# RECENT ADVANCES IN THE CHEMISTRY OF GROUP 9 – PINCER ORGANOMETALLICS

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## Abstract

Tridentate pincer ligands can be tailored to perform functions beyond stereoelectronic influence. This chapter showcases such functions and analyzes their impact in the recent chemistry of group 9 coordination compounds. Hemilabile ligands, redox-active designs, and scaffolds equipped with lone electron pairs or protic groups are described, and their cooperation with metal centers is analyzed. Discussions never lose sight of the different reactivity of cobalt that results from its frequent one-electron chemistry.

## Keywords:

Pincer ligand, Cobalt, Rhodium, Iridium, Hemilabile, Redox-active, Functional ligand, Metal-ligand cooperation.

**Contents**

## 1. INTRODUCTION AND SCOPE

The term “pincer ligand” groups together ligand types that have in common their tridentate meridional (*mer*) coordination mode. Beyond this, ligands may combine different donor atoms and skeletons to attain a variety of stereoelectronic properties and functions, thus becoming very diverse and spanning all areas of metal chemistry. Traditionally, the main goal behind the choice of these ligands was stability: the search for metal-ligand synthons in which decomposition would not be a concern. This way, pincer ligands made possible key findings such as, for example, the observation of methane complexes,[1] or the development of groundbreaking catalytic alkane functionalizations.[2] Yet, the generalized use of these ligands is increasingly showing that they are far from being mere stabilizing auxiliaries, to the point that pincer scaffolds have emerged particularly suited to hold functional objects in the vicinity of metals. Pincer ligand functionalization can comprise a variety of design strategies implicating donor atoms, ligand backbones, peripheral sites or appended groups, which in turn may offer additional electron pairs for cooperative bond activations, protic groups to direct reagent coordination, extended $\pi$ orbitals to temporarily accommodate electrons, etc. Considering that understanding and exploitation of such ligand functions nowadays constitute a major stimulus for research in this area, this contribution focuses on organometallic chemistry driven or facilitated by them.

In its first part (section 2), this chapter addresses the differences between the base and the noble metals of the group in fundamental aspects of their coordination chemistry, also discussing the impact of such differences in elementary organometallic reactions. In its second part (section 3), operation of the various types of functional pincers is analyzed on the basis of group 9 examples, covering the recent evolution of the field in a comprehensive manner.

Even though the goal behind using functional pincers is most often catalysis, this contribution assumes just a brief description of catalytic results, since the topic, in particular Co pincer catalysis, has thoroughly been covered in multiple recent reviews focusing pincers in general[3-7] or specific catalytic applications.[8-10] Pincer architectures without documented functional behavior are not surveyed, at least not specifically, although examples of them are used throughout to illustrate fundamental issues. For perspectives covering evolution of important "classical" scaffolds such as PCP,[11] PSiP,[12,13] those comprising N-heterocyclic carbene- (NHC)[14-19] or S-based[20,21] donor groups, chiral platforms,[22-25] etc., the reader is referred to recent reviews that occasionally include separate coverage of group 9 derivatives. Classical challenges of great relevance for group 9 pincer chemistry such as alkane functionalization by dehydrogenation[26-31] are not addressed either, in the understanding that this area is periodically and carefully reviewed by those authors more directly implicated in their development.

By definition, tridentate ligands that coordinate in the facial (*fac*) mode should be excluded either, although this is often not as clear-cut as it may appear, because most architectures, *fac* or *mer*, are flexible enough to exceptionally adopt the other coordination mode as well as intermediate situations.[32] This is illustrated in Scheme 1 with the help of a *not representative* selection of Ir(PCP) complexes, whose (unarguable pincer) aryl-based ligands offer clear examples of nonmeridional coordination. According to the CCDC database,[33] these PCP designs bind Ir mostly *mer*, although P−Ir−P angles rarely reach 167° because of the intrinsic metric restrictions of the ligand framework. In the examples with electron-withdrawing $P(CF_3)_2$ substituents, reported by Roddick and co-workers,[34-37] the electron-poor P atoms are likely to avoid being mutually trans in order to minimize competition for dπ back-bonding. Yet, ligand coordination to Ir(I) in 4- and 5-coordinate complexes **1** and **2** is not much different from that of electron-rich ligands,[38] although the peculiar electronics definitively favor ligand folding into the *fac* mode in the electron-poorer Ir(III) derivative **3**. Since the backbone is the same, electron-rich versions of this archetypical pincer ligand should also be susceptible of folding into *fac*, although reasons must be different. Example **4** and analogues coordinating other *para*-benzoquinone ligands, recently reported by Jones and co-workers,[39] show that this indeed happens if thermodynamics are properly balanced.

[insert Scheme 1 here]

**Scheme 1** P−Ir−P bond angles in some selected Ir(PCP) pincers

The following pages describe complexes whose structures, like those of $^{\mathbf{R}}\mathbf{2}$, lie half-way between *fac* and *mer*, and hence seem equally accessible by distortion from either mode. Likewise, their reactions might be equally reproduced in nonpincer ligand environments, so that reactivity correlations with their pincer nature, implicit by their inclusion in this review, should be carefully pondered. Although possibilities are too many to be individually commented here, we want to mention at least two ligand architectures that have deserved significant coverage in the following pages whose pincer label is arguable. The first is the xantphos and related POP designs, whose predominant chemistry is that of chelating diphosphines but are increasingly scrutinized with regard to their hemilabile O-coordination.[40] The second comprises Grützmacher's bis(alkene)amine $(trop)_2NH$ (trop = 5-H-dibenzo[*a,d*]cycloheptene-5-yl) and its amide and radical amidyl versions,[41-43] which, to the best of our knowledge, have never been previously referred to as pincer ligands, but certainly have a number of features in common with them.

## 2. METAL OXIDATION STATES, COORDINATION GEOMETRIES AND SPIN STATES

Rh and Ir regularly form low-spin complexes of geometries fully compatible with *mer* tridentate ligands, but this preferred coordination mode of pincers mismatches the tetrahedral geometry often exhibited by Co(I) and Co(II) complexes. Besides, due to the small ligand-field stabilization energy characteristic of 3*d* metals, subtle changes in the coordination environment may become decisive for electronic structure and orbital occupancy, hence for reactivity. As a consequence, the mere use of pincer ligands may interfere cobalt chemistry beyond those effects intentionally introduced through the stereo-electronic features of skeletons and substituents.

## 2.1 Cobalt(II)

Most common procedures for the synthesis of Co pincers draw on bench stable Co(II) dihalogenides or dihalogeno complexes and the corresponding pincer ligand precursors: either the pincers themselves when neutral or deprotonated versions in case of monoanionic, dianionic or trianionic pincers. Hence, Co pincer chemistry frequently starts at $d^7$ paramagnetic species whose characterization requires both X-ray diffraction to know structures, and magnetic susceptibility determinations (SQUID magnetometry,[44] NMR Evans' method,[45,46] etc.) to recognize spin states.

Neutral pincer ligands are expected to form neutral 5-coordinate high-spin Co(II) complexes, but exceptions are numerous and reveal an intricate interplay among pincer ligand features, coordination geometries and spin states. For example, complexes [Co(Cl)$_2${$^{R}$PN(H)P}] (**$^{R}$5**, in Scheme 2) were prepared by the groups of Schneider (R = *t*Bu),[47] Arnold (R = *i*Pr),[48] and Jie and Li (R = Ph),[49] through direct reaction of the corresponding neutral ligands HN(CH$_2$CH$_2$PR$_2$)$_2$ with CoCl$_2$. Complexes were found to exhibit high-spin electronic configuration (S = 3/2). According to density functional theory (DFT) calculations by Beller et al.,[50] the quartet states of **$^{iPr}$5** and **$^{Ph}$5** lie 13.9 and 6.3 kcal mol$^{-1}$, respectively, below the (S = 1/2) low-spin options. The complexes show different geometries in the solid state (Fig. 1): distorted square pyramidal with an axial chloride for **$^{tBu}$5**, and distorted trigonal bipyramidal with the amine and a chlorine atom in the axial positions in the cases of **$^{iPr}$5** and **$^{Ph}$5**. The ligand skeleton demonstrates remarkable conformational flexibility to fit each of the geometries. Going from **$^{tBu}$5** to **$^{iPr}$5** and **$^{Ph}$5,** the PCoP angle closes from 152° to 126° and 117°, at the expense of significant changes in the Co−P and Co−N bond distances, which in the latter case lengthen from 2.18 to 2.34 and 2.38 Å. The latter two values lie well outside the usual range of Co−N bond distances that can be extracted from the CCDC:[33] above 95% of them within the 1.80 - 2.25 Å interval. As a matter of fact, both trigonal bipyramidal derivatives, but $^{\mathbf{Ph}}$**5** in particular, may be regarded as 4-coordinate distorted tetrahedral bearing $\kappa^2$-*P* ligands with pendant free amines. Curiously, this was the description given to the complex when first prepared, without the help of either structural information or calculations, just based on precedents of related PN(R)P ligands.[51] As a counterpoint, Fig. 1 also includes the structure of the square pyramidal bromo derivative $[Co(Br)_2\{^{iPr}PN(H)P\}]$ ($^{\mathbf{iPr}}$**6**), which not only differs from that of its chloro analogue $^{\mathbf{iPr}}$**5,** but also favors low-spin configuration (by just 2 kcal mol$^{-1}$ according to DFT calculations).[50] Note that in both square pyramids ($^{\mathbf{tBu}}$**5** and $^{\mathbf{iPr}}$**6**) the NH points *anti* to the halogeno apex.

[insert Fig 1 here]

**Fig. 1** Crystal structures of Co(II) complexes $[Co(X)_2\{^{R}PN(H)P\}]$ (CCDC codes from left to right: $^{tBu}$**5** ILELOC reported by Schneider et al.;[47] $^{\mathbf{iPr}}$**5** DAJCUO reported by Arnold et al.;[48] $^{\mathbf{Ph}}$**5** ZEVSAX and $^{\mathbf{iPr}}$**6** ZEVRUQ, reported by Beller et al.[50] Hydrogen atoms except NHs are omitted for the sake of clarity.

[insert Scheme 2 here]

**Scheme 2** Examples of cobalt(II) complexes with neutral PNP ligands

Using $CoI_2$ and closely related N-substituted bis(phosphinoethyl)amines $RN(CH_2CH_2PPh_2)_2$ (R = Ph, $CH_2Ph$, etc.), Gray and co-workers obtained 4-coordinate tetrahedral complexes $[Co(I)_2\{^{Ph}PN(R)P\}]$ (**7**) in which the PNP ligand was unequivocally $\kappa^2$-*P* bidentate (Co−N ~ 3.7 Å in solid state).[52] Yet, the EPR spectra in solution of complexes **7** and their magnetism indicated the existence of and equilibrium with the 5-coordinate species **7’** (R-, solvent- and temperature-dependent). In fact, a co-crystal containing in the asymmetric unit both 4- and 5-

coordinate isomers was obtained for R = benzyl. The 5-coordinate structure **7’** (Co−N = 2.08 Å) was in this case square pyramidal, with an iodine atom in the apex, while magnetic measurements indicated low-spin configuration in this environment.

In contrast to the formation of tetrahedral **7**, Shores, Yang and co-workers observed that a $^{tBu}P^{NH}N^{NH}P$ ligand based on the 2,6-bis(amino)pyridine scaffold, reacted with $CoBr_2$ to form the square planar low-spin derivative **8**, after displacement of one bromide to the outer coordination sphere.[53] Complexes **9** and **10**, with related pyridine-centered $^{tBu}PNP$ and $^{tBu}P^{O}N^{O}P$ ligands, respectively, remained 5-coordinate, though exhibited different coordination geometries and spin. In the solid state, the bis(phosphinomethyl)pyridine derivative **9** was found to be high-spin, while the $P^{O}N^{O}P$ complex **10** showed crossover between the doublet and quartet spin-state options.[54] As also occurred in the previous examples, magnetism in solution was further complicated by the lability of ligands (bromides in this case), which is another typical feature of Co(II) complexes.[55]

The reactions of $CoX_2$ with anionic pincer ligands are likely to form 4-coordinate complexes, since at least one of the halogenides should be removed by the deprotonated pincer reagent, commonly an alkaline salt. Still, complexes should choose between distorted tetrahedral high-spin or low-spin square planar geometries. Scheme 3 illustrates some early work from the groups of Fryzuk and Caulton using Fryzuk’s bis(phosphino)amido ligand $N(SiMe_2CH_2PR_2)_2$.[56,57] Monomeric 4-coordinate Co(II) complexes **11** were first prepared for R = Ph and found to exhibit distorted tetrahedral geometries and high-spin, irrespective of the halide. Yet, replacement of the halide ligand with stronger $\sigma$-donors such as alkyls led to the planar low-spin derivatives **$^{Ph}$12**.[58] The bulkier and more basic **$^{tBu}$11** were found to display structures that depended on halide size.[59] The iodo complex remained non-planar high-spin, while the chloro derivative was planar low-spin in solid state but evidenced spin isomers in solution. Change of the aliphatic pincer skeleton to a non-silylated one, as in complex **13** (prepared from the already discussed complex $^{\mathbf{iPr}}$**5** and *n*BuLi), led to planar low-spin structures both in solution and solid state.[60] The square planar structure was also that observed in cationic derivative **15**, despite its essentially different neutral bis(phosphino)amino pincer ligand. Low-spin planar structures were also the preferred option for related derivatives with anionic bis(phosphinomethyl)pyrrolido PNP ligands,[61,62] and for PCP analogues with a variety of skeletons.[11,63] Actually, the free energy difference between pseudotetrahedral high-spin and planar low-spin isomers of a [Co($P^{NMe}C^{NMe}P$)Cl] complex coordinating a 1,3-bis(methylamino)benzene-based PCP ligand was calculated to be up to 19.5 kcal mol$^{-1}$ favorable to the planar option.[64]

[insert Scheme 3 here]

**Scheme 3** Reactions between Co(II) PNP complexes and alkyl lithium reagents. Anion of **15** is tetraphenylborate ($BPh_4^-$).

A singular 4-coordinate Co(II) pincer was reported to escape from the disjunctive between tetrahedral high-spin or square planar low-spin options: the amido(dialkoxo) Co($^{CF3}$ONO) complex **16** represented in Scheme 4.[65] The compound was found to exhibit distorted square planar geometry, with O−Co−O and N−Co−Cl angles of 155° and 160°, respectively, together with uncommon EPR spectra eventually assigned to a S = 3/2 spin state and rationalized on the basis of DFT and crystal field (CF) calculations. Key to the stabilization of this rare species[66] are both the interactions with solvated $Li^+$ cations, that compensate charge of the amido(dialkoxo) trianionic ligand, and the presence of fluorinated groups next to oxygens, that minimize pincer $\sigma$-donation and hence antibonding character of the $d_{x2-y2}$ orbital.

[insert Scheme 4 here]

**Scheme 4** Synthesis and crystal structure of the square planar high-spin complex $[\{Li_2(DME)_2\}\{Co(^{CF3}ONO)Cl\}]$ (**16**) (CCDC code QUZLUU) reported by Stoian, Veige and co-workers.[65] Hydrogen atoms are omitted for the sake of clarity.

Another atypical Co(II) pincer is the 3-coordinate species **18** (Fig 2), obtained from the NNN dianionic ligand 3,5-*t*$Bu_2$-bis(pyrrolyl)pyridine.[67] The 4-coordinate adduct **17** was prepared by reaction between $CoCl_2$ and the *in situ* deprotonated bis(pyrrol)pyridine ligand precursor, in diethylether. It was found to exhibit high-spin and a non-planar structure best described as cis-divacant octahedron, likely resulting from steric encumbrance. The reactions in toluene also afforded a solvent-containing complex, **18**, but the X-ray structure showed that the solvent molecule was in this case interstitial and intercalated between two [Co(NNN)] units rather than coordinated.

[insert Fig 2 here]

**Fig. 2** Crystal structure of Co(II) complexes $[Co(NNN)(OEt_2)]$ (**17**) (CCDC code ASUDEZ) and $[Co(NNN)].C_7H_8$ (**18**) (CCDC code ASUDOJ) reported by Mindiola and co-workers.[67] Hydrogen atoms are omitted for the sake of clarity.

As can be inferred from the previous comments, and also happens for neighboring base metals, spin states and spin-crossover constitute very relevant issues in Co chemistry, in particular for Co(II) complexes. They indeed are a concern for characterization but also a potential source of important magnetic applications.[68] Pincers are not alien to the research in this field; much on the contrary, stability makes them especially attractive candidates for magnetic materials. As a matter of fact, architectures such as the 6-coordinate bis-pincer octahedral complexes based on terpyridines[69] or related NNN ligands,[70-73] have become classic choices for the study of spin-crossover phenomena and their potential applications.[54,74-79]

Besides spin-crossover, Co(II) complexes may display strong first-order spin-orbit coupling and in consequence large magnetic anisotropy (zero-field splitting) in the high-spin state.[80] As a result, complexes may show slow relaxation of their magnetization: a defining property for the so-called single-molecule magnets, or single-ion magnets (SIMs) in case of mononuclear complexes.[81] These molecules represent the smallest possible unit for spin-based data storage and therefore attract great scientific and technological interest.[82,83] Several 5-coordinate Co(II) pincers containing neutral NNN ligands such as 2,6-bis(imino)pyridines,[84] 2,2':6',2''-terpyridine[85,86] or 2,6-bis(pyrazol-1-yl)pyridine (**19**, Fig. 3)[87] were characterized as SIMs. The 6-coordinate Co(II) asymmetric bis-pincer [Co(ONO)($^{H}$ONO)] (**30**), coordinating both a dianionic pyridine-2,6-dicarboxylato ligand and a neutral 2,6-dimethanolpyridine, was also found to display SIM behavior with an unusually slow relaxation.[88]

[insert Fig 3 here]

**Fig. 3** Crystal structures of the Co(II) single-ion magnets [Co(Cl)$_2$(NNN)] (**19**) (CCDC code NIRSOZ) reported by Świtlika, Bieńko and co-workers,[87] and [Co(ONO)($^{H}$ONO$^{H}$)] (**20**) (CCDC code VILBEA) reported by Boča and co-workers.[88] Hydrogen atoms except those at the coordinated oxygens of **20** are omitted for the sake of clarity.

The ubiquitous 6-coordinate bis-terpyridine derivatives also attracted interest as catalysts despite their 19-electron configuration. A handful of [Co(NNN)$_2$]$^{2+}$ bis-pincers were recognized as electrocatalysts for CO$_2$ reduction to CO,[89] although this transformation competed with the production of H$_2$ from the requisite proton source.[90] Consistently with the absence of available empty d orbitals, mechanistic studies suggested catalytic cycles based on protonation and subsequent decoordination of the ligand pyridyl arms, which act as a proton relays, as well as fully ligand-based alternatives.[91] Visible light-driven proton reduction was also found possible for this type of catalysts in the presence photosensitizers.[92] These octahedral bis-pincer derivatives also played a crucial role in characterizing redox-noninnocence[93,94] of bis(imino)pyridine ligands,[95-97] as discussed in following pages.

## 2.2 Cobalt(I)

Often, destination of Co(II) pincer precursors is reduction into Co(I) derivatives, which commonly requires strong reductants such as alkaline metals, potassium graphite ($KC_8$), sodium naphtalenide ($NaC_{10}H_8$), etc. Hydride or alkyl lithium reagents can drive such reductions too,[62,98,99] as already shown in Scheme 3 for the *n*BuLi reduction of $^{\mathbf{iPr}}$**5** into **14**, that competed with the desired dehydrohalogenation to form **13**.[60] In this particular case, selective reduction succeeded using $NaC_{10}H_8$[100] or $NaBH_4$[50] instead of *n*BuLi, whereas selective dehydrohalogenation (of the $^{\mathbf{tBu}}$**5** analogue) was achieved using KO*t*Bu.[47] Many other examples can further illustrate that the outcome of these reductions is highly dependent on the experimental conditions, in particular on the choice of reducing agent. A compelling case is the mercury-bridged dicobalt(I) species (**21**, Fig. 4), obtained after reduction of $[Co(^{tBu}P^{O}C^{O}P)I]$ with Na/Hg amalgam.[63] Also importantly, the frequent choice of dry $N_2$ as "inert" atmosphere for these reductions commonly afforded Co(I) dinitrogen complexes, which have become a relevant class of compounds in Co pincer chemistry.[101-105]

[insert Fig 4 here]

**Fig. 4** Crystal structure of Co(I) complex $[(\mu\text{-Hg})\{Co(^{tBu}P^{O}C^{O}P)\}]$ (**21**) (CCDC code APEVIB) reported by Heinekey and co-workers.[63] Hydrogen atoms are omitted for the sake of clarity.

The experimental conditions under which complexes $^{\mathbf{Ph}}$**11** underwent selective halogenide-by-alkyl metathesis to form $^{\mathbf{Ph}}$**12** (Scheme 3) drove selectively reduction of the bulkier chloro analogue $^{\mathbf{tBu}}$**11** into Co(I) complex **22** (Scheme 5). Despite coordinative unsaturation and likely favored by the sterically demanding ligand, **22** was found to remain mononuclear, adopting a T-shaped high-spin ($d^8$, S = 1) structure.[106,107] Contrarily, the analogue obtained by reduction of

**13** with $KC_8$ turned on the lone pair at imido nitrogen to rearrange into dinuclear complex **23**.[60] This dimer exhibited a Co−Co distance of about 2.42 Å and a low magnetic moment of $0.8 \pm 0.1$ $\mu$B/Co, both suggestive of antiferromagnetic (AF) coupling through a Co−Co bonding interaction. Using a slightly different (aromatic) bis(phosphino)amido skeleton, Mindiola and co-workers found an alternative dinuclear arrangement in which the $Co_2N_2$ core was planar (**24**) instead of bent.[108] This dimer version was found to be diamagnetic with a very short distance between cobalt atoms of about 2.25 Å, altogether suggestive of a Co=Co double bond.

[insert Scheme 5 here]

**Scheme 5** Mononuclear vs dinuclear arrangements of Co(I) (phosphino)amido pincer complexes and their dinitrogen adducts

The 3-coordinate Co(I) complex **22** did not show agostic interactions in the solid state, and evidenced no or limited propensity to bind weak nucleophiles in the vacant fourth site. This was argued to imply that any new Co−L bond will have to provide significant binding energy to overcome that required to induce electron pairing (spin-induced barrier). In agreement with this reasoning, **22** was found to reversibly bind $N_2$ to form square planar diamagnetic dinitrogen complex **26**, in a process calculated to be essentially thermoneutral ($\Delta G°_{298} = 0 \pm 3$ kcal mol$^{-1}$).[59] Yet, the related (enamido)(iminophosphorane)phosphino derivative **25** formed the tetrahedral high-spin complex **29** upon $N_2$ coordination,[109] demonstrating that adduct formation does not necessarily imply electron pairing in the 14-electron precursors. Regardless, high-spin 4-coordinate Co(I) pincers such as **29** or **14** (Scheme 3) are the exception rather than the rule, being restricted to weak-field ligands. As an example, the neutral bis(phosphinomethyl)pyridine derivatives [CoX($^{iPr}$PNP)] were found to be high-spin tetrahedral for X ligands such as chloride (**30**, Fig. 3),[99] triflate, benzoate, alkoxides or aryloxides,[110] but low-spin planar for C-donor ligands such as methyl[99] or 2-benzofuranyl.[110] The X = $CH_2SiMe_3$

derivative lies at the borderline, showing a planar solid-state structure and diamagnetism at low temperature, but broad paramagnetically-shifted NMR resonances at room temperature as a result of the thermal population of the triplet state.[111] Steric effects may once again become determinant, as indicated by diamagnetism of derivative [CoCl($^{tBu}$PNP)] (**31**, Fig. 5), in which the large *t*Bu groups are claimed to inhibit the chloride from distorting from the idealized metal−ligand plane.[98] Consistently with the expected increase of the overall field strength on adding more ligands, the 5-coordinate Co(I) pincers so far reported are all diamagnetic, with structures ranging from trigonal bipyramidal[64,108,112-118] to square pyramidal.[38,99,119,120]

[insert Fig 5 here]

**Fig. 5** Crystal structures of Co(I) complexes [CoCl($^{R}$PNP)] (R = *i*Pr, **30** CCDC code WIYHET; R = *t*Bu, **31** CCDC code LEYNIP) reported by Chirik and co-workers.[98,99] Hydrogen atoms are omitted for the sake of clarity.

In contrast to mononuclear derivatives **22** and **25** (Scheme 5), dimer **23** was found unreactive toward dinitrogen, though the mononuclear dinitrogen adduct **27** was prepared replacing the argon atmosphere by $N_2$ during the synthesis of **23** (hence presumably sequestrating the 3-coordinate synthon prior dimerization).[60] Once again in contrast, dimer **24** was indeed found to reversibly bind $N_2$, in solution and in the solid state, to form the dinuclear adduct **28**. The chemistry around dinuclear complexes **24** and **28** was more intricate than it appears in Scheme 5 since initial reduction of the [CoCl(PNP)] precursor, with sodium naphthalenide under $N_2$, did not stop at Co(I) but directly led to the highly reactive Co(−I) dinitrogen derivative **32** (Fig. 6), which subsequently evolved into complex **28**. **32** was characterized by X-ray diffraction as consisting of two dianionic $d^{10}$ units, each coordinating an end-on $N_2$ ligand, hold together by four solvated (tetrahydrofuran = thf) sodium cations.[108] Cations interact both end-on and side-on with the $N_2$ ligands,[121] and with the metals and the lone pairs at PNP nitrogens. As expected from the low-valent metal center and the framework of extra interactions, the IR νNN frequency of **32**, 1781 cm$^{-1}$, evidenced a significant degree of $N_2$ activation compared to the Co(I) derivatives of Scheme 2: 2004 (**26**), 1999 (**27**), 2024 (**28**) and 2071 (**29**) cm$^{-1}$ (2331 cm$^{-1}$ for free $N_2$). Yet, only the least activated of these species, **29**, was so far found catalytically active in $N_2$ reduction: in this case to produce $N(SiMe_3)_3$ (~200 equiv) in the presence of excess $KC_8$ as reducing agent and $Me_3SiCl$. This silylation method for nitrogen fixation was first reported by Shiina[122] and found practical for several non-pincer Co catalyst precursors,[123-125] as well as for derivatives [Co($^{Cy}$PSiP)($N_2$)($PR_3$)], which contain monoanionic silyl-based ligands.[126] Besides, [Co($^{R}$PNP)($N_2$)] complexes with 2,5-bis(phosphinomethyl)pyrrolide anionic ligands, also developed by Nishibayashi and co-workers,[61] provided the first example of truly catalytic conversion of dinitrogen into ammonia.[127] Under the experimental conditions previously established by Peters and co-workers for 'superstoichiometric' direct formation of $NH_3$ from $N_2$ (large excesses of a strong reducing agent such as $KC_8$ and $HBAr^F_4\cdot 2Et_2O$ as $H^+$ source, in diethylether at −78 °C for 1h),[128] the R = *t*Bu derivative produced 15.9 ± 0.2 equiv of ammonia plus 1.0 ± 0.2 equiv of $NH_2NH_2$.

[insert Fig 6 here]

**Fig. 6** Crystal structure of Co(−I) complex [{$Na_2$(thf)$_3$}{Co(PNP)($N_2$)}]$_2$ (**32**) (CCDC code YEGJAW) reported by Mindiola and co-workers.[108] All hydrogens and the carbon atoms of the thf ligands are omitted for the sake of clarity. Pincer skeletons are represented as wireframes.

### 2.3 Cobalt(0) and below

Dimer **32** constitutes a rare example of Co pincer in oxidation state below Co(I). Other singular reduced species are those represented in Fig. 7. The paramagnetic cationic Co(I)−Co(0) complex [Co($^{iPr}$PN(H)P)]$_2$[$(BEt_3)_2H$] (**33**), again a derivative of **$^{iPr}$5** (Scheme 2), was crystallized from a mixture of products of the reaction with two equivalents of $NaBEt_3H$ in the presence of pinacolborane (Bpin) excess.[100] The Co−Co distance of 2.46 Å is within the range typically associated with a Co−Co single bond, while the metal−ligand bond distances differ significantly between the two cobalt subunits, consistently with a mixed-valence compound. A mononuclear Co(0) derivative with a similar amino ligand, but in $\kappa^2$-P coordination mode, [Co{$^{Cy}$PN(Me)P}(CO)$_2$], was described by Bernskoetter and co-workers.[129] The further N-coordination of the ligand accompanied by the release of CO was proposed to explain an experimentally observed evolution of this complex into a new paramagnetic species, but crystals suitable to prove formation of a pincer could not be obtained. Another amino ligand, the bis(alkene)amine (trop)$_2$NH, hereinafter $\eta^2$N(H)$\eta^2$, was also found to form stable, distorted tetrahedral, neutral Co(0) complexes [Co{$\eta^2$N(H)$\eta^2$}L] with phosphino, phosphito or NHC L ligands, as exemplified by **34** in Fig. 7. Their EPR signals showed g-values and hyperfine couplings indicative of one unpaired electron in an orbital with high d$z^2$ character.[130]

[insert Fig 7 here]

**Fig. 7** Structures of the cation of the Co(I)−Co(0) complex **33** (CCDC code GUKFID) reported by Chirik and co-workers,[100] Co(0) complex **34** (CCDC code LAXVOY) reported by Gianetti, Grützmacher et al., and the mononuclear version of Co(0) pincer **35** (CCDC code WUWNEJ) reported by Peters et al.[131] H atoms except NHs of **34** are omitted for the sake of clarity.

The also spin-doublet Co(0) pincer [Co{$^{iPr}$P$\eta^2$(BC)P}(N$_2$)] (**35**) was prepared by direct reaction of the corresponding borane ligand with CoCl$_2$, followed by treatment with Na/Hg amalgam under nitrogen atmosphere.[131] **35** formed crystals sharing the asymmetric unit with a N$_2$-bridged dinuclear version, although it was proposed to be the main species in solution in view of the observed NN stretching frequency, 2098 cm$^{-1}$. The borane pincer ligand coordinates in the $\kappa^2$-P:$\eta^2$(BC) mode,[132] which is well-known in borane pincers. Details of the bonding and reactivity of this complex will be discussed in the next section.

Wieghardt, Chirik and co-workers reported the mononuclear dinitrogen complexes [Co(NNN)($N_2$)] and [Na(thf)$_3$][Co(NNN)($N_2$)],[133,134] apparently in Co(0) and Co(−I) oxidation states, respectively, though containing redox-noninnocent[93,94] NNN 2,6-bis(imino)pyridine pincer ligands.[135] Their detailed characterization indicated Co(I) oxidation state for both complexes, and reduced versions of the NNN ligand: monoanionic radical and closed-shell dianionic, respectively. Further details of these redox-active pincers will be discussed in the next section. Another complex in deceptive low-valent oxidation state is **36** (Scheme 6), expected to be a Co(−I) derivative coordinating a cationic bis(phosphino)phosphenium PPP ligand. The structure of the complex, however, clearly shows pyramidal geometry about the central phosphorus, indicative of a lone pair at this atom. Hence, the ligand is reduced by two electrons, to an anionic bis(phosphino)phosphide, at the expense of the metal, now in formal oxidation state Co(I).[136] Interestingly, such N-heterocyclic phosphenium reduction seems to be favored in this particular pincer environment,[137] since monodentate and chelating versions of these ligands, phospha-analogues of Fischer carbenes,[138] remain planar at the phosphorus atom after coordination.[139] This has been attributed to the skeleton conformation forced by pincer coordination, which diminished nitrogen-to-phosphorus $\pi$-donation, thus relatively destabilizing cationic phosphonium.[140,141] This Scheme 6 also illustrates a second common entry to cobalt pincers, alternative to that starting from Co(II) salts, which directly leads to low-valent pincers using Co(0) (or Co(−I) in the example) carbonyl or phosphino precursors.

[insert Scheme 6 here]

**Scheme 6** Synthesis and crystal structure of complex [Co(PPP)(CO)$_2$] (**36**) (CCDC code QEJMID) reported by Thomas and co-workers.[136] Hydrogen atoms are omitted for the sake of clarity.

## 2.4 Cobalt(III)

Most Co(III) pincer complexes are low-spin ($d^6$, diamagnetic) and octahedral. Among exceptions, trigonal bipyramidal [Co($P^{Si}N^{Si}P$)(X)$_2$][58] and square pyramidal [Co($P^NC^NP$)(Cl)$_2$][64]

dihalogeno complexes showed magnetic moments consistent with S = 1 intermediate spin-state. Both complexes were obtained from Co(II) precursors via one-electron oxidation, using complexes **$^{Ph}$11** (in Scheme 3) and excess benzylhalides in one case, or $CuCl_2$ against [Co(P$^N$C$^N$P)Cl] in the other.

The square planar derivatives of Scheme 7 constitute another rare case for Co(III) pincers. Analogues **37** and **38** were prepared by the groups of Schneider[47] and Tonzetich,[142] respectively, by oxidation of the corresponding Co(II) chloro precursors with silver salts. Reaction success required the fully dehydrogenated versions of the ligands,[143] since otherwise oxidations resulted in ligand-centered reactions. Dehydrogenation of the bis(phosphinoethyl)amido or bis(phosphinomethyl)pyrrolido aliphatic backbones was achieved at the ligands already coordinated to the corresponding Co(II) chloro precursors, through reactions with the 2,4,6-tert-butylphenoxy radical or 1,4-benzoquinone, respectively. Both Co(III) complexes were paramagnetic, with no observable EPR signals and magnetic susceptibilities in line to those reported for (non-pincer) square planar derivatives of 3d$^6$ configuration and intermediate triplet spin-state.[144]

[insert Scheme 7 here]

**Scheme 7** Square planar Co(III) complexes

The related Co(III) cation **39** was also obtained by oxidation of the corresponding Co(II) neutral precursor with $AgBF_4$.[145] It was characterized by X-ray diffraction as planar, although in this case the complex was diamagnetic and therefore low-spin. Yet, substitution of the pyridine ligand by OH or alkoxydes produced neutral paramagnetic complexes **40**, whose magnetic moments again indicated S = 1 intermediate-spin configuration. Interestingly, the isopropylene linkages between the central pyridine ring and the anilide groups of this NNN ligand played a crucial role to attain oxidation of the metal center, as deduced from the behavior of related complex **41** shown in Scheme 8. In this oxidation attempt reported by Gordon and co-workers,[146] the reaction of the Co(II) precursor with 2 equivalents of trityl chloride produced the Gomberg dimer together with Co(II) dichloro complex **42**, after rearrangement of the symmetric dianionic bis(amido)pyridine ligand into a non-symmetric neutral imino-amino-pyridine. Further cases of noninnocent behavior of pincer ligands will be analyzed below.

[insert Scheme 8 here]

**Scheme 8** Oxidative rearrangement of a noninnocent NNN pincer

### 2.5 Cobalt(I)/cobalt(III) two-electron transformations

As can be inferred from the previous examples, the easiest way to reach Co(III) is from Co(II) precursors via one-electron oxidations. The facile one-electron chemistry of Co, and of base metals in general, contrasts to the typical behavior of their noble neighbors, which undergo instead facile two-electron oxidative addition (OA) and reductive elimination (RE): within the Rh(I)/Rh(III) and Ir(I)/Ir(III) or Ir(III)/Ir(V) manifolds for group 9. Such two-electron processes are essential for activation and catalytic functionalization of many substrates, hence their achievement with earth-abundant and inexpensive 3d metals constitutes a step toward sustainability. A possible strategy in this direction (to be discussed in the following section) relays in redox-active ligands able to accommodate unpaired electrons, which may help to empty or fulfill metal orbitals when required. Alternatively, given that one-electron chemistry benefits from easy access to open-shell high-spin states, their relative destabilization using strong-field ligands should favor the low-spin chemistry characteristic of second- and third-row transition metals.[147] It has been pointed out, nevertheless, that maintaining certain access to high-spin configurations can also be an asset for bond activation and catalysis, since rapid spin crossovers can “cut through” activation barriers leading to spin acceleration.[148-151]

Several examples in Co chemistry support the feasibility of using strong-field pincer ligands to achieve Co(I)/Co(III) two-electron transformations**.** Caulton and co-workers reported the reversible OA of $H_2$ to the already discussed high-spin T-shaped Co(I) complex **22**, to form diamagnetic Co(III) dihydride **43** (Scheme 9).[106,152] DFT calculations indicated that $H_2$ coordination to form a singlet dihydrogen adduct [Co(P$^{Si}$N$^{Si}$P)($H_2$)] leads to the observed product, whereas the alternative triplet intermediate releases back the $H_2$. **22** was found to catalyze ethylene hydrogenation, although failed to hydrogenate higher olefins. The reaction with $PhSiH_3$, another potential OA reagent, also took place, although the facile reaction with multiple silane equivalents only allowed for the characterization of the highly elaborated, non-pincer, Co(V) final product **44**.

[insert Scheme 9 here]

**Scheme 9** Oxidative additions to Co(I) complex [Co($^{tBu}$P$^{Si}$N$^{Si}$P)] (**22**)

Parent Co(I) complexes with non-silylated PNP amine or amide skeletons were also interrogated against $H_2$.[153] Despite the different coordination number, the 4-coordinate high-spin amino complex [CoCl($^{iPr}$PN(H)P)] (**15** in Scheme 3) behaved as **22**, reversibly adding dihydrogen to form a Co(III) cis-dihydride, in this case octahedral. The analogous reaction against $H_3SiPh$ also produced the corresponding Co(III) hydrido-silyl OA product, though irreversibly.[60] An apparently closer analogue of **22**, the 3-coordinate amido synthon [Co($^{iPr}$PNP)] generated *in situ* from low-spin **13** (in Scheme 3), did not add one equiv of $H_2$ but two: one oxidatively to the metal center and another formally across the Co–N bond.[153] This initially resulted in the octahedral Co(III) *mer* trihydride [Co(H)$_3$($^{iPr}$PN(H)P)], which seemingly evolved other species in solution. One of them was identified as a Co(II) dimer [Co(PNP)H]$_2$, which could be prepared independently via a slow, formally dinuclear, $H_2$ addition to the doubly amido-bridged precursor [Co($^{iPr}$PNP)]$_2$ (**23** in Scheme 5). This product adapted its $Co_2N_2$ core from bent to almost planar to shorten the Co–Co distance and become diamagnetic.

Under $H_2$ pressure at low temperature, the Co(I) dimer [($\mu$-Hg){Co($^{tBu}$P$^{O}$C$^{O}$P)}] (**21**, in Fig 4) formed the Co(I) dihydrogen adduct [Co($^{tBu}$P$^{O}$C$^{O}$P)($H_2$)] (**45**) in equilibrium with the Co(III) cis-dihydrido-dihydrogen [Co($^{tBu}$P$^{O}$C$^{O}$P)(H)$_2$(H$_2$)] (**46**, Scheme 10).[63] Interestingly, this outcome was in-between those obtained for Rh and Ir analogues, except for stability, that was precarious for Co. In the case of Rh, the reaction stopped at the initial Rh(I) dihydrogen complex.[154] For Ir, the analogue of **45** was described as solvent-dependent equilibrium between Ir(I) dihydrogen and Ir(III) dihydrido tautomers (or stretched dihydrogen Ir(H···H)),[155] while the best description found for the final IrH$_4$ product was a dihydride coordinating an additional compressed dihydrido ligand: Ir(H)$_2$(H~H).[156,157]

[insert Scheme 10 here]

**Scheme 10** Reaction of H$_2$ with a Co(I) P$^{O}$C$^{O}$P fragment

Deng and co-workers reported the template assembling at the coordination sphere of Co of a CSiC pincer ligand, and the subsequent synthesis of the Co(I) dinitrogen complex **47** (Scheme 11).[158] The compound was diamagnetic, which suggested a square planar geometry, although the structure found in the solid state was highly distorted, with a Si−Co−N angle of 131°. **47** was stable under N$_2$ atmosphere but its replacement with Ar triggered formation of the Co(III) complex **48**, after intramolecular C−H OA of a mesityl substituent. The reaction was found to be readily reversible. The treatment of **47** with 1-napthylamine or 2-pyridinylhydroxide resulted in N−H or O−H intermolecular OA either, to form stable Co(III) hydrides **49** and **50**, respectively. Further examples of intermolecular C−H OA and RE at Co(I) were reported by Tonzetich and co-workers using the bis(phosphinomethyl)pyrrolido square planar derivative [Co($^{Cy}$PNP)(N$_2$)].[159] The complex was also found capable of decarbonylating aldehydes (RCOH) to form [Co($^{Cy}$PNP)(CO)] and the corresponding RH fragments, through a proposed mechanism comprising Co(III) hydride-acyl and -alkyl intermediates. Interestingly, the dinitrogen complex maintained its expected single-electron reactivity towards substrates with more polarized bonds, such as haloalkanes.

[insert Scheme 11 here]

**Scheme 11** C−H, N−H and O−H oxidative additions to a Co(I) CSiC complex

A particularly detailed picture of Co two-electron reactions was taken by the Chirik's group using bis(phosphinomethyl)pyridine ligands. Treatment of Co(I) complex $[Co(CH_3)(^{iPr}PNP)]$ with excess $H_2$, tolylacetylene or methyl iodide formed Co(III) products such as the trihydride *mer*-$[Co(H)_3(^{iPr}PNP)]$, the bis(alkynyl) $[Co(C{\equiv}CTol)_2H(^{iPr}PNP)]$ or the tris(methyl) derivatative $[Co(CH_3)_3(^{iPr}PNP)]$, after OA of H−H, C−H or C−I bonds, respectively, followed by the necessary RE steps.[99] Such a capability of cycling between Co(I) and Co(III) oxidation states stimulated further work in the context of catalytic processes such as C−H bond borylation,[111,160-162] $CO_2$ hydrosilylation,[163] and Suzuki-Miyaura cross-coupling.[110] The thorough mechanistic studies in borylation reactions not only identified active species and confirmed Co(I)/Co(III) cycling, but also elucidated catalyst activation[164] and deactivation pathways,[160] and concluded catalyst design principles for certain combinations of substrates based on their distinct kinetics.[161] Moreover, recognition of the preponderance of electronic factors over sterics and directing group effects in fluoroarene substrates led to their C−H functionalization with selectivities hardly attainable with precious metal catalysts.[165] More recently, the parent cationic complex $[Co(^{iPr}PNP)(N_2)][BAr^F_4]$ ($BAr^F_4 = B[C_6H_3\text{-}3,5\text{-}(CF_3)_2]_4$) was found to reversibly add $H_2$ to form 6-coordinate Co(III) dihydride adducts with solvent or dinitrogen. In contrast, other potential OA reagents such as bis(pinacolborane) afforded one-electron chemistry Co(II) boryl complexes, likely after the rapid comproportionation of initially formed Co(III) species with the Co(I) precursor.[166]

The occurrence of Co(I)/Co(III) catalytic cycles was also substantiated by Fout and co-workers using the strong-field monoanionic ligand bis(aryl-benzimidazol-2-ylidene)phenyl (aryl = 2,6-diisopropylphenyl or mesityl)[119] in catalytic alkyne,[167] alkene[168,169] and nitrile[170] hydrogenation, alkene hydrosilylation,[171] and alkene and nitrile hydroboration.[172] Alkene hydrosilylation used the 4-coordinate low-spin Co(I) dinitrogen complex $[Co(^{DIPP}CCC)(N_2)]$ as catalyst precursor and was found likely to involve an observable hydrido-silyl Co(III) intermediate.[171] Alkene and alkyne hydrogenations were initiated from the 5-coordinate species [Co($^{Mes}$CCC)($PPh_3$)($N_2$)], whose only observable derivative relevant to the hydrogenation cycle was the Co(I) dihydrogen complex [Co($^{Mes}$CCC)($PPh_3$)($H_2$)]. Confirmation of Co(III) dihydrido catalytic intermediates required detailed deuterium labelling and parahydrogen induced polarization (PHIP)[173] transfer experiments.[167,168] The latter technique was also applied to scrutinize intermediates of ethyl propionate and nitrile hydrogenations that used as catalyst precursor the air-stable Co(III) complex [Co($^{Mes}$CCC)(Cl)$_2$(py)] reduced in situ with $NaHBEt_3$ excess. Interestingly, the $BEt_3$ formed in this catalyst activation process was found crucial for catalytic turnover in the case of nitrile substrates, a fact attributed to the formation of nitrile adducts capable of coordinating side-on,[170] as shown for the proposed reaction intermediate **51** in Scheme 12.

[insert Scheme 12 here]

**Scheme 12** (left) Proposed intermediate of Lewis acid-assisted nitrile hydrogenation catalyzed by [Co($^{Mes}$CCC)] complexes. (right) Aryl-aryl reductive elimination from complex [Co($^{iPr}$P$^{O}$C$^{O}$P)(Ph)(SPh)] (**52**)

The feasibility of Co(I)/Co(III) catalytic cycles was also discussed by Ozerov and co-workers in the context of aryl halides coupling catalysis. Aimed at providing examples of RE from Co(III) complexes that compare with previous examples in Rh chemistry,[174] they prepared the 5-coordinate low-spin Co(III) derivative [Co($^{iPr}$P$^{O}$C$^{O}$P)(Ph)(SPh)] (**52**) (Scheme 12).[175] Its thermolysis indeed resulted in intramolecular RE, though instead of the C−S coupling product observed for Rh, the complex underwent C−C RE to couple the aryl of the pincer with the phenyl ligand. While the result confirms the kinetic accessibility of catalytically important C−C RE in Co(III) pincers, it also warns about parallelisms between the reactivity of noble and base metal complexes.

## 2.6 Rhodium and Iridium

The chemistry of Rh and Ir pincers is dominated by M(I) and M(III) low-spin complexes and therefore is more predictable than that of Co. Yet, some pincer platforms enabled stabilization of open-shell complexes and ostensible one-electron transformations. A family of Rh(II) mononuclear compounds with neutral bis(phophinomethyl)pyridine ligands, including cationic and dicationic species such as $[RhCl(^{tBu}PNP)]BF_4$ and $[Rh(^{tBu}PNP)(acetone)](BF_4)_2$, was prepared by Milstein and co-workers through oxidation with silver salts of the corresponding Rh(I) precursors.[176] Synthetic details such as the anion at the oxidant were found crucial since $BF_4$, $PF_6$ and $BAr^F{}_4$ salts attained direct oxidation of the chloro precursor into Rh(II), whereas silver triflate led to chloride abstraction prior to oxidation. The R groups at the phosphorus were also found critical, since synthesis were successful for the *t*Bu-substituted ligand but not for the *i*Pr analogue. The Rh(II) complexes exhibited magnetic moments and EPR spectra according to the expected low-spin $d^7$ electronic configuration. The structure of the chloro cationic complex was distorted square planar while the dicationic acetone derivative showed a square pyramidal geometry with a loosely bound $BF_4$ at the apical position. The reactivity studies could not extend the Rh(II) chemistry beyond the initial synthetic step given that even simple ligands such as phosphines, CO, isonitriles, NO, acetonitrile, etc. led to either oxidation, reduction or disproportionation, occasionally with participation of adventitious water.

The $Ag^+$ one-electron oxidation route to Rh(II) was applied again by the Milstein group to synthesize parent square planar complexes with anionic phosphinito $P^OC^OP$ ligands, starting from an equilibrium between mono- and dinuclear Rh(I) dinitrogen complexes: $[Rh(^{tBu}P^OC^OP)(N_2)]$ and $[(\mu\text{-}N_2)\{Rh(^{tBu}P^OC^OP)\}]$, respectively.[177] Ozerov and co-workers prepared derivatives of the anionic bis(phosphino)diarylamido ligand shown in Scheme 13, which seemingly were more stable than the previous examples.[178] At least, triflate complex **54** allowed for simple anion metathesis reactions toward other $[RhX(^{iPr}PNP)]$ analogues, complexes **55^X^**. Some of these derivatives were alternatively prepared from Rh(III) hydride precursors [RhHX($^{iPr}$PNP)] via H atom abstraction with TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl). Structural studies, EPR spectra and DFT calculations indicated Rh(II) $d^7$ radicals, though spin delocalization in the pincer ligands through two-center, three-electron, Rh−N π-bonds was proposed to be significant. In fact, the amido nitrogen actively participated in reactions such as dihydrogen addition to **53**, or $TiCl_3$ incorporation into [RhCl($^{iPr}$PNP)] (**55**$^{\mathbf{Cl}}$). In the former of these reactions, besides dihydrogen OA, the amido ligand was protonated into the amino version, while in the second case the N changed its coordination mode from terminal to bridging. The early-late heterobimetallic product of this latter reaction was alternatively prepared by treatment of the Rh(I) precursor **53** with $TiCl_4$.[179] Derivatives displaying Rh−Zn bonds were also obtained for this Rh($^{iPr}$PNP) pincer, though in these cases the N did not contribute to bind the Zn.[180]

[insert Scheme 13 here]

**Scheme 13** Synthesis of Rh(II) PNP complexes and reactions with excess $H_2$ and $TiCl_3$

Starting from O atom transfer reagents such as N-methylmorpholine N-oxide or $N_2O$ (inter alia), and the cyclometallated hydrido Rh(III) version[181] of the already discussed T-shaped Co(I) complex **22** (Scheme 5), Caulton and co-workers managed to identify the rare 4-coordinate oxo complex [RhO($^{tBu}$P$^{Si}$N$^{Si}$P)].[182] Although its stability was precarious due to evolution into a newly cyclometallated hydroxyl, the complex was identified as paramagnetic, and calculated to exhibit a planar geometry and a triplet ground state: with the unpaired spin almost equally distributed between Rh and O. Accordingly, despite unsaturation, the complex was found inert to conventional Lewis bases such as pyridines, but capable of nucleophilic oxo attacking to $CO_2$, to form the chelating carbonate [Rh($^{tBu}$P$^{Si}$N$^{Si}$P)($\kappa^2$-$O_2CO$)].[183]

Another amido PNP pincer ligand, the already mentioned vinyl-linked N(CH=CHP*t*Bu$_2$)$_2$, permitted the stabilization of monomeric Ir(II) complexes such as **57** (Scheme 14). In this case, the synthesis entailed oxidative functionalization of the fully saturated amino ligand platform of Ir(III) precursor **56** with 2.5 equiv of benzoquinone as hydrogen acceptor.[184] **57** exhibited a square planar structure, while its magnetic moment and EPR spectra indicated a metal-centered radical (67% of spin density at metal, according to DFT calculations). Consistently with its cyclic voltammogram in thf, which indicated reversible one-electron oxidation and reduction waves at $E_{1/2} = +0.02$ and $-1.8$ V, respectively (vs. $[Fe(C_5H_5)_2]^{0/+}$), chemical oxidation with $AgPF_6$ allowed for the isolation of Ir(III) complex **58**, while chemical reduction with $KC_8$ in the presence of crown ether (15-cr-5) led to the anionic reduction product **59**.[185] Since complexes **57-59** exhibited similar square planar coordination, direct structural comparisons were possible. The Ir–N bond shortened on going from Ir(I) to Ir(II) and Ir(III) (from 2.03 to 1.98 and 1.92 Å, respectively), as N→Ir π-donation increases with rising metal oxidation state. In fact, the strength of this bond component in the Ir(III) state was considered key to attain low-spin (S = 0) electronic configuration in complex **58**.[186] Two more examples of such rare square planar Ir(III) pincers were reported by the same group: an amido analogue of chloro **58**, $[Ir(^{tBu}PNP)(NH\textit{t}Bu)]PF_6$ (vide infra),[187] and the hydroxo complex $[Ir(^{tBu}PNP)(OH)]PF_6$,[188] whose amido ligand was that of the fully saturated ethylene skeleton (that of **56**). The latter was formed along a $O_2$ hydrogenation reaction to be discussed in the next section.

[insert Scheme 14 here]

**Scheme 14** Ir(I)/Ir(II)/Ir(III) redox series of chloro complexes, and Ir(III)/Ir(IV)/Ir(V) series of imido derivatives. Anions are: $PF_6^-$ (**58**), triflate (**60**) and $BF_4^-$ (**62**). Cation of **59** is $[K(15\text{-cr-}5)]^+$

The divinylamide pincer platform of **57-59** was further exploited to prepare series of complexes with rare imido– and nitrido–metal bonds, in collaboration between the Schneider and de Bruin groups. Treatment of **57** with excess lithium *tert*-butylamide, in *tert*-butylamine as solvent, led to chloride-by-amide metathesis to form amido analogues of Ir(II) **57** and, after oxidation with $Ag^+$, of Ir(III) **58**.[187] Adjusting the relative amount of amide base and silver oxidant permitted an alternative transformation of **57** into cation **60** (Scheme 14): a formal Ir(IV) imido, though better described as an Ir(III) species coordinating an imidyl ligand or nitrene radical ($RN•^{-}$, one-electron reduced Fischer-type nitrene ligand).[189] Equivalent electronic descriptions were previously given to the parent neutral nitrido complex [IrN(PNP)],[190-192] its unstable (transient) Rh analogue [RhN(PNP)],[193] and a related isolable N-bridged radical [(PNN)Rh(μ-N)Rh(PNN)],[194] in which the partial radical character of the 'nitridyl' ligands resulted in easy bimolecular N≡N bond formations. Imidyl **60**, however, was found to be more stable and did not react with selected nucleophiles ($PMe_3$), electrophiles ($CO_2$, olefins) or benzylic C–H bonds (toluene). Yet, it was found capable of undergoing both one-electron chemical oxidation and reduction (Scheme 14).[187] Reaction with cobaltocene formed neutral imido **61** which, in contrast to the other square planar Ir(III) complexes aforementioned, exhibited a triplet ground state, without precedents in Ir coordination chemistry. The additional population of an Ir−N $\pi^*$ orbital upon reduction enhanced nitrene reactivity toward both electrophiles such as $CO_2$ and nucleophiles such as $PMe_3$.

Oxidation of **60** with thianthrenium tetrafluoroborate afforded diamagnetic dicationic Ir(V) complex **62**. The NMR spectra indicated $C_{2V}$-symmetric structure in solution and, despite charge and electronic unsaturation, there was no evidence for $BF_4^-$ coordination, a likely consequence of a filled $dz^2$ orbital.[187] The square planar coordination is also singular for this oxidation state, otherwise represented by a handful of 7-coordinate 18-electron neutral tetrahydrides bearing PCP (or $P^OC^OP$),[61] PSiP,[195,196] or PBP[197] anionic pincer ligands. In addition to these examples, the 6-coordinate complex [Ir(SiNN)H(Bpin)$_2$], coordinating a dianionic silyl-amido-quinoline pincer, was described as possibly Ir(V) since an interligand Si−H distance was interpreted as borderline for bonding.[198] Stable Ir(V) complexes, as well as Ir(IV) counterparts, were also reported for the tridentate κ-*N,O,O* meso-2,4-di(2-pyridinyl)-2,4-pentanediolate ligand (dpyp), although ligand coordination mode in these complexes was *fac*.[199] Actually, this made possible octahedral [Ir(dpyp)$_2$] derivatives with four equatorial oxygens and two axial nitrogens: a highly anisotropic ligand field that helps to stabilize high oxidation states.[200,201] An isolated example of Ir(IV) pincer coordinating a bis(phenolato)pyridine ligand was also reported.[202]

Even though examples of stable Ir(V) pincers are scarce, access to this oxidation state was found key to facilitate certain C−H bond additions,[203] and catalytic transformations such as alkene dehydrogenative C−C coupling,[204] or amino-borane and ammonia-borane (de)hydrogenation.[205,206] Besides, Ir(III)/Ir(V) catalytic cycles were recognized as alternatives to the more common Ir(I)/Ir(III) ones for hydrogenation catalysts showing prohibitively high barriers for Ir(III)→Ir(I) C−H RE.[207] In this respect, recent studies by Krogh-Jespersen, Goldman and co-workers indicate that, contrarily to the widely accepted view, such REs (as well as those of N−H bonds)[208] are favored by strongly electron-donating PXP pincers.[209]

To finish this section, it should be mentioned that the oxo species [RhO(NNN)(NN)](ClO$_4$)$_3$, containing a terpyridine pincer ligand as well as either bipyridine or phenantroline NN chelates, remain the only reported complexes in oxidation state Rh(V). Compounds were obtained by oxidation of the corresponding tricationic water complexes with two equivalents of Ce(IV), and could be characterized by NMR due to their diamagnetism.[210]

## 3. FUNCTIONAL PINCERS

From a traditional perspective, transition metal organometallic chemistry takes place at d orbitals of the inner coordination sphere of complexes, where ancillary ligands just determine the space available for reagent coordination and tune the electronic features of the metal. Thus, only the size and shape of ligands, and the still snapshot of their electronics, matter for ligand design. The concept of ligand hemilability,[211] which consists of a reversible decoordination of part of a bi- or polydentate ligand that render the metal temporarily unsaturated, was arguably the first to alter such view of ligands as “passive” entities, also drawing attention to the importance of outer coordination spheres and electronic and atomic reorganizations within ligands. After, several other properties of ligands were identified as potentially capable of playing a role, especially in polydentate ones.[212] They often imply electronic burden beyond traditional “tuning”, through the stabilization of ligand radicals that “change” electronic configurations at metals, or through the input of additional electron pairs that “unlock” mechanistic alternatives for bond cleavage and formation in reagents. Even though such functions equally impact base or noble metal complexes, interest on them is increasingly biasing toward the former, since they may combat odd-electron chemistry and enable catalytic cycling without changes in metal oxidation state.

### 3.1 Hemilabile pincers

Replacing strong-donor arms by labile ones threatens the typical high stability of pincers but may enhance reactivity. After observation by Milstein and co-workers that PNN ligands bearing one amine arm clearly outperformed PNP bis(phosphinomethyl)pyridine symmetric analogues in catalytic alcohol dehydrogenation,[213] phosphine-by-amine substitution became a recurrent strategy to transform fix pincer architectures into hemilabile versions.[32] Examples in group 9 chemistry span ligands such as PNN with pivot groups other than pyridines,[214-218] PSiN,[219] and NCN.[220] A basic design principle for tuning hemilability was deduced from these examples: the longer the amine tether the more labile.[214,220,221] Scheme 15 illustrates a $\kappa^3$-N to $\kappa^2$-N change by dissociation of an amino-tethered enamidophophinimino ligand after a chloride-by-hydride metathesis in Co(II) derivative **63**. Amine dissociation occurred even though the dimeric final product **64** seems more electron deficient than the precursor. The example also illustrates a further ligand coordination change to $\kappa^2$-N:$\eta^6$ upon reduction to Co(I).[222]

[insert Scheme 15 here]

**Scheme 15** Variable coordination to Co of an amine-tethered-enamidophosphinimino ligand.

In general, the hemilabile versions of the ligands enhanced catalytic activity, though not always, since transformations relying in outer-sphere events may be insensitive to the change.[216] Release of hemilabile arms may also diminish steric congestion at the metal coordination spheres, thus augmenting the residence time of reagents. This was claimed to change selectivity in the catalytic transfer hydrogenation of alkynes from ammonia-borane catalyzed by Co(PNP)/Co(PNN) complexes, favoring formation of the thermodynamically more stable E alkenes over kinetically-favored Z ones.[218] Hemilability of classical bis(oxazolino)phenyl NCN ligands (Phebox) was found key to favor dehydrogenative coupling of ethylene to butadiene, which requires a temporary *fac* arrangement of three reactive positions at Ir.[223] Examples of $\kappa^2$ coordination to Co are also known for Phebox[224] and other pincer ligand architectures with imino arms.[225,226]

### *POP pincers*

The $^{Ph}$xantphos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) and other related POP-type ligands may not fit well within the intuitive notion of hemilabile pincer since they do not have any reversibly dissociable arm but a central ether linker that coordinates or not depending on the overall needs of each particular complex. Accordingly, these ligands are just bidentate in many instances, whilst occasional coordination of the O atom can form stable complexes in either *mer* or *fac* mode. The ligands were originally conceived[228] as wide bite-angle diphosphines[229,230] to maximize linear regioisomers in Rh hydroformylation catalysis, their ability to bind tridentate being largely overlooked until recently. Yet, their widespread use in coordination chemistry and homogeneous catalysis has progressively disclosed their coordination flexibility and capability of triggering prominent stoichiometric and catalytic reactions: facts often regarded as cause and effect, respectively. The successful chemistry brought about by POP-type ligands deserved two recent reviews by Adams and Weller,[40] and van Leeuwen and Kamer,[231] respectively. The latter described entries to the various ligand options displaying the 2,2'-bis(phosphino)diarylether skeleton characteristic of the xantphos ligand family, and showcased the wealth of catalytic applications derived from them. A significant part of this successful chemistry corresponds to Rh and Ir complexes, and applications such as hydroformylations and carbonylations, in which pincer coordination of the POP ligand was seldom documented (for an example, see below). On the contrary, tridentate coordination seemed decisive for many other transformations driven by POP complexes in which the variable ligand coordination synchronized other events required for catalytic turnover in the metal coordination sphere. This coordination versatility, together with other potential advantages of wide bite-angle diphosphines such as the promotion of bond-forming REs,[232] was illustrated and discussed in the first of the aforementioned review articles.

The recently reported chemistry of Co(POP) complexes circumscribed to catalytic applications in which catalysts were generated *in situ* from bench-stable precursors, typically $CoCl_2$ or $[Co(acac)_2]$, and ligands such as ${}^{Ph}$xantphos or dpephos (bis{(2-diphenylphosphino)phenyl} ether)**.** In this way, Yoshikai and co-workers developed catalytic additions of azoles[233] and thiazoles[234] to alkynes, as well as various different catalytic sequences comprising initial synthesis of arylzinc derivatives from aryl halides,[235] followed by alkene or alkyne functionalization,[236-239] including borylation in the presence of Cr(III) co-catalysts to afford arylboronic esters.[240] Ge and co-workers applied the Co/xantphos combination in catalytic *gem* diborylation of 1,1-disubstituted vinylarenes,[241] and selective hydrosilylation of alkenes[242] and alkynes.[243] Interestingly, this system showed alkene- and silane-dependent regioselectivity complementary to those obtained with ligands such as bis(diphenylphosphino)ferrocene or the bis(imino)pyridine pincer ligand ${}^{Mes}$NNN, thus allowing access to the desired regioisomer for a variety of alkene/silane combinations.[242]

Since catalyst speciation studies in all these systems remain to be done, the possible participation of pincer catalytic intermediates is unknown. Yet, in view of pronounced ligand effects on selectivity, Mita, Sato and co-workers suggested a prominent role of xantphos $\kappa^3$-P,O,P coordination during Co-catalyzed alkene C−H functionalizations at allylic positions with $CO_2$[244] or ketones.[245] As shown in the simplified mechanistic proposal of Scheme 16, turnover consumed $AlMe_3$ and was proposed to proceed through Co(III) and Co(I) species. Pincer coordination was suggested to favor $\eta^1$- vs. $\eta^3$-allyl Co(I) intermediates, in which the released C=C bond was thought to undergo attack of the electrophilic functionalizing reagent.

[insert Scheme 16 here]

**Scheme 16** Proposed mechanism for the Co-catalyzed allylic C($sp^3$)−H carboxylation with $CO_2$ (adapted from reference[244])

The POP complexes of Rh provided well-characterized examples to illustrate variable ligand coordination and its consequences for reactivity and catalysis. The size of substituents at P may condition the predominant coordination mode, as illustrated by the chloro complexes [RhCl($^R$xantphos)] in Scheme 17. With R = *t*Bu[246] or *i*Pr,[247] complexes were found to be mononuclear and feature *mer* $\kappa^3$-P,O,P xantphos ligands (**66**), whereas the R = Et analogue was formulated as a chloro-bridged dimeric species with $\kappa^2$-P diphosphines (**68**).[248] Likely, the smaller ethyl groups allow closer approach of the metals to form halide bridges at the expense of the weaker O coordination. Interestingly, the derivative with R = Ph, expected to lie between the two extreme possibilities, remains to be structurally characterized, being tentatively described as a coordination polymer (**67**) based on its insolubility.[249] All Rh(I) complexes in Scheme 17 underwent facile OA of $H_2$ to form *cis*-dihydrido complexes whose stability is consistent with the structural trends of the precursors. Thus, while the bulky derivatives, including polymeric **67**, formed stable products **69** (for example $\Delta G^{o}_{298K} = -5$ kcal mol$^{-1}$ for *t*Bu,[246] from DFT calculations), the thermodynamic balance for the ethyl analogue was less favorable, dihydride **70** being only stable under dihydrogen atmosphere.

[insert Scheme 17 here]

**Scheme 17** $H_2$ OA to complexes [RhCl($^{R}$xantphos)]

Hemilability may also condition the course of reactions and their kinetics, as inferred from $H_2$ OA to the parent complex [RhCl($^{tBu}$furPOP)] (**71**) (Scheme 18).[246] As expected from the size of POP substituents, the complex was found to be mononuclear although, in contrast to its analogues **66** that selectively produced stable Rh(III) *cis* dihydrides, **71** permitted the observation of a *trans* dihydride kinetic product **72$_{\mathbf{trans}}$** (ca. 30% of the kinetic distribution). This isomer eventually evolved into the more stable (by ca. 23 kcal mol$^{-1}$, from DFT calculations) *cis* dihydride, although isomerization required prolonged heating. The faster reaction of $H_2$ with a 3-coordinate $\kappa^2$-P species instead of the 4-coordinate **71** was suggested as the most straightforward explanation for the transient but persistent *trans* isomer.

[insert Scheme 18 here]

**Scheme 18** $H_2$ OA to complex [RhCl($^{tBu}$furPOP)] (**71**) and proposed intermediates

The parent cationic derivatives of Scheme 19 illustrate further factors influencing POP coordination mode. Rh(III) dihydrides **74**, which contain tricyclopentylphosphine and $^{Ph}$xantphos ligands, were generated from **73** as an equilibrium mixture in which the *fac* isomer was slightly favored ($\Delta G^{o}_{298K} = -0.45 \pm 0.1$ kcal mol$^{-1}$ in $CD_2Cl_2$) and interconversion was again suggested to involve decoordination of the pincer O atom.[250] Replacing the $^{Ph}$xantphos ligand with dpephos caused notable differences. First, reaction times reduced considerably, from five days in **73** to ten minutes in **75**, under otherwise identical conditions. Considering once again O atom release as the most likely way to achieve the coordination vacancy required for reaction with $H_2$, acceleration seems to reflect a higher lability of dpephos compared to $^{Ph}$xantphos. The same is suggested by the composition of the hydrogenation outcome: a single dihydrido isomer **$76_{fac}$** in equilibrium with the dihydrido-dihydrogen complex **77**.

[insert Scheme 19 here]

**Scheme 19** Reactions of cationic $^{Ph}$xantphos (**73**) and dpephos (**75**) analogues with $H_2$. $BAr^F_4{}^-$ anions are omitted. ($^c$Pe = cyclopentyl)

Early examples of Rh complexes in which $\kappa^3$-P,O,P pincer coordination was recognized useful for catalysis were reported by Julian and Hartwig using amine-substituted xantphos ligands in intramolecular hydroamination of primary aminoalkenes (Scheme 20).[251] In line with pioneering speculations,[252] O atom coordination emerged crucial for selectivity because it blocked the coordination site required for β-hydride elimination in Rh(I) alkyl intermediates, which in the context of these hydroaminations would form undesired imine byproducts. Conversely, the proton transfer step leading to the desired amine products remained unaffected because it is an outer-sphere event. The amino groups on the phosphorus of this POP ligand were observed to enhance rate and selectivity, although their role could not be ascribed to either steric demands or degree of electron donation to the metal center.

[insert Scheme 20 here]

**Scheme 20** Proposed catalytic cycle for intramolecular hydroamination of primary aminoalkenes (adapted from reference[251]). $BF_4^-$ anions are omitted.

A similar exploitation of O atom coordination to hamper undesired side reactions was previously documented by Weller and Willis to avoid catalyst-deactivating acyl decarbonylations in Rh-catalyzed hydroacylation of alkenes and alkynes, though in this case POP ligands also resulted in slow turnover since both desired and undesired products form via inner-sphere pathways.[253] In fact, only the labile dpephos ligand led to a good activity/stability compromise, whereas the more tight skeleton of the xantphos[254] or the presumably stronger-coordinating PSP version of dpephos failed to generate active catalysts.[255] The context of this catalytic hydroacylation was investigated in depth to collect mechanistic evidence on the course of desired and side reactions,[256-259] and to broaden substrate scope.[260] So far, this search has led to optimized conditions to deliver gram scale of product, at essentially quantitative levels, using no excess of either reagent, at very low catalyst loadings, using minimal solvent, with virtually no workup.[261]

Opposite to what was observed in hydroacylation, the rigid xantphos was found to surpass the activity of the more flexible dpephos in alkyne carbothiolation.[262] In this transformation aryl methyl sulfides are combined with alkynes to deliver alkenyl sulfido functionalized products resulting from both C−C and C−S bond formation. Given that the sulfido activating group remains at the functionalized product, the strategy can be used again and again (activating group recycling) to attain further functionalization.[263] Catalytic turnover was found to involve two key intermediates showing *fac* or *mer* $\kappa^3$-P,O,P coordination of the ligand, respectively, which are in slow equilibrium with one another most likely via $\kappa^2$-P species. Only the *fac* isomer is proposed to be an in-cycle intermediate, whereas the more stable *mer* complex constitutes the (out-cycle) catalyst resting state (Scheme 21).[249] Hence, it is to be expected that the slower the equilibrium between *fac* and *mer* isomers, the more the catalyst available for turnover.

[insert Scheme 21 here]

**Scheme 21** Proposed catalytic cycle for phenylacetylene carbothiolation (adapted from reference[40])

O-atom coordination in POP ligands can be exploited not only to hinder undesired side reactions but also to speed up desired ones, whenever rate-determining steps do not depend on empty orbitals but on full ones. This was observed for Rh/xantphos-catalyzed methanol carbonylation,[264] in which interaction between Rh and the xanthene O was found to enhance the nucleophilicity of the catalyst in comparison to structurally related Vaska-type complexes, stabilizing the $S_N2$ transition state for MeI OA to square-planar intermediate [RhI(xantphos)(CO)] (Fig. 8). Consistently, the reverse reaction, MeI RE, was also found to be facile from the closely related $[Rh(I)_2(Me)(dpephos)]$ complex, through a mechanism involving nucleophilic attack of external iodide to the methyl ligand, at both neutral and cationic Rh(III) species.[265] This mechanistic insight suggested the extrapolation of such RE to sulfur and nitrogen external nucleophiles, to form challenging $C(sp^3)-S$ and $C(sp^3)-N$ bonds, respectively.

[insert Fig 8 here]

**Fig. 8** DFT optimized transition state structure for nucleophilic attack on MeI by $[RhI(^{Me}xantphos)(CO)]$ (adapted from reference[264])

Several important contributions to the chemistry of Rh POP pincer complexes originated from reactions of the square-planar Rh(I) hydrides $[RhH(^{R}xantphos)]$ (**78**), first prepared by the groups of Esteruelas (R = *i*Pr)[247] and Goldman (R = *t*Bu).[246] In the presence of reagents such as silanes,[266] boranes or arenes,[267] these hydrides underwent OA/RE sequences leading to silyl-, boryl-, or aryl-analogues of **78** (Scheme 22). The Rh(III) dihydrido intermediates of these sequences were often observable and displayed mutually *trans* hydrides, which suggests the need for an isomerization step into *cis* isomers before RE. Again POP ligand hemilability might facilitate such a rearrangement via 5-coordinate species.

[insert Scheme 22 here]

**Scheme 22** OA/RE sequences in a POP Rh(I) hydride

The OA/RE sequence was also applied to cleave other bonds in small molecules such as C−Cl in chloroarenes,[268] B−B in bis(pinacolato)diboron,[269] or S−F in the chemically inert $SF_6$,[270] and constitutes the backbone of catalytic transformations such as arene borylation,[267] or diphenylsilane alcoholysis.[266] The Rh(I) complexes of Scheme 22 can also insert small molecules such as alkynes or nitriles to furnish catalytic cycles of alkyne diborylation[269] or arene decyanative borylation,[271] respectively. The latter reaction was regarded as a powerful tool in organic synthesis since it may allow working with the cyano group as a boryl equivalent until late stages of synthetic strategies.[272] While experimental investigation of its mechanism only detected $\kappa^3$ POP likely intermediates,[273] DFT calculations featured several other $\kappa^2$ diphosphine key species.[274,275] This was also the case for catalytic ammonia-borane or amine-borane dehydrogenation[276] using **78** as catalyst precursor, which on the basis of calculations was proposed to cycle exclusively through $\kappa^2$-P,P intermediates.[277] Change to cationic catalysts, however, seems to render pincer intermediates more significant for catalytic turnover, as inferred from the various complexes characterized from $[Rh(xantphos)]^+$ precursors in the context of these transformations. These included the dihydrides $[Rh(H)_2(\kappa^3\text{-P,O,P-}{}^{R}xantphos)(\eta^1\text{-}H_3B{\cdot}NMe_3)](BAr^F_4)$ (**79**, R = Ph, Et, *i*Pr)[278,279] and the rare dimetalloborylene singly-charged cation $[\{Rh(\kappa^3\text{-P,O,P-}{}^{iPr}xantphos)\}(\mu\text{-B})]^+$ (**80**), which was proposed to be a dormant end-product of dehydrogenation catalysis (Scheme 23).[248] In catalytic terms, the change from neutral to cationic catalyst precursors had little impact in the efficiency of hydrogen production, but significantly lowered the molecular weight of the polyaminoborane produced from primary amino-boranes.[248] Cationic Rh/xantphos derivatives were also found competent to catalyze the hydroboration of alkenes such as *tert*-buthylethene using $H_3B{\cdot}NMe_3$.[280]

[insert Scheme 23 here]

**Scheme 23** Compounds found in speciation studies of amino-borane dehydrogenation catalyzed by cationic Rh/xantphos complexes. $BAr^F_4{}^-$ anions are omitted.

In view of the subtle energy balances conditioning POP O-atom coordination, it is to be expected that alongside reactions and catalytic transformations in which pincer coordination play a major role, other closely related processes might occur without resorting to tridentate coordination. The latter is the case of anti-Markovnikov hydroamination of alkenes catalyzed by Rh/dpephos complexes,[281,282] in which, contrarily to the intramolecular version discussed above,[251] participation of the POP O atom seems to be irrelevant throughout catalysis. Further examples are the regioselective intramolecular silylation of alkyl C−H bonds catalyzed by Rh/xantphos complexes,[283] in which the possible impact of O coordination on selectivity was investigated and discarded, and the Rh/dpephos-catalyzed coupling of terminal alkynes with carboxylic acids.[284-286]

In contrast to the wealth of Rh chemistry summarized above, Ir POP complexes remain almost anecdotal. Neutral Ir/$^{Ph}$xantphos complexes were prepared and interrogated in the context of alkene hydroformylation using PHIP techniques[173] to detect minor catalytic intermediates.[287] The studies did not evidence POP pincer coordination; on the contrary, the possible dechelation of the diphosphine to form $\kappa^1$-POP intermediates was discussed in view of the dihydride structures obtained in the presence of CO. In the absence of this reagent, however, the parent cationic complexes of Scheme 24 demonstrated once again the versatility of xantphos coordination.[288]

[insert Scheme 24 here]

**Scheme 24** $\kappa^2$-P,P → *fac*-$\kappa^3$-P,O,P → *mer*-$\kappa^3$-P,O,P changes of $^{Ph}$xantphos coordination mode along a reaction sequence. $BAr^F{}_4{}^-$ anions are omitted.

An attempted synthesis of the Ir analogue of Rh(I) chloro complex **$^{iPr}$66** led to the Ir(III) chlorohydride **81** instead, after diastereoselective cyclometalation of a *i*Pr substituent (Scheme 25).[247] Cyclometalation was found to revert through reaction with a variety of reagents, including dihydrogen, silanes,[266] *n*-octane or triflic acid (HOTf), which afforded new Ir(III) products containing the activated reagents. Hence, the preference of Ir for oxidation state Ir(III) together with its ability to cleave C−H bonds turn the simple alkyl substituents at phosphorus into additional ligand functionalities.

[insert Scheme 25 here]

**Scheme 25** Reversal of $^{iPr}$xantphos cyclometalation via protonation or intermolecular C−H bond activation

The xantene and related ether skeletons are known to impart hemilability to ligand platforms other than POP. Replacement of the phosphine arms by silyl groups gave the dianionic xantsil ligand (Scheme 26). The coincidence of two very strong σ-donors seems to encourage highly unsaturated species such as the 14-electron chloro complex **82**, favored over its 16-electron isomer **83** both in solution and in solid state.[289] The X-ray structure of the triflate analogue of **83**, **84** in Scheme 26, suggests that, as tridentate SiOSi ligand, xantsil prefers *fac* coordination (Si−Ir−Si angle 101°) over *mer*. Following a common discussion in 14-electron Ir(III) complexes,[290-295] agostic interactions were found to condition the stability and coordination geometry of **82**, a fact that can give a qualitative idea of the weakness of the competing O-atom coordination. Diamido ligands featuring $-(Me)_2SiOSi(Me)_2-$ or $-(CH_2)_2O(CH_2)_2-$ linkers were applied in Co chemistry by Leznoff and co-workers. They may adopt a variety of coordination modes, including pincer.[296]

[insert Scheme 26 here]

**Scheme 26** Equilibrium between 14- and 16-electron isomers of [IrCl($^{Me}$xantsil)($PCy_3$)] reported by Tobita et al.[289] The X-ray structures of isomer **82** (CCDC code KOBWAB) and a triflato analogue of the 16-electron chloro **83**, complex **84** (CCDC codeKOBWIJ).

### 3.2 Redox-active pincers

Pincer ligands may incorporate skeletons or motifs able to undergo their own redox changes, interfering this way the electronic status quo of the rest of the complex (metal and co-ligands) and its reactivity. Oftentimes, such redox events operate in concert with or in place of redox changes at metals, hence the mere presence of these ligands may cause ambiguity regarding the formal oxidation states of the metal (and possibly that of other ligands). The concept of "ligand redox-noninnocence"[297] was originally coined to account for such ambiguity although nowadays it is widely applied to tag any kind of ligand-centered redox event, even though formal oxidation states can certainly be identified. Redox-active ligands in general were subjected to intense revision in the last years,[93,94,298-301] and some typical examples, such as monodentate imides and nitrides, have already appeared and have been briefly discussed in the preceding pages. The main redox-active pincer architectures were also recently reviewed.[302] In this section we present and discuss noticeably pincer chemistry organized around the redox-active scaffolds that are more significant in group 9 chemistry, namely bis(imino)pyridines, and ligands that contain and/or combine amido and phenolato donor groups.

*Bis(imino)pyridines and related ligands:*

2,6-Bis(imino)pyridine[135,303] pincer complexes are well-known to undergo ligand-centered redox events.[304] Neutral ligands have two low-lying $\pi^*$ orbitals that extend all over the NNN skeleton,[305] in which they can take up to four more electrons while maintaining ligand integrity. Reduction provokes minor changes in C−N and C−C bond distances that are diagnostic for the amount of charge at the ligand.[95] In metal complexes where filled d orbitals and these extended delocalized $\pi^*$ systems are similar in energy, partial (small) overlap can favor interactions that result in singlet (AF-coupled) biradicals (or open-shell singlets), and hence have the character of intramolecular single-electron transfers. Such a result is different from that of classical $d \rightarrow \pi^*$ covalent backdonation, which requires large orbital overlap and therefore a $\pi^*$ orbital concentrated in the atom directly bonded to the metal.

Interactions of this type have been recognized in several bis(imino)pyridine pincer complexes of low-valent metals,[306] as for example the cobalt dinitrogen complex $[Co(^{DIPP}NNN)(N_2)]$ (**86**, Scheme 27), already mentioned in the previous section as seemingly ambiguous with regard of its oxidation state.[133] Its magnetic moment, structural parameters and EPR spectrum, together with DFT calculations, indicated that the complex, formally Co(0), should be better described as a low-spin Co(I) complex with a ligand-centered radical as the SOMO. In Scheme 27, this radical character is denoted by a dot, while the delocalized bond system assumes that the unpaired electron is delocalized over the entire ligand skeleton of the anion radical. Interestingly, further one-electron reduction of **86** afforded diamagnetic anion $[Co(^{DIPP}NNN)(N_2)]^{-}$, which was also characterized as a low-spin Co(I), but now bound to a closed-shell ligand dianion.[133] Similarly, one-electron oxidation of **86** formed diamagnetic cation $[Co(^{DIPP}NNN)(N_2)]^{+}$, which seems to contain true low-spin Co(I) and a neutral, not-reduced not-oxidized, pincer ligand.[307] Then, low-spin $d^8$ electronic configuration at the metal is preserved throughout the redox series of dinitrogen complexes $[Co(^{DIPP}NNN)(N_2)]^{+/0/-}$, since redox events are confined to the ligand.

[insert Scheme 27 here]

**Scheme 27** Selected reactions of bis(imino)pyridine Co pincers.

Related electronic descriptions were deduced for precursor complex **85** and its deprotonated derivative **87**, both diamagnetic and formally Co(I), but consisting of low-spin Co(II) $d^7$ radicals AF-coupled to diamino anion or imino enamido dianion radicals, respectively.[308,309] Consistently with the significance of radicals in the ground-state electronic structures of these pincers, their reactivity may sometimes follow radical pathways.[300,310] As illustrated in Scheme 27, reaction of **87** with benzyl chloride formed **88**, an alkylated analogue of **85**, together with dimer **89**, assembled via C−C coupling of the enamido carbons.[309] This is in agreement with the electronic structures of the putative OA intermediates calculated by DFT, which indicate that radical character accumulates on this particular carbon. In the presence of other long-lived alkyl radicals (such as benzyl, in this example) alkylation of the ligand backbone predominated, but in its absence dimerization was the mayor observed reaction,[309] also for complexes with parent doubly-deprotonated bis(enamido)pyridines.[311] For derivatives of neutral, non-deprotonated, bis(imino)pyridines similar to **86**, which form less localized ligand radicals, reactions with organic halides (RX) led to binuclear oxidative additions,[312] although certain R radicals may also attack at the 3 and 4 positions of the pyridine ring.[313]

The electron-storage capability of bis(imino)pyridines may help metals to avoid less favorable oxidation states, and therefore constitutes a resource for catalytic turnover in transformations based on elementary steps in which multiple electrons are being transferred between the metal and the activated substrates (typically two-electron REs and OAs).[314-317] Notably, this is not the case for the main catalytic application of these ligands in Co chemistry, olefin polymerization and oligomerization,[318-320] which only relies in migratory insertion steps. In fact, the active species in polymerization catalysis were identified as cationic alkyls $[Co(NNN)(R)]^+$: Co(II) low-spin species in which NNN ligand is innocent.[321,322] Despite intense research in alternative ligand architectures, NNN pincers and bis(imino)pyridines in particular remain the preferred option for these polymerization catalysts.[323]

On the contrary, electron-storage in the ligand was recognized in intramolecular $[2\pi + 2\pi]$ cycloadditions of $\alpha,\omega$-dienes catalyzed by **61** and analogous complexes,[321,324] which follow a Co(I)-Co(III) cycle in which the bis(imino)pyridine chelate remains in its one-electron reduced radical anion form ($NNN\bullet^-$) (Scheme 28). Accommodation of the two alkene moieties in the coordination sphere of Co is accompanied by decoordination of an imino arm of the pincer ligand to achieve $\kappa^2$-*N* coordination. The consequential decrease of the overall ligand field strength at the Co(I) center provokes the change to tetrahedral high-spin structure, now AF-coupled with the radical anion. As a result, the SOMO changes from ligand-centered to Co-centered prior to the C−C coupling step.[324]

[insert Scheme 28 here]

**Scheme 28** Proposed cycle for intramolecular [2π + 2π] cycloaddition of $\alpha,\omega$-diene catalyzed by Co complexes with redox-active bis(imino)pyridine pincer ligands.

The electronic versatility of these ligands in combination to 3d metals goes even further in the operation of hydrogenation catalysts. Scheme 29 outlines the mechanism obtained from DFT calculations by Hopman[325] for alkene hydrogenations initially reported by Budzelaar and co-workers,[326] and developed in their asymmetric versions by the group of Chirik.[327,328] It features a relatively conventional monohydride pathway, consisting of migratory olefin insertion and hydrogenolysis by σ-bond metathesis steps, though operated by intermediates which may contain or not radical anions, and display either low-spin or high-spin metal centers.

[insert Scheme 29 here]

**Scheme 29** Calculated mechanism for alkene hydrogenation catalyzed by Co bis(imino)pyridine complexes.

Metal-ligand electronic cooperation was also confirmed by Cundari, Gary et al.[329] on the basis of DFT calculations in catalytic reactions of 1,1-diboration of terminal alkynes.[330] The computations revealed cooperative metal+ligand OA of the B−B bond of bis(pinacolato)diboron to an AF-coupled triplet Co(II) alkynyl intermediate, to form a closed-shell Co(III) singlet:

$$[(\mathrm{NNN}\bullet^{-})^{\downarrow}(\mathrm{HS\text{-}d^{7}\text{-}Co^{II}})^{\uparrow\uparrow\uparrow}(\mathrm{C{\equiv}CR^{-}})] + (\mathrm{BPin})_2 \rightarrow [(\mathrm{NNN})(\mathrm{LS\text{-}d^{6}\text{-}Co^{III}})(\mathrm{C{\equiv}CR^{-}})(\mathrm{BPin^{-}})_2]$$

The calculated transition state (TS) for this process indicated that extensive mixing of the metal d and ligand π orbitals is needed for 3d metal complexes to leverage redox-noninnocence along a catalytic reaction coordinate.

Electron-storage at the pincer ligand also seems likely in other transformations catalyzed by bis(imino)pyridine cobalt complexes, such as dehydrogenative silylation of alkenes,[331] alkene[332] or terminal alkyne[333] hydrosilylation,[334] alkene[335] or terminal alkyne hydroboration,[336] and hydroalumination,[337] although most intermediates of these reactions and their electronic structures remain proposals.[338] Other pincer ligands that maintain, totally or partially, the bis(imino)pyridine skeleton are also likely to retain electron-storage capability.[339] Chiral NNN bis(oxazolino)pyridines,[22,340,341] (oxazolino)(imino)pyridines,[342-347] and (imidazolino)(imino)pyridines,[348] were found to form Co catalysts for hydrogenation,[345] hydroboration,[342,347,348] and hydrosilylation,[341,343,344,346,349] often highly active and enantioselective.[341-345,348,350] Terpyridine Co complexes were also interrogated about their electron-storage capability,[351,352] and were used as alkene hydroboration catalysts.[353] Other formally neutral NNN ligands such as (amino)(imino)pyridines,[354] (oxazolino)bipyridines,[355] and related PNN designs such as (phophino)(imino)pyridines,[356-358] and (phosphino)bipyridines,[359,360] were also investigated in the context of Co-catalyzed hydrometallation reactions.

Further away from bis(imino)pyridines than the latter examples but still neutral and maintaining the central pyridine ring, the CNC bis(arylimidazol-2-ylidene)pyridine scaffold was also recognized to form radical anions in reduced Co chemistry. In complexes such as **90** (Scheme 30), spin density calculations indicated that radicals are essentially pyridine-localized.[361] Consistently, the hydrogen at the 4-position of the pyridine showed unusual downfield $^1$H NMR chemical shifts.[362] Migration of the metal hydride to this position was observed at room temperature under dinitrogen, while reaction with 1,1-diphenylethylene resulted in alkylation, likely after alkene insertion and subsequent selective alkyl migration. This ostensible radical-type reactivity was nevertheless found to be slow, and did not impede efficient catalytic alkene hydrogenation under $H_2$ atmosphere.

[insert Scheme 30 here]

**Scheme 30** Reactions at the 4-position of the pyridine ring of Co pincers of redox-active CNC ligands.

The anionic bis(imino)pyrrolates are π-isoelectronic to bis(imino)pyridines and hence likely to be redox-active as well. Yet, a couple of relevant differences between the two ligand systems should be taken into account.[363] As a result of the angle strain in the five-membered pyrrol ring, the imino arms are more splayed, relatively disfavoring tridentate coordination. Besides, the anionic character together with a smaller π-bonded network results in higher energy HOMOs, which make pyrrolato ligands easier to oxidize.[73] The structure of **91** (Scheme 31) exemplifies the consequences of these facts in a Co(II) complex that contains a bidentate and neutral bis(imino)pyrrolyl ligand radical: one-electron oxidized instead of reduced.[363] It should be noted, nevertheless, that examples in which this architecture supports tridentate[364] and one-electron reduced ligands are also known for metals of other groups.[365] Tridentate complexes are also the norm for closely-related, and also strained,[366] bis(pyridino)pyrrolato ligands.[73,367,368] Alternative dianionic bis(pyrrolyl)pyridine architectures are also possible,[73] as already illustrated in preceding pages (complexes **17** and **18** in Fig. 2).[67]

[insert Scheme 31 here]

**Scheme 31** Examples of Co complexes with potentially redox-active NNN ligands.

The length of imino donor arms can be easily adapted to avoid strain with the aid of different spacers, which have given rise to different families of NNN anionic pincer ligands containing pyrrolyl or isoindolyl cores.[369-375] These NNN architectures have produced dozens of group 9 pincers, though so far without well-characterized examples of redox-active ligands. This is, however, not the general case, since relevant examples of ligand radicals[376] have been reported for derivatives of neighboring metals, such as for example in tripyrrin complexes related to **92** (Scheme 31).[377,378]

2,6-bis(imino)pyridines have also given rise to significant Rh and Ir chemistry, though these noble metals seldom resort to ligand redox-activity.[95] Still, formation of the anionic ligand radical circumvents adoption of the unstable M(0) oxidation state in the Rh analogue of dinitrogen complex **86** (in Scheme 27),[379] being also the favored option for a hypothetical Ir version.[95] On the contrary, electron-storage at the ligand is not anymore the preferred option for Rh(I) and Ir(I) derivatives, although these compounds often show significant "classical" M(I)→NNN π back-donation that modify ligands structural parameters in the same way that electron-storage does.[95] A significant part of this noble metal chemistry was developed by Burger and co-workers,[380] who also discussed electronic distribution in compounds containing bis(imino)pyridines together with other redox-noninnocent ligands such as NO or nitride.[381,382] These authors also explained how, in derivatives of large 4d and 5d metals, the short imino arms of these pincers smooth the barriers for deformation of the metal coordination polyhedron to ease metal-based C−H bond activation reactivity.[380,383]

The terminal nitrido complex **93** provided outstanding examples of outer-sphere bond cleavage, such as those depicted in Scheme 32.[384-386] Related intramolecular C−H activations of the pincer peripheral groups that formed new N−C bonds were reported for putative Co analogues of **93**[387] and nitrene relatives,[67] generated after photo- or thermolysis of azido ligands. Inspired by all these transformations, Cundari et al. explored through calculations the feasibility of methane C−H activation along similar outer-sphere pathways.[388] This author also examined other alternatives for activation of this substrate based on 3d pincers and redox-active ligands.[389,390]

[insert Scheme 32 here]

**Scheme 32** Reactions at the terminal nitride ligand of the bis(imino)pyridine Ir pincer **93**.

*Amido- and phenolato-derived ligands:*

Catechol-, o-aminophenol- and o-phenylenediamino-based bidentate ligands are archetypical redox-active systems that can span three oxidation states when coordinated to a metal (e.g. quinone ($^0$), semiquinone ($\bullet^-$), and catecholate ($^{2-}$) for the κ-*O,O* ligand).[391] These motifs can be integrated into pincer ligand skeletons to generate redox-active pincers. This is illustrated in Scheme 33 for complexes **94**, prepared by Mukherjee and co-workers as either neutral, cationic or anionic derivatives that contain two azo-appended o-amidophenolato pincer ligands.[392] As in other cases illustrated above, going from cation to anion only involved ligand-centered reductions, while Co center remained Co(III). Choosing the cationic derivative as an example, the metric parameters of the amidophenolato fragment (metrical oxidation states),[393] supported by DFT calculations, indicated two o-iminobenzosemiquinonato π-radical ions, AF-coupled through the metal center to result in a diamagnetic cation: [(ON$^{N}$N$^{Ph}$•$^{-}$)$^{\downarrow}$(LS-d$^{6}$-Co$^{III}$)(ON$^{N}$N$^{Ph}$•$^{-}$)$^{\uparrow}$]$^{+}$. In this particular case, the temperature-dependent NMR spectra suggested access to a second electromer, the Co(II) species [(ON$^{N}$N$^{Ph}$)(LS-d$^{7}$-Co$^{II}$)$^{\downarrow}$(ON$^{N}$N$^{Ph}$•$^{-}$)$^{\uparrow}$]$^{+}$, in valence-tautomeric equilibrium.[394] Related ground-state electronic structures were found for analogues coordinating two ligands with appended thioether arms, ONS, though in this case the anionic side of the redox series was identified as a Co(II) derivative.[395]

[insert Scheme 33 here]

**Scheme 33** Redox series of Co(III) octahedral complexes coordinating redox-active amidophenolato-derived ligands. Anion of the cationic version is PF$_{6}^{-}$ and cation of the anionic version is [Co(Cp)$_{2}$]$^{+}$.

The electronic flexibility of these pincers may drive results as counterintuitive as that shown for the neutral square planar complex **95** in Scheme 34. The complex was characterized as an intermediate-spin Co(III) (S = 1) coordinating both a fully reduced amidophenolato and a one-electron oxidized iminosemiquinonato ligand: [(ON$^{OPh2-}$)(IS-d$^{6}$-Co$^{III}$)$^{\uparrow\uparrow}$(ON$^{OPh}$•$^{-}$)$^{\downarrow}$].[396] One-electron oxidation with silver triflate provoked not only structural rearrangement into a six-coordinate species but also electronic rearrangement into a more reduced Co(II) species, [(ONO$^{Ph}$)(HS-d$^{7}$-Co$^{II}$)$^{\uparrow\uparrow\uparrow}$(ONO$^{Ph}$•$^{-}$)$^{\downarrow}$]$^{+}$. Notably, binding of the ligand acyl arm led to neither *mer*- nor *fac*-coordination, but intermediate (O−Co−O angles about 133°), to complete trigonal prismatic geometry around Co. In fact, such geometry was reasoned key to promote metal reduction at the expense of further ligand oxidation. Other examples of redox-controlled ligand hemilability are known for group 9 complexes with related ONS pincer ligands.[397,398] Also, a rare coupling of redox-active naphtoquinone-appended ONO amidophenolato ligands to form spiro oxazine oxazepine derivatives was found to result from a redox cascade triggered by Co(III) complexes in the presence of $O_2$.[399]

[insert Scheme 34 here]

**Scheme 34** Redox-induced ligand-to-metal electron transfer

As already discussed for other amido-based scaffolds, the lone pair at nitrogen may favor ligand rearrangement into bridging to stabilize unsaturated complexes. Scheme 35 shows a redox-active tris(amido) ligand,[400,401] in this case derived from deprotonation of bis(2-isobutyrylamidophenyl)amine, able to reversible arrange this way.[402] The paramagnetic Co(II) dianionic dimer **96** was found to react with $O_2$ stabilizing the anionic superoxo adduct **97**: characterized as a net S = 1/2 species in which high-spin Co(II) couples AF with both a dianionic pincer aminyl radical[403] and a superoxo radical anion: $[(\mathrm{NNN}\bullet^{2-})^{\downarrow}(\mathrm{HS\text{-}d^{7}\text{-}Co^{II}})^{\uparrow\uparrow\uparrow}(\mathrm{OO}\bullet^{-})^{\downarrow}]^{-}$.[404] Hence, the pincer ligand and not the metal underwent one-electron oxidation. Complex **96** was found capable of catalyzing triphenylphosphine oxidation[402] as well as intramolecular benzylic C–H amination of aryl azides.[405] The latter reaction was also explored with related NNN amido pincer ligands bearing sulfonamido end-groups.[406]

[insert Scheme 35 here]

**Scheme 35** Reaction with $O_2$ of a dicolbalt complex featuring a redox-active NNN tris(amido) ligand. Cations are $Et_4N^+$.

Fiedler and co-workers designed a redox-active ON**N**NO skeleton to bridge and hold together two metals in pincer coordination environments (Scheme 36).[407] Cation **98** was found to exhibit a short intermetallic distance of 2.70 Å, which allowed direct overlap of the $dz^2$-based SOMOs localized on each low-spin Co(II) center, to afford a diamagnetic (AF-coupled) dimer. It exhibited an abundance of electrochemical features, arising from both ligand- and metal-based events, over a potential range of nearly 3 V. Upon one-electron oxidation **98** formed a S = 1/2 ligand-based radical, although the unpaired spin was still partially delocalized over the two low-spin Co(II) centers, as deduced form EPR features and DFT calculations.[407] Upon consecutive one-electron reductions, DFT calculations indicated the stepwise generation of high-spin Co(I) centers, which eventually produced a symmetric diamagnetic anion.[408] **98** also underwent reaction with $O_2$ to form the $Co_2$(III) $\mu$-1,2-peroxo complex **99**. In a formally similar two-electron oxidation of the dinuclear core, the reduced $Co_2$(I) anion was proposed to transform protons into hydrides during the electrocatalytic production of $H_2$ driven by **98**, which exploits the $Co_2$ unit to avoid resorting to Co(III).[408]

[insert Scheme 36 here]

**Scheme 36** Reaction with $O_2$ of a dicolbalt complex featuring a redox-active ligand with fused pincer-type coordination sites. Anions are $ClO_4^-$.

o-Phenolates were also used as wingtips[409] to attain redox-active OCO ligands from NHCs, as illustrated in Scheme 37 by the square planar complex **100**. A redox series $[Co(OCO)(S)_n]^{0/+/2+}$ (S = acetonitrile, thf, n = 1-3, respectively) was prepared.[410] The neutral (**100**) and dicationic derivatives were identified as Co(II) low-spin complexes coordinating closed-shell dianionic or neutral (singlet biradical) ligands, respectively, while electronic distribution at the monocation was ambiguous. The redox potential corresponding to the first oxidation was found to be nearly independent of the ligand skeleton, but that of the second oxidation increased up to 400 mV when unsaturated NHC backbones where used, in agreement with ligand-centered redox events. Co(III) complex **101**, a derivative of the neutral complex version obtained by oxidation with $AgCF_3$ (Scheme 37), was found to deliver $\bullet CF_3$ radicals upon visible-light induced homolysis of the $Co{-}CF_3$ bond.[411] This methodology[412] allowed for arene C−H trifluoromethylations that did not require sacrificial oxidants, since reactions also produced $H_2$. Noteworthy, while 5-coordinate **101** was identified as the reactive species, its 6-coordinate adduct was found totally stable under visible-light irradiation.

[insert Scheme 37 here]

**Scheme 37** Visible light-induced $Co{-}CF_3$ bond homolysis causes arene C−H trifluoromethylation.

The pincer ligands based on amido and/or phenolato redox-active functions are scarcely represented in the chemistry of Rh and Ir. Ir(III) complexes with diphenolato imidazolyl-carbene ligands were reported prior to their Co analogues of Scheme 37,[413] and found to undergo reversible oxidation after which the unpaired electron was partially delocalized over the OCO ligand. A valence tautomeric equilibrium between $[(d^6\text{-}Rh^{III})(ONS^{Ph}\bullet^{-})^{\uparrow}(Cl)_2(PPh_3)]$ and $[(d^7\text{-}Rh^{II})^{\uparrow}(ONS^{Ph})(Cl)_2(PPh_3)]$ electromers was characterized for a derivative coordinating a thioether-appended amidophenolato ligand.[414] Besides this couple of examples, the oxidation products of a handful of Rh(III) pincers, unlikely to contain metal centers in higher oxidation state, were subjected to detailed characterization studies to clarify the presumed redox activity of ligands. In derivatives of anionic NNN bis(pyrazolyl)amides, the value of the oxidation potential was correlated with the overall charge at the complex and the nature co-ligands.[415] In dimeric complexes of the dianionic NNN 2,2′-diamidoazobenzene ligand, the extensive delocalization of the N-centered odd electron into the adjoining phenyl ring came out key to attain stability of the oxidized ligand radical.[416] For unsymmetrical NNO ligands containing phenoxido and pyrrolido side arms, spin distribution in the ligand radical was found to involve almost equally these two oxidizable domains.[417]

The Rh(I) cation [Rh($\eta^2$N•$\eta^2$)(bipy)]$^+$ (**102**, Fig 9) was the first reported metal complex coordinating a stable aminyl radical.[43] Ir(I)[42] and Co(I)[41] versions of this complex, as well as Rh(I) analogues with co-ligands other than bipy,[42] were subsequently described. All complexes were prepared via one-electron oxidation of the corresponding neutral amido precursors. A further analogue containing a phosphinyl radical, the Rh(I) neutral complex [Rh($\eta^2$P$^{Ph}$•$\eta^2$)(PPh$_3$)] (**104**), was obtained after one-electron reduction of its cationic bis(phosphino) precursor.[418] The detailed characterization of this family of Rh(I) paramagnetic complexes established that spin distribution between the metal and the (trop)-based ligand may significantly vary depending on the particular features of each complex. In cation **102** for example, the spin density estimated by DFT computations was 56% at the (trop)$_2$N nitrogen atom and 30% at the metal,[43] while in neutral **103** spin allocation was inverse, 41% and 56% respectively, because of a two-center, three-electron Rh−N bonding.[419] Consistently, **102** was found to react with hydrogen donors as expected for a nucleophilic aminyl radical, whereas **103** was much more inert towards H-abstraction. The DFT spin density estimations in **103** also concluded that a negligible amount of the odd electron was localized in the second amide ligand, thus showing that the (trop)$_2$ skeleton plays a role in radical stabilization. Phosphinyl complex **104** was found to consist of two structurally-different electromers that interconverted fast in the EPR time scale. The EPR signals indicated significant spin density at the metal center in both electromers, although one of them showed larger anisotropy of the g tensor and larger hyperfine constants with the P atom of the (trop)$_2$PPh ligand, suggesting that the unpaired electron is highly localized at this Rh−P bond in one of the electromers but delocalized in the other.[418]

[insert Fig 9 here]

**Fig 9** Structures of Rh(I) complexes containing (trop)$_2$N• aminyl and (trop)$_2$P•Ph phosphinyl radical ligands, reported by Grützmacher and co-workers: CCDC codes from left to right:

[**102**]($O_3SCF_3$)[43] FENYAZ; **103**[419] QIPPIQ; [**104**]$PF_6$[418] SUHXAV. H atoms are omitted for the sake of clarity. Phenyl rings of **104** are represented as wireframes.

*Other redox-active ligands and H-atom transfer*

Early work by Milstein and co-workers proved that persistent ligand radicals could be stabilized even within most classical PCP pincer ligand scaffolds, provided that they are equipped with extended π-conjugated systems. The radical complex **105**, with the proposed structure shown in Scheme 38, was obtained by reduction of the dinitrogen-bridged Rh(I) precursor [(μ-$N_2$){Rh($^{iPr}$PCP)}] with K in thf. Its EPR spectrum revealed an unpaired electron confined within the naphthyl moiety of the ligand, despite which the complex was found to undergo metal-centered reactions.[420] The bis(phosphinomethyl)pyridine, another common pincer ligand architecture, provided examples of C−H bond homolysis at the benzylic position in Co complexes (Scheme 38).[98,421] This particular modification of the PNP ligand, which leads to pyridine dearomatization (see below),[422] is commonly achieved by deprotonation with bases, but radical pathways are exceptional. The characterization by Chirik and co-workers of products **107** concluded that radicals were metal-centered, hence low-spin Co(II). Therefore, the overall H-atom release can be viewed as a proton coupled electron transfer (PCET)[423] in which the proton is supplied by the ligand, whereas the electron comes from the accessible Co(I)/Co(II) redox couple. It follows from this that similar C−H bond homolysis should be out of reach for noble Rh and Ir counterparts, not so easily engaged in single-electron transfers. DFT calculations on Co(I) precursors **106** also indicated that open-shell singlet electronic structures [(LS-$d^7$-$Co^{II}$)$^{\uparrow}$($^{iPr}$PNP$\bullet^-$)$^{\downarrow}$(X)], slightly favored over the closed shell alternative for the stronger σ-donor X co-ligands, led to lower C−H bond dissociation energies.[98]

[insert Scheme 38 here]

**Scheme 38** (left) Proposed structure of a Rh(I) complex coordinating a naphthyl-centered pincer ligand radical. Cation is $K^+$. (right) C–H bond homolysis at a Co(I) pincer affording a Co(II) derivative with a dearomatized PNP ligand

As a corollary of the latter reasoning, ligands combining electron storage capability with protonable sites could be expected to act as H-atom reservoirs, a possibility commonly referred to as "chemical noninnocence".[424] The parallelism between proton and electron storage was discussed by Veige and co-workers for certain ONO ligands,[425] while recent work by Anderson et al. showed that pincer ligand-stored H atoms could be transferred to small molecules such as acetonitrile or dioxygen, and regenerated by reaction with $H_2$.[426] Various examples of multiple H-atom removal from pincer backbones in the presence of oxidants or H-atom scavengers have been mentioned and illustrated in the previous chapter (Schemes 7 and 14), as a mean of going from saturated bis(phosphinoethyl)amido[47,143,184,424] or -pyrrolido[142] scaffolds to more inert dehydrogenated versions. Ligands capable of accepting and releasing H atoms are also likely susceptible to isomerization via H-atom shifts, as already illustrated in Scheme 8 by the rearrangement of a symmetric dianionic bis(amido)pyridine ligand into a non-symmetric neutral imino(amino)pyridine. As discussed by Gade and co-workers for 2,5-bis(oxazolinylmethyl)pyrrolido skeletons,[374] such H shifts can be suppressed by ligand designs that "decouple" the central anchor unit from the wingtip donors, using dimethyl-methylidene spacers. This strategy, applied to closely-related ligands, accounts for the different reactivity of **39** and **41** (in Schemes 7 and 8).[145,146]

### 3.3 Functional peripheral sites

A great deal of research has been devoted to decorate pincer architectures for a variety of purposes. Typical examples comprise *para*-functionalization of phenyl or pyridine central rings for goals such as electronic tuning,[427] organization of supramolecular assemblies,[428] catalyst immobilization or dendrimer formation,[429] etc. More inside the perspective of this review are those functional objects poised to interact with metal-bound substrates. Such objects may consist of hydrogen-bond donor or acceptor groups that can act as a proton reservoir or serve to orient and direct substrate coordination through non-covalent interactions,[430,431] or groups providing new electron pairs to be used in concert with the empty orbital at the metal for cooperative bond cleavage.[432] Functional objects should therefore be properly installed or appended to reach the vicinity of metals, for which pincer ligand platforms offer a continuum of possibilities.

Ostensible examples of such appended functions and their utility can be extracted from the PCP designs by Gelman and co-workers, based on dibenzobarrelene scaffolds[433-436] provided with an additional sidearm bearing OH, COOH or $NH_2$ end-groups. These pincers can activate/form chemical bonds via intramolecular interactions between the appended function and metal-bound reagents, as illustrated in Scheme 39 (left) by a reversible protonolysis of Ir hydride **108** to form $H_2$.[437] This strategy led to highly efficient Ir catalysts for acceptorless dehydrogenation of alcohols[438,439] or formic acid,[437] dehydrogenative coupling of alcohols,[440] and chemoselective hydrogenation of nitroarenes to anilines,[441] and was proposed to assist C−H bond formation in catalytic olefin hydroformylation.[442] Loosely coordinating functional tethers are required to preserve access to the coordination vacancy at metal.[443] Related alternative designs by Iluc and co-workers comprising 2-anisolyl (complex **109** of Scheme 39)[444] or 2-pyridyl[445] tethers were found compatible with the intermolecular C−H bond activation at Ir of a range of reagents. In contrast, the reactivity of equivalent PN(R)P platforms with aromatic R groups was strongly conditioned by the backbone fragility and the preferred intramolecular C−H cleavage at R.[446] In line with this latter reaction, it should be observed that conventional C−H metalation of ligand substituents can be regarded in this context as just a particular case of function. Actually, several examples of this resource have been and will be given throughout this chapter, and constitute a main attractive of certain pincer architectures.[447-449] Also, in the limit of this strategy, some pincer ligand designs featured agostic hydrocarbon tethers.[450,451]

[insert Scheme 39 here]

**Scheme 39** (left) Reversible addition of $H_2$ assisted by a carboxylic acid tether. (right) Ir(PCP) pincer equipped with an anisole hemilabile tether.

Miller and co-workers proposed a peripheral functionalization pursuing electronic modification and control over coordination vacancies. It comprised installation, at the N side of a PCN scaffold, of an aza-crown ether substituent, which can act as both a hemilabile arm and a host for cation-crown interactions, enabling the use of simple salts to shift the thermodynamics of ligand binding. It was hypothesized that such a tunable hemilability can gate entry to catalytic cycles, enabling in situ switching between active and inactive states or fine-tuning a balance of activity and stability.[452] This hypothesis was checked in part in Ir chemistry using hydride complex **110**, proposed to participate in the generic equilibrium of Scheme 40. The equilibrium was verified for L = acetonitrile, establishing the ligand capability to exchange among $\kappa^5$-P,C,N,O,O, $\kappa^4$-P,C,N,O and $\kappa^3$-P,C,N coordination modes.[453] In solution, the $\kappa^5$ and $\kappa^4$ modes can be easily distinguished from the $\kappa^3$ binding through the difference in $^1$H NMR chemical shift between each pair of diastereotopic geminal protons of the aza-crown ether, since the effect on them of the diamagnetic anisotropy arising from the metal coordination sphere is different when the fragment is bound but similar when it is released.[454]

[insert Scheme 40 here]

**Scheme 40** Hemilability and cation hosting equilibria of Miller's aza-crown PCN pincers. Anions are omitted.

The equilibrium of Scheme 40 was extrapolated to L = $H_2$ or olefins to account for the acceleration in presence of salts (and deceleration in the presence of base) of reactions such as deuterium incorporation at the hydrido position in the presence of $D_2$,[453] or isomerization of terminal alkenes into internal ones,[455] respectively. Even though cation association constants to these ligands were found to be significantly smaller than those to free crown ethers, addition of salts resulted into rate enhancements as large as 1000-fold, depending on the concentration and identity of the salt: lithium ones leading to the highest responses.[452] The reactivity and catalytic properties of other Ir derivatives of these ligands were also explored in the context of methanol carbonylation,[456,457] where salts were again observed to enhance rate but catalyst stability arose as an issue.[458]

Peripheral ligand implementation with proton-responsive groups may also provide switches for electronic modification and promote new second-sphere interactions. Scaffolds such as NNN 2,6-bis(pyrazolyl)pyridines[72] and NCN phenyl-based analogues[459] were thoroughly interrogated in these respects by the groups of Caulton,[460-463] and Kuwata and Ikariya.[464,465] They gave multiple examples showing that deprotonation of the pyrazolate sites attracts electrophiles there: alkali metal ions or a second transition metal ion, leading to the frequent occurrence of bridging pyrazolates.[460,463] These complexes were also found competent in O-atom transfer reactions,[461,462] and were suggested capable of activating bonds in a concerted manner, as illustrated in Scheme 41. The $CH_2Cl_2$ activation reaction was proposed to immediately follow chemical oxidation of Co(II) precursor **111** in this solvent, which afforded Co(III) derivative **112**.[461] This type of bond activation at metal-ligand Lewis pairs constitutes the main subject of the following pages.

[insert Scheme 41 here]

**Scheme 41** Proposed concerted activation of dichloromethane at a Co(NNN)pincer. Anions are omitted.

Milstein and co-workers found that bis(phosphinomethyl)pyridine PNP complexes (in this context often referred to as lutidine-derived pincers) can display the reaction capabilities illustrated in Scheme 42,[466] which delineate the so-called metal-ligand cooperation by aromatization/dearomatization.[422,467] In the example, the overall reaction is a net trans-addition of $H_2$ to **113** that involves two key steps. First, the Ir(I) precursor equilibrates with a 5-coordinate Ir(III) hydride bearing a deprotonated anionic pincer ligand (**114**). Although, according to DFT calculations,[468,469] this transformation is endergonic by 10.7 kcal mol$^{-1}$, the proposed intermediate could be prepared in an independent experiment by deprotonation of the cationic Ir(III) complex [IrH(Ph)($^{tBu}$PNP)]$PF_6$ with KO*t*Bu, and characterized at low temperature to retard its rapid transformation into **113**. In structurally characterized analogues of this intermediate, the bond distances within the pyridine ring clearly indicated dearomatization into an amide, so as the solution NMR signals. Calculations could not find practical intramolecular pathways for H migration,[470] but it turned out feasible with the help of water molecules that shuttle the proton.

[insert Scheme 42 here]

**Scheme 42** $H_2$ splitting via metal-ligand cooperation by aromatization/dearomatization

The transformation has a profound impact in the reactivity of the complex, not only due to the change of N-donor function but, at least in this particular case, mainly because of the changes at Ir. As explained by Saillard and Hoffmann in their classical theoretical study on OA reactions, $d^8$ square planar complexes display high kinetic barriers to concerted additions because they require a previous severe distortion to a high-energy $C_{2v}$ geometry. Only then the metal can simultaneously offer to the substrate an empty orbital of σ-symmetry for coordination and a filled orbital of π-symmetry to realize bond cleavage.[471] Protonation to Ir(III) indeed solves the half of the problem that concerns the empty orbital, while the basic residue at the deprotonated ligand provides an alternative filled orbital to bring about heterolytic $H_2$ cleavage without resorting to oxidation state Ir(V), through concerted **TS115**. A signature of this mechanism is the mutually trans arrangement of the hydrides in the final product and, when using $D_2$ instead of $H_2$, a D label in the re-protonated methylene. The mechanism resembles in many respects proton-catalyzed strategies to cleave H−H and C−H bonds demonstrated by the teams of Brookhart[472] and Goldman[473] in POCOP and PCP pincers, respectively. In them, Ir(I) square-planar complexes were first protonated by a weak acid to form cationic Ir(III) hydride intermediates that may readily coordinate the reagent. In the absence of an intramolecular basic site, the heterolytic bond cleavage has to be completed intermolecularly, by the conjugated base of the acid.[474-476]

Complex **113** can use this mechanistic resource to cleave bonds other than H−H, such as the sp C−H of phenylacetylene to form [Ir(C≡CPh)H(Ph)($^{tBu}$PNP)],[477] and the O−O bond of the oxygen molecule to give two equiv of [Ir($^{tBu}$PN*P)(OH)(Ph)], which contains the anionic dearomatized version of the PNP.[478] This Ir(PNP) scaffold also demonstrated outstanding capabilities to deal with the $CO_2$ molecule,[479-481] favoring its incorporation at the ligand benzylic position or cleaving it to afford water and a CO ligand. The latter is illustrated in Scheme 43 for the transformation of a related Rh(PNP) hydride (**117**) into a dearomatized carbonyl derivative (**118**), still capable of activating benzene upon UV irradiation. Based on this sequence, a cycle for the photocarbonylation of benzene using $CO_2$ as the feedstock was constructed and demonstrated for the production of benzaldehyde from benzene.[482]

[insert Scheme 43 here]

**Scheme 43** Stoichiometric sequences for benzene carbonylation at Rh(I) PNP pincers ($^{c}$Pe = cyclopentyl)

Building on this new mechanistic paradigm the group of Milstein developed a wealth of new catalytic applications, particularly impacting for Ru chemistry,[483-485] and currently focused on Mn and Co chemistry.[4] Co-catalyzed processes were commonly initiated from Co(II) dichloro precursors, generally activated in situ with $NaHBEt_3$ and KO*t*Bu, and included hydrogenations, of nitriles to amines[486] and of esters to alcohols,[487] and processes that dehydrogenatively couple alcohols with amines into heteroaromatics.[488,489] A variety of different PNN pincer ligands containing the lutidine core was also developed along these catalytic studies. Among them, a $PNN^H$ design meets additional potential for metal−ligand cooperation through the amino/amido function (see below).[490] The Rh analogue of **113**,[484] and closely-related derivatives with smaller substituents at P, demonstrated improved C−H bond activation capabilities and activity in catalytic direct arylation.[491,492] Other teams contributed to this chemistry with different ligand designs, such as those incorporating a NHC arm, by Braunstein, Danopoulos et al.,[493-495] and Paneque, Suárez et al.,[496,497] or those equipped with a pyrazolate, by Caulton and co-workers.[498]

Ozawa and co-workers further modified this type of PNP platforms by replacing the phosphine arms with phosphaalkene units,[499] as in Ir(I) complex **120**. The main difference between this PNP ligand and those aforementioned resides in the P=C double bond, which possess an extremely low-lying $\pi^*$ orbital around the P and thus serve as strong $\pi$ acceptor toward transition metals. The Ir chemistry of this ligand entailed thermodynamically stable unsymmetrical complexes such as **121** and its dearomatized deprotonated form **122**, formed after C–H addition/cyclization of just one of the phosphaalkene arms.[500,501] **122** was found to readily split NH bonds of ammonia (to form **123**) and aniline.[502] Calculations on aniline activation revealed outer-sphere NH deprotonations directly accomplished by the ligand, followed by chloro-by-amido substitution. Ammonia, however, must first coordinate to Ir in order to enhance NH acidity, henceforth adopting a conventional metal-ligand cooperation pathway.[503] This Ir scaffold was also found capable of cleaving acetonitrile C−H bonds,[504] being catalytically active in dehydrative couplings of amines with alcohols to afford N-alkylated amines or imines.[505,506]

[insert Scheme 44 here]

**Scheme 44** Metal-ligand cooperative activation of ammonia at an Ir(PNP) pincer (Mes* = 2,4,6-*t*$Bu_3C_6H_2$).

Van der Vlugt, de Bruin and co-workers brought this metal-ligand cooperation strategy one step forward with the PNN ligand design depicted in Scheme 45, which retains the aromatization/dearomatization capability and incorporates a new reactive (electrophilic) imino arm. In the example, the P arm assists substrate deprotonation while the imine enables reversible storage of the activated sulfonamido reagent at the ligand. The overall reaction was found to be reversible by switching to a more polar solvent. The process was proven to allow for the mono-alkylation of o-toluenesulfonamide when followed by iodomethane OA to the Rh(I) center.[507]

[insert Scheme 45 here]

**Scheme 45** Reversible reaction of o-toluenesulfonamide to generate an aminal Rh complex

Huang and co-workers extrapolated aromatization/dearomatization strategy to pincer ligands displaying one or two NH groups instead of the $CH_2$ arms.[508,509] Since N−H bonds are more acidic and stronger than C−H ones, such systems were expected to display distinct kinetics and thermodynamics. Important differences between the two ligand systems arise from the more localized character of the lone pair generated at the N after deprotonation, and its orientation coplanar with the ligand and pointing outwards the vacant site at the metal. While the former minimizes dearomatization and consequently affects thermodynamics,[510] the latter disqualifies the Lewis pair for direct splitting of bonds, making indispensable the participation of proton shuttles for substrate activations.[511] Yet, this variant of functional pincers also gave outstanding catalytic applications for group 9 complexes. Kempe and co-workers reported various Ir-catalyzed sustainable synthesis of key heteroaromatics,[512-516] combining acceptorless alcohol dehydrogenation with condensation steps. More recently, they developed Co-catalyzed versions of these and related synthesis,[517-519] as well as Co catalysts for hydrogenation of carbonyl compounds.[520] A stoichiometric sequence for benzene carbonylation is depicted in Scheme 43 to compare with the previously mentioned one developed by Milstein et al. This [RhCl($^{cPe}$P$^{NH}$N$^{NH}$P)] system (**119**) utilized CO instead of the greener $CO_2$, but did not require UV irradiation.[521] No intermediates with anionic deprotonated ligands were visible along this sequence, though stable complexes such as [Rh(P$^{NH}$N$^{N}$P)(CO)] were prepared and characterized along previous studies of cooperative H−H and C−H bond activations.[522]

### 3.4 Functions at donor atoms

The lone electron pair can be brought as close to the metal center as to a donor atom of the pincer, as in amido pincer ligands. While for unsaturated early metals this is expected to result in $\pi$-donation to the metal and consequent "cancellation" of the Lewis pair, such a result is less likely for group 9 metals due to the high number of d electrons and concomitant $\pi$-conflicts.[523-525] In low-spin square planar $d^8$ and octahedral $d^6$ complexes, the matching d orbitals are doubly filled, leading to a p$\pi$−d$\pi$ repulsion or, at least, to a lack of $\pi$-bonding. Hence, amido complexes of these types are expected to show highly nucleophilic N atoms.[526] Among usual $d^6$ coordination geometries, only 5-coordinate Y-shaped structures permit N→M $\pi$-donation,[527] therefore being the most likely for unsaturated low-spin M(III) derivatives in the absence of other restraints. Effective ligand designs should also disfavor other possible alternatives for the lone pair, such as the formation of intermetallic amido bridges or its migration via tautomerization: possibilities already illustrated in previous pages. The extent of N→M $\pi$-donation has already been mentioned as an issue for square planar Ir derivatives bearing divinylamido $^{tBu}$PNP ligands in various oxidation states (**57-59**, Scheme 14).[143] Also, a characteristic reaction of the metal-amido Lewis pair manifold such as the heterolytic addition of $H_2$ has been illustrated for the Co(I) mononuclear synthon [Co($^{iPr}$PNP)] displaying a saturated pincer skeleton (generated from **13**, in Scheme 3).[153]

The addition of $H_2$ across a pincer M−N bond was first observed by Fryzuk and co-workers in Rh and Ir complexes of P$^{Si}$N$^{Si}$P amide ligands.[528-531] The related derivative [Ir($^{iPr}$PNP)(H)$_2$] (**124**), bearing a non-silylated version of the amide, was prepared by Abdur-Rashid and co-workers and found to dehydrogenate 2-propanol to form [Ir($^{iPr}$PN(H)P)(H)$_3$] (**125**, Scheme 46). Accordingly, the compound was recognized as an effective catalyst for hydrogen transfer to ketones in the absence of base.[532] Beller et al. reported the transformation of **124** into **125** under $H_2$ as exergonic (by 6.4 kcal mol$^{-1}$ according to DFT calculations), with a free energy activation barrier of 20.3 kcal mol$^{-1}$. They applied catalyst **125** in ester hydrogenation[533] and methanol dehydrogenation in aqueous solution.[534] Recent work by Casado et al. concluded that acetylene C−H bonds can also get cleaved at these Ir−N bonds to form alkynyl derivatives bearing the amino pincer.[535]

[insert Scheme 46 here]

**Scheme 46** Examples of metal-ligand cooperation in Ir amide PNP pincers

Starting from the 18-electron **125**, Hazari and co-workers described the formation of air and moisture stable **126** via outer-sphere insertion of $CO_2$.[536,537] DFT calculations indicated a pathway for insertion initiated by hydride nucleophilic attack on $CO_2$ to form a H-bound formate intermediate (not shown). It was proposed that attack is facilitated by the strong trans influence of the trans hydride, in a genuine example of exploitation of the *mer* ligand coordination environment. The H-bound formate then dissociates to re-coordinate as an O-bound species in **126**.  A non-covalent N−H···O interaction conditions the geometry of the transition states as well as thermodynamics: insertion into the hydride that is *syn* to the N−H is downhill by 4.9 kcal mol$^{-1}$, whereas insertion into the *anti* hydride is uphill by 2.8 kcal mol$^{-1}$ because hydrogen bonding is no longer possible. A $CO_2$ hydrogenation cycle to release formate can be closed from **126** either with $H_2$ in the presence of base, or via electroreduction in presence of a proton source.[538] Notably, the resulting overall $CO_2$ hydrogenation mechanism preserves the N−H bond along the cycle. This is in contrast to the classical bifunctional pathways (Shvo, Noyori or Morris type)[539] that are assumed for this catalyst in ketone hydrogenations or alcohol dehydrogenations, in which both hydride and proton are transferred to (or from) the substrate. Hence, in this case ligand cooperation is limited to anchoring the substrate via hydrogen bonding. A related assistance of a pincer protic moiety was deduced for electroreduction of $CO_2$ to CO and $H_2O$ catalyzed by a Co(SNS) pincer bearing readily protonable sulphido arms.[540]

Scheme 47 intends to illustrate that metal-ligand cooperation in these amido pincers can also involve the simple migration of H between metal and N. Complex **128**, already mentioned in the previous section as a rare example of Ir(III) square planar compound, was obtained by Holthausen, Schneider and co-workers after reaction of the cationic dihydride **127** with oxygen in thf or $CH_2Cl_2$.[188] A cycle for the 4-electron $O_2$ reduction to water was completed via reaction with $H_2$, which restored the hydride complexes **127** and **129** in equilibrium. A key feature of the computed reaction mechanism is the need for traces of water, indispensable for shuttling the NH proton to an Ir-bound peroxo, to give a hydroperoxido intermediate. The second reaction of Scheme 47, reported by Caulton et al.,[541] describes a reverse H migration. **130**, a cyclometallated[542] Ir(III) version of the ${}^{tBu}P^{Si}N^{Si}P$ T-shaped Co(I) complex **22** discussed in the first section (in Scheme 5),[59,106] reacted with $I_2$ to form, as expected, an iodine OA product, **131**. Yet, instead of resorting to C−H RE of the phosphine substituent to circumvent oxidation state Ir(V), the metal transferred its H ligand to the amide. Formally, the hydride ligand transforms this way into a proton with concomitant 2-electron reduction of the metal. Such umpolung of metal hydrides was proposed key to switch selectivity in $CO_2$ hydrogenations catalyzed by parent Ni complexes.[543]

[insert Scheme 47 here]

**Scheme 47** Examples of H migration between Ir and an amide PNP pincer ligand. Anion of **127-129** is $PF_6^-$.

The Rh complexes of the Grützmacher's $(trop)_2N$ amide ligand, mentioned earlier in this section because of its radical chemistry, allowed $H_2$ splitting and alcohol dehydrogenation in oxidation state Rh(I) (Scheme 48). This should result in hydride ligands more nucleophilic than those bonded to Ir(III) and easier hydride transfers.[544] Accordingly, complexes $[Rh(\eta^2N\eta^2)(L)]$ (**132**), coordinating either phosphine[545,546] or NHC[547] L ligands, evidenced exceptional ability to deal with $H^-/H^+$ in a variety of catalytic alcohol dehydrogenative couplings.[547-549] These catalysts and reactions were implemented in innovative anodes for alcohol fuel cells.[550-552]

[insert Scheme 48 here]

**Scheme 48** $H_2$ splitting and alcohol dehydrogenation in amido $Rh(\eta^2N\eta^2)$ pincers

(De)hydrogenation and transfer (de)hydrogenation catalysis based on Co(PNP) amido pincers were first reported by Hanson and co-workers using the Co(II) alkyl precursor $[Co(^{Cy}PNP)(CH_2SiMe_3)]$, activated in situ by Brookhart's acid to form the cationic catalyst **133** (Scheme 49).[553-556] The mechanisms of these reactions were computationally investigated by Yang and co-workers,[557] and catalytic applications were extended by the groups of Jones,[558,559] and Zhang.[560-564] Also, Hanson's and related amido/amino ligand designs were further applied in a variety of Co-catalyzed processes by Beller et al.,[50] Guan et al.,[565] Liu and co-workers,[218,566,567] Milstein et al.,[568] and Bernskoetter et al.[129,569] The rich catalysis associated with these and closely related Co and other base-metal pincer catalysts was reviewed in a comprehensive manner by Schneider at al.,[8] Filonenko, Pidko and co-workers,[570] and by Jiao and Wei from a computational perspective.[571] Alkylation reactions comprising hydrogen borrowing strategies were also included in a review by Irrgang and Kempe.[572] Furthermore, the contribution of these results is significant in reviews covering Co-catalyzed homogeneous hydrogenation,[573] (de)hydrogenation and (de)hydrogenation transfer catalysis,[9] and Co pincer catalysis in general.[3,4] The reader is referred to these very recent reviews for further examples and discussion.

All this recent development of Co catalysts was generally carried out in parallel with studies on neighboring base-metals, and accompanied by computational and experimental mechanistic work. Oftentimes, experiments comparing catalytic performances of N−H and N−Me analogues afforded particularly clear-cut results. As an example, Scheme 49 compares Hanson's catalyst (**133**) with its N-methyl analogue (**133-Me**) in a reversible aceptorless (de)hydrogenation of heterocycles described by Jones and co-workers.[558] Methylation completely inhibited dehydrogenation but not hydrogenation, suggesting a non-bifunctional pathway for the latter. The reverse effect is also possible, as reported, for example, by Bernskoetter et al. in $CO_2$ hydrogenations catalyzed by the Co(I) cationic complex $[Co\{^{iPr}PN(Me)P\}(CO)_2]Cl$ or its NH version.[129] In this case, the N−Me complex clearly outperformed the N−H analogue (29000 vs 450 TONs), showing that potentially bifunctional platforms are not universally advantageous. In this context, recent computational investigation by Dub, Gordon and co-workers reexamined most relevant cases of "accepted" bifunctional hydrogenation mechanisms to assess the actual role of ligand N−H (and C−H) acidic functionalities during catalysis.[574-577] According to this work, even when stoichiometric bifunctional steps such as concerted $H_2$ heterolysis or $H^-/H^+$ transfers proved feasible, they are unlikely to operate during catalysis against alternatives preserving the protic functionality at the ligand: solvent- or product-assisted heterolysis of $\eta^2$-$H_2$ ligands, for example. Yet, the function may contribute stabilizing rate-determining transition states through non-covalent interactions. Whatever the case, it should be highlighted that ligand functionalities are the ultimate responsible for feasible outer-sphere steps allowing catalysis without change of the metal formal oxidation state.

[insert Scheme 49 here]

**Scheme 49** NH vs. NMe Co(II) catalysts in the aceptorless dehydrogenation of 1,2,3,4-tetrahydroquinaldine and reverse hydrogenation of 2-methylquinoline. Anion is $BAr^F_4$.

Some examples in previous pages (complex **7** in Scheme 2, for instance) illustrate that κ$^2$-*P* coordination of amine PNPs is often favored over tridentate binding. Far from hampering ligand functionality, this favors its exploitation at the second coordination sphere as proton relay.[430] In fact, ligands designed to display pendant amine groups have seen tremendous success in electrocatalysts for $H_2$ production and oxidation,[578-581] or $CO_2$ reduction.[582-585] These catalysts break away from the rate−overpotential tradeoff (scaling relations)[586,587] characteristic of inner-sphere catalysts, because their functional moieties lower activation barriers for substrate binding to metal centers. Bidentate functional ligands of this type were mainly applied in Ni and Fe chemistry, but significant examples of their use in Co catalysts were also reported.[582,583,588] Most recent ligand designs incorporate multiple relays at increasing distances from the metal, which facilitate the whole way of protons between the first coordination sphere to the bulk reaction medium.[589]

PNP amido ligand designs with phenylene-linked skeletons,[590] i.e. Ozerov's PNP,[591] are expected to have less accessible lone pairs and are in fact less prone to undergo metal-ligand cooperative reactions. Actually, reaction against $H_2$ of Rh(II) derivative **54**, previously shown in Scheme 13, remains to the best of our knowledge the unique example of (likely) cooperative bond splitting at this type of pincers.[178] Comparison of cyclic voltammetry data from different PNP, PNP' and PNN diarylamido scaffolds, with different metals including Rh, concluded that oxidation events at these complexes were primarily ligand-centered events,[592] which might explain the particular behavior of **54** as resulting from amidyl radical character. Another rare example of metal-ligand reactivity in diarylamido pincers did not involve the amido N, but one of the P arms (Scheme 50). Photolytic or thermal decomposition of the Co(II) azido complex

**134** produced $N_2$ together with dimeric complex **135**, which displayed a planar diamond $Co_2N_2$ core (Co−Co distance 2.57 Å) and two unpaired electrons. Dimer is connected by phosphiniminato bridges, which are proposed to originate from activation of the azido fragment and subsequent insertion of the N atom of a transient nitride into a Co–P bond. The putative nitrido complex was calculated to have considerable nitridyl radical character (0.39 of the spin density vs. 0.58 over the metal). Bridges of **135** were cleaved by HCl to give the new Co(II) pincer [Co($^{iPr}$PN$^{P}$N$^{H}$)Cl] (**136**), in this case distorted tetrahedral.[593]

[insert Scheme 50 here]

**Scheme 50** N-atom transfer to a PNP ligand in a Co(II) pincer

The diarylamido motif was implemented in a variety of other pincer architectures,[215,415,594-596] including parent carbazolido-based PNPs[207,597-599] and CNCs,[600] and the amidophenolato or tris(amido) ligands discussed earlier in this section because of their redox-activity. An alternative scaffold, the NNSi depicted in Scheme 51, gave significant results from the point of view of ligand functionality. Ir and Rh complexes **137** were described as catalysts for dehydrogenative borylation of terminal alkynes and (modest) borylation of arenes, respectively.[198,601,602] The amido site of the ligand emerged capable of accepting a boryl ligand, as shown for the isolable Rh(III) derivative **138**, which was prepared in excess borane.[601] The same reaction, however, favored a different outcome for Ir, complex **139**, already mentioned in this review as a “possible” Ir(V) derivative.[198] Although less stable than its isomer **139** and therefore not experimentally observable, the Ir analogue of **138** was concluded from DFT calculations to be responsible for the observed high catalytic activity in dehydrogenative borylation.[603] Computations indicated easy boryl migrations between Ir and N that contribute to open up coordination vacancies at the metal. Besides, the adaptability of the Si−H interaction with Ir, varying from a moderately perturbed Si−H $\sigma$-complex to full Si−H OA, provides significant flexibility to smooth out other electronic changes at the metal. Such a tunable interaction was identified as a resource of Si-based pincers,[13] and was found to operate in other group 9 systems to, for example, facilitate the exchange between stereoisomers in Ir(PSiP) hydrides.[604] Actually, a family of SiPSi semirigid pincer scaffolds was developed by Sabo-Etienne, Montiel-Palma and co-workers aimed at exploiting the many coordination potentialities of such Si−H moieties.[605-607]

[insert Scheme 51 here]

**Scheme 51** Example of borane reactions with NNSi pincers.

Besides amides, other pincer ligands are known to exhibit donor atoms with lone pairs susceptible of participation in bond activations. Phosphide, for example, is thought to be better than amide in keeping its lone pair away from $\pi$-bonding to metals because phosphorus is less prone than nitrogen to rehybridize from $sp^3$ to $sp^2$.[608] Accordingly, the Ir(I) 18-electron complex [Ir(PPP)(cod)], displaying a bis{(2-diphenylphosphino)phenyl}phosphido ligand (*fac* in this example), was found to react with a variety of Lewis acids to form new P−H, P−C, P−B or P−M bonds.[609] Conversely, related complexes in which the metal center is unsaturated can display Lewis pair reactivity, as illustrated in Scheme 52 for the low-spin Co(I) complex **140**. Just like its already discussed saturated analogue **36** (in Scheme 6), **140** coordinates a PPP pincer with a central N-heterocyclic phosphido moiety that supports a non-bonding lone pair at the P atom.[610] Its reaction with $H_2$ led to addition across the Co−P bond, though the position of the hydride in the reaction product **141**, trans to P, was unexpected for a concerted H−H splitting at a Lewis pair. Preliminary DFT calculations suggested a mechanism in which bond cleavage (OA) takes place at Co, and is followed by proton migration to P. The complex was also observed to cleave the O−H and S−H bonds of phenol and thiophenol, respectively, to form hydrido thermodynamic products.[611] The latter substrate initially afforded a thiolato kinetic isomer **142**, whose evolution into **143** was concluded to be an intermolecular process mediated by the free thiol.

[insert Scheme 52 here]

**Scheme 52** Heterolytic addition of $H_2$ and PhSH across a Co−P bond

Carbenoid pincers[612] are also able to add fragments across the M=C bond without breaking the connection.[613] The reversible reaction of $H_2$ with [IrCl{$^{tBu}$PC(=)P)] to form [IrClH($^{tBu}$PC(H)P)] was first observed by Shaw and co-workers using a bis(phophino)carbene ligand of aliphatic $(CH_2)_2C(CH_2)_2$ skeleton.[614] Later, the reaction was reproduced with other Ir precursors coordinating cyclohexane-,[615] phenylene-,[616] or benzothiophene-based[617] alkylidene diphosphines. In contrast to their group 10 neighbors, found to show polarized M=C bonds featuring nucleophilic carbons,[613] these pincers were described as Fischer carbenes, hence assumed to be electron richer at the metal.[618,619] Consistently, $H_2$ additions were concluded to involve initial OA to Ir(I) followed by carbene migratory insertion into one of the resulting Ir−H bonds.[620] Calculations indicated that such a stepwise pathway is clearly favored over possible cooperative concerted alternatives. Also consistently, no examples are known for the addition of polar reagents across Ir=C bonds, although temporary H accommodation at the C atom was proposed to open up metal coordination vacancies during alcohol dehydrogenation catalyzed by the cyclohexane bis(phosphinito) derivatives [IrCl{$^{tBu}$P$^{O}$C(=)$^{O}$P}].[615] In fact, not only H but also methyl was observed to easily migrate between metal and C in these cyclohexane-based ligands, as illustrated in Scheme 53 by the interconversion between **144** and **145**.[621] The rich hydrogenation/dehydrogenation chemistry of these Ir pincers,[620,622-624] either bis(phosphino)-[625-629] or bis(phosphinito)-tethered,[615,630] was investigated in detail by Wendt and co-workers, who also tested catalytic dehydrogenation of cycloalkanes[630] and trimethylamine.[631] H atom exchange between Ir and PCP ligands was also observed for other aliphatic[632] and cycloheptatriene-based backbones.[633,634]

[insert Scheme 53 here]

**Scheme 53** Metal to C migrations in Ir PCP pincers.

Scheme 54 depicts $H_2$ addition to the 2,3-benzo[*b*]thiophene-linked carbene(bis)phosphine Ir complex **146** developed by Piers and co-workers, together with a characteristic reaction of this and closely related pincers: the formal hydrogenation of $NO_2$ to $N_2$ and $H_2O$. [635,636] Isolable species **147** and **148** were found to mediate this process. The former is represented as an Ir(III) iridaepoxide, whereas dihydride **148** is drawn in the alternative $\eta^2$-carbonyl mode to avoid formal oxidation state Ir(V). Detailed mechanistic studies indicated that overall hydrogenation also involves a (not shown) reactive isomer of **148** displaying O and H groups in mutually cis positions,[617] which favor initial OH formation at the carbon atom. Subsequent OH group migration to the metal followed by water RE would complete the regeneration of carbene precursor **146**.[637] This latter couple of elementary steps was deemed by Young and co-workers as potentially more suitable than double C−H activation[638] for the synthesis of carbene pincers of metals that perform poorly at this reaction.[639,640] The observation proved key to extend the Ir(I) pincer carbenoid chemistry to Rh(I)[639] and Co(I)[641] counterparts, using alcohol or ketone proligands instead of methylenes.

**Scheme 54** $H_2$ splitting and $N_2O$ hydrogenation at a carbenoid Ir pincer.

1,2-Addition of $H_2$ across a Rh=C bond was observed in just one case, and described as very slow at room temperature.[642] Yet, this bond seems to be more reactive than the Ir analogue in insertion chemistry. For example, the reactions of cationic square planar complexes $[M\{^{tBu}PC(=)P\}(CO)][B(Ar^F)_4]$ with excess CO just produced a 5-coordinate adduct for M = Ir, but a new square planar derivative containing a $\eta^2$-ketene moiety in the case of Rh.[643] The only Co system reported so far showed insertion trends similar to Rh, as illustrated by the selected reactions of Scheme 55, although additional easy access to Co(II) stable species was also observed and expected to widen reactivity scope.[641]

[insert Scheme 55 here]

**Scheme 55** Examples of reagent insertions into Rh and Co M=C pincers.

The above C=M-centered reactivity of alkylidene pincer arrays contrasts with the inertness of N-heterocyclic carbene relatives[17] based on imidazole,[644] benzimidazole,[645,646] or perimidine[647-649] central motifs. Rh and Ir PCP designs based on formally divalent carbon(0) moieties such as carbodicarbenes[650,651] or carbodiphosphoranes[652-656] were also described. The electronic description of such tetrylone (carbone) species strongly differs from that of the above tetrylene (carbene) analogues, since they are expected to show highly nucleophilic carbons.[657-659] Still, Rh pincers based on carbodicarbenes performed well as catalysts for diene hydroamination[650] and enantioselective hydroarylation.[651] In contrast, ligand-centered reactivity, often followed by fragmentation, was noticed for carbodiphosphorane Ir pincers.[653-656]

Recent work by Whited, Ozerov and co-workers described the preparation and characterization of cationic 5-coordinate Co(I) silylene pincer **149** (Scheme 56).[660] Related Rh[661,662] species were previously proposed along reactivity studies but never directly observed. **149** was found to exhibit a very electrophilic Si, which was readily attacked by bases such as triflate or pyridine (**150**) to form 5-coordinate Co(I) silyl PSiP pincers. Also, it added water or ethanol across the Co=Si bond to form 6-coordinate Co(III) derivatives such as **151**. The formation of this product was preceded by a kinetic isomer featuring the ethoxy group at Si and the hydride ligand oriented *syn* to one another. Reactions were proposed to involve initial coordination of ethanol to Si, followed by proton transfer to Co. This latter step was likely that driven isomerization too, although a pathway based on Si−H bond RE/OA was not discarded.[660]

[insert Scheme 56 here]

**Scheme 56** Reactions at a Co{$^{iPr}$PSi(=)P} silylene pincer. Anion is BAr$^{F20}$.

Further recent research around silyl PSiP pincers involved Co(I) derivatives closely related to those of Scheme 56, such as [Co{$^{Cy}$PSi(Me)P}(PMe$_3$)(N$_2$)], and the parent Co(II) [Co{$^{Cy}$PSi(Me)P}I], investigated by Turculet and co-workers in the context of H$_2$ or O$_2$ activation, respectively.[663] Derivatives [Co{$^{Cy}$PSi(Me)P}(PR$_3$)(N$_2$)] were also tested as N$_2$ fixation catalysts by Nishibayashi et al.[103,126] Driess et al. prepared new Co(II) pincers using SiNSi scaffolds consisting of central pyridines appended with N-heterocyclic silylenyl arms,[664] and tested them in catalytic arene borylation.[665] Cabeza et al. prepared Ge versions of the N-heterocyclic tetrylene and synthetized a new PGeP pincer ligand as well as derivatives with group 9 metals.[666,667]

Several products and intermediates in Schemes 53 and 54 display pincer ligands with $\eta^2$-coordinating motifs such as C=C or C=O. The design alternatives for these ligands and their typical reactions were recently reviewed by Moret and Verhoeven.[668] More recent work by these authors with the bis(phosphino)ketone ligand of Co pincer **152** (Fig 10) concluded that the C=O moiety is hemilabile and predominantly $\pi$-accepting. Accordingly, the ligand just coordinates $\kappa^2$-P to the high-spin dichloro Co(II) precursor of this complex, but tridentate $\kappa^2$-P:$\eta^2$(CO) to the electron richer Co(I) **152**, also high-spin and distorted tetrahedral.[669] Related conclusions were drawn for bis(phosphino)alkene ligands from the structural parameters of complexes **153**, **154** and related derivatives. $\kappa^2$-P:$\eta^2$ ligand coordination was found in the low-spin Co(I) [CoCl(P$\eta^2$P)] (**153**) and its CO adduct [CoCl(P$\eta^2$P)(CO)], as well as in the square planar Co(II) cation [CoCl(P$\eta^2$P)]$^+$, whereas the ligand was $\kappa^2$-P in the dichloro Co(II) precursor.[670] Complex **154**, bearing a pyrrol-connected bis(phosphino)alkene ligand, was formulated as a Co(II) metallacyclopropane.[117] Iglesias, Oro et al.,[671] reported a particular case of P$\eta^2$P ligand equipped with an N-heterocyclic olefin,[672] capable of coordinating metals either $\eta^2$ or $\kappa$-C through an ylide lone pair. This olefinic moiety was also recognized as hemilabile in Ir complexes, which were found to catalyze formic acid dehydrogenation[673] and hydrogen transfer reactions.[674]

[insert Fig 10 here]

**Fig 10** Structures of bis(phosphino)ketone or bis(phosphino)alkene Co pincers: **152** reported by Moret and Verhoeven,[669] CCDC code VIFWIT; **153** reported by Iluc et al.,[670] CCDC code QONFEG; **154** reported by Li et al.,**[117]** CCDC code YUCZED. H atoms are omitted for the sake of clarity.

Pincer architectures also allow positioning electron-deficient 3-coordinate boron residues in the proximity of metals. Such fragments may directly bind metals as electron-acceptor boranes (Z-type ligands)[675-677] to form the so-called metallaboratranes,[678] or may be cleaved at the metal to form (X-type) boryl ligands.[679] Often, functional group migrations between boron and metal centers are facile,[680] so that both ligand types may interconvert or adopt intermediate structures with the functional groups as bridges (vide infra).[681,682] In either case, Lewis acidic boron atoms may enable cooperative metal-ligand reactivity, now with an inverse organization of the Lewis pairs since metals, required to be electron-rich, act as bases.[539,683-685] An example of reversible (double) $H_2$ activation across a Co−B bond is shown in Scheme 57. The reaction was observed by Peters and co-workers[686] using a diazaboryl $^{tBu}$PBP ligand first reported by Nozaki and Yamashita.[687] This Co pincer system proved active in olefin and amino-borane (de)hydrogenation and transfer (de)hydrogenation catalysis.

[insert Scheme 57 here]

**Scheme 57** Double $H_2$ addition across a Co−B bond, and proposed formation of the coordinatively unsaturated hydrogenation/dehydrogenation catalyst.

The mechanisms of these catalytic reactions were analyzed computationally,[688] as also was the broader context of $H_2$ activation across these polarized bonds[689] and subsequent delivery of hydrides to substrates.[690] Along the pathway referred to as synergetic heterolytic activation, initial $H_2$ coordination occurs at metal, though the boron Lewis acid interacts with one of the H atoms in the H−H cleavage step to directly form a B−H−M bridge.[689] The bonding mode of the resulting hydrides emerged critical, since it conditions nucleophilicity and therefore subsequent reactivity. Computational studies confirmed strong differences in hydricity between H bridges connecting to ($sp^3$) boranes, such as those of **156** (3 center - 2 electron bridges) and those connecting to ($sp^2$) boryls, such as that in **157** (3c-4e).[689] Accordingly, calculations on hypothetical species **157**, thought to be the active hydrogenation catalyst,[688] indicated that incoming alkenes coordinate to Co and insert into the bridging H, while alkane elimination only occurs after scission of a new incoming $H_2$ molecule. Interestingly, formation of catalyst **157** from precursor **155** and just one molecule of $H_2$ was estimated impracticable via either associative or dissociative mechanisms, though the catalyst can readily form from **156** via $H_2$ loss. Also interestingly, the preference of a hypothetical 3-coordinate Co(PBP) fragment for high-spin configuration was found to favor the dissociative route between **155** and **156**, since the triplet energy surface "cuts through" the singlet barrier for $N_2$ decoordination.[688]

Scheme 58 depicts selected transformations observed by Ozerov and co-workers[691-693] using *o*-phenylene-bridged bis(phosphino)boranes first reported by Bourissou.[694] Reactions illustrate, first of all, that facile functional group migration does not restrict to H atoms, since phenyl can be transferred from B to Ir and back under very mild conditions. Actually, group redistribution is so easy that allowed unusual comproportionation reactions such as that of **159** and **160** to form **161**, which completed in 1h at room temperature.[692] The X-ray structures obtained for 5-coordinate Ir(III) boryl derivatives such as **158**, its Rh version, or analogues coordinating hydride instead of phenyl, evidenced the strong trans influence of the boryl moiety, which is able to open coordination positions cis to other strong trans-directing ligands such as hydrides.[691] This property of boryl pincers is shared with other scaffolds that bind through $sp^3$ C or Si atoms.[13]

[insert Scheme 58 here]

**Scheme 58** Selected reactions of [Ir($^{iPr}$PBP)] pincers with *o*-phenylene-based skeletons.

Scheme 58 further illustrates the use of the pincer platform to anchor and orientate reagents prior to their activation at metals. Pyridine coordination to B directed the Ir center to cleave a different C−H bond than in the cases of directing donor coordination to the metal. An example for subsequent C−C bond formation at **162** was given to prove viability of this strategy for *ortho*-regiospecific functionalization of pyridines.[693] O−H, S−H and N−H bond splitting reactions were also observed for the paramagnetic Co(0) derivative [Co{$^{iPr}$P$\eta^2$(BC)P}($N_2$)] (**35**),[131] already mentioned in the first section (in Fig. 7) because of its low oxidation state. N−H activations potentially leading to bidentate $\kappa^2$-N or $\kappa$-N,C ligands such as 8-amidoquinoline or benzo[h]quinolin-10-yl, respectively, formed Co(II) products featuring B−H−Co bridges. In contrast, O−H and S−H activations of phenol or thiophenol just provoked one-electron transformations to give Co(I) high-spin phenolate (X = O) or phenylthiolate (X = S) derivatives [Co{$^{iPr}$PB(Ph)P}(XR)], accompanied by the release of $H_2$.

Aside from the PBP designs shown in Schemes 57 and 58, $P^OB^OP$ and other related ligands based on carborane central motifs,[695] pioneered by Mirkin and co-workers,[696] were applied to group 9 metals. The reader is referred to recent reviews covering boron-based pincers for further examples and catalytic applications.[697-702] It should be mentioned, nevertheless, that a very significant piece of related chemistry was developed by the groups of Hill[703] and Owen,[704] who were also the pioneers of metallaboratranes.[705] Such chemistry was based on a variety of B-based ligand designs commonly and collectively referred to as scorpionates,[680] since as tridentate ligands they coordinate very predominantly in the *fac* mode.[706]

Finally, examples of pincer architectures displaying Lewis acids other than B are depicted in Fig. 11. Common to all ligand designs in the figure, the acidic metal is caged in a polydentate environment, a pincer itself in the Al examples. Coordination around Rh of the dicationic Zn scaffold is rather orthodox for a *mer* ligand. Z-type coordination of Zn was inferred from the significant increase of the CO stretching wavenumbers relative to related Rh(I) derivatives, and calculations confirmed donor/acceptor interactions between an occupied $dz^2$ orbital of Rh and unoccupied s and p orbitals of Zn.[707] The neutral PAlP pincer ligand of the chloro-bridged dimer **164** was also formulated as Z-type Al(III) species, as may be inferred from the lack of pyramidalization[708] at the square-planar $d^8$ Rh(I) center. Upon reduction to **165**, however, the ligand transformed into an anionic X-type Al(I) pincer, that occupies an axial (Al) and two equatorial sites of the trigonal bipyramid around Rh(I).[709]

[insert Fig 11 here]

**Fig. 11** Pincer architectures featuring Zn and Al Lewis acidic donor sites, reported by Tauchert and co-workers[707] ([**163**][$N\{OS(O)_2CF_3\}_2]_2$ CCDC code BIMMAO) and Sasaki, Nakao et al.[709] (**164** CCDC code BICDEZ, **165** CCDC code BICDAV). Hydrogen atoms omitted for the sake of clarity.

## 4. CONCLUDING REMARKS

The immediate conclusion that comes out from a brief inspection of the above chemistry is about the relative contribution of Co to the organometallic chemistry of group 9, which has undergone a spectacular growth: a fact likely extensible to base metals in general when compared to their noble counterparts. Still, the type of studies addressed with each metal remains quite different. While current Co chemistry is most often exploratory, which accounts for the many recent catalytic results, that of Rh and Ir, at least that consigned here, is frequently mechanistic-oriented. Actually, it could be said that most of what we have learned about the functioning of non-spectator pincer ligands comes from experimentation with the noble metals, although it is to be implemented in the base one. Consequently, this chapter was organized to first emphasize the fickle chemistry of Co to then showcase the tools offered by ligands to tame the metal.

If the goal is to imitate noble metals through Co two-electron transformations, a clear option is to maximize ligand field, which only requires “traditional” electronic tuning of donor atoms and their substituents. A second option is to synchronize metal and ligand one-electron events: a strategy proven feasible but still far from being predictable, hence practical, in particular for the high electron counts of Co. Yet, the main message of previous pages is that metal two-electron cycling is not the only way to drive catalytic transformations, since ligands can be equipped with an arsenal of gadgets to assist alternative bond cleavage/formation routes. Electron lone pairs facilitating ligand-assisted bond activations can be placed at virtually any desired distance and orientation relative to the metal. Moreover, protonation of such lone pairs provides H-bonding sites to anchor reagents within the reach of metals and their ligands, in order to promote both inner- and outer-sphere subsequent reactions.

Less evident from the chemistry consigned above is the distinctive role, if any, of *mer* coordination. The planar ligand skeletons required to achieve extended $\pi$-orbitals in redox-active architectures, the face discrimination implicit in some $CO_2$ insertions, or the hemilabile pincer assistance to certain $S_N2$ OAs, seem to harness *mer* coordination in particular cases, but genuine correlations between *mer* binding and reactivity advantages beyond stability remain to be precisely defined.

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