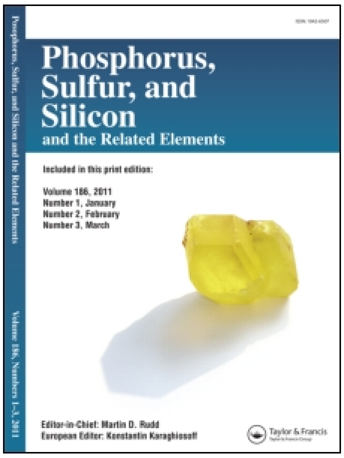

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New Polyfuctional Ligands Derived from Bis(diphenylphosphino)methanide

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To cite this Article Balch, Alan L. and Oram, Douglas E.(1987) 'New Polyfuctional Ligands Derived from Bis(diphenylphosphino)methanide', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 101 — 104
To link to this Article: DOI: 10.1080/03086648708080532
URL: http://dx.doi.org/10.1080/03086648708080532

Phosphorus and Sulfur, 1987, Vol. 30, pp. 101–104
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NEW POLYFUCTIONAL LIGANDS DERIVED FROM BIS(DIPHENYLPHOSPHINO)METHANIDE

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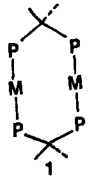
Abstract $Li\{CH(PPh_2)_2\}$ reacts with $HgCl_2$,$SnCl_2$, or $PbCl_2$ in tetrahydrofuran solution to yield the homoleptic complexes $Hg\{CH(PPh_2)_2\}_2$, $Sn\{CH(PPh_2)_2\}_2$,and $Pb\{CH(PPh_2)_2\}_2$ The mecury complex contains two equivalent, carbon bound ligands while the tin and lead compounds contain two different $CH(PPh_2)_2^-$ units: one carbon-bound, the other chelating through two phosphorus atoms. The three coordinate tin or lead ions have pyramidal structures as shown by X-ray studies.

INTRODUCTION

Numerous binuclear transition metal complexes with two trans dpm (bis(diphenylphosphino)methane) ligands have been prepared and found to have a stable $M_2(dpm)_2$ core that can support a broad range of reaction chemistry which involves ligands coordinating in the plane perpendicular to this core.[1,2] We have sought to prepare an analogous set of complexes in which the two phosphines are in cis position and the reactive sites at the two metal ions all adjacent to one another. To do this it appears useful to connect the two dpm-derived ligands via a group X as shown in 2. Thus we have been exploring the chemistry of $LiCH(PPh_2)_2$[3] as a means of preparing 2. Straight forward routes to $(Ph_2P)_2CHCH_2CH(PPh_2)_2$ have failed[4]. Consequently we have turned to introducing a variety of main group elements for the connecting unit X.



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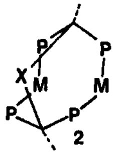

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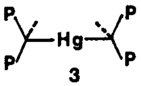

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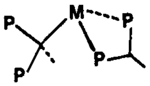

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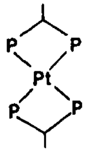
Reaction of $LiCH(PPh_2)_2$ with $HgCl_2$ yields $Hg\{CH(PPh_2)_2\}_2$, 3 (^{31}P NMR: δ, -6.2 ppm; $^2J(P,Hg)$, 88.9 Hz.). Reaction of $SnCl_2$ with $LiCH(PPh_2)_2$ in tetrahydrofuran yields brown $Sn\{CH(PPh_2)_2\}$ (m.p. 145-148 °C dec; ^{31}P NMR, δ_1, -10.3 ppm; $^3J(P,P)$, 25 Hz; $^2J(Sn,P)$, 276, 336 Hz; δ_2, -15.9 ppm; $^2J(Sn,P)$, 1106, 1158 Hz in toluene at 0°). Similarly, reaction of $PbCl_2$ with $LiCH_2(PPh_2)_2$ in tetrahydrofuran yields orange $Pb\{CH(PPh_2)_2\}_2$ (mp 141-146 °C dec; ^{31}P NMR, δ_1, -4.7 ppm; $^1J(P,Pb)$, 1970 Hz; δ_2, -11.6 ppm, $^2J(P,Pb)$, 155 Hz) in toluene at -30°C.

These tin and lead complexes possess structure 4 as indicated by X-ray diffraction studies. $Sn\{CH(PPh_2)_2\}_2 \cdot O(C_2H_5)_2$ crystallizes in the monoclinic space group $P2_1/C$ (No 14) with a=15.124(5) Å, b=14.589(7) Å, c=18.291(8) Å, β=91.50(3)° with Z=4 at 140°K. Refinement yielded R=0.064 for 247 parameters and 1902 reflections with $I > 3\sigma I$. The lead compound is isomorphous. A perspective view is shown in Figure 1, while Figure 2 shows the inner coordination sphere and emphasizes the pyramidal nature of the coordination at P(1), P(2) and Sn and the planarity of the chelate ring. The tin atom is three coordinate with a stereochemically active lone pair. The ether molecule is remote from tin (shortest Sn•••O distance, 6.57(2) Å) and not bonded to it).

These tin(II) and lead(II) complexes are remarkable for a number of reasons. They are the first cases where the $CH(PPh_2)_2^-$ ligand binds in both chelating and C-bound fashions. Other homoleptic conplexes of the ligand can have the C-bound structure 3, a bis-chelate structure 5, a bridging structure 6, or a combination of bridging and C-bound structure 7. The monomeric, three coordination of Sn(II) and Pb(II) is rare. Moreover compounds containing C-Sn(II) and C-Pb(II) as well as P-Sn(II) and P-Pb(II) bonds are unusual. Organotin compounds with R_2Sn stoichiometry have cyclic Sn-Sn bonded structures[8] except for $[\{(CH_3)_3Si\}_2CH]_2$ which is monomeric in solution but dimeric, Sn-Sn bonded in the solid.[9] In 4 the potentially vacant Sn(II) orbitals are filled by the phosphorus donors. Although these tin and lead compounds do not have the structure originally sought, they still should function as ligands since they have potential binding sites at the central metalloid, at the two uncoordinated phosphorus atoms, and at the carbon of the chelating ligand.



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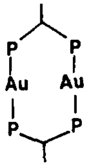

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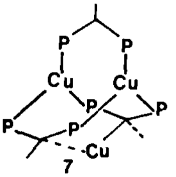

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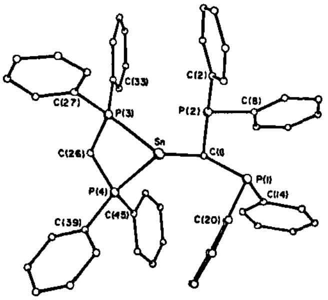

Figure 1. A perspective drawing of Sn{CH$_2$(PPh$_2$)$_2$}$_2$. Bond lengths: Sn-C(1), 2.286(16) Å, Sn-P(3), 2.676(5); Sn-P(4), 2.659(5). Bond angles: P(3)-Sn-P(4), 63.3(2)°; P(3)-Sn-C(1), 99.3(4); P(4)-Sn-C(1), 90.3(4); P(1)-C(1)-P(2), 118.0(8); P(3)-C(26)-P(4), 107,2(8).

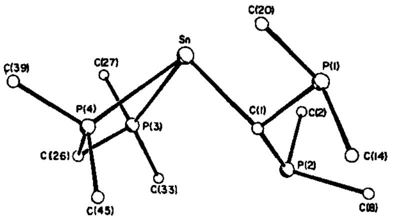

Figure 2. Inner Coordination.