Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Non-Precious Metal Complexes with an Anionic PCP Pincer Architecture

Sathiyamoorthy Murugesan and Karl Kirchner*

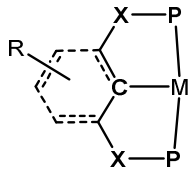
This perspective article provides an overview of the advancements in the field of non-precious metal complexes featuring anionic PCP pincer ligands with the inclusion of aliphatic systems. It covers research from the beginning in 1976 until late 2015 and provides a summary of key developments in this area, which is, to date, limited to the metals nickel, cobalt, iron, and molybdenum. While the research in nickel PCP complexes is already quite extensive, the chemistry of cobalt, iron, and molybdenum PCP complexes is comparatively sparse. With other non-precious metals such as copper, manganese, chromium or vanadium no PCP complexes are known as yet. In the case of nickel PCP complexes already many catalytic applications such as Suzuki–Miyaura coupling, C-S cross coupling, Kharasch and Michael additions, hydrosilylation of aldehydes and ketones, cyanomethylation of aldehydes, and hydroamination of nitriles were reported. While iron PCP complexes were found to be active catalysts for the hydrosilylation of aldehydes and ketones as well as the dehydrogenation of ammonia-borane, cobalt PCP complexes were not applied to any catalytic reactions. Surprisingly, only one molybdenum PCP complex is reported, which was capable of cleaving dinitrogen to give a nitride complex. This perspective underlines that the combination of cheap and abundant metals such as nickel, cobalt, and iron with PCP pincer ligands may result in the development of novel, versatile, and efficient catalysts for atom-efficient catalytic reactions.

Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, AUSTRIA, e-mail: kkirch@mail.tuwien.ac.at

1. Introduction

Transition metal complexes are indispensable tools for every chemist engaged in synthesis. Ideally, any metal-mediated catalytic process should be fast, clean, efficient, and selective. These criteria are especially important when one considers that many of the transition metals employed in catalysis are rare and/or expensive. One of the ways of modifying and controlling the properties of transition metal complexes is the use of appropriate ligand systems. Among the many ligand systems that can be found in the chemical literature pincer ligands play an important role and their complexes have attracted tremendous interest due to their high stability, activity and variability.[1,2] These tridentate ligands are often planar scaffolds consisting of an anionic or neutral central aromatic backbone tethered to two, mostly bulky, two-electron donor groups by different spacers. In recent years, pincers with aliphatic backbones have also received considerable attention. In this family of ligands steric, electronic, and also stereochemical parameters can be manipulated by modifications of the substituents at the donor sites

and/or the spacers allowing the possibility of a rational and modular design enabling the generation of highly active catalysts for a range of chemical transformations with high selectivity. Most common are still pincer systems with phosphine donors tethered to an aromatic benzene backbone, so called PCP pincer ligands. The first PCP pincer complexes were already synthesized in the mid-1970s by Shaw and co-workers.[3] They prepared PCP pincers with bulky tertiary phosphines which were linked with a CH_2 spacer to a deprotonated anionic benzene unit and, in fact, also reported the synthesis of the first nickel PCP pincer complex. However, this area remained comparatively unexplored until in the late 1990s several applications of mostly precious second and third row transition metal pincer complexes in the fields of catalysis, molecular recognition and supramolecular chemistry were discovered turning this area into an intensively investigated subject in organometallic chemistry.



X = CH_2, O, NH, NMe
M = Ni, Co, Fe and Mo
C = sp^2 or sp^3 carbon donor
R = electron withdrawing or donating group

Scheme 1. The aromatic and aliphatic PCP pincer platform with PC*sp*^{2}P and PC*sp*^{3}P frameworks connecting the phosphine donors with various linkers X.

This perspective article provides an overview of the advancements in the field of non-precious metal pincer complexes featuring anionic PCP pincer ligands with the inclusion of aliphatic systems as shown in Scheme 1. It covers research from the beginning in 1976 until late 2015 and provides a summary of key developments in this area, which is, to date, limited to the metals Ni, Co, Fe, and Mo. An overview of all PCP motifs found in the literature in conjunction with non-precious metals is provided in Chart 1.

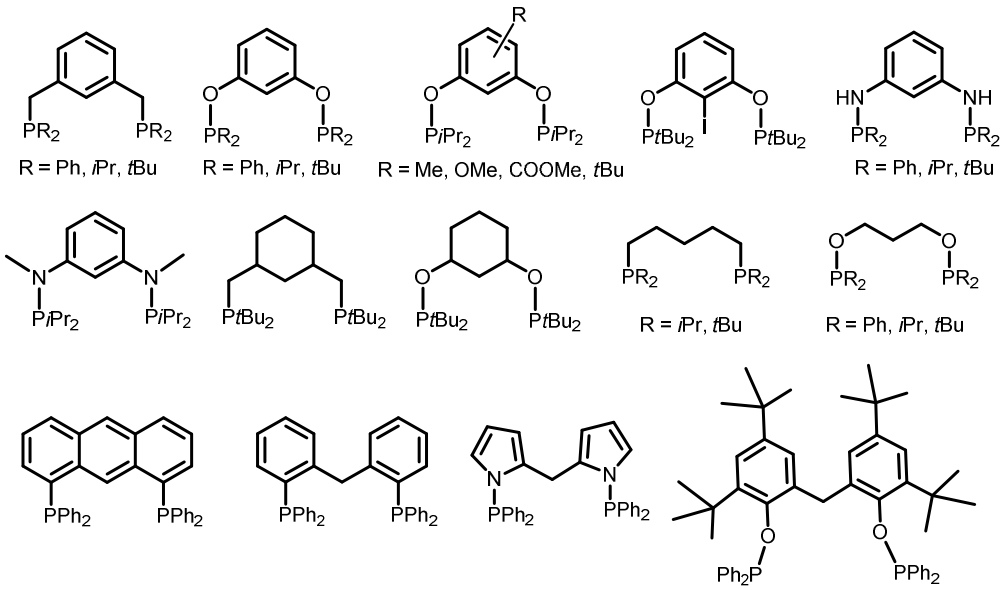


Chart 1 Overview of PCP ligand motifs which are applied to non-precious metals

2. Nickel PCP Pincer Complexes

The first PCP nickel complexes were prepared and characterized by Shaw[3] in 1976. Since then the chemistry of nickel PCP complexes increased significantly particularly in the last decade.[4,5,6,7] Several [Ni(PC*sp*^{2}P)(X)] and [Ni(PC*sp*^{3}P)(X)] (X= Cl, Br, I) complexes, which are the most common synthetic entries into nickel PCP chemistry, were prepared by treating simple nickel halides with the respective pincer ligands in the presence of base. This led to the synthesis of a variety of new nickel complexes as shown in Chart 2.[3,4,6,8,9,10,11,12,13,14,15,16,17,18,19]

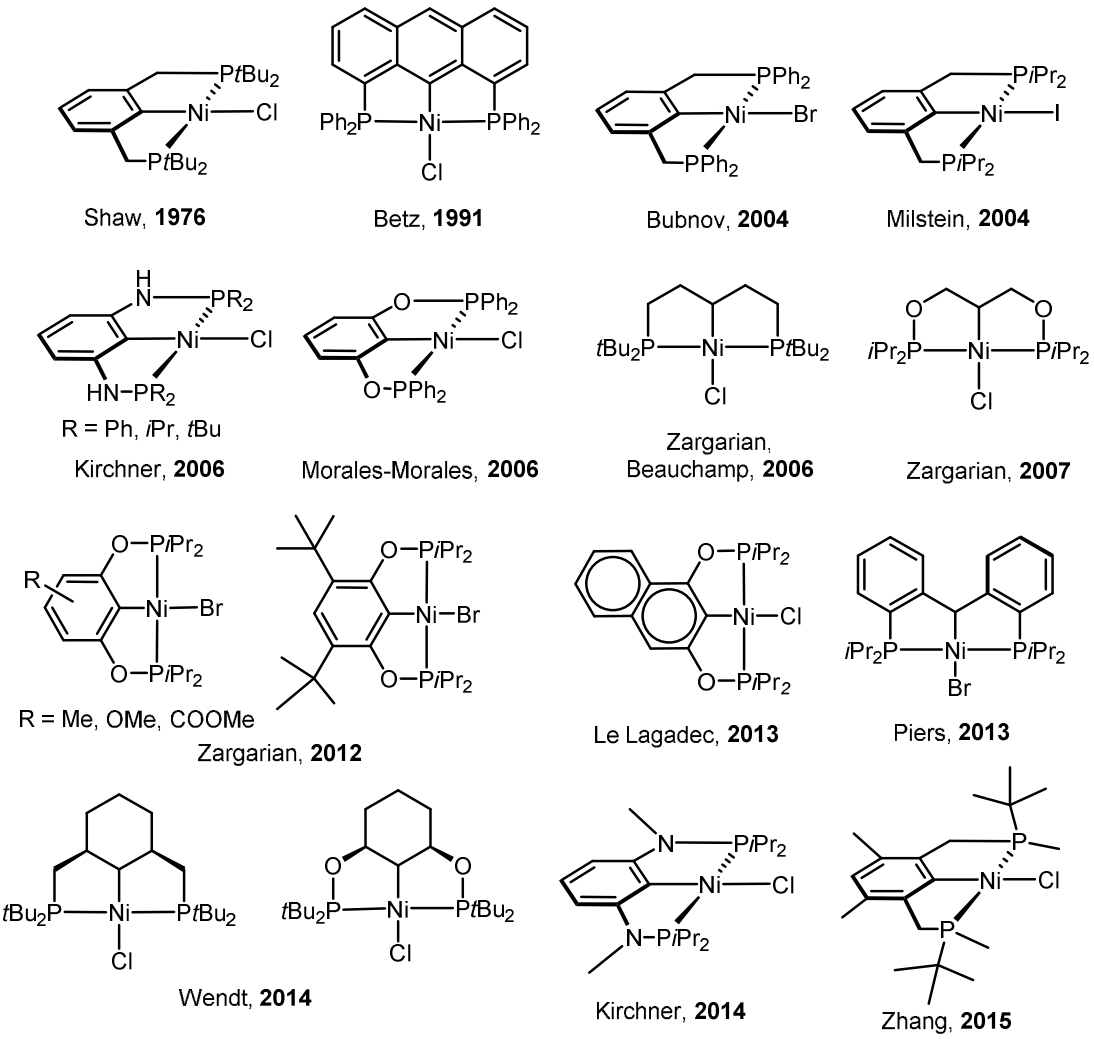
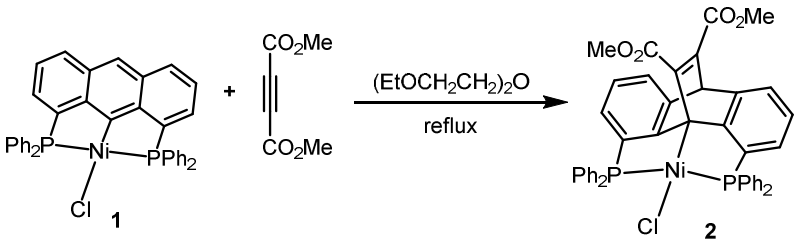


Chart 2 Overview of common Ni(II) PC*sp*^{2}P and PC*sp*^{3}P pincer precursors

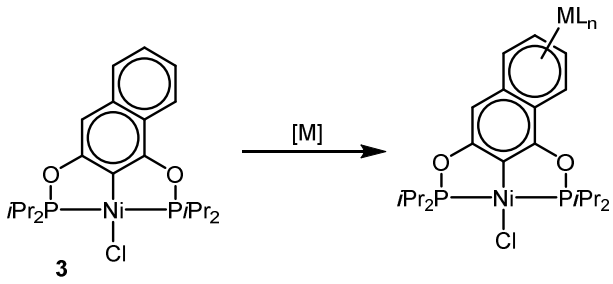
Betz and co-workers prepared complex **1** bearing an anthracene-based PC*sp*^{2}P ligand.[4] This complex was found to react with dimethyl acetylene dicarboxylate as dienophile in a [4+2] Diels-Alder

cycloaddition to yield complex **2**. In the course of this reaction, complex **1** which contains a nickel-Csp^2 bond, is transformed into a complex with a nickel-Csp^3-bond (Scheme 2).[20]



Scheme 2 [4+2] Diels-Alder cycloaddition at the aromatic PCsp^2P backbone of complex **1** with acetylene dicarboxylate

A series of heterobimetallic complexes[17] were prepared in good yields by η^6 coordination of the fragments $[Cp^*Ru]^+$, $[CpRu]^+$, $[CpFe]^+$, and $[Cr(CO)_3]$ to the aromatic ring of the non-symmetric Ni(II) PCP compound **3**. The molecular structures of these new compounds were unequivocally determined by single-crystal X-ray crystallography. The reaction is regiospecific and only coordination at the non-cyclometalated ring was observed (Scheme 3).

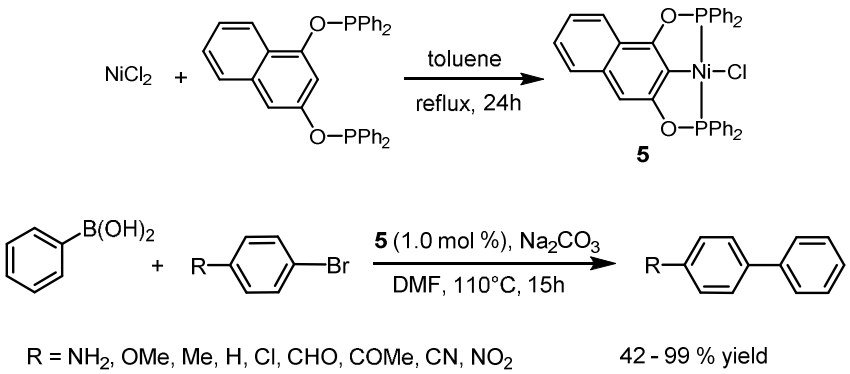


[M] = $[Cp^*Ru(CH_3CN)_3]PF_6$ ML_n = $[Cp^*Ru]PF_6$ **4a**
$[CpRu(CH_3CN)_3]PF_6$ $[CpRu]PF_6$ **4b**
$[Cp_2Fe]$ / NH_4PF_6 $[CpFe]PF_6$ **4c**
$[Cr(C_{10}H_8)(CO)_3]$ $Cr(CO)_3$ **4d**

Scheme 3 Preparation of η^6,η^1-bimetallic nickel PCsp^2P complexes

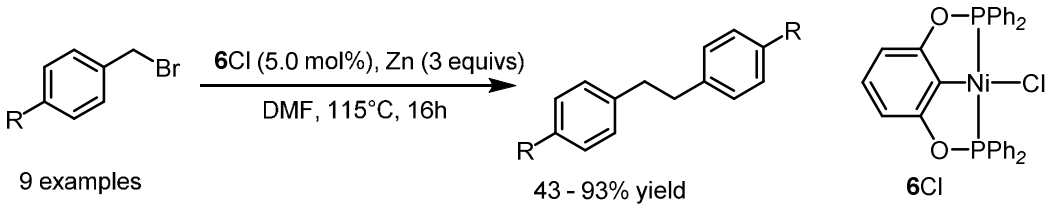
Treatment of anhydrous $NiCl_2$ with a non-symmetric PCP pincer based on a naphthoresorcinol frame under base free conditions afforded the air and moisture stable 16e square-planar complex [Ni(PCsp^2P)(Cl)] (**5**) in good yield (Scheme 4).[21] Complex **5** is a very efficient and robust catalyst which exhibits a comparable performance in the Suzuki–Miyaura cross coupling reactions as that of similar Pd(II) pincer systems albeit with longer reaction periods and larger catalytic amounts of catalysts (1.0% Ni *versus* 0.1% Pd). The cross-coupling of different *para*-substituted bromobenzenes with phenylboronic acid produced high yields of the corresponding biphenyl derivatives (Scheme 4). Another attractive characteristic of the present system is the easy synthesis from cheap commercially available starting

materials and the use of considerable cheaper and biocompatible Ni(II), thus making this system attractive for its potential application in organic synthesis.



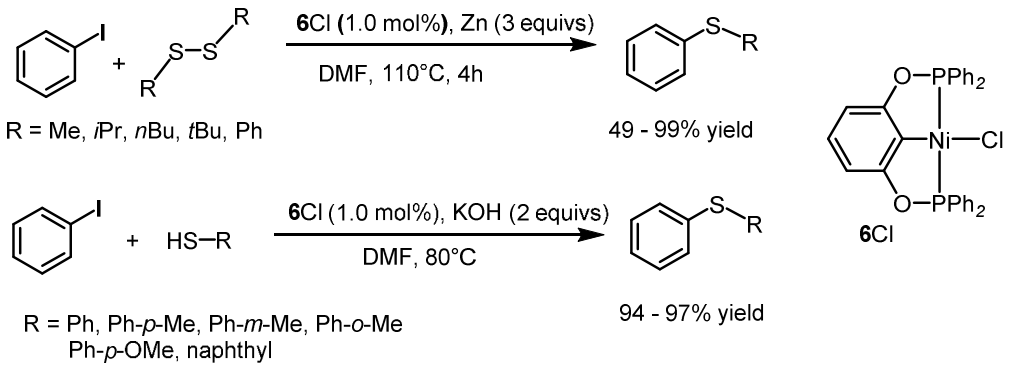
Scheme 4 Synthesis [Ni(PC*sp*^{2}P)Cl] (**5**) and its catalytic activity in the Suzuki-Miyaura cross coupling

Interestingly, the closely related complex **6**Cl featuring a benzene rather than a naphthalene backbone reacted with *para*-substituted benzyl bromides in the presence of Zn as reducing agent to afford only homo coupling products (Scheme 5).[22] The scope of the homo coupling reaction was explored with a variety of functionalized benzyl bromides. Excellent GC yields (75 - 99%) were achieved in most cases. Benzylbromides with electron-donating substituents on the phenyl ring tend to offer slightly better yields than those with electron-withdrawing groups. It was proposed that the Ni(II) PCP complex **6**Cl was reduced to a Ni(I) species which promotes C-Br bond cleavage thereby forming a Ni(II) pincer bromide intermediate along with the benzyl radicals, which underwent dimerization to afford homo coupling products.



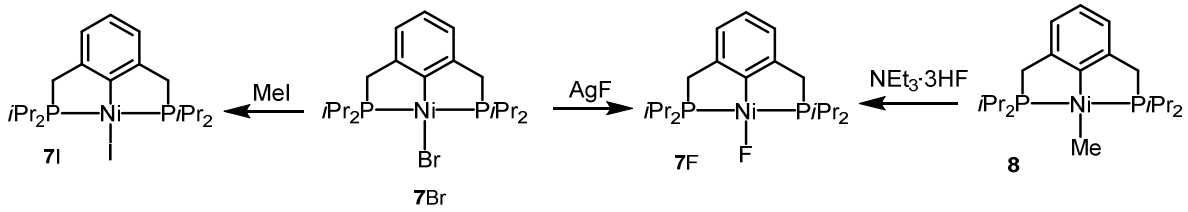
Scheme 5 Homocoupling of *para*-substituted benzylbromides catalyzed by complex **6**Cl

Moreover, complex **6**Cl also efficiently catalyzes the thiolation (C-S cross coupling) of iodobenzene with a broad scope of disulfides in the presence of Zn as reducing agent in DMF at 110°C (Scheme 6).[23] The coupled products were obtained in excellent and, in many cases, nearly quantitative yields. Another interesting direct C-S bond formation was discovered by Guan *et al.*[24] They were able to obtain thioethers in good to excellent yields (49-97%) from the reaction of iodobenzene with different aryl substituted thiols in the presence of **6**Cl (1.0 mol%) and KOH in DMF at 80°C (Scheme 6).



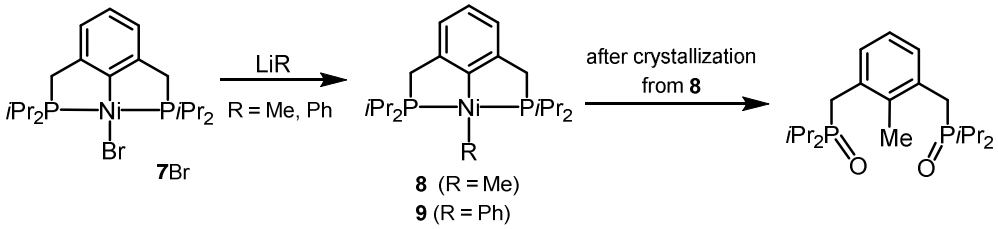
Scheme 6 C-S bond forming reactions catalyzed by the Ni(II) PCsp^2P complex **6**Cl

A series of complexes of the type [Ni(PCsp^2P)(L)] containing the 2,6-bis-(diisopropyl-phosphinomethyl)phenyl pincer ligand and simple monoanionic ligands L (L = F, Cl, Br, H, Me, Ph, NO_3, CF_3SO_3) were synthesized and characterized. The fluoride derivatives were prepared from bromide complexes (**7**Br) by exchange reactions with AgF or, by protonolysis of the methyl complexes [Ni(PCsp^2P)(Me)] (**8**) with $NEt_3 \cdot 3HF$ affording complex **7**F. Upon treatment of complex **7**Br with MeI halogen exchange took place to yield complex **7**I (Scheme 7).[25]



Scheme 7 Formation of halide complexes [Ni(PCsp^2P)(X)] (X = F, Cl, Br, I) (**7**F, **7**Cl, **7**Br, **7**I)

Transmetallation reactions of the halide complex **7**Br with methyl or phenyllithium also proceeded easily affording the corresponding alkyl and aryl derivatives [Ni[(PCsp^2P)(R)] (R = Me, Ph) **8** and **9** in good yields. These complexes are thermally stable, and they resist exposure to air for some time in the solid state. However, during one of the attempts to crystallize the nickel methyl complex colorless crystals were isolated.

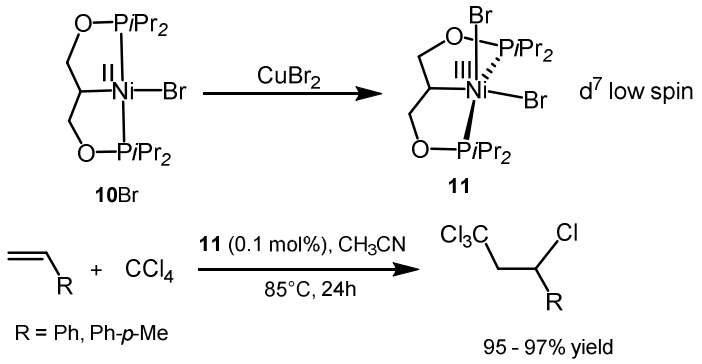


Scheme 8 Synthesis of [Ni(PCsp^2P)(Me)] (**8**) and [Ni(PCsp^2P)(Ph)] (**9**) *via* transmetallation

These were identified as the diphosphine oxide 1-Me-2,6-(iPr$_2$P(O)CH$_2$)$_2$C$_6$H$_3$, where the methyl group saturated the *ipso* position originally bound to nickel, suggesting that the reaction with oxygen induces the reductive coupling of the methyl and the pincer ligand (Scheme 8).[25]

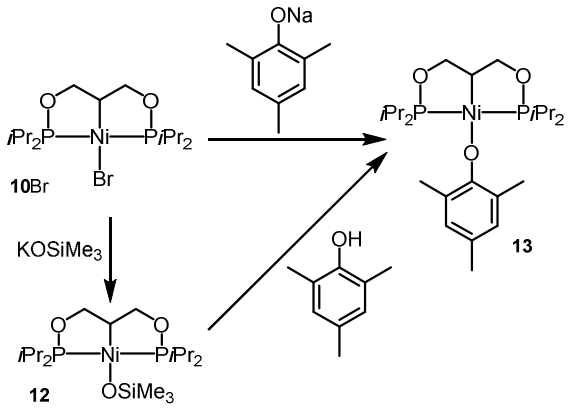
The first paramagnetic Ni(III) PCsp^3P pincer complex [Ni(PCsp^3P)(Br)$_2$] (**11**) was synthesized by reacting complex **10**Br with copper (II) bromide in hexane or acetone solutions (Scheme 9).[26] The paramagnetism of **11** was confirmed by determining the magnetic moment in solution by the Evans method giving a value of μ_{eff} of 1.73 μ_B. This corresponds to one unpaired electron. Later on, related complexes of the type [Ni(PCsp^3P)(X)$_2$] (X = Cl, Br) were also reported by Zargarian and co-workers.[27] Complex **11** was formed due to the facile establishment of the strong Ni-Csp^3 bond and presumably due to the higher flexibility of the aliphatic backbone. On the other hand, the analogous [Ni(PCsp^2P)(Br)] complex,[10,26] which features a Ni-Csp^2 sigma bond and a more rigid aromatic backbone, seems to favor the Ni(II) oxidation state in a square planar geometry and does not react with Cu(II) bromide to form a Ni(III) complex.

The paramagnetic Ni(III) complex **11** promotes the addition of CCl_4 to methyl acrylate, methyl methacrylate, styrene, 4-methylstyrene, acrolein, and acrylonitrile (Kharasch reaction).[26] This reaction takes place in refluxing acetonitrile and afforded functionalized alkanes in 95 - 97% isolated yield (Scheme 9). It has to be noted that related Ni(III) NCN complexes were reported to be catalytically active for the Kharasch addition.[28,29,30]



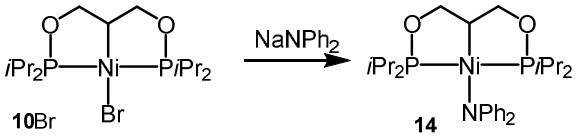
Scheme 9 Synthesis of the Ni(III) complex [Ni(PCsp^3P)(Br)$_2$] (**11**) which promotes the Kharasch addition of CCl_4 to olefins

Zargarian and co-workers prepared a series of Ni(PCsp^3P) complexes which are relevant to catalytic hydroalkoxylation and hydroamination of olefins, C-C and C-X couplings and fluorination of alkyls.[31] Treatment of **10**Br with an excess of potassium trimethylsilanolate and sodium 2,4,6-trimethlyphenolate to afford the thermally stable complexes **12** and **13**, respectively (Scheme 10). Complex **12** was also converted to **13** by protonolysis with mesitol. In contrast to the clean formation of these derivatives, the analogous reaction with KOtBu, under the same conditions, led instead to complete decomposition (Scheme 9).



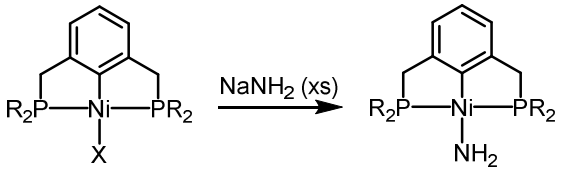
Scheme 10 Synthesis of [Ni(PCsp^3P)(OSiMe$_3$)] (**12**) and [Ni(PCsp^3P)(OMes)] (**13**)

While amides bearing aliphatic N-substituents reacted with **10**Br to unstable derivatives, the diphenylamido derivative **14** was obtained by treatment of complex **10**Br with sodium diphenylamide (Scheme 11).[31] The analogous hexamethyldisilazide derivative also proved to be thermally unstable, leading to intractable yellow solids.



Scheme 11 Synthesis of [Ni(PCsp^3P)(NPh$_2$)] (**14**) *via* halide displacement by diphenylamide

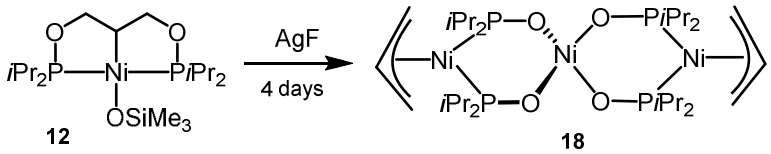
It is interesting to note that related nickel complexes with PCsp^2P backbones based on the bis-2,6-di-*tert*-butylphosphinomethyl- and bis-2,6-di-*iso*-propylphosphinomethylbenzene scaffolds (**7**Br, **15**Cl) reacted with an excess of sodium amide to afford complexes [Ni(PCsp^2P)(NH$_2$)] (**16**, **17**) (Scheme 12).[25,32,33]



Scheme 12 Synthesis of [Ni(PCsp^2P)(NH$_2$)] complexes **16** and **17**

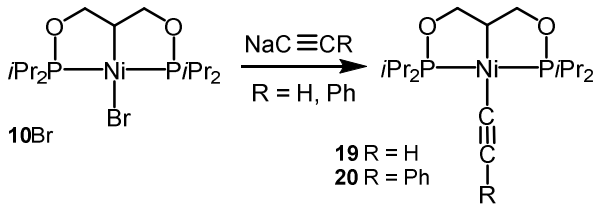
Attempts to obtain the fluoride derivative of **10**Br proved inaccessible as the reaction of **10**Br with AgF led to a colorless solution and an intractable black precipitate. Slow decomposition also resulted from the reaction of **12** with AgF, but in this case the unusual trinuclear complex **18** could be isolated from the

reaction mixture. Complex **18** is a zwitterionic species featuring two allyl $[Ni(\eta^3\text{-}C_3H_5)]^+$ fragments, each coordinated by two phosphorus atoms of the central $[Ni(i\text{Pr}_2\text{PO})_4]^{2-}$ unit. The central Ni atom adopts a tetrahedral coordination geometry defined by four oxygen atoms. The mechanism of this transformation remains elusive, but the finding that ambient light plays a crucial role in initiating the decomposition process implies a radical initiated reaction sequence (Scheme 13).[31] Zwitterions were implicated as a reason for lower yields of aliphatic pincer complexes.[13-15]



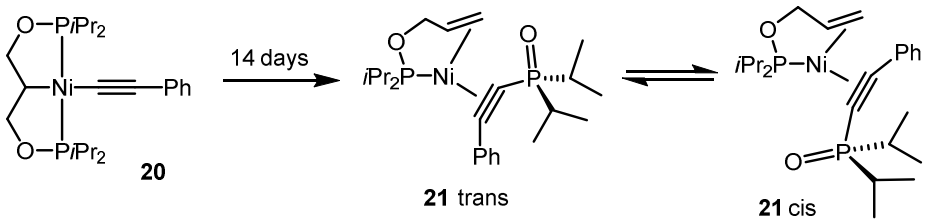
Scheme 13 Formation of a zwitterionic trinuclear nickel complex **18** featuring anionic $\eta^3\text{-}C_3H_5$ and $i\text{Pr}_2\text{PO}$ moieties.

A different but related decomposition reaction of the PC*sp*^{3}P ligand was noted during the synthesis of alkynyl derivatives. Reaction of **10**Br with sodium acetylides (NaC≡CH, NaC≡CPh) at room temperature led to full conversion of the starting material into alkynyl derivatives **19** and **20** (Scheme 14).[31]



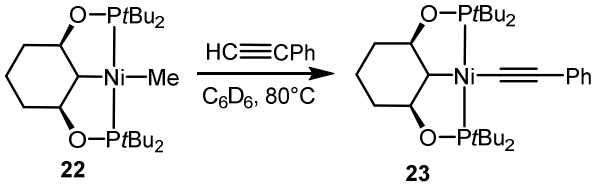
Scheme 14 Synthesis of [Ni(PC*sp*^{3}P)(C≡CR)] (R = H, Ph) (**19** and **20**)

Attempts at growing single crystals of **20** were circumvented by a gradual decomposition. A solution of complex **20** stirred in hexane for two weeks at room temperature resulted in a complex rearrangement reaction to give complex **21** as a mixture of *trans* and *cis* isomers, with the *trans* isomer being the major species. Notably, both isomers of **21** are very stable in non-polar solvents such as hexane, benzene or toluene even at higher temperatures for several hours, whereas in chlorinated solvents decomposition took place even at ambient temperature within a few hours. The structure of the *cis* isomer of **21** was determined by X-ray crystallography and shows that this complex consists of a Ni(0) center ligated by a bidentate phosphinite-alkene and a π-coordinated phosphinoxy alkyne, both originating from the PC*sp*^{3}P and phenylacetylide ligands. The alkyne and alkene fragments can be treated as two-π-electron-donor moieties (Scheme 15).[31]



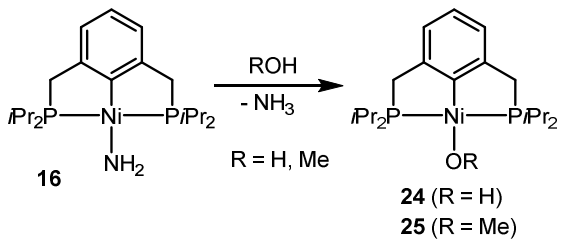
Scheme 15 Unexpected rearrangement of **20** in solution

The cyclohexyl-based PC*sp*^{3}P pincer ligand *cis*-1,3-bis(di-*tert*-butylphosphinito)cyclohexyl) cyclometalated with nickel to generate a series of new Ni(II) complexes including halide, hydride, methyl, and phenyl species.[14] The reactivity of [Ni(PC*sp*^{3}P)(Me)] (**22**) towards phenyl acetylene was also investigated showing a gradual conversion to the acetylide complex **23** over a period of 6 days, upon heating to 80°C. A coincident formation of CH_4 was observed by means of ^{1}H NMR spectroscopy (δ = 0.15 ppm in C_6D_6). However, full conversion of **22** was not achieved even upon prolonged reaction times, but no product was obtained besides **23**, which could be obtained in pure form by crystallization from hexane (Scheme 16).

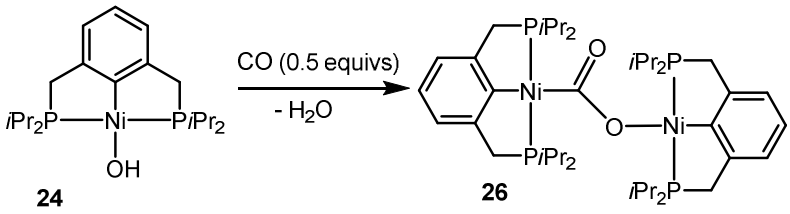


Scheme 16 Synthesis of [Ni(PC*sp*^{3}P)(C≡CPh)] (**23**)

The parent amido complex, [Ni(PC*sp*^{2}P)(NH_2)] (**16**) reacted quantitatively with water and methanol to give the mononuclear hydroxide and methoxide derivatives [Ni(PC*sp*^{2}P)(OH)] (**24**) and [Ni(PC*sp*^{2}P)(OMe)] (**25**), respectively (Scheme 17).[33] Alternatively, [Ni(PC*sp*^{2}P)(OH)] (**24**) was formed also if [Ni(PC*sp*^{2}P)(Br)] (**7**Br) was treated with an excess of KOH or NaOH.[34] Treatment of solution of [Ni(PC*sp*^{2}P)(OH)] (**24**) with 0.5 equivs of carbon monoxide afforded the dinuclear complex {[Ni(PC*sp*^{2}P)]$_2$($\mu$$CO_2$-$\kappa^2$*C,O*)} (**26**) (Scheme 18).[34]

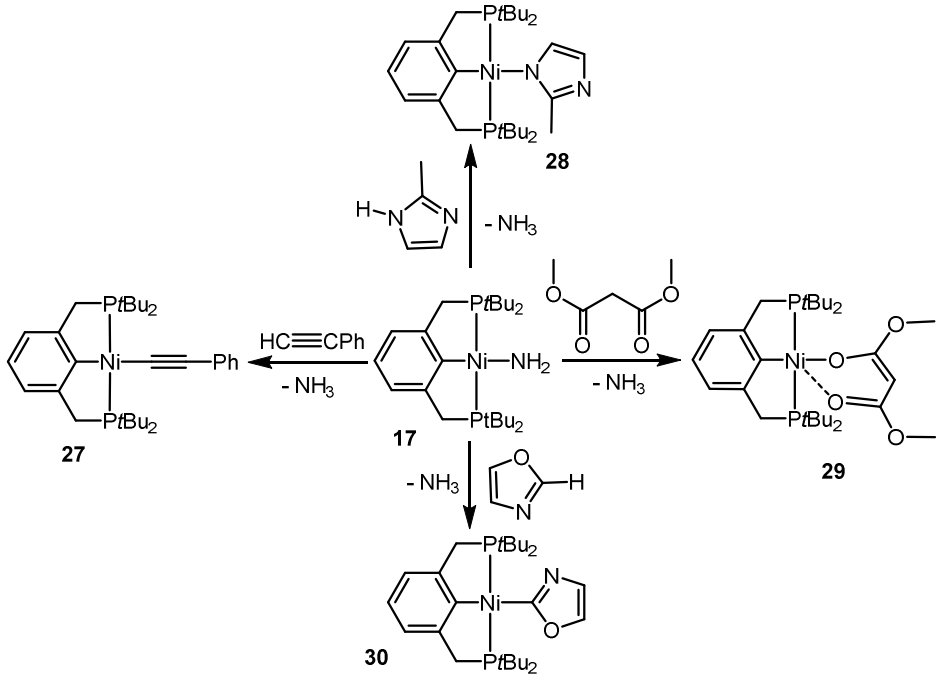


Scheme 17 Synthesis of the hydroxy and methoxy complexes [Ni(PC*sp*^{2}P)(OH)] (**24**) and [Ni(PC*sp*^{2}P)(OMe)] (**25**)

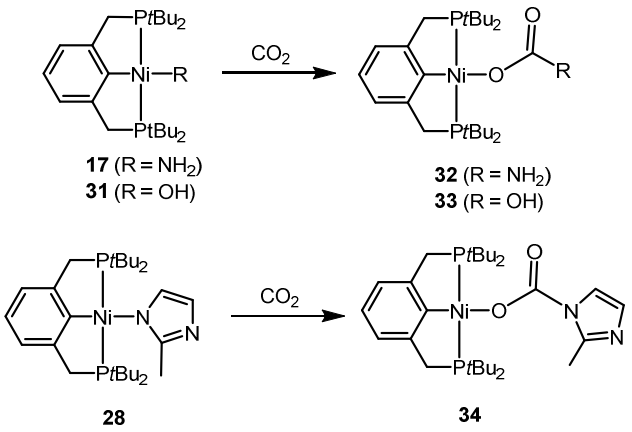


Scheme 18 Insertion of CO into the Ni-O bond of [Ni(PCsp^2P)(OH)] (**24**)

Complex [Ni(PCsp^2P)(NH_2)] (**17**) reacted with several substrates bearing acidic C-H bonds such as phenyl acetylene, imidazole, dimethyl malonate and oxazole to form complexes **27-30**. In the course of this reaction NH_3 is liberated (Scheme 19).[32] These complexes are able to insert carbon dioxide into the nickel-ligand bonds, which is a thermodynamically very favorable process. An example is depicted in Scheme 20. This was shown both experimentally and by means of DFT calculations.[32]

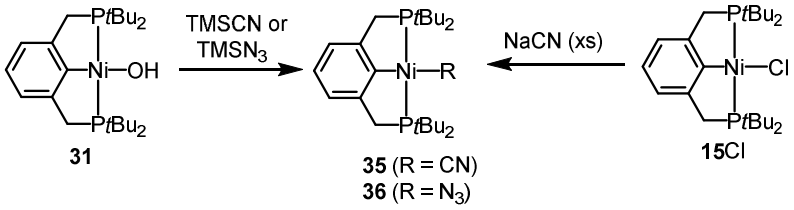


Scheme 19 Liberation of NH_3 gas from [Ni(PCsp^2P)(NH_2)] (**17**) upon treatment with C-H and N-H acidic compounds



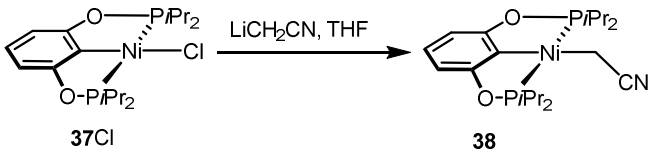
Scheme 20 Carbon dioxide insertion into the nickel-ligand bonds of [Ni(PC*sp*^{2}P)] complexes

Complexes **35** and **36** were prepared by reacting complex [Ni(PC*sp*^{2}P)(OH)] (**31**) with trimethylsilyl cyanide and trimethylsilyl azide, respectively. These two complexes are also able to insert carbon dioxide into the nickel-ligand bond (Scheme 21).[32] The synthesis of complex **35** was also described in an earlier report[3] by the reaction of nickel complex **15**Cl with sodium cyanide in acetone. This complex was, however, not fully characterized.

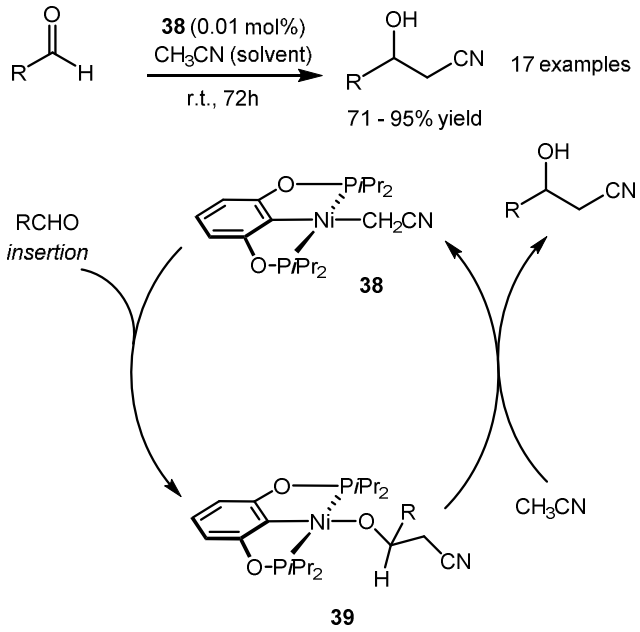


Scheme 21 Synthesis of [Ni(PC*sp*^{2}P)(CN)] (**35**) and [Ni(PC*sp*^{2}P)(N_3)] (**36**)

Guan and co-workers treated Zargarian's complex **37**Cl[10] with $LiCH_2CN$ to obtain the nickel cyanomethyl complex **38** in good isolated yield (Scheme 22).[35] Complex **38** turned out to be an incredibly robust nickel catalyst for the cyanomethylation of aldehydes under base free conditions with unprecedentedly high turnover numbers and frequencies. This was achieved in the presence of merely 0.01 mol % of **38** as catalyst in acetonitrile as solvent (Scheme 23).[35] The reaction was performed at room temperature with a reaction time of 72h. In some cases TONs of 82000 and TOFs of 1139 h^{-1} were achieved. Mechanistic studies suggested reversible insertion of aldehydes into the nickel-carbon bond of the cyanomethyl complex and subsequent C-H bond activation of acetonitrile by the nickel alkoxide intermediate **39**.

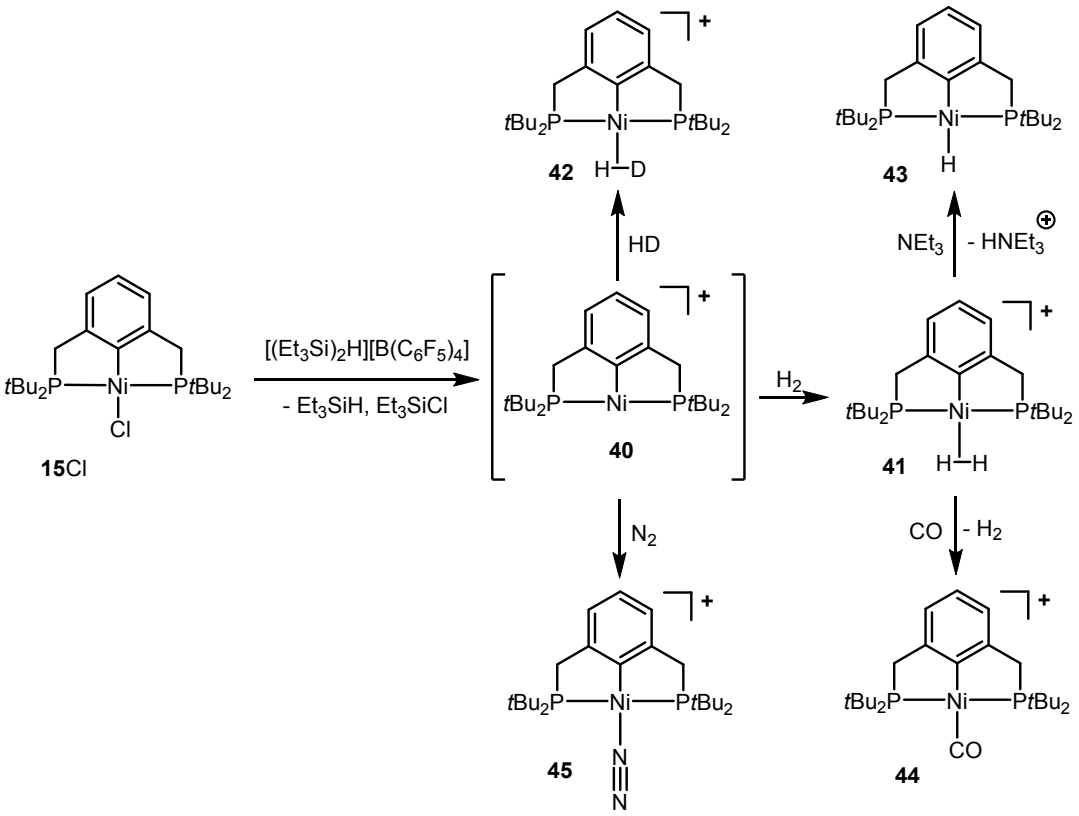


Scheme 22 Synthesis of [Ni(P*Csp*^{2}P)(CH$_2$CN)] (**38**)



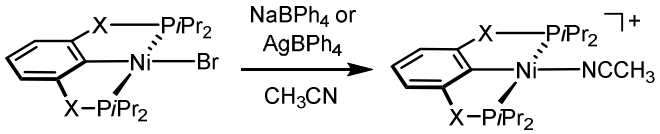
Scheme 23 Cyanomethylation of aldehydes catalyzed by [Ni(PC*sp*^{2}P)(CH$_2$CN)] (**38**)

Kemp and co-workers originally reported[36] the synthesis of the chloro complex [Ni(PC*sp*^{2}P)(Cl)] (**15**Cl). The chemistry of this compound was further investigated by Heinekey and co-workers who prepared several cationic Ni(II) complexes.[37] Upon treatment of complex **15**Cl with {[(Et$_3$Si)$_2$H][B(C$_6$F$_5$)$_4$]} as chloride scavenger, the coordinatively unsaturated intermediate **40** was formed, which reacted readily with both H_2 and HD to form complexes **41** and **42**, respectively. Complex **41** is the first isolated and structurally characterized nickel–dihydrogen complex. The H_2 ligand is heterolytically cleaved in the presence of base to form mono hydride complex **43**. The dihydrogen ligand is also easily displaced by carbon monoxide to yield the carbonyl complex **44** or by dinitrogen to form complex **45** which is a rare example of a Ni(II) terminal dinitrogen complex (Scheme 24).



Scheme 24 Synthesis of several cationic Ni(II) PC*sp*^{2}P complexes after halide abstraction from **15**Cl.

Zargarian and co-workers were exploring some reactivities of neutral [Ni(PCP)(Br)] complexes which contain both PC*sp*^{2}P or PC*sp*^{3}P ligands. Treatment of complexes **7**Br and **37**Br with sodium or silver tetraphenyl borate in the presence of acetonitrile as coordinating solvent afforded cationic complexes of the types **46** and **47** (Scheme 25).[38] These complexes adopt a distorted square-planar geometry around the nickel center.



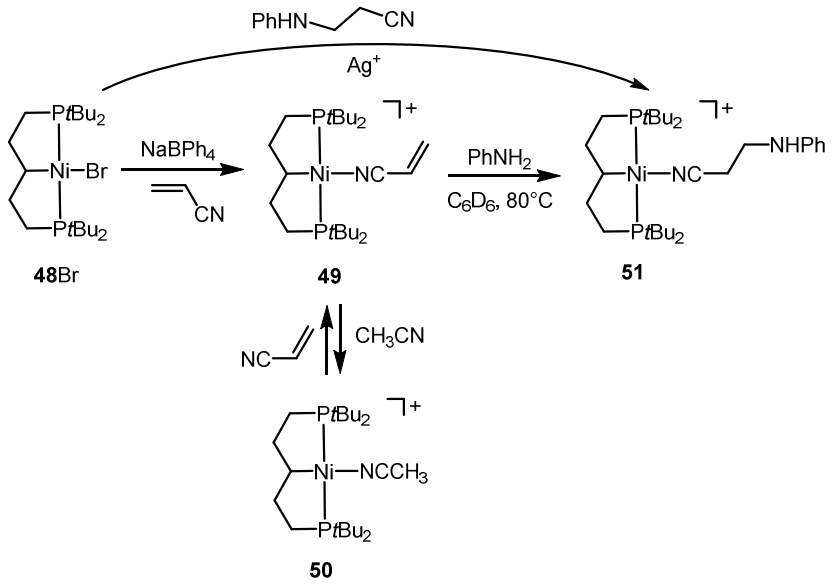
7Br (X = CH_2)
37Br (X = O)

46 (X = CH_2)
47 (X = O)

Scheme 25 Synthesis of the cationic complexes [Ni(PC*sp*^{2}P)(CH_3CN)] (**46, 47**)

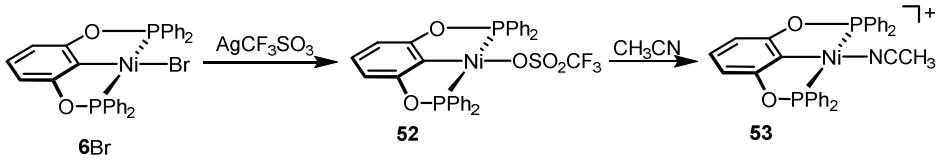
Zargarian, Beauchamp, and co-workers prepared the nitrile complexes **49** and **50** directly *via* the reaction of **48**Br with $NaBPh_4$ in neat acrylonitrile and acetonitrile, respectively (Scheme 26).[15] These complexes, however, were inert towards olefins. On the other hand, complex **50** underwent reversible substitution of the acrylonitrile ligand by acetonitrile.[15] Isolation of **51** from the reaction of **49** with aniline

suggests that these cationic precursors act as Lewis acids that bind the nitrile moiety of acrylonitrile, thereby activating the olefin moiety towards nucleophilic attack by aniline. Alternatively, complex **51** was synthesized by the reaction of complex **48**Br with 3-anilinepropionitrile in presence of a silver salt.[38]



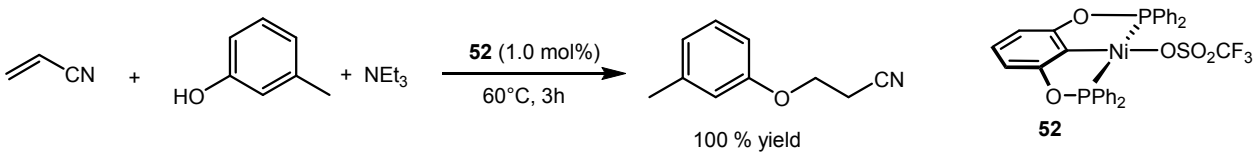
Scheme 26 Synthesis of the cationic complexes [Ni(PCsp^3P)(N≡C-CH=CH_2)] (**49**), [Ni(PCsp^3P)(N≡CCH_3)] (**50**) and [Ni(PCsp^3P)(N≡C-CH_2CH_2NHPh)] (**51**)

Bromide abstraction from complex **6**Br with $AgCF_3SO_3$ in presence of CH_2Cl_2 at room temperature for 3h afforded the air sensitive compound **52**, which was readily converted by addition of acetonitrile to complex **53** which interestingly was resistant towards hydrolysis and/or oxidation (Scheme 27).[39]



Scheme 27 Synthesis of [Ni(PCsp^2P)(CF_3SO_3)] (**52**) and [Ni(PCsp^2P)(CH_3CN)]$^+$ (**53**)

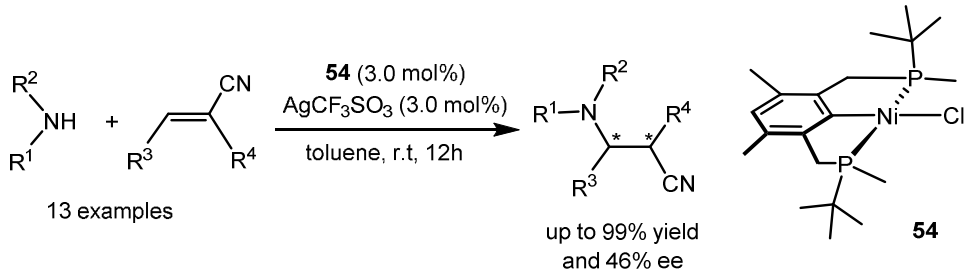
A variety of alcohols were treated with acrylonitrile in the presence of the Ni(II) diphosphinito PCP pincer catalyst **52** and NEt_3, which led to the formation of a C-O bond containing product (Scheme 28).[40,41] Among these alcohols, only with 3-methyl phenol complete conversion could be achieved. Notably, without the addition of NEt_3 no reaction took place. Moreover, this reaction did not succeed with more nucleophilic alcohols such as methanol, ethanol, and isopropanol, due to decomposition of the catalyst.



Scheme 28. Alcoholysis of acrylonitrile catalyzed by the neutral Ni(II) catalyst **52**

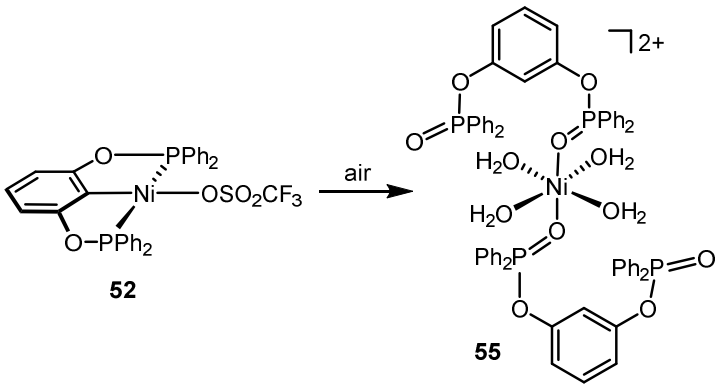
The pincer complex **47** served also as a precatalyst for the regioselective anti-Markovnikov addition of nucleophiles to activated olefins.[41] The catalyzed additions of aliphatic amines to acrylonitrile, methacrylonitrile, and crotonitrile proceed at room temperature and give quantitative yields of products resulting from the formation of C–N bonds. On the other hand, aromatic amines or alcohols are completely inert toward methacrylonitrile and crotonitrile, and much less reactive toward acrylonitrile, requiring added base, heating, and extended reaction times to give good yields. The catalytic reactivities of **47** seem to arise from the substitutional lability of the coordinated acetonitrile that allows competitive coordination of the nitrile moiety in the olefinic substrates. Zargarian and co-workers[10,38,39,40,41] also described in an earlier report that a series of Ni(II) pincer complexes were evaluated as catalysts for the regioselective hydroamination of acrylonitrile. This Michael addition is favored when the generation of cationic Ni(II) species, therefore, α,β-unsaturated nitrile could coordinate to the Ni(II) center, followed by nucleophilic addition of free amine substrate to the activated double bond, then non-reductive elimination of aza-Michael addition product.

Very recently, Zhang and co-workers showed that the P-stereogenic pincer nickel complex **54** is an active catalysts for the asymmetric aza-Michael addition of α,β-unsaturated nitriles providing the products in good to excellent yields (up to 99%) and moderate enantiomeric excesses (up to 46% ee). With 2-phenylacrylonitrile the desired product was obtained in quantitative yield, but without any enantiomeric excess (Scheme 29).[8]



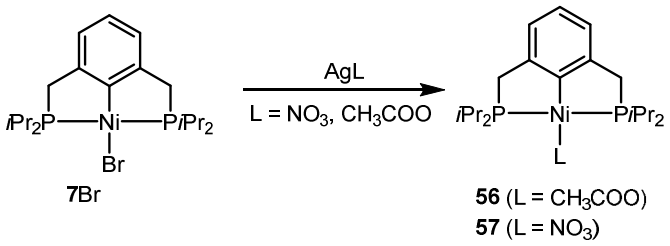
Scheme 29 Hydroamination of crotonitrile catalyzed by the chiral cationic Ni(II) pincer complex **54**

Hydrolytic decomposition[39] of complex **52** at the ambient room temperature in presence toluene as solvent for 2 days resulted the formation of a stable octahedral complex **55**. The formation of this compound presumably proceeds via initial protonation of aryl ring of PCP ligand reforming the aromatic C-H bond followed by oxidation of the phosphine moieties and coordination of water molecules (Scheme 30).



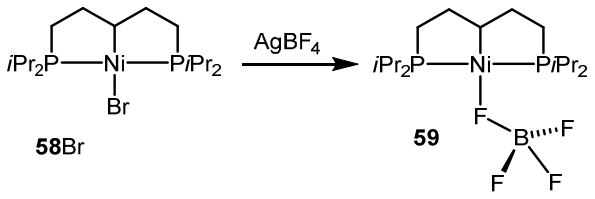
Scheme 30 Synthesis of stable dicationic octahedral Ni(II) complex (**55**) involving protonation and oxidation of the PC*sp*^{2}P ligand

Treatment of complexes **7**Br with stoichiometric amounts of silver salts such as CH_3COOAg and $AgNO_3$ resulted in the formation of complexes **56** and **57**, respectively (Scheme 31). Excess of silver salts caused oxidation of the metal center to give a stable Ni(III) complexes.[25]



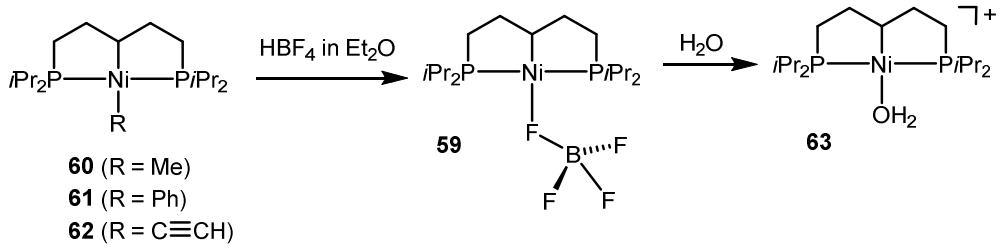
Scheme 31 Synthesis of [Ni(PC*sp*^{2}P)(CH_3OO)] (**56**) and [Ni(PC*sp*^{2}P)(NO_3)] (**57**) by halide displacement

Zargarian and co-workers synthesized the pincer complex [Ni(PC*sp*^{3}P)(κ^1*F*-BF_4)] (**59**) where the weakly coordinating counterion BF_4^- is bound in κ^1*F* fashion (Scheme 32).[42] Accordingly, the BF_4^- ligand is highly fluxional. This species was used to prepare cationic adducts with relatively weak nucleophiles such as water to form for instance the aquo complex [Ni(PC*sp*^{3}P)(H_2O)]$^+$ (**63**) (Scheme 33). Complex **59** was also derived from complexes **60-62** upon addition of tetrafluoroboric acid. Both complexes **59** or **63**

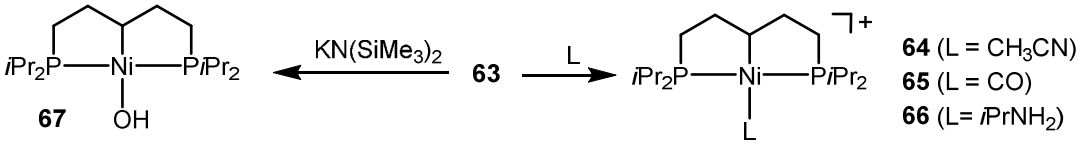


Scheme 32 Synthesis of [Ni(PC*sp*^{3}P)(κ^1*F*-BF_4)] (**59**)

reacted readily with strongly coordinating ligands such as acetonitrile, carbon monoxide, and isopropylamine to afford the cationic complexes **64-66**. In addition, the aquo complex **63** was treated with potassium bis(trimethylsilyl)amide to afford the neutral hydroxo Ni(II) complex **67** (Scheme 34).

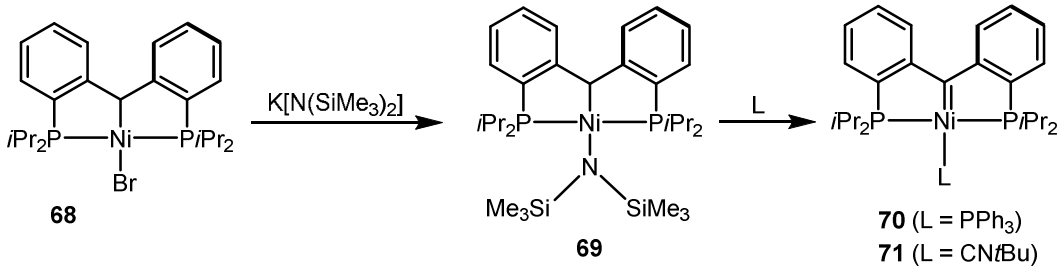


Scheme 33 Synthesis and reactivity of [Ni(PCsp^3P)(κ^1*F*-BF_4)] (**59**)

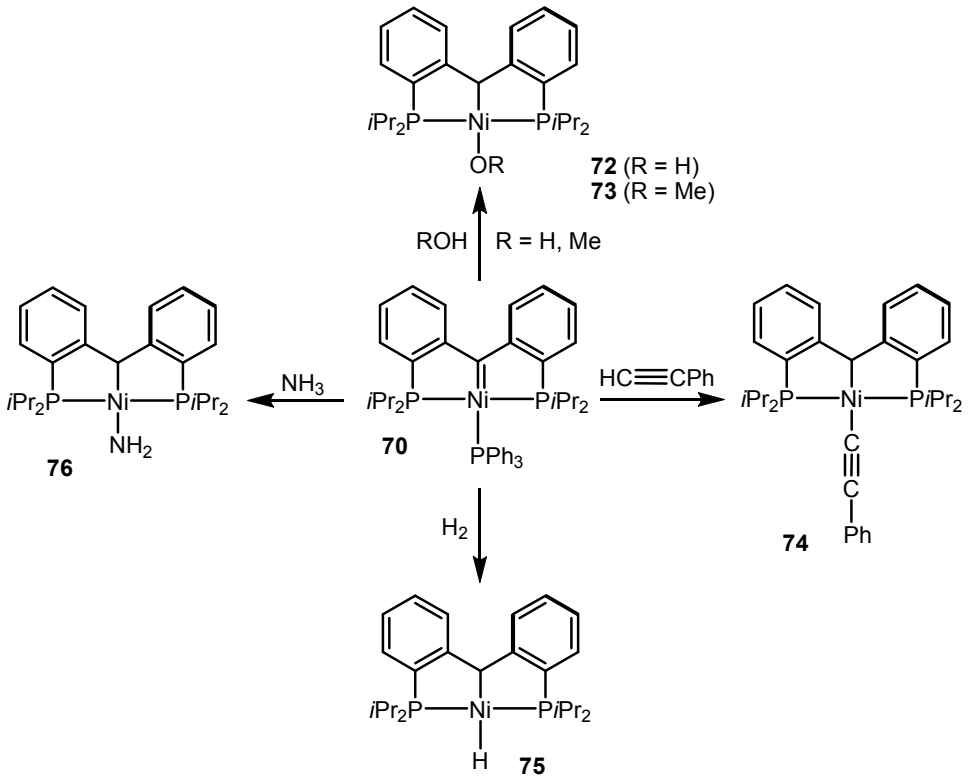


Scheme 34 Reactivity of [Ni(PCsp^3P)(H_2O)]$^+$ (**63**)

Piers and co-workers utilized a $PC_{carbene}P$ ligand framework to prepare new nickel pincer complexes that feature a rare nickel carbene moiety (Scheme 35). These complexes (**70**, **71**) were prepared by treatment of **68** with potassium bis(trimethylsilyl)amide in the presence of the strong ligands PPh_3 or CN*t*Bu in THF as solvent.[16] Intermediate is the bis(trimethylsilyl)amide complex **69**. In these complexes, the nickel carbene donor is non-innocent and engages in a variety of E−H bond activations (E = H, C, N, O), some of which are reversible (Scheme 36).[16] This represents a new mode of bond activation by ligand cooperativity in nickel pincer complexes.

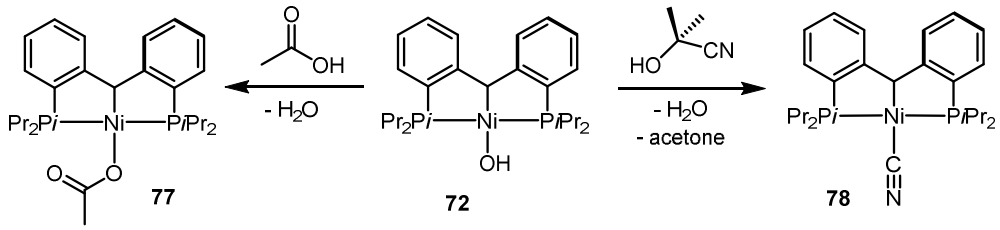


Scheme 35 Synthesis of [Ni($PC_{carbene}P$)(L)] (L = PPh_3, CN*t*Bu) (**70** and **71**)

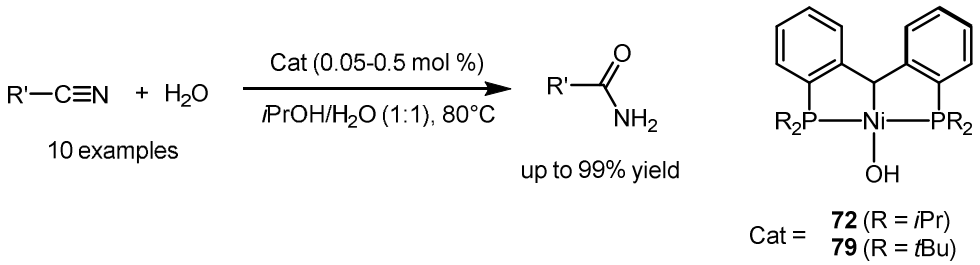


Scheme 36 E−H bond activations (E = H, C, N, O) with the Ni(0) complex **70**

In 2015, Piers and co-workers[43] also described the synthesis of interesting hydroxy PCP complexes of the type [Ni(PC*sp*^{3}P)(OH)] (**72**). The hydroxy group in these complexes is labile as proved by labeling experiments utilizing ^{17}O enriched water and ^{17}O NMR spectroscopy. Compound **72** was shown to react with acetic acid and 2-hydroxy-2-methylpropanenitrile, respectively, to complexes **77** and **78** (Scheme 37). The [Ni(PC*sp*^{3}P)(OH)] complexes (**72** and **79**) are effective catalyst precursors for the selective hydration of nitriles to the corresponding amides under relatively mild conditions (80 °C) and low catalyst loadings (0.05-0.5%). Substrate scope includes aliphatic, vinylic and aromatic nitriles, but substrates with protic groups poison the catalyst abruptly. The catalysts are effective because the electron rich nature of the PCP ligands and their steric bulk renders the hydroxy group labile (Scheme 38).[43]

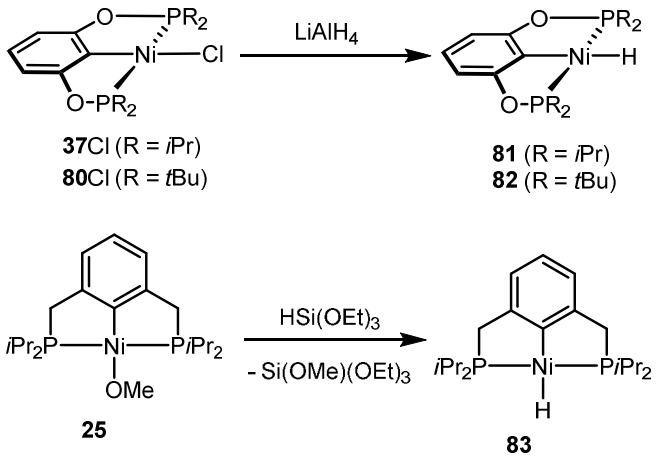


Scheme 37 Synthesis of Ni(II) PC*sp*^{3}P acetate and nitrile complexes



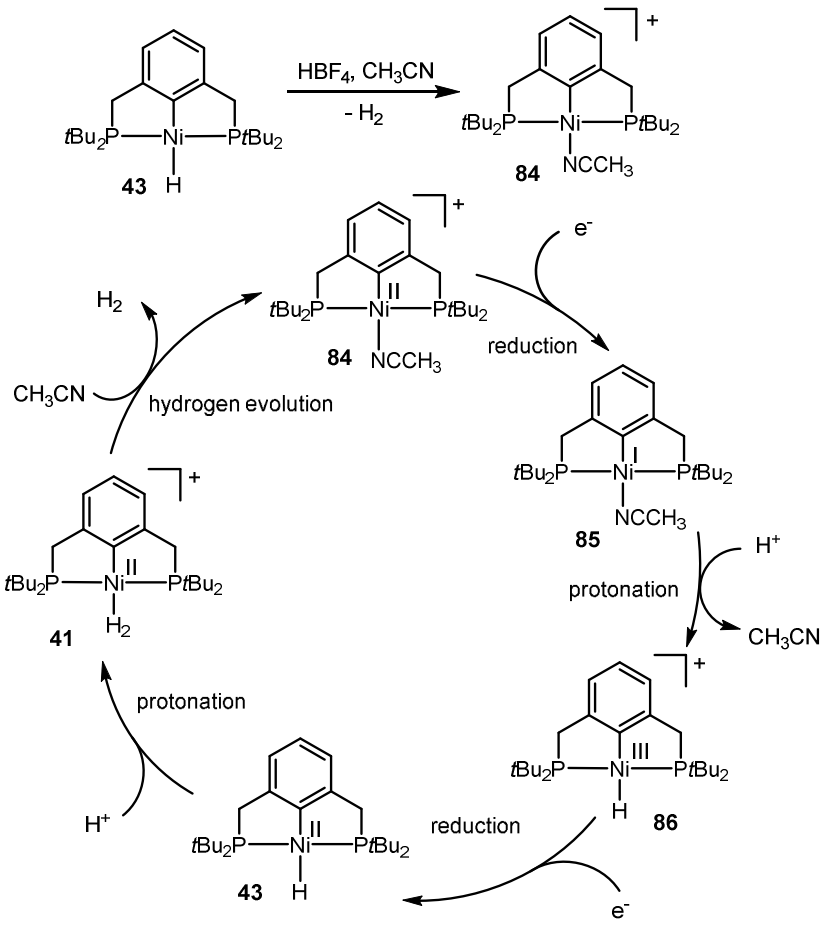
Scheme 38 Hydration of nitriles to amides catalyzed by [Ni(PC*sp*^{3}P)(OH)] (**72** and **79**)

An important class of compounds are hydrides. In the last decade several nickel PC*sp*^{2}P and PC*sp*^{3}P pincer hydride complexes were synthesized.[14,36,44] The typical synthetic route starts from halide complexes. Treatment of **37**Cl and **80**Cl with $LiAlH_4$ in toluene at room temperature for 24h to yield nickel hydride complexes **81** and **82**, respectively (Scheme 39).[45] An alternative synthetic method utilized the nickel methoxy complex **25** and triethoxylsilane to prepare the hydride complex **83** (Scheme 39).[25]



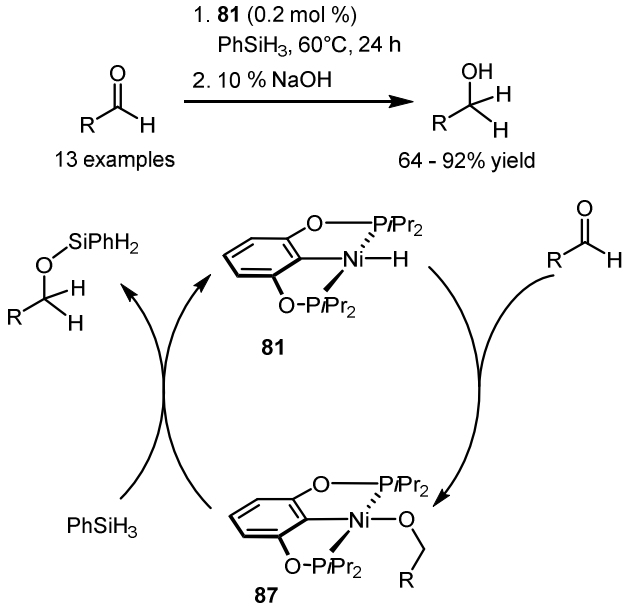
Scheme 39 Synthesis of [Ni(PC*sp*^{2}P)(H)] complexes **81**, **82** and **83**.

Hazari and co-workers reported on the electrocatalytic reduction of protons to H_2 by some nickel pincer complexes. For instance, the Ni(II) PCP pincer hydride complex **43** reacted with HBF_4 in acetonitrile as coordinating solvent to afford the catalytically active cationic nickel complex **84**. Bulk electrolysis experiments were followed by macroscopic determination of the quantity of H_2 produced and demonstrated good Faradaic yields (90 − 95%). Two of the possible intermediate species were isolated and shown to be catalytically active. Computation DFT studies provided corroboration for the proposed catalytic cycle shown in Scheme 40. First, the cationic Ni(II) complex **84** is reduced to give the neutral Ni(I) species **85**. Subsequent protonation displaces the CH_3CN ligand and yields the Ni(III) hydride **86**, which is then reduction to the monohydride Ni(II) species **43**. Protonation gives rise to the dihydrogen Ni(II) species **41** which, in the presence of CH_3CN, finally releases dihydrogen to regenerate the catalyst **84**, thus, completing the catalytic cycle (Scheme 40).[46]



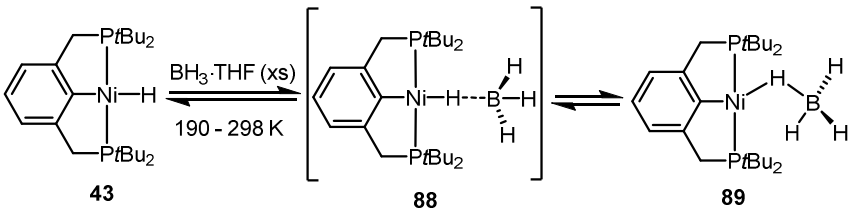
Scheme 40 Proposed catalytic cycle of proton reduction supported by DFT calculations

The hydride Ni(II) PCP pincer complex **81** was tested as catalysts the chemoselective hydrosilylation of C=O bonds of aldehydes and ketones in the presence of other functional groups.[45,47,48] Aldehydes were converted to primary alcohols with 0.2 mol% of catalyst **81** and a slight excess of hydrogen source of phenylsilane followed by basic hydrolysis good to excellent yields (Scheme 41). The mechanism involves C=O insertion into a nickel-hydrogen bond, followed by cleavage of the newly formed Ni-O bond **87** with a silane. It has to be noted that this catalyst did not work well for the hydrosilylation of ketones. For instance, substrates such as acetophenone, cyclohexanone, benzophenone afforded the corresponding alcohols in 18%, 6%, and 60%, respectively, in the presence of 1.0 mol% catalyst at 70°C for 24h.

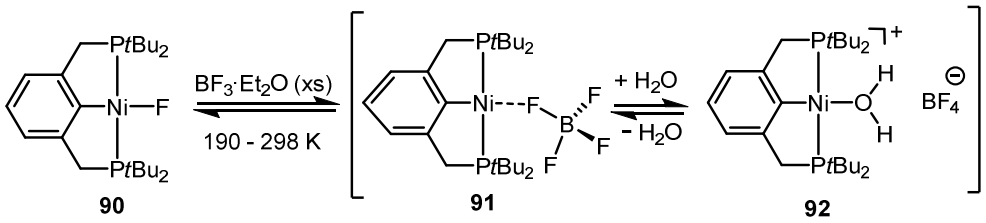


Scheme 41 Hydrosilylation of aldehydes catalyzed by the Ni(II) PCP pincer hydride complex **81**

Peruzzini and coworkers investigated the reactivity of the hydride complex [Ni(PC*sp*^{2}P)(H)] (**43**) towards BH_3 and compared it with the reactivity of the structurally analogous fluoride complex [Ni(PC*sp*^{2}P)(F)] (**90**) with the corresponding BF_3 species (Schemes 42 and 43).[49] The reaction of **43** with BH_3·THF was followed in the 190-298 K temperature range *via* multinuclear ^{1}H, ^{31}P{^{1}H}, and ^{11}B{^{1}H} NMR spectroscopy. The nickel hydride is basic and reacted with BH_3 to form [Ni(PC*sp*^{2}P)(η^1-BH_4)] (**89**) where the borohydride seems to be coordinated in η^1-fashion. In the absence of an X-ray structure this was suggested from DFT calculations. This process is reversible, since the borohydride complex represents the kinetic reaction product and could not be isolated in the solid state. At low temperature intermediate **88** was detected by NMR spectroscopy (Scheme 43). Under similar conditions, the reaction of [Ni(PC*sp*^{2}P)(F)] (**90**) and BF_3 Et_2O yielded the Ni(II) complex **91** with a weakly bound tetrafluoroborate anion. Upon addition of water the aquo complex **88** is formed. The structure of this compound was confirmed by X-ray crystallography (Scheme 43).[49]

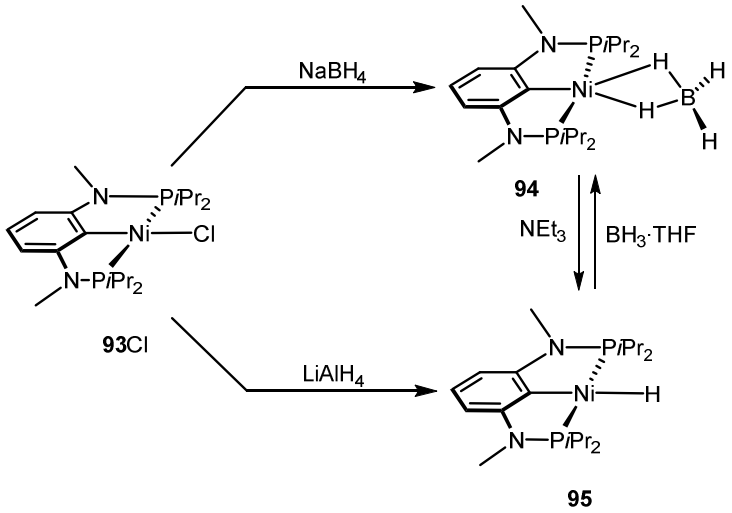


Scheme 42 Reaction of [Ni(PC*sp*^{2}P)(H)] (**43**) with BH_3·THF



Scheme 43 Reaction of [Ni(PCsp^2P)(F)] (**90**) with $BF_3{\cdot}Et_2O$

Kirchner and co-workers are currently focusing on the chemistry of non-precious metal PCP pincer complexes based on the 1,3-diaminobenzene scaffold.[44] In the course of these studies the Ni(II) borohydride complex [Ni(PCsp^2P)(η^2-BH_4)] (**94**) were prepared via two different routes. First, upon treatment of [Ni(PCsp^2P)Cl] (**93**Cl) with an excess of $NaBH_4$ in THF/MeOH (1:1) yields **94** in 91% isolated yield (Scheme 44). The second

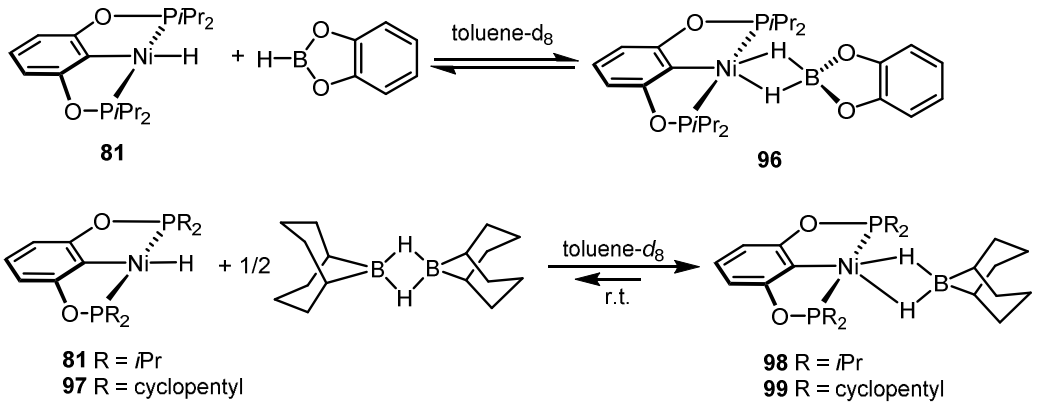


Scheme 44 Synthesis and reactivity of the Ni(II) borohydride [Ni(PCP^{Me}-*i*Pr)(η^2-BH_4)] (**94**) and hydride complexes [Ni(PCP^{Me}-*i*Pr)H] (**95**).

approach makes use of the hydride complex [Ni(PCsp^2P)(H)] (**95**) which was obtained from the reaction of **93**Cl with $LiAlH_4$. It is noteworthy that borane adduct released in presence of trimethylamine as base led to afford [Ni(PCsp^2P)(H)] analogues.[50] Treatment of **95** with $BH_3{\cdot}THF$ at room temperature led to the clean formation of **94** in 93% isolated yield. Heating a toluene solution of **94** at 80°C for 24h in the presence of NEt_3 yields **95** in 93% isolated yield (Scheme 44).[44]

Prior to our findings, Guan and co-workers[50] discovered that nickel hydride complexes react with $BH_3{\cdot}THF$ irreversibly at room temperature to yield BH_4-complexes. Reversing the reactions is possible at higher temperatures if there is a trapping agent available, or under a dynamic vacuum. Other boranes such as 9-Borabicyclo(3.3.1)nonane (9-BBN) and catecholborane (HBcat) are also capable of reacting with nickel hydride complexes such as **81** and **97** to form the corresponding nickel dihydridoborate

complexes **96**, **98** and **99**, unless the hydride moiety is sterically inaccessible (Scheme 45).[50] In these cases, the reactions are reversible at room temperature, allowing nickel hydride species to reform. Under catalytic conditions reduction of CO_2 led to the methoxide level when 9-BBN or HBcat was employed as the reducing agent. The best catalyst involved bulky substituents on the phosphorus donor atoms such as in **81**. Catalytic reactions involving **96** were less efficient because of the formation of dihydridoborate complexes as the dormant species as well as partial decomposition of the catalyst by the boranes (Scheme 45).

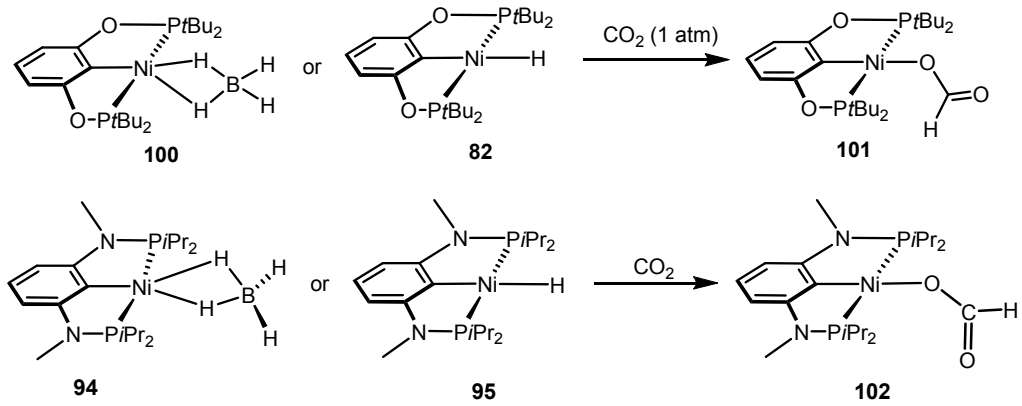


81 R = *i*Pr
97 R = cyclopentyl

98 R = *i*Pr
99 R = cyclopentyl

Scheme 45 Synthesis of [Ni(PC*sp*^{2}P)(borohydride)] derivatives

Both nickel hydride and borohydride complexes were able to reduce carbon dioxide to form the respective formate complexes (Scheme 46). [44,50,51] It has to be mentioned that several pincer complexes of the type [Ni(PCP)(R)] (R = H, OH, Me, allyl) were reported[52,53,54,55] to undergo insertion reactions with CO_2.



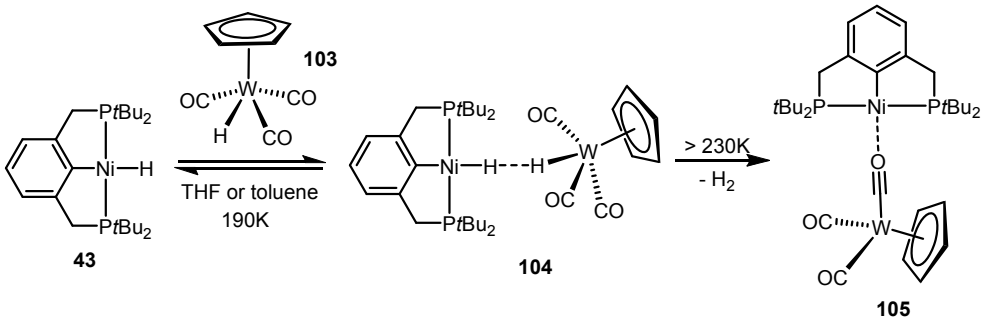
100 **82** **101**

94 **95** **102**

Scheme 46 Reduction of CO_2 by [Ni(PC*sp*^{2}P)(η^2-BH_4)] and [Ni(PC*sp*^{2}P)(H)] to give formate complexes

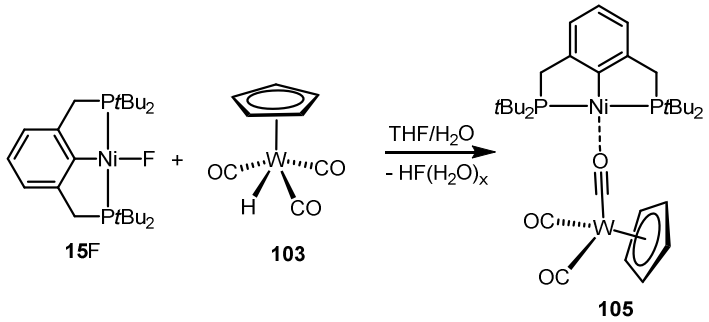
Dihydrogen bond interactions where transition metal hydride complexes serve as both proton acceptor and proton donor in a hydrogen bond are very rare. Peruzzini and co-workers studied the

reaction of the stable electron-rich Ni(II) PCP pincer hydride [Ni(PCsp^2P)(H)] (**43**) with the acidic tungsten(II) complex [WCp(H)(CO)$_3$] (**103**).[56] Stoichiometric amounts of the acid hydride complex [WCp(H)(CO)$_3$] (**103**) and basic hydride complex [Ni(PCsp^2P)(H)] (**43**) reacted in THF or toluene at room temperature to give the bimetallic ion pair complex **105**. In this complex one carbonyl ligand bridges the two metal centers in a rather unconventional "isocarbonylic" mode (Scheme 47). The structure of complex **105** was confirmed by X-ray diffraction analysis. Deuterium exchange H/D was also studied with the isotopomeres [CpW(D)(CO)$_3$] and [Ni(PCsp^2P)(D)]. Complex **104** was an intermediate as suggested by DFT calculations (Scheme 47). Complex **105** dissociates in acetonitrile to produce the adduct [Ni(PCsp^2P)(CH$_3$CN)][CpW(CO)$_3$] that comprises a square-planar nickel(II) PCP cation binding one CH$_3$CN molecule and the piano stool tungsten(II) anion.[56]



Scheme 47 Dihydrogen evolution upon reacting acidic and basic metal hydride complexes

It was shown that water plays an important role in the activation of Ni-F and W-H bonds. The reaction between the nickel(II) PCP pincer fluoride complex **15**F and the tungsten(II) carbonyl hydride **103** led to hydrofluoric acid evolution and formation of the bimetallic isocarbonylic species **105** (Scheme 48). The process was monitored through multinuclear ^{1}H, ^{19}F{^{1}H}, and ^{31}P{^{1}H} variable-temperature NMR spectroscopy.[57] According to DFT calculations four water molecules are involved in the Ni-F and W-H cleavage steps.



Scheme 48 Water assisted hydrofluoric acid evolution upon interaction of complexes **15F** and **103** and formation of **105**

3. Cobalt PCP Pincer Complexes

An overview of all cobalt PCsp^2P and PCsp^3P pincer complexes, which serve as synthetic entries into Co PCP chemistry are depicted in Chart 3.[19,44,58,59,60,61,62,63] These are typically derived from simple Co(0), Co(I) and Co(II) precursors such as $Co(PMe_3)_4$, $Co(Cl)(PMe_3)_3$, $Co(Me)(PMe_3)_4$, and CoX_2 (X = Cl, Br, I).

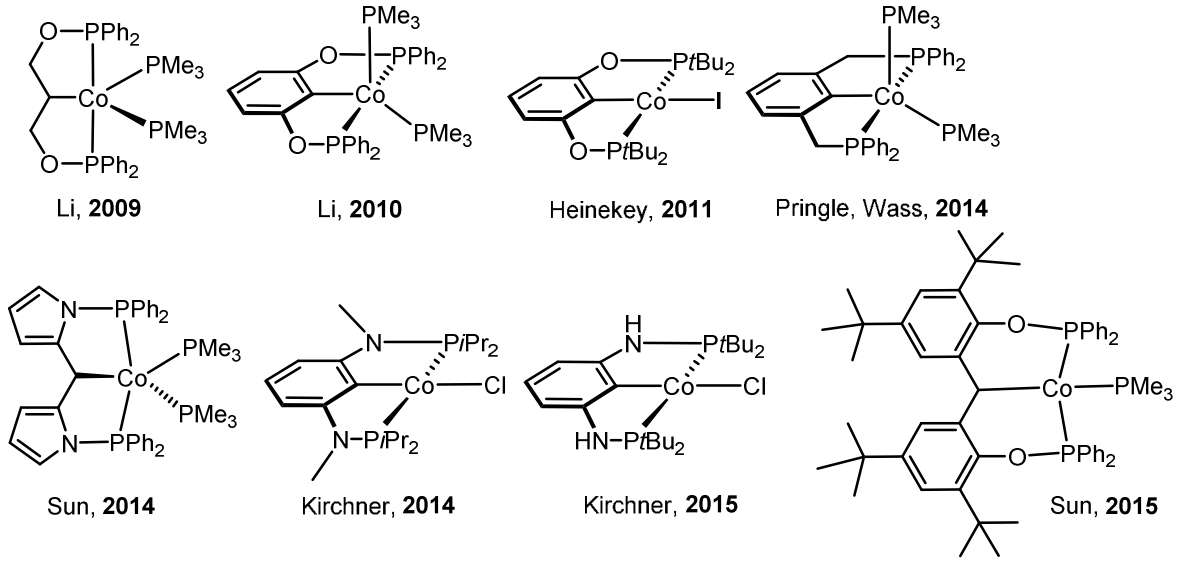
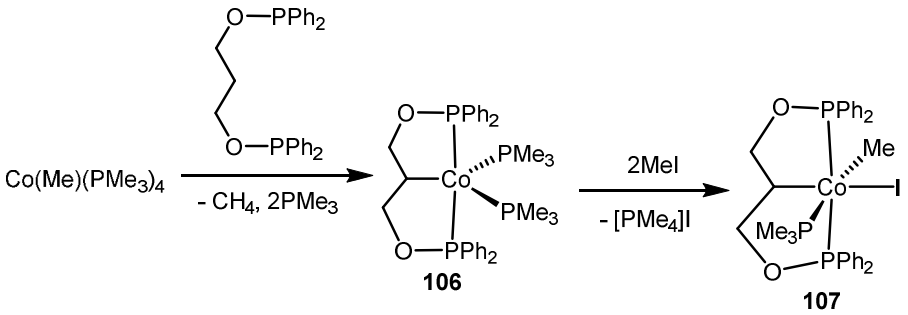


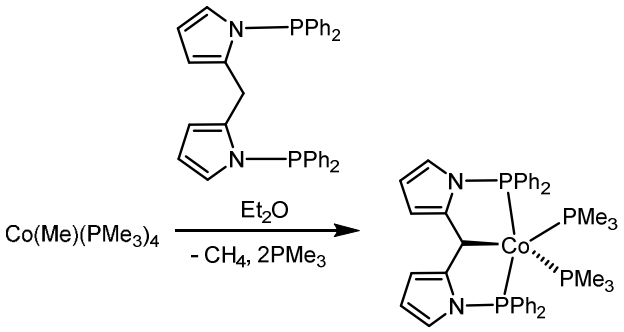
Chart 3 Overview of cobalt PCsp^2P and PCsp^3P pincer complexes

The first cobalt PCP pincer complexes were synthesized by Li and co-workers.[62] This was achieved by the activation of sp^3 C-H bonds induced by electron-rich cobalt species $Co(Me)(PMe_3)_4$ in reaction with aliphatic PCP ligand $(Ph_2POCH_2)_2CH_2$ which led to the formation of the bulky Co(I) PCsp^3P complex **106** (Scheme 49). This process is accompanied by liberation of methane and PMe_3. Complex **106** underwent oxidative addition with MeI which gives rise to the iodomethyl Co(III) complex **107** (Scheme 49). Complex



Scheme 49 Synthesis of Co(I) and Co(III) complexes with a PCsp^3P pincer ligand

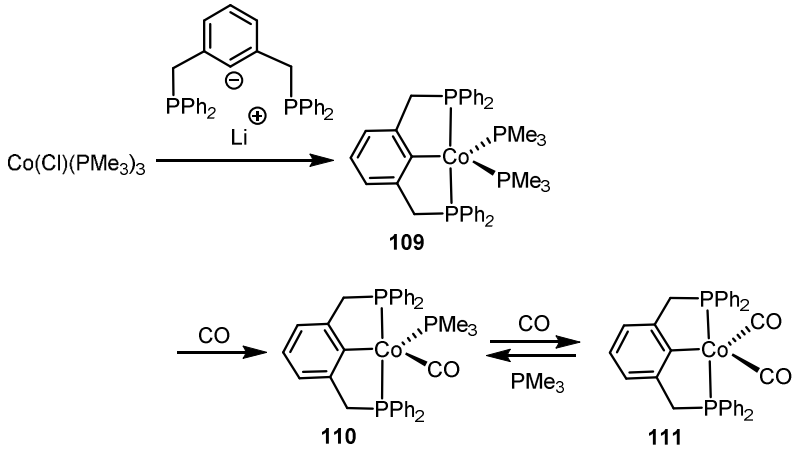
A related reaction was recently reported by Sun and co-workers.[58] They described the coordination chemistry iron, cobalt and nickel complexes with a new PC*sp*^{3}P pincer ligand based on a dipyrromethane backbone. The activation of the Csp^3–H bond was strongly metal-dependent. In the case of cobalt, the Co(I) complex Co(Me)(PMe$_3$)$_4$ reacted readily with the PCP ligand to afford the Co(I) complex PC*sp*^{3}P complex **108** (Scheme 50), while with the Co(0) complex Co(PMe$_3$)$_4$ no PCP pincer complex was formed.



108

Scheme 50. Synthesis of the Co(I) PC*sp*^{3}P complex **108** based on the N,N'-bis(diphenylphosphino)dipyrromethane backbone

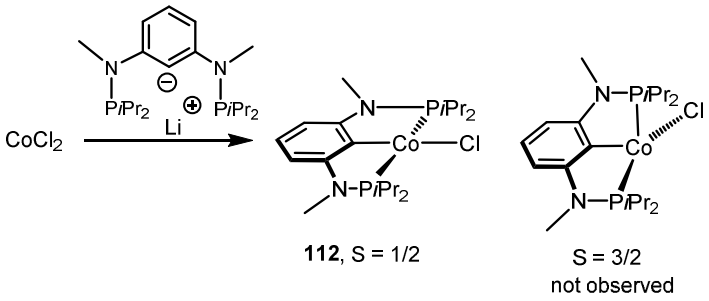
Pringle and co-workers reported the synthesis of the Co(I) PC*sp*^{2}P complex **109** by a transmetalation reaction between 1-lithio-2,6-bis((diphenylphosphino)methyl)benzene and CoCl(PMe$_3$)$_3$.[60] Subsequent exposure of **109** to CO gave the dicarbonyl complex **111**. The synthesis of this complex proceeds via monophosphine intermediate **110**, which was identified by ^{31}P{^{1}H} NMR spectroscopy from the reaction mixture. The conversion of **110** to **111** was shown to be reversible (Scheme 51).



109 **110** **111**

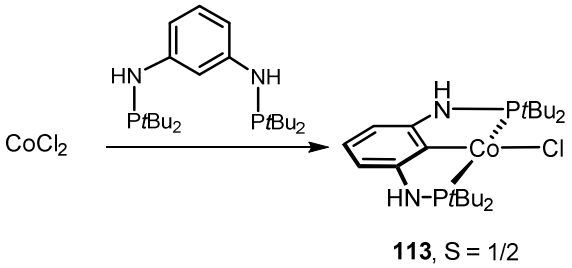
Scheme 51 Synthesis of the Co(I) PC*sp*^{2}P complex **109** and stepwise substitution of PMe$_3$ by CO

Kirchner and co-workers[19,44] reported on the synthesis and reactivity of a series of Co(I), Co(II) and Co(III) PCP complexes bearing pincer ligands based on the 1,3-diaminobenzene scaffold. Treatment of anhydrous $CoCl_2$ with the PCP ligand in the presence of *n*BuLi in THF affords the 15e complex [Co(PC*sp*^{2}P^{Me}-*i*Pr)Cl] (**112**) in 96% isolated yield (Scheme 52).[19] The magnetic moment of μ_{eff} = 2.3(1)μ_B was derived from the temperature dependence of the inverse molar magnetic susceptibility from SQUID



Scheme 52 Synthesis of complex [Co(PC*sp*^{2}P)Cl] (**112**)

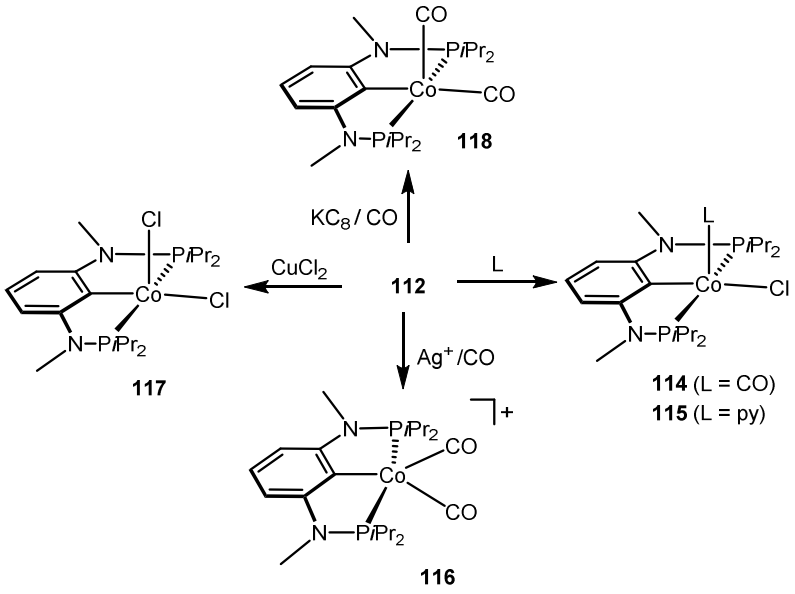
measurements. This value is higher than the one expected for the spin-only approximation and is explained by a spin orbit coupling contribution, being consistent with a low-spin square planar complex. DFT calculations reveal that the corresponding high-spin Co(II) complex with S = 3/2, which adopts a pseudo-tetrahedral geometry, is 19.5 kcal/mol less stable than the square planar low-spin state with S = ½ and was not observed experimentally (Scheme 52). The analogous complex **113**, where the PCP ligand features acidic NH protons and the bulkier *t*Bu substituents, had to be prepared via a different methodology. Refluxing a solution of anhydrous $CoCl_2$ with the corresponding PCP ligand in THF afforded directly **113** albeit in moderate isolated yield (32%) (Scheme 53).[44] In analogy to **112**, complex **113** is a d^7 low spin complex with a solution magnetic moment μ_{eff} of 1.8(1)μ_B as determined in solution by the Evans method.



Scheme 53 Synthesis of complex [Co(PC*sp*^{2}P)Cl] (**113**)

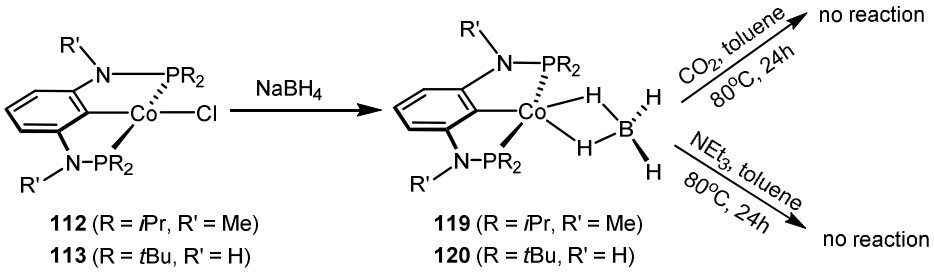
Complex **112** reacted readily with the simple ligands CO and pyridine to afford the five-coordinate square-pyramidal 17e complexes [Co(PC*sp*^{2}P)(CO)Cl] (**114**) and [Co(PC*sp*^{2}P)(py)Cl] (**115**), while in the presence of Ag^+ and CO the cationic complex [Co(PC*sp*^{2}P)(CO)$_2$]$^+$ (**116**) was afforded (Scheme 54). The effective magnetic moments μ_{eff} of all Co(II) complexes were derived from the temperature dependence of the inverse molar magnetic susceptibility by SQUID measurements and are in the range of 1.9 to 2.4μ_B.

This is consistent with a d^7 low spin configuration with some degree of spin orbit coupling. Oxidation of **112** with $CuCl_2$ afforded the paramagnetic Co(III) PCP complex [Co(PC*sp*^{2}P)Cl_2] (**117**), while the synthesis of the diamagnetic Co(I) complex [Co(PC*sp*^{2}P)$(CO)_2$] (**118**) was achieved by stirring **112** in toluene with KC_8 in the presence of CO (Scheme 54).[19]



Scheme 54 Synthesis of five-coordinated Co(I) and Co(II) PC*sp*^{2}P pincer complexes

The first cobalt borohydride PCP pincer complexes were synthesized by Kirchner and co-workers in 2015.[44] The 15e square planar complexes **112** and **113**, respectively, reacted readily with $NaBH_4$ to afford complexes [Co(PC*sp*^{2}P)(η^2-BH_4)] (**119**) and [Co(PC*sp*^{2}P)(η^2-BH_4)] (**120**) in high yields (Scheme 55). The η^2-bonding mode of the borohydride ligand was confirmed by IR spectroscopy and X-ray crystallography. These compounds are paramagnetic with effective magnetic moments of 2.0(1) and 2.1(1)μ_B consistent with a d^7 low spin system corresponding to one unpaired electron. None of these complexes reacts with CO_2 to give formate complexes.[44]



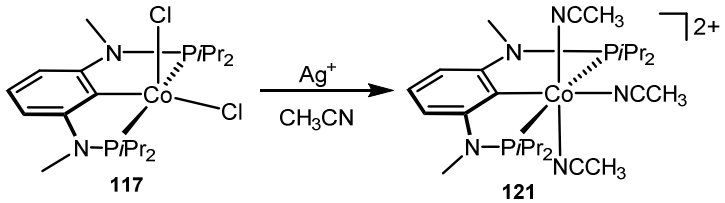
112 (R = *i*Pr, R' = Me)
113 (R = *t*Bu, R' = H)

119 (R = *i*Pr, R' = Me)
120 (R = *t*Bu, R' = H)

Scheme 55 Synthesis of the first Co(II) PC*sp*^{2}P borohydride complexes

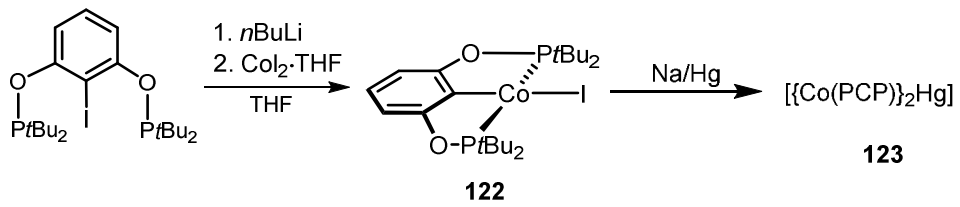
While [Ni(PCsp^2P)(η^2-BH_4)] (**94**) loses readily BH_3 at elevated temperatures in the presence of NEt_3 to form the hydride complex **95** (Scheme 44), the Co(II) complex [Co(PCsp^2P)(η^2-BH_4)] (**119**) did not react with NEt_3 to give a hydride complex. DFT calculations revealed that the formation of the Ni hydride is thermodynamically favorable, while the formation of the Co(II) hydride, in agreement with the experiment, is unfavorable. From the calculations it is apparent that for the Co complexes the BH_4^- coordination is closer to η^2, and the overall geometry can be envisaged as in between square planar and square pyramidal. In complex **94**, the borohydride ligand coordination is closer to η^1, and the overall geometry of the molecule is closer to normal square planar, reflecting the tendency of Ni(II) to form complexes with that geometry, as expected for a d^8 metal.

A facile synthesis of the diamagnetic octahedral tris-acetonitrile Co(III) complex **121** was achieved by treating the Co(III) complex **117** with a silver salt as halide scavenger in acetonitrile as coordinating solvent (Scheme 56).[19]

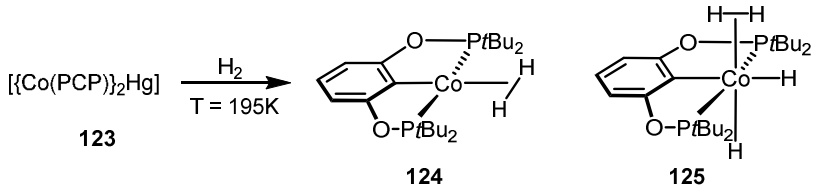


Scheme 56 Synthesis of the six-coordinate trisacetonitrile Co(III) PCP pincer complex [Co(PCsp^2P)($CH_3CN)_3$)]$^{2+}$ (**121**)

Heinekey and co-workers reported[61] the synthesis of the Co(II) iodo PCP complex [Co(PCsp^2P)(I)] (**122**). This compound was prepared in good yield by activation of the ligand with *n*BuLi and the addition of CoI_2·THF (Scheme 57). The magnetic moment of **122** was measured using the Evans method (μ_{eff} = 2.38 μ_B) and is consistent with a paramagnetic complex that contains one unpaired electron. Reduction of **122** was accomplished using sodium amalgam. The isolated product was a mercury-bridged dicobalt species [{Co(PCsp^2P)}$_2$Hg] (**123**). Introduction of H_2 gas to a solution of **123** at 195 K resulted in the formation of a new diamagnetic species. The ^{1}H NMR spectrum in the high-field region exhibited a new resonance (with an integration of two versus other ligand resonances) at δ = -11.6 ppm and was identified as the first cobalt-dihydrogen complex [Co(PCsp^2P)(η^2-H_2)] (**124**) (Scheme 58). Studying solutions of **124** under increased hydrogen pressure allowed observation of a new diamagnetic product identified as [Co(PCsp^2P)(η^2-H_2)($H)_2$] (**125**). In addition to NMR spectroscopy, the identity of the dihydrogen and hydride species were confirmed by means of theoretical calculations.



Scheme 57 Synthesis of complexes [Co(PC*sp*^{2}P)I] (**122**) and reduction to the mercury-bridged dicobalt species [{Co(PC*sp*^{2}P)}$_2$Hg] (**123**)



Scheme 58 Synthesis of [Co(PC*sp*^{2}P)(η^2-H$_2$)] (**124**) and [Co(PC*sp*^{2}P)(η^2-H$_2$)(H)$_2$] (**125**).

4. Iron PCP Pincer Complexes

To date only very few iron PCP complexes are reported in the literature. An overview of iron PC*sp*^{2}P and PC*sp*^{3}P pincer complexes is depicted in Chart 4.[58, 62,63,64] These are typically derived from Fe(0) and Fe(II) precursors such as Fe(PMe$_3$)$_4$, Fe(PMe$_2$Ph)$_4$ and Fe(Me)$_2$(PMe$_3$)$_4$. Remarkably, almost all of the iron PCP complexes are octahedral six-coordinate low-spin d^6 complexes. The only exception is a five-coordinate Fe(II) PCP pincer complex reported recently by Sun *et al* (*vide infra*).[63]

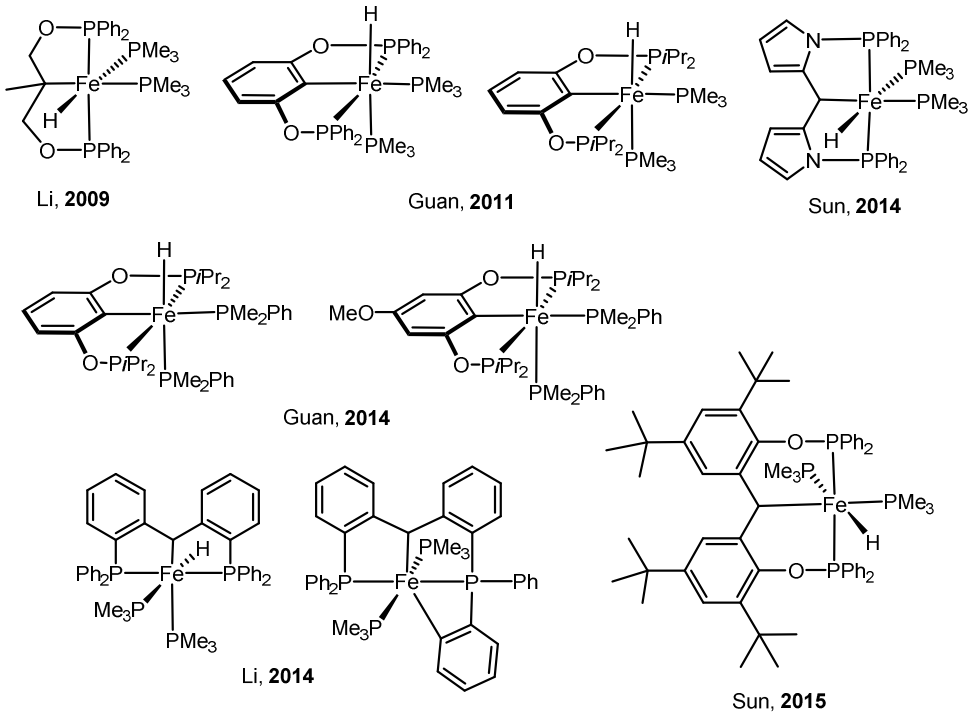
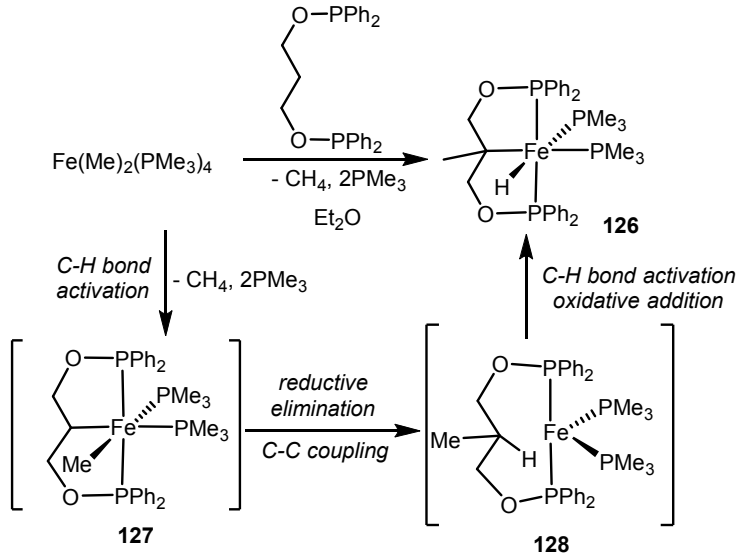


Chart 4 Overview of iron PC*sp*^{2}P and PC*sp*^{3}P pincer complexes

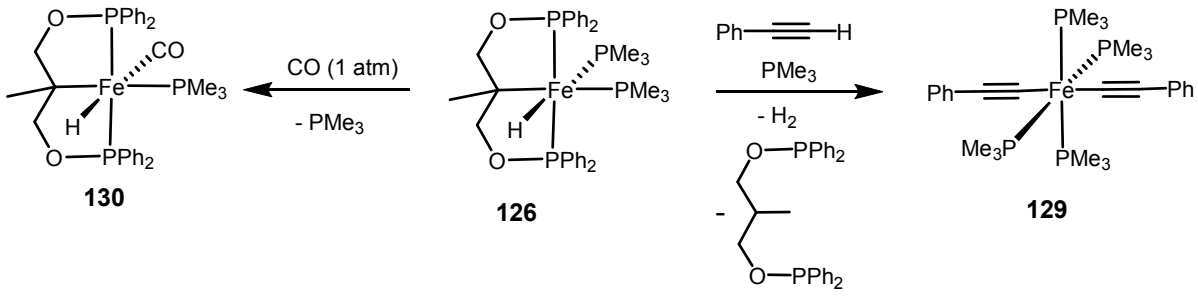
Li and co-workers reported the synthesis of the first iron PCP complex.[62] Treating a diethyl ether solution of the PCP ligand Ph$_2$POCH$_2$)$_2$CH$_2$ with Fe(Me)$_2$(PMe$_3$)$_4$ gave rise to the formation of the hydride-

iron(II) complex [Fe(PC*sp*^{3}P)(PMe$_3$)$_2$(H)] (**126**) (Scheme 59). Similarly to the formation of the related cobalt complex **106** (Scheme 49), the reaction starts with the substitution of two trimethylphosphines and elimination of methane affords to yield intermediate **127**. This step involves a double C-H activation process and C-C coupling between two sp^3-carbons which is an unusual reaction pathway (Scheme 59). Subsequent C-C-coupling between the methyl group and the central carbon atom of the (Ph$_2$POCH$_2$)$_2$CH$_2$ moiety and reductive elimination yields intermediate **128** bearing a new ligand backbone with a sp^3 C-H bond. Finally, a C-H activation process in the new ligand backbone again gives **126** as the final product. (Scheme 59).[62]



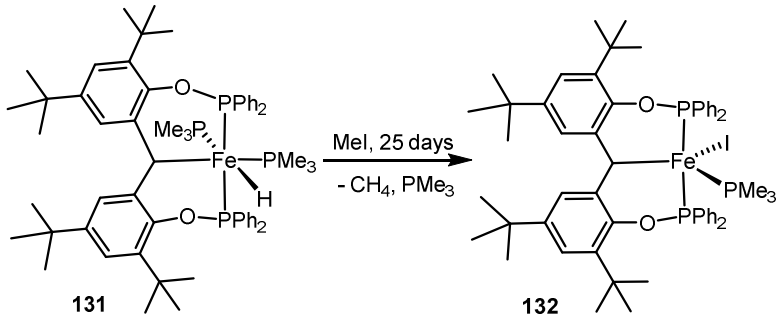
Scheme 59 Synthesis of [Fe(PC*sp*^{3}P)(PMe$_3$)$_2$(H)] (**126**) – a mechanistic rationale

When Fe(II) hydride complex **126** was treated with an excess of phenylacetylene in the presence of two equivs of PMe$_3$, dissociation of the PCP ligand took place and complex **129** was afforded (Scheme 60). This octahedral complex features four PMe$_3$ ligands and two phenylacetylide ligands which are in a mutual trans position.[62] Moreover, in the presence of CO, complex **126** underwent ligand substitution to form the mono CO complex **130**.

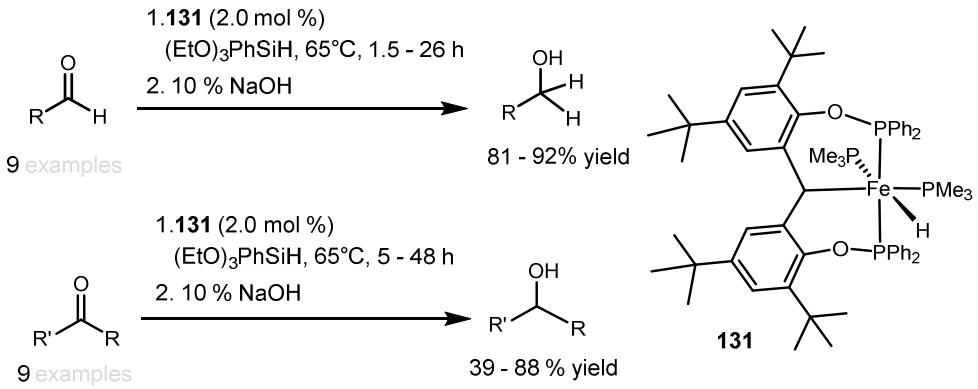


Scheme 60 Reaction of complex **126** with phenylacetylene in the presence of PMe_3 and ligand substitution to give **130**

An interesting reaction was discovered recently by Sun and co-workers.[63] Mixing a diethyl ether solution of the respective PCP ligand with the Fe(0) complex $Fe(PMe_3)_4$ afforded the hydrido iron complex [Fe(PC*sp*^{3}P)$(PMe_3)_2$(H)] (**131**). Surprisingly, the reaction of **131** with iodomethane afforded an unsaturated coordinated complex [Fe(PC*sp*^{3}P)(PMe_3)(I)] (**132**). It should be noted that this is the first five coordinate Fe(II) PCP pincer complex. This compound was characterized by X-ray crystallography and was found to adopt trigonal bipyramidal configuration. Moreover, this compound is a paramagnetic d^6-species with two unpaired electrons as determined by magnetic measurements (Scheme 61). The Fe(II) pincer hydride complex **131** is an active catalyst for the hydrosilylations of aldehydes and ketones utilizing $(EtO)_3SiH$ as the hydrogen source (Scheme 62).[63]



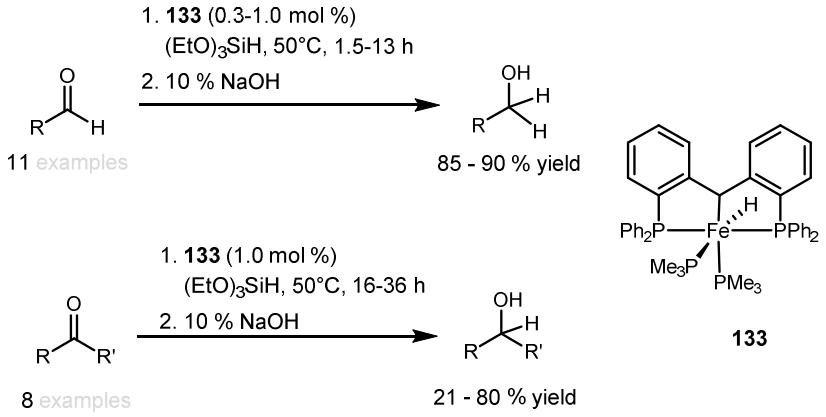
Scheme 61 Formation of the first five-coordinate Fe(II) PCP pincer complex (**132**)



Scheme 62 Hydrosilylation of aldehydes and ketones catalyzed by the Fe(II) hydride complex **131**

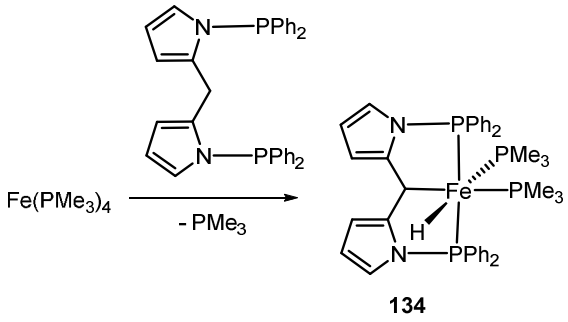
Recently, Li *et al* reported[64] the synthesis of the related PCP complex [Fe(PC*sp*^{3}P)$(PMe_3)_2$(H)] (**133**) via an analogous procedure as reported for the synthesis of **131**. The reaction of PCP pincer ligand $(Ph_2P(C_6H_4))_2CH_2$ with $Fe(PMe_3)_4$ in THF at room temperature resulted in the formation of **133** *via* one oxidative addition process with the substitution of two PMe_3 ligands by two Ph_2P-groups of the pincer

ligand. The new iron hydride complex **133** also showed good activity in the catalytic hydrosilylation of aldehydes and ketones by using $(EtO)_3SiH$ as the hydrogen source under mild conditions (Scheme 63).



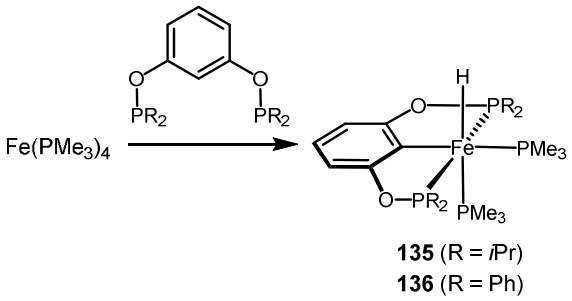
Scheme 63 Hydrosilylation of aldehydes and ketones catalyzed by the Fe(II) PCP hydride complex **133**

Also Sun and co-workers synthesized the hydrido Fe(II) complexes [Fe(PCsp^2P)(H)$(PMe_3)_2$] (**134**) *via* the same cyclometallation route by treatment of the Fe(0) precursor $Fe(PMe_3)_4$ with a dipyrromethane-based PCP pincer ligand. Unfortunately, this complex is inactive for the hydrosilylation of benzaldehyde (Scheme 64).[58]



Scheme 64. Synthesis of the Fe(I) PCsp^3P complex **134** based on the N,N'-bis(diphenylphosphino)-dipyrromethane backbone

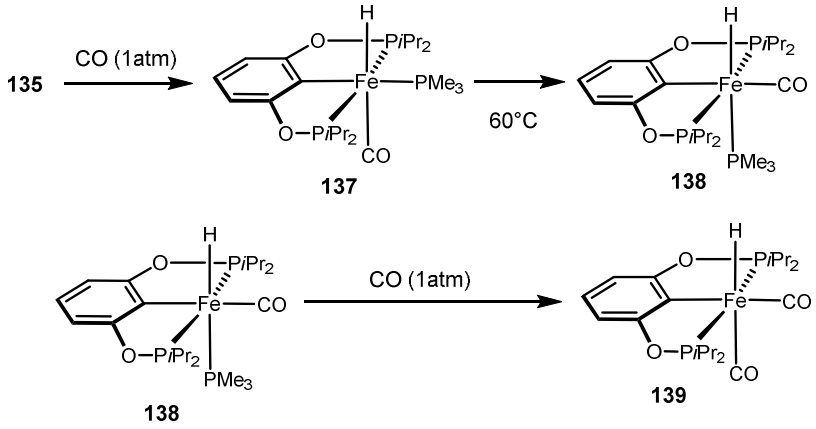
Guan and co-workers synthesized the hydrido Fe(II) complexes [Fe(PCsp^2P)(H)$(PMe_3)_2$] (**135** and **136**) *via* a cyclometallation route by treatment of the Fe(0) precursor $Fe(PMe_3)_4$ with resorcinol-derived bis(phosphinite) PCP ligands pincer ligands (Scheme 65).[65] No reaction took place with a PCP ligand bearing bulky *t*Bu substituents.



135 (R = *i*Pr)
136 (R = Ph)

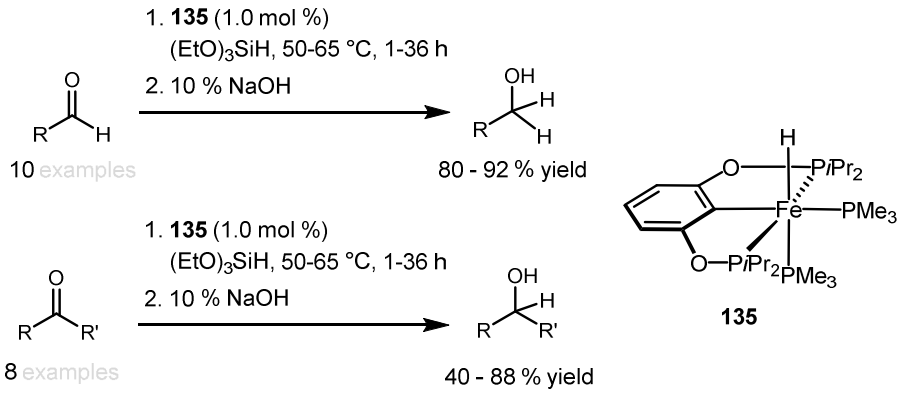
Scheme 65 Synthesis of [Fe(PC*sp*^{2}P)(H)(PMe$_3$)$_2$] (**135**, **136**)

The isopropyl complex **135** undergoes ligand substitution upon mixing with CO to give [Fe(PC*sp*^{2}P)(H)(PMe$_3$)(CO)]. The kinetic product (**137**) of this process contains a CO ligand *trans* to the hydride, whereas the thermodynamic product (**138**) has a CO ligand *cis* to the hydride. The displacement of the PMe$_3$ ligand in **138** by CO takes place only at an elevated temperature, resulting in the formation of *cis*-[Fe(PC*sp*^{2}P)(H)(CO)$_2$] (**139**) (Scheme 66).[65]



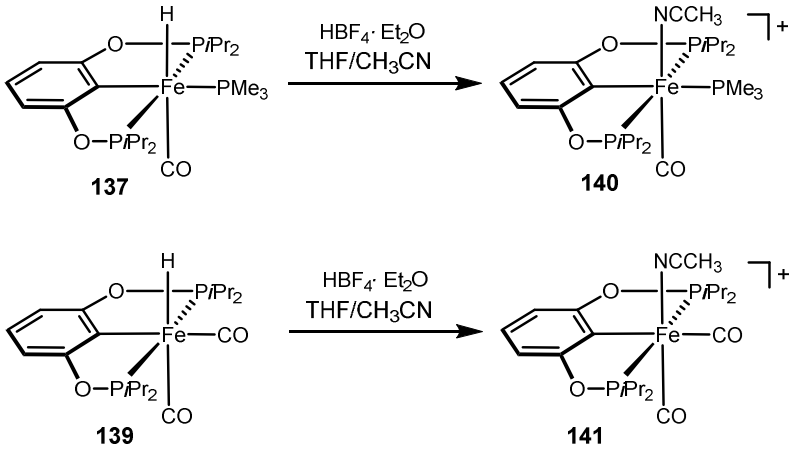
Scheme 66 Ligand substitution reactions of iron PCP hydride complexes

These new iron PCP-pincer hydride complexes catalyze the hydrosilylation of aldehydes and ketones with different functional groups, and **135** turned out to be the most efficient catalyst for this process (Scheme 67).[65] The mechanism of this hydrosilylation with **135** as catalyst was theoretically studied by Wei and co-workers by means of DFT calculations.[66]



Scheme 67 Hydrosilylation of aldehydes and ketones catalyzed by the Fe(II) PCP hydride complex **135**

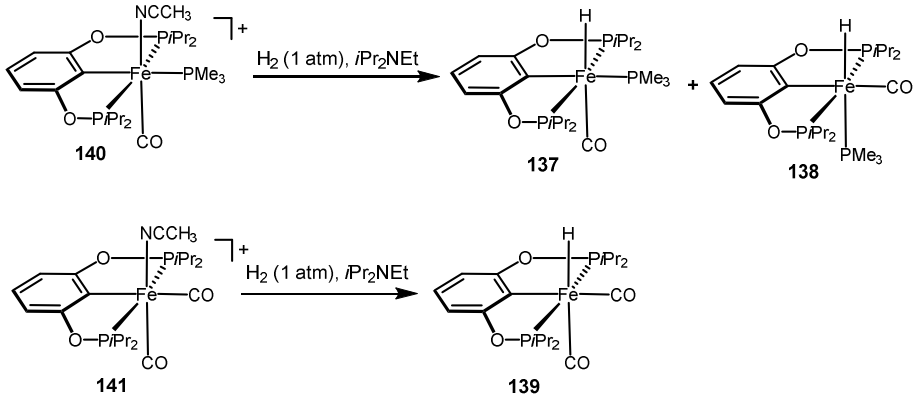
Stoichiometric protonation reactions were carried with neutral Fe(II) PCP pincer hydride complexes **137** and **139**. Addition of HBF_4 led to formation of cationic Fe(II) pincer complexes **140** and **141**, respectively (Scheme 68).[67] A reaction mechanism was described for the formation of complex **140** through either square pyramidal or distorted trigonal bipyramdial intermediate after protonation on **137**, which converted to six coordinate cationic Fe(II) pincer complex by addition of acetonitrile. In contrast, the reaction of **135** with $HBF_4.Et_2O$ led to corresponding cationic complex which was not isolated due to the formation of $HPMe_3^+$, free diphosphinite ligand, and other decomposition products even when the protonation reaction was carried out at low temperatures.[67]



Scheme 68 Protonation of [Fe(PCsp^2P)(H)(PMe_3)(CO)] (**137**) and [Fe(PCsp^2P)(H)$(CO)_2$)] (**139**) with $HBF_4 \cdot Et_2O$

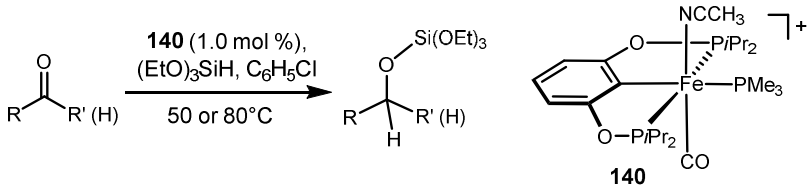
In the presence of Hünig's base (iPr_2NEt), the cationic Fe(II) complex **140** was able to activate dihydrogen which furnished an isomeric mixture of the hydride complexes **137** and **138** (Scheme 69). Likewise, also the cationic bis-carbonyl complex **141** was able to cleave dihydrogen. However, activation of H_2 with **141** was significantly more sluggish. The reaction at room temperature was incomplete even after 11 days with

91% of **141** being converted to **139**. Presumably, the dissociation of CH_3CN from **141** is much slower than from **140**, i.e., **141** is substitutionally more inert than **140**.[67]



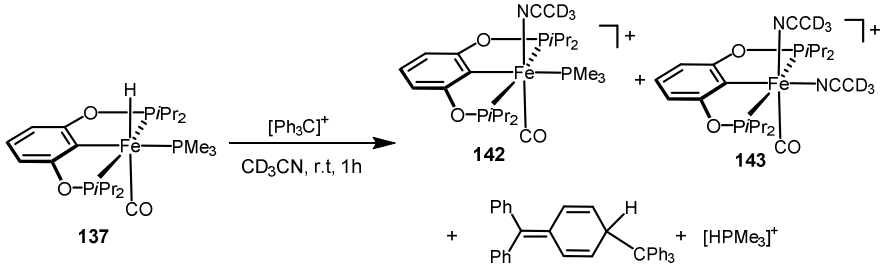
Scheme 69 Activation of dihydrogen by cationic Fe(II) PCP pincer complexes in the presence of base

Although **140** was not a viable catalyst for the hydrogenation of benzaldehyde (under 1 atm of H_2 pressure), both **140** and **141** were effective in catalyzing the hydrosilylation of benzaldehyde and acetophenone and demonstrated an improved activity over the corresponding neutral hydride complexes (Scheme 70).[67]



Scheme 70 Hydrosilylation of aldehydes and ketones catalyzed by Fe(II) PCP complex **140**

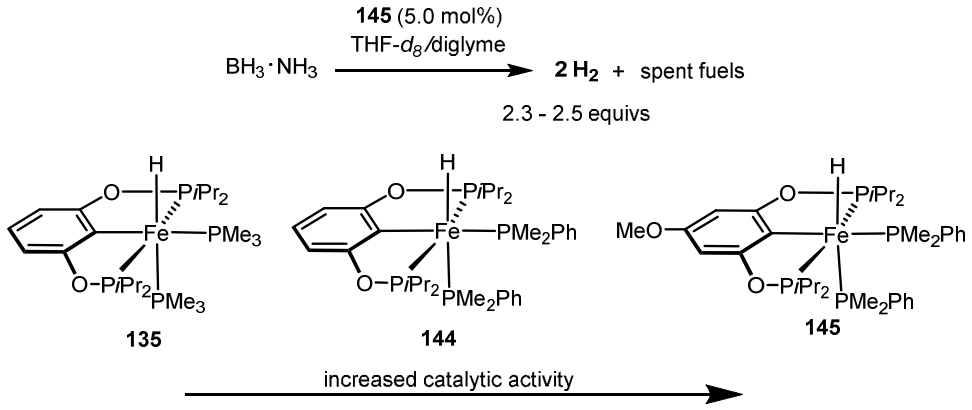
Guan and co-workers also studied the hydride abstraction of the Fe(II) pincer hydride complex **137**. Upon treatment of complex **137** with triphenylmethyl fluoroborate in CD_3CN two new cationic Fe(II) pincer complexes **142** and **143** were formed together with Gomberg's dimer and the phosphonium salt $[HPMe_3][BF_4]$ (Scheme 71).[67]



Scheme 71 Hydride abstraction from the neutral Fe(II) PCP pincer complex **137** in CD_3CN to give cationic PCP pincer complexes

Guan and co-workers studied the dehydrogenation of ammonia-borane (AB) and developed the two new iron PCP pincer based catalysts **144** and **145**. Following a similar procedure used for the synthesis of **135** (Scheme 65), iron PCP-pincer complexes **144** and **145** were prepared from "$Fe(PMe_2Ph)_4$" and the corresponding diphosphinites. In this case, cyclometalation of the diphosphinite ligand is considerably slower, requiring as long as 48 h to complete the reaction. By comparison, synthesis of **135** from $Fe(PMe_3)_4$ is finished within 3 h, probably because PMe_3 is less sterically bulky and more electron donating than PMe_2Ph, resulting in a more facile oxidative addition of the C-H bond.

At room temperature, complex **135** showed no catalytic activity for the dehydrogenation of AB. At 60 °C, however, an immediate gas evolution was observed when a solution of **135** in THF was mixed with a solution of AB (20 equivs) in diglyme. Complex **144**, which differs from **135** only by the ancillary phosphine ligands, showed improved catalytic activity. However, complex **145** turned out to be the superior catalyst in terms of both rate and the extent of H_2 released. After 6 h of mixing, the ^{11}B NMR spectrum of the reaction indicated formation of borazine, polyborazylene, cyclotriborazane, and (cyclodiborazanyl)-aminoborohydride. The described iron-based catalytic system releases 2.3-2.5 equivs H_2 per AB, which is the highest extent of H_2 release among all the iron systems known to date (Scheme 72).[68]

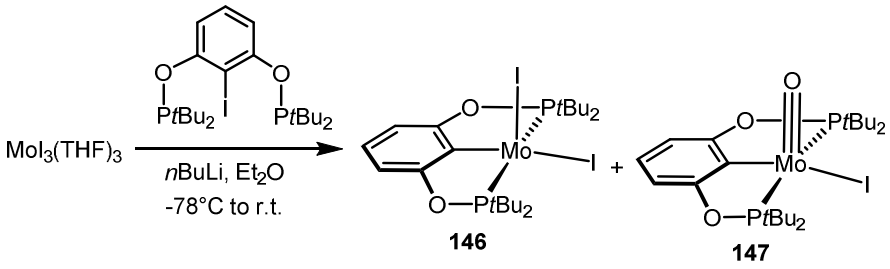


Scheme 72 Dehydrogenation of ammonia-borane catalyzed by Fe(II) PCP pincer complexes

Because more than 2 equiv of H_2 per AB were obtained from the catalytic reactions, it was anticipated that aminoborane (NH_2BH_2) was set free from the iron center. The presence of free aminoborane was probed by using cyclohexene as a trapping agent. Dehydrogenation of AB catalyzed by 5 mol % of **145** was carried out in the presence of 20 equiv of cyclohexene with respect to AB. The trapping product $H_2NB(C_6H_{11})_2$ (47.8 ppm in ^{11}B NMR) was observed.

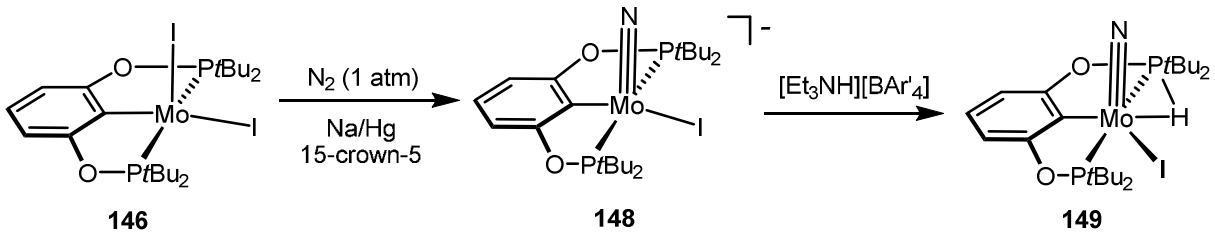
5. Molybdenum PCP Pincer Complexes

The chemistry of molybdenum PCP complexes is hardly developed. The first molybdenum PCP complex was prepared through lithiation of 1-iodo-2,6-[OP(t-Bu)$_2$]$_2$C$_6$H$_3$ and reaction of that lithium reagent with MoI$_3$(THF)$_3$ to give [Mo(PC*sp*^{2}P)(I)$_2$] (**146**) (Scheme 73),[69] a procedure similar to that employed to prepare the cobalt PCP complex **122** (Scheme 57).[61] Compound **146** was obtained in modest yield (46%). However, a diamagnetic impurity was present (10 - 15%), which was proposed to be the Mo(IV) oxo complex (**147**). However, this was merely based on NMR spectroscopy and the fact that MoI$_3$(THF)$_3$ is known to decompose to give Mo=O species and 1,4-di-iodobutane. On the other hand, the lithiation of 1-iodo-2,6-[OP(t-Bu)$_2$]$_2$C$_6$H$_3$ and reaction of that lithium reagent with MoCl$_3$(THF)$_3$ and MoBr$_3$(THF)$_3$ yielded a mixture of several products.[69]



Scheme 73 Synthesis of Mo(III) and Mo(IV) PCP pincer complexes starting from MoI$_3$(THF)$_3$

When a THF solution of **146** (contaminated with **147**) was reduced with NaHg in the presence of 15-crown-5 under N$_2$, the anionic Mo(IV) nitride complex [Mo(PC*sp*^{2}P)(N)(I)]$^-$ (**148**) was obtained as a dark brown solid in 57% yield. This compound was also formed when two or more equivalents of KC$_8$ or Na naphthalenide were used as reducing agents. Upon protonation of **148** by [Et$_3$NH][Bar$'_4$] a diamagnetic compound, presumably **149**, was isolated in 64% yield. Based on NMR data it was proposed that proton addition occurred across the Mo-P bond (Scheme 74).[69]



Scheme 74 Synthesis and reactivity of the anionic Mo(IV) complex [Mo(PC*sp*^{2}P)(N)(I)]$^-$ (**148**)

6. Conclusions

This perspective article provides an overview of the advancements in the field of non-precious metal complexes featuring anionic PCP pincer ligands with the inclusion of aliphatic systems. It covers research from the beginning in 1976 until late 2015 and provides a summary of key developments in this area, which is, to date, limited to the metals Ni, Co, Fe, and Mo. Since the discovery of the first PCP complexes by Shaw and co-workers, who also prepared the first nickel PCP complex, this field has experienced a steady increase in the last decades. While the research in nickel PCP complexes is already quite extensive, the chemistry of cobalt, iron, and molybdenum PCP complexes is comparatively sparse. Surprisingly, with other non-precious metals such as copper, manganese, chromium or vanadium no PCP complexes are known as yet. In the case of nickel PCP complexes already many catalytic applications such as Suzuki–Miyaura coupling, C-S cross coupling, Kharasch and Michael additions, hydrosilylation of aldehydes and ketones, cyanomethylation of aldehydes, and hydroamination of nitriles were reported. While iron PCP complexes were found to be active catalysts for the hydrosilylation of aldehydes and ketones as well as the dehydrogenation of ammonia-borane, cobalt PCP complexes were not applied to any catalytic reactions. Surprisingly, only one molybdenum PCP complex is reported, which was capable of cleaving dinitrogen to give a nitride complex. This perspective underlines that the combination of cheap and abundant metals such as nickel, cobalt, and iron with PCP pincer ligands may result in the development of novel, versatile, and efficient catalysts for atom-efficient catalytic reactions. We are hopeful that the presented reactions will help provide further opportunities to develop novel catalytic transformations and will contribute to further the progress in this field of chemistry.

Acknowledgements

Financial support by the Austrian Science Fund (FWF) is gratefully acknowledged (Project No. P24583-N28). The support and sponsorship of COST action CM1205 “Catalytic Routines for Small Molecule Activation (CARISMA)” is also acknowledged.

References

1 Coining of the name “pincer”: G. van Koten, *Pure App. Chem.* 1989, **61**, 1681.

2 For reviews on pincer complexes, see: (a) R. A. Gossage, L. A. van de Kuil, G. van Koten, *Acc. Chem. Res.* 1998, **31,** 423. (b) M. Albrecht, G. van Koten, *Angew. Chem., Int. Ed.* 2001, **40**, 3750. (c) M. E. van der Boom, D. Milstein, *Chem. Rev.* 2003, **103,** 1759. (d) J. T. Singleton, *Tetrahedron* 2003, **59**, 1837. (e) L. C. Liang, *Coord. Chem. Rev.* 2006, **250,** 1152. (f) The Chemistry of Pincer Compounds; D. Morales-Morales, C. M. Jensen, Eds.; Elsevier: Amsterdam, 2007. (g) H. Nishiyama, *Chem. Soc. Rev.* 2007, **36,** 1133. (h) D. Benito-Garagorri, K. Kirchner, *Acc. Chem.* Res.

2008, **41,** 201. (i) J. Choi, A. H. R. MacArthur, M. Brookhart, A. S. Goldman, *Chem. Rev.* 2011, **111,** 1761. (j) N. Selander, K. J. Szabo, *J. Chem. Rev.* 2011, **111,** 2048. (k) P. Bhattacharya, H. Guan, *Comment Inorg. Chem.* 2011, **32**, 88. (l) S. Schneider, J. Meiners, B. Askevold, *Eur. J. Inorg. Chem.* 2012, 412. (m) G. van Koten, D. Milstein, Eds.; Organometallic Pincer Chemistry; Springer: Berlin, 2013; *Top. Organomet. Chem.* Vol. 40. (n) K. J. Szabo and O. F. Wendt, Pincer and Pincer-Type Complexes: Applications in Organic Synthesis and Catalysis, Wiley-VCH, Germany, 2014. (o) M. Asay, D. Morales-Morales, *Dalton Trans.* 2015, **44**, 17432-17447.

3 C. J. Moulton, B. L. Shaw, *J. Chem. Soc., Dalton. Trans.* 1976, 1020.

4 W. M. Haenel, D. Jakubik, C. Krueger, P. Betz, *Chemische Berichte,* 1991, **124,** 333.

5 (a) K. A. Kozhanov, M. P. Bubnov, V. K. Cherkasov, G. K. Fukin, G. A. Abakumov, *Dalton Trans.,* 2004, 2957. (b) K. A. Kozhanov, M. P. Bubnov, V. K. Cherkasov, N. N. Vavilina, L. Yu. Efremova, O. I. Artyushin, I. L. Odinets, G. A. Abakumov, Dalton Trans. 2008, 2849.

6 D. Benito-Garagorri, V. Bocokic, K. Mereiter, K. Kirchner, *Organometallics,* 2006, **25,** 3817.

7 X. Lefevre, D. M. Spasyuk, D. Zargarian, *J. Organomet. Chem.,* 2011, **696,** 864.

8 Z. Yang, D. Liu, Y. Liu, M. Sugiya, T. Imamoto, W. Zhang, *Organometallics,* 2015, **34**, 1228.

9 V. Boris, L. Fabien, D. Zargarian, *Green Chem.,* 2013, **15,** 3188.

10 V. Pandarus, D. Zargarian, *Organometallics,* 2007, **26,** 4321.

11 M. E. Van der Boom, S. Liou, L. J. W. Shimon, Y. Ben-David, D. Milstein, *Inorg. Chim. Acta.,* 2004, **357,** 4015.

12 V. Gomez-Benitez, O. Baldovino-Pantaleon, C. Herrera-Alvarez, R. A. Toscano, D. Morales-Morales, *Tetrahedron Lett.,* 2006, **47,** 5059.

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

14 K. J. Jonasson, O. F. Wendt, *Chem. Eur. J.,* 2014, **20,** 11894.

15 A. Castonguay, C. Sui-Seng, D. Zargarian, A. L. Beauchamp, *Organometallics,* 2006, **25,** 602.

16 D. V. Gutsulyak, W. E. Piers, J. Borau-Garcia, M. Parvez, *J. Am. Chem. Soc.,* 2013, **135**, 11776.

17 N. A. Espinosa-Jalapa, S. Hernandez-Ortega, X. Le Goff, D. Morales-Morales, J. Djukic, R. Le Lagadec, *Organometallics*, 2013, **32,** 2661.

18 B. Vabre, D. M. Spasyuk, D. Zargarian, *Organometallics,* 2012, **31,** 8561.

19 S. Murugesan, B. Stoeger, M. D. Carvalho, L. P. Ferreira, E. Pittenauer, G. Allmaier, L. F. Veiros, K. Kirchner, *Organometallics,* 2014, **33,** 6132.

20 C. Azerraf, A. Shpruhman, D. Gelman, *Chem. Commun.,* 2009, 466.

21 F. Estudiante-Negrete, S. Hernandez-Ortega, D. Morales-Morales, *Inorg. Chim. Acta,* 2012, **387,** 58.

22 T. Chen, L. Yang, L. Li, K. Huang, *Tetrahedron* 2012, **68,** 6152.

23 V. Gomez-Benitez, O. Baldovino-Pantaleon, C. Herrera-Alvarez, R. A. Toscano, D. Morales-Morales, *Tetrahedron Lett.,* 2006, **47,** 5059.

24 (a) J. Zhang, C. M. Medley, J. A. Krause, H. Guan, *Organometallics,* 2010, **29,** 6393. (b) J. Zhang, A. Adhikary, K. M. King, J. A. Krause, H. Guan, *Dalton Trans.* 2012, **41**, 7959.

25 L. M. Martinez-Prieto, C. Melero, D. Del Rio, P. Palma, J. Campora, E. Alvarez, *Organometallics,* 2012, **31,** 1425.

26 V. Pandarus, D. Zargarian, *Chem. Commun.,* 2007, 978.

27 A. Castonguay, A. L. Beauchamp, D. Zargarian, *Organometallics,* 2008, **27,** 5723.

28 D. M. Grove, G. van Koten, R. Zoet, *J. Am. Chem. Soc.,* 1983, **105**, 1379.

29 A. W. Kleij, R. A. Gossage, R. J. M. K. Gebbink, N. Brinkmann, E. J. Reijerse, U. Kragl, M. Lutz, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.,* 2000, **122**, 12112.

30 L. A. van de Kuil, D.M. Grove, R. A. Gossage, J. W. Zwikker, L. W. Jenneskens, W. Drenth, G. van Koten, *Organometallics,* 1997, **16**, 4985.

31 J. Hao, B. Mougang-Soume, B. Vabre, D. Zargarian, *Angew. Chem. Int. Ed.,* 2014, **53**, 3218.

32 T. J. Schmeier, A. Nova, N. Hazari, F. Maseras, *Chem. Eur. J.* 2012, **18**, 6915.

33 J. Campora, P. Palma, D. Del Rio, M. Mar Caonejo, E. Alvarez, *Organometallics,* 2004, **23**, 5653.

34 J. Campora, P. Palma, D. Del Rio, E. Alvarez, *Organometallics,* 2004, **23**, 1652.

35 S. Chakraborty, Y. J. Patel, J. A. Krause, H. Guan, *Angew. Chem. Int. Ed.,* 2013, **52**, 7523.

36 B. J. Boro, E. N. Duesler, K. I. Goldberg, R. A. Kemp, *Inorg. Chem.* 2009, **48**, 5081.

37 S. J. Connelly, A. C. Zimmerman, W. Kaminsky, D. M. Heinekey, *Chem. Eur. J.,* 2012, **18**, 15932.

38 A. Castonguay, D. M. Spasyuk, N. Madern, A. L. Beauchamp, D. Zargarian, *Organometallics,* 2009, **28,** 2134.

39 (a) A. B. Salah, C. Offenstein, D. Zargarian, *Organometallics,* 2011, **30**, 5352. (b) A. B. Salah, D. Zargarian, *Dalton Trans.*, 2011, **40**, 8977. (c) B. Vabre, P. Petiot, R. Declercq, D. Zargarian *Organometallics* 2014, **33**, 5137.

40 V. Pandarus, D. Zargarian, *Organometallics,* 2007, **26,** 4321.

41 X. Lefèvre, G. Durieux, S. Lesturgez, D. Zargarian, *J. Mol. Catal. A,* 2011, **335**, 1.

42 A. Castonguay, A. L. Beauchamp, D. Zargarian, *Inorg. Chem.,* 2009, **48**, 3177.

43 J. Borau-Garcia, D. Gutsulyak, R. Burford, W. Piers, *Dalton Trans.,* 2015, **44**, 12082.

44 S. Murugesan, B. Stoeger, M. Weil, L. F. Veiros, K. Kirchner, *Organometallics* 2015, **35**, 1364.

45 S. Chakraborty, J. A. Krause, H. Guan, *Organometallics* 2009, **28**, 582.

46 O. R. Luca, J. D. Blakemore, S. J. Konezny, J. M. Praetorius, T. J. Schmeier, G. B. Hunsinger, V. S. Batista, G. W. Brudvig, N. Hazari, R. H. Crabtree, *Inorg. Chem.,* 2012, **51**, 8704.

47 S. Chakraborty, H. Guan, *Dalton Trans.,* 2010, **39,** 7427.

48 S. Chakraborty, P. Bhattacharya, H. Dai, H. Guan, *Acc. Chem. Res.* 2015, **48**, 1995.

49 A. Rossin, M. Peruzzini, F. Zanobini, *Dalton Trans.,* 2011, **40,** 4447.

50 S. Chakraborty, J. Zhang, Y. J. Patel, J. A. Krause, H. Guan, *Inorg. Chem.,* 2013, **52,** 37.

51 S. Chakraborty, J. Zhang, J. A. Krause, H. Guan, *J. Am. Chem. Soc.* 2010, **132**, 8872.

52 T. J. Schmeier, N. Hazari, C. D. Incarvito, J. A. Raskatov, *Chem. Commun.,* 2011, **47**, 1824.

53 S. Chakraborty, Y. J. Patel, J. A. Krause, H. Guan, *Polyhedron,* 2012, **32,** 30.

54 L. M. Martinez-Prieto, C. Real, E. Avila, E. Alvarez, P. Palma, J. Campora, *Eur. J. Inorg. Chem.,* 2013, 5555.

55 H. Suh, T. J. Schmeier, N. Hazari, R. A. Kemp, M. K. Takase, *Organometallics,* 2012, **31,** 8225.

56 A. Vladislava, A. Rossin, N. V. Belkova, M. R. Chierotti, L. M. Epstein, O. A. Filippov, R. Gobetto, L. Gonsalvi, A. Lledos, E. S. Shubina, F. Zanobini, M. Peruzzini, *Angew. Chem. Int. Ed.,* 2011, **50,** 1367.

57 M. R. Chierotti, A. Rossin, R. Gobetto, M. Peruzzini, *Inorg. Chem.,* 2013, **52,** 12616.

58 G. Zhu, X. Li, G. Xu, L. Wang, H. Sun, *Dalton Trans.,* 2014, **43,** 8595.

59 Z. Lian, G. Xu, X. Li, *Acta Crystallogr. Sect. E: Struct. Rep. Online* 2010, **E66**, m636.

60 M. A. Kent, C. H. Woodall, M. F. Haddow, C. L. McMullin, P. G. Pringle, D. F. Wass, *Organometallics,* 2014, **33,** 5686.

61 T. J. Hebden, A. J. St. John, D. G. Gusev, W. Kaminsky, K. I. Goldberg, D. M. Heinekey, *Angew. Chem. Int. Ed.,* 2011, **50,** 1873.

62 G. Xu, H. Sun, X. Li, *Organometallics,* 2009, **28,** 6090.

63 S. Huang, H. Zhao, X. Li, L. Wang, H. Sun, *RSC Adv.,* 2015, **5**, 15660.

64 H. Zhao, H. Sun, X. Li, *Organometallics,* 2014, **33,** 3535.

65 P. Bhattacharya, J. A. Krause, H. Guan, *Organometallics,* 2011, **30**, 4720.

66 W. Wang, P. Gu, Y. Wang, H. Wei, *Organometallics,* 2014, **33,** 847.

67 P. Bhattacharya, J. A. Krause, H. Guan, *Organometallics,* 2014, **33,** 6113.

68 P. Bhattacharya, J. A. Krause, H. Guan, *J. Am. Chem. Soc.,* 2014, **136,** 11153.

69 T. J. Hebden, R. R. Schrock, M. K. Takase, P. Mueller, *Chem. Comm.,* 2012, **48,** 1851.

Graphical Abstract

This perspective article provides an overview of the advancements in the field of non-precious metal PCsp^2P and PCsp^3P pincer complexes.