Alkyl, Silyl, and Phosphane Ligands—Classical Ligands in Nonclassical Bonding Modes

Pierre Braunstein* and Neil M. Boag

Dedicated to Professor Guy Ourisson on the occasion of his 75th birthday

Abstract: Alkyl, silyl, and phosphane ligands are amongst the most familiar and ubiquitous ligands in organometallic and coordination chemistry. The C, Si, and P donor atoms of these ligands are sp^3-hybridized and the ligands are related to each other by the isolobal analogy: (CR$_3$)$^-$(SiR$_3$)$^-$PR$_3$. Herein, we demonstrate that although a number of unusual observations concerning the reactivity and bonding of these ligands appears unrelated at first sight, they in fact provide offer an exiting and consistent picture that may form the basis for new paradigms. The characterization of stable complexes in which alkyl, silyl, and phosphane ligands behave as symmetrical bridges confirms that there is no inherent thermodynamic instability associated with these bonding situations, and, in fact, reactivity studies suggest that these ligands should be able to bridge between metal centers in reaction intermediates or transition states.

Knowledge of the nature of metal–ligand interactions is the crux in understanding the structure and the reactivity of inorganic and organometallic complexes. The bonding modes adopted by ligands in mononuclear chemistry offer few surprises now, although a complete understanding of the intimate nature of the metal–ligand interaction may require the use of high-level theoretical calculations. In dinuclear and cluster chemistry, however, a higher degree of complexity may arise due to the possibility for familiar "monodentate" ligands to adopt bridging roles between all or some of the framework metal atoms. Examples of such complexes have been isolated and provide indispensable structural models for intermediates in ligand-transfer processes, and for understanding the stereochemistry of transmetalations.[1] Critically, solution structures may vary significantly from those in the solid state;[2–4] the latter perhaps represent an intermediate in a fluxional process or reaction profile present in solution with considerable implications in homogeneous catalysis. In such cases, variable-temperature NMR spectroscopy combined with labeling studies is invaluable in probing the nature of the metal–ligand interaction.[5]

In this contribution we focus on recent chemistry dealing with three types of ligands, alkyl, silyl, and phosphane groups, which are certainly amongst the most familiar and ubiquitous ligands in organometallic and coordination chemistry. Their donor atoms, C, Si, and P, respectively, are sp^3-hybridized in all three cases and these ligands are related to each other by the isolobal analogy: $(\mathrm{CR_3})^- \leftarrow\!\circ\!\rightarrow (\mathrm{SiR_3})^- \leftarrow\!\circ\!\rightarrow \mathrm{PR_3}$. A number of unusual observations concerning the reactivity and bonding of these ligands have been recently and independently reported. Although they all appear unrelated at first sight, we would like to show here that they offer an exiting and consistent picture that may form the basis for new paradigms.

1. Bridging Alkyl Ligands

There are currently more examples of bridging alkyl groups than of silyl or phosphane groups; thus, an understanding of the bridging reactivity of these latter ligands will be initially based on alkyl chemistry. Five basic bridging alkyl structural types have been described (Scheme 1), although in practice, complexes can exhibit intermediate geometries and an exact identification is often rendered problematic due the difficulties associated in accurately locating hydrogen atoms when using X-ray data.[6] In discussing the distribution of these structures,

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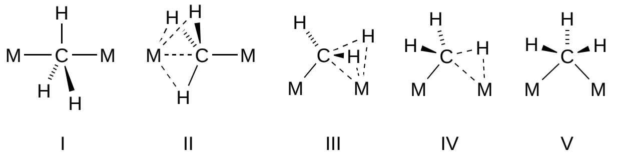
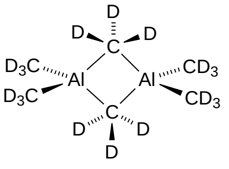


Scheme 1. Possible bridging modes for a methyl group. A metal–metal interaction is possible in modes III–V.

three broad areas may be defined: main group elements, early transition metals/lanthanides, and late transition metals.

Main group elements will not be considered here although many examples are known (for leading references, see ref. [7]) especially the definitive example of a type V structure for [$Al_2(CH_3)_6$], recently confirmed through a powder neutron diffraction study of [$Al_2(CD_3)_6$] (**1**) at 4.5 K, which also established the staggered conformation of the bridges with respect to each other (C_{2h} molecular symmetry).[8] Although this is a common structural type for aluminum,[9] [$(C_6F_5)_3Al(\mu\text{-}CH_3)Al(C_6F_5)_3$]$^-$ has recently been shown to exhibit a type I structure.[10]



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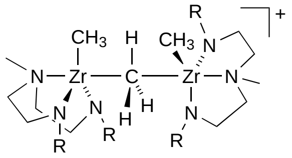
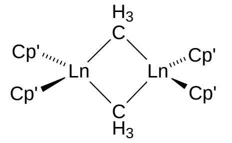
The commercial importance to olefin polymerization of early transition metal and lanthanide metallocenes in conjunction with increasingly sophisticated cocatalysts has led to the isolation of many examples of bridging alkyl groups on these metals. Indeed, the presence of bridging alkyl groups is fundamental to the activity of these complexes.[11] In homodinuclear complexes, only type I (e.g. **2**)[12] or V (e.g. **3**)[13] structures have been reported. The former species is postulated to undergo exchange of the terminal methyl groups through a $Zr(\mu\text{-}CH_3)_3Zr$ intermediate and an example of the latter, **4**, undergoes inversion at the bridging carbon atom.[14] More structural variation is observed in species involving alkyl bridging to Lewis acids with examples of every bridging type.[15]



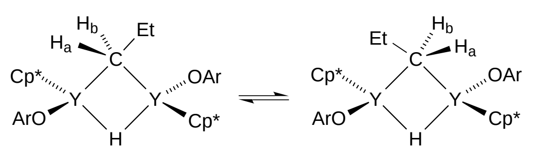
R = mesityl

2



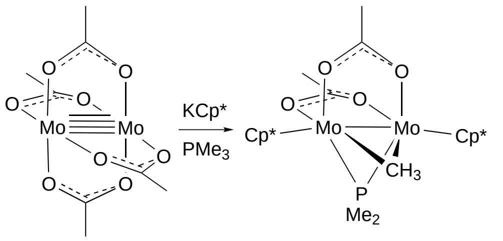
Cp' = $C_5H_4SiMe_2R$ (R = Me,*t*Bu)

3



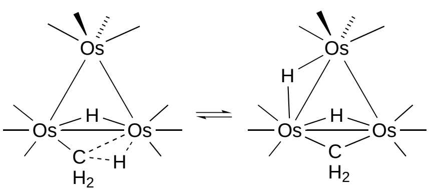
4 Ar = 2,6-tBu$_2$C$_6$H$_3$

Middle and late transition metals offer less diversity and, except in heterodinuclear complexes where the second atom is an alkali metal (e.g. [$(cod)_2Rh_2(\mu\text{-}CH_2SiMe_3)_4Li_2$] (type III; cod = 1,5-cyclooctadiene)[16]) or lanthanide (e.g. [$(i\text{Pr}_2)P(CH_2)_2P(i\text{Pr}_2)Pt(\mu\text{-}Me)_2Yb(C_5Me_5)_2$] (type III)[17]), only exhibit structural types IV and V. There are only a few examples of symmetric bridging alkyl groups and recent ones include **5** (Cp* = C_5Me_5), which results from P–C bond activation of PMe_3 at a dimolybdenum center [Eq. (1)],[18] and [$\{CpV(\mu\text{-}NC_6H_3(i\text{Pr})_2)\}_2(\mu\text{-}Me)$] derived through reductive dimerization using MeMgCl.[19]



5 (1)

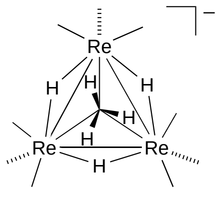
In most cases, however, agostic M⋯C⋯H interactions (Scheme 1, type IV) tend to prevail,[20] as, for example, in the dinuclear complex [$Cp_2Fe_2(\mu\text{-}CH_3)(\mu\text{-}CO)(\mu\text{-}dppm)$]$PF_6$[21] (dppm = bis(diphenylphosphanyl)methane) or in [$HOs_3(CO)_{10}(\mu\text{-}CH_3)$] (**6**), the best known example of a transition metal cluster containing a semibridging alkyl ligand.[22] In these cases, tautomerism between a bridging alkyl group and a methylene hydride is always possible. Cluster **6** exists in solution as a 1:3 mixture of the methyl (**6a**) and methylene (**6b**) tautomers, whereas only the latter is present in the solid state, thus providing an excellent example of the dangers of relying solely on solid-state structures.[22c]



6a **6b**

These varying interactions of alkyl groups on dinuclear centers are of considerable interest for homogeneous and heterogeneous catalysis since they correspond to possible pathways for alkyl migration[23] and dynamic exchange of terminal alkyl[24] or aryl groups[25] between adjacent metals.

A triply bridging bonding mode for the methyl group is best exemplified in $(MeLi)_4$, in which it caps the faces of the Li_4 tetrahedron.[26] However, the bonding is mostly ionic in this case owing to the large difference in electronegativity between Li and C; this can be seen in the isostructural (tBuLi)$_4$ with the rapid migration of *t*Bu groups between faces (or Li atoms between apices) in solution and the solid state.[27] Triply bridging methyl groups in transition metal clusters are extremely rare. There is a solitary example of a symmetrical



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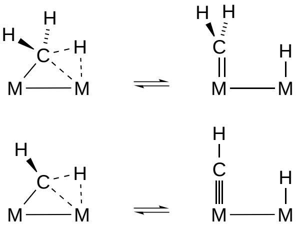
μ_3-CH_3 ligand, $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}CH_3)(CO)_9]^-$ (**7**).[28] The methyl ligand in $[Fe_3(\mu\text{-}H)(\mu_3\text{-}CH_3)(CO)_9]$ exhibits agostic bonding, and the cluster is in equilibrium with two other tautomers, $[Fe_3(\mu\text{-}H)_2(\mu_3\text{-}CH_2)(CO)_9]$ and $[Fe_3(\mu\text{-}H)_3(\mu_3\text{-}CH)(CO)_9]$, clearly revealing the dynamic potential of such systems.[29]

The doubly and triply bridging modes of alkyl groups to transition metals, with or without an agostic component, are relevant to the incipient activation of the C–H bond at a multimetal site,[30] the modes of chemisorption of these groups on metal surfaces, and subsequent heterogeneously catalyzed reactions.[31] Reversible hydrogen elimination/addition from methyl/methylene or methylene/methylidyne groups in particular mimics reactivity found for such groups on surfaces (Scheme 2).

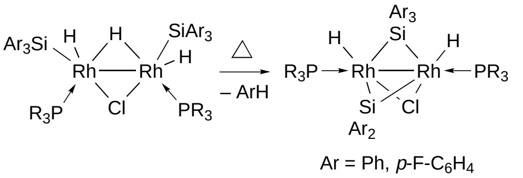


Scheme 2. Ligand transformations on surfaces.

2. Bridging Silyl Ligands

It is interesting now to examine the situation with the heavier silyl analogues. Transition metal silyl complexes have remained of great interest owing to their intrinsic fundamental importance, the possible comparisons they provide with their carbon homologues, and their reactivity and implications in numerous catalytic reactions of considerable (industrial) value.[32]

Until recently, complexes in which a bridging bonding mode for a silyl ligand had been established by X-ray diffraction were limited to boranes[33] and the polynuclear copper complex $[Li(thf)_4][Cu_5Cl_4\{Si(SiMe_3)_3\}_2]$.[34] However, recent studies in dirhodium chemistry have allowed full characterization of the first example in which the silyl ligand occupies a symmetrical bridging position between the metals. These complexes, $[(iPr_3P)(H)Rh(\mu\text{-}Cl)(\mu\text{-}SiAr_2)(\mu\text{-}SiAr_3)Rh(H)(PiPr_3)]$ (Ar = Ph, p-FC_6H_4), were prepared according to Equation (2) and, like bridging alkyl complexes, provide interesting structural models of possible intermediates in ligand-migration reactions.[35] The mirror symmetry of this molecule is noteworthy. The isolation of this dirhodium complex is particularly timely since recent independent studies by different groups, including ours, have concluded that the silyl ligand can migrate intramolecularly from one metal to another in dinuclear complexes. In their studies on diruthenium complexes, Akita, Moro-oka, and co-workers[36] [Eq. (3)] and Girolami and co-workers[37] [Eq. (4)] concluded from variable-temperature NMR studies that the SiR_3 ligand could reversibly flip from one Ru center to the other; an intermediate with a μ-SiR_3 ligand was suggested, although it could not be isolated.



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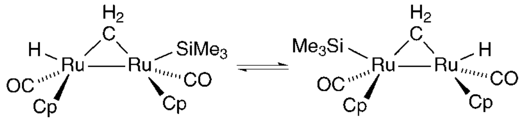

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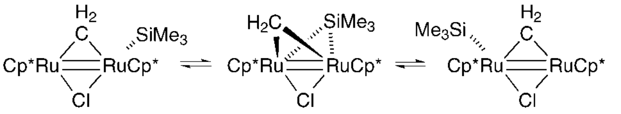
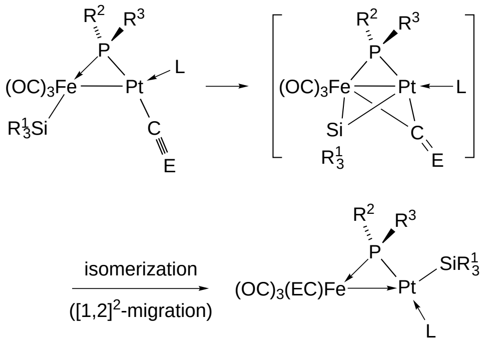


(4)

In our own studies on Fe–Pt complexes, we could actually isolate and structurally characterize isomeric complexes in which a silyl ligand is bound to either Fe or Pt and study the parameters that trigger this unusual isomerization (Scheme 3).[38] This reaction was shown to be intramolecular and it may be promoted by an external nucleophile, such as CO or isonitrile. The course of the silyl group migration was found to depend on a) the steric properties of the SiR^1_3 ligand such that for a given μ-PR^2R^3 bridge ($R^2 = R^3 = Ph$) the migration rate decreases in the order $Si(OMe)_3 > SiMe_2Ph > SiMePh_2 \gg SiPh_3$, b) the phosphido bridge, for which the migration rate decreases in the order μ-$PPh_2 \gg \mu$-$PHCy$ for a given silyl ligand ($R^1 = OMe$), and c) the external nucleophile.



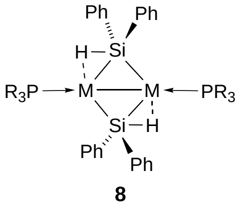
E = O; L = CO, PR_3
E = NR; L = CNR
R^1 = OMe, Me, Ph; R^2, R^3 = H, Ph, Cy
(not all combinations)

Scheme 3. Dyotropic-type concerted mechanism of silyl migration in Fe–Pt complexes.

We have suggested that this dyotropic-type process occurs via an intermediate containing a bridging silyl ligand.[38]

Evidently, these are still rare transformations[39] and the occurrence and intermediacy of such bonding modes are likely to be more general and occur more frequently than is so far realized. In this context, it is noteworthy that recent studies with diruthenium complexes,[36b] analogous to those of Equation (3), and with heteronuclear Mo–Re complexes[40] have shown that an $SnMe_3$ or $SnPh_3$ ligand can also reversibly migrate from one metal center to another.

With mono- or diorganosilyl ligands, the occurrence of agostic M···Si···H interactions dominates, as in **8**, and destroys the symmetry observed in the previous examples.[41] This situation is similar to those in which an alkyl ligand interacts in an unsymmetrical bridging mode, through a M–C σ bond and an agostic M···C···H three-center, two-electron bond with the adjacent metal center. Such an interaction may be considered as representing an "arrested" stage on the reaction coordinate towards full addition of the Si–H bond, a key step in, for example, the metal-catalyzed dehydrocoupling of hydrosilanes leading to silicon oligomers and polymers. In most cases (M = Pd, Pt, Fe, W, Ti), the two $M(\mu\text{-}\eta^2\text{-HSi})$ units are coplanar,[42] but a dirhodium complex has been characterized in which they are almost orthogonal to each other.[43] Exchange between bridging and terminal silyl ligands and terminal and bridging hydrides has been postulated based on the fluxionality observed in some bridged diplatinum complexes (Scheme 4).[42b] This should be kept in mind when examining the situation with phosphane ligands (see Section 3) where terminal bonding was the rule until bridging modes were suggested in reaction mechanisms and eventually structurally demonstrated. It was recently shown that the photochemical reaction of the μ-silyl complex **9** with SiH_2R_2 in a sealed tube at about 5 °C affords the μ-silane complex **10**, whereas reversion to **9** occurs under a CO atmosphere at room temperature [Eq. (5)].[44]



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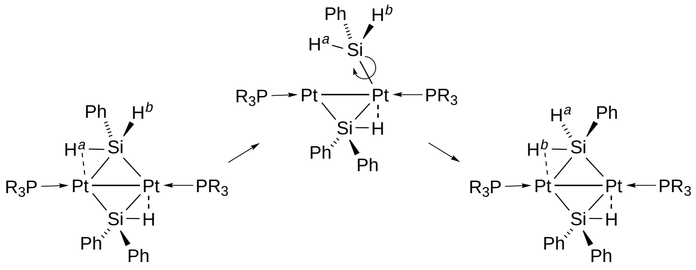
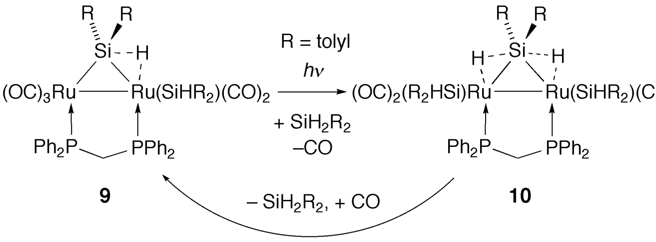
M = Pd, Pt



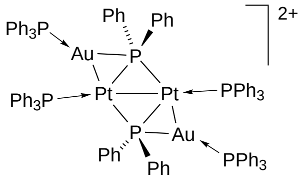
Scheme 4. Fluxionality of bridged diplatinum complexes by the exchange of bridging and terminal silyl and hydride ligands.



(5)

3. Bridging Phosphane Ligands

The isolobal relationship between the alkyl, silyl, and the phosphane ligand $(CR_3)^- \xleftrightarrow{\circ} (SiR_3)^- \xleftrightarrow{\circ} PR_3$ naturally leads to an examination of the bonding situation of phosphanes in dinuclear and cluster complexes. On the basis of the crystal structure determination of the first platinum–gold cluster **11**, the isolobal analogy $Au(PPh_3) \xleftrightarrow{\circ} H$, and theoretical considerations (note the striking similarity between **11** and **8** above!), the prediction was made in 1989 that a doubly bridging bonding mode for phosphane ligands should be possible.[45] However, until very recently, only examples of semibridging phosphanes had been discovered, remarkably in dipalladium chemistry. Following the isolation of **12**[46] and **13**,[47] a few more examples have been described,[48] including complexes containing arylphosphanes whose *ipso*-carbon atom participates in three-center, two-electron bonding such as in **14**.[47, 49] The role played by the P–H and P–C(aryl) σ bonds in complexes of type **12** and **14**, respectively, which provide two extra electrons in an agostic interaction, allows these phosphane ligands to be considered as formally four-electron donors to the metal centers. This is somewhat related



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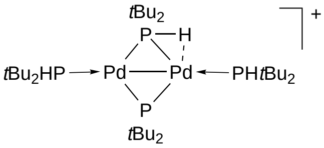

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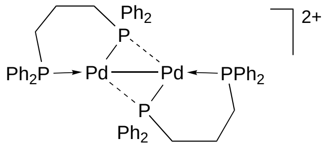

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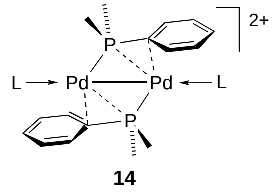

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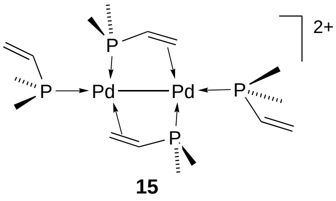

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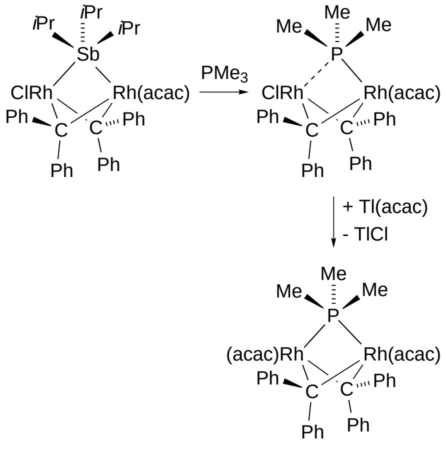
to the situation of the bridging diphenylvinylphosphane in $[\{Pd[\mu\text{-}PPh_2(CH{=}CH_2)][PPh_2(CH{=}CH_2)]\}_2]^{2+}$ (**15**).[50] In this case, however, the phosphorus atom clearly interacts with only one metal center, which leaves such systems out of the scope of the present discussion.

Until very recently, there was no characterized example of a symmetrically bridging $\mu_2\text{-}PR_3$ ligand, although a bonding analysis of the model compound $[\{(H_3P)Cu(\mu\text{-}PPH_3)\}_2]^{2+}$ had been performed.[51] This has been very recently rectified in an elegant study in which Werner and co-workers were able to prepare the unusual dinuclear rhodium complex **16** (Scheme 5); this complex contains a PMe_3 ligand which exhibits almost symmetric bridging between two rhodium centers (Rh–(μ-P) 2.2707(7) and 2.5700(8) Å).[52] Other dirhodium complexes with a semibridging PMe_3 ligand were also reported in this work. The ^{31}P NMR resonance signal of the $\mu\text{-}PMe_3$ ligand in **16** is a triplet, owing to coupling with two equivalent rhodium atoms. This complex is only the second example of a symmetrical bridging situation for an ER_3 ligand in Group 15, and follows the report in 1994 of the related complexes **17** which were the first examples of bridging stibane ligands.[53a,b] The high symmetry of these molecules is reminiscent of that observed with the dinuclear complexes containing a bridging silyl ligand, and consistent with the predictions made earlier.[45] Interestingly, the stibane ligand in **17** could not be directly substituted with PMe_3 to afford **16**, although Sb*i*Pr$_3$ can easily be substituted by smaller stibanes, for example, $SbMe_3$ or $SbEt_3$.[53c]



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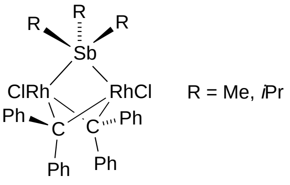
Scheme 5. Synthesis of the first complex with a bridging PMe_3 ligand. acac = acetylacetonate.



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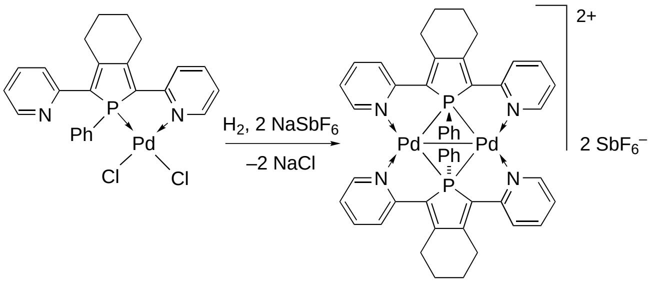
Shortly after complex **16** was reported, Réau, Halet, and co-workers described an elegant access to the dipalladium complex **18** with a symmetrically bridging phosphole ligand [Eq. (6)] and provided a theoretical analysis of the bonding interactions.[54] This bonding situation in a molecule of high symmetry (again!) appears remarkably stable, as a result of highly delocalized Pd–Pd and Pd–P bonding, and this complex does not react with CO or PPh_3.



(6)

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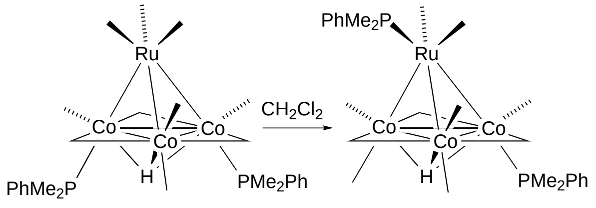
Numerous examples of intramolecular, dynamic exchange of ligands between metal atoms in polynuclear and cluster complexes are known, and this is most common with CO, CNR, and NO ligands.[55] Until very recently, only one study dealt with the intramolecular nature of the rapid exchange (on the NMR time scale) of a phosphane ligand between two metal centers.[56] The isolation of complexes with bridging PR_3 ligands is therefore particularly relevant to such a phenomenon and to reactivity studies recently performed on cluster complexes that strongly suggested the possibility of intramolecular phosphane migration. Thus, it was found in the course of metal site selectivity studies in reactions of tetrahedral MCo_3 (M = Fe, Ru) carbonyl clusters that phosphane migration from one metal center to an adjacent site can easily take place. The quantitative conversion of the kinetic product $[HRuCo_3(CO)_{10}(PMe_2Ph)_2]$ (**19**; [Co-P,Co-P] isomer) of the reaction between $[HRuCo_3(CO)_{11}(PMe_2Ph)]$ and PMe_2Ph into its [Co-P,Ru-P] isomer **20** occurs upon standing in CH_2Cl_2 overnight [Eq. (7)].[57] The interconversion between the [Co-P,Ru-P] and [Co-P,Co-P] isomers **21** and **22**, which involves phosphane migration between Ru and Co has also been discussed [Eq. (8)].[58]



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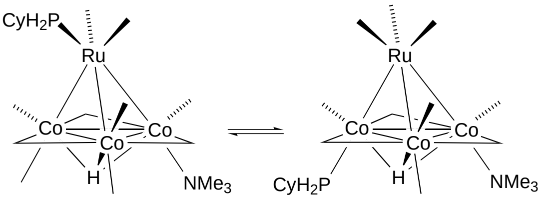
19 **20**

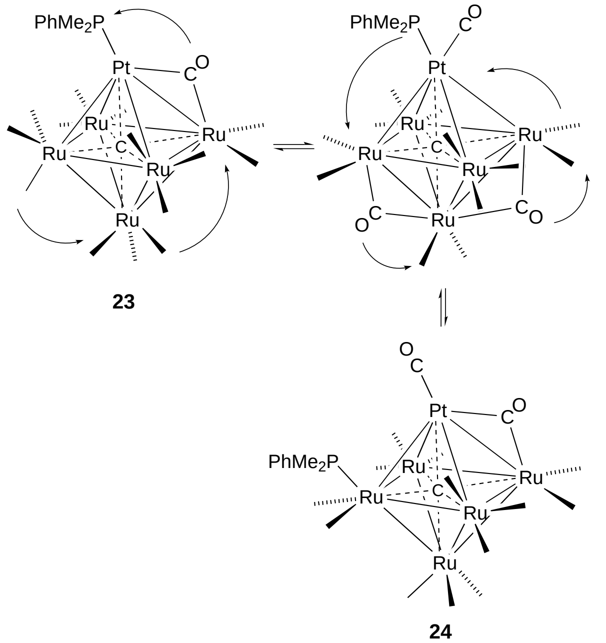


(8)

21 **22**

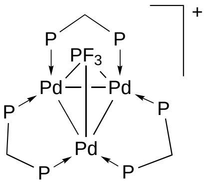
Variable-temperature NMR studies by Adams et al. have now suggested that the interconversion of the platinum–phosphane isomer **23** and the ruthenium–phosphane isomer

24 of the carbido cluster $[PtRu_5(CO)_{15}(PMe_2Ph)(\mu_6\text{-}C)]$ occurs by intramolecular shifts of the phosphane and carbonyl ligands between the metal atoms (Scheme 6).[59] Here again, the very common and stable bridging situations for μ_2-CO and μ_3-CO ligands in carbonyl chemistry contrast with the paucity of data concerning phosphanes, although the latter are amongst the most familiar and ubiquitous ligands in the molecular chemistry of metals.



Scheme 6. Proposed mechanism for cluster isomerization by intramolecular shifts of the phosphane and carbonyl ligands between the metal atoms.

Triply bridging phosphanes should not be excluded from consideration and indeed a complex with a triply bridging phosphane ligand, the palladium cluster **25**, has been described,[60] although the situation of the atypical, strong π-acceptor μ_3-PF$_3$ ligand in **25** should of course be compared to that of the familiar triply bridging CO ligand, also a two-electron donor.



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It is also a striking coincidence that independent reactivity studies concerning the intramolecular migration, whether reversible or not, of the isolobal silyl and phosphane ligands have appeared within such a short period of time.

4. Conclusion and Perspectives

We hope to have provided a useful framework to look at and relate novel and still rare bridging bonding modes for familiar ligands such as alkyl, silyl, and phosphane ligands in dinuclear and cluster chemistry. In addition to having an sp^3-hybridized donor atom, these ligands are mutually related by the isolobal analogy. The characterization of stable complexes in which they behave as symmetrical bridges confirms that there is no inherent thermodynamic instability associated with these bonding situations. Based on experimental observation, it is likely that a higher molecular symmetry is probably necessary for "stopping" these ligands en route from one metal to another although this "stopped intermediate" may involve agostic bonding, a situation particularly favored if the metal framework is not completely symmetrical. The structural investigations are nicely complemented by reactivity studies that suggest or in some cases even show that these ligands should indeed be able to bridge between metal centers in reaction intermediates or transition states. The consistent picture that emerges from these recent investigations strongly suggests that this phenomenon may actually be more general than originally believed and should now be fully considered in reactivity studies, including catalytic mechanisms.

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