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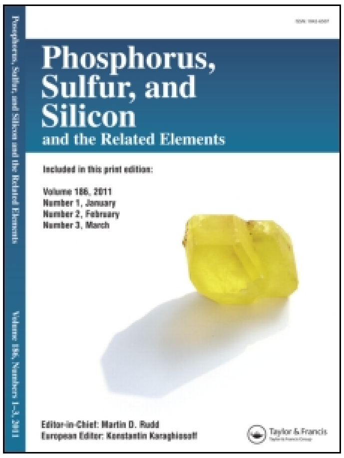

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Anionic Tripod Ligands Containing Phosphorus

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ANIONIC TRIPOD LIGANDS CONTAINING PHOSPHORUS

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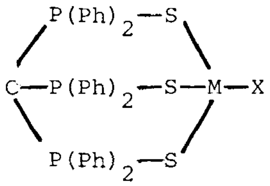
Abstract Tris(diphenylthiophosphinoyl)methanide, $[Ph_2P(S)]_3C^-$, and some analogues, are versatile ligands.

Tris(diphenylphosphino)methane[1], $(Ph_2P)_3CH$, 1, tris(diphenylthiophosphinoyl)methane[1], $[Ph_2P(S)]_3CH$, 2, tris(dimethylphosphino)methane[2], $(Me_2P)_3CH$, 3, and its corresponding trisulfide[2], $[Me_2P(S)]_3CH$, 4 are all relatively new compounds which have three phosphorus atoms attached to the same carbon. 1 has shown interesting properties as a tripod ligand in bonding simultaneously to three metal atoms.[3] Recently, we[4] and Karsch[5] have prepared the stable anions of 2 and 4, respectively, viz. $[Ph_2P(S)]_3C^-$, 5, and $[Me_2P(S)]_3C^-$, 6. This paper reviews (a) the synthesis of these compounds and ions; (b) the synthesis of analogues such as $[Ph_2P(S)][Me_2P(S)]_2CH$, 7, and its anion, 8; (c) the crystal structure of 2[6] and 5[7]; (d) the crystal structure of a complex of 8[8]; (e) the P-31 NMR data for these compounds; (f) and the coordination chemistry of 5 and its analogues.

The unique aspect of the anions 5,6,8 and analogues is that they can function as uninegative, tridentate six electron donors which form cage complexes containing six-membered chelate rings with metals. The only precedent for this type of anionic tripod ligand is the polypyrazolylborate system.[9]



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The thermally- and air-stable anion 5 can be prepared[4] by reaction of 2 with lithium methoxide in methanol followed by metathesis with $[n\text{-}Bu_4N]Br$ to produce crystalline $[n\text{-}Bu_4N]\{[Ph_2P(S)]_3C\}$. The x-ray structural determination[7] shows that the anion 5 is trigonal planar at the central carbon with an average P-C-P bond angle of 119.9°. As expected from a mesomerically stabilized structure, the P-S bond length increases and the P-C bond length decreases compared to those in the neutral parent 2 (see Table). 5 reacts with HgX_2, CdX_2, and other metal halides to give cage complexes of the type 5·MX, where X is Cl, Br, or I.[10]

TABLE

Some Data for $[Ph_2P(S)]_3CH$ and Derivatives

Parameter	2	5	5·Ag(n-Bu_3P)
d(P-S),pm	194.4	198.0	199.2
d(P-C),pm	188.3	175.9	177.6
∠PCP,°	115.3	119.8	115.5
δ(C-13),ppm	52.1	33.1	32.9
δ(P-31),ppm	46.9	44.0	42.7
^2J(P-P), Hz	<2	24.5	12.8
^1J(P-C), Hz	22.3	75.7	50.7

P-31 NMR spectra of these compounds show Hg-199 satellites with J(P-Hg) of the magnitude (90 Hz) expected for two-bond Hg-P coupling. 5 also reacts with $AgNO_3$ in the presence of neutral ligands such as tertiary phosphines to give complexes of the type 5·AgL[11]. The crystal structure of 5·AgP(n-Bu)$_3$ shows the cage structure with P-S and P-C bond lengths in agreement with expectations upon coordination (see Table). The P-31 NMR spectra of the Ag-complexes reveal P-P and P-Ag (107 and 109) coupling.

Finally, the important analogues $[Ph_2P(O)]_n[Ph_2P(S)]_{3-n}CH$ where n=1,2, or 3, and their respective anions have been synthesized.[12] This allows the hardness or softness of the ligands to be varied to suit the appropriate metal. For example, the "soft" trisulfide anion 5 forms stable complexes with typical soft metals such as Hg(II) and Ag(I). Preliminary results indicate that the trioxide anion is a more suitable ligand for the first transition metal series, e.g., Fe(II). However, preliminary evidence indicates $[Ph_2P(O)]_3C^-$ is bidentate in a complex with Fe(II).[13]

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