Mercury-Bis[methanidylenebis(dimethylphosphonium methylide)]: The First Tetra-alkyl Mercurate(II) Compound

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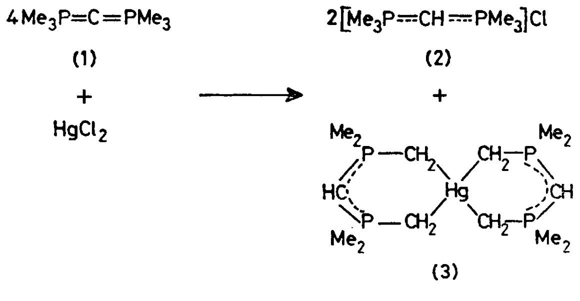
Summary The title compound has been prepared from hexamethylcarbodiphosphorane and mercuric chloride, and its structure deduced from a complete ^{1}H, ^{31}P, and ^{199}Hg n.m.r. analysis.

Dialkylmercurials, in contrast to their zinc and cadmium analogues, are extremely weak acceptor molecules.[1] Therefore, to our knowledge, no trialkyl or tetra-alkyl mercurates(II), HgR_3^- or HgR_4^{2-}, have been observed,[2] whereas the corresponding 'ate-complexes' of zinc and cadmium are described in the early literature of organometallic compounds.[3] Even in the case of perfluoroalkylmercurials only halogenomercurate compounds could be prepared.[4]



Salt-free ylides rank among the most powerful ligand systems for main group and transition metals,[5] and double ylides of the type $R_3P{=}C{=}PR_3$ are particularly versatile, owing to their ambidentate donor properties.[6] In order to obtain a polyalkylated mercurate complex, the reaction of mercury halides with this ligand system was investigated. It was found that these components undergo a smooth reaction in benzene solution at room temperature, in a 1:4 molar ratio, yielding a colourless crystalline precipitate of the chloride[6a,b] (**2**, 98%), and a solution of the title compound. After evaporation of the solvent *in vacuo* and rapid distillation (b.p. 130 °C at 10^{-4} Torr) a pale yellow air-sensitive crystalline solid (**3**) (m.p. 82 °C) was obtained in 67% yield. The mass spectrum of this product, which gives satisfactory elemental analysis, shows the molecular ion at *m/e* 526 (^{200}Hg) with high intensity. The i.r. spectra contain most of the characteristic bands found in other cyclic ylide complexes,[6b] indicating a close structural relationship. The ^{1}H n.m.r. spectra, which are not significantly temperature dependent, provide strong evidence for a symmetrical structure with four equivalent Me_2PCH_2 units. This is also borne out by a singlet resonance in the $\{^1H\}$–^{31}P n.m.r. spectrum. The ^{31}P resonance is accompanied by ^{31}P–^{199}Hg satellites. ^1H–^{199}Hg couplings are likewise observed for the CH_3 and CH_2 proton signals in the ^{1}H n.m.r. spectra. A final convincing test for the validity of the proposed tetra-alkylmercurate structure was offered by a $\{^1H\}$–^{199}Hg experiment (pulsed Fourier transform; Varian XL 100 spectrometer), which gave a 1:4:6:4:1 quintet, independent of temperature over the range from −60 to +35 °C. From this result, a fluxional molecular structure with two- or three-co-ordinate mercury atoms can be ruled out. The pertinent n.m.r. data are summarized in the Table. The low $^1H_2C^{199}Hg$ coupling constants are indicative of a sp^3 hybridisation of the metal, because these ^2J values are significantly higher for alkyl groups at two-co-ordinate (*sp*) mercury.

TABLE. N.m.r. data of compound (**3**)[a]

$\delta(H_3C)$	1·39; $A_6XX'A'_6$, N = 10·9; ^4J(HCPCHg) 2·6
$\delta(H_2C)$	0·54; $A_2XX'A'_2$, N = 9·7; ^2J(HCHg) 72·0
$\delta(HC)$	−0·05, br s, not sensitive to $\{^{31}P\}$
δ(P)	12·85, ^2J(PCHg) 128·0
δ(Hg)	−68·18.

[a] Chemical shifts δ in p.p.m., relative to Me_4Si, H_3PO_4, and Me_2Hg, respectively; coupling constants *J* in Hz; benzene or toluene solvent; 35 °C.

An *X*-ray investigation of the crystals is complicated by the light sensitivity of the material. Crystallographic data are available, however, for analogous dimethylgold(III)[7] and dimethylgallium(III)[8] complexes containing the same ligand system. The structure of the free double ylide (**1**) has been determined by electron diffraction.[9]

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