

CrossMark
click for updatesCite this: *Dalton Trans.*, 2016, **45**,
15762Received 31st May 2016,
Accepted 19th July 2016
DOI: 10.1039/c6dt02184k
www.rsc.org/daltonMetal–ligand cooperation at tethered π -ligands

Dide G. A. Verhoeven and Marc-Etienne Moret*

Metal–ligand cooperativity in homogeneous catalysis is emerging as a powerful tool for the design of efficient transition-metal catalysts. This perspective highlights recent advances in the use of neutral π -coordinating ligands, tethered to a transition-metal center by other donor ligands, as cooperative reaction centers. The state-of-the-art organometallic complexes, including π -coordinating ligands originating from C=C, C=E (E = O, N) and boron containing moieties, are described here, with special attention on their specific reactivity. Geometric and electronic aspects of ligand design and their influence on the coordination mode and reactivity of the π -system are discussed.

1. Introduction

Metal–ligand cooperativity is a fertile area of investigation for the development of modern homogeneous catalysts.^{1,2} Cooperative ancillary ligands do not only stabilize and tune the coordination environment of a metal center, but also engage in chemical reactions with substrate molecules, opening new reactive pathways. In particular, they are proving useful in controlling the reactivity of base metals in view of substituting widely used precious metals catalysts.^{2,3}

*Organic Chemistry & Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands.
E-mail: M.Moret@uu.nl*

Metal–ligand cooperativity can take a number of forms. First, perhaps the simplest of those is hemilability,^{4,5} *i.e.* reversible dissociation of an electron donor (or acceptor) moiety that allows the coordination environment of the metal to adapt to the steric and electronic requirements of different reaction intermediates along a reaction mechanism. Then, redox-active ligands³ act as electron reservoirs during catalysis due to the presence of low lying empty orbitals and/or high-lying filled orbitals at energies comparable to that of the metal d orbitals. This property has been used to facilitate multi-electron processes at metals that tend to undergo one-electron processes or even at redox inactive metals, maintaining the metals oxidation state throughout the process (Fig. 1).^{1,6–10} Finally, the category of bifunctional ligands broadly encompasses ligands that engage in bond-forming and bond-breaking



Dide G. A. Verhoeven

Dide G. A. Verhoeven was born in 1990 in Utrecht, the Netherlands. She received her bachelor degree at the University of Applied Sciences in Utrecht (HU) with a major in Organic Chemistry in 2011, and her MSc degree at Utrecht University (UU) in the group of Organic Chemistry and Catalysis (OCC) with Prof. R. J. M. Klein Gebbink in 2013. Currently she is performing her PhD research in the OCC group, focusing on π -coordinating ligands with a cooperative functionality in base-metal complexes.



Marc-Etienne Moret

Marc-Etienne Moret obtained an MSc degree in chemistry from the Ecole Polytechnique Fédérale de Lausanne (EPFL) in 2005, and a PhD degree from the Eidgenössische Technische Hochschule Zürich (ETHZ) with Prof. P. Chen in 2009. In 2010, he moved to the California Institute of Technology (Caltech) for postdoctoral research in the group of Prof. J. C. Peters on the activation of N₂ by synthetic iron complexes. In 2012, he was appointed assistant professor in the group of Organic Chemistry and Catalysis at Utrecht University (UU). His research interests revolve around ligand design for small-molecule activation and catalysis using first-row transition metals.

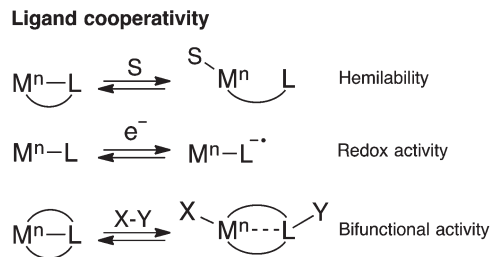
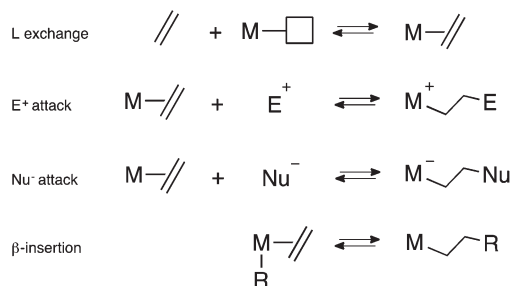


Fig. 1 Ligand cooperativity in substrate activation.

events, working together with the metal in substrate activation *via* functional groups positioned at the ligand. A prominent example of bifunctional ligands are tethered amido ligands (R_2N-M) as found in Noyori-type catalysts for transfer hydrogenation,¹¹ which can accept a proton to become amine ligands ($R_2N(H) \rightarrow M$). This allows dihydrogen to be split heterolytically, leaving a hydride ligand on the metal center, to be subsequently transferred to an unsaturated substrate. Similar mechanisms have been proposed for many of the most efficient catalysts for the hydrogenation of polar bonds, *via* bifunctional H_2 activation involving a variety of internal bases such as deprotonated acidic CH_2 groups^{12–14} or a coordinated cyclopentadienone^{15–20} ligand. Bifunctional substrate activation is of interest for performing bond-making and bond-breaking processes with non-precious metals. In particular, this design principle has recently been used in the development of highly efficient iron-based catalysts for the (de)hydrogenation of polar substrates.^{14,21–25}

The coordination of olefins and other π -ligands to transition metals is a staple of organometallic chemistry. Upon binding, electron density is transferred from the π -bonding orbital to the metal (σ -donation) and, concomitantly, d electrons are partially donated to the π -antibonding orbital. This reduces the bond order and activates the double bond towards both nucleophilic and electrophilic attack. As a result, several elementary steps are available to metal-bound olefins (Scheme 1): (a) ligand exchange where an olefinic substrate binds to the metal *via* a vacant site, (b) electrophilic or (c) a nucleophilic attack while the olefin is already bound to the metal, or (d) concerted processes such as β -insertion (Scheme 1). While these elementary steps are part of the



Scheme 1 Types of olefin activation on a metal center.

mechanism of many catalytic transformations of unsaturated substrates, anchoring such motifs to a metal in a multidentate ligand represents an attractive design principle for cooperative ligand systems.

The relative lability of simple π -ligands requires them to be tethered *via* the ligand backbone, so that dissociation of the ligand will not occur. A stable and robust option are the tridentate pincer type ligands,^{26–37} which gained much attention as robust redox-active or bifunctional ligands. Paralleling the elementary steps outlined in Scheme 1, anchored π -ligands may display a range of cooperative processes. Weakly bound ligands may display hemilability and adaptive coordination. Upon binding of a substrate, the multiple bond can accept either an electrophilic or a nucleophilic fragment, proton (H^+) and hydride (H^-) being prototypical examples. Hence, a small molecule X-Y can split in a heterolytic fashion, adding part of the substrate to the metal center and part to the ligand backbone, and so performing a two-electron bond-breaking process, split over both the ligand and the metal (Fig. 1).

This perspective highlights recent advances in the use of π -coordinating ligands in the design of cooperative ligands. First, pincer ligands incorporating π -coordinating C=C moieties, including aromatic systems, are discussed in section 2. Systems containing an activating borane moiety conjugated with a carbon-based π -system are covered in section 3. Finally, π -interactions of C=E bonds (E = O, NR) are described, including carboxyl and imine based systems (chapter 4).

2. π -Coordinating C=C bonds

2.1 Olefin complexes

A first class of ligands that can be envisioned to act as cooperative ligands in catalysis are olefins. This well known class of ligands has been studied in detail, starting from the first organometallic complex ever reported, *i.e.* Zeise's salt ($K[PtCl_3(C_2H_4)] \cdot H_2O$).³⁸ A metal can bind to an olefinic C=C bond *via* interaction of a d_σ orbital with the ligands π -electrons, forming the σ -bond. Next to this, the metal d_π orbitals can donate electrons to the LUMO of the ligand, the C=C π^* orbital, *via* π -backdonation. Lengthening of the olefinic C=C bond is obtained to which both factors contribute, but the latter effect predominates. The resonance structures that can be drawn for these interactions, shown in Fig. 2a, follow the Dewar–Chatt–Duncanson model; the side-on bound adduct which gives an L-type



Fig. 2 (a) Resonance extremes of an alkene binding to a metal center, left: side-on adduct, right: metallacyclopropane adduct. (b) Addition of a substrate X-Y to this bond, altering the binding mode to form a σ -bond with one of the olefinic carbons.

ligand and the metallacyclopropane adduct which gives an X_2 type ligand.⁷ The difference in the binding mode causes a change in the oxidation state of the metal center, *i.e.* the metal oxidation state remains the same in the L-type bound ligand and it increases by two in the X_2 -type binding, causing ambiguity in the oxidation state of the metal. Throughout this perspective we will generally refer to the lower oxidation state.

Strong bonds are formed with electron rich metal centers, as backdonation will be most efficient.³⁹ This bond can be formed or broken depending on the metal oxidation state, possibly functioning as a hemilabile ligand and directing the system toward bifunctional behavior. One way of activating a small molecule X–Y on such systems is *via* changing the ligands coordination mode, forming a σ -bond with one of the olefinic carbons and adding X to the metal center, together with addition of Y to the second olefinic carbon (Fig. 2b). Internal alkenes and alkynes are classes of ligands that have shown to be suitable as π -coordinating ligands.

The use of phosphine-substituted *trans*-stilbenes as π -coordinating ligands was investigated in detail by several groups. The *ortho*-diphosphine *trans*-stilbene ligand *t*PCH=CHP contains two phosphorus groups to bind the metal center in a bidentate fashion bridged *via* the olefinic ligand backbone which can coordinate to the metal center in a η^2 -fashion (Fig. 3). The incorporation of this ligand in metal complexes was first described by the group of Bennett in 1976.^{40,41} The complexation to rhodium and iridium was described, in which the desired η^2 -coordination of the olefinic backbone was indeed observed, as was shown by NMR analysis and the elongation of the C–C bond in X-ray crystal structure analysis of the ^oTol-Rh–Cl complex. The coordination to group 10 metals Ni, Pd and Pt in the oxidation state of two was shown to result in a different coordination mode, in which a σ -bond was formed with one of the olefinic carbon atoms under elimination of HX.⁴⁰

The Rh and Ir complexes were shown to bind CO and subsequently cleave HCl in a heterolytic fashion over the metal-olefin fragment. This results in the addition of chloride to the metal center and a proton to the ligand backbone, inducing the formation of a C–M σ -bond with one of the olefinic carbon atoms (Scheme 2).⁴¹ The reaction can formally be seen as an electrophilic attack of H^+ at the olefin (Scheme 1). It shows an early example of cooperative behavior of the olefin ligand with the metal center.

A different approach for making a similar ligand was reported by Baratta *et al.* Here, the carbon–carbon double

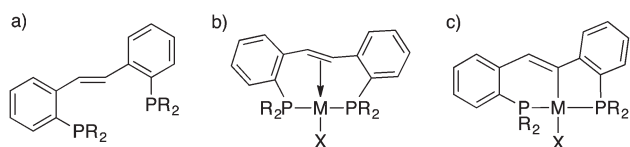
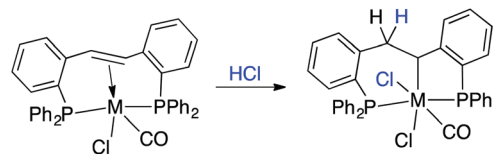


Fig. 3 (a) *trans*-stilbene-type ligand: *t*PCH=CHP, R = *o*-Tol or Ph. (b) η^2 -coordination complexes M = Rh, Ir, R = Ph, X = Cl, Br, I. (c) σ -coordination complexes M = Ni, Pd, Pt, R = Ph, *o*-Tol, X = Cl.

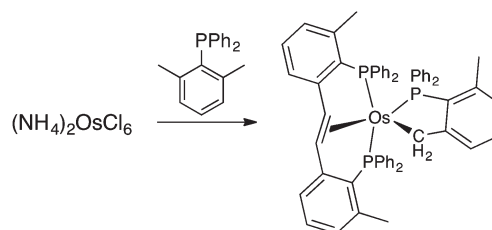


Scheme 2 σ -Complexes after addition of CO and subsequent cooperative addition of HCl, M = Rh, Ir.

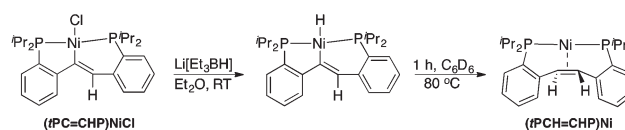
bond was formed from two *o*-methyl groups of two phosphines, as a result of activation of four C–H bonds, leaving an *ortho*-tolyl substituted *trans*-stilbene-type ligand, ^oTol*t*PCH=CHP (Scheme 3). An osmium(II) complex was synthesized of which the X-ray crystal structure showed an elongation of the C=C bond (1.437(4) Å), as a result of η^2 -coordination to Os.⁴²

The use of the *t*PCH=CHP ligand scaffold was extended in the group of Iluc, with the aim of using its backbone as an hydrogen atom reservoir, *i.e.* noncoordination and η^2 -coordination in the neutral form and η^1 -coordination in the vinyl form which could store hydrogen.⁴³ After modification of the ligand by incorporating di-*iso*-propylphenyl ligands, σ -coordination metal complexes were synthesized with Ni, Pd and Pt resulting from C–H activation of the backbone, followed by rapid reductive elimination of HCl. Interestingly, H transfer was observed for the nickel analogue (*t*PC=CHP)NiCl upon addition of Li[Et₃BH], first forming a hydride ligand on the metal center which was then transferred to the backbone resulting in a Ni(0) complex (*t*PCH=CHP)Ni with η^2 -binding of the olefin (Scheme 4).

η^2 -Coordination of the ligand was also established for nickel(II), upon substitution of the olefinic protons for methyl groups, eliminating the possibility of HCl loss. 2 eq. of *t*PCMe=CMeP were mixed with 3 eq. of NiCl₂(dme), resulting



Scheme 3 Synthesis of an Os(II) complex of the ^oTol*t*PCH=CHP ligand from 2,6-xylylPPh₂ and (NH₄)₂OsCl₆ upon activation of four C–H bonds.⁴²



Scheme 4 The (*t*PC=CHP)NiCl complex and the observed H-transfer upon addition of Li[Et₃BH] to (*t*PCH=CHP)Ni.

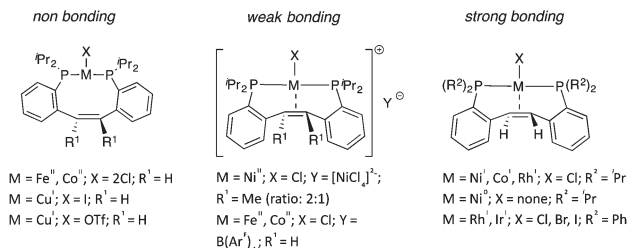
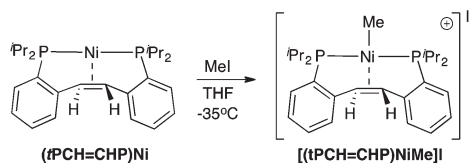


Chart 1 Overview of the non-bonding and η^2 -bonding *trans*-stilbene complexes, arranged by their binding mode.

in a cationic mono chloride species with a NiCl₄²⁻ counteranion, [(*t*PCMe=CMeP)NiCl]₂[NiCl₄]. The complex displays a square-planar geometry around the Ni(II) center and an elongated C–C bond distance for the olefinic backbone (1.398(3) Å vs. 1.330(4) Å).

Synthesis of the more electron-rich analogues Ni(I) *t*PCH=CHP complex, without a counterion, was performed next by a comproportionation reaction using the nickel(II) and nickel(0) precursors NiCl₂(dme) and Ni(cod)₂ (Chart 1). Analysis by single crystal X-ray spectroscopy showed a tetrahedral geometry around the nickel(I) center and an olefinic C–C bond distance of 1.394(3) Å indicative of a η^2 -interaction, without the need to incorporate methyl groups on the ligand backbone. η^2 -Coordination was also observed for the previously described Ni(0) complex (*t*PCH=CHP)Ni, now directly synthesized from the ligand and Ni(cod)₂, which showed activity upon addition of 1 eq. MeI, forming a cationic methyl nickel complex, [(*t*PCH=CHP)NiMe]⁺I⁻ (Scheme 5).⁴³

The hemilability of this system was shown with the Fe and Co analogues.⁴⁴ The Fe(II) and Co(II) complexes (*t*PCH=CHP)MX₂ were synthesized, both containing a non-coordinated olefin moiety, with distances from the metal center to the ligand centroid of 3.596 Å for LFeBr₂ and 3.501 Å for LCoCl₂ (Chart 1). A weak interaction was obtained after halide abstraction of both complexes with Na[Bar^F₄], shown by the slight elongation of the olefinic C–C ligand backbone (ligand: 1.330(4) Å; Fe: 1.332(14) Å; Co: 1.397(6) Å, Chart 1). A strong interaction was obtained after synthesis of the analogous neutral Co(I) complex (*t*PCH=CHP)MCl by reduction of the Co(II) complex with LiAlH₄ (Chart 1). The ¹H NMR spectrum shows a significant upfield shift for the olefinic protons to 2.01 ppm (for *t*PCH=CHP at 8.53 ppm), which is consistent with a bound olefinic moiety with significant π -backdonation. The bond distances were found to be in line with this observation,

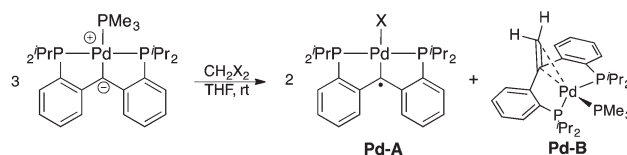


Scheme 5 Reaction of the η^2 -coordinated Ni(0) complex (PCH=CHP)Ni with MeI resulting in [(*t*PCH=CHP)NiMe]⁺.

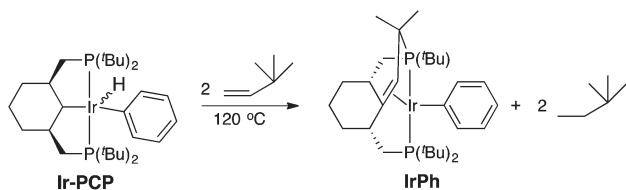
as an elongation was found for the C–C backbone from 1.397(6) Å in the unbound Co(II) complex to 1.442(5) Å in the bound Co(I) complex. The higher degree of backbonding was attributed to the more electron rich Co(I) system compared to the cationic Co(II) species. A similar system was found for the square-planar rhodium analogue (*t*PCH=CHP)RhCl, in which significant π -backdonation of the bound olefin was shown by upfield shifted olefin protons and an elongated C–C distance of 1.432(8) Å (Chart 1). Group 11 metals were explored by the synthesis of the Cu and Ag analogues. Bonding of the olefin was in both cases not observed, although a weak interaction could not be excluded for the Cu(I) complex (*t*PCH=CHP)Cu(OTf): a relatively short distance between the metal and the ligand centroid was observed (2.426 Å), but the olefinic C=C bond lacked elongation (1.294(5) Å). Also the synthesis of cationic divalent complexes, without a halide or triflate ligand, did not lead to interaction with the backbone but afforded linear complexes.⁴⁴

Overall it was observed that the olefinic C=C bond of *t*PCH=CHP elongates upon coordination to a metallic center, predominantly upon binding to an electron rich metal. Bond lengths ranging from 1.40 to 1.44 Å were observed for olefin bound metal complexes, of which the longest C=C length of 1.442(5) Å was observed for (*t*PCH=CHP)CoCl, showing efficient coordination to the electron rich cobalt center. A large upfield shift in both ¹H and ¹³C NMR was observed in all cases for coordination of the olefin backbone, showing the increased electron density on the ligand backbone. *t*PCH=CHP is a promising ligand for the activation of small molecules as it is observed to bind to numerous metal centers and the ligand binding mode shows great versatility.

In a separate study in the group of Iluc toward radical trapping, a Pd complex was obtained with a η^2 -coordinating olefinic moiety in the backbone of the ligand. This complex was synthesized, among others, from a Pd–PCP pincer complex that reacted with CH₂X₂ to obtain Pd-B after CH₂ transfer to the coordinated nucleophilic carbon atom (Scheme 6). This novel type of CH₂ transfer was characterized by X-ray crystal structure analysis, next to other techniques, after direct synthesis of the complex, in which the elongation of the C–C bond was observed probably due to π -backbonding (1.398(3) Å vs. 1.34 Å for a C(sp²)-C(sp²)).⁴⁵ Complex Pd-B could also be independently synthesized by dehydrogenation of the corresponding saturated diphosphine ligand upon coordination to Pd. The 1,1-disubstitution pattern found in this ligand, contrasting with the 1,2-disubstitution pattern in the *trans*-



Scheme 6 Reaction of the Pd–PCP pincer complex with CH₂X₂ to form the expected halide complex Pd-A and unexpected CH₂ transfer product Pd-B.



Scheme 7 The iridium based PCP–pincer complex and its subsequent reaction toward the η^2 -bound complex.

stilbene derivatives, may open up distinct reactive pathways and certainly warrants further investigation.

An iridium-based system in which an internal olefin connected to a cyclohexyl ring binds in a η^2 -fashion was synthesized in the group of Wendt (Scheme 7). The olefin binds in a similar fashion as was found for **Pd-B**, but having both carbon atoms bound to the ligand. The complex was formed from a PCP–pincer complex with a cyclohexyl backbone bound to Ir(III) with a phenyl and a hydride co-ligand. Upon heating in the presence of *tert*-butylethylene as a hydrogen acceptor, the α -carbon of one of the methyl groups of the *t*-butyl substituent was coupled to the Ir-bound carbon atom to form a new coordinated olefin functionality, **IrPh**. This bond-making process was found to be reversible under an H_2 atmosphere at 140 °C.⁴⁶ The formed Ir(I) complex has a distorted square-planar geometry around the metal center, average Ir–C bond lengths of 2.16 and 2.20 Å and a C=C bond length of 1.42 Å, which are all in line with other electron rich Ir–olefin complexes⁴⁷ and the before mentioned distances for the elongation of the olefin backbone.

The olefinic iridium complex was found to be active (Fig. 4) toward the addition of O_2 , performing an oxidative addition

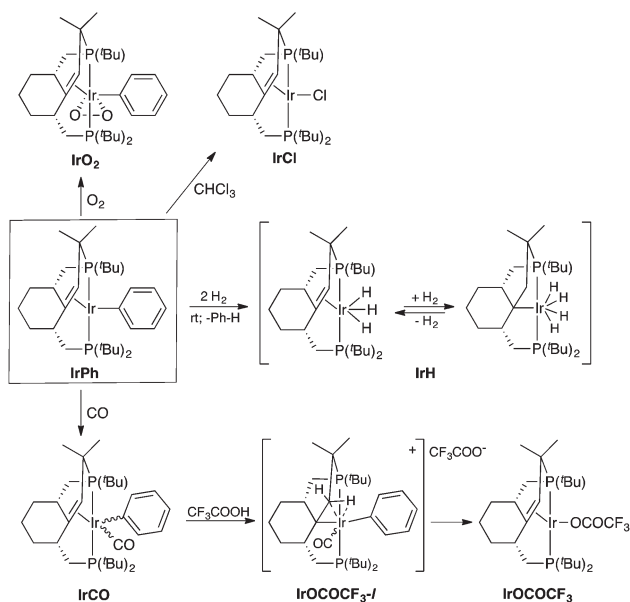


Fig. 4 Reactivity study of the η^2 -bound iridium complex with O_2 , $CHCl_3$, H_2 , and CO with the subsequent reaction of CF_3COOH .

over Ir (**IrO₂**), to $CHCl_3$ by replacing the phenyl ligand for a chloride (**IrCl**), and to CO by addition of a CO molecule to the metal center (**IrCO**). The product of the last reaction was shown to react with trifluoroacetic acid in an interesting way. First the Ir(I)-bound olefinic moiety was protonated, resulting in the unstable Ir(III) alkyl complex **IrOCOCF₃-I**. A similar type of protonation of the backbone was shown before in the example of Bennett with the *trans*-stilbene-type ligands where addition of HCl lead to protonation of the backbone and the addition of Cl to the metal center (*vide supra*). **IrOCOCF₃-I** reacted further cleaving both the phenyl and CO bonds with iridium, forming benzaldehyde together with the proton and forming a bond between Ir and the trifluoroacetate anion (**IrOCOCF₃**).⁴⁸ Further reactivity of **IrPh** was explored with CO_2 and N_2 , but no reaction was observed.⁴⁸ Exposure to H_2 showed the formation of hydride complexes that are in equilibrium, *i.e.* an olefinic complex with three hydride ligands on Ir and a PCP–pincer complex that added another H_2 molecule, split over the metal center and the ligand backbone **IrH**. This addition constitutes an interesting example of cooperative H_2 activation over a metal–olefin reactive center.⁴⁶

Recently, a related PCP–Ir based complex with a terminal olefin was synthesized. Starting from the ligand with a methyl substituted cyclohexyl-group, an equilibrium was observed between an agostic η^2 C–C bond and the non-agostic structure (Fig. 5). Heating of the complex to 80 °C lead to the formation of H_2 *via* β -elimination, and a η^2 -interaction with the olefin. Analysis by X-ray crystallography showed a C=C distance of 1.438(15) Å, which is in line with previously described η^2 -bound complexes.⁴⁹

Besides the previously described systems based on a diphosphine/olefin architecture, related ligands have recently been studied using sulfur as the anchoring ligands, or an alkyne as the π -coordinating ligand.

A family of complexes containing an internal alkene moiety in a thione based ligand was developed in the groups of Han and Jin (SCCS, Fig. 6a).⁵⁰ The metallic center, Ir, Rh or Pd, was bound to the ligand in a bidentate fashion *via* the sulfur atoms and a coordination of the olefinic part was established either directly or after halide abstraction (Fig. 6b and c). The carbon–carbon double bond was found to elongate from 1.325(5) Å to 1.411(5) upon interaction with the metal center in $[(^{Me}SCCS)Ir(Cp^*)]_2Cl$ ($M = Ir, X = Cl, R = Me$, Fig. 6b and 7, C(5)–C(6)).

The coordination of an alkyne ligand can be envisioned in a similar way, *via* π -coordination of the triple bond to the

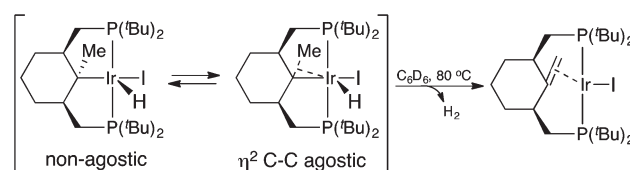


Fig. 5 PCP–Ir complex and its reaction to the η^2 -bound complex.

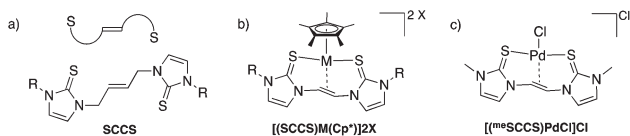


Fig. 6 (a) Schematic (top) and chemical structure (bottom) of SCCS. R = Me, CH=CH₂. (b) General structure of the Ir and Rh complexes. M = Ir, X = Cl, R = Me, CH=CH₂; M = Ir, X = OTf, NO₃, R = Me; M = Rh, X = OTf, R = Me, CH=CH₂. (c) Structure of the Pd complex.

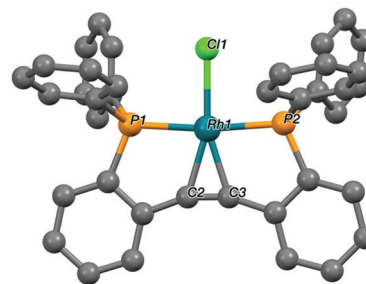


Fig. 9 X-ray crystal structure of Rh(PCCP)Cl.⁵¹

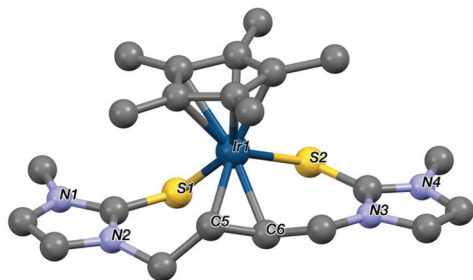


Fig. 7 X-ray crystal structure of [(^meSCCS)Ir(Cp*)]₂Cl.⁵⁰

metal center. Such a system was explored by Ohe *et al.* using *ortho*-diphenylphosphinodiphenylacetylene (PCCP) as the ligand. This ligand contains an internal alkyne moiety connected to two phosphorus groups *via* phenyl rings (Fig. 8a).⁵¹ The reaction of PCCP with an equimolar amount of [RhCl(cod)]₂ (cod = 1,5-cyclooctadiene) resulted in the η²-alkyne-rhodium(i) complex **Rh(PCCP)Cl**, binding PCCP in a pincer-like multidentate fashion (L₃), and a chloride ligand (Fig. 8b). The Rh(i) complex adopts a square planar geometry in which the alkyne carbons lie parallel to the ML₃ plane. When the mixture of PCCP and rhodium precursor was heated

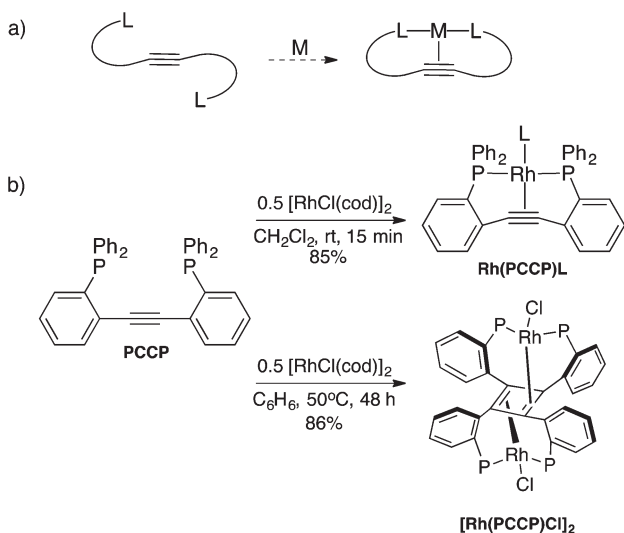


Fig. 8 (a) Schematic representation of the alkyne-M binding. (b) The coordination of PCCP to Rh and the formation of a dimeric-Rh species, L = Cl or L = CO with PF₆⁻; P = PPh₂. Figures adopted from Ohe *et al.*⁵¹

for longer time and at higher temperatures (48 h, 50 °C) a dimeric-rhodium species was synthesized [Rh(PCCP)Cl]₂, and X-ray crystallography showed the formation of a cyclobutadiene ligand generated by the dimerization of the chloride-complex. The cyclobutadiene ring was shown to have two η²-coordinations to the rhodium atoms located on the opposite faces (Fig. 8b). Upon exchanging the chloride ligand of **Rh(PCCP)Cl** for CO, leaving a cationic complex after halide abstraction with NaPF₆, **(Rh(PCCP)CO)** backdonation from Rh to the alkyne ligand was weakened due to the stronger *trans* influence of CO, as shown in the X-ray crystal structure by longer Rh–C bond distances with the acetylenic carbons C(2)–C(3) compared to the chloride bound complex (2.203(7) and 2.199(6) for the Cl vs. 2.107(3) and 2.114(3) for the CO complex, Fig. 9).

Next to olefinic C=C bond coordination, π-coordinating arene groups are also of interest and are discussed next.

2.2 Aromatic complexes

Aromatic ligands containing a six-membered ring can bind to a metal center, forming a η², η⁴ or η⁶-bound complex. Interactions of an aromatic ring with a metal center are in general strong in comparison to hemilabile binding of olefin complexes, and η⁶-arene ligands are often used as robust ancillary ligands. Cooperative activity can nevertheless be observed in such systems if the M–arene interaction is destabilized by strain in the ligand system and/or bulky substituents, or in the case of late transition metals which cannot easily accommodate a 6-electron donor in their valence shell. Heterolytic activation of a small molecule can occur in arene-based systems *via* splitting a molecule, X–Y, over the metal center and the aromatic ring, and so these systems are of interest to explore for their cooperative behavior.

Hemilabile arene coordination was used to prepare two-legged piano stool rhodium complexes that display unusual reversible electrochemical conversion between the oxidation states of I and II, using a 1,4-bis[4-(diphenylphosphino)butyl]-2,3,5,6-tetramethylbenzene (^{ph}PARP) ligand. The ligand was designed to have a long tether between the anchoring phosphine groups close to the metal center and the arene ring, in the form of the butyl chain, to accommodate flexibility of the ligand and its binding mode upon structural or electronic changes of the complex.⁵² A Rh(i) complex was synthesized using ^{ph}PARP and [Rh(THF)₂(COE)₂][PF₆], resulting in a

complex with a rhodium center bound to two phosphorus atoms and an η^6 -coordinated arene ring (Fig. 10a). The complex, $(^{\text{Ph}}\text{PArP})\text{Rh}(\text{I})$, was chemically oxidized using AgPF_6 , resulting in the dicationic $\text{Rh}(\text{II})$ analogue $(^{\text{Ph}}\text{PArP})\text{Rh}(\text{II})$ (Fig. 10a). The arene ring coordinates to the metal center in both oxidation states, but it was shown that the $\text{Rh}(\text{II})$ complex contains generally shorter $\text{Rh}-\text{C}$ bond distances. $(^{\text{Ph}}\text{PArP})\text{Rh}(\text{I})$ showed reactivity toward small molecules, such as CO , acetonitrile and *tert*-butyl isocyanide, in a way that the interaction with the arene ligand was broken upon addition of other ligands (Fig. 10a).⁵³ A tricarbonyl species was formed upon exposure of the $\text{Rh}(\text{I})$ piano-stool complex to 1 atm CO , although reaction was slow and took over 20 days at room temperature.⁵³ Reactions with CO in acetonitrile resulted in binding of a CO and an acetonitrile molecule, and reaction with *tert*-butyl isocyanide resulted in binding of two of these ligands, again breaking the Rh -arene interaction in both cases. Similar reactivity was observed for the $(^{\text{Ph}}\text{PArP})\text{Rh}(\text{II})$ analogue with both CO and *tert*-butyl isocyanide, although reactions proceeded faster as explained by a generally higher reactivity of 17-electron complexes toward substitution reactions compared to their 18-electron counterparts (Fig. 10a). The $\text{Rh}(\text{II})$ complex was additionally reduced under a CO atmosphere or upon addition of *tert*-butyl isocyanide, forming the same complexes as obtained before by reaction of the $\text{Rh}(\text{I})$ analogue, $(^{\text{Ph}}\text{PArP})\text{Rh}(\text{I})(\text{CO})_3$ and $(^{\text{Ph}}\text{PArP})\text{Rh}(\text{I})\text{L}_2$, respectively. One of the key features to obtain this interaction was indeed found to be the tether length, as it needed to be long enough to accommodate structural changes upon complex oxidation. This shows that an arene-based system can contain hemilability in the sense of making and breaking the interaction with the ligand backbone when needed. The interaction between the metal center and the π -electron cloud is broken upon addition of substrates, resulting in vacant sites for these extra incoming ligands. In a next example of an envisioned M -arene

interaction an *m*-terphenyl scaffold was used as the ligand (Fig. 10b). Here, no interaction with the explored metals was obtained as $\text{M}-\text{L}$ distances of 3.51, 3.48 and 3.37 Å were obtained for the nickel, palladium⁵⁴ and rhodium⁵⁵ complexes, respectively. In this case the distance from the metal center to the closest arene-H is mentioned, due to its geometry. Nevertheless, for the rhodium complex containing the significantly shorter $\text{M}-\text{L}$ distance, an interaction between the metal center and the π -electron cloud is observed as shown in the corresponding ^1H NMR spectrum where the aromatic protons of the central arene ring were distributed in a range of δ 6.18–8.04 ppm.⁵⁵

Another strategy to obtain an $\text{Ar}-\text{M}$ interaction is to keep the tether sufficiently short in combination with a flexible ligand backbone, so that the arene moiety is forced in close proximity to the metal center. The combination with a late transition metal (such as $\text{Ni}(0)$) that cannot readily accept 6 electrons from the aromatic ring results in enhanced reactivity. The use of a *p*-terphenyl diphenylphosphine (P_2terph , Fig. 12) ligand was designed and explored in the group of Agapie. The phosphorus groups are on the *ortho* positions of the two peripheral phenyl rings, creating a geometry with a short $\text{M}-\text{L}$ distance upon coordination to a metal. Several systems with this ligand are explored,^{56–59} but only selected cases are described here. In general, two ways of cooperative behavior are described, in which (a) the ligand acts as an electron reservoir in combination with coordinative flexibility to stabilize different oxidation states, or (b) the ligand backbone is activated and can form bonds with H-atoms or small molecules. A prominent recent example of the first case is a Mo -based complex, in which the *p*-terphenyl ligand stabilizes the formal oxidation states of Mo^{II} , Mo^0 , $\text{Mo}^{-\text{II}}$, and $\text{Mo}^{-\text{III}}$ (Fig. 11),⁶⁰ allowing for a remarkable deoxygenative reductive coupling of two metal-bound CO molecules. The redox active behavior of the tethered aromatic ring holds promise for catalytic reactions involving multi-electron transformations, such as the valorization of carbon dioxide.

Chemical cooperativity at the aromatic ring was demonstrated with nickel-based systems. The solid state structure of a $\text{Ni}(0)(\text{P}_2\text{terph})$ complex, formed from a reaction of P_2terph with $\text{Ni}(\text{cod})_2$, showed an interaction of the nickel center with both phosphines and a double bond of the arene backbone with $\text{Ni}-\text{C}$ lengths of 1.992(1) and 2.002(1) Å. The chelation of the nickel center induced a bend of the peripheral aryl rings of 14° inwards relative to *p*-terphenyl.⁶¹ The $\text{Ni}(0)(\text{P}_2\text{terph})$ complex was exposed to $\text{Ni}(\text{II})\text{Cl}_2(\text{dme})$ to perform a comproportionation reaction, resulting in a dinuclear $\text{Ni}^{\text{I}}-\text{Ni}^{\text{I}}$ complex

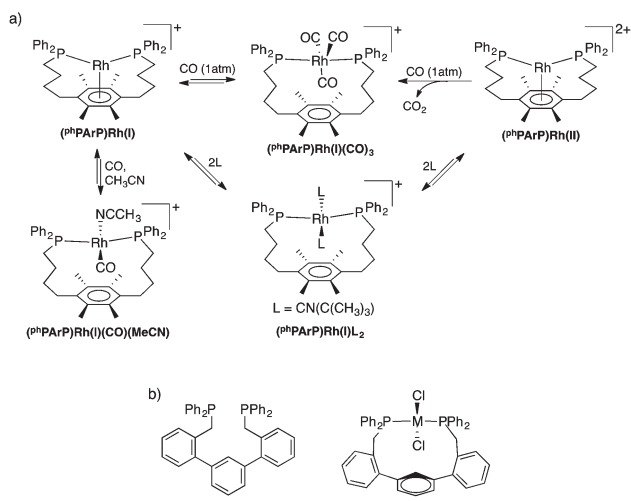


Fig. 10 (a) Two-legged piano stool based rhodium complexes and their reactivity. (b) *m*-Terphenyl based ligand (left) and the corresponding divalent metal complexes (right) $\text{M} = \text{Ni}, \text{Pd}$ or Rh .

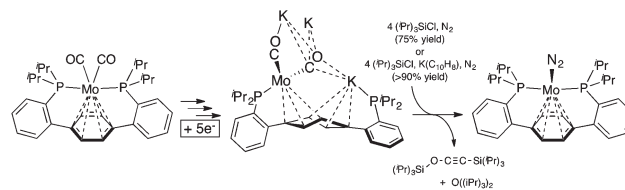


Fig. 11 *p*-Terphenyl based Mo -complexes.

$\text{Ni}_2(\text{P}_2\text{terph})\text{Cl}_2$, coordinated *via* the phosphines in an almost linear PNiNiP fashion. To accommodate this binding, the peripheral aryl rings bent outwards with 16° . Furthermore, two bridging chloride ligands are bound to the nickel centers next to an arene–M interaction *via* two neighboring double bonds in the arene backbone.

Addition of HCl to $\text{Ni}(0)(\text{P}_2\text{terph})$ resulted in oxidative addition of the substrate to the nickel center and loss of the arene–nickel bond ($\text{Ni}-\text{C}_{\text{arene}}: >2.5 \text{ \AA}$) with only a weak interaction with the arene π -system.⁶² Another dinuclear complex was formed upon heating of $\text{Ni}(\text{P}_2\text{terph})\text{HCl}$, resulting in a $\text{Ni}_2(\text{P}_2\text{terphH}_2)\text{Cl}_2$ with two bridging chloride ligands and the phosphorus ligands bound to the Ni(I) centers in a PNiNiP fashion, similar to the previously described dinuclear structure. The protons that were bound to nickel migrated to one of the double bonds of the aromatic rings, resulting in a single bond with a $\text{C}_{\text{ar}}-\text{C}_{\text{ar}}$ distance of $1.5198(1) \text{ \AA}$ breaking the aromaticity. The Ni_2Cl_2 center interacts with the remaining four conjugated carbon atoms in the ring. To study the H-migration, a halide abstraction was performed starting from $\text{Ni}(\text{P}_2\text{terph})\text{HCl}$, affording the positively charged $\text{Ni}(\text{P}_2\text{terph})\text{H}$ complex. Only a H was bound to the nickel center, which was stabilized by a η^2 -interaction of the arene ring ($\text{Ni}-\text{C}_{\text{Ar}}: 2.142(3)$ and $2.157(3) \text{ \AA}$). Analysis by NMR and X-ray crystallography in combination with isotopic labeling experiments shows that the metal hydride can migrate to the aromatic ring, either to the *ipso* or *ortho* carbon (Fig. 12), demonstrating the possibilities of this system to store part of the substrate in the ligand backbone, which is a possible way of introducing cooperative behavior in the system.

Besides the incorporation of a C–H based aromatic ring, the use of heteroatom containing rings is of interest. The incorporation of pyridine in the ligand backbone was investigated, binding the phosphorus tethers on the *meta* positions, keeping a symmetrical ligand system. A diphosphine pyridine (PPyP) ligand was designed, in which the ligand can bind to the metallic center *via* its phosphorus atoms positioned on the *ortho* positions of the peripheral rings, as well as the hetero-

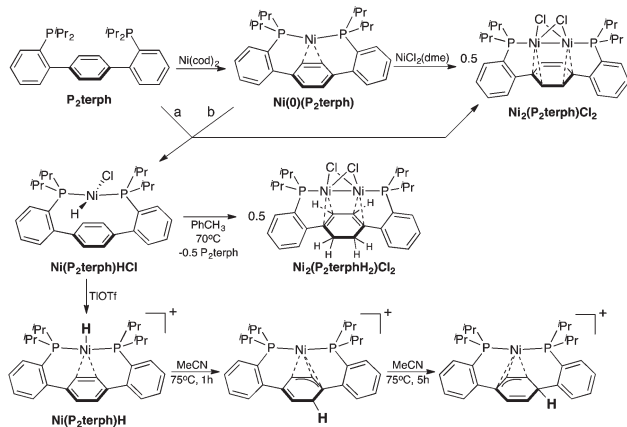


Fig. 12 The *p*-terphenyl based ligand P_2terph and its coordination to nickel. a: $\text{Ni}(\text{cod})_2$, $\text{NiCl}_2(\text{dme})$; b: HCl, Et_2O .

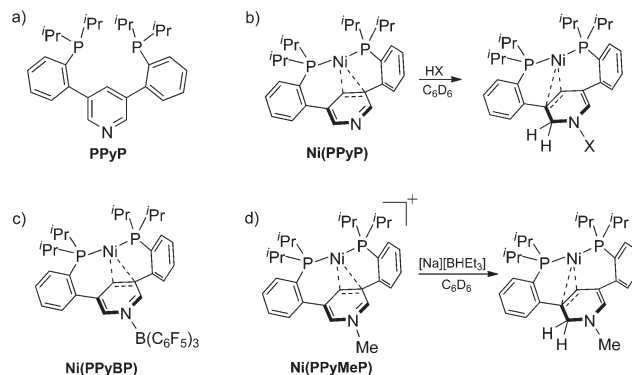


Fig. 13 (a) PPyP ligand. (b) $\text{Ni}(\text{PPyP})$ and its activation of HX, HX = HBPin or H_3PhSi . (c) The $\text{Ni}(\text{PPyBP})$ complex with $\text{B}(\text{C}_6\text{F}_5)_3$ bound to the nitrogen atom of the pyridine ring. (d) $\text{Ni}(\text{PPyMeP})$ and its reaction with $[\text{Na}][\text{BHEt}_3]$.

cycle π system (Fig. 13).^{63,64} Nickel and palladium complexes were synthesized in which the aromaticity was disrupted due to an interaction with one of the carbon–carbon double bonds of the pyridine backbone. This was shown by a significant upfield shift in the ^1H NMR spectrum of $\text{Ni}(\text{PPyP})$ in which the central pyridine protons shifted, *i.e.* the *ortho*-pyridyl shifted to 7.82 ppm and the *para*-pyridyl protons to 4.35 ppm (respectively 8.96 ppm and 7.89 ppm in the free ligand), indicating a severe change in the electronic environment. Binding of a Lewis acidic group such as $\text{B}(\text{C}_6\text{F}_5)_3$ to the pyridine nitrogen atom enhanced the strength of this interaction between the ring and the metal center further, as was evident in further upfield shift of the *para*-pyridyl proton shifted to 3.18 ppm in $\text{Ni}(\text{PPyBP})$ (Fig. 13b). The electron-withdrawing $\text{B}(\text{C}_6\text{F}_5)_3$ group enhances the π -acceptor feature of the ligand, and so enhances the bond strength from the electron rich Ni^0 center to the π -system of the pyridine ligand. Activation of small molecules, such as HBpin, PhSiH_3 and $[\text{Na}][\text{HBET}_3]$ was shown to take place in a stoichiometric fashion by breaking the aromaticity of the pyridine ring. In case of HBpin and PhSiH_3 the heteroatom binds to nitrogen and hydrogen to the carbon at the *ortho* position (Fig. 13c). In case of $[\text{Na}][\text{HBET}_3]$ the activation took place on a methylated version of the nickel complex $\text{Ni}(\text{PPyMeP})$, which was synthesized by addition of methyl triflate resulting in the methylated nitrogen atom and a triflate counter ion. Subsequent reaction with $[\text{Na}][\text{HBET}_3]$ resulted in the breaking of the aromaticity by addition of a hydrogen atom to the carbon at the *ortho* position of nitrogen (Fig. 13d). This ligand-based reactivity was attributed to the metal–ligand bond, in which the pyridine aromaticity was disrupted resulting in a somewhat activated ligand backbone.⁶³

3. π -Systems incorporating a boron atom

The last example showed how introducing an electronegative element in a conjugated π -systems can be used to increase its

affinity for hydrides and enhance reactivity. A similar, maybe stronger, effect can also be achieved by conjugation with an electron deficient group such as a borane.

Boranes themselves can act as Z-type, σ -acceptor ligands that bind to a metal center *via* accepting an electron pair of the metal center, formally forming a retrodonative bond.⁶⁵ They are often tethered to L-type ligands such as a phosphines for stabilization on the metal center, forming so called ambiphilic ligands.⁶⁶ Following the discovery of the first metallaboratrane by Hill in 1999,⁶⁷ ambiphilic ligands have attracted much interest because of their ability to stabilize unusual electronic structures and to act as cooperative ligands, as has been covered in several excellent reviews.^{68–71} In many cases, the boron atom bears conjugated aromatic substituents that can also engage in binding to the metal, resulting in $\eta^2(\text{BC})$ or $\eta^3(\text{BCC})$ coordination modes. The chemistry of acyclic boron-containing π -ligand complexes has been reviewed in 2012 by the group of Emslie.⁷² Here we discuss selected recent examples highlighting the specific reactivity of this motif.

The use of ambiphilic phosphine–borane based ligands in Pd catalyzed Suzuki–Miyaura reactions was explored in the group of Bourissou.^{73,74} Boron-based ligands containing three aromatic substituents, of which one phosphorus-substituted, were synthesized (**PB1** and **PB2**, Fig. 14) and their activity as co-ligands was explored. The addition of **PB1** or **PB2** to a standard cross-coupling reaction with a Pd(II) precursor, such as PdCl₂(cod), Pd(ma)(nbd) or Pd₂dba₃, resulted in good yields for 2-chloropyridine, chloro-N-heterocycles and amino-2-chloropyridines. To better understand the effect of adding a Lewis acidic substituent in the form of a borane to this catalytic reaction, a closer look was taken at the *in situ* formed Pd-complexes. **Pd-PB1** was isolated in which an extra coordinated maleic acid ligand was coordinated to Pd. Ligand **PB1** was found to have a η^3 -interaction with the metal center, *via* the phosphorus atom and a η^2 -interaction with an aromatic double bond of a mesityl substituent (Fig. 14). A new complex was formed upon addition of PhI, **Pd'-PB1**, in which the ligand was still bound *via* the phosphorus atom, but now also with a $\eta^4(\text{BCCCH}_2)$ -interaction of the mesityl bound boron atom, forming an extended π -coordination. This latter complex showed to be significantly less active in catalysis, and is expected to be a product of decomposition. Analysis of a single crystal by X-ray spectroscopy, and NMR analysis both confirm

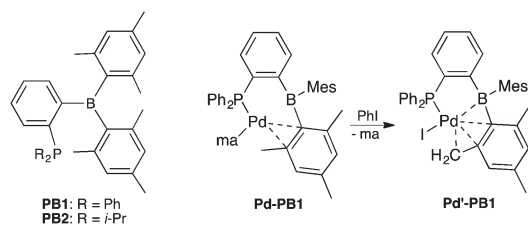


Fig. 14 Left: Phosphine-borane based ligands as synthesized in the group of Bourissou.⁷³ Right: Pd based complex Pd-PB1 and its reaction with PhI to Pd'-PB1.

the formation of **Pd'-PB1**, which was formed *via* an C–H activation on one of the mesityl rings, resulting in a CH₂ group and loss of 1 equivalent of benzene. An upfield shift of about 10 ppm was found in the ¹¹B NMR spectra, from 69.4 ppm for **Pd-PB1** to 52.8 ppm for **Pd'-PB1**, suggesting the presence of some Pd→B interaction. This structure shows a rare example of a η^4 -boratabutadiene complex.

To explore the possibilities of borane-based ligands as supporting ligands in catalysis, the group of Emslie designed multi-dentate ambiphilic ligands with a phosphine donor and a borane acceptor, aiming for π -coordinating systems. The phosphine–borane based TXPB ligand (Fig. 15a) was designed to anchor the metal center *via* the thioxanthene backbone and explored with a variety of metals, amongst which nickel, palladium and rhodium. The ligand was shown to be versatile and gave rise to a broad variety of complexes, but problems were encountered as the central thioether donor group was shown to be easily replaced from the metal center.^{66,75,76} Therefore, a new ligand system was designed containing a bisphosphine moiety instead. A ferrocene group was included to provide increased flexibility, while still remaining a firmly bound complex. The ligand FcPPB (FcPPB = Fe(η^5 -C₅H₄PPh₂)(η^5 -C₅H₄PtBu{C₆H₄(BPh₂)-ortho})), Fig. 15b) was bound to platinum using Pt(nb)₃ (nb = norbornadiene), affording an arylborane complex that binds the two phosphorus atoms, and the borane–phenyl moiety *via* a η^3 -BCC interaction with both the *ipso* and *ortho* carbon atoms.⁷⁵ Similar structures were obtained when performing the metallation with either Ni(cod)₂ or Pd₂(dba)₃, resulting in **Ni(FcPPB)** and **Pd(FcPPB)**, respectively, both containing the η^3 -BCC interaction with the phenyl–boron moiety.⁷⁷

The reactivity of **Pt(FcPPB)** with small molecules was explored. A CO molecule was bound to the Pt center upon exposure to a CO atmosphere, resulting in **Pt(FcPPB)(CO)**, which was characterized as an FcPPB complex connected to

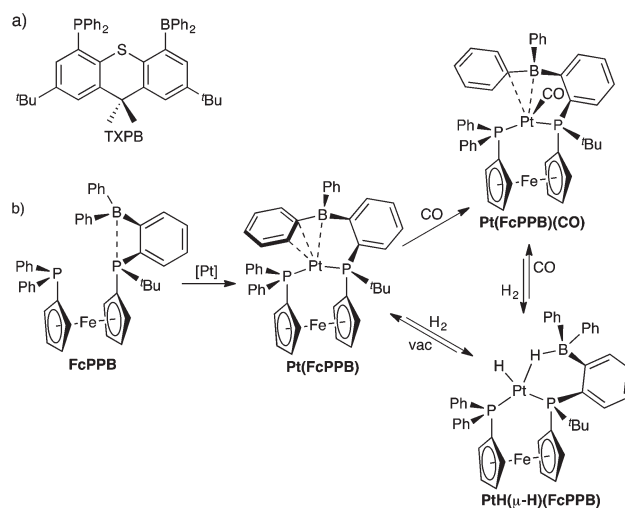


Fig. 15 (a) TXPB ligand. (b) Bisphosphine-ferrocene based ligand FcPPB, the Pt based complexes and their reactivity with CO and H₂.

the ligand *via* the two phosphorus atoms and a η^2 -BC interaction with the borane moiety, next to a CO molecule. Exposure of **Pt(FcPPB)** to an atmosphere of H_2 afforded **PtH(μ -H)(FcPPB)** by inserting a H in the Pt–B bond and adding the other H to Pt. It was shown that H_2 was only weakly bound, as **Pt(FcPPB)** was regained slowly upon storing the complex under argon and rapidly upon applying vacuum. Furthermore, it was possible to gain **Pt(FcPPB)(CO)** upon exposure to a CO atmosphere, and also its reverse reaction was possible.

Ambiphilic, tridentate diphosphanylborane (DPB) ligands, were originally introduced by Bourissou and co-workers in 2006.⁷⁸ In their work on rhodium complexes, only a Rh→B coordination mode was observed. Subsequently, Cu(I) coordination chemistry revealed that this ligand scaffold could also accommodate η^2 (BC) or η^3 (BCC) coordination modes.⁷⁹ Further research on the rhodium system was performed by Ozerov and co-workers, in which the coordination of the borane unit was shown to bind *via* the π -system of the borabenzyl moiety.⁸⁰ Next to this, the product of oxidative addition of the B–C bond was obtained, forming a PBP–pincer complex. The group of Peters explored further possibilities of these ligands. In particular, substitution of the boron–phenyl moiety for the more bulky boron–mesityl group was found to strongly impact the coordination chemistry and the reactivity of the ligand. A nickel–borane complex was formed from a comproportionation reaction with $NiBr_2$ and $Ni(cod)_2$.⁸¹ Analysis by X-ray crystallography showed a coordination of the (^{Mes}DPB^{Ph}) ligand *via* the two phosphorus atoms and a η^2 (B,C) coordination of the boron atom and the *ipso*-carbon atom of the mesityl ring, next to a bound bromide ligand ((^{Mes}DPB^{Ph})NiBr, Chart 2). The complex was reduced using Na/Hg resulting in the Ni(0) complex (^{Mes}DPB^{Ph})Ni, which surprisingly did not bind a solvent molecule. Both of the phosphorus atoms were bound to nickel, as for the Ni(I) complex, but the coordination of the borane substituent changed, as it was now bound in a η^3 -BCC fashion, also binding the *ortho*-carbon atom of the mesityl ring. Whereas a previously synthesized phenyl analogue (^{Ph}DPB^{Ph})Ni(THF) did not show any activity towards H_2 , (^{Mes}DPB^{Ph})Ni showed facile heterolytic activation of the substrate at room temperature in C_6D_6 . The hydrogen-bound complex was identified as the hydrido–borohydrido species (^{Mes}DPB^{Ph})(μ -H)NiH, as shown in Chart 2, and was found to be in a 5:1 equilibrium with (^{Mes}DPB^{Ph})Ni. Similar activity was found when the iron–CO analogue (^{Ph}DPB^{Ph})Fe(CO)₂ was exposed to 1 atm of H_2 , forming (^{Ph}DPB^{Ph}-H)Fe(H)(CO)₂, in which the hemilabile η^3 -BCC interaction participated and hydrogen was added in a heterolytic manner.⁸²

The catalytic possibilities of (^{Mes}DPB^{Ph})Ni were investigated by addition of styrene under a H_2 atmosphere, after which the hydrogenated product ethyl benzene was formed directly. The reaction was monitored by ¹H NMR spectroscopy, showing that the starting complexes were again present in an equilibrium with H_2 after full consumption of the substrate, showing that the catalyst could be recovered after catalysis.⁸¹ Further exploration of (^{Mes}DPB^{Ph})Ni in catalytic reactions showed that it is an efficient catalyst for the hydrosilylation of *para*-substi-

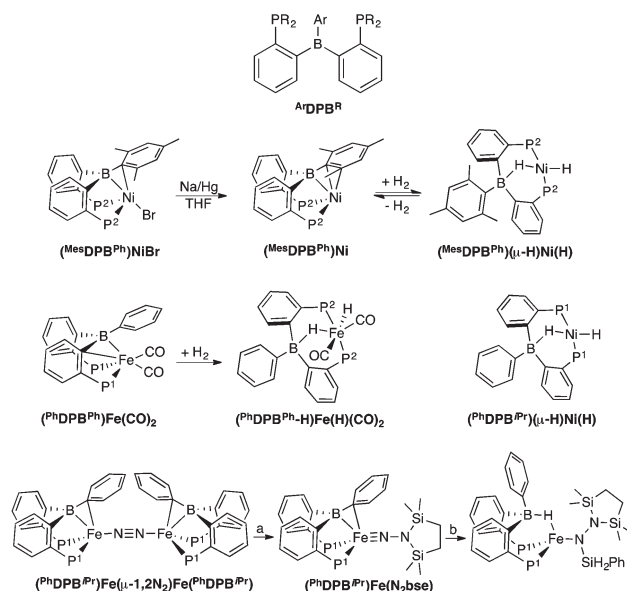


Chart 2 Selected DPB complexes. P = P¹ or P²; P¹ = *i*Pr, P² = Ph; R = Ph or *i*Pr; Ar = Mes or Ph; a = 1,2-bis(chlorodimethylsilyl)ethane, 2.1 equiv. Na/Hg, 1 atm of N₂, b = PhSiH₃.

tuted benzaldehydes with diphenylsilane, *via* the formation of a borohydrido–Ni–silyl species in which SiHPh₂ is bound to nickel and the hydride is inserted in the B–Ni bond.⁸³ Synthesis of the phenyl substituted P¹Pr₂ analogue (^{Ph}DPB^{*i*Pr})Ni showed reactivity toward H_2 as well.⁸⁴ The introduction of the more electron-rich isopropyl substituent in combination with the less bulky phenyl ring on boron tuned the geometric and electronic environment such that the observation of the hydrogen adduct was possible. This unusual Ni–(H_2) complex subsequently reacted to form a similar hydrido–borohydrido species, forming (^{Ph}DPB^{*i*Pr})(μ -H)NiH.

Similar binding modes for the DPB scaffold also play a role in iron-mediated dinitrogen functionalization. The dinitrogen-bridged di-iron complex (^{Ph}DPB^{*i*Pr})Fe(μ -1,2N₂)Fe(^{Ph}DPB^{*i*Pr})⁸⁵ could be functionalized by addition of 1,2-bis(chlorodimethylsilyl)ethane (bse) and 2.1 equivalents of Na/Hg under 1 atm of N₂, forming (^{Ph}DPB^{*i*Pr})Fe(N₂bse). This new complex formed an η^3 (B,C,C)-interaction with the iron center and the phenyl substituted borane tether. Activation of phenylsilane was performed by hydrosilylation of the Fe–N bond, placing SiH₂Ph to N α and H to B. Similar reactivity was found for the Co analogue (^{Ph}DPB^{*i*Pr})Co(N₂), and the substrate scope was extended with both, the iron and cobalt nitrogen bound complexes.⁸⁶

Stephan and co-workers developed ruthenium-based systems containing the ^{Ph}DPB^{Ph} ligand.⁸⁷ The ligand was bound to Ru *via* both phosphorus atoms and an interaction with the phenyl substituent on the borane, forming a positively charged complex with a B(C₆F₅)₄ counterion, *i.e.* [(^{Ph}DPB^{Ph})RuCl]B(C₆F₅)₄. The complex showed reactivity upon addition of PCy₃, binding the phosphorus atom to the interacting phenyl ring on its *ortho*-position, resulting in the cyclohexadienyl (chd) containing Ru-complex (^{chd}DPB^{Ph})Ru(PCy₃)Cl]–

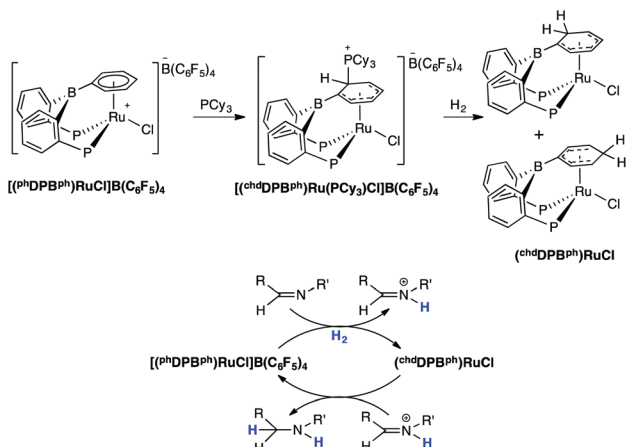


Fig. 16 (DPB)Ru structures and its mechanism for the hydrogenation of imines. P = Ph₂; R = Ph, R' = ^tBu or Ph.

B(C₆F₅)₄. A subsequent reaction was observed upon exposure to H₂, activating it in a heterolytic fashion and cleaving the C_{Ar}–PCy₃ bond. The resulting neutral cyclohexadienyl complex was found to be present in two isomers, with an *ortho* or a *para* addition at the arene ring. [(^{p^h}DPB^{p^h})RuCl]B(C₆F₅)₄ was explored in the hydrogenation of imines, which were shown to proceed at room temperature under high pressures of H₂ (102 atm, 1–10 mol% cat, 83–99% yield). The proposed mechanism proceeds *via* the previously synthesized complex (^{ch^d}DPB^{p^h})RuCl, both the *ortho* or a *para* form. This is consistent with an FLP-type (FLP = frustrated Lewis pair) hydrogenation in which the complex and the substrate act as an FLP to split H₂. The cleaved hydrogen is subsequently delivered to the formed iminium cation (Fig. 16).

These examples show the versatility that incorporation of borane ligands can bring to the coordination chemistry *via* their extended π-system, leading to various coordination modes making them excellent adaptive ligands. The resulting complexes are shown to be active toward small molecule activation *via* a heterolytic pathway transiently accepting hydrides either at the boron site or at a remote carbon site of the conjugated aromatic ring as demonstrated in the last example.

4. π-Bound C=E bonds

In comparison with olefins, the C=E (E = O or N) bond of carbonyls and imines becomes both polar and electron deficient because of the high electronegativity of the element E. Hence, the backdonation interaction is expected to play a dominant role in the description of π-bound C=E bonds. In addition, the presence of lone pairs on the heteroelement may open up reactive pathways that are not accessible to C=C bonds.

Polar C=E bonds can bind to the metal center in either an η¹(E) or η²(C,E)-fashion, the former being by far the most common mode. Here we discuss situations in which the latter (π-coordination) is favored. The incorporation of a carbonyl

will be discussed first, followed by the incorporation of imine and iminium moieties.

4.1 Carbonyl complexes

Carbonyl groups (*i.e.* aldehydes and ketones) are known to bind to a metal center in two distinct ways, *i.e.* η¹(O) to electrophilic metals, by donation of the oxygen lone pair to the metal center, and η²(C,O) to electron-rich metals. The latter case is stabilized by π-backdonation of the metal to the ligand, creating a stronger M–L bond and a weakening of the C=O bond, in line with the binding mode of alkene systems. The C=O interaction can be described by two resonance extremes; the side-on bound extreme and the metallaoxacycle extreme (Fig. 17). Cooperative behavior in such systems can be envisioned arising from the labile (C=O)–M bond, creating the possibility of a hemilabile system. Activation of a small molecule can proceed *via* heterolytic activation, adding part of the substrate to the oxygen of the ligand backbone and part to the metal center, provided that the carbonyl moiety has a η²(C,O) interaction with the metal center. In general, this interaction is scarcely found compared to the η¹(O) bound structure, but it is found more commonly for electron rich systems which can efficiently back donate.³⁹

An early example of a pincer-type ligand incorporating a η²-coordinating ketone was developed in the group of Milstein. The synthesis and characterization of an iridium complex containing a quinone-based ligand was reported.⁸⁸ The ligand was designed with phosphorus groups attached at the *ortho* positions to bind the metal center in a multidentate fashion. Upon synthesis of a cationic complex, a bond between the iridium center and the phosphorus groups was obtained, as well as an interaction with the *ipso* C=O group, establishing the first stable phenoxonium complex (Fig. 18a). The C=O moiety was bound *via* a η²-coordination to the metal, resulting in a stabilized cationic ligand. It was shown that the positive charge was mainly delocalized over the aromatic ring. An X-ray single

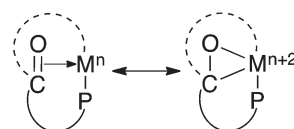


Fig. 17 Resonance extremes of a η²-bound ketone–metal interaction, left: the side-on adduct, right: the metallaoxo-cycle in which the oxidation state is raised by 2.

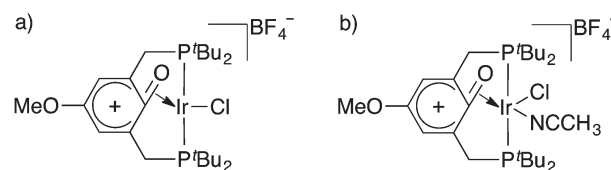


Fig. 18 (a) The pincer-type quinone based iridium complex and (b) the acetoneitrile bound analogue of which an X-ray single crystal structure was obtained.

crystal structure was obtained for the acetonitrile bound PCOP-complex (Fig. 18b). The bond angles inside the ring were found to be close to 120° , of which it was concluded that the system is best described as an Ir(I) complex with a C=O double-bond coordination compared to the Ir(III) three-centered metalla-oxa-cycle structure.⁸⁸

A somewhat analogous structure was obtained by Piers and coworkers⁸⁹ from the reaction of a pincer type iridium $PC_{sp^2}P$ with N_2O to form an iridaepoxide complex. The C=O moiety was formed by exposure of the carbene chloride complex to N_2O , by addition of an oxygen atom to the Ir=C bond, cleanly synthesizing the iridium complex containing the η^2 -coordinated C=O moiety (Fig. 19). The iridaepoxide shows a moderate upfield shift at 65 ppm in ^{13}C NMR. X-ray crystal structure analysis showed a C–O distance of 1.350(7) Å, which is in between a C–O double and single bond, *i.e.* ~ 1.21 Å and ~ 1.45 Å. An Ir–O distance of 2.034(4) Å was found and an Ir–C distance of 2.080(6) Å, both in the range of a single bond.

Hydrogen binds to the iridium center upon exposure of the iridaepoxide to 1 atm H_2 at room temperature, from which H_2O is subsequently eliminated. The mechanism of this formal hydrogenation of N_2O was investigated in detail, in which it was proposed that this elimination occurs *via* migration of a proton to the oxygen atom, forming an alcohol group on the carbene carbon atom and a hydride on the iridium center, as shown in Fig. 20a.⁹⁰ This step can either be seen as a reductive elimination/oxidative addition mechanism when starting from the iridaepoxide extreme, or as a 1,2-insertion/ β -elimination when starting from the η^2 -coordinated C=O extreme (Fig. 20b). In a next step the alcohol group migrates to iridium and H_2O is eliminated.⁹⁰ In this proposed mechanism the metal–ligand system operates in a truly cooperative fashion, storing part of the activated small molecule on the ligand backbone.

A more direct synthetic access to supported metallaepoxide structures is provided by the 2,2'-bis(diphenylphosphine)benzophenone ($^{ph}dppb$) ligand.⁹¹ The use of $^{ph}dppb$ as a chiral ligand was first explored in the group of Ding, where Ru(II)-based Noyori-type systems were developed to perform hydro-

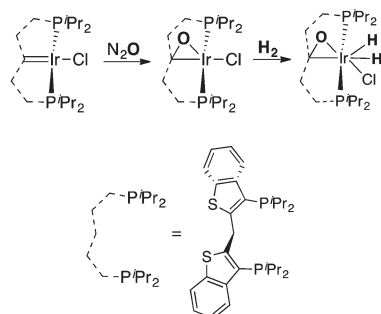


Fig. 19 Schematic representation of the pincer type iridium $PC_{sp^2}P$ iridium complex and its reaction with N_2O , forming the iridaepoxide complex, and the following reaction with H_2 (top) and the schematic and chemical representation of the ligand (bottom).

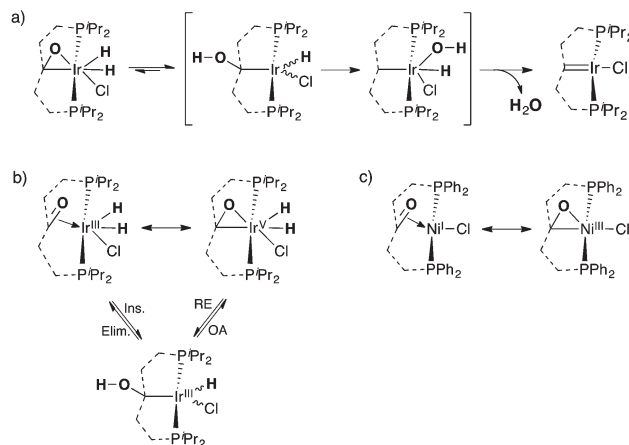


Fig. 20 (a) The iridaepoxide complex with one equivalent of H_2 added and the following H_2O elimination pathway. The ligand is represented schematically as in Fig. 19. (b) Resonance structures of the hydrogen bound iridium complex and the visualization of the proton migration, starting from either Ir(III) or Ir(V) as described by Piers.⁹⁰ (c) Resonance structures for the ($^{ph}dppb$)NiCl complex as described by Moret (*vide infra*).⁹¹

genation reactions. The benzophenone backbone was found to induce enantioselectivity in the catalytic hydrogenation of aromatic systems, in which the coordination of the C=O moiety is believed to be the key feature to obtain high yields and selectivity.⁹² Our group further explored the chemistry by coordination of $^{ph}dppb$ to nickel in the oxidation states of 0, 1 and 2 (Fig. 21). It was found that the ligand ketone moiety does not bind to the metallic center in the high-spin Ni(II) complex ($^{ph}dppb$)NiCl₂ (Ni–C: 3.4031(12) Å, Ni–O: 3.1012(10) Å), but this interaction was induced by reduction of the complex. The synthesis of ($^{ph}dppb$)Ni(I)Cl and ($^{ph}dppb$)Ni(0)PPh₃ both lead to a η^2 (C,O) interaction, leading to shorter bond distances between the ketone moiety and the metallic center (Ni–C: 2.006(2) Å, Ni–O: 1.9740(15) Å for Ni(I) and Ni–C: 2.001(2) Å, Ni–O: 2.0091(14) Å for Ni(0)). Next to this, the C=O bond was elongated from 1.213(3) Å in the Ni(II) structure to 1.310(2) Å in the Ni(I) and 1.330(3) Å in the Ni(0) structure, showing significant π -backdonation from the metal to the C=O moiety in the latter two cases (Fig. 22). NBO analysis of a DFT-computed electron density revealed an increased negative charge on the C=O fragment of $-0.5e$ and $-0.6e$ upon binding to Ni(I)Cl and Ni(0)PPh₃, respectively. This additionally supports the predominantly electron accepting nature of

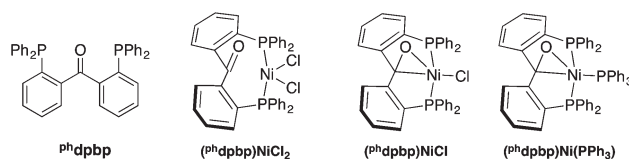


Fig. 21 Left-to-right: Diposphine-ketone ligand 2,2'-bis(diphenylphosphine)-benzophenone ($^{ph}dppb$), and the metal complexes ($^{ph}dppb$)NiCl₂, ($^{ph}dppb$)NiCl and ($^{ph}dppb$)Ni(PPh₃).

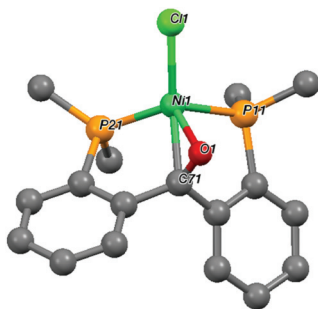


Fig. 22 Crystal structure of $(P^h dpbp)NiCl$ showing the $\eta^2(C,O)$ interaction with the nickel center, phenyl groups on the phosphorus atoms are omitted for clarity except for the bound carbon atom.

the ketone moiety, which can be seen to function as a hemilabile acceptor ligand.⁹¹

In a related study, Ruhland and co-workers explored the use of bisphosphinite ligands for the activation of unstrained $C(sp^2)-C(sp^2)$ bonds. Coordination of the bisphosphinite ligand ($iPr dpobp$, Fig. 23) to nickel,⁹³ rhodium⁹⁴ or iridium⁹⁵ resulted in quantitative oxidative addition of the $PhC-(CO)$ bond, breaking the ligand backbone. This reaction is proposed to proceed *via* a $\eta^2(C,O)$ interaction of the ketone moiety. Such pathways were not observed when using $P^h dpbp$ as the ligand, suggesting that the tether length is of importance to the stability of $\eta^2(C,O)$ complexes.

Coordination of a phosphine-tethered aldehyde ligand was explored in the group of Yeh. The bidentate P,O-chelating ligand *o*-(diphenylphosphine)benzaldehyde (PCHO) in combination with group 6 metals Mo⁹⁶ and W⁹⁷ was described. A complex with an octahedral geometry around the metal center was synthesized in both cases, binding two PCHO ligands and two CO ligands (Fig. 24a). The aldehyde moieties were shown

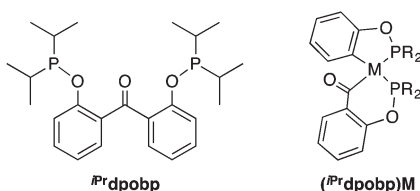


Fig. 23 Bisphosphinite ligand $iPr dpobp$ and the metal complexes. $M = Ni, Rh, Ir$; $R = iPr$.

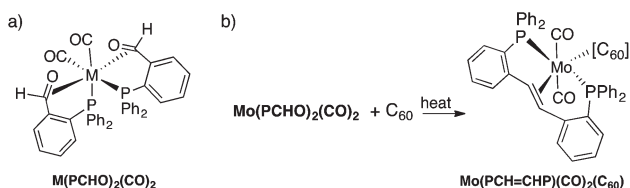


Fig. 24 (a) Octahedral complexes $M(PCHO)_2(CO)_2$, $M = Mo$ or W , PCHO = *o*-(diphenylphosphine)benzaldehyde. (b) Activity study of $Mo(PCHO)_2(CO)_2$ with C_{60} , resulting in the *trans*-stilbene complex $Mo(PCH=CHP)(CO)_2(C_{60})$.

to bind to the metal center in a η^2 -fashion by elongation of the aldehyde $C=O$ bonds upon complexation due to π -backbonding to the empty π^* -orbital of this fragment (Mo, $C-O$: 1.335(4) Å and 1.323(4) Å; W, $C-O$: 1.338(5) Å and 1.357(5) Å). A distinctive shift of the furan proton was observed in 1H NMR, from 10.50 ppm in the free PCHO ligand to 5.38 ppm in case of Mo and 5.12 ppm in case of W. The phosphorus signal was shown to shift from -11.37 ppm in the free PCHO ligand to 18.04 ppm for Mo and 10.03 ppm for W. The reactivity of the molybdenum complex $Mo(PCHO)_2(CO)_2$ with C_{60} was explored: the formed molybdenum complex still contained two CO ligands next to C_{60} , the latter being bound in a η^2 -fashion through a 6:6-ring junction. Furthermore, the two bound PCHO ligands unexpectedly reacted, forming a *trans*-stilbene type ligand, bound *via* the carbon-carbon double bond in the backbone as well as the phosphorus ligands, resulting in $Mo(PCH=CHP)(CO)_2(C_{60})$ (Fig. 24b). This binding is similar to the *trans*-stilbene type ligands shown in section 2.1 (*vide supra*). Analysis by single crystal X-ray diffraction showed a η^2 -bound $C=C$ moiety with a bond length of 1.418(7) Å, which is in the range of the olefinic $C-C$ bonds of the described *trans*-stilbene type ligands that were found to be between 1.40 Å and 1.44 Å.⁹⁶

4.2 Imine complexes

Imines are ubiquitous as ligands for transition metals, forming σ dative bonds by donation of one of the lone pairs of the nitrogen atom. Because this binding mode is generally preferred, π -complexes of $C=N$ bonds are rare (Fig. 25). Here we discuss recent examples where this binding mode is accessed upon formal deactivation of the N-centered lone pair either by coordination to another metal or by substitution to generate an iminium cation.

A rhodium based amido-bridged dinuclear complexes was synthesized in the group of de Bruin, $[Rh(nbd)_2(\mu-bpa)]Cl$ (nbd = norbornadiene, bpa = bis(2-picolyl)amine).⁹⁸ The complex was shown to be susceptible to deprotonation by KO^tBu , resulting in the complex $Rh(nbd)_2(\mu-bpi)$, where the doubly deprotonated bis(2-picolyl)amine ($PyCH_2NHCH_2Py$, bpa) ligand is transformed to a neutral $PyCH=N-CH_2Py$ (bpi) ligand containing an imine functionality (Fig. 26a). The two complexes are related by acid-base chemistry, as the backward reaction is possible by protonation with $NHET_3Cl$. Both the C and N atom of the deprotonated complex have a trigonal geometry, suggesting the formation of a π -coordinating imine $C=N$ frag-

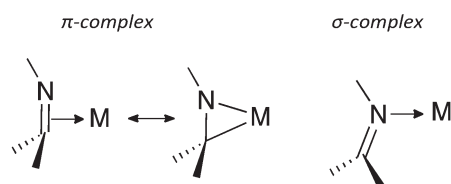


Fig. 25 Left: Schematic representation of the two resonance extremes of an imine π -complex, right: representation of the imine σ -complex.

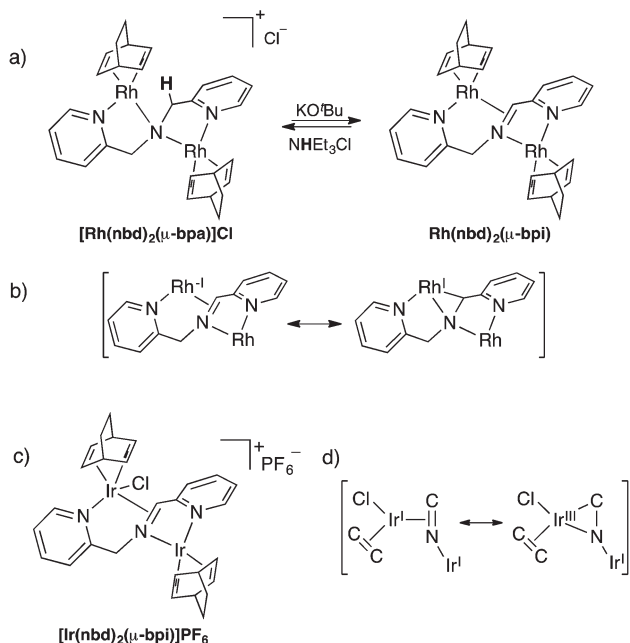


Fig. 26 (a) Rh-based complexes and their acid–base chemistry. (b) Resonance extremes of the Rh–imine bound structure. (c) Structure of the cationic Ir-based complex. (d) Resonance extremes of the Ir–imine bound structure. Figure adapted from de Bruin.^{98,99}

ment (Fig. 26b). Next to this, the C–N distance was found to be shorter upon comparison to the protonated complex, *i.e.* 1.415(4) Å *versus* 1.482(6) Å, respectively. In agreement with further analysis, this complex was described as a mixed valence Rh(–1,1) complex. The complex reacted rapidly with oxygen in benzene, leading to new, mononuclear complexes.⁹⁸ Analogues to this rhodium complex, the synthesis of another group 9 binuclear complex was explored using iridium (Fig. 26c).⁹⁹ An X-ray crystal structure of the cationic complex $[\text{Ir}(\text{nbd})_2(\mu\text{-bpi})]\text{PF}_6$ was obtained, showing a similar complex as the rhodium analogue. The rather unusual bridging π -coordination was again obtained, which was described as the first example of a π -bound imine moiety for iridium. Both of the iridium centers in the complex bind to the imine moiety, of which one adopts a σ -coordination to the imine nitrogen atom, activating the imine for η^2 -coordination to the other iridium center. Next to this, both iridium centers also bear a cod ligand. The η^2 -bound imine was shown to gain substantial π -backdonation, as the C–N bond has a length of 1.407(3) Å which is substantially longer compared to σ -coordinated imines to iridium that have a typical length of \sim 1.30 Å.⁹⁹ As a result it can be concluded that both resonance extremes play a role in binding, *i.e.* the side-on bound Ir(I) extreme and the Ir(III) irida-aza-cyclopropane extreme (Fig. 26d). The iridium complex was shown to be an active pre-catalyst for water oxidation after treatment with cerium ammonium nitrate (Ce^{IV}) as the oxidant.⁹⁹ The research using the bpi ligand was extended to the use of mixed metal systems. Complexes with Rh–Ir¹⁰⁰ and Pd–Ir¹⁰¹ were synthesized, which both still contained the η^2 -bound imine moiety.

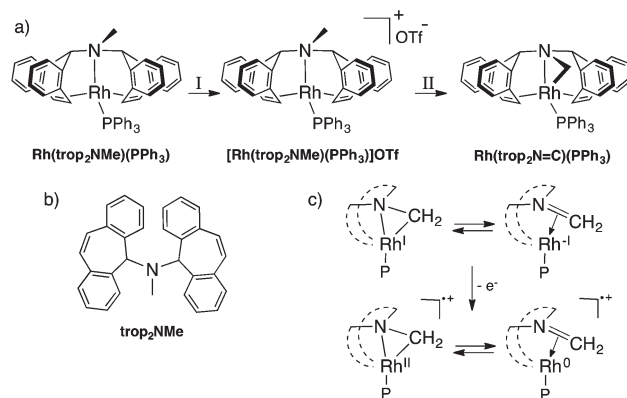


Fig. 27 (a) Synthesis of Rh-based complexes, I = AgOTf ; II = KO^tBu . (b) The ligand trop_2NMe . (c) Binding modes of $\text{Rh}(\text{trop}_2\text{N}=\text{C})(\text{PPh}_3)$ and $\text{Rh}(\text{trop}_2\text{N}=\text{C})(\text{PPh}_3)^+$, the rhodaazacyclopropane and the η^2 -side-on bound (C=N)–M complex.

Other rhodium complexes with a η^2 -bound N=C double bond have been synthesized from a bulky trop_2NMe ligand ($\text{trop} = 5H\text{-dibenzo}[a,d]\text{cyclohepten-5-yl}$).^{102,103} They were formed in multiple steps, starting from trop_2NMe , $\text{Rh}(\mu_2\text{-Cl})_2(\text{cod})_2$ and PPh_3 , resulting in $\text{Rh}(\text{trop}_2\text{NMe})(\text{PPh}_3)$ which was further reacted with AgOTf to yield the positively charged complex $[\text{Rh}(\text{trop}_2\text{NMe})(\text{PPh}_3)]\text{OTf}$. The methyl group was subsequently deprotonated with KO^tBu to form an interaction between C_{Me} and Rh, forming an unsaturated C=N ligand ($\text{Rh}(\text{trop}_2\text{N}=\text{C})(\text{PPh}_3)$) (Fig. 27a and b). The binding of this moiety can either be considered as a rhodaazacyclopropane or as the η^2 -side-on bound (C=N)–M complex (Fig. 27c). The N–CH₂ distance is 1.446(5) Å, which is significantly shorter compared to the N–CH₃ which was found to be 1.505(7) Å, but on the other hand longer than other C=N bonds in iminium ions (1.274–1.301 Å). The rhodaazacyclopropane description has an energetically low-lying π^* -orbital of the N–C bond, and so π -backdonation to the ligand is strong. For these reasons in combination with further analysis by NMR, the metallacycle description is the most accurate for this complex. The properties of $\text{Rh}(\text{trop}_2\text{N}=\text{C})(\text{PPh}_3)$ were explored with cyclic voltammetry in a THF solution, in which the complex could be oxidized. The $\text{Rh}(\text{trop}_2\text{N}=\text{C})(\text{PPh}_3)^+$ complex was stable enough to be analyzed by EPR spectroscopy, from which it was shown that the structural features of the starting complex were retained, obtaining a rhodaazacyclopropyl radical cation. In analogy to the neutral complex, this complex is also best described as a RhNC metallacycle (Fig. 27c), showing the ability of this ligand to stabilize multiple oxidation states with a single geometry.¹⁰³

5. Conclusions

The inclusion of π -coordinating ligands in organometallic complexes is a versatile tool to induce metal–ligand cooperativity. The recent advances described here illustrate how the reactivity of metal-bound π -systems can be controlled by ligand design. In particular, the incorporation of a variety of tethers

to connect the π -coordinating moiety and additional donor groups, mainly based on coordinating P-donors, exerts a strong influence on its coordination mode and reactivity. In the arene based chemistry, the tether length can favor or disfavor coordination of the aromatic π -system: the long, flexible tether in (^{Ph}PArP)Rh complexes combined with steric encumbrance turns a strong η^6 -arene ligand into a hemilabile moiety. Conversely, the rigid *ortho*-phenylene tethers in terphenyl-based ligands impose a close proximity between an aromatic moiety and group 10 metals.

The use of rigid tethers also stabilize unusual coordination modes of certain π -systems, such as the side-on coordination of the C=O moiety in Milstein's quinone based iridium pincer complexes. Similarly, the *ortho*-phenylene tethers in ketone-based pincer ligands favor the $\eta^2(\text{CO})$ binding mode over the $\eta^1(\text{O})$, resulting in hemilabile-acceptor behavior in (^{Ph}dpbp)NiL complexes. Another striking example of tether-imposed binding mode is the unusual coordination mode of the pyridine moiety in Ni(PPyP) complexes: the anchoring of the phosphorus groups on the *meta* positions leads to the nickel center coordinating a C=C bond of the aromatic ring, whereas a pyridine ring usually coordinates *via* its nitrogen atom lone pair. Due to this binding mode, an electron deficient aromatic ring could be generated *via* coordination of Lewis-acidic borane ligand to the lone pair on the pyridine nitrogen atom, leading to enhanced hydride affinity and allowing for bifunctional activation of silanes and boranes.

This last example also illustrates how reactivity at π -ligands can be tuned by electronic effects. Related reactivity was observed upon introduction of electron-deficient borane substituents. Interaction of arylborane moieties with reduced metal centers often involves both the boron atom and the aromatic system in $\eta^2(\text{BC})$ or $\eta^3(\text{BCC})$ coordination modes, as featured in the chemistry of diphosphine-borane (DPB) ligands. Cooperative reactivity of DPB complexes usually involves the boron center functioning as a hydride acceptor, allowing for the activation of a range of small molecules by iron, cobalt, and nickel compounds. Remarkably, a high hydride affinity at the boron-substituted aromatic ring has also been observed in ruthenium chemistry of the ^{Ph}DPB^{Ph} ligand: a hydride can be incorporated on the carbon-backbone of the ligand, allowing the η^6 -bound arene moiety in [^{Ph}DPB^{Ph}RuCl]⁺ to function as a hydride acceptor in frustrated Lewis pair chemistry.

Metal-ligand cooperation is a versatile tool in current efforts to transition from precious to base metals in catalysis. The recent advances discussed herein highlight the incorporation of tethered π -ligands as a promising strategy for the design of new and tuneable cooperative systems, hopefully stimulating further development of this class of compounds for base metal catalysis.

Acknowledgements

The authors would like to thank the Sectorplan Natuur- en Scheikunde (Tenure-track grant at Utrecht University) for financial support.

Notes and references

- J. I. van der Vlugt, *Eur. J. Inorg. Chem.*, 2012, 363–375.
- J. R. Khusnutdinova and D. Milstein, *Angew. Chem., Int. Ed.*, 2015, **54**, 12236–12273.
- P. J. Chirik and K. Wieghardt, *Science*, 2010, **327**, 794–795.
- J. C. Jeffrey and T. B. Rauchfuss, *Inorg. Chem.*, 1979, **18** (10), 2658–2666.
- P. Braunstein and F. Naud, *Angew. Chem., Int. Ed.*, 2001, **40**, 680–699.
- W. I. Dzik, J. I. van der Vlugt, J. N. H. Reek and B. de Bruin, *Angew. Chem., Int. Ed.*, 2011, **50**, 3356–3358.
- O. R. Luca and R. H. Crabtree, *Chem. Soc. Rev.*, 2013, **42**, 1440–1459.
- P. J. Chirik, *Inorg. Chem.*, 2011, **50**, 9737–9740.
- T. W. Myers and L. A. Berben, *J. Am. Chem. Soc.*, 2011, **133**, 11865–11867.
- T. W. Myers and L. A. Berben, *J. Am. Chem. Soc.*, 2013, **135**, 9988–9990.
- R. Noyori, *Angew. Chem., Int. Ed.*, 2002, **41**, 2008–2022.
- E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon and D. Milstein, *Nat. Chem.*, 2011, **3**, 609–614.
- S. P. Semproni, C. Milsmann and P. J. Chirik, *J. Am. Chem. Soc.*, 2014, **136**, 9211–9224.
- R. Langer, G. Leituss, Y. Ben-David and D. Milstein, *Angew. Chem., Int. Ed.*, 2011, **50**, 2120–2124.
- Y. Shvo, D. Czarkie and Y. Rahamim, *J. Am. Chem. Soc.*, 1986, **108**, 7400–7402.
- J. Pearson, R. J. Shively Jr. and R. A. Dubbert, *Organometallics*, 1992, **11**, 4096–4104.
- H.-J. Knölker, E. Baum and R. Klaus, *Tetrahedron Lett.*, 1995, **36**, 7647–7650.
- C. P. Casey and H. Guan, *J. Am. Chem. Soc.*, 2007, **129**, 5816–5817.
- B. L. Conley, M. K. Pennington-Boggio, E. Boz and T. J. Williams, *Chem. Rev.*, 2010, **110**, 2294–2312.
- I. Bauer and H.-J. Knölker, *Chem. Rev.*, 2015, **115**, 3170–3387.
- P. E. Sues, K. Z. Demmans and R. H. Morris, *Dalton Trans.*, 2014, **43**, 7650–7667.
- S. Chakraborty, P. O. Lagaditis, M. Förster, E. A. Bielinski, N. Hazari, M. C. Holthausen, W. D. Jones and S. Schneider, *ACS Catal.*, 2014, **4**, 3994–4003.
- R. Langer, M. A. Iron, L. Konstantinovski, Y. Diskin-Posner, G. Leituss, Y. Ben-David and D. Milstein, *Chem. – Eur. J.*, 2012, **18**, 7196–7209.
- N. Gorgas, B. Stöger, L. F. Veiros, E. Pittenauer, G. Allmaier and K. Kirchner, *Organometallics*, 2014, **33**, 6905–6914.
- S. Chakraborty, H. Dai, P. Bhattacharya, N. T. Fairweather, M. S. Gibson, J. A. Krause and H. Guan, *J. Am. Chem. Soc.*, 2014, **136**, 7869–7872.
- J. I. van der Vlugt and J. N. H. Reek, *Angew. Chem., Int. Ed.*, 2009, **48**, 8832–8846.
- S. Schneider, J. Meiners and B. Askevold, *Eur. J. Inorg. Chem.*, 2012, 412–429.

- 28 C. Gunanathan and D. Milstein, *Acc. Chem. Res.*, 2011, **4**(8), 588–602.
- 29 V. Lyaskovskyy and B. de Bruin, *ACS Catal.*, 2012, **2**, 270–279.
- 30 M. Asay and D. Morales-Morales, *Dalton Trans.*, 2015, **44**, 17432–17447.
- 31 G. van Koten and D. Milstein, *Topics in Organometallic Chemistry, Organometallic Pincer Chemistry*, Springer, 2013.
- 32 A. M. Tondreau, C. C. Hojilla Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis and P. J. Chirik, *Science*, 2012, **335**, 567–570.
- 33 D. Morales-Morales and C. M. Jensen, *The Chemistry of Pincer Compounds*, Elsevier Science, Amsterdam, 2007.
- 34 K. J. Szabó and O. F. Wendt, *Pincer and Pincer-Type Complexes*, Wiley-VCH, Weinheim, 2014.
- 35 M. Albrecht and G. van Koten, *Angew. Chem., Int. Ed.*, 2001, **40**, 3750–3781.
- 36 M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759–1792.
- 37 M. W. O'Reilly and A. S. Veige, *Chem. Soc. Rev.*, 2014, **43**, 6325–6369.
- 38 W. C. Zeise, *Poggendorff's Ann. Phys.*, 1827, **9**, 632–633.
- 39 R. H. Crabtree, *The organometallic chemistry of the transition metals*, Wiley, New Haven, 5th edn, 2009.
- 40 M. A. Bennett and P. W. Clark, *J. Organomet. Chem.*, 1976, **100**, 367–381.
- 41 M. A. Bennett, R. N. Johnson and I. B. Tomkins, *J. Organomet. Chem.*, 1976, **118**, 205–232.
- 42 W. Baratta, E. Herdtweck, P. Martinuzzi and P. Rigo, *Organometallics*, 2001, **20**, 305–308.
- 43 B. J. Barrett and V. M. Iluc, *Organometallics*, 2014, **33**, 2565–2574.
- 44 B. J. Barrett and V. M. Iluc, *Inorg. Chem.*, 2014, **53**, 7248–7259.
- 45 C. C. Comanescu, M. Vyushkova and V. M. Iluc, *Chem. Sci.*, 2015, **6**, 4570–4579.
- 46 A. V. Polukeev, R. Marcos, M. S. G. Ahlquist and O. F. Wendt, *Chem. Sci.*, 2015, **6**, 2060–2067.
- 47 (a) A. Friedrich, R. Ghosh, R. Kolb, E. Herdtweck and S. Schneider, *Organometallics*, 2009, **28**, 708–718; (b) C. Bianchini, E. Farnetti, M. Graziani, G. Nardin, A. Vacca and F. Zanobini, *J. Am. Chem. Soc.*, 1990, **112**, 9190–9197.
- 48 A. V. Polukeev and O. F. Wendt, *Organometallics*, 2015, **34**, 4262–4271.
- 49 K. J. Jonasson, A. V. Polukeev, R. Marcos, M. S. G. Ahlquist and O. F. Wendt, *Angew. Chem., Int. Ed.*, 2015, **54**, 9372–9375.
- 50 L. Zhang, T. Yan, Y.-F. Han, F. E. Hahn and G.-X. Jin, *Dalton Trans.*, 2015, **44**, 8797–8800.
- 51 K. Okamoto, Y. Omoto, H. Sano and K. Ohe, *Dalton Trans.*, 2012, **41**, 10926–10929.
- 52 F. M. Dixon, J. R. Farrell, P. E. Doan, A. Williamson, D. A. Weinberger, C. A. Mirkin, C. Stern, C. D. Incarvito, L. M. Liable-Sands, L. N. Zakharov and A. L. Rheingold, *Organometallics*, 2002, **21**, 3091–3093.
- 53 F. M. Dixon, M. S. Masar III, P. E. Doan, J. R. Farrell, F. P. Arnold Jr., C. A. Mirkin, C. D. Incarvito, L. N. Zakharov and A. L. Rheingold, *Inorg. Chem.*, 2003, **42**(10), 3245–3255.
- 54 R. C. Smith and J. D. Protasiewicz, *Organometallics*, 2004, **23**, 4215–4222.
- 55 B. P. Morgan and R. C. Smith, *J. Organomet. Chem.*, 2008, **693**, 11–16.
- 56 K. T. Horak, A. Velian, M. W. Day and T. Agapie, *Chem. Commun.*, 2014, **50**, 4427–4429.
- 57 K. T. Horak, S. Lin, J. Rittle and T. Agapie, *Organometallics*, 2015, **34**, 4429–4432.
- 58 J. T. Henthorn, S. Lin and T. Agapie, *J. Am. Chem. Soc.*, 2015, **137**, 1458–1464.
- 59 K. T. Horak and T. Agapie, *J. Am. Chem. Soc.*, 2016, **138**, 3443–3452.
- 60 J. A. Buss and T. Agapie, *Nature*, 2016, **529**, 72–75.
- 61 A. Velian, S. Lin, A. J. M. Miller, M. W. Day and T. Agapie, *J. Am. Chem. Soc.*, 2010, **132**, 6296–6297.
- 62 S. Lin, M. W. Day and T. Agapie, *J. Am. Chem. Soc.*, 2011, **133**, 3828–3831.
- 63 K. T. Horak, D. G. VanderVelde and T. Agapie, *Organometallics*, 2015, **34**, 4753–4765.
- 64 G. A. Edouard, P. Kelley, D. E. Herbert and T. Agapie, *Organometallics*, 2015, **34**, 5254–5277.
- 65 M. L. H. Green, *J. Organomet. Chem.*, 1995, **500**, 127–148.
- 66 D. J. H. Emslie, B. E. Cowie, S. R. Oakley, N. L. Huk, H. A. Jemkins, L. E. Harrington and J. F. Britten, *Dalton Trans.*, 2012, **41**, 3523–3535.
- 67 A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1999, **38**(18), 2759–2761.
- 68 G. Bouhadir and D. Bourissou, *Chem. Soc. Rev.*, 2016, **45**, 1065–1079.
- 69 A. Amgoune and D. Bourissou, *Chem. Commun.*, 2011, **47**, 859–871.
- 70 H. Braunschweig and R. D. Dewhurst, *Dalton Trans.*, 2011, **40**, 549–558.
- 71 I. Kuzu, I. Krummenacher, J. Meyer, F. Armbruster and F. Breher, *Dalton Trans.*, 2008, **43**, 5836–5865.
- 72 D. J. H. Emslie, B. E. Cowie and K. B. Kolpin, *Dalton Trans.*, 2012, **41**, 1101–1117.
- 73 R. Malacea, F. Chahdoura, M. Devillard, N. Saffon, M. Gómez and D. Bourissou, *Adv. Synth. Catal.*, 2013, **355**, 2274–2284.
- 74 R. Malacea, N. Saffon, M. Gómez and D. Bourissou, *Chem. Commun.*, 2011, **47**, 8163–8165.
- 75 B. E. Cowie and D. J. H. Emslie, *Chem. – Eur. J.*, 2014, **20**, 16899–16912.
- 76 B. E. Cowie and D. J. H. Emslie, *Organometallics*, 2013, **32**, 7297–7305.
- 77 B. E. Cowie and D. J. H. Emslie, *Organometallics*, 2015, **34**, 4093–4101.
- 78 S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu and D. Bourissou, *Angew. Chem., Int. Ed.*, 2006, **45**, 1611–1614.
- 79 M. Sircoglou, S. Bontemps, M. Mercy, K. Miqueu, S. Ladeira, N. Saffon, L. Maron, G. Bouhadir and D. Bourissou, *Inorg. Chem.*, 2010, **49**(9), 3983–3990.

- 80 W.-C. Shih, W. Gu, M. C. MacInnis, S. D. Timpa, N. Bhuvanesh, J. Zhou and O. V. Ozerov, *J. Am. Chem. Soc.*, 2016, **138**, 2086–2089.
- 81 W. H. Harman and J. C. Peters, *J. Am. Chem. Soc.*, 2012, **134**, 5080–8082.
- 82 D. L. M. Suess and J. C. Peters, *J. Am. Chem. Soc.*, 2013, **135**, 12580–12583.
- 83 S. N. MacMillan, W. H. Harman and J. C. Peters, *Chem. Sci.*, 2014, **5**, 590–597.
- 84 W. H. Harman, T.-P. Lin and J. C. Peters, *Angew. Chem., Int. Ed.*, 2014, **53**, 1081–1086.
- 85 D. L. M. Suess and J. C. Peters, *J. Am. Chem. Soc.*, 2013, **135**, 4938–4941.
- 86 M. A. Nesbit, D. L. M. Suess and J. C. Peters, *Organometallics*, 2015, **34**(19), 4741–4752.
- 87 M. P. Boone and D. W. Stephan, *J. Am. Chem. Soc.*, 2013, **135**, 8508–8511.
- 88 A. Vigalok, B. Rybtchinski, Y. Gozin, T. S. Koblenz, Y. Ben-David, H. Rozenberg and D. Milstein, *J. Am. Chem. Soc.*, 2003, **125**, 15692–15693.
- 89 L. E. Doyle, W. E. Piers and J. Borau-Garcia, *J. Am. Chem. Soc.*, 2015, **137**, 2187–2190.
- 90 L. E. Doyle, W. E. Piers, J. Borau-Garcia, M. J. Sgro and D. M. Spasyuk, *Chem. Sci.*, 2016, **7**, 921–931.
- 91 B. W. H. Saes, D. G. A. Verhoeven, M. Lutz, R. J. M. Klein Gebbink and M.-E. Moret, *Organometallics*, 2015, **34**, 2710–2713.
- 92 Q. Jing, C. A. Sandoval, Z. Wang and K. Ding, *Eur. J. Org. Chem.*, 2006, 3606–3616.
- 93 K. Ruhland, A. Obenhuber and S. D. Hoffman, *Organometallics*, 2008, **27**, 3482–3495.
- 94 A. Obenhuber and K. Ruhland, *Organometallics*, 2011, **30**, 4039–4051.
- 95 A. Obenhuber and K. Ruhland, *Organometallics*, 2011, **30**, 171–186.
- 96 C.-S. Chen, C.-S. Lin and W.-Y. Yeh, *J. Organomet. Chem.*, 2011, **696**, 1474–1478.
- 97 W.-Y. Yeh and C.-S. Lin, *Organometallics*, 2004, **23**, 917–920.
- 98 C. Tejel, M. A. Ciriano, M. Pilar del Rio, F. J. van den Bruele, D. G. H. Hetterscheid, N. Tschlis i Spithas and B. de Bruin, *J. Am. Chem. Soc.*, 2008, **130**, 5844–5845.
- 99 W. I. Dzik, S. E. Calvo, J. N. H. Reek, M. Lutz, M. A. Ciriano, C. Tejel, D. G. H. Hetterscheid and B. de Bruin, *Organometallics*, 2011, **30**, 372–374.
- 100 C. Tejel, L. Asensio, M. P. del Río, B. de Bruin, J. A. López and M. A. Ciriano, *Eur. J. Inorg. Chem.*, 2012, 512–519.
- 101 C. Tejel, L. Asensio, M. P. del Río, B. de Bruin, J. A. López and M. A. Ciriano, *Angew. Chem., Int. Ed.*, 2011, **50**, 8839–8843.
- 102 T. Büttner, F. Breher and H. Grützmacher, *Chem. Commun.*, 2004, 2820–2821.
- 103 P. Maire, A. Sreekanth, T. Büttner, J. Harmer, I. Gromov, H. Rügger, F. Breher, A. Schweiger and H. Grützmacher, *Angew. Chem., Int. Ed.*, 2006, **45**, 3265–3269.