The Chemistry of π-Cyclopentadienyl Nitrosyl Molybdenum Complexes. Part IV.[1] Further Studies of Compounds Containing Bridging Sulphur Ligands

By **J. A. McCleverty** * and **D. Seddon**, Chemistry Department, The University, Sheffield S3 7HF

Reaction of $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ (X = Br or I) with RSH (R = Me, Et, Pr, Bu^t, Bu, or CH_2Ph) gave $[(\pi\text{-}C_5H_5)\text{-}Mo(NO)(X)(SR)]_2$ and reduction of this (X = Br) with zinc dust (X = Br) afforded $[(\pi\text{-}C_5H_5)Mo(NO)SR]_2$. The oxidation of the last with Cl_2 or Br_2 is briefly discussed. Treatment of $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ with $NaSBu^n$ (X = Br) gave $[(\pi\text{-}C_5)Mo(NO)(SPr^n)_2]_2$ and with $NaSPr^i$ (X = I) both $[(\pi\text{-}C_5H_5)Mo(NO)(SPr^i)]_2$ and $[(\pi\text{-}C_5H_5)\text{-}Mo(NO)(SPr^i)_2]_2$. The mass, n.m.r., i.r., and electronic spectra of the compounds are described.

In an earlier paper,[2] we described the formation of the complexes $[(\pi\text{-}C_5H_5)Mo(NO)(SR)_x]_n$ (R = Ph or CH_2Ph; $x = 1$ or 2), and two isomers of $[(\pi\text{-}C_5H_5)Mo(NO)(I)\text{-}(SCH_2Ph)]_2$. These compounds are of some structural interest. Thus $[(\pi\text{-}C_5H_5)Mo(NO)(SR)_2]_2$ is apparently dimeric in the solid and gas phases, but is monomeric (co-ordinatively unsaturated) in non-polar solvents; the mixed iodo-thiol dimers may be similar. The reduced species $[(\pi\text{-}C_5H_5)Mo(NO)(SR)]_2$, appear to be similar to $[(\pi\text{-}C_5H_5)Cr(NO)(SPh)]_2$[3] (*i.e.* containing a metal–metal bond and bridging SR groups), but i.r. data obtained from the former suggest[2] that the NO groups are bridging whereas in the latter, they are terminal.

The preparations of the molybdenum compounds were somewhat fortuitous and in order to develop a rational and general synthetic procedure, we have studied, systematically, the reactions of $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ (X = Br or I) with thiols and thiolates. The new compounds prepared have been studied spectrally in order to obtain further information about their structures in solution.

EXPERIMENTAL

All reagents were used as purchased without further purification, except $[(\pi\text{-}C_5H_5)Mo(NO)(CO)_2]$,[4] $[(\pi\text{-}C_5H_5)Mo(NO)I_2]_2$,[2,3] and $[(\pi\text{-}C_5H_5)Mo(NO)Br_2]_2$,[4] which were prepared as described in the literature.

Conductivity measurements were made at room temperature using a Phillips conductivity meter. Molecular weights were determined osmometrically and mass spectrally (AEI MS 12). I.r. spectra were obtained using Infracord 457 and Unicam SP 100 spectrophotometers, and electronic spectra using a Unicam SP 700 instrument. N.m.r. spectra were obtained with Varian HA 100 and Perkin-Elmer R12A spectrometers.

Microanalyses were performed by the Microanalytical Laboratory of this Department, and all m.p.s are uncorrected. All yields are quoted relative to the starting material.

Synthesis of Di[bromo(alkanethiolato)(nitrosyl)-π-cyclopentadienylmolybdenum] Complexes, $[(\pi\text{-}C_5H_5)Mo(NO)(Br)\text{-}(SR)]_2$.— Bis[dibromo(nitrosyl)-π-cyclopentadienylmolybdenum], in a mixture of n-hexane or n-pentane (20 ml) and just sufficient ethanol to dissolve the solid, was treated with an excess of the appropriate alkanethiol (RSH) (when R = Me, cooling was necessary). After the mixture had been stirred for a further 10 min, the yellow microcrystalline powder which had formed was filtered off, washed with n-pentane, and dried and stored *in vacuo*. The yields and m.p.s of the compounds are as follows: $[(\pi\text{-}C_5H_5)Mo(NO)\text{-}(Br)(SMe)]_2$ 90%, 194°; $[(\pi\text{-}C_5H_5)Mo(NO)(Br)(SEt)]_2$, 61%, 159°; $[(\pi\text{-}C_5H_5)Mo(NO)(Br)(SPr)]_2$, 100%, 146°; $[(\pi\text{-}C_5H_5)\text{-}Mo(NO)(Br)(SBu^t)]_2$, 88%, 133°; $[(\pi\text{-}C_5H_5)Mo(NO)(Br)\text{-}(SBu)]_2$, 88%, 132°; $[(\pi\text{-}C_5H_5)Mo(NO)(Br)(SCH_2Ph)]_2$, 85%, 181°.

Synthesis of Di[alkanethiolato(nitrosyl)-π-cyclopentadienylmolybdenum], $[(\pi\text{-}C_5H_5)Mo(NO)(SR)]_2$.—The appropriate di-[bromo(alkanethiolato)(nitrosyl)-π-cyclopentadienylmolybdenum] (*ca.* 1·0 g) was refluxed under nitrogen for several hours in the presence of zinc dust (1·0 g). The solution was then filtered and the filtrate was evaporated to dryness *in vacuo*. Ethanol was then added to the solid, the mixture was shaken, and the soluble fraction was removed. The residue was recrystallised from dichloromethane and ethanol, affording the complex as yellow crystals. The refluxing time, yields, and m.p.s for the compounds are as follows: $[(\pi\text{-}C_5H_5)Mo(NO)(SMe)]_2$, 4 h, 70%, 220°; $[(\pi\text{-}C_5H_5)Mo(NO)\text{-}(SEt)]_2$, 3 h, 30%, 220°; $[(\pi\text{-}C_5H_5)Mo(NO)(SBu^t)]_2$, overnight, 50%, 197° (phase change at *ca.* 175°); $[(\pi\text{-}C_5H_5)Mo\text{-}(NO)(SCH_2Ph)]_2$, overnight, 70%, 194°.

Bis[di(propanethiolato)(nitrosyl)-π-cyclopentadienylmolybdenum], $[(\pi\text{-}C_5H_5)Mo(NO)(SPr)_2]_2$.—To a warm solution of bis[dibromo(nitrosyl)-π-cyclopentadienylmolybdenum] (1·4 g) in acetone (100 ml) was added dropwise in ethanol (50 ml) a solution of sodium (0·2 g) and propane-α-thiol (0·7 ml). The mixture was refluxed under nitrogen for 1 h, during which time its colour changed from deep green to magenta; it was then cooled to room temperature, filtered, and evaporated to dryness. n-Hexane (150 ml) was added to the residue, and the insoluble material was filtered off; the hexane solution was evaporated *in vacuo*. The residue was redissolved in ethanol which was then slowly evaporated, using a water pump, leaving the complex as a deep purple oil.

Bis[iodo(ethanethiolato)(nitrosyl)-π-cyclopentadienylmolybdenum], $[(\pi\text{-}C_5H_5)Mo(NO(I)(SEt)]_2$.—Bis[di-iodo(nitrosyl)-π-cyclopentadienylmolybdenum] (1·0 g), dissolved in acetone (*ca.* 30 ml), was treated with ethanethiol (0·2 ml) and the mixture was stirred for 30 min. The solution was evaporated *in vacuo* and the product was washed with ethanol (to remove the starting material) and n-pentane; it was then dried and stored *in vacuo*. The yield was 0·9 g (100%), but the complex could not be satisfactorily characterised by elemental analysis. It was too insoluble for

---

[1] Part III, J. A. McCleverty and D. Seddon, *J.C.S. Dalton*, 1972, 2526.

[2] J. A. McCleverty and T. A. James, *J. Chem. Soc.* (*A*), 1971, 1068.

[3] R. B. King, *Inorg. Chem.*, 1967, **6**, 30.

[4] J. F. Preston and R. L. Reed, *Chem. Comm.*, 1966, 51; T. A. McPhail and G. A. Sim, *J. Chem. Soc.* (*A*), 1968, 1858; G. R. Knox, personal communication.

^{1}H n.m.r. spectral studies, but was characterised by its electronic, i.r., and mass spectra.

Bis[iodo(propanethiolato)(nitrosyl)-π-cyclopentadienylmolybdenum], $[(\pi\text{-}C_5H_5)Mo(NO)(I)(SPr)]_2$.—To bis[di(iodo)(nitrosyl)-π-cyclopentadienylmolybdenum] (1·0 g) dissolved in acetone (50 ml) was added, during 15 min and with stirring, propane-α-thiol (0·3 ml). The solvent was then removed *in vacuo* and the remaining oil was left to crystallise at 0°. Ethanol and n-hexane were then added, the product was filtered off, washed with n-hexane, and dried and stored *in vacuo* (0·7 g, 80%, m.p. 180°).

TABLE 1

Analysis of complexes $[(\pi\text{-}C_5H_5)Mo(NO)XY]_2$

X	Y	Calc. (%) C	H	N	S	Hal	Found (%) C	H	N	S	Hal	*M* [a]
Br	SMe	22·6	2·5	4·4	10·1	25·2	23·2	2·8	4·2	10·2	24·8	
Br	SEt	25·3	3·0	4·2	9·7	24·1	25·4	3·1	4·1	9·9	24·4	620 [b]
Br	SPr	27·7	3·5	4·0	9·3	23·1	28·1	3·9	4·1	9·3	23·2	606 [c]
Br	SBu^i	30·1	3·9	3·9	8·9	22·2	30·1	4·1	3·8	9·0	22·5	
Br	SBu	30·1	3·9	3·9	8·9	22·2	30·6	4·3	3·8	9·2	22·0	625 [d]
Br	SCH_2Ph	36·5	3·0	3·6	8·1	20·3	36·4	3·2	3·7	8·1	20·2	
I	SPr	24·4	3·1	3·6	8·1	32·3	23·6	3·2	3·4	8·3	32·2	615 [e]
I	SCH_2Ph	32·7	2·7	3·2	7·3	28·9	32·1	2·6	2·8	7·3	28·9	
	SMe	30·3	3·4	5·9	13·5		30·5	3·7	6·0	13·6		
	SEt	33·3	4·0	5·6	12·7		33·0	4·1	5·7	12·6		
	SPr	36·1	4·5	5·3	12·0		35·8	4·2	5·3	12·1		
	SBu^i	38·6	5·0	5·0	11·4		38·9	5·2	4·9	11·3		
	SCH_2Ph	45·9	3·8	4·5	10·2		46·1	4·1	4·5	10·2		
SPr	SPr	38·7	5·6	4·1	18·8		37·5	5·2	4·6	18·3		360
SPr^i	SPr^i	36·1	4·5	5·3	12·0		36·2	4·8	5·5	11·7		

[a] Osmometrically in chloroform unless otherwise indicated. [b] Calc. 664. [c] Calc. 692. [d] Calc. 720. [e] Calc. 786. [f] Calc. 682; in acetone.

Bis[iodo(toluene-α-thiolato)(nitrosyl)-π-cyclopentadienylmolybdenum], $[(\pi\text{-}C_5H_5)Mo(NO)(I)(SCH_2Ph)]_2$.—To bis[di(iodo)(nitrosyl)-π-cyclopentadienylmolybdenum] (1·0 g), dissolved in acetone (50 ml) was added, during 15 min, and with stirring, toluene-α-thiol (0·3 ml). To this mixture, n-hexane (150 ml) was added, and the stirring was continued for a further 15 min. The product, which had precipitated, was filtered off, washed with n-pentane, and dried and stored *in vacuo* (0·3 g, 30%), m.p. 169°.

Bis[(propanethiolato)(nitrosyl)-π-cyclopentadienylmolybdenum], $[(\pi\text{-}C_5H_5)Mo(NO)(SPr)]_2$.—To bis[di-iodo(nitrosyl)-π-cyclopentadienylmolybdenum] (4·5 g) in warm acetone (50 ml) was added dropwise and with stirring an ethanol (60 ml) solution containing sodium (0·6 g) and propane-α-thiol (1·7 ml). The mixture was refluxed under nitrogen for 10 min, and was then cooled to 0° when the complex which had crystallised (0·8 g) was filtered off. The filtrate was evaporated to dryness and the residue dissolved in chloroform. After filtration, the chloroform solution was evaporated to dryness, ethanol was added and, after filtration, a further amount (0·8 g) of the complex was obtained. On evaporation of the ethanol filtrate, more product (0·5 g) was isolated. The compound was purified by recrystallisation from dichloromethane and ethanol [combined yield 2·1 g (79%), m.p. 181°].

Reaction of Bis[di-iodo(nitrosyl)-π-cyclopentadienylmolybdenum], with Sodium Propane-2-thiolate.—To a hot solution of $[(\pi\text{-}C_5H_5)Mo(NO)I_2]_2$ (2·0 g) in acetone (50 ml) was added an ethanol (50 ml) solution containing sodium (0·23 g) and propane-2-thiol (1·0 ml). The mixture was refluxed under nitrogen for 10 min, and then allowed to cool for 1 h. After filtration, *bis[(propane-2-thiolato)(nitrosyl)-π-cyclopentadienylmolybdenum]*, which was recrystallised from dichloromethane and ethanol, washed with n-pentane, and dried *in vacuo*, was obtained. The filtrate was evaporated *in vacuo*, and the residue was extracted with n-hexane. The extract was filtered and reduced *in vacuo* affording a purple oil. This oil was dissolved in methanol, and the solvent was evaporated slowly using a water pump giving *bis{di(propane-2-thiolato)(nitrosyl)-π-cyclopentadienylmolybdenum}* as a crystalline solid (0·8 g, 47%).

Bis[iodo(nitrosyl)-π-cyclopentadienylmolybdenum], $[(\pi\text{-}C_5H_5)Mo(NO)I]_2$.—The complex $[(\pi\text{-}C_5H_5)Mo(NO)(CO)_2]$ (2·5 g) dissolved in benzene was refluxed with allyl iodide (1·0 ml) for 72 h. The solvent was then removed *in vacuo* and the complex repeatedly washed with ethanol, and air dried (0·5 g, 16%).

RESULTS AND DISCUSSION

The compounds described here are of three types, $[(\pi\text{-}C_5H_5)Mo(NO)(X)(SR)]_2$, (I), $[(\pi\text{-}C_5H_5)Mo(NO)(SR)_2]_2$, (II), and $[(\pi\text{-}C_5H_5)Mo(NO)(SR)]_2$, (III). All, with one exception (II; R = Pr), were obtained as crystalline solids and were characterised satisfactorily by elemental analyses and molecular-weight measurements (Table 1).

Synthetic Studies.—Four general reactions were carried out: treatment of $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ (X = Br or I) with RSH in cold acetone, or with NaSR in refluxing acetone and/or ethanol, reduction of $[(\pi\text{-}C_5H_5)Mo(NO)Br(SR)]_2$ (X = Br or I) with zinc dust, and oxidation of $[(\pi\text{-}C_5H_5)Mo(NO)(SR)]_2$ with X_2 (X = Cl or Br) (see general reaction scheme).

Treatment of $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ (X = Br or I) with alkanethiols, RSH (R = Me, Et, Pr, Bu^i, Bu, or CH_2Ph), in cold acetone afforded the mixed halogeno-thiol dimers, (I) (see Table 1). In the solid state the bromo-complexes were yellow and microcrystalline whereas their iodo-analogues were red-brown powders or crystals. In solution, however, the species (I; X = Br) were deep green whereas the compounds (I; X = I), which were significantly less soluble in chloroform, dichloromethane, or acetone than (I; X = Br), were yellow. Neither group of complexes exhibited significant conductivity in acetone, indicating that species such as $[\{(\pi\text{-}C_5H_5)Mo(NO)(SR)\}_2X]^+$ or $[(\pi\text{-}C_5H_5)Mo(NO)(SR)_2]^{2+}$ were absent. However, it is possible that dissociation of the types

$$(\pi\text{-}C_5H_5)Mo(NO)(X)(SR)]_2 \rightleftharpoons [(\pi\text{-}C_5H_5)Mo(NO)(SR)]_2 + X_2 \quad (1)$$

or

$$[(\pi\text{-}C_5H_5)Mo(NO)(X)(SR)]_2 \rightleftharpoons [(\pi\text{-}C_5H_5)Mo(NO)X]_2 + (RS)_2$$

could occur (see spectral studies) and, indeed, molecular-weight determinations indicate a significant lowering from the expected value for the dimer, which is not consistent with the presence of the appropriate monomer.

TABLE 2

Mass spectral data obtained from some representative new molybdenum complexes *

Complex	m/e [a]	Relative intensity	Assignment
$[(\pi\text{-}C_5H_5)Mo(NO)Br(SEt)]_2$	496	5	$[(C_5H_5)_2Mo_2(NO)_2(SEt)_2]^+ + ([M - 2Br]^+)$
	467	2	$[(C_5H_5)_2Mo_2(NO)_2(SEt)S]^+$
	437	1	$[(C_5H_5)_2Mo_2(NO)(SEt)S]^+$
	$427 \rightarrow 375$		Continuum of peaks
	327	37	$[(C_5H_5)Mo(NO)Br(SEt)]^+ ([M/2]^+)]$
	297	17	$[(C_5H_5)MoBr(SEt)]^+$
	268	30	$[(C_5H_5)MoBrS]^+$
	236	12	$[(C_5H_5)MoBr]^+$
	210	12	$[(C_3H_3)MoBr]^+$
	189	100	$[(C_5H_5)MoS]^+$
$[(\pi\text{-}C_5H_5)Mo(NO)I(SPr)]_2$	524	2	$[(C_5H_5)_2Mo_2(NO)_2(SPr)_2]^+ ([M - 2I]^+)$
	481	2	$[(C_5H_5)_2Mo_2(NO)_2(SPr)S]^+$
	441	82	$[(C_5H_5)Mo(NO)I_2]^+$
	411	91	$[(C_5H_5)MoI_2]^+$
	389	80	$[(C_5H_5)Mo(NO)(I)(SPr)]^+ ([M/2]^+)$
	344	19	$[(C_5H_5)_2Mo_2S]^+$
	316	60	$[(C_5H_5)MoIS]^+$
	284	100	$[(C_5H_5)MoI]^+$
	258	7	$[(C_3H_3)MoI]^+$
	197	56	$[(C_5H_5)MoS]^+$
$[(\pi\text{-}C_5H_5)Mo(NO)(SPr^i)]_2$	524	100	$[(C_5H_5)_2Mo_2(NO)_2(SPr^i)_2]^+ ([M]^+)$
	481	60	$[(C_5H_5)_2Mo_2(NO)_2(SPr^i)S]^+$
	451	3	$[(C_5H_5)_2Mo_2(NO)(SPr^i)S]^+$
	439	30	$[(C_5H_5)_2Mo_2(NO)_2S_2H]^+$
	$427 \rightarrow 376$		Continuum
	$366 \rightarrow 313$		Continuum
$[(\pi\text{-}C_5H_5)Mo(NO)(SBu^i)]_2$	626	1·2	$[(C_5H_5)_2Mo_2(NO)_2(SBu^i)_3]^+$
	552	100	$[(C_5H_5)_2Mo_2(NO)_2(SBu^i)_2]^+ ([M]^+)$
	537	1	$[(C_5H_5)_2Mo_2(NO)_2(S_2C_7H_{15})]^{+}$ [c]
	522	2	$[(C_5H_5)_2Mo_2(NO)_2(S_2C_6H_{12})]^{+}$ [c]
	495	43	$[(C_5H_5)_2Mo_2(NO)_2S(SBu)S]^+$
	$408 \rightarrow 378$		Continuum
	$348 \rightarrow 316$		Continuum

[a] Peak position relative to $^{92}Mo^{79}Br$. [b] Very weak peak. [c] Loss of CH_3 from preceding ion.

* Mass spectral data for the following compounds have been deposited as Supplementary Publication No. 20,562 (7 pp.): $[(\pi\text{-}C_5H_5)Mo(NO)Br(SPr)]_2$, $[(\pi\text{-}C_5H_5)Mo(NO)Br(SCH_2Ph)]_2$, $[(\pi\text{-}C_5H_5)Mo(NO)I(SCN_2Ph)]_2$, $[(\pi\text{-}(C_5H_5)Mo(NO)Br(SCH_2Ph)]_2$, and $[(\pi\text{-}C_5H_5)Mo(NO)I(SCH_2Ph)]_2$. Details of the deposition scheme are given in Notices to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

Although (I; X = Br) was not attacked by an excess of alkanethiol, reaction of $[(\pi\text{-}C_5H_5)Mo(NO)Br_2]_2$ with NaSPr afforded $[(\pi\text{-}C_5H_5)Mo(NO)(SPr)_2]_2$ (II; R = Pr). This process is similar to that described [2] for the synthesis of (II; R = CH_2Ph) from $[(\pi\text{-}C_5H_5)Mo(NO)I_2]_2$. However, when the di-iodo-dimer was treated with $NaSPr^i$, both (II; R = Pr^i) and the mono-thiol dimer (III; R = Pr^i) were formed. The species (II) were monomeric in solution, as expected.[2]

Reduction of (I; X = Br) with zinc dust in refluxing acetone afforded (III; R = Me, Et, Pr, Bu^i, or CH_2Ph). Treatment of (I; X = I; R = Pr or CH_2Ph) with PbO or $Hg(NO_3)_2$ gave similar compounds (III; R = Pr or CH_2Ph) which, although not isolated, were characterised spectrally. Compound (III; R = CH_2Ph) was entirely similar to $[(\pi\text{-}C_5H_5)Mo(NO)(SCH_2Ph)]_2$ obtained,[2] somewhat fortuitously, in the reaction between $[(\pi\text{-}C_5H_5)Mo(NO)I_2]_2$ and $PhCH_2SH$ in acetone. Solution and mass spectral molecular-weight determinations showed unequivocally that this class of compounds is binuclear.

Treatment of $[(\pi\text{-}C_5H_5)Mo(NO)(SR)]_2$ with chlorine or bromine in chloroform–ethanol resulted in the formation of $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ (X = Cl or Br)*. These halogeno-dimers were not isolated, but were identified spectroscopically[1] in solution, and, when the solution believed to contain $[(\pi\text{-}C_5H_5)Mo(NO)Cl_2]_2$ was treated with PPh_3, $[(\pi\text{-}C_5H_5)Mo(NO)Cl_2(PPh_3)]$ was isolated (this compound was identical to an authentic sample prepared as described elsewhere [1]).

Spectral Studies.—The mass spectra of the compounds were obtained at temperatures within the range 150—200°. The spectra of (I; X = Br) (Table 2) did not

---

* This is not inconsistent with equation (1) which represents an equilibrium, since the reaction conditions referred to were more drastic than those implied in equation (1).

exhibit molecular ions, the higher fragments having *m/e* values corresponding to $[M - 2Br]^+$. This ion fragmented giving the species $[M - 2Br - R]^+$, $[M - 2Br - 2R]^+$, $[M - 2Br - 2R - NO]^+$, $[M - 2Br - 2R - 2NO]^+$, $[M - 2Br - 2R - 2NO - S]^+$, $[M - 2Br - 2R - 2NO - 2S]^+$, and $[(C_5H_5)Mo_2S_2]^+$. This spectral behaviour was identical to that of the brown isomer of (I; X = I, R = CH_2Ph).[2] No ions of the type $[(C_5H_5)Mo(NO)Br]^+$ or $[(C_5H_5)_2Mo_2(NO)_2(Br)(SR)]^+$ were detected, and the implication is that the species (I; X = Br) have terminal Br and bridging SR groups. The presence of Br in (I; X = Br) was, of course, confirmed by the observation of ions corresponding to $[M/2]^+$. This half-molecular ion fragmented with apparently sequential loss of NO, RS, and Br, respectively. No ions of the type $[(C_5H_5)Mo(NO)Br_2]^+$ or $[(C_5H_5)Mo(NO)(SR)_2]^+$ were observed, suggesting that (I; X = Br) has a symmetrical structure.

However, not only did the spectra of (I; X = I) contain the ions $[M - 2I]^+$ and $[M/2]^+$, as expected, but $[(C_5H_5)Mo(NO)I_2]^+$ was also present. Such an ion could arise *via* thermal rearrangement at the probe in the mass spectrometer, and we are not inclined to believe that the structure of (I; X = I) is significantly different from that of (I; X = Br).

The mass spectra of (II; R = Pr and CH_2Ph) were similar to that reported previously[2] for (II; R = CH_2Ph).

The spectra of (III) were essentially similar to that of (III; R = CH_2Ph)[2]. Thus, molecular ions were detected, and the ions derived from these were identical to those described for the fragmentations of the ion $[M - 2Br]^+$ obtained from (I; X = Br). Between *m/e* = 427 and 377, a continuum of peaks was observed. These could not be assigned, but three ions, $[(C_5H_5)_2Mo_2(NO)S_2]^+$, $[(C_5H_5)_2Mo_2S_2O]^+$, and $[(C_5H_5)_2Mo_2S_2]^+$, could be responsible. The corresponding chromium compound (R = Ph)[3] fragmented similarly, the chromocene ion, $[(C_5H_5)_2Cr]^+$, being very strong; in the new compounds the molybdocene ion was extremely weak or non-existent. On the basis of our previous discussion of these spectra,[2] our view that (III) contains bridging SR groups and a metal–metal bond, as in $[(\pi\text{-}C_5H_5)Cr(NO)(SR)]_2$,[3] seems to be confirmed.*

The ^{1}H n.m.r. spectra obtained from (I), (II), and (III) (Table 3) were, with the exception of the species having R = CH_2Ph, relatively unexceptional, and confirmed the formulation of the compounds. Generally the τ-values of the cyclopentadienyl protons in (I) and (II) occurred at fields lower than those of (III). However, within the series (I) and (III), the $\pi\text{-}C_5H_5$ proton resonances of (I; X = Br or I, R = CH_2Ph) and (III; R = CH_2Ph) occurred at noticeably higher fields than those of their simple alkyl analogues, presumably because of increased shielding arising from the ring currents of the phenyl groups.

The methylene proton resonances in (I; X = Br or I, R = CH_2Ph) occurred as an AB pair, which is consistent with several structures, including A and B.†

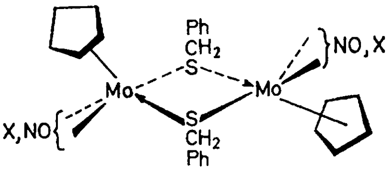
TABLE 3

^{1}H N.m.r. spectra obtained from $[(\pi\text{-}C_5H_5)Mo(NO)XY]_2$ in $CDCl_3$

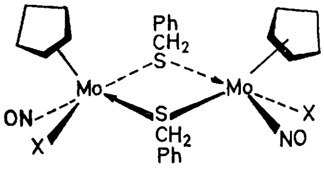
X	Y	τ	Rel. area ^{a}	Assignments and Remarks
Br	SEt ^{b}	3·96	5	$\pi\text{-}C_5H_5$, single
		7·90	2	$-\mathit{CH}_2Me$; quartet
		8·67	3	$-CH_2-\mathit{CH}_3$; triplet
Br	SCH_2Ph ^{b}	2·65	5	$-C_6H_5$; multiplet
		4·31	5	$\pi\text{-}C_5H_5$; singlet
		5·62	2	$-\mathit{CH}_2Ph$; AB pair (J_{AB} 13·0 Hz)
I	SPr ^{c}	3·81	5	$\pi\text{-}C_5H_5$; singlet
		7·05	2	$-\mathit{CH}_2CH_2CH_3$; multiplet
		8·25	2	$-CH_2\mathit{CH}_2Me$; multiplet
		8·80	3	$-CH_2CH_2\mathit{CH}_3$; triplet
I	SCH_2Ph ^{c}	2·60	5	$-C_6H_5$; multiplet
		4·29	5	$\pi\text{-}C_5H_5$; singlet
		5·60	2	$-\mathit{CH}_2Ph$; AB pair (J_{AB} Hz)
SPr	SPr ^{c}	4·12	5	$\pi\text{-}C_5H_5$; singlet
		6·37	2	$-\mathit{CH}_2CH_2Me$; triplet
		8·22	2	$-CH_2\mathit{CH}_2Me$; double triplet
		9·00	3	$-CH_2CH_2\mathit{CH}_3$; triplet
—	SEt ^{b}	4·29	5	$\pi\text{-}C_5H_5$; singlet
		7·10	2	$-CH_2Me$; quartet
		8·50	3	$-CH_2\mathit{CH}_3$; triplet
—	SPr^i ^{c}	4·48	5	$\pi\text{-}C_5H_5$; singlet
		6·90	1	$-C\mathit{H}Me_2$; quintet
		8·36	6	$-CH(\mathit{CH}_3)_2$; doublet
—	SCH_2Ph ^{b}	2·50	5	$-C_6H_5$; multiplet
		4·71	5	$\pi\text{-}C_5H_5$; singlet
		5·80	2	$-\mathit{CH}_2Ph$; sharp singlet

* ^{1}H N.m.r. data for compounds having X and Y as follows are given in Supplementary Publication No. 20562 (see footnote to Table 2). X(Y): Br (SMe), Br (SPr), Br (Bu^t), Br (SBu), — (SMe), — (SPr), — (SPr^i), and — S(Bu^s).

^{a} Relative area. ^{b} At 100 MHz. ^{c} At 60 MHz.



A



B

The methylene resonances in (III; R = CH_2Ph) occur as a sharp singlet, and the resonances due to the isopropyl group in (III; R = Pr^i) occur as a simple quintet (H)

---

* The R and NO groups are lost before S, and there is a predominance of Mo_2-containing fragments, consistent with an Mo–Mo bond.

† In A, an AB spectrum, because of the asymmetry of the S atom environment, would be predicted whether the relative arrangement of the NO and X groups were mutually *cis* or *trans*, but in B, the methylene protons as shown are diastereotopic (NO and X groups mutually *trans*) whereas in the corresponding form with *cis*-NO and *cis*-X groups, the protons would be enantiotopic and so should give a singlet proton resonance.

TABLE 4

NO Stretching frequencies obtained from new molybdenum complexes

Compound	ν_{NO} (cm^{-1}) KBr	Nujol	CH$_2$Cl$_2$
$[(\pi\text{-}C_5H_5)Mo(NO)(Br)(SMe)]_2$	1678		1660
	1650		
$[(\pi\text{-}C_5H_5)Mo(NO)(Br)(SEt)]_2$	1638		1659
$[(\pi\text{-}C_5H_5)Mo(NO)(Br)(SPr)]_2$	1640		1658
$[(\pi\text{-}C_5H_5)Mo(NO)(Br)(SBu^i)]_2$	1626		1655
	1662		
$[(\pi\text{-}C_5H_5)Mo(NO)(Br)(SBu)]_2$	1642		1648
	1669		
$[(\pi\text{-}C_5H_5)Mo(NO)(Br)(SCH_2Ph)]_2$	1652		1660
	1633		
$[(\pi\text{-}C_5H_5)Mo(NO)(I)(SEt)]_2$	1695		
	1650		
$[(\pi\text{-}C_5H_5)Mo(NO)(I)(SPr)]_2$	1648		
$[(\pi\text{-}C_5H_5)Mo(NO)(I)(SCH_2Ph)]_2$	1650 [a,b]		1661 [b]
$[(\pi\text{-}C_5H_5)Mo(NO)(SPr)_2]_2$	1640 [c]		
$[(\pi\text{-}C_5H_5)Mo(NO)(SMe)]_2$	1590	1593	1618
	1560	1565	1579
$[(\pi\text{-}C_5H_5)Mo(NO)(SEt)]_2$	1578	1580	1600sh
		1569	1578
$[(\pi\text{-}C_5H_5)Mo(NO)(SPr)]_2$	1601	1601	1612
	1570	1570	1574
$[(\pi\text{-}C_5H_5)Mo(NO)(SPr^i)]_2$	1617	1619	1612
	1599	1600	1573
	1586	1585	
	1566	1565	
$[(\pi\text{-}C_5H_5)Mo(NO)(SBu^t)]_2$	1591	1595	1612
	1568	1570	1576
$[(\pi\text{-}C_5H_5)Mo(NO)(SCH_2Ph)]_2$	1600	1601	1616
	1581	1583	1578
	1559	1562	

[a] Prepared as in this work; ν_{NO}. [b] From ref. 2. [c] As an oil on NaCl plate.

TABLE 5

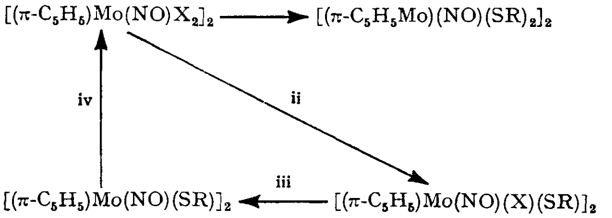
Electronic spectra data obtained from new molybdenum complexes

Complex	R	Temp. (°C)	$\lambda_{max.}$(RK) (ε in l mol^{-1} cm^{-1})
$[(\pi\text{-}C_5H_5)Mo(NO)Br(SR)]_2$	Me	−30	18·51 (890sh); 25·77 (1660sh); 33·55 (9240sh); 37·03 (17,950)
		+20	16·80 (167); 24·39 (2240); 32·36 (7450sh); 38·16 (12,130sh)
	Et	−30	16·58 (215); 24·15 (2150); 32·57 (8300sh); 38·02 (15,050sh)
		+20	16·58 (893); 24·03 (6240); 30·76 (9500)
	Pr	−30	17·09 (186); 24·15 (3000); 32·46 (8400); 37·45 (11,650sh)
		+20	16·61 (703); 23·98 (6100); 30·76 (9960); 37·31 (8600sh)
	Bu	−30	17·24 (241); 24·21 (3300); 32·15 (8760); 37·59 (13,600)
		+20	16·61 (834); 24·03 (7250); 30·58 (11,540); 37·31 (9440sh)
	CH$_2$Ph	−30	17·21 (200sh); 24·03 (3450); 32·05 (9340sh); 37·03 (14,560sh)
		+20	16·61 (604); 24·21 (5710); 36·76 (10,080)
$[(\pi\text{-}C_5H_5)Mo(NO)(SR)_2]$	Me	+20	18·01 (124); 30·76 (12,400); 39·06 (14,400)
	Et	+20	17·30 (215); 31·84 (7840); 39·37 (18,100)
	Pr	+20	30·76 (14,250); 37·31 (14,050)
	Pr^i	+20	30·76 (14,100); 38·02 (14,100)
	Bu^s	+20	30·21 (13,040); 37·31 (10,880sh)
	CH$_2$Ph	+20	30·39 (13,800); 38·16 (14,300sh)
$[(\pi\text{-}C_5H_5)Mo(NO)(I)SR]_2$	Et	+20	11·82 (158); 19·0 (1910); 25·44 (8760); 31·44 (8380)
	Pr	+20	16·00 (785sh); 19·19 (1200sh); 22·57 (5450); 28·81 (8650); 31·15 (10,380)
	CH$_2$Ph	+20	16·80 (536sh); 22·62 (3330); 28·57 (9600sh); 31·84 (11,600sh)
$[(\pi\text{-}C_5H_5)Mo(NO)(SR)_2]_2$	Pr	+20	17·98 (6100); 24·33 (8900); 29·23 (8550); 35·46 (9730)
$[(\pi\text{-}C_5H_5)Mo(NO)I]_2$		+20	15·19 (265); 21·78 (1640sh); 25·00 (13,800); 29·23 (5090); 27·39 (6040)

and a doublet (Me). These data are consistent with either structure C or D.

In their i.r. spectra, the new complexes exhibited NO stretching frequencies (Table 4) in the range 1560—1680 cm^{-1}. Frequencies from the middle to the top end of this range are assigned to the stretching modes of terminally bound NO, whereas those frequencies at the bottom end of the range have been associated with bent M–N–O bonding arrangements or even bridging NO groups.

In (I; X = Br or I), ν_{NO} (in solution) occurred as a single absorption, and was generally 50 cm^{-1} higher than ν_{NO} in the corresponding species (III). The position of the NO stretching frequency was influenced by the electronegativity of X but not apparently by R. The spectra of (III) in solution contained two NO stretching frequencies, separated by 37 cm^{-1}, and it seems likely that this is due to the presence of two isomers (C and D possibly).*



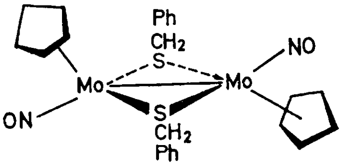
SCHEME i, SR⁻ in hot ethanol; ii, RSH in cold ethanol or acetone; iii, Zn dust in hot acetone (X = Br); iv, X_2 (X = Cl or Br)

The electronic spectra of (I), (II), and (III) are recorded in Table 5. There were distinct spectral differences between (I; X = Br) and (I; X = I), and we discovered that the spectrum of (I; X = Br) in chloroform was temperature dependent. The spectra of (I; X = Br) at 20° bear similarities to the spectra of (III) at the same temperature, but the spectra of the former at low temperature are unique. Considering these

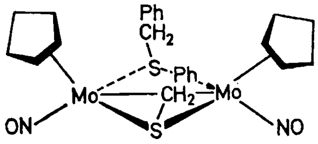
---

* It is possible, but does not seem very likely, that two ν_{NO} could arise from either isomer C or D, being caused by the relative configurations of the SR groups, *i.e. syn* or *anti*. Alternatively, coupling between the NO groups in isomer D could occur, although there are no reported examples of this phenomenon in similar types of metal carbonyls and isonitriles.

data together with the molecular-weight determinations in the same solvent, we suggest that a partial dissociation of the type in (1) can occur. The spectra of (I; X = I) at 20 °C are different to that of $[(\pi\text{-}C_5H_5)Mo(NO)I]_2$ indicating that dissociation, if it occurs in this series, must be similar to that proposed for (I; X = Br).



C



D

Conclusions.—The data we have obtained from (I) suggest that the molecule is a dimer containing terminal NO and X, and bridging SR. Unfortunately the ^1H n.m.r. spectra of (I; R = CH_2Ph or Pr^i) do not permit an identification of the particular isomers formed. It seems, on the basis of the limited data obtained here and previously,[2] that (II) has a similar structure where (X) is replaced by SR, but that these molecules, unlike (I), readily dissociate into (co-ordinatively unsaturated) monomers in solution. The species (III) clearly contain a metal–metal bond and probably bridging SR groups. However, contrary to our previous suggestions,[2] there seems to be little convincing evidence that the NO groups are also bridging. Thus, (III) seems most likely to exist as a mixture of isomers (C and D), analogous to $[(\pi\text{-}C_5H_5)Cr(NO)(SPh)]_2$[3]; this is consistent with ^1H n.m.r. and i.r. spectral data.

We thank the S.R.C. for a studentship (D. S.), Dr. T. A. James for discussions, and Mrs. J. Bray for experimental assistance.

[2/642 *Received, 20th March*, 1972]