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Coordination Versatility of sp^3-Hybridized Pincer Ligands toward Ligand–Metal Cooperative Catalysis

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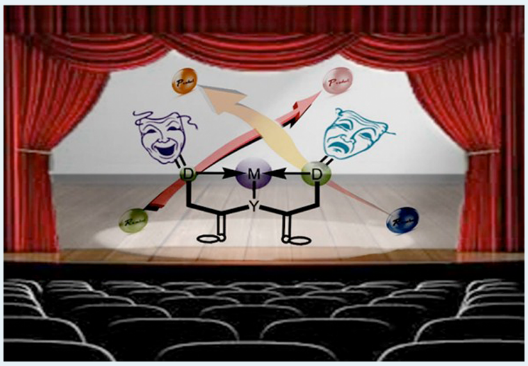
ABSTRACT: Pincer-type complexes occupy a very important position in chemistry and chemistry-related disciplines. In this article we have selected several spectacular examples of pincer systems and demonstrate that reversible structural changes in the ligand backbone may have a dramatic impact on the reactivity of their metal complexes. This perspective aims to focus on some recent exciting developments in the chemistry of "cooperating" PN(sp^3)P and PC(sp^3)P pincer ligands relevant to catalytic applications.



KEYWORDS: *ligand–metal cooperation, non-innocent ligands, pincer complexes, catalysis*

1. INTRODUCTION

Pincer-type ligands belong to a family of tridentate ligands where the central anionic or neutral donor site is flanked by two neighboring donor groups (Y = C, N, Si; D is a neutral two-electron donor, see Figure 1). Their DYD η^3-mer coordination to transition or main group metals gives rise to the formation of Y-M bond-sharing bicyclic structures[1,2] that are often translated into robust materials featuring exceptional thermodynamic stability.[3,4] On the other hand, structural modification of the coordinating environment helps to control reactivity of the complexes by controlling steric, as well as, electronic properties of the metal center.[5−7] Combination of these factors placed these fascinating compounds in a domain of very intensive research activity and eventually made them very popular in many branches of catalysis,[8−12] basic organometallic and coordination chemistry.[13−15] Moreover, pincer complexes are rapidly entering the areas traditionally occupied by inorganic or organic materials such as design of high-performance materials,[16−19] bioinorganic[20,21] and supramolecular chemistry.[22−25]

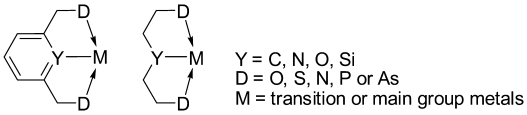


Figure 1. Schematic representation of pincer complexes.

Aliphatic pincer complexes (Figure 1, right) actually preceded aromatic counterparts (Figure 1, left): their synthesis was first described in the late 1970s, the outset of the "pincer era".[26−29] However, further exploration of the sp^3-hybridized pincer ligands has been overshadowed for quite a long time by more structurally simple and robust ligands based on (hetero)aromatic moiety. This is not surprising because easy manipulation of the aromatic or heteroaromatic rings facilitates an access to diverse DYD pincer ligands by modifying one or more of the parameters in the general structure of the ligand, that is, the donor and spacer groups, the (hetero)aromatic skeleton itself and its substitution, thus marking the sp^2-hybridized pincer complexes as more suitable candidates for systematic studies of structure/reactivity relationships than the corresponding aliphatic compounds. Moreover, three donor groups of the aromatic [2,6-$(DCH_2)_2C_5H_3Y$] ligands, meridionally coordinated to a metal center, are essentially coplanar, which guarantees efficient communication between the metal-centered d_{xz} orbitals and the π orbitals of the aromatic backbone.[30−32] This, together with high sensitivity of the (hetero)arene moieties toward electronic nature of the substituents in *para* position, allows for easier fine-tuning of the electronic properties of the metals.

Nevertheless, during the past decade we have witnessed a remarkable renaissance of the sp^3-hybridized pincer ligands. The new wave of interest[33] mainly started after reversible switching between different coordination modes found earlier in these compounds were brought to practice. For example, metal-amide/metal-amine interconversion[34−37] in heteroaromatic[38] and aliphatic PNP systems[39−41] was proven to facilitate heterolytic bonds cleavage (Figure 2, top). In a similar manner, strongly σ-donating anionic C(sp^3)-hybridized pincer ligands increase electron density at the metal center, which in combination with a high flexibility of the aliphatic scaffolds

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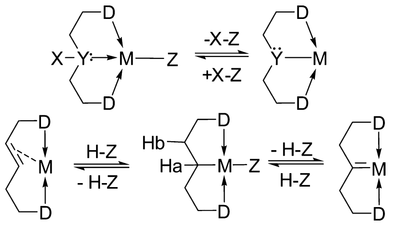


Figure 2. Reversible switching between different coordination modes toward bond activation/formation.

and the presence of labile hydrogens in α- and β-positions, induce bond activation/formation via dynamic interplay between carbometalated and α- or β-H eliminated species (Figure 2, bottom).[42] This coordination versatility characteristic of sp^3-hybridized pincer complexes opens new practical reactivity patterns in nonoxidative (i.e., alternative to the conventional oxidative addition/reductive elimination sequence) activation and formation of polar and nonpolar bonds and, thus, very much compensates for their less robust nature and justifies further efforts toward their diversification and toward more detailed studies of their properties.

An additional aspect advantageously distinguishing the sp^3- from the sp^2-based pincer complexes is their dimensionality. For example, the vast majority of aromatic complexes of this type are approximately planar.[43−51] Arguably, this structural simplicity is reflected in a relatively limited number of successful catalytic applications in stereoselective synthesis.[11,52] Unlike those, three-dimensional steric environment around the metal center created by sp^3-based ligands provides a unique opportunity to design new pincer catalysts with a better enantio-differentiating ability.

This survey aims to focus on some recent exciting developments in the chemistry of PN(sp^3)P and PC(sp^3)P pincer complexes.

2. COORDINATION VERSATILITY IN N(SP^3)-BASED PINCER LIGANDS

2.1. Aliphatic Disilylamido PN(sp^3)P Pincer Ligands: The Prototype. 16-electron pincer complexes of iridium(I) and rhodium(I) bearing aliphatic disilylamido PNP ligands (Figure 3) have been reported by Fryzuk et al. as efficient catalysts for the homogeneous hydrogenation of simple olefins.[53]

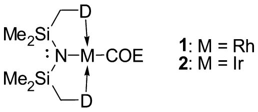
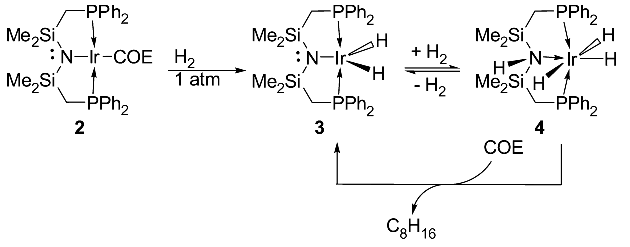


Figure 3. Prototypical PN(sp^3)P pincer ligands.

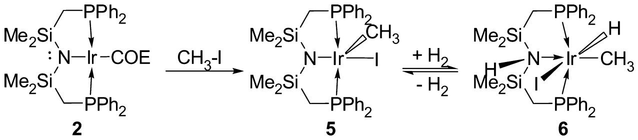
However, this rather expected reactivity was accompanied by a high degree of double bond isomerization. For example, when **1** or **2** were used as catalyst precursors, isomerization of 1-hexene into *cis/trans* 2-hexene occurred 1.5 times faster than its hydrogenation. Moreover, unlike the classical oxidative addition/reductive elimination mechanism that is known to be sensitive to the steric properties of substrates, hydrogenation of internal olefins using the PNP catalysts was as fast as that of terminal ones. Considering this anomalous reactivity, a ligand−metal cooperative mechanism for heterolytic hydrogen splitting was suggested. According to this hypothesis, nonoxidative 1,2-addition via interplay between the amide-stabilized dihydride **3** and amine-stabilized trihydride **4** takes place over the course of the catalytic cycle (Scheme 1).[54] The key species **4** were only observed spectroscopically because of their inherent instability toward the loss of dihydrogen.

Scheme 1. Ligand-Metal Cooperative Mechanism for Heterolytic Splitting of H_2 by PN(sp^3)P Pincer Complexes



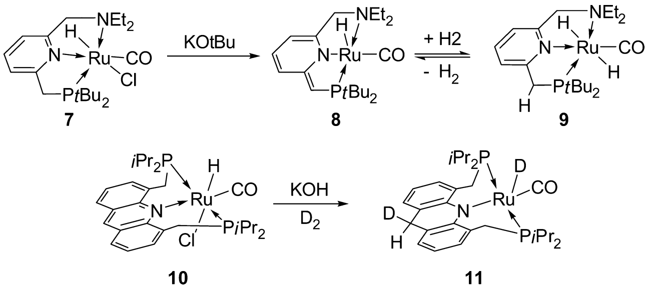
Attempted heterolytic activation of hydrogen by the amide-stabilized **5** led to the formation of the amine-stabilized complex **6** that can be formally seen as a product of the desired transformation, but with the wrong (anti) stereochemistry (Scheme 2). According to X-ray analysis of **6**, the hydride ligand was located trans to the N−H bond.[40] This, of course, does not rule out the suggested mechanism, although questions its kinetic control that should have led to the formation of a *cis* isomer.[55] Nevertheless, these fundamentally important observations encouraged further evolution of ligand−metal cooperating PNP pincer catalytic systems.

Scheme 2. Stereochemistry of Heterolytic Activation of H_2

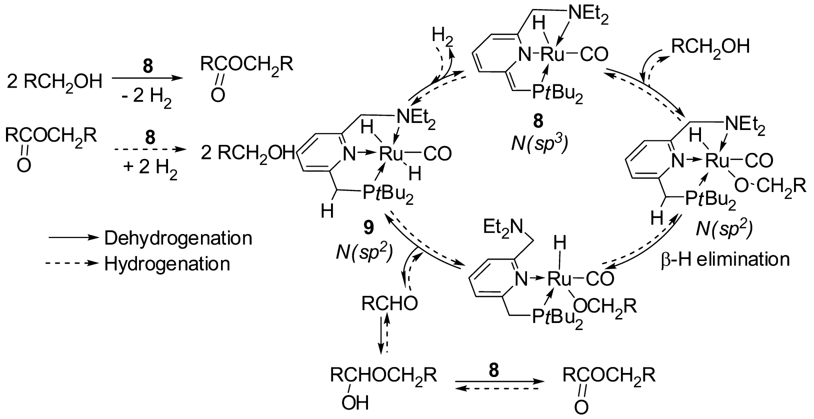


2.2. Pyridine-Based PNP and PNN Pincer Complexes. A different mode of ligand−metal cooperation involving very interesting coordination switches was found by Milstein and co-workers in a series of ruthenium and iridium pincer complexes bearing PNP or PNN ligands. As was demonstrated, deprotonation of 18-electron heteroaromatic Ru(II) PNN complex **7** at the benzylic position causes dearomatization of the pyridine moiety, followed by elimination of the chloride ligand, to yield (en)amide N(sp^3)-based **8** (Scheme 3, top). The existence of the complex in its dearomatized form was

Scheme 3. Non-Oxidative Hydrogen Splitting via "Short- and Long-Range" Dearomatization PNP Pincer Ligands



Scheme 4. Plausible Mechanism of Ru-Catalyzed Dehydrogenative Coupling of Primary Alcohols and Vice Versa



supported by X-ray analysis that clearly points to nonequivalent bond lengths within the side arms (1.350 Å versus 1.505 Å).

Although such N(sp^3)-(en)amide ligands are expected to be strongly π-donating in combination with metals having empty orbitals of d_π-symmetry, this 16-electron dearomatized complex readily restores aromaticity upon nonoxidative hydrogen splitting (Scheme 3, top).[56] Density functional theory (DFT) calculations predict that the presence of water may assist in the proton transfer step in the heterolytic 1,4-addition.[57]

Being reversible, this process represents a conceptually different mode of ligand−metal cooperation because switching between the metal-"enamide" (dearomatized) and metal-"imine" (aromatized) coordination modes is accompanied by the change in hybridization of the coordinating nitrogen. Thus, these reversible chemical transformations within the pincer backbone strongly vary coordinating properties of the ligand: from π-donating (amido form) to π-accepting (imino form).

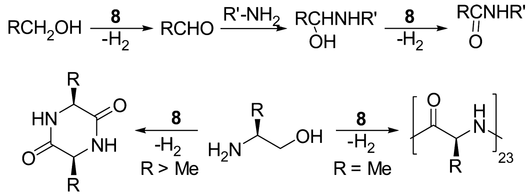
A similar scheme also takes place in a "long-range" fashion via dearomatization of the central ring in the extended acridine-based PNP complexes such as **10** (Scheme 3, bottom).[58] However, reactivity of **10** is apparently different from that of **7**. The most likely reaction mechanism involves base-promoted reductive elimination of HCl to form Ru(0) species that readily oxidatively add dihydrogen generating Ru(II) dihydride species that, in due turn, dearomatize upon migration of the hydride ligand to the C-9 position of acridine scaffold. According to DFT calculations, this migration pathway has a lower barrier than nonoxidative addition of dihydrogen as in previously described pyridine-based systems.

On the basis of these key transformations, novel catalytic reactions have been developed. Thus, acceptorless dehydrogenative coupling of primary alcohols to form esters under neutral conditions was realized using **8** as a catalyst (Scheme 4). Since a base is not involved in this process, formation of esters is explained by tandem dehydrogenation/hemiacetalyzation/dehydrogenation reactions but not via a classical Tischenko reaction.[56] The catalyst **8** demonstrated 950 TOs and excellent conversions under relatively mild heating.

The same catalyst was found capable of operating the reverse reaction, namely, hydrogenation of esters to alcohols.[59] Indeed, employing 0.01 mol % of **8** under 5−6 atm of hydrogen at 115 °C for the reduction of ethyl benzoate lead to the quantitative formation of corresponding benzyl and ethyl alcohols. The catalyst is equally active in hydrogenation of aliphatic (e.g., ethyl butyrate) and aromatic (e.g., dimethyl terphthalate) esters, although sensitive to steric bulk of the substrates (low conversion was observed for *tert*-butyl acetate).

Even more challenging transformations can be performed using these catalysts capable of the reversible hybridizational M-N(sp^2)/M-N(sp^3) switch. For example, it was demonstrated that the same catalyst **8** can be successfully applied to the mixtures of primary alcohols and primary amines to synthesize amides via dehydrogenative (waste-free!) pathway.[60] According to this synthetic scheme, **8** converts primary alcohol into an aldehyde that is readily attacked by the present amine to form aminal that is dehydrogenated to the corresponding amide, in due turn (Scheme 5). The reaction proceeds at 110−135 °C in an open system to ensure complete hydrogen removal, showing excellent conversions of alcohols and fair to excellent yields of amides, depending on the steric bulk of an amine component. This protocol was even applied to the synthesis of linear and cyclic peptides and pyrazines from β-amino alcohols,[61] as well as of moderate molecular weight (10−30 kDa) polyamides from diols and diamines.[62,63] Selectivity toward cyclic or linear peptides is strongly dependent on the steric properties of the substrates. For example, while (*S*)-(+)-2-amino-1-propanol cleanly form a polymer consisting of 23 repeating units, larger substituents in an α-position form cyclic dipeptides, in good to excellent yield. No racemization was ever detected.

Scheme 5. Dehydrogenative Coupling of Primary Alcohols and Amines



Nowadays, an arsenal of such non-innocent pincer ligands includes various PNPs and PNNs that differ in lability of the side arms (Figure 4) which was proven to be influential on the reaction outcome. For example, while **8** serves as an excellent catalyst for the clean dehydrogenative coupling of alcohols and amines to form amides, employment of the analogous PNP complex **12** under essentially identical reaction conditions leads to the synthesis of aliphatic and aromatic imines in good to excellent selectivity. Remarkably, liberated hydrogen is not intercepted in this case with hydrogenation of imine to the

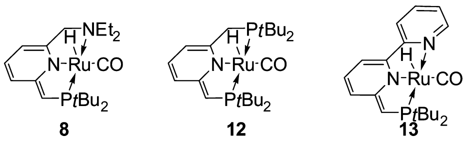


Figure 4. PNP and PNN pincer complexes developed by Milstein and co-workers.

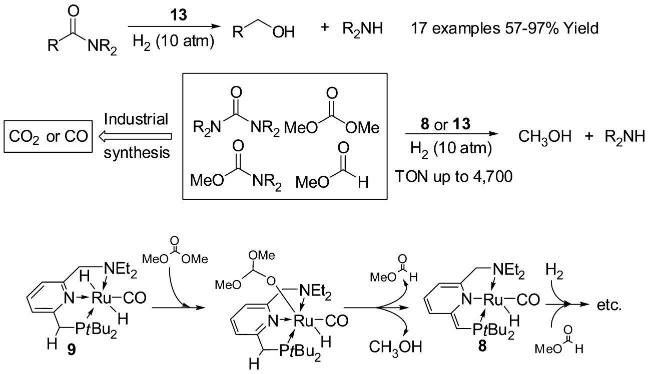
corresponding amine as was reported for other catalytic systems (Scheme 6).[64,65]

Mechanistically, this difference in reactivity is attributed to the lability of the amine versus phosphine donor group (Scheme 6). Presumably, successful β-H elimination step requires reversible dissociation of a side arm. If so, in the case of **8** bearing a more labile amine side arm, the aminal intermediate forms from the metal-coordinated aldehyde that favors further dehydrogenation to produce amide product, while in the analogous **12**, rapid phosphine-side arm closure displaces the aldehyde intermediate product, so that the nucleophilic attack by amine leads to a condensed imine product.

Also in this case, the reactions were found to be reversible which engendered a series of extremely useful mild hydrogenation protocols. Thus, it was found that both **8** and more thermally stable **13** are capable of hydrogenating amides[66] and even ureas[67] to the corresponding amines and alcohols (stoichiometry depends on the substrate), under 10−14 atm of hydrogen at 110−140 °C.

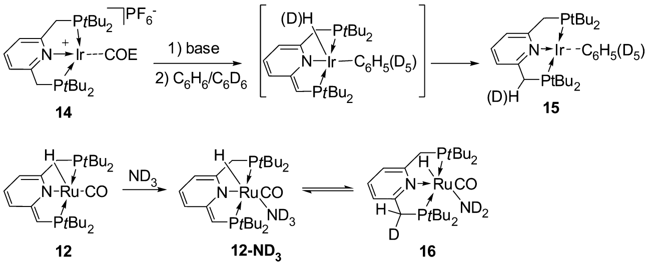
Similarly, **8** and **13** were found active in unprecedented hydrogenation of organic formates, carbamates, and even carbonates to methanol.[68] This process is important from the conceptual and practical points of view because it offers an alternative indirect route to produce methanol from CO and CO_2 (Scheme 7). The reactions proceed efficiently and selectively under mild, neutral conditions using mild hydrogen pressure, without the generation of any waste or byproducts (such as CO) and with high turnover numbers (TONs). Moreover, hydrogenation of dimethyl carbonate and methyl formate proceeds very well also in absence of solvent, representing ultimate "green" reactions.

Scheme 7. Ru-Catalyzed Mild Hydrogenation of Organic Formates, Carbamates, Carbonates, and Ureas



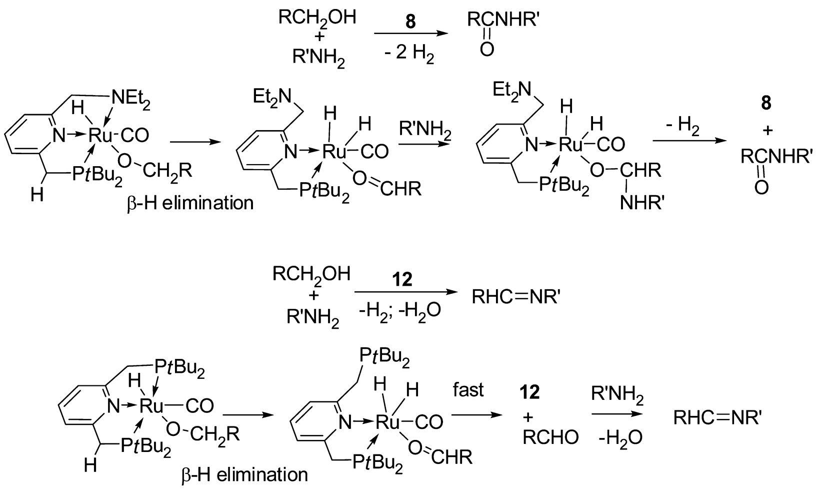
Mechanistically these processes are similar to those described earlier. For example, hydrogenation of carbamates proceeds via dearomatization of the dihydride **9** (prepared in situ by addition of H_2 to **8**) that takes place readily in the presence of dimethyl formate to deliver methyl formate and methanol. Aromatization of the latter in the presence of H_2 initiates the next cycle of the sequence.

Scheme 8. C−H and N−H Activation via Dearomatization PNP Pincer Ligands

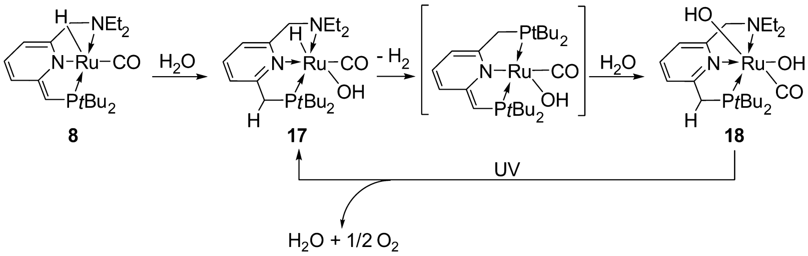


Remarkably, the bond activation via the hybridizational interplay is not limited to hydrogen. Milstein and co-workers recently demonstrated that C−H[69,70] and N−H[71] bonds can be successfully cleaved by the dearomatized PN(sp^3)P-based complexes (Scheme 8). When a benzene solution of the dearomatized Ir(I) PNP **14** was mildly heated at 60 °C for 2 h, quantitative C−H activation to form **15** (with no overall change in oxidation state), took place. Upon reaction of complex **14** with C_6D_6, deuterium incorporation into a benzylic group of

Scheme 6. Ru-Catalyzed Dehydrogenative Formation of Imines versus Amides Catalyzed by 8 and 12



Scheme 9. Potential Catalytic Cycle for Catalytic Splitting of Water



complex **15** was observed revealing only three benzylic protons according to ^1H NMR. Although no intermediates were directly observed in the C−H activation process, intermediacy of the Ir(III) complex is a viable possibility (Scheme 8, top).

To probe the possibility of ammonia activation, complex **12** was reacted with an excess of ND_3 in C_6D_6 and led to the selective formation of the deuterated analogue **12-ND$_3$** 5 min after addition (Scheme 8, bottom). The reaction was highly stereospecific as only one of the two CH_2 arm hydrogen signals in the ^1H NMR spectrum disappeared. Although it could not be determined exactly which of the two CH_2 hydrogens was exchanged, such dramatic selectivity suggests that the activation process occurs on only one face of the ligand and in an intramolecular manner with one coordinated molecule of ND_3. Although no catalysis has been described so far, it seems likely that practical applications of these ligand−metal cooperating systems will follow.

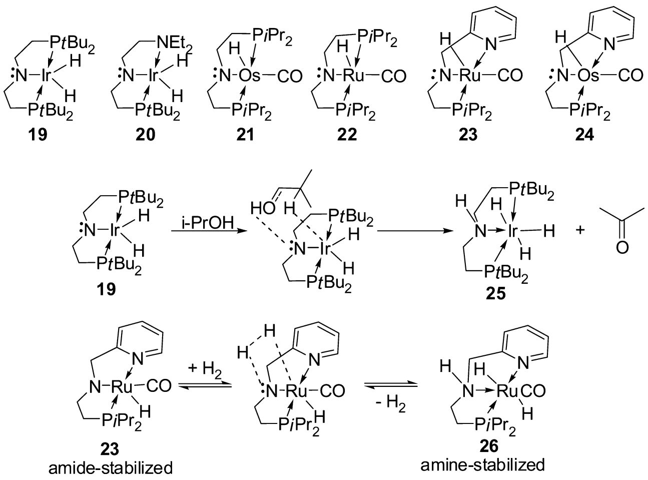
Water splitting was probed using this powerful bond activation approach.[72] As was demonstrated, the dearomatized PNN complex **8** readily reacts with water in THF at room temperature, resulting in the formation of the aromatizated *trans*-hydrido-hydroxo complex **17** (Scheme 9). According to DFT studies, this compound is probably formed by a mechanism involving water coordination at the vacant site trans to the hydride, followed by proton migration to the side arm, as was suggested for earlier cases.[73] Even more interestingly, the latter complex reacts with water under mild heating forming the *cis*-dihydroxo complex **18** and one equivalent of H_2. As previously, DFT studies predict that this process involves H_2 formation via interaction of the side arm proton with the hydride ligand, followed by addition of H_2O to the dearomatized intermediate. Furthermore, irradiation of **18** under UV regenerates **17** with liberation of O_2 in an intramolecular fashion according to crossover experiments (Scheme 9).

Although the thermal and photochemical reactions have been demonstrated only as independent systems, the system may offer great potential for catalytic splitting of water.

2.3. Aliphatic PN(sp^3)P Pincer Complexes. Structurally simpler all-aliphatic PNP ligands were also found capable of a similar ligand−metal interplay. As was demonstrated by Gusev and co-workers, ruthenium, osmium, and iridium complexes bearing these ligands (**19**−**24**) appeared to be active in heterolysis of polar and nonpolar bonds.[4,41,74−76] For instance, stirring solutions of the iridium amide **19** under the atmosphere of H_2 or its exposure to isopropanol afforded the expected amine-stabilized trihydride **25** (Scheme 10). Similar reactivity was observed for the analogous **23**. On the basis of these transformations, efficient protocols for transfer hydrogenation of ketones have been developed.

More thermally stable **21**−**24** were also employed as precatalysts in acceptorless dehydrogenation of alcohols and hydrogenation of esters.[4,75,76] In particular, a catalyst derived from **23** has shown an unmatched efficiency under neutral conditions by giving TONs up to 18000, while the catalyst derived from **24** proved to be particularly useful for hydrogenation of esters. Also remarkably, hydrogenation with this catalyst is chemoselective in the presence of double bonds, so that it could be applied for hydrogenation of triglycerides, allowing production of unsaturated fatty alcohols directly from olive oil. Unlike Milstein's catalysts, this reaction is operated by the metal-amide N(sp^3)/metal-amine N(sp^3) interconversion.

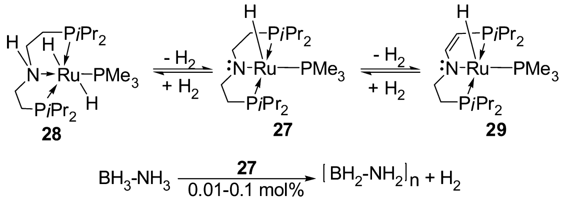
Scheme 10. Ligand-Metal Cooperation in Aliphatic PN(sp^3)P Pincer Complexes



Another structurally simple catalytic system for the heterolytic activation of H_2 was discovered by Schneider and co-workers.[77−79] They described a bifunctional Ru(II)PNP catalyst **27** capable of an unexpected mode of ligand−metal cooperation. Thus, it was found that **27** quantitatively adds hydrogen in solution under H_2 atmosphere via the earlier described metal-amide N(sp^3)/metal-amine N(sp^3) switch (to form **28**), but also slowly releases H_2 under argon atmosphere at room temperature over several days forming a nonpyridine analogue of the Milstein's catalyst (**29**) (Scheme 11). The amido complex **27** was used for the room temperature dehydrogenation of ammonia-borane showing up to 21 s^{-1} turnover frequency (TOF) and TON of 8300.

Although the mechanistic information about the outstanding activity of **27** is lacking, a large kinetic isotope effect (KIE, ca. 8) observed in dehydrogenation of the deuterated ammonia-borane strongly suggests concerted metal-centered N−H and B−H bond cleavages as the rate-limiting step.[77] Moreover, slow H_2 elimination from complex **28** indicates that the spontaneous loss of H_2 to regenerate **27** cannot be of relevance for the catalytic cycle and it is more likely to proceed through the enamide intermediate **29**. DFT calculations show that the

Scheme 11. Metal-Amide/Metal-Enamide Coordination Switch in Aliphatic PN(sp^3)P Pincer Complexes



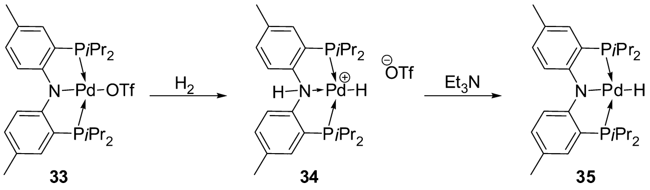
enamido ligand in **29** exhibits significantly different donor properties, compared to the parent **27**. Therefore, if the suggested mechanism is operative, this system will represent a third conceptually unique mode of ligand−metal cooperation in PN(sp^3)P pincer complexes driven by metal-amide/metal-enamide coordination switch, where π donation by the amido N(sp^3) nitrogen atom can be controlled by the reversible chemical changes within the ligand backbone.

Hydrogenolysis of a terminal nitrido ligand in the Ru(IV) PNP complex (**30**) was described by Schneider, Holthausen, and co-workers.[80] As was concluded from the X-ray and IR characterization studies and confirmed by DFT calculations, the stronger π donation exerted by the amido N(sp^3) atom significantly weakens the usually π-donating nitride. The more nucleophilic nature of the nitride ligand in **30** was also supported by the reaction of it with π-acidic CO to form the corresponding isocyanate complex **32**.

On the other hand, the bifunctional nature of the PNP facilitated heterolytic activation of hydrogen and led to the formation of ammonia via the unusual sequence of the reactions that includes apparently rate-determining heterolytic activation of hydrogen and subsequent protonation of the nitrido ligand (Scheme 12). Indeed, the ligand assistance is predicted by DFT calculations as the lowest free-energy path for this sequence which rules out the oxidative addition pathway as unreasonable.

2.4. Diphenylamine-Based PN(sp^3)P Pincer Complexes. Heterolytic splitting of polar H-X bonds at cationic PdPN(sp^3)P complexes was studied by Ozerov and co-workers.[81] Unlike complexes of other transition metals described in this section, PN(sp^3)P in the cationic d^8 complexes such as **33** should not have a strongly pronounced π-donor character because all orbitals of d$_\pi$-symmetry at Pd are filled and, therefore, enhances nitrogen-centered reactivity. Indeed, it was demonstrated that **33** is capable of heterolytic 1,2-addition of small molecules across the Pd−N(sp^3) bond upon exposure to H_2, terminal acetylenes and thiols. However, the attempted 1,2-elimination in this case led to deprotonation of the Pd-HN(sp^3) moiety toward the formation of the corresponding neutral species such as **35** (Scheme 13). DFT calculations rule out the competitive Pd(II)/Pd(IV) oxidative addition route.

Scheme 13. Reactivity of Diphenylamine-Based PN(sp^3)P Pincer Complexes



3. COORDINATION VERSATILITY IN C(SP^3)-BASED PINCER COMPLEXES

The arsenal of the PC(sp^3)P ligands is relatively limited. For example, alkyl chain,[26] cyclohexane,[82] adamantane,[83] cyclo-

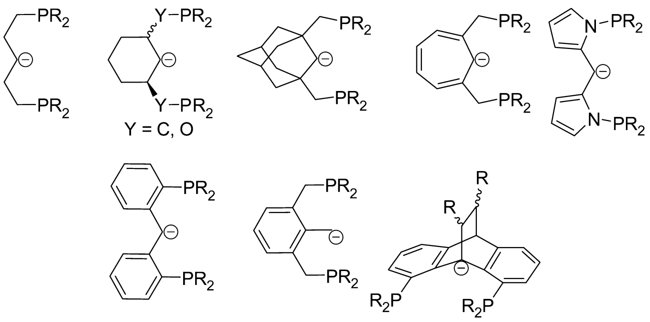
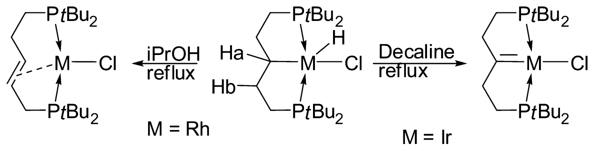
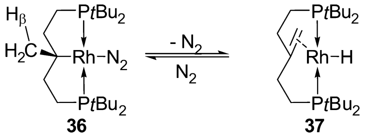


Figure 5. Known PC(sp^3)P ligands.

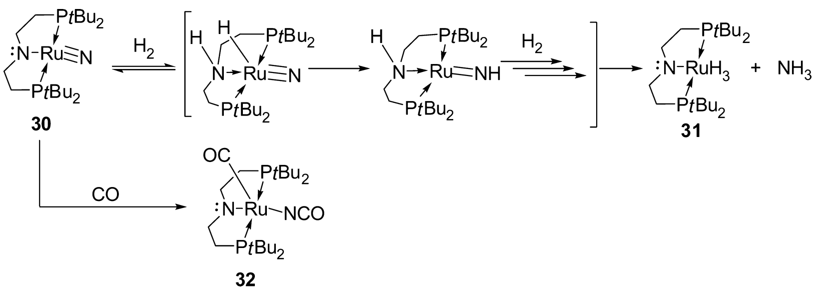
Scheme 14. Coordination Flexibility in Carbometalated PC(sp^3)P Complexes



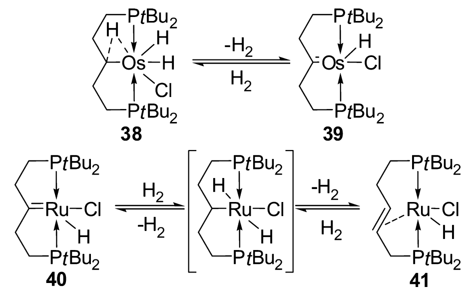
Scheme 15. Reversible Switching between Different Coordination Modes in Rh(I) PC(sp^3)P Pincer Complexes



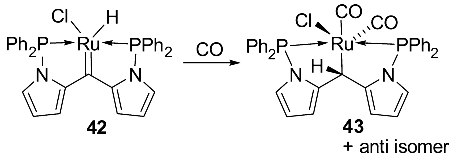
Scheme 12. Reactivity of Nitrido Ru(IV) PNP Complex



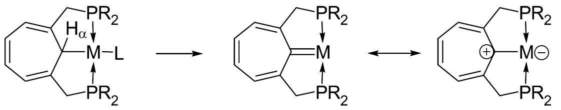
Scheme 16. Reversible Activation of H_2 by Osmium and Ruthenium $PC(sp^3)P$ Pincer Complexes



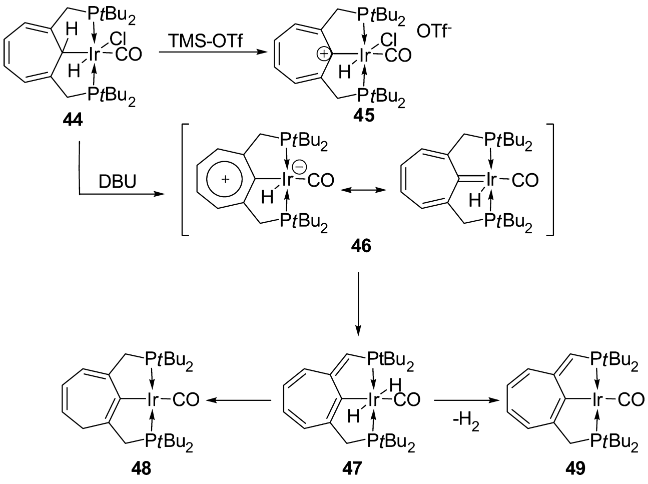
Scheme 17. 1,2-Hydrogen Shift in Ruthenium Carbene Pincer Complexes



Scheme 18. Cycloheptatriene-Based $PC(sp^3)P$ Pincer Complexes with a Reversed Polarity



Scheme 19. Attempted Synthesis of the Ir Carbene Cycloheptatriene-Based $PC(sp^3)P$ Pincer Complexes



heptatriene,[84] arylmethane,[85] diarylmethane,[86,87] and dibenzobarrelene[88] derivatives have been employed as platforms for their construction (Figure 5).

Expectedly, trans-influence of the strongly σ-donating $C(sp^3)$-hybridized pincer ligands is clearly pronounced. On the average, comparative IR studies indicate 10−30 cm^{-1} lower ν vibrations of the M-L bonds located trans to the metalated $C(sp^3)$ position compared with the analogous aromatic sp^2-metalated compounds, suggesting a more electron-rich character of the metal centers and, consequently, a more reactive carbon−metal bond.[26]

The tendency of transition metal complexes bearing all-aliphatic ligands to lose hydrogen presumably via to α- and β-hydride elimination to form isomeric carbene or olefin chelate complexes, evidencing the high reactivity of the $C(sp^3)$-metal bond, was postulated by Shaw and co-workers during their pioneering studies (Scheme 14).[89−92]

Later, Vigalok et al. reported that dinitrogen Rh(I) complex **36** and the β-H eliminated **37** are found in the temperature dependent equilibrium under nitrogen atmosphere (Scheme 15).[93] Remarkably, unlike classical migratory insertion processes requiring *cisoid* coordination of the participating ligands, this reaction proceeds via direct trans insertion. Similar transformation has been reported for ruthenium complexes.[94]

Gusev and co-workers studied organometallic and coordination chemistry of the osmium and ruthenium $PC(sp^3)P$ complexes possessing both α- and β-hydrogens.[42] As shown, osmium carbometalated compound **38** demonstrates a clear agostic interaction between the osmium center and the methine hydrogen that facilitates hydrogen extrusion to form the thermodynamically stable carbene complex **39**. Moreover, ruthenium carbene (**40**) and olefin (**41**), are, apparently, interconvertable via competitive α- and β-hydride elimination from the presumed Ru(IV) dihydride intermediate (Scheme 16).

Similar coordination versatility was also observed in less flexible $PC(sp^3)P$ transition metal pincer complexes. Interestingly, the stability of the $PC(sp^3)P$ pincer complexes of this type is metal-dependent. For example, exposure of the carbene complex **42**, prepared from $[RuCl_2(cymene)]_2$ and dipyromethane diphosphine, to strongly coordinating ligands such as CO, induces a quantitative 1,2-H shift (Scheme 17).[86]

A seminal design of the $PC(sp^3)P$ pincer ligands taking advantage of cycloheptatriene platform was introduced by Kaska, Mayer, and co-workers.[84] Significance of the tropylium resonance form leading to the lability the α-methine hydrogen is the most striking difference between the all-aliphatic and the cycloheptatriene-based sp^3-metalated pincer ligands because the corresponding transition metal pincer complexes must be regarded as organometallic species of a reversed polarity (Scheme 18).

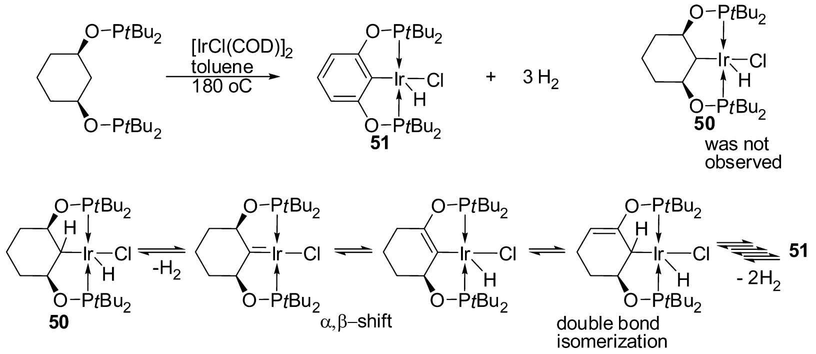
Indeed, treatment of the $C(sp^3)$-metalated **44** with one equivalent of TMS-OTf leads to the formation of a stable tropylium derivative **45** (Scheme 19) that is expectedly characterized by a longer ν (Ir-CO) vibration, 2030 cm^{-1} in **45** vs 2000 cm^{-1} in **44**.[95]

However, attempted treatment of **44** with DBU to form carbene-tropylium product **46** led to the formation of the sp^2-carbometalated **47**-**49**.[96] As was suggested, HCl is removed from the cycloheptatrienyl PCP pincer **44** across the $C(sp^3)$−Ir bond forming a carbene structure as outlined in Scheme 19. The proposed carbene, however, was not observed because of the fast rearrangement affording **47**, that, in due turn, may rearrange into **48** or expel H_2 to form **49**. Indeed, DFT calculations predict the **46** as the least stable species being destabilized by 10.7 kcal/mol in comparison to **48** and by 26.6 kcal/mol to **49**. Considerably higher stability of the $C(sp^2)$-Ir bond is, apparently, a driving force for the isomerization processes.

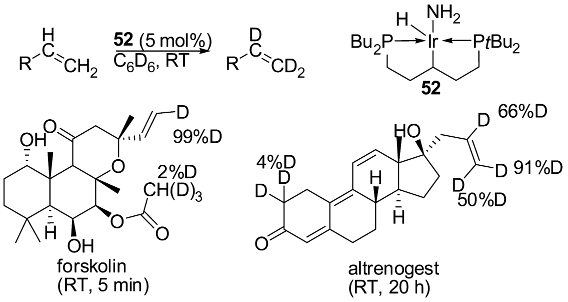
Coordination flexibility in $PC(sp^3)P$ pincer complexes has not found yet as many practical catalytic applications as $N(sp^3)$-based systems, however, some interesting developments in the field must be spotted.

Interesting aromatization of *cis*-1,3-bis(di-*t*-butylphosphinito)cyclohexane ligand accompanied by extrusion of 3 equivalents of dihydrogen was discovered by Wendt and

Scheme 20. Dehydrogenative Aromatization of the Ligand Backbone Proceeding via Ligand-Metal Cooperation



Scheme 21. Regio- and Chemoselective Isotopic Labeling of Olefins Catalyzed by the All-Aliphatic Ir(III) Amido Hydride Pincer Complexes



co-workers upon attempted synthesis of the corresponding Ir PC(sp^3)P complex **50**.[97] Arguably, this unusual transformation may proceed either via iridium-catalyzed acceptorless dehydrogenation of cyclohexane ligand into the known aromatic POCOP (**50**) followed its facile metalation, or, alternatively, via the formation of the hypothetical POC(sp^3)OP Ir(III) hydride species (**50**) that undergoes α-elimination of hydrogen, followed by α,β-hydride shift and double bond isomerization (Scheme 20).

Zhou and Hartwig utilized all-aliphatic Ir(III) amido hydride complex **52**[98] to design a very efficient catalyst for H/D exchange at vinyl groups that operates under very mild conditions and without isomerization of the double bonds.[99] As was demonstrated, **52** induces very fast (minutes to hours) room temperature deuteration of internal and terminal double bonds with absolute regioselectivity. In addition to absolute regioselectivity, the method is highlighted by excellent functional group compatibility. For example, nitriles, primary amines, alcohols, esters and ketones can be present, although acidic α-hydrogens to the electron-withdrawing groups may suffer from partial exchange. Aliphatic hydrogens do not react under the developed reaction conditions. This regio- and chemoselectivity allowed efficient isotopic labeling of some biologically active molecules and natural products (Scheme 21).

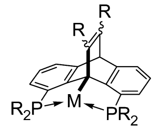
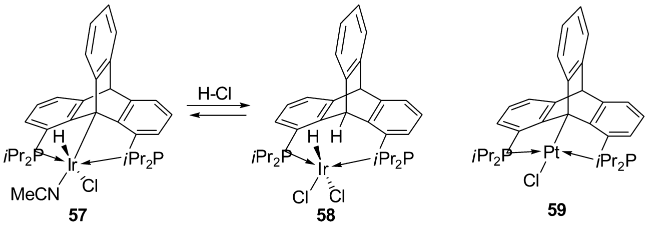
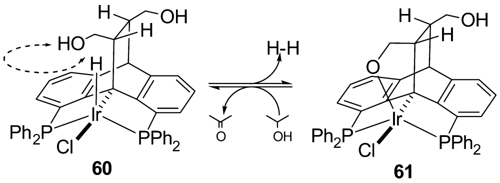


Figure 6. Schematic representation of the dibenzobarrelene-based PC(sp^3)P pincer complexes developed by Gelman and co-workers.

Scheme 23. Heterolytic Addition of HCl Across the Metal−C(sp^3) Bond in Ir(III) and Pt(II) PC(sp^3)P Pincer Complexes

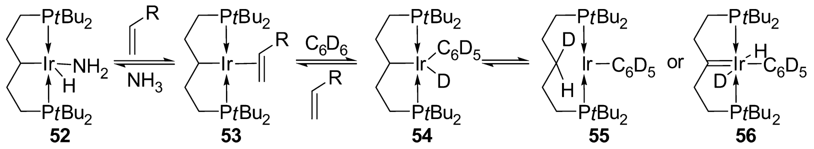


Scheme 24. Ligand-Metal Cooperation toward Acceptorless Dehydrogenation of Alcohols by the Dibenzobarrelene-Based Ir(III) PC(sp^3)P Pincer Complexes

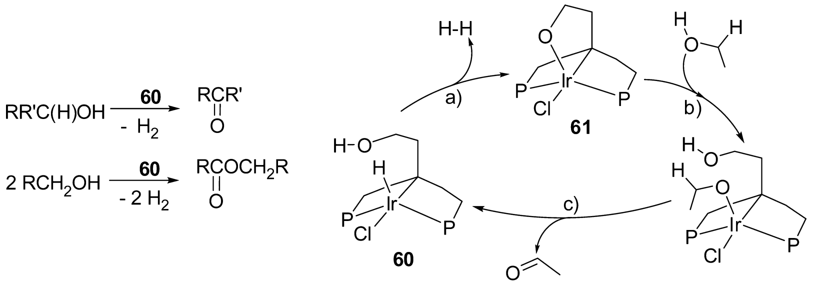


Aromatic pincer complexes were found practically inactive under the described conditions and, therefore, it is suggested the reaction is operated by a mechanism in which the methine position of the backbone acts as a shuttle. If so, the following mechanistic scheme may be suggested: after dissociation of olefin, the iridium(I) fragment (**53**) (generated by reductive elimination of NH$_3$ from **52**) undergoes oxidative addition of the aryl deuterium bond to form **54**. Subsequent reversible C-D reductive elimination involving the methine carbon center on

Scheme 22. Plausible Mechanism of Ir(III) PC(sp^3)P -Catalyzed H/D Exchange



Scheme 25. Plausible Mechanism of Ir(III) PC(sp^3)P -Catalyzed Acceptorless Dehydrogenation of Alcohols



the ligand could generate the aryl iridium(I) complex **55**. Alternatively, the complex resulting from the oxidative addition of the arene (**54**) could undergo reversible α-hydrogen elimination from the ligand backbone to give the iridium(III) carbene species **56** (Scheme 22). A parallel process with the vinylic C−H bonds would lead to incorporation of deuterium into the olefinic substrates.

More recently, Gelman and co-workers studied possible metal ligand-cooperation in dibenzobarrelene-based PC(sp^3)P pincer complexes (Figure 6).[88] A synthetic approach to such compounds is very modular as it is accomplished through the use of reliable Diels−Alder cycloaddition methodology that guarantees facile access to a readily modifiable platform and allows tailoring their steric and electronic properties.

Structural analysis of a series of different transition metal complexes bearing such ligands revealed a common structural feature: a strong deviation of the metal−C(sp^3) bond from the geometry characteristic of sp^3-hybridized atoms.[88,100−103] For example, in the vast majority of the structurally defined complexes the C−C(sp^3)−M angles (highlighted in Figure 6) range between 116 and 129° instead of the tetrahedral 109°. It has been suggested that this strong deformation may be reflected in a lability of the carbon−metal bond in the new three-dimensional PC(sp^3)Ps despite the stabilizing "pincer effect".

To check this hypothesis, possible heterolytic addition of HCl across the metal−C(sp^3) bond in iridium (**57**) and platinum (**59**) complexes has been examined. Theoretical DFT calculations predicted that protonation of **57** by HCl is nearly thermoneutral, while protonation of **59** is moderately exergonic (DG_{rx} = 0.5 kcal/mol for Ir, −4.3 kcal/mol for Pt).[104]

Indeed, it was found that treatment of **57** with gaseous HCl in $CDCl_3$ over 18 h at room temperature results in a gradual transformation of the starting material into the chelate complex **58** in which the metal center is surrounded with mutually trans coordinated phosphine and chloride ligands, while the *transoid* hydride and the methine proton complete the almost perfect pseudooctahedral geometry. The last proton was found in the difference Fourier map and refined. Although the location determined by X-ray analysis is not particularly accurate, the H1···Ir and Ir···C1 contacts are very short (1.89 and 2.696 Å, respectively), and, therefore, are definitely defined as agostic. A similar transformation, albeit in a less selective fashion, was observed for **59**, proving that activation of small molecules may be achieved via 1,2-cleavage of the carbon−metal bond in PCP complexes possessing an appropriate topology. The reversed process of the regeneration of the carbon−metal bond via elimination of H−Cl is not surprising and is routinely used for the preparation of pincer complexes (Scheme 23).

Another mode of metal−ligand cooperation in the dibenzobarrelene-based PC(sp^3)P pincer complexes relies on their three-dimensionality. Molecular complexity of these systems was utilized for the design of multifunctional catalytic systems.[105] For example, iridium hydride pincer complex **60** possessing an acidic side arm, that is capable of interacting with the catalytic site, was synthesized. Initial investigation of its properties revealed that **60** is moderately stable in solution and gradually, but selectively, transforms into **61** upon extrusion of molecular hydrogen. Organometallic product **61** was identified as the arm-closed species, which features strongly distorted trigonal bipyramidal geometry around the iridium center (Scheme 24). More interestingly, addition of isopropyl alcohol to the resulting solution of **61** recovers the parent **60**.

This simple stoichiometric experiment points to a hypothetical catalytic cycle through which the acceptorless dehydrogenation of alcohols may proceed (Scheme 25): (a) H_2-forming step, leading to the formation of the arm-closed iridium species **61**; (b) ligand exchange step, leading to the arm-open iridium alkoxide species; and (c) regeneration of the Ir−H catalyst **60** by β-hydride elimination with subsequent formation of the oxidized product.

Indeed, this transformation was realized under catalytic conditions: 0.1 mol % of **60** or **61** in the presence of 5 mol % of Cs_2CO_3 dehydrogenate secondary alcohols into ketones showing TONs of 1100, while acceptorless dehydrogenation of primary alcohols leads to the formation of the corresponding esters and lactones. Mechanistically, formation of these Tischenko products can be rationalized, as in previously published works,[56] by tandem dehydrogenation/hemiacetalyzation/dehydrogenation reactions. This scenario may explain why some electron-rich substrates produce mixtures of the corresponding ester and aldehyde upon full conversion of the starting alcohols: obviously, electron-releasing substituents must have the opposite effects on the rates of the subsequent dehydrogenation and acetalyzation.

4. CONCLUDING REMARKS

In this Article, recent developments in the chemistry of PN(sp^3)P, PN(sp^3)N and PC(sp^3)P pincer ligands have been described. This perspective focused on "cooperating" ligand systems capable of reversible structural changes in the ligand backbone that control their coordination mode and coordination properties.

Different ligand−metal cooperation mechanisms have been disclosed. Metal-amide/metal-amine, aromatization/dearomatization and metal-amide/metal-enamide switches are characteristic of N(sp^3)-based systems, while interplay between C(sp^3)-metalated and carbene/olefin chelate species via reversible α-/β-hydride migration, and metal−ligand side arm cooperation add to coordination flexibility of the PC(sp^3)P pincer ligands.

Noteworthy, the coordination versatility of the carbometalated PC(sp^3)P systems makes them particularly attractive for further developments, because, by comparison, metal centers in prototypal aromatic PCP pincer complexes, are often insufficiently reactive owing to the very rigid coordination by the anionic tridentate ligands. Thus, ligand−metal cooperation may significantly enrich their chemistry and, even more important, further enhance their potential in catalysis. Moreover, the above-mentioned ligand−metal cooperation patterns have already found notable applications for the design of very efficient catalysts capable of nonoxidative (i.e., alternative to the conventional oxidative addition/reductive elimination sequence) activation and formation of polar and nonpolar bonds.

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Notes

The authors declare no competing financial interest.

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