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Anionic Phosphito-P-Mercury Complexes $[Hg\{P(O)(OEt)_2\}^n]^{(n-2)-}$, n = 3,4

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The title compounds were formed from HgL_2 and NaL (HL = $HP(O)(OEt)_2$) and characterized by ^{31}P and ^{199}Hg NMR spectroscopy. Symmetric anionic mercurates $[HgL_n]^{(n-2)-}$ n = 3 or 4, have been characterized with L = halide [1], pseudohalide [1], -SR [2], -SeR [2], -TeR [2], $-S_2CNEt_2$ [3] (diethylcarbamodithioato), $-SiR_3$ [4], $-GeR_3$ [5] and $-Co(CO)_4$ [6]. Furthermore methylmercury complexes (L = Me) have been discussed as possible intermediates in the exchange between methylmercury and methyllithium [7]. We report here on the first symmetric mercurates involving Hg-P bonds.

Results and Discussion

Formation of $[Hg\{P(O)(OEt)_2\}_3]^-$ and $[Hg\{P(O)(OEt)_2\}_4]^{2-}$

We have obtained tris(diethylphosphito)mercurate and tetrakis(diethylphosphito)mercurate* by reaction 1. No compounds

$$HgL_2 + nNaL \rightarrow Na_n[HgL_{(n+2)}]\ n = 1, 2 \qquad (1)$$

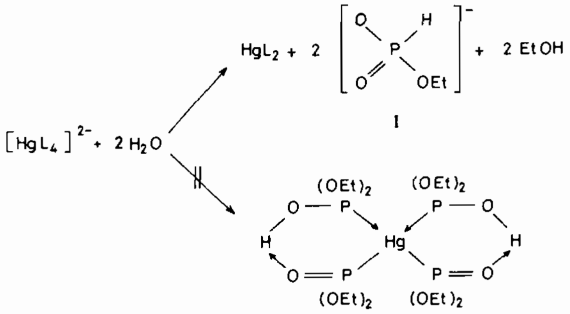
$[HgL_n]^{(n-2)-}$, with $n > 4$ could be detected.

HgL_2 co-ordinates two equivalents of L^- in an exothermic reaction leading to crystalline Na_2HgL_4. The compound is readily soluble in DMSO and pyridine but only slightly soluble in THF, acetonitrile, benzene or methylene chloride. On the other hand mixtures of HgL_2 and NaL 1/1 are readily soluble in DMSO, THF, diethylether or benzene. Evaporation of the solvent yielded only glassy samples of $NaHgL_3$. Attempts to crystallize the tris(phosphito)mercurate anion with large counterions (*e.g.* as tetraphenylphosphonium salt) were unsuccessful. 31-Phosphorus NMR spectroscopy revealed the tris-phosphito complex in solution to be in a disproportionation equilibrium with HgL_2 and $[HgL_4]^{2-}$ (eqn. 2):

$$2[HgL_3]^- \rightleftharpoons HgL_2 + [HgL_4]^{2-} \qquad (2)$$

This equilibrium seems to move to the right with increasing donor qualities of the solvent.

All the compounds are water sensitive, except for HgL_2 which is stable to water [9]. Hydrolysis of tetrakis(phosphito)mercurate leads to the sodium salt of phosphoricacid monoethylester (I) but no conjugate acid H_2HgL_4 (II) is formed. Compounds of type II are common for many transition metals [8].



II

31-Phosphorus and ^{199}Hg NMR Spectroscopy of $[HgL_n]^{(n-2)-}$

The new mercurates were characterized by ^{31}P and ^{199}Hg NMR spectroscopy: 199-Mercury NMR spectra show the appropriate multiplicity (1:3:3:1 quartet and 1:4:6:4:1 quintet) confirming the number of phosphito ligands co-ordinated to mercury to be 3 and 4. The co-ordination of phosphito ligands to HgL_2 is accompanied by high frequency shift of the mercury resonance (Table I). Surprisingly, the value of $\delta(^{199}Hg)$ for $[HgL_3]^-$ is slightly higher than for $[HgL_4]^{2-}$.

The size of the coupling constants (Table I) indicates a one bond coupling, indicating that the P/O ambidentate [8] phosphito ligands are P-bonded. The decrease in the coupling constants from the bisphosphito- to the tetrakis-phosphito-mercury complex is similar to that observed for $^3J(^{199}Hg,H)$ in $[Hg(SiMe_3)_n]^{(n-2)-}$, n = 2–4 [4], which has been correlated to the change in mercury hybridization from sp to sp^3.

The 31-phosphorus chemical shift increases upon coordination of the third phosphito ligand to 132 ppm, this representing the highest value observed for a phosphito-mercury compound. Co-ordination of the fourth ligand results in a decrease of $\delta(^{31}P)$. Similar

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*The nomenclature complies with that used in the review of Roundhill *et al.* [8].

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TABLE I. NMR Parameters of $Hg\{P(O)(OEt)_2\}_n]^{(n-2)-}$.[a]

n	$\delta(^{31}P)$	$\delta(^{199}Hg)$	$^1J(^{199}Hg, ^{31}P)$
2[b]	106	1142	7135
2[c]	105	1061	7375
3[b]	132	–	5206
3[c]	129	1956	5283
4[b]	111	1909	3863
4[c]	109	1930	3975

[a] Chemical shifts in ppm to high frequency of 85% H_3PO_4 or aqueous $Hg(ClO_4)_2$ (2 mmol HgO/cm^3 60% $HClO_4$). [b] DMSO, 295 K. [c] MeOH, 233 K.

effects were observed for phosphine coordination complexes of phosphito-mercury compounds [10].

Dynamic Behaviour of $[HgL_3]^-$ and $[HgL_4]^{2-}$

The phosphito ligands in $[HgL_3]^-$ and $[HgL_4]^-$ were found to be labile on the NMR time scale in contrast to that of HgL_2: the 31-phosphorus NMR spectrum of a mixture of HgL_2 and NaL 1/1 in pyridine displays broadened peaks and partial collapse of the ^{199}Hg couplings, indicating intermolecular exchange of phosphito groups. The bandwidth at half-height of the species $[HgL_n]^{(n-2)-}$, n = 2–4, present in this solution according to eqn. 2 decreases in the order $[HgL_3]^- \geqslant HgL_2 > [HgL_4]^{2-}$. Corresponding results are obtained for a solution in DMSO, except for linewidths being generally larger than in pyridine. The exchange path according to eqn. 3 seems to be predominant. This exchange

$$\mathit{Hg}L_2 + [HgL_3]^- \rightleftharpoons [\mathit{Hg}L_3]^- + HgL_2 \quad (3)$$

mechanism has also been found to be effective in the system $Hg(SiMe_3)_2/[Hg(SiMe_3)_3]^-$ [4]. Upon addition of $HP(O)(OEt)_2$ or $[P(O)(OEt)_2]^-$ to the tetrakisphosphito-mercury complex, the ^{31}P resonances remained unaffected, indicating that there is no exchange between coordinated phosphito ligands and $HP(O)(OEt)_2$ or free phosphito groups respectively occurring on the NMR time scale (eqn. 4).

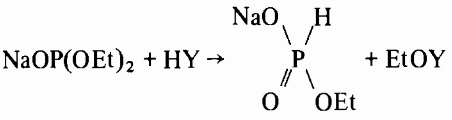
$$\begin{aligned} &[HgL_4]^{2-} + H\mathit{L} \xrightleftharpoons{DMSO} [\mathit{L}HgL_3]^{2-} + HL \\ &[HgL_4]^{2-} + \mathit{L}^- \rightleftharpoons [\mathit{L}HgL_3]^{2-} + L^- \end{aligned} \quad (4)$$

Preparation of NaL

NaL, obtained according to the literature [11] from elemental sodium and HL according to eqn. 5, was found to contain the sodium salt of phosphoric acid monoethylester (I) and ethylphos-

$$HL + Na \rightarrow NaL + \tfrac{1}{2}H_2 \quad (5)$$

phonic acid diethylester together with trans-esterification products. These contaminations could not be separated by crystallization, owing to very similar solubilities. They are thought to be formed by reaction 6,



$$NaOP(OEt)_2 + HY \rightarrow (NaO)(H)P(=O)(OEt) + EtOY \quad (6)$$

(HY = $HP(O)(OEt)_2$), which occurs during the exposure of HL to NaL in the course of any slow deprotonation of HL. NaL also reacts with EtOH according to eqn. 6 showing why the use of ethanol as catalyst for reaction 5, as recommended in the literature [12], results in increased amounts of I as by-product.

Greater purity of NaL can be obtained by the reaction of Na metal with HgL_2 according to eqn. 7:

$$HgL_2 + 2Na \rightarrow Hg + 2NaL \quad (7)$$

Depending on the solvent (*vide supra*), Na_2HgL_4 may precipitate as intermediate. This reaction is also accessible to other alkali metals.

Experimental

NMR spectra were recorded on a multinuclear WP-80 FT spectrometer, chemical analyses were obtained with a Heraeus EA-415. Preparation of Na_2HgL_4: upon mixing 0.5 mmol HgL_2 [13] and 1 mmol NaL in 3 cm^3 of acetonitrile, Na_2HgL_4 precipitates as a colorless, crystalline solid. The mixture is warmed for a short time to 80 °C, and the acetonitrile is discarded. The product is then treated with another 3 cm^3 of acetonitrile as above. Yield *ca.* 90%, m.p. 129–131 °C; C: 23.5, H: 4.6; calculated for $C_{16}H_{40}HgNa_2O_{12}P_4$, C: 24.1, H: 5.0.

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