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Cooperative Catalysis

Neutral Tridentate PNP Ligands and Their Hybrid Analogues: Versatile Non-Innocent Scaffolds for Homogeneous Catalysis

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C–H activation · cooperative catalysis · N,P ligands · tridentate ligands · homogeneous catalysis

Ligands in coordination chemistry and homogeneous catalysis are traditionally "static" spectators that do not actively participate in the catalytic cycle. However, such classic systems do not provide additional "handles" that could facilitate or trigger alternative productive reaction pathways. Recent advances in the use of novel nitrogen-centered pincer systems have unveiled interesting opportunities for cooperative catalysis. The chemistry of pyridine-derived, neutral ligands is discussed, with a specific focus on their non-innocent behavior and potential as facilitators for metal-mediated organic transformations. This overview should provide inspiration and an incentive to incorporate non-innocent ligands and their metal complexes within old and new homogeneously catalyzed reactions.

1. Introduction

Cooperative catalysis, which involves 'participating ligand fragments', is a ubiquitous concept in the chemistry of biological systems.[1] This principle covers many seemingly unrelated types of functionalities wherein the protein scaffold or cofactors around the active site actively facilitate substrate turnover. The mode of action of, for example, the enzyme galactose oxidase[2] and the hydrogenases[3] are most likely based (in part) on cooperative effects induced by the ligand sphere around the metal active site.

In contrast to the (bioinspired) application of multimetallic cooperative systems for selective transformations, the design and utilization of cooperative ligand systems for applications in synthetic (inorganic) chemistry and metal-mediated homogeneous catalysis is still in its infancy. It is only relatively recently that the targeted design of adaptive, cooperative ligand frameworks has been recognized as a promising way to approach synthetic problems related to the selective conversion of substrates and the uncovering of new reactivity and previously unknown transformations. Ligand-assisted reactivity is particularly attractive for hydrogenation-related catalysis, which involves heterolytic H_2 activation as a key step in the overall processes. These assemblies operate through an intramolecular acid or base functionality located in the ligand framework, akin to the hydrogenase active site.[4] For example, much attention has been paid to redox-active ligands, which are based on units such as quinones, dithiolenes, or α-diimines.[4] Ligand–metal assemblies are even more timely and are extremely useful in catalytic applications. Most of these cooperative catalytic systems incorporate reversible alcohol–ketone[5] or reversible amine–amide functionalities.[6] Impressive activities and mechanistic insights have been obtained for a number of these bioinspired molecular systems and for various types of substrates, including examples that deal with self-complementary monophosphorus ligands.[7,8] These developments in turn allow a wider range of activity than that traditionally provided by metal-based catalysis alone.

For many applications, in particular those that concern late-transition-metal systems, phosphorus-based ligands have made a huge impact on the progress of homogeneous catalysis. Besides the well-known examples of bidentate diphosphorus frameworks, tridentate scaffolds that lead to selective coordination around a metal center stand out as a particularly useful class of ligands. Several hybrid systems that combine different heteroatom donor groups are available.

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Among the plethora of bulky phosphorus-containing tridentate 'pincer ligand' systems applied in coordination and organometallic chemistry during the last decades,[9] many are based on formally monoanionic scaffolds.[10] The robustness, activity, and variability, of these pincer-type ligands and their metal complexes means that they are attracting increasing interest in catalysis, the development of molecular devices, and soft matter.[11] Typical examples include frameworks **1–5** (Figure 1).[12–21] Reviews on recent developments of these innocent monoanionic tridentate ligand systems, in particular those that carry a central amido functionality, are available.[10,22]

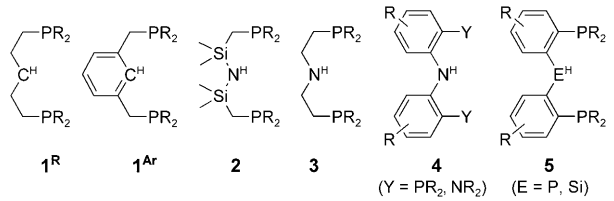

Figure 1. Generalized structures of representative monoanionic pincer ligand scaffolds **1–5** generated after formal deprotonation of the central unit.

Formally neutral tridentate ligand systems have seen a surge in recent decades. These ligands offer complementary chemistry to their monoanionic derivatives, for example, when focusing on low-valent metal centers (e.g., Rh^{I} or Ir^{I}) or if coordinatively unsaturated dicationic complexes (such as Pt^{II}) are targeted. These ligands range from the ubiquitous 2,2′,6′,2″-terpyridine[23] (tpy, **6** in Figure 2) to bis(imino)pyridine systems **7**, studied for late-transition-metal alkene polymerizations,[24] and related pyridine-based scaffolds such as **8**[25] and **9**.[26] Other neutral tridentate frameworks, including structures **10**[27] and **11**,[28] have also recently been developed, but little emphasis has so far been placed on catalytic applicability of these systems.

However, none of the aforementioned neutral ligand types display any significant cooperative character during catalytic turnover, with the exception of **6** and **7**, which have been demonstrated to exhibit extensive redox noninnocence. Furthermore, phosphorus-based fragments offer unique properties for synthetic modularity, electronic control, and steric tuning of the ligand characteristics.

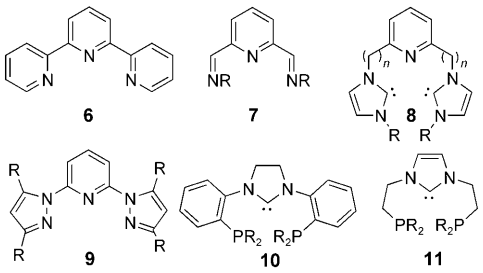

Figure 2. Non-exhaustive overview of common and newly developed neutral tridentate ligand scaffolds **6–11**.

Recently, a specific class of aromatic, neutral tridentate ligands based on lutidine, and close analogues thereof, has been developed.[29,30] One special feature of these 2,6-lutidine-derived systems is their ease of deprotonation of the methylene spacer group, which effectively renders this ligand class "non-innocent".[31] The aim of this Minireview is to give a tantalizing overview of the interesting and useful chemistry available with this type of ligands, with a particular emphasis on the non-innocent (cooperative) ligand reactivity and (potential) applications in catalysis. The mode of action and type of reactions accessible with this kind of ligand–metal cooperative reactivity differs significantly from that observed in previously studied acid–base switching systems.[5,6] We will first introduce the various skeletons available for this type of neutral, tridentate ligands that have a central nitrogen atom. Thereafter, the most significant developments with Group 7–10 transition metals will be described.

2. Synthesis

2.1. Pyridine-Based Diphosphines

Three synthetic routes have been used for the straightforward synthesis of tridentate ligands with a central pyridyl fragment. Direct nucleophilic substitution of 2,6-bis(chloromethyl)pyridine by sodium diphenylphosphide led to the

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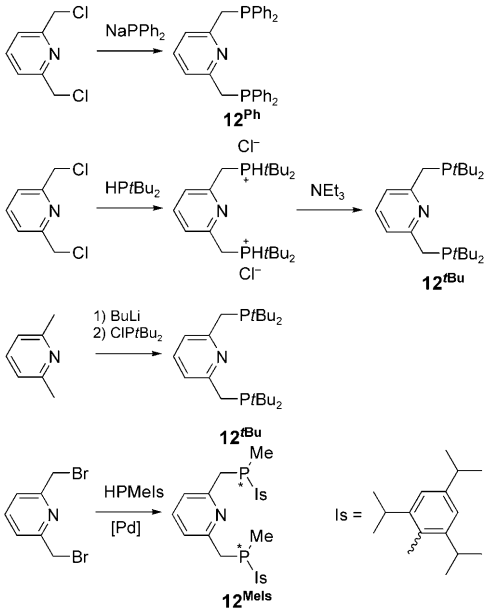
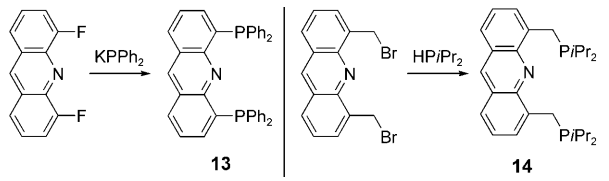


Scheme 1. Formation of PNP ligands $\mathbf{12^R}$ from readily available starting materials.

corresponding PNP^{Ph} ($\mathbf{12^{Ph}}$, Scheme 1) as the first derivative of this class of ligands.[29] Addition of a secondary phosphine to 2,6-bis(chloromethyl)pyridine followed by selective deprotonation using triethylamine was described specifically for the *tert*-butyl analogue $\mathbf{12^{tBu}}$ by Milstein and co-workers, but this method is more general and circumvents potential issues with unstable phosphide intermediates.[32] Rieger and co-workers described the phenyl-, tolyl-, and mesityl-substituted PNP^{Ar} ligands by following the same procedure.[33] Kawatsure and Hartwig reported the selective lithiation of 2,6-lutidine (2,6-dimethylpyridine) and subsequent reaction of the lithiated species with chlorophosphine reagents, which again showcases the *tert*-butyl analogue $\mathbf{12^{tBu}}$.[34] The yield for this latter reaction tends to be slightly lower than for the two-step addition using secondary phosphines, but the reagents are more readily accessible and less expensive. Scriban and Glueck recently reported a platinum-catalyzed asymmetric phosphination of 2,6-bis(bromomethyl)pyridine with PHMeIs (Is = 2,4,6-tris(isopropyl)phenyl) to generate the corresponding P-stereogenic diphosphine $\mathbf{12M^{eIs}}$ in up to 72% *ee*.[35] To date, no application of these chiral PNP derivatives to coordination chemistry or stoichiometric/catalytic reactivity studies has been reported.

In a cumbersome overall four-step synthesis (only the last step is displayed), Haenel and co-workers prepared the acridine-based ligand **13** (from 2-amino-3-fluorobenzoic acid and 2-fluoridobenzene). This ligand features a highly rigid

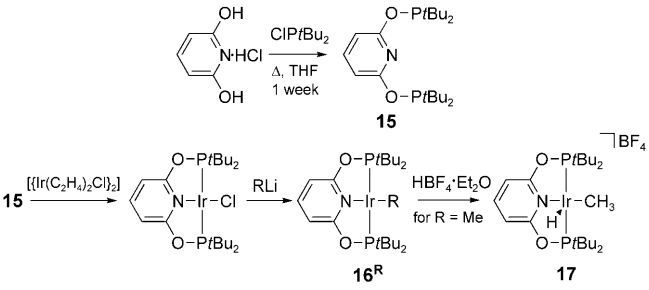


Scheme 2. Synthesis of acridine-related PNP ligands **13** and **14**.

tridentate PNP pocket that lacks the folding or twisting motion commonly observed with PNP^R-derived complexes.[36] Gunanathan and Milstein recently reported the synthesis of the structurally related but more flexible ligand **14** (Scheme 2). This ligand was prepared from 4,5-bis(bromomethyl)acridine, which is available in one step from acridine and bromomethyl methyl ether, by reaction with the secondary phosphine $HPiPr_2$ in good yield.[37]

2.2. Other Pyridine-Based Phosphorus Ligands

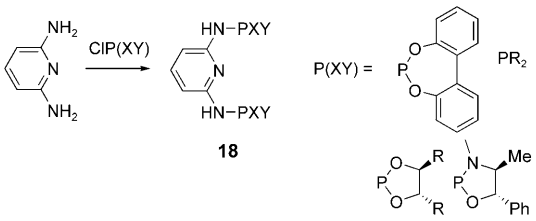
In addition to CH_2 spacers that separate the central pyridine functionality and the peripheral donor (e.g., phosphine) groups, other linkers have also been explored. The pyridine analogue **15** of Brookhart's $POCOP^R$ ligand,[38] which features two phosphinite groups and is derived from the corresponding HCl salt of the dialcohol, has only very recently been synthesized by the same research group.[39] To date, only the *tert*-butyl substituted analogue has been described. The corresponding Ir^ICl complex was readily converted into the methyl- or phenyl derivative $\mathbf{16^R}$. Surprisingly, $\mathbf{16^{Me}}$ underwent smooth and clean protonation with strong acid to furnish the rare five-coordinate cationic Ir^{III} alkylhydrido species **17** (Scheme 3).



Scheme 3. Synthesis of PONOP ligand **15** and the rare cationic Ir^{III} alkylhydrido complex **17**.

The pyridine-derived bis(dipyrrolylphosphine) analogue of Milstein's π-accepting PCP^{Pyrr} compound[40] remains unknown. This is unfortunate, since the latter by itself is a nonclassical pincer-type diphosphine ligand, as the highly electron-poor P atoms induce a strikingly different reactivity. The introduction of heteroatoms into the skeleton of the PNP system has also been explored by Kirchner and co-workers, who prepared the tridentate ligand class **18**,[41] which is derived from 2,6-diaminopyridine The NH spacers allow a wide range of phosphorus-based substituents, including diols and aminoalcohols, which provide a modular approach to vary the electronic character of the tridentate ligand backbone (Scheme 4).

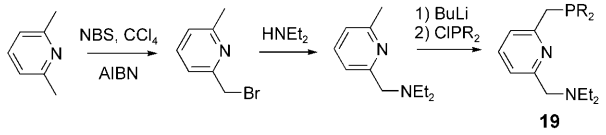
There are several examples of lutidine-based ligand scaffolds with less common phosphorus-based side groups such as phosphaalkenes, phospholes, and phosphinines, which allow access to widely different electronic characters of the PNP ligands. We will not discuss these in detail here and refer the reader to the appropriate references.[42–45] Furthermore,



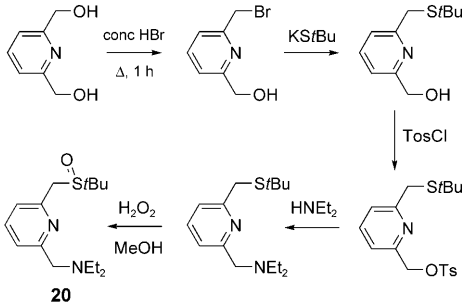
Scheme 4. Neutral PNP ligand class **18**, which is derived from 2,6-diaminopyridine and has more versatility for the facile introduction of (chiral) phosphorus side groups, including the formation of bis(phosphoramidito)pyridines.

the oxides, sulfides, and phosphoranimines of ligand structure $\mathbf{12^R}$ have found some application, but these are considered to be outside the scope of this Minireview.[46] Ligands that feature a direct bond between the pyridine ring and the phosphorus unit are related to the phosphoranimines; these ligands are then modified as the oxo, sulfido, or imido analogues for tridentate chelation.[47]

Some hybrid or mixed ligand systems based on the lutidine skeleton have also been designed, notably scaffolds **19** and **20**, which both contain a diethylamine side group. Compound **19** still contains one PR_2 sidearm donor (Scheme 5),[31] while this group has been replaced by a less (oxygen)-sensitive *tert*-butylsulfoxide unit in **20** (Scheme 6).[48]



Scheme 5. Synthesis of hybrid, non-innocent ligand skeleton **19**.



Scheme 6. Synthetic route to lutidine-derived mixed ligand **20**, featuring *tert*-butylsulfoxide and diethylamine side groups.

The synthesis of these lutidine-based mixed-donor systems is slightly more elaborate than the corresponding symmetric (diphosphine) derivatives, especially for the latter species. In fact, compound **20** is prepared from 2,6-bis(hydroxymethyl)pyridine in a five-step synthesis that involves monobromination with HBr, followed by reaction with KS*t*Bu to give the thioether functionality (Scheme 6). Tosylation of the remaining hydroxy group allows the introduction of the diethylamine group. Lastly, the thioether is selectively oxidized with H_2O_2 to give the final product.

In complexes with ligand **20**, the methylene spacer near the sulfoxide group is easily and selectively deprotonated with one equivalent of base to result in a highly delocalized anionic charge, which renders the ligand relatively insusceptible to reprotonation. From preliminary coordination chemistry investigations, it was concluded that the ligand is a weaker σ donor than the corresponding PNP analogue. IR spectroscopy and X-ray crystallography confirmed that coordination of the sulfoxide group takes place solely through the sulfur atom.

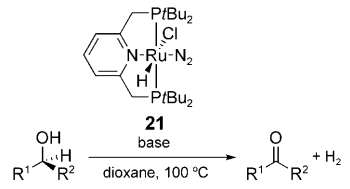
3. Ruthenium

3.1. Cooperative Catalysis

The facile deprotonation of the PNP backbone at one of the methylene spacers, concomitant with the dearomatization of the pyridine ring, is becoming more important for the preparation of dedicated cooperative catalysts. Similar chemistry is not available for the structurally related PCP ligands because the benzene ring is less easily dearomatized.[49] This non-innocent, charge-switching character of the PNP scaffold has long been overlooked or underappreciated as a possible tool for cooperative catalysis.[50] In fact, it was recognized only a few years ago as a potential blessing rather than an inconvenient side effect of this particular ligand type.

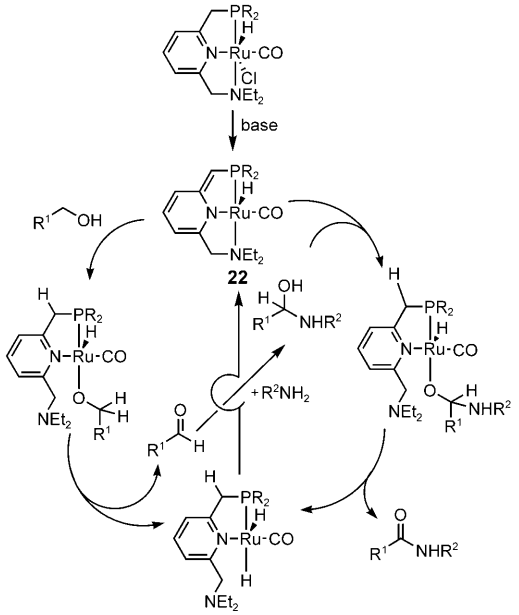
Early studies on the application of complexes with non-innocent ligand $\mathbf{12^{tBu}}$ focused on ruthenium-catalyzed acceptorless dehydrogenation of alcohols to ketones with complex **21** (Scheme 7).[51] At that time, no clear mention was made of the possible involvement of a complex that featured the dearomatized structure of the ligand backbone **12** during catalysis. The molecular structure for a Ru complex with the dearomatized analogue of $\mathbf{12^{iPr}}$ was determined recently.[52]

Subsequent research mainly focused on the mixed PNN ligand **19** for a number of unprecedented reactions that specifically utilize the facile dearomatization–reprotonation sequence exhibited by this scaffold. The hemilabile[53] coordination of the amine functionality also proved an essential feature for successful applications. The diethylamine fragment is proposed to act as a hemilabile switch, which creates a vacant site that allows for productive turnover at the Ru center. The first application of dearomatization–reprotonation was the highly efficient ruthenium-based system **22** for the acceptorless dehydrogenation of alcohols, wherein the combined metal and dearomatized ligand act in a cooperative manner to convert, for example, primary alcohols to esters[31] or secondary alcohols to ketones, with the concomitant



Scheme 7. Acceptorless dehydrogenation of alcohols with non-dearomatized complex **21**.

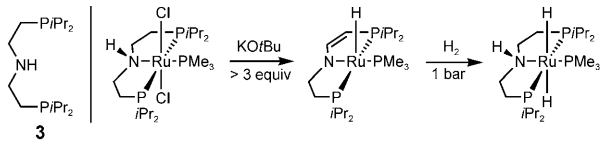
extrusion of H_2.[54] The reverse reaction, that is, the catalytic hydrogenation of non-activated esters to alcohols was also discussed.[52] Most notable was the recent finding that the straightforward coupling of alcohols and amines to form amides, with extrusion of H_2, could also be effectively catalyzed by Ru complex **22**.[55] The proposed catalytic cycle is depicted in Scheme 8.



Scheme 8. Proposed catalytic cycle for the direct dehydrogenative coupling of alcohols and amines utilizing the facile dearomatization–reprotonation chemistry displayed by complex **22**.

It is essential that the hemiaminal remains coordinated to the Ru^{II} center, followed by a dehydrogenation to yield the amide, as this mechanism prevents unwanted dehydration of the same intermediate to give the corresponding imine compound (or after subsequent hydrogenation the secondary amine product). Use of the "'parent" PNP^{tBu} ligand instead of the flexidentate PNN derivative resulted in a dramatic reduction of activity. The alcohol group was observed to be coordinated, which was mediated by dissociation of one of the phosphine units, but recoordination of this strong donor is too fast to allow efficient catalysis. Similar observations were made previously for the dehydrogenation of alcohols to form esters.[31]

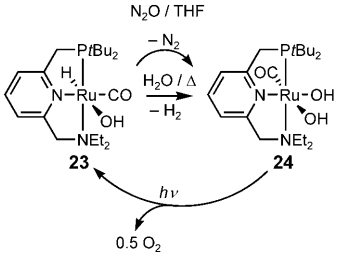
Recently, Schneider and co-workers reported a similar feature for the monoanionic derivative (under strongly basic conditions) of the aliphatic PNP ligand **3**, in which additional equivalents of base could lead to an unsaturation in the ligand backbone (Scheme 9).[56] This led to cooperative behavior in



Scheme 9. Cooperative behavior of aliphatic PNP backbone **3** with certain Ru complexes.

the ruthenium-catalyzed dehydrogenation of ammonia–borane with high activity and at low catalyst loading.

Milstein and co-workers recently reported that, in a similar manner to aliphatic alcohols, water also could be activated using the Ru complex **22**.[57] It was shown that reaction of **22** with water (or isotopically labeled derivatives thereof) led to reprotonation of the PNP backbone, concomitant with formation of the Ru complex **23** in good yield (Scheme 10). This research and the resulting activity of this

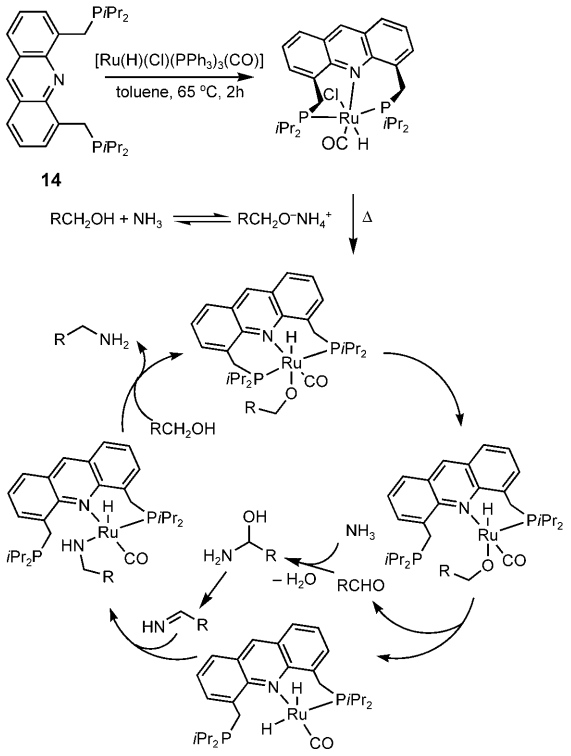


Scheme 10. Activation of water or oxygen-atom transfer using complex **23** and subsequent photolysis of bis(hydroxo)ruthenium complex **24** to generate O_2.

system toward water splitting through the intermediacy of complex **24** has been recently highlighted, and will therefore not be discussed here.[58] However, in contrast to the other studies in which complex **22** was used, no mention was made of the need for this flexidentate ligand with respect to the water-splitting reaction. This poses the question whether other non-innocent meridional systems, including $\mathbf{12^R}$ or **20**, could also facilitate similar very interesting and potentially useful reactivity.

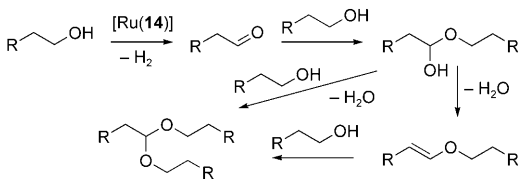
The newly developed ligand **14** was recently employed for the direct conversion of alcohols to amines (Scheme 11).[59] Drawbacks of the current process, in which NH_3 could be used as a substrate, are the high temperature necessary (up to 135 °C), long reaction times, and moderate selectivity for the primary amine (for aliphatic alcohols). The originally proposed catalytic mechanism (Scheme 11) is similar to the dehydrogenative coupling of alcohols and amines, but with two distinct differences. No hemilabile amine side-arm functionality is available and there is no lutidine scaffold present to allow for the same facile dearomatization mechanism, as observed with ligand $\mathbf{12^{tBu}}$. The observed selectivity towards the primary amine probably relates (in part) to the use of a diphosphine-based ligand, which most likely shows significantly reduced hemilabile character and enables the dehydration of the intermediate hemiaminal to give the imine compound that is subsequently hydrogenated. It was originally hypothesized that one phosphine arm would dissociate from the Ru center to leave an open coordination site. However, a non-anticipated non-innocent role of the acridine backbone, which is known to be susceptible to nucleophilic addition reactions, can not be excluded on the basis of these results.

The direct dehydrogenative coupling of alcohols to form acetals (under neutral conditions) or esters (at pH > 7) was subsequently reported for the [Ru(**14**)(H)(CO)(Cl)] system



Scheme 11. Originally proposed mechansim—with hemilabile coordination of a phosphorus donor functionality—for the ruthenium-catalyzed formation of primary amines from alcohols and ammonia, using acridine-based PNP ligand **14**.[59]

(Scheme 12),[60] which is in striking contrast with the inactivity of complex **22** in the same reaction. Although no unequivocal evidence has been presented to date, it was speculated that ligand **14**, in particular the acridine framework, could display cooperative behavior during catalysis. The acridine N atom could act as a hemilabile donor (the Ru–N bond length is larger than that in the related complex **21**), thereby also facilitating the intramolecular nucleophilic addition (or transfer) of a proton from the metal site to the 9 position of the acridine fragment. Preliminary DFT modeling studies have shown that this 9 position is spatially well-positioned over the Ru center, so this that process can easily occur. This arrangement would, in effect, lead to a dearomatization of the acridine ring system,[36] thereby providing a new type of non-innocent, cooperative ligand scaffold. Alternatively, the acridine N atom could act as an internal base. Such a favorable interaction would be facilitated by a large dihedral angle of approximately 168° between the P–Ru–P plane and the Ru–*N*-acridine plane; this angle leads to a highly bent



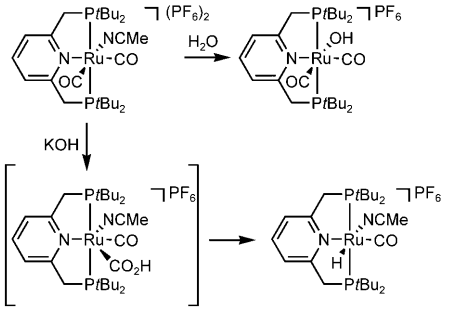
Scheme 12. Catalytic formation of acetals by dehydrogenative coupling of alcohols with [Ru(**14**)].

structure. The Ru–N bond, which is long compared to that found in **22**, is an indication for weak binding of the acridine fragment. ^{1}H NMR spectroscopic investigations showed that the subsequently dearomatized structure also existed in solution, but more definitive experiments are required to substantiate this potentially novel example of a cooperative ligand effect.

3.2. Other Chemistry with Ruthenium

Van Koten and co-workers showed that the dehydrative coupling of functionalized diols with anilines gave the corresponding *N*-(ω-hydroxyalkyl)anilines and arylpiperazines in moderate yield when ligand **12^{Ph}** was used.[61] This result can be related to the recent reactivity observed by Milstein and co-workers for analogous Ru complexes.[55]

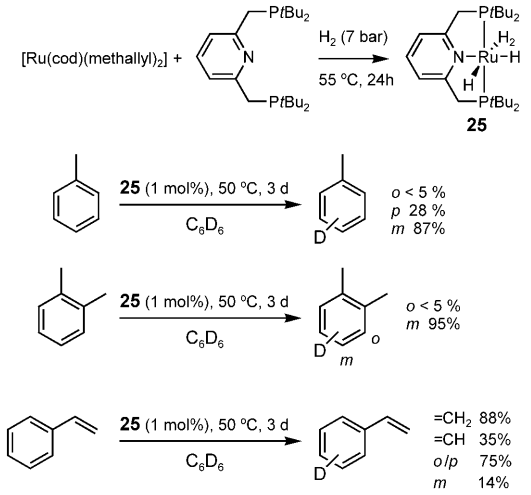
Gibson et al. independently reported the formation of some Ru complexes with **12^{tBu}** in 2004 (Scheme 13),[62] simultaneously with the first application of this catalyst



Scheme 13. Reactivity of a Ru complex of **12^{tBu}** toward H_2O and KOH.

system for the acceptorless dehydrogenation of alcohols by Milstein and co-workers.[51] In the former report, a Ru–OH species that arose from facile deprotonation of an elusive intermediate aquo complex was also discussed, as well as some other interesting compounds. No mention was made of the potential involvement of the PNP backbone during these reactions. It appears worthwhile to revisit this chemistry in light of the recently established reactivity of related Ru complexes with water.

Leitner and co-workers have discussed the synthesis of the nonclassical hydride complex **25** from a Ru precursor and **12^{tBu}**, and its potential use in H–D exchange reactions (Scheme 14).[63] Reversible exchange of the H_2 ligand for N_2 was observed and was subsequently used as a starting point for a theoretical investigation into the applicability of **25** as a catalyst for N_2 reduction.[64] More notably, rapid H–D exchange was noted when complex **25** was treated with [D_8]toluene, with a high preference for exchange at the sp^2 carbon atoms. Initial deuteration occurred at the *para*-CH as well as the CH_2 spacer groups, with subsequent additional scrambling into the hydride and *tert*-butyl fragments. Similar observations were made when D_2 was applied during the synthesis of **25**. Therefore it was concluded that the selective formation of [D_4]-**25** is not feasible, as it leads to subsequent



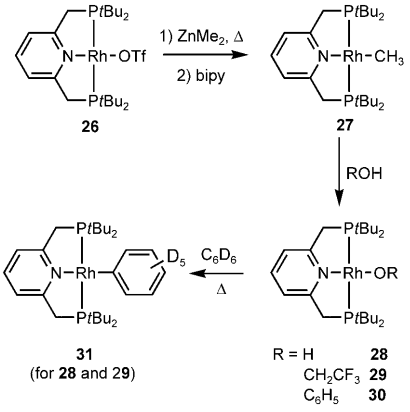
Scheme 14. Formation of Ru complex **25** with a nonclassical hydride and ligand **12^{tBu}**, and subsequent catalytic H–D exchange reactions with toluene, *o*-xylene, and styrene.

H–D scrambling with H atoms in the ligand backbone.[65] The results from DFT calculations suggested σ-bond metathesis as a key step in the exchange mechanism, with a large directing effect from the steric hindrance inferred by the ligand sidearm groups.

4. Group 8 Metals

4.1. Rhodium

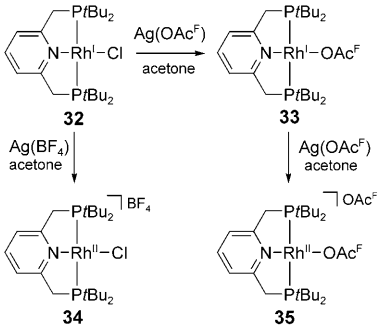
Goldberg's research group recently discussed the synthesis and reactivity of rare Rh(PNP^{tBu}) hydroxide and alkoxide complexes **28**–**30**.[66] To avoid the facile deprotonation–dearomatization of the PNP methylene group, which was observed after the addition of MeLi to the cationic dinitrogen adduct [Rh(PNP^{tBu})(N$_2$)](OTf), an elaborate synthetic route was devised, which started from the triflate adduct **26** and proceeded via the methyl complex **27** as an intermediate species (Scheme 15).



Scheme 15. Formation of the Rh^{I} methyl complex **27** with **12^{tBu}** and subsequent reactivity with water to give species **28**. The phenoxo species **30** catalyzes the H–D exchange between D_2O and benzene.

Reaction of either complex **27** with wet C_6D_6 or of the isolated complexes **28** and **29** with C_6D_6 led to formation of the phenylene complex **31** (albeit not cleanly). The phenoxide derivative **30** proved stable against exchange with benzene, even for extended periods of time at elevated temperatures. However, this latter complex was shown to be an effective catalyst for the H–D exchange between D_2O and benzene. The methylene spacers in the ligand backbone were found to interact in an unspecified way, as deuteration experiments revealed incorporation of D atoms in these positions. Further investigations revealed that the C–H bond activation mechanism is accelerated by the addition of phenol and that the mechanism differs from that of reported Ru^{II} or Ir^{III} systems, as it is concluded (from kinetic studies) to proceed by dissociation of the phenoxide ligand.[67] The related acetate complex also showed the same catalytic activity.

Amidst the elegant work carried out on Rh^{I} species with lutidine-derived PNP^{R} systems, the recent finding by Milstein and co-workers concerning the facile formation of analogous (rare) mononuclear Rh^{II} complexes is of interest.[68] Depending on the counterion of the Ag salt, either direct oxidation of the ubiquitous complex [RhCl(**12^{tBu}**)] (**32**) to complex **34**, or a two-step reaction to Rh^{I} derivative **33** and subsequent oxidation to **35** is observed (Scheme 16). The square planar,



Scheme 16. Oxidation of defined Rh^{I} complexes **32** with ligand **12^{tBu}** to the corresponding Rh^{II} derivatives. OAc^{F} = OC(O)CF$_3$.

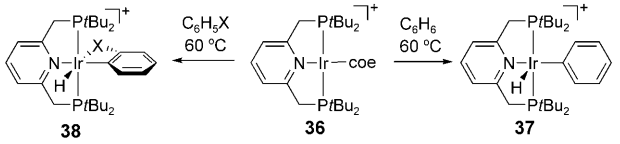
paramagnetic mononuclear Rh^{II} species **34** showed subtle but significant alterations in, for example, the Rh–P and Rh–Cl bond lengths, which are attributable to the change in the metal oxidation state. Furthermore, a pronounced effect of the phosphine side groups was noted, as analogous PNP^{iPr}-based Rh^{I} species yielded mixtures of diamagnetic compounds, which was explained by the lower steric shielding of the Rh center. Compounds **34** and **35** did not react with O_2, H_2, or ethylene, but NO cleanly added to these fragments to give a Rh^{III} complex featuring a bent NO ligand.

To date, no explicit use has been made of the non-innocent character of ligand scaffold **12^{R}** in rhodium-centered chemistry. This may in part be due to the relatively large steric crowding that this ligand imposes on the Rh center.

4.2. Iridium

The Ir^{I} complex **36**, which bears ligand **12^{tBu}**, was shown to readily activate C–H bonds of benzene in a stoichiometric

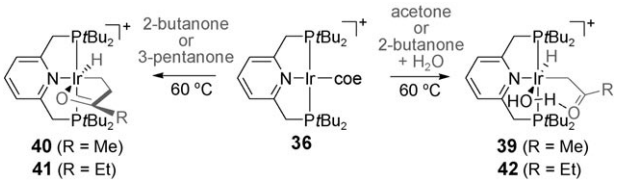
fashion to produce the rare square-pyramidal Ir^{III} analogue **37**.[69] Moreover, the first selective *ortho*-C–H activation of haloarenes using the same precursor was reported (Scheme 17). While no regioselectivity was observed for



Scheme 17. *ortho* C–H activation of halobenzenes using Ir^{I} complex **36** with ligand $\mathbf{12^{Ph}}$. coe = cyclooctene.

fluorobenzene, selectivities of around 4:2:1 for *ortho*/*meta*/*para* chloro- and bromobenzene were observed during reaction in the neat halobenzene at 50 °C. After complete consumption of **36** and raising the temperature to 60 °C, **38** (X = Cl, Br) was formed, which indicated reversible oxidative addition for the *meta*- and *para*-activated species and a directing role of the halogen atom.

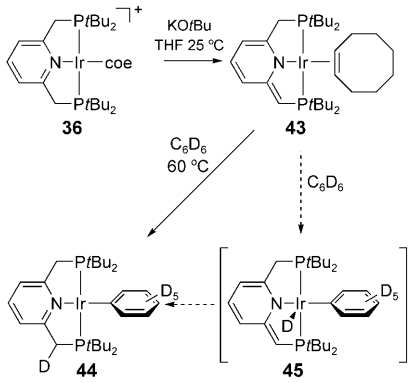
The same Ir complex **36** was later shown to also induce selectivity for the activation of sp^3 C–H bonds of ketones.[70] Water plays an important role in this reaction: when absent, selective activation of a β-C–H bond was observed for 2-butanone and led to the formation of the five-membered iridacyclic complex **40**, with the C=O group also coordinated to the Ir^{III} center (Scheme 18). Use of 3-pentanone resulted in



Scheme 18. Selective β-C–H activation of sp^3 C–H bonds of aliphatic ketones with complex **36**.

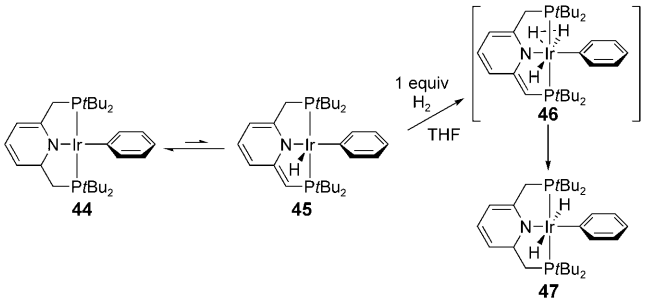
the analogous complex **41**. However, the presence of water led to a drop in regioselectivity and to the activation of the terminal α-C–H bond in around 40% yield, with complex **40** as the remaining product. This result was explained and verified by spectroscopic data and DFT analysis, which confirmed the existence of a hydrogen-bonding interaction that occurs between the carbonyl functionality and an aquo ligand in complex **42** to form a six-membered ring with an Ir^{III} center. A similar activation and coordination was observed for acetone (Scheme 18). It was demonstrated that the formation of species **42** is reversible, since the application of a vacuum and redissolution of the resulting solid product in dry CH_2Cl_2 resulted in full conversion of the **40**/**42** mixture to complex **40**. The specific role of the facile deprotonation of the ligand backbone was not further elucidated for these particular stoichiometric transformations.

Subsequent research with complex **36** focused on the non-innocent character of the PNP backbone of ligand $\mathbf{12^{tBu}}$ when it is coordinated to a metal center.[71] As such, this feature proved instrumental to facilitate the C–H activation of benzene by the deprotonated Ir^{I} complex **43**, which selectively led to the neutral four-coordinated Ir^{I} complex **44**. The possible intermediate Ir^{III} species **45** initially formed after a metal-centered oxidative addition of benzene (Scheme 19) was not detected.



Scheme 19. C–H activation of benzene with non-innocent complex **43**. The dashed arrows indicate a potential reaction pathway, although the intermediate **45** was not detected.

To further investigate this C–H activation process, complex **37**, which is the cationic derivative of **45**, was treated with one equivalent of base at low temperature to yield compound **45**. This product converted to species **44** over the course of 10 hours at −50 °C. The reactive nature of the dearomatized backbone was further demonstrated by the activation of H_2 using **44**, which led to the sole formation of the *trans*-dihydride **47**. This result strongly suggests the intermediacy of species **45**, with subsequent formation of the dihydrogen complex **46**, which was not observed, and heterolytic splitting of the H_2 ligand to rearomatize the PNP backbone to yield complex **47** (Scheme 20).

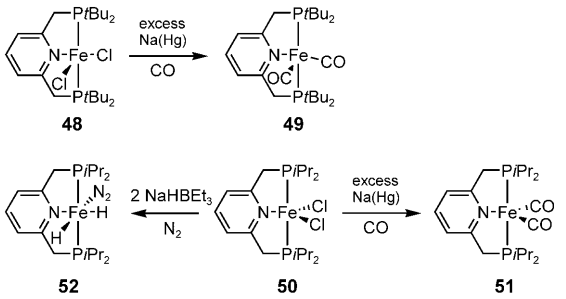


Scheme 20. Bifunctional activation of H_2 by complex **45**.

5.1. Iron

The research groups of Milstein[72] and Goldman[73] independently characterized a molecular structure of the $FeCl_2$ complex of $\mathbf{12^{tBu}}$ (species **48**) but subtle differences (i.e., different space groups) where observed between the two

structures. Reduction of this Fe^{II} species under an atmosphere of CO led to the formation of the corresponding complex [$Fe^0(CO)_2$(**12**^{tBu})] (**49**).[73] Similar chemistry was performed by Chirik and co-workers on the related Fe complex **50** (with PNP^{iPr}), but noticeable differences were found for the geometry around the Fe^0 center (Scheme 21).[74] A distorted

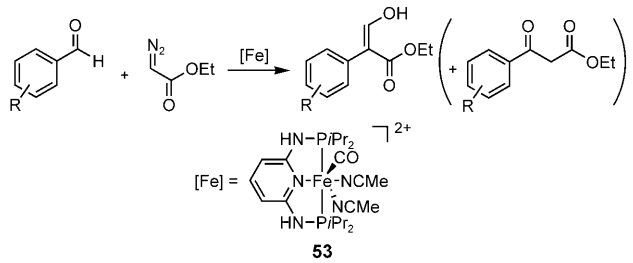


Scheme 21. Fe complexes **48**–**52** demonstrate subtle differences in steric hindrance of the phosphine side groups on the geometry of the obtained complexes.

square-pyramidal coordination was discerned with the bulkier PNP^{tBu} ligand, while a trigonal bipyramidal structure (**51**) could be elucidated with the less sterically congested PNP^{iPr} system. Reaction of $NaBHEt_3$ with **50** under an N_2 atmosphere led to formation of the corresponding dihydrido–dinitrogen complex **52**.

To date, no exploration of the non-innocent character of ligand scaffold **12** with Fe chemistry has been reported, despite the precedent of a growing body of relevant research with the heavier congener Ru (see Section 3).[75] This trend is very surprising, but it is believed that the Fe chemistry will be taken up by researchers soon, especially in light of the rapidly developing application of iron-based catalysis in organic synthesis.[76]

Benito-Garagorri and Kirchner prepared octahedral Fe^{II} complexes with a 2,6-diaminopyridine-derived PNP ligand type **18**. These examples include some complexes that contain bipyridine as coligand, as well as homoleptic complexes.[77] This rich coordination chemistry is typically inaccessible with more sterically encumbered phosphine derivatives. Deprotonation of one of the NH units using basic alumina was observed, and gave rise to a formally monoanionic ligand scaffold. Some of these Fe^{II} complexes, including complex **53** (Scheme 22), were applied in the coupling of aromatic aldehydes with ethyl diazoacetate to give 3-hydroxyacrylates



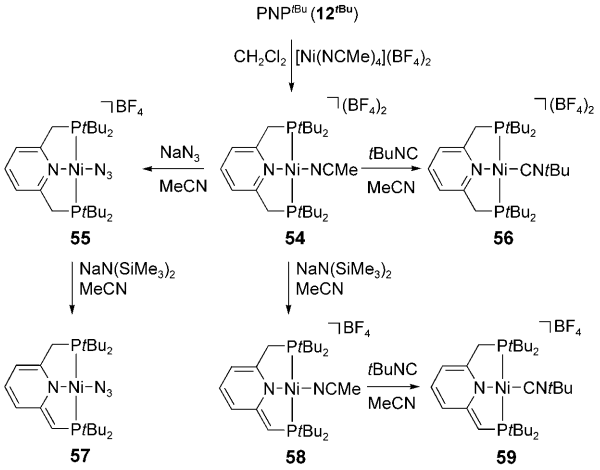
Scheme 22. Iron-catalyzed coupling of benzaldehydes and ethyl diazoacetate using complex **53**, which is based on ligand class **18**.

as main product. The first coordination sphere around the Fe^{II} ion did have a significant influence on the catalyst performance.

It remains to be seen if the amino linker of ligand **20**, like its CH_2 analogues, will be available for cooperative catalysis (as observed for the METAMORPhos type sulfonamidophosphoramidites[7,8]). This reaction would, in principle, offer new possibilities for this versatile subclass of tridentate PNP ligands.

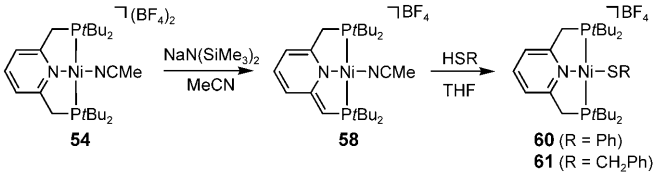
5.2. Nickel

Complex **54**, which contains a labile MeCN ligand, was used as a starting material to study the character of the dearomatized ligand PN$^-$P^{tBu} (**12**$^-$), using suitable signaling coligands (as in complexes **55**–**59**; Scheme 23).[78] Besides NMR spectroscopy, IR spectroscopy proved useful as a tool to probe the nature of the heterocyclic N atom, either as a neutral pyridine or a monoanionic amide.



Scheme 23. Synthesis of complexes **55**–**59** with ligand **12**^{tBu} by employing the non-innocent character of the PNP backbone.

Compound **54** also provided, via the isolable dearomatized, monocationic analogue **58**, a convenient route into the formation of monomeric, terminal Ni thiolate species **60** and **61**, in which the thiol substrate first reprotonates the PNP backbone before substitution of the acetonitrile coligand occurs (Scheme 24). The chemistry of nickel thiolate complexes is attracting increasing interest because of their likely role in biocatalytic systems such as NiFe hydrogenase.[79] Both compounds **60** and **61** feature a mononuclear four-coordinate



Scheme 24. Synthesis of the rare monomeric terminal thiolato Ni complexes **60** and **61** with ligand **12**^{tBu}.

nickel center with a single Ni–thiolate linkage (Figure 3). Such species remain quite rare, and only a handful of complexes have been described recently,[80] most of which feature similar low-spin, square-planar geometries, as in the two displayed examples.

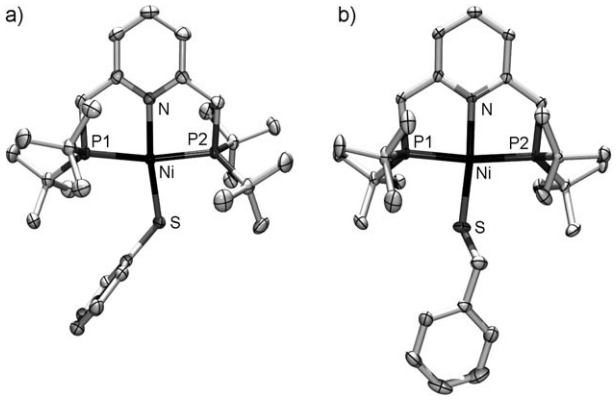
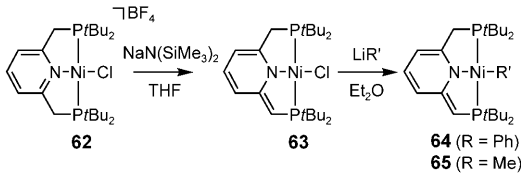


Figure 3. X-ray crystal structures of the cationic parts of complexes **60** (a) and **61** (b).

Besides nickel thiolates, nickel alkyl complexes have gained increasing importance as these species are inferred as catalytic intermediates for a range of organic transformations, such as hydrovinylation, Heck, and Kumada coupling, and polymerization reactions. Insight into the directed synthesis and controlled reactivity of such alkyl species might aid the development of more active or selective catalyst systems. Facile deprotonation of complex **62** ([NiCl(**12**$^{t\mathrm{Bu}}$)]BF_4)[78] resulted in the clean formation of complex **63**; subsequent reactivity of this species toward nucleophiles is strictly limited to the Ni^{II} center. The reactivity was probed by addition of either PhLi or MeLi, and led to the formation of the corresponding Ni alkyl species **64** and **65**, respectively (Scheme 25).

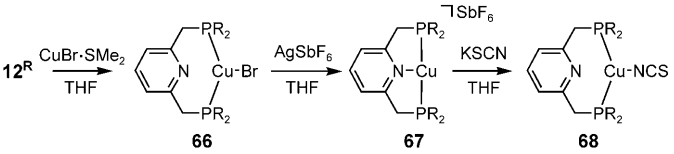


Scheme 25. Synthesis of the Ni–alkyl complexes **64** and **65** that feature the deprotonated version of ligand **12**$^{t\mathrm{Bu}}$.

Investigation of the potential for redox chemistry with the neutral Ni^{II} complex **63**, which incorporates the non-innocent **12**$^{t\mathrm{Bu}}$ ligand is interesting, as it might lead to unusual reactivity, given its close resemblance to the monoanionic Ni complex with ligand **4**, as recently described by Mindiola and co-workers.[81] It was demonstrated that ligand **4** can behave as a redox-based non-innocent ligand under certain reaction conditions.

5.3. Copper

The first example of a complex in which the central N atom of ligand **12** unexpectedly acts as a hemilabile moiety—reminiscent of the speculated behavior of the acridine ligand **14**—was recently discussed (complexes **66**–**68**; Scheme 26 and Figure 4).[82] In this case, IR spectroscopy proved to be a useful tool for assessing the coordination mode of the lutidine fragment. Surprisingly, no appreciable reactivity of complex **67** with O_2 has been observed so far.



Scheme 26. Hemilabile coordination of the pyridyl N atom of ligand backbone **12**^{R} to Cu^{I}.

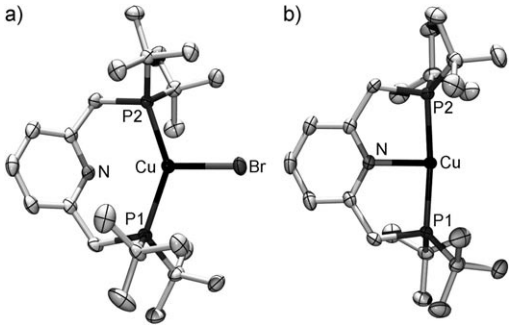
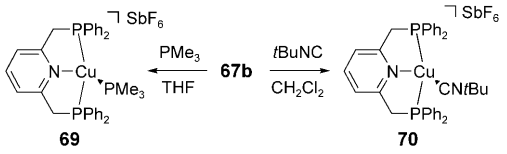


Figure 4. Molecular structures for complexes **66** (a) and the cationic part of **67** (b).

The reactivity of the Cu center strongly depends on the steric demands of the ligand backbone. Coordination of additional donor ligands such as PMe_3, CO, or isocyanide to complex **67a** was unsuccessful, whereas for the less hindered Cu center in compound **67b** (generated from **66b**), which features phenyl rings on the phosphorus side groups, the process proved to be facile and led to complexes **69** and **70** (Scheme 27 and Figure 5).

Furthermore, a combined experimental and theoretical study focused on the neutral T-shaped analogue **71**. This species, which was obtained by dearomatization of complex **67** with strong base, proved reactive toward electrophiles, including for example, MeOTf, which led to selective C–C bond formation at the ligand backbone (Scheme 28).[83] This reactivity might lead to new opportunities for the synthesis



Scheme 27. Synthesis of complexes **69** and **70** by coordination of additional donor ligands to compound **67b**.

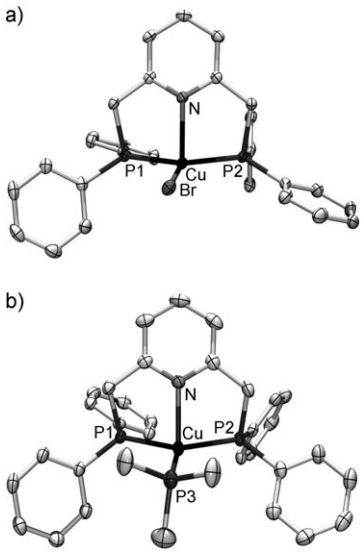
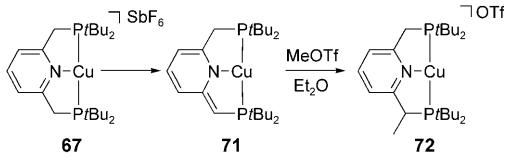


Figure 5. Molecular structure of complexes **66b** (a) and the cationic part of **69** (b).



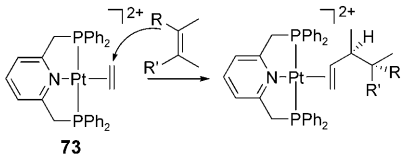
Scheme 28. Reactivity of complex **71**, which is the neutral, dearomatized analogue of **67a**, toward MeOTf. The reaction results in C–C bond formation in the backbone of ligand $\mathbf{12^{tBu}}$ whilst retaining the T-shaped configuration around Cu^{I} in complex **72**.

and exploration of modified, perhaps even chiral analogues of ligand scaffold $\mathbf{12^{tBu}}$. In general, the potential for cooperative catalysis with first-row transition metals such as copper is high, and it is a very attractive area to explore, provided the coordination behavior of the various states of the non-innocent ligand backbone can be controlled and tuned properly. Strikingly, Cu^{II} coordination has so far been elusive with this kind of tridentate ligand scaffolds.

6. Palladium and Platinum

Sacco and co-workers reported the first case of non-innocent behavior of the 'parent' pyridyl-derived PNP^{Ph} ligand during their studies on the carbonylation of Pd- and Pt-alkoxo complexes.[84] As such, they described the facile deprotonation of the PNP backbone at one of the methylene spacers, concomitant with the dearomatization of the pyridine ring, in the absence of CO.[85]

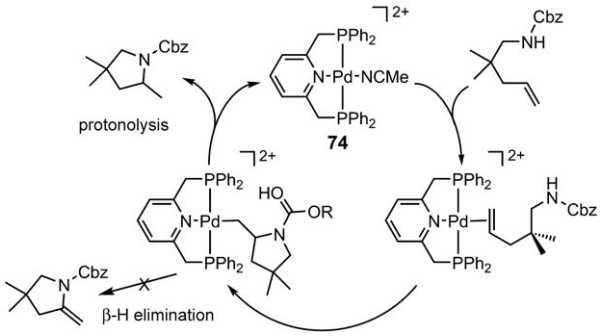
Vitagliano and co-workers have shown that the dicationic complex [Pt($\mathbf{12^{Ph}}$)] (**73**) is a suitable starting compound for stoichiometric reactions that involve nucleophilic attack of alcohols or amines onto coordinated alkenes (e.g., ethene).[86,87] In a related study (Scheme 29), they demonstrated that the same complexes can act as catalysts for the co-dimerization of ethene and internal alkenes (also known as the hydrovinylation reaction).[88]



Scheme 29. Co-dimerization of ethylene and 2,3-disubstituted butene substrates catalyzed by dicationic Pt($\mathbf{12^{Ph}}$) complex **73**.

The Pd analogue was subsequently shown to catalyze the same co-dimerization activity, but cyclopropanation was observed as a significant side reaction. In some cases, the cyclopropanation turned out to be even the dominating product pathway.[89] The catalytic hydroxylation of arenes was also demonstrated with catalyst **73** and the intermolecular cross-coupling of the Pt- or [Pd(η^1-allyl)] complex with complex **73** (or its Pd analogue) was reported to occur rapidly.[90]

Another recent application of the induced electrophilicity onto alkene substrates by the dicationic solvated Pd complex [Pd($\mathbf{12^{Ph}}$)(NCMe)]$(BF_4)_2$ **74** was reported by Michael and co-workers (Scheme 30).[91] The intramolecular hydroamination

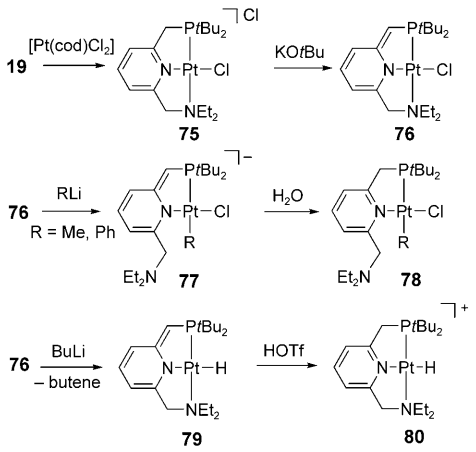


Scheme 30. Proposed catalytic cycle for the catalytic intramolecular hydroamination of unactivated, N-protected aminoalkenes using Pd catalyst **74**, which features ligand $\mathbf{12^{Ph}}$. Cbz = carboxybenzyl.

of unactivated, N-protected aminopentenes was shown to be efficiently catalyzed, and led to 2-methyl-substituted pyrrolidines in good yields. Six-membered piperidine derivatives and 2,6-disubstituted piperazines[92] were also accessible by using this methodology. There is a notable effect of the N-protecting group on the efficiency of the ring-closing reaction, with the best results obtained for amide-based N-groups and no turnover for the tosylated analogues. Remarkably, other quite similar tridentate ligand structures as well as common bidentate diphosphines did not give any conversion. Furthermore, the Pt analogue of **74** proved inactive as well. In principle, these reactions could potentially also benefit from the cooperative interaction of the PNP ligand and the reactive metal center, but no reports have appeared to date that utilize this concept with Pd and Pt.

Milstein and co-workers reported some interesting substitution chemistry on neutral Pt complex **76** that featured the dearomatized version of the hybrid ligand **19**, which was made in a straightforward fashion using **75** as an intermediate

species.[93] For instance, it was demonstrated that this species preferentially underwent addition of alkyllithium species, to form anionic compounds of the formula [{Pt(**19**$^-$)(R)Cl}Li], species **77**, rather than substitution of the halide coligand (Scheme 31). Protonation of the dearomatized PN$^-$N backbone with, for example, water, yielded the neutral [Pt(**19**)(R)Cl] complex **78**, wherein the dialkylamino arm of the ligand remains uncoordinated. Formation of Pt–H species **79** was accomplished when butyllithium was employed, concomitant with formation of butene as a side product (by β-H elimination). Subsequent addition of a strong acid led to the selective reprotonation of the dearomatized backbone, with formation of the cationic Pt–hydrido species **80**.



Scheme 31. Formation of the dearomatized Pt complex **76** and its versatile substitution chemistry, leading to the formation of, inter alia, monoanionic Pt complex **79**, facilitated by hemilabile coordination of the dialkylamino side arm in ligand **19**.

7. Summary and Outlook

In summary, we have provided a comprehensive overview on the recently expanded field of neutral tridentate pyridine-based PNP ligands and close analogues thereof. The pyridine and lutidine scaffold has proven to be a very versatile building block for the construction of a wide array of phosphorus-functionalized ligands. The main focus to date has been the exploration of the coordination chemistry of such systems, especially with 2nd and 3rd row transition metals. The versatility of these tridentate ligands has been showcased in various types of (stoichiometric) activation reactions. Some of these frameworks display non-innocent behavior, which is linked to facile deprotonation of the backbone and leads to charge-switching from neutral to monoanionic. Dearomatization plays a key role in this behavior, and therefore the choice of the ligand backbone is of crucial importance. Lutidine pincer scaffolds have relatively low dearomatization energies and therefore are well-suited for cooperative catalysis. In addition, the deprotonation–dearomatization process can be conveniently followed by both IR and NMR spectroscopy. This dearomatization principle should be taken into account as a design feature for the construction of new scaffolds.

Of particular interest are the recent significant breakthroughs in cooperative catalysis with these non-innocent building blocks. This approach has led to unprecedented transformations such as the dehydrogenative coupling of alcohols and amines. Future developments will surely be directed to making further use of the non-innocent character of these versatile compounds, with much attention for hybrid or flexidentate ligand scaffold. Besides lutidine- or dialkylamine-derived backbones, it is to be expected that other new types of non-innocent structures (e.g., acridine-based) will find use once their specific mode of cooperative action is clarified. We also forsee particular interest in the development and application of chiral cooperative ligands to allow for asymmetric catalysis; breakthroughs in this area are therefore anticipated.

It is clear that the combination of a flexidentate ligand with a non-innocent cooperative framework provides ample opportunity for novel types of reactivity that will extend far beyond the realm of ruthenium-based chemistry. In general, there is a remarkable absence of examples of cooperative catalysis that utilize the biologically relevant, economically attractive, and late-first-row transition metals that undergo one-electron redox steps. We envision that there is much to be gained if ways can be found to translate existing chemistry with higher homologues (e.g., Ru versus Fe) of these overlooked metals. Nature also has accomplished fascinating chemistry by combining non-innocent ligands with these first-row transition metals. Cascade catalysis is another interesting concept that might benefit from cooperative catalysis, especially when linked to selective evolution of reactive reagents, as in the case of the dehydrogenative coupling of alcohols (i.e., H_2). The successful application of non-innocent, cooperative ligands in new types of reactions is likely only a matter of time.

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