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SUBSTITUTION REACTIONS OF [MoBr(π-allyl)(CO)$_2$(L)$_2$] COMPLEXES (L = ACETONITRILE, PYRIDINE) WITH XANTHATES AND DITHIOCARBAMATES

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Summary

The substitution reactions of the [MoBr(π-allyl)(CO)$_2$(L)$_2$] complexes (L = acetonitrile, pyridine) with several xanthates and dithiocarbamates have been studied. The reaction leads to the formation of M^I[Mo(S,S)$_2$(π-allyl)(CO)$_2$] complexes [(S,S) = methyl-, ethylxanthate or *N*-ethyl-, *N*-methyl- and *N,N*-diethyldithiocarbamate; M^I = Na or K] for L = acetonitrile and to [Mo(S,S)-(π-allyl)(CO)$_2$(py)] complexes for L = pyridine. The new compounds have been characterized by elemental analysis, conductance measurements, and IR and ^{1}H NMR spectroscopy.

Introduction

This paper describes the substitution reactions of complexes of the type [MoBr(π-allyl)(CO)$_2$(L)$_2$], [L = CH$_3$CN, pyridine (py)], with anionic (S,S)-donors, namely xanthates (Rxant) and dithiocarbamates (RR'dtc). These anionic species can be regarded as three-electron donors when they act as bidentate ligands. The principal purpose of the work was to study the influence of the N-donor ligand present in the starting complex on the type of substitution reaction. However, the alkyl radicals of the xanthate and dithiocarbamate ligands can also influence the stability of the complexes formed.

Few examples of substitution reactions of halogen by anionic (S,S)-donor ligands are known. However, Brisdon et al. [1] have studied the reaction of the complex [MoBr(π-allyl)(CO)$_2$(bipy)] (bipy = 2,2'-bipyridine) with *N,N*-dialkyldithiocarbamates in the presence of pyridine to give the complexes

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[Mo(RR'dtc)(π-allyl)$(CO)_2$(py)] (R = R' = Me, Et). These two compounds are the only known examples of π-allyl-1,1-dithioligand carbonyl molybdenum(II) complexes. It was expected that the reactions of [MoBr(π-allyl)$(CO)_2(py)_2$] with *O*-alkyldithiocarbonate, *N*-alkyl-dithiocarbamates and *N*,*N*-dialkyl-dithiocarbamates would also lead to neutral complexes, of the type [Mo(S,S)-(π-allyl)$(CO)_2$(py)].

Results and discussion

A) [MoBr(π-allyl)$(CO)_2(CH_3CN)_2$] reacts rapidly with alkaline xanthates and dithiocarbamates at room temperature with replacement of the bromine and both acetonitrile molecules by two dithio ligands, to give anionic complexes of the type M^I[Mo$(S,S)_2$(π-allyl)$(CO)_2$], according to eq. 1.

$$[\mathrm{MoBr}(\pi\text{-allyl})(\mathrm{CO})_2(\mathrm{CH_3CN})_2] + 2\,\mathrm{M^I(S,S)} \rightarrow \mathrm{M^I}[\mathrm{Mo(S,S)_2}(\pi\text{-allyl})(\mathrm{CO})_2] + 2\,\mathrm{CH_3CN} + \mathrm{M^IBr} \quad (1)$$

M^I = Na, K; (S,S) = Rxant, RR'dtc.

The compounds containing methyl- and ethyl-xanthate, *N*-methyl-, *N*-ethyl- and *N*,*N*-diethyl-dithiocarbamate were isolated as pure, microcrystalline solids, whereas the corresponding benzyl- and tert-buthylxanthate complexes were too unstable to be isolated.

These complexes containing two dithio ligands, are always formed independent of the molar ratio 1 : 1 or 1 : 2 (Mo : dithio-lig.) of the reaction. In the reaction with ethylxanthate two isomers of different properties and stabilities were isolated. The red, unstable, isomer is formed only with a 1 : 1 molar ratio, whereas the yellow, more stable, isomer is obtained with a 1 : 2 molar ratio. The formation of two compounds of different colour (yellow and reddish orange) was also observed in the reaction with sodium benzylxanthate.

All these complexes behave as 1 : 1 electrolytes. Their stability varies with the nature of the sulfur-donor ligand present in the compound, the xanthate complexes being more stable than the corresponding dithiocarbamate complexes, which gradually decompose even when kept at low temperature in an inert atmosphere in the absence of light. All the compounds are soluble in DMSO, DMFA and acetone, and insoluble in hexane and water, but decompose rapidly in the presence of oxygen in most solvents.

B) [MoBr(π-allyl)$(CO)_2(py)_2$] reacts instantaneously with alkaline xanthates and dithiocarbamates at room temperature with substitution of bromine and a single pyridine molecule by a dithio ligand, to give yellow solids, according to eq. 2.

$$[\mathrm{MoBr}(\pi\text{-allyl})(\mathrm{CO})_2(\mathrm{py})_2] + \mathrm{M^I(S,S)} \rightarrow [\mathrm{Mo(S,S)}(\pi\text{-allyl})(\mathrm{CO})_2(\mathrm{py})] + \mathrm{py} + \mathrm{M^IBr} \quad (2)$$

M^I = Na, K; (S,S) = R-xant, RR'-dtc.

The complexes are non-electrolytes in DMFA, and the derivatives of methylxanthate, ethylxanthate and *N*-ethyldithiocarbamate are quite stable. The benzylxanthate complex is an oil above —10° C, and was identified by its IR spectrum only.

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR THE COMPLEXES OF TYPE A, $M^I[Mo(S,S)_2(\pi\text{-ALLYL})(CO)_2]$, AND OF TYPE B, $[Mo(S,S)(\pi\text{-ALLYL})(CO)_2(py)]$

(S,S)ligand (complex)	Colour	Yield (%)	Elemental analysis. Found (calcd.) (%)				M.p. (°)	Λ_M (ohm^{-1} cm^2 mol^{-1})
			C	H	N	Mo		
Mexant(A)	Yellow	80.7	24.58 (24.22)	2.44 (2.46)		21.35 (21.49)	114—120 [a]	37.6 [c]
Etxant(A)	Yellow	84.3	28.08 (27.85)	3.22 (3.16)		19.96 (20.22)	122—138 [a]	23.6 [d] 41.2 [c]
Etxant(A)	Red	85.8	28.05 (27.85)	3.25 (3.16)		20.36 (20.22)	93—106 [a]	22.0 [d]
Medtc(A)	Yellow	84.4	23.84 (25.24)	3.21 (3.03)	6.32 (6.54)	22.38 (22.40)	57—61 [a]	57.8 [c]
Etdtc(A)	Yellow	45.3	27.88 (28.95)	3.86 (3.76)	5.79 (6.14)	—	—	42.3 [c]
Et_2dtc(A)	Yellow-orange	55.3	32.29 (35.16)	4.38 (4.88)	4.54 (5.48)	—	122—126	33.5
Mexant(B)	Yellow	79.1	37.90 (37.99)	3.44 (3.43)	3.61 (3.69)	25.43 (25.30)	103—106 [a]	8.8 [c]
Etxant(B)	Yellow-orange	45	38.97 (39.71)	3.80 (3.81)	3.57 (3.56)	24.33 (24.40)	84—85	3.8 [c]
Medtc(B)	Yellow	75.0	35.21 (38.11)	3.65 (3.70)	7.39 (7.40)		104—106 [a]	—
Etdtc(B)	Yellow	70.3	38.90 (39.81)	3.99 (4.08)	6.92 (7.14)		108—126 [b]	9.2
Et_2dtc(B)	Yellow	71.3	42.78 (42.86)	4.75 (4.76)	6.45 (6.66)	22.67 (22.84)		12.0 [c]

[a] Decomposition. [b] Decomposition with melting. [c] In DMFA (dimethylformamide). [d] In DMSO (dimethylsulfoxide).

Products of the composition $[Mo(S,S)(\pi\text{-allyl})(CO)_2(py)]$ are always formed, independent of the molar ratio of the reactants. The complex $[Mo(Et_2dtc)(\pi\text{-allyl})(CO)_2(py)]$ obtained by this reaction is identical with that isolated by Brisdon et al. [1] from the reaction of $[MoBr(\pi\text{-allyl})(CO)_2(bipy)]$ with an excess of sodium *N,N*-dialkyldithiocarbamate in the presence of pyridine. The complexes of this series are quite stable. They are soluble in benzene, DMSO, DMFA, acetone, ethanol, diethyl ether and chloroform, and insoluble in hexane and water.

Analytical and physical data for the new complexes are given in Table 1.

Infrared spectra

The infrared spectra of all these complexes show two strong bands of approximately the same intensity, centred at ca. 1930 and 1840 cm^{-1}, which are typical of the stretching vibrations of two *cis*-carbonyl groups [1,2]. Sometimes these bands are split or have weak shoulders, suggesting that isomers might be present.

The π-coordination of the allyl ligand can be deduced from the absence of the characteristic bands of a σ-coordinated allyl group [3].

Table 2 summarizes some significative infrared frequencies of the complexes.

TABLE 2

INFRARED SPECTRAL DATA (cm^{-1}) FOR THE COMPLEXES A $M^I[Mo(S,S)_2(\pi\text{-ALLYL})(CO)_2]$ AND COMPLEXES B, $[Mo(S,S)(\pi\text{-ALLYL})(CO)_2(py)]$ [a]

(S,S)ligand (complex)	ν(C—C—R)	ν(C—O)	ν(C$\cdots$N)	ν(C—N)	ν(C=S)	ν(C≡O)
Mexant(A)	1204s	1153s			1033vs	1917vs 1843vs
Etxant(A)$_{red}$	1258vs	1112s			1025vs	1960vs 1932vs 1886vs
Etxant(A)$_{yellow}$	1217vs 1195vs	1118s			1025vs	1967vs 1953vs 1912(sh) 1830vs 1805(sh)
Medtc(A)			1526s [b] 1500s	1160s [b]	950s [b]	1938vs 1906s 1832vs
Etdtc(A)			1510s [b] 1482s	1150s [b]	965s [b]	1926vs 1828vs
Et$_2$dtc(A)			1515(sh) 1493s	1197s	980m 950m	1946vs 1914vs 1858s 1836vs
Mexant(B)	1233vs(br)	1171s			1040s	1932vs 1829vs
Etxant(B)	1232vs(br)	1116s			1039	1940(sh) 1925vs 1839vs
Bzxant(B) [c]	1260s	1192vs(br) 1175(sh)			1060s 1068s	1949sv 1845vs
Medtc(B)			1536s	1166m	960s	1905vs 1830vs
Etdtc(B)			1494s	1150m	973s	1911vs 1813vs
Et$_2$dct(B)			1499s	1149m	1000m	1921vs 1838vs

[a] In KBr disks. [b] In Nujol mulls. [c] Oil.

A) $M^I[Mo(S,S)_2(\pi\text{-allyl})(CO)_2]$ complexes. As mentioned above, the substitution reaction leading to these complexes can be regarded as a replacement of two acetonitrile molecules and the bromine ligand by two dithio ligands. Either or both of these ligands can be both bidentate, or one can be monodentate. An increase of the coordination number could take place with respect to the starting complex in the case of two bidentate (S,S)-ligands. In the IR spectra of the dithiocarbamate complexes a strong band and a shoulder which appear in the 1482—1526 cm^{-1} region can be assigned to the stretching frequencies ν(C$\cdots$N), and this would be consistent with presence of both bidentate and monodentate dithio ligands [4].

The $M^I[Mo(Etxant)_2(\pi\text{-allyl})(CO)_2]$ isomers show different ν(C≡O) (carbonyl group) stretching frequencies and ν(C—O—R) (xanthate ligand) appears at higher frequency in the red than in the yellow isomers, so that a greater contribution of the resonance form $R\text{—}\overset{+}{O}\text{=}C\genfrac{}{}{0pt}{}{\diagup S^-}{\diagdown S^-}$ can be inferred for the red isomer.

B) [Mo(S,S)(π-allyl)(CO)$_2$(py)] complexes. The high values at which the stretching frequencies ν(C—O—R) of the xanthate and ν(C$\overset{\cdots}{-}$N) of the dithiocarbamate appear are indicative of a chelating character of both ligands [4]. The IR spectra of all these new complexes exhibit the characteristic bands of the coordinate pyridine ligand.

^{1}H NMR spectra

The ^{1}H NMR spectra confirm the π-coordination of the allyl group [1,5,6], and so the Mo(CO)$_2$(π-allyl) moiety is conserved in these reactions.

Tables 3 and 4 give the chemical shifts and coupling constants for all these compounds.

A) M^I[Mo(S,S)$_2$(π-allyl)(CO)$_2$] complexes. The ^{1}H NMR spectra of these complexes show a single resonance signal for the alkyl groups of the xanthate and dithiocarbamate ligands, which is what would be expected for a single type (monodentate or bidentate) of ligand. This could be explained by fluxional behaviour in solution, which is very common in the π-allyldicarbonylmolybdenum complexes [7—9]. The two ethyl groups of the *N,N*-diethyldithiocarbamate ligand also give a single resonance, being both chemically equivalent on the NMR time scale. This can be attributed to a free rotation around the C—N bond.

In the complex K[Mo(Mexant)$_2$(π-allyl)(CO)$_2$] the presence of a methyl resonance signal characteristic of the ionic species Mexant$^-$ can be explained by a partial substitution of the Mexant ligand by C_2D_6SO in the complex, to give rise to the species [Mo(Mexant)(C_2D_6SO)(π-allyl)(CO)$_2$] and K$^+$Mexant$^-$ in

TABLE 3

^{1}H NMR CHEMICAL SHIFT (δ, ppm) AND COUPLING CONSTANT DATA (J, Hz) FOR THE COMPLEXES M^I[Mo(S,S)$_2$(π-ALLYL)(CO)$_2$]

(S,S) ligand	CH$_3$		CH$_2$		π-allyl	
	δ	J	δ	J	δ	J
Mexant	4.04s				1.07d (H$_a$)	9.7
	3.78s [a]				1.16d (H$_a$) [a]	9.7
					3.25m (H$_s$)	
Etxant$_{\text{yellow}}$	1.36t	7	4.49q	7	1.07d (H$_a$)	9.5
					3.18d (H$_s$)	6.5
					3.77m (H')	
Etxant$_{\text{red}}$	1.32t	7	4.49q	7	1.30d (H$_a$)	10
					3.22d (H$_s$)	6.5
					4.25m (H')	
Medtc	2.88s, br				1.14d (H$_a$)	9.7
					3.20d (H$_s$)	6.7
					4.00m (H')	
Etdtc	1.07t	7			1.12d (H$_a$)	9.3
					3.20d (H$_s$)	6.0
					3.94m (H')	
Et$_2$dtc	1.15t	7.3.	3.76q	7.3	1.19d (H$_a$)	10

[a] Resonances of the new species present in solution of C_2D_6SO. s: singlet, d: doublet, t: triplet, q: quartet, b: broad.

TABLE 4

^{1}H NMR CHEMICAL SHIFT (δ, ppm) AND COUPLING CONSTANT DATA (J, Hz) FOR THE COMPLEXES [Mo(S,S)(π-allyl)(CO)$_2$(py)]

(S,S) ligand	(S,S)		pyridine	π-allyl	
	δ	J	δ	δ	J
Mexant	(CH_3) 4.10s		(H_m) 7.50m	(H_a) 1.33d	10
	(CH_3) 3.97s [a]		(H_p) 7.91m	(H_a) 1.47d [a]	10
			(H_o) 8.73m	(H_s) 3.24m	
Etxant	(CH_3) 1.33t	7.3	(H_m) 7.52m	(H_a) 1.34d	10
	(CH_2) 4.52q	7.3	(H_p) 7.91m	(H_s) 3.17m	
			(H_o) 8.75m	(H') 4.43m	
Etxant [b]	(CH_3) 1.29t	7.3	(H_m) 7.38m	(H_a) 1.49d	10
	(CH_2) 4.42q	7.3	(H_p) 7.48m	(H_s) 3.19d	6.7
			(H_o) 8.88d	(H') 4.24m	
Medtc	(CH_3) 2.85d	4.7	(H_m) 7.52m	(H_a) 1.22d	10
			(H_p) 7.95m	(H_s) 3.15d	6
			(H_o) 8.75m	(H') 4.00m	
Etdtc	(CH_3) 1.05t	7.3	(H_m) 7.51m	(H_a) 1.21d	10
	(CH_2) 3.27m		(H_p) 7.95m	(H_s) 3.15d	6
			(H_o) 8.76m	(H') 3.98m	
Et$_2$dtc	(CH_3) 1.09t	7.3	(H_m) 7.95m	(H_a) 1.20d	11
	(CH_2) 3.74q	7.3	(H_p) 7.91m	(H_s) 3.14d	6.3

[a] Resonances of the new species present in solution of C_2D_6SO. [b] In $CDCl_3$.

solution. The ionic nature of these complexes is confirmed also by comparison of their ^{1}H NMR data with those of the neutral complexes [Mo(S,S)(π-allyl)(CO)$_2$(py)]. Thus, in agreement with literature data [8], our complexes show the following trends for the allylic proton chemical shifts: δ(H_a, anionic complexes) < δ(H_a, neutral complexes) and δ(H_s, anionic complexes) > δ(H_s, neutral complexes) (Tables 3 and 4) (H_a = *anti*-proton, H_s = *syn*-proton of the π-allyl ligand).

The values of the ^{1}H NMR chemical shifts for the π-allyl protons of the isomeric complexes K[Mo(Etxant)$_2$(π-allyl)(CO)$_2$] are also different, but the IR and ^{1}H NMR spectral data are insufficient for deciding which isomer is which. A structural study by X-ray crystallography is to be carried out for this purpose.

B) [Mo(S,S)(π-allyl)(CO)$_2$(py)] complexes. The ^{1}H NMR spectra in C_2D_6SO of these complexes are consistent with the proposed formula. The split signals which appear for the H_a and H_s allylic protons and for the methyl protons in the ^{1}H NMR spectrum of the methylxanthate complex seem to indicate a change in the coordination mode of the xanthate ligand by a partial reaction with the solvent C_2D_6SO. This reaction could give rise to the formation in solution of the new species [Mo(Mexant)(C_2D_6SO)(π-allyl)(CO)$_2$(py)], in which the methylxanthate ligand should be monodentate.

There are two possible stereochemistries (a or b) (Fig. 1), for the [Mo(S,S)(π-allyl)(CO)$_2$(py)] complexes. From the nature of the reaction, the ^{1}H NMR spectra at low temperature, and the structural data for the similar complexes [Mo(pd)(π-allyl)(CO)$_2$(py)] (pd = pentane-2,4-dionate [10], it seems likely that

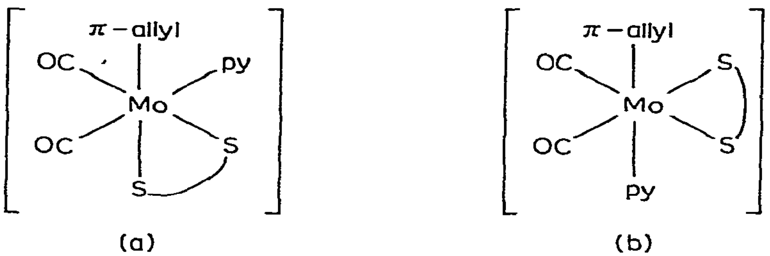

Fig. 1. Two possible stereochemistries for $[Mo(S,S)(\pi\text{-allyl})(CO)_2py]$ complexes.

the stereochemistry in the solid state is (a). However, the splitting patterns of the allylic proton signals of the ^1H NMR spectra at room temperature indicate that in solution the stereochemistry is (b), [1].

Experimental

All experiments were carried out under oxygen-free dry nitrogen. Solvents were dried by standard methods and saturated with dry nitrogen.

Reagents

Potassium methylxanthate, potassium ethylxanthate, potassium t-butylxanthate and sodium benzylxanthate were prepared as described in the literature [11], as were sodium N-methyldithiocarbamate, sodium *N*-ethyldithiocarbamate, and sodium *N,N*-diethyldithiocarbamate [12].

The starting complexes $[MoBr(\pi\text{-allyl})(CO)_2(L)_2]$, $[L = CH_3CN$, pyridine (py)], were prepared as reported by Tom Dieck and Friedel [6].

Analyses

C, H, N analyses were carried out by the Elemental Micro-Analysis Ltd. Laboratories, Amberley, Beaworthy (Devon) England. Molybdenum was determined gravimetrically [13].

Physical measurements

Conductance measurements were performed in DMSO or DMFA at room temperature with a Philips conductivity bridge, Model No CM 4144 and a cell PR 9512/00. Infrared spectra in the 4000—200 cm^{-1} region were recorded on Perkin-Elmer 325 and 457 spectrophotometers, using KBr disks or Nujol mulls. ^1H NMR spectra were measured at 60 MHz with a Perkin-Elmer R12 spectrometer in deuterodimethylsulfoxide solution, with TMS as internal standard.

Preparation of the complexes

A) $M^I[Mo(S,S)_2(\pi\text{-allyl})(CO)_2]$ *complexes,* $[M^I = Na, K; (S,S) = RR'dtc,$ *Rxant].* A solution of $[MoBr(\pi\text{-allyl})(CO)_2(CH_3CN)_2]$ in acetone was added to a solution (or suspension) of the corresponding alkaline xanthate or dithiocarbamate in the same solvent in a molar ratio 1 : 2. An instantaneous reaction took place with formation of a light, white precipitate. The mixture was stirred for 20—45 min at room temperature and the white solid filtered off. The filtrate was evaporated under vacuum until an oil or oily solid separated, and the complexes were precipitated by addition of diethyl ether with stirring. In the case of the *N*-methyl- and *N*-ethyl-dithiocarbamate complexes, n-hexane was added to the diethyl ether solution to precipitate the product. Sometimes the precipitate redissolved, in such cases the solution was concentrated under vacuum, with stirring, and cooled in an acetone/liquid N_2 bath.

The complex formed was filtered off, washed with diethyl ether or ether/hexane and dried under vacuum.

Potassium di(ethylxanthate) π-allyl dicarbonyl molybdate(II) (red isomer). This complex was similarly prepared using a molar ratio 1 : 1 of reactants. A red solid was precipitated by addition of diethyl ether to the red oil initially formed. Sometimes a yellow product separated, and this was redissolved by adding more diethyl ether. The red solid was filtered off, washed with diethyl ether, and dried under vacuum. On standing at 0°C the filtrate gave more red solid in crystalline form (yield 85%).

B) [Mo(S,S)(π-allyl)(CO)$_2$(py)] complexes, [(S,S) = Rxant, RR'dtc]. The complexes were obtained by addition of a solution of the corresponding alkaline xanthate or dithiocarbamate in acetone (30 ml) to a suspension of [MoBr(π-allyl)(CO)$_2$(py)$_2$] in benzene (50 ml), the molar ratio of reactants being 1 : 1. An instantaneous reaction was observed. After stirring for 45 min the mixture was filtered and the filtrate was concentrated at reduced pressure until an oil or oily solid formed. After addition of a little diethyl ether, n-hexane was added with vigorous stirring and cooling at 0°C, to give a yellow precipitate. This was filtered off, washed with hexane at 0°C, and dried under vacuum. Sometimes this yellow solid redissolved, and in such cases we used the procedure described above for the type A complexes. The ease of isolating the yellow solid determines the yield of the reaction.

The reaction can be carried out in acetone. After stirring for 45 min, the volume of the reaction mixture was reduced to a half by evaporation, and the complex was precipitated by addition of water. The yellow solid so formed was filtered off, washed with water, and dried under vacuum on P_2O_5. Sometimes an oil separated instead of a solid.

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