

CARBONYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN WITH SULFUR DONORS

IV *. PYRIDINE REPLACEMENT REACTIONS OF $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})$ COMPLEXES ((S,S) = XANTHATE AND DITHIOCARBAMATE)

M.F. PERPIÑÁN, L. BALLESTER,

Facultad de Ciencias Químicas, Departamento de Química Inorgánica, Universidad Complutense, Madrid-3 (Spain)

and A. SANTOS

Instituto de Química Inorgánica "Elhuyar", C.S.I.C., Serrano 113 bis, Madrid-6 (Spain)

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Summary

The reactions of $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})$ [(S,S) = methylxanthate, *N*-ethylthiocarbamate and *N,N*-diethylthiocarbamate] with various N- and P-donor mono- and bi-dentate ligands has given four types of mono- and bi-nuclear complexes: $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{L})$ [(S,S) = Mexant, EtHdtc, Et₂dtc; L = PPh₃], $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{L-L})$ [(S,S) = Mexant, (L-L) = bipy, phen, DDH, GBCHI; (S,S) = EtHdtc, (L-L) = bipy, phen, GBCHI; (S,S) = Et₂dtc, (L-L) = phen], $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2]_2(\mu\text{-L-L})$ [(S,S) = Mexant, EtHdtc, Et₂dtc; (L-L) = 4,4'-bipy, 4,4'-DTBP, dppe], and $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{L-L})]_2(\mu\text{-CO})_2$ [(S,S) = EtHdtc, Et₂dtc; L-L = dppe]. In some cases the pyridine replacement is accompanied by a change in the coordination mode of the 1,1-dithiolato ligand.

Introduction

Complexes of general formula $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})$. (S,S = xanthate, dithiocarbamate) have been prepared by the reaction of $\text{MoBr}(\pi\text{-allyl})(\text{CO})_2(\text{py})_2$ with the corresponding alkali metal salt [2]. An excess of the 1,1-dithiolate ligand gives the same products, the second pyridine molecule being not displaced. This fact has motivated the present study, which deals with the substitution reactions of $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})$ complexes [(S,S) = Mexant (methylxanthate), EtHdtc

* Part I, II and III: see refs. 1, 2 and 3, respectively.

(*N*-ethylthiocarbamate), Et₂dtc (*N,N*-diethylthiocarbamate)] with carbon monoxide and a series of mono- and bi-dentate, N- or P-donor ligands: 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), diacetyldihydrazone (DDH), 4,4'-bipyridine (4,4'-bipy), 4,4'-dithiobipyridine (4,4'-DTBP), 1,2-bis(diphenylphosphine)ethane (dppe), triphenylphosphine (PPh₃) and glyoxalbis(cyclohexylimine) (GBCHI).

The reactions with 2,2'-bipyridine could be expected to give the same complexes as were obtained from the direct reaction of MoBr(π -allyl)(CO)₂(bipy) with the corresponding alkaline xanthate or dithiocarbamate [3]. On the other hand the reaction of Mo(S,S)(π -allyl)(CO)₂(py) complexes with dppe can be a convenient method of preparing complexes containing (S,S), CO, π -allyl and dppe ligands, which could not be obtained by the reaction of MoBr(π -allyl)(CO)₂(dppe) with the alkaline xanthates and dithiocarbamates we used [3].

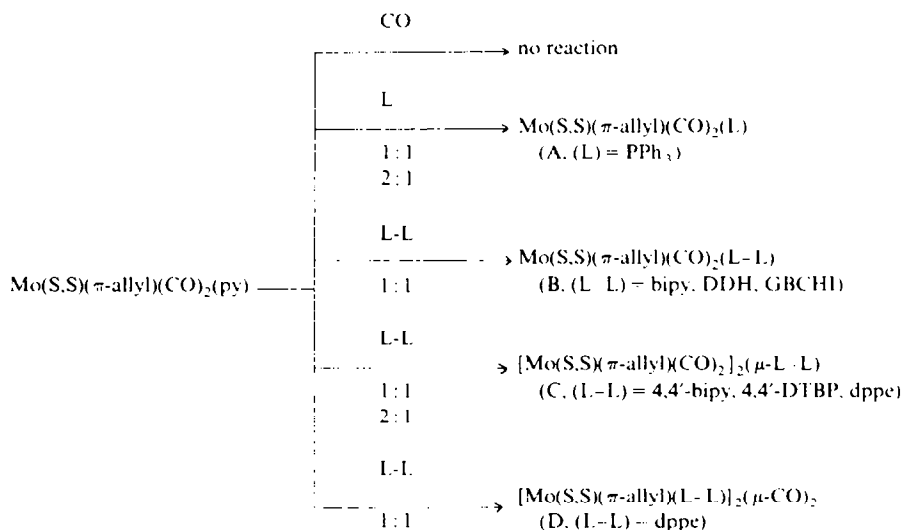
The reaction type and products should also be influenced by whether the bidentate ligands are chelating or non-chelating.

Results and discussion

The reactions of the Mo(S,S)(π -allyl)(CO)₂(py) complexes with the ligands mentioned above give several types of mono- and bi-nuclear compounds, according to Scheme 1.

Most of the reactions occur immediately and the products separate from the reaction medium either spontaneously or after addition of water. The complexes behave as non-electrolytes in several solvents and decompose before melting or melt with decomposition. They are rather stable, except for some of the dithiocarbamate derivatives (4,4'-bipy; 4,4'-DTBP; GBCHI) which decompose slowly in air. All these complexes have low solubilities in ordinary organic solvents, which makes NMR studies difficult.

SCHEME 1



[(S,S) = Mexant, EtHdte, Et₂dte]

No reaction was observed on bubbling carbon monoxide through a solution of $\text{Mo}(\text{Mexant})(\pi\text{-allyl})(\text{CO})_2(\text{py})$ or $\text{Mo}(\text{EtHdtc})(\pi\text{-allyl})(\text{CO})_2(\text{py})$ in acetone, and the recovered solids were spectroscopically (IR) identical with the starting compounds. The starting complexes or decomposition products were isolated from the reactions of DDH with $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})$ [(S,S) = EtHdtc, Et₂dtc] or GBCHI with $\text{Mo}(\text{Et}_2\text{dtc})(\pi\text{-allyl})(\text{CO})_2(\text{py})$. The new compounds obtained in the remaining reactions can be regarded as derived from the $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})$ complexes by replacement of the pyridine ligand, accompanied in some cases by a change in the coordination mode of the 1,1-dithiolate ligand, as discussed below. Table 1 summarizes analytical data and some physical properties for the isolated products.

The reaction of the $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})$ complexes with PPh_3 in a 1/1 molar ratio yields simple substitution products, $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{PPh}_3)$ (type A). An excess of PPh_3 gives the same results.

In the case of potentially chelating N,N-donor ligands, compounds of type B are formed. The 2,2'-bipyridyl derivatives $\text{Mo}(\text{Mexant})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})$ (I) and $\text{Mo}(\text{EtHdtc})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})$ (IX) so obtained are identical with those isolated from the reaction of $\text{MoBr}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})$ with KMexant and NaEtHdtc [3]. As in earlier studies [3,4] a compound of composition $\text{Mo}(\text{Et}_2\text{dtc})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})$ could not be isolated from the reaction of the N,N-diethyldithiocarbamate derivative.

The reactions with bridging N,N-donor ligands yield binuclear species of type C, independent of the molar ratio 1/1 or 2/1 of reactants (molybdenum complex/N,N-donor ligand). However the reaction with the potentially bridging or chelating P,P-donor ligand dppe leads to the formation of two types of binuclear compounds, which contain the dppe bridging molecule (type C) [(S,S = Mexant, EtHdtc, Et₂dtc)] or two bridging CO molecules (type D) [(S,S = EtHdtc, Et₂dtc). Thus from the reaction in 1/1 molar ratio the orange solid which immediately precipitates corresponds to the dppe bridging species $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2]_2(\mu\text{-dppe})$, but the solution contains traces of $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{dppe})]_2(\mu\text{-CO})_2$. Upon stirring of the reaction mixture for a longer time (2 h for the Et₂dtc derivative or 2 days for the EtHdtc derivative) CO evolution is observed and the precipitate disappears giving a red solution, from which only the compound of type D is precipitated upon addition of water. The reaction in 2/1 (starting complex/dppe) molar ratio is similar, the complex $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2]_2(\mu\text{-dppe})$ immediately separates out and is converted slowly upon stirring of the mixture to the D complex. Unidentified decomposition products are also formed. The complex C → complex D conversion takes place also upon stirring of the isolated complex $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2]_2(\mu\text{-dppe})$ in acetone. This conversion cannot be reversed by bubbling CO for 1 h through a solution of $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{dppe})]_2(\mu\text{-CO})_2$.

The dppe bridged complexes do not react with carbon monoxide at room temperature, but a bridge cleavage of the $[\text{Ml}_2(\text{CO})_2(\text{dppe})]_2(\mu\text{-dppe})$ (M = Mo, W) compounds occurs upon treatment with CO to give $\text{Ml}_2(\text{CO})_2(\text{dppe})$ and $\text{Ml}_2(\text{CO})_2(\text{dppe})_2$ [5].

All these results are summarized in Scheme 2.

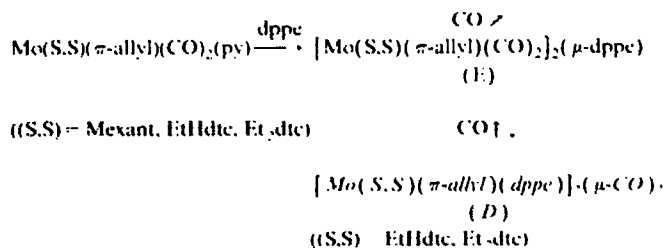
TABLE I
ANALYTICAL AND PHYSICAL DATA FOR THE NEW COMPLEXES

Compound	Elemental analysis (Found (calcd.)) (%)			λ_{max} (nm cm^{-1})	Colour
	C	H	N		
I Mo(Mexant)(π -allyl)(CO) ₂ (bipy) ⁺	47.14 (47.50)	3.51 (3.33)	6.39 (5.83)	ϵ : 0.07 ¹⁰	deep red
II Mo(Mexant)(π -allyl)(CO) ₂ (phen)	32.67 (31.89)	4.51 (4.34)	13.02 (13.52)	ϵ : 0.21 ¹⁰	reddish-orange
III Mo(Mexant)(π -allyl)(CO) ₂ (DDH)	47.81 (48.47)	6.18 (6.15)	5.86 (5.38)	25.6 ¹⁰	violet
IV Mo(Mexant)(π -allyl)(CO) ₂ (GBCHH)	52.76 (53.34)	3.94 (4.09)		ϵ : 0.20 ¹⁰	orange
V Mo(Mexant)(π -allyl)(CO) ₂ (PPh ₃)	38.12 (38.10)	3.16 (3.17)	3.84 (3.71)	1.9 ¹⁰	orange
VI [Mo(Mexant)(π -allyl)(CO) ₂] ₂ (μ -4,4'-Bipy)	34.60 (35.13)	2.82 (2.92)	3.36 (3.41)	2.0 ¹⁰	orange-yellow
VII [Mo(Mexant)(π -allyl)(CO) ₂] ₂ (μ -4,4'-DTBP)	47.49 (48.11)	3.99 (4.00)		0.38 ¹⁰	orange
VIII Mo(EtHdic)(π -allyl)(CO) ₂ (bipy) ⁺	48.22	3.92	8.17	3.4 ¹⁰	orange-red
IX Mo(EtHdic)(π -allyl)(CO) ₂ (phen)	48.681	3.851	(8.51)		

XI	$\text{Mo}(\text{EtHdtc})(\pi\text{-allyl})(\text{CO})_2(\text{GBCHI})$	50.06 (49.52)	6.59 (6.56)	7.67 (7.87)	8.2 ^c	green
XII	$\text{Mo}(\text{EtHdtc})(\pi\text{-allyl})(\text{CO})_2(\text{PPh}_3)$	53.87 (54.27)	4.09 (4.52)	2.20 (2.43)	2.9 ^c	orange
XIII	$[\text{Mo}(\text{EtHdtc})(\pi\text{-allyl})(\text{CO})_2]_2(\mu\text{-4,4'-Bipy})$	40.30 (39.91)	3.81 (3.83)	8.31 (7.16)	2.0 ^c	reddish-brown
XIV	$[\text{Mo}(\text{EtHdtc})(\pi\text{-allyl})(\text{CO})_2]_2(\mu\text{-dppe})\cdot 2 \text{ acetone}$	49.30 (49.32)	5.52 (5.08)	2.44 (2.45)	16.64 ^d	orange
XV	$[\text{Mo}(\text{EtHdtc})(\pi\text{-allyl})(\text{dppe})]_2(\mu\text{-CO})_2$	57.45 (58.00)	5.11 (5.12)	1.99 (2.05)	0.60 ^a	orange
XVI	$\text{Mo}(\text{Et}_2\text{dtc})(\pi\text{-allyl})(\text{CO})_2(\text{phen})$	49.76 (49.72)	4.71 (4.33)	7.75 (7.90)	0.14 ^a	deep-red
XVII	$\text{Mo}(\text{Et}_2\text{dtc})(\pi\text{-allyl})(\text{CO})_2(\text{PPh}_3)$	55.18 (55.73)	4.59 (4.97)	2.20 (2.32)	< 0.16 ^a	orange
XVIII	$[\text{Mo}(\text{Et}_2\text{dtc})(\pi\text{-allyl})(\text{CO})_2]_2(\mu\text{-4,4'-Bipy})$	42.08 (42.97)	4.43 (4.53)	6.54 (6.68)	< 0.17 ^a	reddish-red
XIX	$[\text{Mo}(\text{Et}_2\text{dtc})(\pi\text{-allyl})(\text{CO})_2]_2(\mu\text{-4,4'-DTBP})$	39.87 (39.92)	4.31 (4.21)	6.49 (6.20)	13.3 ^d	yellow
XX	$[\text{Mo}(\text{Et}_2\text{dtc})(\pi\text{-allyl})(\text{CO})_2]_2(\mu\text{-dppe})$	50.34 (51.13)	5.16 (5.00)	2.59 (2.59)	7.48 ^a	orange
XXI	$[\text{Mo}(\text{Et}_2\text{dtc})(\pi\text{-allyl})(\text{dppe})]_2(\mu\text{-CO})_2$	59.09 (59.09)	5.50 (5.48)	1.85 (1.97)	0.54 ^a	orange

^a In CHCl_3 , ^b In acetone, ^c In DMSO, ^d In DMFA. ^e See ref. 2.

SCHEME 2



The influence of the substituent Y of the dithiolate ligands YCS₂ on the behaviour of the compounds (different reaction time, stability, reactivity, etc. for dithiolate compounds with Y = OR, NRH) is evident [2,3,6]. This may be related to the different electron-releasing abilities of Y [7].

Infrared spectra

Table 2 lists the most significant infrared frequencies of the CO, xanthate and dithiocarbamate ligands in the new complexes. The compounds of the type A, B and C show two strong bands of approximately the same intensity, which are typical of the stretching vibrations $\nu(\text{CO})$ of two *cis*-carbonyl groups [4]. The almost constant frequencies ($1930 \pm 20 \text{ cm}^{-1}$ and $1840 \pm 20 \text{ cm}^{-1}$) of both $\nu(\text{CO})$ bands in the π -allyldicarbonyl complexes can be considered as evidence of the presence of the π -allyl group [8]. The absence of the characteristic bands of a σ -allyl group confirms the π -coordination of the allyl ligand [9]. Sometimes the $\nu(\text{CO})$ bands show splittings or weak shoulders; this may be due to the presence of isomers, which is more probable for the binuclear complexes.

The complexes of type D show a single $\nu(\text{CO})$ stretching vibration in the region of the bridging carbonyl ligands [10], so that these compounds are formulated as CO-bridged binuclear species.

The $\nu(\text{C}-\text{O}-\text{R})$ and $\nu(\text{C}=\text{N})$ stretching frequencies of the xanthate and dithiocarbamate ligands in the complexes are commonly used to identify the mono- or bi-dentate coordination of the 1,1-dithiolate ligands [11,12], except the cases in which the $\nu(\text{C}=\text{N})$ value fall in the 1480-90 region. The high values of these $\nu(\text{C}-\text{O}-\text{R})$ and $\nu(\text{C}=\text{N})$ frequencies in the complexes of types A and C seem to indicate the presence of a bidentate ligand, which is consistent with a simple replacement of pyridine in the $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})$ complexes without change in the bidentate coordination mode of the dithiolate ligand.

On the other hand in the most of complexes of the type B, $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{L} \cdot \text{L})$, the (S,S) ligands are clearly monodentate. However, in $\text{Mo}(\text{Et}_2\text{dte})(\pi\text{-allyl})(\text{CO})_2(\text{phen})$, $\nu(\text{C}=\text{N})$ appears at 1512 cm^{-1} , frequency value typical of the bidentate dithiocarbamates. This implies either an increasing of the coordination number with respect to the starting carbonyl complex or monodentate coordination of the phenanthroline molecule. Some examples of the monodentate coordination of phenanthroline have been described [13]. However we lack the structural and NMR data to decide between both possibilities, because of the low solubility of this complex.

The formation of the CO-bridged complexes $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{dppe})]_2(\mu\text{-CO})_2$, probably involves an increase in the coordination number with respect to the

TABLE 2

INFRARED SPECTRAL DATA (cm^{-1}) FOR THE COMPLEXES OF THE TYPE (A): $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{L})$, (B): $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{L-L})$, (C): $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2]_2(\mu\text{-L-L})$ AND (D): $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{dppc})]_2(\mu\text{-CO})_2$

Compound (type)	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{C-O-R})$	$\nu(\text{C-O})$	$\nu(\text{C}\cdots\text{N})$	$\nu(\text{C=S})$	$\nu(\text{N-H})$
I (B)	1942 vs 1870 vs	1204 s	1145 m		1036 vs	
II (B)	1957 vs 1862 vs 1936 vs	1199 m	1127 m		1039 s	
III (B)	1954 vs 1873 vs 1939 vs 1858 vs	1198 m	1143 m		1028 vs	
IV (B)	1930 vs 1857 vs	1188 s	1136 m		1041 s	
V (A)	1919 vs 1842 vs	1222 vs 1218 vs	1162 m		1042 m	
VI (C)	1914 vs 1836 vs	1227 vs 1213 sh	1160 s		1036 s	
VII (C)	1934 vs 1841 vs 1923 vs 1833 vs	1214 vs 1223 vs	1166 s		1040 s	
VIII (C)	1940 vs 1856 vs	1216 s	1167 m		1037 m	
IX (B)	1925 vs 1839 vs			1486 s	948 s	3394 m
X (B)	1931 vs 1840 vs			1474 m	952 s	3378 m
XI (B)	1912 vs 1811 vs			1487 m	967 s	3350 m
XII (A)	1924 vs 1854 vs			1508 sh 1498 s	982 m	3360 m
XIII (C)	1923 vs 1833 vs			1515 s	975 m	3150 m
XIV (C)	1918 vs 1844 vs			1516 s	969 m	3190 m
XV (D)	1798 vs			1509 sh 1496 s	980 m	3375 m
XVI (B)	1939 vs 1862 vs			1512 m	985 s	
XVII (A)	1919 vs 1843 vs			1489 s	998 m	
XVIII (C)	1921 vs 1837 vs			1496 s		
XIX (C)	1925 vs 1832 vs			1494 s	998 m	
XX (C)	1937 vs 1839 vs 1917 sh			1486 s	999 m	
XXI (D)	1791 sh 1781 vs			1484 s		

basically octahedral $\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})$ complexes, to give 18-electron, seven-coordinate species (the bidentate and monodentate xanthate and dithiocarbamate ligands are considered as three- and one-electron donors respectively) [4]. Seven-coordination is very common in molybdenum(II) chemistry [14].

Some *N*-ethyldithiocarbamate derivatives show a broader $\nu(\text{NH})$ band than the starting complex, shifted towards lower frequencies. In the complex $[\text{Mo}(\text{EtHdte})(\pi\text{-allyl})(\text{CO})_2]_2(\mu\text{-dppc}) \cdot n$ acetone there is probably interaction between the NH group of EtHdte and the acetone molecule, which causes a shift of the $\nu(\text{CO})$ stretching vibration of the acetone towards lower frequencies (1693 cm^{-1}). In the other cases, the low values of the $\nu(\text{NH})$ frequency in the solid state can be attributed to interactions between NH groups of different molecules; higher $\nu(\text{NH})$ frequency (3400 cm^{-1}) are observed in the solution spectrum.

The IR spectra of all these complexes clearly shows the characteristic vibration

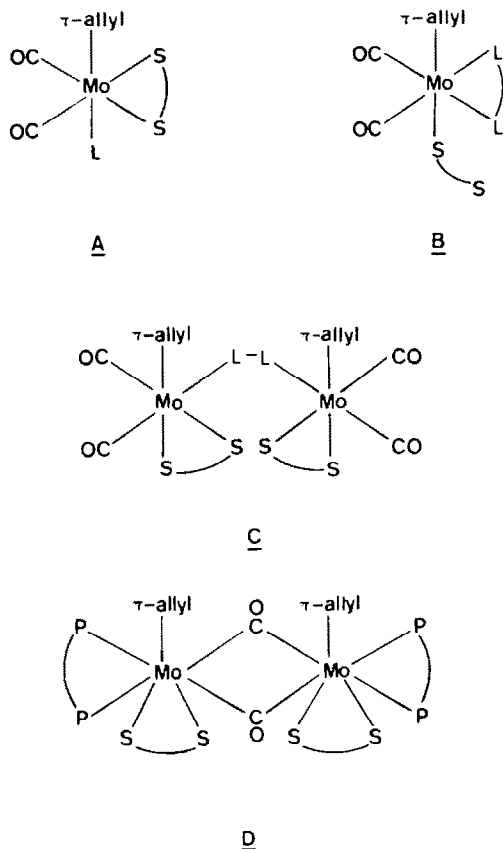


Fig. 1. Probable structural formulae for the complexes of type A, B, C, and D.

bands of the P- or N-donor ligands.

Figure 1 shows the probable structural formulae of the new compounds.

¹H-NMR spectra

Table 3 shows the chemical shift and coupling constant data for some of the complexes obtained. Unfortunately in several cases the NMR spectra could not be obtained because of the low solubility of the products. The spectra are consistent with the proposed formulae and with those of similar complexes previously studied [2-4,8]. The resonances of the allyl group definitively confirm the π -coordination of this ligand. The ethyl groups of the *N,N*-diethyl dithiocarbamate ligand give a single resonance, thus both are equivalent on the NMR time scale, because of free rotation around the C-N bond.

Electronic spectra

Electronic spectra of a selection of products and starting compounds were recorded in the 245-900 nm region. Table 4 summarizes the absorption maxima observed for these compounds. The assignment of these spectra is difficult because of the π -electron systems present in various ligands and the low symmetry of the

TABLE 3

¹H NMR CHEMICAL SHIFT (δ , ppm) AND COUPLING CONSTANT DATA (J , Hz) FOR SEVERAL COMPLEXES

Complex	(S,S)		L or L-L		π -allyl	
	δ	J	δ	J	δ	J
I	(CH ₃) 4.14 s		7.73 m		(H _a) 1.40 m	
			8.28 m		(H _c) 3.19 s, (br)	
			8.57 m		(H ¹) 3.17 m	
III	(CH ₃) 4.19 s		(CH ₃) 1.93 s		(H _a) 1.33 d	10
			(NH ₂) 6.63 s, (br)		(H _c + H ¹) 3.44 m	
V	(CH ₃) 4.08 s		(Ph) 7.48 m		(H _a) 1.35 d	10
VI	(CH ₃) 4.09 s		(H _m) 7.94 m		(H _a) 1.34 d	10
			(H _n) 8.85m		(H _c) 3.25 s, (br)	
VII	(CH ₃) 4.09 s		(H _m) 7.50 d	6	(H _a) 1.32 d	10.3
			(H _n) 8.71 d	6	(H _c) 3.23 s, (br)	
IX	(CH ₃) 1.39 t		7.60 m		(H _a) 1.39 m	
			8.07 m		(H _c) 3.20 d	6.3
			8.53 m			
			8.82 m			
XVIII	(CH ₃) 1.15 t	7.3	(H _m) 7.98 d	6	(H _a) 1.24 d	9.7
	(CH ₂) 3.77 q	7.3	(H _n) 8.90 d	6	(H _c) 3.14 d	6
					(H ¹) 3.94 m	

complexes. The absorption maxima appearing in the 385–550 nm region are due probably to $d \rightarrow d$ transitions, accompanied in some cases of a transfer charge $M \rightarrow L$ transition. Likewise the absorption bands in the range 290–300 nm include probably a $TC M \rightarrow \pi^*(CO)$ transition. The absorption maximum at 270 nm in the phenanthroline complex can be unambiguously assigned to a $\pi \rightarrow \pi^*$ intraligand transition [15].

TABLE 4

ELECTRONIC SPECTRAL DATA

Compound	$\lambda(\epsilon)$
Mo(Mexant)(π -allyl)(CO) ₂ (py)	398 sh (928), 315 (4000), 256 (10,320)
Mo(Mexant)(π -allyl)(CO) ₂ (Pph ₃)	430 sh (336), 307 sh (3266), 264 (14674)
Mo(Mexant)(π -allyl)(CO) ₂ (phen)	505 sh (1864), 432 (2208), 314 (26080), 290 sh (18240), 270 (34560)
[Mo(Mexant)(π -allyl)(CO) ₂] ₂ (μ -dppe)	450 sh (600), 385 (2001), 338 (6303), 315 (8104), 251 (20610)
Mo(Et ₂ dte)(π -allyl)(CO) ₂ (py)	380 sh (1200), 298 (10400), 250 (30400)
[Mo(Et ₂ dte)(π -allyl)(CO) ₂] ₂ (μ -4,4'-Bipy)	550 sh (60), 298 sh (15616), 247 (44925)
[Mo(Et ₂ dte)(π -allyl)(CO) ₂] ₂ (μ -dppe)	300 sh (16800), 248 (52800)
[Mo(Et ₂ dte)(π -allyl)(dppe)] ₂ (μ -CO) ₂	470 sh (960), 360 (9600), 292 (16000), 250 sh (56800)

Experimental

Several experiments were carried out under oxygen-free dry nitrogen. Analytical grade solvents were used. The starting complexes, $\text{Mo}(S,S)(\pi\text{-allyl})(\text{CO})_2(\text{py})$ [(S,S) = Mexant, EtHdtc, Et₂dte], were prepared as described in the literature [2]. Elemental analyses were carried out by the Elemental Micro Analysis Ltd. Laboratories, Amberley, Beaworthy (Devon) England. Conductance measurements were performed in several solvents 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 and 599 B Perkin Elmer spectrophotometers, using KBr disks. ¹H NMR spectra were measured at 60 MHz with a Perkin Elmer R12 spectrometer in deuterodimethyl sulfoxide solution with TMS as internal standard. Electronic spectra were recorded in chloroform solution on a Kontron Uvikon 820 Spectrophotometer.

Preparation of the complexes

The yields of the following reactions were very high or almost quantitative.

$\text{Mo}(S,S)(\pi\text{-allyl})(\text{CO})_2(L-L)$ complexes [I, (S,S) = Mexant, L-L = bipy; II, (S,S) = Mexant, L-L = phen; IX, (S,S) = EtHdtc, L-L = bipy; X, (S,S) = EtHdtc, L-L = phen; XVI, (S,S) = Et₂dte, L-L = phen]. The L-L ligand (phen or bipy) was added in a 1/1 molar ratio to a solution of $\text{Mo}(S,S)(\pi\text{-allyl})(\text{CO})_2(\text{py})$ in the minimum amount of acetone. An immediate reaction took place with formation of a red precipitate. After some minutes of stirring at room temperature the solid was filtered off, washed with acetone, and dried under vacuum over P_2O_5 . If the filtrate was coloured, water was added to precipitate more solid.

$\text{Mo}(\text{Mexant})(\pi\text{-allyl})(\text{CO})_2(\text{DDH})$ (III). To a solution of $\text{Mo}(\text{Mexant})(\pi\text{-allyl})(\text{CO})_2(\text{py})$ in the minimum amount of acetone diacetyldihydrazone was added in 1/1 molar ratio. An immediate reaction was observed. After stirring for some minutes water was added to yield a reddish-orange precipitate, which was filtered off, washed with water and dried under vacuum over P_2O_5 . The yield was almost quantitative.

$\text{Mo}(\text{Mexant})(\pi\text{-allyl})(\text{CO})_2(\text{GBCHI})$ (IV). The reaction was carried out in acetone and under oxygen-free nitrogen by stirring of $\text{Mo}(\text{Mexant})(\pi\text{-allyl})(\text{CO})_2(\text{py})$ and GBCHI in 1/1 molar ratio. After stirring for 30 min water was added to the brown solution to give a violet solid and after centrifugation this was washed with acetone/ H_2O and dried under vacuum over P_2O_5 .

$\text{Mo}(S,S)(\pi\text{-allyl})(\text{CO})_2(\text{PPh}_3)$ complexes [V, (S,S) = Mexant; XII, (S,S) = EtHdtc; XVII, (S,S) = Et₂dte]. These compounds were prepared in acetone and under N_2 by stirring of equimolecular amounts of $\text{Mo}(S,S)(\pi\text{-allyl})(\text{CO})_2(\text{py})$ and PPh_3 . After 30 min the solvent was partially evaporated at reduced pressure and an orange precipitate was separated by addition of water. Sometimes an oil or oily solid was formed, and this was crystallized by scratching the walls of the Schlenk tube or by vigorous stirring. The solid formed was filtered off, washed with water, and dried under vacuum over P_2O_5 .

$\text{Mo}(\text{EtHdtc})(\pi\text{-allyl})(\text{CO})_2(\text{GBCHI})$ (XI). A solution of 1 molar equivalent of GBCHI in CH_2Cl_2 was added to a solution of $\text{Mo}(\text{EtHdtc})(\pi\text{-allyl})(\text{CO})_2(\text{py})$ in acetone. A dark green solution was immediately formed. After stirring for 15 min under N_2 the mixture was concentrated under reduced pressure to give an oily solid.

Then water was added, and the oil was crystallized as described above. The green solid formed was filtered off, washed with water and dried under vacuum over P_2O_5 .

$[Mo(S,S)(\pi\text{-allyl})(CO)_2]_2(\mu\text{-}4,4'\text{-Bipy})$ complexes [VI, (S,S) = Mexant; XIII, (S,S) = EtHdc; XVIII, (S,S) = Et₂dte]. The reaction was carried out under nitrogen. Mo(S,S)(π -allyl)(CO)₂(py) and 4,4'-Bipy in 2/1 molar ratio were stirred in acetone for 10 min, then the solvent was partially evaporated under vacuum and water was added. An orange, reddish-brown or reddish-orange precipitate was formed, and this was filtered off, washed with water, and dried under vacuum over P_2O_5 . If an oil appeared, it was crystallized by addition of water, as described above.

$[Mo(\text{Mexant})(\pi\text{-allyl})(CO)_2]_2(\mu\text{-}4,4'\text{-DTBP})$ (VII). A solution of 4,4'-DTBP in CH_2Cl_2 was added to a solution of 2 molar equivalents of Mo(Mexant)(π -allyl)(CO)₂(py) in acetone. The reaction mixture was stirred for 30 min and concentrated almost to dryness. Water was added with vigorous stirring and scratching of the vessel walls. The solid obtained was filtered off, washed with water and dried under vacuum over P_2O_5 .

$[Mo(Et_2dte)(\pi\text{-allyl})(CO)_2]_2(\mu\text{-}4,4'\text{-DTBP})$ (XIX). The reaction was carried out under N_2 . Mo(Et₂dte)(π -allyl)(CO)₂(py) and 4,4'-dithiobipyridine in 2/1 molar ratio were stirred in CH_2Cl_2 for 40 min, during which the colour of the solution became topaz. n-Hexane was added to precipitate a yellow solid. If the precipitate redissolved, it was recovered by concentration under vacuum, with stirring and cooling in an acetone/liquid N_2 bath. The complex formed was filtered off, washed with hexane and dried under reduced pressure.

$[Mo(S,S)(\pi\text{-allyl})(CO)_2]_2(\mu\text{-dppe})$ complexes [VIII, (S,S) = Mexant; XIV, (S,S) = EtHdc; XX, (S,S) = Et₂dte]. 1,2-Bis(diphenylphosphine)ethane was added to a solution of 2 molar equivalents of Mo(S,S)(π -allyl)(CO)₂(py) in the minimum amount of acetone. An orange solid separated immediately. The mixture was stirred for 2½ hours (Mexant derivative) or 10 min (EtHdc and Et₂dte derivatives) under nitrogen. The product formed was filtered off, washed with small amounts of acetone and dried under vacuum.

$[Mo(S,S)(\pi\text{-allyl})(dppe)]_2(\mu\text{-CO})_2$ complexes [XV, (S,S) = EtHdc; XXI, (S,S) = Et₂dte]. To a solution in acetone of the starting molybdenum complex 1 molar proportion of dppe was added. After few minutes an orange solid separated. The mixture was stirred under nitrogen until redissolution of precipitate (2 h for Et₂dte derivative and 2 days for EtHdc derivative). After filtration of the mixture and addition of water a reddish-orange precipitate was formed, which was filtered off, washed with water and dried under vacuum over P_2O_5 .

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