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Bonding and Organic and Inorganic Reactivity of Metal-Coordinated Phosphinoenolates and Related Functional Phosphine-Derived Anions[†]

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1. Introduction

In molecular chemistry, a detailed understanding of the physical properties and stoichiometric or catalytic reactivity of metal complexes represents a prerequisite for the improvement of the property considered, for higher efficiency and better applicability. To this end, it is helpful to try to differentiate, at least in a formal sense, the influence of the metal center(s) from that of the ligands in order to better identify, analyze, and understand the parameters that are responsible for the property under consideration. We shall focus here on chemical rather than physical properties, but it is clear that the design and synthesis of molecular-based materials with advanced physical properties represents a growing field of science. A separate analysis of the contributions of the ligands and the metal(s) to molecular properties is not always as easy as it might seem because of the intricate and synergistic nature of the metal−ligand interactions. This interaction is at the very core of coordination chemistry and has implications in fields extending from the design of molecular catalysts to the preparation of molecular-based nanomaterials.[1] Furthermore, spectator ligands, which by definition do not participate directly in the reaction investigated, often play a considerable role in controling the molecular reactivity. In turn, chemical modifications within the molecule may trigger the emergence of reactivity at the spectator ligand, which then loses its original quality to become an actor! Understanding these effets is obviously of fundamental importance in order to be able to orient and fine-tune molecular reactivity.

[†] Gratefully dedicated to Professor G. Ourisson on the occasion of his 80th birthday, with most sincere congratulations and wishes.

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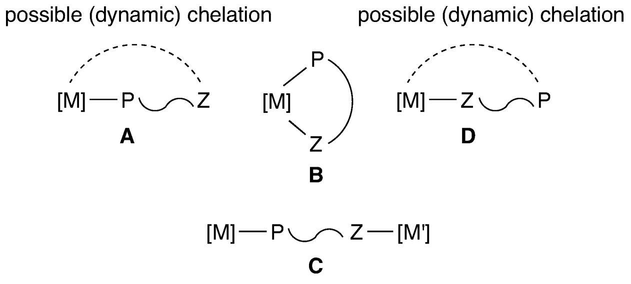
The differentiation introduced in the coordination sphere of a metal center by donor groups of significantly different electronic and/or steric properties allows higher selectivities to be reached, in particular in asymmetric catalysis. As an example, a chelating ligand with such donor groups will induce a strong stereochemical differentiation in the *trans* (electronic factor) and *cis* (steric factor) positions of a square-planar complex (Scheme 1). This contrasts with the "degenerate" situation induced by a symmetrical chelate of C_2 symmetry.

Scheme 1. Coordination Site Differentiation Resulting from the Presence of Donor Groups with Very Different Stereoelectronic Properties

The concept of electronic differentiation resulted from early studies by Faller, who used isosteric ligands such as CO and NO to control allylic alkylation on molybdenum.[2] This was further extended to palladium systems by using ligands of different σ-donor/π-acceptor properties.[3] These ideas, together with Achiwa's "respective control concept",[4] have contributed much to the rapid developments witnessed in careful ligand design associated with the selection of the most appropriate metal for a given transformation.[5,6] Mostly developed for mononuclear complexes containing chelating ligands, these efforts should be extended to the more complex but also more versatile chemistry of multinuclear complexes.

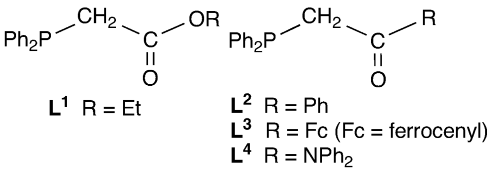
The anionic ligands that are the focus of this review derive from molecules called functional phosphines. By this, we mean phosphine ligands which contain an additional functional group Z usually capable of coordinating to a metal center, in at least one of the phosphorus substituents, as in RR′P∼Z (R, R′ = alkyl or aryl). The role of the function Z may be to modify the physical properties of the ligand and its complexes (e.g. solubility in water upon introduction of sulfonato groups) and/or to modify its electronic properties either by direct interaction with the metal or indirectly, via the spacer connecting the phosphorus donor to the Z function. Most such hybrid ligands, i.e., that associate within the same molecule at least two chemically different functions, are expected to give rise to selective and differentiated bonding interactions with the metal center(s).[1,5−9] These effects will be enhanced when the functions P and Z are chosen to be very different from each other, as observed when combining hard and soft donors. The possible metal−ligand interactions involving such a P∼Z ligand are illustrated in Scheme 2.

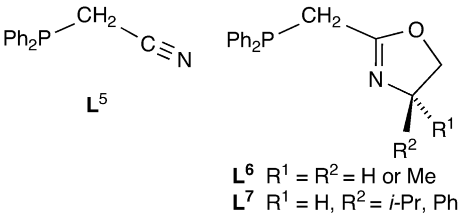
Scheme 2. Bonding Modes of a Hybrid P∼Z Ligand

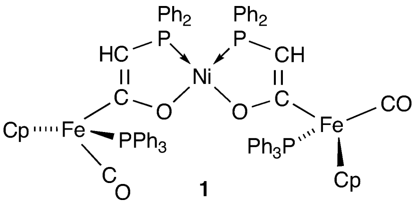


When these ligands behave as monodentate P-donors (Scheme 2A), i.e., with soft metal centers, the influence of the Z group will manifest itself best when it directly interacts with the metal(s) in either a chelating (Scheme 2B) or bridging (Scheme 2C) mode. Depending on the kinetic lability of the M−Z interaction, chelation can be reversible, and this gives rise to the interesting phenomenon of hemilability, which is gaining increasing significance in chemistry with applications in the fields of molecular activation, homogeneous catalysis, molecular sensors, etc.[7−10] It is clear that if the affinity of the function Z for the metal considered is greater than that of the phosphorus donor atom, a monodentate behavior of type D may result, but here again, reversible chelation may follow, this time by coordination of the P donor. This bonding versatility is particularly significant in early−late heterometallic chemistry.[11] At variance with these functional phosphines, α-stabilized phosphoylides of the type $R_3P{=}CH{-}Z$ do not interact with metals via the P atom and will not be considered here; their behavior has been discussed elsewhere.[12,13]

In our case, the function Z will represent an ester,[14] a carboxylate,[15] a ketone,[16] an amide,[17−19] a nitrile group,[14] or an oxazoline moiety[20,21] situated in the β-position to the phosphorus atom as in ligands L^1 to L^7, respectively. The synthetic principle that first led to L^2 and L^3, namely the reaction of the corresponding lithium enolate $Li[CH_2C(O)R]$ with a chlorophosphine,[16,22] has found numerous applications. These include the synthesis of functional tridentate ligands starting from $RPCl_2$[16,20] and the diastereoselective synthesis of the heterotrinuclear phosphinoenolate complex **1** containing the chiral auxiliary $FeCp(CO)(PPh_3)$.[23]







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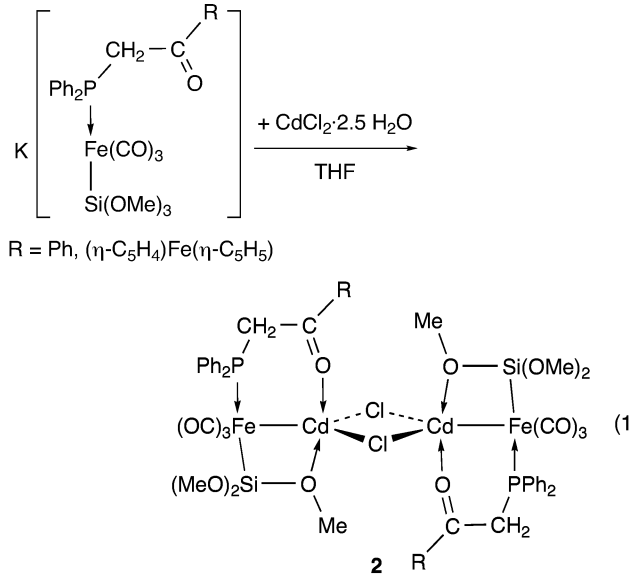
Except for L^5, these ligands will predominantly lead to P-monodentate or to five-membered ring chelating behavior,[9] but in still very rare cases, bridging modes have been encountered in dinuclear complexes such as **2** (eq 1)[24] or **3**.[25] The occurrence in **2** of an additional bridge formed by the alkoxysilyl ligand is noteworthy, but the dynamic behavior and numerous applications in bimetallic chemistry of such μ-η^2-Si−O units, first discovered in 1989,[26] have been discussed elsewhere.[27]



(1)

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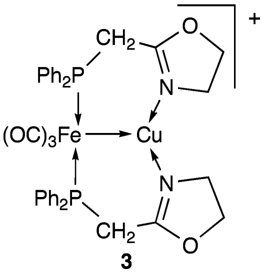

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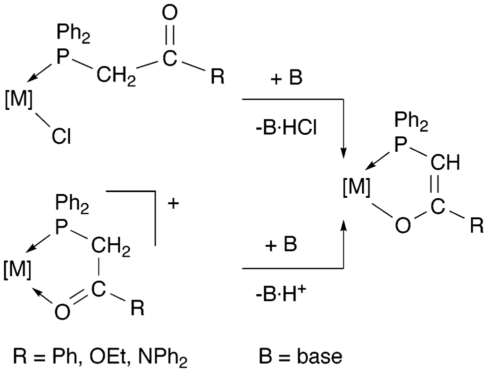
In contrast to L[1] to L[4], which readily form chelates as in the Pd(II) complex **4**, the phosphinonitrile ligand L[5] cannot do so, owing to the rigidity of the $CH_2C{\equiv}N$ moiety. Instead, formation of the dinuclear complex **5** was observed in which L[5] acts as a bridging ligand (Scheme 3).[28]

At an early stage of our studies, we noticed that the acidity of the PCH_2 protons is significantly enhanced by coordination of the phosphorus atom, even more so when chelation of the P∼Z ligand occurs. Facile deprotonation, e.g. with KH/THF, affords stable metal complexes which contain a carbanionic center in the α position to the phosphorus (Scheme 4).[28,29] Stronger bases are needed to deprotonate the free ligand, and the resulting functional carbanions should then best be used *in situ*. We shall see below that the remarkable stabilization of phosphinoenolates and related anionic ligands brought about by their coordination to a transition metal is not accompanied by a loss of reactivity but rather allows its fine-tuning.

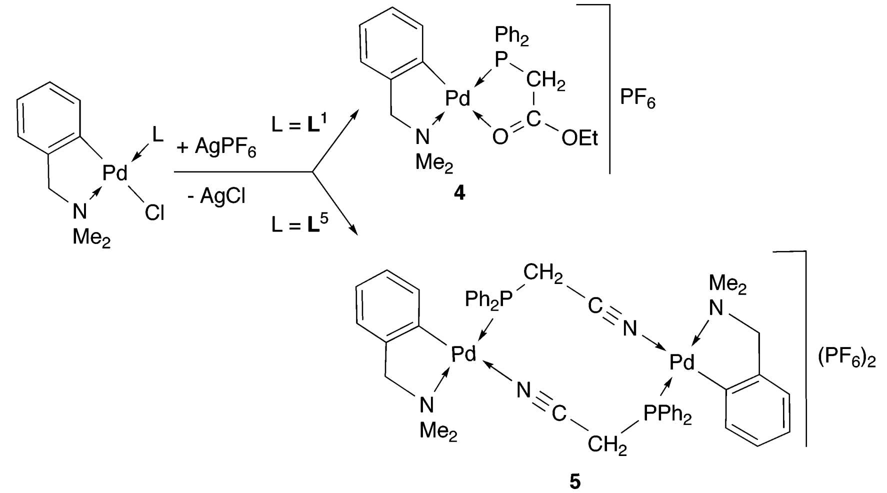
Scheme 4. Formation of *β*-Phosphinoenolate and *β*-Phosphinoenamidate Metal Complexes



It is to be anticipated that the nature of the function Z in monoanionic ligands of the type $R_2P{-}CH^{(-)}{-}Z$ will greatly influence the reactivity of the carbanionic center. Conversely, the bonding behavior and reactivity of this function will be affected by the adjacent negative charge. These mutual influences will be facilitated by the expected electronic delocalization of the negative charge onto the Z function. Furthermore, owing to the presence of the P donor group, various coordination modes to one or more metal centers are concievable for such functional carbanions that should also affect the reactivity of the system. The main bonding modes to be discussed in the following are shown in Scheme 5. In some cases, their occurrence is still very rare.

At this point, one should also mention the existence of α-phosphinoenolates, $[R_2PC(\overset{\cdots}{-}O)(\overset{\cdots}{-}CH_2)]^-$, which are obtained by deprotonation of acetylphosphines and can be regarded as positional isomers of those derived from L[2] to L[4] (cf. bonding mode J). They have been used

Scheme 3. Contrasting Bonding Behavior of Ligands L[1] and L[5]



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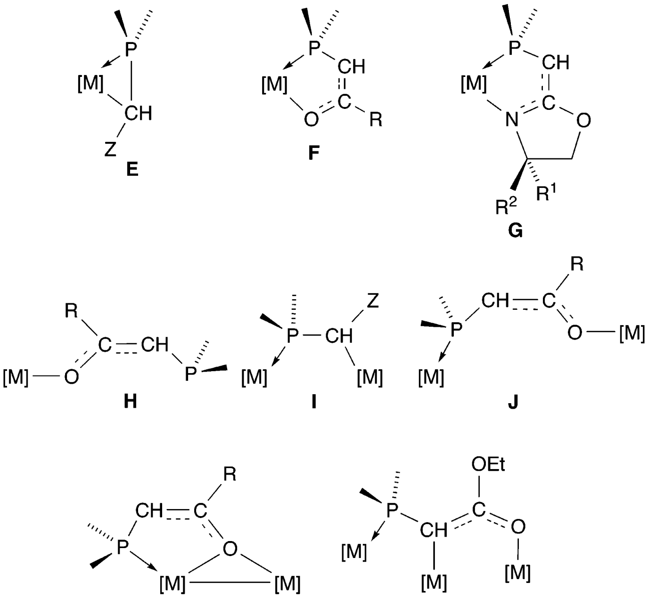
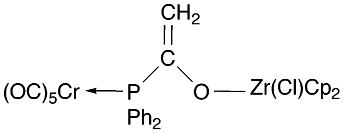
Scheme 5. Bonding Modes Encountered in the Coordination Chemistry of Functional Phosphine-Derived Carbanions



as bridging ligands in early−late dimetallic chemistry, as shown with complex **6**.[30]



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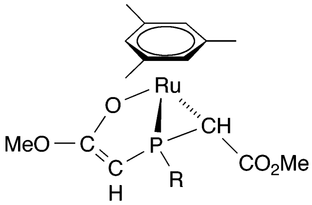
In the following, we shall first briefly examine how to generate the structures depicted in Scheme 5 and then concentrate on the ligand-based reactivity of complexes of type F, which represents the most frequently encountered bonding mode, toward organic or metallic electrophiles. We will therefore not discuss here the properties of complexes where $R_2P{-}CH^{(-)}{-}Z$ remains a spectator ligand, although it can have a considerable influence on the reactivity of the complex considered. This is clearly the case for the phosphinoenolate chelating ligand in, e.g., Pd-induced stepwise ethene and/or methyl acrylate/CO insertion reactions into a Pd−C bond[31] and in catalytic reactions as important as the oligomerization of ethylene to linear α-olefins (M = Ni),[32−34] the polymerization of ethylene,[35−39] the ethene/CO copolymerization (M = Pd),[40] the transfer dehydrogenation of alkanes (M = Rh),[41] and, in the case of isoelectronic phosphinooxazoline-derived ligands of type G, the transfer hydrogenation of ketones with propan-2-ol (M = Ru).[42]

2. Bonding Modes of Functional Phosphine-Derived Carbanions

These are represented in Scheme 5 and have all been characterized by X-ray diffraction analysis of the corresponding metal complexes.

2.1. Bonding Mode E (κ^2-*P,C*)

Whereas transition metal complexes containing a three-membered ring structure based on η^2-CH_2PR_2 and related ligands have been known for ca. 30 years,[43,44] this is not the case with phosphinoenolate ligands, owing to their much stronger preference for the formation of five-membered ring structures of type F (see below). However, deprotonation of the Ru(II)-coordinated trifunctional phosphine $RP[CH_2C(O)OMe]_2$ led to the (κ^3-*P,C,O*)-bonded tripod-type ligand in **7** which features a three-membered Ru−P−C ring.[45] Recently,



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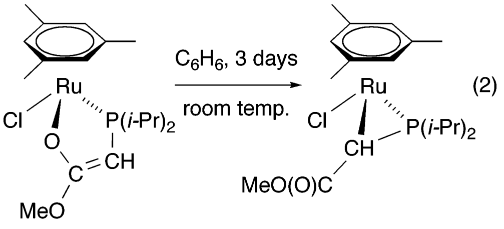
an unusual example of thermal isomerization of a Ru(II) phosphinoester enolate, **8a**, from a five- to a three-membered ring structure, has been fully characterized by Werner et al. (eq 2).[46] A phosphinomethanide Os(II) complex related to **8b** is also known.[47]



8a **8b**

A complex with three-membered Pt−P−C rings could not be isolated from the reactions of the functional carbanions $Li(Ph_2PCHZ)$ (Z = CN, C(O)OEt, $C(O)NPh_2$) with $[PtCl_2(NCPh)_2]$ although this could have been the result of nucleophilic displacement of the chlorides and of the labile benzonitrile ligands. Instead, nucleophilic attack of the functional carbanions occurred on the coordinated nitrile, as will be discussed in section 3.5.[48−50]

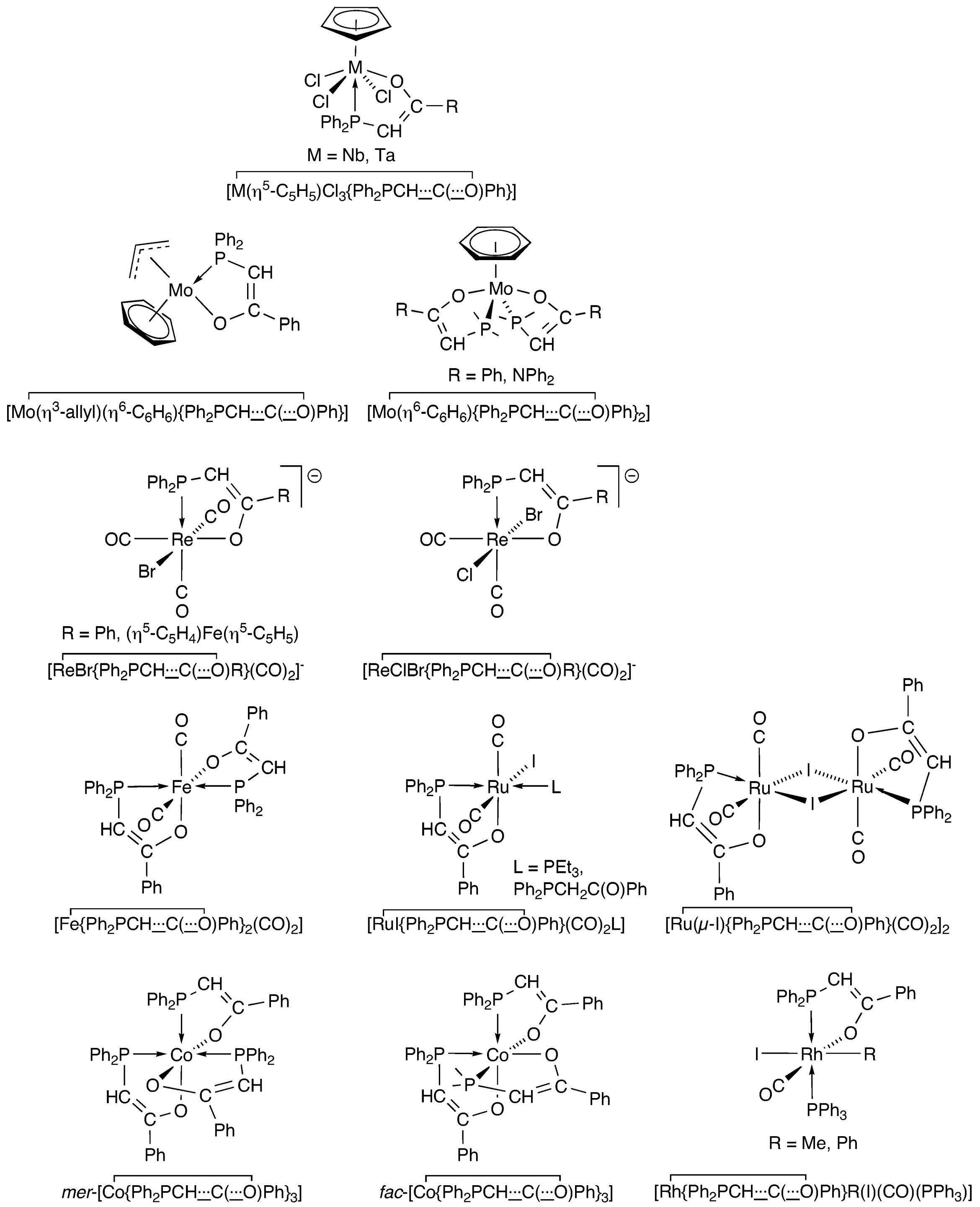
2.2. Bonding Mode F (κ^2-*P,O*)

Although P,O-chelated complexes can be obtained from metal halides by anion exchange using the lithium salt of a functional carbanion $R_2P{-}CH^{(-)}{-}Z$, deprotonation of the PCH_2 group of a P-coordinated neutral functional ligand of type L^1 to L^4 is more convenient and readily leads to stable five-membered ring structures containing a monoanionic, 3e donor P,O chelate (Scheme 4).

The metallacycles formed by the chelating phosphinoenolates are characterized by shorter C−C (ca. 1.37 Å) and longer C−O distances (ca. 1.30 Å) than those in the complexes containing the corresponding neutral chelates $Ph_2PCH_2C(O)R$ (ca. 1.50 and 1.25 Å, respectively). For comparison, the enolate C−C and C−O bond distances in [K(Kryptofix-2,2,2)][$Ph_2PCH{\cdots}C({\cdots}O)Ph$] are 1.404(9) and 1.268(6) Å, respectively.[51] Such data are consistent with an increasing double bond character for the C−C bond and a decreasing C−O bond order when going from the neutral to the anionic ligand. Similar trends are observed in structures of type G with the phosphino-oxazoline C−C and C−N bonds.[52] For convenience, we shall picture these metallacycles with a C=C double bond, although electron delocalization within the enolato or enaminate moiety obviously involves the oxygen or the nitrogen atom, respectively.

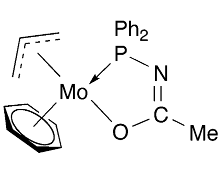
The synthesis of phosphinoenolate complexes by deprotonation of a P-coordinated, neutral functional phosphine

Scheme 6. Phosphinoenolate Complexes with Group 5−9 Metals



ligand has turned out to be rather general and has been successfully applied not only to various group 10 metal complexes, whose reactivity has been studied to a much larger extent (see below), but also to group 5−9 metals, as illustrated in Scheme 6 with Nb(V), Ta(V),[53] Mo(II),[54] Re(I), Re(III),[55] Fe(II),[56] Ru(II),[57] Co(III),[58] and Rh(III)[59] complexes. The resulting complexes are generally air-stable, which contrasts with the case of the phosphinoenolates of the alkali metals.

More recently, similar deprotonation reactions have been extended to another P,O ligand, the acetamide-derived phosphine $Ph_2PNHC(O)Me$. This resulted in phosphinoiminolate complexes such as the three-legged piano stool complex **9**, which was the first example to be structurally characterized,[60] a dinuclear Rh(I) complex,[61] and the square-planar complex **10**.[62]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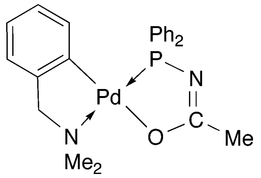
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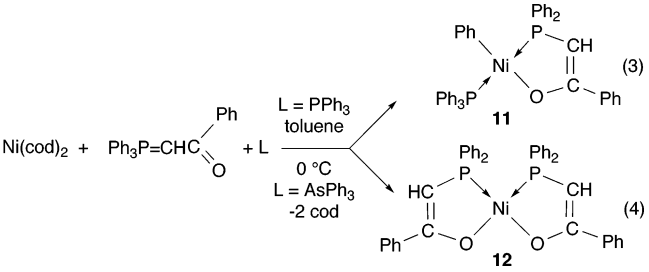
There is a synthetic procedure to access complexes containing a chelating phosphinoenolate ligand that is unique to Ni(II): the oxidative-addition of ketophosphorus ylides $Ph_3P{=}CHC({=}O)R$ to Ni(0) complexes such as $[Ni(cod)_2]$, in the presence of a two-electron donor phosphine ligand (eq 3), which leads to the migration of a phenyl group from phosphorus to nickel.[63−65] The resulting square-planar complexes, such as **11**, contain both a nickel−carbon σ-bond and a bidentate, three-electron donor P,O chelating ligand. These complexes are established precursors to the active species responsible for the catalytic polymerization or oligomerization of ethylene into linear α-olefins, as in the Shell Higher Olefins Process (SHOP).[34,38,63,64,66] In this catalytic system, the most reactive site in the molecule is the Ni−Ph bond, but the chelating, spectator P,O ligand is very important in tuning the performances of the catalyst.

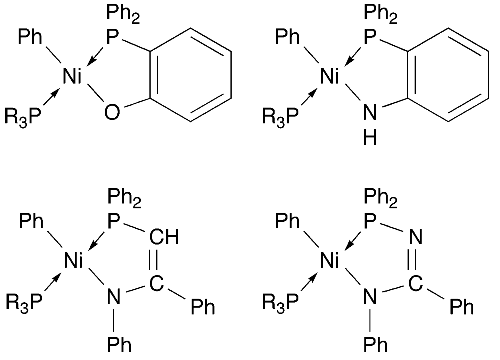
The outcome of the reaction of these ketophosphorus ylides with [Ni(cod)$_2$] is very dependent on the nature of the added two-electron donor ligand (Scheme 7). When the phosphine ligand used in eq 3 was replaced with AsPh$_3$, the bis-phosphinoenolate Ni(II) complex **12** was obtained instead (eq 4).[65] This complex corresponds to the deactivated form of oligo- or polymerization catalysts of type **11**.[37,38] X-ray diffraction studies have established the *cis* geometry of **12** and related square-planar complexes,[37,38,65,67] but with the sterically bulkier P(*t*-Bu)$_2$ groups in place of PPh$_2$, a *trans* P−Ni−P arrangement is adopted.[68]

Scheme 7. Influence of the Ligand L on the Reaction of Ketophosphorus Ylides with [Ni(cod)$_2$]



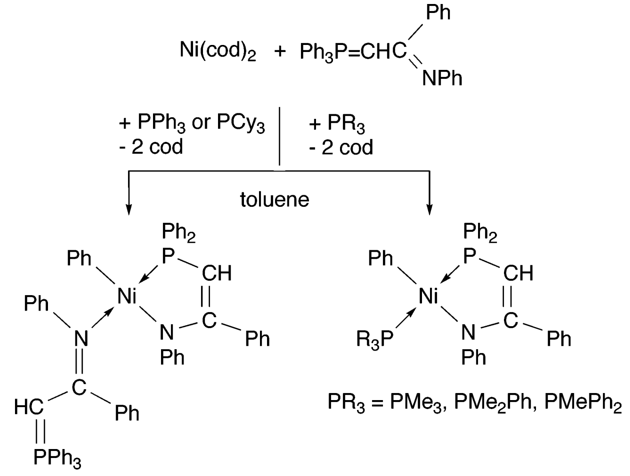
The synthetic procedure shown in eq 3 has been extended to other chelating P,O[69] and P,N systems,[70,71] as shown in Scheme 8. Depending on the nature of the added two-electron donor phosphine ligand, it was found that coordination of an intact α-iminophosphorus ylide can occur instead (Scheme 9).[70]

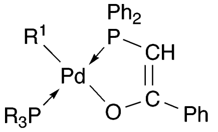
Scheme 8. Ni(II) Complexes with Anionic P,O or P,N Chelates Prepared from the Corresponding Phosphorus Ylides



To prepare Pd(II) analogues to the Ni(II) SHOP-type catalysts and compare their catalytic properties, a different synthetic approach had to be used since the oxidative-addition of a phosphorus ylide P-aryl bond is limited to Ni(0) precursors. Deprotonation of a Pd(II)-coordinated phosphine L^2 or L^4 readily afforded the desired products **13** and **14**, respectively.[72−74]

Scheme 9. Oxidative Addition of an α-Iminophosphorus Ylide to Ni(0) and N-Coordination of the Intact Ylide or P-Coordination of the Added Phosphine[70]





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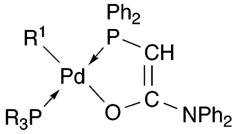

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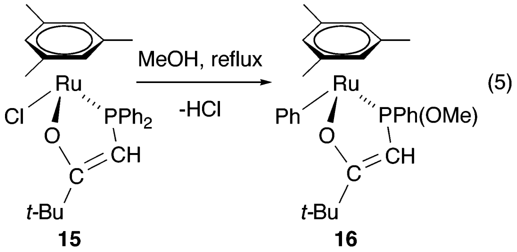
R^1 = Me or Ph

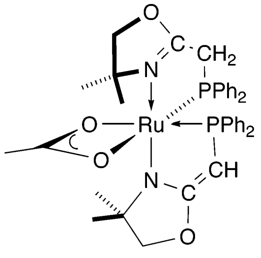
Interestingly, the synthesis of phosphinoenolate metal complexes can in some cases be achieved by transmetalation reactions, despite the anionic and chelating behavior of the ligand. Such reactions have been found to occur from Pd(II) to Pd(II) centers[75] and from Ni(II) to Pd(II)[75,76] or Pt(II)[76] centers and are driven by the formation of the thermodynamically most stable complex (see section 3.7). Other examples involving Ti(IV), Zr(IV), and Pd(II) complexes will be examined in section 2.6 (see below).

We will see that, despite the stability of the five-membered ring structures of type F, they are often associated with a very rich and versatile carbon- or oxygen-centered reactivity of the chelating ligand (remember that the reactivity of metal complexes in which the P,O chelate behaves as a spectator ligand will not be examined here). Furthermore, reactivity at phosphorus has been observed in one instance: an easy cleavage of a P−Ph bond in the Ru(II) complex **15** afforded **16** as the result of a [1,2]-phenyl migratory process (eq 5).[77]



2.3. Bonding Mode G (κ^2-*P,N*)

Similarly to the synthesis of complexes of type F, the first anionic P,N chelates derived from the phosphino-oxazolines L^6 and L^7 have been obtained by deprotonation of the coordinated ligand. This afforded the octahedral Ru(II) complex **17**, an efficient catalyst precursor for the transfer-hydrogenation of ketones with propan-2-ol (M = Ru),[42] and the square-planar Pd(II) complex **18**.[52]



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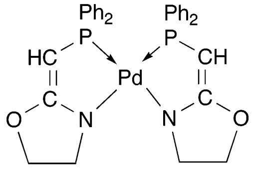

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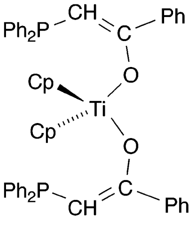
2.4. Bonding Mode H (κ^1-*O*)

Although we are not aware of phosphinoenolates bound to a metal center solely through the carbon atom, complexes with O-bound phosphinoenolate ligands have recently been characterized. As expected, their synthesis requires the use of an oxophilic metal center. Reaction of $\mathrm{Li[Ph_2PCH\overset{\cdot\cdot}{-}C(\overset{\cdot\cdot}{-}O)Ph]}$ with $[Cp_2TiCl_2]$ afforded the bis-phosphinoenolate complex **19**, which displays a very interesting reactivity (see section 2.6). The monophosphinoenolato titanocene **20** and the bis(phosphinoenolato) zirconocene complexes **21** were obtained from a D-camphor-derived phosphine ligand, and the latter complex has been characterized by X-ray diffraction.[78] Obviously, one of the objectives in this research was to apply such complexes as synthons in the assembling of early−late heterodimetallic complexes by taking advantage of their pendant phosphine function (see section 2.6).



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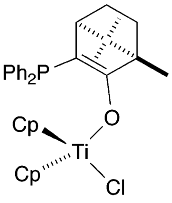

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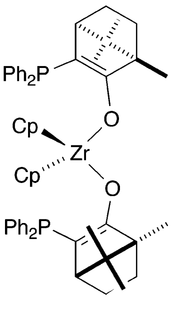

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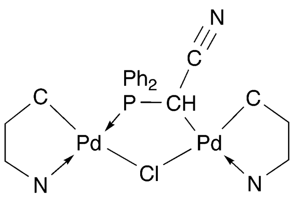
2.5. Bonding Mode I (μ_2-*P,C*)

This bonding mode was first structurally characterized in palladium chemistry.[29] Reaction of the chloride-bridged dinuclear complexes $[\mathrm{Pd}(\overline{C\ N})(\mu\text{-Cl})]_2$ with an equivalent of $\mathrm{Li[Ph_2PCH\overset{\cdot\cdot}{-}C(\overset{\cdot\cdot}{-}O)OEt]}$ afforded complex **22** (Scheme 10).[28,29] The enolate function behaves here as a donor ligand through the carbon, as in structures of type E but in contrast to situation F or H. The ambident or ambifunctional[79] behavior of these phosphinoenolates parallels that well-known for usual organic enolates.[80,81]

In the reaction of Scheme 10, one of the 3e donor bridging chlorides of the Pd(II) precursor seems to have been directly replaced by the functional enolate. However, chemical labeling experiments established that the reaction proceeds in fact via the intermediate formation of the mononuclear, five-membered ring chelate complex **23a**, thus demonstrating the possible conversion of bonding mode F to I (see section 3.7). The dmba or 8-mq Pd(II) complexes **24** containing the carbanion derived from ligand L[5] and analogous to **22** have also been characterized, but a mononuclear intermediate could not be isolated, in contrast to the case of **23a**. The presence of a stereogenic carbon center in the μ-P,C bridge of **22** or **24** manifests itself in the complex ^{1}H NMR patterns for the C(O)OEt and NMe$_2$ protons of the dmba chelates.[28]



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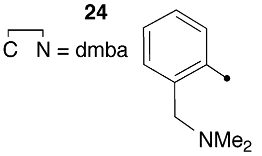

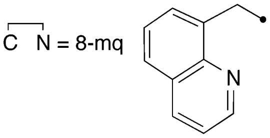

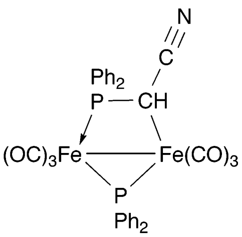

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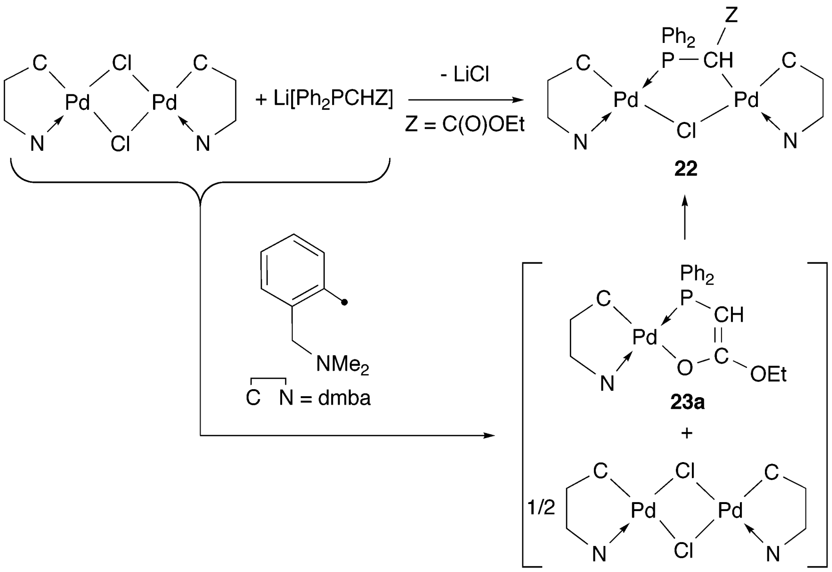
These reactions appear to have been the first examples of direct formation from the free functional carbanion of dinuclear complexes containing a M{μ-R$_2$*P*−*C*H(Z)}M

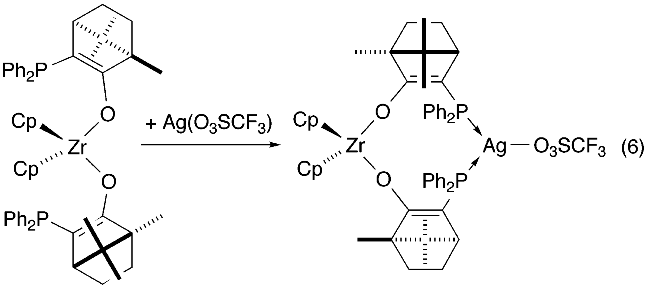
Scheme 10. Formation of the First Phosphinoenolate Complex with a μ_2-P,C Bridge[29]



moiety.[29] Other complexes with such a moiety were obtained in a stepwise manner by coupling of a phosphido ligand with an organic reagent. This has been the case for W−Os complexes[82] and for the dinuclear Fe complex **25**, which was one of the several products formed in the reaction between $[(CO)_3\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}CO)Fe}(CO)_2(PPh_2H)]^-$ and ICH_2CN.[83]

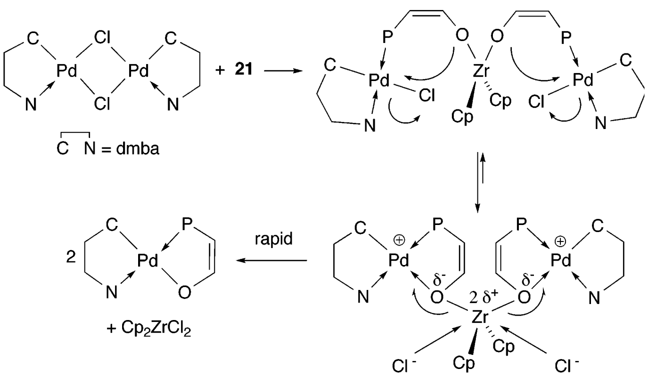
2.6. Bonding Mode J (μ_2-*P,O*)

Starting from the Zr(IV) metal complex **21** containing O-bound monodentate phosphinoenolate ligands, heterodinuclear complexes which display bonding mode **J** as in **26** have been prepared by reaction of the pendant phosphorus donor with a late transition metal complex (eq 6).[78] In such situations, the anionic P,O ligand acts as an assembling ligand suitable for early−late metal chemistry. Whereas a Zr/Cu complex similar to **26** was also obtained, attempts to form Zr/Pd or Zr/Pt complexes failed and, instead, a rearrangement that led to the complete transfer of the phosphinoenolate ligand from the Zr(IV) to the d^8 metal center occurred (Scheme 11). The stability of the resulting five-membered ring chelate of type **F** represents the driving force for this reaction.[78] This is reminiscent of the transmetalation reactions evoked in section 2.2.



21 **26**

Scheme 11. Suggested Mechanism for the Transfer of the Phosphinoenolate Ligand from the Zr(IV) Complex 21 to a Pd(II) Center[78]



Reaction of the Ti(IV) complex **19** with $[Mo(nbd)(CO)_4]$ led to the heterodimetallic complex **27**.[84] However, complete transmetalation of the phosphinoenolate ligand occurred upon reaction with $[Pd(or)PtCl_2(cod)]$ (Scheme 12). With the hope of preventing this transmetalation, **19** was reacted with the Pt(0) complex $[Pt(C_2H_4)(PPh_3)_2]$ and an unprecedented metal−metal bonded Ti−Pt complex **28** was obtained in which one phosphinoenolate acts as a bridging ligand, whereas the other has transferred to Pt (Scheme 12).[84] This complex was structurally characterized and extended Hückel molecular orbital calculations indicated the presence of a quasi-covalent Ti(III)−Pt(I) bond (2.721(2) Å).

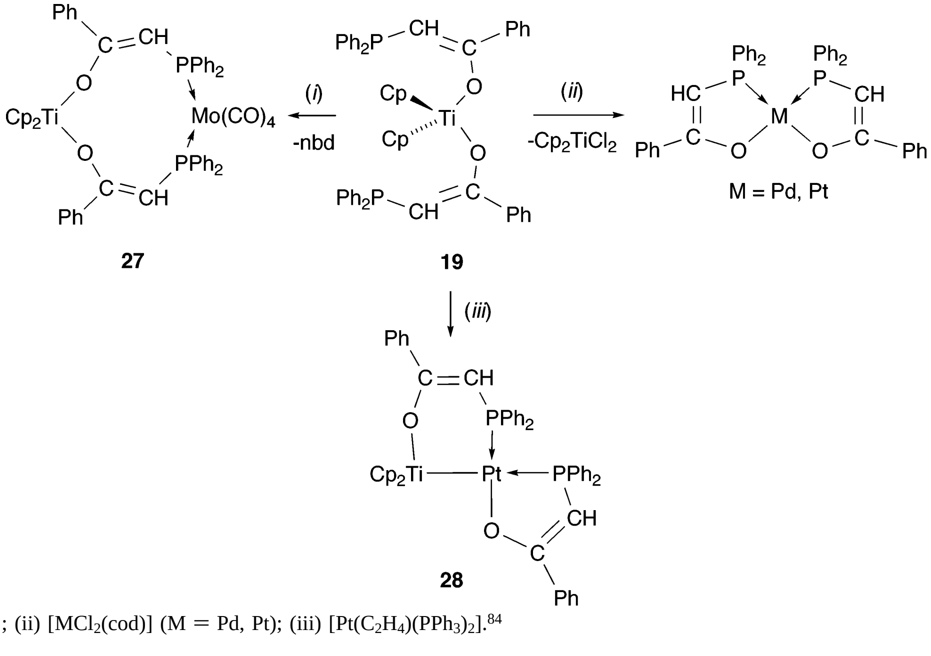
During attempts to use L^2 or L^4 as assembling ligands in Fe−Sn chemistry, the reaction shown in eq 7 led to spontaneous deprotonation of the PCH_2 group and formation of a six-membered ring in complex **29**.[85]

A related bridging situation for an anionic P,O ligand was observed in the dirhodium(II) phosphinophenolate complex **30** which resulted from demethylation of one of the methoxy groups of the ligand tris(2,4,6-trimethoxyphenyl)phosphine by $[Rh_2(\mu\text{-}O_2CMe)_4(MeOH)_2]$ in refluxing ethanol.[86]

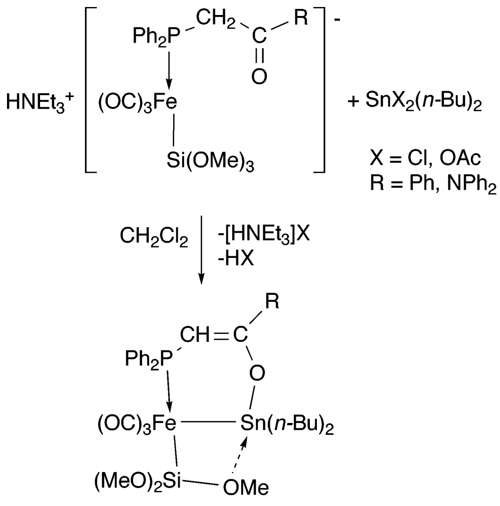
2.7. Bonding Mode K (μ-κ^1(*O*):κ^2(*P*,*O*))

Only one example of a phosphinoenolate ligand adopting this bonding mode appears to be known. It was observed in the triruthenium cluster **31** and resulted from thermal PC−H bond cleavage of $[Ru_3(CO)_{11}(L^2)]$ or $[Ru_3(CO)_{10}(L^2)_2]$.[87] In a reversible reaction, protonation of **31** by HBF_4 in the presence of CO afforded the corresponding cationic cluster

Scheme 12. Reactivity of the Ti(IV) Metalloligand 19[a]



[a] (i) $[Mo(nbd)(CO)_4]$; (ii) $[MCl_2(cod)]$ (M = Pd, Pt); (iii) $[Pt(C_2H_4)(PPh_3)_2]$.[84]



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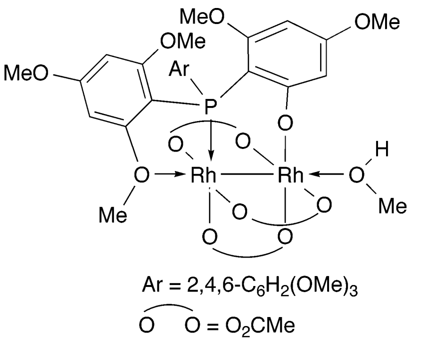

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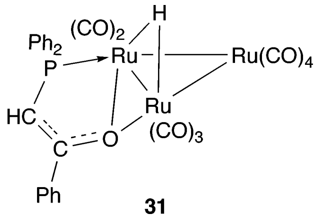
[Ru$_3$(μ-H)(μ-L^2)(CO)$_{10}$]$^+$ containing a P,O-bridging β-ketophosphine ligand.[87,88]



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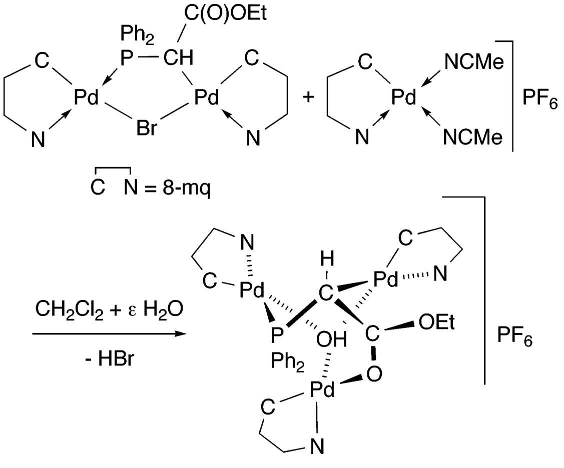
2.8. Bonding Mode L (μ_3-*P,C,O*)

In this bonding mode, all three functionalities available on the phosphinoenolate ligand are involved in bonding to metal centers. It remains exceptional, and the first such example, the tripalladium(II) complex **32**, was obtained by the reaction shown in eq 8, in which a mononuclear Pd(II) cationic complex was added to a dinuclear complex of type **I**.[89] In **32**, the μ_3-functional phosphinoenolate acts as an assembling, 5e donor ligand, like the water-derived μ_3-OH ligand that also caps the Pd$_3$ unit. Note that this cluster also provided the first example of a μ_3-OH ligand in palladium chemistry.

In this section, we have seen that phosphinoenolates are versatile ligands which can act as 1e donors, when they are monodentate O-bound ligands, as 3e donors when they are P,O-chelating or μ_2-P,O or μ_2-P,C bridging ligands, or as 5e donors, when they behave as μ_3-P,C,O bridging ligands.

It is often possible to convert one bonding mode into another, as we have seen for F → E (eq 2), F → I (Scheme 10), or I → L (eq 8), which is important to keep in mind when considering the fine-tuning of the properties of the complexes. The major reactivity patterns encountered in this chemistry will be analyzed below, with an emphasis on the chelating P,O systems of type F. Less data are available for the systems derived from the phosphino-oxazoline ligands L^6 and L^7, whose chelating anions (see G) have only recently been reported.[42,52]



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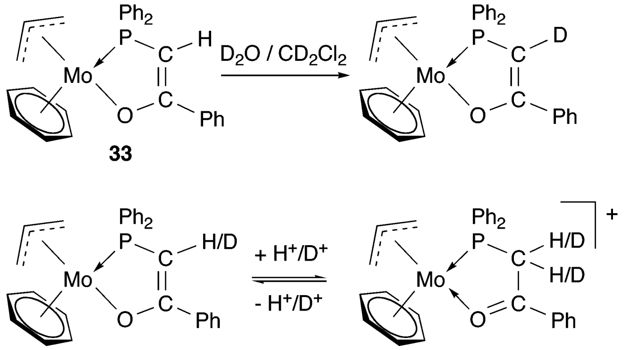
3. Carbon-Based Reactivity

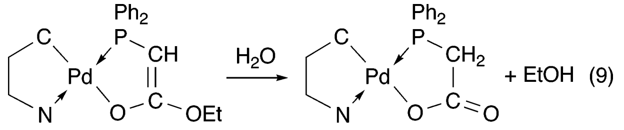
3.1. Protonation Reactions

Protonation of metal complexes containing phophinoenolate and related ligands typically occurs at the enolate carbon, and these reactions are generally reversible. An unprecedented hydrogen−deuterium exchange was observed with **33**, which is isoelectronic to **9**, and its protonated form in D$_2$O (Scheme 13).[54]

Scheme 13. Hydrogen−Deuterium Exchange Involving 33 and Its Protonated Form[54]



As mentioned above, protonation of **31** afforded cationic clusters containing a bridging, ketophosphine ligand L^2.[87,88] However, hydrolysis of the ester function of **23a,b** led to the phosphinocarboxylate complexes **34a,b** (eq 9), which could be obtained directly by reaction of [Pd($\overline{\text{C N}}$)(μ-Cl)]$_2$ with Ph$_2$PCH$_2$CO$_2$Na.[15] Likewise, reaction of 2 equiv of this salt with [PdCl$_2$(NCPh)$_2$] afforded *cis*-[$\overline{\text{Pd\{Ph}_2\text{PCH}_2\text{C(O)O}}$}$_2$],[15] which was recently characterized by X-ray diffraction.[90]



23a C N = dmba
23b C N = 8-mq

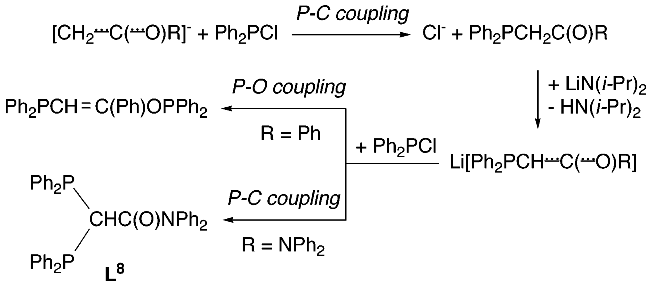
34a C N = dmba
34b C N = 8-mq

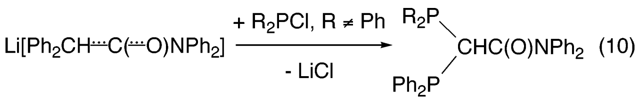
3.2. Reactions with P–Cl Bonds

Organic enolates are known to be ambident reagents, and the fact that the reaction of $Li[CH_2{\cdots}C({\cdots}O)Ph]$ with Ph_2PCl in THF afforded the ketophosphine $Ph_2PCH_2C(O)Ph$ (L^2), by a chemoselective P—C bond formation, was somewhat surprising in view of the known oxophilicity of this P(III) reagent. The same holds true for $Li[CH_2{\cdots}C({\cdots}O)NPh_2]$, which similarly led to $Ph_2PCH_2C(O)NPh_2$ (L^4).[17,19]

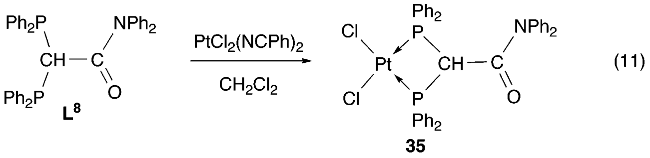
In contrast, reaction of the lithium phosphinoenolate $Li[Ph_2PCH{\cdots}C({\cdots}O)Ph]$ with Ph_2PCl occurred by formation of a P—O bond and yielded the phosphine−phosphinite-type ligand $Ph_2PCH{=}C(Ph)OPPh_2$ (see Scheme 14 and section 4.1).[91] However, the presence of the more electron donating group NPh_2 in $Li[Ph_2PCH{\cdots}C({\cdots}O)NPh_2]$ reverses the chemoselectivity of the reaction with Ph_2PCl in Et_2O or THF and only the P—C enolate coupling product L^8 was observed (Scheme 14).[50] The synthesis of new chiral, functional diphosphine ligands should become readily accessible by selective P−C coupling reactions of $Li[Ph_2PCH{\cdots}C({\cdots}O)NPh_2]$ with different chlorophosphines (eq 10).

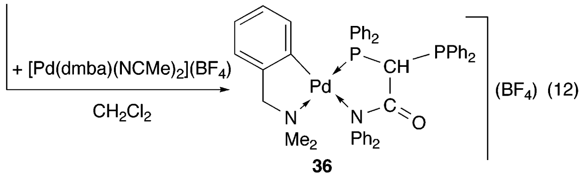
Scheme 14. Selective P−C or P−O Coupling Reactions



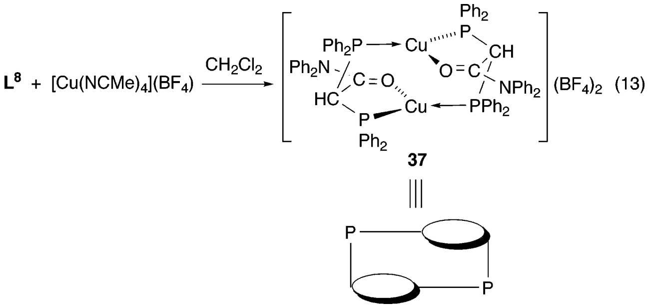


The new ligand L^8 can chelate metal centers by forming four- or five-membered rings depending on the nature of the other ligands present.[50] In the former case (eq 11), the angular flexibility of the two chloride ligands in **35** compensates for the reduced P−Pd−P angle and thus provides stability to the molecule. This is not the case with **36** (eq 12), in which a P,N chelate is formed which, interestingly, contains a pendant phosphorus donor function.

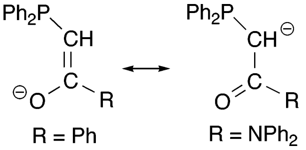




Ligand L^8 can also display a μ_2-η^3 tripod-like bonding as observed in the centrosymmetric dinuclear Cu(I) complex **37,** in which each copper atom is P,O-chelated by one ligand and P-bonded to the other ligand (eq 13). An eight-membered $Cu_2P_4C_2$ ring and a ten-membered $Cu_2P_2C_4O_2$ ring are thus formed with the functional diphosphine ligand. The hemilability observed for this complex, which results from reversible oxygen−metal dissociation in the presence of donor solvents such as MeCN or SMe_2, has been investigated by variable temperature $^{31}P\{^1H\}$ NMR spectroscopy.[50]



As far as the reactivity of $[Ph_2PCH{\cdots}C({\cdots}O)R]^-$ is concerned, one may therefore say that it behaves toward P—Cl bonds according to two limiting forms depending on the nature of the R group:

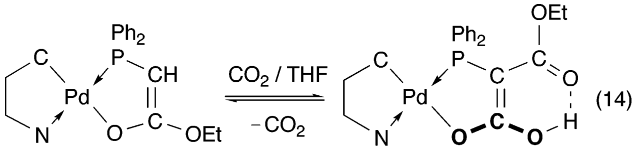


These contrasting chemoselectivities should be related to the different electron donor properties of the R group and/or to the structures of the alkali metal phosphinoenolate reagents in solution as a function of the R group. In this context, it is interesting to note the structural effect of the counterion since the solid-state structures of K(18-crown-6)$[Ph_2PCH{\cdots}C({\cdots}O)Ph]$ and of K(Kryptofix-2,2,2)$[Ph_2PCH{\cdots}C({\cdots}O)Ph]$ are composed of monomeric entities[51] whereas that of $[Na\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}]_4$ is of the cubane type.[92]

3.3. Reactions with Heterocumulenes

3.3.1. Reactions with CO_2

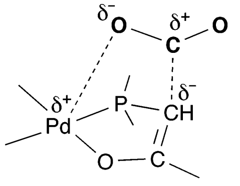
The most surprising reaction in this category was that of the air-stable Pd(II) complexes **23a,b** (C N = dmba, 8-mq) with CO_2. Indeed, bubbling dry CO_2 under ambient conditions through a THF solution of these complexes at room temperature led to an immediate reaction (eq 14).



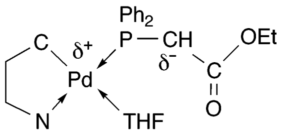
23a C N = dmba
23b C N = 8-mq

38a C N = dmba
38b C N = 8-mq

A structural analysis by X-ray diffraction of the product **38b** established that insertion of CO_2 in the P*C*—*H* bond had taken place with formation of a new C—C bond.[28] This reaction was monitored in solution by the disappearance of the ^{1}H NMR resonance of the PCH proton at 3.15 or 3.31 ppm, for the dmba or 8-mq complexes **23a** and **23b**, respectively, while a new resonance appears for the O—H proton of **38a,b** at 13.9 ppm. Bubbling argon or nitrogen through a THF solution of **38a,b** releases CO_2, and **23a,b** were recovered quantitatively within a few seconds (eq 14). This remarkable reaction, which can be performed for a large number of cycles without any decomposition, provided the first example where a reversible CO_2 insertion in a molecular complex has been fully characterized by X-ray diffraction as resulting from a C—C coupling process.[28] The nature of the ancillary chelate on palladium plays a crucial role in this reaction: the high *trans* influence of the σ-bonded carbon atom accounts for the labilization of the Pd—O bond in both the precursor and the CO_2 complex. On the other hand, the $C_{(P)}\overset{..}{-}C_{(CO2)}$ bond of **38a,b** is weakened by the —C(O)OEt substituent in the α position, and this allows the reaction to become easily reversible. Complexes **23a,b** are thus reversible CO_2 carriers operating under mild conditions which perform a trifunctional activation of CO_2 by nucleophilic attack at the carbon and stabilization of the oxygen atoms by the electrophilic centers Pd and H. Note that no isolable CO_2 insertion product was formed when $Li[Ph_2PCH\overset{..}{-}C(\overset{..}{-}O)OEt]$ was treated with CO_2, which emphasizes the key role played by the palladium center in this reaction. One can envisage an approach of CO_2 from above the metal coordination square-plane as depicted below in M which is favorable from an electrostatic point of view and appears most reasonable from a theoretical standpoint.[51]



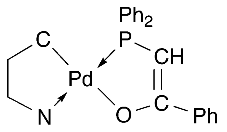
M



N

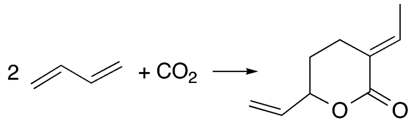
The reaction with CO_2 occurs best in THF solution, where one could assume that the five-membered ring chelate displays a pronounced 1,3-dipolar character or even opens up under the influence of THF coordination, as shown in N. Such solvent effects were not considered in the theoretical investigation.[51] Both this CO_2 reaction and the formation of **22** in Scheme 10 provide strong evidence for the carbanionic character of the CH group α to the phosphorus atom.

It became obviously interesting to evaluate the chemical reactivity toward CO_2 of complexes related to **23a,b** and differing only by the nature of the organic substituent at the C—O group. Thus, complexes **39** were prepared from the β-ketophosphine $Ph_2PCH_2C(O)Ph$ (L^2) according to Scheme 4,[16] but they did not react with CO_2 under the conditions where **23a,b** led to carbon—carbon bond coupling.[93] This may be explained by a decreased carbanionic character of the carbon atom α to the phosphorus upon replacement of OEt by Ph and illustrates a major reactivity difference between the phosphinoenolates derived from L^1 and L^2.



39a C N = dmba
39b C N = 8-mq

The CO_2 activation reaction of eq 14, which results for this triatomic molecule in a bent structure related to that of the radical anion $CO_2^{\bullet-}$, suggested that its molecular activation may translate into catalytic properties. In the context of investigating the possiblity to use CO_2, which is an abundant and clean source of carbon, for the synthesis of added-value chemicals, the catalytic properties of these CO_2 complexes were investigated for the telomerization reaction of butadiene with CO_2, which can lead to lactones (eq 15), acids, or esters.[93−97] Complex **23a** was shown to be the first example of a reversible CO_2 carrier showing catalytic activity in CO_2 chemistry.[93] Considering the lack of reactivity of **39a,b** toward CO_2 and their inactivity in butadiene-CO_2 telomerization, this study allowed us to establish that, at least in this case, CO_2 fixation (activation) by a metal complex was a prerequisite for catalytic activity but did not represent a sufficient condition since **23b** reversibly binds CO_2 but does not display catalytic activity. This latter observation was explained by the stronger rigidity of the 8-mq chelate compared to dmba, which limits the accessibility to the Pd center. Using a modified catalytic system, CO_2 telomers were obtained in 76% yield and formation of the δ-lactone **40** was achieved with a selectivity of 96%.[93,94]



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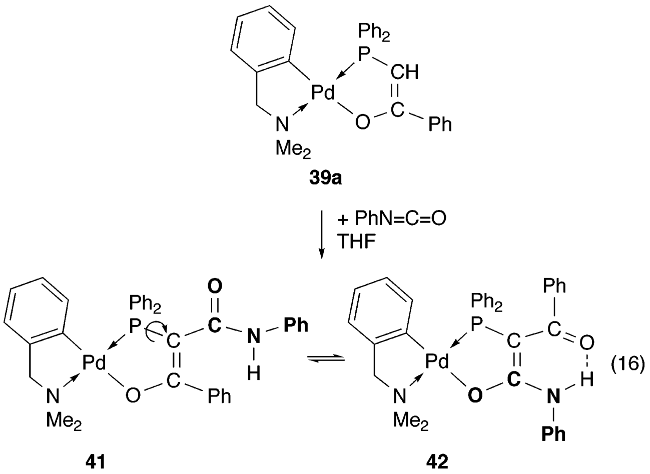
3.3.2. Reactions with Organic Isocyanates

Although the carbanionic character of the enolate carbon of complexes **39a,b** is not sufficient to allow their reaction with CO_2, it is high enough to give rise to the insertion into the P*C*—*H* bond of a heterocumulene more reactive than CO_2, such as PhNCO. This reaction afforded two isomeric complexes **41** and **42** which were shown to be in dynamic equilibrium (eq 16).[98,99] Cross-experiments established that this isomerization did not proceed via PhNCO deinsertion/reinsertion.[99] Thus, the necessary Pd—O bond dissociation

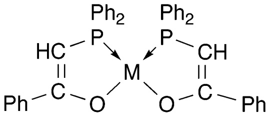


(16)

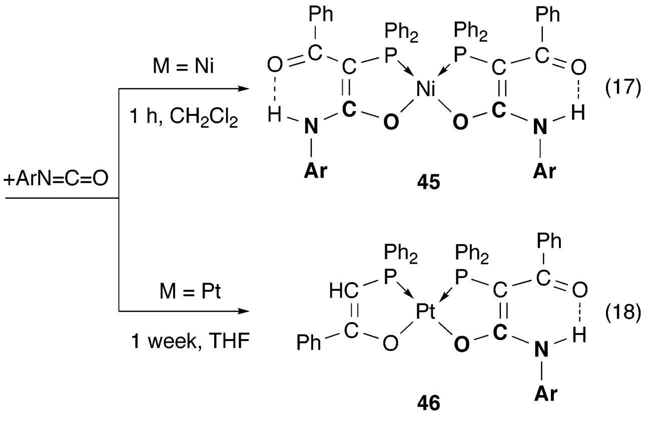
for this isomerization to occur is facilitated by the high *trans*-influence of the cyclometalated C atom and is followed by easy rotation of the ligand about the P−C and the C(P)−C(Ph) bonds. Whereas the former isomer may be viewed as the direct Michael-addition product of **39a** and PhNCO, without the need to open the P,O chelate, the latter is similar to the CO_2 complex **38a** (eq 14). The hemilabile behavior[9] of this new multifunctional ligand shows that one should be cautious in deciding the sequence of events in such reactions between phosphinoenolate complexes and organic electrophiles. Does the reaction first occur with retention of the P,O-chelating bonding mode, with subsequent opening and isomerization, or does it first proceed by opening of the chelate? In the CO_2 chemistry of eq 14, there has been no evidence for a primary product resulting from CO_2 insertion into the P*C*−*H* bond with retention of the original P,O chelate.

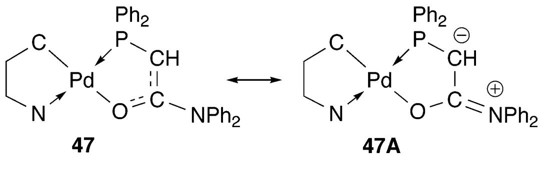
Since organic isocyanates are more reactive than CO_2, as just illustrated with complex **39a**, which did not react with CO_2, it is not surprising that the more reactive complexes **23a,b** also reacted with PhNCO. In this case, however, only the isomer corresponding to **42** was obtained,[99] probably because, as in **38**, the better electron donor OEt group favors H-bonding and the resulting cyclic structure for the ligand moiety.

The greater reactivity of the Ni(II) vs Pt(II) phosphinoenolates **43** and **44** is illustrated by the reactions of eqs 17 and 18: both P,O-chelates of **43** undergo coupling with ArNCO to give **45**, in contrast to only one chelate in the case of the Pt(II) complex which afforded **46**.[99]

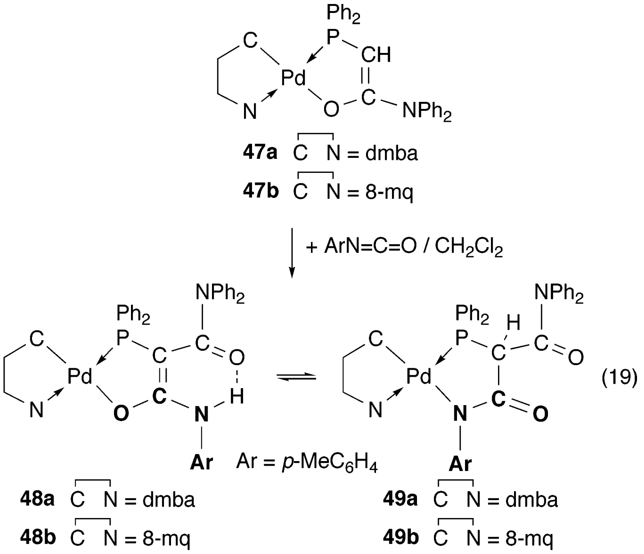


43 M = Ni
44 M = Pt

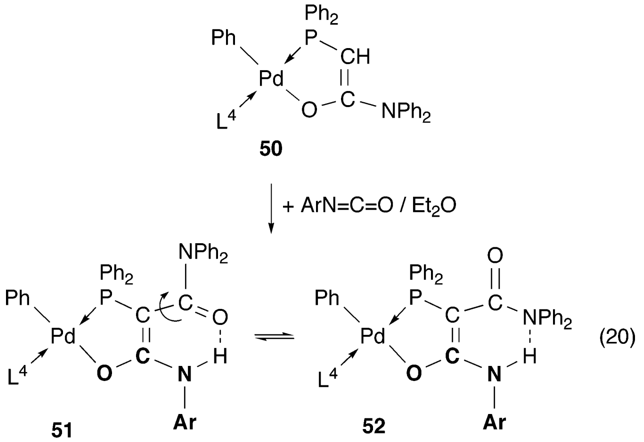




Comparative studies with phosphinoenolate complexes **47a,b**, prepared from 2-diphenylphosphino-*N*,*N*-diphenylacetamide L,^{4} showed that their enolate carbon is more electron-rich than in those derived from L^2. Structural data indicated that the resonance form **47A** significantly contributes to the overall structure.[50] Accordingly, the Pd(II) complexes **47a,b** reacted with arylisocyanates to give the products **48a,b**, analogous to **42**, which are in solvent-dependent equilibrium with yet another isomeric structure, **49**, characterized by a P,N chelating mode of the ligand (eq 19).[50]



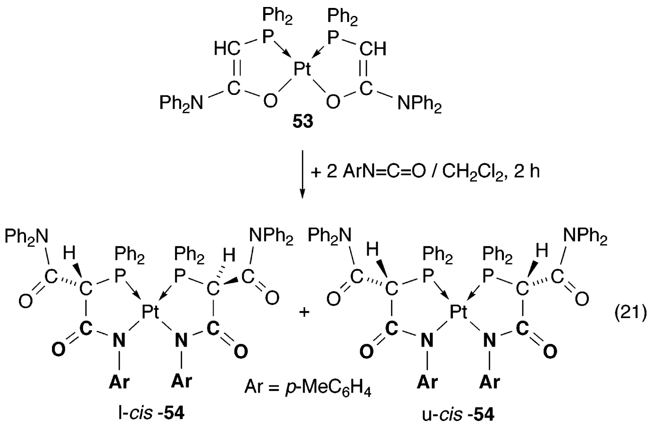
In the case of the Pd(II) phenyl complex **50**, two isomers of the Michael-addition product with ArNCO were identified and the ratio **51**:**52** of ca. 1:3 was determined by NMR spectroscopy (eq 20).[74] A similar result was obtained with the acetyl ligand in place of the phenyl group.



$L^4 = Ph_2PCH_2C(O)NPh_2$
Ar = p-MeC_6H_4

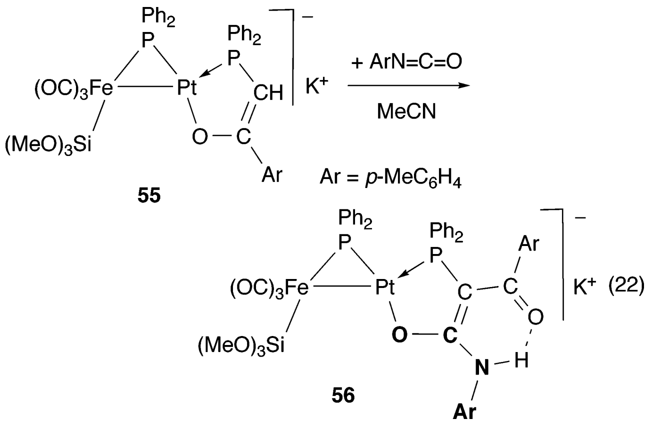
In contrast to the reaction of eq 18, the bis-chelated Pt(II) complex **53** reacted smoothly with ArNCO to give **54** after isocyanate insertion into *each* of the chelate C−H bonds (eq 21). Only one geometrical isomer was formed, and the ratio of the diastereoisomers *l-cis*-**54**:*u-cis*-**54**, which contain chiral bifunctional phosphine ligands, was determined to be ca. 1:1 by NMR spectroscopy.[50] This reaction provides additional evidence for the higher reactivity of phosphinoenolate complexes derived from L^4 as compared to L^1. Their reactivity is, however, not sufficient to give rise to a reaction with CO_2 under similar conditions to those for the complexes derived from L^1 (see section 3.3.1).

The first heterodimetallic complexes containing a chelating phosphinoenolate ligand[100] were also rare examples of



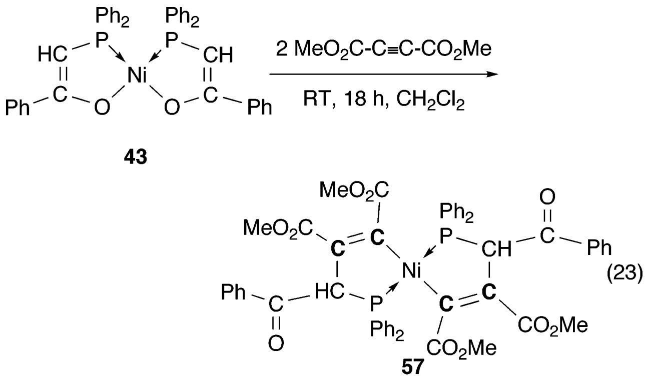
(21)

anionic phosphinoenolate metal complexes.[55] They were therefore expected to readily react with electrophilic reagents. The quantitative reaction of **55** with ArNCO to give **56** (eq 22)[100] was indeed much faster (ca. 2 h) than that in the case of the neutral platinum complex **44**, which required several days (eq 18). This enhanced reactivity results from a combined effect of the dimetallic nature of **55** and of its anionic charge. For comparison, the phosphinoenolate rhenium complex $[\mathrm{NMe_4}][\mathrm{Re}\overline{\mathrm{ClBr\{Ph_2PCH{\cdots}C({\cdots}O}}\mathrm{)Ph\}(CO)_2}]$ (see Scheme 6) did not react with organic isocyanates, despite its negative charge.[55]



(22)

In conclusion, phosphinoenolate metal complexes insert organic isocyanates into their P*C*—*H* bond with increasing facility in the sequence Pt < Pd < Ni. Owing to the unsymmetrical structure of these heterocumulenes when compared to CO_2 (see section 3.3.1), they afford a diversity of isomeric, 3e donor P,O or P,N chelating multifunctional ligands depending on the metal, the nature of the substituent on the enolate moiety, and the reaction conditions. These situations are depicted in Scheme 15. Bonding modes P and R correspond to that observed for the more symmetrical heterocumulene O═C═O molecule in complexes **37** (eq 14). Carbon—carbon bond formation reactions involving organic isocyanates are relevant to a number of organic transformations catalyzed by transition metal complexes.[101]



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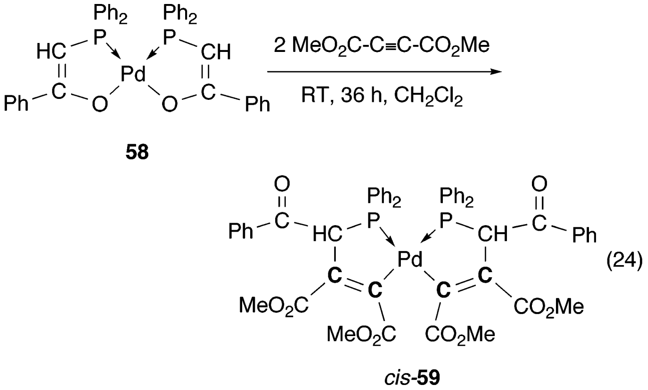

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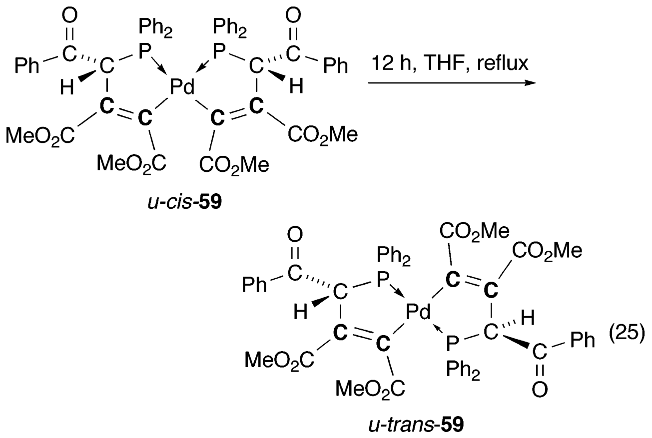


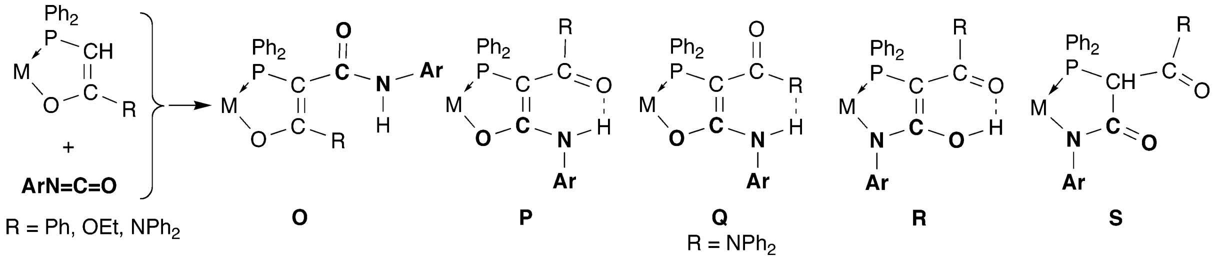
(25)

3.4. Reactions with Alkynes, Tetracyanoethylene, and Azo Compounds

3.4.1. Reactions with the Alkyne DMAD

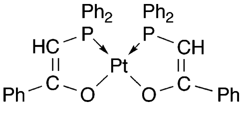
The ease with which carbon—carbon coupling reactions between the Ni-, Pd-, and Pt-phosphinoenolate complexes

Scheme 15. Isomeric Structures Identified for the Coupling Products of the Group 10 Metal-Coordinated Phosphinoenolates with Organic Isocyanates

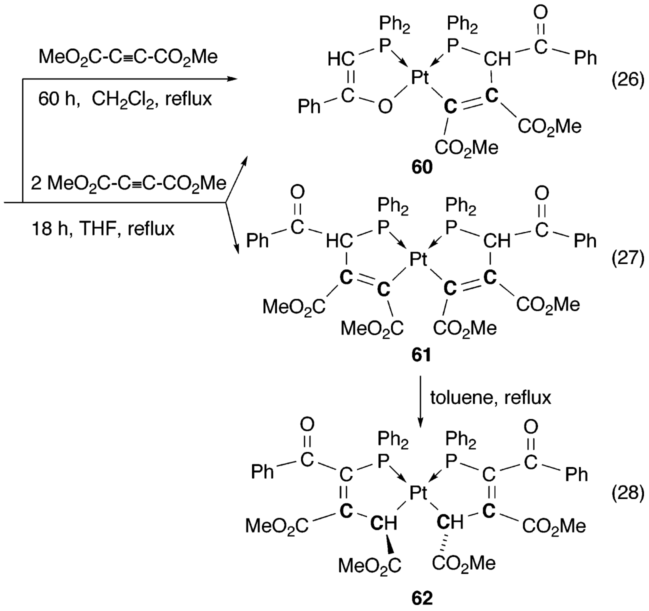


and the activated alkyne $MeO_2C{-}C{\equiv}C{-}CO_2Me$ (DMAD) occur was also found to follow the order Ni > Pd > Pt.[102,103] In the *trans*-bis(alkenyl) Ni(II) complex **57** formed from **43** (eq 23), two stereogenic centers have been generated and the complex was isolated as a mixture of diastereoisomers. With the Pd(II) precursor **58**, the reaction was slightly slower and the *cis* product **59** was obtained in the form of two diastereoisomers (eq 24). The *u-cis* isomer of this bis(alkenyl) complex was shown to thermally isomerize to the *u-trans* form (eq 25). This is suggestive of an intramolecular isomerization involving a tetrahedral transition state.

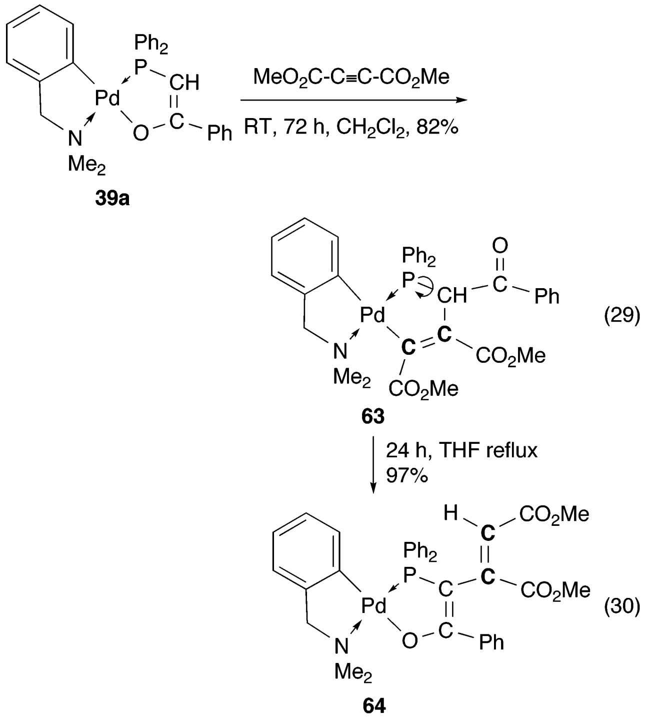
In the reaction with the Pt(II) complex **44**, only one P,O chelate reacted with the alkyne in refluxing CH_2Cl_2 to give the alkenyl complex **60** (eq 26) (cf. the similarity with the isocyanate insertion reaction of eq 18), but in refluxing THF, a bis-coupling reaction afforded **61** (eq 27). Increasing the reaction temperature by working in refluxing toluene led to a 1,3-H shift, and the bis-alkyl complex **62** of *l* configuration was formed diastereoselectively (eq 28).[103] Its higher stability is likely due to the resulting electronic conjugation within the ligand.

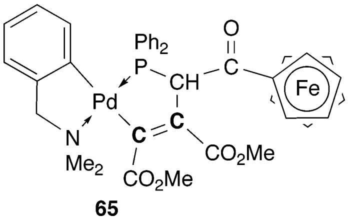


44



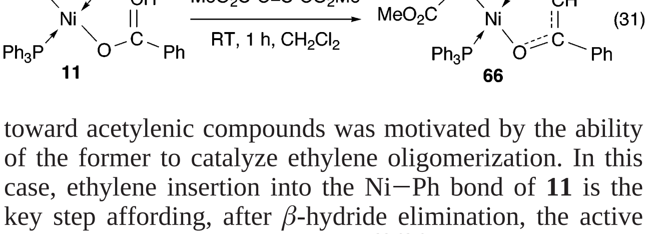
With the Pd(II) bicyclic complex **39a**, the phosphinoenolate moiety was found to be more reactive toward DMAD than the Pd–C bond of the C,N chelate since the C–C coupling product **63** was formed first (eq 29).[103,104] As with **58** (eq 24), this reaction occurred at room temperature. A product similar to **63**, **65**, was obtained with the ferrocenylphosphinoenolate derived from ligand L[3,104] and with the ester-derived Pd(II) phosphinoenolate complex **23a**.[105] Thermal isomerization of **63** via Pd–C bond breaking and H migration afforded **64**, which has a conjugated ligand system and corresponds to the formal insertion of the alkyne into the C–H bond of the P,O chelate (eq 30). This reaction restores a P,O chelate, in contrast to the case of the Pt(II) bis(alkenyl) complex **61**, whose isomerization product **62** retains the Pt–C bonds (eqs 27 and 28). Again, having analyzed the reaction sequence leading to **64** was important since if **63** had not been isolated, one could have assumed a direct *cis*-insertion of the alkyne DMAD into the enolate C–H bond of **39a** without opening of its Pd–O bond. It is also interesting to note that a related isomerization was observed to be reversible in the aryl isocyanate chemistry (eq 16).[98] With manganese carbonyl derivatives, insertion of DMAD into the $PC_{sp^2}{-}H$ bond of a chelating diphosphanylmethanide ligand has recently been found to occur with retention of the four-membered ring $\overline{\mathrm{Mn{-}P{-}C{-}P}}$.[106]



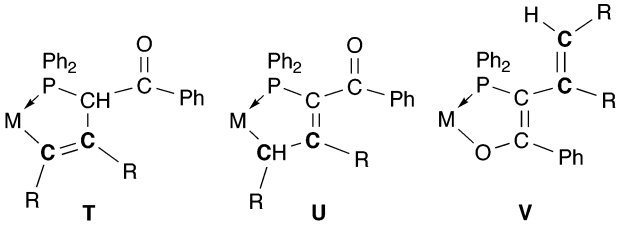


65

It is interesting to contrast the lack of reaction of the Pd–C bond in **39a**[103] with the chemoselective insertion of DMAD into the Ni–Ph bond of **11** (eq 31) and not into the Ni–phosphinoenolate moiety, as observed in the case of complex **43** (eq 23). A comparison of the reactivity of **11** and **43** toward acetylenic compounds was motivated by the ability of the former to catalyze ethylene oligomerization. In this case, ethylene insertion into the Ni–Ph bond of **11** is the key step affording, after *β*-hydride elimination, the active species containing a Ni–H bond.[33,63,64] Similarly, DMAD



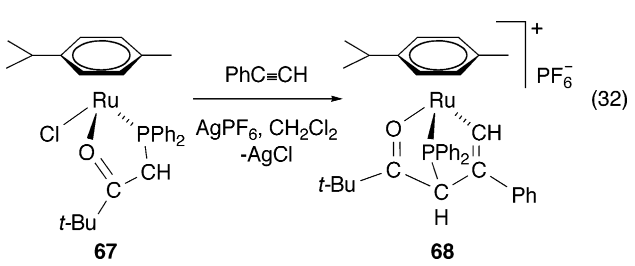
Scheme 16. Isomeric Structures Identified for the Coupling Products of the Group 10 Metal-Coordinated Phosphinoenolates with the Alkyne DMAD (R = CO_2Me)



inserts into the Ni−Ph bond of **11** to give **66** (eq 31), and likewise for diphenylacetylene or CO_2.[64,107]

In contrast to the classical methods used to generate a metal−alkenyl bond by alkyne insertion into a M−C or M−H bond, those described here did not involve a carbon center directly bonded to the metal. In summary, all three types of isomeric structures T through V have been encountered (Scheme 16). The primary reaction products have a ligand arrangement of type T and may be thermally isomerized to forms U and V, which contain a conjugated ligand system. More data are required for a rigorous comparison of the conditions for the occurrence of all the possible isomeric products, including the choice of the metal center.

These structures are reminiscent of the bonding modes encountered above when examining the reactivity of the heterocumulenes with CO_2 or ArNCO (see section 3.3, eq 14, and Scheme 15). In these cases, however, an immediate H-shift restored a P−C_{sp^2} linkage, except in the case of the phosphinoenolate derived from L^4, and the ligand structure in complexes **49a,b** and **54** is related to that in type T complexes (eqs 19 and 21). Interestingly, a C−C bond formation reaction related to those in eqs 23 and 24 was observed between the Ru(II) phosphinoenolate complex **67** and PhC≡CH but the preferred octahedral coordination geometry of the metal allowed formation of a *fac*-tripodal ligand involving the phosphine, the oxygen atom of the keto group, and a σ-coordinated vinyl fragment in **68** (eq 32).[108]



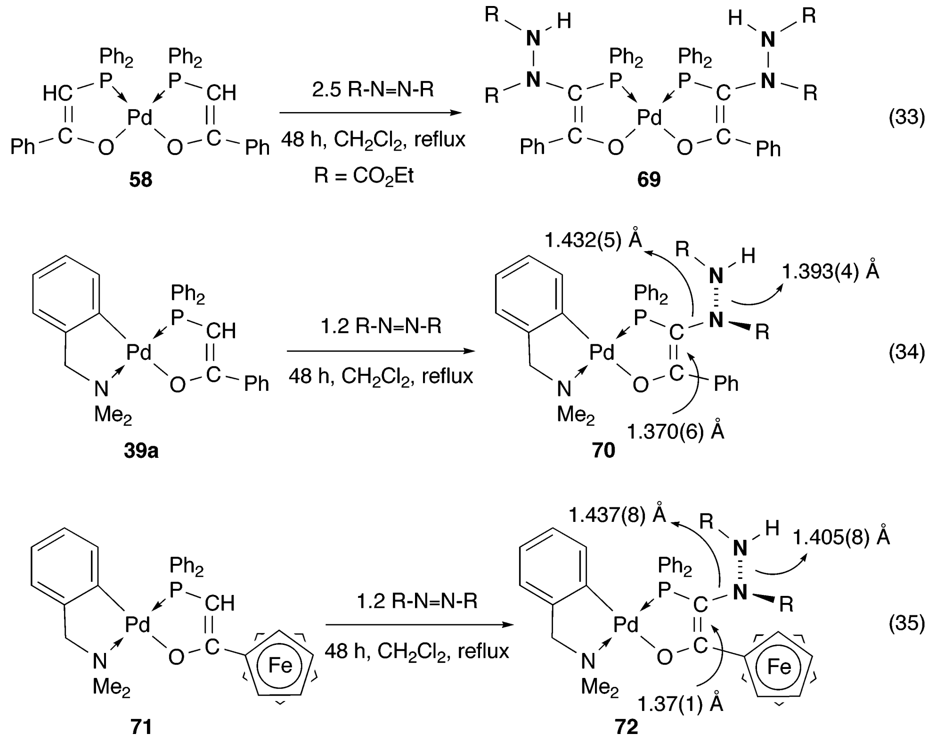
3.4.2. Reaction with Tetracyanoethylene

The complex **23a**, which readily reacts with CO_2 (see section 3.3.1), also undergoes C−C bond formation with tetracyanoethylene (TCNE) to form an alkyl complex. This reaction is closely related to that between this complex and DMAD, which afforded an analogue of **63**.[105]

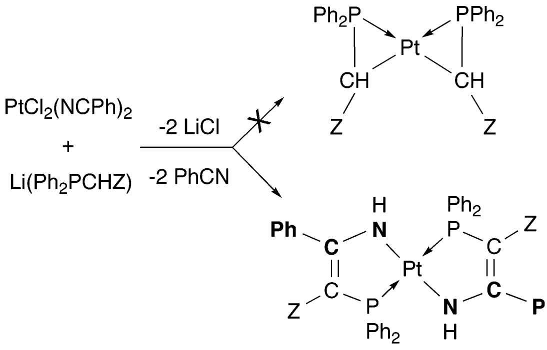
3.4.3. Reactions with Diethyl Azodicarboxylate $EtO_2C—N{=}N—CO_2Et$

The alkyne couling reactions of eqs 24 and 29 involving Pd(II) complexes were extended to the formation of C−N bonds using diethyl azodicarboxylate $MeO_2C—N{=}N—CO_2Me$ as the Michael acceptor.[109] The bis(phosphinoenolate) Pd(II) complex **58** reacted stepwise (one enolate after the other) to afford **69** (eq 33). As in the case of the alkyne DMAD (eq 29), complex **39a** reacted with $EtO_2C—N{=}N—CO_2Et$, specifically with the enolate function, to afford **70** (eq 34), which is related to **64**. An isomeric structure similar to **63** was not observed. The ferrocenyl derivative **71** similarly afforded **72** (eq 35). Both **70** and **72** have been characterized by X-ray diffraction (Scheme 17).[109]

Scheme 17. Formation of C(enolate)−N Bonds by Reaction of Phosphinoenolate Pd(II) Complexes with R−N=N−R (R = CO_2Et)[109]



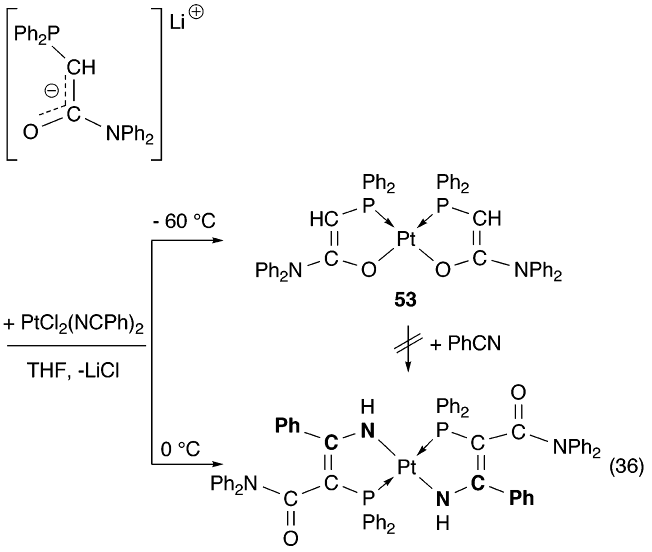
Scheme 18. Nucleophilic Attack of Functional Phosphino-carbanions on Coordinated Organonitriles



73a Z = CN
73b Z = C(O)OEt
73c Z = C(O)NPh2

3.5. Reactions with Coordinated Organonitriles

As briefly mentioned in section 2.1, the reactions of the functional carbanions $\text{Li}(\text{Ph}_2\text{PCHZ})$ (Z = CN, C(O)OEt, C(O)NPh_2) with $[\text{PtCl}_2(\text{NCPh})_2]$ occurred by nucleophilic attack on the coordinated nitriles, rather than by simple nucleophilic displacement of the chlorides and of the labile benzonitrile ligands (Scheme 18). In the resulting complexes, *trans*-$[\text{Pt}(\text{Ph}_2\text{PC(Z)}{=}\text{C(Ph)NH})]$ (**73**), the benzonitrile ligand ends up formally inserted into the P*C*—*H* bond of the enolate moiety. These were, to the best of our knowledge, the first examples of reactions of a carbanion on a coordinated nitrile.[48] When $\text{Li}[\text{Ph}_2\text{PCH}\overset{...}{-}\text{C}(\overset{...}{-}\text{O})\text{NPh}_2]$ was reacted with $[\text{PtCl}_2(\text{NCPh})_2]$ in THF at −60 °C, the *cis* complex **53** was isolated in high yield. It is analogous to *cis*-$\text{Pt}[\text{Ph}_2\text{PCH}\overset{...}{-}\text{C}(\overset{...}{-}\text{O})\text{Ph}]_2$ (**44**). However, when this reaction was performed at 0 °C, the *trans* complex **73c** was isolated instead (eq 36).[50] It was shown that **53** does not react with uncoordinated benzonitrile, which confirms that formation of **73** results from the nucleophilic attack of the carbon atom of $[\text{Ph}_2\text{PCH}\overset{...}{-}\text{C}(\overset{...}{-}\text{O})\text{NPh}_2]^-$ on the CN carbon atom of the coordinated benzonitrile ligand, this being followed by proton transfer from the enolate carbon to the nitrogen atom.



53

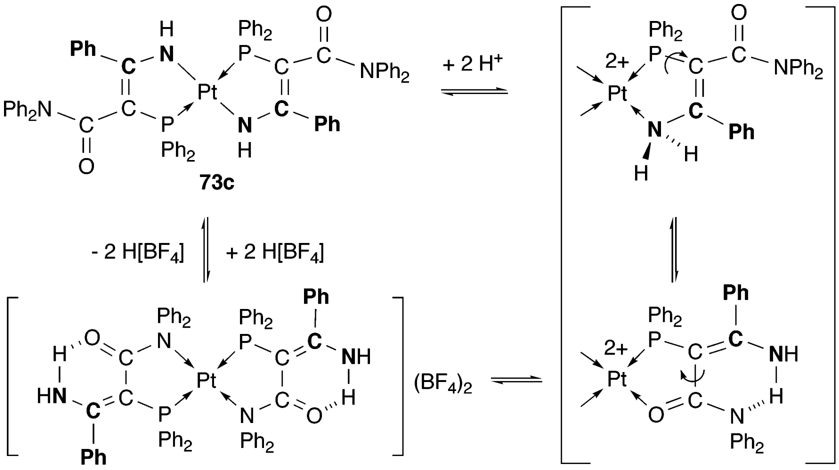
73c

Protonation of complex **73c** occurred at the coordinated ligand with formation of **74**, which contains unusual phosphine amide, enamine ligands (Scheme 19). Protonation is likely to occur at the coordinated nitrogen atom (although alternatives are conceivable) and would be followed by rotation of the ligand about the P−C bond and coordination of the NPh_2 donor group.

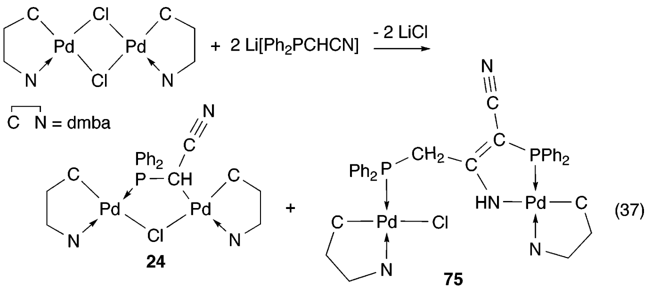
A further example of the C-based reactivity of a Pd-coordinated functional carbanion is that of $(\text{Ph}_2\text{PCHC}{\equiv}\text{N})^-$. It is related to the reaction in Scheme 18 dealing with the nucleophilic attack of the carbanion on the coordinated nitrile ligand of a Pt(II) complex, giving the complexes *trans*-$[\text{Pt}(\text{Ph}_2\text{PC(Z)}{=}\text{C(Ph)NH}]$ **73**. The reaction of 2 equiv of $(\text{Ph}_2\text{PCHC}{\equiv}\text{N})^-$ with the dinuclear complexes $[\text{Pd}(\overline{\text{C N}})(\mu\text{-Cl})]_2$ led to **24** and to the unusual dinuclear Pd(II) complex **75** (eq 37). Likely intermediates in the formation of **75** are shown in Scheme 20. First, intermediate "$[\text{Pd}(\overline{\text{C N}})(\text{Ph}_2\text{PCHC}{\equiv}\text{N})]$" would react with the complex $[\text{Pd}(\overline{\text{C N}})\text{Cl}(\text{Ph}_2\text{PCH}_2\text{C}{\equiv}\text{N})]$ **76**, itself formed by reaction of $[\text{Pd}(\overline{\text{C N}})(\mu\text{-Cl})]_2$ with the residual phosphine $\text{Ph}_2\text{PCH}_2\text{C}{\equiv}\text{N}$ left unreacted during the preparation of the carbanion.[49]

Since in **76** the nitrile function of the Pd-coordinated phosphine $\text{Ph}_2\text{PCH}_2\text{C}{\equiv}\text{N}$ (L^5) is little perturbed compared to that in the free ligand, this reaction expands the scope of

Scheme 19. Reversible Protonation at the Phosphine Amide, Enamine Ligand of 73c



74



(37)

nucleophilic reactions of functional carbanions on coordinated nitriles.[110,111]

Going back to the Pt(II) complexes **73a**−**c** in Scheme 18, one could formally consider their P,N chelate as resulting from nucleophilic attack of uncoordinated benzonitrile by “$[\mathrm{Pd}(\overline{\mathrm{C\ N}})(\mathrm{Ph_2PCHC{\equiv}N})]$”, although the actual synthesis occurred via the opposite sequence of events: addition of the uncoordinated carbanion to the Pt-coordinated benzonitrile ligands.[48,49] However, there is a striking similarity between complexes **73a**−**c** and the products described in sections 3.3.1−3.3.3 which resulted from a carbon-based nucleophilic attack of the metal-coordinated α-phosphino-stabilized carbanions on various Michael acceptors (eq 14 and Schemes 15 and 16). In particular, bonding mode U in Scheme 16 corresponds to the arrangement found in complexes **73a**−**c**.

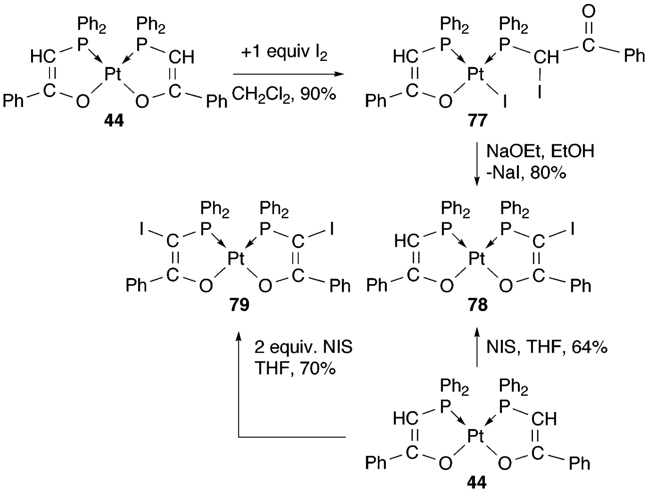
3.6. Reaction with Iodine or *N*-Iodosuccinimide

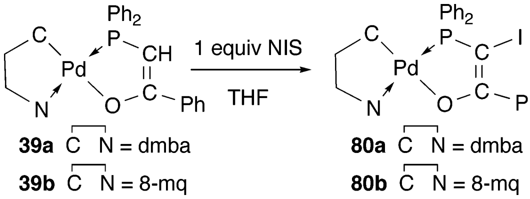
To increase the scope of possible functionalizations of coordinated phosphinoenolates, replacement of the PC−H bond with a PC−I bond would be desirable, and two procedures were employed to this end. The Pt(II) complex **44** was reacted with iodine, and the *β*-iodo(phosphinoenolate) complex **78** was obtained after deprotonation of the *β*-iodo(ketophosphine) in **77** (Scheme 21).[112] The formation of Pt−I and C−I bonds in complex **77** illustrates the heterolytic I^-/I^+ behavior of iodine.

Complex **78** and the bis[*β*-iodo(phosphinoenolate)] complex **79** were directly obtained from **44** and 1 or 2 equiv of *N*-iodosuccinimide (NIS), respectively (Scheme 21).

The oxidation reaction with iodine did not allow us to isolate the desired products with the analogous Ni(II) or Pd(II) precursors **43** and **58**, respectively. However, reaction of the milder reagent NIS with **39a,b** afforded the *β*-iodo(phosphinoenolate) complexes **80a,b** (eq 38). The reactions of NIS with **44** and **39a,b** appear to be the first direct functionalization reactions of a phosphinoenolate C−H bond.[112]

Scheme 21. Formation of the *β*-Iodo(phosphinoenolate) Complexes 78 and 79

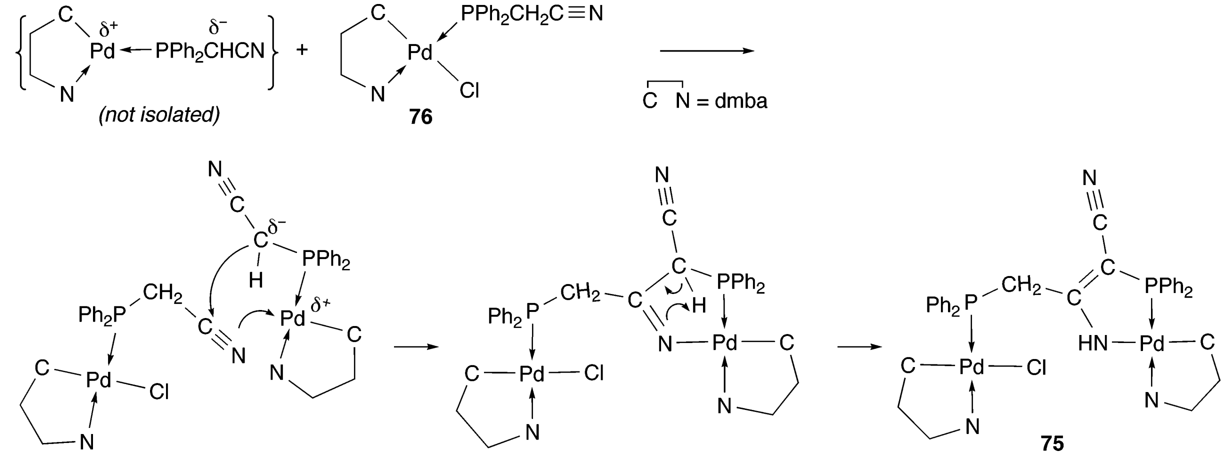


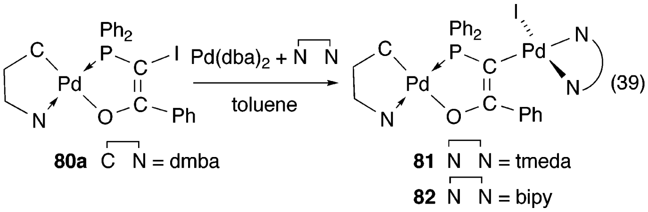


(38)

In attempts to exploit the newly formed C−I bond for further reactivity, no reaction was observed with HC≡CPh or $HC{\equiv}CSiMe_3$ in the presence of $[Pd(PPh_3)_4]$ and CuI. This could be due to a lack of reactivity of the C−I bond toward Pd(0), and such oxidative insertion of the metal represents a key step in the catalytic Heck reaction. Indeed, no reaction was observed between **80a** and $[Pd(PPh_3)_4]$ in toluene at 60 °C. However, this Pd(II) complex reacted with $[Pd(dba)_2]$ in the presence of nitrogen donor ligands such as tetramethylethylenediamine (tmeda) or 2,2′-bipyridine (bipy) (but not in the presence of PPh_3) by oxidative addition of the C−I bond accross the Pd(0) to give complexes **81** and **82** (eq 39).[112] The tmeda ligand in **81** is not displaced by bipy to afford **82**, nor is it displaced by dppe. The kinetic inertness of **81** is most likely due to steric factors, and an X-ray

Scheme 20. Possible Mechanism Accounting for the Formation of the Dinuclear Pd(II) Complex 75[49]





(39)

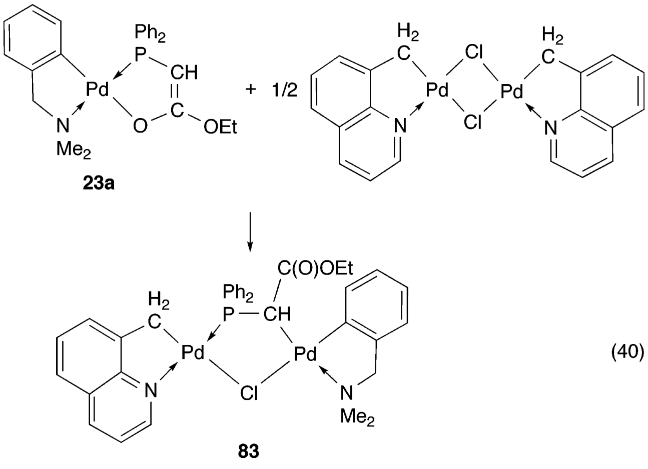
diffraction study of its molecular structure established that the coordination planes of the two palladium atoms are almost orthogonal to each other, so that easy access to a five-coordinate transition state at the tmeda-chelated Pd center may well be sterically prevented. The Pd$-$C$_{sp^2}$ bond of the complexes is reactive toward protic reagents.

In complexes **81** and **82**, the phosphinoenolate P,O ligand behaves as a 4e donor, doubly negatively charged ligand. It is interesting to contrast these homodinuclear complexes containing a P$-$C$_{sp^2}$ bridge between the metal centers with those described below in section 3.7 in which a P$-$C$_{sp^3}$ bridge results from electrophilic attack of a metal complex on the phosphinoenolate carbon atom, which thus retains its C$-$H bond.

3.7. Reactions with Metal Electrophiles

Reactions of coordinated phosphinoenolates with electrophilic metal centers predominantly occur at the softer carbon center, although we will see in section 4.4 that the donor ability of the metal-coordinated enolate oxygen toward other metal centers has also been demonstrated.

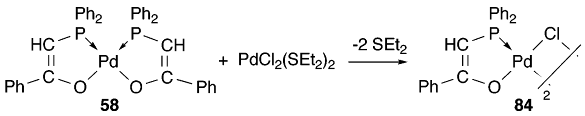
An early study clearly demonstrated the carbon-based reactivity of the coordinated phosphinoenolates with metal centers. Thus, when the dimethylbenzylamine complex **23a** was reacted with [Pd(8-mq)(μ-Cl)]$_2$, the dinuclear complex **83**, with a different $\overline{\text{C N}}$ chelate on each Pd(II) center, was obtained in high yield (eq 40).[28] This reaction clearly demonstrated that, notwithstanding the stability of mononuclear phosphinoenolate complexes such as **23**, their enolate carbon is sufficiently nucleophilic to open the bridge of chloride-bridged dinuclear Pd(II) complexes. This palladium "tagging experiment" allowed us to unambiguously establish the sequence of reactions shown in Scheme 10 where the mononuclear complex **23a** was rapidly formed and then reacted with the remaining chloride-bridged dinuclear Pd(II) precursor, since only half of it is consumed at this stage of the reaction, to afford the final product **22**.



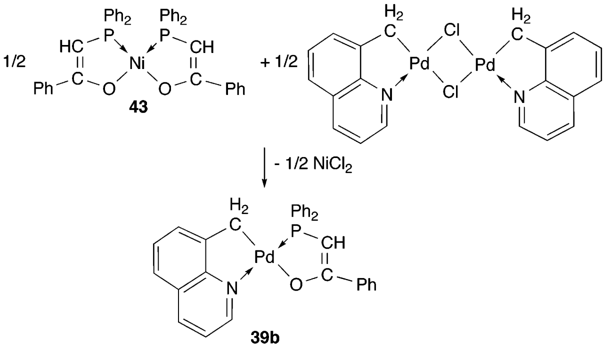
(40)

Although a mononuclear complex containing the phosphinoenolate derived from L^5 could not be isolated, it could likewise explain the formation of complex **24** (eq 37) and it was invoked as an intermediate in the reactions of Scheme 20.

Transmetalation reactions in which a chelating phosphinoenolate ligand is transferred from Pd(II) to another Pd(II) center (eq 41)[75] or from Ni(II) to a Pd(II) (eq 42)[75] or Pt(II) center (eq 43)[76] also involve nucleophilic attack of the enolate carbon on the other metal.



(41)



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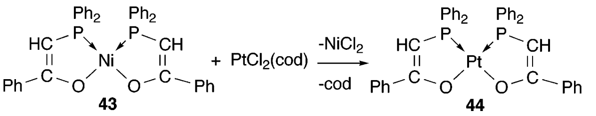
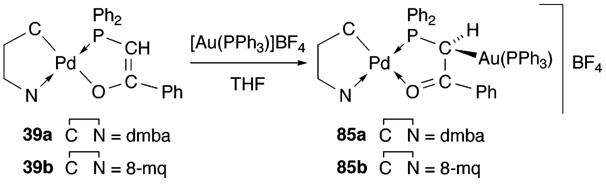


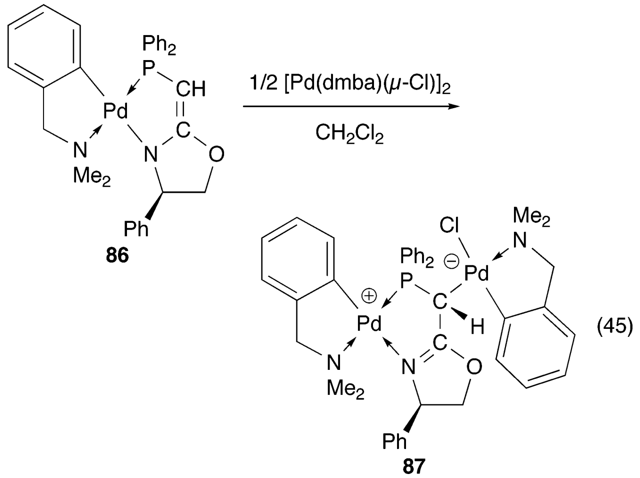
(43)

Further reactions involving the carbon center of coordinated phosphinoenolates include those with Au(I) reagents (eq 44).[76] In the products **85a,b**, a stereogenic C center has been generated and the C$-$O bond order has increased, as in the reactions of **39a,b** with the isolobal proton. However, in the IR spectrum, an absorption around 1510 cm^{-1} was observed instead of the ν(CO) band at 1570 cm^{-1} found in $[(\overline{\text{C N}})\overline{\text{Pd}(\text{Ph}_2\text{PCH}_2\text{C}(\text{O}})\text{Ph})]^{+}$.[76]



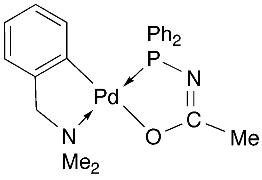
(44)

Related to **39a**, complex **86** (see bonding mode G in Scheme 5) contains an anionic P,N chelate obtained by deprotonation of the Pd(II)-coordinated chiral phosphinooxazoline ligand (of the L^7 type) (4-(*R*)-phenyl-2-oxazoline-2-ylmethyl)diphenylphosphine (abbreviated (*R*)-PCH$_2$ox$^{\text{Ph}}$). It reacted with [Pd(dmba)(μ-Cl)]$_2$ to afford diastereoselectively the dinuclear complex $[\{\overline{\text{Pd(dmba)Cl}}\}\text{-}(R)\text{-}\{\overline{\text{CHPPh}_2\text{-}(R)\text{-ox}^{\text{Ph}}}\}\text{Pd(dmba)}]$, **87**, in which a Pd(dmba)Cl moiety is directly bonded to the carbon atom α to P, which results in an unusual zwitterionic structure (eq 45).[113] Although this



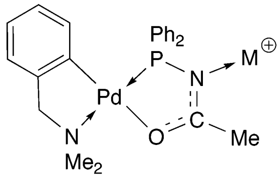
(45)

reaction was diastereoselective, generation of both the *R* and *S* configurated stereogenic P−*C* centers is generally expected in reactions of phosphinoenolates with metal centers such as that shown in eq 44. With the aim of simplifying this matter, the replacement of the PCH functionality with the isoelectronic PN group of phosphinoiminolates, as in **88**, was envisaged since the nitrogen atom could retain a planar coordination geometry upon metalation. Furthermore, the simple exchange of a CH group by a N atom can bring about interesting electronic and geometric differences in molecular complexes, as shown with the phosphines $Ph_2PNHC(O)R$ and $Ph_2PCH_2C(O)R$.[114]

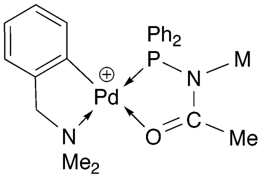


88

The interaction between the iminolate N atom of **88** and a metal cation could be formally envisaged as resulting from a dative bond involving its lone pair, as in a type W structure, or from a more covalent interaction, as shown in X, resulting in the positive charge of the complex being more localized on the Pd(II) center than on the metal M. Intermediate situations between these limiting forms are also conceivable.



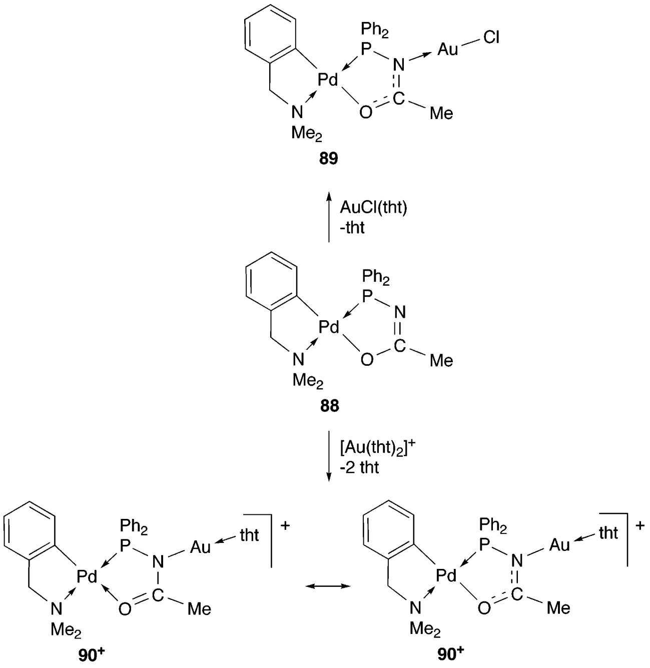
W



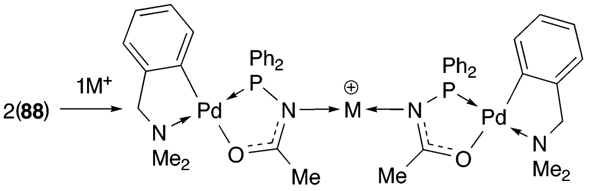
X

When **88** was reacted with 1 equiv of [AuCl(tht)], which contains the labile tht (tetrahydrothiophene) ligand, the expected product **89** was isolated in good yield (Scheme 22).[115] Formally, **88** behaves here as a neutral, 2e donor ligand (L-type) toward the Au(I) center, which retains its usual 14e electronic configuration. However, the metalloligand **88** behaves formally as an X-type ligand in the cationic complex $\mathbf{90}^+$, obtained by reaction with $[Au(tht)_2]^+$.

Scheme 22. Behavior of the Phosphinoiminolate Complex 88 as a Formal L- or X-Type Metalloligand



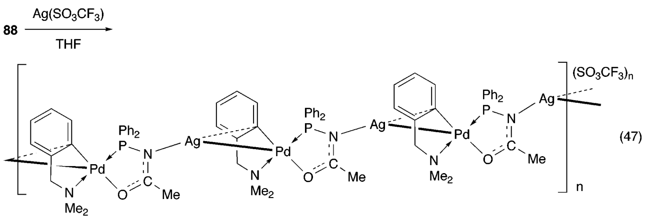
The trinuclear complexes **91**−**93** containing two linearly coordinated metalloligands **88** were obtained from Cu(I), Ag(I), and Au(I) precursors (eq 46).[62,115]



(46)

91 M = Cu
92 M = Ag
93 M = Au

The reaction of **88** in THF with pure, acid-free $Ag(SO_3CF_3)$, in a 1:1 stoichiometry, afforded the first 1-D coordination/organometallic polymer containing Ag−Pd bonds, **94**·OTf, which was characterized by X-ray diffraction (eq 47).[62]



(47)

94·SO_3CF_3

The Ag^+ cation is, as anticipated, linked to the iminolate nitrogen atom, which retains its planar coordination geometry, but instead of the triflate remaining coordinated to the silver ion, the latter prefers to find the required additional electron density in the Pd−carbon σ bond involving the cyclometalated ligand of another complex molecule. This results in a Ag−Pd dimetallic repeat unit generating a 1-D coordination/organometallic wire (Figure 1).[62] The bonding between the Ag center of one unit and the adjacent complex has been analyzed by extended Hückel and density functional theory calculations and corresponds to a multicentered

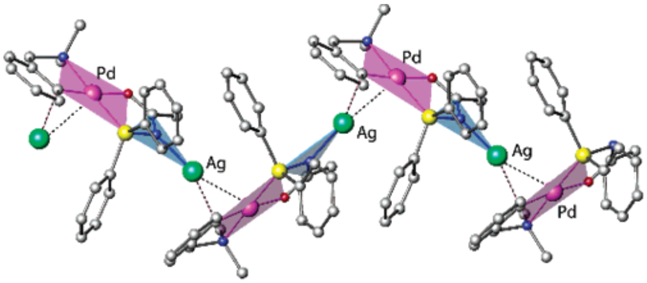


Figure 1. View of the 1-D coordination/organometallic Ag−Pd polymer **94**·OTf.[62] (Reproduced with permission from ref 62. Copyright 2004 Wiley-VCH.)

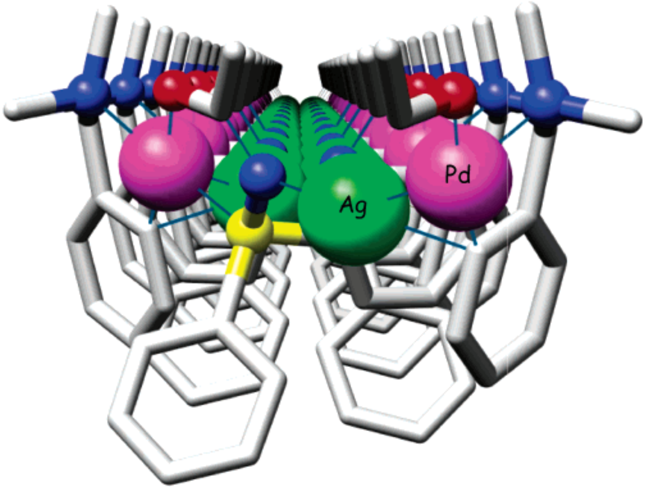


Figure 2. Perspective view of the 1D coordination/organometallic Ag−Pd polymer **94**·OTf.[62] (Reproduced with permission from ref 62. Copyright 2004 Wiley-VCH.)

interaction resulting in the donation of σ and π electron density from the Pd−C (p_z orbital) and Pd-bound aryl regions to the coordinatively unsaturated silver. A view along the *a* axis (Figure 2) shows the adjacent rows of silver atoms flanked by two rows of palladium atoms and also illustrates that the lipophilic aromatic rings are all on one side of the planes containing the metals, which leads to an unusual layered structure in the crystal.[62]

The term "coordination polymer" was coined ca. 40 years ago,[116] and the corresponding research area continues to grow in significance. The structure of **94**·SO_3CF_3 represents an unprecedented example of perfectly alternating metals in an ordered 1-D *heterodimetallic* polymeric structure and also the first molecular wire containing Ag−Pd bonds. The synthetic approach used opens up interesting perspectives in coordination/organometallic supramolecular chemistry.[62]

These recent results provide important extensions to previous studies on phosphino-enolate or -enaminate complexes such as **39** and **86**, respectively, which led to homo- and heterodinuclear (μ-P,C)-bridged complexes (see **22**, **83**, **85**, and **87**). The palladium phosphinoiminolate complex **88** represents an interesting building block toward electrophilic coinage metal complexes. The reactions occur by selective coordination of the metal to the sp^2-hybridized nitrogen atom of the *P*,*O*-chelate and with retention of the planar coordination geometry at the nitrogen atom. They led to novel homo- and heterodi- or polynuclear (μ-P,N)-bridged complexes.

4. Oxygen-Based Reactivity

4.1. Reactions with P–Cl Bonds

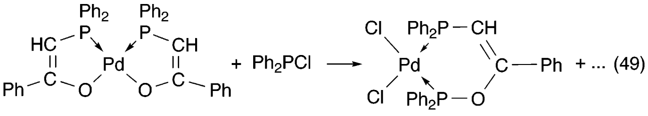
Reaction of the lithium phosphinoenolate Li[Ph$_2$PCH$\overset{...}{-}$C($\overset{...}{-}$O)Ph] with Ph$_2$PCl resulted in the formation of a P−O bond to yield a phosphine−phosphinite-type ligand (eq 48).[91]

$$\mathrm{Li[Ph_2PCH\overset{...}{-}C(\overset{...}{-}O)Ph]} \xrightarrow[\text{-LiCl}]{\text{+Ph}_2\text{PCl / Et}_2\text{O}} \mathrm{Ph_2PCH{=}C(Ph)OPPh_2} \quad (48)$$

This ligand, previously encountered in the carbonyl complex W(CO)$_4$(Ph$_2$PCH═C(Ph)OPPh$_2$),[117] has also been generated in the coordination sphere of a metal by reaction of the coordinated phosphinoenolate with free or coordinated Ph$_2$PCl[118] (see eq 49) or by thermal activation of the coordinated ketophosphine.[16]

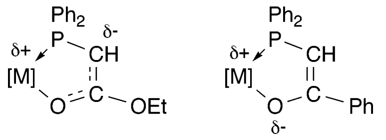
That selective P−O coupling would take place in eq 48 might have been anticipated on the basis of the known oxophilicity of chlorophosphines, although reaction of the lithium enolate of acetophenone, Li[CH$_2\overset{...}{-}$C($\overset{...}{-}$O)Ph], with Ph$_2$PCl exclusively led to P−C bond formation and yielded the corresponding ketophosphine ligand Ph$_2$PCH$_2$C(O)Ph in high yield (see section 3.2).[16] For comparison, the functional enolate Li[Ph$_2$PCH$\overset{...}{-}$C($\overset{...}{-}$O)NPh$_2$] undergoes selective P−C coupling with Ph$_2$PCl to afford the new diphosphine ligand (Ph$_2$P)$_2$CHC(O)NPh$_2$ (L^8) (see Scheme 14). The chemoselectivity of these synthetically useful reactions is thus strongly dependent upon the nature of the substituent on the enolate carbon.

The reactions of transition metal-coordinated phosphinoenolates with chlorophosphines occur with breaking of the original M−O bond and formation of a P−O bond. Thus, the bis-chelated complex **58** reacted with Ph$_2$PCl to afford the six-membered ring complex **95**, which contains a phosphine−phosphinite chelating ligand (eq 49).[118]



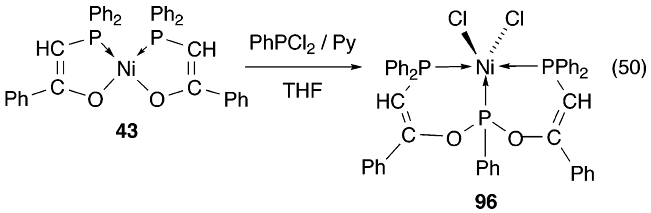
58 **95**

The facts that **58** did not react with CO$_2$ (see section 3.3.1) and that **95** resulted from O−P bond formation would be consistent with the negative charge of the enolate moiety being more C-localized when R = OEt and O-localized when R = Ph. This is also in agreement with the well-known electronic effects of these groups and the more olefinic character of the PC−H proton in the latter case (δ ca. 5 ppm, compared with ca. 3.2 when R = OEt).[16]

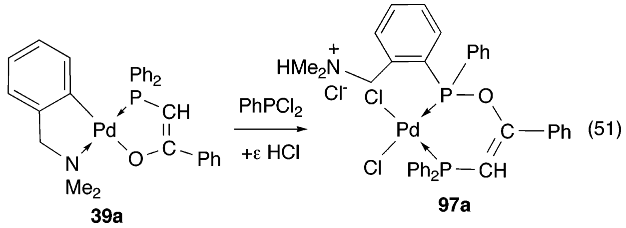


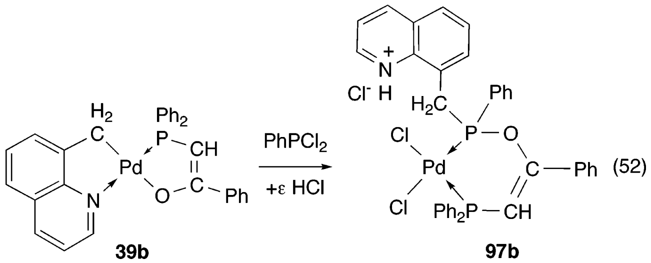
The phosphine−phosphinite complex **95** was also formed quantitatively upon controlled thermolysis of [PdCl$_2${Ph$_2$PCH$_2$C(O)Ph}$_2$].[16]

A new phosphorus double functionalization reaction was discovered upon reaction of the bis-phosphinoenolate Ni(II) complex **43** with PhPCl$_2$, which afforded the pentacoordinate Ni(II) complex **96** (eq 50).[119] One can also view this template condensation reaction as a formal insertion of a P−R moiety into the Ni−O bonds of the precursor.

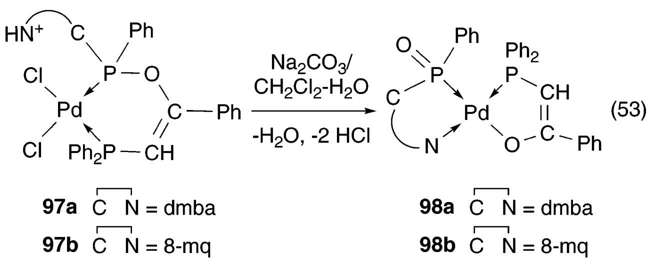


When the precursor metal complex contains two different uninegative chelating ligands, a phosphinoenolate and a cyclometalated ligand, as in **39**, which provides the metal center with four chemically different ligated atoms, a new reaction was found with $PhPCl_2$ which afforded in one pot a novel chiral phosphorus ligand (eqs 51 and 52).[118,119] The selectivity of the coupling between phosphorus and the originally *trans* donor atoms, C and O, is remarkable. These P−C coupling reactions were the first examples involving the carbon atom of cyclometalated complexes, and they should have a wide scope since they operate equally well with sp^2- or sp^3-hybridized carbon atoms, as shown with the formation of **97a** and **97b**, respectively. The potential of these new functionalization reactions involving air-stable organometallic precursors deserves therefore further investigations.





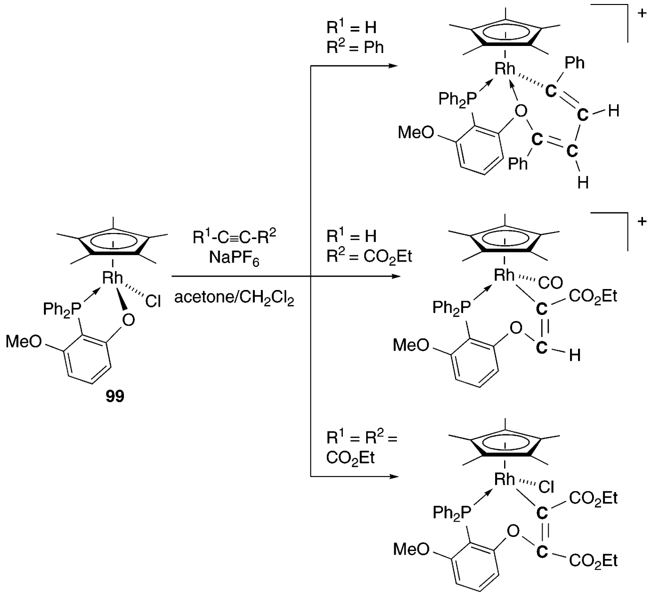
Nucleophilic attack of OH^- on the phosphinite donor of the coordinated phosphine−phosphinite ligand in **97a,b** led to cleavage of the P−O bond, which regenerated the phosphinoenolate ligand, and formation of a oxodiarylphosphoranido ligand (eq 53).[118] The presence of a stereogenic phosphorus center in **98** was indicated by ^1H NMR spectroscopy and confirmed by X-ray diffraction.



4.2. Reactions with Alkynes

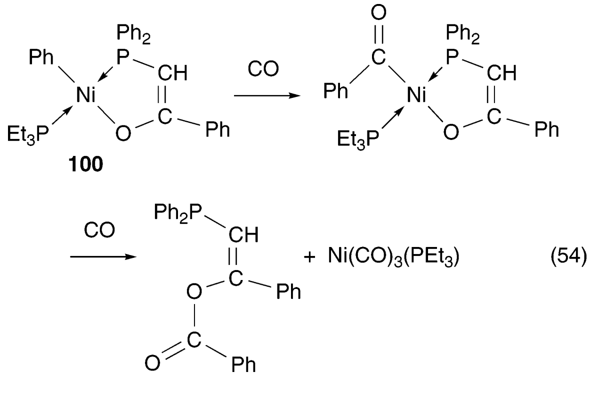
The reactivity of a $M-O_{enolate}$ bond in a phosphinophenolate complex has been evidenced in unprecedented reactions consisting of single and double insertion of alkynes into the Rh−O σ-bond of the Rh(III) cationic complex generated from **99**. These reactions afforded five-, six-, and seven-membered metallacycles (Scheme 23).[120] These reactions contrast with the carbon-based reactivity of the phosphinoenolate complexes examined in section 3. In the case of phosphinophenolate complexes such as **99**, reaction at the carbon would result in loss of aromaticity, which explains the preference for oxygen-based reactivity.

Scheme 23. Single and Double Insertion of Alkynes into the Rh−O σ-Bond of the Rh(III) Cationic Complex Generated from 99[120]



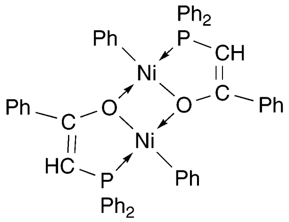
4.3. Reactions with a Coordinated Benzoyl Ligand

In the course of studies on the reactivity of the Ni(II) complex **100**, a catalyst precursor for ethylene oligo- and polymerization and the alternating copolymerization of ethylene with CO, researchers at Du Pont found that it reacts with CO to give first the expected benzoyl derivative, which then, under CO, leads to $C-O_{enolate}$ reductive coupling and elimination of the unusual ester $Ph_2PCH{=}C(Ph)OC(O)Ph$ (eq 54).[121]



4.4. Reactions with Metal Centers

The donor ability of a metal-coordinated phosphinoenolate oxygen atom is clearly demonstrated in situations where it binds to a metal center while retaining the original M−O bond. This is the case in the dinuclear Ni(II) complex **101**, which corresponds to a deactivated form of the ethylene oligomerization SHOP-type catalyst,[37,38] in the dinuclear Rh(I) phosphinoiminolate complex **102**,[61] and in the heterometallic, paramagnetic Ni/Co complex **103**.[76] Related situations have been described in Zr(IV) chemistry (see **104**), although the synthetic approach was completely different.[122,123] It is interesting to relate the structure of **103** to that of the product **105** obtained when the bis(phosphinoenolate) Ni(II) complex **43** is converted into an active ethylene polymerization catalyst by reaction with an aluminum alkyl.[37]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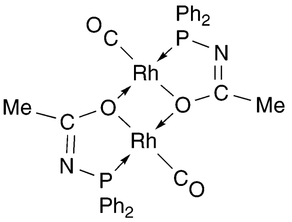
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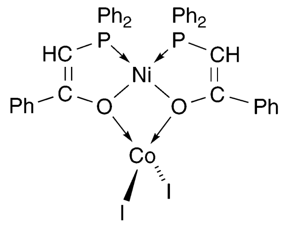
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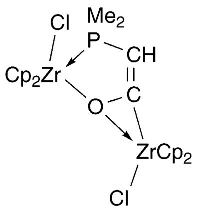
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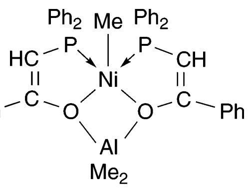
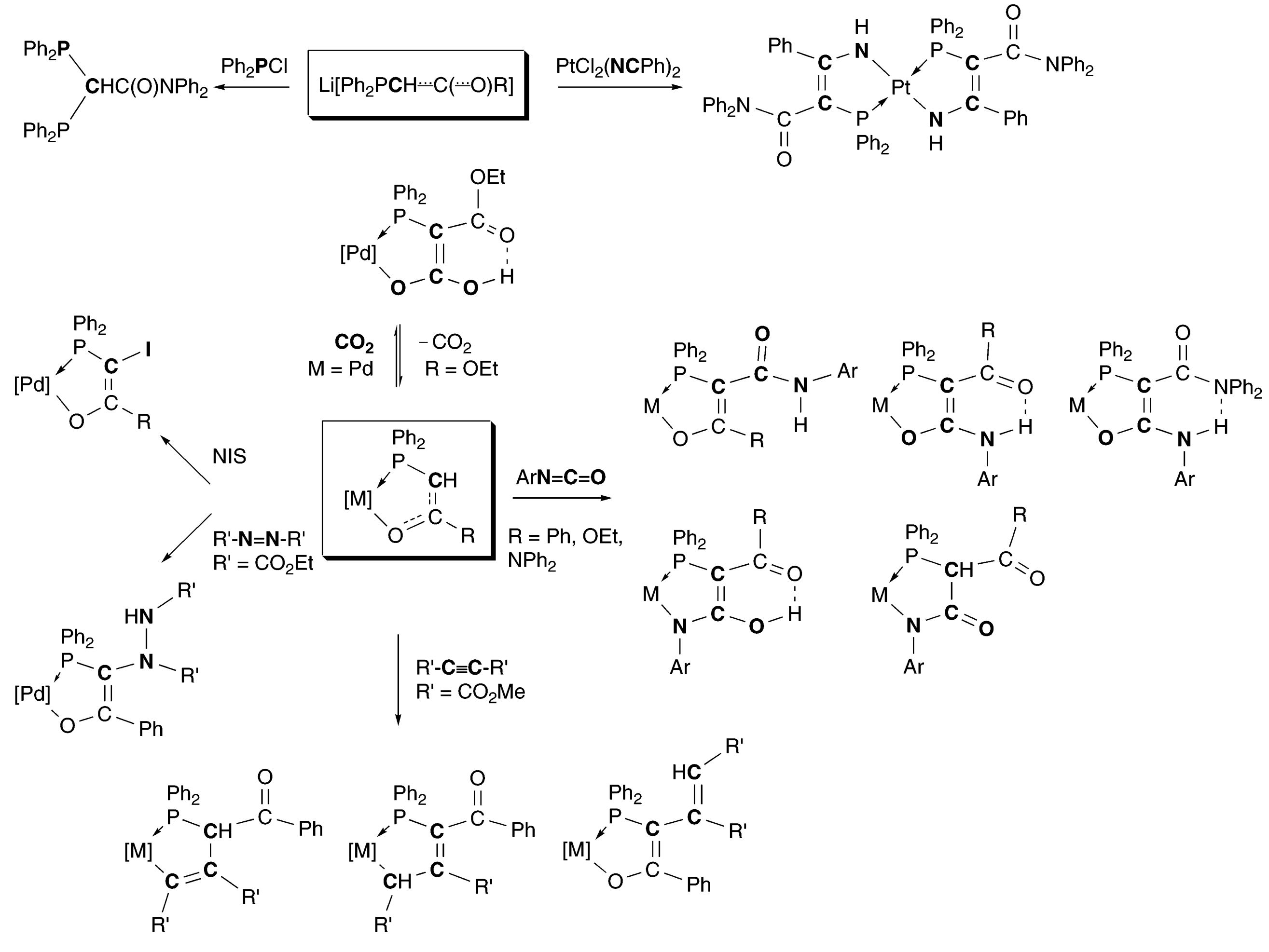

105

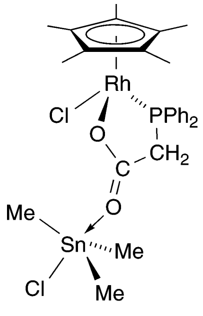
In reaction iii of Scheme 12, which led to the phophinoenolate-stabilized Ti–Pt complex **28**, formal insertion of the Pt(0) fragment into a Ti(IV)–O bond of the precursor occurred. Also, the transmetalation observed with Pd(II) or Pt(II) complexes (reaction ii of Scheme 12) involved rupture of a Ti(IV)–O bond.[84] These examples illustrate the reactivity of M–O bonds toward metal centers in phosphinoenolate metal complexes. The coordinated oxygen atom of phosphino-enolate or -iminolate complexes remains sufficiently electron-rich to allow further coordination to a metal center, thus leading to unusual heterodinuclear metal complexes.

When a phosphinocarboxylate ligand chelates a metal center, the C=O oxygen is expected to be a better donor than the M–O oxygen. Accordingly, the carboxylate function of the Rh(III) complex $Cp^*\overline{RhCl[Ph_2PCH_2C(O)O}]$, obtained by reaction of $Ph_2PCH_2CO_2Na$ with $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$,[15] acts as a Lewis base toward Sn(IV) reagents, as in **106**.[90] A

Scheme 24. Summary of the Carbon-Based Reactivity of Phosphinoenolates and Related Metal Complexes toward Organic Reagents: Formation of C–P, C–C, C–I, and C–N Bonds



similar situation was observed with an arene Ru(III) complex.[90]

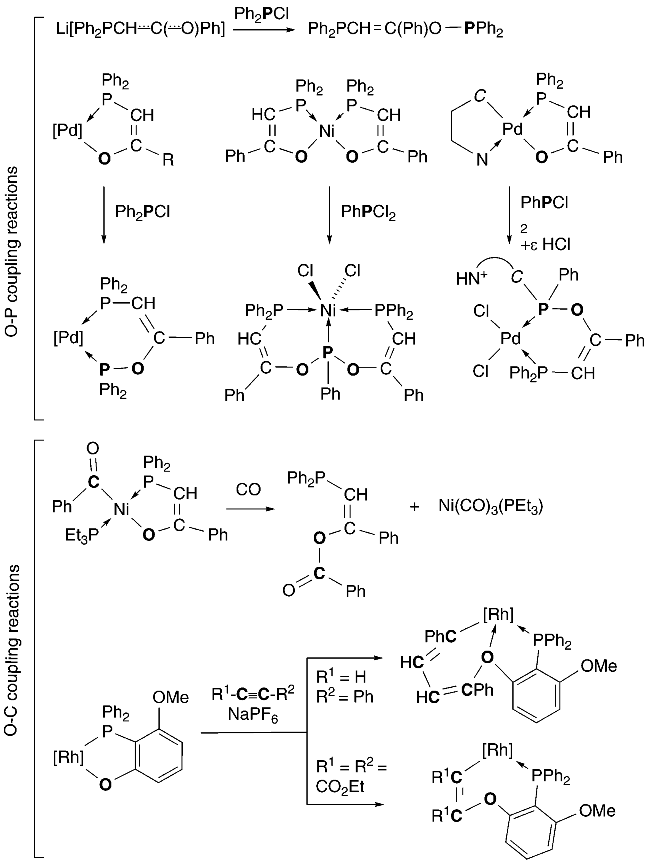


106

5. Summary and Outlook

Organic enolates have long held a central position in synthetic chemistry and display versatile bonding and reactivity patterns when associated with metals owing to their well-known ambident behavior.[124−131] Their formation and reactivity play a crucial role in a number of key transformations, as shown, for example, in the case of nickel with aldol reactivity[132] and in the case of palladium with the arylation of esters, ketones, or acrylates, aldol-like and Mannich-type reactions, the insertion of CO, and the copolymerization of ethylene and acrylates.[133,134] The chemistry of the functional phosphine-derived carbanions, including phosphinoenolates, and of the phosphinoiminolates described in this review is characterized by an increasing diversity and has gained much significance over the years. The ability of transition metals to influence and drive the reactivity of the enolate or iminolate functionality is due, in particular, to the presence of a coordinating heteroatom. Whereas the ambident behavior of the enolate function in organic systems and in β-phosphinoenolates is most characteristic, the presence in the latter of a coordinating phosphorus donor increases the diversity of bonding modes (see Scheme 5) to be observed and exerts a profound influence on the reactivity of the enolate moiety. Furthermore, it allows isolation and full characterization of metal complexes which would otherwise be too elusive.

Scheme 25. Summary of the Oxygen-Based Reactivity of Phosphinoenolates and Related Metal Complexes toward Organic Reagents: Formation of O−P and O−C Bonds



Scheme 26. Summary of the Reactivity of Metal-Coordinated Functional Phosphine-Derived Anions toward Metal Complexes

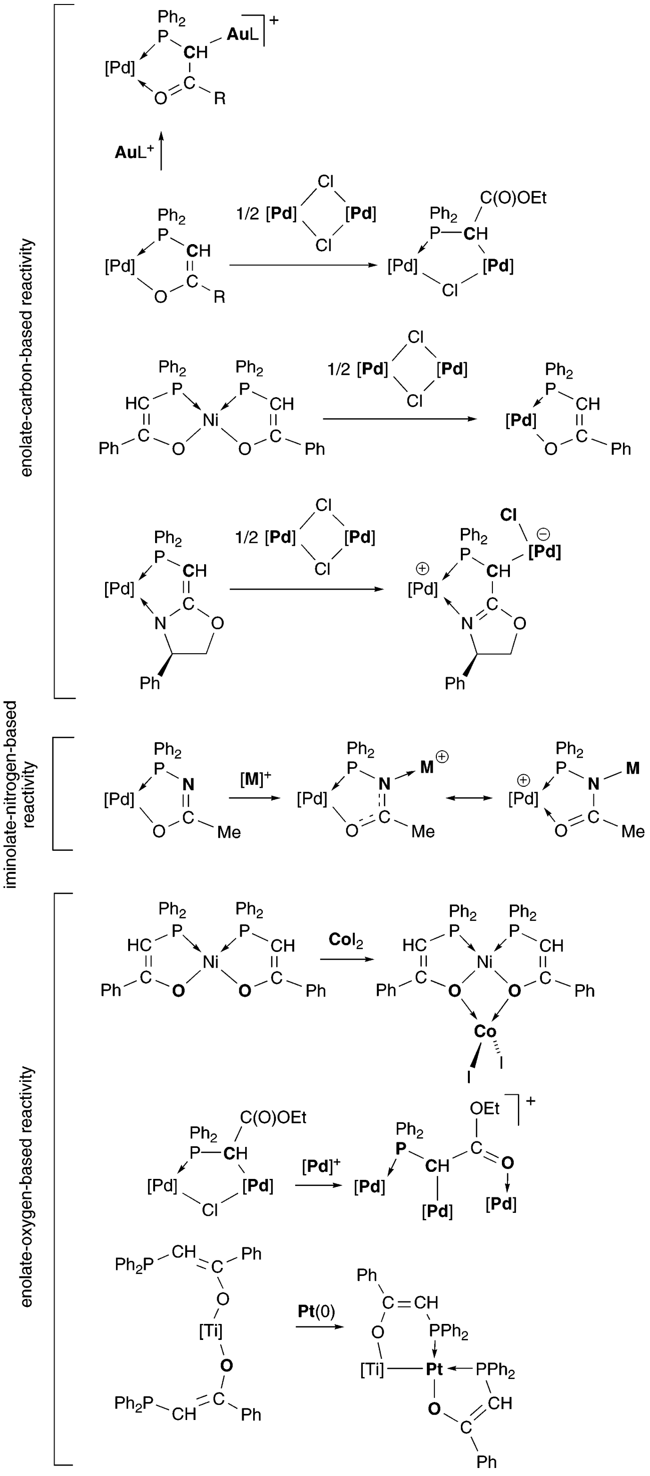
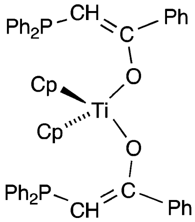
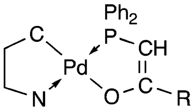
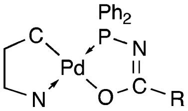
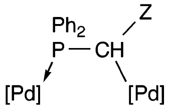
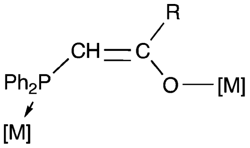
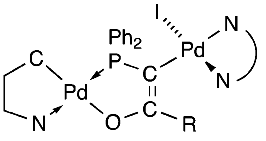
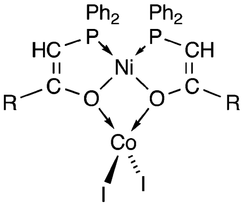
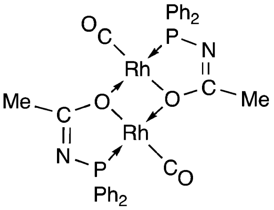
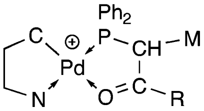
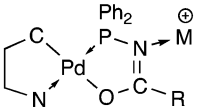
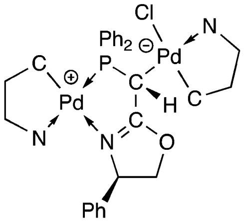
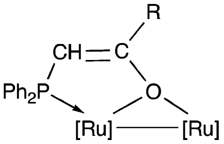
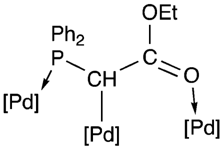


Table 1. Bonding Modes for Phosphino-carbanions and Phosphino-iminolates in Their Metal Complexes[a]

P,O or *P,N* ligand	1e donor	3e donor	4e donor	5e donor
formal charge	-1	-1	-2	-1
in complexes		   		      

[a] The electron donicity is given when considering the ligand as a neutral entity.

Organic enolates generally bind to soft metals via their carbon atom, but the reverse is true for β-phosphinoenolates, which readily chelate the metal via the phosphorus and the enolate oxygen atoms because of the stabilizing effect due to formation of a five-membered ring chelate. Such structures have been characterized with group 5−10 metals.

The reactivity of metal-coordinated phosphine-derived anions is very rich and diversified, and it has led to a number of unprecedented reactions. It also provides examples of conversion from one bonding mode into another, as observed in the cases F → E (eq 2), F → I (Scheme 10), and I → L (eq 8), which are relevant to a better understanding of the subsequent reactivity of the metal complexes.

The ambident behavior of the enolate moiety accounts for the occurrence of carbon- and oxygen-based reactions. Those involving organic reagents are summarized in Schemes 24 and 25, respectively, whereas reactions with metal complexes are illustrated in Scheme 26.

To the category of carbon-based reactions (Scheme 24) belong (i) the P−C coupling reactions involving Li[$Ph_2PCH\overset{\cdot\cdot}{-}C(\overset{\cdot\cdot}{-}O)NPh_2$] and Ph_2PCl which generate functional dppm-type ligands, (ii) C−C coupling reactions involving coordinated organonitriles which result in the formal insertion of the nitrile into the enolate PC−H bond, (iii) C−C coupling reactions with CO_2 which led to the discovery of unique carriers able to reversibly bind CO_2 under ambient conditions of temperature and pressure and allow the selective telomerization of CO_2 with butadiene to give a δ-lactone, (iv) reactions with other heterocumulenes such as organic isocyanates which result in a number of bonding patterns for the ligands depending on the substituents on the phosphinoenolates and on the nature of the metal center, (v) reactions with activated alkynes (C−C coupling), such as DMAD, or with diethylazodicarboxylate (C−N coupling), which generate multifunctional ligands in isomeric structures whose bonding patterns and relative stability were shown to be very metal-dependent, (vi) reactions with iodine and *N*-iodosuccinimide which transform the PC−H into a PC−I bond into which insertion of Pd(0) becomes possible, and (vii) the formation of unique homo- or heterodi- or polynuclear complexes (Scheme 26).

Reactions of functional phosphine-derived carbanions, including phosphinoenolates, which correspond to an oxygen-based reactivity (Scheme 25) include (i) the reaction of Li[$Ph_2PCH\overset{\cdot\cdot}{-}C(\overset{\cdot\cdot}{-}O)Ph$] with Ph_2PCl which yielded the P−$O_{enolate}$ coupling product $Ph_2PCH{=}C(Ph){-}O{-}PPh_2$, (ii) metal-templated reactions of Ni(II) and Pd(II) phosphinoenolates with Ph_2PCl which afforded mono- or bis(phosphine−phosphinite) complexes and led to the discovery of new P−O and P−C coupling reactions involving chemically different Pd(II)-bound P,O and C,N chelates, (iii) CO-induced acyl/enolate−oxygen reductive coupling, (iv) the coupling of alkynes, and (v) reactions with electrophilic metals which resulted in oxygen-bridged heterodimetallic complexes (Scheme 26).

Reactions involving electrophilic metal centers are summarized in Scheme 26 and include both enolate carbon-based or iminolate nitrogen-based and oxygen-based reactivity. They include transmetalation reactions and additions to phosphinoenolates or phosphinoiminolates. The resulting heterometallic complexes contain a μ-P−C, μ-P−O, or μ-P−N bridge (Scheme 26) and extend to an unprecedented

1-D coordination/organometallic heterodimetallic polymer containing Pd−Ag bonds (eq 47, Figures 1 and 2).

We have seen throughout this review that the thermodynamic stabilization brought about by the transition metal is still compatible with a very rich reactivity and that the metals to which the functional phosphine-derived carbanion is bound and the nature of their coordination sphere have a considerable influence on its reactivity. Obviously, the inorganic component and the organic substituents of the functional phosphine-derived ligands are essential parameters available for fine-tuning of the properties of the systems, and this will provide further inspiration in the field.

From an electronic point of view, the functional phosphine-derived carbanions and phosphino-iminolates discussed in this review have been encountered in different bonding situations where they formally behave as 1e, 3e, 4e, or 5e donors toward the metal(s) to which they are bonded. This is summarized in Table 1.

A further aspect of the unique properties confered by the phosphinoenolate and related ligands to their metal complexes is found in their numerous catalytic applications. This includes the Pd-catalyzed telomerization of CO_2 and butadiene,[93,94] the Ni-catalyzed oligomerization[32−34] and polymerization of ethylene,[35−39] the Rh-catalyzed transfer dehydrogenation of alkanes,[41] and, in the case of isoelectronic phosphinooxazoline-derived ligands, the Ru-catalyzed transfer hydrogenation of ketones with propan-2-ol.[42] As mentioned in the Introduction, these reactions did not involve reactivity at the phosphinoenolate moiety, except in the case of the CO_2 activation, and were therefore not discussed here. However, the considerable influence of these chelates, even as spectator ligands, on the catalytic properties of their metal complexes clearly suggests that new ligands and complexes obtained by reactions at the phosphinoenolate moiety could have important catalytic applications.

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