

REACTIONS OF SUBSTITUTED CARBONYL COMPLEXES OF MOLYBDENUM(0), $\text{Mo}(\text{CO})_4(\text{DAB})$ AND $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{DAB})$, WITH HgX_2 ($\text{X} = \text{Cl}, \text{I}, \text{SCN}$) AND SnCl_4 (DAB = 1,4-DIAZABUTADIENE)

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(Received April 7th, 1983)

Summary

Reactions of the complexes $\text{Mo}(\text{CO})_4\text{DAB}$ [DAB = diacetyldihydrazone (DDH), glyoxalbis(cyclohexylimine (GCy))] and $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{DAB})$ [DAB = glyoxaldihydrazone (GDH), (GCy)], with HgX_2 ($\text{X} = \text{Cl}, \text{I}, \text{SCN}$) and SnCl_4 were studied. They give products which can be regarded as the result of oxidative addition with or without elimination of CO or PPh_3 , and which contain Mo–M' or Mo–M'–Mo bonds (M' = Hg, Sn). An adduct of composition $\text{Mo}(\text{CO})_4(\text{DDH}) \cdot \text{SnCl}_4$ has also been isolated and characterized.

Introduction

Reactions of carbonyl complexes of the type $\text{M}(\text{CO})_4(\text{LL})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; LL = bipy, phen, diphos) with mercury halide [1–3] and pseudohalide [4] have been described as have the reactions of $\text{M}(\text{CO})_4(\text{bipy})$ ($\text{M} = \text{Mo}, \text{W}$) with germanium and tin halides [5]. These reactions give heteronuclear metal–metal bonds, and most of them involve an oxidative addition with or without elimination of ligands, adducts being formed in some cases. Similar reactions of substituted carbonyl complexes containing DAB ligands (DAB = 1,4-diazabutadiene: $\text{R}^1\text{N}=\text{C}(\text{R}^2)-\text{C}(\text{R}^2)=\text{NR}^1$) have not been reported, and so we decided to examine the reactions of two series of substituted carbonyl complexes of general formula, $\text{Mo}(\text{CO})_4(\text{DAB})$ [DAB = diacetyldihydrazone (DDH), glyoxalbis(cyclohexylimine)(GCy)] and $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{DAB})$ [DAB = glyoxaldihydrazone (GDH), (GCy)] with HgX_2 ($\text{X} = \text{Cl}, \text{I}, \text{SCN}$) and SnCl_4 . The DAB ligands are in some respects similar to the 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (dmp) ligands, and we hoped to elucidate the influence of the N,N'-donor ligand on the reaction type and nature of the reaction products.

The $\text{Mo}(\text{CO})_4(\text{DAB})$ and $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{DAB})$ complexes have been extensively studied by tom Dieck et al. [6–9] and Staal et al. [10].

TABLE I
ANALYTICAL AND PHYSICAL DATA FOR THE COMPLEXES OBTAINED BY REACTION OF $M\alpha(CO)_4DAB$ AND $M(CO)_2(PPh_3)_2DAB$ WITH HgX_2
(X = Cl, SCN, I) AND $SuCl_4$

Compound	color	M.p. (°C) (dec.)	ΔM ohm ⁻¹ cm ² mol ⁻¹	Analyses (Found (calcd.) (%))				
				C	H	N	P	X
$M\alpha(CO)_3(DDH)Cl(HgCl)$ (I)	yellow-orange	170	33	15.6 (14.9)	2.0 (1.8)			9.5 (9.9)
$[M\alpha(CO)_3(DDH)]_2Hg(SCN)_2$ (II)	light brown	158	32	20.0 (21.2)	2.2 (2.2)			14.4 (14.8)
$[M\alpha(CO)_4(DDH)]_2HgI_2$ (III)	yellow-orange	157	20	18.7 (17.5)	2.0 (1.9)			10.8 (10.8)
$M\alpha(CO)_4(DDH) \cdot SnCl_4$ (IV)	copper	220	6	15.1 (16.5)	1.7 (1.9)			9.5 (9.6)
$[M\alpha(CO)_3(DDH)]_2SnCl_4 \cdot (CH_3)_2CO$ (V)	orange	200	3	27.4 (27.3)	3.6 (3.7)			10.1 (11.1)
$M\alpha(CO)_3(GCy)ClHgCl$ (VI)	crimson	250	18	29.6 (29.8)	3.6 (3.5)			4.1 (4.1)

$[\text{Mo}(\text{CO})_3(\text{GCy})]_2\text{Hg}(\text{SCN})_2$ (VII)	violet	300	45	20.8 (20.7)	2.2 (2.3)	6.8 (7.3)
$\text{Mo}(\text{CO})_3(\text{GCy})\text{ClSnCl}_3$ (VIII)	red	140	< 3	29.0 (30.9)	3.5 (3.6)	4.1 (4.2)
$\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GDH})\text{Cl}(\text{HgCl})\text{HgCl}_2 \cdot 0.5 \text{PPh}_3^a$ (IX)	reddish-brown	200	88	31.8 (31.7)	2.6 (2.4)	4.9 (4.8)
$\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GDH})(\text{NCS})(\text{HgSCN}) \cdot \text{Hg}(\text{SCN}) \cdot 0.5 \text{PPh}_3^a$ (X)	light-brown	145	32	34.6 (33.2)	2.2 (2.3)	8.7 (8.8)
$\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GDH})(\text{HgI})_2$ (XI)	reddish-brown	183	< 1	22.9 (22.9)	1.8 (1.8)	4.9 (4.8)
$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GDH}) \cdot 2\text{SnCl}_4$ (XII)	brown	180	< 5	37.1 (37.4)	3.2 (2.8)	4.2 (4.3)
$[\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GCy})]_2\text{HgCl}_2 \cdot 0.3 \text{PPh}_3^a$ (XIII)	violet	73	< 6	56.4 (56.0)	6.2 (5.1)	3.1 (3.3)
$\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GCy})(\text{NCS})(\text{HgSCN})$ (XIV)	violet	70	< 7	44.3 (45.4)	4.1 (4.1)	5.8 (5.8)
$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy})2\text{SnCl}_4$ (XV)	brownish-violet	200	< 10	44.1 (44.0)	4.0 (3.8)	2.0 (2.0)

^a In these cases the analysis shows that the product contains an excess of PPh_3 . This PPh_3 may be present as molecules of crystallisation or as an impurity very difficult to remove.

Results and discussion

Reactions of the compounds $\text{Mo}(\text{CO})_4(\text{DAB})$ and $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{DAB})$ with mercury halides and pseudohalides and with SnCl_4

The reactions of the compounds $\text{Mo}(\text{CO})_4(\text{DAB})$ (DAB = DDH, GCy) with HgCl_2 in molar ratio 1/1 are typical oxidative elimination reactions [11], giving products of composition $\text{Mo}(\text{CO})_3(\text{DAB})(\text{HgCl})(\text{Cl})$, analogous to $\text{Mo}(\text{CO})_3(\text{bipy})(\text{HgCl})(\text{Cl})$ [12]. However, the reactions with $\text{Hg}(\text{SCN})_2$ do not have the same stoichiometry, although they can also be regarded as oxidative elimination reactions, and the products have the composition $[\text{Mo}(\text{CO})_3(\text{DAB})]_2\text{Hg}(\text{SCN})_2$, and are thus of the same type as those formed in the reaction of the compounds $\text{Mo}(\text{CO})_3(\text{PPh}_3)(\text{NN})$ (NN = bipy, phen) with $\text{Hg}(\text{SCN})_2$ [4], except that in this latter case the reaction involves elimination of PPh_3 instead of CO. It must be emphasized that the reaction of the $\text{Mo}(\text{CO})_4(\text{DAB})$ compounds with $\text{Hg}(\text{SCN})_2$ is different from that of the $\text{Mo}(\text{CO})_4(\text{NN})$ compounds (NN = bipy, phen, dmp); which give $\text{Mo}(\text{CO})_3(\text{NN})(\text{HgSCN})(\text{NCS})$ [4]. The reaction with HgI_2 yields an adduct $[\text{Mo}(\text{CO})_4(\text{DAB})]_2\text{HgI}_2$ only when DAB = DDH, and there is no reaction when DAB = GCy. Probably steric hindrance by the cyclohexyl group prevents reaction. From the reaction of $\text{Mo}(\text{CO})_4(\text{DDH})$ with SnCl_4 an 1/1 adduct or a product of composition $[\text{Mo}(\text{CO})_3(\text{DDH})]_2\text{SnCl}_4(\text{Me}_2\text{CO})$ can be isolated, so that this is also an oxidative elimination reaction. As the reaction is instantaneous and it is difficult to control the quantity of SnCl_4 , it has not been possible to establish the conditions under which either product is formed exclusively. Nevertheless the reaction of $\text{Mo}(\text{CO})_4(\text{GCy})$ with SnCl_4 can be regarded as a typical oxidative elimination reaction involving formation of $\text{Mo}(\text{CO})_3(\text{GCy})(\text{SnCl}_3)(\text{Cl})$.

The reactions of the $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{DAB})$ compounds in general are oxidative addition reactions with or without elimination of PPh_3 , and in no case is CO eliminated. In some cases (IX, X, XIII) some of released phosphine remains in the product as molecules of crystallisation or as an impurity very difficult to remove. In these cases we assume that only one molecule of PPh_3 remains coordinated to Mo. In reactions with HgCl_2 and $\text{Hg}(\text{SCN})_2$ products of composition $\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GDH}) \cdot 2\text{HgX}_2$ (X = Cl, SCN), $\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GCy})_2\text{HgCl}_2$ and $\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GCy}) \cdot \text{Hg}(\text{SCN})_2$ are obtained in which the HgX_2 content is lower for the derivatives of GCy than for the derivatives of GDH. On the other hand, the reaction between HgI_2 and the GDH derivative gives $\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GDH})(\text{HgI})_2$. No reproducible reaction products were obtained from the reaction of $\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GCy})$ with HgI_2 . Reactions with SnCl_4 give compounds of composition $\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{DAB}) \cdot 2\text{SnCl}_4$, which, on the basis of their IR spectra can be regarded as oxidative addition products.

Table 1 gives the analytical results and the physical properties of the products isolated. The conductivity measurements in DMF correspond to non-electrolytes or in some cases lie in the range for 1/1 electrolytes, indicating a dissociation in solution such as has been observed in similar cases [11].

The compounds are highly coloured and very slightly soluble in organic solvents of low polarity. In polar solvents the compounds derived from $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{DAB})$ complexes are considerably more soluble than those derived from $\text{Mo}(\text{CO})_4(\text{DAB})$ complexes and the solutions gradually decompose. The rate of decomposition is greater the higher the polarity of the solvent.

Infrared spectra

Table 2 gives the frequencies (cm^{-1}) of the more significant bands which appear in the spectra of the new products, together with those of the starting compounds. In general, the IR spectra are the most characteristic features of the type of compound formed and allow the adducts to be clearly distinguished from the products formed in an oxidative elimination. Thus in the spectra of adducts formed from $\text{Mo}(\text{CO})_4(\text{DAB})$ complexes, the four bands corresponding to the $\nu(\text{CO})$ stretching frequencies are relatively close to those of the starting compounds, whilst in the case of products of oxidative elimination reactions only three bands appear and these are displaced towards higher frequencies because of the lowering of the electronic density on the metal as a result of its oxidation, which lowers the back-bonding to the CO ligands.

The bands corresponding to the stretching frequencies $\nu(\text{C}=\text{N})$ are generally weak in the products and are not significantly displaced. The bands corresponding to $\delta(\text{MCO})$ appear in the $540\text{--}640\text{ cm}^{-1}$ region; there are four in the case of the adducts and three in the oxidative elimination reaction products. The same occurs with the $\nu(\text{Mo}-\text{C})$ stretching frequencies in the $360\text{--}500\text{ cm}^{-1}$ region. In this case, there is a characteristic intense band between 360 and 390 cm^{-1} in the starting compounds and in the adducts. This band corresponds to one of the $\nu(\text{Mo}-\text{C})$ stretching frequencies, and is absent from the oxidative addition products. Between 225 and 250 cm^{-1} there are one or two weak bands which may be assigned to $\nu(\text{Mo}-\text{N})$ stretching frequencies, and do not seem to be much affected by the type of compound formed. In products of the reactions with HgCl_2 there are two bands in the range $270\text{--}305\text{ cm}^{-1}$ which are assigned to $\nu(\text{M}-\text{Cl})$ frequencies. These bands are displaced towards the lower frequency compared with HgCl_2 , and one of them may be a $\nu(\text{Mo}-\text{Cl})$ and the other a $\nu(\text{Hg}-\text{Cl})$ vibration. In the products from reactions of $\text{Hg}(\text{SCN})_2$, the $\nu(\text{C}\equiv\text{N})$ stretching frequencies appear as a structured band with maxima at 2100 and $2060\text{--}2080\text{ cm}^{-1}$. The first maximum could be due to terminal SCN groups coordinated with Hg through S. However $\nu(\text{C}\equiv\text{N})$ thiocyanate bands at $2075\text{--}2079$ and 2105 cm^{-1} have been assigned to SCN groups coordinated with Mo through N in $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2(\text{N},\text{N})(\text{NCS})]$ (N,N = bipy, phen) [13] and $[\text{Me}_4\text{N}][\text{Mo}(\text{CO})_5(\text{NCS})]$ [14], respectively, the coordination mode of thiocyanate being confirmed in the first case by determination of structure [15,16]. A medium or strong band at 310 cm^{-1} , which appears in all products from $\text{Hg}(\text{SCN})_2$, could be assigned to a $\nu(\text{Hg}-\text{S})$ or to a $\nu(\text{Mo}-\text{N})$ stretching frequency involving the S or N atoms of the thiocyanate. On the other hand the $\nu(\text{CS})$ band cannot be observed because of the presence of strong ligand bands in the same region. From the results we cannot decide between the formulation $[\text{Mo}(\text{CO})_3(\text{DAB})]_2\text{Hg}(\text{SCN})_2$, with terminal SCN groups coordinated with Hg through S, and $[\text{Mo}(\text{NCS})(\text{CO})_3(\text{DAB})]_2\text{Hg}$, with terminal NCS groups coordinated with Mo through N. Both formulae imply the presence of Mo-Hg-Mo bonds with the mercury four coordinated in the first case and two-coordinated in the second. However the fact that the coordination number of the mercury atom in $\text{Cp}(\text{CO})_3\text{Mo}(\text{HgSCN})$ was not raised in several attempted addition reactions [17] favours the second possibility. In the spectra of the products from SnCl_4 , the bands which appear in the $270\text{--}340\text{ cm}^{-1}$ range are also assigned to $\nu(\text{M}-\text{Cl})$ stretching frequencies; the higher ones must correspond to $\nu(\text{Sn}-\text{Cl})$ vibrations and that at about 270 cm^{-1} in all the products of oxidative elimination reactions with SnCl_4 or HgCl_2 may be a $\nu(\text{Mo}-\text{Cl})$ vibration.

(Continued on p. 82)

TABLE 2
THE MOST RELEVANT IR FREQUENCIES (cm^{-1}) OF THE COMPOUNDS $\text{Mo}(\text{CO})_4\text{DAB}$, $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2$ AND THOSE OF THEIR REACTION PRODUCTS

Compounds	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{CO})$	$\nu(\text{M}-\text{C})$	$\nu(\text{M}-\text{X})$	$\nu(\text{Hg}-\text{S})$	$\nu(\text{M}-\text{N})$
$\text{Mo}(\text{CO})_4\text{DDH}$		2020 s, 1910s 1870 s, 1835 s	500 m, 470 m 460 sh 380 s			240 m, 220 w
$\text{Mo}(\text{CO})_3(\text{DDH})\text{Cl}(\text{HgCl})$ (I)		1920 s, 1910 s 1880 s	490 m, 470 m 450 m	285 s, br		250 w, 230 w
$[\text{Mo}(\text{CO})_3(\text{DDH})]_2\text{Hg}(\text{SCN})_2$ (II)	2100 s, 2080 s	1980 s, 1960 s 1875 s	500 m, 480 m 450 m		310 m 300 sh	246 w, 225 w
$[\text{Mo}(\text{CO})_4(\text{DDH})]_2\text{HgI}_2$ (III)		2020 s, 1980 s 1865 s, 1845 s	500 m, 470 m 420 m, 380 s			235 w, 215 w
$\text{Mo}(\text{CO})_4\text{DDH}\cdot\text{SnCl}_4$ (IV)		2005 s, 1910 s 1870 s, 1835 s	490 m, 450 m 410 mw, 370 s	318 s, 307 s 290 s, 283 s		240 m, 225 w
$[\text{Mo}(\text{CO})_3(\text{DDH})]_2\text{SnCl}_4\cdot(\text{CH}_3)_2\text{CO}$ (V)		2110 s, 1970 s 1930 s	500 m, 460 m 415 w	305 s, 296 s 285 s, 270 s		245 w, 225 w
$\text{Mo}(\text{CO})_4(\text{GCy})$		2020 s, 1930 s 1880 s, 1810 s	490 m, 470 m 460 m, 370 f			248 w, 230 w
$\text{Mo}(\text{CO})_3(\text{GCy})\text{Cl}(\text{HgCl})$ (VI)		2000 s, 1980 s 1920 s, 1890 s, 1880 s	450 m ^a	287 s, 270 s		218 vw

$[\text{Mo}(\text{CO})_2(\text{GCy})_2\text{Hg}(\text{SCN})_2]$ (VII)	2100 s, 2060 s	1980 s, br 1900 s, br 2020 s, 1960 s 1920 s 1830 s, 1750 s	490 w, 450 w ^a	310 s 300 sh	245 w, 228 w
$\text{Mo}(\text{CO})_3(\text{GCy})\text{Cl}(\text{SnCl}_3)$ (VIII)			^a	340 s, 320 s 270 s	236 vw, 220 vw
$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GDH})$		1830 s, 1750 s	455 m, 418 m		230 w, 215 w
$\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GDH})\text{Cl}(\text{HgCl})\cdot\text{HgCl}_2$ (IX)		1910 s, 1850 vs	450 w, 415 w	315 m, 295 s 284 sh 278 sh	247 w, 228 w
$\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GDH})(\text{NCS})\text{Hg}(\text{SCN})\cdot\text{Hg}(\text{SCN})_2$ (X)	2118 vs 2100 sh 2080 s, 2060 sh	1900 m, 1830 s	460 m, 420 m	310 m 300 sh 270 m	245 w, 225 w
$\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GDH})(\text{Hgl})_2$ (XI)		1905 s, 1844 vs	450 w, 415 w		248 w, 225 w
$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GDH})\cdot 2\text{SnCl}_4$ (XII)		1960 s, 1880 vs		325 s, br 320 s 305 m, 280 w	240 w, 230 w
$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy})$		1850 s, 1770 s, 1760 s	480 w, 450 w		262 w, 230 m
$[\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GCy})]_2\text{HgCl}_2$ (XIII)		1915 s, 1890 s 1825 s, 1795 s 1885 s	480 m 450 m	330 m, 290s	230 w, 220 w
$\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GCy})(\text{NCS})(\text{HgSCN})$ (XIV)	2020 vs, br 2060 sh		490-485 w	310 s	248 w, 228 w
$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy})\cdot 2\text{SnCl}_4$ (XV)		1915 s, 1845 s		337 s, 325 sh 305 s, 275 m	236 w, 222 w

^a Bands difficult to see in the $\text{Mo}(\text{CO})_4(\text{CGy})$ derivatives.

As far as products from $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{DAB})$ complexes are concerned, two bands corresponding to $\nu(\text{CO})$ stretching frequencies are generally observed; these are considerably displaced towards higher frequencies, suggesting that an oxidative addition always takes place, whether or not accompanied by phosphine elimination. Two bands are also observed between 495 and 540 cm^{-1} , and another two between 415 and 490 cm^{-1} , and these are assigned to the $\delta(\text{MoCO})$ bending and to the $\nu(\text{Mo}-\text{C})$ stretching frequencies, respectively. However, the product of the reaction of $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy})$ with $\text{Hg}(\text{SCN})_2$ shows only one $\nu(\text{CO})$ band and one $\nu(\text{Mo}-\text{C})$ band, which could be due to a more symmetrical configuration of this compound compared to the others.

The bands corresponding to $\nu(\text{C}=\text{N})$ vibrations of the DAB ligands are not observed due to the presence of the phosphine phenyl bands. The $\nu(\text{C}\equiv\text{N})$ vibrations of the thiocyanates in the products of reactions between $\text{Hg}(\text{SCN})_2$ and $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GDH})$ show a structured band with maxima at 2118, 2100, 2080 and 2060 cm^{-1} , which may be due to the presence of various classes of terminal thiocyanates, some coordinated through N to Mo (2060 cm^{-1}) and others through S to Hg. The $\nu(\text{C}\equiv\text{N})$ band in the product of the reaction with $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy})$ appears at a lower frequency, as a broad band between 2020 and 2060 cm^{-1} , favouring the presence of SCN terminal groups coordinated to Mo without excluding the presence of thiocyanate groups coordinated through S to Hg. This suggests formulae of the type $\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GDH})(\text{HgSCN})(\text{NCS}) \cdot \text{Hg}(\text{SCN})_2$ and $\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GCy})(\text{HgSCN})(\text{NCS})$, respectively, for these two compounds.

The products from HgCl_2 and SnCl_4 show bands in the 275–340 cm^{-1} region which are assigned to $\nu(\text{M}-\text{Cl})$ stretching frequencies. It is difficult to distinguish between $\nu(\text{Mo}-\text{Cl})$ and $\nu(\text{Hg}-\text{Cl})$ in the products from HgCl_2 . Two formulae are possible for the product from $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy})$, namely $[\text{ClMo}(\text{CO})_2(\text{PPh}_3)(\text{GCy})]_2\text{Hg}$ and $[\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GCy})]_2\text{HgCl}_2$, both with Mo–Hg–Mo bonds. Products of the reactions of both $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{DAB})$ compounds with SnCl_4 show several bands in the 275–340 cm^{-1} region, of which that with the lowest frequency (275–280 cm^{-1}) could be assigned to $\nu(\text{Mo}-\text{Cl})$. This suggests that these compounds could have the formula $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{DAB})(\text{SnCl}_3)(\text{Cl}) \cdot \text{SnCl}_4$ (DAB = GDH, GCy), in which case the DAB ligand would be monodentate. However a bidentate coordination of the DAB ligand seems more probable, in which case the band at 275–280 cm^{-1} could be assigned to a bridging Sn–Cl–Sn bond. As has also been seen in the reactions with $\text{Hg}(\text{SCN})_2$, several of the products of the reactions contain HgX_2 or SnCl_4 of crystallisation, a relatively common occurrence in compounds with heteronuclear Mo–Hg bonds produced by reactions with mercury halides or pseudohalides [11]. The bands which appear in the 225–250 cm^{-1} region can be assigned to $\nu(\text{Mo}-\text{N})$ vibrations.

Electronic spectra

The electronic spectra of the reaction products are quite similar to those of the starting compounds. All show one or two bands between 270 and 290 nm which, because of their high intensity and their position, are assigned to CT transitions $\pi^*(\text{CO}) \leftarrow d\pi(\text{Mo})$. There is also another band, which for $\text{Mo}(\text{CO})_4(\text{DDH})$, $\text{Mo}(\text{CO})_4(\text{GCy})$, $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GDH})$ and $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy})$ and their corresponding derivatives appears in the ranges 296–328 nm, 320–372 nm, 320–352 nm, and 320–350 nm, respectively. Because of its relatively high intensity it is also

assigned to a CT transition $\pi^*(\text{DAB}) \leftarrow \pi(\text{DAB})$ in the tetracarbonyls and their derivatives, whilst in the dicarbonyl complexes it is probably due to a CT transition $\pi^*(\text{Ph}) \leftarrow \pi(\text{Ph})$ of the PPh_3 ligand. In these last compounds the bands appearing in the range 390–455 nm are assigned to CT transitions $\pi^*(\text{DAB}) \leftarrow \pi(\text{DAB})$.

The most interesting bands are those in the lower energy region; in the starting compounds these are called solvatochromic bands because they vary with the polarity of the solvent and have been assigned to CT transitions $\pi^*(\text{DAB}) \leftarrow d \pi(\text{Mo})$ [18–20]. They are very strong bands for $\text{Mo}(\text{CO})_4(\text{DAB})$ complexes and are considerably displaced towards the red when the polarity of the solvent is increased [6,18]. Complexes $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{DAB})$ also show solvatochromic bands, but they are much weaker and less sensitive to the polarity of the solvent.

The similarity between the electronic spectra of the starting compounds and those of the products may be because all the fairly intense bands are due to CT transitions and are less affected by the changes in symmetry and coordination of the metal in the oxidative addition or elimination reactions. The solvatochromic bands are also the most shifted in the products with respect to those of the starting compounds. Table 3 lists the absorption maxima of the bands of highest wavelength appearing in the electronic spectra of the starting compounds and their products, in benzene and in DMF.

The spectra of $\text{Mo}(\text{CO})_4(\text{DDH})$ and its reaction products with $\text{Hg}(\text{SCN})_2$ and HgI_2 show a structured solvatochromic band with two maxima, which are displaced towards the red in the latter, whilst the spectra of the products from HgCl_2 and SnCl_4 in the same solvent show two clearly separated bands, and the displacement towards the red of the lower frequency band is very pronounced. The spectra in DMF show a single band which corresponds to that of higher frequency appearing in the spectra in benzene. Only the SnCl_4 derivatives show two bands similar to those of the spectra in benzene but displaced towards the blue.

In the spectra of $\text{Mo}(\text{CO})_4(\text{GCy})$ and its derivatives the solvatochromic band is very sensitive to the polarity of the solvent. In benzene this band for the products is displaced towards the red, and in the spectra in DMF, show, in addition to the displacement towards the red, two additional maxima one of them towards the lower frequency values.

Because of the high insolubility of the products from $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GDH})$, in the majority of the cases no bands are observed in the range where the solvatochromic band appears for the starting compounds, especially in benzene. However, in spite of the low solubility, a solvatochromic band towards 570 nm has been observed in the spectra of the reaction products of $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy})$, and a component of lower energy sometimes appears in DMF.

We conclude that all the new compounds are the result of oxidative addition reactions, along, in some cases with elimination of CO or PPh_3 . These oxidative addition reactions can be classified into three general types:

- (a) Oxidative addition reactions with elimination of CO or PPh_3 and formation of a seven-coordinate molybdenum compound containing a Mo–HgX or Mo– SnCl_3 bond and, in most cases, a Mo–X bond (I, VI, VIII–XI, XIV).
- (b) Oxidative addition reactions with elimination of CO or PPh_3 and formation of six- or seven-coordinate molybdenum compounds containing Mo–M–Mo bonds (M = Hg, Sn) (II, V, VII, XIII).
- (c) Oxidative addition reactions with formation of seven-coordinate molybdenum

(Continued on p. 86)

TABLE 3
ELECTRONIC ABSORPTION MAXIMA λ (nm) (ϵ) FOR THE $\text{Mo}(\text{CO})_4\text{DAB}$ AND $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2$ DAB COMPOUNDS AND THOSE OF THEIR REACTION PRODUCTS IN THE 900–300 nm RANGE

Compounds	$\pi^*(\text{Ph}) \leftarrow \pi(\text{Ph})$ (PPh_3)		$\pi^*(\text{DAB}) \leftarrow \pi(\text{DAB})$		$\pi^*(\text{DAB}) \leftarrow d\pi(\text{Mo})$	
	Benzene	DMF	Benzene	DMF	Benzene	DMF
$\text{Mo}(\text{CO})_4(\text{DDH})$			304	308(2000)	392(2300)	432(3000) 390(1880)
$\text{Mo}(\text{CO})_3(\text{DDH})\text{Cl}(\text{HgCl})$			296 w	312(4000)	400 w	456 w 440(800)
[$\text{Mo}(\text{CO})_3(\text{DDH})_2$] ₂ Hg(SCN) ₂ (I)			304(570)	308(6200)	400(2500)	435(3000) 400(2300)
[$\text{Mo}(\text{CO})_3(\text{DDH})_2$] ₂ HgI ₂ (II)			328 sh	304(23636)	416(2200)	460(3500) 384(2300)
[$\text{Mo}(\text{CO})_3(\text{DDH})_2$] ₂ SnCl ₄ (III)			300 ^a		384 ^a	496(2800) 370(2000) 456(3000)
$\text{Mo}(\text{CO})_4(\text{GCy})$ (IV)			372(30041)	375(51392)	535(143768)	490(127404)
$\text{Mo}(\text{CO})_3(\text{GCy})\text{Cl}(\text{ClH})$ (VI)			320(27190)	340 sh	580(32751)	519(23551) 622(25362)

$\text{Mo}(\text{CO})_3(\text{GCy})\text{Hg}(\text{SCN})_2$ (VII)	370(7415)	535(31516)	540(658)	744(282)
$\text{Mo}(\text{CO})_3(\text{GCy})\text{Cl}(\text{SnCl}_3)$ (VIII)	365 ^a	290(6000)	495(2195)	626(2390)
$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GDH})$ $\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GDH})\text{Cl}(\text{HgCl})\cdot\text{HgCl}_2$ (IX)	412 sh 336 sh 352 sh	416 sh 560(4800)	552(2200) 582 vw	
$\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GDH})(\text{NCS})\cdot(\text{HgSCN})\cdot\text{Hg}(\text{SCN})_2$ (X)	344 vw		450 vw	
$\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GDH})(\text{Hgl})_2$ (XI)	320 sh 352 sh	459 vw	444 vw	
$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GDH})\cdot 2\text{SnCl}_4$ (XII)	336 sh	438 vw		
$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy})$ $[\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GCy})]_2\text{HgCl}_2$ (XIII)	350 s 350 sh, 360 sh 390 sh 445 w	390 sh(110000) 580 s 585 m	595(113333) 500(1000)	
$\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GCy})(\text{NCS})(\text{HgSCN})$ (XIV)	335 sh, 360 sh 320 sh	400 sh 570 m	555(1120)	770(320)
$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy})\cdot 2\text{SnCl}_4$ (XV)	416 sh		570 w	

^a When the solubility is very low the intensity of the bands is indicated by the notation usually employed in IR spectroscopy.

compounds containing Mo–Hg–Mo (III) or Mo–Sn bonds (XII, XV).

In some cases residual HgX_2 ($X = \text{Cl}, \text{SCN}$) or SnCl_4 is present in the products from these compounds. The HgX_2 and SnCl_4 plays the role of the lattice water in hydrates, and stabilize the crystalline complexes [11].

We were not able to isolate the products from reactions with Ph_3SnCl or Me_3SnCl .

Experimental

The starting complexes $\text{Mo}(\text{CO})_4(\text{DAB})$ and $\text{Mo}(\text{CO})_2(\text{DAB})(\text{PPh}_3)_2$ were made as described in the literature [7,8].

All experiments were performed under oxygen-free dry nitrogen. Organic solvents were purified by conventional methods. Analyses for C, H, N, Cl and P were carried out by Elemental Micro-Analysis Ltd. Laboratories, Amberley, Beaworthy (Devon, England). Infrared spectra in the $4000\text{--}200\text{ cm}^{-1}$ region were recorded with KBr discs or Nujol mulls on a Perkin–Elmer 325 spectrometer.

Electronic spectra were recorded on a Uvikon 820 Kontron Spectrophotometer. Conductance measurements were performed in benzene and DMF at room temperature with a Philips conductivity bridge, Model N° CM 4144 and a PR 9512/00 cell.

Reactions of $\text{Mo}(\text{CO})_4(\text{DDH})$ and $\text{Mo}(\text{CO})_4(\text{GCy})$

$\text{Mo}(\text{CO})_3(\text{DDH})\text{Cl}(\text{HgCl})$ (I). A solution of HgCl_2 (0.17 g, 0.6 mmol) in CH_2Cl_2 was added to a solution of $\text{Mo}(\text{CO})_4(\text{DDH})$ (0.2 g, 0.6 mmol) in 15 ml of the same solvent and the mixture was stirred at room temperature for 3 h. The orange precipitate initially formed redissolved with evolution of CO and an orange-yellow precipitate appeared. This was isolated by decantation, washed several times with diethyl ether (10 ml each), and dried in a vacuum at room temperature (yield 60%).

$[\text{Mo}(\text{CO})_3(\text{DDH})]_2\text{Hg}(\text{SCN})_2$ (II). $\text{Hg}(\text{SCN})_2$ (0.20 g, 0.64 mmol) was added to a solution of $\text{Mo}(\text{CO})_4(\text{DDH})$ (0.2 g, 0.6 mmol) in CH_2Cl_2 (20 cm^3) with stirring. Evolution of CO was observed. After 3 h of stirring at room temperature the light brown solid formed was filtered off, washed several times with diethyl ether, and dried for 2 h in a vacuum at room temperature (yield 70%).

$[\text{Mo}(\text{CO})_4(\text{DDH})]_2\text{HgI}_2$ (III). HgI_2 (0.30 g, 0.6 mmol) was added to a solution of $\text{Mo}(\text{CO})_4(\text{DDH})$ (0.2 g, 0.6 mmol) in CH_2Cl_2 (15 cm^3) and the mixture was stirred at room temperature for 18 h. Addition of diethyl ether gave a reddish-brown precipitate, which was separated by decantation, washed several times with diethyl ether and dried in a vacuum at room temperature (yield 45%).

$\text{Mo}(\text{CO})_4(\text{DDH})\text{SnCl}_4$ (IV) and $[\text{Mo}(\text{CO})_3(\text{DDH})]_2\text{SnCl}_4 \cdot (\text{CH}_3)_2\text{CO}$ (V). Carefully dried solvents were used in this reaction. Two or three drops of SnCl_4 were distilled into a solution of $\text{Mo}(\text{CO})_4(\text{DDH})$ (0.2 g, 0.6 mmol) in 15 cm^3 of acetone with vigorous stirring; a bright red precipitate of $\text{Mo}(\text{CO})_4(\text{DDH}) \cdot \text{SnCl}_4$ was formed immediately on the addition of the first drop of SnCl_4 . The mixture was stirred for 1 h at room temperature then the precipitate was filtered off under dry N_2 , washed with diethyl ether and dried in vacuum for 5 h at room temperature. The dried product was reddish-violet in colour (yield 40%).

The reaction in CH_2Cl_2 as solvent gave a violet solid which could not be isolated, and decomposed quickly to a brown material.

Sometimes instead of the adduct we isolated $[\text{Mo}(\text{CO})_3(\text{DDH})]_2\text{SnCl}_4(\text{CH}_3)_2\text{CO}$.

As the reaction is instantaneous it is very difficult to stop it at the correct point.

$Mo(CO)_3(GCy)ClHgCl$ (VI). $HgCl_2$ (0.16 g, 0.6 mmol) was added to a solution of $Mo(CO)_4(GCy)$ (0.26 g, 0.6 mmol) in 15 cm³ of CH_2Cl_2 and the mixture was stirred at room temperature for 6 h. The precipitate initially formed redissolved with evolution of CO and a red precipitate appeared. This was filtered off, washed several times with diethyl ether, and dried in vacuum for 3 h (yield 80%).

$[Mo(CO)_3(GCy)]_2Hg(SCN)_2$ (VII). A solution of $Hg(SCN)_2$ (0.19 g, 0.6 mmol) in acetone was added with stirring to a solution of $Mo(CO)_4(GCy)$ (0.26 g, 0.6 mmol) in the same solvent. Evolution of CO was observed. After 3 h stirring the reaction was complete and the evolution of CO had ceased. Partial evaporation of solvent and addition of diethyl ether gave a deep red precipitate, which was filtered off and dried in a vacuum for 4 h at room temperature (yield 70%). No reaction took place in CH_2Cl_2 as solvent.

Attempted reactions of the same starting complex with HgI_2 under various conditions (involving different solvents, molar ratios of reactants, temperatures and reaction times) were unsuccessful.

$Mo(CO)_3(GCy)ClSnCl_3$ (VIII). The conditions used were similar to those for the reaction of $Mo(CO)_4(DDH)$ with $SnCl_4$. Two or three drops of $SnCl_4$ were distilled slowly into a solution of $Mo(CO)_4(GCy)$ (0.26 g, 0.6 mmol). The colour of the solution changed immediately to bright red and a red precipitate immediately appeared. After 30 min stirring at room temperature the precipitate was filtered off, washed several times with CH_2Cl_2 , and dried for 2 h at room temperature in a vacuum (yield 95%).

Reactions of $Mo(CO)_2(PPh_3)_2(GDH)$ and $Mo(CO)_2(PPh_3)_2(GCy)$

$Mo(CO)_2(PPh_3)(GDH)Cl(HgCl)(HgCl_3)$ (IX). $HgCl_2$ (0.14 g, 0.52 mmol) were added to a solution of $Mo(CO)_2(PPh_3)_2(GDH)$ (0.20 g, 0.26 mmol) in 20 cm³ of CH_2Cl_2 . After 1 h stirring at room temperature a reddish-brown precipitate appeared, and this was filtered off, washed several times with 5 cm³ of petroleum ether, and dried for 3 h at room temperature (yield 60%).

$Mo(CO)_2(PPh_3)(GDH)(NCS)(HgSCN) \cdot Hg(SCN)_2$ (X). $Hg(SCN)_2$ (0.16 g, 0.5 mmol) was added to a solution of $Mo(CO)_2(PPh_3)_2(GDH)$ (0.19 g, 0.25 mmol) in 20 cm³ of CH_2Cl_2 . After 45 min stirring at room temperature the brown precipitate was filtered off, washed several times with 5 cm³ petroleum ether, and dried at room temperature for 3 h in vacuum (yield 70%).

$Mo(CO)_2(PPh_3)(GDH)(HgI)_2$ (XI). HgI_2 (0.28 g, 0.62 mmol) was added with stirring to a solution of $Mo(CO)_2(PPh_3)_2(GDH)$ (0.24 g, 0.31 mmol) in CH_2Cl_2 (20 cm³). After 1 h stirring at room temperature the brown precipitate formed was filtered off, washed several times with petroleum ether (5 cm³ each), and dried at room temperature for 3 h in vacuum (yield 50%).

$Mo(CO)_2(PPh_3)_2(GDH) \cdot 2SnCl_4$ (XII). Four drops of $SnCl_4$ were distilled into a solution of $Mo(CO)_2(PPh_3)_2(GDH)$ (0.24 g, 0.31 mmol) in CH_2Cl_2 (15 cm³). After 15 min stirring diethyl ether (20–30 cm³) was added and the brown precipitate formed was filtered off, washed several times with diethyl ether (5 cm³ each), and dried for 2 h at room temperature in vacuum (yield 60%).

$[Mo(CO)_2(PPh_3)(GCy)]_2HgCl_2$ (XIII). $HgCl_2$ (0.06 g, 0.22 mmol) was added to a solution of $Mo(CO)_2(PPh_3)_2(GCy)$ (0.20 g, 0.22 mmol) in CH_2Cl_2 (20 cm³) and the mixture was stirred for 18 h at room temperature. A violet solution was formed.

Evaporation of the solvent under reduced pressure left a solid, which was dissolved in the minimum amount of CH_2Cl_2 . Addition of petroleum ether (20 cm^3) gave a violet precipitate, which was filtered off, washed several times with petroleum ether and dried for 3 h at room temperature in vacuum (yield 50%).

$\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{GCy})(\text{NCS})(\text{HgSCN})$ (XIV). $\text{Hg}(\text{SCN})_2$ (0.07 g, 0.23 mmol) was added with stirring at room temperature to a solution of $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy})$ (0.21 g, 0.23 mmol) in CH_2Cl_2 (20 cm^3). After 1 h stirring the solvent was evaporated at reduced pressure, and the solid residue was dissolved in the minimum amount of CH_2Cl_2 . Addition of petroleum ether (20 cm^3) gave a violet precipitate, which was filtered off, washed several times with petroleum ether (5 cm^3 each), and dried at room temperature in vacuum for 3 h (yield 50%).

Attempted reactions between $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy})$ and HgI_2 under various conditions failed to yield a definite product.

$\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy}) \cdot 2\text{SnCl}_4$ (XV). This compound was prepared by the procedure described for $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GDH})$, starting from 0.27 g (0.30 mmol) of $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{GCy})$ (yield 60%).

Acknowledgement

Financial support of this work by the Comisión Asesora de Investigación Científica y Técnica (Project No 3727-79) is gratefully acknowledged.

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