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**SUBSTITUTION REACTIONS OF $[\text{MBr}(\pi\text{-ALLYL})(\text{CO})_2(\text{L-L})]$
COMPLEXES ($\text{M} = \text{Mo}, \text{W}$; $\text{L-L} = 2,2'$ -BIPYRIDINE,
1,2-BIS(DIPHENYLPHOSPHINE)ETHANE) WITH XANTHATES AND
DITHIOCARBAMATES**

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Summary

The complexes $[\text{MBr}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ ($\text{M} = \text{Mo}, \text{W}$, $\text{bipy} = 2,2'$ -bipyridine) react with alkylxanthates ($\text{M}^{\text{I}}\text{Rxant}$), and *N*-alkyldithiocarbamates ($\text{M}^{\text{I}}\text{RHdtc}$) ($\text{M}^{\text{I}} = \text{Na}$ or K), yielding complexes of general formula $[\text{M}(\text{S,S})\text{-}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ ($\text{M} = \text{Mo}$, $(\text{S,S}) = \text{Rxant}$ ($\text{R} = \text{Me}, \text{Et}, \text{t-Bu}, \text{Bz}$), RHdtc ($\text{R} = \text{Me}, \text{Et}$); $\text{M} = \text{W}$, $(\text{S,S}) = \text{Extant}$). A monodentate coordination of the (S,S) ligand was deduced from spectral data. The reaction of $[\text{MoBr}(\pi\text{-allyl})(\text{CO})_2\text{-}(\text{bipy})]$ with MeHdtc and Mexant gives the same complexes whether pyridine is present or not. The complexes $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ ($(\text{S,S}) = \text{MeHdtc}$, Mexant) do not react with an excess of (S,S) ligand and pyridine.

No reaction products were isolated from reaction of $[\text{MoBr}(\pi\text{-allyl})(\text{CO})_2\text{-}(\text{dppe})]$ with xanthates or *N*-alkyldithiocarbamates.

Introduction

In a previous paper [1] we described substitution reactions of the complexes $[\text{MoBr}(\pi\text{-allyl})(\text{CO})_2(\text{L})_2]$ ($\text{L} = \text{MeCN}, \text{py}$) with the anionic (S,S) -donor ligands *O*-alkyldithiocarbonates (xanthates, Rxant) *N*-alkyldithiocarbamates (RHdtc) and *N,N*-dialkyldithiocarbamates (R_2dtc), both MeCN molecules or a pyridine molecule being replaced along with the Br ligand to yield the anionic or neutral complexes $\text{M}^{\text{I}}[\text{Mo}(\text{S,S})_2(\pi\text{-allyl})(\text{CO})_2]$ ($\text{M}^{\text{I}} = \text{Na}$ or K) or $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})]$, respectively. The possibility of monodentate or bidentate coordination of the (S,S) -donor ligands in both types of complexes was discussed. We now describe a study of the reactions of the same (S,S) -donor ligands with

similar complexes, $[\text{MBr}(\pi\text{-allyl})(\text{CO})_2(\text{L-L})]$ ($\text{M} = \text{Mo}, \text{W}$), containing the chelating ligands 2,2'-bipyridine (bipy) or 1,2-bis(diphenylphosphine)ethane (dppe).

Brisdon et al. [2] have studied the reactions of complexes of this same type, $[\text{MX}(\pi\text{-allyl})(\text{CO})_2(\text{L-L})]$ [$\text{M} = \text{Mo}, \text{W}$; $\text{L-L} = \text{bipy}$, di-(2-pyridyl)amine (dpa); $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{MeCO}_2\text{CF}_3\text{CO}_2, \text{PhSO}_2, p\text{-MeC}_6\text{H}_4\text{SO}_2$), with an excess of a three-electron donor anionic ligand, such as pentane-2,4-dionate (pd), *N,N*-dialkyldithiocarbamate (R_2dtc) or salicylaldehyde (sal), in the presence of pyridine. These reactions give $[\text{Mo}(\text{A})(\pi\text{-allyl})(\text{CO})_2(\text{py})]$ ($\text{A} = \text{pd}, \text{Me}_2\text{dtc}, \text{Et}_2\text{dtc}$) or $[\text{Mo}(\text{sal})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$. The formation of the latter led the authors to postulate the existence of a $[\text{Mo}(\text{A})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ complex as intermediate in all the reactions. These results prompted us to investigate similar reactions with *N*-alkyldithiocarbamates and xanthates. The possible end products of these reactions, $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})]$, have been reported [1], and the corresponding intermediates, $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$, are described in this work.

Results and discussion

These reactions can be described as a simple substitution of Br by a xanthate or dithiocarbamate ligand, according to eq. 1.



($\text{M}^{\text{I}} = \text{Na}$ or K ; $\text{M} = \text{Mo}$, (S,S) = Rxant ($\text{R} = \text{Me}, \text{Et}, \text{Bz}, \text{t-Bu}$), RHdtc ($\text{R} = \text{Me}, \text{Et}$); $\text{M} = \text{W}$, (S,S) = Etxant)

The chelating bipyridine ligand is not displaced by an excess of xanthate or dithiocarbamate.

Several attempts to synthesize the corresponding *N,N*-dialkyldithiocarbamate derivatives failed, the Mo^{V} compound $[\text{Mo}_2\text{O}_3(\text{Et}_2\text{dtc})_4]$ sometimes being isolated from the reaction of $[\text{MoBr}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ with $\text{M}^{\text{I}}\text{Et}_2\text{dtc}$ in acetone.

The reaction of $[\text{WBr}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ leads to the desired complex only in the case of the reaction with ethyl xanthate. In the case of the remaining xanthates the starting complex was recovered, sometimes impure.

The reaction of alkyldithiocarbamates MeHdtc yields traces of $[\text{W}(\text{MeHdtc})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$, the starting complex being mainly recovered. The low reactivity of $[\text{WBr}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ was also manifested in the absence of reaction with *N,N*-dialkyldithiocarbamates [2].

Table 1 lists the analytical data and physical properties of the isolated complexes, together with the yields. The complexes are stable to air and atmospheric moisture, and their stabilities are independent of the alkyl radical present in the (S,S) ligand. These compounds are non-electrolytes in DMFA and insoluble in most common solvents.

Infrared spectra

Table 2 gives the principal IR frequencies of the carbonyl, xanthate and dithiocarbamate ligands. All these complexes show two strong bands, approxi-

TABLE 1
ANALYTICAL AND PHYSICAL DATA FOR THE [M(S,S)(π -allyl)(CO)₂(bipy)] COMPLEXES

M	(S,S) Ligand	Colour	Yield (%)	Elemental analysis (Found (calcd.) (%))				M.p. (°C)	Λ_M^c (ohm ⁻¹ cm ² mol ⁻¹)
				C	H	N	M		
Mo	Mexant	deep red	87.5	44.63 (44.75)	3.85 (3.51)	5.93 (6.14)	20.83 (21.03)	165 ^a	0.07
Mo	Etant	deep red	91.2	45.56 (45.97)	3.72 (3.83)	5.82 (5.95)	20.40 (20.41)	190–200 ^a	7.2
Mo	t-Buxant	deep red	90.2	47.94 (48.21)	4.03 (4.42)	5.88 (5.62)	19.37 (19.26)	148–153 ^a	11.4
Mo	Bzxant	reddish-orange	87.4	50.81 (51.89)	3.91 (3.76)	5.38 (5.26)	18.01 (18.02)	151–153 ^b	6.3
Mo	MeHdte	red	81.3	45.09 (44.85)	3.74 (3.73)	8.99 (9.23)	21.00 (21.07)	185–190 ^a	1.4
Mo	EtHdte	red	78.9	45.90 (46.07)	4.03 (4.05)	8.74 (8.95)	19.90 (20.45)	176–186 ^a	1.5
W	Etant	deep red	85.0	37.92 (38.73)	3.20 (3.22)	4.85 (5.01)	32.94 (32.80)	215–220 ^a	3.2

^a Decomposition. ^b Melting with decomposition. ^c In DMFA.

TABLE 2
 INFRARED SPECTRAL DATA FOR THE $[M(S,S)(\pi\text{-allyl})(CO)_2(\text{bipy})]$ COMPLEXES

M	(S,S) ligand	$\nu(\text{C-O-R})$	$\nu(\text{C-O})$	$\nu(\text{C=N})$	$\nu(\text{C-N})$	$\nu(\text{C=S})$	$\nu(\text{C=O})$
Mo.	Mexant	1204s	1145m			1036vs	1942vs 1870vs
Mo	Etxant	1205s	1118m			1037vs	1947vs 1870vs 1845(sh)
Mo	t-Buxant	1239m	1131s			1010s 994s	1940vs 1848vs
Mo	Bzxant	^a	1140s			1049s	1932vs 1926(sh) 1861(sh) 1843vs
Mo	MeHdtc			1488s 1493(sh)	1157s	936vs	1925vs 1852vs
Mo	EtHdtc			1486s	1158m	948s	1925vs 1839vs
W	Etxant	1209s	1117m			1038s	1920vs 1845vs 1820(sh)

^a Any band of similar characteristics with those observed for the remaining xanthates do not appear in the same spectral region.

mately of the same intensity, in the $\nu(\text{CO})$ stretching frequencies region, typical of the *cis*-dicarbonyl complexes [2,3]. The absence of bands characteristic of the σ -bonded allyl group, together with the presence of bands corresponding to a π -bonded C—C—C system [4,5], are indicative of π -coordination of this group. Small splittings and shoulders are observed in the carbonyl stretching bands, which could be due to the presence of isomers. This fact is consistent with the greater basic character of tungsten, which increases the π -back-bonding $M \rightarrow \text{CO}$ [6].

The $\nu(\text{C=N})$ ($<1490 \text{ cm}^{-1}$) and $\nu(\text{C-O-R})$ stretching frequencies of the $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ complexes correspond to monodentate coordination of the (S,S) ligand [7,8]. These frequencies are lower than those in the $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})]$ [1] and $[\text{M}(\text{Rxant})_2(\text{CO})_2(\text{PPh}_3)]$ [9] complexes, which contain bidentate (S,S) ligands. The new complexes seem to retain the six-coordination present in the starting compounds.

Several strong bands characteristic of the bipyridine ligand are clearly observed in the IR spectra of the complexes.

¹H NMR spectra

The ¹H NMR spectra of the complexes were measured in $(\text{CD}_3)_2\text{SO}$. In spite of the limited resolution of these spectra, owing to the low solubility, the spectral data obtained are consistent with the proposed formulae. Table 3 lists the chemical shifts (δ , ppm) and coupling constants (J , Hz) of these complexes. The signals of the $>\text{NH}$ group protons present in the *N*-alkyldithiocarbamate ligands are obscured by the resonances of the aromatic bipyridine protons. The CH_2 multiplet of the *N*-ethylthiocarbamate ligand cannot be clearly observed.

TABLE 3

¹H NMR CHEMICAL SHIFT (δ , ppm) AND COUPLING CONSTANT DATA (J , Hz) FOR THE [Mo(S,S)(π -allyl)(CO)₂(bipy)] COMPLEXES

(S,S) ligand	(S,S) protons		Aromatic protons.	π -allyl protons		
	δ	J		δ	J	
Mexant	(CH ₃) 4.14s		bipy	{ 7.73m 8.28m 8.75m	(H _a) 1.40m (H _s) 3.19s(br) (H') 3.17m	
Etixant	(CH ₃) 1.51t (CH ₂) 4.65q	7.0 7.0	bipy	{ 7.76m 8.27m 8.78m	(H _a) 1.32d (H _s) 3.19s	8.7
t-Buxant	(CH ₃) 1.84s		bipy	{ 7.75m 8.28m 8.66m 8.87m	(H _a) 1.37m (H _s) 3.16m	
Bzxant	(CH ₂) 5.76s		bipy + Bzxant	{ 7.60m 8.21m 8.75m	(H _a) 1.42m (H _s) 3.18s(br)	
MeHdte	(CH ₃) 2.84m		bipy	{ 7.58m 8.05m 8.53m 8.81m	(H _a) 1.17d (H _s) 3.17d (H') 3.85m	10 6.3
EtHdte	(CH ₃) 1.39t	7.0	bipy	{ 7.50m 8.07m 8.53m 8.82m	(H _a) 1.39m (H _s) 3.20d	6.3

The chemical shifts and coupling constants of the allyl group confirm definitely the π -coordination of this ligand [2,10]. Figure 1 shows the probable structural formula of these complexes, on the basis of the reaction used for the preparations and the IR and ¹H NMR spectral data.

Reactions of [MoBr(π -allyl)(CO)₂(dppe)] with potassium methylxanthate and sodium N-methyldithiocarbamate

The reaction of the orange complex [MoBr(π -allyl)(CO)₂(dppe)] with potassium methylxanthate in acetone leads to a beige xanthate-free compound, whose IR spectrum differs only in the ν (CO) stretching frequencies (1935vs, 1848s and 1778s cm⁻¹) from that of the starting compound (1847vs, 1935vs,

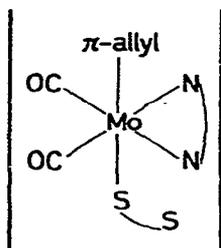


Fig. 1. Probable structural formula of the [M(S,S)(π -allyl)(CO)₂(bipy)] complexes ((S,S) = Rxant, RHdte).

1805(sh) cm^{-1}). The beige product may be a binuclear species with carbonyl and/or halogen bridges.

The reaction of $[\text{MoBr}(\pi\text{-allyl})(\text{CO})_2(\text{dppe})]$ and NaMeHdtc , in a 1/1 molar ratio with acetone/dichloromethane as solvent and under N_2 gives after several days a product which differs from the starting complex only in the presence of a weak carbonyl band at 1877 cm^{-1} . From these results we can conclude that the complex $[\text{MoBr}(\pi\text{-allyl})(\text{CO})_2(\text{dppe})]$ does not react with these (S,S)-donor ligands under the conditions of the experiments, the starting complex being mainly recovered.

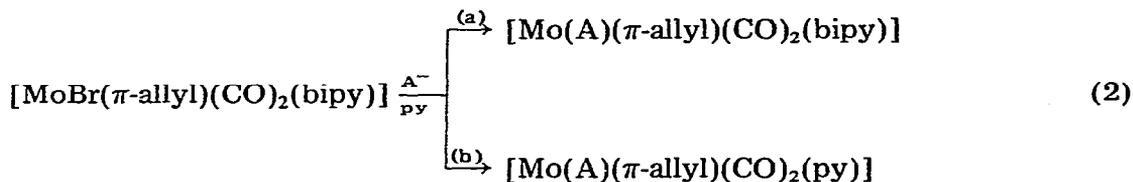
Reactions of $[\text{MoBr}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ and $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ ((S,S) = MeHdtc, Mexant) with sodium N-methyldithiocarbamate and potassium methylxanthate in the presence of pyridine

These reactions should lead to the complexes $[\text{Mo}(\text{MeHdtc})(\pi\text{-allyl})(\text{CO})_2(\text{py})]$ and $[\text{Mo}(\text{Mexant})(\pi\text{-allyl})(\text{CO})_2(\text{py})]$, previously described [1], if the (S,S) ligands behaved as they do in the reaction of $[\text{MoBr}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ with dialkyldithiocarbamates [2].

The reactions of $[\text{MoBr}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ with an excess of NaMeHdtc (1/4) in the presence of pyridine always yields $[\text{Mo}(\text{MeHdtc})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ along with a second product, nature and quantity depending on the reaction time. After 2–4 h traces of the desired product $[\text{Mo}(\text{MeHdtc})(\pi\text{-allyl})(\text{CO})_2(\text{py})]$ were obtained, while after 3 days an appreciable amount of $[\text{Mo}(\text{CO})_3(\text{bipy})(\text{py})]$ was also formed. The reaction with KMexant gives similar results, $[\text{Mo}(\text{Mexant})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ being present after a short reaction time (2–3 h) and a mixture of products containing $[\text{Mo}(\text{CO})_3(\text{bipy})(\text{py})]$ after several days.

On the other hand the reactions of the $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ complexes (S,S = MeHdtc, Mexant), similar to the hypothetical intermediate $[\text{Mo}(\text{A})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ mentioned above [2], with an excess of (S,S) ligand and pyridine yield a mixture of decomposition products from which no $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})]$ could be isolated whatever reaction time was used.

From these results we deduce that the reaction of the $[\text{MoBr}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ with xanthate- and N-alkyldithiocarbamate ligands in the presence of pyridine is different from that described by Brisdon et al. [2] for other three-electron donor anionic ligands, including the N,N-dialkyldithiocarbamates. Two pathways, shown in eq. 2, seem possible:



a) A = RHdtc, Rxant, sal

b) A = R₂dtc, pd

The stability of the end complex could determine the choice of path.

We can also conclude that the $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ complexes

(S,S = Rxant, RHdtc), isolated and described in this work, cannot be regarded as intermediates in the formation of $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{py})]$, since they do not react with pyridine. The postulated function of $[\text{Mo}(\text{R}_2\text{dtc})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ as an intermediate also seems unlikely since such complexes were not isolated by Brisdon et al. [2] and we would not obtain $[\text{Mo}(\text{Et}_2\text{dtc})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ by direct synthesis from $[\text{MoBr}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ and NaEt_2dtc .

We conclude that the reaction of $[\text{MoX}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ with anionic three-electron donor ligands (A) in the presence of pyridine gives $[\text{Mo}(\text{A})(\pi\text{-allyl})(\text{CO})_2(\text{py})]$ complexes only when the complexes $[\text{Mo}(\text{A})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ cannot be formed, as is the case in the reaction with diethyldithiocarbamate. In the case of stable isolable $[\text{Mo}(\text{A})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ complexes the reaction stops at this stage, the bipyridine complexes being the end products.

Experimental

All experiments were carried out under oxygen-free dry nitrogen.

Reagents

Potassium methyl-, ethyl- and t-butylxanthate and sodium benzylxanthate were prepared as described in the literature [11]; sodium *N*-methyl-*N*-ethyl- and *N,N*-diethyldithiocarbamate were also obtained by literature methods [12]. The complexes $[\text{MoBr}(\pi\text{-allyl})(\text{CO})_2(\text{L-L})]$ (L-L = bipy, dppe) were prepared as reported by tom Dieck and Friedel [10]. $[\text{WBr}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ was prepared by refluxing $[\text{W}(\text{CO})_3(\text{bipy})(\text{py})]$ [13] with allyl bromide in THF [14].

Analyses

C, H, N analyses were carried out by the Elemental Micro Analysis Lmted Laboratories, Amberley, Beaworthy (Devon) England. Mo and W were determined gravimetrically by standard methods [15].

Physical measurements

Conductance measurements were performed in DMFA at room temperature with a Philips conductivity bridge, Model No CM 4144 and a PR 9512/00 cell. Infrared spectra in the 4000–200 cm^{-1} region were recorded with KBr discs on Perkin-Elmer 325 and 457 spectrophotometers. ^1H NMR spectra were measured at 60 MHz with a Perkin-Elmer R12 spectrometer in $(\text{CD}_3)_2\text{SO}$ solution, with TMS as internal standard.

Preparation of the complexes $[\text{Mo}(\text{S,S})(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$

A solution of the alkaline xanthate or dithiocarbamate in acetone was added under nitrogen with stirring to a suspension of $[\text{MoBr}(\pi\text{-allyl})(\text{CO})_2(\text{bipy})]$ in the same solvent, in a molar ratio 1/1 of reactants. A gradual change in colour was observed, always in the range orange-deep red. The mixture was allowed to proceed for several hours (3–7) to ensure complete reaction. The product was isolated by precipitation with water or by evaporation of solvent to leave a very small volume of solution. The solid formed was filtered off, washed with

water, and dried over P_2O_5 under vacuum for several hours.

In the case of the dithiocarbamate derivatives the reaction time can be reduced considerably (10–30 min) by heating the mixture at 30–40°C.

Preparation of [W(Etxant)(π -allyl)(CO)₂(bipy)]

A suspension of [WBr(π -allyl)(CO)₂(bipy)] (0.28 g, 0.5 mmol) and potassium ethylxanthate (0.080 g, 0.5 mmol) was stirred for 7 days under N_2 . The product was precipitated with water, filtered off, washed with water and dried over P_2O_5 under vacuum for several hours (yield 0.26 g, 85%).

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