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REACTIONS OF THE CARBONYL COMPLEXES $M(CO)_3(L)_3$ (L = py, M = Mo, W; L = NH_3, M = Mo) AND $M(CO)_4(2\text{-}Mepy)_2$ (M = Mo,W) WITH HgX_2 (X = Cl, CN, SCN)

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Summary

The reactions of the substituted Group VI metal carbonyls of the type $M(CO)_4(2\text{-}Mepy)_2$ (M = Mo, W) and $M(CO)_3(L)_3$ (L = py, M = Mo, W; L = NH_3, M = Mo) with mercuric derivatives HgX_2 (X = Cl, CN, SCN) have given rise to three series of tricarbonyl complexes: $M(CO)_3(py)HgCl_2 \cdot 1/2HgCl_2$ (M = Mo, W); $2[M(CO)_3(L)]Hg(CN) \cdot nHg(CN)_x$ (L = py, M = Mo, W, $n = 1/2$, $x = 2$; L = 2-Mepy, $x = 1$; M = Mo, $n = 3$; M = W, $n = 1$); and $[M(CO)_3(L)Hg(SCN)_2 \cdot nHg(SCN)_2]$ (L = py, M = Mo,W, $n = 0$; L = 2-Mepy, M = Mo, W, $n = 1/2$; L = NH_3, M = Mo, $n = 0$) depending on which mercuric compound is employed. All the reactions with $Hg(SCN)_2$ give isolable products whereas those with $Hg(CN)_2$ and $HgCl_2$ did so far only the reactions with $[M(CO)_4(2\text{-}Mepy)_2]$ and $M(CO)_3(py)_3$. The greater reactivity of $Hg(SCN)_2$ than of $Hg(CN)_2$ and $HgCl_2$ is consistent with the various acceptor capacities of the groups bonded to the mercury atom.

The reactions studied always involve displacement of the N-donor ligand of the original complex and partial or total displacement of the halide or pseudohalide groups of the mercury compound to give in all cases compounds containing M–Hg bonds. In addition, elimination of a CO group in the tetracarbonyl complexes $M(CO)_4(2\text{-}Mepy)_2$ occurs.

Introduction

It is well known that the complexes of the type $\widehat{NN}M(CO)_4$ (M = Mo, W, $\widehat{NN}$ = bipy, phen, x-phen) react with $HgCl_2$ to form compounds with heteronuclear metal–metal bonds [1,2]. The determination of the crystal structure of several of such products has demonstrated the presence of metal–mercury bonds [3]. Most of the reactions studied give tricarbonyl complexes via an oxidative elimination reaction in which one CO ligand is displaced and HgX or HgX_2 units are added to the metal. However, in a few cases the reactions of tetracarbonyl complexes with the

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HgX_2 species gave the formation of adducts [1,2].

In earlier work we investigated the reactions of the tricarbonyl complexes $\overset{\frown}{NN}M(CO)_3(PPh_3)$ (M = Mo, W; $\overset{\frown}{NN}$ = bipy, phen) with the Lewis acids HgX_2 (X = Cl, CN, SCN), and showed them to lead to new tricarbonyl derivatives containing M–Hg bonds [4]. In most cases the reaction occurs without elimination of any of the ligands present in the initial complex. This can be explained in terms of the soft character of the phosphorous atom of the PPh_3 ligand and the chelating nature of the bipy or phen. Different behaviour would be expected for the tricarbonyl species with monodentate N-donor ligands, and so we undertook a study of the behaviour of tricarbonyl complexes of the type $M(CO)_3(L)_3$ (L = py, 2-Mepy, M = Mo, W; L = NH_3, M = Mo) towards HgX_2 species. Since the attempted synthesis of $M(CO)_3(2\text{-Mepy})_3$ gave only the $M(CO)_4(2\text{-Mepy})_2$ complexes, we studied the reactions of the latter with the mercury salts.

Results and discussion

Reactions with $HgCl_2$

Reactions of $HgCl_2$ with the tricarbonyl complexes $M(CO)_3(L)_3$ (M = Mo, L = NH_3, py; M = W, L = py), as with the tetracarbonyl complexes $[M(CO)_4(2\text{-Mepy})_2]$ (M = Mo, W), gave isolable compounds only in the case of the pyridine derivatives; in the other cases the products rapidly decompose.

The reactions of $M(CO)_3(py)_3$ (M = Mo, W) with $HgCl_2$, carried out as described in the experimental section, gave two new compounds, which can be formulated as tricarbonyl species, $M(CO)_3(py)_2HgCl_2 \cdot 1/2HgCl_2$, on the basis of the analytical and spectroscopic data (see Tables 1 and 2). The compounds are microcrystalline solids, insoluble in most common solvents, and behave as non-electrolytes in DMSO.

Table 2 summarizes some significant infrared frequencies for the new complexes obtained and for the starting carbonyl compounds. The infrared spectra of the $HgCl_2$ derivatives in the $\nu(CO)$ region exhibit two broad bands strongly shifted towards higher frequencies with respect to those of the parent compounds. This is consistent with a substantial decrease of the electron density on the transition metal atom. Two bands are observed in the lower frequency region (300–200 cm^{-1}); Kubicki et al. [5], in species $M(Cp)_2(HgX)_2 \cdot xHgX_2$, assigned the band at 280 cm^{-1} to the ν(Hg–Cl) stretching vibration of the Mo–HgCl bond.

The presence of lattice HgX_2 in complexes has often been reported [6–9]. The ν(Hg–Cl) frequency in the lattice HgX_2 lies in the 310–270 cm^{-1} region, this region also being characteristic of the ν(Hg–X) stretching vibrations of the groups HgX bonded to transition metals. Thus, the bands at 275 and 253 cm^{-1} in the molybdenum complex and at 282 and 258 cm^{-1} in the tungsten complex, may be assigned to the ν(Hg–Cl) vibrations of the two types of Hg–Cl bands present in the complexes. The lower ν(Hg–X) frequencies in the new complexes with respect to those in free $HgCl_2$ (375 cm^{-1}) [10] and MeHgCl (315 cm^{-1}) [11] may indicate the presence of a strong covalent interaction between the mercury atom and the carbonyl complex species. This fact and the marked shift of the $\nu(CO)$ band is consistent with the presence of a Mo–Hg bond. The IR spectra of the two complexes exhibit bands attributable to the bending and stretching vibrations of the M–CO bonds and to the bands of the coordinated pyridine ligand.

The electronic spectra of the two complexes in DMSO solution are equivalent,

TABLE 1

ANALYTICAL DATA

Compound	Analyses (Found (calcd.) (%))			Colour
	C	H	N	
$Mo(CO)_3(py)_2HgCl_2\cdot 1/2HgCl_2$	20.54	1.34	3.64	brown-yellow
	(20.98)	(1.34)	(3.76)	
$W(CO)_3(py)_2HgCl_2\cdot 1/2HgCl_2$	18.24	1.20	3.16	green-yellow
	(18.76)	(1.20)	(3.36)	
$Mo(CO)_3(NH_3)Hg(SCN)_2\cdot 1/3$ acetone	13.35	1.11	7.97	orange
	(13.52)	(0.94)	(7.88)	
$Mo(CO)_3(py)Hg(SCN)_2$	20.75	0.83	7.11	orange
	(20.86)	(0.86)	(7.29)	
$W(CO)_3(py)Hg(SCN)_2$	17.84	0.87	6.57	orange
	(18.10)	(0.75)	(6.33)	
$Mo(CO)_3(2\text{-}Mepy)Hg(SCN)_2\cdot 1/2Hg(SCN)_2$	19.32	1.03	6.99	orange
	(19.26)	(0.93)	(7.48)	
$W(CO)_3(2\text{-}Mepy)Hg(SCN)_2\cdot 1/2Hg(SCN)_2$	17.33	0.89	6.32	orange
	(17.24)	(0.84)	(6.69)	
$2[Mo(CO)_3(py)]Hg(CN)\cdot 1/2Hg(CN)_2$	24.24	0.98	6.36	brown
	(24.82)	(1.14)	(6.42)	
$2[W(CO)_3(py)]Hg(CN)\cdot 1/2Hg(CN)_2$	20.44	1.09	5.38	yellow-earth
	(20.65)	(0.95)	(5.35)	
$2[Mo(CO)_3(2\text{-}Mepy)]Hg(CN)\cdot 3Hg(CN)$	19.11	0.79	5.75	orange-yellow
	(18.19)	(0.96)	(5.78)	
$2[W(CO)_3(2\text{-}Mepy)]Hg(CN)\cdot 1Hg(CN)$	19.31	1.10	4.66	yellow
	(20.44)	(1.19)	(4.76)	

and this fact is consistent with the presence of analogous environments around the transition metal atom. In both cases there are three bands in the 390–260 nm region. The maximum at about 260 nm is probably due to the $M \rightarrow \pi^*(CO)$ CT transition accompanied by a $\pi \rightarrow \pi^*$ transition of pyridine ligand. The absorption at 310 nm is assigned to the $M \rightarrow \pi^*$ (CO) CT transition along with a $M \rightarrow L_{py}$ CT transition. The maximum at 385 nm is tentatively assigned to $d \rightarrow d$ transition accompanied by a $M \rightarrow L_{py}$ CT transition. These attributions are based on the data in the literature for tetracarbonyl complexes [12] and arenetricarbonyl complexes [13].

Reactions with $Hg(CN)_2$

Reactions of $Hg(CN)_2$ with the carbonyl complexes $M(CO)_4(2\text{-}Mepy)_2$ and $M(CO)_3(py)_3$ (M = Mo, W) give rise to isolable bimetallic compounds by elimination of CO and 2-methylpyridine ligands from the tetracarbonyl complexes and elimination of two pyridine ligands from the tricarbonyl complexes. When $Hg(CN)_2$ reacts with $Mo(CO)_3(NH_3)_3$ a yellow compound is formed, but decomposes rapidly.

The isolated compounds can be formulated as tricarbonyl complexes, $2[M(CO)_3(py)]HgCN \cdot 1/2Hg(CN)_2$ (M = Mo, W) and $2[M(CO)_3(2\text{-}Mepy)]$ $HgCN \cdot nHg(CN)$ ($M = Mo$, $n = 3$; $M = W$, $n = 1$), on the basis of their analytical data (Table 1). All these complexes contain two $M(CO)_3(L)$ units (L = py, 2-Mepy) for Hg(CN) group accompanied by $Hg(CN)_2$ molecules or Hg(CN) groups probably bonded through pseudo-bridging interactions. Thus a hexacoordinated environment can be assigned to the transition metal.

TABLE 2

INFRARED SPECTRAL DATA

Compound	ν(CO)			ν(CN)
$Mo(CO)_4(2\text{-}Mepy)_2$	1900s,	1860s,	1808s	
$W(CO)_4(2\text{-}Mepy)_2$	1885s,	1848s,	1800s	
$Mo(CO)_3(py)_3$	1890s,	1855sh,	1759vs	
$W(CO)_3(py)_3$	1879vs,	1745vs		
$Mo(CO)_3(NH_3)_3$	1870s,	1710vs		
$Mo(CO)_3(py)_2 1.5HgCl_2$	1933s,	1843s		
$W(CO)_3(py)_2 1.5HgCl_2$	1923s,	1826s		
$2[Mo(CO)_3py]HgCN \cdot 1/2Hg(CN)_2$	1966s br,	1890sh,	1857s	2101m, 2055sh
$2[W(CO)_3py]HgCN \cdot 1/2Hg(CN)_2$	1960s br,	1864s br,		2105m, 2040sh
$2[Mo(CO)_3(2\text{-}Mepy)]HgCN \cdot 3HgCN$	1970s br,	1890s br,		2122m, 2055m
$2[W(CO)_3(2\text{-}Mepy)]HgCN \cdot HgCN$	1960s br,	1860s br,	1810sh	2120sh, 2150m, 2040m
$Mo(CO)_3pyHg(SCN)_2$	1976s,	1905sh,	1884s	2138m, 2108m
$W(CO)_3pyHg(SCN)_2$	1963s,	1895sh,	1869s	2136m, 2099m
$Mo(CO)_3(2\text{-}Mepy)Hg(SCN)_2 \cdot 1/2Hg(SCN)_2$	1975s,	1909sh,	1889s	2130m, 2115br
$W(CO)_3(2\text{-}Mepy)Hg(SCN)_2 \cdot 1/2Hg(SCN)_2$	1970s br,	1875s br,		2130m, 2110br
$Mo(CO)_3(NH_3)Hg(SCN)_2 \cdot 1/3$ acetone	1975s,	1911sh,	1873s	2130m, 2109br

Analogous structures have been reported for several other complexes containing two transition elements to each mercury atom; for example for the compound $Hg[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, in which the crystal structure demonstrated the presence of linear Mo–Hg–Mo bonds [14].

The complexes isolated in these reactions are microcrystalline solids, unstable in air and insoluble in the most common solvents. Conductance measurements show them to be covalent species.

The IR spectra of the new complexes in the 2000–1800 cm^{-1} region show two very intense broad and split bands which are assigned to the ν(CO) stretching vibrations of the carbonyl groups. As in the case of $HgCl_2$ derivatives, these bands are strongly shifted towards higher frequencies with respect to those of the parent compounds. The presence of two bands in the 2122–2040 cm^{-1} region assigned to the $\nu(C\equiv N)$ vibrations implies a strong modification in the nature of the CN groups in the species formed with respect to that in free $Hg(CN)_2$ (2195 cm^{-1}) [15]. Such low values for these frequencies have been found for other molybdenum complexes with $Hg(CN)_2$ [5], and attributed to an increase in the ionic nature of the interaction and in the negative charge on the nitrogen atom. On the other hand, bands observed in the 2130–2030 cm^{-1} region have been assigned to the $\nu(C\equiv N)$ vibrations in cyano-complexes of molybdenum [16].

The assignment of the ν(Hg–CN) vibration is uncertain because of the presence in the relevant region of bands for some vibrations of the M–CO bonds, but weak bands, in the 350–370 cm^{-1} region in our complexes are tentatively attributed to the ν(Hg–CN) vibrations. The shifting of ν(Hg–CN) towards lower frequencies with respect to its value in the free $Hg(CN)_2$ (450 cm^{-1}) [15] is consistent with the existence of interactions similar to those between the $Hg(CN)_2$ and conventional bases [17–19].

The remaining bands of the spectrum are attributable to characteristic vibrations

δ(MCO)+ ν(MCO)	ν(Hg–CN)	ν(HgCl)	ν(HgS)
590m		275sh 253s	
592m		288w 258s	
579s, 510m, 493w			
575m, 515w, 458w	352w		
563m, 500w	354w		
570w, 470w, 450w	370m		
580m			248w
585m, 565m			248w
578m			248w
570m			250w
580s, 500s, 450s			255w

of the M–CO bonds (Table 2) and the N-donor ligand.

The diffuse reflectance spectra of the cyano complexes in all cases show 3 bands in the 900–190 nm region which are not significantly changed by the change in the metal atom or the N-donor ligand. The similarity in the number of bands and in their position suggests the presence of similar environments in the isolated complexes. Table 3 shows the observed absorption maxima and their assignments for these compounds and for the mercuric thiocyanate derivatives.

Reactions with $Hg(SCN)_2$

The reactions of $Hg(SCN)_2$ with the initial carbonyl complexes in all cases give new derivatives which have been characterized as tricarbonyl species. The new complexes, which can be formulated on the basis of their analytical data (see Table 1) as $M(CO)_3(py)Hg(SCN)_2$, $M(CO)_3(2\text{-Mepy})Hg(SCN)_2 \cdot 1/2Hg(SCN)_2$ ($M = Mo$, W) and $Mo(CO)_3(NH_3)Hg(SCN)_2 \cdot n$ acetone, are formed by displacement of CO and 2-methylpyridine ligands from the complexes $M(CO)_4(2\text{-Mepy})_2$, and of two N-donor ligands (py or NH_3) from the tricarbonyl complexes $M(CO)_3L_3$ ($L = py$, NH_3). The products are yellow-orange solids, unstable in air and light, insoluble in the most common organic solvents, and non-electrolytes in DMSO.

In the reactions carried out $Hg(SCN)_2$ was more reactive than $Hg(CN)_2$ and $HgCl_2$. This is consistent with the greater electronegativity of the SCN (3.91) than of the CN (3.84) and Cl (3.0) groups. (These Pauling electronegativity values were calculated by the electronegativity equalization method [20]).

The new derivatives may be regarded as hexacoordinated complexes in which the metal environment involves three CO groups, one N-donor ligand, and the two Hg(SCN) and NCS groups.

In the IR spectra of these complexes we can assign the most characteristic vibrations of CO groups and the Hg(SCN) bands (Table 2). All the complexes show

TABLE 3

DIFFUSE REFLECTANCE SPECTRAL DATA

Compound	λ_{max}	Assignment [a]
$2[Mo(CO)_3(py)]HgCN \cdot 1/2Hg(CN)_2$	785w	$d \to d$
	410	$d \to d + \mathrm{IL}(\pi \to \pi^\star)$
	260	$\mathrm{CT}(\mathrm{M} \to \pi^\star\mathrm{CO}) + \mathrm{IL}(\pi \to \pi^\star)$
$2[Mo(CO)_3(2\text{-}Mepy)]HgCN \cdot 3Hg(CN)$	790w	$d \to d$
	410	$d \to d + \mathrm{IL}(\pi \to \pi^\star)$
	260	$\mathrm{CT}(\mathrm{M} \to \pi^\star\mathrm{CO}) + \mathrm{IL}(\pi \to \pi^\star)$
$2[W(CO)_3(2\text{-}Mepy)]HgCN \cdot Hg(CN)$	400	$d \to d + \mathrm{IL}(\pi \to \pi^\star)$
	260	$\mathrm{CT}(\mathrm{M} \to \pi^\star\mathrm{CO}) + \mathrm{IL}(\pi \to \pi^\star)$
$Mo(CO)_3(NH_3)Hg(SCN)_2 \cdot 1/3$ acetone	775	$d \to d$
	430	$d \to d$
	348	$d \to d + \mathrm{CT}(\mathrm{M} \to \pi^\star\mathrm{CO})$
	258	$\mathrm{CT}(\mathrm{M} \to \pi^\star\mathrm{CO}) + \mathrm{IL}(\pi \to \pi^\star)$
$Mo(CO)_3(py)Hg(SCN)_2$	808	$d \to d$
	440	$d \to d + \mathrm{CT}(\mathrm{M} \to \mathrm{L})$
	345	$d \to d + \mathrm{CT}(\mathrm{M} \to \pi^\star\mathrm{CO})$
	260	$\mathrm{CT}(\mathrm{M} \to \pi^\star\mathrm{CO}) + \mathrm{IL}(\pi \to \pi^\star)$
$Mo(CO)_3(2\text{-}Mepy)Hg(SCN)_2 \cdot 1/2Hg(SCN)_2$	795	$d \to d$
	439	$d \to d + \mathrm{CT}(\mathrm{M} \to \mathrm{L})$
	366	$d \to d + \mathrm{CT}(\mathrm{M} \to \pi^\star\mathrm{CO})$
	260	$\mathrm{CT}(\mathrm{M} \to \pi^\star\mathrm{CO}) + \mathrm{IL}(\pi \to \pi^\star)$
$W(CO)_3(2\text{-}Mepy)Hg(SCN)_2 \cdot 1/2Hg(SCN)_2$	830	$d \to d$
	398	$d \to d + \mathrm{CT}$
	260	$\mathrm{CT}(\mathrm{M} \to \pi^\star\mathrm{CO}) + \mathrm{IL}(\pi \to \pi^\star)$

[a] CT = charge transfer, IL = intraligand transition.

in the $\nu(CO)$ region two strong broad bands centred at 1969 ± 6 and 1879 ± 10 cm^{-1}. As with the $HgCl_2$ and $Hg(CN)_2$ derivatives, the $\nu(CO)$ vibrations are at lower frequencies in the tungsten complexes than in the molybdenum complexes. These frequencies are substantially shifted with respect to those of the parent complexes, and this effect is greater than that observed in the compounds with $Hg(CN)_2$ and $HgCl_2$. Thus our complexes show the following trends for the $\nu(CO)$ frequency shifts: $Hg(SCN)_2 > Hg(CN)_2 > HgCl_2$, this sequence is consistent with sequence of electronegativities assigned to the bonded groups to the mercury atom.

The bands in the 2138–2106 cm^{-1} region are assigned to the $\nu(C{\equiv}N)$ vibrations of the SCN group. The frequencies of these bands are consistent with the presence of HgSCN groups bonded to transition metal [21] or of NCS groups coordinated to the molybdenum or tungsten atom [16]. A band at ca. 250 cm^{-1} is assigned to a $\nu(Hg{-}SCN)$ stretching frequency. In complexes with Mo–Hg(SCN) bonds a band at 258 cm^{-1} was assigned to this vibration [5]. The presence of CO groups and the N-donor ligand complicates the assignment of the $\nu(CS)$ and $\nu(SCN)$ vibrations.

The reflectance spectra of the thiocyanate derivatives have been recorded (Table 3). The spectra are similar for all the complexes derived from $Hg(SCN)_2$ and so equivalent environments around the molybdenum or tungsten atom are proposed.

Experimental

All experiments were carried out under oxygen-free dry nitrogen. Analytical grade solvents were used.

The starting complexes, $M(CO)_3(py)_3$ (M = Mo, W) and $Mo(CO)_3(NH_3)_3$ were prepared as previously described [22–24]. The tetracarbonyl complexes, $M(CO)_4(2\text{-}Mepy)_2$ (M = Mo, W), were obtained by reaction of $M(CO)_6$ with reflux 2-methylpyridine for 30 min in the case of the molybdenum and 2.5 h in the case of the tungsten complex. After the refluxing the mixture was cooled to room temperature and water was added to yield a yellow precipitate, which was filtered off, washed with water and dried under vacuum over P_2O_5. The yields of both reactions were almost quantitative. The tungsten derivative is stable to air, whereas the molybdenum complex decomposes gradually.

Elemental analyses were carried out by Elemental Micro Analyses Ltd. Laboratories, Amberley Beaworthy (Devon) England. Conductance measurements were performed in DMSO at room temperature with a Philips conductivity bridge, Model CM 4144 and a cell PR 9512/00. Infrared spectra in the 4000–200 cm^{-1} region were recorded on a 325 Perkin–Elmer spectrophotometer, using KBr disks or Nujol mulls. Electronic spectra in DMSO solution of the complexes $M(CO)_3(py)_2HgCl_2 \cdot 1/2HgCl_2$ were recorded on a Kontron Uvikon 820 Spectrophotometer. The diffuse reflectance spectra of the solid compounds were measured using the same spectrophotometer with the standard Kontron diffuse reflectance accesory and barium sulfate as the reference sample. The solid samples were slightly diluted with $BaSO_4$.

Preparation of the complexes

$M(CO)_3(py)_2HgCl_2 \cdot 1/2HgCl_2$ (M = Mo, W). The tricarbonyl complexes $M(CO)_3(py)_3$ (M = Mo, W) and $HgCl_2$ in 1/1 molar ratio were stirred together in acetone. After 1.5 h for the molybdenum complex and 2.5 h for the tungsten complex the yellow solid formed was filtered off, washed with acetone, and dried under vacuum.

$2[M(CO)_3(py)]Hg(CN) \cdot 1/2Hg(CN)_2$ (M = Mo, W). The complexes were obtained by stirring the starting carbonyl complex, $M(CO)_3(py)_3$ (M = Mo, W) and $Hg(CN)_2$ in 1/1 molar ratio in acetone at room temperature. The reaction was allowed to proceed for several hours (2 or 3) to ensure completion. The brown solid formed was filtered off, washed with acetone and dried under vacuum.

$2[Mo(CO)_3(2\text{-}Mepy)]Hg(CN) \cdot 3Hg(CN)$. To a solution of the $Mo(CO)_4(2\text{-}Mepy)_2$ (0.788 g, 2 mmol) in 8ml of acetone was added $Hg(CN)_2$ (0.505 g, 2 mmol). Stirring for 10 min at 0°C gave an orange-yellow precipitate, which was filtered off, washed with acetone, and dried under vacuum. Addition of diethyl ether to the filtrate gave additional quantities of the product.

$2[W(CO)_3(2\text{-}Mepy)]Hg(CN) \cdot 1Hg(CN)$. $Hg(CN)_2$ was added in 1/1 molar ratio to a solution of $W(CO)_4(2\text{-}Mepy)_2$ in the minimum amount of acetone. After 10 min stirring at 0°C the mixture was filtered and 100 ml of diethyl ether was added to the filtrate to give a yellow precipitate, which was filtered off, washed with ether and dried under vacuum.

$Mo(CO)_3(NH_3)Hg(SCN)_2 \cdot n$ acetone. When $Hg(SCN)_2$ (0.158 g, 0.5 mmol) was added to a suspension of $Mo(CO)_3(NH_3)_3$ (0.115 g, 0.5 mmol) in 8 ml of acetone an immediate reaction was observed. The mixture was stirred at 0°C for 10 min and

then filtered. Addition of 150 ml of diethyl ether to the filtrate gave an orange precipitate, which was isolated by filtration, washed with diethyl ether, and dried under vacuum.

$M(CO)_3(py)Hg(SCN)_2$ ($M = Mo, W$). Equimolecular amounts of $M(CO)_3(py)_3$ ($M = Mo$, W) and $Hg(SCN)_2$ were stirred together in acetone for 1.5 h at room temperature. The orange solid formed was filtered off, washed with acetone, and dried under vacuum.

$M(CO)_3(2\text{-}Mepy)Hg(SCN)_2 \cdot 1/2Hg(SCN)_2$ ($M = Mo, W$). A one molar equivalent of $Hg(SCN)_2$ was added to a solution of the tetracarbonyl complex $M(CO)_4(2\text{-}Mepy)_2$ ($M = Mo$, W), in the minimum amount of acetone. An immediate reaction took place with formation of an orange precipitate. After 5–10 min stirring at 0°C the solid was filtered off, washed with acetone, and dried under vacuum.

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