REACTIONS OF TRICARBONYLPYRIDINE COMPLEXES (NN)(py)M(CO)$_3$ (M = Mo, W; NN = 2,2'-BIPYRIDINE, 1,10-PHENANTHROLINE) WITH MERCURIC DERIVATIVES HgX$_2$ (X = Cl, CN, SCN)

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Summary

Treatment of mercury(II) halides and pseudohalides with complexes (NN)(L)M(CO)$_3$ (L = py; NN = 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen); M = Mo, W) gives new tricarbonyl complexes. In all cases elimination of the pyridine ligand occurs and in some cases there is partial displacement of halogen from the mercuric halide. Treatment of bipy(py)W(CO)$_3$ with mercuric chloride gives only an adduct. Conductivity, IR and electronic absorption are given, and possible formulations suggested.

Introduction

It is well known that interaction of transition metal complexes with Lewis acid metal derivatives can give heteronuclear complexes. Basic complexes containing the CO ligand have been most widely investigated because the CO stretching vibration frequencies are extremely sensitive to changes in the formal oxidation state of the metal. The interaction of an acceptor molecule with the central metal atom leads to an increase in the ν(CO) vibration, which is associated with a decrease in the electron density at the metal atom, and with weaking of $d_\pi M - p\pi^*$(CO) dative bonds.

In the carbonyl hexa-coordinated complexes, the coordination of the acceptor gives a final product by elimination of a neutral ligand molecule, usually CO (the so-called oxidative elimination), as, for example, in the following reaction [1]:

$$(bipy)M(CO)_4 + 2HgCl_2 \leftrightarrows bipy(CO)_4M \cdot 2HgCl_2 \xrightarrow{-CO}$$
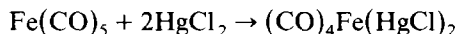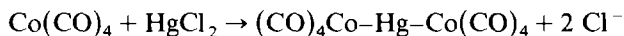
$$HgCl_2 + bipy(CO)_3MCl(HgCl)$$
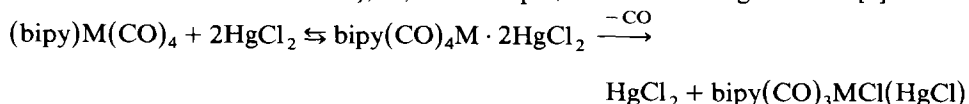
On the other hand donor-acceptor interactions can also result in nucleophilic displacement of the ligand from the metallic acceptor; the following examples [2,3]

TABLE 1

ANALYTICAL DATA AND SOME PHYSICAL PROPERTIES FOR THE NEW COMPOUNDS

Compound [a]	Colour	Yield (%)	Analyses (Found (calcd.) (%))			M.p. [b] (°C)	Conductivity [c] (Λ_M) (ohm^{-1} cm^2 mol^{-1})
			C	H	N		
bipy(CO)$_3$MoHgCl	orange	55	27.31 (27.28)	1.34 (1.39)	4.73 (4.89)	160–167	12.39
phen(CO)$_3$MoHgCl	orange	87	30.66 (30.21)	1.47 (1.34)	4.81 (4.69)	156	13.96
bipy(py)(CO)$_3$W·1.5HgCl$_2$	red	27	23.78 (23.74)	1.40 (1.40)	4.47 (4.61)	124	26.60
phen(CO)$_3$WHgCl	orange	72	26.94 (26.33)	1.46 (1.16)	3.88 (4.09)	137	11.31
bipy(CO)$_3$MoHg(SCN)$_2$	orange	51	27.17 (27.60)	1.20 (1.22)	8.41 (8.58)	99	<0.08
phen(CO)$_3$MoHg(SCN)$_2$	orange	88	30.07 (30.15)	1.14 (1.18)	8.03 (8.27)	100–105	<0.07
bipy(CO)$_3$W·1.5Hg(SCN)$_2$	orange	16	21.07 (21.37)	0.93 (0.89)	7.69 (7.78)	64	24.32
phen(CO)$_3$WHg(SCN)$_2$	orange	74	26.20 (26.69)	0.98 (1.05)	6.91 (7.32)	117–121	4.82
[bipy(CO)$_3$Mo]$_2$Hg(CN)$_2$·0.5Hg(CN)$_2$	yellow	65	33.26 (33.13)	1.63 (1.52)	9.41 (9.32)	144	20.51
[phen(CO)$_3$Mo]$_2$Hg(CN)$_2$·0.5Hg(CN)$_2$	yellow	54	36.18 (36.05)	1.42 (1.45)	8.68 (8.91)	173–180	55.22
[phen(CO)$_3$W]$_2$Hg(CN)$_2$·0.5Hg(CN)$_2$	orange	31	30.82 (31.08)	1.14 (1.25)	7.99 (7.68)	174	[d]

[a] All the compounds are diamagnetic. [b] Decomposition temperature. [c] In DMFA at 22 °C for c ca. 10^{-3}–10^{-4} M. [d] Insoluble.

illustrate the nature of such reactions:

$$Co(CO)_4 + HgCl_2 \rightarrow (CO)_4Co-Hg-Co(CO)_4 + 2\ Cl^-$$

$$Fe(CO)_5 + 2HgCl_2 \rightarrow (CO)_4Fe(HgCl)_2$$

In this type of reaction the formation of basic metal-mercury halide complexes may involve complete displacement of halide to give metal–mercury bonds [4], partial halide displacement to give complexes of HgX^+ [3,5] or retention of both halides to give simple adducts of HgX_2 [6,7]. The stronger metal bases appear to promote the first type of reaction and weakest tend to favour the last.

Some previous papers in this series [8,10] have been concerned with the preparation of complexes containing metal–mercury bonds. We now report the preparation of complexes by reaction of mercuric halides and pseudohalides with $(NN)(py)M(CO)_3$ (M = Mo, W; NN = bipy, phen) in which the presence of pyridine ligand increase the basicity of the tricarbonyl complex compared with $(NN)M(CO)_4$.

Results and discussion

Mercury(II) halides and pseudohalides were found to react with metal tricarbonylpyridine complexes $(NN)(py)M(CO)_3$ (NN = bipy, phen; M = Mo, W) in three different ways: (a) reactions characterized by expulsion of a ligand pyridine and its replacement by the mercuric derivative, (b) reactions involving pyridine expulsion and halide displacement from the HgX_2 group and (c) formation of adducts. The first type of reaction is observed when the Lewis acid is $Hg(CN)_2$ or $Hg(SCN)_2$; hovewer with $HgCl_2$ only products corresponding to the second and third type of reaction are isolated.

The analytical data (Table 1) for the yellow-orange reaction products are consistent with the proposed formulations. The complexes are insoluble in organic solvents and the conductivity data in DMFA solution are indicative of their neutral character. They are unstable to air and light, and in suspension give a deposit of metallic Hg. All the new complexes are diamagnetic.

In most cases the molar ratio of mercuric cyanide or thiocyanate to the basic metal is one or greater. The presence of additional HgX_2 is frequently found in this type of compounds, and can be accounted for in terms of $Hg-X \cdots X$ interactions as a stabilizing factor in these compounds.

Reactions of (NN)(py)M(CO)₃ with Hg(CN)₂ and Hg(SCN)₂

The mercuric cyanide or thiocyanate always causes the elimination of pyridine ligand, and displacement of cyanide or thiocyanate groups from the mercury atom is not observed. Compounds which contain two $(NN)M(CO)_3$ units per mol of $Hg(CN)_2$ (Table 1) are always formed in the reactions with $Hg(CN)_2$. This can be explained in terms of the tendency of the mercury atom to reach four-coordination, which is possible by addition of two basic groups such as $(NN)M(CO)_3$ to a linear C–Hg–C bond present in the $Hg(CN)_2$.

Different behaviour is found in the reactions with $Hg(SCN)_2$, and the compounds isolated are of the type $(NN)(CO)_3M \cdot Hg(SCN)_2 n Hg(SCN)_2$.

Reactions with HgCl₂

When an acetone solution of a $(NN)M(CO)_3$ complex is treated with mercuric

chloride in molar ratio 1/1 an orange precipitate is obtained, except in the case of the complex with M = W and NN = bipy, which gives a red compound, which was characterized as a simple adduct bipy(CO)$_3$W · 1.5HgCl$_2$. The analytical data for the other products show them to be of the type (NN)(CO)$_3$MHgCl (NN = bipy, phen, M = Mo; NN = phen, M = W). Analytical data and some physical properties are listed in Table 1. These complexes are unstable in air and relatively stable to light. They are insoluble in common organic solvents and the conductivity data in DMFA show their neutral character.

IR spectra

The (solid state) IR spectra data for the new complexes and the parent compounds are shown in Table 2. The same three band pattern appears in the carbonyl stretching region. In all cases the ν(CO) bands are strongly shifted towards the

TABLE 2A

INFRARED SPECTRAL DATA IN THE 2000–1700 cm^{-1} REGION

Compound	ν(CO)	ν(CN)
bipy(py)Mo(CO)$_3$	1885vs, 1847sh, 1755vs	
phen(py)Mo(CO)$_3$	1890vs, 1750vs	
bipy(py)W(CO)$_3$	1875vs, 1837sh, 1745vs	
phen(py)W(CO)$_3$	1875vs, 1780sh, 1740vs	
bipy(CO)$_3$MoHgCl	1947s, 1935s, 1885sh, 1832vs	
phen(CO)$_3$MoHgCl	1985s, 1938s, 1897s, 1870s, 1822s	
phen(CO)$_3$WHgCl	1955vs, 1905vs, 1860vs	
bipy(py)(CO)$_3$W · 1.5HgCl$_2$	1975sh, 1953vs, 1870vs, 1843sh	
bipy(CO)$_3$MoHg(SCN)$_2$	1975sh, 1958vs, 1855vs	2100vs, 2070sh
phen(CO)$_3$MoHg(SCN)$_2$	1977sh, 1957vs, 1870vs	2100vs, 2070sh
bipy(CO)$_3$W · 1.5Hg(SCN)$_2$	1970s, 1938s, 1863vs	2110vs, 2050s
phen(CO)$_3$WHg(SCN)$_2$	1975s, 1960sh, 1869vs	2090vs, 2070sh
[bipy(CO)$_3$Mo]$_2$Hg(CN)$_2$·0.5Hg(CN)$_2$	1960s, 1945s, 1870sh, 1838vs	2100sh, 2090m
[phen(CO)$_3$Mo]$_2$Hg(CN)$_2$·0.5Hg(CN)$_2$	1975sh, 1950s, 1870s, 1823vs	2100sh, 2085m
[phen(CO)$_3$W]$_2$Hg(CN)$_2$·0.5Hg(CN)$_2$	1960sh, 1940s, 1855vs, 1815vs	2100sh, 2090w

TABLE 2B

INFRARED SPECTRAL DATA IN THE 600–200 cm^{-1} REGION

Compound	δ(MCO)+ν(MCO)	ν(HgX)
bipy(CO)$_3$MoHgCl	592s, 510s, 486m, 455m	265s, 251s
phen(CO)$_3$MoHgCl	593vs, 575vs, 510vs, 480m, 458s	285vs, 270vs, 250s
phen(CO)$_3$WHgCl	585s, 565m, 515vs, 475w, 462s	287vs, 275vs
bipy(py)(CO)$_3$W · 1.5HgCl$_2$	590s, 568m, 503m, 475m, 455m	355m, 287s, 272vs, 243s
bipy(CO)$_3$MoHg(SCN)$_2$	587s, 515s, 505sh, 460s, 437w	245m
phen(CO)$_3$MoHg(SCN)$_2$	587s, 515s, 486m, 460s, 445w	240vs
bipy(CO)$_3$W · 1.5Hg(SCN)$_2$	587s, 515s, 508sh, 460br	247m
phen(CO)$_3$WHg(SCN)$_2$	589m, 570m, 512m, 460sbr, 448m	245s
[bipy(CO)$_3$Mo]$_2$Hg(CN)$_2$·0.5Hg(CN)$_2$	582s, 518s, 493m, 450s	332m
[phen(CO)$_3$Mo]$_2$Hg(CN)$_2$·0.5Hg(CN)$_2$	590s, 518s, 485m, 452m	325s
[phen(CO)$_3$W]$_2$Hg(CN)$_2$·0.5Hg(CN)$_2$	585s, 510s, 490m, 452m	335m, 302m

higher frequencies (60–120 cm^{-1}) with respect to those of the parent compounds. These shifts are consistent with an increase in the formal oxidation state of transition metal. The variation of these shifts for the various acceptor molecules HgX$_2$ is in the order ca. X = Cl > X = SCN > X = CN.

In addition the cyano and thiocyanate complexes exhibit ν(CN) stretching vibrations in the ca. 2110 cm^{-1} region, which are shifted with respect to those of free Hg(CN)$_2$ and Hg(SCN)$_2$ [11,12]. The low values of the frequencies, 2085 and 2100 cm^{-1}, observed for the cyano derivatives are indicative of an increase in the ionic nature of CN group, which it is possibly due to a pseudo-bridging character of the CN ligand [13]. Two bands in the 2110–2050 cm^{-1} region observed in the thiocyanate complexes may be indicative of the presence of a Mo–SCN bond or of inter/intra molecular interactions via the SCN group.

In the lower frequency region (400–200 cm^{-1}) all the complexes show bands corresponding to ν(HgX) stretching vibrations. For X = Cl, the bands are observed about 280–240 cm^{-1}, considerably shifted with respect to the HgCl$_2$ [14]. A weak Hg–X bond involving a mercury atom bonded to the transition metal is suggested. In addition the adduct bipy(py)(CO)$_3$W · 1.5HgCl$_2$ exhibits one band at 355 cm^{-1} which is attributed to the presence of HgCl$_2$ lattice molecules.

The thiocyanate complexes show one band at ca. 245 cm^{-1}, which is assigned to ν(Hg–SCN) stretching vibration. This vibration appears at 258 cm^{-1} in the complexes containing Mo–HgSCN bonds [13].

In the cyano complexes the bands at 330 cm^{-1} are assigned to the ν(HgCN) stretching vibration. The position is significantly different from that for free Hg(CN)$_2$ [11], and the shifts are consistent with those observed for the complexes of the mercuric cyanide with conventional bases [15,17].

The formation of all these new complexes is accompanied by an increase in ν(CO) and a decrease in ν(HgX) frequencies, which is consistent with donation of electronic density from the metal to the Hg atom. On this basis the complexes formed by nucleophilic displacement reactions, like the simple adducts, may be regarded as metal basic-metal acceptor complexes.

Electronic spectra

The electronic spectra of the new tricarbonyl derivatives were recorded in DMFA solution from 267 to 650 nm. The absortion maxima, λ_{max}, and intensites (log ϵ) are listed in Table 3. The nature of the absortion maxima were assigned by comparison with data for other tricarbonyl complexes [18] and the corresponding hexacarbonyls [19]. The absortion spectra within each series of compounds are similar, with small differences depending on the ligand.

The IR and electronic data for the tricarbonyl complexes described in this paper, obtained by reactions of NN(py)M(CO)$_3$ and HgX$_2$ (X = Cl, CN; SCN), and for those obtained by reactions of NNM(CO)$_4$ and the same Lewis acids [1,10] suggest that formation a corresponding product by both routes is possible only in the case of the Hg(CN)$_2$. The small differences observed in both derivatives with Hg(CN)$_2$ are due to the presence of additional lattice molecules of Hg(CN)$_2$. For the chloro and thiocyanate tricarbonyl derivatives isolated by both routes it is possible to think in terms of different coordination at the transition metal atom.

The reactions reported in this paper can be classified as "oxidative elimination reactions" in the general sense of the elimination of the pyridine ligand and increase

TABLE 3

ELECTRONIC SPECTRAL DATA

Compound	10^5 Concentration (mol 1^{-1})	λ (nm)	$\log \epsilon$	Assignment
bipy(CO)$_3$MoHgCl	13.0	430	3.09	$M \rightarrow L_{NN}$
		283	4.20	$M \rightarrow \pi^*(CO)$
phen(CO)$_3$MoHgCl	10.4	435	3.44	$M \rightarrow L_{NN}$
		325sh	3 27	$M \rightarrow \pi^*(CO) + d \rightarrow d$
		295sh	4.06	$M \rightarrow \pi^*(CO)$
		272	4.34	$\pi L_{NN} \rightarrow \pi^* L_{NN}$
bipy(py)(CO)$_3$W·1.5HgCl$_2$	9.82	462	3 36	$M \rightarrow L_{NN}$
		345sh	3.44	$M \rightarrow Lpy + d \rightarrow d$
		318sh	3 95	$M \rightarrow \pi^*(CO) + d \rightarrow d$
		287	4.24	$M \rightarrow \pi^*(CO)$
phen(CO)$_3$WHgCl	10.9	446	3.54	$M \rightarrow L_{NN}$
		355	3.53	$M \rightarrow \pi^*(CO) + d \rightarrow d$
		297sh	4.16	$M \rightarrow \pi^*(CO)$
		274	4.37	$\pi L_{NN} \rightarrow \pi^* L_{NN}$
bipy(CO)$_3$MoHg(SCN)$_2$	4.75	393	3.36	$M \rightarrow L_{NN} + d \rightarrow d$
		297sh	4.09	$M \rightarrow \pi^*(CO)$
		283	4.22	$M \rightarrow \pi^*(CO)$
phen(CO)$_3$MoHg(SCN)$_2$	5.15	403	3.46	$M \rightarrow L_{NN} + d \rightarrow d$
		293sh	4 11	$M \rightarrow \pi^*(CO)$
		270	4.44	$\pi L_{NN} \rightarrow \pi^* L_{NN}$
bipy(CO)$_3$W·1.5Hg(SCN)$_2$	3.89	460	3.17	$M \rightarrow L_{NN}$
		395	3.19	$M \rightarrow \pi^*(CO) + d \rightarrow d$
		300sh	3.98	$M \rightarrow \pi^*(CO)$
		280	4.26	$M \rightarrow \pi^*(CO)$
phen(CO)$_3$WHg(SCN)$_2$	6.58	450	3.56	$M \rightarrow L_{NN}$
		343	3.64	$M \rightarrow \pi^*(CO) + d \rightarrow d$
		293sh	4.25	$M \rightarrow \pi^*(CO)$
		271	4.56	$\pi L_{NN} \rightarrow \pi^* L_{NN}$
[bipy(CO)$_3$Mo]$_2$Hg(CN)$_2$·0.5Hg(CN)$_2$	7.10	440	3.50	$M \rightarrow L_{NN}$
		395sh	3 51	$M \rightarrow \pi^*(CO) + d \rightarrow d$
		287	4 46	$M \rightarrow \pi^*(CO)$
[phen(CO)$_3$Mo]$_2$Hg(CN)$_2$·0.5Hg(CN)$_2$	3.12	440	3.45	$M \rightarrow L_{NN}$
		387sh	3 49	$M \rightarrow \pi^*(CO) + d \rightarrow d$
		295sh	4.31	$M \rightarrow \pi^*(CO)$
		270	4.76	$\pi L_{NN} \rightarrow \pi^* L_{NN}$
[phen(CO)$_3$W]$_2$Hg(CN)$_2$·0.5Hg(CN)$_2$ [a]	–	–	–	–

[a] Insoluble.

of formal oxidation state of the metal when HgCl, Hg(CN)$_2$ or Hg(SCN)$_2$ units are added.

Experimental

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

Reagents. The complexes (NN)(py)M(CO)$_3$ (M = Mo, W; NN = bipy, phen) were prepared as previously described [20,24]. Commercially available mercuric salts were 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 4000–200 cm^{-1} region were recorded on a Perkin–Elmer 325 spectrophotometer with KBr disks or Nujol mulls.

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

Electronic spectra in the 650–267 nm region were recorded in DMFA solution on an Kontron Uvikon 820 spectrophotometer.

Preparation of the complexes

(NN)(CO)$_3$MHgCl (M = Mo, NN = bipy, phen; M = W, NN = phen). The tricarbonyl complexes NN(py)M(CO)$_3$ (M = Mo, NN = bipy, phen; M = W, NN = phen) and HgCl$_2$ in 1/1 molar ratio were stirred together in acetone in the dark. After several minutes for the molybdenum complexes and 6 h for the tungsten complex, the orange solid formed was filtered off, washed with acetone and dried under vacuum.

Bipy(py)W(CO)$_3$ · 1.5HgCl$_2$. 0.14 g (0.05 mmol) of HgCl$_2$ in ca. 10 ml of acetone was added in the dark to a 10 ml suspension of 0.25 g (0.05 mmol) of bipy(py)W(CO)$_3$ in acetone. The solution inmediately changed colour. The suspension was stirred for 5 h and then filtered. Addition of 150 ml of diethyl ether to the filtrate gave a red precipitate which was filtered off, washed with diethyl ether, and dried under vacuum.

(NN)(CO)$_3$M · nHg(SCN)$_2$ (M = Mo, NN = bipy, phen, n = 1; M = W, NN = phen, n = 1; M = W, NN = bipy, n = 1.5). A molar equivalent of Hg(SCN)$_2$ was added to a suspension of the tricarbonyl complex NN(py)M(CO)$_3$ (M = Mo, W; NN = bipy, phen) in the dark. An inmediate reaction was observed. The mixture was stirred for several minutes. In the case of the phen derivatives the orange precipitate was filtered off, washed with acetone and dried under vacuum. For bipy derivatives the suspension was filtered off, and addition of diethyl ether to the filtrate gave an orange precipitate which was isolated by filtration, washed with diethyl ether, and dried under vacuum. In all cases the reactions were carried in the light absence.

[NN(CO)$_3$M]$_2$Hg(CN)$_2$ · 0.5Hg(CN)$_2$ (M = Mo, NN = bipy, phen; M = W, NN = phen). Equimolecular amounts of NN(py)M(CO)$_3$ (M = Mo, NN = bipy, phen; M = W, NN = phen) and Hg(CN)$_2$ were stirred together in acetone for several hours at room temperature and in the dark. The solid formed was filtered off, washed with acetone, and dried under vacuum.

Acknowledgement

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