

Phosphorus-31 and Mercury-199 NMR Measurements of Cationic Mercury Phosphite Complexes

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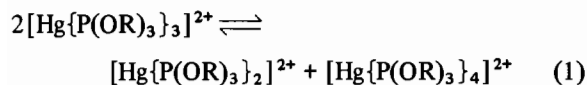
Whilst phosphine coordination compounds of mercury of the type $[\text{HgX}_2(\text{PR}_3)_n]$, $[\text{HgX}(\text{PR}_3)_n]^+$ and $[\text{Hg}(\text{PR}_3)_n]^{2+}$ have received much study in the recent years [1-10], there is only one report on mercury tertiary phosphite complexes, concerning $[\text{HgX}_2\{\text{P}(\text{OR})_3\}_n]$ with X = Cl, I; R = Et and n = 1, 2 [11]. We report here on cationic mercury phosphite complexes $[\text{Hg}\{\text{P}(\text{OR})_3\}_n]^{2+}$, n = 1-4.

Results and Discussion

Mercury(II)trifluoromethanesulfonate (which was preferred to mercury(II)perchlorate in view of the explosive nature of $\text{Hg}(\text{ClO}_4)_2$ in contact with oxidising materials) and tertiary phosphites ($\text{P}(\text{OMe})_3$ and $\text{P}(\text{OEt})_3$) in the stoichiometry 1:1 form coordination complexes $[\text{HgP}(\text{OR})_3]^{2+}$ in dichloromethane. This and the other complexes were identified according to its ³¹P and ¹⁹⁹Hg NMR spectra (*vide infra*). The existence of an 1:1 adduct is in contrast to the reaction of tertiary phosphines with $\text{Hg}(\text{ClO}_4)_2$, where no evidence for the formation of 1:1 adducts was observed [10].

Addition of a second equivalent of $\text{P}(\text{OR})_3$ leads to $[\text{Hg}\{\text{P}(\text{OR})_3\}_2]^{2+}$. Such species were already inferred from electrochemical measurements [12].

Upon addition of one further equivalent of $\text{P}(\text{OR})_3$, $[\text{Hg}\{\text{P}(\text{OR})_3\}_3]^{2+}$ is formed, which underwent partial disproportionation into the bis and tetrakis complex according to eqn. 1:



This disproportionation is not observed for the corresponding phosphine complexes $[\text{Hg}(\text{PR}_3)_3]^{2+}$ [10]; cationic silver(I) phosphite complexes $[\text{Ag}\{\text{P}(\text{OR})_3\}_3]^+$ have however been reported to disproportionate in the above way [13]. Integration of the respective signals leads to the equilibrium constants $K = ([\text{Hg}\{\text{P}(\text{OR})_3\}_2]^{2+}[\text{Hg}\{\text{P}(\text{OR})_3\}_4]^{2+})/[\text{Hg}\{\text{P}(\text{OR})_3\}_3]^{2+} = 0.01$ (R = Me) and $K = 0.1$ (R = Et).

In solutions of the stoichiometry $\text{Hg}^{2+}:\text{P}(\text{OR})_3 = 1:4$ the complex $[\text{Hg}\{\text{P}(\text{OR})_3\}_4]^{2+}$ is formed. No

complexes $[\text{Hg}\{\text{P}(\text{OR})_3\}_n]^{2+}$ with n > 4 could be detected.

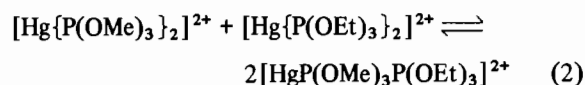
Table I presents the ³¹P and ¹⁹⁹Hg NMR parameters of the new complexes. The one bond mercury-phosphorus coupling of the complexes $[\text{Hg}\{\text{P}(\text{OR})_3\}_n]^{2+}$ represent the largest ¹J(¹⁹⁹Hg, ³¹P) and,

TABLE I. NMR Parameters of $[\text{Hg}\{\text{P}(\text{OR})_3\}_n](\text{O}_3\text{SCF}_3)_2^{\text{a}}$.

R	n	δ(³¹ P)	δ(¹⁹⁹ Hg)	¹ J(¹⁹⁹ Hg, ³¹ P)	T, K
Me	1	98.2	826	17528	253
Me	2	120.4	1041	11123	253
Me	3	132.3	1722	6756	173
Me	4	117.8	1933	4410	173
Et	1	90.8	823	17323	253
Et	2	115.0	1031	10645	253
Et	3	128.8	1720	6630	173
Et	4	111.5	1965	4308	173

^a0.25 mmol/cm⁻³ CH₂Cl₂, in ppm to high frequency of 85% H₃PO₄ or aqueous Hg(ClO₄)₂ (2 mmol HgO (cm⁻³ 60% HClO₄); coupling constants in Hz.

as far as we are aware, the largest ¹J(M,P) values reported so far. This should be associated with very short Hg-P bonding distances [14]. The Hg-P one bond coupling constants thus cover the remarkable range from 143 Hz (for $[\text{Hg}\{\text{P}(\text{O})(\text{OEt})_2\}_2(\text{PPh}_3)_2]$ [15]) to 17528 Hz for $[\text{Hg}\{\text{P}(\text{OMe})_3\}_n]^{2+}$, i.e. more than two orders of magnitude. The Hg-P coupling of $[\text{Hg}\{\text{P}(\text{OR})_3\}_n]^{2+}$ decreases with increasing n, as has been observed for $[\text{Hg}(\text{PR}_3)_n]^{2+}$ [10] and this is attributed to the s character of the HgP bond [16]. ¹H NMR spectra of $[\text{Hg}\{\text{P}(\text{OMe})_3\}_2]^{2+}$ exhibit a pseudo triplet pattern due to virtual coupling in the AA'X₉X'₉' spin system, this indicating a large two bond phosphorus-phosphorus coupling. More accurate [16] estimates of ²J(³¹P, ³¹P) were expected from the asymmetric complexes $[\text{HgP}(\text{OR})_3\text{P}(\text{OR}')_3]^{2+}$ containing two chemically non-equivalent phosphorus atoms, allowing straightforward analysis of the spectrum. The compound $[\text{Hg}\{\text{P}(\text{OMe})_3\}_2]^{2+}$ is formed by synproportionation of the respective symmetric compounds [eqn. 2):



A near statistical distribution of the species (eqn. 2) arises at equilibrium (K ≈ 4). The two bond coupling ²J(P,P) of the asymmetric complex has been determined to be 567 Hz and is smaller than for $[\text{Hg}\{\text{P}(\text{O})(\text{OMe})_2\}_2]$ (700 Hz in CDCl₃) [17].

The AB spectrum has been assigned using ¹H³¹P selective off resonance decoupling (Table II). The phosphorus chemical shift of $\text{P}(\text{OMe})_3$ is at higher

TABLE II. NMR Parameters of $[\text{HgP}(\text{OR})_3\text{P}(\text{OR}')_3](\text{O}_3\text{SCF}_3)_2^{\text{a}}$.

R	R'	$\delta(\text{P}(\text{OMe})_3)$	$\delta(\text{P}(\text{OEt})_3)$	$^1\text{J}(\text{Hg}, \text{P}(\text{OMe})_3)$	$^1\text{J}(\text{Hg}, \text{P}(\text{OEt})_3)$	$\delta(^{199}\text{Hg})$
Me	Me	120.4		11123		1041
Me	Et	121.5	113.8	10717	11029	1036
Et	Et		115.0		10645	1031

^a0.25 mmol Hg/cm⁻³ in CH₂Cl₂, 253K.

frequency for $[\text{HgP}(\text{OMe})_3\text{P}(\text{OEt})_3]^{2+}$ than for $[\text{Hg}\{\text{P}(\text{OMe})_3\}_2]^{2+}$ whilst $^1\text{J}(\text{Hg}, \text{P}(\text{OMe})_3)$ is smaller for $[\text{HgP}(\text{OMe})_3\text{P}(\text{OEt})_3]^{2+}$ than for $[\text{Hg}\{\text{P}(\text{OMe})_3\}_2]^{2+}$. The opposite is true when comparing $[\text{HgP}(\text{OMe})_3\text{P}(\text{OEt})_3]^{2+}$ with $[\text{Hg}\{\text{P}(\text{OEt})_2\}_2]^{2+}$. This proves the *trans*-influence [18] of $\text{P}(\text{OEt})_3$ to be higher than for $\text{P}(\text{OMe})_3$. The ^{31}P coordination shifts of $[\text{Hg}\{\text{P}(\text{OR})_3\}_n]^{2+}$ are negative, as usually observed for phosphite ligands coordinated to metals, and amount up to 47.2 ppm. The position of the ^{31}P resonance decreases in the order $n = 3 > 2 > 4 > 1$ (Table I), whilst $\delta(^{31}\text{P})$ shifts progressively as the number of ligands increases in $[\text{Hg}(\text{PR}_3)_n]^{2+}$ and $[\text{Ag}\{\text{P}(\text{OR})_3\}_n]^+$. The ^{199}Hg resonances of $[\text{Hg}\{\text{P}(\text{OR})_3\}_n]^{2+}$ are shifted to high frequency with increasing n , as has been observed for cationic mercury(II)phosphine complexes. Interestingly, the addition of the fourth phosphite (to give $[\text{Hg}\{\text{P}(\text{OR})_3\}_4]^{2+}$) produces a much larger change in mercury chemical shift than the addition of a fourth phosphine (to give $[\text{Hg}(\text{PR}_3)_4]^{2+}$) [10].

The metal phosphorus bond in the complexes $[\text{Hg}\{\text{P}(\text{OR})_3\}_n]^{2+}$, R = Me, Et; $n = 1, 2$ is kinetically stable on the NMR time scale at ambient temperature. The corresponding complexes with triphenylphosphite are kinetically labile above 213K ($n = 1$) or 183K ($n = 2$) as shown by the loss of the Hg–P coupling. These results reflect the σ donor capability to decrease in the order $\text{P}(\text{OR})_3 > \text{P}(\text{OPh})_3$. Solutions of the stoichiometry $\text{Hg}^{2+}:\text{P}(\text{OR})_3 = 1:3$ display only one broad ^{31}P signal at 253K which resolves upon cooling (173K for R = Me, 193K for R = Et) to the coupled spectra of the species $[\text{Hg}\{\text{P}(\text{OR})_3\}_n]^{2+}$, $n = 2-4$ (*vide supra*). The ^{31}P chemical shift at 253K nearly equals $\Sigma\delta_{\text{nPn}}$ or $[\text{Hg}\{\text{P}(\text{OR})_3\}_n]^{2+}$, $n = 2-4$ at 193K. This indicates that there is ligand exchange but no dissociation of the complexes. The complexes $[\text{Hg}\{\text{P}(\text{OR})_3\}_4]^{2+}$ are kinetically labile at temperatures above 193K (R = Et).

Experimental

The NMR spectra were recorded on a multinuclear Bruker WP-80 spectrometer in the FT mode, temperatures being adjusted using a B-VT-1000 accessory. NMR spectra were calculated with PANIC on a Bruker Aspect 2000 computer.

$[\text{Hg}(\text{DMSO})_6](\text{O}_3\text{SCF}_3)_2$ was prepared according to the literature [19]; all other reagents were

commercial and used without purification. The mercury phosphite complexes (R = Me, Et) seem to melt below ambient temperature. The complexes decompose upon standing at room temperature with formation of elemental mercury. Dialkylphosphito-P-mercury complexes could be identified as decomposition intermediates.

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