high trans influence from this $POC_{sp3}OP$ ligand, despite the electron withdrawing effect of the oxygen atoms in the pincer arms.

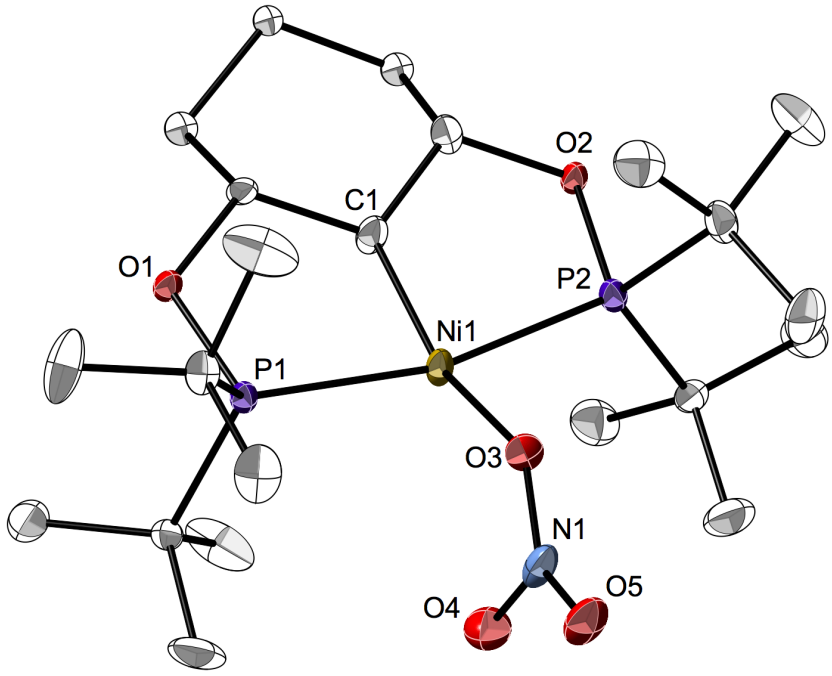


Figure 1. Molecular structure of **2** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.913(3), Ni1–P1 = 2.2348(9), Ni1–P2 =2.2339(9), Ni1–O3 = 1.994(5), O3–N1 = 1.256(6), N1–O4 = 1.316(6), N1–O5 = 1.230(7), C1–Ni1–O3 = 158.28(19), P1–Ni1–P2 =164.00(4), P1–Ni1–C1 = 82.09(9), P2–Ni1–C1 = 81.92(9), P1–Ni1–O3 = 101.53(12), P2–Ni1–O3 = 93.56(12).

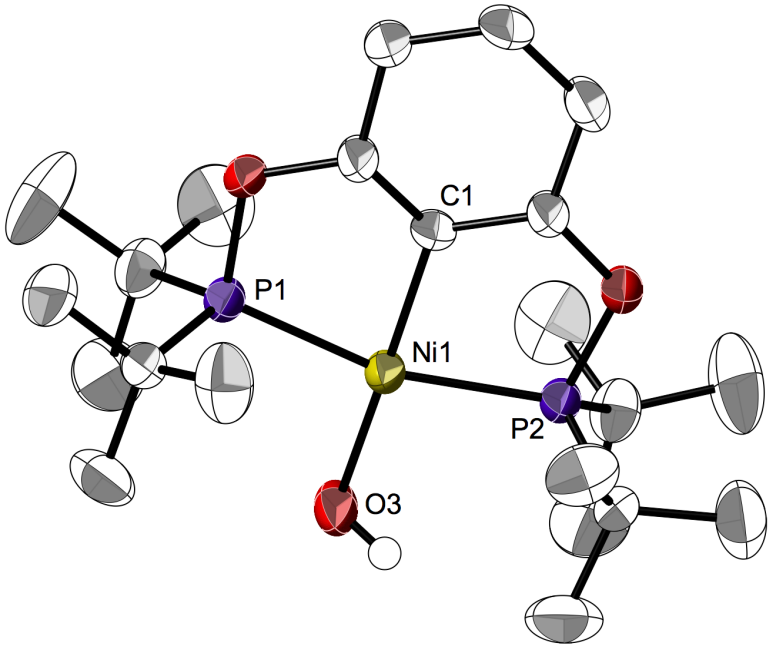
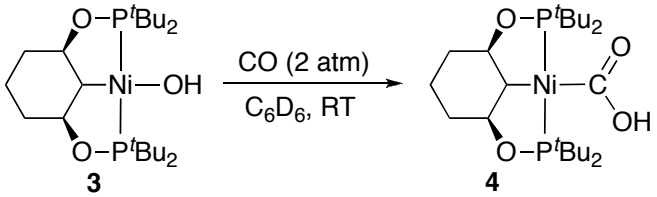


Figure 2. Molecular structure of **3** at the 30% probability level. Hydrogen atoms except the hydroxide are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.942(4), Ni1–P1 = 2.1917(14), Ni1–P2 = 2.1888(14), Ni1–O3 = 1.911(3), C1–Ni1–O3 = 176.9(2), P1–Ni1–P2 = 164.14(6), P1–Ni1–C1 = 82.01(15), P2–Ni1–C1 = 82.15(15), P1–Ni1–O3 = 97.46(13), P2–Ni1–O3 = 98.39(13).

Reacting a degassed C_6D_6 solution of **3** with 2 atm CO gives a clean conversion over a period of 3 days to the corresponding hydroxycarbonyl complex **4** through insertion into the Ni–OH bond (Scheme 2). The course of the reaction was followed by means of ^{31}P NMR spectroscopy, and no formation of any bridged dimeric μ-CO_2-κ^{2}C,O species was indicated under these conditions, as was previously reported by the group of Cámpora[6a] through a suggested decarbonylation sequence between two (PCP)NiCOOH complexes (PCP = C_6H_3-2,6-($CH_2P^iPr_2$)$_2$). Lee and coworkers reported on the same type of dinuclear compounds formed from PNP pincer supported nickel hydoxycarbonyl complex (PNP = N[2-P^iPr_2-4-Me-C_6H_3]$_2$) in a subsequent condensation reaction with 1 eq of the corresponding (PNP)NiOH complex. The same authors also report the formation of the hydroxycarbonyl with the PNP ligand is substantially faster and that degassing and heating on a solution of their (PNP)NiCOOH complex results in full decomposition with the β-hydride elimination product (PNP)NiH as the major product. This closely resembles our previous observations for the similar (PCP)PdCOOH complex (PCP = C_6H_3-2,6-($CH_2P^tBu_2$)$_2$) that isomerizes to form the analogous formate complex upon heating in a closed

vessel, probably via β-hydride elimination to form the hydride, followed by CO_2 insertion into the Ni–H bond.[15] With this in mind, additional studies should be made concerning the stability and further reactivity of complex **4**. The acidic proton was not observed in the ^{1}H NMR spectrum and the carbonyl carbon was also hardly detectable by ^{13}C NMR spectroscopy at accessible concentrations.



3 **4**

Scheme 2

A C_6D_6 solution of the hydroxycabonyl complex **4** forms crystals suitable for X-ray diffraction upon standing at RT for several days. The X-ray structure confirms the molecular structure and reveals a crystal lattice where two molecules are oriented to form a hydrogen-bonded pair (Figure 3). This resembles the structural features of previously reported hydroxycabonyl complexes with pincer ligands, such as (PNP)NiCOOH by Lee[13] (PNP = N[2-P^{i}Pr$_2$-4-Me-C$_6$H$_3$]$_2$) and ($PC_{Ar}P$)PdCOOH by our group[15] ($PC_{Ar}P$ = C$_6$H$_3$-2,6-(CH$_2$P^{t}Bu$_2$)$_2$). The O–O distance of the hydrogen bond is 2.681 Å, indicating a fairly strong interaction in consistence with those previously reported for hydroxycarbonyl complexes.

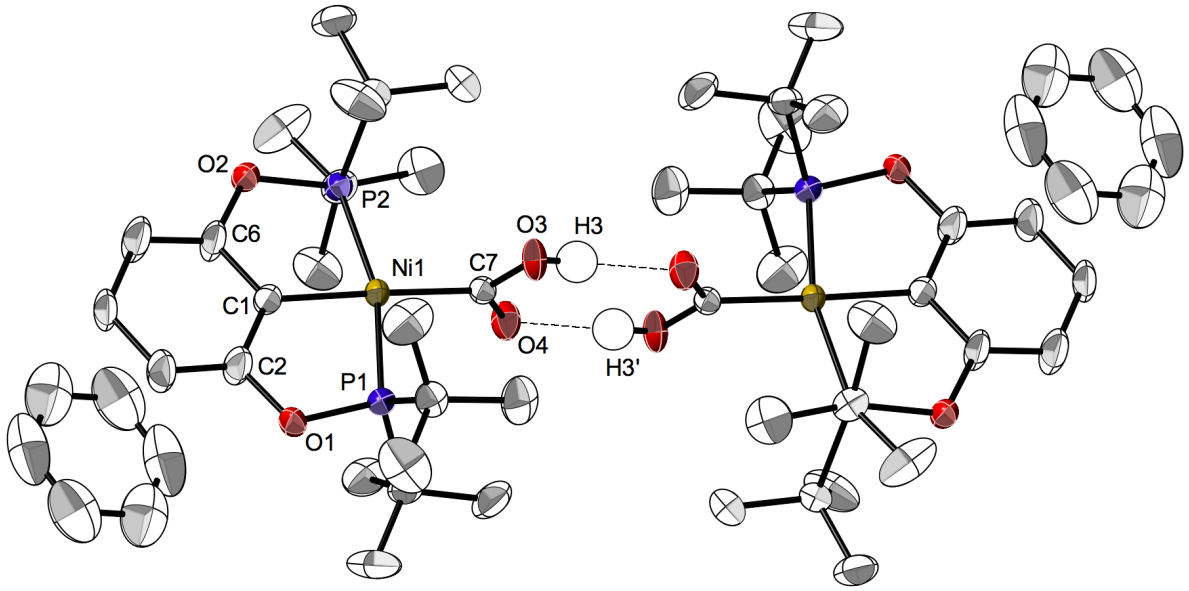
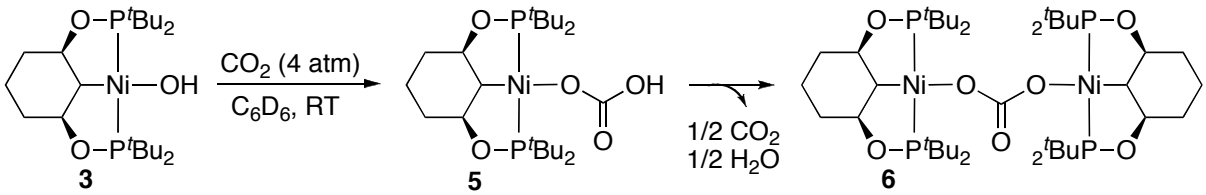


Figure 3. Molecular structure of **4** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.956(4), Ni1–P1 = 2.179713), Ni1–P2 = 2.1787(13), Ni1–C7 = 1.899(4), C7–O3 = 1.299(5), C7–O4 = 1.297(5), O3–H3 = 0.8200, O4–H3' = 1.890, P1–Ni1–P2 = 164.05(5), C1–Ni1–C7 = 177.7(2), Ni1–C7–O3 = 121.6(3), O3–C7–O4 = 117.5(4), C7–O3–H3 = 109.5, P1–Ni1–C1 = 82.27(14), P2–Ni1–C1 = 81.78(14), P1–Ni1–C7 = 96.82(14), P2–Ni1–C7 = 99.12(14).



Scheme 3

Reaction between complex **3** and CO_2 almost immediately gives a mononuclear hydrogen carbonate complex **5** (Scheme 3) that was characterized by NMR spectroscopy and X-ray crystallography. However, upon concentration *in vacuo* complex **5** dimerizes to form the bridged carbonate complex **6** under decarboxylation and water elimination. This reactivity mirrors the one previously reported by Cámpora for similar aromatic (PCP)NiOCOOH complexes (PCP = C_6H_3-2,6-

$(CH_2P^iPr_2)_2$).[6b] It is suggested to take place through an initial elimination of CO_2 to generate the corresponding (PCP)NiOH complex that immediately reacts with residual bicarbonate complex, forming the $\{(PCP)Ni\}_2\mu$-(CO_3) dimer. They further report on the reversibility of this process, reforming the bicarbonate by absorbing CO_2 during reflux in wet solutions. Their binuclear carbonate also undergoes hydrolysis and decarboxylation upon heating under open reflux and in presence of water, to regenerate the hydroxide complex – a reactivity not yet investigated for the here reported system. The NMR spectra of **5** and **6** are very similar, due to the symmetrical structure of the latter that makes the two PCP fragments appear as one set of resonances. The acidic bicarbonate proton of **5** is revealed as a characteristically broad singlet around 12.4 ppm. However, as opposed to Cámpora's work, the difference in chemical shifts of both the carbonate carbon and the nickel bound α-carbon ^{13}C resonances are insignificant between **5** and **6**. The shift of the α-carbon has been observed to be directly related to the σ-donating capacity of the ligand coordinated in *trans* position, and thus the expected tendency would be a slight shift downfield of the corresponding resonance for the stronger σ-donator CO_3^{2-} relative the less basic HCO_3^-.[19] Similarly, the $^{31}P\{^1H\}$ NMR signals of the PCP complexes are expected to correlate with the electronegativity of the ligating atom, and accordingly the ^{31}P NMR shift is shifted upfield to some extent for complex **6** relative **5**, although the difference indeed is not significant. Overall, this indicates that the electronic nature of the $(POC_{sp3}OP)Ni$ is closer to that of a proton compared to the $(PC_{Ar}P)Ni$ framework.

Slow evaporation of a C_6D_6 solution gave X-ray quality crystals of complex **5**, while complex **6** crystallized from C_6D_6 in a sealed NMR tube upon standing at room temperature over night. Despite the very close resemblance of their spectroscopic signatures, characterization in the solid state unambiguously assigns **5** and **6** as two unique structures (Figures 4 and 5). In the crystal structure of **5** the complex forms hydrogen bonded dimers similarly to what has been observed for both Pd and Ni hydrogen carbonate complexes. In the structure the two $(POC_{sp3}OP)Ni$ cores are related by symmetry whereas the hydrogen carbonate ligands have unique positions in each of the two halves giving rise twice as many positions for the hydrogen carbonate atoms with an apparent occupancy of one half. As previously reported by the group of Cámpora for their $(PC_{Ar}P)NiOCOOH$ complex ($PC_{Ar}P$ = C_6H_3-2,6-$(CH_2P^iPr_2)_2$), we observe a NiO–C distance in the bicarbonate complex **5** that is shorter than the C–OH bond and more comparable to the C=O bond.[6b] This indicates

a mix of the lone-electron pairs on the nickel-bound oxygen with the carbonyl π bond, giving delocalization of the negative charge resulting from the polarized Ni–O bond. The quality of the crystals of **6** was very poor (Rint = 0.42) and any quantitative interpretations must be done with utmost care. However, the structure clearly shows the connectivity and dinuclear character of the molecule.

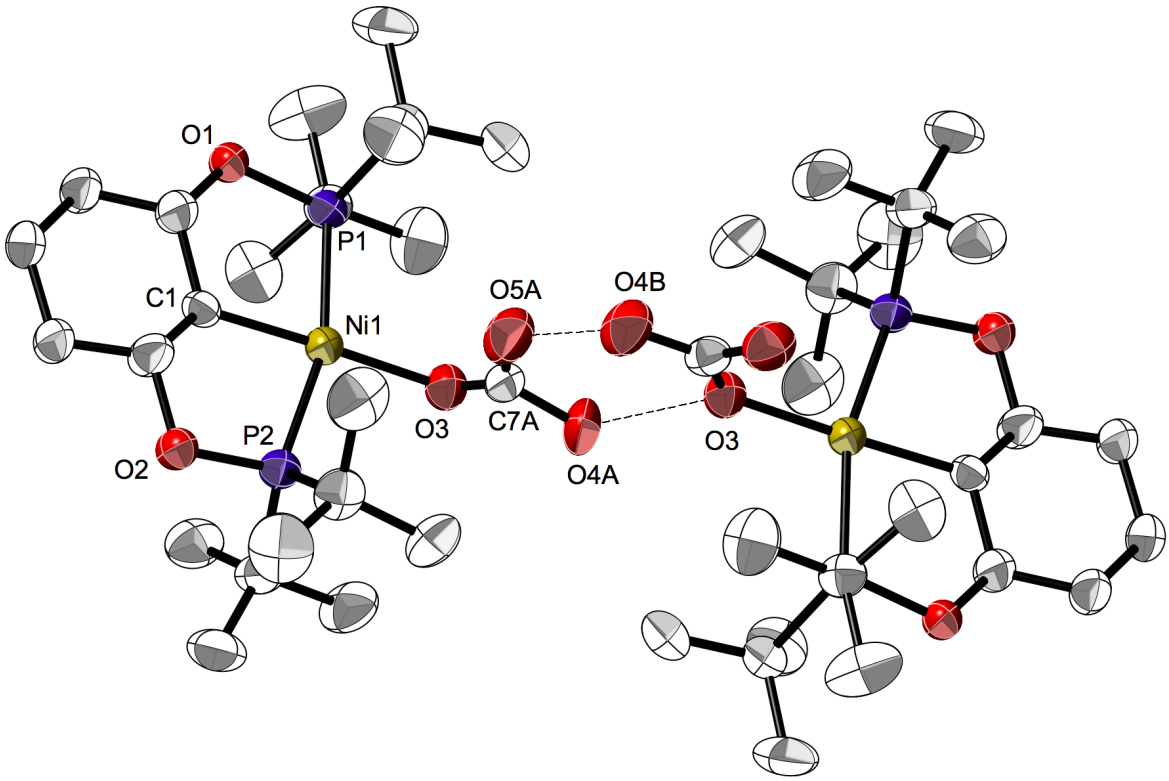


Figure 4. Molecular structure of **5** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ni1–C1 = 1.942(4), Ni1–P1 = 2.2341(12), Ni1–P2 = 2.2297(12), Ni1–O3 = 1.965(3), C7A–O3 = 1.091(13), C7A–O4A = 1.386(11), C7A–O5A = 1.259(14), O5A–O4B = 2.577, O4A–O3 = 2.981, P1–Ni1–P2 = 163.13(5), C1–Ni1–O3 = 177.60(17), Ni1–O3–C7A = 124.7(7), O3–C7A–O4A = 116.4(13), O3–C7A–O5A = 125.4(10), P1–Ni1–O3 = 99.45(10), P2–Ni1–O3 = 97.42(10), P1–Ni1–C1 = 81.53(12), P2–Ni1–C1 = 81.62(12).

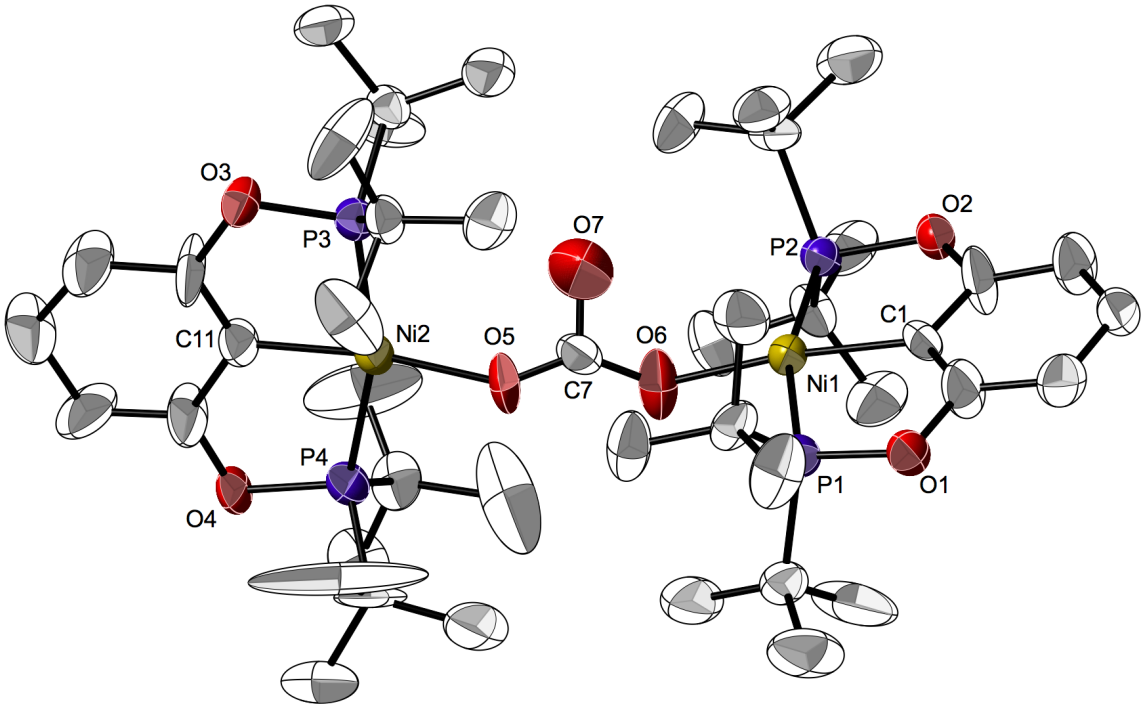


Figure 5. Molecular structure of **6** at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Crystal data and collection and refinement details for compounds **2-6.**

	2	**3**	**4**	**5**	**6**
formula	$C_{22}H_{45}NNiO_5P_2$	$C_{22}H_{46}NiO_3P_2$	$C_{23}H_{46}NiO_4P_2$	$C_{23}H_{46}NiO_5P_2$	$C_{45}H_{90}Ni_2O_7P_4$
Fw	524.25	479.24	507.25	523.25	984.48
space group	$P2_1/c$	$P2_1/c$	P-1	$P2_1/c$	P-1
a/Å	15.3227(7)	16.9353(10)	8.6469(9)	8.2261(8)	12.110(5)
b/Å	12.8587(3)	11.0050(4)	11.5350(10)	21.399(2)	15.166(5)
c/Å	15.7585(8)	16.2191(8)	17.1695(8)	16.3594(17)	17.078(5)
α/deg	90	90	76.775(8)	90	65.992(5)
β/deg	118.248(7)	116.413(7)	77.895(9)	101.165(8)	87.490(5)
γ/deg	90	90	68.895(9)	90	86.117(5)
V/Å^3	2734.2(2)	2707.3(2)	1539.2(3)	2825.2(5)	2858.3(17)
Z	4	4	2	4	2
D_{calcd}/g cm^{-3}	1.274	1.176	1.179	1.230	1.144
μ/mm^{-1}	0.856	0.852	0.760	0.828	0.810
θ/ range/deg	2.55-28.86	2.34-28.82	2.44-28.76	2.52-28.84	2.33-29.03
no. reflns collected	35327	34317	20293	35349	38789
no. of unique reflns	6617	6515	7039	6786	13511
$R(F)$ (I>2σ(I))[a]	0.0593	0.0695	0.0734	0.0685	0.1444
$wR2(F^2)$ (all data)[b]	0.1855	0.2328	0.1743	0.213	0.4253
S[c]	1.017	0.984	1.057	1.131	1.000
R_{int}	0.0821	0.1410	0.1081	0.1179	0.4236

[a] $R = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$. [b] $wR2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma|F_o|)^2]^{1/2}$. [c] $S = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma|F_o|)^2]^{1/2}$.

Conclusions

In summary, a nickel(II) hydroxo complex (**3**) supported by a cyclohexyl based $POC_{sp3}OP$ pincer ligand ($POC_{sp3}OP$ = *cis*-1,3-Bis-(di-*tert*-butylphosphinito)cyclohexyl) has been synthesized and spectroscopically and crystallographically characterized. The reactivity of complex **3** towards CO and CO_2 has been studied; reaction with CO generates the corresponding hydrocarbonyl complex, ($POC_{sp3}OP$)NiCOOH (**4**) that is seemingly stable towards dimerisation or β elimination at room temperature and atmospheric pressure. Reacting **3** with CO_2 affords a mononuclear bicarbonate species (**5**) that under reduced pressure loses ½ eq. of H_2O and CO_2 to give a binuclear, bridged carbonate complex (**6**). Complexes **4**-**6** were also characterized spectroscopically and in the solid state.

Supporting information

All crystallographic data in CIF format and NMR spectra for compounds **3**-**6**.

Acknowledgement

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Catalytic dehydrogenation of cyclooctane and triethylamine using aliphatic iridium pincer complexes[†]

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[†] Dedicated to John Bercaw on the occasion of his 70th birthday

Abstract

The majority of the known pincer iridium based catalysts for dehydrogenation of alkanes has arene-based backbones. Here, the catalytic activity of aliphatic iridium pincer complexes, *viz.* the cyclohexane-based phosphine complex (PCyP)IrHCl (**4**) (PCyP = {*cis*-1,3-bis-[(di-*tert*-butylphosphino)methyl]cyclohexane}$^-$) and the 2-methylpropane-based phosphinite complex (POCOP)IrHCl (**5**) (POCOP = 1,3-bis-(di-*tert*-butylphosphinito)-2-methylpropane$^-$), in dehydrogenation of cyclooctane and triethylamine was studied. They give TONs that are in the range of 0-70. In addition, improved procedures for synthesis and metallation of the PCyP ligand (**3**) are presented.

Keywords: dehydrogenation, iridium, pincer complexes, homogeneous catalysis, hydrogen transfer

1. Introduction

The conversion of cheap and abundant, but relatively inert, alkanes into more reactive olefins is an industrially important process.[1] Significant efforts have been made to develop catalysts that provide selective alkane dehydrogenation under mild conditions,[2-5] and iridium PCP pincer complexes have been dominating the field for the last two decades.[6] The majority of the ligands studied are composed of an arene backbone, *e.g.* benzene,[7-13] antracene [13,14] or a 7-6-7 fused-ring based systems (Figure 1). [15] In contrast, iridium pincer complexes with aliphatic backbones have received relatively little attention and their performance in catalytic dehydrogenation of alkanes has not been reported.

To fill this gap, we here present a study on the catalytic activity of a cyclohexane-based (PCyP)IrHCl complex (**4**) (PCyP = {*cis*-1,3-bis-[(di-*tert*-butylphosphino)methyl]cyclohexane}$^-$),[16] and a 2-methylpropane-based phosphinite complex (POCOP)IrHCl (**5**) (POCOP = 1,3-bis-(di-*tert*-butylphosphinito)-2-methylpropane$^-$).[17] We also report on an improved synthesis of compound **4**.

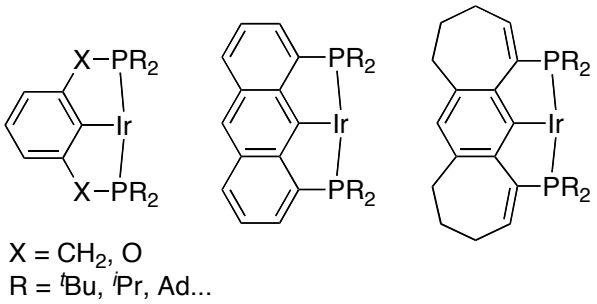


Figure 1. Arene-based pincer complexes, used in alkane dehydrogenation (14e particles are shown).

2. Experimental

2.1. General experimental procedures

All manipulations were carried out under an Ar or N_2 atmosphere using standard Schlenk or glovebox techniques, unless otherwise stated. All catalytic experiments were performed under Ar. Hydrocarbon solvents were degassed and distilled from Na/benzophenone. Chlorinated solvents and triethylamine were degassed and distilled from CaH_2. Commercially available reagents were used as received. NMR spectra were recorded on a Varian Unity INOVA 500 MHz instrument and referenced to the residual solvent peaks for ^1H and ^{13}C measurements, and to external 85% H_3PO_4 for ^{31}P measurements. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

2.2. Synthesis of cis-1,3-bis(iodomethyl)cyclohexane (2)

Iodine (10.24 g, 40.4 mmol) was added portion-wise to a stirred mixture of Ph_3P (10.59 g, 40.4 mmol) and imidazole (2.64 g, 38.8 mmol) in CH_2Cl_2 (200 mL) at 0 °C. The mixture was stirred for 30 min at 0°C and 1 hour at RT, before a solution of *cis*-1,3-bis(hydroxymethyl)cyclohexane (**1**) (2.82 g, 19.6 mmol) in THF (40 mL) was added dropwise at 0°C. The reaction mixture was allowed to warm to RT and was stirred for an additional hour. Further steps could be done in air. After addition of pentane (200 mL) the mixture was filtered through a pad of silica and concentrated in vacuum. The residue was re-dissolved in pentane (60 mL), filtered through another pad of silica and washed out with additional pentane. Concentration in vacuum afforded *cis*-1,3-bis(iodomethyl)-cyclohexane as a colourless oil which readily solidified slightly below RT. Yield: 6.32 g (89%). (R_f=0.49 in hexane). Anal. Calc. for $C_8H_{14}I_2$: C, 26.40; H, 3.88. Found C, 26.41, H, 3.89. ^{1}H NMR ($CDCl_3$): δ 3.12 (d, J = 6.2 Hz, 4H, -CH_2I), 2.03 (d of m, J = 12.6 Hz, 1H, 1-CH_AH$_B$), 1.86-1.78 (m, 3H, 3-CH_AH$_B$ + 4-CH_AH$_B$), 1.52-1.44 (m, 2 H, -CH-), 1.34 (m, 1H, 4-CH$_A$$H_B$), 0.89 (m 2H, 3-CH$_A$$H_B$), 0.70 (apparent q, J = 11.9 Hz, 1H, 1-CH$_A$$H_B$). ^{13}C NMR ($CDCl_3$): δ 40.16 (1-$CH_2$), 39.73 (-CH-), 33.08 (3-CH_2), 25.48 (4-CH_2), 15.18 (-CH_2I).

2.3. Synthesis of cis-1,3-bis-[(di-tert-butylphosphino)methyl]cyclohexane, (PCyP)H (3)

To a -78 °C solution of *cis*-1,3-bis(iodomethyl)-cyclohexane (5.37 g, 14.8 mmol) in Et_2O (100 mL) a solution of ^{t}BuLi in pentane (1.6 M, 46.2 mL, 74.0 mmol) was slowly added. The reaction mixture was stirred for 1 hour at 0°C and 2 hours at RT. ^{t}Bu$_2$PCl (8.43 mL, 44.4 mmol) was added dropwise at -78 °C and the reaction was stirred at RT overnight. The solvent was removed under vacuum before hexane (400 mL) and degassed water (100 mL) were added, and the resulting mixture was stirred for 10 min. The organic phase was separated, dried over

$MgSO_4$ and concentrated in vacuum. The residue was dried for ca. 5 h at 50 °C under 10^{-3} mbar vacuum to give a pale yellow oil, which solidifies upon standing. This material was crystallized from CH_2Cl_2/MeOH and dried under vacuum to give a white powder. Yield: 4.0 g (68%). NMR spectra are consistent with the literature. [18]

2.4. Synthesis of (PCyP)IrHCl (4)

The (PCyP)H ligand **3** (1.500 g, 3.74 mmol) and $[Ir(COD)Cl]_2$ (1.258 g, 1.87 mmol) were placed into a Straus flask inside a nitrogen glovebox and 35 ml of toluene was added. The flask was sealed and heated on an oil bath for 6 h at 170 °C. After reaching RT, the solution was degassed, cooled to -196 °C and the flask was refilled with H_2. The reaction mixture was heated for 5 h at 160 °C under H_2 atmosphere. The volatiles were evaporated and the resulting red powder was washed with cold hexane and dried in vacuum to give 2.261 g (96%) of **4**. NMR spectra are consistent with the literature data. [16]

2.5. Dehydrogenation of cyclooctane in the presence of tert-butylethylene

In a typical experiment, the catalyst (0.0116 mmol) and ^{t}BuONa (0.0017 g, 0.0177 mmol, 1.5 eq) were placed into a Straus flask and cyclooctane (COA) (4.74 ml, 35.2 mmol, ca. 3030 eq) as well as *tert*-butylethylene (TBE) (4.54 ml, 35.2 mmol, ca. 3030 eq) was added. The flask was sealed and immersed into a pre-heated oil bath with the specified temperature for 24 h. After that, the flask was cooled by a stream of air and the sample was analysed by NMR spectroscopy. Two runs were performed to determine average TONs. No compounds other than COA, cyclooctene (COE), TBE and *tert*-butylethane (TBA) could be detected by ^{1}H NMR spectroscopy.

2.6. Acceptorless dehydrogenation of cyclooctane by complex 4

Complex **4** (0.0073 g, 0.0116 mmol) and ^{t}BuONa (0.0017 g, 0.0177 mmol, 1.5 eq) were placed into a Schlenk flask and COA (4.74 ml, 35.2 mmol, ca. 3030 eq) was added. The flask was connected to a reflux condenser, immersed into an oil bath pre-heated to 170 °C and the mixture was refluxed for 18 h while passing a slow flow of argon above the reflux condenser. After cooling with a stream of air, the sample was analysed by NMR spectroscopy.

2.7. Dehydrogenation of triethylamine in the presence of tert-butylethylene

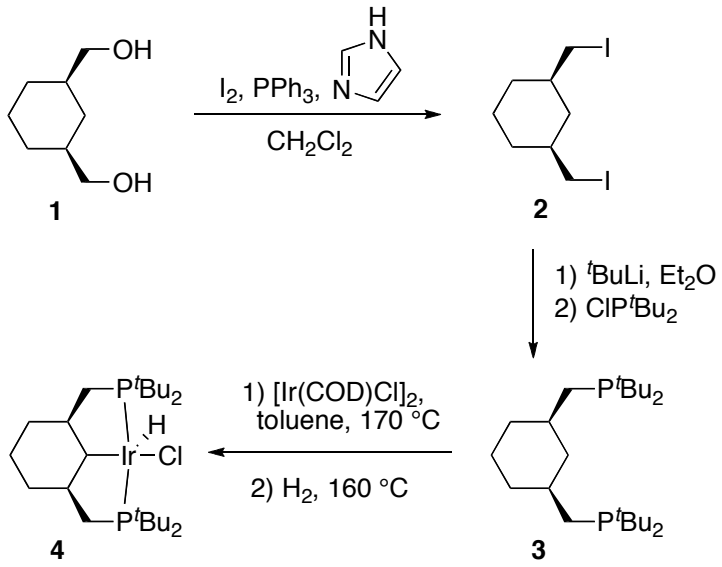
In a typical experiment, catalyst (0.0086 mmol) and ^{t}BuONa (0.0012 g, 0.0125 mmol, 1.5 eq) were placed into a Straus flask, and the specified amounts of NEt_3 (10 or 100 eq), TBE (20 or 200 eq) as well as 1.5 ml of toluene were added. The flask was sealed and immersed into a pre-heated oil bath at 120 °C for 18 h. Subsequently, the flask was cooled by a stream of air and the sample was analysed by NMR spectroscopy. An average of two runs were performed to determine TONs. No compounds other than NEt_3, N,N-diethylvinylamine, N,N-divinylethylamine, TBE and TBA could be detected by ^{1}H NMR spectroscopy.

3. Results and discussion

3.1 Improved synthesis of 4

While the previously reported procedure [18] can give good yields of the cyclohexane-based pincer ligand **3**, difficulties in the handling of the highly unstable *cis*-1,3-bis[(trifluoromethylsulfonyloxy)methyl]cyclohexane intermediate [19] makes the synthesis inconsistent in the reproducability of the yields. For the same reason it is also impractical for large-scale synthesis. Metallation of **3** according to the literature procedure gives **4** in a moderate yield (62%). [16] In addition, ^{1}H and ^{31}P{^{1}H} NMR spectra indicate that this protocol always gives trace

impurities in the resulting samples of **4**, and thus we wanted to develop an overall more robust and convenient route to **4**.



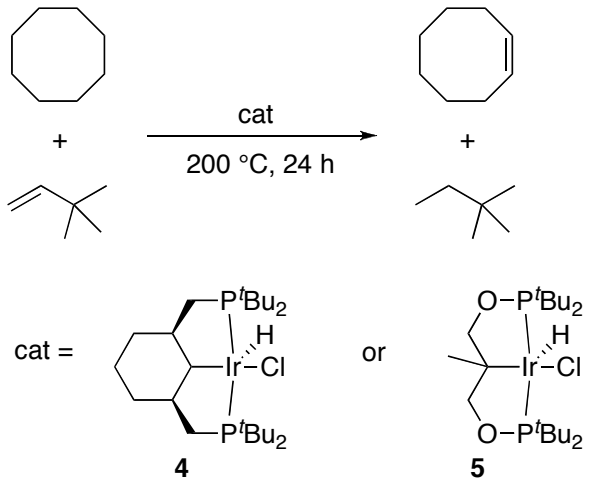
Scheme 1. New synthetic route to (PCyP)IrHCl (**4**).

To obtain a more stable intermediate in the synthesis of ligand **3** we wanted a good leaving group other than triflate. The diol **1** was made through reduction of commercially available *cis*-1,3-cyclohexanedicarboxylic acid with an excess of BH_3 in THF, according to the previously published procedure. [19] The hydroxyl groups were then iodinated by reaction with PPh_3/I_2/imidazole in anhydrous CH_2Cl_2 [20] (Scheme 1) affording the diiodo compound **2** in 89% yield. In contrast to the corresponding triflate, **2** is air and moisture-stable and can be stored in the freezer for at least several months without any signs of decomposition. Attempts to directly substitute the iodides with HP^tBu_2 failed, but lithiation of **2** followed by reaction with ClP^tBu_2 gave the desired ligand **3** in a 68% yield. The improved metallation protocol includes treatment of the reaction mixture with hydrogen at elevated temperatures. At these conditions, all by-products are converted to complex **4**. Hence very pure **4** is obtained and no further purification is required, except for washing with hexane in order to get rid of traces of grease.

3.2 Dehydrogenation reactions

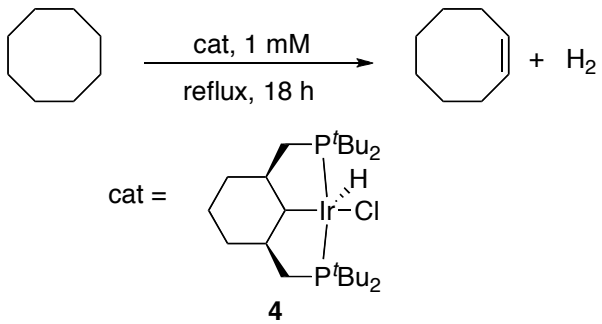
A common test reaction used to compare catalytic activity in dehydrogenation of alkanes is the transfer dehydrogenation of cyclooctane (COA) in the presence of *tert*-butylethylene (TBE), which acts as hydrogen acceptor. The reaction is known to be inhibited by both the hydrogen acceptor (TBE) and the dehydrogenation product (cycloctene, COE),[6] and thus it is important to compare activity using the same ratio of catalyst, COA and TBE. We chose COA/TBE/cat = 3030/3030/1, the same conditions Brookhart and coworkers used for their (POCOP)Ir catalysts such as [2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$]IrHCl (**6**),[8] since most literature data refers to this work. ^{t}BuONa (1.5 eq) was also added in order to remove HCl from **4** and **5** and generate an active 14e species. All catalytic results are summarised in Table 1. After heating the mixture for 24 h at 200 °C, complex **4** demonstrated a turnover number (TON) of 50. Longer heating, as well as raising the temperature to 240 °C did not improve this result. At lower temperature (150 °C) we obtained almost the same TON (45). In comparison, catalyst **6** [8] is reported to give a TON of 1583 in 40 h. To validate our results we performed the reaction using our conditions and **6** as a catalyst, obtaining comparable results. It is known that the catalytic activity can be inhibited by traces of N_2 [21] and given the higher electron-donating nature of aliphatic pincer ligands this effect can be even stronger for these systems. Indeed, carrying out the catalysis under high vacuum (10^{-3} mbar) instead of an Ar atmosphere raised the TON, but only slightly; 70 equivalents of COE were observed. Unfortunately, no products of dehydrogenation were observed when complex **5** was used, indicating a lack of activity. This result is in line with the poor thermal stability reported for **5** [17] and it is likely that the stability of the catalytically active species is even lower. The same reason is probably behind the inferior performance of **4**. Dehydrogenation of the ligand is noticeable for the parent hydrido-chloride complex around 200 °C and monitoring the reaction mixture by means of ^{31}P NMR-spectroscopy after activation with ^{t}BuONa indicate

complete decomposition of the catalytically active species after several hours at 150 °C. A thorough investigation of the decomposition routes of complex **4** is currently in progress.



Scheme 2. Transfer dehydrogenation of COA by iridium pincer complexes with aliphatic backbones.

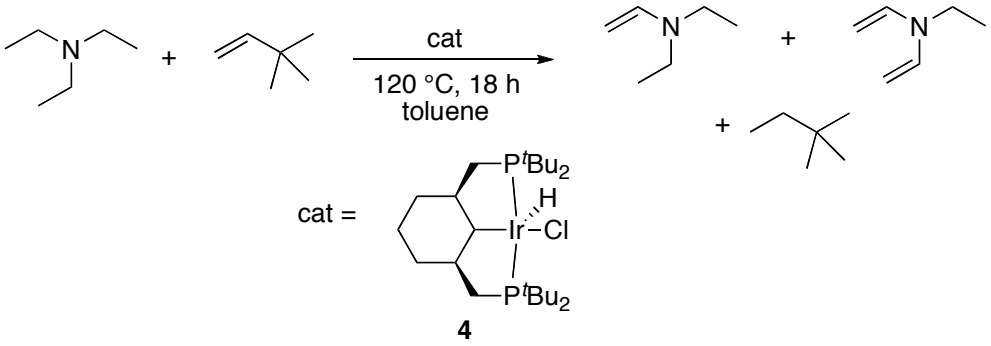
Acceptorless dehydrogenation of COA by **4** resulted in 5 turnovers, which can be compared to 105 for benzene-based complex [2,6-(^{t}Bu$_2$PCH$_2$)$_2$C$_6$H$_3$]IrH$_2$ (**7**).[22] Probably the decomposition of **4** is quite fast already at the COA boiling point of 149 °C. [23]



Scheme 3. Acceptorless dehydrogenation of COA by complex **4**.

Considering the low thermal stability of active species derived from **4**, we decided to test it in a reaction that does not require high temperature such as the

dehydrogenation of tertiary amines, which was reported to proceed at 90 °C with **7** as a catalyst. [24] A toluene solution instead of neat reactants was used to suppress inhibition by the generated products. In our case, the reaction was too slow at 90 °C, but heating a 100/200/1 NEt_3/TBE/cat mixture in toluene at 120 °C afforded a TON of 18.9, with the yields of N,N-diethylvinylamine and N,N-divinyl-ethylamine being 15.7 and 1.6 %, respectively. Complex **7** has been reported to give a TON of 6.5 and 65% yield of N,N-diethylvinylamine using a 10/10/1 NEt_3/TBE/cat ratio and a TON of 11.4 with 64% yield of N,N-diethylvinylamine and 25 % yield of N,N-divinyl-ethylamine using a 10/30/1 NEt_3/TBE/cat ratio. [24] For a more direct comparison with literature data, we carried out the dehydrogenation using 10/20/1 NEt_3/TBE/**4** ratio, and 4.3 turnovers with 43% yield of N,N-diethylvinylamine was observed. NMR monitoring showed that in this case interactions with the toluene lead to formation of catalytically inactive species prior to complete decomposition of the catalyst. Thus, the low TON presumably reflects a kinetic competition between these unwanted processes and interaction with NEt_3. When COA was used as a solvent, competition between dehydrogenation of COA and NEt_3 was observed; on a per mol basis, selectivity is around 1:10. However, in view of the large excess of COA, high yields of vinylamines could not be achieved.



Scheme 4. Transfer dehydrogenation of triethylamine by complex **4**.

Table 1. Catalytic dehydrogenation using different substrates and iridium catalysts.

Entry	Catalyst	Substrate	Acceptor	TON	Reference
1	**4**	COA	TBE	50	this work
2	**5**	COA	TBE	0	this work
3	**6**	COA	TBE	1583	8
4	**6**	COA	TBE	1918	this work
5	**4**	COA	-	5	this work
6	**7**	COA	-	105	22
7	**4**	NEt_3 100 eq	TBE 200 eq	18.9	this work
8	**4**	NEt_3 10 eq	TBE 20 eq	4.3	this work
9	**7**	NEt_3 10 eq	TBE 10 eq	6.5	24
10	**7**	NEt_3 10 eq	TBE 30 eq	11.4	24

4. Conclusions

In conclusion we have presented an improved synthetic route to the cyclohexane-based PCyP ligand **3**, suitable for multigram scale, and improved the metallation procedure for the complex (PCyP)IrHCl (**4**). The latter, together with the aliphatic phosphinite complex **5**, was tested for several catalytic dehydrogenations. The activity was found to be relatively low compared to the corresponding aromatic complexes, and this is primarily due to the low thermal stability of the catalytically active species.

Acknowledgements

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PC(sp^3)P Pincer Carbonyl Complexes with Iridium. Oxidative Addition of Methyl Iodide and Subsequent Reductive Elimination of an C(sp^3)–C(sp^3) Bond

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Abstract

The previously reported complex *trans*-[IrHCl{*cis*-1,3-Bis-(di-*tert*-butylphosphino)methyl}cyclohexane] (**2**) forms the 18-electron carbonyl compound *trans*-[Ir(CO)HCl{*cis*-1,3-Bis-((di-*tert*-butylphosphino)methyl)}cyclohexane] (**5a**) upon reaction with 1 atm CO. The structural isomer *trans*-[IrH(CO)Cl{*cis*-1,3-Bis-((di-*tert*-butylphosphino)methyl)}cyclohexane] (**5b**) is obtained directly upon complexation of the ligand (**1**) with $IrCl_3 \cdot H_2O$ in refluxing DMF. Both compounds **5a** and **5b** afford the reduced complex *trans*-[Ir(CO){*cis*-1,3-Bis-((di-*tert*-butylphosphino)methyl)}cyclohexane] (**4**) upon treatment with KO^{t}Bu. Complex (**4**) was also synthesised in a more straightfoward fashion from the previously known terminal nitrogen complex *trans*-[Ir(N_2){*cis*-1,3-Bis-((di-*tert*-butylphosphino)methyl)}cyclohexane] (**3**) under atmospheric CO. The complexes **4**, **5a** and **5b** were characterised spectroscopically and in the solid state. Methyl iodide oxidatively adds to complex **3**, affording *trans*-[IrMeI{*cis*-1,3-Bis-((di-*tert*-butylphosphino)methyl)}cyclohexane] (**6**), that transforms into the *trans*-[IrHI{*cis*-1,3-Bis-((di-*tert*-butylphosphino)methyl)-2-methyl}cyclohexane] (**7**) *via* an unusual 1,2-methyl migration, presumed to involve the reductive elimination of a C(sp^3)–C(sp^3) bond and the C(sp^3)–H activation of a tertiary carbon.

Introduction

The chemistry of iridium PCP pincer-type complexes has been continuously developed over the last decades, mainly owing to their applications as active homogeneous catalysts in the dehydrogenation[1] of alkanes,[2-6] alcohols[7-8] and amine-boranes.[9-10] Oxidative additions and reductive eliminations are fundamental processes in these and many other catalytic transformations and stoichiometric reactions, and are highly influenced by the electronic properties of the metal centre.[11] In this aspect, the application of all-aliphatic pincer backbones is a relevant task, since the properties of a C(sp^3)- compared to the more common C(sp^2)-based PCP complex might differ significantly due to electronic factors such as stronger *trans* influence by the metallated carbon and a metal centre with higher nucleophilicity.[12] Also the hybridization is expected to influence the rate of any concerted reaction.[13, 14] Carbon monoxide has been long known to coordinatively add to both PC(sp^2)P-[15] and PC(sp^3)P-supported[16] iridium(III) complexes, and such iridium carbonyl complexes have later been found to be involved in catalytic transformations such as transfer dehydrogenations of ketones[8] and olefin hydroformylation.[17] PCP iridium(I) carbonyl complexes are well known for aromatically based pincer structures,[7, 18-22] and has been reported to catalyze the decarbonylation of 2-naphtaldehyde[23] and the partial deoxygenation of diols[24] and glycerol,[25] but there are no PC(sp^3)P-supported iridium(I) carbonyl complexes reported to this date.

Here we report on the synthesis and interconversion of PC(sp^3)P pincer carbonyl complexes with iridium(I) and iridium(III). Furthermore we report on the oxidative addition of methyl iodide to an iridium(I) centre, followed by an unusual 1,2-methyl migration from the metal to the ligand backbone.

Experimental Section

General Comments. All manipulations were performed under a nitrogen or argon atmosphere using standard Schlenk or glovebox techniques, except where noted. Solvents were purified by vacuum distillation from sodium/benzophenone ketyl radical. The ligand **1** and the complexes **2** and **3** were prepared according to previously reported procedures.[26-27] All other chemicals were purchased from commercial suppliers and used as received. ^{1}H-, ^{13}C- and ^{31}P-NMR experiments were recorded on a Varian Unity INOVA 500 spectrometer, operating at 499.76 MHz (^{1}H). For ^{1}H- and ^{13}C-NMR spectra, the residual solvent peak was used as an internal

reference. ^{31}P-NMR spectra were referenced externally using 85% H_3PO_4 at δ = 0 ppm. Multiplicities are abbreviated as follows: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet, (br) broad, (v) virtual. IR sprectra were obtained on a Bruker ALPHA FT-IR. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

Crystallography. XRD-quality crystals of compounds **4**, **5a** and **5b** were obtained through recrystallization from toluene or hexane. Intensity data were collected with an Oxford Diffraction Excalibur 3 system, using ω-scans and MoKα (λ = 0.71073 Å) radiation.[28] The data were extracted and integrated using Crysalis RED.[29] The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL5.1.[30] Molecular graphics were generated using CrystalMaker® 8.3.5.[31]

Preparation of *trans*-[Ir(CO){*cis*-1,3-Bis-((di-*tert*-butylphosphino)methyl)}-cyclohexane] (4). Compound **3** (10.0 mg, 0.016 mmol) was dissolved in toluene (3 mL), and the solution was freeze-pump-thawed prior to addition of CO (1 atm). After stirring at room temperature for 1.5 h, the solvent was removed *in vacuo*, and the yellow solid residue was recrystallized from hexane. Yield: 7.8 mg (78%). ^{1}H-NMR (C_6D_6): δ 2.32-2.27 (m, PC*H*$_2$CH, 2 H), 2.22-2.19 (m, Cy, 2 H), 2.02-1.98 (br m, Cy, 1 H), 1.73-1.64 (m, Cy, 2 H), 1.52 (tt, J = 4.0 Hz, J = 13.5 Hz, PC*H*$_2$CH, 2 H), 1.48-1.42 (m, Cy, 1 H), 1.32 (vt, J_{PH} = 13.0 Hz, ^{t}Bu, 18 H), 1.26 (vt, J_{PH} = 13.0 Hz, ^{t}Bu, 18 H), 1.19 (t, J = 11.0, *H*C–Ir, 1 H), 0.95 (dq, J = 3.5 Hz, J = 12.5 Hz, Cy, 2 H). ^{13}C{^{1}H}-NMR (C_6D_6): δ 194.8 (vt, J_{PC} = 15 Hz, Ir–*C*O, 1 C), 71.6 (vt, J_{PC} = 7.2 Hz, H*C*–Ir, 1 C), 50.3 (vt, J_{PC} = 19 Hz, PCH_2, 2 C), 36.9 (vt, J_{PC} = 25 Hz, Cy, 2 C), 36.4 (vt, J_{PC} = 21 Hz, *C*$(CH_3)_3$, 2 C), 35.8 (vt, J_{PC} = 22 Hz, *C*$(CH_3)_3$, 2 C), 34.9 (vt, J_{PC} = 19 Hz, Cy, 2 C), 29.8 (vt, J_{PC} = 5.6 Hz, C$(CH_3)_3$, 6 C), 29.7 (vt, J_{PC} = 5.2 Hz, C$(CH_3)_3$, 6 C), 27.7 (vt, J_{PC} = 2.8 Hz, $CH_2CH_2CH_2$, 1 C). ^{31}P{^{1}H}-NMR (C_6D_6): δ 81.8 (s). IR (NaCl/nujol) ν_{CO} = 1917 cm^{-1}.

Preparation of *trans*-[Ir(CO)HCl{*cis*-1,3-Bis-((di-*tert*-butylphosphino)methyl)}-cyclohexane] (5a). Compound **2** (25.0 mg, 0.040 mmol) was dissolved in THF (3 mL), and the solution was freeze-pump-thawed prior to addition of CO (1 atm). A color change from deep red to colorless was observed within seconds. After stirring at room temperature for 2 h, the solvent was removed *in vacuo*, and the white solid residue was recrystallized from hexane. Yield: 22.2 mg (85%). ^{1}H-NMR (C_6D_6): δ 1.89-1.84 (m, PC*H*$_2$CH, 2 H), 1.82-1.77 (br m, Cy, 2 H + 1 H), 1.61 (t, J = 10.5 Hz, *H*C–Ir, 1 H), 1.51-1.45 (br m, PC*H*$_2$CH, 2 H + Cy, 1 H), 1.41 (vt, J_{PH} = 13.0 Hz, ^{t}Bu, 18 H), 1.37

(vt, J_{PH} = 13.0 Hz, ^{t}Bu, 18 H), 1.12 (tt, J = 3.5 Hz, J = 14.0 Hz, Cy, 2 H), 0.90 (dq, J = 4.0 Hz, J = 13.0 Hz, Cy, 2 H) -8.59 (dt, J_{HH} = 1.5 Hz, J_{PH} = 17.0 Hz, Ir–*H*, 1 H). $^{13}C\{^1H\}$-NMR (C_6D_6): δ 226.7 (s, Ir–*C*O, 1C), 51.5 (vt, J_{PC} = 11 Hz, *C*H–Ir, 1 C), 37.8 (vt, J_{PC} = 27 Hz, PCH_2, 2 C), 36.8 (vt, J_{PC} = 21 Hz, Cy, 2 C), 36.2 (vt, J_{PC} = 23 Hz, *C*$(CH_3)_3$, 2 C), 33.9 (vt, J_{PC} = 17 Hz, *C*$(CH_3)_3$, 2 C), 32.7 (s, Cy, 2 C), 30.8, (vt, J_{PC} = 3.2 Hz, C$(CH_3)_3$, 6 C), 30.6 (vt, J_{PC} = 3.0 Hz, C(*C*$H_3)_3$, 6 C), 27.8, (s, $CH_2CH_2CH_2$, 1 C). $^{31}P\{^1H\}$-NMR (C_6D_6): δ 50.2 (s). IR (ATR) ν_{CO} = 1977 cm^{-1}. Anal. Calcd for $C_{25}H_{51}ClIrOP_2$ (657.29): C, 45.68; H, 7.82. Found: C, 45.60; H, 7.65.

Preparation of *trans*-[IrH(CO)Cl{*cis*-1,3-Bis-((di-*tert*-butylphosphino)methyl)}-cyclohexane] (5b). *cis*-1,3-Bis-[(di-*tert*-butylphosphino)methyl]cyclohexane (**1**) (24.8 mg, 0.062 mmol) and $IrCl_3 \cdot H_2O$ (18.6 mg, 0.062 mmol) was mixed with dry degassed DMF (4 mL) under a stream of N_2. The mixture was heated to 150 °C for 24 h. Upon cooling to RT a yellow precipitate came out of solution. The solvent was removed *in vacuo*, followed by repeated crystallisation from THF to afford **5b** as a pale yellow crystalline powder. Yield: 23.2 mg (54%). ^{1}H-NMR (C_6D_6): δ 2.61-2.52 (m, PC*H*$_2$CH, 2 H), 2.09-2.01 (m, PC*H*$_2$CH, 2 H + Cy, 2 H), 1.86-1.81 (m, Cy, 1 H), 1.55 (vt, J_{PH} = 13.5 Hz, ^{t}Bu, 18 H), 1.53-1.51 (m, Cy, 1 H) 1.42 (t, J = 11.0 Hz, *H*C–Ir, 1 H), 1.15 (tt, J = 4.0 Hz, J = 14.0 Hz, Cy, 2 H), 1.06 (vt, J_{PH} = 12.5 Hz, ^{t}Bu, 18 H), 0.92 (dq, J = 3.5 Hz, J = 13.0 Hz, Cy, 2 H), -18.7 (t, J_{PH} = 13.0 Hz, Ir–*H*, 1 H). $^{31}P\{^1H\}$-NMR (C_6D_6): δ 56.4 (d, J_{PH} = 13.0 Hz). IR (ATR) ν_{CO} = 1989 cm^{-1}. Anal. Calcd for $C_{25}H_{51}ClIrOP_2$ (657.29): C, 45.68; H, 7.82. Found: C, 45.59; H, 7.79.

Preparation of *trans*-[IrMeI{*cis*-1,3-Bis-((di-*tert*-butylphosphino)methyl)}-cyclohexane] (6). To a toluene (3 mL) solution of compound **3** (40.0 mg, 0.064 mmol) was added MeI (7.9 μL, 0.127 mmol) and within 1 h the reaction turned burgundy red. The reaction mixture was allowed to stir at RT over night. Concentration in vacuo afforded **6** a solid material. Yield: 41.8 mg (89 %). ^{1}H-NMR (C_6D_6): δ 2.15 (t, J = 5.5 Hz, Ir–C*H*$_3$, 3H), 2.06-2.03 (m, Cy, 2 H) 1.95 (t, J = 10.5, *H*C–Ir, 1 H), 1.87-1.82 (m, PC*H*$_2$CH, 2 H and Cy, 1 H), 1.61-1.57 (m, Cy, 2 H), 1.38-1.34 (br m, Cy, 1 H), 1.27 (vt, J_{PH} = 12.0 Hz, ^{t}Bu, 18 H), 1.21 (vt, J_{PH} = 12.5 Hz, ^{t}Bu, 18 H), 1.19-1.13 (m, PC*H*$_2$CH, 2 H), 1.07-0.99 (m, Cy, 2 H). $^{13}C\{^1H\}$-NMR (C_6D_6): δ 52.5 (br s, *C*H–Ir, 1 C), 46.6 (vt, J_{PC} = 14.6 Hz, PCH_2*C*H, 2 C), 36.6 (vt, J_{PC} = 20.6 Hz, *C*$(CH_3)_3$, 2 C), 36.1 (vt, J_{PC} = 16.6 Hz, *C*$(CH_3)_3$, 2 C), 34.3 (vt, J_{PC} = 23.4 Hz, C*H*CH_2CH_2, 2 C), 33.9 (vt, J_{PC} = 18.5 Hz, PCH_2, 2 C), 30.09 (vt, J_{PC} = 3.0 Hz, C(*C*$H_3)_3$, 6 C), 30.05 (vt, J_{PC} = 4.3 Hz, C(*C*$H_3)_3$, 6 C), 27.0 (s, $CH_2CH_2CH_2$, 1 C), -27.8 (vt, J_{PC} = 9.9 Hz, Ir–*C*H_3, 1 C). $^{31}P\{^1H\}$-NMR (C_6D_6): δ 32.39 (s).

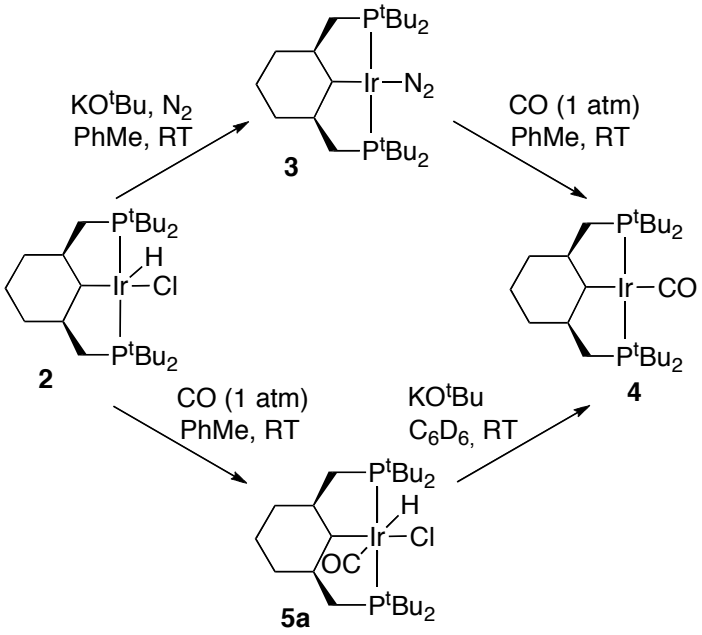
Preparation of *trans*-[IrHI{*cis*-1,3-Bis-((di-*tert*-butylphosphino)methyl)-2-methyl}cyclohexane] (7). A toluene solution (3 mL) of compound **6** (41.8 mg, 0.057 mmol) was heated to 60 °C over night, turning from burgundy red to pale orange/pink. The solvent was removed *in vacuo* and the solid residue was dissolved in a minimum amount of hexane. Storing at -28 °C afforded crystalline **7** (23.4 mg, 56 %). ^{1}H-NMR (C_6D_6): δ 1.69-1.57 (m, PCH_2CH, 4 H) 1.47 (dvt, J_{PH} = 13.0 Hz, J_{HH} = 2 Hz, ^{t}Bu, 18 H), 1.36 (dvt, J_{PH} = 12.5 Hz, J_{HH} = 2 Hz, ^{t}Bu, 18 H), 1.35-1.32 (m, Cy, 2 H), 1.28-1.18 (m, Cy, 4 H), 1.16-1.10 (m, Cy, 2 H), -1.02 (t, J = 2.0 Hz, IrC–CH_3, 3 H), -28.4 (br t, J = 13.0 Hz, Ir–*H*, 1 H). ^{13}C{^{1}H}-NMR (C_6D_6): δ 51.2 (vt, J_{PC} = 12.8 Hz PCH_2CH, 2 C), 38.4 (vt, J_{PC} = 21.9 Hz, *C*(CH_3)$_3$, 2 C), 35.0-34.8 (two merged vt's, Cy, 2 C and *C*(CH_3)$_3$, 2 C), 31.60 (vt, J_{PC} = 16.9 Hz, PCH_2, 2 C), 31.56 (vt, J_{PC} = 5.2 Hz, C(*C*H_3)$_3$, 6 C), 31.0 (vt, J_{PC} = 4.0 Hz, C(*C*H_3)$_3$, 6 C), 26.5 (s, $CH_2CH_2CH_2$, 1 C). ^{31}P{^{1}H}-NMR (C_6D_6): δ 68.56 (s).

Results and Discussion

We have earlier reported on the cyclometallation of ligand **1** with [Ir(COD)Cl]$_2$ to give *trans*-[IrHCl{*cis*-1,3-Bis-(di-*tert*-butylphosphino)methyl}cyclohexane] (**2**), and also on the reduction of this compound with metallic potassium under a N_2 atmosphere at elevated temperatures, affording the Ir(I) terminal nitrogen complex **3**.[26] We here report an alternative synthesis of **3** from **2** under slightly milder conditions and in comparable yields, using KO^{t}Bu (Scheme 1) as was previously reported by Milstein and Frech for the preparation of a naphtyl based PCP Rh(I) η^1-N_2 complex.[32] Complex **3** readily underwent ligand substitution with CO, to form the Ir(I) carbonyl complex **4**. Upon addition of CO to a degassed toluene solution of **3**, a colour change from orange to yellow was observed within minutes, in consistence with what is expected for the more high-field CO ligand. Following this route, complex **4** was isolated and characterised IR and NMR spectroscopy and the structure was confirmed by means of X-ray crystallography. It shows a characteristic carbonyl shift at 194.8 ppm in the ^{13}C-NMR spectrum. Complex **4** failed to give satisfactory elemental analysis, possibly due to a limited stability at room temperature similarly to what was found for complex **3**. The molecular structure of compound **4** is shown in Figure 1, and the crystallographic data for the compounds **4**-**5** are given in Table 1. The structure adopts a distorted square planar geometry around iridium. While the angle between the PCP coordinated carbon and the carbonyl ligand is close to ideal (177.1°), the P–Ir–P angle is much more distorted

(164.46°) due to the geometric constraints imposed by the chelating pincer arms. With respect to bond lengths and angles around iridium, complex **4** resembles its aromatic analogue very closely,[7] and the sp^3-hybridisation instead of an sp^2-hybridisation has a surprisngly small effect on the π-back donation to CO; there is no substantial change of the Ir–CO or C–O distances ($PC_{Ar}P$ mean distances: Ir–CO = 1.863 Å; C–O = 1.147 Å, 4: Ir–CO = 1.860(7) Å; C–O = 1.143(7)), and the ν_{CO} stretching frequency of **4** is 1917 cm^{-1}(nujol), which is in good agreement with the value reported for the aromatic analogue (ν_{CO} = 1913 cm^{-1}, KBr).[19]

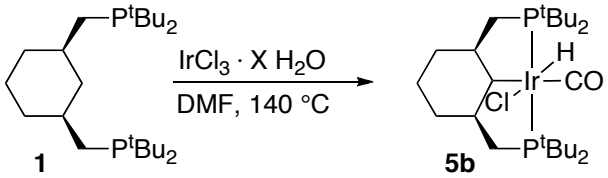
Subjecting the deep red solution of complex **2** to 1 atm CO resulted in a colourless solution of the 18 electron complex **5a** within seconds. Treating a C_6D_6 solution of **5a** with an excess of KO^{t}Bu afforded reduction to the iridium(I) complex **4**, as confirmed by comparison with the NMR-spectrum of the isolated compound. The lower route is, however, slower and slightly less clean than the synthesis starting from compound **3 (**Scheme 1).



Scheme 1. Synthesis of iridium(I) complexes 3 and 4 and iridium(III) complex 5a

Refluxing ligand **1** and $IrCl_3 \cdot H_2O$ in DMF gave a yellow solid material that was shown to be complex **5b**, a *cis-trans* isomer of **5a**. This type of cyclometallation where the solvent is the carbonyl source, was previously observed by Azerraf and Gelman in the formation of a dibenzobarrelene based $PC(sp^3)P$ iridium complex.[8a, 8c]

The structural isomers **5a** and **5b** are clearly distinguishable by means of NMR-spectroscopy, most notably in the ^{31}P-NMR shifts (δ = 50.2 ppm and 56.4 ppm respectively in C_6D_6) and the ^{1}H-NMR hydride shifts (δ = -8.59 ppm and -18.7 ppm respectively in C_6D_6), and both compounds are seemingly resistant towards isomerisation upon standing in solution at room temperature for several days. A significantly lower solubility of compound **5b** made attempts to obtain a satisfactory ^{13}C-NMR spectrum of this compound unsuccessful. However, crystallographic and IR spectroscopic data clearly confirm the presence of a carbonyl ligand. The ν_{CO} stretching frequencies for **5a** and **5b** are found at 1977 cm^{-1} and 1989 cm^{-1} respectively, which are both really close to the value reported for the aromatic analogue of **5a** (ν_{CO} = 1985 cm^{-1}, KBr),[15] and again there is thus no observable trend in different π-back donation *trans* to a C(sp^2)-carbon, a C(sp^3)-carbon and a hydride ligand. As expected the ν_{CO} values in the Ir(III) complexes **5a** and **5b** are substantially higher than the value in the Ir(I) complex **4**.



Scheme 2. Synthesis of compound 5b

The molecular structure of compound **5a** and **5b** are given in Figures 2 and 3 respectively. Notably, the two isomers **5a** and **5b** have different orientations of their respective hydride ligands relative the α-hydrogen, as illustrated in Figure 4. In case of **5a**, the hydride and α-hydrogen are located *anti* to each other, while in **5b** they are *syn*. Consistent with this, the hydride signals in the ^{1}H-NMR spectra, only display a $^{2}J_{HH}$ coupling (J = 1.5 Hz) in complex **5a**. Previously reported PC(sp^3)P complexes with iridium[26, 33] show an *anti* configuration and this seems to be the preferred outcome of a metallation involving a concerted oxidative addition process via a C–H σ-complex. This is therefore what is observed in the fast CO addition to **2** which has an *anti* configuration. Gelman observed that the quality of the DMF influenced the outcome of the cyclometallation reaction, affording a PC(sp^3)PIrH(CO)Cl complex in the presence of water and a PC(sp^3)PIr(CO)(Cl)$_2$ complex in dry solvent,[8c] but **5b** is analogous to the complex reported in wet DMF, featuring the carbonyl ligand located in a *trans* position and the hydride and chloride both in *cis* position to the

metallated PCP carbon. For the present reaction **5b** was the predominant species formed when using DMF freshly distilled from CaH_2, which might indicate traces of water being present although that could not be spectroscopically confirmed. When using DMF straight from the bottle without any drying the course of the reaction was less clean and seemingly gave rise to another pincer coordinated non-hydridic compound as byproduct, although isolation and characterization of this species proved unsuccessful. The observations by Gelman and the *syn* configuration of the hydride ligand and α-hydrogen in **5b** could indicate that the mechanism for formation of the cyclometallated species in DMF is not a simple C–H oxidative addition but involves several deprotonation/protonation steps. This indicates that the *syn* configuration is thermodynamically more stable than the *anti* one.

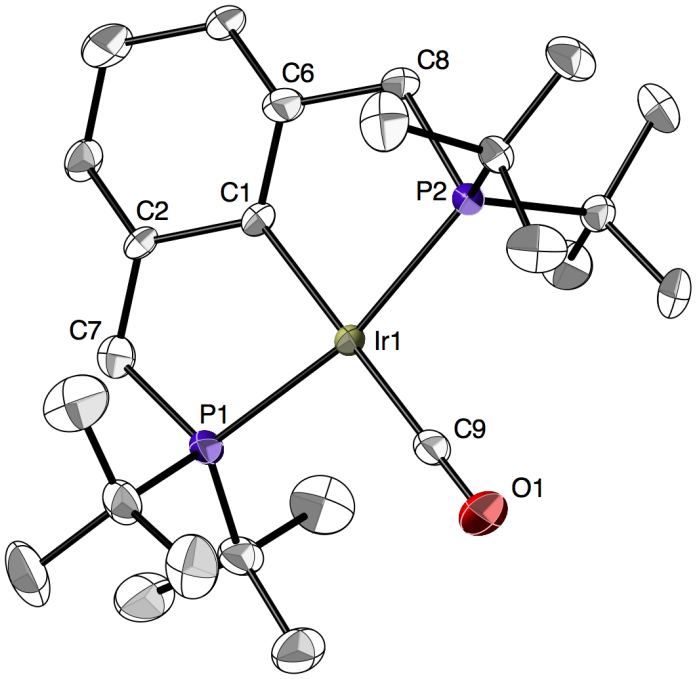


Figure 1. Molecular structure of **4** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ir1–C1 = 2.143(6), Ir1–C9 = 1.860(7), C9–O1 = 1.143(7), Ir1–P1 = 2.3073(16), Ir1–P2 = 2.3060(15), P1–Ir1–P2 = 164.46(6), C1–Ir–C9 = 177.1(3), Ir1–C9–O1 = 179.1(7), P1–Ir1–C1 = 82.38(16), P2–Ir1–C1 = 82.14(16).

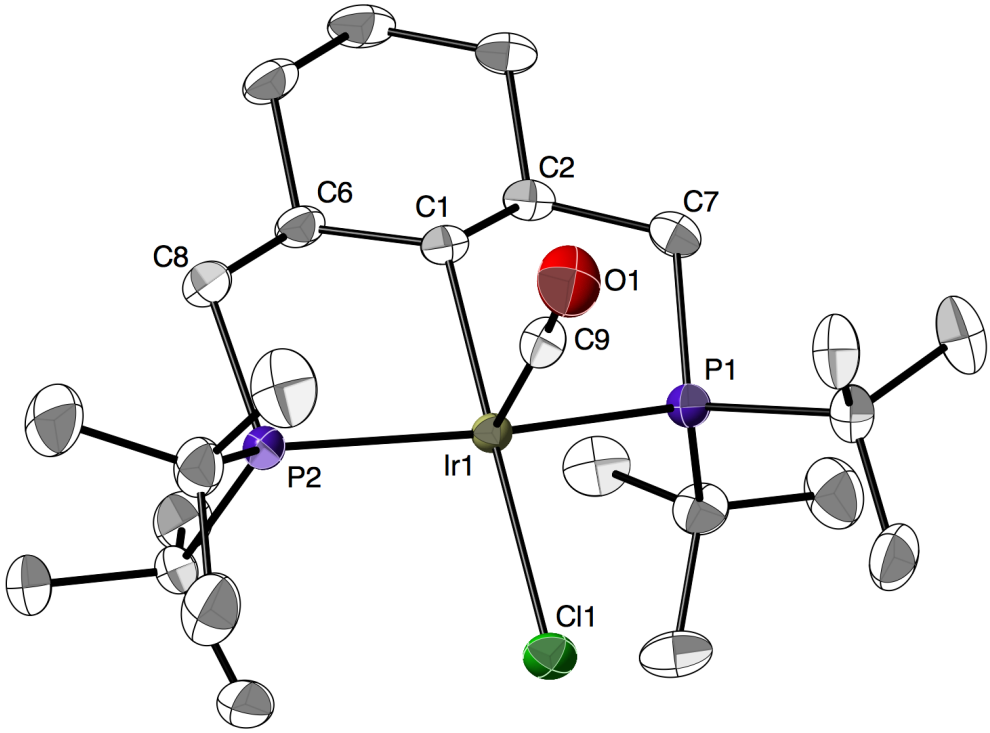


Figure 2. Molecular structure of **5a** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ir1–C1 = 2.137(4), Ir1–C9 = 1.943(4), C9–O1 = 1.101(5), Ir1–Cl1 = 2.5374(10), Ir1–P1 = 2.3591(10), Ir1–P2 = 2.3643(10), P1–Ir1–P2 = 158.44(4), C1–Ir–C9 = 87.16(16), Ir1–C9–O1 = 173.7(4), C1–Ir1–Cl1 = 179.40(11), P1–Ir1–Cl1 = 95.53(4), P2–Ir1–Cl1 = 96.39(4).

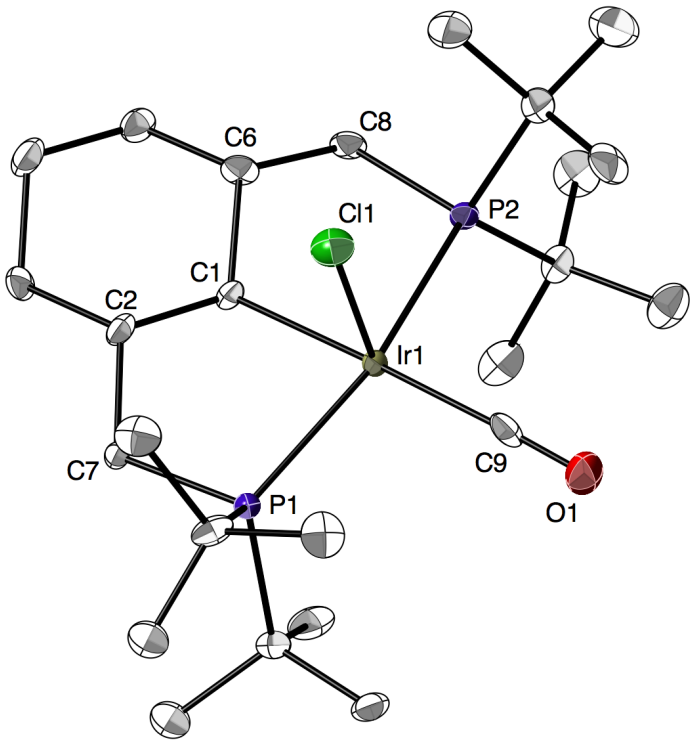


Figure 3. Molecular structure of **5b** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ir1–C1 = 2.159(4), Ir1–C9 = 1.909(5), C9–O1 = 1.111(6), Ir1–Cl1 = 2.5340(12), Ir1–P1 = 2.3578(11), Ir1–P2 = 2.3555(11), P1–Ir1–P2 = 161.82(4), C1–Ir–C9 = 174.72(18), Ir1–C9–O1 = 174.1(4), C1–Ir1–Cl1 = 90.49(12), P1–Ir1–Cl1 = 94.15(4), P2–Ir1–Cl1 = 94.44(4).

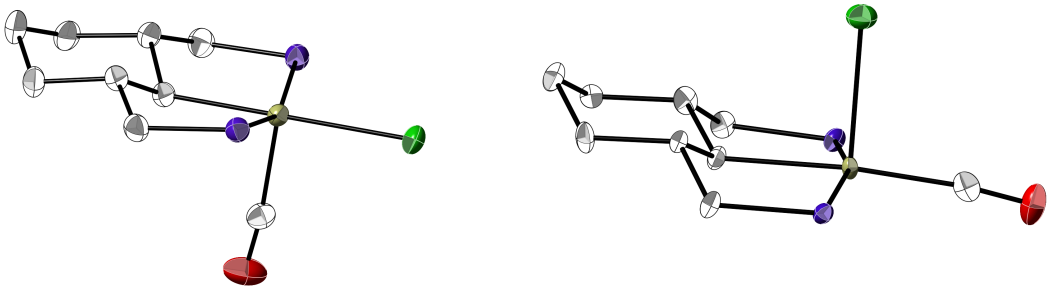


Figure 4. Side view of complexes **5a** (left) and **5b** (right) in the solid state, illustrating the α-hydrogen and metal hydride positioned *syn* and *anti* to each other, respectively. Hydrogen atoms and substituents on phosphorus are omitted for clarity.

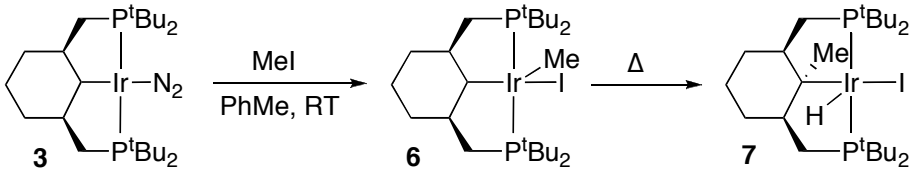
Subjecting the terminal nitrogen iridium(I) complex **3** to methyl iodide results in full conversion to compound **6** within hours (Scheme 3). The compound displays a triplet at 2.15 ppm in the ^{1}H-NMR spectrum and a triplet at -27.8 ppm in the ^{13}C-

NMR spectrum corresponding to the Ir–CH_3 moiety, in analogy with the previously reported aromatic counterpart.[34] The presence of a characteristic broadened triplet at 1.95 ppm corresponding to the α-proton of the cyclohexyl ring is indicative of a PCP-coordinated structure. The molecular structure of compound **6** is given in Figure 5, along with the crystallographic data for **6** and **7** in Table 2. Complex **6** adopts a distorted square pyramidal geometry around iridium with the methyl ligand in apical position with an *anti* realationship to the α-hydrogen.

Upon heating a toluene solution of **6** to 60 °C the colour turns from burgundy red to pale pink/orange within several hours. This transformation also takes place in room temperature over a period of days, but a hexane or toluene solution of **6** is stable at -28 °C for several weeks. The single product formed was characterized as complex **7**, the result of a 1,2-methyl migration from the metal to the metallated PCP carbon. The mechanism for this transformation is likely to proceed via reductive elimination of the C(sp^3)–C(sp^3) bond to give a non-metallated intermediate, which undergoes an oxidative addition of the remaining C–H bond in the previous α-position of the cyclohexyl backbone. A simliar result have been reported by Xu *et al.*[35] upon the complexation of an acyclic POC(sp^3)OP ligand with $Fe(Me)_2(PMe_3)_4$, but the examples of C(sp^3)–C(sp^3) reductive eliminations at iridium in the literature are limited.[34] The group of van Koten has reported on a reductive elimination and C(sp^2)–C(sp^3) bond formation from a NC(sp^2)N platinum(II) pincer complex upon treatment with methyl, alkyl or benzyl halides, generating an arenium platinum(II) complex.[36] Also, the group of Milstein has reported on the reverse process, where a C(sp^2)–C(sp^3) bond cleavage occurs upon complexation of a tolyl-based ligand with rhodium,[37] iridium,[38] platinum[39] and ruthenium,[40] with a net transfer of a methylene moiety.[41] The unambiguous presence of a hydride shift at -28.4 ppm in the ^{1}H-NMR spectrum of **7**, perfectly integrating 1:3 with the methyl protons at -1.02 ppm, argues for the suggested structure rather than a non-metallated η^2 C–C agostic species, as previously observed by Frech and Milstein for a cationic rhodium(I) complex with a naphtyl-based PCP ligand backbone.[32] The quaternary α-carbon was not visualized in the ^{13}C-NMR spectrum at the attempted concentrations and neither was the methyl carbon, probably due to its strong coordination to the metal, however a HMQC correlation to the methyl protons is apparent at ~5 ppm.

Frech and Milstein further report on the steric impact from the phosphorus substituents on the reactivity of naphtyl-based PCP rhodium(III) methyl idodide complexes towards carbon monoxide, giving simple coordination to form a mixture

of isomeric octahedral rhodium(III) carbonyl complexes in case of *iso*-propyl, and inducing reductive elimination of methyl iodide to form a four-coordinated rhodium(I) carbonyl complex in case of *tert*-butyl substituents.[32] Reacting complex **6** with 1 atm of carbon monoxide did not result in any formation of **4**, but rather a slow decomposition to a mixture of several compounds of which none was successfully isolated or characterized.



Scheme 3. Synthesis of 6 and subsequent transformation to compound 7.

Table 1. Crystallographic data for compounds **4**-**5**

	4	**5a**	**5b**
formula	$C_{25}H_{49}IrOP_2$	$C_{25}H_{50}ClIrOP_2$	$C_{25}H_{50}ClIrOP_2$
Fw	619.78	656.24	656.24
space group	Pbca	$P2_1/n$	Pbca
a/Å	12.4581(9)	12.5453(2)	12.3770(2)
b/Å	15.3030(9)	15.2101(3)	15.3452(2)
c/Å	29.2263(16)	15.5649(3)	28.8663(4)
α/deg	90	90	90
β/deg	90	93.996(2)	90
γ/deg	90	90	90
V/Å^3	5571.9	2962.80	5482.51
Z	8	4	8
D_{calcd}/g cm^{-3}	1.478	1.469	1.590
μ/mm^{-1}	4.920	4.718	5.100
θ/ range/deg	2.47-28.12	2.42-28.96	2.23-33.14
no. reflns collected	90480	70507	39527
no. of unique reflns	6596	7422	9768
$R(F)$ (I>2σ(I))[a]	0.0520	0.0332	0.0389
$wR2(F^2)$ (all data)[b]	0.1167	0.1030	0.1221
S[c]	1.224	1.425	1.124
R_{int}	0.126	0.0594	0.0317

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|)^2]^{1/2}$. [c] $S = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|)^2]^{1/2}$.

The structure of **7** was confirmed by an X-ray analysis and it is given in Figure 6. Complex **7** also has a square pyramidal geometry around iridium with the hydride ligand in apical position. The hydride atom was found in the Fourier map 0.85(4) Å from the metal center with a C1–Ir1–H1 angle of 100(2)°, in an *anti* configuration with respect to the methyl substituent on the α-carbon (although omitted from the molecular structure for clarity). The distance between the methyl substituent and the metal (Ir1–C9) in compound **7** is 2.449 Å, which clearly indicates an interaction, as already confirmed by the negative ^{1}H-NMR shifts of the methyl protons. This interaction gives rise to bond angles around the α-carbon that strongly deviates from the ideal tetrahedral geometry. Complex **7** further displays an unusual metal coordination with the PCP carbon in an axial position, resulting in a tilt of the cyclohexyl ring relative the coordination plane (Figure 7). It can be noted that this is the expected geometry resulting from two concerted elimination-addition reactions

as suggested above. Importantly it also supports previous suggestions that reductive elimination goes with configurational retention.[42]

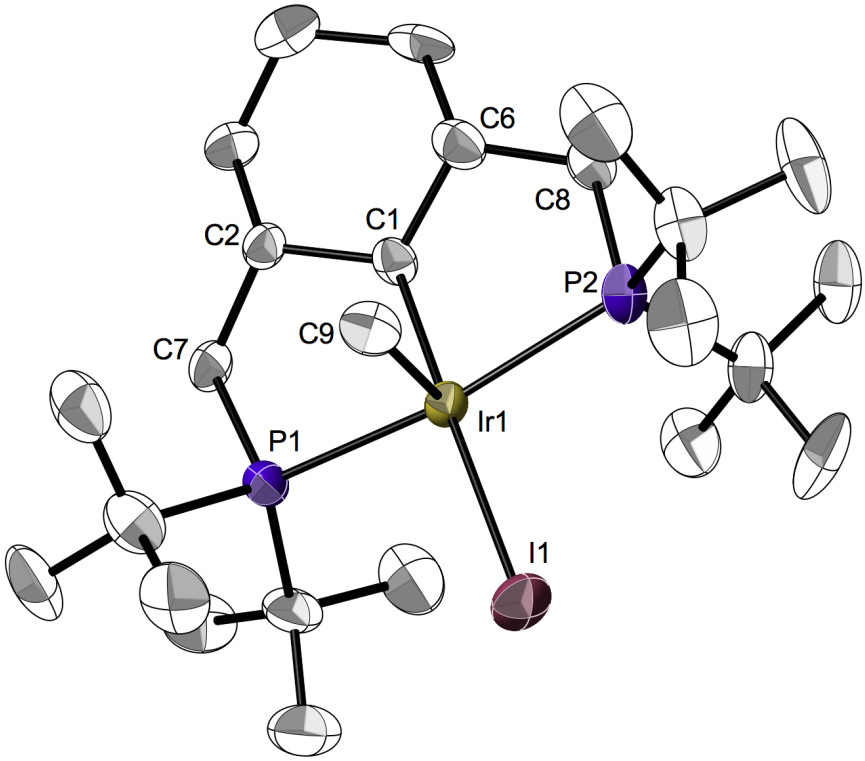


Figure 5. Molecular structure of **6** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ir1–C1 = 2.094(8), Ir1–C9 = 2.065(19), Ir1–I1 = 2.7837(8), Ir1–P1 = 2.344(2), Ir1–P2 = 2.354(3), P1–Ir1–P2 = 162.74(9), C1–Ir–C9 = 92.7(4), C9–Ir1–I1 = 91.5(3), C1–Ir1–I1 = 175.8(3), P1–Ir1–I1 = 97.44(6), P2–Ir1–I1 = 97.32(7).

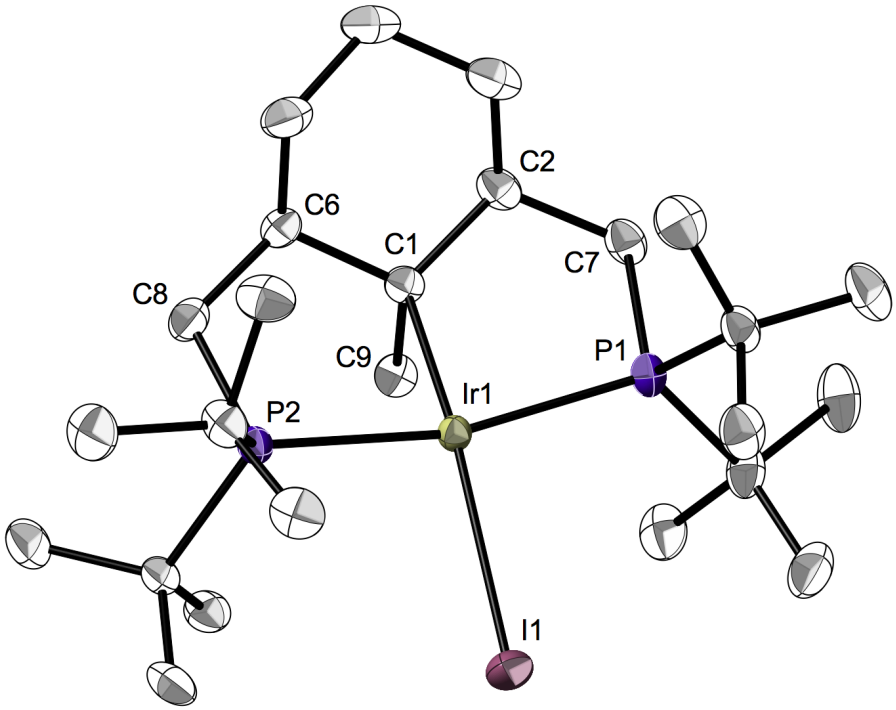


Figure 6. Molecular structure of **7** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Ir1–C1 = 2.087(3), C1–C9 = 1.553(4), Ir1–I1 = 2.8051(3), Ir1–P1 = 2.3397(8), Ir1–P2 = 2.3401(8), P1–Ir1–P2 = 166.59(3), C1–Ir–C9 = 83.19(18), C2–C1–C9 = 110.3(3), C2–C1–Ir1 = 118.9(2), C1–Ir1–I1 = 159.10(9), P1–Ir1–I1 = 95.84(2), P2–Ir1–I1 = 96.15(2).

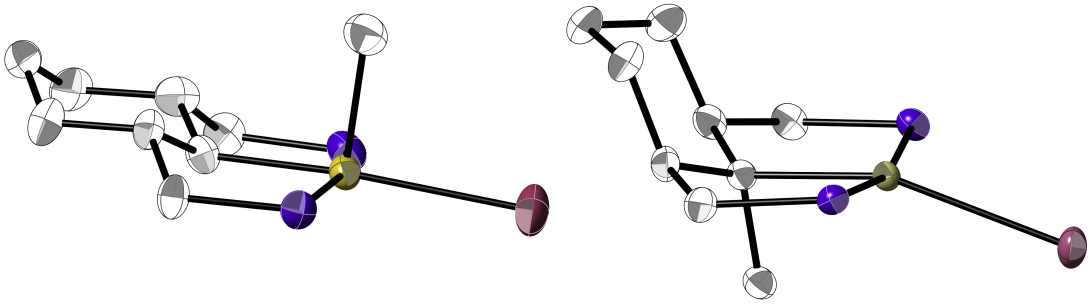


Figure 7. Side view of the complexes **6** (left) and **7** (right), displaying the PCyP carbon coordinated to the metal in an axial position in complex **7**. Hydrogen atoms and substituents on phosphorus are omitted for clarity.

Table 2. Crystallographic data for compounds **6**-**7**

	6	**7**
formula	$C_{25}H_{52}IrP_2I$	$C_{25}H_{52}IrP_2I$
Fw	733.74	733.74
space group	Pbca	$P2_1/c$
a/Å	17.1711(3)	12.4916(7)
b/Å	17.9192(3)	16.1841(8)
c/Å	18.9036(4)	15.2699(9)
α/deg	90	90
β/deg	90	103.920(6)
γ/deg	90	90
V/Å^3	5816.49	2996.4(3)
Z	8	4
D_{calcd}/g cm^{-3}	1.676	1.626
μ/mm^{-1}	5.773.	5.603
θ/ range/deg	2.37-29.05	2.52-28.88
no. reflns collected	74221	39037
no. of unique reflns	7398	7169
$R(F)$ (I>2σ(I))[a]	0.0670	0.0258
$wR2(F^2)$ (all data)[b]	0.1875	0.0605
S[c]	1.207	1.186
R_{int}	0.1468	0.0367

[a] $R = \Sigma(||F_o| - |F_c||)/ \Sigma|F_o|$. [b] $wR2 = [\Sigma w(|F_o| - |F_c|)^2/ \Sigma|F_o|)^2]^{1/2}$. [c] $S = [\Sigma w(|F_o| - |F_c|)^2/ \Sigma|F_o|)^2]^{1/2}$.

Conclusions

In summary, we have described the synthesis of new cyclohexyl-based PCP carbonyl complexes with iridium(I) and iridium(III). Characterization by means of X-ray crystallography and IR spectroscopy showed a good agreement of the CO bond lengths and IR bands with the previously reported aromatic PCP analogues, and thus no increased *trans*-influence or π-back donation was indicated as a result of the sp^3-hybridized PCP carbon in the present case. We further report on the oxidative addition of methyl iodide to a PCP iridium(I) terminal nitrogen complex, and a subsequent transformation to an iodo hydride complex via an unusual 1,2-methyl migration to the PCP carbon. The obtained geometry of this compound is consistent with concerted reductive elimination of a C(sp^3)–C(sp^3) bond and oxidative addition of a C(sp^3)–H bond.

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Bis{μ-*cis*-1,3-bis[(di-*tert*-butylphosphanyl)oxy]cyclohexane-κ^2P:P'}bis[carbonylnickel(0)] including an unknown solvent molecule

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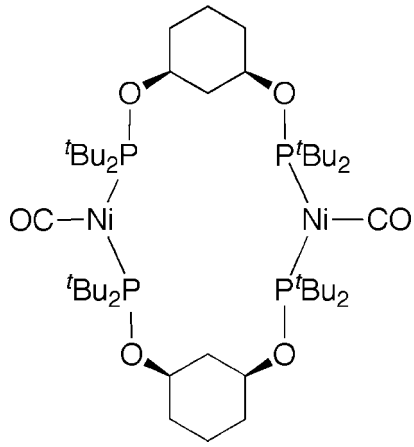
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.004 Å; R factor = 0.050; wR factor = 0.125; data-to-parameter ratio = 26.5.

The title compound, $[Ni_2(C_{22}H_{46}P_2O_2)_2(CO)_2]$, is located about a centre of inversion with the Ni^0 atom within a distorted trigonal–planar geometry. The cyclohexyl rings are in the usual chair conformation with the 1,3-*cis* substituents equatorially oriented. No specific intermolecular interactions are noted in the crystal packing. A region of disordered electron density, most probably a disordered deuterobenzene solvent molecule, was treated using the SQUEEZE routine in *PLATON* [Spek (2009). *Acta Cryst.* D**65**, 148–155]. Its formula mass and unit-cell characteristics were not taken into account during refinement.

Related literature

For similar 16-atom macrocyclic dimers with Ni^{II}, see: Johnson & Wendt (2011); Castonguay *et al.* (2008); Pandarus *et al.* (2008). For 16-atom macrocyclic dimers of Pd^{II} and Pt^{II} with *cis*-1,3-bis-(di-alkylphosphinito)cyclohexane ligands, see: Sjövall *et al.* (2001) and Olsson *et al.* (2007), respectively. For other examples of Ni^0 atoms adopting a close to trigonal–planar geometry, see: Rosenthal *et al.* (1990); Maciejewski *et al.* (2004); Brun *et al.* (2013). For an example of a carbon monoxide-induced reductive elimination from a PNP pincer-supported Ni^{II} hydride complex to form a tetrahedral Ni^0 dicarbonyl species (PNP = $[N(2\text{-}PR_2\text{-}C_6H_3)_2]^-$), see: Liang *et al.* (2012).



Experimental

Crystal data

$[Ni_2(C_{22}H_{46}O_2P_2)_2(CO)_2]$
M_r = 982.50
Monoclinic, $C2/c$
a = 31.7851 (9) Å
b = 8.5449 (2) Å
c = 21.3311 (5) Å
β = 90.995 (2)°
V = 5792.7 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.80 mm^{-1}
T = 120 K
0.20 × 0.15 × 0.05 mm

Data collection

Agilent Xcalibur Sapphire3 diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.883, T_{max} = 1.000
27324 measured reflections
6958 independent reflections
4948 reflections with $I > 2\sigma(I)$
R_{int} = 0.073

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.125
S = 1.09
6958 reflections
263 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (CrystalMaker, 2001); software used to prepare material for publication: *SHELXL97*.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5304).

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supplementary materials

Acta Cryst. (2014). E**70**, m176–m177 [doi:10.1107/S1600536814007818]

Bis{μ-*cis*-1,3-bis[(di-*tert*-butylphosphanyl)oxy]cyclohexane-κ^2P:P'}bis[carbonylnickel(0)] including an unknown solvent molecule

Klara J. Jonasson and Ola F. Wendt

1. Chemical context

2. Structural commentary

The title compound is formed through a carbon monoxide induced dimerization of a previously synthesized POCOP pincer Ni^{II} hydride complex. The course of the reaction is likely to proceed *via* a reductive elimination of a C—H bond between the metallated carbon and the hydride ligand. In the absence of carbon monoxide the POCOP pincer Ni^{II} hydride complex is stable towards reductive elimination in solution, even at 80 °C and upon addition of 1 eq. diphenylacetylene. Tricoordinate nickel(0) species are coordinately unsaturated, and the steric bulk of the *tert*-butyl substituents on the phosphorus atoms is likely to have a crucial stabilizing impact on the title compound. It decomposes over a period of hours upon exposure to air.

The title compound has a low solubility in C_6D_6 and attempts to obtain ^{1}H– and ^{13}C-NMR spectra has been unsatisfactory. Dissolving the red crystals of the title compound in $CDCl_3$ results in a yellow/green solution and decomposition to several compounds, as indicated by ^{31}P-NMR spectroscopy; none was successfully isolated or characterized.

3. Supramolecular features

4. Database survey

5. Synthesis and crystallization

A C_6D_6 solution of the compound *trans*-[NiH{*cis*-1,3-Bis-(di-*tert*-butylphosphinito) cyclohexane}] (10.0 mg, 0.021 mmol) was degassed with repeated freeze-pump-thaw cycles, before addition of CO (3 atm, 0.2 mmol, 10 eq.). Upon standing at room temperature the solution turned gradually darker, and within 48 h deep-red crystals of bis[μ-[*cis*-1,3-bis-[(di-*tert*-butyl)phosphinito]cyclohexane]-κ^2-P,*P*′]- bis[carbonylnickel(0)] were formed. These were used directly in the X-ray diffraction experiment, but were dried in high-vacuum prior to the elemental analysis. Yield: 8.7 mg (82%). ^{31}P{1H} NMR: (202.3 MHz, C_6D_6) δ: 177.8 (*s*). Anal. Calcd for $C_{46}H_{92}Ni_2O_6P_4$ (982.52): C 56.23, H 9.44. Found: C 56.02, H 9.47.

6. Refinement

The H atoms were positioned geometrically and treated as riding on their parent atoms with C—H distances of 0.96–0.98 Å, and with U_{iso}(H) = 1.2–1.5 U_{eq}. The asymmetric unit contains half a molecule of the title complex and half a molecule of benzene but this could not be modelled successfully. Solvent contributions were therefore removed from the diffraction data with *PLATON* using the SQUEEZE procedure (Spek, 2009). SQUEEZE estimated the electron count in the void volume of 680 Å^3 to be 140 which is in reasonable agreement with a total number of four benzene molecules in

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the unit cell.

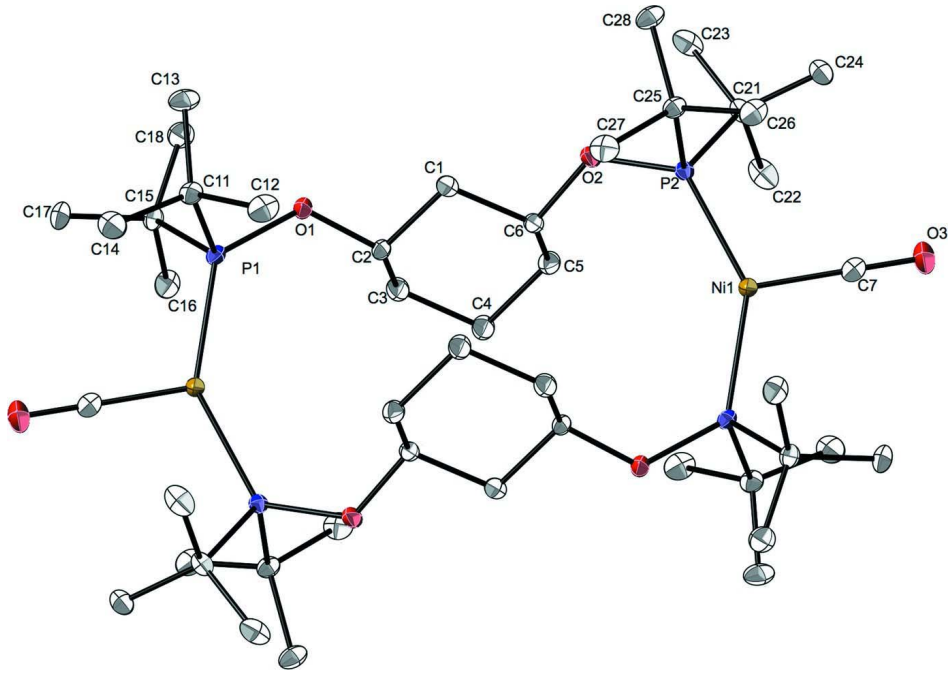

Figure 1

The molecular structure of the centrosymmetric title compound with atom labels and 30% probability displacement ellipsoids. Unlabelled atoms are related by the symmetry operation: 3/2-*x*, 1/2-*y*, -*z*. H-atoms are omitted for clarity.

Bis{*μ*-*cis*-1,3-bis[(di-*tert*-butylphosphanyl)oxy]cyclohexane-κ^2*P*:*P*′}bis[carbonylnickel(0)]

Crystal data

$[Ni_2(C_{22}H_{46}O_2P_2)_2(CO)_2]$
M_r = 982.50
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 31.7851 (9) Å
b = 8.5449 (2) Å
c = 21.3311 (5) Å
β = 90.995 (2)°
V = 5792.7 (3) Å^3
Z = 4
F(000) = 2128
D_x = 1.127 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 6436 reflections
θ = 2.5–29.1°
μ = 0.80 mm^{-1}
T = 120 K
Plates, red
0.2 × 0.15 × 0.05 mm

Data collection

Agilent Xcalibur Sapphire3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1829 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.883, T_{max} = 1.000
27324 measured reflections
6958 independent reflections
4948 reflections with $I > 2\sigma(I)$
R_{int} = 0.073
θ_{max} = 29.1°, θ_{min} = 2.5°
h = −42→35
k = −11→11
l = −26→26

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