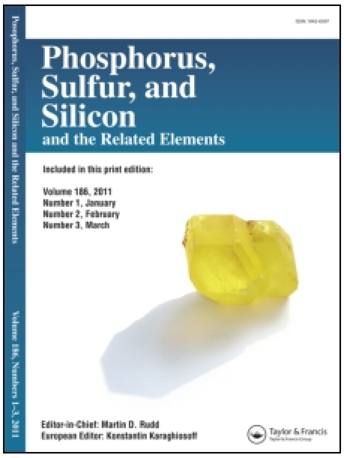

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HOMOLEPTIC DISILYLPHOSPHIDO COMPLEXES $\{M[P(SiR_3)_2]_x\}_n$ AND THEIR USE AS PRECURSORS TO PHOSPHIDE SEMICONDUCTOR NANOCLUSTERS

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<u>Abstract</u> Several homoleptic disilylphosphido complexes are described, which are relatives of the well-known homoleptic disilylamido complexes. The differing properties of the amido and phosphido ligands are ascribed to normal periodic relationships.

We are pursuing the synthesis, structural characterization, and reactivity studies of the first members of a new class of inorganic compounds: homoleptic disilylphosphido complexes of general formula $M[P(SiR_3)_2]_x$. The $P(SiMe_3)_2$ ligand is a heavier congener to the well-known $N(SiMe_3)_2$ ligand; homoleptic disilylamido complexes make up the largest known class of amido-metal complexes.[1]

We have now prepared a variety of homoleptic $P(SiMe_3)_2$ complexes, which allows the first comparison of homologous, binary amido and phosphido complexes. Our results show that $P(SiMe_3)_2$ complexes generally exhibit higher molecularities and higher coordination numbers than do the corresponding disilyamido complexes. Additionally, we find that terminal $P(SiMe_3)_2$ ligands invariably exhibit pyramidal configurations in the homoleptic compounds whereas terminal $N(SiMe_3)_2$ ligands were shown to exhibit planar configurations.[1] To our knowledge, the data below provide the first direct demonstration of the stronger bridging tendencies of phosphido ligands relative to amido ligands. The differing behaviors of disilylamido and disilylphosphido ligands may be ascribed to normal periodic trends, which distinguish the properties of N and P.[2]

Efforts to prepare homoleptic diaryl- and dialkylphosphido (PR_2) complexes were initiated by Issleib and coworkers 30 years ago,[3] and several bulky dialkylphosphido complexes are now known. However, homoleptic $P(SiMe_3)_2$ complexes had not been described (except for alkali-metal salts). We initially became interested in $P(SiMe_3)_2$

complexes as precursors in solution-phase routes to inorganic phosphides; see eq 1.[4] We have now obtained $M[P(SiMe_3)_2]_x$ derivatives of monovalent, divalent, and trivalent metals.

$$1/2\{Cd[P(SiMe_3)_2]_2\}_2 + 4MeOH \xrightarrow{-4MeOSiMe_3} 1/3Cd_3P_2 + 4/3PH_3 \quad (1)$$

The new complexes of divalent metals **1** - **6** are prepared in 68-90% yields by the exchange reaction of eq 2. Compound **6** crystallizes as a THF adduct, but the THF ligand is easily lost in vacuo giving $\{Mn[P(SiMe_3)_2]_2\}_2$. The molecular structures of **1** - **3**, and **5** are shown below.

$$M[N(SiMe_3)_2]_2L + 2HP(SiMe_3)_2 \longrightarrow 1/n\{M[P(SiMe_3)_2]_2\}_2L + 2HN(SiMe_3)_2 \quad (2)$$

M = Zn (**1**)	L = none
Cd (**2**)	none
Hg (**3**)	none
Sn (**4**)	none
Pb (**5**)	none
Mn (**6**)	THF

The *unsolvated* alkali-metal complexes of the $P(SiMe_3)_2$ ligand **7** - **9** are prepared similarly; see eq 3. The structures of the lithium and sodium complexes (**7** and **8**) have been determined; **8** is shown below.

$$M[N(SiMe_3)_2] + HP(SiMe_3)_2 \longrightarrow 1/n\{M[P(SiMe_3)_2]\}_n + HN(SiMe_3)_2 \quad (3)$$

M = Li (**7**)	n = 6
Na (**8**)	∞
K (**9**)	?

Several other examples are obtained from alkyl or alkoxide precursors as shown in eqs 4 and 5. The solid-state structures of **10**·2dioxane, **11**·py, **12**, and **13** have been determined, and the latter three are shown below.

$$MR_x + xHP(SiMe_3)_2 \longrightarrow M[P(SiMe_3)_2]_x + xRH \quad (4)$$

$M = Mg$ (10) $\quad R = CH_2CMe_3 \quad x = 2$

In (11) $\quad CMe_3 \quad 3$

$$M(OR)_x + xHP(SiMe_3)_2 \longrightarrow 1/n\{M[P(SiMe_3)_2]_x\}_n + xROH \quad (5)$$

$M = Cu$ (12) $\quad R = CMe_3 \quad x = 1 \quad n = 6$

Bi (13) $\quad CMe_2Et \quad 3 \quad 1$

We have also prepared a series of disilylphosphido complexes containing the bulkier $P(SiPh_3)_2$ ligand; see eq 6. All are two-coordinate monomers. The solid-state structure of the cadmium complex 15 is depicted below.

$$M[N(SiMe_3)_2]_2 + 2LiP(SiPh_3)_2 \longrightarrow M[P(SiPh_3)_2]_2 + 2LiN(SiMe_3)_2 \quad (6)$$

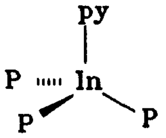
$M = Zn$ (14)

Cd (15)

Hg (16)

Sn (17)

Cadmium phosphide nanoclusters are prepared from the methanolysis of the new disilylphosphido precursor 15, and are isolated as a very dark, pyridine-soluble solid. Transmission electron microscopy reveals nanoclusters with ca. 30 – 40 Å diameters. The Cd_3P_2 nanoclusters retain large numbers of –OMe and $-SiPh_3$ residues as surface substituents, which are responsible and necessary for arresting particle growth in the nanometer regime.[5]



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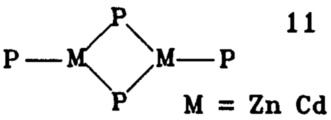

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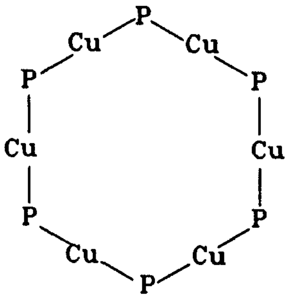

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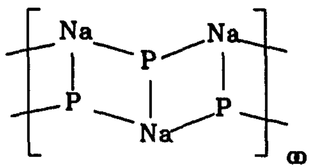

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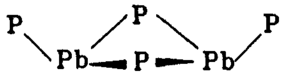

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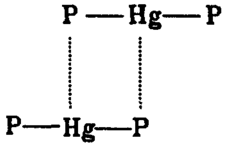

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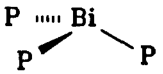

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