The Chemistry of π-Cyclopentadienyl Nitrosyl Molybdenum Complexes Part III.[1,2] Dichloro- and Dibromo-compounds and their Lewis Base Adducts

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The stoicheiometric reaction of $[(\pi\text{-}C_5H_5)Mo(NO)(CO)_2]$ with chlorine or bromine affords $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ (X = Cl or Br). These species react with Lewis bases L (L = PPh_3, $AsPh_3$, PMe_2Ph, pyridine, or bipyridyl) or halide ion (X = Cl or Br) giving $[(\pi\text{-}C_5H_5)Mo(NO)X_2L]$, $[(\pi\text{-}C_5H_5)Mo(NO)Br(PMe_2Ph)_2]Br$, $[(\pi\text{-}C_5H_5)Mo(NO)Cl(bipy)]Cl$ and $[(\pi\text{-}C_5H_5)Mo(NO)X_3]^-$. The spectral properties of these compounds are compared with those of the corresponding iodides. The synthesis of $[(\pi\text{-}C_5H_5)Mo(NO)(CN)Br]_n$ is briefly reported.

IN a previous paper[1] we described the formation of the metal–metal-bonded species $[(\pi\text{-}C_5H_5)Mo(NO)I]_2$, by reduction of $[(\pi\text{-}C_5H_5)Mo(NO)I_2]_2$ using $[(\pi\text{-}C_5H_5)Mo(NO)(CO)_2]$. Because of the relatively low solubility of both iodides, however, we were unable to study in detail their properties, reactions, and structures in solution. In an attempt to improve the solubility of this class of binuclear complexes we have attempted to prepare $[(\pi\text{-}C_5H_5)Mo(NO)X_n]_2$ (where X = Cl or Br and n = 1 or 2), and our results are described in this paper.

The binuclear complexes $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ are believed[1,3] to contain terminal NO, and both terminal and bridging X. The halogen bridges should be readily cleaved by Lewis bases, L, and by an excess of halide ion, X^-, affording $[(\pi\text{-}C_5H_5)Mo(NO)X_2L]$, $[(\pi\text{-}C_5H_5)Mo(NO)XL_2]X$ and $[(\pi\text{-}C_5H_5)Mo(NO)X_3]^-$. A number of complexes of this type have been reported[2,3] where X = I, and herein we describe the formation of a series of compounds where X = Cl or Br and L = PPh_3, $AsPh_3$, PMe_2Ph, pyridine (py) or bipyridyl (bipy); these new compounds are compared with the corresponding iodides.

RESULTS AND DISCUSSION

Reaction of $[(\pi\text{-}C_5H_5)Mo(NO)(CO)_2]$ with the stoicheiometric amounts of chlorine or bromine afforded $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_n$, X = Cl or Br. Chlorination led only to low yields of the oxidised nitrosyl, the major product being an air- and moisture-sensitive green oil, probably $[Mo(NO)_2Cl_2]_n$, which afforded the known[4] $[Mo(NO)_2(PPh_3)_2Cl_2]$ on treatment with PPh_3 in refluxing benzene. The corresponding bromide, $[Mo(NO)_2Br_2]_n$, was produced similarly and afforded $[Mo(NO)_2(bipy)Br_2]$ on treatment with 2,2′-bipyridyl. The π-cyclopentadienyl dihalides were soluble only in polar solvents, only slightly more so than their iodo-analogues, but were satisfactorily characterised by elemental analyses (Table 1).

TABLE 1

Analytical and conductivity data obtained from new compounds

	Analytical data								
	Found				Calc.				
Compound	C	H	N	Hal	C	H	N	Hal	Λ [a]
$[(\pi\text{-}C_5H_5)Mo(NO)Cl_2]_2$	22·6	1·9	5·5	25·2	22·9	1·9	5·3	27·1	
$[(\pi\text{-}C_5H_5)Mo(NO)Br_2]_2$	17·7	2·0	3·6	45·4	17·1	1·4	4·0	45·6	
$[Et_4N][(\pi\text{-}C_5H_5)Mo(NO)Cl_3]$	36·7	5·7	6·6	23·1	36·5	5·8	6·6	24·9	
$[Et_4N][(\pi\text{-}C_5H_5)Mo(NO)Br_3]$	27·7	4·5	5·0	38·6	27·8	4·5	5·0	42·8	73·9 [b]
$[(\pi\text{-}C_5H_5)Mo(NO)Cl_2(py)]$	34·9	3·4	8·1	20·1	35·2	2·9	7·9	20·8	
$[(\pi\text{-}C_5H_5)Mo(NO)Cl_2(PPh_3)]$	53·1	4·2	2·7	13·5	52·7	3·8	2·7	13·6	
$[(\pi\text{-}C_5H_5)Mo(NO)Cl_2(AsPh_3)]$	48·7	3·9	2·4	12·4	48·6	3·5	2·5	12·5	26·5 [c] 12·4 [b]
$[(\pi\text{-}C_5H_5)Mo(NO)Cl_2(PMe_2Ph]$; A	39·2	4·1	3·9	17·9	39·2	4·0	3·5	17·8	2·1 [c] 11·4 [b]
$[(\pi\text{-}C_5H_5)Mo(NO)Br_2(py)]$	28·3	2·8	6·5	36·9	27·9	2·3	6·5	37·2	
$[(\pi\text{-}C_5H_5)Mo(NO)Br(bipy)]Br$	35·4	2·8	8·2	22·4	35·5	2·6	8·3	31·5	29·2 [b]
$[(\pi\text{-}C_5H_5)Mo(NO)Br_2(PPh_3)]$	45·7	3·7	2·3	25·9	45·0	3·3	2·3	26·1	
$[(\pi\text{-}C_5H_5)Mo(NO)Br_2(AsPh_3)]$	42·0	3·2	2·1	24·5	42·0	3·2	2·1	24·4	9·0 [c] 45·2 [b]
$[(\pi\text{-}C_5H_5)Mo(NO)Br_2(PMe_2Ph)]$, A	32·4	3·8	2·8	32·8	31·9	3·3	2·9	32·8	
$[(\pi\text{-}C_5H_5)Mo(NO)Br_2(PMe_2Ph)]$, B	32·6	3·6	2·9	32·8	31·9	3·3	2·9	32·8	2·2 [c] 24·7 [b]
$[(\pi\text{-}C_5H_5)Mo(NO)Br(PMe_2Ph)_2]Br$	40·2	4·5	2·2	25·5	40·4	4·3	2·3	25·7	131·4 [c] 26·9 [b]
$[(\pi\text{-}C_5H_5)Mo(NO)(CN)Br]_2$	24·3	1·9	9·1	27·3	24·2	1·7	9·4	26·9	

[a] In $cm^2\ mol^{-1}\ \Omega^{-1}$. [b] In Me_2SO; for typical 1 : 1 electrolyte Λ = 50. [c] In acetone; for typical 1 : 1 electrolyte Λ = 150—170.

Treatment of $[(\pi\text{-}C_5H_5)Mo(NO)(CO)_2]$ with cyanogen

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

[2] Part II, T. A. James and J. A. McCleverty, *J. Chem. Soc.* (*A*), 1971, 1596.

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

[4] F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, 1964, **3**, 1609.

or cyanogen bromide in sealed evacuated tubes afforded yellow microcrystalline solids which were insoluble in most solvents with the exception of dimethyl sulphoxide (DMSO) or pyridine. Satisfactory elemental analyses could not be obtained from the product of the cyanogen reaction although, from i.r. spectral data, $(\pi\text{-}C_5H_5)$, NO, and CN groups, but not CO, were clearly present. Analytical data obtained from the product of the reaction with BrCN suggested an empirical formula $[(\pi\text{-}C_5H_5)Mo(NO)(CN)Br]_n$. The compound apparently formed an adduct with pyridine whose mass spectrum exhibited ions at $m/e \simeq 1000$; no satisfactory explanation of these, or any other ions in the spectrum, nor an adequate elemental analysis of the adduct, could be obtained. The ^1H n.m.r. spectrum of $[(\pi\text{-}C_5H_5)Mo(NO)(CN)Br]_n$ in DMSO consisted of three resonances of unequal intensity in the range τ 6—6·5 which can presumably be assigned to $\pi\text{-}C_5H_5$ proton resonances (see later); the multiplicity of signals may indicate a mixture, isomers, or stereochemically non-equivalent $\pi\text{-}C_5H_5$ groups in an oligo- or poly-meric species.

Both the dichloro- and dibromo-complexes underwent reactions with Lewis bases, L, (*e.g.* PPh_3, PMe_2Ph, $AsPh_3$, pyridine or 2,2′-bipyridyl, *e.g.*

$$[(\pi\text{-}C_5H_5)Mo(NO)X_2]_n + nL \rightleftharpoons n[(\pi\text{-}C_5H_5)Mo(NO)LX_2]$$

These reactions are entirely analogous to those of the corresponding iodide.[2,3] With PMe_2Ph, two isomers (A and B) could be obtained, the former by reaction of $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ with the Lewis base in cold ethanol, and the latter by heating the former in acetone.* Treatment of $[(\pi\text{-}C_5H_5)Mo(NO)(PMe_2Ph)Br_2]$ with an excess of PMe_2Ph afforded, as expected,[2] $[(\pi\text{-}C_5H_5)Mo(NO)(PMe_2Ph)_2Br_2]$; the corresponding reaction with the dichloride afforded an uncharacterised green oil. The species $[(\pi\text{-}C_5H_5)Mo(NO)X_3]^-$ were obtained by treating $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_n$ with X^-, and were isolated as the salts of the $[Et_4N]^+$ cation.

The conductivities (Table 1) of the new compounds were measured in acetone and DMSO. In no case was Λ shown to be time dependent, in contrast to the data obtained [2] from the related iodo-species. In acetone, dissociation of the neutral adducts appears to be minimal, and in DMSO, only for $[(\pi\text{-}C_5H_5)Mo(NO)(AsPh_3)Br_2]$ does Λ approach the value for a 1 : 1 electrolyte. Thus, it seems that only the iodo-complexes, $[(\pi\text{-}C_5H_5)Mo(NO)LX_2]$ (X = I) dissociate readily in DMSO, and this may be rationalised partly on steric and partly on electronegativity grounds. The bipyridyl complex $[(\pi\text{-}C_5H_5)Mo(NO)(bipy)Br_2]$ was too insoluble in acetone for conductivity measurements, but in DMSO afforded values of Λ considerably less than those expected for a 1 : 1 electrolyte. This may be due to ion-pairing or dissociation of PMe_2Ph, since a reasonable formulation would seem, by analogy with the iodide analogue,[3] to be $[(\pi\text{-}C_5H_5)Mo(NO)(bipy)Br]^+Br^-$. The compound $[(\pi\text{-}C_5H_5)Mo(NO)(PMe_2Ph)_2Br_2]$ behaved similarly in DMSO, but Λ in acetone was entirely consistent with the species formulation as $[(\pi\text{-}C_5H_5)(Mo)(NO)(PMe_2Ph)_2Br]^+Br^-$.

Attempts to reduce the dihalides, $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ $[(\pi\text{-}C_5H_5)Mo(NO)X]_2$ (X = Cl or Br), using sodium amalgam, zinc dust, $NaBH_4$, or $[(\pi\text{-}C_5H_5)Mo(NO)(CO)_2]$ were unsuccessful. Treatment of $[(\pi\text{-}C_5H_5)Mo(NO)(CO)_2]$ with allyl iodide in a variety of solvents has afforded low yields of $[(\pi\text{-}C_5H_5)Mo(NO)I]_2$, but similar reactions using allyl bromide have been unsuccessful in providing the analogous bromo-dimer.

Spectral Studies.—*Mass spectra.* The mass spectra of $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_n$ (X = Cl or Br) are summarised in the Experimental section. Both compounds, in common with the iodide, X = I, failed to exhibit parent molecular ions, but weak ions were detected which corresponded to the fragmentation of $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2^+$. Hence, it would appear that $n = 2$, but confirmation of this in solution is impossible because of low solubility.† The strongest ions in the spectra of these compounds, however, were derived from $[(\pi\text{-}C_5H_5)Mo(NO)X_2]^+$.

The mass spectra of the Lewis base adducts were unexceptional (that of $[(\pi\text{-}C_5H_5)Mo(NO)(PPh_3)Cl_2]$ is included in the Experimental section), and again no molecular ion was observed. The heaviest ions corresponded to $[(\pi\text{-}C_5H_5)Mo(NO)X_2]^+$, but peaks arising from the fragmentation of the Lewis base could also be detected.

^1H N.m.r. spectra. The ^1H n.m.r. spectra of $[(\pi\text{-}C_5H_5)Mo(NO)LX_2]$ and $[(\pi\text{-}C_5H_5)Mo(NO)L_2X]X$ were recorded in $CDCl_3$ and $(CD_3)_2SO$, and the data are summarised in Table 2. Information obtained from $[(\pi\text{-}C_5H_5)Mo(NO)(AsPh_3)I_2]$ and ‘ *cis* ’-$[(\pi\text{-}C_5H_5)Mo(NO)(PMe_2Ph)I_2]$ are also included.[2]

In our earlier discussion [2] of the n.m.r. spectral properties of $[(\pi\text{-}C_5H_5)Mo(NO)(PMe_2Ph)I_2]$ we suggested that the molecule could exist as either *cis*- or *trans*-isomers.‡ We further proposed that, in this species, the relative orientation of the PMe_2Ph group in the molecule was such that the phenyl group pointed away from the molecule, either between an NO group and an I atom (*cis*-isomer) or between two I atoms (*trans*-isomer). This assumption of stereospecificity was justified on the grounds of the relative bulk of the PMe_2Ph ligand in relation to the size of the I atoms and the NO group. As a consequence the interpretation of the ^1H n.m.r. spectra of the di-iodide, in non-polar solvents and in DMSO,§ was greatly simplified: the methyl resonances of the co-ordinated PMe_2Ph in the ‘ *cis* ’-form appeared as a

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* Under similar conditions in cold acetone $[(\pi\text{-}C_5H_5)Mo(NO)I_2]_2$ afforded a mixture of ‘ *cis* ’- and ‘ *trans* ’-$[(\pi\text{-}C_5H_5)Mo(NO)(PMe_2Ph)I_2]$, whereas in hot acetone, only the *cis*-form was produced.[2]

† A dimeric formulation with two bridging and two terminal X, and terminal NO, would allow each Mo atom to have an 18-electron configuration; there is no formal Mo–Mo bond and each metal atom has the preferred 3—4 co-ordination ($\pi\text{-}C_5H_5 \equiv 3$ co-ordination sites).

‡ The geometry is defined by the relative position of the iodine atoms in the basal ligand set, assuming the usual 3 : 4 or ‘ four-legged piano-stool ’ configuration of mono-π-cyclopentadienyl molybdenum complexes.

§ In non-polar solvents $[(\pi\text{-}C_5H_5)Mo(NO)(PMe_2Ph)I_2]$ was not dissociated, but in DMSO it formed $[(\pi\text{-}C_5H_5)Mo(NO)(PMe_2Ph)(DMSO)_2]^{2+}$.

TABLE 2

^{1}H n.m.r. data obtained from $[(\pi\text{-}C_5H_5)Mo(NO)LX_2]$ and $[(\pi\text{-}C_5H_5)Mo(NO)L_2X]^+$

X	L	Solvent	τ	Rel. area [a]	Assignments and remarks	Δ_{Me} [b]
Cl	py	$CDCl_3$	1·86	1	m; C_5H_5N	
			3·81	1	s; $\pi\text{-}C_5H_5$	
	$AsPh_3$	$(CD_3)_2SO$	2·65	3	m (7 lines); As $(C_6H_5)_3$	
			3·81	1	s; $\pi\text{-}C_5H_5$	
	PMe_2Ph; A [c]	$(CD_3)_2SO$	2·30	5	m; C_6H_5 of $PMe_2(C_6H_5)$	
			4·07	5	d; $\pi\text{-}C_5H_5$ (J_{HP} 3·0 Hz)	
			7·93 7·98	6	dd; inequivalent CH_3 of $P(CH_3)_2Ph$ (J_{HP} 11·0 Hz)	5
	PMe_2Ph; A	$CDCl_3$	2·40	5	m; C_6H_5 of $PMe_2(C_6H_5)$	
			4·21	5	d; $\pi\text{-}C_5H_5$ (J_{HP} 3·0 Hz)	
			7·76 7·91	6	dd; inequivalent CH_3 of $P(CH_3)_2Ph$ (J_{HP} 12·0 Hz)	15
	PMe_2Ph; B [d]	$(CD_3)_2SO$	2·30	5	m; C_6H_5 of $PMe_2(C_6H_5)$	
			4·01	5	d; $\pi\text{-}C_5H_5$ (J_{HP} 3·0 Hz)	
			7·90 7·94	6	dd; inequivalent CH_3 of $P(CH_3)_2Ph$ (J_{HP} 12·0 Hz)	4
	PMe_2Ph; B	$CDCl_3$	2·40	5	m; C_6H_5 of $PMe_2(C_6H_5)$	
			4·33	5	d; $\pi\text{-}C_5H_5$ (J_{HP} 3·0 Hz)	
			7·88	6	t; two overlapping doublets; inequivalent CH_3 of $P(CH_3)_2Ph$ (J_{HP} 11·0 Hz)	11
Br	py	$CDCl_3$	1·50	1	broad m; C_5H_5N	
			3·75	1	s; $\pi\text{-}C_5H_5$	
	bipy [e]	$(CD_3)_2SO$	1·55	8	m; $C_{10}H_8N_2$	
			2·43	5	s; $\pi\text{-}C_5H_5$	
	$AsPh_3$	$(CD_3)_2SO$	2·67	3	m (9 lines); $As(C_6H_5)_3$	
			3·71	1	s; $\pi\text{-}C_5H_5$	
	Br [f]	$CDCl_3$	3·89	5	s; $\pi\text{-}C_5H_5$	
			6·64	8	d; CH_2 $(C_2H_5)_4N^+$	
			8·64	12	t; CH_3	
	PMe_2Ph; A	$(CD_3)_2SO$	2·40	5	m; C_6H_5 of $PMe_2(C_6H_5)$	
			4·02	5	d; $\pi\text{-}C_5H_5$ (J_{HP} 4·0 Hz)	
			7·86 7·89	6	dd; inequivalent CH_3 of $P(CH_3)_2Ph$ (J_{HP} 11·0 Hz)	3
	PMe_2Ph; A	$CDCl_3$	2·40	5	m; C_6H_5 of $PMe_2(C_6H_5)$	
			4·31	5	d; $\pi\text{-}C_5H_5$ (J_{HP} 2·0 Hz)	
			7·74 7·89	6	dd; inequivalent CH_3 of $P(CH_3)_2Ph$ (J_{HP} 9·5 Hz)	15
Br	PMe_2Ph; B	$(CD_3)_2SO$	2·40	5	m; C_6H_5 of $PMe_2(C_6H_5)$	
			4·02	5	d; $\pi\text{-}C_5H_5$ (J_{HP} 4·0 Hz)	
			7·90	6	d; two overlapping doublets (J_{HP} 11·0 Hz)	0 [g]
	PMe_2Ph; B	$CDCl_3$	2·50	5	m; C_6H_5 of $PMe_2(C_6H_5)$	
			4·32	5	d; $\pi\text{-}C_5H_5$ (J_{HP} 3·0 Hz)	
			7·74 7·85	6	dd; inequivalent CH_3 of $P(CH_3)_2Ph$ (J_{HP} 11·0 Hz)	11
	$(PMe_2Ph)_2$ [h]	$(CD_3)_2SO$	2·40	10	m; C_6H_5 of $PMe_2(C_6H_5)$	
			3·99	5	t; $\pi\text{-}C_5H_5$ (J_{HP} 2·0 Hz)	
			7·82	12	asymmetric q; CH_3 of $P(CH_3)_2Ph$ (J_{HP} 5·0 Hz)	
I	$AsPh_3$	$(CD_3)_2SO$	2·62	3	m; C_6H_5 of $As(C_6H_5)_3$	
			3·58	1	s; $\pi\text{-}C_5H_5$	
	PMe_2Ph [i]	$CDCl_3$	2·38	5	m; C_6H_5 of $PMe_2(C_6H_5)$	
			4·36	5	d; $\pi\text{-}C_5H_5$ (J_{HP} 3·0 Hz)	
			7·63 7·77	6	dd; inequivalent CH_3 of $P(CH_3)_2Ph$ (J_{HP} 10·0 Hz)	14

[a] Relative area. [b] Δ_{Me} = separation of two doublets in PMe_2Ph signal; in Hz. [c] Isomer A. [d] Isomer B. [e] bipy = 2,2′-Bipyridyl $C_{10}H_8N_2$, as Br^- salt. [f] $[Et_4N]^+$ salt. [g] This assignment is preferred to that offered for *trans*-$[(\pi\text{-}C_5H_5)Mo(NO)(PMe_2Ph)I_2]$ in $(CD_3)_2SO$, where *trans*-$[(\pi\text{-}C_5H_5)Mo(NO)(PMe_2Ph)\{(CD_3)_2SO\}_2]^{2+}$ is apparently formed: there is no conductivity evidence for this in the bromo-complex. [h] As the Br^- salt. [i] '*cis*'-Isomer.

double doublet ($J_{HP} \geqslant 10$ Hz) whereas, in the '*trans*'-form, they appeared as a single doublet ($J_{HP} \leqslant 9$ Hz). If these assumptions are tenable in the corresponding dichloro- and dibromo-complexes then, of course, similar spectra should be observed.

The spectra of both isomers of [(π-C_5H_5)Mo(NO)(PMe_2Ph)X_2] (X = Cl or Br) in $CDCl_3$ or DMSO consisted of resonances due to the phenyl protons, a doublet due to the π-C_5H_5 protons (J_{HP} *ca.* 3 Hz) and a double doublet due to the (inequivalent) methyl groups in PMe_2Ph. Thus it is impossible to say whether isomer A or B is the '*cis*'- or '*trans*'-form, or whether they have the same overall isomeric structure but different orientations of the PMe_2Ph ligand with respect to the other ligands. This may be due to the smaller size of Cl or Br atoms relative to I. It may be of significance that the separation between the doublet components of the methyl signals obtained from isomer A (X = Cl or Br) in $CDCl_3$ are very similar to that obtained from '*cis*'-[(π-C_5H_5)Mo(NO)(PMe_2Ph)I_2]. The chemical shifts of the cyclopentadienyl and of the methyl resonances were dependent on X, the solvent and the isomer.

I.r. Spectra.—The nitrosyl stretching frequencies of the new complexes, together with their iodo-analogues are summarised in Table 3. The values of ν_{NO} for the new complexes lie in the range 1630—1660 cm^{-1} (KBr disc), fairly typical of terminal NO bonded to molybdenum.

TABLE 3

Nitrosyl stretching frequencies of π-cyclopentadienyl-nitrosyl molybdenum complexes

	ν_{NO} (KBr; cm^{-1})		
Complex	X = Cl	X = Br	X = I [a]
[(π-C_5H_5)Mo(NO)X_2]$_2$	1670	1670	1670
[Et_4N][(π-C_5H_5)Mo(NO)X_3]	1635	1655	1650
[(π-C_5H_5)Mo(NO)X_2(py)]	1650	1656	1661 [b]
[(π-C_5H_5)Mo(NO)X_2(PPh_3)$_4$]	1654	1660	1660 [b]
[(π-C_5H_5)Mo(NO)X_2($AsPh_3$)]	1650	1652	1661 1650
[(π-C_5H_5)Mo(NO)X_2(PMe_2Ph)]	1635 [c]	1643 [c]	1650 [d]
[(π-C_5H_5)Mo(NO)X(bipy)]$^+X^-$		1660	*b*
[(π-C_5H_5)Mo(NO)X-(PMe_2Ph_2]$^+X^-$		1652s 1633s	1652
[(π-C_5H_5)Mo(NO)(CN)Br]$_2$		1680 [e]	

[a] Data from ref. 1 and 2. [b] Data from ref. 3. [c] No difference in ν_{NO} between isomers A and B. [d] '*cis*'-Isomers. [e] ν_{ON} = 2182 cm^{-1}.

The nitrosyl stretching frequency depends on the nature of X (with exception of [(π-C_5H_5)Mo(NO)X_2]$_2$ and L, and on the charge on the complex (when comparing species with the same basic co-ordination unit [(π-C_5H_5)-Mo(NO)X_3]). Thus in a species in which L remains constant, but X is varied, ν_{NO} decreases with increasing electronegativity of X. When X remains constant but L is varied, the approximate order of ν_{NO} is L = PPh_3 > pyridine > $AsPh_3$ > PMe_2Ph which follows reasonably closely the σ-donor/π-acceptor characteristics of L. The spectrum of [(π-C_5H_5)Mo(NO)(PMe_2Ph)Br]$^+Br^-$ exhibited two NO stretching frequencies, separated by 19 cm^{-1}. This is perhaps too large to be explained by solid-state splitting effects, and may arise because of '*cis*'-'*trans*' isomerism in the complex (this was not detected by n.m.r. spectroscopy). The NO stretching frequencies of [(π-C_5H_5)Mo(NO)(PMe_2Ph)X_2](X = Cl or Br), isomer A or B, were identical.

EXPERIMENTAL

All reagents were used as purchased, without further purification, except [(π-C_5H_5)Mo(NO)(CO)$_2$] and PMe_2Ph which were prepared by literature methods, or modifications thereof.

Conductivity measurements were made at room temperature using a Phillips Conductivity meter. I.r. spectra were recorded using an Infracord 475 and Unicam SP 100 spectrophotometers, and ^{1}H n.m.r. spectra using a Varian HA 100 instrument mass spectra were recorded using an AEI MS9 spectrometer.

Microanalyses were carried out by the microanalytical laboratory of this Department. All melting points are uncorrected and yields are quoted relative to either [(π-C_5H_5)Mo(NO)(CO)$_2$] or [(π-C_5H_5)Mo(NO)X_2]$_2$, where appropriate.

Bis(dichloronitrosyl-π-cyclopentadienylmolybdenum), [(π-C_5H_5)Mo(NO)Cl_2]$_2$.—Chlorine (250 ml at N.T.P) in a stream of N_2 gas, was passed through a solution of [(π-C_5H_5)Mo-(NO)(CO)$_2$] (2·5 g) in degassed (N_2) chloroform (30 ml). After 45 min, the solution was filtered under N_2; on addition of n-hexane (30 ml) to the filtrate, dark red crystals (0·45 g, 17%) of the complex (m.p. 241°) were precipitated.

Bis(dibromonitrosyl-π-cyclopentadienylmolybdenum), [(π-C_5H_5)Mo(NO)Br_2]$_2$.—To an ice-cold, stirred, solution of bromine (3·3 g) in dichloromethane (30 ml) was added a solution of [(π-C_5H_5)Mo(NO)(CO)$_2$] (10·0 g) in dichloromethane (30 ml). After 10 min, light petroleum (b.p. 60—80°; 60 ml) was added, the mixture filtered, and the filtrate reduced to half its volume *in vacuo*. During this procedure dark red-brown crystals formed and these were filtered off, washed with light petroleum, and air-dried (7·9 g, 56%), m.p. 240°.

Tetraethylammonium Trichloronitrosyl-π-cyclopentadienylmolybdenum, [Et_4N][(π-C_5H_5)Mo(NO)Cl_3].—A slurry of [(π-C_5H_5)Mo(NO)Cl_2]$_2$ (0·2 g) and [Et_4N]Cl (0·25 g) in anhydrous ethanol (50 ml) was stirred for 1 h, by which time a solution had formed. This was filtered and n-hexane (40 ml) was added. The mixture was set aside overnight, and the pale yellow-green microcrystalline powder which had precipitated was filtered off, washed with n-hexane and dried in a desiccator (0·2 g, 90%), m.p. 135—140° with decomp.

Tetraethylammonium Tribromonitrosyl-π-cyclopentadienylmolybdenum, [Et_4N][(π-C_5H_5)Mo(NO)Br_3].—This complex was prepared in the same way as its trichloro-analogue, using [(π-C_5H_5)Mo(NO)Br_2]$_2$ (0·7 g) and [Et_4N]Br (0·3 g), and by refluxing the mixture for 1 h. The compound was obtained as orange-red needles (0·5 g, 45%), m.p. 205—208°.

The Lewis Base Adducts [(π-C_5H_5)Mo(NO)X_2L].—The complexes where X = Cl or Br and L = PPh_3, $AsPh_3$, pyridine and bipyridyl (X = Br only) were obtained by treating an anhydrous ethanol solution or suspension of [(π-C_5H_5)Mo(NO)X_2]$_2$ with the ligand L dissolved in anhydrous ethanol. The adduct which formed after shaking was filtered off, washed with n-pentane or ether, and was air-dried. The colours, yields and m.p.s of these compounds are as follows: $[(\pi\text{-}C_5H_5)Mo(NO)Cl_2(py)]$, yellow, 52%, 150—155°; $[(\pi\text{-}C_5H_5)Mo(NO)Cl_2(PPh_3)]$, yellow, 100%, 165°; $[(\pi\text{-}C_5H_5)Mo(NO)Cl_2(AsPh_3)]$, yellow, 92%, 278° with decomp.; $[(\pi\text{-}C_5H_5)Mo(NO)Br_2(py)]$, yellow-brown, 74%, 179—181°; $[(\pi\text{-}C_5H_5)Mo(NO)Br(bipyr)]Br$, yellow-green, 14%, decomp. in the range 280—308° when melting occurs; $[(\pi\text{-}C_5H_5)Mo(NO)Br_2(PPh_3)]$, yellow, 80%, 170°; $[(\pi\text{-}C_5H_5)Mo(NO)Br_2(AsPh_3)]$, yellow, 96%, 230°.

Dibromo(dimethylphenylphosphine)nitrosyl-π-cyclopentadienylmolybdenum, $[(\pi\text{-}C_5H_5)Mo(NO)Br_2(PMe_2Ph)]$.—*Isomer A*. An ethanol solution (30 ml) of $[(\pi\text{-}C_5H_5)Mo(NO)Br_2]_2$ (0·53 g) was treated with PMe_2Ph (0·3 ml) in anhydrous ethanol (10 ml), and the yellow microcrystalline solid which formed was filtered off, washed with ether, and air-dried (0·5 g, 68%, m.p. 204°).

Isomer B. An acetone solution (30 ml) of isomer A (0·2 g) was refluxed for 15 min. The solvent was then partially evaporated, and n-pentane (80 ml) was added. The yellow compound which precipitated was filtered off, washed with ether, and air-dried (0·2 g, 100%, m.p. 197°).

The isomers of $[(\pi\text{-}C_5H_5)Mo(NO)Cl_2(PMe_2Ph)]$ were obtained similarly (Isomer A, 88%, 203°; Isomer B, 50%, 203°).

Bromobis(dimethylphenylphosphine)nitrosyl-π-cyclopentadienylmolybdenum Bromide, $[(\pi\text{-}C_5H_5Mo(NO)Br(PMe_2Ph)_2]$-$Br$.—A solution of $[(\pi\text{-}C_5H_5)Mo(NO)Br_2]_2$ (0·5 g) and PMe_2Ph (0·7 ml) in acetone (40 ml) was refluxed for 2 h. The mixture was cooled, and the bright yellow solid which precipitated was filtered off, washed with n-pentane, and dried *in vacuo* (0·6 g, 60%, m.p. 205° with decomp.).

Bis(bromocyanonitrosyl-π-cyclopentadienylmolybdenum), $[(\pi\text{-}C_5H_5)Mo(NO)(CN)Br]_2$.—A solution of $[(\pi\text{-}C_5H_5)Mo(NO)(CO)_2]$ (2·0 g) and cyanogen bromide (0·8 g) in degassed (N_2) dichloromethane (30 ml) was heated at 100° for 2 h in a sealed evacuated tube. A yellow solid formed and, after cooling and opening of the tube, this was collected by filtration; it was washed with n-pentane and air-dried (2·0 g, 84%), m.p. >230°).

Mass Spectral Data. Obtained at source temperature of 200 °C and pressure 10^{-7} mmHg (*m/e* calculated using ^{98}Mo, ^{35}Cl, ^{79}Br, and ^{81}Br).

$[(\pi\text{-}C_5H_5)Mo(NO)Cl_2]_2$. *m/e* = 263, $[C_5H_5MoNOCl_2]^+$ (25%); 233, $[(C_5H_5)MoCl_2]^+$ (100%); 198, $[C_5H_5MoCl]^+$ (41%); 168, $[MoCl_2]^+$ (19%); 133, $[MoCl]^+$ (15%); 98, $[Mo]^+$ (5%); 65, $[C_5H_5]^+$ (8%).

$[(\pi\text{-}C_5H_5)Mo(NO)Br_2]_2$. *m/e* = 353, $[C_5H_5MoNOBr_2]^+$ (54%); 323, $[C_5H_5MoBr_2]^+$, (100%); 242, $[C_5H_5MoBr]^+$ (96%); 216, $[C_3H_3MoBr]^+$ (28%); 176·5, $[C_5H_5MoNOBr_2]^{2+}$; 161·5, $[C_5H_5MoBr_2]^{2+}$.

$[(\pi\text{-}C_5H_5)Mo(NO)Cl_2(PPh_3)]$. *m/e* = 277, $[C_{10}H_{10}Mo\text{-}NCl]$? (8%); 263, $[C_5H_5MoNOCl_2]^+$ (42%); 262 $[PC_{18}H_{15}]^+$ (100%); 233, $[C_5H_5MoCl_2]^+$ (29%); 198, $[C_5H_5MoCl]^+$ (11%); 183 $[PC_{12}H_8]^+$ (95%); 172, $[C_3H_3MoCl]^+$ (5%); 152 $[C_{12}H_8]^+$ (20%); 116·5 $[C_5H_5MoCl_2]^{2+}$; 108, $[PC_6H_5]^+$ (53%).

We are grateful to the S.R.C. for a studentship (D. S.), to Dr. T. A. James for discussion, and to Mrs. J. Bray and Mr. G. A. Wright for technical assistance.

[2/428 *Received, 24th February*, 1972]