The Chemistry of Cyclopentadienyl Nitrosyl Complexes of Molybdenum. Part 11.[1] Monohapto-allylic Species and their Reactions with Electrophiles†

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Treatment of $[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)I(NO)]$ or $[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)(NO)(NCMe)][PF_6]$ with NaS_2CNR_2 or $AgOCOC_2F_5$ affords $[Mo(\eta^5-C_5H_5)(\eta^1-C_3H_5)(NO)(S_2CNR_2)]$, (1; R = Me or Et) and $[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)(NO)\{OC(:O)C_2F_5\}]$, respectively. The structures of these compounds are discussed. Treatment of (1) with electrophiles (EX) gives either cyclisation products, $[Mo(\eta^5-C_5H_5)(CHCH_2EXCH_2)(NO)(S_2CNR_2)]$, [EX = $C_2(CN)_4$ or $(CF_3)_2CO$] or insertion products $[Mo(\eta^5-C_5H_5)(EXCH_2CH:CH_2)(NO)(S_2CNMe_2)]$ (EX = $CF_3C_2CF_3$ or SO_2). Treatment of (1; R = Me) with HCl and $SOCl_2$ affords $[Mo(\eta^5-C_5H_5)Cl(NO)(S_2CNMe_2)]$ and $[Mo(\eta^5-C_5H_5)(C_3H_5SOCl_2)(NO)(S_2CNMe_2)]$, respectively. The properties of (1) are compared with those of $[Mo(\eta^5-C_5H_5)(\eta^1-C_5H_5)(NO)(S_2CNMe_2)]$ and $[Mo(C_5H_5)_2I(NO)]$.

IN a previous paper[2] we discussed the fluxional properties of $[Mo(C_5H_5)_2X(NO)]$ (X = I, Me, C_5H_5, and S_2CNR_2), and have observed that the apparent equivalence of the C_5H_5 groups could arise *via* electronic interchange of the two rings through η^5-, η^3-, and η^1-bonding modes. We have developed a series of chemical tests to probe the validity of our ideas, demonstrating that $[Mo(C_5H_5)_2I(NO)]$, in solution at least, can behave[3,4] as though one ring is pentahapto while the other exists, either in an intermediate or transition state, in an η^1-bonding mode.

We have also attempted to determine whether η^3-bonding modes play a significant role in the description of $[Mo(C_5H_5)_2I(NO)]$, but it has proved impossible to specifically design a system containing the $\eta^3-C_5H_5$ group. However, the recent *X*-ray crystallographic study of $[W(C_5H_5)_2(CO)_2]$ established[5] unequivocally that trihapto-cyclopentadienyl groups do exist. In a previous contribution to this discussion, we investigated[1] the spectral and chemical properties of $[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)I(NO)]$ and concluded that this η^3-allylic species was an inappropriate model for $[Mo(\eta^5-C_5H_5)(\eta^3-C_5H_5)I(NO)]$.

However, a more realistic comparison between $[Mo(C_5H_5)_2I(NO)]$ and related non-cyclic allylic species could be made if complexes containing the group $\{Mo(\eta^5-C_5H_5)(\eta^1-C_3H_5)(NO)\}$ could be synthesised. In this paper, we describe the conversion of $[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)(NO)X]$ into $[Mo(\eta^5-C_5H_5)(\eta^1-C_3H_5)(NO)Y]$ and compare the behaviour of these new species with electrophiles with that of $[Mo(\eta^5-C_5H_5)(\eta^1-C_5H_5)(NO)(S_2CNMe_2)_2]$ and $[Mo(C_5H_5)_2I(NO)]$. A preliminary report of some of our work has been published.[6]

EXPERIMENTAL

All reactions were carried out under dry nitrogen, and all solvents were degassed prior to use. All commercially available reagents were used as obtained without further purification. The complexes $[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)I(NO)]$ and $[Mo(\eta^5-C_3H_5)(NCMe)(NO)][PF_6]$ were prepared as described previously.[1]

I.r. spectral data were obtained with PE 180 and 457 spectrophotometers. ^1H N.m.r. spectra were measured using a Varian HA100 spectrometer, while ^{13}C and ^{19}F n.m.r. spectra were obtained using a JEOL PFT90 instrument. Molecular-weight determinations were made osmometrically. Elemental analyses were determined by the Microanalytical Laboratory of this Department, and all yields are quoted relative to the starting material.

$[Mo(\eta^5-C_5H_5)(\eta^1-C_3H_5)(NO)(S_2CNMe_2)]$ (1; R = Me).—To a solution of $[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)I(NO)]$ (2.0 g) in dichloromethane (50 cm^3) was added $NaS_2CNMe_2 \cdot 2H_2O$ (0.8 g). The mixture was stirred overnight, ethanol (*ca.* 10 cm^3) was added, and the solution then gently evaporated at room temperature *in vacuo* to about 30 cm^3. During this time the product formed as a yellow solid which was filtered off and recrystallised from dichloromethane–ethanol. The *complex* was obtained as yellow crystals (87%).

The compound could also be obtained by treating $[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)(NCMe)(NO)][PF_6]$ (0.6 g) in acetone (50 cm^3) with $NaS_2CNMe_2 \cdot 2H_2O$ (0.25 g). After stirring overnight, the solvent was then removed *in vacuo* and the residues were extracted with dichloromethane (20—30 cm^3) and filtered. Methanol (*ca.* 4 cm^3) was added to the filtrate and the solution was evaporated to low bulk *in vacuo*, the product forming as a yellow solid. Recrystallisation from dichloromethane–methanol afforded the *complex* as yellow crystals (85%).

The compound $[Mo(\eta^5-C_5H_5)(\eta^1-C_3H_5)(NO)(S_2CNEt_2)]$, (1; R = Et), could be similarly prepared by either method (yields >80%).

$[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)(NO)(OCOC_2F_5)]$.—To a solution of $[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)(NCMe)(NO)][PF_6]$ (0.55 g) in dichloromethane (40 cm^3) was added silver(I) pentafluoropropionate (0.35 g). The mixture was stirred for 2 h, filtered, and the solvent evaporated off *in vacuo*. The residual oil was treated with n-pentane and set aside for several days at −10 °C. During this time, the *complex* formed as golden-brown crystals (*ca.* 40%).

$[Mo(\eta^5-C_5H_5)\{\eta^1-CHCH_2C(CN)_2C(CN)_2CH_2\}(NO)(S_2CNMe_2)]$, [2; EX = $(NC)_2C:C(CN)_2$, R = Me].—To a solution of $[Mo(\eta^5-C_5H_5)(\eta^1-C_3H_5)(NO)(S_2CNMe_2)]$ (0.2 g) in dichloromethane (40 cm^3) was added tetracyanoethylene (0.1 g). After stirring the mixture for 2 h, ethanol (*ca.* 8 cm^3) was added and the solution was partially evaporated *in vacuo*. The product gradually formed as a yellow solid which was filtered off and recrystallised from dichloromethane–ethanol. The *complex* was obtained as yellow crystals (95%). The compound $[Mo(\eta^5-C_5H_5)\{\eta^1-$

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† No reprints available.

$\overline{\mathrm{CHCH_2C(CN)_2C(CN)_2C}}\mathrm{H_2\}(NO)(S_2CNEt_2)]}$, [2; EX = $\mathrm{(NC)_2C{:}C(CN)_2}$, R = Et] was obtained similarly.

$[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})\{\eta^1\text{-}\overline{\mathrm{CHCH_2C(CF_3)_2OC}}\mathrm{H_2}\}(\mathrm{NO})(\mathrm{S_2CNMe_2})]$, (2; EX = $\mathrm{(CF_3)_2CO}$, R = Me].—A solution of $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^1\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{S_2CNMe_2})]$ (0.1 g) and hexafluoroacetone (*ca.* 1 cm^3) in dichloromethane (10 cm^3) was shaken in a sealed, evacuated Carius tube at room temperature for 20 h. The tube was then opened, its contents treated with methanol (*ca.* 5 cm^3), the mixture filtered, and the filtrate partially evaporated *in vacuo*. The product gradually formed as a yellow solid which was recrystallised from dichloromethane–methanol affording the *complex* as yellow crystals (*ca.* 80%).

$[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})\{\eta^1\text{-}\mathrm{C(CF_3){:}C(CF_3)CH_2CH{:}CH_2}\}(\mathrm{NO})(\mathrm{S_2CNMe_2})]$, [2; EX = $\mathrm{CF_3C_2CF_3}$, R = Me].—This complex was obtained in the same way as that described above for the hexafluoroacetone adduct, using $\mathrm{CF_3C{\equiv}CCF_3}$ (*ca.* 1 cm^3).

$[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{SO_2CH_2CH{:}CH_2})(\mathrm{NO})(\mathrm{S_2CNMe_2})]$ [2; EX = $\mathrm{SO_2}$, R = Me].—Sulphur dioxide gas was passed through a solution of $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^1\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{S_2CNMe_2})]$ (0.1 g) in dichloromethane (15 cm^3) for *ca.* 1 h. Pentane was then added to the solution until a faint cloudiness was apparent. On setting aside this mixture at −10 °C overnight, the *complex* was obtained as golden-yellow crystals (55%).

Reaction of $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^1\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{S_2CNMe_2})]$ *with* HCl.—Anhydrous HCl gas was passed through a solution of $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^1\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{S_2CNMe_2})]$ in dichloromethane for *ca.* 15 min. Methanol was then added to the mixture which was then partially evaporated *in vacuo*. Gradually orange crystals of $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cl}(\mathrm{NO})(\mathrm{S_2CNMe_2})]$ formed, and this was identified by comparison of its m.p. and i.r. spectrum with that of an authentic sample.[2]

Reaction of $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^1\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{S_2CNMe_2})]$ *with* $\mathrm{SOCl_2}$; $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{C_3H_5SOCl_2})(\mathrm{NO})(\mathrm{S_2CNMe_2})]$.—Upon addition of thionyl chloride (0.11 g) to a solution of $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^1\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{S_2CNMe_2})]$ (0.3 g) in dichloromethane (20 cm^3), the mixture changed from yellow to golden-brown in colour. Methanol (*ca.* 5 cm^3) was then added and the mixture was partially evaporated *in vacuo*. The product gradually formed as golden-brown crystals (42%).

RESULTS AND DISCUSSION

Synthesis and Structure of $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^1\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{S_2CNR_2})]$ *and* $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{OCOC_2F_3})]$.—Treatment of $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{I}(\mathrm{NO})]$ or $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{NCMe})][\mathrm{PF_6}]$ with $\mathrm{NaS_2CNR_2}$ (R = Me or Et) afforded species initially formulated as $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{S_2CNR_2})]$ (analytical data, Table 1). From ^{1}H (Table 2) and ^{13}C (Table 3) n.m.r. spectral data taken together, it was immediately clear that the allylic group in these new complexes is η^1-bonded while the dithiocarbamate ligand is bidentate. It may be noted that the proton signals due to the Me groups in $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^1\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{S_2CNMe_2})]$ (1; R = Me) appear as a singlet, and this must be due to accidental degeneracy, since the ^{13}C resonances of the associated carbon atoms occur as two singlets. Two distinct signals would be expected for restricted rotation about the $\mathrm{S_2C{-}NMe_2}$ group bound to an asymmetric metal atom, a very common phenomenon in metal dithiocarbamato-complexes. A variable-temperature ^{13}C n.m.r. spectral study of (1; R = Me) established that it was stereochemically rigid, unlike $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^1\text{-}\mathrm{C_5H_5})(\mathrm{NO})(\mathrm{S_2CNMe_2})]$,[2] except, of course, for rotation about the $\mathrm{S_2C{\cdots}NMe_2}$ bond which causes collapse of the carbon signals of the $\mathrm{NMe_2}$ group at *ca.* 90 °C.

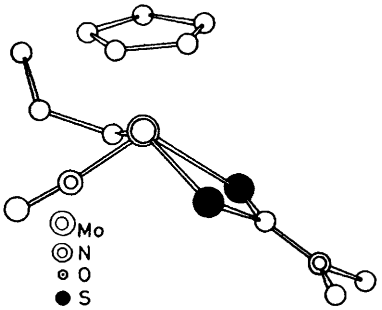

FIGURE 1 Mo–C (ring) 2.26—2.44 Å; Mo–N 1.79 Å; $\mathrm{S_2C{-}NMe_2}$ 1.36 Å; Mo–C(allyl) 2.28 Å

The structure of (1; R = Me) has been confirmed by a single-crystal *X*-ray structure determination.[6,7] This reveals (Figure 1) that the molecule has the 'four-legged piano-stool' structure typical of most η-cyclopentadienyl molybdenum(II)/(III) complexes, and is very similar to $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^1\text{-}\mathrm{C_5H_5})(\mathrm{NO})(\mathrm{S_2CNMe_2})]$.[8]

Treatment of $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{I}(\mathrm{NO})]$ or $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{NCMe})][\mathrm{PF_6}]$ with $\mathrm{AgOCOC_2F_5}$ afforded a species initially formulated as $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{C_3H_5})(\mathrm{NO})(\mathrm{O_2CC_2F_5})]$. The i.r. spectrum of this complex exhibits a band at 1 715 cm^{-1} which may be assigned to the unco-ordinated carbonyl group of a monodentate pentafluoropropionate ligand. The value of ν(NO) is

TABLE 1

Analytical data obtained for the molybdenum complexes

	Analytical results (%)							
	Found				Calculated			
Complex	C	H	N	S	C	H	N	S
$[\mathrm{Mo(C_5H_5)(C_3H_5)(NO)(S_2CNMe_2)}]$	37.1	4.8	7.7	18.6	37.5	4.6	8.0	18.2
$[\mathrm{Mo(C_5H_5)(C_3H_5)(NO)(S_2CNEt_2)}]$	40.7	5.1	7.5	16.9	41.1	5.3	7.4	16.8
$[\mathrm{Mo(C_5H_5)(C_3H_5)(NO)(OCOC_2F_5)}]$	32.8	2.8	3.8		33.4	2.5	3.5	
$[\mathrm{Mo(C_5H_5)\{C_3H_5C_2(CN)_2\}(NO)(S_2CNMe_2)}]$	42.6	3.6	17.8	13.3	42.5	3.3	17.5	13.3
$[\mathrm{Mo(C_5H_5)\{C_3H_5C_2(CN)_2\}(NO)(S_2CNEt_2)}]$	44.8	4.0	16.7	12.5	44.9	3.9	16.9	12.6
$[\mathrm{Mo(C_5H_5)\{C_3H_5C(CF_3)_2O\}(NO)(S_2CNMe_2)}]$	32.5	3.4	5.2	12.2	32.4	3.1	5.4	12.4
$[\mathrm{Mo(C_5H_5)\{C_3H_5C_2(CF_3)_2\}(NO)(S_2CNMe_2)}]$	34.9	3.1	5.8	12.9	35.0	3.1	5.5	12.5
$[\mathrm{Mo(C_5H_5)\{C_3H_5SO_2\}(NO)(S_2CNMe_2)}]$	31.4	3.8	6.9	23.3	31.7	3.9	6.7	23.1
$[\mathrm{Mo(C_5H_5)\{C_3H_5SOCl_2\}(NO)(S_2CNMe_2)}]$	27.8	3.3	6.2	19.7	28.0	3.4	6.0	20.4

TABLE 2

I.r. and ^1H n.m.r. spectral data

Complex	ν(NO) [a]	δ(A) [b]	Assignment *
$[Mo(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_3H_5)(NO)(S_2CNMe_2)]$ (1; R = Me)	1 598	6.15(1)	10-line m; H_x of C_3H_5
		5.56(5)	s; C_5H_5
	(1 543) [c]	4.70(1)	Complex d; H_c of C_3H_5; (J_{xc} 16.0 Hz)
		4.50(1)	dd; H_d of C_3H_5 (J_{xd} 10.0 Hz, J_{cd} 3.0 Hz)
		3.29(6)	s; Me of S_2CNMe_2
		2.52(2)	Complex d; H_a and H_b of C_3H_5
$[Mo(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_3H_5)(NO)(S_2CNEt_2)]$ (1; R = Et)	1 601	6.16(1)	10-line m; H_x of C_3H_5
		5.54(5)	s; C_5H_5
	(1 518)	4.70(1)	d; H_c of C_3H_5 (J_{xc} 16.0 Hz)
		4.49(1)	dd; H_d of C_3H_5 (J_{xd} 10.0 Hz, J_{cd} 3.0 Hz)
		3.81(4)	q; CH_2 of S_2CNEt_2 (J_{HH} 7.0 Hz)
		2.51(2)	Complex d; H_a and H_b of S_2CNEt_2
		1.26(6)	t; Me of S_2CNEt_2 (J_{HH} 7.0 Hz)
$[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(NO)(OCOC_2F_5)]$	1 654	6.33(1)	Complex m; *H*$_c$ of η^3-C_3H_5
	(1 715;[d]	6.15(9) 5.98(1) (5)	s; C_5H_5; '*endo*' isomer s; C_5H_5; '*exo*'-isomer
	1 160,[e]	4.98(1)	d; H(*syn*) of C_3H_5
	1 210[e])	4.18(1)	Complex m; H(*syn*) of C_3H_5
		3.67(1)	dd; H(*anti*) of C_3H_5
		2.70(1)	Complex m; H(*anti*) of C_3H_5
$[Mo(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}CHCH_2C(CN)_2C(CN)_2CH_2\}(NO)(S_2CNMe_2)]$ [2; EX = $(NC)_2C{=}C(CN)_2$, R = Me]	1 626	5.73(5)	s; C_5H_5
		3.33(3)	s; Me of S_2CNMe_2
		3.31(3)	s; Me of S_2CNMe_2
		3.32—2.60 (5)	Complex m; C_3H_5
$[Mo(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}CHCH_2C(CN)_2C(CN)_2CH_2\}(NO)(S_2CNEt_2)]$ [2; EX = $(NC)_2C{=}C(CN)_2$, R = Me]	1 621	5.92(5)	s; C_5H_5
		3.80(4)	2 q; CH_2 of S_2CNEt_2, sepn. 1.5 Hz (J_{HH} 7.0 Hz)
		3.60—2.70 (5)	Complex m; C_3H_5
		1.26(6)	2 t; Me of S_2CNEt_2, sepn. 1.5 Hz (J_{HH} 7.0 Hz)
$[Mo(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}CHCH_2C(CF_3)_2OCH_2\}(NO)(S_2CNMe_2)]$ [2; EX = $(CF_3)_2CO$, R = Me]	1 621	5.89(5)	s; C_5H_5
		4.50(1)	m; H of $C_6H_5OF_6$
		4.01(1)	m; H of $C_6H_5OF_6$
		3.34(6)	s; Me of S_2CNMe_2
		2.83—2.38 (4)	m; H of $C_6H_5OF_6$
$[Mo(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}C(CF_3){=}C(CF_3)C_3H_5\}(NO)(S_2CNMe_2)]$ [2; EX = $CF_3C_2CF_3$, R = Me]	1 612	7.23(1)	d; =CH– of C_3H_5 (sepn. 15 Hz)
		6.61—5.72 (2)	m; $=CH_2$ of C_3H_5
		5.73(5)	s; C_5H_5
		3.45—3.15 (2)	m; CH_2 of C_3H_5
		3.32(3)	s; Me of S_2CNMe_2
		3.29(3)	s; Me or S_2CNMe_2
$[Mo(\eta^5\text{-}C_5H_5)\{S(:O)_2C_3H_5\}(NO)(S_2CNMe_2)]$	1 651 (1 175,[f]	6.23—5.64 6.04 (6)	m; =CH– of C_3H_5 s; C_5H_5
	1 048[f])	5.44—5.18 (2)	m; $=CH_2$– of C_3H_5
		4.30—3.52 (2)	m; CH_2 of C_3H_5
		3.38(3)	s; Me of S_2CNMe_2
		3.34(3)	s; Me of S_2CNMe_2

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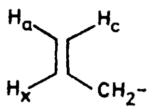


[a] In cm^{-1} in KBr. [b] From $SiMe_4$ in $(CD_3)_2CO$ (relative intensity in parentheses). [c] ν(CN) of $S_2C\overset{\cdots}{-}NR_2$. [d] ν(CO) of $OC(:O)C_2F_5$. [e] ν(CF). [f] ν(SO) of SO_2R.

very close to that of the related species $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(NO)X]$ (X = halide, NCO, or NCS; 1 641—1 658 cm^{-1})[1] and is significantly different from that of (1; R = Me or Et). From the ^1H n.m.r. spectrum of the pentafluoropropionate it is clear that the chemical shifts of the protons in the allyl group are very similar to those observed in $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(NO)X]$[1] and are consistent with an η^3-bonding mode for this ligand. Further, the occurrence of two cyclopentadienyl proton signals (relative ratio 9 : 1) can be explained, as in the case of other species of the type $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(NO)X]$,[1,9] in terms of the presence of *exo* and *endo* isomers of $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(NO)\{OC(:O)C_2F_5\}]$ (Figure 2).

Reactions of $[Mo(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_3H_5)(NO)(S_2CNMe_2)]$ (1; R = Me) *with Electrophiles.*—It has been shown[10-12] that

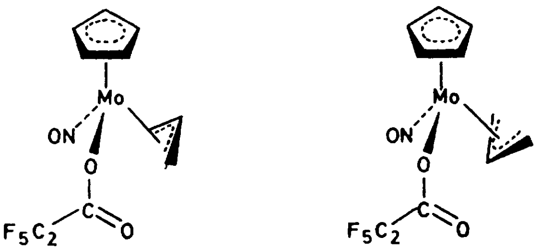
TABLE 3

^{13}C and ^{19}F n.m.r. spectra obtained from molybdenum nitrosyl complexes

Complex	δ * (p.p.m.)	Assignment
$[Mo(\eta^5-C_5H_5)(\eta^1-C_3H_5)(NO)(S_2CNMe_2)]$	32.80	allylic-CH_2
	38.30	N*Me*
	38.80	N*Me*
	102.80	$\eta^5-C_5H_5$
	106.10	allylic-CH_2
	144.90	$CH_2\mathit{C}HCH_2$
	202.90	$S_2\mathit{C}NMe_2$
$[Mo(\eta^5-C_5H_5)\{\overline{CHCH_2C(CN)_2C(CN)_2CH_2}\}(NO)(S_2CNEt_2)]$	12.56	$N(CH_2\mathit{C}H_3)$
	34.10	Mo-*C*H
	44.65 45.26 47.50	$\mathit{C}(CN)_2$ or $CH\mathit{C}H_2C(CN)_2$
	50.36	$N(\mathit{C}H_2)$
	103.67	$\eta^5-C_5H_5$
	112.97	CN
	113.51	CN
	200.81	$S_2\mathit{C}NEt_2$
$[Mo(\eta^5-C_5H_5)\{\overline{CHCH_2C(CF_3)_2OCH_2}\}(NO)(S_2CNMe_2)]$	75.30	CF_3 (q; J_{FF} 9.0 Hz)
	76.44	CF_3 (q; J_{FF} 9.0 Hz)
$[Mo(\eta^5-C_5H_5)\{C(CF_3){:}C(CF_3)CH_2CH{:}CH_2\}(NO)(S_2CNMe_2)]$	58.14	CF_3 (q; J_{FF} 8.8 Hz)
	58.22	CF_3 (q; J_{FF} 8.8 Hz)

* For ^{13}C resonances, δ relative to $SiMe_4$, recorded in $(CD_3)_2CO$; for ^{19}F resonances, δ relative to $CFCl_3$, recorded in $(CD_3)_2CO$.

η^1-allylmetal complexes, particularly those bonded to the groups $\{Fe(\eta^5-C_5H_5)(CO)_2\}$, $\{Mo(\eta^5-C_5H_5)(CO)_3\}$, and $\{Mn(CO)_5\}$, readily react with electrophiles, E=X [*e.g.* $(NC)_2C{=}C(CN)_2$, $(CF_3)_2C{=}O$, $CF_3C{\equiv}CCF_3$, SO_2, *etc.*].



exo *endo*

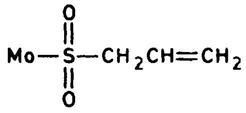
FIGURE 2

These reactions usually result either in a (3 + 2) cycloaddition between the EX molecule and the η^1-allyl group which is accompanied by a 1,2-metal migration, or in insertion of the EX molecule into the metal-carbon σ-bond. Although we expected that (1; R = Me or Et) would undergo such reactions with electrophiles, it was of interest to establish whether the presence of ligands other than CO would significantly influence the course of these reactions, and also, as indicated earlier, to compare the behaviour of the new η^1-allyl complexes with that of $[Mo(\eta^5-C_5H_5)(\eta^1-C_5H_5)(NO)(S_2CNMe_2)]$ and $[Mo(C_5H_5)_2I(NO)]$ towards EX, particularly tcne and $CF_3C{\equiv}CCF_3$.

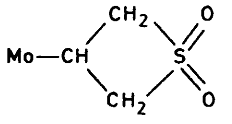
Treatment of (1; R = Me or Et) with $(NC)_2C{=}C(CN)_2$ and $(CF_3)_2C{=}O$ (E=X) afforded air-stable yellow complexes $[Mo(\eta^5-C_5H_5)(C_3H_5EX)(NO)(S_2CNR_2)]$, [2; EX = $(NC)_2C{=}C(CN)_2$ or $(CF_3)_2C{=}O$, R = Me or Et]. These compounds exhibit NO stretching frequencies significantly higher than those of the η^1-allyl precursors. The ^1H n.m.r. spectra contained resonances due to the η^5-C_5H_5 and dithiocarbamate ligands (restricted rotation about the $S_2C \overset{..}{-} R_2$ bond gives rise, of course, to two sets of signals associated with the Me or Et protons). However, because of the complexity of the signals and their poor resolution, we could obtain little definitive information from the ^1H n.m.r. spectra of the C_3H_5EX groups, other than to note that they are generally similar to those observed in $[Fe(\eta^5-C_5H_5)(C_3RR'_2EX)(CO)_2]$ (R, R' = H or Me).[11,12] No resonance associated with C_3H_5EX occurred below δ = 4.5, and hence it is clear that there are no $-CH{=}$ protons as could be expected in an insertion product containing the group $\{MoEXCH_2{-}CH{=}CH_2\}$. More useful information can be obtained from ^{13}C n.m.r. spectroscopy. Thus, the ^{13}C resonances of the $C_3H_5C_2(CN)_4$ group in [2; EX = $(NC)_2C{=}C(CN)_2$, R = Et] (Table 3) have notable similarities to comparable resonances in $[Fe(\eta^5-C_5H_5)\{C_3H_4MeC_2(CN)_4\}(CO)_2]$.[12] Thus, the signal in the former occurring at δ 34.10 may be related to that in the latter at δ 33.68 which is due to the carbon atom directly bonded to the metal. The resonances due to the tcne fragment in the two species occur at very similar chemical shifts, and this would certainly not be the case in an insertion product. The ^{19}F n.m.r. spectrum of [2; EX = $(CF_3)_2CO$, R = Me] (Table 3) exhibits two signals which are consistent either with an insertion or a cyclisation product.

The cyclic nature of the $C_3H_4MeC_2(CN)_4$ group in $[Fe(\eta^5-C_5H_5)\{C_3H_4MeC_2(CN)_4\}(CO)_2]$ has recently been confirmed[13] by *X*-ray crystallography and so, taking this and our spectral data into account, we conclude that the tcne and $(CF_3)_2CO$ adducts of $[Mo(\eta^5-C_5H_5)(\eta^1-C_3H_5)(NO)(S_2CNR_2)]$ are similar, *i.e.* they have the structure shown in Figure 3.

Reaction of (1; R = Me) with $CF_3C{\equiv}CCF_3$ or SO_2 affords yellow adducts of lower stability towards air than [2; EX = $(NC)_2C{=}C(CN)_2$ or $(CF_3)_2CO$, R = Me]. The NO stretching frequencies of these adducts are noticeably different to those of [2; EX=$(NC)_2C{=}C(CN)_2$ or $(CF_3)_2CO$, R = Me], suggesting that insertion rather than cyclisation had occurred at the allyl group in the precursor. The i.r. spectrum of (2; EX = SO_2) also exhibited strong bands at 1 175 and 1 048 cm^{-1}. These may be due to an SO_2R group and, on the basis of previous i.r. spectral studies[14] of the products formed between SO_2 and metal-bonded allylic and acetylenic fragments, we may conclude that only two structures for the $C_3H_5SO_2$ fragment need be considered, *i.e.* (*A*) and (*B*).



(*A*)



(*B*)

Due to low solubility and poor resolution, the ^1H n.m.r. spectra of (2; $EX = CF_3C_2CF_3$, R = Me) and (2; $EX = SO_2$, R = Me) were of poorer quality than those of [2; $EX = (NC)_2C{=}C(CN)_2$ or $(CF_3)_2CO$, R = Me]. However, a qualitative difference was detectable, especially in the observation of signals at δ 7.23 ($EX = CF_3C_2CF_3$) and between δ 6.23 and 5.64 ($EX = SO_2$) which must be assigned to the unique proton in a $-CH_2CH{=}CH_2$ group. Such low-field resonances do not occur in the cyclisation products, and in the case of the SO_2 adduct, this rules out a structure containing (*B*). The ^{19}F n.m.r. spectrum of (2; $EX = CF_3C_2CF_3$, R = Me) consists of a doublet of poorly-resolved quartets centred at δ 58.18 (Table 3). The value of J_{FF} (8.81 Hz) is typical of two CF_3 groups in a mutually-*cis* configuration (*i.e.* the CF_3 groups must be in different environments).[15] A second smaller doublet of quartets centred at δ 57.25 (J_{FF} 8.3 Hz) was at first thought to be due to an isomer of the principle species, but as the intensities of these signals varied from sample to sample and increased significantly when traces of acid were added to (2; $EX = CF_3C_2CF_3$, R = Me) in solution, they were attributed to a decomposition product, possibly $C_3H_6C_2(CF_3)_2$. Therefore, we conclude that the treatment of $[Mo(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_3H_5)(NO)(S_2CNMe_2)]$ with $CF_3C{\equiv}CCF_3$ and SO_2 affords insertion products, *i.e.* as in Figure 4 and $[Mo(\eta^5\text{-}C_5H_5)\{S(\dot{:}O)C_3H_5\}(NO)(S_2CNMe_2)]$, respectively.

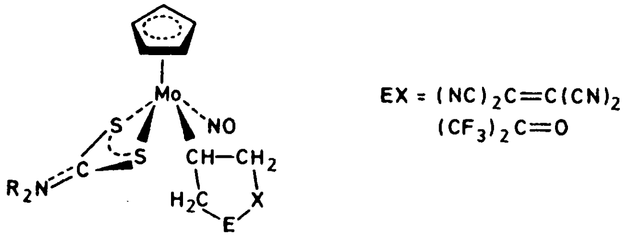


FIGURE 3

Treatment of (1; R = Me) with thionyl chloride in dichloromethane afforded a complex which analysed satisfactorily as (2; $EX = SOCl_2$, R = Me). However, because of the insolubility of this complex, we were unable to obtain n.m.r. spectra and consequently cannot propose a definite structure for this species. However, it is probably a cyclisation product like [2; $EX = (NC)_2C{=}C(CN)_2$ or $(CF_3)_2C{=}O$]. There was no reaction between (1; R = Me) and $RC{\equiv}CR$ (R = Ph, CH_2OH, or CO_2Me), perfluorocyclobutene, CF_3CN, CS_2, PhNSO, or $C_6H_{11}NC$. However, a reaction was observed with C_2F_4, but the products were formed in very low yield and were too unstable to permit characterisation.

From a comparison of the behaviour towards electrophiles of (1; R = Me or Et) with that of $[Fe(\eta^5\text{-}C_5H_5)(\eta^1\text{-allyl})(CO)_2]$ and related Mo and Mn complexes, it may be seen that the presence of NO and S_2CNMe_2 instead of carbonyl ligands has no significant influence over the course of the reactions. Thus tcne and $(CF_3)_2CO$ form cyclic products, whereas $CF_3C{\equiv}CCF_3$ and SO_2 engage predominantly in insertion reactions.

Treatment of (1; R = Me) with anhydrous HCl affords the known $[Mo(\eta^5\text{-}C_5H_5)Cl(NO)(S_2CNMe_2)_2]$ with, presumably, loss of propene. This reaction parallels exactly the behaviour of $[Mo(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(NO)(S_2CNMe_2)]$ and $[Mo(C_5H_5)_2I(NO)]$ with HCl,[2] in which $[Mo(\eta^5\text{-}C_5H_5)Cl(NO)(S_2CNMe_2)]$ and $[Mo(\eta^5\text{-}C_5H_5)Cl(I)(NO)]_2$, respectively, are formed with the loss, in both cases, of cyclopentadiene. These reactions are entirely typical of a metal–carbon σ-bond. With tcne, (1) forms a cyclic product and so do $[Mo(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(NO)(S_2CNMe_2)]$ and $[Mo(C_5H_5)_2I(NO)]$, although the latter two afford[4] norbornenyl derivatives attached to the metal *via* the bridgehead carbon atom [see *e.g.* (4) in ref. 4]. Whereas (1; R = Me or Et) reacts with $CF_3C{\equiv}CCF_3$ affording an insertion product (3; $EX = CF_3C_2CF_3$)(see Figure 4), the bis(cyclopentadienyl) complexes form[4] cyclic products derived from Diels–Alder (3 + 2) addition to an η^1-cyclopentadienyl ring [see (3) and (5) in ref. 4] as indeed does $[Fe(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(CO)_2]$.[11] In conclusion, we may state that the reactions of (1; R = Me or Et) with electrophiles are entirely those expected of a $Mo(\eta^1\text{-}C_3H_5)$ species, and further serve to strengthen the view that $[Mo(C_5H_5)_2I(NO)]$ behaves in solution as though it contains an $\eta^1\text{-}C_5H_5$ ring.

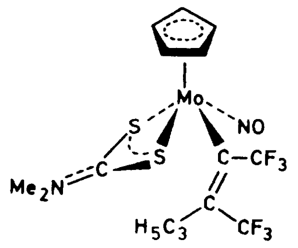


FIGURE 4

A notable difference between (1) and $[Mo(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(NO)(S_2CNMe_2)]$, however, is the lack of fluxionality in the former when compared to the latter. Whereas the $\eta^1\text{-}C_5H_5$ ring in the latter engages in 1,2-shifts about the metal and also in electronic role-interchange with the η^5-ring, the η^1-allyl group in the former is rigid. It has been suggested by Cotton[16] that the bending of the Mo–N–O bond angle in the bis(cyclopentadienyl) dithiocarbamate facilitates ring role interchange, and in so doing permits the metal, in the transition state, to maintain its 18-electron configuration. It would therefore seem likely that Mo–N–O bond-angle bending would also occur in (1), thereby allowing the allyl group to undergo 1,3-shifts. That this does not occur would seem to suggest that there need be no participation of the NO group in the fluxional behaviour of these species. It would appear more reasonable, as we have suggested,[2] to propose progressive tilting of the C_5H_5 rings either *via* $\eta^5 \leftrightarrow \eta^3 \leftrightarrow \eta^1$ or $\eta^5 \leftrightarrow \eta^4 \leftrightarrow \eta^3 \leftrightarrow \eta^2 \leftrightarrow \eta^1$ interchange, ring rocking modes perhaps peculiar to bis(cyclopentadienyl) complexes.

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