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Jonasson, Klara

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

Klara Jonasson

LUND UNIVERSITY

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Fakultetens opponent är Prof. Timo Repo, Helsingfors Universitet.
Title:
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, CO₂ activation, catalysis

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

Klara Jonasson

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

-Voltaire
Populärvetenskaplig sammanfattning


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*

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

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$^2$P: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*

*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
1Pr 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
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>^Bu</td>
<td>tert-butyl</td>
</tr>
<tr>
<td>Tf</td>
<td>Trifluoromethanesulfonyl</td>
</tr>
<tr>
<td>TBA</td>
<td>2,2-dimethylbutane</td>
</tr>
<tr>
<td>TBE</td>
<td>3,3-dimethyl-1-butene</td>
</tr>
<tr>
<td>TFA</td>
<td>Trifluoroacetate</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>T.M.</td>
<td>Transmetallation</td>
</tr>
<tr>
<td>TMEDA</td>
<td>Tetramethylethylenediamine</td>
</tr>
<tr>
<td>TMS</td>
<td>Tetramethylsilane</td>
</tr>
<tr>
<td>TON</td>
<td>Turn over number</td>
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<tr>
<td>WGS</td>
<td>Water-gas shift</td>
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<tr>
<td>XRD</td>
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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

![Figure 1.1. Schematic representation of pincer complexes.](attachment:image)

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(sp³)–H bond relative the C(sp²)–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 dπ orbitals and the π-system of the aromatic backbone, variation of the substituents in para-position allow for fine electronic tuning of the PC₄Ar₃P complexes.⁷⁻¹⁰
After the establishment of pincer complexes as potent catalysts for several chemical transformations, 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 \( \sigma \)-donating \( sp^3 \)-hybridised PCP carbon will have a greater \textit{trans}-influence on the ligand in the forth coordination site, than will an \( sp^2 \)-hybridised PC_{Ar}P carbon. Thus, over the past decades a slowly growing collection of pincer ligands with saturated backbones have been reported, \textit{cf.} Figure 1.3. Along with the straight alkyl chain featured already in Shaw’s work, examples of cyclohexane, \textit{e.g.} arylmethane, adamantane, dibenzobarrelene, cycloheptatriene and diarylmethane-based scaffolds are known from the literature.

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. The synthesis of trialkylphosphine 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.
1.3 Complexation and coordination

The PCP pincer complex features an $\eta^3$-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. 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 < 'Bu, suggesting a higher impact from steric than from electronic effects. 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.

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.
1.5 References

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.

\[
\text{Scheme 2.1. Shaw’s complexation of an acyclic PCP ligand with rhodium and iridium, achieving cyclometallation and formation of non-metallated dimers.}
\]

In the same fashion, Shaw obtained 16-atom cyclic dimers as the major species upon attempted cyclometallation of $\text{R}_2\text{P(CH}_2)_3\text{PR}_2$ 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 $\text{C}_{\text{sp}3}-\text{H}$ 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 $\text{PC}_{\text{sp}3}\text{PNiBr}$ complex upon heating to 110 °C in the presence of DMAP.$^5$
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. 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.
2.1.2. \(\alpha\) - and \(\beta\) -hydrogen elimination of the ligand framework

One weak point of the aliphatic pincer complexes is the presence of labile \(\alpha\) - and \(\beta\)-hydrogen atoms in the backbone, which significantly reduce their coordination stability. Indeed the most powerful catalytic transformations utilising PC\(\text{sp}^3\)P complexes as catalysts concerns complexes with bi- or tricyclic PC\(\text{sp}^3\)P pincer scaffolds such as dibenzobarrelene\(^8\) and adamantane\(^9\) derivatives, lacking \(\alpha\)- and/or \(\beta\)-hydrogens to avoid such plausible decomposition routes.

![Scheme 2.3](image)

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

The studies of Shaw report on the release of \(H_2\) upon thermolysis of a PC\(\text{sp}^3\)P iridium(III) chloro hydride complex, forming the carbene complex through a presumed \(\alpha\)-H elimination (Scheme 2.4).\(^1\) The analogous rhodium complex instead undergoes \(\beta\)-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 \(\alpha\)-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.

![Scheme 2.4](image)

**Scheme 2.4.** Shaw’s reversible \(\alpha\)-elimination of an acyclic PCP iridium(III) complex.
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.  

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 temperatures (Scheme 2.6). NaH reduction of the same complex under a N₂ atmosphere afforded a terminal nitrogen Rh(I) complex, which also induced a reversible β-elimination forming the hydride.

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. 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. 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 and in presence of H₂. 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 ³¹P-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, utilising DMF as a carbonyl source. This protocol renders full decomposition of the ligand backbone and formation of $^{1}$Pr$_2$P(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. 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 $\beta$-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.\textsuperscript{21}

![Scheme 2.8. Zargarian’s isolated decomposition products from attempted formation of a POC$_{sp3}$OP nickel fluoride complex.](image-url)
Scheme 2.9. Zargarian’s isolated decomposition products from a POC\textsubscript{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\textsubscript{sp3}P ligand showed the same trend as reported by Shaw and co-workers for acyclic PC\textsubscript{sp3}P ligands concerning the influence from the phosphorus substituents,\textsuperscript{22} giving cyclometallation only in the tert-butyl substituted case\textsuperscript{23} and an 8-membered cyclic cis-coordinated complex with phenyl substituents (Scheme 2.10).\textsuperscript{24} However, complexation with this type of ligand is generally straightforward and has been subsequently reported with rhodium,\textsuperscript{25} ruthenium,\textsuperscript{26} platinum\textsuperscript{27} and iridium.\textsuperscript{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.\textsuperscript{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[(phosphinato)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

![Chemical structures](image)

**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.](image)

![Scheme 2.13. Olsson and Wendt’s cyclometallation attempts of a cyclohexyl-based POC(sp3)OP ligand with platinum.](image)

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.  

![Scheme 2.14. A ring flip from diaxial to diequatorial conformation, suggested to precede cyclometallation.](image)

The work presented in this thesis involves the cyclometallation of cis-1,3-bis-(diter-t-butylphosphinite)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.

\[
\text{Scheme 2.15. Synthesis of new } \text{PC}_{\text{sp}3}\text{P and POC}_{\text{sp}3}\text{OP complexes with nickel.}
\]

2.2.2 Aromatisation

The cyclohexyl-based pincer complexes have proved to be more stable towards \(\alpha\)- and \(\beta\)-hydrogen elimination reaction of the ligand backbone as compared to their acyclic counterparts. However, attempted cyclometallation of the \(\text{cis-1,3-bis-(di-tert-butylphosphinito)cyclohexane ligand with iridium resulted in an acceptorless dehydrogenation and aromatisation of the cyclohexyl scaffold.}^{28}\) This unusual transformation has been suggested to proceed via consecutive \(\alpha\)-eliminations and \(\alpha,\beta\)-hydrogen shift reactions (Scheme 2.16).\(^{30}\) Gusev and co-workers observed \(\text{H-elimination from the corresponding bis(phosphine) complex on ruthenium, obtaining a}

\[
\text{Scheme 2.16. Suggested pathway for the dehydrogenation and aromatisation of a cyclohexyl pincer backbone.}
\]
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 \( \alpha \)- and \( \beta \)-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.

2.4 References

2. Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Odell, K. J.; Shaw, B. L. J. Am. Chem. Soc. 1980, 102, 4373.
3. Cyclohexyl-based PCP complexes with nickel. CO\textsubscript{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.\textsuperscript{1} Early in the development of coupling reactions, 1\textsuperscript{st} 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 Eiichi Negishi, Akira Suzuki and Richard F. Heck for pioneering work in this area.\textsuperscript{2-3} While the general catalytic cycle for cross-coupling reaction (Figure 3.1) commonly constitutes a Pd\textsuperscript{0}/Pd\textsuperscript{II} sequence, there has been a revived interest in developing nickel-based catalysts for various coupling reactions in recent years.\textsuperscript{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,\textsuperscript{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.\textsuperscript{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.\(^\text{11}\) A later study by the same group reported on similarly low and variable yields for aromatically based bis(phosphinite) pincer complexes.\(^\text{12}\)

\[
\text{R}^1\text{X} + \text{R}^2\text{MgY} \xrightarrow{\text{catalyst}} \text{R}^1\text{R}^2
\]

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.\(^\text{13-14}\) 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.\(^\text{15-17}\)
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 and alkylations of heterocycles. 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. 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.

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 and , 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. Zargarian also utilised acyclic POCsp3OP nickel(III) complexes as catalysts for the Kharasch addition, a reaction previously reported by van Koten and co-workers for aromatic NCN pincer complexes.
**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.
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)P11, 37-38 and POC(sp2)OP27, 39 nickel complexes, underpinning the greater electron donation ability of a sp3-hybridised carbon atom.

![Scheme 3.5. Guan’s proposed mechanism for nickel catalysed CO2 reduction with HBCat.](image)

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

![Scheme 3.6. Novel cyclohexyl-based pincer nickel complexes.](image)
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.\textsuperscript{36} 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\textsuperscript{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.](image)

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

<table>
<thead>
<tr>
<th></th>
<th>8a</th>
<th>8b</th>
<th>9a</th>
<th>9b</th>
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<td>2.3764(4)</td>
<td>2.2497(14)</td>
<td>2.4303(4)</td>
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<td>1.939(2)</td>
<td>1.990(4)</td>
<td>1.998(2)</td>
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<tr>
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<td>2.2163(7)</td>
<td>2.2346(11)</td>
<td>2.2402(7)</td>
</tr>
<tr>
<td>Ni–P2</td>
<td>2.1933(9)</td>
<td>2.2156(7)</td>
<td>2.2251(11)</td>
<td>2.2325(7)</td>
</tr>
<tr>
<td>C1–Ni–X</td>
<td>173.20(10)</td>
<td>179.44(8)</td>
<td>178.81(18)</td>
<td>169.48(7)</td>
</tr>
<tr>
<td>P–Ni–P</td>
<td>163.69(4)</td>
<td>163.50(3)</td>
<td>170.83(5)</td>
<td>168.48(3)</td>
</tr>
</tbody>
</table>
Figure 3.3. Cyclic voltammetry scans of $10^{-3}$ M solutions of compounds 8-9 at a Pt electrode in CH$_2$Cl$_2$ (0.1 M ("Bu$_4$N)PF$_6$ scan rate 0.1 V s$^{-1}$).

The POC$_{sp^3}$OP complexes 8a and 8b have a smaller P–Ni–P angle than their PC$_{sp^3}$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.

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.
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 \( ^{iPr}POC_{sp3}OP \)-based hydride or alkyl nickel complexes has been unsuccessful due to a limited thermal stability.\(^{40} \) They still postulated the \( ^{iPr}POC_{sp3}OP \) nickel methyl complex as an in situ generated reactive intermediate in the Kumada-Corriu-Tamao cross coupling reaction, where the \( ^{iPr}POC_{sp3}OP \) nickel chloride complex had comparable reactivities to the \( ^{iPr}PC_{sp3}P \) 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.

\[ \text{Scheme 3.8. Synthesis of compounds 11 and 12.} \]

**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 react 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 CO₂ insertion into the POC₃sp³OPNi–H bond, we wanted to study the reactivity of analogous Ni–Me bond for the same type of CO₂ insertion. The formation of a metal carboxylate in this fashion is a proposed key step in many transition-metal catalysed conversions of CO₂ into more valuable products, which is of general interest to the scientific community. The CO₂ 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 PC₆⁺P nickel methyl complex by Hazari and co-workers (PC₆⁺P = [2,6-C₆H₃(CH₂P'Bu₂)₂]), 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 CO₂ has been reported to proceed without initial coordination for both PC₆⁺PNi–Me and PC₆⁺PPd–Me complexes.

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\textsubscript{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\textsubscript{Ar}PNi–NH\textsubscript{2} complex through reaction with sodium amide, was not accessible for the present system.\textsuperscript{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\textsubscript{Ar}OPNiCl (POC\textsubscript{Ar}OP = [2,6-C\textsubscript{6}H\textsubscript{3}(OPPh\textsubscript{2})\textsubscript{2}]).\textsuperscript{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\textsubscript{Ar}P palladium complexes (PC\textsubscript{Ar}P = [2,6-C\textsubscript{6}H\textsubscript{3}(CH\textsubscript{2}PPr\textsubscript{2})\textsubscript{2}]).\textsuperscript{45}

![Scheme 3.11. Synthesis of complex 16 through a direct route or via complex 15.](image)

The hydroxide complex 16 readily inserts CO\textsubscript{2} to form the bicarbonate species 17 (Scheme 3.12). Upon concentration \textit{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\textsubscript{Ar}PNiOCOOH complex (PC\textsubscript{Ar}P = [2,6-C\textsubscript{6}H\textsubscript{3}(CH\textsubscript{2}PPr\textsubscript{2})\textsubscript{2}]). They suggest a reversibility of the initial CO\textsubscript{2} insertion, so that the dimerisation takes place through a CO\textsubscript{2} elimination from the bicarbonate complex to regenerate the (PCP)NiOH complex,
which then reacts with residual bicarbonate complex, forming a \((\text{PCP})\text{Ni}\)\(_2\)\(\mu\)-(CO\(_3\)) dimer.\(^{46}\)

\[
\begin{align*}
\text{O-P}^\text{Bu}_2 & \\
\text{Ni-OH} & \quad \text{CO}_2 \quad (1 \text{ atm}) \quad \text{toluene, } 150^\circ C \\
\text{O-P}^\text{Bu}_2 & \quad \text{CO} \quad (1 \text{ atm}) \quad \text{toluene, } 80^\circ C \\
\text{O-P}^\text{Bu}_2 & \\
\text{16} & \quad \text{17} & \quad \text{18} & \quad \text{19}
\end{align*}
\]

**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 \(\mu\)-CO\(_2\)\(-\kappa^2\)C,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 \(\sigma\)-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 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 hydroxycarbonyl complexes with pincer ligands, such as (PNP)NiCOOH by Lee\(^{48}\) (PNP = N[2-P\(^3\)Pr\(_2\)-4-Me-C\(_6\)H\(_3\)]\(_2\)) and (PC\(_{Ar}\)P)PdCOOH by Wendt\(^{49}\) (PC\(_{Ar}\)P = [2,6-C\(_6\)H\(_3\)(CH\(_2\)P\(^3\)Bu\(_2\))\(_2\)]). 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.
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-C₆H₄PR)₂]⁺, R = Ph, 'Pr, Cy), affording a P,P’-coordinated dicarbonylic tetrahedral nickel(0) complex. Examples of tricoordinate 16e nickel(0) complexes like 20 are relatively rare in the literature, and typically require the stabilisation by a bulky ligand.
3.2. 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{$^1$H}-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{$^1$H}-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$_6$D$_6$ 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$_6$D$_6$).

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\textsubscript{2} insertion reactions, the cyclohexyl-based POC\textsubscript{sp3}OP essentially show comparable reactivity to similar aromatic PC\textsubscript{Ar}P and POC\textsubscript{Ar}OP complexes. Insertion of CO into a POC\textsubscript{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\textsubscript{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\textsubscript{2} insertion into the Ni–H bond of the POC\textsubscript{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\textsubscript{2} reduction to methanol derivatives, using boranes or other reducing agents.

3.4. References

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 cyclooctene (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.](image)

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\textsuperscript{6} has been thoroughly studied by Goldman and co-workers.\textsuperscript{25} Insertion of TBE into an Ir–H bond of (PCP)IrH\(_2\) (PCP = [2,6-C\(_6\)H\(_3\)(CH\(_2\)P\(_t\)Bu\(_2\))\(_2\)]\(^{+}\)) 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\(_6\)H\(_3\)(CH\(_2\)P\(_t\)Bu\(_2\))\(_2\)]\(^{+}\)).
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. 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$^\text{sp3}$OPIrHCl (1) (POC$^\text{sp3}$OP = 1,3-bis-(di-tert-butylphosphinito)-2-methylpropane) and PC$^\text{sp3}$PIrHCl (21) (PC$^\text{sp3}$P = cis-1,3-bis-[(di-tert-butylphosphino)methyl]cyclohexane) (Figure 4.3).

![Figure 4.3. Pincer complexes tested in the transfer dehydrogenation experiments.](image)

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. 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\textsuperscript{15}, using COA/TBE/catalyst = 3030/3030/1, and thus these conditions were applied also in our study. NaO'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).
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 N₂ in the Ar atmosphere used in the above-described experiments could inhibit the catalytic activity through formation of relatively stable bridged N₂-dimers, and this tendency could be stronger for a more electron rich PC₅₃P-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

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<th>Substrate</th>
<th>Acceptor</th>
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<td>21</td>
<td>COA</td>
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<tr>
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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 NEt₃ dehydrogenation required a slightly higher reaction temperature than in the protocol reported by Goldman 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.

4.4. References

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-\textsuperscript{1} and PC_{sp3}P-supported\textsuperscript{2} iridium(III) complexes. Such iridium carbonyl complexes are suggested to be involved in catalytic transformations such as olefin hydroformylation reactions\textsuperscript{3} and transfer dehydrogenations of ketones.\textsuperscript{4-5} PCP iridium(I) carbonyl complexes are known for aromatically based pincer structures,\textsuperscript{6-11} and has been reported to catalyse the decarbonylation of 2-naphtaldehyde\textsuperscript{12} and the partial deoxygenation of diols\textsuperscript{13} and glycerol.\textsuperscript{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 $\sigma$-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.\textsuperscript{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.\textsuperscript{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\textsubscript{3}, obtaining simple coordination in the first case but oxidative addition of an N–H bond in the latter.\textsuperscript{17}

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

Complex 21 has been previously reported to form the terminal N\textsubscript{2}-complex 24 under reductive conditions in presence of N\textsubscript{2} (Scheme 5.1).\textsuperscript{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 \textit{trans}-position to the PCP carbon. This complex can in turn be converted to complex 25 by addition of KO\textsuperscript{t}Bu (Scheme 5.1).


Refluxing the cyclohexyl-based bis(phosphine) ligand 27 with IrCl\textsubscript{3}⋅H\textsubscript{2}O 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 \textit{trans}-position and the hydride and chloride both in \textit{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 $\alpha$-carbon, as illustrated in the molecular structures in Figure 5.1. In complex 26 the hydride and $\alpha$-hydrogen are located \textit{anti} to each other, while in 28 they are \textit{syn}. The \textit{anti} configuration is the previously reported outcome for cyclohexyl-based PC$_{sp^3}$P complexes with iridium and is, thus, the expected for a concerted oxidative addition process via a C–H $\sigma$-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 \textit{syn}-H in 28. The more upfield shift for complex 28 compared to complex 26 ($\delta = -8.59$ ppm and -18.7 ppm respectively in C$_6$D$_6$) is in agreement with the higher \textit{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$_{sp^2}$P complexes,$^{18}$ \textit{i.e.} the Ir–CO bond lengths and the $\nu$$_{CO}$ stretching frequencies do not indicate any substantial electronic impact from the supposedly more strongly $\sigma$-donating PC$_{sp^3}$P-ligand relative its PC$_{sp^2}$P counterpart.

\textbf{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.
5.3. Oxidative addition of MeI and subsequent elimination of a C\textsubscript{sp3}–C\textsubscript{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\textsubscript{3} moiety, in analogy with the previously reported aromatic counterpart.\textsuperscript{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 $\eta^2$ C–C agostic species.

![Figure 5.2. $^1$H-NMR spectra of the hydride shifts of complexes 26 and 28.](image)

**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(PMe3)4. However, literature examples of C(sp3)–C(sp3) reductive eliminations at iridium centres are very limited. 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. Figure 5.3 also visualises the interaction between the methyl carbon and the metal centre in compound 30, as already confirmed by the negative 1H-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.
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

Klara J. Jonasson, Nanna Ahlsten, Ola F. Wendt

Centre for Analysis and Synthesis, Department of Chemistry, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

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Reaction of 2 equivalents of 1,3-bis-(di-tert-butyolphosphinito)-2-methyl-propane (1a) with [Ir(COD)Cl]2 affords the first aliphatic diphosphinite PCP pincer complex with iridium, Ir(H){(t-Bu2POCH2)2C(Me)}Cl (2). The poor yield of 2 is partly explained by the formation of a di-nuclear byproduct [IrCl(COD)]2(μ-Cl)(μ-[(t-Bu2POCH2)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 IrCl3/C1H2O in DMF leads to complete decomposition of the pincer ligand under the formation of Ir(H)(i-Pr2P(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 PCsp3P ligand readily cyclometallates with palladium, platinum and iridium, the corresponding 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-Bu2POCH2)2C(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 CaH2 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 (1H- and 13C NMR) using residual solvent peaks or H3PO4 (d 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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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 overnight. C6H5Bu2 (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 Et2O. 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%).

1H NMR (C6D6): δ 3.84–3.79 (m, 2H, OCH2), 3.72–3.67 (m, 2H, OCH2), 2.05 (oct, 3JH1 = 6.4 Hz, 1H, CH3(CH2)2), 1.13 (d, 3JH1 = 11.2 Hz, 18H, (CH3)3C), 1.12 (d, 3JH1 = 11.1 Hz, 18H, 2(CH3)2C), 0.94 (d, 3JH1 = 6.9 Hz, 3H, CH3(CH2)2). 13C{1H} NMR (C6D6): δ 75.9 (d, JRECI = 20.9 Hz, CH3O), 38.0 (t, JRECI = 7.5 Hz, CH3(CH2)2), 35.4 (d, JRECI = 26.2 Hz, (CH3)2C), 35.2 (d, JRECI = 25.7 Hz, (CH3)2C), 27.7 (d, JRECI = 15.5 Hz, (CH3)2C), 27.6 (d, JRECI = 15.5 Hz, (CH3)2C), 14.6 (s, CH3). 31P{1H} NMR (C6D6): δ 161.5 (s).

2.3. Preparation of 1,3-bis-(di-iso-proplyphosphino)-2-methylpropene (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 CIPPr2 (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 pale yellow oil, that was used without further purification (Yield: 0.490 g, 91%).

1H NMR (C6D6): δ 3.79–3.73 (m, 2H, OCH2), 3.68–3.62 (m, 2H, OCH2), 2.02 (oct, 3JH1 = 6.4 Hz, 1H, CH3(CH2)2), 1.69–1.59 (m, 4H, CH(CH2)2), 1.16–1.11 (m, 12H, 2(CH3)2C), 1.05–0.98 (m, 12H, 2(CH3)2C), 0.93 (d, 3JH1 = 6.9 Hz, 3H, CH3(CH2)2). 13C{1H} NMR (C6D6): δ 74.4 (d, JRECI = 19.5 Hz, 2CH2O), 37.9 (t, JRECI = 7.2 Hz, CH2O(CH2)2), 28.3 (d, JRECI = 17.9 Hz, 4(CH2)2CH), 18.2 (d, JRECI = 5.0 Hz, (CH2)2CH), 18.0 (d, JRECI = 5.1 Hz, (CH2)2CH), 17.1 (d, JRECI = 1.4 Hz, (CH2)2CH), 17.0 (d, JRECI = 1.3 Hz, (CH2)2CH), 14.1 (s, CH3). 31P{1H} NMR (C6D6): δ 152.4 (s).

2.4. Preparation of Ir(H)[(Bu2PCH2)2C(Me)]Cl (2) and [IrCl2(COD)][µF][(Bu2PCH2)2C(Me)] (3)

Inside a nitrogen atmosphere glovebox, [Ir(COD)Cl2] (79 mg, 0.12 mmol) was added to a solution of 1a (90 mg, 0.24 mmol) in CH2Cl2 (1 mL) in a J. Young NMR tube. The tube was evacuated under high vacuum and H2 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%). 1H NMR (C6D6): δ 5.35–5.27 (m, 4H, CH2), 3.87–3.82 (m, 2H, OCH2), 3.70–3.66 (m, 2H, OCH2), 3.62–3.57 (m, 4H, CH=C), 2.21–2.12 (m, 4H, 2CH=CH-CH=C), 2.04–1.98 (m, 4H, 4H, 2CH=CH-CH=C), 1.94–1.90 (m, 1H, CH3(CH2)2), 1.57–1.48 (m, 8H, 4H, 4H, CH=CH-CH=C), 1.50 (s, 18 H, 2(CH3)2C), 1.47 (s, 18 H, 2(CH3)2C), 0.74 (d, JHH = 6.9 Hz, 3H, CH3). 31P{1H} NMR (C6D6): δ 142.7 (s). Anal. Calcd. for C50H52Cl2Ir2O2P2: 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%). 1H NMR (C6D6): δ 3.28–3.19 (m, 2H, OCH2), 3.04–3.00 (m, 2H, OCH2), 1.50 (vt, JHH = 14.0 Hz, 18 H, 2(CH3)2C), 1.29 (vt, JHH = 13.5 Hz, 18 H, 2(CH3)2C), 1.13 (s, 3H, CH3(CH2)2), –37.4 (t, JHH = 13.4 Hz, 1H, Ir-H). 13C{1H} NMR (toluene-d8): δ 90.0 (vt, JHC = 6.7 Hz, OCH2), 46.6 (vt, JHC = 24.1 Hz, C(CH3)2), 45.8 (vt, JHC = 26.7 Hz, C(CH3)2), 39.0 (d, JHC = 5.5 Hz, Ir-C), 33.8 (vt, JHC = 5.7 Hz, (CH3)2C), 33.4 (vt, JHC = 6.2 Hz, (CH3)2C), 32.7 (s, CH3). 31P{1H} NMR (C6D6): δ 180.0 (d, JPH = 13.4).

2.5. Preparation of Ir(H)(i-Pr2P(OMe)2)(COD) (4)

IrCl3·H2O (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: ν(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). The data were extracted and integrated using Crysalis RED. The structures were solved by direct methods and refined by full-matrix least-squares calculations on $F^2$ (all data) using SHELXTL 5.1. 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 in 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.
and the fact that the angle C11–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 iPr-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 diphosphinates is further illustrated by the reaction between 1b and IrCl3.H2O in DMF, resulting in compound 4, where the ligand backbone has been fully decomposed, forming i-Pr3P(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-Pr2POCH2)2C(Me)Cl or Ir(H)(i-Pr2POCH2)2C(Me)Cl could be detected, by means of 31P{1H} 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 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)(i-Bu2POCH2)(i-Bu2POCH2)2C(Me)Cl (2). The poor yield of 2 is partly explained by the formation of a di-nuclear byproduct [IrCl(COD)]2([μ-(i-Bu2POCH2)(i-Bu2POCH2)CH(Me)]) (3). Reaction of 1,3-bis-(di-isopropylphosphinito)-2-methyl-propane (1b) under the same condition does not give any cyclometallation, and reaction with IrCl3.H2O in DMF leads to complete decomposition of the pincer ligand under the formation of Ir(H)(i-Pr3P(OH))3(CO) (4), underpinning the comparatively low thermal stability of aliphatic phosphinite pincer systems.

Acknowledgements

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Appendix A. Supplementary material

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

Klara J. Jonasson, Ola F. Wendt

Centre for Analysis and Synthesis, Department of Chemistry, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

**Article Info**

**Abstract**

The coordination behaviour of the aliphatic pincer ligand cis-1,3-bis-((di-tert-butylphosphino)methyl)cyclohexane with NiCl₂ and NiBr₂ 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], hydroammonations [7], hydroisilylations [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 were 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...
499.76 MHz (1H). Chemical shifts are given in ppm downfield from TMS, using residual solvent peaks (1H and 13C) or H3PO4 (31P) 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 Microanalytical Laboratory, 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 o-scans and Mo Kα (λ = 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 F2 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)cyclohexane [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 NiCl2 (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, and the resultant solution was analyzed by GC.

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). 1H NMR (CD2Cl2): δ 1.83–1.79 (m, Cy, 2H), 1.73–1.67 (m, Cy, 1H and m, PCH2CH2, 2H), 1.55–1.50 (m, Cy, 2H), 1.49 (vt, J = 12.5 Hz, 3Bu, 18H), 1.46 (vt, J = 12.0 Hz, 3Bu, 18H), 1.30–1.22 (m, Cy, 1H, 12.5 Hz, HC–Ni), 1.11–1.05 (m, PCH2CH2, 2H), 0.81–0.73 (m, Cy, 2H). 13C{1H} NMR (CD2Cl2): δ 56.3 (t, JPC = 11 Hz, CH2–Ni), 38.7 (vt, JPC = 19 Hz, CH2CH2CH3), 37.7 (vt, JPC = 11 Hz, C(CH3)2), 37.7 (vt, JPC = 11 Hz, C(CH3)2), 32.8 (vt, JPC = 14 Hz, C(CH3)2), 32.8 (vt, JPC = 18 Hz, P–CH2), 30.7 (vt, JPC = 4.7 Hz, C(CH3)2), 29.7 (vt, JPC = 4.5 Hz, C(CH3)2), 27.2 (s, CH2CH2CH3), 31P{1H} NMR (CD2Cl2): δ 61.79 (s). Anal. Calcd for C24H49BrNiP2 (493.74): C, 53.56; H, 9.18. Found: C, 53.48; H, 9.10.

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 MgSO4 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 Zargar and coworkers for the non-cyclic 1,5-bis(phosphinito) pentane ligand [10b], but increasing the amount of NiX2 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 31P 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 Zargar 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 mono-coordinated 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 31P{1H} 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 3Bu protons as virtual triplets in 1H NMR spectra. The characteristic pattern of virtual triplets is also observed in the 13C{1H} 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 18Perep3P nickel complex [10a], underpinning the greater trans-influence from a sp3-hybridized coordinated carbon compared to its sp2-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.](image-url)
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 NaBH4 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 LiAlH4 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 PCsp3P nickel bromide complex to a rare nickel carbene complex through dehydrobromination with Kn(SiMe3)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 1Bu-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 sterically demanding 1Pr-groups is a topic for future investigations.

4. Conclusion

The complexation behaviour of the cyclohexyl-based PCsp3P ligand cis-1,3-bis-((di-tert-butylphosphino)methyl)cyclohexane towards NiCl2 and NiBr2 has been studied, giving two new PCsp3P-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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Pincer complexes

Synthesis and characterisation of a new family of POC$_{sp3}$OP pincer complexes with nickel. Reactivity towards CO$_2$ and phenyl acetylene

Klara J. Jonasson, and Ola F. Wendt$^{[a]}$

**Abstract:** A cyclohexyl based POC$_{sp3}$OP pincer ligand (POC$_{sp3}$OP = cis-1,3-Bis-(di-tert-butylphosphinopheno)cyclohexyl) cyclometalates 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-butylphosphinopheno)cyclohexane)]$_2$ (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$_{sp3}$OP)NiCl (2a) and (PC$_{sp3}$OP)NiCl (2a) (PC$_{sp3}$OP = 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)NiO(CO)H (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 $\sigma$-donating anionic C(sp$_3$)-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 $\alpha$- and $\beta$-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 $\alpha$- or $\beta$-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 Zargarin on the

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$^[a]$ K. J. Jonasson, Dr. O. F. Wendt
Centre for Analysis and Synthesis
Department of Chemistry
Lund University
P.O. Box 124, S-22100 Lund, Sweden
Tel.: (+46)46 228153
E-mail: ola.wendt@chem.lu.se

Supporting information for this article is available on the WWW under http://www.XXXXXX or from the author.
complexation of acyclic POCOP OP pincer ligands with nickel,[12] we wanted to attempt cyclometallation of our similar cyclohexyl-based POCOP 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 cyclisation by Ni pincer complexes involve various cross-coupling reactions.[13-14] direct alkylations,[15] alkene hydroformations,[16] hydroaminations,[17] hydrosilylations[18] and reduction of carbon dioxide to methane.[19]

We here report on the first successful cyclometallation of cis-1,3-bis-(di-tert-butylphosphinato)cyclohexane and present a series of new POCOP OP supported Ni(II) complexes, including the halide, hydride, methyl and phenyl species. We further report on the reactivity of these compounds towards phenyl acetylene and CO2. There is a major interest in transition metal mediated functionalization of CO2, 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 CO2, where insertion into a metal-hydrogen bond in many cases is an essential step.[21] Another approach towards CO2 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 CO2 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 Zaragarian and coworkers for their non-cyclic 1,5-bis(phosphinato)pentane ligand.[12] Complexes 1a and 1b are the first cyclometallated complexes with this ligand and indeed the first POCOP OP nickel complexes with tert-butyl substituents. Altering the NiX2 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 31P-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. Zaragarian 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 nickel 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-butylphosphinato)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 H2O in the solvent, despite using conventional drying procedures. This oxidation proceeds slowly even without presence of NiX2, and hence there is no evident metal mediation. For non-cyclic POCOP 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 31P{1H} NMR spectra of the here reported pincer complexes display a singlet resonance that confirms the equivalence of the two phosphoryl nuclei, in line with the expected trans geometry. This is consistent with the appearance of the Ph protons as two (although sometimes slightly merged) virtual triplets in the 1H NMR spectra. The characteristic pattern of virtual triplets is also observed in the 13C{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 (δPh ≈ 11 Hz) in CD2Cl2.

![Scheme 1. Synthesis of (POCOP OP)NiCl (1a) and (POCOP OP)NiBr (1b).](image)

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 POCOP OP complexes have a more narrow P-Ni-P angle than their POCOP counterparts,[28] in case of 1a 163.6° 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 POCOP 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 (PC₅sp³P)NiCl complex is unreactive towards hydride sources and base. The Ni–X bond lengths of 1a and 1b are slightly shorter than in their PC₅sp³P 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 (POC₅ArOP)Ni–Cl[29] or (POC₅ArOP)Ni–Br[30-31] complexes, and also slightly longer than those of the corresponding acyclic (POC₅sp³OP)Ni–X complexes.[12] Crystal data and collection and refinement details for compounds 1a, 1b, 3 and 4 are presented in Table 1.

The redox properties of the POC₅sp³OP complexes 1a and 1b, alongside the recently reported PC₅sp³P 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 PC₅sp³P and POC₅sp³OP 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 E₁/₂ values of 1a and 1b compare to those reported by Zargarian for acyclic POC₅sp³OP 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 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–C6 = 1.440(4), C1–Ni1–C1 = 81.79(7), P1–Ni1–C1 = 81.73(7), P1–Ni1–Cl1 = 98.71(9), P2–Ni1–Cl1 = 98.68(2).
separate the traces of state for several days. Recrystallization 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.

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 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 (PCP)NiCl complex that readily reacts with MeMgCl or allylMgCl to form the methyl and allyl complex respectively, in good yields. 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. The Ni–Me moiety of 3 is characterised by high-field triplets in the 1H (-0.24 ppm) and 13C (-19.95 ppm) NMR spectra (C6D6). 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.

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 (PCP)NiMe (PCP = C2H8–2,6-(CH2–P–Bu)2). ftw compared to 2.026 Å (Figure 5). The expectedly stronger trans influence from a coordinated sp3 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 = Pr2P(CH2)iPr) reported by Zargarian and co-workers and the (PCP)NiX complexes (PCP = C2H8–2,6-(CH2–P–Pr)2) reported by Câmara and co-workers. 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 1H-NMR spectrum.

Compound 1a is readily converted to the nickel hydride complex by reduction with LiAlH4 (Scheme 3), following the synthetic route used by Guan for the aromatic analogue. The 1H NMR spectrum of 5 reveals a typical hydride resonance as a triplet at -8.58 ppm (JHH = 52.0 Hz). A concentrated hexane
solution of complex 5 afforded X-ray quality crystals upon storing at -28 °C under N₂ 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 N₂ 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.

The reaction of (POC₆OP)NIH (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 CH₄ was observed by means of ¹H NMR spectroscopy (δ = 0.15 ppm in CD₃OCD). 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 POC₆OP ligand, which reacts already at room temperature. The reaction is also somewhat slower than with a palladium methyl complex with an aromatic PCP ligand (PCP = C₆H₅-2,6-(CH₃PBU₂)₂). The lower reactivity is possibly of steric origin since the fastest reaction is observed for the nickel PC₆OP complex which bears 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 ³¹P(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 = C₆H₅-2,6-(OPBU₂)₂), where the hydride complexes are highly reactive forming acetylide complexes in addition to small amounts of the β-phenylvinyl complex. The higher reactivity of the hydride is expected for the proposed α-bond metathesis mechanism. Also, in the present case a α-bond metathesis mechanism is plausible but no H₂ formation was observed by ¹H-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-phenylvinyllic byproduct from 1,2-insertion into the Ni–H bond could for example not be supported by any clear olefinic proton shifts in the ¹H NMR spectrum.

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 = 2.204(10), Ni1–P2 = 2.1423(9), Ni1–C11 = 1.971(3), C1–Ni1–C11 = 73.81(16), P1–Ni1–P2 = 161.61(4), P1–Ni1–C1 = 81.04(10), P2–Ni1–C11 = 81.19(10), P1–Ni1–C11 = 100.65(10), P2–Ni1–C11 = 97.52(10).

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 = 98.3(12), P2–Ni1–H11 = 95.8(12).
C(alkyne) bond length (1.889(3) Å) that is significantly shorter than the Ni–C bond lengths in (POC$_{3}$OP)Ni–Me (3, 2.016(3) Å) and (POC$_{3}$OP)Ni–Ph (4, 1.971(3) Å), in consistency with the hybridization of the concerned carbon atoms. Like in the similar (PC$_{3}$P)NiCCP complex (PC$_{3}$P = C$_{6}$H$_{5}$-2,6-(CH$_{3}$PPh$_{2}$)$_{2}$) previously reported by Schmeier et al.,$^{[23a]}$ 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°.

The formate complex 7 was obtained via direct CO$_{2}$ insertion into the Ni–H bond (Scheme 5), analogously to the previously reported reaction with the corresponding (POC$_{3}$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 singlet resonance at δ 8.50 ppm and $^{13}$C NMR displays a singlet corresponding to the carbonyl at δ 175.3 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.

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 $\eta^1$-bound carbonate 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 $sp^3$-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-hydrocarbonyl 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 that of (PCP)Pd complexes and on par with aromatic (PCP)Ni complexes.

The 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 = 1.225(4), C8–Ni1–C7 = 177.74(16), P1–Ni1–P2 = 164.18(4), C7–C8–C11 = 176.14(4), P1–Ni1–C1 = 82.17(10), P2–Ni1–C1 = 82.01(10), P1–Ni1–C7 = 94.48(11), P2–Ni1–C7 = 97.37(11).

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 = 1.225(4), C8–Ni1–C7 = 177.74(16), P1–Ni1–P2 = 164.18(4), C7–C8–C11 = 176.14(4), P1–Ni1–C1 = 82.17(10), P2–Ni1–C1 = 82.01(10), P1–Ni1–C7 = 94.48(11), P2–Ni1–C7 = 97.37(11).

The insertion of CO$_{2}$ into the Ni–H 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 $\eta^1$-bound carbonate 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 $sp^3$-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-hydrocarbonyl 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 that of (PCP)Pd complexes and on par with aromatic (PCP)Ni complexes.

**Scheme 5.** Synthesis of (POC$_{3}$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 $\eta^2$ coordination, in consistency with other reported crystallographically characterized nickel formate complexes.$^{[19a, 23b, 37]}$ Similarly, the molecular structure of 8 confirms the $\eta^1$ 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$_{3}$P)NiOAc complex (PC$_{3}$P = C$_{6}$H$_{5}$-2,6-(CH$_{3}$PPh$_{2}$)$_{2}$) previously reported by Zargarian and
Gives the hydrocarbyl and hydride complexes an unprecedented stability and allows for the first isolation of such complexes involving a (POC$_{3}$OP)Ni core. Also, the current system is completely unreactive towards C–O bond cleavage of the ligand, which is otherwise a major stibibility issue of POC$_{3}$OP complexes. Despite the increased stability the methyl complex reacts with phenyl acetylene to give a Ni(II) acetylide complex under the release of CH$_{x}$. 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.

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4 R = Σ |F$_{o}$| - |F$_{c}$| / Σ|F$_{o}$| . 5 wR2 = Σ[w(F$_{o}$ - |F$_{c}$|)$^2$] / Σ|F$_{o}$|.$^2$ . 6 S = Σ|w(F$_{o}$ - |F$_{c}$|)$^2$] / Σ|F$_{o}$|.$^2$.

Conclusion

We here report on the first metallation of a cyclohexyl-based POC$_{3}$OP ligand; a new family of POC$_{3}$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...
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-butylphosphinophenoxy)cyclohexane) was synthesized according to previously reported procedures.\(^\text{[10]}\) All other chemicals purchased from commercial suppliers and used as received. \(^{1}H\), \(^{13}C\) and \(^{31}P\) NMR experiments were reported on a Varian Unity INOVA 500 spectrometer, operating at 499.76 MHz \((J)\). 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\(_3\)PO\(_4\) at 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 Nicolet Magna 550 FT-IR.

Crystallography. XRD-quality crystals of compounds 1a, 1b and 3e–8 were obtained through recrystallization from benzene, toluene or hexane. Intensity data were collected with an Oxford Diffraction Xcalibur 3 system, using \(\omega\)-scans and Mo Ka (\(\lambda = 0.71073\) Å) radiation.\(^\text{[27]}\) The data were extracted and integrated using Crystalsal RED.\(^\text{[28]}\) The structure was solved by direct methods and refined by full-matrix least-squares calculations on \(F^2\) using SHELXTL5.1.\(^\text{[29]}\) Molecular graphics were generated using CrystalMaker® 8.3.5.\(^\text{[30]}\)

### Table 2. Crystal data and collection and refinement details for compounds 5–8.

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### Synthesis and characterisation of compounds

trans-\[Ni(cis-1,3-Bis-(di-tert-butylphosphinophenoxy)cyclohexane)\] (1a): To a stirred mixture of the cis-1,3-bis-(di-tert-butylphosphinophenoxy)cyclohexane ligand (25.2 mg, 0.062 mmol) and anhydrous NiCl\(_2\) (22.6 mg, 0.123 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\(_3\)) \(\delta = 3.60\) (dt, \(J = 3.5, 7.5\) Hz, CH\(_2\)CO, 2 H), 2.03 (s, CH\(_2\)CH\(_2\)CH\(_2\)CO, 2 H) and \(J_{CH=CH} = 11.0\) Hz, 1 H), 1.48 (vt, \(J = 12.0\) Hz, CH\(_2\), 18 H), 1.32 (vt, \(J = 15.0\) Hz, CH\(_2\)CH\(_2\), 2 H)

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-butylphosphinophenoxy)cyclohexane) was synthesized according to previously reported procedures.\(^\text{[10]}\) All other chemicals purchased from commercial suppliers and used as received. \(^{1}H\), \(^{13}C\) and \(^{31}P\) NMR experiments were reported on a Varian Unity INOVA 500 spectrometer, operating at 499.76 MHz \((J)\). 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\(_3\)PO\(_4\) at 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 Micronanalytisches Laboratorium, M"uhlen 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 Xcalibur 3 system, using \(\omega\)-scans and Mo Ka (\(\lambda = 0.71073\) Å) radiation.\(^\text{[27]}\) The data were extracted and integrated using Crystalsal RED.\(^\text{[28]}\) The structure was solved by direct methods and refined by full-matrix least-squares calculations on \(F^2\) using SHELXTL5.1.\(^\text{[29]}\) Molecular graphics were generated using CrystalMaker® 8.3.5.\(^\text{[30]}\)
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%). H NMR (CD$_3$OD): 1.3-7.71 (m, CH$_3$CH$_2$O, 2 H), 2.29-2.24 (m, CH$_3$CH$_2$O, 2 H), 1.79 (dt, J = 2.0 Hz, J = 11.0 Hz, CH$_3$O–Ni, 1 H), 1.73-1.68 (m, CH$_3$CH$_2$O, 1 H), 0.34 (q, J = 6.0 Hz, CH$_3$, 6 H). IR (ATR): ν$_{max}$ = 3434 cm$^{-1}$, 2967 cm$^{-1}$, 1712 cm$^{-1}$, 1640 cm$^{-1}$, 1408 cm$^{-1}$, 1367 cm$^{-1}$, 1234 cm$^{-1}$, 1157 cm$^{-1}$, 1076 cm$^{-1}$, 1036 cm$^{-1}$, 974 cm$^{-1}$, 913 cm$^{-1}$, 873 cm$^{-1}$, 850 cm$^{-1}$, 746 cm$^{-1}$, 718 cm$^{-1}$, 676 cm$^{-1}$, 618 cm$^{-1}$, 565 cm$^{-1}$.

Acknowledgements

Financial support from the Swedish Research Council, the Knut and Alice Wallenberg Foundation and the Royal Physiographical Society in Lund is gratefully acknowledged. We thank Flavia Pop and Dr. Narcis Avarvari for experimental assistance in the cyclic voltammetry measurements.

Keywords: aliphatic pincer ligands • bis(phosphinite) POPCOP complexes • nickel • cyclometallation • CO$_2$ insertion


[41] CrystalMaker® Software; Begbroke Science Park, Sandy Lane, Yarnton, Oxfordshire, OX5 1PF, United Kingdom (2010).

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Synthesis and characterization of a new family of POC\textsubscript{sp3}OP Pincer complexes with nickel. Reactivity towards CO\textsubscript{2} and phenyl acetylene

Klara J. Jonasson, Ola F. Wendt\textsuperscript{1}
Centre for Analysis and Synthesis, Department of Chemistry, Lund University,
P.O. Box 124, S-221 00 Lund, Sweden
Received XXXX XX, 2014

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2. NMR-spectra ................................................................. S3

\textsuperscript{1} Corresponding author. Tel.: +46 46 2228153. E-mail address: ola.wendt@chem.lu.se
(O.F. Wendt).
1. Characterisation of cis-1,3-bis-(di-tert-butylphosphinate)cyclohexane

cis-1,3-bis-(di-tert-butylphosphinate)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\(_6\)D\(_6\)): \(\delta\) 4.47-4.41 (m, CH\(_2\)C=H, 2 H), 2.93-2.91 (m, OCHC\(_2\)H\(_2\)CHO, 1 H), 1.97-1.95 (m, CH\(_2\)CH\(_3\)CHO, 2 H), 1.36 (vt, \(J_{PH} = 26.0\) Hz, tBu, 36 H), 1.11-1.04 (m, CH\(_2\)CH\(_3\)CHO, 2 H), 0.88-0.80 (m, CH\(_2\)CH\(_3\)CH\(_2\), 1 H).

\(^{31}\)P\(^{1}\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 63.7 (s).
2. NMR-spectra

$^1$H-NMR (C$_6$D$_6$) of compound 3. The Ni–Me protons are displayed as a triplet at -0.24 ppm.

$^{13}$C-NMR (C$_6$D$_6$) of compound 3. The Ni–Me carbon are displayed as a triplet at -20 ppm. Trace amounts of 1a are notable, especially for its more intense shifts i.e. the CH$_2$CHO carbons at 87 ppm, the C(CH$_3$)$_3$ carbons around 28 ppm and the CH$_3$CH$_2$CH$_2$ carbon at 21 ppm. The singlet at 30 ppm corresponds to Apiezon brand H grease, and the singlet at 1 ppm is silicon grease.
$^{31}\text{P-NMR (C}_6\text{D}_6)$ of compound 3.

$^1\text{H-NMR (C}_6\text{D}_6)$ 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$_6$D$_6$) of compound 5.

$^{13}$C-NMR (C$_6$D$_6$) 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$_2$CHO 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

Klara J. Jonasson and Ola F. Wendt*

Centre for Analysis and Synthesis, Department of Chemistry, Lund University,
P.O. Box 124, S-221 00 Lund, Sweden. E-mail: ola.wendt@chem.lu.se

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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 $\frac{1}{2}$ eq. of H$_2$O 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. 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, and also to play an important part in several biological systems. 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, in order to prevent formation of species with higher nuclearity such as bridged Ni(II)–(OH)–Ni(II) or doubly bridged Ni(II)(OH)$_2$Ni(II) complexes.

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, but also for synthetic applications in the development of transition metal mediated functionalisations of CO$_2$, e.g. in the synthesis of organic carbonates. The potential utilization of cheap and abundant CO$_2$ as a synthetic C1 source remains a major target for making the chemical industry sustainable.

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.\textsuperscript{11b,12} This process has been subject to biomimetic reactivity studies with Ni(II) pincer complexes, with hydroxycarbonyl species as proposed intermediates.\textsuperscript{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).\textsuperscript{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.\textsuperscript{13}

Whereas the reactivity of group 10 PC\textsubscript{A}P hydroxo and alkoxo complexes towards CO and CO\textsubscript{2} is well documented, \textsuperscript{4d, 5, 6b, 15} the chemistry of their PC\textsubscript{sp3}P counterparts has not been studied. Yet coordination of an sp\textsuperscript{3}-hybridised PCP carbon expectedly gives a higher electron density at a metal centre relative an sp\textsuperscript{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\textsubscript{sp3}OP pincer ligand, affording tridentate chelate (POC\textsubscript{sp3}OP)NiX complexes (X = Cl, Br).\textsuperscript{16} We here report on the synthesis of the analogous hydroxo complex (POC\textsubscript{sp3}OP)NiOH (3) via two alternative pathways. Reaction of 3 with CO or CO\textsubscript{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 \textit{trans}-[NiCl\textsubscript{cis}-1,3-Bis-(di-tert-butylphosphinito)cyclohexane] (1) was synthesized according to known procedures.\textsuperscript{16} All other chemicals were purchased from commercial suppliers and used as received. \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{31}P NMR experiments were recorded on a Varian Unity INOVA 500 spectrometer, operating at 499.76 MHz (\textsuperscript{1}H). For \textsuperscript{1}H and \textsuperscript{13}C NMR spectra, the residual solvent peak was used as an internal reference. \textsuperscript{31}P NMR spectra were referenced externally using 85\% H\textsubscript{3}PO\textsubscript{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. The data were extracted and integrated using CrysAlis RED. The structure was solved by direct methods and refined by full-matrix least-squares calculations on \( F^2 \) using SHELXTL5.1. 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\(_2\)O and evaporation of the solvent afforded 2 as a brick red, microcrystalline solid. Yield: 32.3 mg (77%). \(^1\)H NMR (C\(_6\)D\(_6\)): \( δ \) 3.42 (dt, \( J = 3.5 \) Hz, \( J = 10.5 \) Hz, CH\(_2\)CHO, 2 H), 1.85 (t, \( J = 11.0 \) Hz, HC–Ni, 1 H), 1.77–1.72 (m, CH\(_2\)CH\(_2\)CHO, 2 H), 1.36 (vt, \( J = 13.5 \) Hz, tBu, 36 H), 1.37–1.35 (m, CH\(_2\)CH\(_2\)CH\(_2\) 1 H), 0.92–0.79 (m, CH\(_2\)CH\(_2\)CHO, 2 H and CH\(_2\)CH\(_2\)CH\(_2\) 1 H). \(^1^3\)C\([\text{H}]\) NMR (C\(_6\)D\(_6\)): \( δ \) 87.6 (vt, \( J_{\text{PC}} = 14.3 \) Hz, CH\(_2\)CHO, 2 C), 54.1 (t, \( J_{\text{PC}} = 14 \) Hz, HC–Ni, 1 C), 39.4 (vt, \( J_{\text{PC}} = 11.3 \) Hz, C(CH\(_3\))\(_2\), 2 C), 37.8 (vt, \( J_{\text{PC}} = 17.3 \) Hz, C(CH\(_2\))\(_3\), 2 C), 33.4 (vt, \( J_{\text{PC}} = 11.6 \) Hz, CH\(_2\)CH\(_2\)CHO, 2 C), 27.8 (vt, \( J_{\text{PC}} = 6.7 \) Hz, C(CH\(_2\))\(_3\), 6 C), 27.5 (vt, \( J_{\text{PC}} = 6.3 \) Hz, C(CH\(_2\))\(_3\), 6 C), 21.3 (s, CH\(_2\)CH\(_2\)CH\(_2\) 1C). \(^31^\text{P}[\text{H}]\) NMR (C\(_6\)D\(_6\)): 180.3 \( δ \) (s). IR (ATR): \( ν_{\text{as}}(\text{NO}) = 1465 \) cm\(^{-1}\), \( ν_{\text{s}}(\text{NO}) = 1287 \) cm\(^{-1}\), \( ν(\text{NO}) = 1021 \) cm\(^{-1}\). Anal. Calcd for C\(_{22}\)H\(_4\)NNiO\(_3\)P\(_2\) (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\(_4\)D\(_6\)): \( δ \) 3.52–3.46 (m, CH\(_2\)CHO, 2 H), 1.96–1.93 (m, CH\(_2\)CH\(_2\)CHO, 2 H), 1.56 (t, \( J_{\text{PH}} =
11.5, HC-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, CH₂CH₂CH₂, 1 H), 1.03-0.93 (m, CH₂CH₂CHO, 2 H and CH₂CH₂CH₂, 1 H), -2.71 (t, J₁H = 6.0, Ni-OH, 1 H). ¹³C¹H NMR (C₆D₆): δ 87.8 (vt, JPC = 17 Hz, CH₂CHO, 2 C), 54.6 (t, JPC = 16 Hz, HC-Ni, 1 C), 39.3 (vt, JPC = 10 Hz, C(CH₃)ₓ, 2 C), 37.3 (vt, JPC = 16 Hz, C(CH₃)ₓ, 2 C), 33.7 (vt, JPC = 12 Hz, CH₂CH₂CHO, 2 C), 28.4 (vt, JPC = 7.2 Hz, C(CH₃)ₓ, 6 C), 28.0 (vt, JPC = 4.4 Hz, C(CH₃)ₓ, 6 C), 22.1 (s, CH₂CH₂CH₂, 1C). ³¹P¹H NMR (C₆D₆): 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 C₆D₆ (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 (C₆D₆): δ 9.08 (s, Ni-COOH, 1H), 3.55-3.50 (m, CH₂CHO, 2 H), 2.07-2.04 (m, CH₂CH₂CHO, 2 H), 1.65 (t, J₁H = 11.5 Hz, HC-Ni, 1H), 1.57-1.52 (m, CH₂CH₂CH₂, 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, CH₂CH₂CHO, 2 H and CH₂CH₂CH₂, 1 H). ¹³C¹H NMR (C₆D₆): δ 227.9 (s, Ni-COOH, 1 C), 85.8 (vt, JPC = 14.2 Hz, CH₂CHO, 2 C), 68.6 (t, JPC = 26.9 Hz, HC-Ni, 1 C), 40.4 (vt, JPC = 15.8 Hz, C(CH₃)ₓ, 2 C), 38.5 (vt, JPC = 20.7 Hz, C(CH₃)ₓ, 2 C), 33.9 (vt, JPC = 12.1 Hz, CH₂CH₂CHO, 2 C), 28.6 (vt, JPC = 5.5 Hz, C(CH₃)ₓ, 6 C), 28.3 (vt, JPC = 5.3 Hz, C(CH₃)ₓ, 6 C), 22.4 (s, CH₂CH₂CH₂, 1C). ³¹P¹H NMR (C₆D₆): δ 193.4 (s).

**Reaction of 3 with CO₂.** 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)Ni₂(µ-CO₂)] (6).** A degassed hexane solution (7 mL) of 3 (35 mg, 0.073 mmol) was treated with 1 atm CO₂ 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 C₆D₆ under 4 atm CO₂ gave 5 as the predominant species in solution within 3h, and full conversion of 3. Removal of the C₆D₆ 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 (C₆D₆): δ 12.4 (br s, Ni-OC(O)OH, 1H), 3.47-3.42 (m, CH₂CHO, 2 H), 1.81-1.77 (m, CH₂CH₂CHO, 2 H), 1.75 (t, J₁H = 11.0 Hz, HC-Ni, 1H), 1.48 (vt, J = 12.5 Hz, tBu, 36 H), 1.37-1.33 (m, CH₂CH₂CH₂, 1H), 0.93-0.87 (m, CH₂CH₂CHO, 2 H
and CH₂CH₂CH₂, 1 H). ¹³C[¹H] NMR (C₆D₆): δ 161.50 (br s, Ni–OCOOH, 1 C), 87.50 (vt, Jₑᵥ = 15.5 Hz, CH₂CHO, 2 C), 53.54 (t, Jₑᵥ = 29.4 Hz, HC–Ni, 1 C), 39.48 (vt, Jₑᵥ = 10.9 Hz, C(CH₃)₃, 2 C), 37.72 (vt, Jₑᵥ = 16.3 Hz, C(CH₃)₂, 2 C), 33.48 (vt, Jₑᵥ = 10.9 Hz, CH₂CH₂CHO, 2 C), 28.10 (vt, Jₑᵥ = 6.5 Hz, C(CH₃)₆, 6 C), 27.79 (vt, Jₑᵥ = 6.2 Hz, C(CH₃)₃, 6 C), 21.55 (s, CH₂CH₂CH₂, 1 C). ³¹P[¹H] NMR (C₆D₆): δ 178.2 (s). IR (ATR): νₑᵥ(CO₂) = 1615 cm⁻¹, νₑᵥ(CO₂) = 1369 cm⁻¹.

Complex 6: ¹H NMR (C₆D₆): δ 3.50-3.45 (m, CH₂CHO, 4 H); 1.93-1.89 (m, CH₂CH₂CHO, 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 (HC–Ni, 2H); 1.36-1.32 (m, CH₂CH₂CH₂, 2H); 1.02-0.90 (m, CH₂CH₂CHO, 4 H and CH₂CH₂CH₂, 2 H). ¹³C[¹H] NMR (C₆D₆): δ 161.50 (br s, μ-CO₂, 1 C), 85.79 (vt, Jₑᵥ = 13.6 Hz, CH₂CHO, 4 C), 53.5 (t, Jₑᵥ = 27.6 Hz, HC–Ni, 2 C), 39.46 (vt, Jₑᵥ = 9.9 Hz, C(CH₃)₃, 4 C), 37.77 (vt, Jₑᵥ = 15.2 Hz, C(CH₃)₂, 4 C), 33.66 (vt, Jₑᵥ = 11.6 Hz, CH₂CH₂CHO, 4 C), 29.14 (vt, Jₑᵥ = 6.4 Hz, C(CH₃)₆, 12 C), 28.61 (vt, Jₑᵥ = 6.2 Hz, C(CH₃)₃, 12 C), 21.81 (s, CH₂CH₂CH₂, 2 C). ³¹P[¹H] NMR (C₆D₆): δ 176.1 (br s).

Results and discussion

Synthesis of the (POC₃sp³OP)NiOH complex 3 from the chloride 1 was attempted according to the previously reported anion metathesis route used for making similar nickel hydroxide complexes.⁴³,⁶a 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 (PC₃sp³P)Pd pincer complexes,⁶a,²¹ that 1 is readily converted to the corresponding nitrate complex 2 in a reaction with AgNO₃, 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 (POC₃sp³OP)NiH¹⁶ in a reaction with H₂O, 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 ³¹P containing species.

Thus, complex 2 was obtained in good yield upon stirring 1 with AgNO₃ 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)NiONO₂ complex that gave the stable side product (PCP)Ni³⁺(ONO₂)₂ when exceeding a 1:1 ratio between (PCP)NiCl and AgNO₃ (PCP = C₆H₃-2,6-(CH₂PPr₂))₂. The ³¹P 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 ¹H NMR spectrum differs significantly as complex 2 displays a complete coalescence of the two characteristic virtual triplets corresponding to the 36 'Bu-protons. The FTIR data is clearly indicative of a η¹ coordinated nitrate ligand, and the observed bands are in good agreement with those reported by Campora. The ¹H NMR spectrum of 3 displays a triplet resonance corresponding to the hydroxide proton at δ = -2.71 ppm (J_HH = 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.

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. 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 Zargar;\textsuperscript{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](image-url)

**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 C₆D₆ 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 ³¹P NMR spectroscopy, and no formation of any bridged dimeric μ-CO₂-κ²C,O species was indicated under these conditions, as was previously reported by the group of Cámpora through a suggested decarbonylation sequence between two (PCP)NiCOOH complexes (PCP = C₆H₃-2,6-(CH₂PPr₂)₂). Lee and coworkers reported on the same type of dinuclear compounds formed from PNP pincer supported nickel hydroxycarbonyl complex (PNP = N[2-PPr₂-4-Me-C₆H₃]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 = C₆H₃-2,6-(CH₂P'Bu₂)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 CO₂ 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 ¹H NMR spectrum and the carbonyl carbon was also hardly detectable by ¹³C NMR spectroscopy at accessible concentrations.

Scheme 2

A C₆D₆ 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 Lee¹³ (PNP = N[2-PPr₂-4-Me-C₆H₃]₂) and (PC₅ArP)PdCOOH by our group¹⁵ (PC₅ArP = C₆H₃-2,6-(CH₂P'Bu₂)₃). 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 = 2.1797(13), Ni1–C7 = 1.999(4), C7–O3 = 1.297(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 CO₂ 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 = C₆H₅-2,6-
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 $\{(\text{PCP})\text{Ni}\}_2\mu$(CO$_2$) 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 $\alpha$-carbon $^{13}$C resonances are insignificant between 5 and 6. The shift of the $\alpha$-carbon has been observed to be directly related to the $\sigma$-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 $\sigma$-donator CO$_3^{2-}$ relative the less basic HCO$_3^{-}$. Similarly, the $^{31}$P{${}^1$H} 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$_6$D$_6$ solution gave X-ray quality crystals of complex 5, while complex 6 crystallized from C$_6$D$_6$ 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$_6$H$_3$-2,6-(CH$_3$PPr$_2$)$_2$), 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. This indicates
a mix of the lone-electron pairs on the nickel-bound oxygen with the carbonyl $\pi$ bond, giving delocalization of the negative charge resulting from the polarized Ni–O bond. The quality of the crystals of 6 was very poor ($R_{\text{int}} = 0.42$) 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.

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* R = Σ(|Fo| - |Fc|) / Σ|Fo|. ** wR2 = [Σw(|Fo|² - |Fc|²)]² / Σ|Fo|². ** S = [Σw(|Fo|² - |Fc|²)]² / Σ|Fo|² / 2. ** C = Σw(|Fo|² - |Fc|²) / Σ|Fo|² / 2².

Conclusions

In summary, a nickel(II) hydroxo complex (3) supported by a cyclohexyl based POC₃sp(OP pincer ligand (POC₃sp(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 CO₂ has been studied; reaction with CO generates the corresponding hydrocarbonyl complex, (POC₂spOP)NiCOOH (4) that is seemingly stable towards dimerisation or β elimination at room temperature and atmospheric pressure. Reacting 3 with CO₂ affords a mononuclear bicarbonate species (5) that under reduced pressure loses ½ eq. of H₂O and CO₂ 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†

Alexey V. Polukeev, Roman Gritcenko, Klara J. Jonasson and Ola. F. Wendt*

Centre for Analysis and Synthesis, Department of Chemistry,
PO Box 124, 22100 Lund, Sweden.
Ph: +46-46-2228153. E-mail: ola.wendt@chem.lu.se

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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-butylphosphinato)-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).](image)

2. Experimental

2.1. General experimental procedures

All manipulations were carried out under an Ar or \( \text{N}_2 \) 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 \(^1\)H and \(^{13}\)C measurements, and to external 85\% H\(_3\)PO\(_4\) 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 Ph₃P (10.59 g, 40.4 mmol) and imidazole (2.64 g, 38.8 mmol) in CH₂Cl₂ (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 C₈H₁₄I₂: C, 26.40; H, 3.88. Found C, 26.41, H, 3.89. ¹H NMR (CDCl₃): δ 3.12 (d, J = 6.2 Hz, 4H, -CH₂I), 2.03 (d of m, J = 12.6 Hz, 1H, 1-C₄H₄), 1.86-1.78 (m, 3H, 3-CH₃H₈ + 4-CH₄H₈), 1.52-1.44 (m, 2 H, -CH-), 1.34 (m, 1H, 4-CH₃H₈), 0.89 (m 2H, 3-CH₃H₈), 0.70 (apparent q, J = 11.9 Hz, 1H, 1-CH₃H₈). ¹³C NMR (CDCl₃): δ 40.16 (1-CH₃), 39.73 (-CH-), 33.08 (3-CH₃), 25.48 (4-CH₂), 15.18 (-CH₂I).

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 Et₂O (100 mL) a solution of '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. 'Bu₂PCl (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$_2$Cl$_2$/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 '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 'H NMR spectroscopy.
2.6. Acceptorless dehydrogenation of cyclooctane by complex 4

Complex 4 (0.0073 g, 0.0116 mmol) and tBuONa (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 tBuONa (0.0012 g, 0.0125 mmol, 1.5 eq) were placed into a Straus flask, and the specified amounts of NEt₃ (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 NEt₃, N,N-diethylvinylamine, N,N-divinylethylamine, TBE and TBA could be detected by ¹H 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[(trifluoromethyl)sulfonyloxy)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, ¹H and ³¹P[¹H] NMR spectra indicate that this protocol always gives trace
impurities in the resulting samples of 4, and thus we wanted to develop an over-
all more robust and convenient route to 4.

![Scheme 1](image.png)

**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 BH₃
in THF, according to the previously published procedure. [19] The hydroxyl
groups were then iodinated by reaction with PPh₃/I₂/imidazole in anhydrous
CH₂Cl₂ [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 HPtBu₂ failed, but lithiation of 2 followed by
reaction with CIPtBu₂ 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,
ext 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-(Bu₂PO)₂C₆H₃]IrHCl (6),[8] since most literature data refers to this work. '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 N₂ [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 ³¹P NMR-spectroscopy after activation with 'BuONa indicate
complete decomposition of the catalytically active species after several hours at 150 ºC. 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-(Bu₂PCH₂)₂C₆H₃]IrH₂ (7).[22] Probably the decomposition of 4 is quite fast already at the COA boiling point of 149 ºC. [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 NEt₃/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 NEt₃/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 NEt₃/TBE/cat ratio. [24] For a more direct comparison with literature data, we carried out the dehydrogenation using 10/20/1 NEt₃/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 NEt₃. When COA was used as a solvent, competition between dehydrogenation of COA and NEt₃ 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.

\[
\text{Scheme 4. Transfer dehydrogenation of triethylamine by complex 4.}
\]
Table 1. Catalytic dehydrogenation using different substrates and iridium catalysts.

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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<sub>4</sub> (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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References


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

Klara J. Jonasson, Ola F. Wendt*

Centre for Analysis and Synthesis, Department of Chemistry, Lund University,
P.O. Box 124, S-221 00 Lund, Sweden. E-mail: ola.wendt@chem.lu.se

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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⋅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'Bu. Complex (4) was also synthesised in a more straightforward 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-[IrHII{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 amineboranes.\(^9\)-\(^10\) 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.\(^17\) PC 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$_3$PO$_4$ 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 Mikroanalytisches 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 $\omega$-scans and MoK$\alpha$ ($\lambda = 0.71073$ 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$_6$D$_6$): $\delta$ 2.32-2.27 (m, PC$_2$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$_2$H$_2$CH, 2 H), 1.48-1.42 (m, Cy, 1 H), 1.32 (vt, $J_{PH} = 13.0$ Hz, 'Bu, 18 H), 1.26 (vt, $J_{PH} = 13.0$ Hz, 'Bu, 18 H), 1.19 (t, $J = 11.0$, HC–Ir, 1 H), 0.95 (dq, $J = 3.5$ Hz, $J = 12.5$ Hz, Cy, 2 H). $^{13}$C($^1$H)-NMR (C$_6$D$_6$): $\delta$ 194.8 (vt, $J_{PC} = 15$ Hz, Ir–CO, 1 C), 71.6 (vt, $J_{PC} = 7.2$ Hz, HC–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$_2$CH$_2$CH$_2$, 1 C). $^{31}$P($^1$H)-NMR (C$_6$D$_6$): $\delta$ 81.8 (s). IR (NaCl/nujol) $\nu_{CO} = 1917$ 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$_6$D$_6$): $\delta$ 1.89-1.84 (m, PCH$_2$CH, 2 H), 1.82-1.77 (br m, Cy, 2 H + 1 H), 1.61 (t, $J = 10.5$ Hz, HC–Ir, 1 H), 1.51-1.45 (br m, PCH$_2$CH, 2 H + Cy, 1 H), 1.41 (vt, $J_{PH} = 13.0$ Hz, 'Bu, 18 H), 1.37
(vt, $I_{PH} = 13.0$ Hz, '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, $I_{HH} = 1.5$ Hz, $I_{PH} = 17.0$ Hz, Ir–H, 1 H). $^{13}$C($^1$H)-NMR (C$_6$D$_{18}$): δ 226.7 (s, Ir–CO, 1C), 51.5 (vt, $I_{PC} = 11$ Hz, CH–Ir, 1 C), 37.8 (vt, $I_{PC} = 27$ Hz, PCH$_2$, 2 C), 36.8 (vt, $I_{PC} = 21$ Hz, Cy, 2 C), 36.2 (vt, $I_{PC} = 23$ Hz, C(CH$_3$)$_3$, 2 C), 33.9 (vt, $I_{PC} = 17$ Hz, C(CH$_3$)$_3$, 2 C), 32.7 (s, Cy, 2 C), 30.8, (vt, $I_{PC} = 3.2$ Hz, C(CH$_3$)$_3$, 6 C), 30.6 (vt, $I_{PC} = 3.0$ Hz, C(CH$_3$)$_3$, 6 C), 27.8, (s, CH$_2$CH$_2$CH$_2$, 1 C). $^{31}$P($^1$H)-NMR (C$_6$D$_{18}$): δ 50.2 (s). IR (ATR) ν$_{CO}$ = 1977 cm$^{-1}$. Anal. Calcd for C$_{25}$H$_{51}$ClIrOP$_2$ (657.29): C, 46.68; 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$_3$·H$_2$O (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$_6$D$_{18}$): δ 2.61-2.52 (m, PCH$_2$CH, 2 H), 2.09-2.01 (m, PCH$_2$CH, 2 H + Cy, 2 H), 1.86-1.81 (m, Cy, 1 H), 1.55 (vt, $I_{PH} = 13.5$ Hz, 'Bu, 18 H), 1.53-1.51 (m, Cy, 1 H) 1.42 (t, $J = 11.0$ Hz, HC–Ir, 1 H), 1.15 (tt, $J = 4.0$ Hz, $J = 14.0$ Hz, Cy, 2 H), 1.06 (vt, $I_{PH} = 12.5$ Hz, 'Bu, 18 H), 0.92 (dq, $J = 3.5$ Hz, $J = 13.0$ Hz, Cy, 2 H), -18.7 (t, $I_{PH} = 13.0$ Hz, Ir–H, 1 H). $^{31}$P($^1$H)-NMR (C$_6$D$_{18}$): δ 56.4 (d, $I_{PH} = 13.0$ Hz). IR (ATR) ν$_{CO}$ = 1989 cm$^{-1}$. Anal. Calcd for C$_{25}$H$_{51}$ClIrOP$_2$ (657.29): C, 46.68; H, 7.82. Found: C, 45.59; H, 7.79.

**Preparation of trans-[IrMe\{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$_6$D$_{18}$): δ 2.15 (t, $J = 5.5$ Hz, Ir–CH$_3$, 3H), 2.06-2.03 (m, Cy, 2 H) 1.95 (t, $J = 10.5$ Hz, HC–Ir, 1 H), 1.87-1.82 (m, PCH$_2$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, $I_{PH} = 12.0$ Hz, 'Bu, 18 H), 1.21 (vt, $I_{PH} = 12.5$ Hz, 'Bu, 18 H), 1.19-1.13 (m, PCH$_2$CH, 2 H), 1.07-0.99 (m, Cy, 2 H). $^{13}$C($^1$H)-NMR (C$_6$D$_{18}$): δ 52.5 (br s, CH–Ir, 1 C), 46.6 (vt, $I_{PC} = 14.6$ Hz, PCH$_2$CH, 2 C), 36.6 (vt, $I_{PC} = 20.6$ Hz, C(CH$_3$)$_3$, 2 C), 36.1 (vt, $I_{PC} = 16.6$ Hz, C(CH$_3$)$_3$, 2 C), 34.3 (vt, $I_{PC} = 23.4$ Hz, CH$_2$CH$_2$CH$_2$, 2 C), 33.9 (vt, $I_{PC} = 18.5$ Hz, PCH$_2$, 2 C), 30.09 (vt, $I_{PC} = 3.0$ Hz, C(CH$_3$)$_3$, 6 C), 30.05 (vt, $I_{PC} = 4.3$ Hz, C(CH$_3$)$_3$, 6 C), 27.0 (s, CH$_2$CH$_2$CH$_2$, 1 C), -27.8 (vt, $I_{PC} = 9.9$ Hz, Ir–CH$_3$, 1 C). $^{31}$P($^1$H)-NMR (C$_6$D$_{18}$): δ 32.39 (s).
Preparation of trans-[IrH{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\(_{6}\)D\(_{6}\)): \(\delta\) 1.69-1.57 (m, PC\(_{2}\)H\(_{2}\)CH, 4 H) 1.47 (dvt, \(J_{PH} = 13.0\) Hz, \(J_{HH} = 2\) Hz, tBu, 18 H), 1.36 (dvt, \(J_{PH} = 12.5\) Hz, \(J_{HH} = 2\) Hz, tBu, 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\(_{6}\)D\(_{6}\)): \(\delta\) 51.2 (vt, \(J_{PC} = 12.8\) Hz PCH\(_{2}\)CH, 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(CH\(_{3}\))\(_{3}\), 6 C), 31.0 (vt, \(J_{PC} = 4.0\) Hz, C(CH\(_{3}\))\(_{3}\), 6 C), 26.5 (s, CH\(_{2}\)CH\(_{2}\)CH\(_{2}\), 1 C). \(^{31}P\){\(^{1}H\)}-NMR (C\(_{6}\)D\(_{6}\)): \(\delta\) 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 KOtBu (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, and the sp³-hybridisation instead of an sp²-hybridisation has a surprisingly small effect on the π-back donation to CO; there is no substantial change of the Ir–CO or C–O distances (PC₆₃P 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 C₆D₆ solution of 5a with an excess of KO'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 IrCl₃·H₂O 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(sp³)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 ($\delta = 50.2$ ppm and 56.4 ppm respectively in C$_6$D$_6$) and the $^1$H-NMR hydride shifts ($\delta = -8.59$ ppm and -18.7 ppm respectively in C$_6$D$_6$), 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 $\nu_{CO}$ 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 ($\nu_{CO} = 1985$ cm$^{-1}$, KBr), and again there is thus no observable trend in different $\pi$-back donation trans to a C(sp$^3$)-carbon, a C(sp$^3$)-carbon and a hydride ligand. As expected the $\nu_{CO}$ 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](image)

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 $\alpha$-hydrogen, as illustrated in Figure 4. In case of 5a, the hydride and $\alpha$-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 $^3$$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 metallaion involving a concerted oxidative addition process via a C–H $\sigma$-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$^3$)P$\text{IrH(CO))Cl}$ complex in the presence of water and a PC(sp$^3$)P$\text{Ir(CO)(Cl)}_2$ 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 CaH₂, 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(15), P1–Ir1–C1 = 164.46(16), 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–Ir1–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 ^1H-NMR spectrum and a triplet at -27.8 ppm in the ^13C-
NMR spectrum corresponding to the \(\text{Ir-CH}_3\) moiety, in analogy with the previously reported aromatic counterpart.\textsuperscript{34} The presence of a characteristic broadened triplet at 1.95 ppm corresponding to the \(\alpha\)-proton of the cyclohexyl ring is indicative of a PCP-coordinated structure. The molecular structure of compound \textbf{6} is given in Figure 5, along with the crystallographic data for \textbf{6} and \textbf{7} in Table 2. Complex \textbf{6} adopts a distorted square pyramidal geometry around iridium with the methyl ligand in apical position with an \textit{anti} relationship to the \(\alpha\)-hydrogen.

Upon heating a toluene solution of \textbf{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 \textbf{6} is stable at -28 °C for several weeks. The single product formed was characterized as complex \textbf{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 \(\text{C(sp}^3\text{)--C(sp}^3\text{)}\) bond to give a non-metallated intermediate, which undergoes an oxidative addition of the remaining C–H bond in the previous \(\alpha\)-position of the cyclohexyl backbone. A similar result have been reported by Xu \textit{et al.}\textsuperscript{35} upon the complexation of an acyclic \(\text{POC(sp}^3\text{)OP}\) ligand with \(\text{Fe(Me)}_2(\text{PMe}_3)_4\), but the examples of \(\text{C(sp}^3\text{)--C(sp}^3\text{)}\) reductive eliminations at iridium in the literature are limited.\textsuperscript{34} The group of van Koten has reported on a reductive elimination and \(\text{C(sp}^3\text{)--C(sp}^3\text{)}\) bond formation from a \(\text{NC(sp}^3\text{)N}\) platinum(II) pincer complex upon treatment with methyl, alkyl or benzyl halides, generating an arenium platinum(II) complex.\textsuperscript{36} Also, the group of Milstein has reported on the reverse process, where a \(\text{C(sp}^3\text{)--C(sp}^3\text{)}\) bond cleavage occurs upon complexation of a tolyl-based ligand with rhodium,\textsuperscript{37} iridium,\textsuperscript{38} platinum\textsuperscript{39} and ruthenium,\textsuperscript{40} with a net transfer of a methylene moiety.\textsuperscript{41} The unambiguous presence of a hydride shift at -28.4 ppm in the \(\text{^1H-NMR}\) spectrum of \textbf{7}, perfectly integrating 1:3 with the methyl protons at -1.02 ppm, argues for the suggested structure rather than a non-metallated \(\eta^2\ \text{C–C}\) agostic species, as previously observed by Frech and Milstein for a cationic rhodium(I) complex with a naphtyl-based PCP ligand backbone.\textsuperscript{32} The quaternary \(\alpha\)-carbon was not visualized in the \(\text{^{13C-NMR}}\) 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.\textsuperscript{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

<table>
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<th></th>
<th>4</th>
<th>5a</th>
<th>5b</th>
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<tbody>
<tr>
<td>formula</td>
<td>C_{25}H_{49}IrOP&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C_{25}H_{50}ClIrOP&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C_{25}H_{50}ClIrOP&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>Fw</td>
<td>619.78</td>
<td>656.24</td>
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<tr>
<td>space group</td>
<td>Pbca</td>
<td>P2&lt;sub&gt;1&lt;/sub&gt;/n</td>
<td>Pbca</td>
</tr>
<tr>
<td>a/Å</td>
<td>12.4581(9)</td>
<td>12.5453(2)</td>
<td>12.3770(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>15.3030(9)</td>
<td>15.2101(3)</td>
<td>15.3452(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>29.2263(16)</td>
<td>15.5649(3)</td>
<td>28.8663(4)</td>
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<tr>
<td>α/deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>β/deg</td>
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<td>93.996(2)</td>
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<td>γ/deg</td>
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<td>90</td>
<td>90</td>
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<td>V/Å³</td>
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</tr>
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<td>7422</td>
<td>9768</td>
</tr>
<tr>
<td>R(I) (I&gt;2σ(I))&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.0520</td>
<td>0.0332</td>
<td>0.0389</td>
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<td>wR2(F&lt;sup&gt;2&lt;/sup&gt;) (all data)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.1167</td>
<td>0.1030</td>
<td>0.1221</td>
</tr>
<tr>
<td>S&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.224</td>
<td>1.425</td>
<td>1.124</td>
</tr>
<tr>
<td>R&lt;sub&gt;int&lt;/sub&gt;</td>
<td>0.126</td>
<td>0.0594</td>
<td>0.0317</td>
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</tbody>
</table>

<sup>a</sup> R = Σ(|F<sub>o</sub>| - |F<sub>c</sub>|) / Σ|F<sub>c</sub>|. <sup>b</sup> wR2 = [Σw(|F<sub>o</sub>| - |F<sub>c</sub>|)<sup>2</sup> / Σ|F<sub>c</sub>|<sup>2</sup>)<sup>1/2</sup>. <sup>c</sup> S = [Σw(|F<sub>o</sub>| - |F<sub>c</sub>|)<sup>2</sup> / Σ|F<sub>c</sub>|<sup>2</sup>)<sup>1/2</sup>.

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 <sup>1</sup>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.\textsuperscript{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

<table>
<thead>
<tr>
<th></th>
<th>6</th>
<th>7</th>
</tr>
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<tr>
<td></td>
<td>( \text{C}<em>{25}\text{H}</em>{52}\text{IrP}_{2}\text{I} )</td>
<td>( \text{C}<em>{25}\text{H}</em>{52}\text{IrP}_{2}\text{I} )</td>
</tr>
<tr>
<td>Fw</td>
<td>733.74</td>
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<td>space group</td>
<td>PbcA</td>
<td>P2₁/c</td>
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<tr>
<td>( a/\text{Å} )</td>
<td>17.1711(3)</td>
<td>12.4916(7)</td>
</tr>
<tr>
<td>( b/\text{Å} )</td>
<td>17.9192(3)</td>
<td>16.1841(8)</td>
</tr>
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<td>( c/\text{Å} )</td>
<td>18.9036(4)</td>
<td>15.2699(9)</td>
</tr>
<tr>
<td>( a/\text{deg} )</td>
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<td>90</td>
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<tr>
<td>( \beta/\text{deg} )</td>
<td>90</td>
<td>103.920(6)</td>
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<td>( \gamma/\text{deg} )</td>
<td>90</td>
<td>90</td>
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<tr>
<td>( V/\text{Å}^3 )</td>
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<td>2996.4(3)</td>
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<td>( Z )</td>
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<td>( D_{\text{calc}}/\text{g cm}^{-3} )</td>
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<td>( \mu/\text{mm}^{-1} )</td>
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<td>2.52-28.88</td>
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<td>no. of unique reflns</td>
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<td>7169</td>
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<td>( R(F) ) (I&gt;2( \sigma(I) ))^a</td>
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<tr>
<td>( wR2(F^2) ) (all data)^b</td>
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<tr>
<td>( S^c )</td>
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<tr>
<td>( R_{\text{int}} )</td>
<td>0.1468</td>
<td>0.0367</td>
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\(^a R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| \cdot \ ^b wR^2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma F^2)^{1/2} \cdot \ ^c S = (\Sigma w(|F_o| - |F_c|)^2/\Sigma F^2)^{1/2}.\)

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 \( \pi \)-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.
References

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[34] Xu, G. Q.; Sun, H. J.; Li, X. Y. Organometallics 2009, 28, 6090.
Bis[μ-cis,1,3-bis[(di-tert-butylphosphanyloxy)cyclohexane-κ²P,P']bis[carbonylnickel(0)]] including an unknown solvent molecule

Klara J. Jonasson and Ola F. Wendt*

Centre for Analysis and Synthesis, Department of Chemistry, Lund University, PO Box 124, S-221 00 Lund, Sweden
Correspondence e-mail: ola.wendt@chem.lu.se

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

The title compound, [Ni₂(C₂₂H₄₆O₂P₂)(CO)₂] including an unknown solvent molecule, is located about a centre of inversion with the Ni⁰ 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)]. Its formula mass and unit-cell characteristics were not taken into account during refinement.

Related literature

For similar 16-atom macrocyclic dimers with Ni⁰, see: Johnson & Wendt (2011); Castonguay et al. (2008); Pandarus et al. (2008). For 16-atom macrocyclic dimers of Pd⁰ and Pt⁰ with cis-1,3-bis-(di-alkylphosphino)cyclohexane ligands, see: Sjövall et al. (2001) and Olsson et al. (2007), respectively. For other examples of Ni⁰ 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 Ni⁰ hydride complex to form a tetrahedral Ni⁰ dicarbonyl species (PNP = [N(2-PR₂-C₆H₃)₂]²⁻), see: Liang et al. (2012).

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

metal-organic compounds
supplementary materials

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 NiII 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 NiII 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 C₆D₆ and attempts to obtain ¹H- and ¹³C-NMR spectra has been unsatisfactory. Dissolving the red crystals of the title compound in CDCl₃ results in a yellow/green solution and decomposition to several compounds, as indicated by ³¹P-NMR spectroscopy; none was successfully isolated or characterized.

3. Supramolecular features

4. Database survey

5. Synthesis and crystallization

A C₆D₆ 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}-κ²-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%). ³¹P{¹H} NMR: (202.3 MHz, C₆D₆) δ: 177.8 (s). Anal. Calcd for C₄₆H₉₂Ni₂O₆P₄ (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 Å³ to be 140 which is in reasonable agreement with a total number of four benzene molecules in
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.

\[
\text{Bis(μ-cis-1,3-bis[(di-tert-butylphosphanyl)oxy)cyclohexane-κ²P:P]bis[carbonylnickel(0)]}
\]

Crystal data

\[\text{[Ni}_2\text{C}_{22}\text{H}_{46}\text{O}_2\text{P}_2\text{(CO)}_2]}\]

\[M_r = 982.50\]

Monoclinic, \(C2/c\)

Hall symbol: \(-C\ 2\ yc\)

\[a = 31.7851 (9) \text{ Å}\]

\[b = 8.5449 (2) \text{ Å}\]

\[c = 21.3311 (5) \text{ Å}\]

\[β = 90.995 (2)°\]

\[V = 5792.7 (3) \text{ Å}^3\]

\[Z = 4\]

\[F(000) = 2128\]

\[D_x = 1.127 \text{ Mg m}^{-3}\]

Mo Ka radiation, \(λ = 0.71073 \text{ Å}\)

Cell parameters from 6436 reflections

\[θ = 2.5–29.1°\]

\[μ = 0.80 \text{ mm}^{-1}\]

\[T = 120 \text{ K}\]

Plates, red

\[0.2 \times 0.15 \times 0.05 \text{ mm}\]

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

\(\text{CrysAlis PRO}; \text{Agilent, 2011}\)

\[T_{\text{min}} = 0.883, T_{\text{max}} = 1.000\]

27324 measured reflections

6958 independent reflections

4948 reflections with \(I > 2σ(I)\)

\(R_{\text{int}} = 0.073\)

\[θ_{\text{max}} = 29.1°, θ_{\text{min}} = 2.5°\]

\[h = -42→35\]

\[k = -11→11\]

\[l = -26→26\]