Synthesis of the Compounds $[Hg\{PPh_2[M(CO)_5]\}_2]$ (M = Cr, Mo, or W)

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The stable title compounds have been prepared by mercuriation of $[M(CO)_5(PPh_2H)]$ using $Hg[N(SiMe_3)_2]_2$ and characterized by ^{31}P and ^{199}Hg n.m.r. and mass spectroscopy. The values of $^1J(^{31}P-^{199}Hg)$ (525—725 Hz) are the smallest observed so far for Hg–P bonds.

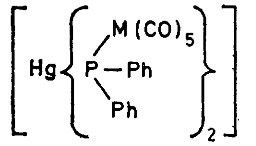
THE sole stable phosphidomercury compound reported so far[1] is $[Hg(PBu^t_2)_2]$. Attempts to prepare various other phosphidomercury compounds have resulted in the formation of elemental mercury and the corresponding P–P bonded product,[1,2] presumably by homolytic fission of intermediate Hg–P bonds.[1] This reaction has been used[1] as a high-yield preparative route to diphosphines, equation (1).

$$HgBu^t_2 + 2PR_2H \longrightarrow [Hg(PR_2)_2] \longrightarrow (PR_2)_2 + Hg \quad (1)$$

We have found that Hg–P bonds of phosphidomercury compounds are stabilized when the phosphorus atoms are co-ordinated to low-valent transition-metal compounds. Hence, we report here on the synthesis of three new phosphidomercury compounds using this technique.

RESULTS AND DISCUSSION

The novel hetero-trinuclear phosphido-bridged compounds (1)—(3) were prepared according to a versatile synthetic route for Hg–P bonded compounds[3] by mercuriation of the corresponding phosphines, $[M(CO)_5(PPh_2H)]$, using the mercury(II) 'salt' of bis(trimethylsilyl)amine, equations (2) and (3). The products (1)—(3) are formed in a smooth reaction (ambient temperature or faster by gentle warming in toluene) *via* the asymmetric mercury intermediates (1a)—(3a) [equation (2)] which were detected by following the reaction with n.m.r. spectroscopy. Compounds (1)—(3) were isolated as stable yellow crystals, soluble in common organic solvents. Compounds (1) and (3) melt with only slight decomposition, but considerable formation of elemental mercury is observed for the molybdenum complex (2).


(1; M = Cr)
(2; M = Mo)
(3; M = W)

$$Hg[N(SiMe_3)_2]_2 + [M(CO)_5(PPh_2H)] \longrightarrow [(Me_3Si)_2NHg(PPh_2)M(CO)_5] + NH(SiMe_3)_2 \quad (2)$$

(1a; M = Cr)
(2a; M = Mo)
(3a; M = W)

$$[(Me_3Si)_2NHg(PPh_2)M(CO)_5] + [M(CO)_5(PPh_2H)] \longrightarrow [Hg\{PPh_2[M(CO)_5]\}_2] + NH(SiMe_3)_2 \quad (3)$$

Phosphorus-31 and ^{199}Hg n.m.r. data for (1)—(3) confirm the structures by showing the expected coupling patterns (^{199}Hg: $I = \frac{1}{2}$, 16.8%) and are given in Table 1.

TABLE 1

N.m.r. parameters for $[M(CO)_5(PPh_2H)]$ and $[Hg\{PPh_2[M(CO)_5]\}_2]$ [a]

	$[M(CO)_5(PPh_2H)]$ [b]	$[Hg\{PPh_2[M(CO)_5]\}_2]$ [c]		
M	$\delta(^{31}P)$	$\delta(^{31}P)$	$\delta(^{199}Hg)$	$^1J(^{31}P-^{199}Hg)$
Cr	30.5	77.2	1 278	640
Mo	4.2	50.5	1 290	525
W	−16.0 [d]	27.4 [e]	1 293	725

[a] In p.p.m. to high frequency of 85% H_3PO_4 or aqueous $Hg[ClO_4]_2$ (2 mmol HgO per cm³ of 60% $HClO_4$), coupling constants in Hz. [b] 1 mol dm⁻³ in toluene. [c] 0.125 mol dm⁻³ in CH_2Cl_2. [d] $^1J(^{31}P-^{183}W) = 229$ Hz. [e] $^1J(^{31}P-^{183}W) = 148$ Hz.

Substitution of H by Hg in the phosphines $[M(CO)_5(PPh_2H)]$ is associated with a shift of $\delta(^{31}P)$ to high frequency as has been observed for other P–H systems (Table 2). There seems to be a rough correlation between this shift and $^1J(^{31}P-^{199}Hg)$ (Table 2). The relatively high chemical shift of $[Hg(PBu^t_2)_2]$ is possibly due to intermolecular Hg–P co-ordination, which is known to shift $\delta(^{31}P)$ of the ligand to high frequency.[4]

TABLE 2

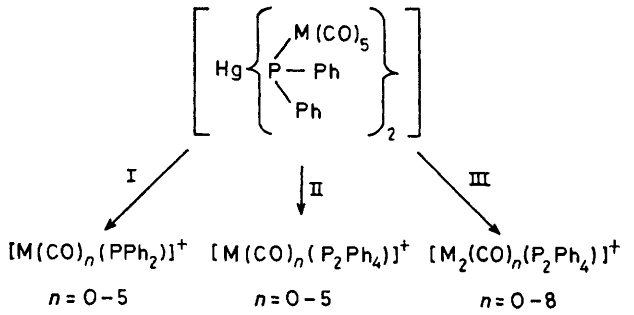
N.m.r. parameters for HgL_2 [a]

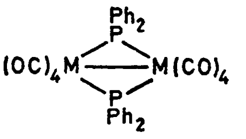
L	$\Delta\delta(^{31}P)$ [b]	$^1J(^{31}P-^{199}Hg)$	$\delta(^{199}Hg)$	Ref.
$P(OEt)_2O$	101.3	7 347	1 294	*c, d*
$PPh(OBu^n)O$	92.9	5 310	1 217	*d*
PBu^t_2O	77.0	2 945	1 511	*e*
PBu^t_2	81.6	*f*	2 128	1, 3
$PPh_2[Cr(CO)_5]$	46.7	640	1 278	This work

[a] In p.p.m. to high frequency of aqueous $Hg[ClO_4]_2$ (2 mmol HgO per cm³ of 60% $HClO_4$), coupling constants in Hz. [b] $\delta(HgL_2) - \delta(HL)$. [c] J. Benett, A. Pidcock, C. R. Waterhouse, P. Coggon, and A. T. McPhail, *J. Chem. Soc. A*, 1970, 2094. [d] J. Eichbichler and P. Peringer, *Inorg. Chim. Acta*, 1980, **43**, 121. [e] P. Peringer and J. Eichbichler, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2033. [f] No coupling observed, presumably due to intermolecular PBu^t_2 exchange (see ref 3).

The ^{199}Hg chemical shifts of (1)—(3) were found in the region typical for other symmetric Hg–P species (Table 2). However, $\delta(^{199}Hg)$ of $[Hg(PBu^t{}_2)_2]$ is outside this range, presumably indicating again the presence of intermolecular Hg–P co-ordination, which is expected to shift $\delta(^{199}Hg)$ to high frequency.[4,5] The one-bond phosphorus–mercury coupling constants are among the smallest observed so far for Hg–P bonds; $^1J(^{31}P-^{199}Hg)$ of HgL_2 decreases in the order L = phosphito > phosphonito > phosphinito > phosphido (Table 2), *i.e.* electronegative substitution at the phosphorus atom causes $^1J(^{31}P-^{199}Hg)$ to increase, as has been reported for platinum complexes.[6] The small coupling constants of (1)—(3) are expected to be accompanied by a rather large Hg–P bonding distance.[7] It is interesting to note that the value of $^1J(^{31}P-^{199}Hg)$ for (1)—(3) does not vary progressively within Group 6B, but is smallest for the molybdenum and largest for the tungsten compound. Substitution of H by Hg in $[W(CO)_5(PPh_2H)]$ causes a considerable decrease in $^1J(^{31}P-^{183}W)$ (Table 1).

The mass spectra of (1)—(3) showed no molecular ions. Three main fragmentation or decomposition pathways according to the scheme below were observed. At low temperatures fission of the Hg–P bonds of (1)—(3) yields the species $[M(CO)_n(PPh_2)]^+$ (n = 0—5) and Hg (pathway I). At higher temperatures, around the melting points, a mononuclear $M(CO)_5$ complex (M = Cr, Mo, or W) of tetraphenyldiphosphane is formed as well as ions $[M(CO)_n(P_2Ph_4)]^+$, n = 0—5, corresponding to successive loss of CO (pathway II). In a third decomposition pathway for (2) and (3), peaks corresponding to $[M_2(CO)_n(P_2Ph_4)]^+$, n = 0—8, appear. These could either be due to fragments of the binuclear complexes $[(OC)_5M(Ph_2PPPh_2)M(CO)_5]$ or, in view of the maximum value of n being 8, to the four-membered M–M bonded phosphido-bridged species depicted below. All peaks displayed patterns corresponding to the polyisotopic elements contained in the appropriate fragments.





No triphenylphosphine co-ordination complexes of (1)—(3) are formed down to 173 K. This could either reflect very weak acceptor qualities of the Hg atoms or be due to steric reasons.

According to preliminary results, (1)—(3) are also formed by reaction of the metallated phosphines $[Li\{PPh_2[M(CO)_5]\}]$ with mercury(II) compounds, and compounds analogous to (1)—(3) are formed with other transition metals and phosphines.

EXPERIMENTAL

The n.m.r. spectra were recorded on a Bruker WP-80 spectrometer operating in the Fourier-transform mode, the mass spectra on a Varian MAT CH7, and the i.r. spectra on a Perkin-Elmer 180 instrument. Chemical analyses were obtained with a Heraeus EA 415.

All reactions were carried out in dried solvents under dinitrogen. The compounds $[M(CO)_5(PPh_2H)]$ (M = Cr, Mo, or W) and $Hg[N(SiMe_3)_2]_2$ were prepared according to the literature.[8,9]

Preparation of $[Hg\{PPh_2[Mo(CO)_5]\}_2]$ (2).—The compounds $[Mo(CO)_5(PPh_2H)]$ (422 mg, 1 mmol) and $Hg[N(SiMe_3)_2]_2$ (260 mg, 0.5 mmol) were dissolved in toluene (2 cm^3) and allowed to react at ambient temperature for 10 d. (The reaction may be accelerated by warming to 60 °C.) The solvent and $NH(SiMe_3)_2$ were removed *in vacuo*. Recrystallization from toluene–light petroleum yielded (2) in *ca.* 80% yield, m.p. 142—144 °C (Found: C, 39.1; H, 1.9; O, 15.2. Calc. for $C_{34}H_{20}HgMo_2O_{10}P_2$: C, 39.2; H, 1.9; O, 15.3%), i.r. bands [ν(CO), toluene] at 2 071, 2 068, 1 988, and 1 945br cm^{-1}.

The following compounds were prepared analogously: (1), m.p. 143.5—144.5 °C (Found: C, 42.5; H, 2.1; O, 16.5. Calc. for $C_{34}H_{20}Cr_2HgO_{10}P_2$: C, 42.8; H, 2.1; O, 16.8%), i.r. bands at 2 061, 2 057, 1 982, and 1 943br cm^{-1}; (3), m.p. 160—161 °C (Found: C, 33.7; H, 1.6; O, 12.8. Calc. for $C_{34}H_{20}HgO_{10}P_2W_2$: C, 33.5; H, 1.7; O, 13.1%), i.r. bands at 2 069, 2 066, 1 981, and 1 945br cm^{-1}.

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