Synthesis and NMR spectroscopy of $[\text{t-Bu}_2\text{PHg}(\mu\text{-PPh}_2)\text{M(CO)}_5]$, M = Cr, Mo, W and X-ray structure for M = Cr, W

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Abstract

The title complexes (M = Cr (1), Mo (2) and W (3)) are prepared in almost quantitative yield from $[\text{t-Bu}_2\text{PHgN(SiMe}_3)_2]$ and $[\text{M(HPPh}_2)(\text{CO})_5]$ or in 70% yield by synproportionation of $[\text{Hg(t-Bu}_2\text{P})_2]$ and $[\text{Hg}\{(\mu\text{-PPh}_2)\text{M(CO)}_5\}_2]$. The compounds are crystalline, air-stable in the solid state but oxygen-sensitive in solution. The solid state structures of 1 and 3 consist of dimers containing four-membered $(\text{Hg–P})_2$ rings with asymmetric phosphido bridges (252.2(2) pm and 268.9(2) pm for 1). The coordination geometry of Hg is almost planar. According to ^{31}P and ^{199}Hg NMR spectroscopy, the solution structure consists of dimers at 173 K, whilst dissociation into monomers occurs at ambient temperature. © 1997 Elsevier Science S.A.
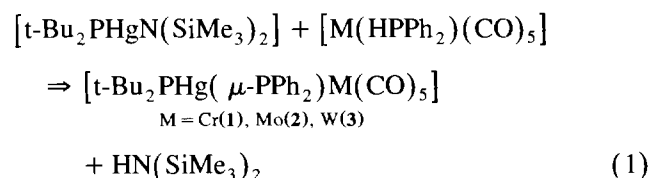
1. Introduction

The bonding mode of the phosphido group in mercury complexes $[\text{R}_2\text{PHgX}]$ depends on the nature of X. Terminal phosphido groups are present in $[\text{Hg(t-Bu}_2\text{P})_2]$ which was described as having a two-coordinate linear geometry in the solid state [1]. A similar structure was reported for $[\text{Hg}\{(\text{Me}_3\text{Si})_2\text{P}\}_2]$ [2]. Both complexes are monomeric in solution. The solution phase structure of $[\text{t-Bu}_2\text{PHgN(SiMe}_3)_2]$ also contains terminal dibutylphosphido ligands [3]. Bridging phosphido ligands are formed in compounds $[\text{R}_2\text{PHgX}]$, where X causes sufficient acceptor qualities of the mercury centre. Six-, eight- and ten-membered rings, whose cores are comprised of alternating Hg and P atoms were shown to be present for $\text{X} = \text{O}_3\text{SCF}_3^-$, SO_4^{2-} and the triazenato ligand $(2\text{-FC}_6\text{H}_4)_2\text{N}_3^-$ [4–6]. These structures were derived from ^{31}P and ^{199}Hg solution NMR spectroscopy, but no solid state structures have been determined. We report here on the synthesis, the solution and solid state structures of $[\text{t-Bu}_2\text{PHg}(\mu\text{-PPh}_2)\text{M(CO)}_5]$, M = Cr, Mo, W.
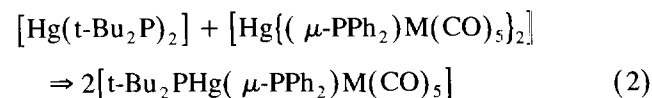
2. Results and discussion

2.1. Synthesis

The asymmetric dinuclear phosphido complexes 1–3 were obtained at ambient temperature by the substitution reaction of Eq. (1) in quantitative yield.

$$[\text{t-Bu}_2\text{PHgN(SiMe}_3)_2] + [\text{M(HPPh}_2)(\text{CO})_5]$$
$$\Rightarrow [\text{t-Bu}_2\text{PHg}(\mu\text{-PPh}_2)\text{M(CO)}_5]$$
$$\text{M} = \text{Cr(1), Mo(2), W(3)}$$
$$+ \text{HN(SiMe}_3)_2 \qquad\qquad (1)$$

The synthetic strategy of Eq. (1), the proton transfer reaction from HP functions to N(SiMe₃)₂ ligands coordinated to mercury and other metals [2] has previously been applied in the synthesis of $[\text{Hg}\{(\mu\text{-PPh}_2)\text{M(CO)}_5\}_2]$ [7], $[\text{Hg(t-Bu}_2\text{P})_2]$ and $[\text{t-Bu}_2\text{PHgN(SiMe}_3)_2]$ [3]. A more recent example is the formation of $[\text{Hg}\{(\text{Me}_3\text{Si})_2\text{P}\}_2$ [2].

An alternative pathway is the synproportionation Eq. (2).

$$[\text{Hg(t-Bu}_2\text{P})_2] + [\text{Hg}\{(\mu\text{-PPh}_2)\text{M(CO)}_5\}_2]$$
$$\Rightarrow 2[\text{t-Bu}_2\text{PHg}(\mu\text{-PPh}_2)\text{M(CO)}_5] \qquad (2)$$

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Table 1
Crystal data for (1) and (3): M = Cr for (1), W for (3)

	(1)	(3)
Molecular formula	$C_{50}H_{56}Cr_2Hg_2O_{10}P_4$	$C_{50}H_{56}Hg_2O_{10}P_4W_2$
Formula weight	1446.01	1709.7
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (No.2)	$P\bar{1}$ (No. 2)
Unit cell dimensions		
a (pm)	1073.9(2)	1077.3(3)
b (pm)	1086.7(1)	1094.8(2)
c (pm)	1233.3(2)	1240.1(3)
α (deg)	96.00(1)	95.99(2)
β (deg)	94.50(1)	94.08(2)
γ (deg)	99.96(1)	100.26(2)
Volume (nm^3)	1.4029(4)	1.4253(6)
Z	1	1
Temperature (K)	223(2)	213(2)
Density (calculated) ($Mg\,m^{-3}$)	1.712	1.992
Absorption coefficient (mm^{-1})	5.997	9.554
Color, habit	yellow, prism	yellow, prism
Crystal size (mm^3)	$0.5 \times 0.3 \times 0.25$	$0.3 \times 0.15 \times 0.09$

The equilibrium was found to lie to the right of the asymmetric species. The products were isolated as yellow crystalline air-stable solids. Solutions of 1–3 are oxygen sensitive and are converted to the corresponding dibutylphosphinito complexes 1a–3a (Eq. (3)) which were characterised by ^{31}P NMR spectroscopy.

$$2[t\text{-}Bu_2PHg(\mu\text{-}PPh_2)M(CO)_5] + O_2$$
$$\Rightarrow 2[t\text{-}Bu_2P(O)Hg(\mu\text{-}PPh_2)M(CO)_5] \quad (3)$$
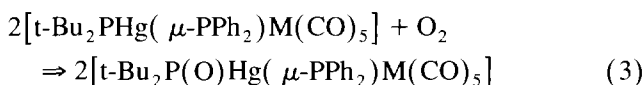
2.2. Solid state structure

Compounds 1 and 3 were characterised by single crystal X-ray diffraction. Crystal data are collected in

Table 2
Distances (pm) and bond angles (deg) for (1) and (3): M = Cr for (1), W for (3)

	(1)	(3)
Hg(1)–P(1)	245.1(2)	244.7(3)
Hg(1)–P(2)	252.2(2)	252.6(3)
Hg(1)–P(2a)	268.9(2)	266.0(3)
M(1)–P(1)	243.0(2)	255.2(3)
M(1)–C(1)	190.5(9)	208.0(13)
M(1)–C(5)	186.3(8)	199.5(13)
P(1)–Hg(1)–P(2)	148.52(6)	147.73(10)
P(1)–Hg(1)–P(2a)	124.95(5)	125.78(9)
P(2)–Hg(1)–P(2a)	86.53(5)	86.48(9)
M(1)–P(1)–Hg(1)	116.76(7)	115.74(11)
P(1)–M(1)–C(5)	175.7(3)	175.1(4)
P(1)–M(1)–C(4)	91.3(2)	92.4(3)
P(1)–M(1)–C(3)	89.1(3)	95.9(3)
P(1)–M(1)–C(2)	95.0(2)	89.3(3)
P(1)–M(1)–C(1)	86.7(2)	85.4(3)
C(6)–P(1)–C(12)	100.3(3)	100.5(5)
C(19)–P(2)–C(18)	112.6(3)	112.8(5)

Table 1, relevant distances and angles are given in Table 2. The chromium and tungsten complexes 1 and 3 are strictly isostructural. The molecular structure of 1 is shown in Fig. 1. In the solid state two $[t\text{-}Bu_2PHg(\mu\text{-}PPh_2)M(CO)_5]$ units are associated in a pairwise fashion about a crystallographic inversion centre. The resulting four-membered $(Hg\text{-}P)_2$ ring is substantially asymmetric. The short Hg–P bridge distance is 252.2(2) pm, the longer one amounts to 268.9(2) pm. This is distinctly longer than the Hg–P bond lengths in $[Hg(t\text{-}Bu_2P)_2$ (244.2(3) and 245.1(3) pm) [1]. The value of 268.9 pm exceeds the sum of the covalent radii (258 pm) [8]. An Hg–P distance of 261.3(4) pm has recently been reported for the complex $[Hg(dppe)_2](O_3SCF_3)_2$ (dppe = bis(diphenylphosphino)ethane) [9].

Even longer Hg–P distances, namely 316 pm in $[Hg(t\text{-}Bu_2P)_2]$ and 324.6(1) pm in $[Hg\{(Me_3Si)_2P\}_2$, were proposed to correspond to secondary interactions [2], which exist only in the solid state (vide infra). These are only slightly below the van der Waals sum of 335 pm. The different bonding lengths in the four-membered $(Hg\text{-}P)_2$ rings of 1 and 3 are accompanied by different P–Hg–P angles where the shorter Hg–P distance is involved in the larger P–Hg–P angle (148.52(6)°). An increase in the P–Hg–P angle leads to an increase of the metal–ligand overlap population and consequently to stronger bonds [10]. The Hg–PPh$_2$ separation is 245.1(2) pm. This is slightly longer than for $[Hg\{(\mu\text{-}PPh_2)Cr(CO)_5\}_2]$ for which 242.7(2) and 243.0(2) pm were observed [11]. The overall geometry of mercury is distorted trigonal planar: the mercury centre is 0.8 pm out of the plane defined by the three adjacent phosphorus atoms, but the P–Hg–P angles are not equal to 120°.
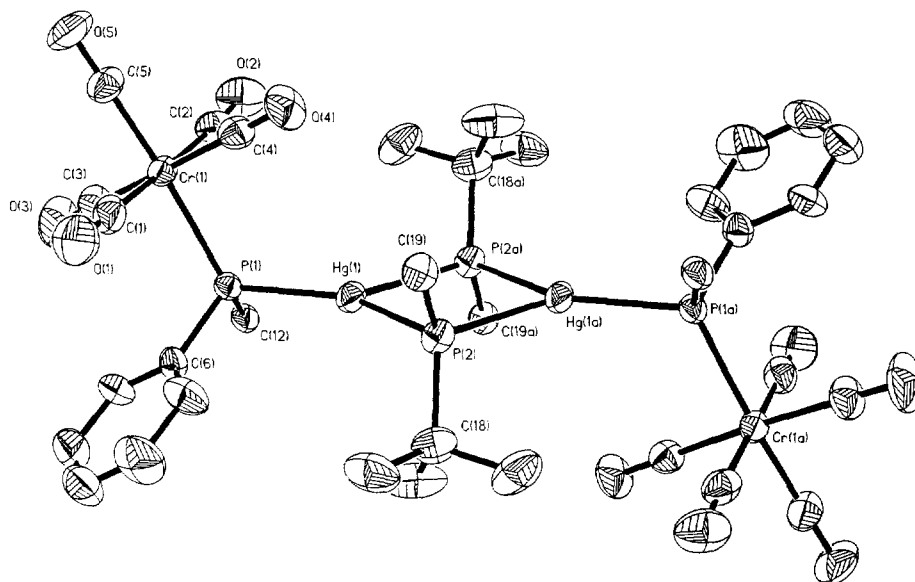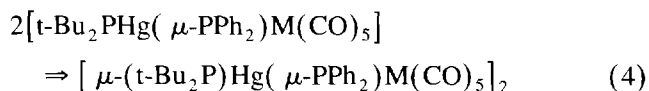
Fig. 1. Molecular structure of **1**.

The mercury–mercury separation is 378.12 pm, which excludes any Hg–Hg interaction.

2.3. NMR spectroscopy

The NMR patterns of **1** recorded at 173 K are consistent with a dimeric structure involving symmetric dibutyl-phosphido bridges. The equivalence of the t-Bu$_2$P–Hg bonds may be the consequence of fluxional behaviour at this temperature. NMR spectra at even lower temperatures were, however, precluded by an insufficient solubility. The ^{199}Hg NMR spectrum of the isotopomer containing one ^{199}Hg nucleus (abundance 28.01%) shows interactions to two equivalent dibutyl-phosphido-phosphorus atoms and to two PPh$_2$-phosphorus atoms via one and three bonds respectively. The value of ^1J HgP involving the dibutyl-phosphido ligands (201 Hz) is extraordinary small when compared to a range of 125 to 17528 Hz for one bond couplings between ^{199}Hg and ^{31}P [12,13]. This is probably related to the decreased s-character of the mercury–dibutyl-phosphido bond as a result of a weak coordination to the second Hg. In this context the Hg–P coupling constants of [Hg(t-Bu$_2$P)$_2$] and [Hg{(Me$_3$Si)$_2$P}$_2$] would be of interest. These were, however, not observed, presumably because of intermolecular phosphido-group exchange. The ^{31}P NMR spectrum consists of two resonances flanked by ^{199}Hg satellites. The assignment to the dibutyl and diphenyl-phosphido groups was readily done according to the values of the Hg–P coupling constants. Full NMR data are given in Section 3.

The NMR spectra are strongly temperature dependent. At ambient temperature, the ^{31}P signal of the dibutyl-phosphido groups is broadened ($W_{1/2} = 60$ Hz) and shows no ^{199}Hg satellites. The chemical shift moves

ca. 50 ppm to low frequencies. This is attributed to the equilibrium Eq. (4)

$$2[\text{t-Bu}_2\text{PHg}(\ \mu\text{-PPh}_2)\text{M(CO)}_5]$$
$$\Rightarrow [\ \mu\text{-(t-Bu}_2\text{P})\text{Hg}(\ \mu\text{-PPh}_2)\text{M(CO)}_5]_2 \qquad (4)$$

which appears to lie to the right at 173 K whereas at ambient temperature dissociation to the monomer takes place. The temperature dependence of the chemical shift is rationalised by a positive coordination shift which is usually observed for Hg complexes with phosphine ligands. The temperature dependence of the ^{31}P shift may also reflect changes in angles and stereochemistry at the phosphorus atom as a result of the formation of the four-membered (HgP)$_2$ ring [14,15]. The presence of only one signal for the dibutyl-phosphido ligands of the monomer and dimer demonstrates the interconversion of these species on the NMR time scale. The absence of Hg satellites indicates intermolecular dibutyl-phosphido ligand exchange. It is interesting to note that the ^{31}P NMR spectra of [Hg{(Me$_3$Si)$_2$P}$_2$] are consistent with a monomeric solution phase structure and were temperature invariant in the range of −78 to +70 °C [2].

3. Experimental section

3.1. Physical measurements

NMR spectra were recorded on Bruker WP 80 and AC 200 instruments. ^{31}P shifts are referenced against 85% H$_3$PO$_4$, ^{199}Hg chemical shifts are positive to high frequency of an aqueous Hg(ClO$_4$)$_2$ solution (2 mmol HgO/1 cm^3 60% HClO$_4$). Microanalyses were per-

formed on a Heraeus EA 415 apparatus. Mass spectra were obtained on a Varian Mat CH7 (70 eV).

3.2. Preparation of the compounds

[t-Bu$_2$PHgN(SiMe$_3$)$_2$] [3], [M(HPPh$_2$)(CO)$_5$] [16], [Hg(t-Bu$_2$P)$_2$] [3,17] and [Hg{(μ-PPh$_2$)M(CO)$_5$}$_2$] [7] were prepared according to published procedures. The following reactions were carried out under an atmosphere of dinitrogen.

3.2.1. [t-Bu$_2$PHg(μ-PPh$_2$)M(CO)$_5$]

(a) Samples of [Hg{(μ-PPh$_2$)M(CO)$_5$}$_2$] (0.72 mmol) and of [Hg(t-Bu$_2$P)$_2$] (355 mg, 0.72 mmol) were suspended in toluene (CH$_2$Cl$_2$ for M = Mo) (5 ml). The suspension is heated while stirring until a clear solution is obtained. Upon cooling the product crystallises as yellow needles in ca. 70% yield. The molybdenum complex 2 crystallises as the CH$_2$Cl$_2$ adduct (2 · 0.5CH$_2$Cl$_2$). The CH$_2$Cl$_2$ content has been determined by ^{1}H NMR and can be readily removed in vacuo.

1: m.p. 156 °C (decomp.). Anal. Found: C, 41.4; H, 3.7; O, 10.6. C$_{25}$H$_{28}$CrHgP$_2$O$_5$. Calcd.: C, 41.53; H, 3.90; O, 11.06. MS: 722, [M$^+$]. ^{31}P{^{1}H} NMR (− 100 °C, ambient temperature in parentheses, CD$_2$Cl$_2$): 172.4(122.4) (Bu$_2$P, ^1JHgP = 201 Hz, ^2JPP = 50 Hz), 55.4(68.7) (Ph$_2$P, ^1JHgP = 1545 Hz, ^3JHgP = 104 Hz). ^{199}Hg{^{1}H} NMR (− 100 °C, ambient temperature in parentheses, CD$_2$Cl$_2$): 2225(1785).

2: m.p. 122 °C (decomp.). Anal. Found: C, 39.1; H, 3.7; O, 10.2. C$_{25}$H$_{28}$HgMoP$_2$O$_5$. Calcd.: C, 39.15; H, 3.68; O, 10.43. MS: 727, [M − C$_3$H$_5^+$]. ^{31}P{^{1}H} NMR (− 100 °C, ambient temperature in parentheses, CD$_2$Cl$_2$): 167.8(122.5) (Bu$_2$P), 32.9(42.6) (Ph$_2$P).

3: m.p. 130 °C (decomp.). Anal. Found: C, 35.1; H, 3.4; O, 9.4. C$_{25}$H$_{28}$HgP$_2$O$_5$W. Calcd.: C, 35.12; H, 3.30; O, 9.36. MS: 854, [M$^+$]. ^{31}P{^{1}H} NMR (− 100 °C, ambient temperature in parentheses, CD$_2$Cl$_2$): 170.3(122.8) (Bu$_2$P), 12.1(22.8) (Ph$_2$P). ^{199}Hg{^{1}H} NMR (− 100 °C, CD$_2$Cl$_2$): 2234.

(b) Equimolar amounts of [t-Bu$_2$PHgN(SiMe$_3$)$_2$], and [M(HPPh$_2$)(CO)$_5$] are mixed in toluene. The reaction is complete at ambient temperature within 1 h. The solvent and HN(SiMe$_3$)$_2$ is removed in vacuo leaving the product in quantitative yield.

^{31}P{^{1}H} NMR data of the phosphinito complexes (ambient temperature, CD$_2$Cl$_2$); 1a: 145.1 (Bu$_2$PO, ^2JPP = 133 Hz), 52.7 (Ph$_2$P); 2a: 144.8 (Bu$_2$PO, ^2JPP = 127 Hz), 30.2 (Ph$_2$P); 3a: 144.6 (Bu$_2$PO, ^2JPP = 137 Hz), 10.2 (Ph$_2$P).

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