The Chemistry of Cyclopentadienyl Nitrosyl and Related Complexes of Molybdenum. Part 8.[1] Carboxylato- and β-Diketonato-complexes, Their Reactions with Water, Hydrogen Sulphide, and Alcohols, and the Treatment of Bis(cyclopentadienyl)iodonitrosylmolybdenum with Some Acids

By **Martin M. Hunt**, **W. George Kita**, and **Jon A. McCleverty**,* Chemistry Department, The University, Sheffield S3 7HF

Reaction of [Mo(C_5H_5)$_2$I(NO)] with RCO_2H, or of [{Mo(η^5-C_5H_5)(NO)X_2}$_2$] with Ag[O_2CR], affords [Mo(η^5-C_5H_5)(NO)(O_2CR)X] (X = I, R = Me, Et, Pr^n, Pr^i, or Ph; X = Br, R = Me); the carboxylate group is bidentate. Treatment of [Mo(C_5H_5)$_2$I(NO)] with $RCOCH_2OCR$, or of [{Mo(η^5-C_5H_5)I_2(NO)}$_2$] with Tl[RCOCHOCR], affords [Mo(η^5-C_5H_5)I(NO)(RCOCHOCR)] (R = Me, CF_3, or Ph). Reaction of [Mo(η^5-C_5H_5)(σ-C_5H_5)(NO)(η^2-S_2CNMe_2)] with CF_3CO_2H gives [Mo(η^5-C_5H_5)(NO)(σ-O_2CCF_3)(η^2-S_2CNMe_2)], but a similar reaction does not occur with $MeCO_2H$. Both [Mo(η^5-C_5H_5)I(NO)(O_2CMe)] and [Mo(η^5-C_5H_5)I(NO)(MeCOCHOCMe)] react with MeOH or $PhCH_2OH$ to give [{Mo(η^5-C_5H_5)I(NO)(OR)}$_2$] (R = Me or CH_2Ph), and methanolysis of [{Mo(η^5-C_5H_5)(NO)(O_2CCF_3)$_2$}$_2$] affords [{Mo(η^5-C_5H_5)(NO)(O_2CCF_3)(OMe)}$_2$]. With 'wet' alcohols (ROH; R = Et, Pr^n, or Bu^n) or water, [Mo(η^5-C_5H_5)I(NO)(O_2CMe)] affords [{Mo(η^5-C_5H_5)I(NO)(OH)}$_n$], and the corresponding deuteroxide is obtained *via* D_2O. Reaction of the acetatoiodide with H_2S gives [{Mo(η^5-C_5H_5)I(NO)(SH)}$_n$]. Treatment of [Mo(C_5H_5)$_2$I(NO)] with HPF_6 or HBF_4 in the presence of PPh_3 or $Ph_2PCH_2CH_2PPh_2$ gives [Mo(η^5-C_5H_5)I(NO)(PPh_3)$_2$][PF_6] or [Mo(η^5-C_5H_5)I(NO)($Ph_2PCH_2CH_2PPh_2$)][BF_4], respectively. With HI or $PhCH_2SH$, [Mo(C_5H_5)$_2$I(NO)] affords [{Mo(η^5-C_5H_5)I_2(NO)}$_2$] and [{Mo(η^5-C_5H_5)I(NO)(SCH_2Ph)}$_2$], respectively.

IN the previous paper[1] we suggested that [Mo(C_5H_5)$_2$I(NO)], in *solution*, might exist transitionally as [Mo(η^5-C_5H_5)(σ-C_5H_5)I(NO)] (possibly solvated) in which the η^5 and σ rings are rapidly exchanging their electronic roles. Although it has not been possible to provide direct spectroscopic evidence to support this view, we reasoned that such a species containing a σ-cyclopentadienyl ring should undergo reactions typical of M–C σ bonds. Thus, with acids HX, protolysis should occur with loss of C_5H_6 and formation of M–X. In this paper we describe first the reaction of [Mo(C_5H_5)$_2$I(NO)] with carboxylic acids and some β-diketones, alternative syntheses of the molybdenum carboxylates and β-diketonates so formed, and the reactions of these new complexes with some alcohols, water, and H_2S. Secondly we report on the treatment of [Mo(C_5H_5)$_2$I(NO)] with HPF_6 or HBF_4 in the presence of PPh_3 and $Ph_2PCH_2CH_2PPh_2$, and briefly describe the reaction of the bis(cyclopentadienyl)complex with HI and $PhCH_2SH$.

RESULTS AND DISCUSSION

Carboxylato- and β-*Diketonato-complexes*.—Treatment of [Mo(C_5H_5)$_2$I(NO)] with carboxylic acids RCO_2H (R = Me, Et, Pr^n, Pr^i, or Ph) afforded the species [Mo(η^5-C_5H_5)I(NO)(O_2CR)] (analytical and m.p. data in Table 1). These complexes may also be prepared by the reaction of [{Mo(η^5-C_5H_5)I_2(NO)}$_2$] with Ag[O_2CR] in acetone. Similar treatment of [{Mo(η^5-C_5H_5)Br_2(NO)}$_2$] afforded the corresponding acetatobromide. Since these complexes, particularly the bromide, react readily with water, they must be handled in very dry solvents

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[1] Part 7, preceding paper.

[2] J. A. McCleverty and D. Seddon, *J.C.S. Dalton*, 1972, 2526; R. B. King, *Inorg. Chem.*, 1967, **6**, 30.

and maintained in moisture-free conditions. The ^1H n.m.r. spectra of these complexes are entirely consistent with their formulation (Table 2). The i.r. spectra exhibited an NO stretching frequency in the range 1 655–1 675 cm^{-1} typical of other neutral species of the type $[Mo(\eta^5-C_5H_5)L(NO)X_2]$.[3] The strong frequencies in the 1 425—1 495 cm^{-1} region are typical of the asymmetric OCO stretching mode of a bidentate carboxylate group,[3] and no bands due to co-ordinated RCO_2 were observed at $>1\ 600\ cm^{-1}$. Accordingly, the carboxylato-species may be formulated as the monomeric $[Mo(\eta^5-C_5H_5)(NO)(\eta^2-O_2CR)X]$ (X = Br or I).

TABLE 1

Analytical and m.p. data obtained for the new molybdenum complexes

	Analysis (%)								
	Calc.				Found				
Complex	C	H	N	X	C	H	N	X	M.p. (θ_c/°C)
$[Mo(\eta^5-C_5H_5)X(NO)(O_2CR)]$									
X = I, R = Me	22.3	2.1	3.7	33.7	22.6	2.2	3.6	33.5	99—102
Et	24.6	2.6	3.6	32.4	25.1	2.9	3.9	32.9	108—110
Pr^n	26.7	3.0	3.5	31.3	27.0	3.3	3.6	31.5	92—95
Pr^i	26.7	3.0	3.5	31.3	26.8	3.3	3.1	31.1	104—105
Ph	32.8	2.3	3.2	28.9	32.8	2.5	2.9	28.9	160—162
X = Br, R = Me	25.5	2.4	4.3	24.2	25.3	2.6	4.2	24.0	110
$[Mo(\eta^5-C_5H_5)I(NO)(RCOCHOCR)]$									
R = Me	28.8	2.9	3.4	30.4	28.3	3.1	3.4	30.2	118—120
Ph	44.4	3.0	2.6	23.5	45.2	3.4	2.5	23.7	185—187
CF_3	22.9	1.1	2.7	24.2	23.0	1.4	2.4	23.9	*a*
$[Mo(\eta^5-C_5H_5)(NO)(O_2CCF_3)(S_2CNMe_2)]$	28.3	2.6	6.6	15.1	28.4	2.8	6.5	15.4	176—178
$[\{Mo(\eta^5-C_5H_5)(NO)(OR)X\}_n]$									
X = I, R = Me	20.7	2.3	4.0	36.4	20.8	2.7	4.0	36.5	168 (decomp.)
X = Br, R = Me	23.9	2.7	4.6	26.5	24.1	2.9	4.8	26.3	*a*
X = I, R = $PhCH_2$	33.9	2.9	3.3	29.9	33.7	3.0	3.2	29.7	115—117
X = F_3CCO_2, R = Me	28.7	2.3	4.2		28.8	2.6	4.0		*a*
X = I, R = H	17.9	1.8	4.2	37.9	18.3	2.0	4.0	37.9	*a*
$[\{Mo(\eta^5-C_5H_5)I(NO)(SH)\}_n]$ [b]	17.2	1.4	4.0	36.3	17.5	1.9	3.6	36.2	*a*
$[Mo(\eta^5-C_5H_5)I(NO)(PPh_3)_2][PF_6]$	49.9	3.7	1.4	12.9	12.9	3.8	1.4	13.0	*a*
$[Mo(\eta^5-C_5H_5)I(NO)(Ph_2PCH_2CH_2PPh_2)][BF_4]$	46.3	3.6	1.7	15.8	46.4	4.0	1.6	16.3	*a*

[a] Not measured. [b] S: found 9.1, calc. 9.2%.

Reaction of $[Mo(C_5H_5)_2I(NO)]$ with $RCOCH_2OCR$ (R = Me, Ph, or CF_3), or treatment of $[\{Mo(\eta^5-C_5H_5)I_2(NO)\}_2]$ with 2 mol of Tl[RCOCHOCR], afforded $[Mo(\eta^5-C_5H_5)I(NO)(RCOCHOCR)]$. However, the yields obtained by the former route were significantly lower than those obtained by the latter. These complexes, like their carboxylato-analogues, are moisture sensitive and must be handled under dry conditions. The NO stretching frequency of $[Mo(\eta^5-C_5H_5)I(NO)(F_3CCOCHOCCF_3)]$ occurred at 1 690 cm^{-1}, some 40 cm^{-1} higher than that in the pentane-2,4-dionato- and 1,3-diphenylpropane-1,3-dionato-complexes. This is probably due to the strong electron-withdrawing properties of the CF_3 groups. Two signals were observed for the protons of the methyl groups in $[Mo(\eta^5-C_5H_5)I(NO)(MeCOCHOCMe)]$, due to the asymmetry of the molybdenum complex and the concomitant inequivalence of the methyl groups.

Reactions of $[Mo(\eta^5-C_5H_5)(\sigma-C_5H_5)(NO)(\eta^2-S_2CNMe_2)]$ [1] with trifluoroacetic acid afforded $[Mo(\eta^5-C_5H_5)(NO)(O_2CCF_3)(\eta^2-S_2CNMe_2)]$. The dicyclopentadienyl complex did not react with acetic acid at room temperature, $[Mo(\eta^5-C_5H_5)I(NO)(\eta^2-S_2CNMe_2)]$ did not form an acetato-complex with $Ag[O_2CMe]$, and $[Mo(\eta^5-C_5H_5)I(NO)(O_2CMe)]$ reacted with $Na[S_2CNMe_2]$ to give the known $[Mo(\eta^5-C_5H_5)I(NO)(\eta^2-S_2CNMe_2)]$.[4] The i.r. spectrum of $[Mo(\eta^5-C_5H_5)(NO)(O_2CCF_3)(\eta^2-S_2CNMe_2)]$ contained a strong band at 1 720 cm^{-1}, typical of the group M–O–C(=O)CF_3, indicating that this complex contains a unidentate trifluoroacetate group.[3] The frequency at 1 550 cm^{-1} is assigned to the stretching mode of the S_2C-NMe_2 group. The occurrence of the methyl proton resonances of the dithiocarbamate group as a doublet is consistent with the asymmetry of the molybdenum complex, the probability that the sulphur ligand is bidentate, and that there is hindered rotation about the C–N bond of the S_2C-NMe_2 ligand. Accordingly, we formulate this complex as $[Mo(\eta^5-C_5H_5)(NO)(\sigma-O_2CCF_3)(\eta^2-S_2CNMe_2)]$.

Reactions of the Carboxylates and β-Diketonates with Some Alcohols, Water, and H_2S.—During attempts to prepare $[Mo(\eta^5-C_5H_5)I(NO)(O_2CMe)]$ in methanol, and

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[3] S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, 1973, 1912; K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1963 and refs. therein.

[4] T. A. James and J. A. McCleverty, *J. Chem. Soc.* (*A*), 1970, 3308.

TABLE 2

Infrared and ^1H n.m.r. spectral data obtained for the new molybdenum complexes

Complex	I.r. (cm^{-1})			^1H N.m.r.	
	$\nu(NO)$	$\nu(CO)$	Other [a,b]	τ [c]	Assignment
$[Mo(\eta^5\text{-}C_5H_5)(NO)(O_2CR)X]$					
X = I, R = Me	1 655	1 480		2.01(3) [d]	s, CH_3
				6.36(5)	s, C_5H_5
Et	1 655	1 495s		1.10(3) [d]	t, CH_3 [J(HH) 8.0 Hz]
		1 470s		2.36(2)	q, CH_2
				6.37(5)	s, C_5H_5
Pr^n	1 675	1 495m		0.94(3) [d]	t, CH_3 [J(HH) 7.0 Hz]
		1 475s		1.65(2)	sxt, CH_2
				2.30(2)	t, CH_2
				6.36(5)	s, C_5H_5
Pr^i	1 665	1 485s		1.12(6) [d]	d, $(C\mathit{H}_3)_2CH$ [J(HH) 8.0 Hz]
		1 440s		2.53(1)	spt, $C\mathit{H}Me_2$
				6.38(5)	s, C_5H_5
Ph	1 665	1 450s		6.26(1) [e]	s, C_5H_5
		1 425m		7.70(1)	m, C_6H_5
X = Br, R = Me	1 655	1 480		*f*	
$[Mo(\eta^5\text{-}C_5H_5)I(NO)(RCOCHOCR)]$					
R = Me	1 655	1 570s		2.02(3) [d]	s} inequivalent CH_3
		1 525s		2.05(3)	s} of $C\mathit{H}_3COCHOCC\mathit{H}_3$
				5.74(1)	s, $MeCOC\mathit{H}OCMe$
				6.28(5)	s, C_5H_5
Ph	1 650	1 525s		6.31(5) [e]	s, C_5H_5
		1 485m		6.92(1)	s, $PhCOC\mathit{H}OCPh$
				7.80(10)	m, C_6H_5
CF_3	1 690	1 640s		4.43(1) [d]	s, $F_3CCOC\mathit{H}OCCF_3$
		1 620m		6.54(5)	s, C_5H_5
$[Mo(\eta^5\text{-}C_5H_5)(NO)(O_2CCF_3)(S_2CNMe_2)]$					
	1 650s	1 720s	1 550m(C–N)	2.38(3) [d]	s} inequivalent
			1 100—1 200s (C—F)	2.39(3)	s} $S_2CH(C\mathit{H}_3)_2$
				6.18(5)	s, C_5H_5
$[\{Mo(\eta^5\text{-}C_5H_5)(NO)(OR)X\}_n]$					
X = I, R = Me	1 640	1 000		3.20(3) [g]	s, OCH_3
				4.99(3)	s, OCH_3
				6.25(10)	s, C_5H_5
X = Br, R = Me	1 630	1 000		3.21(3) [g]	s, OCH_3
				6.26(5)	s, C_5H_5
X = I, R = CH_2Ph	1 670	1 020		4.50(1) [g]	s, $OCH_2\mathit{Ph}$
				6.00(1)	s, $OC\mathit{H}_2Ph$
				6.24(5)	s, C_5H_5
				7.29(5)	m, C_6H_5
X = O_2CCF_3, R = Me	1 670s	1 720s	1 395m (OCO sym str.)	3.50 [e] 3.82 3.95 4.29 } (3)	s, OCH_3
				6.22 6.24 6.25 6.28 } (5)	s, C_5H_5
X = I, R = H	1 670s		3 320m (O–H)	5.40(1) [g,h]	br s, O–H
				6.25(5)	s, C_5H_5
$[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(SH)\}_n]$	1 660s		2 400 (SH)	3.10(1) [d,h]	br s, SH
				6.34(5)	s, C_5H_5

[a] Measured in KBr discs. [b] Assignment in parentheses. [c] Relative to $SiMe_4$; relative peak areas are given in parentheses. [d] In $(D_3C)_2CO$ solution. [e] In $CDCl_3$ solution. [f] Not measured. [g] In $(D_3C)_2SO$ solution. [h] Signal disappears when D_2O is added.

also in trying to recrystallise the authentic acetate from that solvent, we observed that the carboxylate group was readily displaced by methoxide. In fact, all the carboxylato-and β-diketonato-complexes reacted with methanol affording $[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(OMe)\}_2]$. A similar reaction occurred with benzyl alcohol, giving $[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(OCH_2Ph)\}_2]$, and $[Mo(\eta^5\text{-}C_5H_5)Br(NO)(O_2CMe)]$ afforded, with methanol, the corresponding bromo(methoxide). A limited yield of $[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(OMe)\}_2]$ could also be recovered from a solution of $[\{Mo(\eta^5\text{-}C_5H_5)I_2(NO)\}_2]$ in methanol after 24h. Because of their low solubility, we were unable to establish unequivocally the dimeric nature of the alkoxides. However, by analogy with $[\{Mo(\eta^5\text{-}C_5H_5)(NO)X_2\}_2]$,[5] and in view of the ^1H n.m.r. spectral results (see below), we think that a binuclear formalism is reasonable and consistent with the ' 18-electron ' rule.

Treatment of $[\{Mo(\eta^5\text{-}C_5H_5)(NO)(O_2CCF_3)_2\}_2]$ [6] with

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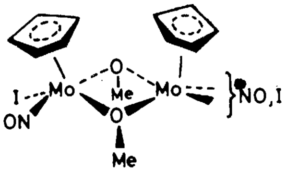
[5] T. A. James and J. A. McCleverty, *J. Chem. Soc.* (*A*), 1971, 1068.

[6] R. B. King and R. N. Kapoor, *J. Organometallic Chem.*, 1968, **15**, 457.

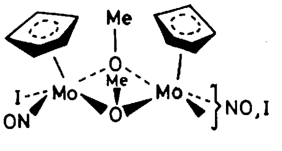
methanol afforded only $[\{Mo(\eta^5\text{-}C_5H_5)(NO)(OMe)(O_2CCF_3)\}_2]$. However, when this reaction was carried out in the presence of CO, in an attempt to prepare $[Mo(\eta^5\text{-}C_5H_5)\{C(=O)(OMe)\}(NO)(O_2CCF_3)]$, only the starting material (in substantial amounts) could be recovered.

Reaction of $[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(OMe)\}_2]$ with $CF_3COCH_2OCCF_3$ afforded $[Mo(\eta^5\text{-}C_5H_5)I(NO)(CF_3COCHOCCF_3)]$, but neither pentane-2,4-dione nor 1,3-diphenylpropane-1,3-dione behaved similarly.

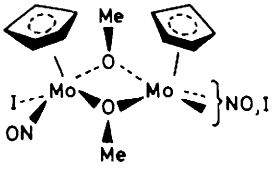
The i.r. spectra of the methoxo- and benzyloxo-complexes exhibited ν(NO) in the range expected for such molybdenum complexes containing *O*-donor ligands, *viz.* 1 630—1 670 cm^{-1}. For $[\{Mo(\eta^5\text{-}C_5H_5)(NO)(OMe)(O_2CCF_2)\}_2]$, the frequency at 1 720 cm^{-1} was assigned to the asymmetric O–C–O stretching mode of a unidentate carboxylate group. The ^1H n.m.r. spectra of $[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(OR)\}_2]$ (R = Me or $PhCH_2$) exhibited *one* signal due to the cyclopentadienyl ring protons and *two* singlets due to the methyl or methylene protons. This behaviour can only be satisfactorily accounted for by assuming that the alkoxide species are binuclear. Thus, *two* methyl or methylene proton signals could arise from a mixture of species such as (1) and (2), or from (4), or from (1) or (2) in which isomerism is caused by the relative positions of the two NO and I groups [these could be mutually *cis* or *trans* with respect to $Mo_2(OR)_2$], or even from (4) in which similar isomerism is possible.* While the spectrum of $[\{Mo(\eta^5\text{-}C_5H_5)Br(NO)(OMe)\}_2]$ contained only one methoxide proton resonance, that of $[\{Mo(\eta^5\text{-}C_5H_5)(NO)(OMe)(O_2CCF_3)\}_2]$ contained four,t ogether with four signals due to the cyclopentadienyl protons. This carboxylate clearly exists as a number of isomers in solution.



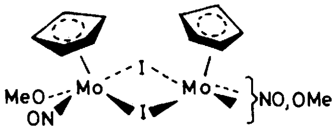
(1)



(2)



(3)



(4)

In attempts to obtain the corresponding ethoxides, propoxides, and butoxides, we treated $[Mo(\eta^5\text{-}C_5H_5)I(NO)(O_2CMe)]$ with ROH (R = Et, Pr^n, Pr^i, or Bu^n). In all of these reactions we used ostensibly dry alcohols but obtained invariably $[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(OH)\}_n]$. This hydroxide could be obtained essentially quantitatively by reaction of $[Mo(\eta^5\text{-}C_5H_5)I(NO)(O_2CMe)]$ with water, and the corresponding deuteroxide was prepared *via* D_2O. The reactions with alcohols other than MeOH and $PhCH_2OH$ was surprising, especially since 'wet' methanol afforded the methoxide with $[Mo(\eta^5\text{-}C_5H_5)I(NO)(O_2CMe)]$. A careful study of the reactions failed to provide any evidence of olefin elimination occurring *via* dehydration of these alcohols. Indeed, when scrupulously dry alcohols (other than MeOH and $PhCH_2OH$) were used no reaction occurred with the acetate. Accordingly, we must assume that trace amounts of moisture in the routinely dried alcohols must have been responsible for the formation of the hydroxide. We can offer no explanation for the failure to obtain $[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(OR)\}_2]$ (R = Et, Pr^n, Pr^i, or Bu^n).† Treatment of $[Mo(\eta^5\text{-}C_5H_5)I(NO)(O_2CMe)]$ with H_2S in diethyl ether afforded the hydrogensulphide $[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(SH)\}_n]$, which is the first member of the series $[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(SR)\}_2]$ (R = alkyl or aryl) which we have described elsewhere.[5,7] The i.r. spectrum of $[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(XH)\}_n]$ (X = O or S) exhibited absorptions due to ν(XH) in the expected regions. The ^1H n.m.r. spectra of the hydroxide and hydrogensulphide showed broad singlets due to X–H which disappeared when solutions containing the complexes were treated with D_2O. Because of the relative insolubilities and involatilities of these complexes we were unable to determine the extent of oligomerisation but by analogy with the corresponding alkoxides and thiolates [5,7] they must be at least dimeric.

We have attempted to extend the generality of the reaction of $[Mo(\eta^5\text{-}C_5H_5)(NO)(O_2CMe)X]$ (X = Br or I) with compounds containing 'acidic' protons. Thus with anhydrous NH_3 and primary and secondary amines, brown, rather insoluble, powders were formed. Although these did not give reproducible analytical data,[8] it was clear that both the acetate and cyclopentadienyl groups were removed. With PhNHNNPh, however, $[Mo(\eta^5\text{-}C_5H_5)I(NO)(O_2CMe)]$ afforded the known triazenide $[Mo(\eta^5\text{-}C_5H_5)I(NO)(PhN_3Ph)]$, and with aryl- and dialkyl-hydrazines a series of hydrazido-(1—) and -(2—) complexes can be obtained.[9] With $F_3CC{\equiv}CH$, $PhC{\equiv}CH$, and PPh_2H, however, there was no reaction.

Finally, we may compare the η-cyclopentadienyl

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* Similar isomers containing *trans*-cyclopentadienyl rings are also possible, but the occurrence of sharp singlets for these protons in $[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(OR)\}_2]$ seems to diminish the possibility of there being mixtures of *cis*- and *trans*-bis(cyclopentadienyl) complexes unless the complexes are fluxional. We could detect no broadening of the proton resonances in either complex down to −60 °C below which the complexes crystallised.

† Attempts to prepare the alkoxoiodides *via* reaction of $[\{Mo(\eta^5\text{-}C_5H_5)I_2(NO)\}_2]$ and Na[OR] led to extensive decomposition.

[7] J. A. McCleverty and D. Seddon, *J.C.S. Dalton*, 1972, 2588.

[8] M. M. Hunt, J. A. McCleverty, and J. Williams, unpublished work.

[9] W. G. Kita, J. A. McCleverty, B. E. Mann, D. Seddon, G. A. Sim, and D. I. Woodhouse, *J.C.S. Chem. Comm.*, 1974, 132; W. G. Kita, J. A. McCleverty, and D. Seddon, *J. Less-Common Metals*, 1974, **36**, 203; N. A. Bailey, P. D. Frisch, J. A. McCleverty, N. W. Walker, and J. Williams, *J.C.S. Chem. Comm.*, 1975, 350; P. D. Frisch, M. M. Hunt, J. A. McCleverty, D. Seddon, and J. Williams, unpublished work.

alkoxides with the similar tris(pyrazolyl)borates $[Mo\{HB(pyz)_3\}(NO)(OR)X]$ (pyz = $C_3H_3N_2$ or 3,5-$Me_2C_3HN_2$: X = Cl, Br, or I; R = Me, Et, or Pr^i).[10] While the former are binuclear, the latter, because of the steric bulk of the pyrazolylborate ligand, are monomers. Furthermore, the chemical shifts of the protons α to the carbon atom adjacent to oxygen in $[\{Mo(\eta^5\text{-}C_5H_5)(NO)(OMe)X\}_2]$ resonate at ' normal ' positions (δ 3.20—4.99 p.p.m.) unlike those in the tris(pyrazolyl)borate complexes where the shifts are at significantly lower field. This suggests that the metal atom in the η-cyclopentadienyl complexes is slightly more ' electron rich ' than the metal atom in $[Mo\{HB(pyz)_3\}(NO)(OR)X]$.

Reaction of $[Mo(C_5H_5)_2I(NO)]$ *with Other Acids.*—Cleavage of σ-C_5H_5 ring from $[Mo(C_5H_5)_2I(NO)]$ by acids containing non-co-ordinating anions should cause transient formation of $[Mo(\eta^5\text{-}C_5H_5)I(NO)]^+$. The latter is formally a 14-electron species and so should readily accept two neutral ligands L giving $[Mo(\eta^5\text{-}C_5H_5)IL_2(NO)]^+$. Thus, treatment of the bis(cyclopentadienyl) complex with HPF_6 or HBF_4 afforded a deep red-brown species which subsequently reacted with PPh_3 or $Ph_2PCH_2CH_2PPh_2$ giving $[Mo(\eta^5\text{-}C_5H_5)I(NO)(PPh_3)_2]^+$ or $[Mo(\eta^5\text{-}C_5H_5)I(NO)(Ph_2PCH_2CH_2PPh_2)]^+$ (isolated as $[PF_6]^-$ or $[BF_4]^-$ salts). The cationic triphenylphosphine complex has been described previously.[2]

Reaction of $[Mo(C_5H_5)_2I(NO)]$ with aqueous HI in acetone–dichloromethane afforded $[\{Mo(\eta^5\text{-}C_5H_5)I_2(NO)\}_2]$ essentially quantitatively. A strong smell of cyclopentadiene was detected during the course of this reaction. Treatment of the bis(cyclopentadienyl) complex with $PhCH_2SH$ afforded the known[7] $[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(SCH_2Ph)\}_2]$. The iodide and thiolate were identified mass spectrometrically.

In conclusion, we may observe that the reactions of $[Mo(C_5H_5)_2I(NO)]$ with acids appear to be characteristic of a species containing a Mo–C_5H_5 σ bond. What we cannot say, however, is whether this is as a result of the existence of $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)I(NO)]$ *prior* to reaction with HX, or whether a σ-bonded ring is generated during the reaction in an intermediate or a transition state.

EXPERIMENTAL

The complexes $[\{Mo(\eta^5\text{-}C_5H_5)(NO)X_2\}_2]$ (X = Br or I),[11] $[Mo(C_5H_5)_2I(NO)]$,[12] and $[\{Mo(\eta^5\text{-}C_5H_5)(NO)(O_2CCF_3)_2\}_2]$ [6] were prepared as described previously. Infrared spectra were recorded using Perkin-Elmer 457 and 180 spectrophotometers, and ^1H n.m.r. spectra using a Varian HA100 instrument. Elemental analyses were by the Microanalytical Laboratory of this Department. All the melting points are uncorrected and yields are quoted relative to molybdenum-containing starting materials.

Carboxylato-complexes, $[Mo(\eta^5\text{-}C_5H_5)I(NO)(O_2CR)]$.—The methods described herein are general for the carboxylato-complexes prepared in this work, and the synthesis of $[Mo(\eta^5\text{-}C_5H_5)I(NO)(O_2CR)]$ is illustrative.

Acetato(η-cyclopentadienyl)iodonitrosylmolybdenum, $[Mo(\eta^5\text{-}C_5H_5)I(NO)(O_2CMe)]$. *Method A.* The complex $[Mo(C_5H_5)_2(NO)I]$ (1.0 g, 2.65 mmol) and glacial acetic acid (0.16 g, 2.66 mmol) were stirred together in acetone (50 cm^3) under N_2 for 48 h. The resulting orange-brown solution was filtered and reduced in volume *in vacuo* to near dryness. Slow addition of diethyl ether afforded brown crystals of $[Mo(\eta^5\text{-}C_5H_5)I(NO)(O_2CMe)]$ which were filtered off, washed with n-pentane, and dried *in vacuo* (0.7 g, 70%).

Method B. The complex $[\{Mo(\eta^5\text{-}C_5H_5)I_2(NO)\}_2]$ (1.0 g, 1.12 mmol) and silver(I) acetate (0.4 g, 2.4 mmol) were stirred together in acetone (50 cm^3) under N_2 for 24 h. The resulting precipitate of silver iodide was filtered off and the orange-brown filtrate concentrated to near dryness *in vacuo.* Slow addition of diethyl ether afforded brown crystals of $[Mo(\eta^5\text{-}C_5H_5)I(NO)(O_2CMe)]$ which were filtered off, washed with pentane, and dried *in vacuo* (0.6 g, 70%).

The complex $[Mo(\eta^5\text{-}C_5H_5)Br(NO)(O_2CMe)]$ was prepared similarly from $[\{Mo(\eta^5\text{-}C_5H_5)Br_2(NO)\}_2]$.

β-Diketonato-complexes, $[Mo(\eta^5\text{-}C_5H_5)I(NO)(RCOCHOCR)]$.—The methods described below are general for the β-diketonato-complexes prepared in this work, and the synthesis of $[Mo(\eta^5\text{-}C_5H_5)I(NO)(MeCOCHOCMe)]$ is illustrative.

(η-Cyclopentadienyl)iodonitrosyl(pentane-2,4-dionato)molybdenum, $[Mo(\eta^5\text{-}C_5H_5)I(NO)(MeCOCHOCMe)]$. *Method A.* The complex $[Mo(C_5H_5)_2I(NO)]$ (0.5 g, 1.31 mmol) and pentane-2,4-dione (0.14 g, 1.4 mmol) were stirred together in acetone (25 cm^3) under N_2 for 24 h. The resulting orange-brown solution was filtered and evaporated to near dryness *in vacuo.* Slow addition of diethyl ether afforded brown crystals of $[Mo(\eta^5\text{-}C_5H_5)I(NO)(MeCOCHOCMe)]$ which were filtered off, washed with n-pentane, and dried *in vacuo* (0.45 g, 80%).

Method B. The complex $[\{Mo(\eta^5\text{-}C_5H_5)I_2(NO)\}_2]$ (2.0 g, 2.25 mmol) and Tl[MeCOCHOCMe] (1.4 g, 4.61 mmol) were stirred together in acetone under N_2 for 24 h. The resulting yellow precipitate of thallium(I) iodide was filtered off and the brown filtrate was evaporated to near dryness *in vacuo.* Slow addition of diethyl ether gave the complex as brown crystals, which were filtered off, washed with pentane, and dried *in vacuo* (0.90 g, 50%). The species $[Mo(\eta^5\text{-}C_5H_5)I(NO)(RCOCHOCR)]$ (R = Ph or CF_3) were similarly obtained in yields of 50%.

Reaction of $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNMe_2)]$ *with Trifluoroacetic Acid; (η-Cyclopentadienyl)(dimethyldithiocarbamato)nitrosyl(trifluoroacetato)molybdenum,* $[Mo(\eta^5\text{-}C_5H_5)(NO)(O_2CCF_3)(S_2CNMe_2)]$.—The complex $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNMe_2)]$ (0.5 g, 1.32 mmol) and trifluoroacetic acid (0.2 g, 1.75 mmol) were stirred together in dichloromethane (50 cm^3) under N_2 for 24 h. The resulting yellow-orange solution was evaporated *in vacuo* and the residue dissolved in dichloromethane and filtered. Addition of diethyl ether to the filtrate, followed by slow evaporation under reduced pressure, afforded yellow crystals of $[Mo(\eta^5\text{-}C_5H_5)(NO)(O_2CCF_3)(S_2CNMe_2)]$. These were filtered off, washed, with diethyl ether, and dried *in vacuo* (0.5 g, 60%).

Bis[(η-cyclopentadienyl)iodo(methoxo)nitrosylmolybdenum], $[\{Mo(\eta^5\text{-}C_5H_5)I(NO)(OMe)\}_2]$.—*Method A.* The complex $[Mo(\eta^5\text{-}C_5H_5)I(NO)(O_2CMe)]$ (0.15 g) was dissolved

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in dichloromethane (20 cm^3) and the solution was filtered. To the filtrate was added methanol (10 cm^3) and orange-brown crystals of the *complex* were formed on slow evaporation *in vacuo*. These were filtered off, washed with methanol, and dried *in vacuo* (0.08 g, 60%).

Method B. The complex $[Mo(\eta^5-C_5H_5)I(NO)(MeCOCHOCMe)]$ (0.2 g) was dissolved in dichloromethane (20 cm^3) and the solution was filtered and treated with methanol (an excess). On slow evaporation *in vacuo* the *complex* was formed as orange-brown crystals and purified as above (0.1 g, 60%).

These reactions were general for the carboxylates (R = Et, Pr^n, Bu^t, or Ph) and β-diketonates (R = CF_3 or Ph).

Reaction between $[\{Mo(\eta^5-C_5H_5)I_2(NO)\}_2]$ *and Methanol*.—The complex $[\{Mo(\eta^5-C_5H_5)I_2(NO)\}_2]$ (0.5 g) was stirred under nitrogen in methanol–acetone (30 cm^3, 1 : 1) for 24 h. The resulting orange-brown solution was evaporated to dryness *in vacuo* and, on addition of dichloromethane (15 cm^3) to the residue, dark purple crystals of the starting material were obtained. These were filtered off, washed with a small portion of dichloromethane, and dried *in vacuo* (0.2 g, 40%). To the filtrate was added methanol and, on slow evaporation *in vacuo*, orange-brown crystals of $[\{Mo(\eta^5-C_5H_5)I(OMe)\}_2]$ were formed. These were filtered off, washed with methanol, and dried *in vacuo* (0.15 g, 40%).

Bis[bromo(η-cyclopentadienyl)methoxonitrosylmolybdenum], $[\{Mo(\eta^5-C_5H_5)Br(NO)(OMe)\}_2]$.—The complex $[Mo(\eta^5-C_5H_5)Br(NO)(O_2CMe)]$ (0.6 g) was dissolved in dichloromethane (40 cm^3) and an addition of an excess of methanol to the filtered solution followed by slow evaporation of the mixture *in vacuo* afforded the *complex* as orange crystals. These were filtered off, washed with methanol, and dried *in vacuo* (0.4 g, 70%).

Bis[benzyloxo(η-cyclopentadienyl)iodonitrosylmolybdenum], $[\{Mo(\eta^5-C_5H_5)I(NO)(OCH_2Ph)\}_2]$.—The complex $[Mo(\eta^5-C_5H_5)I(NO)(O_2CMe)]$ (0.5 g) was dissolved in dichloromethane (15 cm^3) and the solution was filtered. To the filtrate was added benzyl alcohol (10 cm^3) and the mixture was stirred for 24 h. Partial evaporation of this solution *in vacuo* afforded the *complex* which was filtered off, washed with diethyl ether, and dried *in vacuo* (0.4 g, 70%).

(η-Cyclopentadienyl)methoxonitrosyl(trifluoroacetato)-molybdenum, $[Mo(\eta^5-C_5H_5)(NO)(OMe)(O_2CCF_3)]$.—The complex $[\{Mo(\eta^5-C_5H_5)(NO)(O_2CCF_3)_2\}_2]$ (1.0 g) was dissolved in dichloromethane (20 cm^3) and methanol (20 cm^3) was added. The solution was partially evaporated *in vacuo* and yellow-orange crystals of the *complex* were formed. These were filtered off, washed with methanol, and dried *in vacuo* (0.6 g, 70%). When this reaction was carried out in methanol which had been saturated with CO the methoxide was not formed, and the starting material was recovered (80%).

Reaction of $[Mo(\eta^5-C_5H_5)I(NO)(O_2CMe)]$ *with Water to give* $[\{Mo(\eta^5-C_5H_5)I(NO)(OH)\}_n]$.—The complex $[Mo(\eta^5-C_5H_5)I(NO)(O_2CMe)]$ (0.9 g) was dissolved in dichloromethane (20 cm^3) and the solution was filtered. To the filtrate was added 'wet' ethanol (30 cm^3 containing 1% v/v water), and the solution was allowed to stand for 15 min. Partial evaporation *in vacuo* afforded orange-brown crystals of $[\{Mo(\eta^5-C_5H_5)I(NO)(OH)\}_n]$. These were filtered off, washed with ethanol, and dried *in vacuo* (0.7 g, 90%). The corresponding *deuteroxide*, $[\{Mo(\eta^5-C_5H_5)I(NO)(OD)\}_n]$, was prepared by treating the starting material with acetone containing D_2O. It was precipitated (80%) as a brown powder.

The hydroxide is also formed in reactions between $[Mo(\eta^5-C_5H_5)I(NO)(O_2CMe)]$ and 'wet' ROH (R = Et, Pr^n, Pr^i, Bu^t, or Bu^n) but with 'wet' methanol (up to 5% v/v water) only $[\{Mo(\eta^5-C_5H_5)I(NO)(OMe)\}_2]$ could be isolated. In dry alcohols, with the exception of MeOH and $PhCH_2OH$, only unchanged $[Mo(\eta^5-C_5H_5)I(NO)(O_2CMe)]$ (50% yields) could be recovered.

(η-Cyclopentadienyl)iodomercaptonitrosylmolybdenum, $[\{Mo(\eta^5-C_5H_5)I(NO)(SH)\}_n]$.—Dry dihydrogen sulphide was passed slowly for a few minutes through a stirred suspension of $[Mo(\eta^5-C_5H_5)I(NO)(O_2CMe)]$ (1.0 g) in diethyl ether (30 cm^3). A dark brown precipitate formed which was filtered off, washed well with diethyl ether, and dried *in vacuo* (0.8 g, 80%).

(η-Cyclopentadienyl)iodonitrosylbis(triphenylphosphine)-molybdenum Hexafluorophosphate, $[Mo(\eta^5-C_5H_5)I(NO)(PPh_3)_2][PF_6]$.—The complex $[Mo(C_5H_5)_2I(NO)]$ (0.5 g) and aqueous HPF_6 (0.2 g, slight excess; 60% aqueous solution) were stirred in dichloromethane–acetone (75 cm^3, 1 : 1) for 15 min, during which time the solution changed from deep green to dark red-brown. Triphenylphosphine (0.7 g, slight excess) was added and the colour changed to deep yellow. After 20 min the solution was evaporated *in vacuo* and the residue redissolved in dichloromethane (*ca.* 20 cm^3). This solution was filtered and to the filtrate was added n-hexane (*ca.* 10 cm^3), the mixture being slowly and partially evaporated *in vacuo*. As soon as the yellow precipitate had begun to form the mixture was cooled at 0 °C overnight. The resulting microcrystalline *product* was collected, filtered off, washed with n-pentane, and dried in air (1.25 g, 70.0%).

[1,2-Bis(diphenylphosphino)ethane](η-cyclopentadienyl)-iodonitrosylmolybdenum Tetrafluoroborate, $[Mo(\eta^5-C_5H_5)I(NO)(Ph_2PCH_2CH_2PPh_2)][BF_4]$.—A filtered solution of $[Mo(C_5H_5)_2I(NO)]$ (1.0 g) in dichloromethane (30 cm^3) containing aqueous HBF_4 (0.7 g, 40% aqueous solution) was treated with $Ph_2PCH_2CH_2PPh_2$ (1.2 g) in acetone (25 cm^3). The mixture was stirred for 2 h, during which time the solution changed from deep green to red-brown. The solution was then filtered, evaporated *in vacuo*, and the brown residue redissolved in dichloromethane. This solution was filtered through phase-separating paper, ethanol and light petroleum (b.p. 120—160 °C) were added, and the mixture slowly and partially evaporated *in vacuo*. The brown crystals of the *product* were collected by filtration, washed with n-pentane, and dried *in vacuo* (0.65 g, 65.0%).

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