

PREPARATION AND NMR SPECTROSCOPY OF $[\text{Hg}\{(\mu\text{-PEt}_2)\text{Cr}(\text{CO})_5\}_3]^-$

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Summary

The new tetranuclear phosphido-bridged compound $[\text{Hg}\{(\mu\text{-PEt}_2)\text{Cr}(\text{CO})_5\}_3]^-$ has been obtained by reaction of $[\text{Hg}\{(\mu\text{-PEt}_2)\text{Cr}(\text{CO})_5\}_2]$ with $\text{Li}[\text{Cr}(\text{CO})_5\text{PEt}_2]$. The coordination of $[\text{Cr}(\text{CO})_5\text{PEt}_2]^-$ results in an unprecedented increase in $J(\text{Hg},\text{P})$, whereas an increase in the number of phosphorus ligands coordinated to mercury is usually accompanied by a decrease in the magnitude of $J(\text{Hg},\text{P})$. This anomaly is interpreted in terms of Cr–Hg donor acceptor interactions.

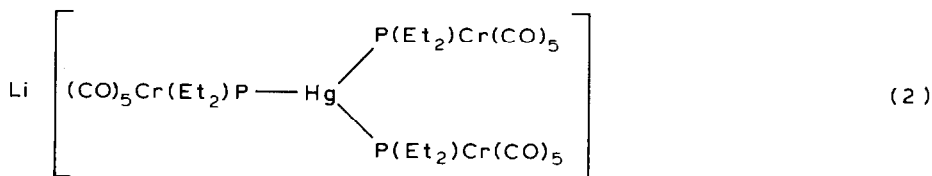
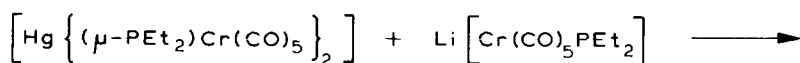
Introduction

The structural flexibility of bridging phosphido ligands is demonstrated by the extremes in the $\text{M}-(\mu\text{-PPh}_2)\text{-M}$ angle of 65 and 116° associated with metal–metal distances of 2.34 and 4.33 Å [1]. Metal–metal interactions may or may not be involved. The diagnosis is often ambiguous, especially when there is no need for a metal–metal bond in electron counting terms. Experimental assignments are based on the metal–metal distance or on the position of the ^{31}P NMR shift of the $\mu\text{-PR}_2$ ligand. Resonances of 50 → 300 ppm imply the presence of metal–metal bonds, whereas values of 50 → –300 ppm are observed when the PR_2 ligands bridge two metal centers not joined by a metal–metal bond [2–6]. Some exceptions are known, however [7,8]. We propose here that the value of the Hg–P coupling constant can provide an additional indicator for metal–metal interactions in phosphido-bridged mercury-transition metal complexes.

Results and discussion

We have previously described the synthesis of heterotrimetallic complexes of the type $[\text{Hg}\{(\mu\text{-PR}_2)\text{M}(\text{CO})_5\}_2]$ where $\text{R} = \text{Ph}$ and $\text{M} = \text{Cr}, \text{Mo}$ and W [9]. Very small Hg–P coupling constants were noted [9] (525–725 Hz depending on M). The coordination of various O and N donor ligands to mercury results in an anomalously large increase in the Hg–P coupling constant (e.g. 2231 Hz for $[\text{Hg}(\text{phen})\{(\mu\text{-$

$\text{PPh}_2\text{W}(\text{CO})_5\}_2$], phen = 1,10-phenanthroline) and in a large shift of the ^{31}P resonance to low frequencies [10]. Homoleptic phosphidomercurates $[\text{Hg}\{(\mu\text{-PPH}_2)\text{M}(\text{CO})_5\}_n]^{2-n}$ with $n=3$ or 4 do not exist. This is attributed to steric factors, since the acceptor ability of the Hg in $[\text{Hg}\{(\mu\text{-PPH}_2)\text{M}(\text{CO})_5\}_2]$ is demonstrated by the formation of other addition complexes, as mentioned above [10]. We therefore used the sterically less demanding bridging group PEt_2 , and were able to obtain the tetranuclear complex **1** by the reactions shown in eqs. 1 and 2.



(1)

NMR data for complex **1** are consistent with the proposed structure: the $^{199}\text{Hg}\{^1\text{H}\}$ NMR spectrum reveals a 1/3/3/1 quartet of signals centered at 2504 ppm, showing that the mercury centre is coupled to three equivalent phosphorus atoms. The coordination of $\text{Li}[\text{Cr}(\text{CO})_5\text{PEt}_2]$ to $[\text{Hg}\{(\mu\text{-PEt}_2)\text{Cr}(\text{CO})_5\}_2]$ is accompanied by a high frequency shift of the ^{199}Hg resonance. Corresponding results were obtained for the addition of halide to HgX_2 to give $[\text{HgX}_3]^-$ [11], and for the addition of a neutral or anionic phosphorus donor ligand (denoted by phos) to $[\text{Hg}(\text{phos})_2]^{2+}$ or $[\text{Hg}(\text{phos})_2]$ to give $[\text{Hg}(\text{phos})_3]^{2+}$ or $[\text{Hg}(\text{phos})_3]^-$ [12–14]. The ^{31}P NMR data for **1** and $[\text{Hg}\{(\mu\text{-PEt}_2)\text{Cr}(\text{CO})_5\}_2]$ are included in Table 1.

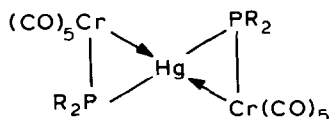
TABLE 1

NMR DATA FOR $[\text{Hg}(\text{phos})_n]^{2+}$ AND $[\text{Hg}(\text{phos})_n]^{2-n}$ ($n = 2,3$)

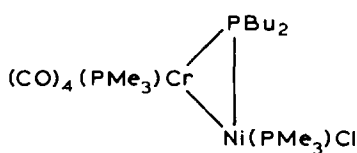
phos	n	$J(\text{Hg,P})$ (Hz)	$\delta(\text{P})$ (ppm)
$(\mu\text{-PEt}_2)\text{Cr}(\text{CO})_5$ ^a	2	751	62.4
	3	921	28.7
PPh_3 ^b	2	5010	
	3	3120	
$\text{P}(\text{OEt})_3$ ^c	2	10645	
	3	6630	

^a This work; solvent THF. ^b From ref. 14. ^c From ref. 13.

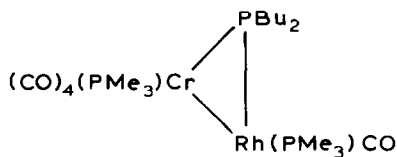
Particularly interesting is the fact that the Hg–P coupling constant for **1** is larger than that of $[\text{Hg}\{(\mu\text{-PEt}_2)\text{Cr}(\text{CO})_5\}_2]$, i.e. the coordination of $[\text{Cr}(\text{CO})_5\text{PEt}_2]^-$ seems to be associated with an increase in the Hg–P coupling constant. In contrast, *all* other complexes of the type $[\text{Hg}(\text{phos})_3]^{2+}$ or $[\text{Hg}(\text{phos})_3]^-$, exhibit smaller $J(\text{Hg},\text{P})$ values than those for of the corresponding complexes $[\text{Hg}(\text{phos})_2]^{2+}$ or $[\text{Hg}(\text{phos})_2]$ [12–14]. Some examples are given in Table 1. This effect arises from the higher degree of *s*-orbital character associated with the $[\text{Hg}(\text{phos})_2]^{2+}$ or $[\text{Hg}(\text{phos})_2]$ species, and has been observed for complexes of other metals. We propose that this anomaly arises from intramolecular mercury–chromium interactions in $[\text{Hg}\{(\mu\text{-PR}_2)\text{Cr}(\text{CO})_5\}_2]$ of the type depicted below, which lead to unexpectedly small



Hg–P coupling constants as discussed below. Lewis acid-base adducts in which a transition metal in a neutral transition metal organometallic compound acts as a donor towards mercury(II) halides, are well known, and have been reviewed recently [15]. The structural formulation involves seven-coordinate chromium atoms. This is less common than for Mo or W, but X-ray structures of the closely related examples $[(\text{CO})_4(\text{PMe}_3)\text{Cr}(\mu\text{-}t\text{-Bu}_2\text{P})\text{Ni}(\text{PMe}_3)\text{Cl}](\text{Cr}\text{--}\text{Ni})$ (**2**) and $[(\text{CO})_4(\text{PMe}_3)\text{Cr}(\mu\text{-}t\text{-Bu}_2\text{P})\text{RhCO}(\text{PMe}_3)](\text{Cr}\text{--}\text{Rh})$ (**3**) have been reported [16].

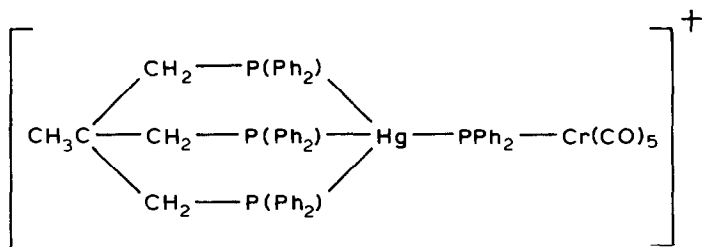


(2)



(3)

We suggest that the Hg–P coupling in $[\text{Hg}\{(\mu\text{-PR}_2)\text{M}(\text{CO})_5\}_2]$ can be divided into $^1J(\text{Hg},\text{P})$ and $^2J(\text{Hg},\text{P})$ contributions. The one-bond Hg–P coupling constant is expected to be near to 3000 Hz. This is based on the value of 3082 Hz observed for $[\text{Hg}\{\eta^3\text{-CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3\}\{(\mu\text{-PPh}_2)\text{Cr}(\text{CO})_5\}]^+$ (**4**) [17], in that type of complex



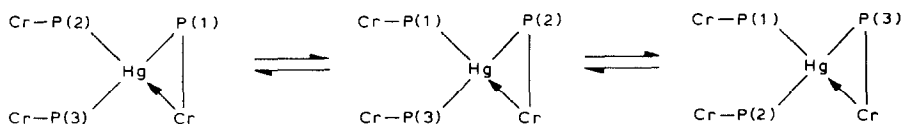
(4)

the mercury is tetracoordinate, and this renders additional Hg–Cr interactions unlikely. The Hg–P coupling constant involving the monodentate phosphorus ligand of other complexes $[\text{Hg}\{\eta^3\text{-CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3\}(\text{phos})]^{2+}$ falls within the

range associated with $[\text{Hg}(\text{phos})_2]^{2+}$ type complexes because of a special hybridization [17]. Two-bond Hg–P coupling constants in a HgMP linkage can be very large [18,19]: values of up to 583 Hz were observed for a HgMP *cis* geometry and those up to 3879 Hz for *trans* geometry. Opposite signs for $^1J(\text{Hg,P})$ and $^2J(\text{Hg,P})$ would account for the very small Hg–P coupling constants in $[\text{Hg}\{\mu\text{-PR}_2\}_2\text{M}(\text{CO})_5\}_2$.

Cleavage of the Cr–Hg donor acceptor bond of $[\text{Hg}\{\mu\text{-PEt}_2\}\text{Cr}(\text{CO})_5\}_2$ by the better donor ligand $[\text{Cr}(\text{CO})_5\text{PEt}_2]^-$ leads to **1**. This results in an increase in $J(\text{Hg,P})$ despite the concomitant reduction of the *s*-character of the Hg–P bonds, because of the elimination of the two bond Hg–P coupling contribution. Other work has shown that metal–metal donor acceptor bonds in heterobimetallic phosphido-bridged complexes can be cleaved by a variety of nucleophiles [20].

It is not known if a Hg–Cr interaction is still present in **1**; mercury can achieve a maximum coordination number of 4 when 3 phosphorus donor ligands are involved. On the other hand, the acceptor ability of Hg is certainly reduced on going from $[\text{Hg}(\text{phos})_2]$ to $[\text{Hg}(\text{phos})_3]^-$, but complexes of the type $[\text{Hg}(\text{phos})_4]^{2-}$ are known [12]. The equivalence of the phosphorus ligands in **1** demonstrates that any Hg–Cr interaction must be fluxional on the NMR time scale as in the scheme below (the substituents on P and Cr are omitted):



A decision on whether any Hg–Cr interaction is still present must await an X-ray study or the availability of NMR data for a compound of the type $[\text{Hg}\{\mu\text{-PR}_2\}_4\text{M}(\text{CO})_5\}_4]^{2-}$.

Experimental

$\text{Cr}(\text{CO})_5\text{PEt}_2\text{H}$ ($\delta(\text{P})$ 14.5 ppm, $J(\text{P,H})$ 322 Hz) and $[\text{Hg}\{\mu\text{-PEt}_2\}\text{Cr}(\text{CO})_5\}_2$ were prepared by published procedures [9,21]. All other reagents were supplied commercially. All manipulations were performed in dried solvents under N_2 .

NMR spectra were recorded on a Bruker WP-80 spectrometer, chemical shifts are in ppm (with positive shifts to high frequency) relative to external 85% H_3PO_4 or aqueous $\text{Hg}(\text{ClO}_4)_2$ (2 mmol HgO/ml 60% HClO_4). Coupling constants are in Hz.

Preparation of $\text{Li}[\text{Hg}\{\mu\text{-PEt}_2\}\text{Cr}(\text{CO})_5\}_3]$

A solution of $\text{Li}[\text{Cr}(\text{CO})_5\text{PEt}_2]$, prepared in situ by adding *n*-BuLi to a stirred solution of $\text{Cr}(\text{CO})_5\text{PEt}_2\text{H}$ in THF, was added to a THF solution of $[\text{Hg}\{\mu\text{-PEt}_2\}\text{Cr}(\text{CO})_5\}_2$ at -60°C . ^{31}P NMR spectroscopy data showed the reaction to be almost quantitative. Attempts to crystallize **1** as the Li^+ , $[\text{NEt}_4]^+$, $[\text{PPh}_4]^+$ or $[\text{PPh}_3\text{NPPH}_3]^+$ salts were unsuccessful.

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