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Hemilability of Hybrid Ligands and the Coordination Chemistry of Oxazoline-Based Systems

Pierre Braunstein* and Frédéric Naud*

Dedicated to Professor Henri B. Kagan on the occasion of his 70th birthday

Ligand design is becoming an increasingly important part of the synthetic activity in chemistry. This is of course because of the subtle control that ligands exert on the metal center to which they are coordinated. Ligands which contain significantly different chemical functionalities, such as hard and soft donors, are often called hybrid ligands and find increasing use in molecular chemistry. Although the interplay between electronic and steric properties has long been recognized as essential in determining the chemical or physical properties of a complex, predictions remain very difficult, not only because of the considerable diversity encountered within the Periodic Table—different metal centers will behave differently towards the same ligand and different ligands can completely modify the chemistry of a given metal—but also because of the small energy differences involved. New systems may—even through serendipity—allow the emergence of useful concepts that can gain general acceptance and help design molecular structures orientated towards a given property. The concept of ligand hemilability, which finds numerous illustrations with hybrid ligands, has gained increased acceptance and been found to be very useful in explaining the properties of metal complexes and in designing new systems for molecular activation, homogeneous catalysis, functional materials, or small-molecule sensing. In the field of homogeneous enantioselective catalysis, in which steric and/or electronic control of a metal-mediated process must occur in such a way that one stereoisomer is preferentially formed, ligands containing one or more chiral oxazoline units have been found to be very valuable for a wide range of metal-catalyzed reactions. The incorporation of oxazoline moieties in multifunctional ligands of increasing complexity makes such ligands good candidates to display hemilabile properties, which until recently, had not been documented in oxazoline chemistry. Herein, we briefly recall the definition and scope of hemilabile ligands, present the main classes of ligands containing one or more oxazoline moieties, with an emphasis on hybrid ligands, and finally explain why the combination of these two facets of ligand design appears particularly promising.

Keywords: coordination chemistry · homogeneous catalysis · hybrid ligands · ligand design · sensors

1. Introduction

Recent years have witnessed considerable and increasingly fruitful activity in the two, originally independent, research areas of coordination and organometallic chemistry that we would like to combine and examine herein: the hemilability of polydentate hybrid ligands when coordinated to transition metals and the properties of complexes containing oxazoline-based ligands. The reasons for studying hemilabile ligands derives from their ability to provide open coordination sites at the metal during reaction that are "masked" in the ground-state structure, and to stabilize reactive intermediates. Originally interest centered on reversible coordination, stoichiometric and catalytic activation, and transport of small molecules. Thus, metal complexes containing hemilabile ligands have been found to be catalytically active in a range of reactions, including hydrogenation, carbonylation or its reverse, hydroformylation of olefins and epoxides, allylation, epoxydation, olefin (co)dimerization and copolymerization and ring-opening metathesis polymerization (ROMP).[1, 2] More recently, the activation of small molecules through reversible coordination to a metal center has been directed towards small-molecule sensing, in particular of CO.[3, 4] The small energy differences, often in the order of 50 kJ mol^{-1}, involved in the dynamic processes which form the basis of hemilability, explains the difficulty, but also the chal-

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lenge, in designing systems endowed with specific properties. The concepts and analytical tools developed over the years in the context of molecular coordination and organometallic chemistry have stimulated new approaches in other disciplines, notably in heterogeneous catalysis, surface sciences, and bioinorganic chemistry. Although such aspects will not be discussed here, it is interesting to note that some metalloenzymes operate through a mechanism of activation similar to hemilability; for example, the opening of a zinc–cysteine bond allowing coordination of a water molecule occurs when going from an inactive to an active form of a metalloenzyme.[5, 6] Furthermore, doubly functionalized porphyrins with imidazole-containing "arms" reversibly bind O_2 or CO through a hemilabile mechanism involving displacement of one imidazole arm.[7] Hybrid ligands which contain significantly different chemical donor functions, such as hard and soft donor atoms or groups, find increasing use in molecular chemistry, largely because of their aptitude to display hemilabile behavior in the coordination sphere of a metal complex.

Oxazoline-based ligands have aroused considerable interest since their first use, in 1986, for asymmetric catalysis. They were used in the monophenylation of diols[8, 9] and the hydrosilylation of ketones.[10–12] The metal complexes used in asymmetric catalysis should contain a chiral ligand which sterically and/or electronically controls a metal-mediated process in such a way that one stereoisomer is preferentially formed.[13] Ligands containing one or more chiral oxazoline units have been found very useful for a wide range of metal-catalyzed reactions.

Herein, we would first like to briefly recall the definition and scope of hemilabile ligands and examine some extensions of this concept, then present the main classes of ligands containing one or more oxazoline moieties, and finally explain why the combination of these two categories of ligands appears particularly promising by summarizing some of our own recent results in this area.

2. Hemilabile Ligands

The transition metal coordination chemistry of hemilabile ligands has been recently presented in an excellent review article.[1] We shall therefore focus here only on those aspects of hemilability that are relevant to the present discussion. The term "hemilabile" ligand was introduced about 20 years ago[14] although the phenomenon itself had been observed earlier.[15] The concept of ligand hemilability has since been used to encompass various situations; it is therefore necessary to briefly summarize what it now commonly covers.

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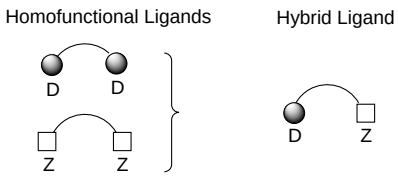
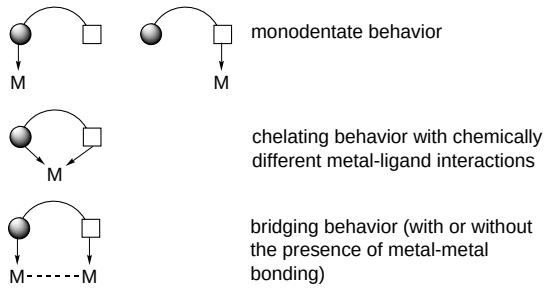
2.1. Definitions

Hybrid ligands are polydentate ligands that contain at least two different types of chemical functionality capable of binding to metal centers (Scheme 1). These functionalities



Scheme 1. A hybrid ligand contains at least two chemically different donor functions.

are often chosen to be very different from each other to increase the differentiation between their resulting interactions with the metal center(s) and thereby their chemoselectivity (Scheme 2). In turn, these functionalities will



Scheme 2. Bonding modes of hybrid ligands.

influence the bonding/reactivity of the other ligands bound to the metal, in particular those in the *trans* position. Combining hard and soft donors in the same ligand—often called a hybrid or heteroditopic ligand[2]—has represented one of the greatest endeavors, the hope being that different and contrasting chemistries could be associated within the same molecule, thus leading to novel and unprecedented properties for the resulting metal complexes.

An essential feature of hemilabile ligands is to have at least one substitutionally labile donor function Z while the other donor group(s) D remain firmly bound to the metal center(s). They were first encountered in mononuclear complexes where numerous examples have now been identified, but the concept of hemilability can easily be extended to dinuclear complexes,[16] and metal clusters[17, 18] where the labile coordination site does not need be at the metal ligated by the strong donor D but could be at an adjacent metal site (Scheme 2). The lability which leads to selective breaking of the Z→metal interaction in a mononuclear, dinuclear, or cluster complex may occur under different circumstances (Scheme 3). Type I corresponds to the spontaneous "opening" of the $\widehat{DZ}$ chelate (mononuclear system) or bridge (di- or polynuclear system), type II to the intramolecular competition with another donor function and type III to the coordination of an external reagent. The latter obviously applies equally to dinuclear or cluster complexes, for simplicity these have not been represented in Scheme 3. These various possibilities will be detailed in Section 2.2.

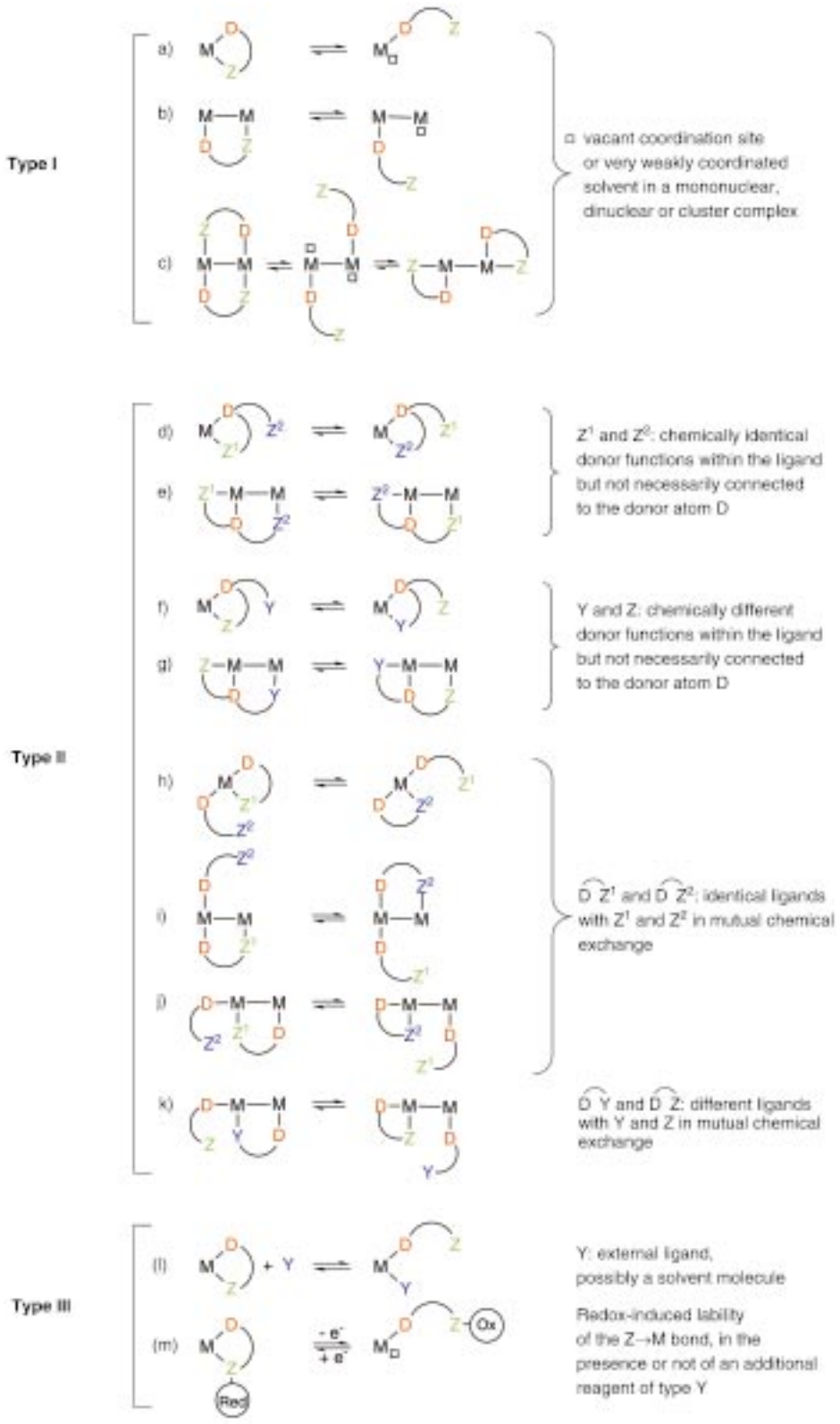
Although symmetrical, homofunctional bidentate ligands such as $Ph_2PCH_2PPh_2$ or $Ph_2PCH_2CH_2PPh_2$ may also change their coordination mode from bridging or chelating to monodentate or vice versa, such systems should not be categorized as hemilabile ligands since the resulting metal–donor interactions are not intrinsically different, in contrast to the situations in Scheme 2. If these donor groups behave differently, this will be the result of the presence at the metal center of other chemically different ligands, for example in a position *trans* to the metal–donor interaction concerned.

We suggest that another essential criterion to consider before assigning hemilabile character to a ligand is the reversibility of the formation/displacement of the Z→metal interaction. Although this may appear somewhat restrictive since in an irreversible "opening" of a chelating ligand $\widehat{DZ}$ to give a $\widehat{ZD}$→M monodentate system, "half" ("hemi") of the ligand was indeed labile. Our limitation emphasizes the importance of having relatively small energy differences between the "open" and "closed" situations, which should be an important property of hemilabile ligands. The irreversible "opening" or "closing" of a chelate with or without participation of an external reagent is of course a sign of reactivity, but not of hemilability in the sense that we wish to use herein. This is like comparing a wind–screen wiper with a single cleaning sweep!

2.2. Occurence of Hemilability

After the opening of the Z→metal bond has taken place, recoordination of the Z functionality may restore the original situation, as typically observed in fluxional processes (e.g. in Scheme 3a and b), or in the reversible binding of a small molecule (Scheme 3 part l). Recoordination may also take place after a chemical transformation has occurred within the metal coordination sphere. Thus for example, decoordination of the Z functionality may allow—or result from—fixation of a small molecule like CO to a metal alkyl complex which may lead to migratory insertion and formation of an acyl ligand. This transformation liberates a coordination site to which the function Z can coordinate. Alternatively, the migratory–insertion step may be promoted by the entropically favored tendency of the $\widehat{DZ}$ ligand to chelate the metal center (Scheme 4). Note that a possible consequence of the chelating ability of the $\widehat{DZ}$ ligand is to force the newly formed ligand to adopt a position in the final complex different from that expected on the basis of the mechanism of the elementary step concerned, for example, CO insertion versus alkyl migration (Scheme 4). Such an example will be described in Section 2.2.1.

As indicated in Section 2.1, the presence of a hemilabile ligand in a complex may significantly influence the reactivity of incoming substrates and promote transformations that would not otherwise occur. Such an example is presented in Scheme 5. Whereas the complexes *trans*,*cis*,*cis*-[$RuCl_2(\eta^2$-P,O)$_2$] (P,O = iPr$_2$PCH$_2$CH$_2$OMe, iPr$_2$PCH$_2$C(O)OMe) react with HC≡CPh to give the vinylidene complexes [$RuCl_2(\eta^1$-*P*-P,O)(η^2-P,O)(=C=CHPh)] in which one of the P,O chelates



Scheme 3. Various hemilabile situations. Type III extends to dinuclear or cluster complexes.

has opened to provide a coordination site for the vinylidene unit, related Ru^{II} complexes with the ligand P*i*Pr_3 instead of P,O do not perform this isomerization.[19] The rapid intramolecular exchange in the chelating behavior of the two P,O ligands (Scheme 3h) is characterized by a free enthalpy of activation of 41 and 53 kJ mol^{-1}, for the ether and ester phosphanes, respectively.

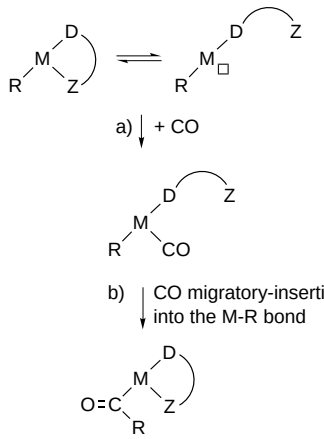
It was recently suggested that the cycloreversion process of **1** that leads to complexes **3** and **4** (Scheme 6) occurs via intermediate **2**, with a decoordinated phosphane sidearm.[20a] Recoordination of the phosphane would liberate either CO or diphenylethyne. This is consistent with the observation that **3** does not undergo a thermal ligand-exchange process with diphenylethyne to give **4**.

Numerous other examples have been reported in recent years of cyclopentadienyl-based hemilabile ligands where, for example, an olefin, amine, phosphane, ether, or thioether function tethered to the ring reversibly coordinates to the metal center in the presence of an external substrate (Scheme 3l).[1, 20b] This often leads to dramatic rate enhancements in catalytic reactions, as exemplified in ethylene polymerization with Cr, Ti, and rare-earth metal complexes.[21, 22]

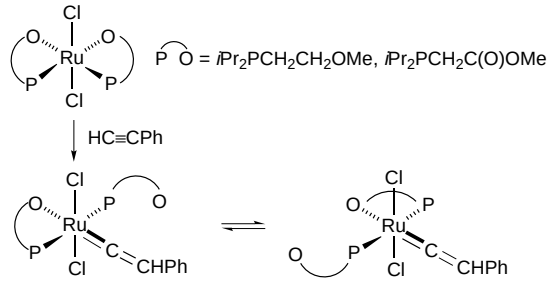
Other types of labile donor functions that are often involved in hemilabile behavior are E–H groups which can form agostic bonds to the central metal atom, in most cases E is carbon. This type of bonding plays a central role in olefin polymerization (Scheme 7) where coordination of the monomer is facilitated by the easy opening of the β-agostic bond involving the growing alkyl chain.[23] An early example was reported for half-sandwich Co^{II} complexes.[24, 25]

The sequence of events shown in Scheme 4 is typical of that found in numerous catalytic cycles, this further emphasizes the significance of hemilabile ligands in homogeneous or supported catalysis where the "opening" step allows coordination, activation, and transformation of a substrate molecule at the metal site while the "closing" step leads to stabilization of the metal coordination sphere and favors elimination of the product.[1, 2, 26–28]

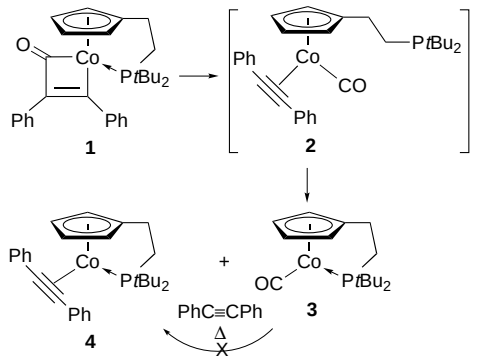
Furthermore, the "opening and closing" mechanism is not restricted to the precursor or product of a reaction but may also occur in the intermediate species. Thus, it was shown by



Scheme 4. The steps of CO coordination a) can initiate the "opening" of the chelate ring or take place on the vacant site created by spontaneous "opening". The CO migratory-insertion step b) may occur spontaneously and be followed by "closing" of the chelate or, alternatively, may be triggered by it.

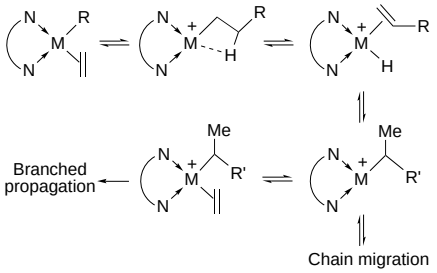


Scheme 5. Reactions with organic substrates may be promoted by hemilabile P,O ligands. Whereas [RuHCl(CO)($P i Pr_3$)$_2$], for example, does not convert HC≡CPh into the corresponding vinylidene complex [Ru=C=CHPh], this transformation is possible when ether–phosphane or ester–phosphane ligands are used.[19]



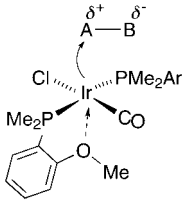
Scheme 6. Cycloreversion reaction of the cobaltacyclobutenone chelate complex **1** leading to complexes **3** and **4** via intermediate **2** with a decoordinated phosphane sidearm.[20]

Shaw et al. that the oxidative addition of MeI to Ir^{I} complexes of the type [IrCl(CO)(PR_3)$_2$] was about 100 times faster with the phosphane ligand PMe_2(*o*-$MeOC_6H_4$) than with PMe_2Ph or PMe_2(*p*-$MeOC_6H_4$).[29] It was suggested that the *ortho*-methoxy group can temporarily coordinate to Ir^{I}, thus making the metal center more electron-rich, thereby facilitating the oxidative-addition reaction ("anchimeric assistance"; Scheme 8). An electronic effect acting through the phosphorus was ruled out for PMe_2(*o*-$MeOC_6H_4$) by comparison with



Scheme 7. Involvement of β-agostic C–H···M interactions in the mechanism of ethylene polymerization with Ni and Pd α-diimine complexes.[23]

PMe_2(*p*-$MeOC_6H_4$) since electronic effects should be more pronounced with the latter ligand. Interestingly, in the ground-state structure of the precursor Ir^{I} complex and the Ir^{III} product, the PMe_2(*o*-$MeOC_6H_4$) ligand was exclusively P-bound to the metal center.



Scheme 8. Even temporary chelation of the hybrid ligand is sufficient to increase the electron density at the metal center and enhance its reactivity ("anchimeric assistance").[29]

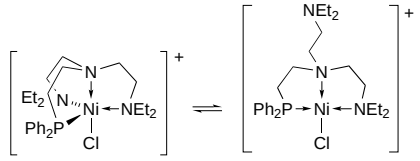
In organolithium chemistry a hemilabile amino ether ligand has been shown to impart, among other things, dramatic rate accelerations in lithium diisopropylamide (LDA) mediated dehydrohalogenations or α- and β-eliminations of epoxides.[30, 31] This acceleration was related to the behavior of the difunctional ligand which forms a weakly coordinated monodentate linkage in the reactant but a strongly coordinated bidentate linkage in the transition structure which stabilizes this species.

Ligand hemilability has recently been used to control catalyst turnover frequency and enantioselectivity in the alkylation of aldehydes.[32]

Let us now briefly examine the various categories of hemilabile behavior depicted in Scheme 3.

2.2.1. Type (I) Hemilability

The situations in Scheme 3a–c are typically encountered with metal centers which have easily variable coordination numbers: $3 \rightleftharpoons 2$ (e.g. d^{10} ML_3/ML_2 complexes), $4 \rightleftharpoons 3$ (e.g. d^8 ML_4/ML_3 complexes), $5 \rightleftharpoons 4$ (e.g. d^8 ML_5/ML_4 complexes), and $6 \rightleftharpoons 5$ (e.g. d^6 ML_6/ML_5 complexes). Ligands other than bidentate ones can of course give rise to such hemilabile behavior and examples of the reversible change in coordination number from 5 to 4 and from 6 to 5 are shown in Equations (1)[33] and (2),[34] respectively.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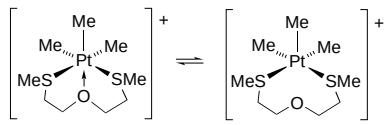
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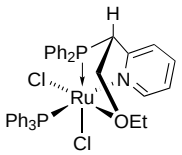
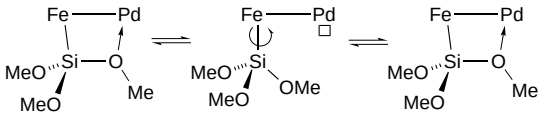


5

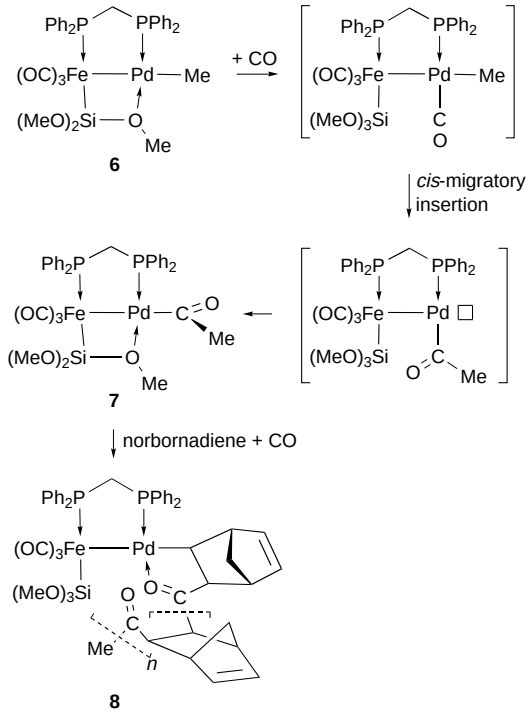
A further example is provided by the Ru^{II} complex **5** which contains an optically active P,N,O ligand. The hemilabile behavior was detected by variable-temperature NMR spectroscopy.[35] Quite surprisingly, it is the pyridyl ring that reversibly coordinates to the metal center and not the harder ether function. This could be explained by the higher *trans* influence of the PPh_3 ligand compared to that of the chloride ion.

Ligand hemilability in dimetallic complexes (Scheme 3b), is exemplified by the dynamic behavior of the bridging trimethoxysilyl ligand in a number of Fe–Pd complexes. The equivalence of the OMe protons on the NMR time scale was explained by rapid "rotation" of the $Si(OMe)_3$ ligand about the Fe–Si axis.[16, 36] Below coalescence temperature the complex was static (Scheme 9).



Scheme 9. Formation and dynamic behavior of a η^2-μ_2-Si-O interaction (the ancillary ligands are omitted for clarity).

The hemilability of the trimethoxysilyl ligand results in the existence of a "masked" coordination site at the Pd center in complex **6** accessible to small molecules that may coordinate, sometimes reversibly, to the metal center (Scheme 10). If the spontaneous opening of the O→Pd bond had not been detected in solution by variable-temperature NMR spectroscopy, one could argue that reversible coordination of a small molecule would actually correspond to a situation of type (III) where an external reagent triggers the opening of the O→Pd bond. The readily available coordination site at the Pd center has been exploited for the coordination of small molecules like isonitriles, CO, or olefins and has led to the formation of poly(iminomethylenes)[37] and polyketones resulting from the alternating insertion of CO and olefins into a palladium–carbon bond (Scheme 10).[37, 38]



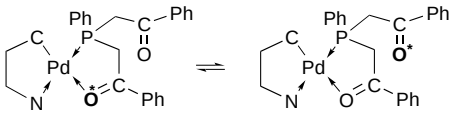
Scheme 10. "Opening" and "closing" steps of the η^2-μ_2-Si-O bridge during sequential CO/olefin insertion.

By design, the CO molecule has to occupy a coordination site *cis* to the alkyl group in such complexes, which facilitates the migratory-insertion step. It was shown by trapping experiments that the resulting acyl ligand is originally *trans* to the PPh_2 group and then flips to a position *trans* to the metal–metal bond in **7**.[16, 39] This isomerization allows (or was induced by) recoordination of the methoxy oxygen atom to the palladium center. Insertion of an olefin into the metal–acyl bond may then occur. This reaction results in the reopening of the SiO→Pd bond, driven by the chelation of the carbonyl group and leading to a five-membered chelate which is preferred over the four-membered μ_2-η^2-Si-O bridge. Since CO insertion into the metal–alkyl bond is faster than olefin insertion, a new metal–acyl bond forms which restores a situation similar to that in **7**. However, CO insertion into a metal–acyl bond is thermodynamically unfavorable, so an olefin molecule inserts into the metal–acyl bond to give a metal–alkyl bond, into which a CO inserts, and so on. This leads to the growth of a perfectly alternating polyketone chain in **8**. Such polyketones are of considerable current interest,[40–48] as demonstrated with the commercial developments of Carilon[49, 50] by Shell and Ketonex[51, 52] by BP Chemicals.[53] The lability of the SiO→Pd bond in related Fe–Pd complexes has also been invoked to explain the considerable catalytic activity of some of these dimetallic complexes for the dehydrogenative coupling of stannanes.[54, 55]

In Scheme 3c two bridging hybrid ligands convert into two chelates as a result of the spontaneous opening of the Z→M bonds.

2.2.2. Type (II) Hemilability

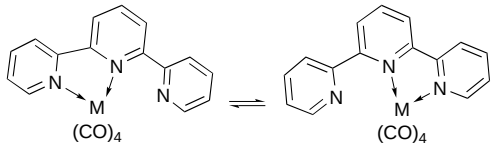
In the following examples, intramolecular competition between donor functions is responsible for ligand hemilability. In Scheme 3d, the hemilability of the chelate is associated with an intramolecular fluxional process that may be frozen at lower temperature.[56–59] An example is given in Equation (3) where above the coalescence temperature the two carbonyl



(3)

groups of the phosphane ligand bind alternately to the Pd center.[60, 61] The mutual exchange of the two carbonyl functions is facilitated by the proximity of the uncoordinated one while the phosphorus donor serves as an anchor.

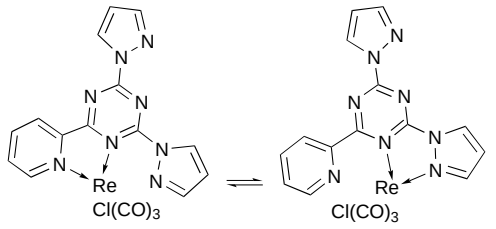
Another example of this type of fluxional process is provided by the pyridine-group exchange observed with the terpyridine ligand in tetracarbonyl complexes $[M(CO)_4$-(terpy-*N*,*N*)] (M = Mo, W) [Eq. (4)].[62] The latter dynamic behavior has been termed a "tick-tock twist".



(4)

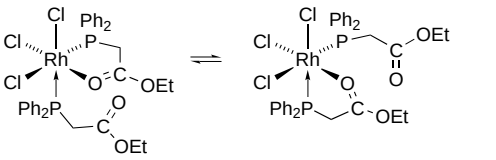
Scheme 3e shows an exchange between two chemically identical arms of a hybrid ligand that may act as a chelate or a bridge between two metal centers.

The reactions in Scheme 3f and 3g require a suitable trifunctional ligand and have therefore been less frequently studied or observed.[63] An example is given in Equation (5)[64, 65] and a further one can be found later [Eq. (18)].[66]



(5)

The reaction in Scheme 3h involves two independent but identical ligands in mutual intramolecular exchange owing to the lability of their Z function. This phenomenon was recognized at a very early stage in studies on hybrid ligands and an example is illustrated in Equation (6).[15]

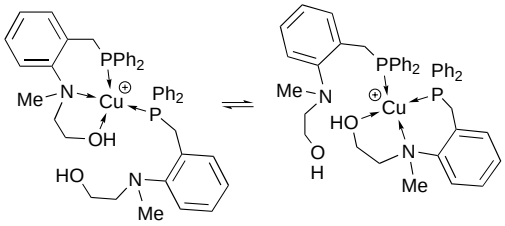


(6)

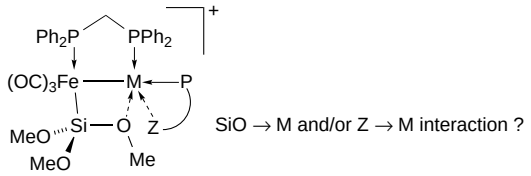
Most systems in this category involve two or more hemilabile hybrid ligands interacting with one metal center.[27, 67, 68] The resulting dynamic situation has often been described in terms of a "wind-screen wiper" mechanism.[69] A recent example involving a P,N,O tridentate ligand and the complexation of a Cu^+ ion is shown in Equation (7).[70]

In Scheme 3i and 3j the reactions follow a similar pattern but involve two different metal centers.

The situation in Scheme 3k has been examined recently for two chemically different hemilabile ligands (with the donor atoms D being Si and P, respectively) which carry different oxygen functionalities able to compete for the same coordination site, as shown in Scheme 11.[71]



(7)

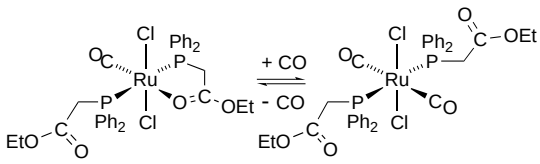


Scheme 11. Possible competition between labile donor groups for a coordination site at M. $\overset{\frown}{P\,Z}$ = various hybrid phosphane ligands; M = Pd or Pt.

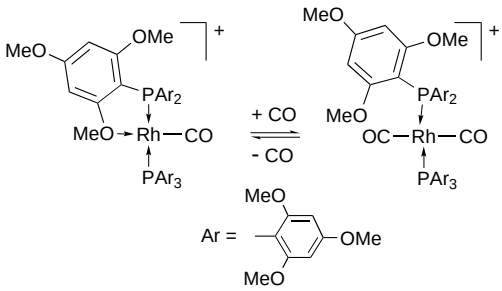
2.2.3. Type (III) Hemilability

In these examples, an external reagent Y, which can be electrons in the case of redox reactions, is involved in the breaking of the labile ligand–metal bond. The reaction in Scheme 3 part l covers a range of possibilities depending on the nature of Y. Systems where the external reagent Y is a small molecule, such as CO, which, depending on its partial pressure can reversibly coordinate to the metal, are illustrated in Equations (8)–(10).[3, 4, 26, 72, 73]

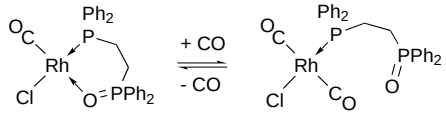
The Rh system shown in Equation (10) was used as a catalyst in methanol carbonylation.[26] It is interesting that the analogous P,S ligand did not show any hemilabile behavior but gave rise to enhanced catalysis, showing that other effects are at work.[74–76] Further reactions of the kind shown in Sche-



(8)

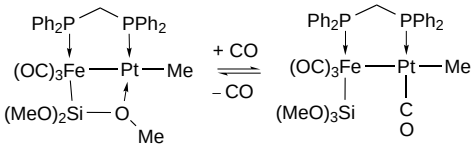


(9)

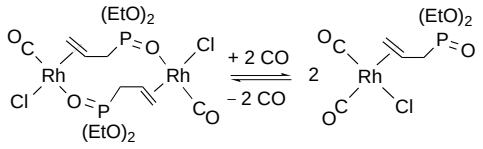


(10)

me 31 come from the dimetallic chemistry of hemilabile $Si(OMe)_3$ ligands[77] or from dinuclear complexes with bridging allylphosphonate ligands[78, 79] [Eq. (11) and (12)].

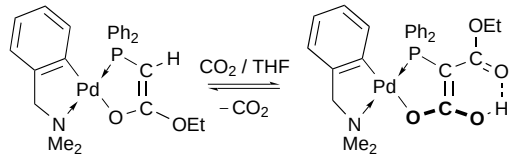


(11)



(12)

Finally, the possibility to promote an "opening and closing" type situation from a nondynamic chelate by the reversible reaction of the metal complex with an external reagent is worth mentioning. This is illustrated in Equation (13) by a



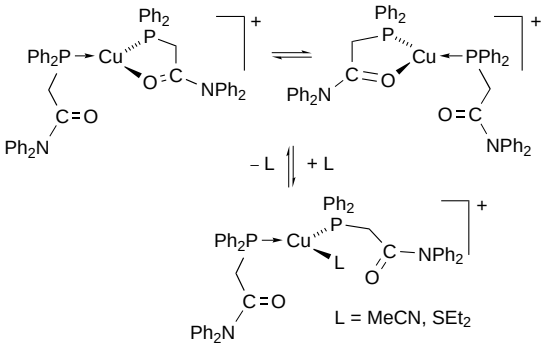
(13)

palladium complex which reversibly binds CO_2, under ambient conditions, with the formation of a C–C bond.[80] The phosphino ester enolate ligand in the precursor acts as a three-electron donor and coordinates through the P and O atoms to form a stabile chelate ring. However, after incorporation of CO_2, a new P,O chelate is formed in which the O–Pd bond is reversibly cleaved when CO_2 is eliminated. This restores the original O–Pd bond. Therefore, the reversible opening of the O–Pd bond is entirely because of the external reagent, although the chemical nature of this oxygen function changes during the reaction.

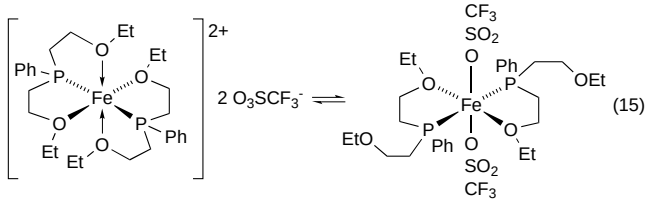
The reversible uptake of small molecules (e.g. CO, CO_2, SO_2) may be used as a means to "detect" them in the gas phase and can be applied in molecular sensors.[3, 4, 28, 81, 82] Thus, for example, the Rh^I phosphane–ether complex in Equation (9) was incorporated into thin films and shown by optical-based sensing to selectively and reversibly coordinate CO in the presence of O_2, CO_2, N_2, and H_2 under ambient conditions.[3, 4]

A solvent molecule may also displace the kinetically more labile Z→M bond, as shown with the Cu^I complexes in Equation (14).[83] In the absence of a donor solvent, only hemilabile behavior of the type shown in Scheme 3h is observed. By exploiting their spectroscopic properties, Ru^{II} bipyridyl complexes containing a hemilabile phosphane ether ligand have been used as sensors for molecules such as DMSO, MeCN, or SMe_2.[84]

Furthermore, Y may also represent a potentially coordinating counter ion that can compete with a donor function and displace it reversibly from the metal center. This is exemplified by the displacement of the oxygen arm of a P,O,O ligand [Eq. (15)][85] and of a P,P,O ligand in [Eq. (16)].[86]



(14)



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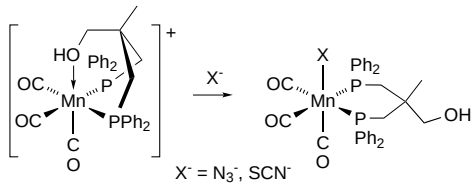
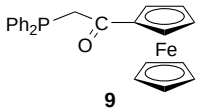


(16)

Bischelated P,N aminophosphane Pt^{II} complexes that exhibit in vitro activity against cisplatin-resistant tumor cells readily attack the DNA base thymine through a chelate ring-opening mechanism. It was shown that the latter can be controlled by the substituents on the N atom, the size of the chelate ring, the pH, and the concentration of an external reagent such as the Cl^- ion.[87]

Finally, functional ligands with a redox-active center may exhibit a hemilabile behavior of the type shown in Scheme 3h, as in Cu^I complexes with the ferrocenyl keto-phosphane ligand $[Ph_2PCH_2C(O)Fc]$ **9** (Fc = ferrocenyl),[79] or an electron-transfer induced hemilability of the type in Scheme 3m, as encountered in a recently developed class of so-called "redox switchable" ligands [Eq. (17)].[88]



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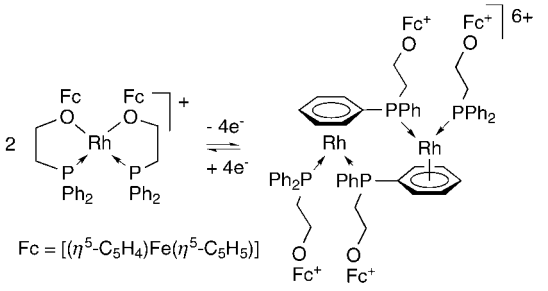


(17)

Potential applications of redox-switchable hemilabile ligands include the development of new catalysts the reactivity of which may be tuned by the redox active centers, the preparation of electroactive films for metal complexation, and

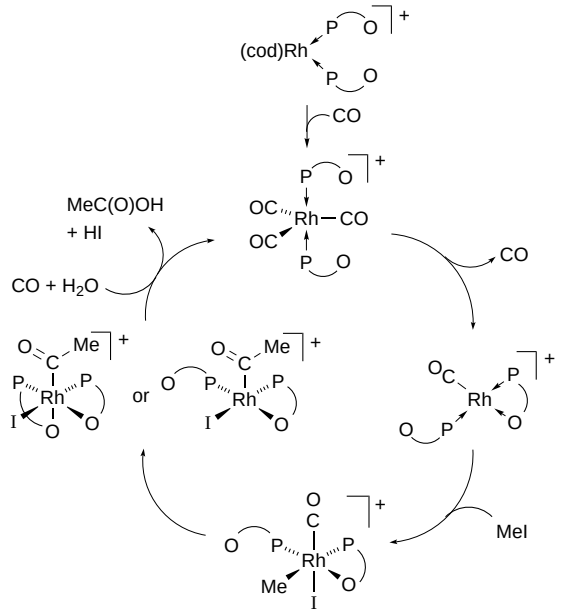
the synthesis of novel materials for molecule separation technologies.[1, 88, 89]

Considering the ubiquitous role of phosphorus-based ligands in coordination and organometallic chemistry, it is not surprising that the most investigated class of hemilabile ligands is that of functional phosphanes.

2.3. Hemilabile Functional Phosphanes

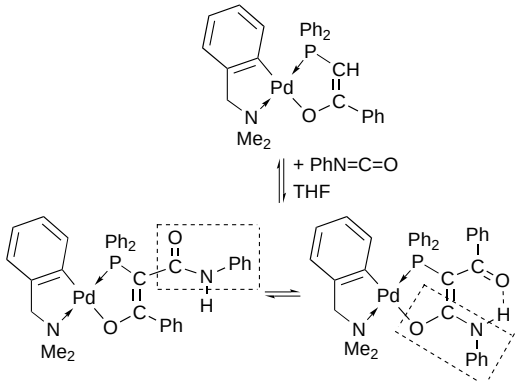
Endowed with soft and hard donor groups, phosphorus–oxygen and phosphorus–nitrogen based ligands represent the most studied class of functional phosphanes and many such examples have been presented in the previous section. The oxygen functional groups associated with the phosphorus donor come from alcohol, ether, ketone, ester, amide, and phosphane oxide or phosphonate groups.[1, 2, 26, 27, 43, 78, 90–94] Although these various functions will impart significant changes in the coordination properties and hemilability of the corresponding P,O ligands, it is generally observed that phosphorus–oxygen ligands are the most weakly chelating type of ligand. It is therefore not surprising that their complexes have been utilized in homogeneous and supported catalysis (by anchoring onto solid supports or sol–gel processing),[28] where temporary protection and facile generation of vacant, reactive sites at the metal centers constitute a prerequisite. Successful catalysis was observed in reactions such as the carbonylation of methanol into acetic acid and methylacetate (Co, Rh), the hydrocarbonylation of methanol into acetaldehyde using synthesis gas (Co, Rh), hydrovinylation (Ni), hydrogenation of aldehydes and ROMP (Ru), hydrogenation of (prochiral) alkenes and alkynes (Rh), hydroformylation (Rh), and ethylene/CO copolymerization (Pd). An example of a catalytic cycle showing how the opening and closing mechanism involving P,O ligands facilitates the elementary steps involved (oxidative addition, methyl migration) is shown in Scheme 12 for ether–phosphane ligands such as $R_2PCH_2CH_2OMe$ (R = Ph, *n*Pr).[2]

A specific class of P,O ligands, the phosphino enolate and related types, has been shown to confer very interesting properties to their metal complexes. They can behave as spectator ligands as in organonickel(II) complexes which contain three-electron-donor anionic P,O chelates such as $[Ph_2PCH_2C(O)O]^-$ or $[Ph_2PCH{\cdots}C({\cdots}O)Ph]^-$ and which are efficient catalyst precursors for the highly selective oligomerization of ethylene into linear α-olefins, a reaction which forms the basis of the industrial Shell Higher Olefin Process (SHOP).[95–102] However, the postulated mechanism of this catalytic reaction does not imply hemilabile behavior of the P,O chelate but instead involves a hydrido nickel species of the type NiH(P,O) which is electronicaly unsaturated and allows the coordination and subsequent insertion of ethylene.[96, 97, 103] In palladium(II) chemistry such anionic P,O chelates may also behave as reactive moieties towards a wide range of electrophilic organic or inorganic reagents. In these cases, the covalent $Pd{-}O_{enolate}$ bond does not display any lability.[66, 80, 104–109] However, an example of a hemilabile phosphino enolate ligand was found in the course of reactivity



Scheme 12. Carbonylation of MeI catalyzed by ether–phosphane rhodium complexes.[2a]

studies on palladium(II) complexes with organic isocyanates which led to new multifunctional systems [Eq. (18)].[66] The hemilability of the new ligand corresponds to the situation in Scheme 3 f. It is noteworthy that a substitutionally inert



(18)

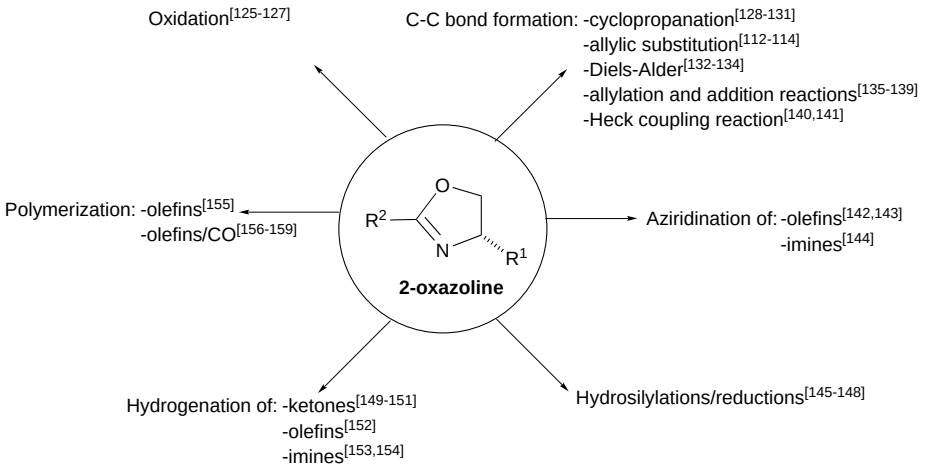
palladium–oxygen bond can acquire hemilabile character after appropriate chemical transformations. A related phenomenon was described above in Equation (13).

Amine and pyridine moieties are the most common donors associated with phosphorus–nitrogen ligands but amides, imines, or nitriles have also been used as the weakly coordinating end of P,N chelates.[110] These hybrid ligands often display hemilabile behavior but it is generally observed that the lability of the nitrogen moiety is lower than that of the oxygen moiety of P,O ligands. However, the beneficial effect of P,N ligands, for example, on the rhodium-catalyzed hydroformylation of olefins is documented.[111]

The dominant position of P,O and P,N donors in studies on hybrid and hemilabile ligands contrasts with the absence, to the best of our knowledge, of studies describing the dynamic behavior of phosphane-oxazoline ligands, which could in

principle behave as P,O or P,N donors. This is even more surprising when one considers the increasingly successful use of phosphane-oxazoline chelates in organometallic chemistry and homogeneous catalysis.[112–115]

We would now like to address this point and examine some of our own results on the coordination properties of tridentate phosphane-oxazoline ligands and analyze the conditions that lead to their hemilabile behavior.



Scheme 13. Applications of oxazoline-based ligands in homogeneous catalysis.

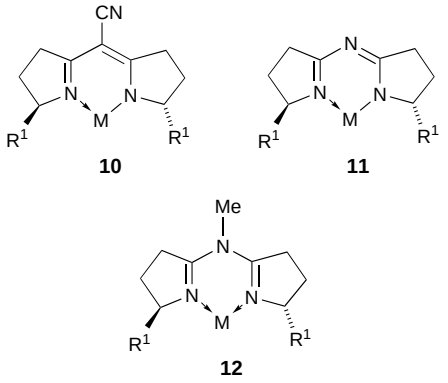
3. Oxazoline-Based Ligands

Metal-catalyzed asymmetric synthesis is a powerful tool since large amounts of optically active products can be synthesized using a small amount of optically active catalyst.[116–121] Most of these catalysts are metal complexes containing a chiral organic ligand which sterically and/or electronically controls a metal-mediated process in such a way that one stereoisomer is preferentially formed.[13]

It is only since 1986 that oxazoline-based ligands have been used in asymmetric catalysis, originally for the monophenylation of diols[8, 9] and later the hydrosilylation of ketones.[10–12] This initiated considerable research activity in the field and triggered the synthesis of numerous chiral ligands containing at least one oxazoline structural unit.[122–124] In a short space of time these ligands have been used successfully in many metal-catalyzed reactions. The stability of oxazolines towards hydrolysis and oxidation is a great advantage compared to phosphanes which are readily converted into phosphane oxides in reactions carried out under (slightly) oxidative conditions. The number of applications is steadily growing and a less than exhaustive list is given in Scheme 13.

Oxazoline units are expected to readily coordinate a metal center and they have indeed been shown to bind to a wide range of transition metals (Scheme 14).

The successful use of oxazoline-based ligands was paralleled by that of semicorrin ligands (see **10**–**12**),[123, 177] the first examples of which were also published in 1986.[178] The advantage of these ligands ist that the two stereogenic centers

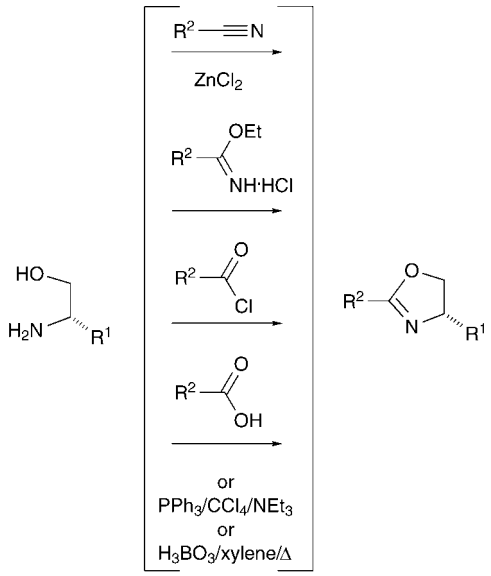


are held in close proximity to the metal and thus have a strong and direct influence on the stereochemical course of a metal-catalyzed process.

Semicorrin ligands were successfully applied to the copper-catalyzed cyclopropanation of olefins and the cobalt-catalyzed conjugate reduction of α,β-unsaturated carboxylic esters and amides. The related structure of oxazoline compared to semicorrin prompted several research groups to investigate the synthesis and the potential of bis(oxazoline) ligands in asymmetric catalysis. One major advantage that such ligands offer the synthetic chemist is that chiral oxazolines can readily be prepared in enantiomerically pure form from simple precursors (chiral pool; Scheme 15).[179] In fact, various optically pure amino alcohols are commercially

Sc	***Ti*** [147,160 161]	***V*** [125,162]	**Cr**	***Mn*** [165]	***Fe*** [122b,167]	***Co*** [122b,124, 143]	***Ni*** [165,170]	***Cu*** [122b,128, 132,175,176]	***Zn*** [135, 137]
Y	***Zr*** [155]	**Nb**	***Mo*** [58,163, 164]	**Tc**	***Ru*** [126,130, 149,151]	***Rh*** [145,146, 168,169]	***Pd*** [131,136, 143, 169, 171]	**Ag**	**Cd**
La	***Hf*** [155]	**Ta**	***W*** [163]	***Re*** [58,166]	**Os**	***Ir*** [153,154]	***Pt*** [172,173]	***Au*** [174]	**Hg**

Scheme 14. Oxazoline donor ligands coordinate to a wide range of transition metals, those in italics (references given in parenthesis).



Scheme 15. Preparation of enantiomerically pure oxazolines from readily available precursors.

available (e.g. $R^1 = i$Pr, sBu, tBu, Me, Ph) or can be readily prepared by reduction of the corresponding α-amino acids.[180, 181] Using these methods several chiral oxazoline-based ligands have been synthesized. They can be divided into two main classes: 1) neutral ligands, which behave as electron donors but also as π acceptors and can bind electrophilic, cationic metal centers, and 2) anionic ligands with stronger electron-donating properties, which can reduce the electrophilicity of a metal ion or allow coordination to early transition metals. Oxazoline-based cationic ligands have been far less developed (see Section **3.3**).

3.1. Oxazoline-Based Neutral Ligands

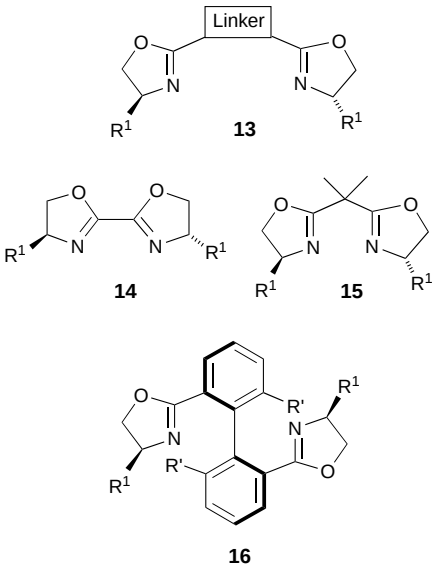
Most oxazoline-based ligands belong to this class and it is possible to distinguish them according to their potential coordination behavior, namely monodentate, bidentate, tridentate, and multidentate.

3.1.1. Monodentate Behavior

Although monodentate oxazolines have been encountered in coordination chemistry,[182] it is only very recently that a modentate chiral oxazoline has been used in metal-catalyzed asymmetric synthesis. This first example concerned a nickel-catalyzed multicomponent tandem coupling.[183]

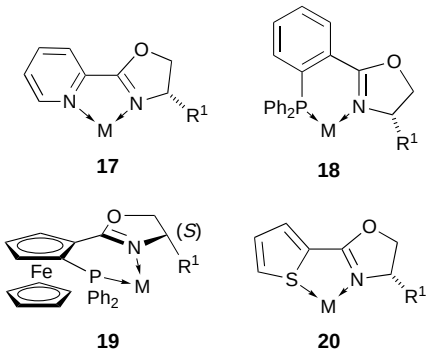
3.1.2. Bidentate Behavior

Owing to the excellent results obtained with semicorrin ligands, many C_2 symmetric bidentate bis(oxazoline) ligands have been synthesized to vary the nature, size, and flexibility of the link between the oxazoline moieties and also the nature of the substituent (R^1) held by the oxazoline stereogenic center (see **13**). A selection is depicted below, ligands **14**–**16**.



A recent review by Gosh et al.[124] nicely summarizes the different C_2 ligands reported and their use in various metal-catalyzed asymmetric syntheses.

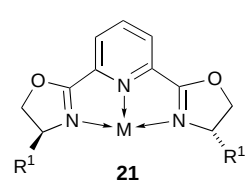
As seen above with other heterofunctional ligands, increased selectivity can be induced by the (stereo)electronic properties of the donor atoms. This applies to heterofunctional N,N′ ligands such as **17**[10, 184] and to P,N **18**,[115] **19**,[150, 151] or S,N **20** ligands[185, 186] and has resulted in the high enantioselectivities obtained in asymmetric allylic alkylation with Pd complexes bearing the P,N ligand **18**.[112–114]



3.1.3. Tridentate Behavior

Several research groups have taken advantage of the versatility of the oxazoline synthesis to introduce a donor atom into the link between the oxazoline rings to give a potentially tridentate ligand. It is anticipated that the tridentate ligands will form a deeper chiral concave pocket around the metal center than the corresponding chiral bidentate ligands. This has led to the development of several ligands, among these Nishiyama's tridentate bis(oxazoline) "Pybox" system **21** which has been particularly useful (e.g. for the asymmetric hydrosilylation of ketones and the cyclopropanation of olefins).[130, 145, 187] In systems **21** and **22** the planarity of the link allows only a meridional (*mer*) coordination mode of the ligand, while in **23** and **24**, the sp^3 character

of the donor atom combined with the flexibility of the backbone is expected to allow both *mer* and facial (*fac*) coordination modes. No coordination chemistry has been



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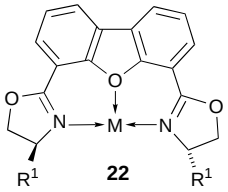

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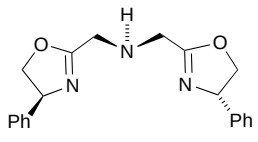

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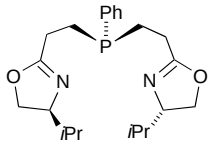

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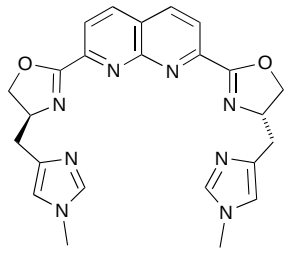
reported for **23** and **24** although these ligands allow good to excellent activities and enantioselectivities in ruthenium-catalyzed asymmetric transfer hydrogenation reactions.[188, 189]

3.1.4. Multidentate Behavior

Interest is also growing in the design of polydentate ligands such as **25**[190, 191] and **26**[146] which could form di- and polynuclear complexes.



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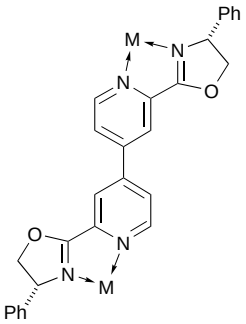

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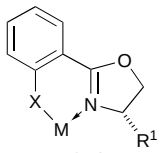
Recent studies indicate the considerable potential that dinuclear and cluster complexes have for catalysis,[192] and for modeling the catalytic activity of metalloenzymes.[193] Several examples demonstrate that dinuclear metal complexes can display distinct advantages over mononuclear metal catalysts and mixed-metal systems offer the additional potential of selective activation of two different substrates.[192, 194] Such complexes can mediate multielectron transfers,[195] activate a substrate by simultaneous coordination to two (or more) metal centers[196, 197] or, in the case where metal–metal bonding is present, allow direct insertion of a substrate into such a bond, a process that does not require ligand dissociation to generate coordinative unsaturation.[198] Although the potential of multidentate oxazoline-based ligands is obvious, reports describing their use are still limited.

3.2. Oxazoline-Based Anionic Ligands

Chiral anionic ligands containing oxazolines have been prepared to allow the fine tuning of the electronic properties of the metal center, and also to strengthen the complexation by creating a covalent bond between the metal and the ligand.[169, 172] This class of ligands has allowed the preparation of very efficient catalysts[129, 136, 138] although there are fewer examples of such ligands than of their neutral analogues. As with the neutral ligands, the anionic ligands can be divided into several families according to their potential coordination behavior. An important additional feature which allows differentiation is whether the anionic charge is carried by an external atom as in systems such as **27**,[125, 160, 162, 165, 199, 200] **28**,[143] **29**,[137, 138] **30**,[131, 169, 172] **31**,[191] or on the pyrrole nitrogen of pyrrole oxazolines,[201] or largely localized on the oxazoline nitrogen atom as in **32**.[128, 129, 136, 147, 161, 168, 202] A further example will be shown below with **40**.[210, 211]



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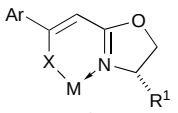

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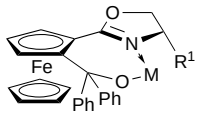

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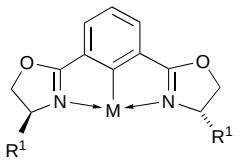

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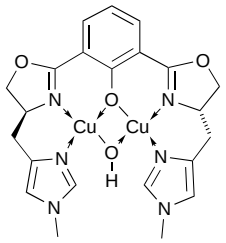

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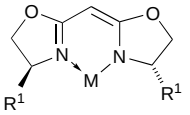
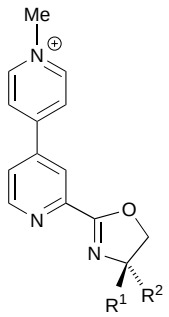


32

3.3. Oxazoline-Based Cationic Ligands

With the hope of preorganizing the electron-donating substrate in the Rh^{I}-catalyzed enantioselective hydrosilylation by charge-transfer effects, the electron-accepting ligand **33** has been prepared.[203]



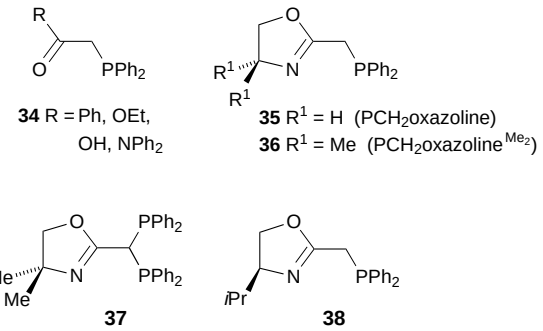
33

4. Hemilabile Phosphorus–Oxazoline Hybrid Ligands

4.1. Bidentate P,N Ligands

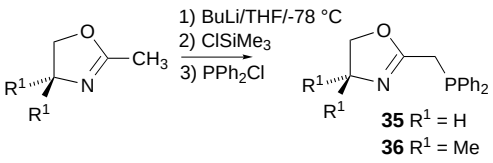
As an extension of our studies on the coordination chemistry of, and catalysis with, the ligands β-phosphino-

ketones,[67, 204–206] -ester,[15] -acids, or -amides,[83, 90] of type **34**, we became interested in using oxazoline moieties for the design of new functional phosphane ligands.



Our first approach was to synthesize P,N ligands (**35** and **36**) analogous to the P,O type ligand **34** by a similar method which involved the reaction of the carbanion derived from 2-methyl-2-oxazoline with PPh_2Cl. This approach failed because of the deprotonation of the expected monophosphorylated product by the oxazoline carbanion present in solution, which resulted in the formation of a diphosphorylated oxazoline ligand **37** among other products.[207, 208]

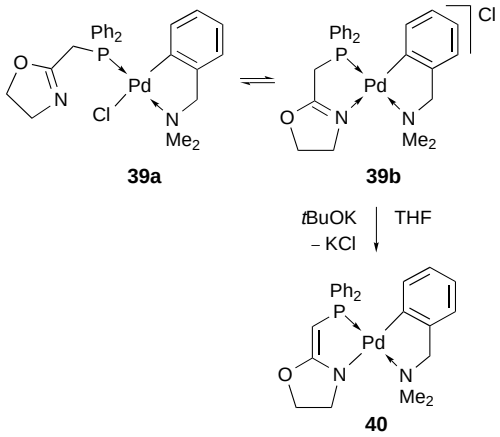
We then adapted a one-pot procedure recently described by Helmchen et al. for the preparation of **38** which consists first of the deprotonation of the corresponding 2-methyl-2-oxazoline in THF at $-78\,^{\circ}C$, followed by the addition at this temperature of Me_3SiCl to form the *N*-silyl derivative which finally reacts with PPh_2Cl as shown in Equation (19).



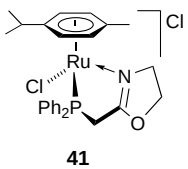
(19)

To examine the coordination properties of the new ligands, we first considered four-coordinate palladium(II) complexes and generally observed the formation of stable P,N chelates in complexes such as $[PdMe(Cl)(PCH_2oxazoline)]$ and $[PdMe(SMe_2)(PCH_2oxazoline)](O_3SCF_3)$ with the ligand PCH_2oxazoline.[207] The bidentate coordination of the ligand strongly differentiates the positions *trans* to P and N. Thus, as observed in the copolymerization of CO and ethylene, the ligand induces a mutual *cis* arrangement of the incoming substrate and the growing polymeric chain. Opening of the chelate is possible and upon reaction of two equivalents of PCH_2oxazoline with one equivalent of $[\{Pd(dmba)(\mu\text{-}Cl)\}_2]$, (dmba = *N*-benzyldimethylamine) the species **39a** and **39b** were found to be in rapid equilibrium in solution (Scheme 16).[211]

This behavior corresponds to the hemilability in Scheme 31 and it was clearly established by the presence in the IR spectrum of **39** in CH_2Cl_2 of two vibration bands assigned to coordinated and uncoordinated oxazoline moieties. This



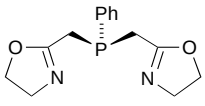
Scheme 16. Hemilabile behavior of the PCH_2oxazoline ligand in **39** and transformation into the stable chelate complexes **40** upon deprotonation.

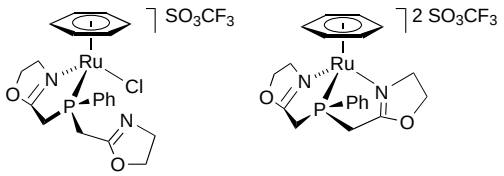


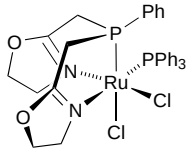
dynamic situation is suppressed upon deprotonation of the PCH_2 group which gives in **40** a static, three-electron-donor anionic chelating ligand (Scheme 16).[210, 211] In contrast to **39**, the PCH_2oxazoline ligand in compound **41** does not exhibit any hemilabile behavior although the chloride counterion could have occupied a coordination site on the Ru center. This situation illustrates how the coordination mode of the phosphinooxazoline ligand is tuned by the choice of the metal center.

4.2. Tridentate N,P,N and Related Ligands

Since the PCH_2oxazoline ligand seemed to preferentially form strong chelates and is fairly inert toward competition from external ligands, we introduced with the new N,P,N ligand bis(oxazolinyl)(phenyl)phosphane (**42**, NPN) the possibilty of an intramolecular competition between two equivalent oxazoline arms within the same ligand (Scheme 3 d).[208]



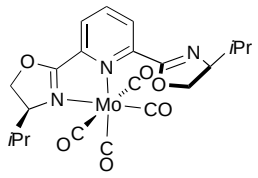




Surprisingly, the NPN ligand in complex **43a** behaves only as a static N,P chelate. Removal of the chloride by treatment with $Ag(O_3SCF_3)$ led to the expected chelation of the pendent arm of the ligand giving compound **44a**.[208] This tridentate bonding mode is also observed in complex **45** where NPN coordinates in a *fac* manner. This coordination mode seems to be preferred to *mer* since varying the Ru precursors and the reaction conditions (solvent, temperature) led only to the formation of complexes containing NPN in either *fac* (**45**) or pseudo-*fac* geometry (**44a**).

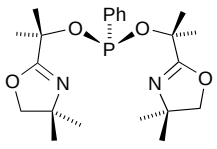
Owing to the increasing interest in new catalysts that allow hydrogenation reactions under mild conditions and preferably in the absence of hydrogen gas,[212, 213] complex **45** was tested for the transfer hydrogenation of acetophenone in propan-2-ol. This complex is a very active catalyst precursor which gives yields of phenethylalcohol up to 97% and turnover frequencies as high as 112000 h^{-1}.[208]

Note that Heard et al. examined the coordination properties of Nishiyama's Pybox ligand in hexacoordinated Pt, Re, Mo, and W complexes. They found evidence for a dynamic process where the bidentate bonding mode of Pybox in **46** is associated with a fluxional exchange of pendent and coordinated oxazolines.[58, 166] This process occurs according to a "tick-tock twist" [see Eq. (4)] and/or a "rotation" mechanism. Thus, comparing our bis(oxazolinyl)-(phenyl)phosphane ligand **42** to the Pybox ligand, it can be seen that a change in the nature of the donor atom of the linker between the two oxazolines (sp^2-hybridized N vs. sp^3-hybridized P in **42**), although keeping the same chelate size, leads to different coordination behavior.

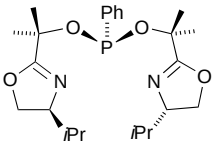


46

We then designed a new ligand, larger than NPN, anticipating that a longer link between the phosphorus and oxazoline units would offer more flexibility and thus allow a *mer* coordination mode. The new bis(oxazoline)(phenyl)-phosphonite ligands, **47** and **48**, were prepared by the reaction



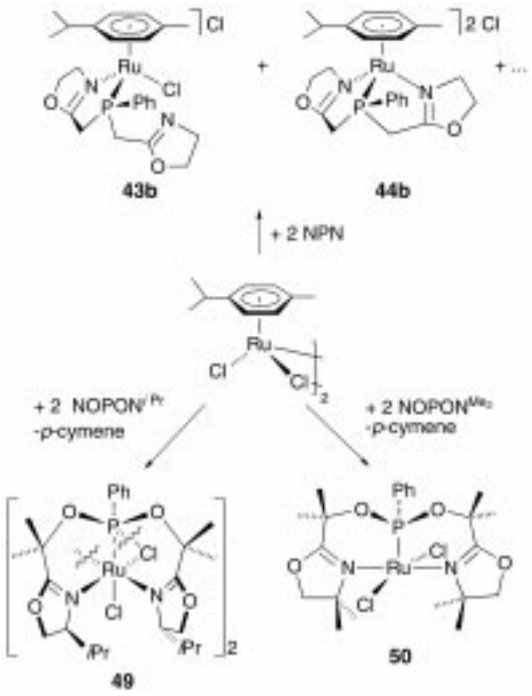
NOPON^{Me_2} **47**



NOPON^{iPr} **48**

of two equivalents of the corresponding 2-(α-hydroxyalkyl)-2-oxazolines with one equivalent of $PPhCl_2$ in the presence of excess NEt_3.[214] The complexation of these new NOPON ligands to Ru^{II} centers differs from that of the NPN ligands and is influenced by the substituents on the oxazolin ring: the reactions in Scheme 17, performed under identical conditions (6 h, THF, reflux), show that depending upon the ligand used three different products can be obtained.

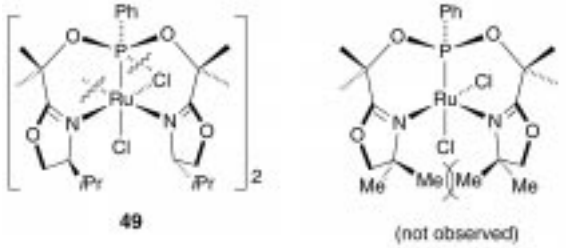
In contrast to the bis(oxazolinyl)(phenyl)phosphonite ligands, NPN did not displace the *p*-cymene ligand from Ru^{II}



Scheme 17. Contrasting behavior of the ligands NPN, NOPON^{Me_2}, and NOPON^{iPr} in Ru^{II} complexes.

but formed monocationic (**43b**) and dicationic (**44b**) complexes in which NPN displays bidentate or tridentate coordination, respectively. Therefore, the size of the chelate (five vs. six-membered) and/or the nature of the phosphorus donor atom (phosphonite vs. phosphane) appears to play an important role for the substitution of the *p*-cymene ligand. Furthermore, the nature of the oxazoline substituents in NOPON^{Me_2} and NOPON^{iPr} must be considered to explain their different coordination behavior. NOPON^{Me_2} (**47**) gives *mer* tridentate coordination in a pentacoordinate, square-pyramidal complex **50** while NOPON^{iPr} **48** gives *fac* tridentate coordination in a hexacoordinate dinuclear complex **49**. In **47** both oxazolin rings each have two methyl substituents at the C4 atom whereas **48** has only an isopropyl group at the *S*-configured C4 center. Thus in ligand **48** if two oxazolines are placed in close proximity, as in a *fac* coordination mode, the *i*Pr groups can avoid each other. Whereas if **47** was to adopt a *fac* coordination mode, two of the four methyl groups would point towards each other and thus create an unfavorable steric clash (Scheme 18).

This is not the case in the *mer* situation. Moreover, the fact that no compound of the type [$RuCl_2$(*mer*-NOPON^{iPr})] could

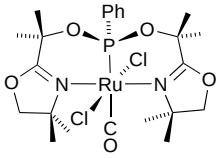


Scheme 18. The presence of two methyl groups on the oxazoline C4 center prevents facial coordination of the NOPON^{Me_2} ligand.

be detected indicates that, when given the choice, this new class of ligands prefers to bind in a *fac* coordination mode.

Compound **49** represents a rare example of a fully characterized complex where a tridentate chiral bis(oxazoline) ligand coordinates in a nonmeridianal fashion. We performed preliminary studies for the asymmetric transfer hydrogenation of acetophenone in propan-2-ol and obtained a conversion of 98% with 26% *ee* of the secondary alcohol product.[214]

Bubbling CO into a solution of complexes [{Ru(μ-Cl)Cl(NOPON$^{i\mathrm{Pr}}$)}$_2$] (**49**) and [RuCl$_2$(NOPON$^{\mathrm{Me_2}}$)] (**50**) leads to carbonyl complexes in which the carbonyl group is incorporated into to the vacant sixth coordination site or by opening of the chloride bridge, respectively. No further coordination of CO occurs, consistent with the stability of the tridentate *mer* or *fac* coordination modes. Comparison between the IR data for the ν(CO) vibration and between the chemical behavior of CO in [RuCl$_2$(CO)(NOPON$^{\mathrm{Me_2}}$)] (**51**)[214] and [RuCl$_2$(CO)(Pybox$^{i\mathrm{Pr}}$)] (**52**)[130] indicates that the Ru–CO bond in **51** is weaker than that in **52**, because the *trans* influence of the P donor in NOPON$^{\mathrm{Me_2}}$ is greater than that of the N donor in the Pybox ligand. This difference underlines the importance of the electronic effects induced by the multidonor ligand on the reactivity of the complex.



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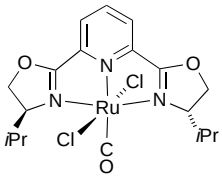
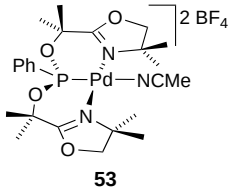


52

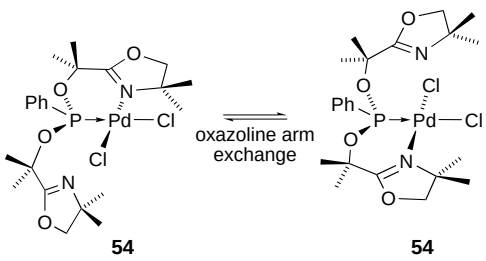
As the hemilabile behavior of the PCH$_2$oxazoline ligand is strongly dependent on the metal center, the Pd chemistry of NOPON$^{\mathrm{Me_2}}$ was examined.[209] Again the difference between NPN and NOPON$^{\mathrm{Me_2}}$ is striking since while reaction of NOPON$^{\mathrm{Me_2}}$ with [Pd(NCMe)$_4$](BF$_4$)$_2$ cleanly afforded compound **53**, reaction with NPN under similar conditions led to the formation of uncharacterized products. Interestingly, excess acetonitrile did not dissociate one arm of the oxazoline ligand from the Pd center in **53**.



53

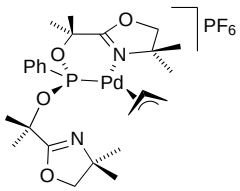
The bis(oxazoline)(phenyl)phosphonite ligand in compound **54** exhibits a dynamic bidentate coordination mode where the two oxazoline arms exchange rapidly as shown by variable-temperature NMR spectroscopy [Eq. (20)].[209]

This dynamic process corresponds to the hemilability shown in Scheme 3d and prompted us to investigate the behavior of NOPON$^{\mathrm{Me_2}}$ complexes in which an additional ligand can also display changes in hapticity. The allyl ligand which can easily adopt either η^1- or η^3-bonding modes appeared to be the candidate of choice.[215] The η^3-bonding



54 **54** (20)

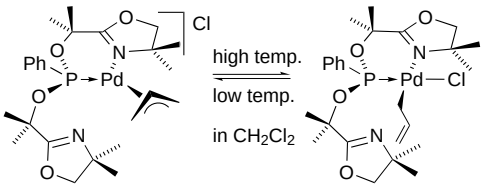
mode is the most generally observed case while η^1-allyl complexes have been isolated mainly with platinum[216–218] or early transition metals.[219–221] The manner in which an allyl fragment coordinates to a transition metal center and its ability to change its coordination geometry will influence the stereochemistry of reactions proceeding via allyl intermediates.[215, 222] For instance, it is well known in palladium–allyl chemistry that an η^3-η^1-η^3 mechanism may operate and that it can be either detrimental to or favorable for enantioselectivity. Therefore, it appears important to recognize the bonding mode of an allyl ligand in a (catalytic) system to understand or rationalize its reactivity. Many Pd–allyl complexes with an η^3-coordination mode of the allyl unit have been isolated. Only a few Pd complexes containing η^1-allyl ligands have been reported although they are either the reactive species or the proposed intermediates in C–C coupling reactions. To study the mutual influence of the allyl and NOPON$^{\mathrm{Me_2}}$ ligands, we first investigated the allyl complex **55** obtained from the reaction of NOPON$^{\mathrm{Me_2}}$ with 0.5 equivalents of [{Pd(η^3-C$_3$H$_5$)(μ-Cl)}$_2$] and one equivalent of NH$_4$PF$_6$. This compound displays behavior similar to that of [PdCl$_2$(NOPON$^{\mathrm{Me_2}}$-N,P)] in that the oxazoline N donors of the dynamic bidentate-coordinated ligand are continually exchanging with one another. The allyl ligand remains coordinated in an η^3 fashion over the temperature range 200–395 K. Thus, in contrast to literature reports on the chemistry of Pd–allyl complexes with P,N,N and N,N,N ligands,[223, 224] we could not isolate a complex of the type [Pd(η^1-C$_3$H$_5$)(NOPON$^{\mathrm{Me_2}}$-N,P,N)]$^+$.



55

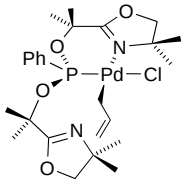
We then examined the situation where the chloride ligand from the Pd precursor ([{Pd(η^3-C$_3$H$_5$)(μ-Cl)}$_2$]) is not replaced by the PF$_6^-$ ion and could therefore influence the dynamic behavior of the ligands by coordination to the metal. The complex thus obtained (**56**) exhibits, under the same conditions as for **55**, fluxional behavior of the allyl ligand, as indicated by variable-temperature ^{1}H and ^{13}C{^{1}H}NMR spectroscopy. Again spectroscopic data show that NOPON$^{\mathrm{Me_2}}$ is a dynamic N,P chelate, while the additional fluxional behavior of the allyl unit is related to the presence of the chloride ion [Eq. (21)].[209]

This competition between the η^3-bonding mode of the allyl and the coordination of the Cl$^-$ ion, meets the requirements of reversible opening and low energy cost for a hemilabile situation of the type in Scheme 3l, although strictly speaking this qualification is not appropriate since an η^3-bonded allyl



56a **56b** (21)

ligand has two identical terminal carbons. It also appears that the dynamic behavior depends on the solvent since changing from CH_2Cl_2 to toluene displaces the equilibrium towards a complex with a static η^1-bonded allyl ligand as detected by ^1H and $^{13}C\{^1H\}$NMR spectroscopy at 260 K.



56b
in toluene solution and in the solid state

The geometry of complex **56b** was confirmed by solid-state ^{13}C NMR spectroscopy and X-ray diffraction.[209] This is only the second crystal structure of an η^1-allyl unit bound to Pd and the first one of a *cis* chloro – allyl transition metal complex. We have demonstrated the influence of the counter ion and the solvent on the bonding mode of the allyl unit, a key feature for the stereoselectivity observed in asymmetric allylic substitution reactions where ion and solvent effects have a significant influence on the rate and enantioselectivity of the reaction.[225, 226] It is unclear whether the hemilabile $NOPON^{Me_2}$-N,P chelate is or is not a simple spectator ligand. The relative positions and mutual influence of the η^1-allyl and the chloride ligands seen in this complex have not been observed with bidentate ligands, including phosphinoaryl-oxazolines[112, 113] and phosphinoferrocenyl-oxazolines.[227] This ligand arrangement has however been invoked for intermediates proposed in the dynamic processes of η^3-allyl palladium complexes.[228]

In conclusion, it was found that (phosphinomethyl)oxazoline ligands do not always behave as stable chelates as often assumed but may exhibit hemilabile behavior. This was established for a situation where the oxazoline nitrogen competes with an external donor ligand, such as chloride, for coordination sites. This situation results in a hemilabile behavior of the type shown in Scheme 3l and is suppressed when the external donor ligand is removed. Such ligand-competition reactions are of course dependent on the nature of the metal center and of the ancillary ligands. This is illustrated by the comparative behavior of the PCH_2oxazoline ligand in Pd complexes **39** and Ru complex **41**; only in **39** could an external chloride ion compete with the N-donor ligand for a coordination site.

For a study of hemilabile behavior of the type shown in Scheme 3d, the N,P,N ligand **42** was designed which contains two identical oxazoline arms. Surprisingly, this ligand was found to adopt only *fac* tridentate or static bidentate coordination modes. No opening/closing mechanism resulting from competition between these two arms was observed.

The new bis(oxazoline)(phenyl)phosphonite ligand **47** was prepared and found to adopt either static *fac* or *mer* tridentate coordination modes or a dynamic bidentate hemilabile behavior as shown in Scheme 3d. The introduction of a chiral oxazoline as in **48** alters the coordination properties and leads exclusively to *fac* tridentate coordination. Obviously the size of the chelate ring and the nature of the P donor atom play a crucial role in the occurrence of hemilability. In the presence of an external donor ligand like chloride, which has a tendency to coordinate to the metal center, one could have expected an enhanced dynamic behavior that could parallel that described above with **39**. However the reaction shown in [Eq. (21)] provided an unexpected result because the external chloride triggered the coordination of the allyl ligand in a terminal η^1 mode while the $NOPON^{Me_2}$ ligand remained bidentate. This led to the stabilization of the first *cis* η^1-allyl chloride transition metal complex.[209]

5. Conclusion

The hemilability of hybrid ligands is a property that attracts increasing interest as documented by the current research efforts aimed at understanding its occurrence and scope. The diversity of situations encountered and illustrated in Scheme 3 also indicates the number of parameters and the subtlety with which they need to be tuned for this phenomenon to occur. The importance of hemilability was first demonstrated in homogeneous catalysis where it continues to provide new and exciting results. More recently ligand hemilability has also been applied to the development of new molecular-based sensors and materials. The introduction of oxazoline moieties in hybrid ligands has opened the door to studies on their involvement in hemilabile systems that can readily carry and transfer chiral information. It can be anticipated that such studies will continue to provide new and exciting results.

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