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A new uninegative ligand, *tris*-(diphenylthiophosphinyl)methanide[1]

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Abstract—The reaction of *tris*-(diphenylthiophosphinyl)methane, $[(C_6H_5)_2P(S)]_3CH$, with mercury(II) halides produces complexes of the type $[(C_6H_5)_2P(S)]_3CHgX$, where X is Cl, Br and I.

We report here the first coordination compound of *tris*-(diphenylthiophosphinyl)methanide, the prototype of a new class of uninegative ligands. Reaction of the neutral parent compound, *tris*-(diphenylthiophosphinyl)methane,[2–4] with mercuric halides in ethanol produces compounds with the stoichiometry $[(C_6H_5)_2P(S)]_3CHgX$, where X is Cl, Br and I. The compounds are air-stable, high-melting, diamagnetic, monomeric crystalline solids. The analogous cadmium halide complexes are prepared similarly except that the addition of triethylamine to the reaction medium facilitates removal of the methine proton from the neutral starting ligand. Molecular weight determinations establish the monomeric nature of the complexes and thus preclude the possibility of dimeric mercury(I) compounds.

The ^{31}P NMR spectrum of the chloro compound, for example, at room temperature consists of a singlet (δ_P = 44.1 ppm vs 85% H_3PO_4, coordination shift = 2.2 ppm) flanked by mercury-199 ($I = 1/2$, relative abundance = 16.4%) satellites with $^2J(Hg199\text{-}P31) = 91$ Hz. This indicates that the three phosphorus atoms are equivalent. The observation of two-bond ^{31}P–^{199}Hg coupling in phosphine sulphide complexes at room temperature is unusual since such ligands are labile[5] on the NMR time scale with the result that sharp mercury satellites in the phosphorus spectrum are not usually observed. The ^{31}P NMR spectra of the other complexes in this study are similar.

Additional evidence for the existence of the anion form of the ligand is (a) the failure to observe a signal for the methine proton in the ^1H NMR spectrum of the complexes, whereas the neutral parent ligand has an easily detectable methine proton signal at 6.04 ppm (quartet, $^2J(PCH) = 16.5$ Hz); and the failure to observe the methine carbon in the ^{13}C NMR spectra of the complexes, undoubtedly due to the long relaxation time of the protonless carbon.

These data are consistent with two possible structures: (a) a four-coordinate mercury (II) complex, approximately tetrahedral, with the ligand bonded in a tridentate fashion through the three sulphur atoms or (b) a two-coordinate mercury(II) complex, approximately linear, with the ligand bonded via the methine carbon to the mercury. We currently favor the tridentate ligand structure since space filling models of the neutral parent ligand indicate that the methine proton is sterically very crowded, and replacement of this small proton with a large mercury atom would be very difficult indeed. An X-ray structural determination of an analogue of these compounds is currently in progress.

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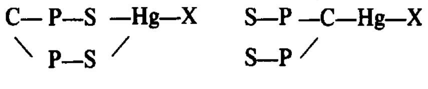

(a) (b)

Possible structures of $[(C_6H_5)_2P(S)]_3CHgX$ with phenyl groups omitted for clarity.

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