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Preparation and Properties of Phosphito-P(triazenato-N^1, N^3) mercury Compounds and their PPh_3 Coordination Complexes

JOHANN EICHBICHLER and PAUL PERINGER*

Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

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Various redistribution systems 1 and 2

1 $HgT_2 + HgY_2 \rightleftharpoons 2THgY$

2 $HgL_2 + HgY_2 \rightleftharpoons 2LHgY$

(T = Ar–N–N=N–Ar = 1,3 diaryl-1-triazenato; L = phosphito, phosphonito and phosphinito – all bonded through P, Y = Cl, Br, I, CN, SCN, Ph, EtS, PhS, PhSe and $Mn(CO)_5$) have been investigated in the past few years [1–10]. Interest developed in (i) synthetic aspects (depending on the position of the redistribution equilibrium in the solid state), (ii) the position of the redistribution equilibrium in solution, (iii) ligand exchange processes, (iv) the ambidentate P/O system for compounds involving L, (v) the bonding mode of the triazenato (= triaza-allyl) ligands in solution and in the solid state and (vi) monitoring the *trans* influence.

This work deals with synthesis and properties of $(EtO)_2P(O)HgT$, compounds, involving a phosphorus–mercury–nitrogen bond sequence, and their PPh_3 coordination complexes.

Results and Discussion

The new compounds $(EtO)_2P(O)HgN_3(2XC_6H_4)_2$ (X = H, Me, F, Cl, Br, I, NO_2) were made by synproportionation of the respective symmetric compounds in solution (eqn. 1)

$$HgL_2 + HgT_2 \rightleftharpoons 2LHgT \qquad L = (EtO)_2P(O) \qquad (1)$$

The redistribution equilibrium was found (by NMR) to position completely on the (right) side of the asymmetric mercury compounds. In view of the S/N ratio obtained $K = [THgL]^2/([HgL_2]\ [HgT_2])$ is greater than 10^4. This corresponds thus to L = Ph [4, 6, 7] and $Mn(CO)_5$ [5] (eqn. 1) whereas for L = Cl, Br, I, CN, SCN, SPh and SePh [7, 8] the corresponding symmetric compounds are also present in the equilibrium. As monitored by ^{31}P NMR the reaction takes about thirty minutes in pyridine at ambient temperature and proceeds considerably slower in (more apolar) CH_2Cl_2. An alternative route is the reaction of equimolar amounts of HgT_2 and LH according to eqn. 2. Analogous to other Hg–N or Hg–O bonded species [11] this reaction proceeds

$$HgT_2 + LH \rightleftharpoons LHgT + TH \qquad L = (EtO)_2P(O) \qquad (2)$$

completely to the right side. The reaction takes about a day in pyridine at room temperature.

Some of the compounds were isolated in the solid state as orange yellow, well crystalline, air and moisture stable substances, readily soluble in organic solvents. Analytical data are given in Table I.

The ^{31}P and ^{199}Hg NMR parameters are presented in Table I. The size of $J(^{31}P–^{199}Hg)$ indicates one bond coupling and thus direct bonding of phosphorus to mercury, as has been observed for other phosphito–mercury compounds [1, 3, 10].

TABLE I. NMR[a] and Analytical Data of $(2XC_6H_4)_2N_3Hg(O)P(OEt)_2$.

X	$^1J(^{31}P–^{199}Hg)$[b]	$\delta(^{199}Hg)$[c]	$\delta(^{31}P)$[c]	mp[d]	C[e]	H[e]	N[e]	C[f]	H[f]	N[f]
H	11856	1086	70.4	142	35.5	3.7	7.7	36.0	3.8	7.9
CH_3	11898	1097	69.1	103–108	37.9	4.3	7.4	38.5	4.3	7.5
F	12012	1052	66.0	150–156	33.5	3.0	7.5	33.7	3.2	7.4
Cl	12617	1093	66.3	133–139	32.2	2.9	7.1	31.9	3.0	7.0
Br	12844	1098	66.8	159–160	27.6	2.6	6.3	27.8	2.6	6.1
I	12920	1103	69.6	170–172	24.4	2.1	5.4	24.5	2.3	5.3
NO_2	13127	1055	64.2	136–140	31.0	2.7	11.3	30.8	2.9	11.2

[a] 0.5 m in pyridine, 300 K. [b] In Hz. [c] In ppm to high frequency of aqueous $Hg(ClO_4)_2$ (2 mmol HgO/ml 60% $HClO_4$) or 85% H_3PO_4. [d] °C, uncorrected. [e] Found. [f] Calculated.

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*Author to whom correspondence should be addressed.

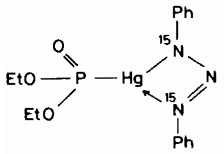
TABLE II. NMR[a] Data of $(2XC_6H_4)_2N_3Hg(O)P(OEt)_2 \cdot (PPh_3)$.

X	$\delta(^{31}P)^b$ L	$\delta(^{31}P)^b$ PPh_3	$\delta(^{199}Hg)^b$	$^1J(^{31}P-^{199}Hg)^c$ L	$^1J(^{31}P-^{199}Hg)^c$ PPh_3	$^2J(^{31}P-^{31}P)^c$ L-PPh_3
CH_3	88.8	39.1		10641	1569	280
F	89.8	43.3	1762	10768	1839	284
Cl	87.5	43.2	1701	11031	2039	286
I	89.1	40.1		11324	2072	289
NO_2	86.7	43.4		10970	2509	295

L = $P(O)(OEt)_2$. [a]0.25 *M* in methylenechloride, 173 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.

$^1J(^{31}P-^{199}Hg)$ of LHgY have been correlated with the *trans* influence of the group Y [1, 3]. The size of $^1J(^{31}P-^{199}Hg)$ for Y = T was found in the region of Y = Br [1] although it should be noted that the *trans* influence is defined for linear P–Hg–Y configurations whereas the bonding mode of the triazenato group is bidentate (*vide infra*).

^{31}P and ^{199}Hg NMR have also been used to estimate the kinetic behaviour of the mercury ligand bonds involved. The addition of HgL_2 or HgT_2 to a solution of THgL gives rise to the ^{31}P or ^{199}Hg features of both the symmetric and the asymmetric species. This and the observation of $^1J(^{31}P-^{199}Hg)$ demonstrates the kinetic stability of the metal–ligand bonds involved on these NMR time scales. On the other hand a solution of I in pyridine displays two broad ^{199}Hg resonances at ambient temperature. At 253 K the ^{199}Hg spectrum consists of sharp doublets of triplets due to mercury coupling with one $^{31}P(^1J(^{31}P-^{199}Hg)$ = 12011 Hz) and two equivalent ^{15}N nuclei [$^1J(^{15}N-^{199}Hg)$ = 178 Hz]. This indicates the occurrence of intermolecular triazenato ligand exchange processes on this NMR time scale.



The equivalence of the terminal triazenato nitrogen atoms was found to persist down to 233 K. This is compatible either with π triazaallyl bonding or rapid intramolecular Hg exchange between the terminal nitrogen atoms [9]. An X-ray crystal structure [5] of another mixed triazenato mercury compound, $(2ClC_6H_4)_2N_3HgMn(CO)_5$ revealed slightly different Hg–N bond distances in the crystalline state.

Mixed LHgT can also synthesized for L = $(t\text{-}Bu)_2$-P(O) or PH(BuO)P(O) the latter decompose like other phosphonito–Hg compounds of this type, with formation of elemental mercury [3].

The compounds $(EtO)_2P(O)HgT$ coordinate one equivalent of triphenylphosphine as could be shown to be ^{31}P and ^{199}Hg NMR (Table II).

Whereas at room temperature the complexes are dissociated in part and fast exchange between 'free' and coordinated PPh_3 is observed at low temperatures the PPh_3 complex is formed quantitatively and the Hg–PPh_3 bond becomes kinetically stable (with exception of X = H). The kinetic lability of the PPh_3 complexes varies with the substituent in *ortho* position of the aryl groups of the triazenato ligand and was found to decrease in the order H > Me > F > I ≈ Cl > NO_2. The bonding mode of the triazenato group in these complexes could not be determined: at 173 K in CH_2Cl_2 the triazenato group of the triphenyl-phosphine complex of 1 is still involved in intermolecular exchange dynamics.

Attempts to coordinate a second equivalent of PPh_3 failed. The ^{31}P NMR spectrum of a mixture $(EtO)_2P(O)HgT:PPh_3$ = 1:2 displayed at 173 K the pattern of the mono PPh_3 adduct besides noncoordinated PPh_3.

The interpretation of the coordination effects in ^{31}P and ^{199}Hg NMR corresponds largely to that of phosphine coordination complexes of other phosphito mercury compounds [12].

The complex $(2NO_2C_6H_4)N_3Hg(O)P(OEt)_2 \cdot PPh_3$ has been isolated in the solid state.

Experimental

The NMR spectra were recorded in the FT-mode on a Bruker WP-80 multinuclear spectrometer equipped with a Bruker B-VT-1000 variable temperature unit. Chemical analysis were obtained with a Heraeus EA 415, mass spectra with a Varian Mat CH 7 (70 eV). The symmetric HgT_2 and HgL_2 compounds were prepared as described previously [7, 13].

The following procedure is typical for the preparatin of mixed THgL compounds:

731 mg (1 mmol) $Hg[(2ClC_6H_4)_2N_3]_2$ and 475 mg (1 mmol) of $Hg[(EtO)_2P(O)]_2$ are allowed to react in 3 ml of pyridine at room temperature for one hour. After evaporation of the solvent recrystallisation from toluene–petrolether yields bis(2-chlorophenyl)-1-triazenato-N^1,N^3(diethylphosphito-P)mercury in almost quantitative yield (m/e: 601 (M^+ for ^{35}Cl and ^{200}Hg)).

Bis(2-nitrophenyl)-1-triazenato-N(diethylphosphito-P) (triphenylphosphine-P)mercury was obtained by slow evaporation of a equimolar solution of $(EtO)_2P(O)HgN_3(2NO_2C_6H_4)_2$ and PPh_3 in toluene as red crystals.

M.p.: 98–105 °C, C: 46.2(46.1), H: 3.6(3.8), N: 8.1(7.9).

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