

Phosphine complexes of the early metals and the lanthanoids

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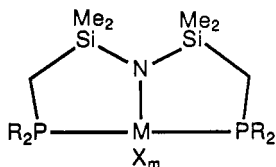
Abstract. The coordination chemistry of the mixed-donor tridentate ligand $\text{-N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2$ with the early transition metals of groups 3 and 4 and the lanthanide elements will be presented. This ancillary ligand has allowed for the formation of phosphine complexes of these hard elements which has in turn induced new reactivity patterns for hydrocarbyl ligands.

The stability and reactivity of metal complexes are a function of both the position of the metal in the periodic table and the nature of the ligands. While the former provides for diverse chemical reactivity, it is the latter feature which allows the reactivity patterns of a given metal be fine tuned (ref 1).

Because much of this paper involves ligand design it will be useful to emphasize certain terms. A complex is given the general formula L_nMX_m , where L_n represent *ancillary ligands* and X_m are defined as *reactive ligands*. *Ancillary ligands* are defined as those ligands that provide the appropriate steric and electronic environment around the central element but remain innocent in any transformation that the compound undergoes. In contrast, the *reactive ligands* are those groups that undergo changes. Some typical examples of reactive ligands would be hydrocarbyl groups which could undergo insertion with CO, or hydrides that would undergo olefin insertion. By distinguishing the ligands around a central element M into these two subgroups, attention is given to the fact that it is the *ancillary ligands* that allow one to fine-tune the chemistry of the *reactive ligands*. More importantly, one might anticipate that new types of *ancillary ligands* could generate new and unusual chemistry.

Our particular ancillary ligand design has centred on two donor types: amides, -NR_2 , and phosphines, PR_3 . These particular ligands were picked because of the following observations: it was apparent in the literature that amides were well-suited ligands for the early metals and the lanthanide elements (ref. 2) but not particularly well known for the later transition elements (ref. 3). In contrast, phosphine ligands are considered ubiquitous for the later transition elements (ref. 4), yet they are not that common for early transition elements (ref. 5). In particular, phosphine complexes of the group 3 metals and the lanthanide elements are extremely rare with only a few genuine derivatives having been reported (ref. 6). The paucity of such compounds has been ascribed to the hard acid nature of these metals and the soft base nature of the phosphine donor, which results in a mismatch of donor and acceptor. However, while there might not be a preference for phosphine donors to bind to these elements, given no other choice but phosphine ligands, such complexes should be attainable. It would appear to be a matter of selecting the appropriate solvent (i.e., avoiding ethers) and ensuring that hard ligands are not present in excess.

Our strategy for overcoming this apparent mismatch of phosphine donor and early-metal acceptor was to use the hybrid chelating ligand $\text{-N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)$ ($\text{R} = \text{Me}, \text{Pr}^i, \text{Ph}$). It was anticipated that the hard amide donor -NR_2 would serve as an anchor to the hard metal thereby inducing chelation of the pendant soft phosphine donors by virtue of their close proximity to the metal. In this paper we outline some of our work in this area concentrating on groups 3 and 4 and some of our forays into the lanthanide series of metals.

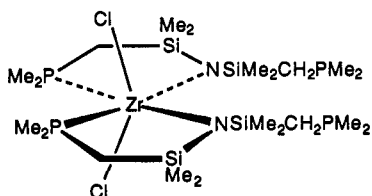
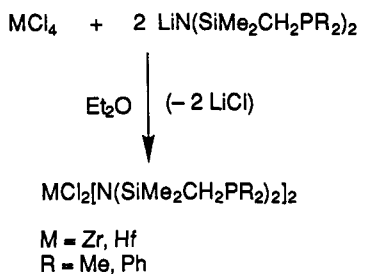
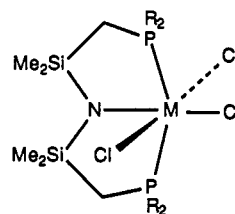
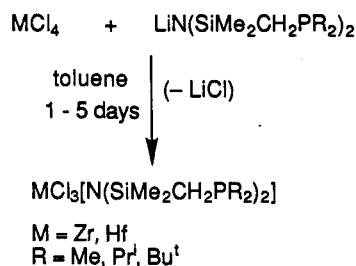


M = groups 3, 4 & lanthanides

R = Me, Ph, Pr^i , Bu^t

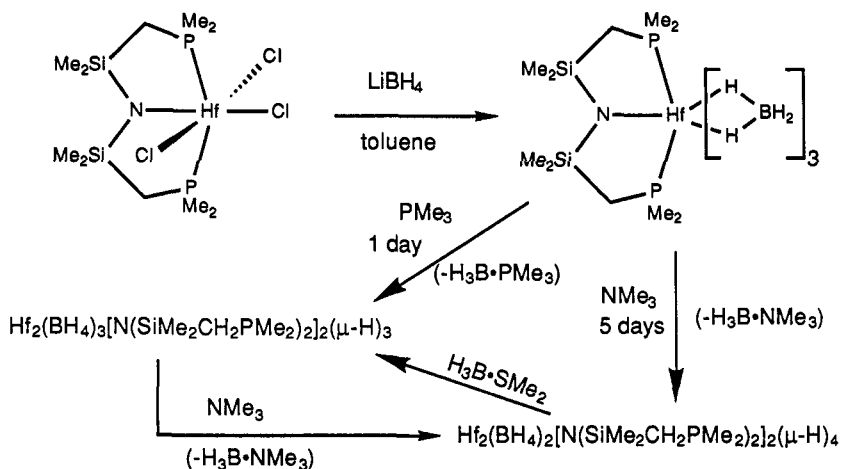
X_m = hydride, alkyl, aryl

Phosphine Complexes of Group 4. Our earliest experiments in attempting to generate phosphine complexes of the early metals centred on Zr and Hf. The reaction of the $\text{LiN}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2$ ($\text{R} = \text{Me}, \text{Ph}$) with either ZrCl_4 or HfCl_4 in diethyl ether generated the bis(ligand) complexes $\text{MCl}_2[\text{N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2]_2$ (Scheme 1) (ref. 7). In all of these derivatives the ancillary ligand binds in a bidentate fashion even though each ligand is capable of tridentate coordination; interestingly, these complexes were shown to be chiral both in solution and in the solid state. Attempts to introduce reactive ligands such as hydrocarbyl ligands by metathesis with organolithium reagents or Grignards failed presumably because the chloride ligands are protected sterically by the ligand substituents.

Scheme 1**Scheme 2**

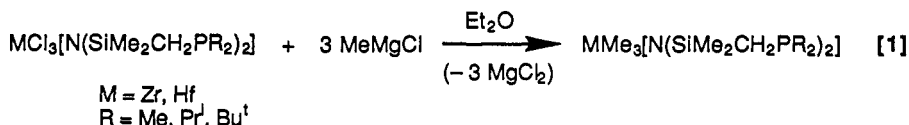
As the bis(ligand) complexes of Zr and Hf could not be further elaborated by the introduction of *reactive ligands* such as hydrocarbyl or hydride groups, monoligand complexes were investigated (ref. 8). Addition of one equivalent of the lithium salt of the ligand to a suspension of MCl_4 in toluene produced the desired complexes (Scheme 2); high dilution and long reaction times were required for the ligand having methyl substituents.

The monoligand complexes were found to be amenable to further elaboration either by LiBH_4 , Grignard and organolithium reagents. For example, a series of binuclear hafnium hydride-borohydride complexes was prepared starting from the tris(tetrahydroborate) complex $\text{Hf}(\text{BH}_4)_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2]$ as shown in Scheme 3 (ref. 9).

Scheme 3

The binuclear derivative having three bridging hydrides was structurally characterized. Both of the complexes having bridging hydrides show a downfield binomial quintet in the ^1H NMR spectrum; for $\text{Hf}_2(\text{BH}_4)_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2]_2(\mu\text{-H})_3$, $\delta(\mu\text{-H})_3$ is at 8.68 ppm and for $\text{Hf}_2(\text{BH}_4)_2[\text{N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2]_2(\mu\text{-H})_4$, $\delta(\mu\text{-H})_4$ is at 9.65 ppm.

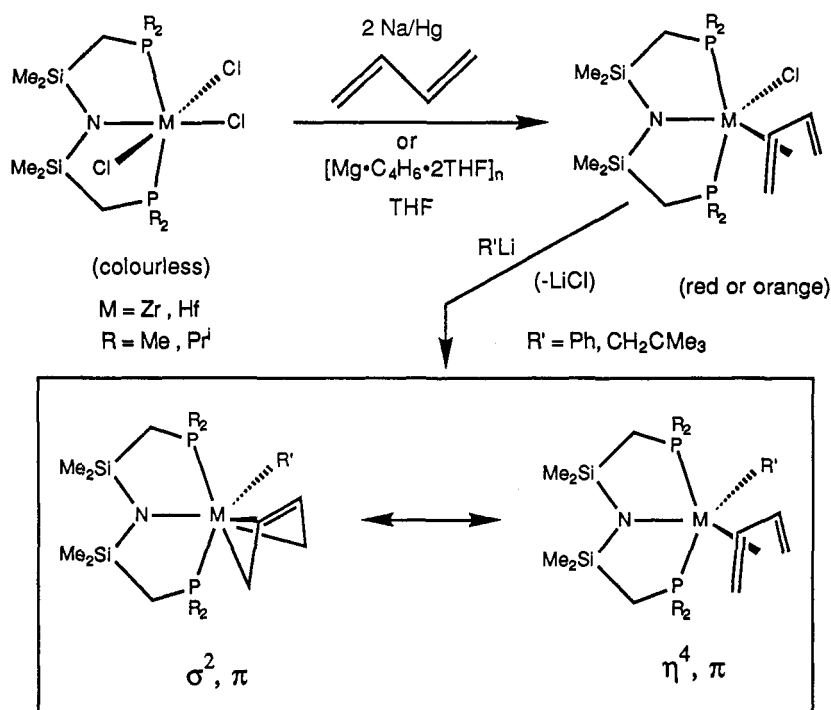
Replacement of the chlorides on the monoligand complexes with methyl groups generates the trimethyl complexes as shown in equation 1 (ref. 10).



These molecules are fluxional even down to -90°C showing only one type of methyl environment in the ^1H NMR spectrum at all temperatures; phosphine dissociation of one of the arms of the tridentate ligand to a five-coordinate intermediate could rationalize this process.

Butadiene complexes of zirconium and hafnium have also been generated via two reductive procedures as shown in Scheme 4 (ref. 11).

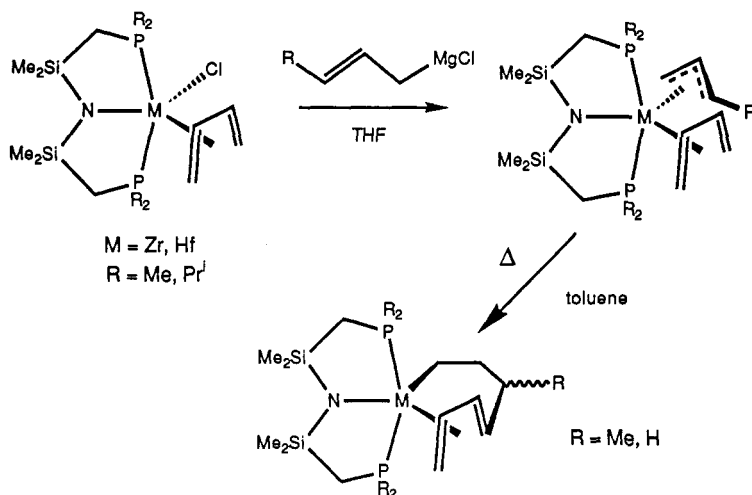
Scheme 4



Diene complexes of the group 4 elements have been shown to be fluxional. In particular, metallocene derivatives of the general formula $\text{Cp}_2\text{M}(\text{diene})$ are proposed to be undergoing an "envelope-flip" mechanism via the σ^2, π resonance form (ref. 12). In the butadiene complexes shown in Scheme 4, this process was shown not to be occurring and a better rationalization of the observed solution behaviour is that the diene is undergoing fast rotation on the NMR time scale (ref. 11). Such a distinction is important as it provides support for the fact that this particular ancillary ligand changes the nature of the reactive ligands, in this case a butadiene fragment, as compared to the same metal with other ancillary ligands (i.e., cyclopentadienyl ligands).

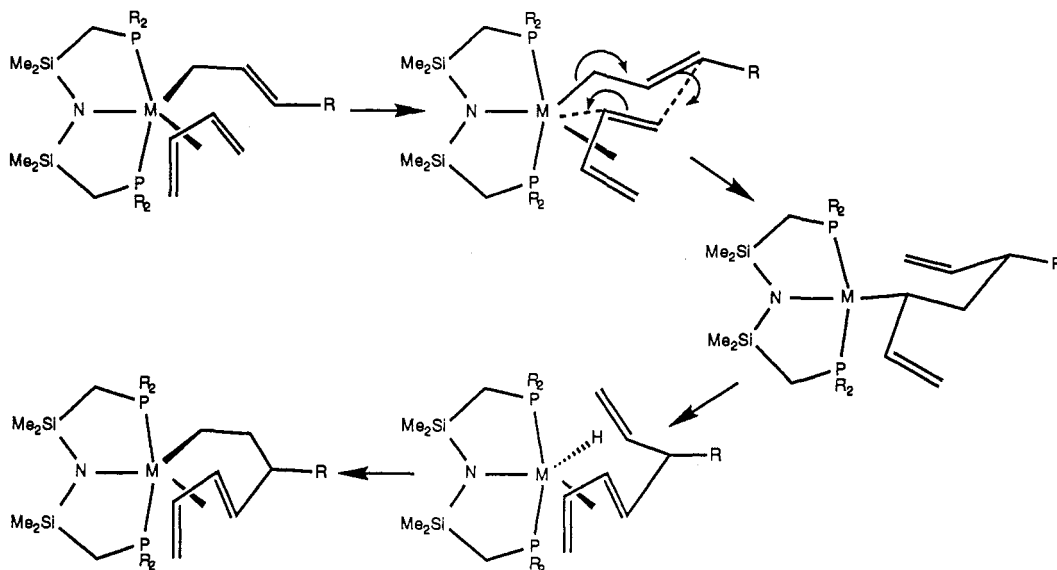
Another example of the dramatic effect of this tridentate ancillary ligand system is the carbon-carbon coupling reaction of a butadiene fragment with an allyl moiety at either zirconium or hafnium as shown in Scheme 5 (ref. 13).

Scheme 5



This coupling reaction is unique. If one changes the ancillary ligand to Cp or Cp*, the analogous diene allyl complexes Cp'M(diene)(allyl), M = Zr, Hf, do not undergo any C-C coupling reaction. The mechanism of this reaction can be rationalized in terms of a six-membered transition state followed by β -elimination and hydride migration (Scheme 6).

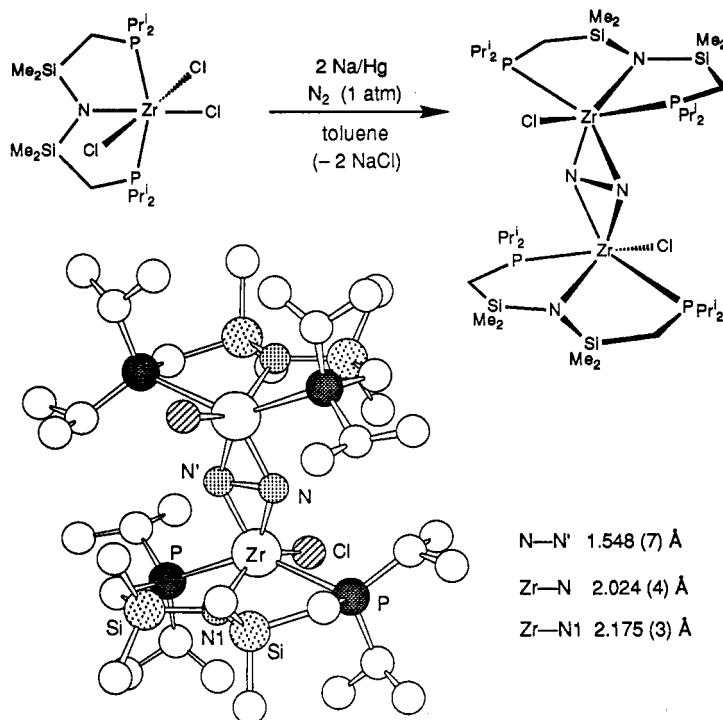
Scheme 6



Another example of how this tridentate *ancillary ligand* system can change the properties of *reactive ligands* coordinated to zirconium concerns the reduction chemistry in the presence of dinitrogen (ref. 14). Addition of two equiv of Na/Hg to $\text{ZrCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$ under an atmosphere of N_2 generates a binuclear dinitrogen complex; the structure of this complex is shown in Scheme 7. There are two interesting aspects to this X-ray structure: (i) the N_2 binding mode is side-on bridging, only the second example of such a bonding interaction for an N_2 ligand, and (ii) the N-N bond length is 1.548 (7) Å, the longest N-N bond distance for any transition metal dinitrogen complex.

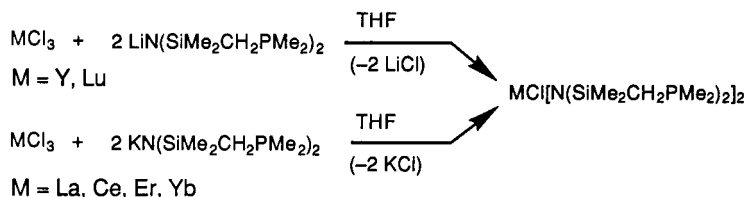
By comparison, in the related dinitrogen complex $[\text{Cp}^*_2\text{ZrN}_2]_2(\mu\text{-N}_2)$, the bridging N_2 ligand is end-on (i.e., $\text{Zr-N}\equiv\text{N-Zr}$), the more typical mode of binding of N_2 ligands to transition metals (ref. 15). The reactivity of the side-on bridged N_2 derivative is also quite different to that the permethylzirconocene dinitrogen complex since addition of H_2 , CO or olefins does not displace the N_2 ligand of $\{[\text{Pr}^i_2\text{PCH}_2\text{-SiMe}_2)_2\text{N}]\text{ZrCl}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$. This is consistent with a strongly bound hydrazido (4-) ligand, i.e., N_2^{4-} .

Scheme 7



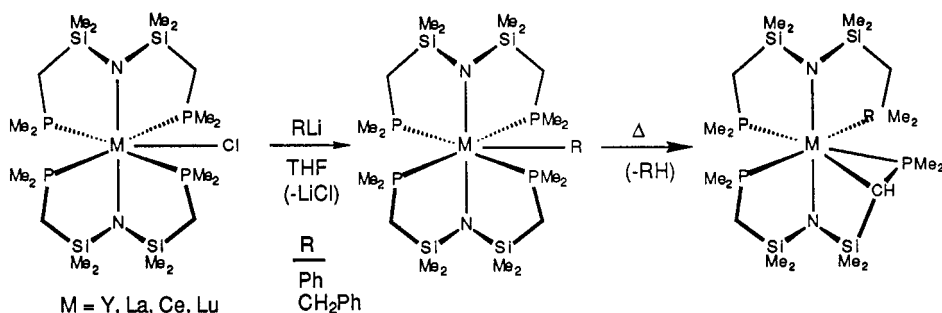
Phosphine Complexes of Group 3 and the Lanthanides. When this work was initiated in 1980 there were no authentic phosphine complexes of group 3 and the only lanthanide derivative was $\text{Cp}_3\text{Yb}(\text{PR}_3)$ where PR_3 could be a variety of secondary and tertiary phosphines (ref. 16). By applying the identical synthetic strategies, already described for group 4, to the heavier members of the group 3 metals and a number of the lanthanide elements, access to *bona fide* phosphine derivatives of these elements was achieved (refs. 17,18). This is summarized in Scheme 8.

Scheme 8



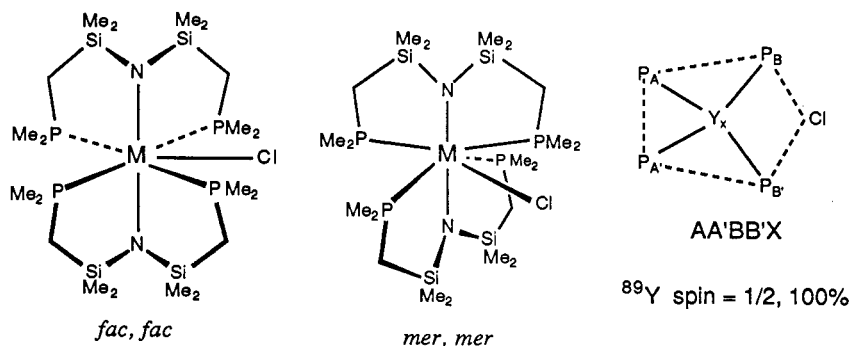
In contrast to the bis(ligand) derivatives of the group 4 metals, these bis(ligand) derivatives are reactive to certain organolithium and organopotassium reagents to generate hydrocarbyl derivatives. For $\text{M} = \text{Y}$ and Lu , these hydrocarbyl derivatives can be isolated; however, for $\text{M} = \text{La}$ and Ce , cyclometallation of the ligand backbone occurs spontaneously by elimination of hydrocarbon. For the Y and Lu derivatives, heating to 50°C is required for the cyclometallation. The site of the metallation was determined by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy to be one of the methylene protons (PCH_2Si) and confirmed by a single-crystal X-ray structure (Scheme 9) (ref. 19).

Scheme 9



Those seven-coordinate bis(ligand) complexes of the general formula $\text{MX}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2]_2$ ($\text{X} = \text{Cl}$ or hydrocarbyl) are fluxional. At low temperatures, this process can be frozen out on the $^{31}\text{P}\{^1\text{H}\}$ NMR time scale and the spectra analyzed. The lutetium-phenyl complex exhibits an AA'BB' spin system. For the yttrium derivatives, the presence of the 100% naturally abundant spin = 1/2 ^{89}Y nucleus generates AA'BB'X spin systems which also provide information of yttrium-phosphorus coupling constants. Unfortunately, the stereochemistry of the low temperature limiting structures of these bis(ligand) derivatives is not known. As shown in Scheme 10, geometries based on a pentagonal bipyramid satisfy the low temperature NMR data, but we are unable to distinguish between a *fac, fac* or a *mer, mer* configuration; for that reason, either is used interchangeably.

Scheme 10



Studies are in progress on the formation and reactivity of monoligand complexes of the the group 3 and the lanthanide elements (ref. 19).

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