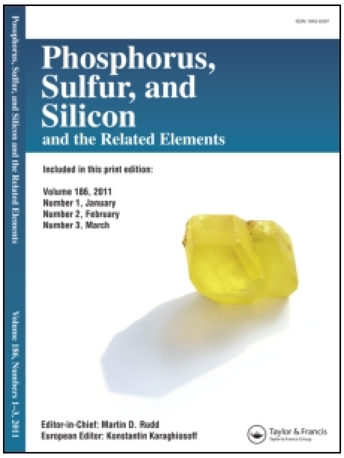

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Phosphinomethyl Compounds: Versatile Tools in Organometallic Chemistry

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To cite this Article Karsch, Hans H. and Appelt, Armin(1983) 'Phosphinomethyl Compounds: Versatile Tools in Organometallic Chemistry', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 287 — 290
To link to this Article: DOI: 10.1080/03086648308076022
URL: http://dx.doi.org/10.1080/03086648308076022

Phosphorus and Sulfur, 1983, Vol. 18 pp. 287-290
0308-664X/83/1801-0287/$18.50/0

PHOSPHINOMETHYL COMPOUNDS: VERSATILE TOOLS IN ORGANOMETALLIC CHEMISTRY

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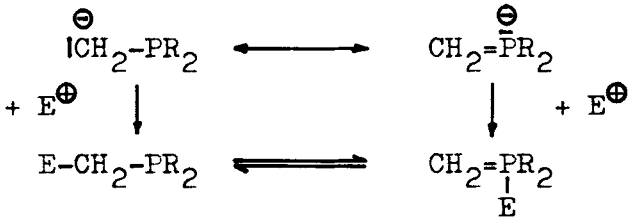
Abstract The preparation and properties of some main group and transition element compounds (Al, Si, Sn, P, Zr, Fe, Co, Ni), containing phosphinomethyl substituents, are described.

INTRODUCTION

The reactivity and ambidentate nature of phosphinomethanides, i.e. $[(R_2P)_nCH_{(3-n)}]^-$ has attracted our attention in the past, e.g. Eq. (1)[1].



$$\begin{array}{ccc} \overset{\ominus}{|CH_2-PR_2} & \longleftrightarrow & \overset{\ominus}{CH_2=\overline{P}R_2} \\ +E^{\oplus}\ \downarrow & & \downarrow\ +E^{\oplus} \\ E-CH_2-PR_2 & \rightleftharpoons & CH_2=\underset{\underset{E}{|}}{P}R_2 \end{array} \qquad (1)$$

Thus phosphinomethyl substituted phosphines have been obtained according to Eq. (2)[2].

$$Me_{(3-n)}PCl_n + n\ LiCH_2PMe_2 \longrightarrow Me_{(3-n)}P(CH_2PMe_2)_n \qquad (2)$$

NEW RESULTS

We have now extended our studies to various other kinds of electrophiles. Thus a simple access to novel mono- to tetradentate phosphine ligands is available, Eq. (3). Methyl substituents at the phosphorus atom and heteroelement bridges distinguish these colourless, air sensitive and distillable liquids.

$$Me_{(4-n)}ECl_n + n\ LiCH_2PMe_2 \longrightarrow Me_{(4-n)}E(CH_2PMe_2)_n \quad (3)$$

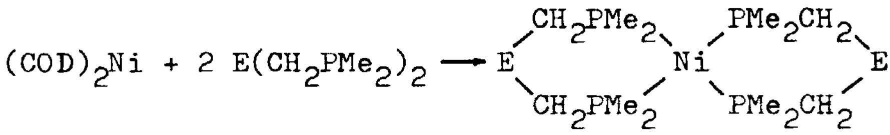
$[E = Si, Sn]$

The same type of reaction is also observed in the analogous organoaluminum system, thus combining electrophilic and nucleophilic centers in one molecule ("amphoteric ligand"), Eq. (4).

$$\begin{tikzcd} AlCl_3 + 3\ LiCH_2PMe_2 \arrow[r] & \text{"}Al(CH_2PMe_2)_3 \arrow[d, "+\ 2\ AlMe_3"] \\ & 3\ \text{"}Me_2AlCH_2PMe_2\text{"} \end{tikzcd} \quad (4)$$

The colourless crystals obtained, by means of spectroscopic and cryoscopic evidence, contain dimeric, six membered ring molecules. No monomeric adducts may be isolated on the addition of Lewis bases, e.g. PMe_3 or THF, whereas on the addition of $LiCH_2PMe_2$ aluminate ions are formed, i.e. $Li[Me_2Al(CH_2PMe_2)_2]$ and $Li[Al(CH_2PMe_2)_4]$.

The new diphosphines act as six ring chelate ligands in transition metal complexes, Eq. (5).



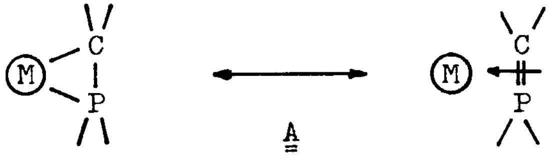
$$(COD)_2Ni + 2\ E(CH_2PMe_2)_2 \longrightarrow E\begin{matrix} CH_2PMe_2 \\ CH_2PMe_2 \end{matrix}Ni\begin{matrix} PMe_2CH_2 \\ PMe_2CH_2 \end{matrix}E \quad (5)$$

$[E = PMe, SiMe_2]$

In the phosphine/iron(O) complex system[3], cyclometalation occurs at the methylene carbon atom and novel ferrabicyclic complexes are formed, i.e. $[E(CH_2PMe_2)_2](H)Fe[Me_2PCHECH_2PMe_2]$ $(E = H_2C, Me_2C,$

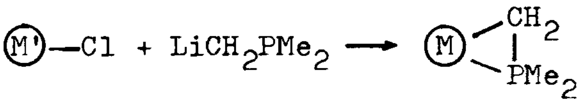
Me_2Si, Me_2Sn, MeP). Reactions with CO, and (in the case of E = CH_2) with N_2, CO_2 and PR_3 yield pentacoordinated iron(0) complexes and thus demonstrate the existence of a reversible equilibrium with the iron(0) isomers $[E(CH_2PMe_2)_2]_2Fe$.

The structural unit of a η^2-phosphinomethanide ligand, i.e. the three membered ring **A** seems to account for the stability of these complexes.



A

This structural feature is also dominant in other phosphinomethyl substituted transition metal complexes, obtained by a similiar route to Eqs. (2), (3) and (4), i.e. Eq. (6).



$$\text{Ⓜ'}\text{—Cl} + LiCH_2PMe_2 \longrightarrow \text{Ⓜ}(CH_2PMe_2) \qquad (6)$$

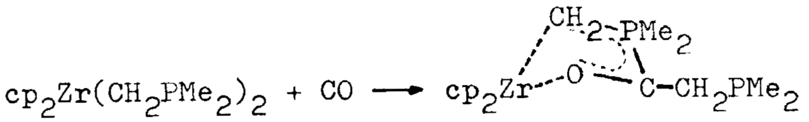
[Ⓜ = L_3Co, $L_2(CO)Co$, L_3Ni^+, $L_3(H)Fe$, $L_3(Me)Fe$ and $L_2(Me)_2Co$; L = PMe_3]

In contrast to this, the phosphinomethyl group binds to early transition metals in a η^1- manner, Eq. (7)[4].

$$\begin{array}{l} cp_2ZrCl_2 + LiCH_2PMe_2 \longrightarrow cp_2Zr(Cl)CH_2PMe_2 \\ cp_2ZrCl_2 + 2\,LiCH_2PMe_2 \longrightarrow cp_2Zr(CH_2PMe_2)_2 \end{array} \qquad (7)$$

The bis(phosphinomethyl) derivative may act as a chelating diphosphine ligand, e.g. according to Eq.(5) [E = cp_2Zr], thus combining electron rich [Ni(0), d^{10}] and electron deficient [Zr(IV), d^0] metal centers by phosphinomethyl bridges. This has remarkable consequences for the properties of the resulting complex: it forms dark green solutions, from which black crystals may be obtained (THF).

The presence of two nucleophilic phosphinomethyl groups is also responsible for the reaction course according to Eq. (8), whereby a novel "heterodiene" complex is obtained.



(8)

From these and other findings, we conclude, that the introduction of the phosphinomethyl group in organometallic systems, which is easily achieved by means of phosphinomethanides, may play an important and growing role both in organophosphorus and in organometallic chemistry in the future.

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