

REACTIONS OF CARBONYL COMPLEXES $(NN)(Ph_3P)M(CO)_3$ ($M = Mo, W$; $NN = 2,2'$ -BIPYRIDINE, 1,10-PHENANTHROLINE) WITH MERCURY HALIDES AND PSEUDOHALIDES

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(Received December 21st, 1982)

Summary

The reactions of mercuric derivatives HgX_2 ($X = Cl, CN$ or SCN) with the substituted Group VI carbonyl derivatives $(NN)(Ph_3P)M(CO)_3$ ($NN = 2,2'$ -bipyridine (bipy), 1,10-phenanthroline (phen); $M = Mo, W$) give three types of tricarbonyl compounds $(NN)(Ph_3P)(CO)_3 M \cdot nHgX_2$ ($M = Mo, NN = bipy, phen, X = CN, n = 1.5$; $M = W, NN = bipy, X = Cl, SCN, n = 1$; $M = W, NN = phen, X = Cl, n = 1.5$); $(NN)(Ph_3P)(CO)_3MHgX \cdot nHgX_2$ ($M = Mo, NN = bipy, phen, X = Cl, n = 0.5$) and $[(NN)(CO)_3M]_2Hg(SCN)_2$ ($M = Mo, NN = bipy, phen; M = W, NN = phen$), depending on the mercuric derivative employed. Only in the case of the reaction of the tungsten carbonyl complexes with mercuric cyanide does decomposition occur. Conductivity, IR, UV-VIS and magnetic data are given and possible formulations suggested. All the new complexes may be regarded as donor-acceptor compounds, the transition metal acting as the donor base and the mercury derivative as the acceptor. The reactions involve either partial halogen displacement from the mercuric salts to yield HgX complexes or retention of both halogens to give adducts, with or without elimination of the phosphine ligand.

Introduction

It is well known that many transition metal complexes have nucleophilic properties and can act as bases in acid-base interactions.

There have been previous reports of complexes containing metal-mercury bonds formed by reactions of Lewis acids, HgX_2 , with a number of substituted Group VI carbonyl derivatives [1–4]. The tetracarbonyl complexes, $(NN)M(CO)_4$ ($M = Mo, W$; $NN = bipy, phen$) have been most investigated, and they react to give complexes of the type $(NN)(CO)_3M(HgX)(X)$ by elimination of a CO group and a change in the oxidation state of the central metal. The crystal structure of $[(bipy)(CO)_3-$

Mo(HgCl)(Cl)] [5] shows the presence of a Mo–Hg bond in this compound.

The reactions of Mo,W-tricarbonyl derivatives have been studied and two types of complexes with M–Hg bonds, $\text{Hg}[\text{C}_5\text{H}_5(\text{CO})_3\text{M}]_2$ (A) and $(\text{arene})(\text{CO})_3\text{M} \cdot n\text{HgX}_2$ (B), have been reported. These compounds were formed by reaction of mercuric cyanide or mercuric halide with the corresponding anionic $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3]^-$ or neutral $(\text{arene})\text{M}(\text{CO})_3$ derivatives [2,3]. The crystal structure of $\text{Hg}[(\pi\text{-C}_5\text{H}_5)(\text{CO})_3\text{Mo}]_2$ [6] has been determined and reveals the presence of the linear Mo–Hg–Mo bonds.

The complexes of the type B can be formulated as 1:1 or 1:2 adducts, having one or two mercury atoms coordinated to the transition metal. An ionic formulation cannot be excluded for these compounds.

The complexes of the type B show a notable increase in the stretching frequency $\nu(\text{CO})$ with respect to that of the starting carbonyl compounds, and can be regarded as metal basic-metal acceptor compounds. The formation of the type A complexes can be also regarded as a metal-base acceptor complex reaction, as indicated by the increase of $\nu(\text{CO})$ in the salt with respect to the carbonyl anion. Which type of complex is formed probably depends on the nucleophilic character of the starting complex.

In this paper we describe the reactions of HgCl_2 with tricarbonyl complexes of the type $(\text{NN})(\text{Ph}_3\text{P})\text{M}(\text{CO})_3$ prepared from $(\text{NN})\text{M}(\text{CO})_4$ compounds by replacement of a CO group by a phosphine ligand. This substitution increases the metal basicity. We have also studied the corresponding reactions with mercury pseudohalides, $\text{Hg}(\text{CN})_2$ and $\text{Hg}(\text{SCN})_2$.

Results and discussion

We made three series of compounds, of the types $(\text{NN})(\text{Ph}_3\text{P})(\text{CO})_3\text{M} \cdot n\text{HgX}_2$ ($\text{M} = \text{Mo}$, $\text{NN} = \text{bipy}$, phen , $\text{X} = \text{CN}$, $n = 1.5$; $\text{M} = \text{W}$, $\text{NN} = \text{bipy}$, $\text{X} = \text{Cl}$, SCN , $n = 1$; $\text{M} = \text{W}$, $\text{NN} = \text{phen}$, $\text{X} = \text{Cl}$, $n = 1.5$) (I); $(\text{NN})(\text{Ph}_3\text{P})(\text{CO})_3\text{MHgX} \cdot n\text{HgX}_2$ ($\text{M} = \text{Mo}$, $\text{NN} = \text{bipy}$, phen , $\text{X} = \text{Cl}$, $n = 0.5$) (II) and $[(\text{NN})(\text{CO})_3\text{M}]_2\text{Hg}(\text{SCN})_2$ ($\text{M} = \text{Mo}$, $\text{NN} = \text{bipy}$, phen , $\text{M} = \text{W}$, $\text{NN} = \text{phen}$) (III) by acid-base reactions. The new complexes and some of their physical properties are listed in Table 1. They are microcrystalline solids, unstable in air and light, insoluble in polar organic solvents, and non-electrolytes in DMFA solution. In suspension in acetone the compounds produce a deposit of metallic mercury.

On exposure to light the tungsten derivatives undergo a rapid photochemical reaction but they are quite stable in the dark. They have been characterized by elemental analysis, IR and UV-VIS spectroscopy.

In most cases the molar ratio of mercuric halide to transition metal base is one or greater. The presence of lattice HgX_2 may be responsible for the stability of the compounds [7–10], owing to extensive $\text{Hg-X} \cdots \text{Hg}$ interactions. The general pattern observed for the reaction products with mercuric halides and pseudohalides involves retention of both halides to produce simple adducts of HgX_2 , (compounds of the type I). Only the reactions of the $(\text{NN})(\text{Ph}_3\text{P})\text{Mo}(\text{CO})_3$ compounds with HgCl_2 give complexes of HgX^+ , via partial halide displacement (type II).

The reaction with $\text{Hg}(\text{SCN})_2$ occurs with elimination of the phosphine ligand of the $(\text{NN})(\text{Ph}_3\text{P})\text{M}(\text{CO})_3$ complexes ($\text{M} = \text{Mo}$, $\text{NN} = \text{bipy}$; $\text{M} = \text{Mo}$, W , $\text{NN} = \text{phen}$).

TABLE I
ANALYTICAL AND OTHER DATA FOR THE NEW COMPOUNDS

Compound ^a	Colour	Yield (%)	Elemental Analysis (%) ^b			M.p. ^c (°C)	Conductivity ^d Ω_M (ohm ⁻¹ cm ² mol ⁻¹)
			C	H	N		
bipy(Ph ₃ P)(CO) ₃ MoHg(CN) ₂ ·0.5Hg(CN) ₂ (I)	yellow	47	42.25 (41.78)	2.49 (2.35)	7.21 (7.16)	166	27.81
phen(Ph ₃ P)(CO) ₃ MoHg(CN) ₂ ·0.5Hg(CN) ₂ (II)	orange	56	45.07 (45.02)	2.28 (2.29)	6.66 (6.99)	107–115	23.93
bipy(Ph ₃ P)(CO) ₃ MoHgCl·0.5HgCl ₂ (III)	orange	68	38.31 (38.38)	2.37 (2.34)	2.89 (2.67)	182–190	19.50
phen(Ph ₃ P)(CO) ₃ MoHgCl·0.5HgCl ₂ (IV)	orange	75	40.03 (39.89)	2.28 (2.31)	2.82 (2.81)	145	22.33
bipy(Ph ₃ P)(CO) ₃ WHgCl ₂ (V)	red	28	28.70 (28.88)	2.32 (2.40)	2.53 (2.93)	117	18.06, 58.37 ^e
phen(Ph ₃ P)(CO) ₃ W·1.5HgCl ₂ (VI)	yellow	60	35.93 (35.46)	1.98 (2.05)	2.39 (2.50)	129	12.90, 38.18 ^e
bipy(Ph ₃ P)(CO) ₃ WHg(SCN) ₂ (VII)	orange	31	39.13 (39.52)	2.21 (2.29)	5.44 (5.58)	149	19.93, 60.52 ^e
[bipy(CO) ₃ Mo] ₂ Hg(SCN) ₂ (VIII)	orange	57	33.05 (34.00)	1.68 (1.62)	8.19 (8.49)	127–129	< 0.07
[phen(CO) ₃ Mo] ₂ Hg(SCN) ₂ (IX)	orange	66	36.78 (37.05)	1.45 (1.54)	7.98 (8.09)	143–147	< 0.09
[phen(CO) ₃ W] ₂ Hg(SCN) ₂ (X)	orange	50	30.99 (31.68)	1.33 (1.32)	6.94 (6.92)	153–158	16.84

^a All the compounds are diamagnetic. ^b Analytical data calculated for these complexes are in parentheses. ^c Decomposition temperature. ^d In DMFA at 22°C for conc. ca. 10⁻³ M. ^e For solutions containing excess mercuric derivative.

In these cases the complexes obtained (type III) contain two $(NN)M(CO)_3$ units per mol of $Hg(SCN)_2$. However the reaction with $[(bipy)(Ph_3P)W(CO)_3]$ yields an 1 : 1 complex without elimination of any of the ligands, as in the reactions mentioned above which give compounds of type I.

All these new complexes are diamagnetic.

The mass spectra of some of these compounds generally show very few metastable ions, and none of these involves a M–Hg bond. Usually the $HgCl_2^+$, $HgCl^+$, Hg^+ and their doubly-charged counterparts were identified as stable species in the case of the chloro-derivatives. However in the compound $(bipy)(Ph_3P)(CO)_3W \cdot HgCl_2$, unstable $HgCl_2^+$ and $HgCl^+$ ion peaks were not detected. The presence of triphenylphosphine ligand was revealed for this complex. The molecular ion could be not observed, probably because of mercury–mercury interactions. The unstable MHg^+ ion was not detected for some compounds. Although the metal–mercury bond is chemically strong, it is thermally unstable, and mercury is immediately deposited on heating.

The IR spectra in the solid state of these new complexes and the parent compounds are reported in Table 2. The pattern of bands observed in the carbonyl stretching region is different for complexes I–VII, in which the molar ratio mercury/metal base is 1 or 1.5, from that for complexes VIII–X, in which the molar ratio metal base/mercury is 2.

Complexes I–VII show a three band spectrum (s,s,s) centered at ca. $60\text{--}80\text{ cm}^{-1}$ above the $\nu(CO)$ frequencies of the tricarbonyl starting compounds, whereas in the complexes VIII–X the $\nu(CO)$ bands are strongly split and shifted towards the higher frequencies ($80\text{--}50\text{ cm}^{-1}$) with respect to those of the parent compounds. These shifts are consistent with an increase in the formal oxidation state of the transition metal. The compounds I–VII show the NN ligand bands, and exhibit the typical triphenylphosphine bands in the $1600\text{--}500\text{ cm}^{-1}$ region [11]. However no trace of the phosphine ligand could be detected in the 2 : 1 complexes VIII–X.

The cyano and thiocyanate derivatives (I,II,VII–X) exhibit $\nu(CN)$ bands in the 2100 cm^{-1} region which are shifted with respect to those of $Hg(CN)_2$ and $Hg(SCN)_2$ [12,13]. The low frequency (2090 cm^{-1}) of the $\nu(CN)$ band in the cyano complexes $[(NN)(Ph_3P)(CO)_3MoHg(CN)_2 \cdot 0.5Hg(CN)_2]$ (NN = bipy, phen) is indicative of an increase in the ionic nature of CN group possibly due to a pseudo-bridged character of the CN^- ligands, each of which interacts with at least two mercury atoms [14]. Two bands at ca. $2100, 2050\text{ cm}^{-1}$ in the thiocyanato derivatives may indicate the presence of inter- or intra-molecular interactions via the SCN group. As expected the complexes show bands in the $400\text{--}200\text{ cm}^{-1}$ region corresponding to $\nu(Hg\text{--}X)$ stretching vibrations.

For $X = Cl$ in complexes III–VI, bands were observed at about 280 cm^{-1} . The positions are not significantly different from those obtained by Coates and Ridley [15] for $\nu(HgCl)$ in $(bipy\ BPh_2)(HgCl_3)$, suggesting either an increase in the coordination number of mercury or/and weak Hg–X bonds involving a mercury atom bonded to a transition metal. In keeping with the frequency shifts expected for a donation of electron density from metal (Mo, W) to Hg, the formation of all these complexes is accompanied by an increase in $\nu(CO)$ and a decrease in the average $\nu(Hg\text{--}X)$ frequency. On the basis of infrared spectra it is possible that the adducts obtained, like the complexes formed by nucleophilic displacement reactions, may be regarded as metal basic-metal acceptor complexes.

TABLE 2
INFRARED SPECTRAL DATA (ν in cm^{-1})

Compound	$\nu(\text{CO})$	$\nu(\text{C-N})$	$\nu(\text{HgX})$
bipy(Ph ₃ P)Mo(CO) ₃	1903vs, 1818vs, 1775vs		280m
phen(Ph ₃ P)Mo(CO) ₃	1907vs, 1808vs, 1773vs		280s, 253s
bipy(Ph ₃ P)W(CO) ₃	1900vs, 1800vs, 1768vs		230m
phen(Ph ₃ P)W(CO) ₃	1890vs, 1810vs, 1753vs		285w, 260s, 248s
bipy(Ph ₃ P)(CO) ₃ WHgCl ₂	1970s, 1883s, 1832s		287s, 253s, 240m
phen(Ph ₃ P)(CO) ₃ W · 1.5HgCl ₂	1946s, 1875s, 1845s		337s, 310s
bipy(Ph ₃ P)(CO) ₃ WHg(SCN) ₂	1953s, 1868s, 1843s	2095s-2050sh	327s, 305m
bipy(Ph ₃ P)(CO) ₃ MoHgCl · 0.5HgCl ₂	1970sh, 1948sh, 1933vs, 1830vs		240m
phen(Ph ₃ P)(CO) ₃ MoHgCl · 0.5HgCl ₂	1985sh, 1947vs, 1848s, 1825vs	2090m	239m
bipy(Ph ₃ P)(CO) ₃ MoHg(CN) ₂ · 0.5Hg(CN) ₂	1960s, 1940vs, 1865vs, 1830vs	2050s	
phen(Ph ₃ P)(CO) ₃ MoHg(CN) ₂ · 0.5Hg(CN) ₂	1975sh, 1950s, 1870s, 1823vs		
[bipy(CO) ₃ Mo] ₂ Hg(SCN) ₂	1982vs, 1950vs, 1900sh, 1825vs	2100sh-2060s	
[phen(CO) ₃ Mo] ₂ Hg(SCN) ₂	1980vs, 1950vs, 1895sh, 1837vs	2090sh-2070s	
[phen(CO) ₃ W] ₂ Hg(SCN) ₂	1975s, 1935s, 1900sh, 1885s, 1828s		

TABLE 3
ELECTRONIC SPECTRAL DATA

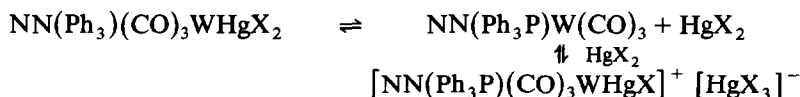
Compound	Concentration (mol l ⁻¹)	λ (nm)	log ϵ	Assignment
bipy(Ph ₃ P)(CO) ₃ MoHg(CN) ₂ ·0.5Hg(CN) ₂	4.95 × 10 ⁻⁵	485	3.14	<i>d</i> → <i>d</i> + M → L _{NN}
		390	3.68	<i>d</i> → <i>d</i> + M → π*CO
		285	4.40	M → π*CO
		450	2.71	<i>d</i> → <i>d</i>
		328	3.37	<i>d</i> → <i>d</i> + M → π*CO
phen(Ph ₃ P)(CO) ₃ MoHg(CN) ₂ ·0.5Hg(CN) ₂	8.41 × 10 ⁻⁴	275	4.41	πL _{NN} → π*L _{NN}
		440	3.41	M → L _{NN}
		390	3.40	<i>d</i> → <i>d</i> + M → π*CO
		315sh	3.98	M → π*CO
		285	4.37	M → π*CO
bipy(Ph ₃ P)(CO) ₃ MoHgCl·0.5HgCl ₂	8.70 × 10 ⁻⁵	438	3.38	M → L _{NN}
		395	3.36	<i>d</i> → <i>d</i> + M → π*CO
		330sh	3.46	<i>d</i> → <i>d</i> + M → π*CO
		293sh	4.17	M → π*CO
		277	4.46	πL _{NN} → π*L _{NN}
bipy(Ph ₃ P)(CO) ₃ WHgCl ₂ ^a phen(Ph ₃ P)(CO) ₃ W·1.5HgCl ₂ ^a bipy(Ph ₃ P)(CO) ₃ WHg(SCN) ₂ ^a [bipy(CO) ₃ Mo] ₂ Hg(SCN) ₂	6.05 × 10 ⁻⁵	—	—	—
		—	—	—
		—	—	—
		453	3.65	M → L _{NN}
		380	3.73	<i>d</i> → <i>d</i> + M → π*CO
[phen(CO) ₃ Mo] ₂ Hg(SCN) ₂	4.08 × 10 ⁻⁵	285	4.44	M → π*CO
		445	3.62	M → L _{NN}
		395	3.70	<i>d</i> → <i>d</i> + M → π*CO
		293sh	4.28	M → π*CO
		270	4.52	πL _{NN} → π*L _{NN}
[phen(CO) ₃ W] ₂ Hg(SCN) ₂	3.82 × 10 ⁻⁵	450	3.87	M → L _{NN}
		350	4.05	<i>d</i> → <i>d</i> + M → π*CO
		295sh	4.56	M → π*CO
		270	4.90	πL _{NN} → π*L _{NN}

^a The complexes undergo dissociation in solution (see text).

Conductivity measurements (Table 1) correspond to non-ionic compounds in DMFA solutions. Only the tungsten complexes $[(\text{NN})(\text{Ph}_3\text{P})(\text{CO})_3\text{W} \cdot n\text{HgX}_2]$ ($\text{X} = \text{Cl}, \text{SCN}$) (V–VII) undergo dissociation in solution. A change in colour from yellow to violet is observed, and the IR and UV-VIS spectra of the solution show the presence of the starting compound.

The presence of a large excess of mercuric chloride or mercuric thiocyanate increase the conductivities of the tungsten complexes $[(\text{NN})(\text{Ph}_3\text{P})(\text{CO})_3\text{W} \cdot n\text{HgX}_2]$ ($\text{NN} = \text{bipy}, \text{phen}; \text{X} = \text{Cl}, \text{SCN}$), which approach those expected for a uni-univalent electrolyte (Table 1). The dissociation of the complex to give the starting carbonyl compound and mercuric halide or pseudohalide would reduce the conductivity.

In the light of the discussion above, the existence in solution of the following equilibria can be postulated:



The tricarbonyl derivatives I–IV, which are not dissociated in solution, can be formulated as seven-coordinate complexes with a coordination geometry analogous to that of $(\text{NN})(\text{CO})_3\text{M}(\text{HgX})(\text{X})$ complexes [2].

The splitting of the bands in the carbonyl stretching region of the 2:1 complexes VIII–X is also observed in the $\text{M}^{\text{II}}[\text{M}(\text{CO})_3\pi\text{-C}_5\text{H}_5]_2$ ($\text{M}^{\text{II}} = \text{Zn}, \text{Cd}, \text{Hg}; \text{M} = \text{Cr}, \text{Mo}, \text{W}$) compounds [16]. Fischer and Noack interpreted these spectra in terms of a single isomer with a “skew” configuration of the $\text{M}(\text{CO})_3\text{C}_5\text{H}_5$ groups about a linear $\text{M}-\text{Hg}-\text{M}$ system [3]. The IR spectra of our compounds are quite similar in the carbonyl stretching region, and so the presence of analogous systems is suggested.

The reactions we have studied can be classified as “oxidative addition reactions”, the formal oxidation state of the metal being increased as HgX or HgX_2 units are added.

The UV-VIS of the new tricarbonyl complexes were recorded in DMFA solution from 267 to 650 nm, and the absorption maxima (λ_{max}) and intensities ($\log \epsilon$) are listed in Table 3. The nature of the absorption bands has been assigned by comparing the spectra with one another and with those of the corresponding hexacarbonyls [17], diamine-tetracarbonyl [18] and arenetricarbonyl complexes [19]. The absorption spectra within each series of compounds are similar, the small differences depending on the ligand.

Experimental

All reactions were carried out under nitrogen using standard Schlenk tube techniques and freshly distilled, dried, and degassed solvents.

Reagents. The complexes $(\text{NN})(\text{Ph}_3\text{P})\text{M}(\text{CO})_3$ ($\text{M} = \text{Mo}, \text{W}; \text{NN} = \text{bipy}, \text{phen}$) were prepared as described in the literature [20,21].

Commercially available mercuric salts were used without purification.

Analyses. C,H,N analyses were carried out by the Elemental Micro-Analyses Ltd. Laboratories, Amberley, Beaworthy (Devon) England.

Physical measurements. Infrared spectra in the $4000\text{--}200\text{ cm}^{-1}$ region were recorded on a Perkin–Elmer 325 spectrophotometer, with KBr disks or Nujol mulls.

Conductance measurements were performed in DMFA at room temperature with a Philips conductivity bridge, Model No CM 4144 and a PR9512/00 cell.

Electronic spectra in DMFA solution were scanned in the 650–267 nm region with a Kontron Uvikon 820 spectrophotometer.

Mass spectra were recorded on a Varian MAT 711 apparatus operating at 100 eV.

Preparation of the complexes

The $(\text{NN})(\text{Ph}_3\text{P})(\text{CO})_3\text{M} \cdot n\text{HgX}_2$ ($\text{M} = \text{Mo}$, $\text{NN} = \text{bipy}$, phen , $\text{X} = \text{CN}$, $n = 1.5$; $\text{M} = \text{W}$, $\text{NN} = \text{bipy}$, $\text{X} = \text{Cl}$, SCN , $n = 1$; $\text{M} = \text{W}$, $\text{NN} = \text{phen}$, $\text{X} = \text{Cl}$, $n = 1.5$) (I) and $(\text{NN})(\text{Ph}_3\text{P})(\text{CO})_3\text{MHgX} \cdot n\text{HgX}_2$ ($\text{M} = \text{Mo}$, $\text{NN} = \text{bipy}$, phen , $\text{X} = \text{Cl}$, $n = 0.5$) (II) compounds were prepared by the addition of HgX_2 ($\text{X} = \text{Cl}$, CN , SCN) in acetone to a suspension of $(\text{NN})(\text{Ph}_3\text{P})\text{M}(\text{CO})_3$ in that solvent.

The $[(\text{NN})(\text{CO})_3\text{M}]_2\text{Hg}(\text{SCN})_2$ ($\text{M} = \text{Mo}$, $\text{NN} = \text{bipy}$, phen ; $\text{M} = \text{W}$, $\text{NN} = \text{phen}$) (III) compounds were prepared similarly by the addition of suspensions of $\text{Hg}(\text{SCN})_2$ in acetone to the tricarbonyl complex in the dark.

As typical example, 0.08 g (0.29 mmol) of HgCl_2 dissolved in ca. 10 ml of acetone was added to a 10 ml suspension of 0.20 g (0.29 mmol) of $\text{bipy}(\text{Ph}_3\text{P})\text{W}(\text{CO})_3$ in acetone. The solution immediately changed colour and a red precipitate was formed. The suspension was stirred for 30 min, and the solid was filtered off on a glass filter and washed 4–5 times with 5–10 ml portions of acetone and ether.

Acknowledgement

Financial support from the Comision Asesora de Investigación Científica y Técnica (CAICYT) for this work is gratefully acknowledged (Project No. 3727/79). The authors thank P. Tigeras for recording the IR spectra.

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