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Polydentate Ligands Containing Phosphorus. 7. The Molecular Structure of a Mercury Complex of a New Uninegative Tridentate Ligand, Bis(dimethylthiophosphinyl)(diphenylthiophosphinyl)Methanide [1]

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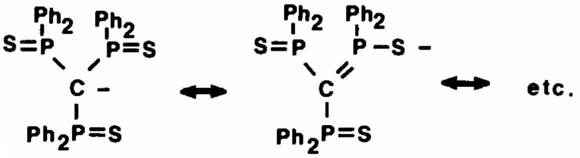
We report here the first molecular structure determination of a coordination compound, $\{[Me_2P(S)]_2[Ph_2P(S)]C\}HgCl$, which contains a member of an unusual and potentially versatile class of novel ligands, *viz.*, tris(diorganothiophosphinyl)methanide, $[R_2P(S)]_3C^-$. The ligands are derived by proton abstraction from the methine carbon of the neutral tris(diorganothiophosphinyl)methane parents, $[R_2P(S)]_3CH$ [2–6]. The resulting resonance stabilized carbanions can behave as uninegative, tridentate, six-electron donors. By coordination to a metal atom through the three sulfurs, the ligand forms a cage containing three six-membered chelate rings (Fig. 1). The coordination behavior thus mimics the polypyrazolylborates [7], (and the related polypyrazolylgallates [8]) the only precedent for this type of uninegative tridentate ligand.



We recently synthesized some coordination compounds of these ligands [1, 9], *viz.*, $\{[Ph_2P(S)]_3C\}MX$ and $\{[Me_2P(S)]_2[Ph_2P(S)]C\}MX$ where M = Hg or Cd and X = Cl, Br, or I. There are two obvious possibilities for metal–ligand bonding. The ligand coordinates (1) in a tridentate fashion through the sulfurs or (2) as a monodentate ligand via the central carbon. Although the great affinity of mercury for sulfur would favor the former bonding scheme, some NMR evidence [9] for the complex in solution seems to favor the latter. We have determined the crystal structure of $\{[Me_2P(S)]_2[Ph_2P(S)]C\}HgCl$ and found a tridentate S-bonded ligand (Fig. 1). The salient features of the structure are given below.

Mercury is in a distorted tetrahedral coordination geometry with mean SHgS and SHgCl bond angles of 102.1° and 115.8°, respectively, but with significant deviations from the means (see Table I). As is expected upon coordination the P–S bonds are considerably longer (mean, 203.2 pm) than the P–S bonds in simple uncoordinated tertiary phosphine sulfides, which range from 192.8 pm in $(p\text{-}CH_3C_6H_4)_3PS$ [10] to 196.6 pm in $(C_6H_{11})_3PS$ [11]. Also, the phosphorus-central carbon bond lengths are significantly smaller (mean, 176.9 pm) than the P–C single bonds in tertiary phosphine sulfides (181.5 pm in $(m\text{-}CH_3C_6H_4)_3PS$ [10], 181.7 in $(C_6H_5)_3PS$ [12], and 183.9 in $(C_6H_{11})_3PS$ [11], but longer than ylide P–C bonds (which average about 171 pm) [13] which contain considerable double bond character.

TABLE I. Some Important Bond Lengths and Angles in $\{[Me_2P(S)]_2[Ph_2P(S)]C\}HgCl^a$.

Bond lengths (pm)		Bond angles (°)	
P(1)–C	176.5(7)	P(1)–C–P(2)	116.4(4)
P(2)–C	179.0(7)	P(1)–C–P(3)	117.0(4)
P(3)–C	175.3(8)	P(2)–C–P(3)	115.7(4)
P(1)–S(1)	204.2(3)	S(1)–Hg–S(2)	107.5(1)
P(2)–S(2)	203.4(3)	S(1)–Hg–S(3)	95.5(1)
P(3)–S(3)	201.9(3)	S(2)–Hg–S(3)	103.4(1)
Hg–S(1)	252.2(3)	S(1)–Hg–Cl	123.1(1)
Hg–S(2)	255.0(3)	S(2)–Hg–Cl	114.0(1)
Hg–S(3)	271.6(3)	S(3)–Hg–Cl	110.3(1)
Hg–Cl	240.8(3)		

[a] Numbering of the atoms is shown in the Figure.

The PCP bond angles around the central carbon average 116.4°, which indicates that the C-hybrid orbitals contain s-character intermediate between sp^3 and sp^2-hybrids, and would seem consistent with the resonance delocalization suggested except that this argument is clouded by several facts. First, the central carbon is part of a cage containing six-membered rings which impose their own geometric requirements on carbon and second, the PCP bond angles [4] in the analogous neutral uncoordinated-ligand, $[Ph_2P(S)]_3CH$, average 115.3°, which is only slightly less than that observed in this complex of the anionic ligand. The molecular structure of the neutral parent ligand, $[Me_2P(S)]_2[Ph_2P(S)]CH$, is not known, but would be of interest for comparison with the structure of the anionic ligand.

Full details of this crystal and molecular structure will be published elsewhere, as will be additional coordination chemistry of these novel ligands.

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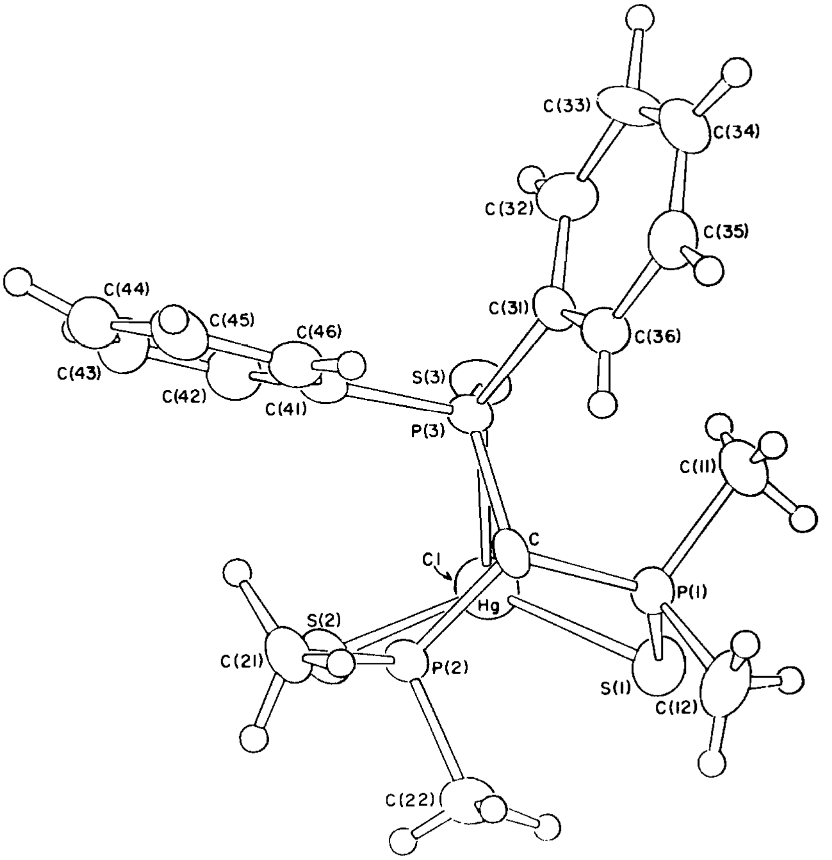

Fig. 1. The molecular structure of $\{[(C_6H_5)_2P(S)][(CH_3)_2P(S)]_2C\}HgCl$ as viewed along the mercury–chlorine axis. The Cl lies beneath the Hg.

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References

1 Part 6. S. O. Grim, P.H. Smith, L. C. Satek, I. J. Colquhoun and W. McFarlane, *Polyhedron, 1,* 137 (1982).
2 K. Issleib and H. P. Abicht, *J. Prakt. Chem., 312,* 456 (1970).
3 S. O. Grim, L. C. Satek and J. D. Mitchell, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., 35B,* 832 (1980).
4 I. J. Colquhoun, W. McFarlane, J.-M. Bassett and S. O. Grim, *J. Chem. Soc., Dalton Trans.,* 1645 (1981).
5 H. H. Karsch, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., 34B,* 1178 (1979).
6 S. O. Grim and E. D. Walton, *Phosphorus Sulfur, 9,* 123 (1980).
7 (a) S. Trofimenko, *J. Am. Chem. Soc., 88,* 1842 (1966); (b) S. Trofimenko, *Acc. Chem. Res., 4,* 17 (1971); (c) S. Trofimenko, *Chem. Rev., 72,* 497 (1972).
8 K. R. Breakell, S. J. Rettig, D. L. Singbeil, A. Storr and J. Trotter, *Can. J. Chem., 56,* 2099 (1978).
9 S. O. Grim, P. H. Smith, S. Nittolo, H. L. Ammon, L. C. Satek, S. A. Sangokoya, R. K. Khanna, I. J. Colquhoun, W. McFarlane and J. R. Holden, to be published.
10 T. S. Cameron, K. D. Howlett, R. A. Shaw and M. Woods, *Phosphorus, 3,* 71 (1973).
11 K. A. Kerr, P. M. Boorman, B. S. Misener and J. G. H. van Roode, *Can. J. Chem.., 55,* 3081 (1977).
12 P. W. Codding and K. A. Kerr, *Acta Crystallogr., B34,* 3785 (1978).
13 J. C. J. Bart, *J. Chem. Soc., Sect. B,* 350 (1969).