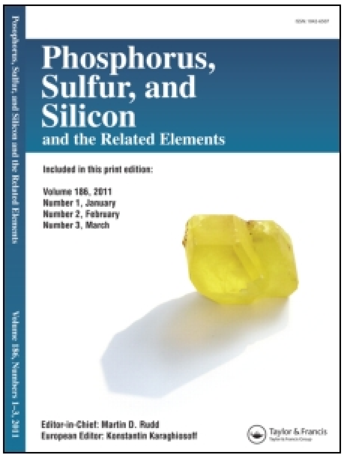

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Hard Metal Centers with Soft Phosphine Type Ligands

HANS H. KARSCH, VOLKER GRAF and MANFRED REISKY

Anorganisch-chemisches Institut, Technische Universität München, Lichtenberg-str.4, D-85747 Garching, Germany

Phosphine complexes of metals which normally do not coordinate phosphines readily, as exemplified by the rare earth or the alkaline earth metals, are obtained by using anionic phosphine ligands.

Keywords: rare earth; alkaline earth metals; phosphine complexes; anionic phosphine ligands

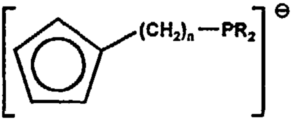
INTRODUCTION

In contrast to transition metals, where phosphine complexes play a dominant role, hard metal centers like the rare earth metals or the alkaline earth metals normally do not form complexes with simple phosphines, **I**. The generation of these complexes seems worthwhile mainly for two reasons:

1. To enter a new field always is a challenge. The combination soft/hard seems disadvantageous, but it is like entering a long-known house not by the main entrance but by a side-door: new insights can be expected. The soft phosphine donors may donate new properties to the metal centers, which may lead to new basic results (nature of metal-phosphorus bond, role of d-orbitals with alkaline earth metals, low valency, new coordination behavior, metal-metal bonding, weak interactions, etc.)
2. New properties may give rise to new applications. Realistic efforts in this respect are aimed to organic synthesis, catalysis, CVD, and materials.

The obvious strategy for phosphine coordination to hard metal centers involves the introduction of the organophosphorus ligand as an anion. In fact, stable compounds exhibiting metal-phosphorus bonding have been obtained within the alkaline earth and rare earth metal series in recent years by using phosphanides, **II**. In contrast to phosphines, however, phosphanides are two-coordinate. Two anionic ligands which more resemble phosphines are the phosphinomethanides **III** and phosphinoalkyl substituted cyclopentadienyl ligands **IV**, since phosphorus is tricoordinate and the negative charge is not centered on phosphorus.

R_3P $R_2P^{\ominus}$ $[R_2P-CXY]^{\ominus}$



I **II** **III** **IV**

We have demonstrated that phosphinomethanide ligands of type **III**, in particular diphosphinomethanides (X = PR_2, Y = $SiMe_3$), are excellently suited to achieve phosphine coordination to rare earth metals[1] and up to 8 Ln-P bonds can be generated in this way[2]. Therefore, these ligands seem ideal candidates to achieve phosphine bonding to group 2 metals[3]. Group 12 metal centers are also included for comparison.

On the other hand, ligands of type **IV** are particularly interesting in the rare earth metal series: cyclopentadienyl ligands play a dominant role in the exploitation of these metals centers for synthetic and catalytic purposes, but the available range of suitable systems is restricted. Many of the involved species are neither monomeric, nor free of solvent or alkali metal halides.

By an additional coordination of phosphine functionalities - weak and reversible, but effective - one may overcome this problem. Moreover, these ligands seem suitable to form bridges to other metal centers, i. e. an access to lanthanoide-transition metal heteronuclear complexes seems at hand. Therefore, ligands of type **IV** were included in the study.

Complexes of both ligand types **III** and **IV** should gain additional stability by their chelating character. Furthermore, neutral complexes may be expected, which are soluble in hydrocarbons and may even exhibit some volatility.

RESULTS

Stable complexes **1-3**, exhibiting four metal-phosphorus bonds, which are readily soluble in hydrocarbons, are obtained according to eq. (1)[4].

$$MCl_2 + 2\ Li[(Me_2P)_2C(SiMe_3)] \xrightarrow{THF} \underset{1-3}{(THF)_nM[(Me_2P)_2C(SiMe_3)]_2} \quad (1)$$

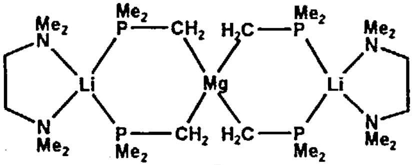
(1: M = Be, n = 0; 2: M = Mg, n = 2; 3: M = Ca, n = 3)

The magnesium complex 2 is easily transformed to the magnesate 4 (eq. 2) exhibiting six magnesium-phosphorus bonds[4]. The anion of 4 , as expected, is isostructural to $Al[(Me_2P)_2C(SiMe_3)]_3$[5].

$$2 + Li[(Me_2P)_2C(SiMe_3)] \xrightarrow[Et_2O]{12\text{-crown-4}} \underset{4}{Li[12\text{-crown-4}]_2\{Mg[(Me_2P)_2C(SiMe_3)]_3\}} \quad (2)$$

Another kind of magnesate complex 5, internally charge balanced by lithium coordination is obtained according to eq. (3).

$$MgCl_2 + 4\ LiCH_2PMe_2 \xrightarrow{TMEDA}$$

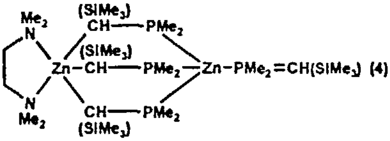


5

(3)

Whereas in solution at r.t., an exchange of $PMe_2CH_2^-$-bridging sites is observed, at low temperature (-90°C) the trinuclear 5 is the only detectable species. Its structure is confirmed by X-ray diffraction. An unusual dinuclear zinc complex 6 is obtained according to eq. (4). The two isomers of 6 are observed in a 1:1 ratio.

$$ZnCl_2 + 2\ Li[CH(PMe_2)(SiMe_3)]\cdot TMEDA \xrightarrow{THF}$$



6

(4)

Anhydrous rare earth chlorides MCl_3 (M = Y, La, Nd, Lu) with $Li[Cp(CH_2)_2PR_2]$ (R = Me, Ph, ^{t}Bu, Cy) give mononuclear complexes 7 free of LiCl and solvent (eq. 5).

$$MCl_3 + 2\ LiCp(CH_2)_2PR_2 \longrightarrow \underset{7}{M[Cp(CH_2)_2PR_2]_2Cl} \quad (5)$$

(7: e.g. M = Y, La, Nd, Lu; R = Me, Ph, ^{t}Bu, Cy)

The complexes are soluble in hydrocarbons and may be converted by reactions with various nucleophiles to give again mononuclear, solvent free products **8** (eq. 6).

$$M[Cp(CH_2)_2PR_2]_2Cl + M'R' \xrightarrow[-M'Cl]{} \underset{\mathbf{8}}{M[Cp(CH_2)_2PR_2]_2R'} \qquad (6)$$

$$(\mathbf{8}: M' = Li, Na;\ R' = CH_3, Cp, CH_2PMe_2, Cp(CH_2)_2PR_2)$$

Further reactions of these new rare earth complexes are straightforward. Thus, $[Cp(CH_2)_2PMe_2]_3La$ is converted with CH_3I to the tris-phosphonium salt and with sulfur to the trisphosphinetrisulfide derivative. Starting from $[Cp(CH_2)_2PMe_2]_2YCH_3$, the monocation $\{[Cp(CH_2)_2PMe_2]_2Y^+\}$ is obtained free of solvent in high yield as the BPh_4^- salt. Similar complexes are obtained using $MeP[(CH_2)_2Cp]_2^{2-}$ as ligand. The complexes are fully characterized by analytical and spectroscopic means and, in part, by X-ray analysis.

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