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Reactivity of diphosphines towards methyl- and phenyl-mercury(II) ions. Crystal structure of $[Hg(Ph_2PCH_2CH_2PPh_2)_2][O_3SCF_3]_2$*

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Methyl- and phenyl-mercury(II) ions reacted, in the molar ratio 2 : 1, with bidentate phosphines L–L to give binuclear complexes of general formula $[RHg(L\text{–}L)HgR]^{2+}$. [L–L = $Ph_2P(CH_2)_nPPh_2$, n = 1–3]. When an excess of the phosphine ligand is present an intermolecular exchange process occurs which leads to the formation of the symmetrically substituted compounds, HgR_2 and $[Hg(L\text{–}L)_2]^{2+}$. The reactions in solution have been studied by multinuclear NMR spectroscopy; the structure of the bimetallic species was deduced with the aid of computer simulation. The single-crystal structure of $[Hg(Ph_2PCH_2CH_2PPh_2)_2][O_3SCF_3]_2$ [orthorhombic, space group *Pbcn*, a = 17.141(3), b = 20.158(3), c = 15.614(9) Å, Z = 4] showed the mercury atom to be in a distorted-tetrahedral configuration.

The importance of methylmercury compounds in processes connected with environmental pollution is well known.[1] Recent studies on the detoxification of organomercurials in naturally occurring biological systems[2] have stimulated renewed interest in the co-ordination chemistry of the methylmercury ion.

Few complexes of organomercury(II) with tertiary phosphines have been previously described.[3] Although organomercury(II) ions have high affinity for tertiary phosphines and react easily with them, generally the so-called symmetrization reaction occurs[3c] with the formation of a complex of Hg^{2+} along with a diorganomercurial. The first examples of tetrahedral complexes of the type $[HgR\{N(CH_2CH_2PPh_2)_3\}]^+$ (R = Me, Et or Ph) were recently reported by us.[4,5]

The reaction of the covalent species HgMe(Cl) with $Ph_2PCH_2CH_2PPh_2$ (dppe) has been reported but the product $[Hg(dppe)Cl_2]$, was poorly characterized.[3b]

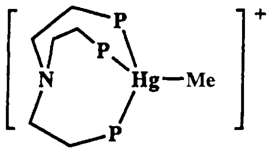
We now report on the interaction between the ions $[HgR]^+$ (R = Me or Ph) and the bidentate phosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1, dppm; n = 2, dppe; n = 3, dppp). The structure of the previously reported[6] complex $[Hg(dppe)_2]^{2+}$ has been now determined by X-ray diffractometry. The only previously reported structure of a mercury(II)–dppe complex was that of the polymeric compound $[Hg(dppe)(CN)_2]$.[7]

Experimental

General considerations

All solvents and chemicals were of reagent grade and used as received. The complexes $[HgMe(dmso)][(O_3SCF_3]$ and $[HgPh(dmso)][(O_3SCF_3)]\cdot dmso$ (dmso = dimethyl sulfoxide) were prepared as previously described.[4]

Proton and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded at 200.13 and 50.32 MHz respectively on a Bruker AC-200 spectrometer. Peak positions are relative to $SiMe_4$ as external reference. The $^{31}P\text{-}\{^1H\}$ and $^{199}Hg\text{-}\{^1H\}$ spectra were recorded on the same instrument, operating at 81.015 and 35.85 MHz respectively. Chemical shifts are relative to external 85% H_3PO_4 and external 0.1 mol dm^{-3} $Hg(ClO_4)_2$ in 0.1 mol dm^{-3} $HClO_4$ respectively. **CAUTION**: Organomercurials are extremely toxic, and all experimentation involving these reagents should be carried out in a well vented fume-hood.



$[HgMe\{N(CH_2CH_2PPh_2)_3\}]^+$

The NMR spectral simulation was performed by means of the computer program CAHOS (computer analysis of highly overlapped spectra)† running on a personal computer. The NMR spectra were transferred as sequences of intensity values at constant frequency intervals from the Aspect computer of the spectrometer to the personal computer by means of the Bruker software package WIN-NMR.[8] This program, which allows the simultaneous refinement of chemical shifts, linewidths and homo- and hetero-nuclear coupling constants, uses the Powell conjugate directions method[9] as minimization algorithm and the well known mathematical algorithm of LAOCN3[10] for simulation of the spectra. A preliminary version of the program was used by us previously.[11] A detailed description of the procedure is available as SUP 57145.

Synthesis of $[Hg(dppe)_2][O_3SCF_3]_2$

The complex $[HgPh(dmso)][O_3SCF_3]\cdot dmso$ (0.585 g, 1 mmol) and dppe (0.398 g, 1 mmol) were dissolved in dichloromethane (30 cm^3). After the solution was allowed to stand for 4 h in the dark, toluene (15 cm^3) was added and the solvent was evaporated in a current of nitrogen until colourless crystals precipitated (yield 85%) (Found: C, 50.20; H, 3.80; P, 9.40. Calc. for $C_{54}H_{48}F_6O_6P_4S_2$: C, 50.05; H, 3.75; P, 9.55%). Selected NMR data (CD_2Cl_2, 0.32 mol dm^{-3}, 298 K): $^{31}P\text{-}\{^1H\}$, δ 21.4 [s with satellites, ^1J(Hg–P) = 2160 Hz]; $^{199}Hg\text{-}\{^1H\}$, δ 2125 [qnt, ^1J(Hg–P) = 2160 Hz].

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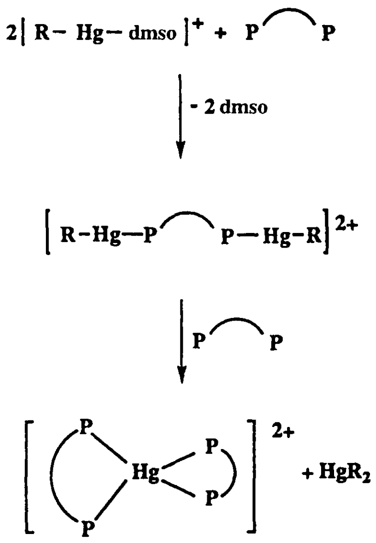
* *Supplementary data available* (No. SUP 57145, 4 pp.): computer analysis of the NMR spectra. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

† To obtain a copy of the program please contact A. Vacca (E-mail: vacsab@chiml.unifi.it).



Scheme 1

Crystallography

Diffraction data 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 centred reflections. Crystal data and data collection details are given in Table 2. The intensities I as well as the standard deviations $\sigma(I)$ were calculated as described, by using the value of 0.03 for the instability factor k.[12] After scaling, the intensities were corrected for Lorentz-polarization and an empirical correction for absorption using ψ scans was applied.[13]

All the calculations were carried out on an Hewlett-Packard 486/50 personal computer, using the SHELXS 86,[14] SHELXL 93[15] and ORTEP[16] programs. Atomic scattering factors for neutral atoms were taken from ref. 17. Both $\Delta f'$ and $\Delta f''$ components of the anomalous dispersion were included for all non-hydrogen atoms.[18] The structure was solved by the heavy-atom method with Patterson and Fourier maps. Full-matrix least-squares refinements were carried out on F^2, with anisotropic thermal parameters 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. During the refinement the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, the weights, w, being defined as $1/[\sigma^2(F_o) + (0.0532P)^2 + 99.12P]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/98.

Results and Discussion

The reaction of dppe with [HgMe(dmso)]$^+$ in dichloromethane solution (0.2 mol dm^{-3} HgMe^{II}), at room temperature (Scheme 1), was monitored by ^{1}H and ^{31}P-{^{1}H} NMR spectroscopy. When the molar ratio (r) dppe:[HgMe]$^+$ is less than 0.5:1 the proton spectra show the presence of two methylmercury species (Fig. 1): the singlet at δ 1.16 with satellites [^3J(Hg–H) = 255 Hz] is due to the MeHg protons of [HgMe(dmso)]$^+$ whereas the multiplet centred at δ 1.12 with two pairs of satellites is attributed to the MeHg^{II} protons of the new dinuclear species [MeHg(Ph$_2$PCH$_2$CH$_2$PPh$_2$)HgMe]$^{2+}$ (see below). When r = 0.5:1 there is no resonance due to the ion [HgMe(dmso)]$^+$.

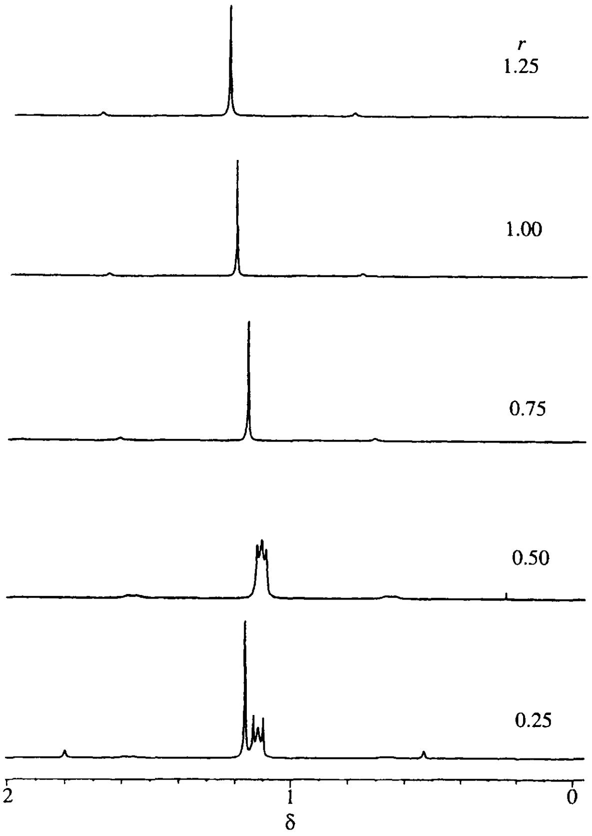


Fig. 1 Proton NMR spectra of the system [HgMe(dmso)]$^+$–dppe, (MeHg resonance region), at variable molar ratio r = [dppe]/[HgMe(dmso)$^+$], in CD$_2$Cl$_2$ solution (0.2 mol dm^{-3} HgMe) at 298 K

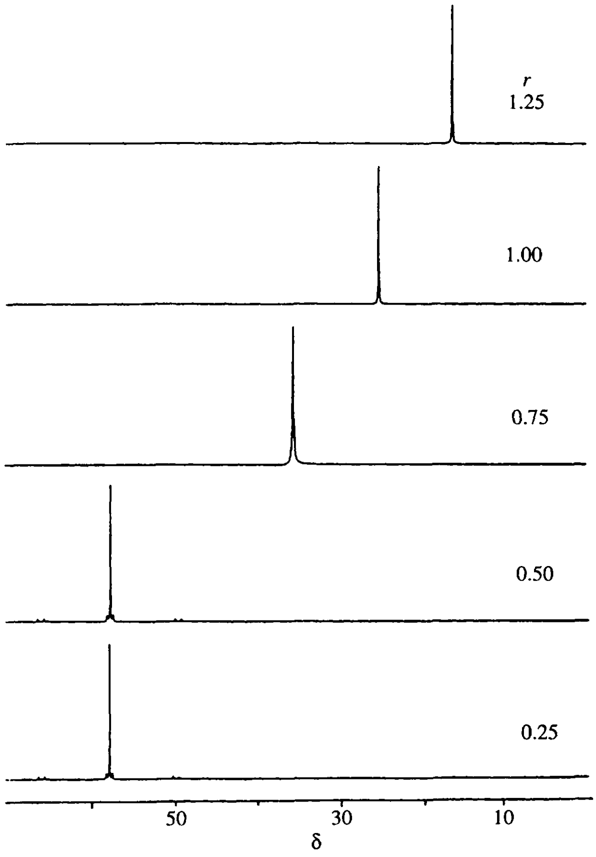


Fig. 2 The ^{31}P-{^{1}H} NMR spectra of the system [HgMe(dmso)]$^+$–dppe, at variable molar ratio r = [dppe]/[HgMe(dmso)$^+$]; conditions as in Fig. 1

The corresponding $^{31}P\text{-}\{^1H\}$ NMR spectrum (Fig. 2) shows only a single pattern centred at δ 57.43 which we assign to the dinuclear complex. Although the dinuclear complex appears to be stable indefinitively in solution no crystals could be isolated. When an excess of ligand is present in the solution ($r > 0.5:1$) the ^{31}P spectrum consists of a singlet the chemical shift of which is the weighted average of those of the signals of the dinuclear complex and free dppe (δ −12.5). This singlet moves to high field as the amount of the added dppe increases, the limit being the resonance of free dppe (Fig. 2). The trend of the $MeHg^{II}$ resonance in the corresponding ^1H NMR spectra is consistent (Fig. 1). When the temperature of the solutions with $r > 0.5:1$ is decreased the ^{31}P singlet broadens. Similar behaviour is shown by the $^{199}Hg\text{-}\{^1H\}$ resonance: a singlet, broad even at room temperature, becomes very broad at low temperature (223 K). These results indicate that a rapid exchange process is taking place for the systems with $r > 0.5:1$, even at the lowest accessible temperature. We propose a ligand association exchange, such as that shown in Scheme 2. Fully analogous dinuclear complexes were obtained with dppm or dppp.

Solutions of $[HgMe(dmso)]^+$ and dppe with $r > 0.5:1$ slowly degrade at room temperature. After 24 h the $^{31}P\text{-}\{^1H\}$ NMR spectra show a new signal centred at δ 21.4 [s with satellites, $^1J(Hg\text{–}P) = 2160$ Hz] which we attribute to the previously reported species $[Hg(dppe)_2]^{2+}$.[6] The corresponding ^1H spectra show lines due to the protons of dimethylmercury, $HgMe_2$ [δ 1.1, $^2J(Hg\text{–}P) = 103$ Hz]. Taken together, the $^{31}P\text{-}\{^1H\}$ and ^1H spectra indicate that a symmetrization process is occurring (Scheme 1).

The reaction of the 1:1 mixture is complete, at room temperature, in *ca.* 20 d. The reactions of dppe with $[HgPh(dmso)]^+$ are similar but the symmetrization reaction is faster with phenyl- than with methyl-mercury. A stoichiometric mixture of phenylmercury and dppe yields only symmetrization products in *ca.* 3 h.

Analysis of the NMR spectra of the dinuclear species

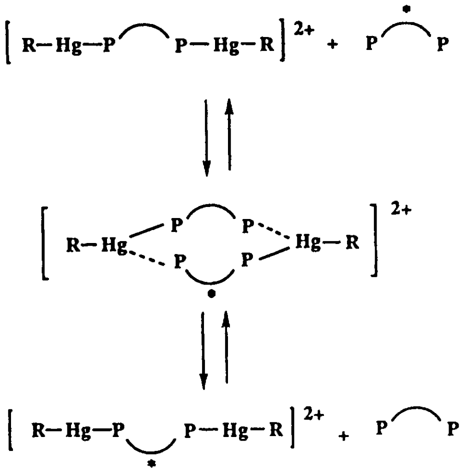
The ^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$ and $^{199}Hg\text{-}\{^1H\}$ NMR spectra of the mercury complexes obtained by reaction (1) (R = Me;

$$2\,[HgR]^+ + L\text{–}L \longrightarrow [RHg(L\text{–}L)HgR]^{2+} \qquad (1)$$

L–L = dppm, dppe or dppp; R = Ph, L–L = dppe) were successfully simulated assuming a symmetric structure. As an example we show below the spin system for R = Me and L–L = dppe, together with the labelling of the relevant nuclei.

$H_3C\text{-}Hg\text{-}P\text{-}H_2C\text{-}CH_2\text{-}P\text{-}Hg\text{-}CH_3$
H A Y P B B′ P′ Y′ A′H′

The experimental NMR spectra containing the multiplets employed in the simulation are shown in Fig. 3. The ^1H and $^{31}P\text{-}\{^1H\}$ spectra contain satellites on the main resonances due to the presence of isotopomers. Satellites are also present, but less visibly, in the $^{13}C\text{-}\{^1H\}$ spectra. Since ^{199}Hg has a natural abundance of 16.84% the binuclear ion $[MeHg(dppe)HgMe]^{2+}$ will exist as three isotopomers: a species with no ^{199}Hg atoms (69.16% abundance), one with a single ^{199}Hg atom (28.01%) and one with two ^{199}Hg atoms (2.84%). As a consequence any signal which is affected by the presence of a mercury nucleus will have three components. For example, the proton resonance of the methyl groups attached to the mercury atoms will relate to three spin systems: HH′PP′ (in which H = ^1H and P = ^{31}P), contributing 69.16% to the total intensity, HH′PP′Y (in which Y = ^{199}Hg) contributing 28.01% and HH′PP′YY′ which will contribute only 2.84%. However, if we make the reasonable assumption that coupling between the protons on the two methyl groups is negligible as they are at opposite ends of the molecule, we may calculate the spin subsystems and contributions as follows: HPP′, 69.16; HPP′Y, 14.00; HPP′Y′, 14.00; and HPP′YY′, 2.84%. The agreement factors obtained at the end of the refinement are 2.8, 1.7, 1.1 and 2.3% for the ^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$ and $^{199}Hg\text{-}\{^1H\}$ NMR spectra, respectively. The simulated signals are shown as the upper trace of the insets in Fig. 3.



Scheme 2

Although the calculated and observed ^{13}C chemical shifts are in excellent agreement, the observed intensity pattern is not exactly as expected because of the well known limitations which affect quantitative intensity measurements in ^{13}C NMR spectroscopy.[19]

In the experimental ^1H and ^{31}P NMR spectra the satellites are broader and less well resolved than the central resonances as a result of the enhanced spin–lattice relaxation of the ^{199}Hg nucleus *via* chemical shift anisotropy.[20] In order to obtain a satisfactory fit of both the central resonances and the satellites two different sets of values for the linewidth at half height had to be refined, one for the calculation of the subspectra of isotopomers containing the monitored nucleus no more than two bonds away from a ^{199}Hg nucleus and the other when this condition does not apply. Whereas the refined linewidth values of the two ^{13}C nuclei in the methyl groups are not significantly different (4 ± 2 and 2.6 ± 0.1) this is not the case for the ^1H and the ^{31}P spectra. Where a significant coupling with the ^{199}Hg nucleus is present the linewidths are about three times as large as in those spectra where this coupling is absent: 6 ± 2 as against 2.1 ± 0.1 in the case of the ^1H nucleus of the methyl group and 12 ± 1 as against 4.1 ± 0.1 for the ^{31}P nucleus.

Selected spectral parameters of the diphosphine complexes are given in Table 1. The coupling constants $^2J(Hg\text{–}H)$ have values which are comparable with those of other methylmercury(II) phosphine complexes (167–174 Hz).[3] They are slightly higher than those found for thiolate derivatives of RHg^{II} (150–164 Hz).[21] These data are consistent with a decrease in the s character of the C–Hg bond and thus indicate the RHg–P bonds to have a lot of covalent character.

Little data have been published on ^{13}C NMR spectra of organomercury phosphine complexes. It is noteworthy that the ^{13}C resonance of the Me group is found more than 12 ppm to lower field than for the cation $[HgMe\{N(CH_2CH_2PPh_2)_3\}]^+$.[4] Moreover the value of the coupling constant $^2J(P\text{–}C) = 73$ Hz is more than twice the corresponding value for the latter complex (32 Hz). In the case of $[HgPh]^+$ the chemical shift of the carbon atom linked to the metal is virtually the same as that found for the $N(CH_2CH_2PPh_2)_3$ derivative (δ 161 *vs.* 162) whereas the value of $^1J(P\text{–}C)$ is halved on passing from the two- to the four-co-ordinated complex (from 99 to 45 Hz). The ^{13}C chemical shift of the CH_2 group of the ligand dppe is at

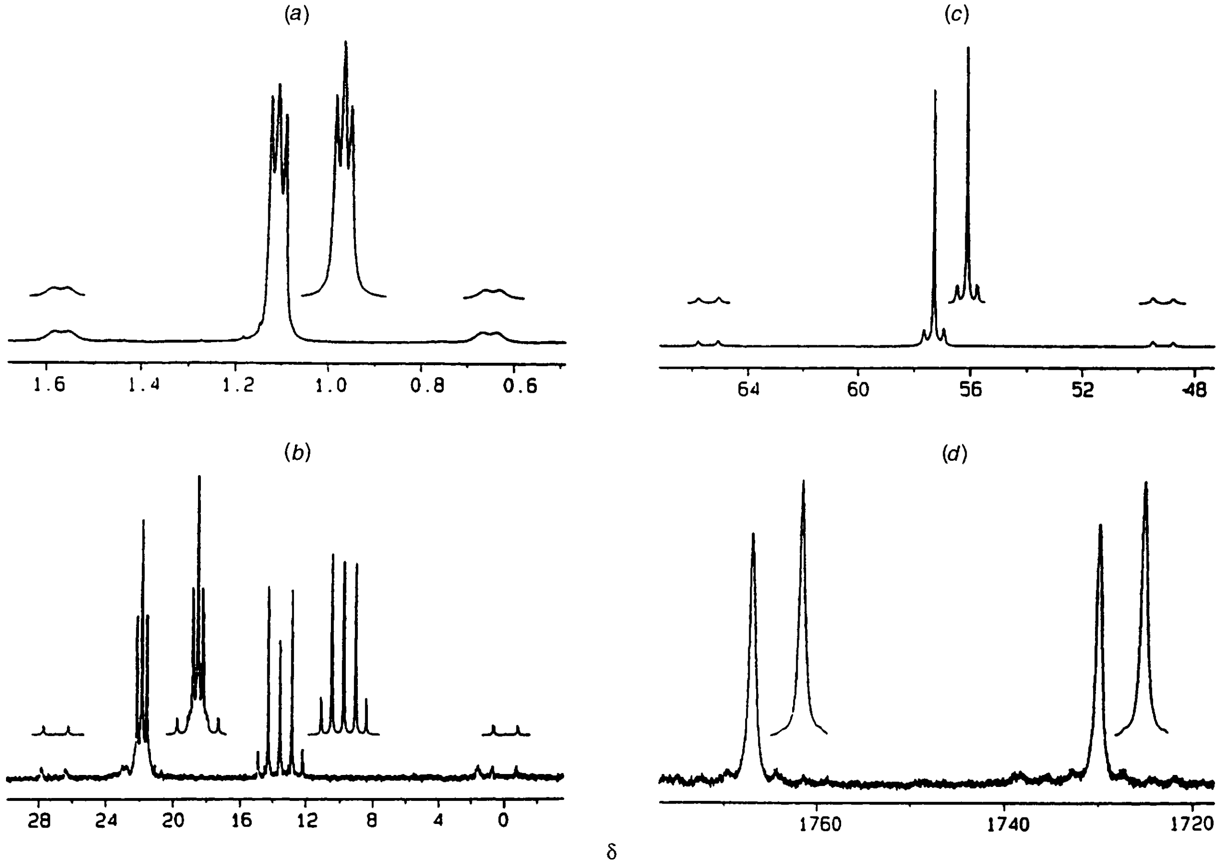


Fig. 3 Experimental (lower) and calculated (upper) NMR spectra of the complex $[MeHg(dppe)HgMe]^{2+}$: (*a*) ^1H (MeHg resonance region), (*b*) ^{13}C-$\{^1H\}$ (MeHg and CH_2 region), (*c*) ^{31}P-$\{^1H\}$ and (*d*) ^{199}Hg-$\{^1H\}$

Table 1 Selected NMR spectral parameters[a] for the dimeric cations $[RHg(L\text{–}L)HgR]$ in CD_2Cl_2 solution

		$[MeHg(dppm)HgMe]^{2+}$ [b]	$[MeHg(dppe)HgMe]^{2+}$ [c]	$[MeHg(dppp)HgMe]^{2+}$ [d]	$[PhHg(dppe)HgPh]^{2+}$ [e]
^1H					
CH_3	δ	0.65 (d with satellites)	1.11 (m with satellites)	1.05 (d with satellites)	
	^2J(Hg–H)	125	183	183	
	^3J(P–H)	6	6.6	6.9	
CH_2	δ	4.9 (t)	3.25 (d)	3.2 (m, PCH_2)	3.4 (s)
				2.1 (m)	
^{13}C-$\{^1H\}$					
HgC	δ	13.5 (m)	13.5 (m)	13.9 (d)	160.7 (m)
	^2J(P–C)	74	73	73	99
CH_2	δ	23.8 (t)	21.9 (t)	27.8, (s, PCH_2)	22.4 (t)
				21.1 (m)	
	^1J(P–C)	23	15		30
^{31}P-$\{^1H\}$					
	δ	50.8 (s with satellites)	57.3 (s with satellites)	55.1 (m with satellites)	50.8 (s with satellites)
	^1J(Hg–P)	1510	1320	1380	2070
	^3J(P–P′)		57		60
^{199}Hg-$\{^1H\}$					
		1760 (d)	1750 (d)	1760 (d)	1390 (d)

[a] Chemical shifts in ppm, coupling constants in Hz. [b] 0.8 mol dm^{-3} Solution of $HgMe^+$ at 253 K. [c] 0.2 mol dm^{-3} Solution of $HgMe^+$ at 298 K. [d] 0.4 mol dm^{-3} Solution of $HgMe^+$ at 298K. [e] 0.2 mol dm^{-3} Solution of $HgPh^+$ at 298K.

significantly higher field for the organomercury complexes as compared to those of other dppe metal complexes such as $[MoX(alkyne)(dppe)_2]$ (X = F, Cl or Br) (δ 28–30).[22]

The ^{31}P chemical shift of the dinuclear complexes are close to that observed for the triphenylphosphine derivative $[HgMe(PPh_3)]^+$ (δ 56.3).[23] The values of the ^1J(Hg–P) coupling constants are higher than those found for the $N(CH_2CH_2PPh_2)_3$ derivatives (60–430 Hz) and comparable with those for other methylmercury monophosphine complexes (PPh_3, 1305;[23] PMe_3, 1875;[3c] PMe_2Ph, 2543[3c] Hz). The coupling constant between the two magnetically non-equivalent phosphorus nuclei [^3J(P–P) = 57 Hz] is significantly higher than those reported for a series of uncomplexed asymmetrical diphosphines containing the dppe backbone (25–30 Hz)[24] and other values, in the range 32–37 Hz, for monobridged dppe carbonyl complexes of Cr, Mo and W.[25]

The ^{199}Hg chemical shifts, shown in Table 1, are lower than those of the $N(CH_2CH_2PPh_2)_3$ complexes (δ 2400–2200). It is interesting that we have been able to determine the coupling constant over five bonds between the two magnetically non-

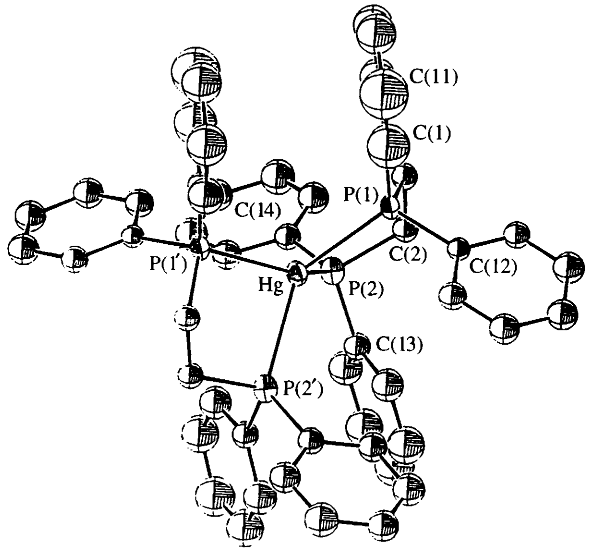


Fig. 4 Perspective view of the complex cation $[Hg(dppe)_2]^{2+}$

Table 2 Crystal data and data-collection details for $[Hg(dppe)_2][O_3SCF_3]_2$

Empirical formula	$C_{54}H_{48}F_6HgO_6P_4S_2$
M	1295.58
T/K	293(2)
λ/Å	0.710 70
Crystal system	Orthorhombic
Space group	*Pbcn*
a/Å	17.141(3)
b/Å	20.158(3)
c/Å	15.614(9)
U/Å^3	5395.1(11)
Z	4
D_c/Mg m^{-3}	1.595
μ/mm^{-1}	3.118
Transmission factors (%)	73.78–98.70
$F(000)$	2584
Crystal size/mm	0.50 × 0.45 × 0.20
Scan speed/° min^{-1}	1.10–8.24
Scan width	0.70 + 0.35 tan θ
Scan method	ω–2θ
Background time	Half scan time
Standards (maximum deviation in %)	3 every 2 h (< 3)
θ Range for data collection/°	2.61–22.47
hkl Ranges	0–18, 0–21, 0–16
Reflections collected	3930
Independent reflections	3506 (R_{int} = 0.0000)
Data, restraints, parameters	3506, 0, 112
Goodness of fit on F^2	1.048
Final $R1$ and $wR2$ indices [$I > 2\sigma(I)$]	0.0643, 0.1452
(all data)	0.1230, 0.1828
Largest difference peak and hole/e Å^{-3}	1.268, −1.132

equivalent mercury-199 nuclei in $[MeHg(dppe)HgMe]^{2+}$. The refined value, ^5J(Hg–Hg) = 86 ± 17 Hz, is, notwithstanding the relatively high estimated error, significantly large for such long-range coupling.

Structure of the complex $[Hg(dppe)_2][O_3SCF_3]_2$

The molecular structure of this compound consists of $[Hg(dppe)_2]^{2+}$ cations and $[CF_3SO_3]^-$ anions. Fig. 4 shows a perspective view of the complex cation. Bond distances and angles are given in Table 3.

Table 3 Selected bond lengths (Å) and angles (°)

Hg–P(1)	2.512(4)	P(2)–C(13)	1.810(10)
Hg–P(2)	2.613(4)	P(2)–C(14)	1.814(8)
P(1)–C(11)	1.807(10)	P(2)–C(2)	1.83(1)
P(1)–C(12)	1.817(7)	C(1)–C(2)	1.51(2)
P(1)–C(1)	1.82(1)		
P(1)–Hg–P(2)	83.0(1)	C(11)–P(1)–C(1)	104.9(6)
P(1)–Hg–P(1′)	119.3(2)	C(12)–P(1)–C(1)	107.3(6)
P(1)–Hg–P(2′)	136.0(1)	Hg–P(2)–C(13)	113.5(4)
P(2)–Hg–P(2′)	107.6(2)	Hg–P(2)–C(14)	123.7(4)
Hg–P(1)–C(11)	119.4(4)	Hg–P(2)–C(2)	100.7(5)
Hg–P(1)–C(12)	114.7(3)	C(13)–P(2)–C(14)	105.5(5)
Hg–P(1)–C(1)	102.7(5)	C(13)–P(2)–C(2)	102.2(6)
C(11)–P(1)–C(12)	106.7(5)	C(14)–P(2)–C(2)	109.2(6)

Symmetry transformation used to generate equivalent atoms: ′ $-x, y, -z + \frac{1}{2}$.

In the complex cation the mercury atom lies on a two-fold axis and is in a distorted-tetrahedral configuration. The distortion is mainly attributable to the chelating nature of the dppe ligand which has particular steric and electronic requirements. The angle P(1)–Hg–P(2) is only 83.0(2)°. This value is clearly much less than the ideal one but it falls however in the range of values reported for other chelating five-membered rings {see for example the [Hg(*cis*-$Ph_2PCH{=}CHPPh_2)Br_2$] complex, where the P–Hg–P angle is 80.5(1)°[26]}. Furthermore, the P(1)–Hg–P(1′) angle of 119.3(2)° is significantly larger than P(2)–Hg–P(2′) [107.6(2)°]. Assuming that no residual absorption error has affected the final atomic parameters, this deformation seems to be responsible for the different Hg–P bond distances, 2.512(4) and 2.613(4) Å for Hg–P(1) and Hg–P(2) respectively (sum of the covalent radii, 2.58 Å[27]). An increase in the P–Hg–P angle leads to an increase of the metal–ligand overlap population and consequently to stronger bonds.[28] None of the intermolecular contact distances is unusual.

Interestingly in the unique reported structure of a mercury complex containing four phosphorus donor atoms, *i.e.* the $[Hg(PMe_2Ph)_4]^{2+}$ cation,[29] the Hg–P(1) and Hg–P(2) distances display values of 2.53 and 2.55 Å, with corresponding bond angles P(1)–Hg–P(1′) and P(2)–Hg–P(2′) of 111.8 and 102.4° respectively. In the latter complex the other four angles of the polyhedron are close to the tetrahedral value, owing to the nature of the monotertiary phosphine, which does not impose any steric constraints on the structure.

Acknowledgements

We gratefully acknowledge the financial support of EU for the HCM programme Metals and Environmental Problems (1995–1997). Thanks are also due to Mr. Francesco Nuzzi for technical assistance.

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Received 18*th December* 1995; *Paper* 5/08204H