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REACTIONS OF THE MOLYBDENUM(II) DICARBONYL COMPLEXES WITH MERCURY(II) HALIDES AND PSEUDOHALIDES

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Summary

The reactions of the molybdenum(II) dicarbonyl complexes, $[MoBr(\pi\text{-allyl})(CO)_2(L)_2]$ ($L = CH_3CN$, py) and $[MoBr(\pi\text{-allyl})(CO)_2(L,L)]$ (L,L = bipy, phen, dppe) with HgX_2 (X = Cl, CN, SCN) give several new complexes via a displacement reaction involving Br or/and L ligands or a simple adduct formation reaction.

Introduction

One of the methods known for the formation of heteronuclear complexes with M–Hg bonds involves the reaction of basic metal complexes with mercury(II) derivatives and the behaviour of the molybdenum(0) carbonyls with mercury halides and pseudohalides has been studied extensively [1–6]. Although molybdenum(II) Mo(II) carbonyl complexes are expected to have a lower basicity, some examples of reactions of such complexes with mercury halides have been reported, e.g. $[Mo(\pi\text{-}C_5H_5)(CO)_2(L)(R)]$ ($R = CH_3$, $OCCH_3$) compounds react with HgX_2 to give compounds of the type $[Mo(\pi\text{-}C_5H_5)(CO)_2(L)HgX]$, involving displacement of R by the HgX group [7].

In the light of the above results we decided to study the reactions of molybdenum(II) dicarbonyl complexes with metallic derivatives of Lewis acid character. We describe below the reactions of HgX_2 (X = Cl, CN, SCN) with $[MoBr(\pi\text{-allyl})(CO)_2(L)_2]$ ($L = CH_3CN$, py) and $[MoBr(\pi\text{-allyl})(CO)_2(L,L)]$ (L,L = bipy, phen, dppe), in which the influence of the variation in the nature of the Mo–L or Mo–(L,L) bond should be apparent.

Results and discussion

The behaviour of the $[MoBr(\pi\text{-allyl})(CO)_2(L)_2]$ complexes, where L is an N-donor monodentate ligand, towards HgX_2 derivatives varies according to the nature of L

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and X. Thus several types of compounds can be obtained: (i) unidentified decomposition products (when $L = CH_3CN$ and $X = Cl$, CN; $L = py$ and $X = Cl$); (ii) products in which all the ligands of the starting complex are retained, e.g.: $[MoBr(\pi\text{-allyl})(CO)_2(py)_2 \cdot Hg(SCN)_2]$; and (iii) compounds in which Br and/or ligands L have been displaced. Thus the reaction of $Hg(SCN)_2$ with $[MoBr(\pi\text{-allyl})(CO)_2(CH_3CN)_2]$ involves elimination of bromine and the two acetonitrile ligands to give a new compound which can be formulated as $[Mo(NCS)(\pi\text{-allyl})(CO)_2Hg(SCN)_2 \cdot \text{acetone}]$ on the basis of analytical and spectroscopic data. The solid is unstable in air and a non-electrolyte in DMSO solution. The IR and ^1H NMR spectra are consistent with the absence of acetonitrile and the presence of acetone ($\nu(C{=}O)$ 1694 cm^{-1}, $\delta = 2.10$ (ppm)). X-Ray fluorescence analysis shows the absence of bromine in the new complex. On the other hand, the pyridine derivative reacts with HgX_2 ($X = CN$, SCN) to give two new compounds. The reaction with $Hg(SCN)_2$ yields a complex of the adduct type, $[MoBr(\pi\text{-allyl})(CO)_2(py)_2 \cdot Hg(SCN)_2]$, but with $Hg(CN)_2$ one molecule of pyridine is eliminated, to give $[MoBr(\pi\text{-allyl})(CO)_2(py) \cdot Hg(CN)_2]$. The two new complexes are microcrystalline solids, unstable in air, and non-electrolytes in DMSO.

The reaction of the $[MoBr(\pi\text{-allyl})(CO)_2(L,L)]$ complexes with the mercury derivatives gives compounds in which all the ligands of the parent complexes are retained. This is consistent with the generally less labile character of bidentate ligands compared to pyridine or acetonitrile ligands. The complexes characterized, which have the general formula $[MoBr(\pi\text{-allyl})(CO)_2(L,L) \cdot nHgX_2]$ ($n = \frac{1}{4}-\frac{1}{2}$), are stable in air and non-electrolytes in DMF or DMSO solutions.

The products of formula $[MoBr(\pi\text{-allyl})(CO)_2(L)_2 \cdot nHgX_2]$ or $[MoBr(\pi\text{-allyl})(CO)_2(L,L) \cdot nHgX_2]$ can be regarded as adducts in which n varies with the N- or P-donor ligand and the acceptor nature. Formation of adducts with HgX_2 is known for some organometallic and organic compounds, although these involve a whole number of HgX_2 molecules. However, the presence of the lattice HgX_2 has been noted in complexes such as $[MCp_2(HgX)_2 \cdot nHgX_2]$, $n = 0, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}, 1$, and may stabilize the compounds through Hg–X...Hg interactions [8].

The IR spectra (Table 2) of all the compounds isolated show two strong bands of approximately the same intensity, which are typical of the $\nu(CO)$ stretching vibrations of the two *cis*-carbonyl groups [9]. These bands are very little different from those of the starting carbonyls; this is characteristic of the π-allyldicarbonyl complexes, which always present two $\nu(CO)$ vibrations at almost constant frequencies (1930 ± 20 cm^{-1} and 1850 ± 20 cm^{-1}) [10]. The absence of the characteristic bands of a σ-allyl group confirms the π-coordination of the allyl ligand.

On the other hand, the characteristic vibrations of the HgX_2 acceptor are much modified upon formation of the adduct. The values of the $\nu(Hg–Cl)$ vibrations in the new derivatives (Table 2) are similar to those found in compounds with Mo–Hg–X bonds [8]. The decrease in the $\nu(Hg–Cl)$ frequency with respect to that in free $HgCl_2$ [11] suggests a weakening of the Hg–Cl bond or/and an increase in the coordination number of the Hg atom. The result is consistent with adduct formation [12].

In the $Hg(CN)_2$ and $Hg(SCN)_2$ derivatives the $\nu(Hg–X)$ frequencies cannot be assigned probably because of their low intensities; such behaviour is known for simple adducts of $Hg(CN)_2$ [13].

On the other hand, the displacement to lower frequencies of $\nu(C{\equiv}N)$ vibrations in the $Hg(CN)_2$ derivatives is consistent with the formation of a simple adduct with terminal CN groups [13]. However, the $\nu(C{\equiv}N)$ vibration in the thiocyanate derivatives is displaced to higher frequencies with respect to that of free $Hg(SCN)_2$. This is possibly associated with bridging by the SCN groups [14]. The appearance of several $\nu(C{\equiv}N)$ bands in the $[Mo(NCS)(\pi\text{-allyl})(CO)_2Hg(SCN)_2 \cdot \text{acetone}]$ complex can be attributed so to the presence of coordinated $Hg(SCN)_2$ [15] with the NCS group bonded to the molybdenum atom [11].

The IR spectra of the new pyridine derivatives show two characteristic bands of the pyridine ligand in the 780–680 cm^{-1} region. In the adduct with $Hg(SCN)_2$ these bands are split, as in the starting complex, whereas such splitting is not observed in the $Hg(CN)_2$ derivative, in accord with the proposed formulae. The IR spectra of the $[MoBr(\pi\text{-allyl})(CO)_2(L,L) \cdot nHgX_2]$ complexes exhibit the characteristic bands of the coordinated NN or PP donor ligands.

Unfortunately, in most cases the ^1H NMR spectra could not be obtained because of low solubility, but the few data recorded confirm the π-coordination of the allyl group. For example, the spectrum in $CDCl_3$ of the $[MoBr(\pi\text{-allyl})(CO)_2(dppe) \cdot \frac{1}{2}Hg(SCN)_2]$ shows three resonances at δ 7.52m (C_6H_5), δ 3.6–2.0m [H^s–H^1(π-allyl)] and δ 1.68s (br) [H^a(π-allyl)] indicating that, the $[Mo(\pi\text{-allyl})(CO)_2]$ moiety is retained in all reactions. This would be expected, since a marked stability of this moiety in π-allyl molybdenum(II) dicarbonyl complexes is evident in many of their reactions.

Electronic spectra of the new complexes and starting compounds were recorded in the 260–900 nm region. Table 2 summarizes the absorption maxima (λ_{max}, nm) and the intensities (ϵ) for these compounds. The assignment of the these spectra is difficult because of the π-electron systems present in various ligands and the low symmetry of the complexes. However, it can be seen that the presence of the mercury derivatives in the complexes results in only small modifications of λ_{max} with respect to those of the parent compounds. This fact, and the small shifts of the $\nu(CO)$ bands in the bimetallic derivatives with respect to those of the starting π-allyldicarbonyl complexes suggest that the oxidation state of the molybdenum is not changed by incorporation of the mercury salts.

Experimental

All experiments were carried out at room temperature under oxygen-free dry nitrogen. Analytical grade solvents were used. The starting carbonyl complexes were prepared as previously described [9]. C, H, N analyses (Table 1) were carried out by Elemental Micro-analysis Ltd Laboratories, (Devon) England. Conductance measurements were performed at room temperature using a Philips conductivity bridge PW 9510160. Infrared spectra in the 4000–200 cm^{-1} region were recorded on a 325 Perkin–Elmer spectrophotometer, using KBr disks. Electronic spectra were recorded with DMSO solutions on a Kontron Uvikon 820 Spectrophotometer. ^1H NMR spectra were measured at 60 Mhz with a Perkin–Elmer R12 spectrometer in deuterodimethylsulphoxide or deuterochloroform with TMS as internal standard. Infrared and electronic spectral data are listed in Table 2.

Preparation of the complexes

$[Mo(NCS)(\pi\text{-allyl})(CO)_2Hg(SCN)_2\text{acetone}]$. Equimolecular amounts of $[MoBr(\pi\text{-allyl})(CO)_2(CH_3CN)_2]$ (0.355 g) and $Hg(SCN)_2$ (0.317 g) were stirred in acetone.

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TABLE 1

ANALYTICAL AND PHYSICOCHEMICAL DATA FOR THE NEW COMPLEXES

Compound	Colour	M.p. (°C) (decomp.)	Elemental analysis (Found (calcd.) (%))					Λ_M (ohm^{-1} cm^2 ml^{-1}) [a]
			C	H	N	Hg	Mo	
Mo(NCS)(π-allyl)(CO)$_2$Hg(SCN)$_2$·acetone	bright yellow	104	20.70 (21.11)	1.60 (1.76)	6.5 (6.71)			10.2 [b]
MoBr(π-allyl)(CO)$_2$(py)$_2$·(Hg(SCN)$_2$	yellow	155	28.74 (27.31)	2.04 (2.01)	8.18 (7.49)		13.72 (12.83)	17.7 [b]
MoBr(π-allyl)(CO)$_2$(py)Hg(CN)$_2$	yellow	105	25.05 (23.88)	1.76 (1.66)	6.84 (6.94)			5.1 [b]
MoBr(π-allyl)(CO)$_2$(bipy)·$\frac{1}{2}$Hg(CN)$_2$	red	196	33.84 (34.60)	2.23 (2.34)	7.11 (7.56)	17.76 (18.06)		15.9 [c]
MoBr(π-allyl)(CO)$_2$(phen)·$\frac{1}{2}$Hg(CN)$_2$	red	195	38.76 (37.34)	2.47 (2.24)	7.55 (7.25)			21.7 [c]
MoBr(π-allyl)(CO)$_2$(dppe)·$\frac{1}{2}$Hg(CN)$_2$	yellow	143	46.23 (48.19)	3.60 (3.64)	1.85 (1.75)	12.16 (12.58)		27.7 [c]
MoBr(π-allyl)(CO)$_2$(bipy)·$\frac{1}{4}$HgCl$_2$	purple	175	35.97 (36.26)	2.63 (2.62)	5.66 (5.64)			5.9 [b]
MoBr(π-allyl)(CO)$_2$(phen)·$\frac{1}{3}$HgCl$_2$	orange	200	36.63 (37.56)	2.24 (2.39)	5.03 (5.15)			12.3 [b]

[a] For concentrations ca., 10^{-3}–10^{-4} *M*. [b] In DMSO solution. [c] In DMF solution.

TABLE 2

INFRARED AND ELECTRONIC SPECTRAL DATA FOR THE REACTANT AND PRODUCT COMPLEXES

Compound	IR data (cm^{-1}) [a]		Electronic data [b]	
	ν(CO)	Other bands	λ_{max}(nm)	c
[MoBr(π-allyl)(CO)$_2$(CH$_3$CN)$_2$]	1942 vs		262	3436
	1834 vs		355 sh	875
			377	984
[Mo(NCS)(π-allyl)(CO)$_2$Hg(SCN)$_2$·acetone]	1938 vs	2160sh	270	7002
	1856 vs	2142s ν(C≡N)	386	1086
		2093sh		
[MoBr(π-allyl)(CO)$_2$(py)$_2$]	1907 vs		260	6219
	1809 vs		343	1041
			380	1257
[MoBr(π-allyl)(CO)$_2$(py)$_2$·Hg(SCN)$_2$]	1934 vs	2130 s ν(C≡N)	261	12795
	1848 vs	2070 sh	385	1232
[MoBr(π-allyl)(CO)$_2$(py)Hg(CN)$_2$]	1940 vs	2120 s ν(C≡N)		
	1850 vs			
[MoBr(π-allyl)(CO)$_2$(bipy)]	1938 vs		261	10159
	1845 vs		291	12110
			298 sh	11874
			343	2324
			377	1797
[MoBr(π-allyl)(CO)$_2$(bipy)·$\frac{1}{2}$Hg(CN)$_2$]	1949 vs	2130 s ν(C≡N)	267	7920
	1865 vs		275 sh	7632
			302 sh	5092
			316	5479
			349	2080
			380	1941
			466 sh	1579
[MoBr(π-allyl)(CO)$_2$(bipy)·$\frac{1}{4}$HgCl$_2$]	1938	277m ν(Hg–Cl)	261	13675
	1841		292	16317
			298 sh	16084
			348	3099
			374	2282
[MoBr(π-allyl)(CO)$_2$(phen)]	1925 vs		266	11926
	1847 vs		276 sh	11768
			293 sh	8289
			325 sh	1818
			388	1417
			468	1268
[MoBr(π-allyl)(CO)$_2$(phen)·$\frac{1}{2}$Hg(CN)$_2$]	1951 vs	2135 vs ν(C≡N)	271	25925
	1871		293 sh	11520
			323 sh	3061
			404	2451
			465	1851
[MoBr(π-allyl)(CO)$_2$(phen)·$\frac{1}{2}$HgCl$_2$]	1940 vs	271 m ν(Hg–Cl)	271	51150
	1855 vs		291 sh	23067
			361 sh	5316
			388	4133
			457	3617
[MoBr(π-allyl)(CO)$_2$(dppe)]	1935 vs		264	7771
	1843 vs		417	864
[MoBr(π-allyl)(CO)$_2$(dppe)·$\frac{1}{2}$Hg(CN)$_2$]	1944 vs	2110 sh ν(C≡N)	264	22565
	1874 vs	2088 m	400	944

[a] In KBr. [b] In DMSO for conc. ca. 10^{-4} *M*.

After 5 h, the yellow solid formed was filtered off, washed with acetone, and dried under vacuum for 30 h.

When the reaction was carried out with a 1/2 molar ratio of Mo complex to Hg(SCN)$_2$ the same solid was formed immediately.

[MoBr(π-allyl)(CO)$_2$(py)$_2$Hg(SCN)$_2$]. This was made from [MoBr(π-allyl)(CO)$_2$(py)$_2$] (0.431 g) and Hg(SCN)$_2$ (0.317 g) 1/1 molar ratio) in acetone. After 4 h the yellow precipitate was filtered off, washed with acetone, and dried under vacuum.

[MoBr(π-allyl)(CO)$_2$(py)Hg(CN)$_2$]. A solution of 1 molar equivalent of Hg(CN)$_2$ in acetone was slowly added to a solution of [MoBr(π-allyl)(CO)$_2$(py)$_2$] in the same solvent. After 30 min stirring the solution was concentrated under reduced pressure and diethyl ether was added. The yellow precipitate formed was filtered off, washed with an acetone/diethyl ether mixture, and dried under vacuum.

[MoBr(π-allyl)(CO)$_2$(bipy) $\cdot$ $\frac{1}{2}$Hg(CN)$_2$]. A mixture of equimolecular amounts of the starting molybdenum complex and Hg(CN)$_2$ in acetone was stirred for 115 h. Concentration of the solution in vacuo followed by addition of an excess of diethyl ether gave a red precipitate, which was filtered off, washed with diethyl ether, and dried under vacuum.

[MoBr(π-allyl)(CO)$_2$(phen) $\cdot$ $\frac{1}{2}$Hg(CN)$_2$]. A 1/1 mixture of [MoBr(π-allyl)(CO)$_2$(phen)] and Hg(CN)$_2$ in acetone was stirred for 6 days. The red precipitate was filtered off, washed with diethyl ether, and dried under vacuum. Addition of diethyl ether to the filtrate gave the product.

[MoBr(π-allyl)(CO)$_2$(dppe) $\cdot$ $\frac{1}{2}$Hg(CN)$_2$]. A 1/1 mixture of [MoBr(π-allyl)(CO)$_2$(dppe)] and Hg(CN)$_2$ in acetone was stirred for 2 h during which the initially yellow solution became brown-orange. The solvent was partially evaporated off, to give a green-yellow precipitate, which was filtered off, and dried under vacuum. Addition of diethyl ether to the filtrate precipitated a green-yellow solid, which was filtered off, washed with diethyl ether, and dried under vacuum. The two green-yellow products were identical.

[MoBr(M-allyl)(CO)$_2$(bipy) $\cdot$ $\frac{1}{4}$HgCl$_2$]. A 1/1 mixture of [MoBr(π-allyl)(CO)$_2$(bipy)] and HgCl$_2$ in acetone was stirred for 3.5 days, during which the initially light red solution became dark red. The solvent was partially evaporated off under reduced pressure, and diethyl ether was added to give a dark purple precipitate. This was filtered off, washed with diethyl ether, and dried under vacuum.

[MoBr(π-allyl)(CO)$_2$(phen) $\cdot$ $\frac{1}{3}$HgCl$_2$]. A mixture of [MoBr(π-allyl)(CO)$_2$(phen)] (0.453 g) and HgCl$_2$ (0.271 g) in acetone was stirred for 19 h. The orange precipitate obtained was filtered off, washed with acetone, and dried under vacuum.

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