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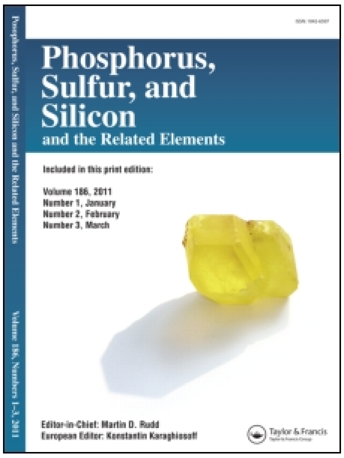

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Ambidentate, Anionic Phosphine Ligands in Organoelement Chemistry

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AMBIDENTATE, ANIONIC PHOSPHINE LIGANDS IN ORGANOELEMENT CHEMISTRY

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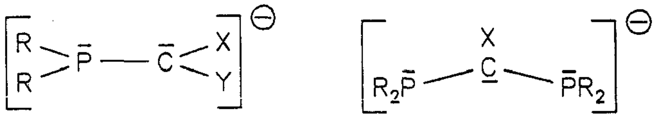
Abstract: Phosphinomethanides bind to electrophiles either via phosphorus or carbon. The resulting compounds usually are fluctional and/or may rearrange from carbon to phosphorus coordination or vice versa. Selective oxidative coupling reactions of the phosphinomethanide ligands are found with metal centers in high oxidation states, whereas these ligands are stable to reduction. Thus, low valent species can be stabilized. In addition, diphosphinomethanides are useful ligands to promote high coordination numbers with main group ("hypervalent compounds"), transition or lanthanoide elements.

INTRODUCTION

Mono-and diphosphinomethanides



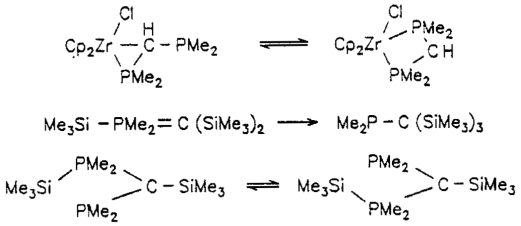
monophosphinomethanides *diphosphinomethanides*

X,Y = H, $SiMe_3$, PMe_2; R = Me, Ph

represent a unique class of compounds, where both, the same coordination number and the same valence electronic number of directly connected carbon and phosphorus allow for a comparison of reactivity towards electrophiles. The nucleophilicity can be tuned by the choice of substituents: $SiMe_3$ and/or PMe_2 substituents at carbon reduce its nucleophilicity to an extent, where both carbon and phosphorus exhibit similar nucleophilicity.

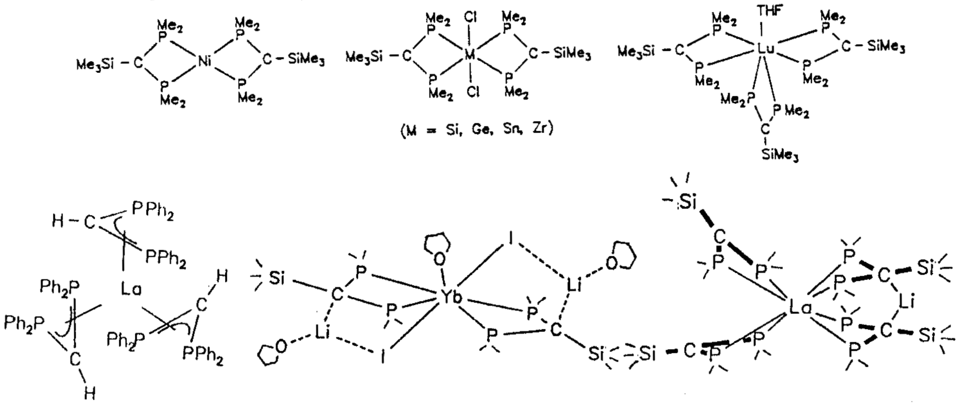
RESULTS

Equilibria with both coordination modes may be found, e.g.



Fluctionality also is quite common and rearrangements may also occur.

High coordination numbers with phosphine donor ligands are feasible using diphosphinomethanides. Thus, main group, transition and even lanthanoide element complexes with up to eight element-phosphorus bonds are obtained. Some examples are given below:



Particularly interesting are the compounds $R_2Si[C(PMe_2)_2$-$(SiMe_3)]_2$. For R = Me, the solid state structure represents a "frozen transition state" between tetra- and hexacoordination.

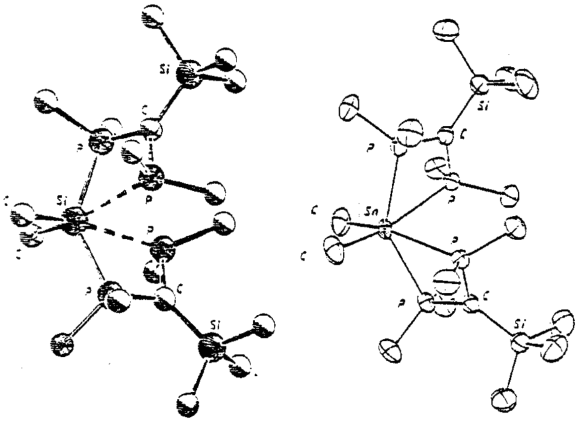
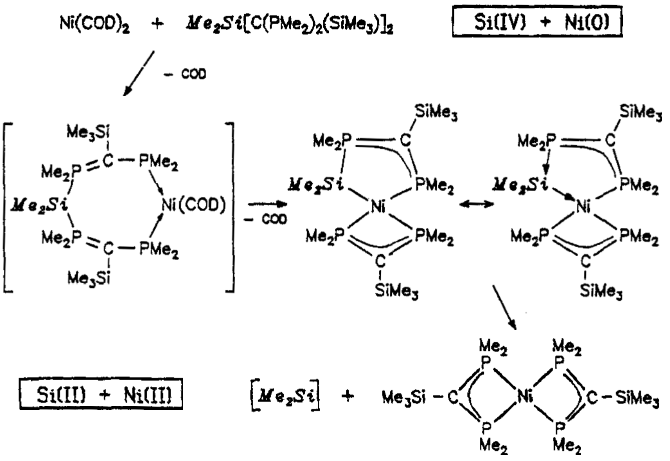
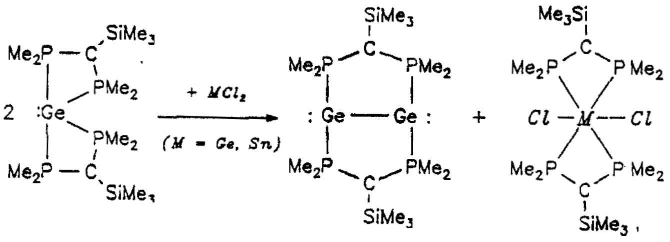


Fig.1. Molecular Structure of $Me_2E[C(PMe_2)_2(SiMe_3)]$

Compounds of this kind are a unique source for transient silylenes. The intermediate phosphine donor stabilized silylene complex liberates R_2Si on heating.



Stable, phosphine donor stabilized Si(II), Ge(II), Sn(II) and Pb(II) compounds are likewise accessible with diphosphinomethanide ligands. The germanium derivatives are unique in exhibiting a rich, unusual chemistry including an unusual redox reactivity:



Thus $SnCl_2$ is oxidized by a Ge(II) derivative, which at least partially, is due to the essentially nonpolar Ge-P bond. This property seems also responsible for the outstanding nucleophilic behaviour of the resulting dinuclear Ge(I) compound.

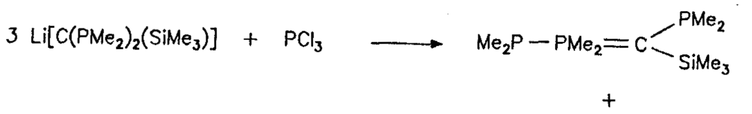
Oxidative C-C, P-C and P-P coupling reactions selectively are observed in the reactions of phosphinomethanides with Cp_2TiCl_2, depending on the substitution pattern and the reaction conditions.

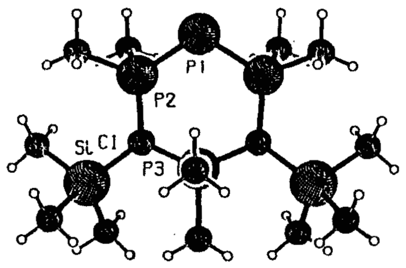
$$2\ LiCH_2PMe_2 \xrightarrow[(C-C)]{Cp_2TiCl_2} Me_2PCH_2CH_2PMe_2$$

$$2\ LiCH(SiMe_3)(PMe_2) \xrightarrow[(P-C)]{Cp_2TiCl_2} Me_3SiCH_2PMe_2{=}C(SiMe_3)(PMe_2)$$

$$2\ LiC(SiMe_3)_2(PMe_2) \xrightarrow[(P-P)]{Cp_2TiCl_2} (Me_3Si)_2C{=}PMe_2{-}PMe_2{=}C(SiMe_3)_2$$

As oxidizing reagent, amongst others, also $BiCl_3$ can be used, provided that more than one heteroatom substituent at the carbanion is present (P-C and P-P coupling). Elemental bismuth is formed as the by-product. In contrast, with PCl_3 stable low valent phosphorus intermediates can be isolated. Thus, e.g. adding three equivalents of $Li[C(PMe_2)_2(SiMe_3)]$ slowly to a solution of PCl_3 in diethyl ether at low temperature, a novel $1\lambda^3$, 2, 4,6 λ^5-Tetraphosphonine ("Tetraphosphabenzene") may be isolated and structurally characterized





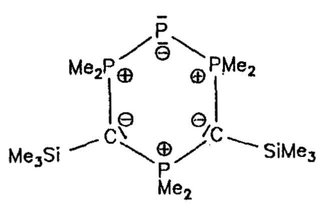


Fig.2. Molecular Structure of 1

CONCLUSION

Phosphinomethanide ligands give an access to a variety of novel structures, reactivities and dynamic features which is unprecedent in organoelement chemistry and which is mainly due to the ambidentate nature and high nucleophilicity of this class of organophosphorus compounds.