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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 $[HgX_2(PR_3)_n]$, $[HgX(PR_3)_n]^+$ and $[Hg(PR_3)_n]^{2+}$ have received much study in the recent years [1–10], there is only one report on mercury tertiary phosphite complexes, concerning $[HgX_2\{P(OR)_3\}_n]$ with X = Cl, I; R = Et and n = 1,2 [11]. We report here on cationic mercury phosphite complexes $[Hg(P(OR)_3)_n]^{2+}$, n = 1–4.

Results and Discussion

Mercury(II)trifluoromethanesulfonate (which was preferred to mercury(II)perchlorate in view of the explosive nature of $Hg(ClO_4)_2$ in contact with oxidising materials) and tertiary phosphites ($P(OMe)_3$ and $P(OEt)_3$) in the stoichiometry 1:1 form coordination complexes $[HgP(OR)_3]^{2+}$ in dichloromethane. This and the other complexes were identified according to its ^{31}P and ^{199}Hg NMR spectra (*vide infra*). The existence of an 1:1 adduct is in contrast to the reaction of tertiary phosphines with $Hg(ClO_4)_2$, where no evidence for the formation of 1:1 adducts was observed [10].

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

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

$$2[Hg\{P(OR)_3\}_3]^{2+} \rightleftharpoons [Hg\{P(OR)_3\}_2]^{2+} + [Hg\{P(OR)_3\}_4]^{2+} \quad (1)$$

This disproportionation is not observed for the corresponding phosphine complexes $[Hg(PR_3)_3]^{2+}$ [10]; cationic silver(I) phosphite complexes $[Ag\{P(OR)_3\}_3]^+$ have however been reported to disproportionate in the above way [13]. Integration of the respective signals leads to the equilibrium constants $K = ([Hg\{P(OR)_3\}_2]^{2+}[Hg\{P(OR)_3\}_4]^{2+})/[Hg\{P(OR)_3\}_3]^{2+} = 0.01$ (R = Me) and K = 0.1 (R = Et).

In solutions of the stoichiometry $Hg^{2+}:P(OR)_3 = 1:4$ the complex $[Hg\{P(OR)_3\}_4]^{2+}$ is formed. No complexes $[Hg\{P(OR)_3\}_n]^{2+}$ with $n > 4$ could be detected.

Table I presents the ^{31}P and ^{199}Hg NMR parameters of the new complexes. The one bond mercury–phosphorus coupling of the complexes $[HgP(OR)_3]^{2+}$ represent the largest $^1J(^{199}Hg, ^{31}P)$ and, 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 $[\underline{Hg}(P(O)(OEt)_2)_2(\underline{P}Ph_3)_2]$ [15]) to 17528 Hz for $[\underline{HgP}(OMe)_3]^{2+}$, *i.e.* more than two orders of magnitude. The Hg–P coupling of $[Hg\{P(OR)_3\}_n]^{2+}$ decreases with increasing n, as has been observed for $[Hg(PR_3)_n]^{2+}$ [10] and this is attributed to the s character of the HgP bond [16]. ^1H NMR spectra of $[Hg(P(OMe)_3)_2]^{2+}$ exhibit a pseudo triplet pattern due to virtual coupling in the $AA'X_9X_9'$ spin system, this indicating a large two bond phosphorus–phosphorus coupling. More accurate [16] estimates of $^2J(^{31}P,^{31}P)$ were expected from the asymmetric complexes $[HgP(OR)_3P(OR')_3]^{2+}$ containing two chemically non-equivalent phosphorus atoms, allowing straightforward analysis of the spectrum. The compound $[HgP(OMe)_3P(OEt)_3]^{2+}$ is formed by synproportionation of the respective symmetric compounds [eqn. 2):

TABLE I. NMR Parameters of $[Hg\{P(OR)_3\}_n](O_3SCF_3)_2$ [a].

R	n	$\delta(^{31}P)$	$\delta(^{199}Hg)$	$^1J(^{199}Hg,^{31}P)$	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

[a] 0.25 mmol/cm^{-3} CH_2Cl_2, in ppm to high frequency of 85% H_3PO_4 or aqueous $Hg(ClO_4)_2$ (2 mmol HgO (cm^{-3} 60% $HClO_4$); coupling constants in Hz.

$$[Hg\{P(OMe)_3\}_2]^{2+} + [Hg\{P(OEt)_3\}_2]^{2+} \rightleftharpoons 2[HgP(OMe)_3P(OEt)_3]^{2+} \quad (2)$$

A near statistical distribution of the species (eqn. 2) arises at equilibrium ($K \cong 4$). The two bond coupling $^2J(P,P)$ of the asymmetric complex has been determined to be 567 Hz and is smaller than for $[Hg\{P(O)(OMe)_2\}_2]$ (700 Hz in $CDCl_3$) [17].

The AB spectrum has been assigned using $\{^1H\}^{31}P$ selective off resonance decoupling (Table II). The phosphorus chemical shift of $P(OMe)_3$ is at higher

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TABLE II. NMR Parameters of $[HgP(OR)_3P(OR')_3](O_3SCF_3)_2$[a].

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

[a] 0.25 mmol Hg/cm^{-3} in CH_2Cl_2, 253K.

frequency for $[HgP(OMe)_3P(OEt)_3]^{2+}$ than for $[Hg\{P(OMe)_3\}_2]^{2+}$ whilst $^1J(\underline{Hg},\underline{P}(OMe)_3)$ is smaller for $[HgP(OMe)_3P(OEt)_3]^{2+}$ than for $[Hg\{P(OMe)_3\}_2]^{2+}$. The opposite is true when comparing $[HgP(OMe)_3P(OEt)_3]^{2+}$ with $[Hg\{P(OEt)_2\}_2]^{2+}$. This proves the *trans*-influence [18] of $P(OEt)_3$ to be higher than for $P(OMe)_3$. The ^{31}P coordination shifts of $[Hg\{P(OR)_3\}_n]^{2+}$ 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 $\delta(^{31}P)$ shifts progressively as the number of ligands increases in $[Hg(PR_3)_n]^{2+}$ and $[Ag\{P(OR)_3\}_n]^+$. The ^{199}Hg resonances of $[Hg\{P(OR)_3\}_n]^{2+}$ 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 $[Hg\{P(OR)_3\}_4]^{2+}$) produces a much larger change in mercury chemical shift than the addition of a fourth phosphine (to give $[Hg(PR_3)_4]^{2+}$) [10].

The metal phosphorus bond in the complexes $[Hg\{P(OR)_3\}_n]^{2+}$, 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 $P(OR)_3 > P(OPh)_3$. Solutions of the stoichiometry $Hg^{2+}:P(OR)_3 = 1:3$ 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 $[Hg\{P(OR)_3\}_n]^{2+}$, n = 2–4 (*vide supra*). The ^{31}P chemical shift at 253K nearly equals $\Sigma\delta_np_n$ or $[Hg\{P(OR)_3\}_n]^{2+}$, n = 2–4 at 193K. This indicates that there is ligand exchange but no dissociation of the complexes. The complexes $[Hg\{P(OR)_3\}_4]^{2+}$ 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.

$[Hg(DMSO)_6](O_3SCF_3)_2$ 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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