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Journal of Organometallic Chemistry 555 (1998) 255–262

Journal of Organo metallic Chemistry

Interaction of methylmercury(II) with the bifunctional ligand *o*-diphenylphosphinobenzoate, dpb. Synthesis and characterization of [(dpb)HgMe] and [(dpbo)HgMe], dpbo = *o*-diphenylphosphinoxidebenzoate

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Received 10 October 1997

Abstract

The complex [(dpb)HgMe] (**1**) is obtained by reaction of MeHg(OH) with *o*-diphenylphosphinobenzoic acid (Hdpb); alternatively the solvate [(dpb)HgMe] · $0.5H_2O$ · $0.5C_5H_5N$ (**1bis**) can be prepared by reacting MeHgCl with Hdpb and pyridine. The derivative [(dpbo)HgMe] (**2**), where dpbo is *o*-diphenylphosphinoxidebenzoate, is formed by reaction of **1** or **1bis** solutions with atmospheric oxygen. Crystal data for **1bis**: monoclinic, space group $P2/n$, $a = 10.413(4)$, $b = 9.831(3)$, $c = 20.674(3)$ Å, $\beta = 102.51(3)°$, $Z = 2$. Crystal data for **2**: triclinic, space group $P\bar{1}$, $a = 11.535(2)$, $b = 12.897(5)$, $c = 13.275(7)$ Å, $\alpha = 88.31(4)$, $\beta = 73.65(4)$, $\gamma = 85.27(4)°$, $Z = 2$. In **1bis** the mercury atom displays a distorted linear fashion, being coordinated to a methyl group and to the phosphorus atom of the dpb ligand. Two additional weaker linkages cause the packing in pairs of the molecules. In **2** the mercury is linearly linked to a methyl group and to an oxygen atom of the carboxylic group of the dpbo ligand. Also in this case the coordination around the mercury center is completed by two weaker additional bond interactions, which, involving the oxygen atoms of the adiacent moiety, determine the dimerization of the molecule. The multinuclear magnetic resonance spectra of **1** (or **1bis**) which have been compared with those of the related complex $[(PPh_3)HgMe](CF_3SO_3)$ (**3**) and of the solution containing **1** and CF_3SO_3H (molar ratio 1:1.5), do not seem to unambigously support a dimeric configuration of the complex in solution. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Methylmercury; Phosphine complexes; Crystal structure; NMR spectroscopy

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1. Introduction

Most researches on the coordination chemistry of methylmercury(II) have been aimed at the understanding of its toxic effects on living organisms and at the design of specific sequestering agents. Renewed interest stems from the mechanism of the biological processes of detoxification of this very dangerous organometallic species [1].

During our recent investigations about the interactions of organomercury(II) ions with polydentate phosphines, we have found that the coordination of more than one phosphorus atom to the metal center strongly facilitates the cleavage of the Hg–C linkage (protonolysis or symmetrization processes) [2,3].

Now here we report the synthesis and the structural characterization of the complex [(dpb)HgMe] and of the closely related [(dpbo)HgMe] one, where dpb and dpbo are *o*-diphenylphosphinobenzoate and *o*-diphenylphosphinoxidebenzoate, respectively (Scheme 1). The simultaneous presence in the dpb ligand of both

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PII S0022-328X(97)00713-4

a soft and an hard donor atom may be of interest, because similar situation occurs in simple models for the methylmercury-protein interaction such as methyl-L-cysteinatomercury(II) [4]. In the dbp case, the presence of P as soft donor atom in place of S, gives the possibility of monitoring the complex behaviour in solution through NMR.

Although the synthesis of $[(PR_3)HgMe]X$ complexes had been reported in 1964 by Coates et al. [5], these compounds have been scarcely investigated, maybe because of their propensity to undergo symmetrization reactions [5,6]. As a matter of fact only $[(PMe_3)HgMe]Cl$ [7] and $[(PPh_3)HgMe]NO_3$ [8] have been properly characterized through ^{1}H- and ^{13}P-NMR or X-ray analysis, respectively.

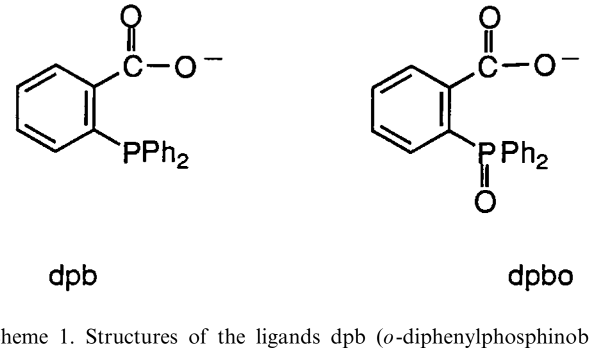
2. Experimental

All the reactions were performed under an atmosphere of dry nitrogen. Solvents were purified and dried by standard methods. *O*-diphenylphosphino benzoic acid [9] and methylmercury triflate [2] were prepared by the previously reported methods. The other starting materials were reagent grade and were used without further purification.

2.1. Syntheses

2.1.1. [(dbp)HgMe] (1)

Methylmercury hydroxide (233 mg, 1 mmol) in water (3 cm^3) was added to a solution of Hdpb (306.3 mg, 1 mmol) in ethanol (10 cm^3). The resulting solution was stirred at room temperature for 10 min, then all the solvents were removed under vacuum. The solid was dissolved in dichloromethane (10 cm^3), and the resulting solution was filtered. Addition of ethyl ether (60 cm^3) caused the precipitation of colourless crystals. These were filtered, washed with ethyl ether and dried under a stream of nitrogen. Yield: 443 mg (85%). (Found C, 46.35; H, 3.40; Hg, 38.45; Calc. for $C_{20}H_{17}HgO_2P$: C, 46.11; H, 3.29; Hg, 38.51).



dpb dpbo

Scheme 1. Structures of the ligands dpb (*o*-diphenylphosphinobenzoate) and dpbo (*o*-diphenylphosphinoxidebenzoate).

2.1.2. [(dbp)HgMe] · 0.5H$_2$O · 0.5Py (**1bis**)

Pyridine (0.242 cm^3, 3 mmol) was added to a solution of methylmercury chloride (251 mg, 1 mmol) and Hdpb (306.3 mg, 1 mmol) in ethanol (15 cm^3). Addition of water (20 cm^3) and evaporation of ethanol under a stream of nitrogen allowed the precipitation of the complex. This was filtered, washed with water and dried under vacuum at room temperature. Yield: 388 mg (68%). (Found: C, 47.35; H, 3.55; N, 1.15; Hg, 34.95; Calc. for $C_{45}H_{41}Hg_2NO_5P_2$: C, 47.46; H, 3.63; N, 1.23; Hg, 35.22).

2.1.3. [(dbpo)HgMe] (2)

Hydrogen peroxide (36%, *m*/*v*) (0.5 cm^3, 0.5 mmol) was added at room temperature to a solution of the complex **1** (260 mg, 0.5 mmol) in dichloromethane (10 cm^3)/ethanol (2 cm^3). The resulting solution was stirred for 12 h, then all the solvent was removed under vacuum. The solid was dissolved in dichloromethane and the resulting mixture was filtered. Addition of ethyl ether caused the precipitation of colorless crystals which were collected as described for **1**. Yield: 498 mg (93%). (Found: C, 44.55; H, 3.25; Hg, 37.45. Calc. for $C_{20}H_{17}HgO_3P$: C, 44.74; H, 3.19; Hg, 37.36).

2.1.4. [(PPh$_3$)HgMe](CF$_3$SO$_3$) (3)

A solution of triphenylphosphine (262 mg, 1 mmol) in dichloromethane (10 cm^3) was added to a solution of $[MeHg(DMSO)]CF_3SO_3$ (442 mg, 1 mmol) in the same solvent (10 cm^3). *n*-hexane (15 cm^3) was added to the resulting solution and the solvent was evaporated under a current of nitrogen until a colorless oil separated. The solvent was decanted off and the oil was dissolved in ethanol (10 cm^3). Addition of *n*-heptane (10 cm^3) and slow evaporation of the solvent allowed the precipitation of colorless crystals which were filtered, washed with *n*-hexane and dried under a stream of nitrogen. Yield: 524 mg (88%). (Found: C, 38.55; H, 3.05; Hg, 31.75. Calc. for $C_{20}H_{18}F_3HgO_3PS$: C, 38.31; H, 2.89; Hg, 31.99).

2.2. Crystallography

Diffraction data of **1bis** and **2** were collected at room temperature on an ENRAF NONIUS CAD4 automatic diffractometer. Unit cell parameters were determined by least-squares refinement of the setting angles of 25 carefully centered reflections. Crystal data and data collection details are given in Table 1. The intensities I as well as the standard deviations $\sigma(I)$ were calculated by using the value of 0.03 for the instability factor k [10]. The intensities were corrected for Lorentz-polarization effects and an empirical absorption correction was applied using y scans [11].

All the calculations were carried out on a 486 IBM personal computer, using the SHELXS86 [12], SHELXL93

Table 1
Crystal data and structure refinement for **1bis** and **2**

	1bis	**2**
Formula	$C_{45}H_{41}Hg_2NO_5P_2$	$C_{40}H_{34}Hg_2O_6P_2$
Formula weight	1137.90	1073.79
Temperature, K	293(2)	293(2)
Wavelength, Å	0.7107	0.7107
Crystal system	Monoclinic	Triclinic
Space group	$P2/n$	$P\bar{1}$
a, Å	10.413(4)	11.535(2)
b, Å	9.831(3)	12.897(5)
c, Å	20.674(3)	13.275(7)
α, deg	90	88.31(4)
β, deg	102.51(3)	73.65(4)
γ, deg	90	85.27(4)
Volume, Å^3	2066.2(11)	1888.5(13)
Z	2	2
Density calc., g cm^{-3}	1.829	1.888
Absorption coeff., cm^{-1}	75.5	82.5
Absorption correc. range	0.573–1.000	0.320–1.000
$F(000)$	1094	1024
Crystal size, mm	$0.38 \times 0.18 \times 0.10$	$0.50 \times 0.30 \times 0.10$
Theta range, θ	2.88–22.48	2.52–22.48
Index ranges	$-11 \le h \le 10$ $0 \le k \le 10$ $0 \le l \le 22$	$-11 < h \le 12$ $-13 \le k \le 13$ $0 \le l \le 14$
Method	ω–2θ	
Scan speed, deg min^{-1}	1.03–8.24	1.27–8.24
Scan width, deg	$0.7 + 0.35 \tan \theta$	$0.8 + 0.35 \tan \theta$
Background time	Half the scan time	
Standards	3 every 120 min	
Reflections collected	2774	4917
Independent reflections	2694	4917
Refinement method	Full matrix least-squares on F^2	
Data/restraints/parameters	2694/0/88	4917/0/155
Goodness-of-fit on F^2	1.039	0.925
Final R [$I > 2\sigma(I)$]	$R_1 = 0.037$, $wR_2 = 0.084$	$R_1 = 0.044$, $wR_2 = 0.11$
Final R [all data]	$R_1 = 0.059$, $wR_2 = 0.094$	$R_1 = 0.057$, $wR_2 = 0.12$

[13] and ORTEP [14] programs. Atomic scattering factors for neutral atoms were taken from ref. [15]. Both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms [16]. The structures were solved by heavy atom method and full-matrix least-squares refinements were carried out on F^2 with anisotropic thermal factors assigned to mercury and phosphorus atoms. The phenyl rings were treated as rigid bodies of D_{6h} symmetry. Hydrogen atoms were introduced in calculated positions, riding on their attached carbon atoms with isotropic thermal parameters 20% larger than those of the latter. The function minimized during the refinement was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where w is defined as $1/\sigma^2[(F_o^2) + (0.0406P)^2 + 14.54P]$ and $1/\sigma^2[(F_o^2) + (0.0685P)^2 + 23.91P]$ in **1bis** and **2**, respectively [$P = (\max(F_o^2, 0) + 2F_c^2)/3$].

2.3. NMR measurements

The ^1H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker Avance DRX-500 spectrometer operating at 500.132, 125.76 and 202.46 MHz, respectively, and equipped with a variable temperature control unit accurate to ± 0.1°C. ^1H, ^{13}C chemical shifts are relative to tetramethylsilane, whereas ^{31}P chemical shifts are relative to external 85% H_3PO_4. $^{199}Hg\{^1H\}$-NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 35.85 MHz. ^{199}Hg chemical shifts are relative to external 0.1 mol dm^{-3} $Hg(ClO_4)_2$ in 0.1 mol dm^{-3} $HClO_4$. Downfield values of the chemical shifts are reported as positive. The assignments of the signals resulted from 2D ^1H COSY, 2D ^1H NOESY and proton detected 2D ^1H, ^{13}C and ^1H, ^{31}P correlations using non-spinning samples. J_{HH} and J_{PH} coupling constants were obtained from heteronuclear decoupling experiments as well as from 1D-NMR spectra. 2D-NMR spectra were recorded using pulse sequences suitable for phase-sensitive representations, using TPPI. Double-quantum filtered ^1H COSY experiments [17] were recorded with 1024 increments of size 2K (with eight scans each) covering the full range (ca. 5000 Hz) in both dimensions. The ^1H NOESY measurements [18] were recorded with 1024 increments of size 2K (with 16 scans each) covering the full range (ca. 5000) in both dimensions and using a mixing time of 0.8 s. The ^1H, ^{13}C correlations [19] were recorded using the standard HMQC sequence with no decoupling during acquisition, 1024 increments of size 2K (with 16 scans each) were collected covering 5000 Hz range in $F2$ and 22 000 Hz range in $F1$. Standard pulse sequence was employed for the ^1H, ^{31}P correlations [20].

3. Results and discussion

The complex [(dbp)HgMe] is obtained from the reaction of MeHg(OH) with Hdpb in water/ethanol solution. Alternatively the solvate [(dpb)-HgMe] · $0.5H_2O$ · 0.5Py can be prepared by reacting MeHgCl with Hdpb and pyridine. The compound which is soluble in common organic solvents such as ethanol, dichloromethane, acetone, thf, slowly decomposes in solution, separating metallic mercury. The complex [(dpb)HgMe] reacts in dichloromethane solution with [(DMSO)HgMe](CF_3SO_3) to form Hg metal and untractable products. The complex very slowly reacts with atmospheric oxygen to form the

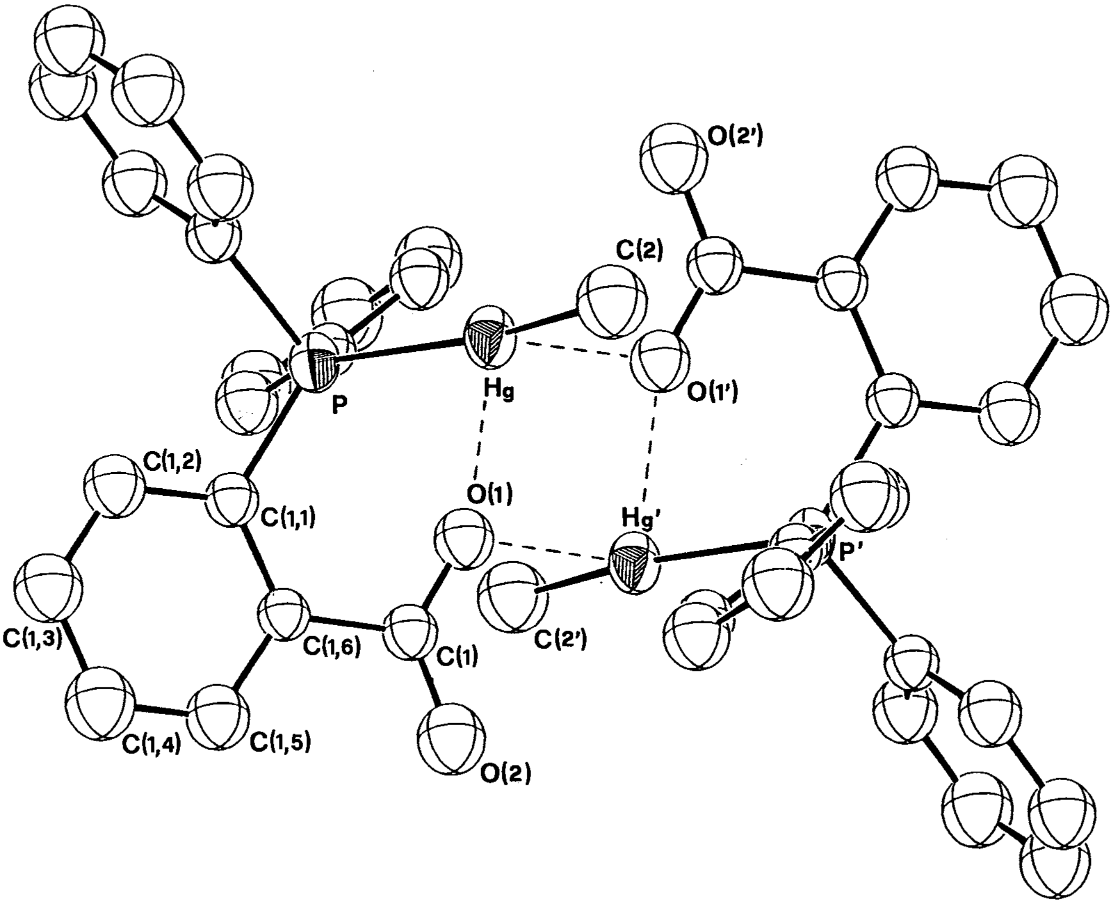


Fig. 1. Perspective view of the dimer [(dpb)HgMe]$_2$. ORTEP drawing with 30% probability ellipsoids.

phosphinoxide derivative [(dbpo)HgMe]. This latter can be properly prepared through oxidation of [(dbp)HgMe] by H_2O_2. The complex [(PPh_3)HgMe](CF_3SO_3) was prepared for comparison raisons by reaction of PPh_3 with [(DMSO)HgMe](CF_3SO_3).

3.1. Description of the structures

The molecular structure of **1bis** may be described as consisting of [(dbp)HgMe]$_2$ dimers, the two monomeric units being related by an inversion center, with a Hg..Hg separation of 4.616 Å. Pyridine and water solvent molecules are interspersed in the latice. Fig. 1 shows the perspective view of the dimeric unit and Table 2 reports selected bond distances and angles.

In each half of the dimer the mercury is linked in a slightly distorted linear fashion to a methyl group and to the phosphorus atom of the phosphine group (Me–Hg–P = 165.8(3)°). Besides the two strong covalent bonds there are additional linkages, which allow the formation of the dimer. Indeed the two metal centers are held together by two bridging oxygen atoms of the carboxylic groups which display secondary interactions with the mercury atoms (Hg...O(1′) 2.64, Hg...O(1) 2.84 Å). Therefore, we face a 2 + 2 coordination which represent a common feature in the stereochemistry of the mercury atom, made possible via overlap with vacant 6p orbitals of the metal. The values of the secondary bondings are effectively much larger than the values of normal covalent Hg–O bond distances (2.00–2.35 Å) [4,21], but are also appreciably shorter than the sum of the Van der Waals radii (3.00 Å [22], and 3.23 Å [23,24]) and actually may be considered indicative of some interactions.

As far as the distribution of the solvent molecules in the latice is concerned, while pyridine does not show any significative contact, the oxygen of the water molecule displays hydrogen bonding interactions with the oxygen (O(2)) of the carboxylic group not involved in the interactions with the mercury atom. The value of such contact, 2.88 Å, is in between the values of twice the Van der Waals radii of oxygen, as reported by Pauling (2.84 Å) [25] and by Bondi (3.04 Å) [24].

It seems interesting to recall the structure of the L-cysteinate methylmercury hydrate [4], where a carboxylic group interacts with mercury atom forming a six-membered ring, with an intra Hg..O contact matching that found in our compound (2.85 Å). It seems anyway noteworthy that while in the phosphine ben-

Table 2
Selected bond lengths (Å) and angles (°) for **1bis**

Hg–P	2.413(3)
Hg–C(2)	2.065(12)
Hg...O(1)	2.842(6)
Hg...O(1′)	2.641(6)
P–C(1,1)	1.824(5)
P–C(1,2)	1.836(5)
P–C(1,3)	1.799(5)
O(1)–C(1)	1.248(10)
O(2)–C(1)	1.251(11)
C(1)–C(6,1)	1.510(10)
P–Hg–C(2)	165.8(3)
P–Hg–O(1′)	102.6(2)
C(2)–Hg–O(1′)	91.4(4)
C(1,1)–P–C(1,2)	104.6(3)
C(1,1)–P–C(1,3)	108.8(3)
C(1,2)–P–C(1,3)	103.7(3)
C(1,1)–P–Hg	114.1(2)
C(1,2)–P–Hg	106.9(2)
C(1,3)–P–Hg	117.4(2)
C(1)–O(1)–Hg′	116.7(6)
O(1)–C(1)–O(2)	124.9(9)
O(1)–C(1)–C(6,1)	116.3(8)
O(2)–C(1)–C(6,1)	118.8(8)

Symmetry transformations used to generate equivalent atoms: $-x+1$, $-y$, $-z+1$.

zoate complex the formation of the dimer occurs through interactions involving the mercury atom, in the cysteinato complex the metal atom does not present any interactions with the neighbouring molecule, the packing in pairs of molecules being achieved through hydrogen bonding only between the oxygen and nitrogen atoms of the ligands.

The molecular structure of **2** (Fig. 2) consists of [(dpbo)HgMe]$_2$ dimers, the two halves being linked through mercury–oxygen bond interactions (Hg..Hg separation 4.142 Å). As a matter of fact in each monomer [(dpbo)HgMe] the metal atom is bonded to a methyl unit and to one oxygen atom of the carboxylic group in a slightly distorted linear fashion (Me–Hg–O = 169.2(5)°), the phosphorus atom being definitely away from the mercury center. Also in this case the coordination around each mercury atom is completed by two weaker additional bond interactions, which involve the oxygen atoms of the phosphinoxide and of the carboxylic group of the adiacent molecule. Table 3 reports selected bond distances and angles of **2**.

In both the structures the values of the bond distances involving mercury atom fit very well with the values previously reported, both as strong covalent [4,21] either as weak [26] interactions. In particular as concerns the Hg–P bond distance, (2.413(3) Å) values of 2.37–2.40 Å have been observed in structures containing nearly linear P–Hg–X units with P–Hg–X angles in the range 158–166° [8,27].

The above structures highlight the better bonding capabilities towards Hg(II) ions of the phosphine with respect to the carboxilic group, provided the lone pair on the phosphorus is available.

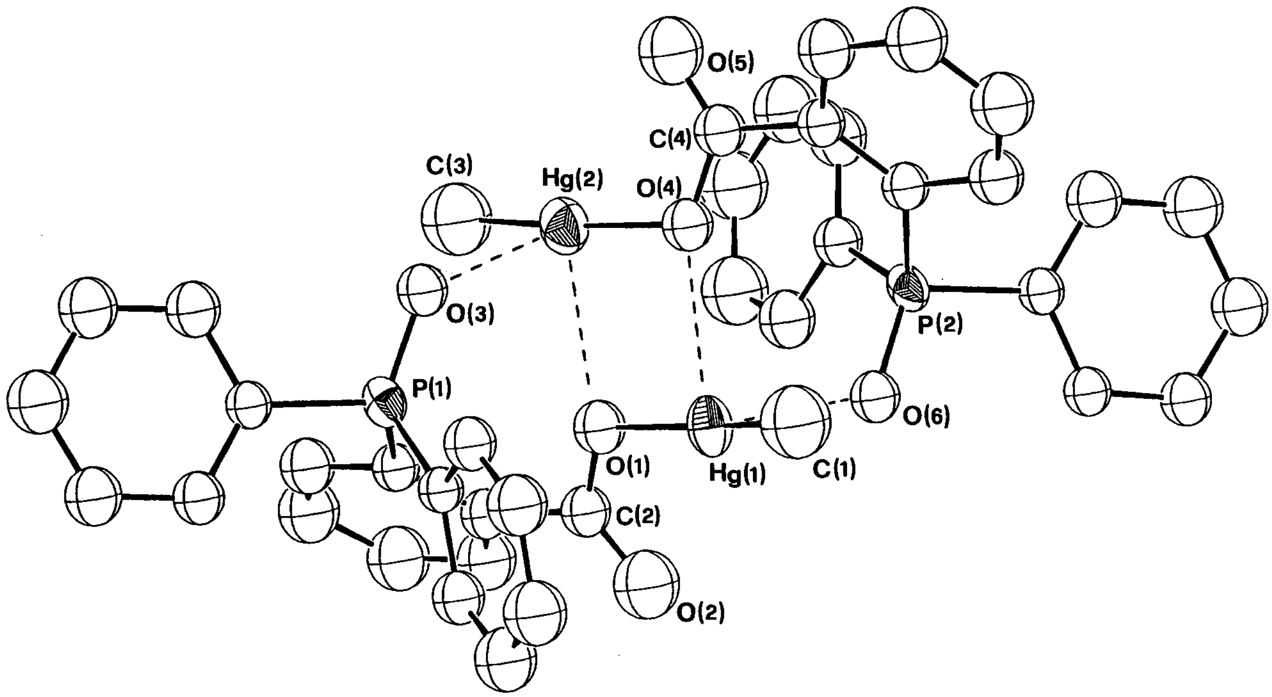


Fig. 2. Perspective view of the dimer [(dpbo)HgMe]$_2$. ORTEP drawing with 30% probability ellipsoids.

Table 3
Selected bond lengths (Å) and angles (°) for **2**

Hg(1)–C(1)	2.05(2)
Hg(1)–O(1)	2.086(7)
Hg(1)...O(4)	2.874(8)
Hg(1)...O(6)	2.732(8)
Hg(2)–C(3)	2.04(2)
Hg(2)–O(4)	2.101(7)
Hg(2)...O(1)	2.817(8)
Hg(2)...O(3)	2.814(8)
P(1)–O(3)	1.485(7)
P(1)–C(1,3)	1.806(5)
P(1)–C(1,2)	1.817(5)
P(1)–C(1,1)	1.855(5)
P(2)–O(6)	1.491(7)
P(2)–C(1,5)	1.815(5)
P(2)–C(1,6)	1.816(6)
P(2)–C(1,4)	1.836(5)
O(1)–C(2)	1.276(12)
O(2)–C(2)	1.216(13)
O(4)–C(4)	1.290(12)
O(5)–C(4)	1.215(13)
C(2)–C(6,1)	1.505(11)
C(4)–C(6,4)	1.480(11)
C(1)–Hg(1)–O(1)	169.2(5)
C(3)–Hg(2)–O(4)	172.8(5)
O(3)–P(1)–C(1,3)	110.4(4)
O(3)–P(1)–C(1,2)	114.6(4)
C(1,3)–P(1)–C(1,2)	103.6(3)
O(3)–P(1)–C(1,1)	113.8(4)
C(1,3)–P(1)–C(1,1)	104.7(3)
C(1,2)–P(1)–C(1,1)	108.8(3)
O(6)–P(2)–C(1,5)	110.6(3)
O(6)–P(2)–C(1,6)	112.6(4)
C(1,5)–P(2)–C(1,6)	102.3(3)
O(6)–P(2)–C(1,4)	114.5(4)
C(1,5)–P(2)–C(1,4)	105.0(3)
C(1,6)–P(2)–C(1,4)	110.9(3)
C(2)–O(1)–Hg(1)	119.9(6)
C(4)–O(4)–Hg(2)	112.1(6)
O(2)–C(2)–O(1)	125.1(10)
O(2)–C(2)–C(6,1)	120.4(9)
O(1)–C(2)–C(6,1)	114.5(8)
O(5)–C(4)–O(4)	122.9(10)
O(5)–C(4)–C(6,4)	121.5(9)
O(4)–C(4)–C(6,4)	115.6(8)

3.2. NMR spectra

Selected NMR spectral data for the complex [(dpb)HgMe] (**1**) are reported in Table 4. The corresponding data for the complex [(PPh$_3$)HgMe](CF$_3$SO$_3$) (**3**) and for a solution containing [(dpb)HgMe] and CF$_3$SO$_3$H (molar ratio 1:1.5) are also reported for comparison. The values of the $^2J_{\mathrm{HgH}}$ coupling constant, as well as the ^{31}P{^{1}H} and ^{199}Hg{^{1}H} data, are consistent with the coordination of the phosphorus atom to the mercury in each case, but, while a static complex forms even at room temperature in the presence of triflic acid, a dynamic process takes place in the case of **1** and **3**, the slow exchange limit being reached only at 198 K. This different dynamic behaviour can be attributed to a rapid MeHg$^+$ exchange among phosphine ligands due to an associative pathway in the case of **1** and **3** (as previously reported for [(PMe$_3$)HgMe]$^+$ [7]), whereas in the solution containing **1** and an excess of triflic acid any free phosphine is clearly protonated and thus uncoordinating. Indeed, traces of free phosphine are likely present in solutions of **1** and **3** because of exiguous decomposition processes [28], whilst we have found that the addition of CF$_3$SO$_3$H to a solution of [(PPh$_3$)HgMe]$^+$ analogously cancels out the exchange process at room temperature.

The ^{1}H- and ^{13}C-NMR spectra of **1** and **1**/triflic acid have been investigated in greater detail. All the resonances have unambiguously been assigned through 1D- and 2D-NMR techniques (see experimental). The results are reported in Table 5. These data show that the two phenyl phosphino rings are NMR equivalent in **1**, a single set of resonance being observed for all the ring nuclei. This apparently rules out that, unlike in the solid-state structure, a rigid chelate ring may exists in the NMR time scale, involving the metal center, the phosphorus atom and the carboxylate group in the solution structure of **1**. This seems consistent with a weakening of the secondary interactions found in the solid state due to the solvation process. Accordingly,

Table 4
Selected NMR spectral data for the dbp complexes[a]

Complex	Temp. (K)	^{1}H (CH$_3$)	^{31}P{^{1}H}	^{199}Hg{^{1}H}
[(dbp)HgMe] **1**	295	0.92 (s with satell., br) $^2J_{\mathrm{HgH}} = 179$	58.0 (br)	—[b]
	198	0.90 (d with satell.) $^3J_{\mathrm{PH}} = 7.0$, $^2J_{\mathrm{HgH}} = 178$	57.4 (s with satell.) $^1J_{\mathrm{HgP}} = 2665$	1710 (d)
[(PPh$_3$)HgMe](CF$_3$SO$_3$) **3**	295	1.26 (s with satell., br) $^2J_{\mathrm{HgH}} = 177$	57.4 (br)	—[b]
	198	1.13 (d with satell.) $^3J_{\mathrm{PH}} = 5.0$, $^2J_{\mathrm{HgH}} = 177$	55.9 (s with satell.) $^1J_{\mathrm{HgP}} = 1345$	1747 (d)
[(dbp)HgMe]/CF$_3$SO$_3$H[c]	295	1.14 (d with satell.) $^3J_{\mathrm{PH}} = 7.4$, $^2J_{\mathrm{HgH}} = 175$	65.9 (s with satell.) $^1J_{\mathrm{HgP}} = 1493$	1725 (d)

[a] CD$_2$Cl$_2$ solutions 0.05 M. Abbreviations: br, broad; s, singlet, d, doublet. Chemical shifts in ppm, coupling constants in Hz.
[b] We were unable to record any signal in the ^{199}Hg spectrum after 12 h long experiment.
[c] Mole ratio 1:1.5.

Table 5

^{13}C-NMR and ^{1}H-NMR chemical shifts (ppm) and coupling constants (Hz) for the dbp complexes[a]

Complex												
	C1	C2	C1,1	C2,1	C3,1	C4,1	C5,1	C6,1	C_{ipso}	C_{ortho}	C_{meta}	C_{para}
[(dbp)HgMe] **1**	169.58	9.19 (br)	127.82 $^1J_{CP} = 59.9$	135.13 $^2J_{CP} = 7.0$	130.24 $^3J_{CP} = 9.7$	132.44	132.53 $^3J_{CP} = 9.2$	132.5	127.86 $^1J_{CP} = 59.9$	134.34 $^2J_{CP} = 13.1$	129.86 $^3J_{CP} = 11.0$	131.76
[(dbp)HgMe] /CF_3SO_3H[c]	168.91	13.50 $^2J_{CP} = 78.0$	128.12 $^1J_{CP} = 49.9$	136.88 $^2J_{CP} = 5.4$	134.62 $^3J_{CP} = 6.1$	134.08	133.90 $^3J_{CP} = 6.8$	—[b]	126.80 $^1J_{CP} = 56.0$	134.59 $^2J_{CP} = 13.1$	130.77 $^3J_{CP} = 11.9$	133.59
	H2	H2,1	H3,1	H4,1	H5,1	H_{ortho}	H_{meta}	H_{para}				
[(dbp)HgMe] **1**	0.92 (br)	6.78 $^3J_{HP} = 11.9$; $^3J_{3,1} = 7.6$; $^4J_{4,1} = 1.3$	7.26 $^4J_{HP} = {}^4J_{5,1} = 1.3$; $^3J_{2,1} = {}^3J_{4,1} = 7.6$	7.18 $^5J_{HP} = {}^4J_{2,1} = 1.3$; $^3J_{3,1} = {}^3J_{5,1} = 7.6$	7.59 $^4J_{HP} = 12.6$; $^4J_{3,1} = 1.3$; $^3J_{4,1} = 7.6$	7.46 (m)	7.45 (m)	7.51 (m)				
[(dbp)HgMe] /CF_3SO_3H[c]	1.14 $^3J_{HP} = 7.4$	7.04 $^3J_{HP} = 13.3$; $^3J_{3,1} = 7.7$; $^4J_{4,1} = 1.3$	7.67 $^4J_{HP} = {}^4J_{5,1} = 1.3$; $^3J_{2,1} = {}^3J_{4,1} = 7.7$	7.78 $^5J_{HP} = {}^4J_{2,1} = 1.3$; $^3J_{3,1} = {}^3J_{5,1} = 7.7$	8.45 $^4J_{HP} = 5.0$; $^4J_{3,1} = 1.3$; $^3J_{4,1} = 7.7$	7.45 (m) $^3J_{HP} = 14.3$	7.56 (m) $^4J_{HP} = 2.7$	7.65 $^5J_{HP} = 2.2$; $^3J_{HH} = 7.5$; $^4J_{HH} = 1.1$				

[a] CD_2Cl_2 solutions 0.05 M, 294 K. Abbreviations: br, broad; m, multiplets.

[b] Masked by other resonances.

[c] Mole ratio 1:1.5.

the solution structure of **1** is likely better described in terms of monomers than dimers. Analogous conclusions can be drawn out for the complex obtained from **1** by the reaction with triflic acid. In addition, considering that: (i) the $^{31}P\{^1H\}$ and $^{199}Hg\{^1H\}$ parameters of the **1**/triflic acid solution closely resemble those recorded for the cationic complex **3** at low temperature, (ii) the down field shift of the ^1H and ^{13}C resonances of the **1**/triflic acid solution, as compared to those of **1**, can be attributed to a positive charge located on the complex, (iii) the $^1H(H2)$ and $^{13}C(C2)$ signals appear as sharp doublets, we identify the complex formed by the addition of CF_3SO_3H to **1** as the CO_2-protonated cationic complex [(dpbH)HgMe](CF_3SO_3). Finally, it is worth notice the remarkable difference in the $^1J_{HgP}$ coupling constant found for the neutral complex **1** (2665 Hz) as compared to that found for **3** and for [(dpbH)HgMe](CF_3SO_3) (1345 and 1493 Hz, respectively). We attribute this difference to cationic nature of the two latter compound, whose coupling constants fall in the range normally observed for other phosphine organomercury complexes [2,7,29].

The ^1H- and $^{31}P\{^1H\}$-NMR spectra of the complex **2** are straightforward: the methyl ^1H signal is a singlet at 0.90 ppm with satellites ($^2J_{HgH} = 219$ Hz) whereas the ^{31}P resonance of the P=O group occurs at 30 ppm as a singlet.

4. Supplementary material

Supplementary materials consist of coordinates, thermal parameters, complete bond distances and angles and Fo/Fc listings.

Acknowledgements

We gratefully acknowledge the financial support of EU for HCM program 'Metals and Environmetal Problems' (1995–1997), through Grant ERBCHRX-CT94-0632.

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