Cationic Mono-phosphine Complexes of Mercury

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Cationic mercury–phosphine complexes of the type $[Hg(PR_3)_n]^{2+}$, $n = 2,3,4$, are well known [1, 2], but no evidence of the formation of cationic 1/1 adducts $[HgPR_3]^{2+}$ was found for any of a range of tertiary phosphines studied [1]. In solutions containing 1/1 ratios of $Hg(ClO_4)_2$ and phosphine, the 1/2 complex and unchanged $Hg(ClO_4)_2$ are present (eqn. (1)) [1]. This has been recently confirmed

$$Hg^{2+} + PR_3 \begin{cases} \not\rightarrow [HgPR_3]^{2+} \\ \rightarrow 0.5\,[Hg(PR_3)_2]^{2+} + 0.5Hg^{2+} \end{cases} \quad (1)$$

for $[Hg(Me_2SO)_6](O_3SCF_3)_2$ and tricyclohexylphosphine or tri-n-butylphosphine [2]. On the other hand, cationic monophosphine complexes of mercury containing an anionic ligand [4], $[HgL(PR_3]^+$, as well as 1/1 complexes of Hg^{2+} and tertiary phosphites [3], $[HgP(OR)_3]^{2+}$, are known.

Results and Discussion

The non-existence of complexes $[HgPR_3]^{2+}$ may be due to thermodynamic reasons; *i.e.*, the synproportionation equilibrium (eqn. 2) lies on the left side. Alternatively, it may be due to kinetic reasons, when

$$Hg^{2+} + [Hg(PR_3)_2]^{2+} \rightleftharpoons 2\,[HgPR_3]^{2+} \quad (2)$$

$[Hg(PR_3)_2]^{2+}$ is formed first and the synproportionation (eqn. (2)) does not occur despite a favourable position of the synproportionation equilibrium. The first (thermodynamic) reason seems very unlikely since synproportionation reactions usually proceed in favour of the asymmetric species HgXY whenever the donating atoms or groups X and Y (eqn. (3)) differ appreciably in electronegativity [5]. Except-

$$HgX_2 + HgY_2 \rightleftharpoons 2HgXY \quad (3)$$

tions are scarce, e.g., the spontaneous symmetrization of 2,3,5,6 tetrafluoro-4 methoxyphenylmercury trifluoromethanesulfonate [6]. The kinetic reason could be rationalized as follows. The rate of formation of the mono-phosphine complex (eqn. (4)) is slow compared with the rate of coordination of a second phosphine (eqn. (5)). This behaviour can be

$$Hg^{2+} + PR_3 \xrightarrow{\text{slow}} [HgPR_3]^{2+} \quad (4)$$

$$[HgPR_3]^{2+} + PR_3 \xrightarrow{\text{fast}} [Hg(PR_3)_2]^{2+} \quad (5)$$

explained in terms of the *trans* effect [7] of the phosphine in $[HgPR_3]^{2+}$. A corresponding kinetic behaviour is observed in the course of the formation of $LHgP(O)(OEt)_2$ (L = OAc or triazenato-N^1,N^3) from HgL_2 and diethylphosphite (eqn. (6)). The *trans* effect of the diethylphosphito ligand in LHg-

$$HgL_2 + HP(O)(OEt)_2 \longrightarrow LHgP(O)(OEt)_2 + HL \quad (6)$$

$P(O)(OEt)_2$ causes an 'overshoot' (eqn. (7)) with formation of $Hg[P(O)(OEt)_2]_2$ which reacts with unchanged HgL_2 in a slower synproportionation reaction (eqn. (8)) to the desired product.

$$LHgP(O)(OEt)_2 + HP(O)(OEt)_2 \longrightarrow Hg[P(O)(OEt)_2]_2 + HL \quad (7)$$

$$Hg[P(O)(OEt)_2]_2 + HgL_2 \longrightarrow 2LHgP(O)(OEt)_2 \quad (8)$$

Mercury trifluoromethanesulfonate $[Hg(Me_2SO)_6](O_3SCF_3)_2$ (which was preferred to mercury perchlorate in view of violent redox reactions reported for the latter in contact with oxidisable organic material [8]) was found to react with tri-n-butylphosphine or tricyclohexylphosphine in 1/1 stoichiometry according to eqn. (1) as has been reported [2]. In contrast, a 1/1 complex is formed with triphenylphosphine. When using pyridine as solvent, 1/1 adducts $[HgPR_3]^{2+}$ were also obtained for tri-n-butylphosphine and tricyclohexylphosphine. Mono-phosphine complexes thus seem to be formed in the presence of the neutral ligands Me_2SO (for PPh_3) or pyridine (for the more basic phosphines PBu_3 and PCy_3). The effect of the neutral ligands may be again of thermodynamic or of kinetic nature: either the synproportionation equilibrium (eqn. (2)) is shifted to the right side, corresponding to a stabilization of the asymmetric species by the ligand (the 1/1 complexes $[HgPR_3]^{2+}$ are thought to exist as solvates $[Hg(PR_3)L_n]^{2+}$ (L = Me_2SO or pyridine)), or the synproportionation reaction is catalyzed by the ligands. We favour the kinetic version since the synproportionation reaction also proceeds in the presence of one half pyridine per mercury (although much slower).

An alternative route to cationic mono-phosphine mercury complexes was found in the transfer of phosphine from silver(I) to mercury(II). The transmetallation reaction of $[AgPR_3]^+$ with $[Hg(Me_2SO)_6](O_3SCF_3)_2$ in methanol or methylenechloride results instantly and quantitatively in the formation

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TABLE I. NMR Parameters of $[HgPR_3]^{2+}$ [a]

R	Solvent	$\delta(^{31}P)$	$\delta(^{199}Hg)$	$^1J(^{199}Hg, ^{31}P)$	T (K)
Ph	methanol	35.1		10069	303
	pyridine	33.1	1167	9032	233[b]
n-Bu	methanol	38.7		8838	303
	pyridine	35.2	1199	8123	303
Cy	methanol	72.5		8171	303
	pyridine	68.2	1260	7402	303

[a]0.1 mmol/cm^3 solvent; chemical shifts in ppm to high frequency of 85% H_3PO_4 or aqueous $Hg(ClO_4)_2$ (2 mmol HgO/cm^3 60% $HClO_4$), coupling constants in Hz. [b]Kinetically labile on the NMR time scale at temperatures above 233 K.

of the mono-phosphine complex of mercury (eqn. (9)):

$$[AgPR_3]^+ + Hg^{2+} \longrightarrow [HgPR_3]^{2+} + Ag^+ \quad (9)$$

The new complexes $[HgPR_3]^{2+}$ were characterized by ^{31}P and ^{199}Hg NMR spectroscopy (Table I). The ^{199}Hg NMR spectra consist of doublets, proving the 1/1 stoichiometry of the complexes. The ^{31}P NMR resonances appear at lower frequencies than those of the corresponding bis-phosphine complexes [1]. The mercury–phosphorus couplings are considerably larger than for the complexes $[Hg(PR_3)_2]^{2+}$ [1]. Both facts are in keeping with the concept of *trans* influence [9].

Experimental

The NMR spectra were recorded on a multinuclear Bruker WP-80 spectrometer operating in the FT mode. $[Hg(Me_2SO)_6](O_3SCF_3)_2$ was prepared as previously described [10]. The complexes $[AgPR_3]O_3SCF_3$ were obtained in situ upon addition of stoichiometric quantities of PR_3 to AgO_3SCF_3. All other reagents were commercially available.

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