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(O-n-Butyl-P-phenyl-phosphonito-P)–Mercury Complexes

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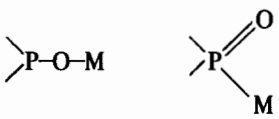
Phosphonito–mercury compounds $C_6H_5(n\text{-}C_4H_9O)P(O)HgX$, (X = $C_6H_5(n\text{-}C_4H_9O)P(O)$, Cl, Br, I, CN, C_6H_5, OAc, O_3SCF_3, SCN, SC_6H_5, SC_2H_5 and 2,5-pyrrolidindionato-N) were prepared from the corresponding phosphinic acid ester with HgO or with HgO and HgX_2. The new compounds are characterized by a Hg–P bond and decompose easily with fission of this bond. $\delta(^{31}P)$, $\delta(^{199}Hg)$ and $^1J(^{31}P\text{–}^{199}Hg)$ data are reported.

Introduction

Metal complexes involving phosphorus compounds for which the following tautomeric equilibrium can be written, exhibit a

diversity of bonding modes [1]: Firstly, the neutral ligand may coordinate to the metal, secondly the deprotonated ligand is ambivalent, *i.e.* the metal may be bonded through the phosphorus or through the oxygen atom



All bonding types have been described [2] for mainly transition metal complexes derived from phosphonic acid diesters** $(RO)_2P(O)H$ and phosphine oxides** $R_2P(O)H$.

This paper deals with mercury complexes with a deprotonated phosphinic acid ester $R(R'O)P(O)H$.

The compounds will be named phosphonito complexes in analogy to the nomenclature used in the review article of Round-hill *et al.* [2] being derived from the ligand in its three-coordinate form regardless of the specific bonding mode.

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**Name of the predominant tautomer.

Results and Discussion

Bis(O-n-butyl-P-phenylphosphonito-P)–mercury (*2*) was obtained according to reactions (1a) and (1b).

$$2C_6H_5(n\text{-}C_4H_9O)P(O)H + HgO \rightarrow \underset{1}{} \underset{2}{[C_6H_5(n\text{-}C_4H_9O)P(O)]_2Hg} + H_2O \quad (1a)$$

$$2C_6H_5(n\text{-}C_4H_9O)P(O)H + Hg(OAc)_2 \rightarrow [C_6H_5(n\text{-}C_4H_9O)P(O)]_2Hg + 2HOAc \quad (1b)$$

Whilst being stable below 263 K, the compound was found to decompose at room temperature even in the dark according to eqn. (2).

$$[C_6H_5(n\text{-}C_4H_9O)P(O)]_2Hg \rightarrow [C_6H_5(n\text{-}C_4H_9O)P(O)]_2 + Hg \quad (2)$$

The hypophosphonic acid derivative $[C_6H_5(n\text{-}C_4H_9O)P(O)]_2$ has been identified by mass spectroscopy: m/e 394 M^+, 339 $(M - C_4H_7)^+$, 283 $(339 - C_4H_8)^+$, 265 $(283 - H_2O)^+$ and others.

An analogous cleavage of mercury–phosphorus bonds has been reported for some phosphinito [3] ($R_2P(O)$–) and phosphido [4] (R_2P–) mercury complexes and has been used synthetically for the formation of P–P bonds [5, 6]. Homolytic fission of the Hg–P bond seems most likely as a first step, although no ESR signals could be detected when carrying out the reaction in an ESR spectrometer. This may be due either to the free radical concentration being too low to be detected or to a radical cage mechanism [7]. Compound *2* turned out, however, to be stable enough for NMR spectroscopic characterization.

Mixed mercury complexes of the type $C_6H_5(n\text{-}C_4H_9O)P(O)HgX$ were obtained according to reaction (3).

$$2C_6H_5(n\text{-}C_4H_9O)P(O)H + HgO + HgX_2 \rightarrow 2C_6H_5(n\text{-}C_4H_9O)P(O)HgX + H_2O \quad (3)$$

X = Cl, Br, I, CN, C_6H_5, OAc, O_3SCF_3, SCN, SC_6H_5, SC_2H_5 and 2,5-pyrrolidindionato-N.

These compounds are unstable too and could not, like *2*, be isolated analytically pure. Decomposition can be thought to proceed either *via* the asymmetric species itself or *via* *2* formed according to the equilibrium (4) (lying far on the side of the asymmetric product).

$$2C_6H_5(n\text{-}C_4H_9O)P(O)HgX \rightleftharpoons [C_6H_5(n\text{-}C_4H_9O)P(O)]_2Hg + HgX_2 \quad (4)$$

The first possibility seems to be more reasonable because some $C_6H_5(n\text{-}C_4H_9O)P(O)HgX$ decompose faster than $[C_6H_5(n\text{-}C_4H_9O)P(O)]_2Hg$. In the course of decomposition of $C_6H_5(n\text{-}C_4H_9O)P(O)HgCl$ in benzene, a white solid precipitated which was identified as mercurous chloride, resulting presumably from recombination of two HgCl radicals. Formation of $(HgCl)_2$ by a symmetrization reaction according to eqn. (5) could be excluded.

$$2C_6H_5(n\text{-}C_4H_9O)P(O)HgCl + Hg \rightarrow [C_6H_5(n\text{-}C_4H_9O)P(O)]_2Hg + (HgCl)_2 \quad (5)$$

When conducted in pyridine, subsequent dismutation of $(HgCl)_2$ took place as expected eqn. (6).

$$(HgCl)_2 \xrightarrow{\text{pyridine}} HgCl_2 \cdot py_2 + Hg \quad (6)$$

Whenever the corresponding mercurous compound was not stable, direct formation of elemental mercury was observed.

The NMR spectroscopic investigation of the asymmetric mercury compounds was possible, however, with the exception of X = O_3SCF_3 and SCN, where no ^{199}Hg NMR data could be obtained because of the instability of the compounds.

The ^{31}P and ^{199}Hg NMR parameters are presented in Table I. The very high ^{31}P–^{199}Hg coupling constants observed for the phosphonito mercury complexes indicate one bond coupling and thus direct bonding of phosphorus to mercury. This is further supported by ^{199}Hg NMR resonances occurring at rather high frequencies whereas mercury–oxygen bonded species would be expected to absorb around 0ppm.

The bonding mode of the phosphonito ligand corresponds to structures observed for phosphito (X-ray structure determinations have been carried out of $[(MeO)_2P(O)]_2Hg$ [8] and $(EtO)_2P(O)HgCl$ [9]) and for phosphinito mercury compounds [3].

The variation of $^1J(^{31}P\text{–}M)$ (M = ^{195}Pt and ^{199}Hg) and related coupling constants [10] according to the ligand opposite was frequently explained in terms of the *trans*-influence [11] of that group. The Hg–P bond, exhibiting presumably essentially σ-bond character, is weakened in the order $O_3SCF_3 < OAc < Cl < Br <$ 2,5-pyrrolidindionato-N $< SCN < I < CN < SC_6H_5 < SC_2H_5 < C_6H_5(n\text{-}C_4H_9O)P(O) < C_6H_5$. This sequence corresponds essentially to that found for the respective diethylphosphito–mercury compounds collected in Table II, for phosphinito–mercury compounds [3] and for the cationic mercury complexes $[(Me_3P)HgX]^+$ [10]. Classification according to the element E bonded to mercury (neglecting some special substituents at E) yields a *trans*-influence order C > P > S > O(N)* closely resembling that found for platinum complexes [11]. The size of $^1J(^{31}P\text{–}^{199}Hg)$ of the phosphonito–mercury complexes was higher compared with the respective

*In the case of the oxoanions O_3SCF_3 and OAc coordination of the solvent pyridine to mercury is assumed.

TABLE I. NMR Parameters of Phosphonito–mercury Compounds $C_6H_5(n\text{-}C_4H_9O)P(O)HgX$[a].

X	$\delta(^{199}Hg)$[b]	$\delta(^{31}P)$[b]	$^1J(^{31}P\text{–}^{199}Hg)$[c]
Cl	1231	85.6	10525
Br	1132	86.1	10288
I	921	89.9	9684
CN	1254	88.1	9136
C_6H_5	1356	116.7	4608
$C_4H_4NO_2$[d]		81.6	10277
$C_6H_5(n\text{-}C_4H_9O)P(O)$	1217	111.3	5506
OAc	964	77.5	10902
O_3SCF_3		75.4	11080
SCN		89.5	9975
SC_6H_5	1309	94.2	7904
SC_2H_5	1391	98.7	7271

[a] *Ca.* 0.75 *M* solutions in pyridine, 300 K.
[b] In ppm to high frequency of aqueous $Hg(ClO_4)_2$ (2 mmol HgO/ml 60% $HClO_4$) or 85% H_3PO_4.
[c] In Hz.
[d] 2,5-Pyrrolidindionato-N.

TABLE II. NMR Parameters of Phosphito Mercury Compounds $(EtO)_2P(O)HgX$[a].

X	$\delta(^{199}Hg)$[b]	$\delta(^{31}P)$[b]	$^1J(^{31}P–^{199}Hg)$[c]
Cl	1283	69.2[e]	13630[e]
Br	1184	72.8[e]	13313[e]
I	983	79.2[e]	12563[e]
CN	1298	78.5	11635
C_6H_5	1371	112.6	5993
$C_4H_4NO_2$[d]	–	71.6	12820
$(EtO)_2P(O)$	1294	103.4[e]	7601[e]
OAc	1012	63.8[e]	14034[e]
O_3SCF_3	1004	61.4	14580
SCN	1383	71.7	13127
SC_6H_5	1353	85.4	10165
SC_2H_5	1420	91.7	9266

[a] 0.5 *M* solutions in pyridine, 300 K.
[b] In ppm to high frequency of aqueous $Hg(ClO_4)_2$ (2 mmol HgO/ml 60% $HClO_4$) or 85% H_3PO_4.
[c] In Hz.
[d] 2,5-Pyrrolidindionato-N.
[e] Similar values have been reported in ref. 9.

phosphinito compounds but lower than in the phosphito–mercury compounds. Electronegative substitution at the phosphorus atom caused thus the $^{31}P–^{199}Hg$ coupling constant to increase. This effect has also been observed for $^1J(^{31}P–^{195}Pt)$ in related platinum complexes.

Substitution at phosphorus also seems to affect the relative *trans*-influence of the phosphorus-ligand. Decreasing *trans*-influence with increasing electronegative substitution at the phosphorus atom is indicated by Table III.

TABLE III. Selected $^1J(^{31}P–^{199}Hg)$ of $R_1R_1P(O)HgX$ in Hz.

R_1	R_2	$X = R_1R_2P(O)$	C_6H_5
EtO	EtO	7601[a]	5993[a]
C_6H_5	n-C_4H_9O	5506[a]	4608[a]
t-C_4H_9	t-C_4H_9	2829[b]	3094[b]

[a] This work.
[b] Ref. 3.

The ^{31}P NMR absorptions were found to be shifted to high frequencies when going from C_6H_5(n-C_4H_9O)P(O)H to C_6H_5(n-C_4H_9O)P(O)HgX analogously to the corresponding phosphito (Table II) and phosphinito compounds [3]. As can be seen from Fig. 1, there is a qualitative linear connection between $\delta(^{31}P)$ and $^1J(^{31}P–^{199}Hg)$. A similar relation can be drawn for the phosphito mercury complexes.

The ^{199}Hg resonances of the asymmetric phosphonito (Table I) and phosphito compounds (Table II) were found between the values of the respective symmetric compounds with the exception of C_6H_5(n-C_4H_9O)P(O)HgCl. There seems to be a qualitative connection between the resonance position of the

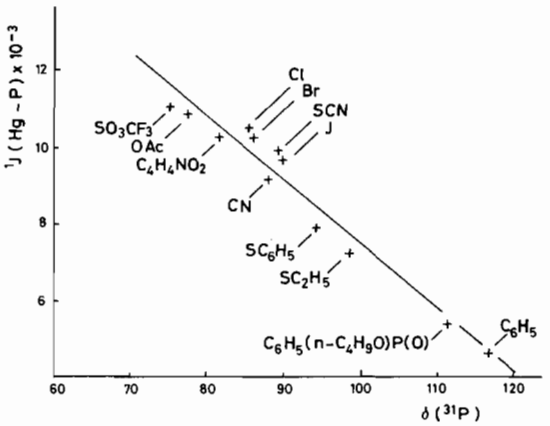

Fig. 1. Plot of $\delta(^{31}P)$ versus $^1J(^{31}P–^{199}Hg)$ of various complexes C_6H_5(n-C_4H_9O)P(O)HgX [$C_4H_4NO_2$ = 2,5-pyrrolidindionato-N].

asymmetric compound relative to those of the respective symmetric compounds and the relative *trans*-influence of the ligands involved. No ^{199}Hg resonance could be detected for (O-n-butyl-P-phenyl-phosphonito-P)-2,5-pyrrolidindionato-N–mercury and the respective diethylphosphito compound presumably due to scalar relaxation of the second kind of ^{199}Hg by ^{14}N [13].

Mixtures of C_6H_5(n-C_4H_9O)P(O)HgX and C_6H_5(n-C_4H_9O)P(O)HgY display ^{199}Hg NMR doublets due to $^{31}P–^{199}Hg$ coupling intermediate in size compared with $^1J(^{31}P–^{199}Hg)$ of the pure compounds. This indicates rapid ligand exchange according to eqn. (7) for X, Y = Cl, Br, I; X ≠ Y.

$$C_6H_5(n\text{-}C_4H_9O)P(O)\underline{Hg}X + C_6H_4(n\text{-}C_4H_9O)P(O)HgY \rightleftharpoons C_6H_5(n\text{-}C_4H_9O)P(O)\underline{Hg}Y + C_6H_4(n\text{-}C_4H_9O)P(O)HgX \quad (7)$$

Experimental

^{31}P and ^{199}Hg NMR spectra were recorded in the FT-mode on a multinuclear Bruker WP-80 spectrometer.

Phenylphosphinic acid butylester (*1*) was made from phenylphosphonous dichloride and n-butanol [14]. $\delta(^{31}P)$, pyridine = 23.2 ppm, $^1J(^1H-^{31}P) = 560$ Hz. MS: m/e 143$(M - C_4H_8)^+$, 100%, 125$(M - OBu)^+$, 25% and others.

Bis(O-n-butyl- P-phenyl-phosphonito-P)–mercury (*2*) was prepared by treating *1* with an equivalent amount of yellow mercuric oxide in benzene at 50 °C.

The mixed compounds $C_6H_5(n\text{-}C_4H_9O)P(O)HgX$ (X = Cl, Br, I, CN, C_6H_5, O_3SCF_3, OAc, SCN, SC_6H_5, SC_2H_5 and 2,5-pyrrolidindionato-N) were obtained by reacting equivalent quantities of *1*, mercuric oxide and HgX_2 in pyridine.

The HgX_2 used were either commercial (X = Cl, Br, I, CN, SCN, OAc, C_6H_5) or prepared as described in the literature [15, 16].

The phosphito mercury complexes $(EtO)_2P(O)$-HgX (X as specified above) were synthesized according to the literature [18] (X = Cl, Br, I, OAc, SCN) or analogously to the phosphonito complexes above (X = CN, C_6H_5, O_3SCF_3, SC_6H_5, SC_2H_5 and 2,5-pyrrolidindionato-N). Attempts to prepare $(EtO)_2P(O)HgC_6H_5$ according to the method of Mukaiyama *et al.* [20] were unsuccessfull.

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