The Chemistry of Cyclopentadienyl Nitrosyl and Related Complexes of Molybdenum. Part 9.[1] Reactions of Bis(cyclopentadienyl) Complexes with Dienophilic Acetylenes and Olefins

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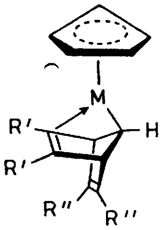
Reaction of [Mo(C$_5$H$_5$)$_2$I(NO)] with F$_3$CC$\equiv$CCF$_3$ and (NC)$_2$C=C(CN)$_2$ affords [Mo(η^5-C$_5$H$_5$){C$_7$H$_5$(CF$_3$)$_2$}I(NO)] and [Mo(η^5-C$_5$H$_5$)I{C$_7$H$_5$(CN)$_4$}I(NO)], respectively. Treatment of [Mo(η^5-C$_5$H$_5$)(σ-C$_5$H$_5$)(NO)(η^2-S$_2$CNMe$_2$)] with RC$\equiv$CR (R = CF$_3$ or CO$_2$Me), (NC)$_2$C=C(CN)$_2$, and maleic anhydride gives [Mo(η^5-C$_5$H$_5$){C$_7$H$_5$R$_2$}(NO)(η^2-S$_2$CNMe$_2$)], [Mo(η^5-C$_5$H$_5$){C$_7$H$_5$(CN)$_4$}(NO)(η^2-S$_2$CNMe$_2$)], and [Mo(η^5-C$_5$H$_5$){C$_7$H$_5$(CO)$_2$O}(NO)(η^2-S$_2$CNMe$_2$)]. In all of these complexes the acetylene or olefin has added in a Diels–Alder fashion to a cyclopentadienyl group, and in the first complex the F$_3$CC$\equiv$CCF$_3$ group is probably co-ordinated to the metal.

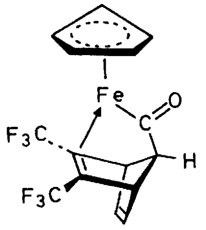
In an earlier paper[2] we suggested that [Mo(C$_5$H$_5$)$_2$I(NO)] might exist in solution as [Mo(η^5-C$_5$H$_5$)(σ-C$_5$H$_5$)I(NO)] (possibly solvated). We have shown that the bis(cyclopentadienyl) complex reacts in solution in a way typical of species containing M–C σ bonds. That is, with acids such as HI, RCO$_2$H, or RCOCH$_2$OCR, cleavage of cyclopentadiene occurred[1] with formation of the appropriate iodide, carboxylate, or β-diketonate.

A further reaction which might be expected of a species containing a σ-cyclopentadienyl ring is the formation of Diels–Alder adducts by reaction with dienophilic acetylenes and olefins. Wilkinson and Piper[3] showed that Hg(C$_5$H$_5$)$_2$ accepted two molecules of maleic anhydride and proposed that this was evidence for the existence of σ-cyclopentadienyl groups in the organomercurial. More recently, Clark and Stone and their respective co-workers demonstrated that F$_3$CC$\equiv$CCF$_3$ reacts with [Pt(C$_8$H$_{12}$)(σ-C$_5$H$_5$)$_2$] (C$_8$H$_{12}$ = cyclo-octa-1,5-diene) and [Fe(η^5-C$_5$H$_5$)(σ-C$_5$H$_5$)(CO)$_2$] forming[4] (1a) and (2) respectively. However, it may also be observed that [Ni(C$_5$H$_5$)$_2$], a species having a '20-electron' configuration,[5] and apparently containing two η^5 rings, reacts with RC$\equiv$CR (R = CO$_2$Me[6] or CF$_3$[7]) to give (1b).

In an attempt to study the behaviour of [Mo(C$_5$H$_5$)$_2$I(NO)] in solution, we have treated it, and the related [Mo(η^5-C$_5$H$_5$)(σ-C$_5$H$_5$)(NO)(η^2-S$_2$CNMe$_2$)],[2] with a series of dienophilic acetylenes and olefins.



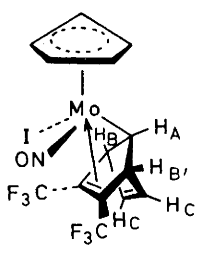
(1a) M = Pt, R' = H, R'' = CF$_3$
(1b) M = Ni, R' = CF$_3$ or CO$_2$Me, R'' = H



(2)

RESULTS AND DISCUSSION

Reaction of [Mo(C$_5$H$_5$)$_2$I(NO)] with F$_3$CC$\equiv$CCF$_3$ occurred in a sealed tube over 3 weeks, and afforded [Mo(η^5-C$_5$H$_5$){C$_7$H$_5$(CF$_3$)$_2$}I(NO)] (3). With tetracyanoethylene, however, reaction was quicker, and after 4 h the insoluble [Mo(η^5-C$_5$H$_5$){C$_7$H$_7$(CN)$_4$}I(NO)] (4) was recovered. We were unable, however, to detect reactions between the bis(cyclopentadienyl) complex and RC$\equiv$CR' (R = R' = CO$_2$Me or Ph; R = CF$_3$, R = H), (NC)HC=CH(CN), maleic anhydride, or (F$_3$C)$_2$CO either at room temperature or in refluxing acetone. We were also unable to isolate characterisable products from the reaction between [Mo(C$_5$H$_5$)$_3$(NO)] and F$_3$CC$\equiv$CCF$_3$.



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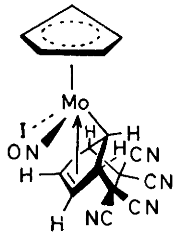

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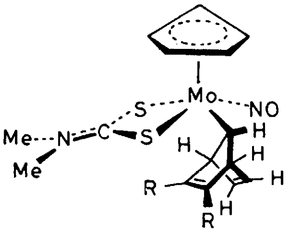
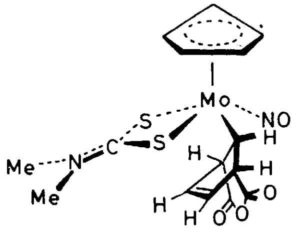


(5) R = CF3
(6) R = CO$_2$Me



(8)

Treatment of [Mo(η^5-C$_5$H$_5$)(σ-C$_5$H$_5$)(NO)(η^2-S$_2$CNMe$_2$)][2] with F$_3$CC$\equiv$CCF$_3$ gave [Mo(η^5-C$_5$H$_5$){C$_7$H$_5$(CF$_3$)$_2$}(NO)(η^2-S$_2$CNMe$_2$)] (5) in 1 d. A similar adduct, [Mo(η^5-C$_5$H$_5$){C$_7$H$_5$(CO$_2$Me)$_2$}(NO)(η^2-S$_2$CNMe$_2$)] (6), was obtained with dimethyl acetylenedicarboxylate, and with (NC)$_2$C=C(CN)$_2$ and maleic anhydride the

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[1] Part 8, preceding paper.

[2] Part 7, M. M. Hunt, W. G. Kita, B. E. Mann, and J. A McCleverty, *J.C.S. Dalton*, 1978, 467.

[3] G. Wilkinson and T. S. Piper, *J. Inorg. Nuclear Chem.*, 1956, **2**, 32.

[4] J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1976, 2044; H. C. Clark, D. G. Ibbott, N. C. Payne, and A. Shaver, *J. Amer. Chem. Soc.*, 1975, **97**, 3555.

[5] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley–Interscience, New York, 1974.

[6] M. Dubeck, *J. Amer. Chem. Soc.*, 1960, **82**, 6193.

[7] D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1964, 1752; L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 1963, **2**, 714.

species $[Mo(\eta^5\text{-}C_5H_5)\{C_7H_5(CN)_4\}(NO)(\eta^2\text{-}S_2CNMe_2)]$ (7) and $[Mo(\eta^5\text{-}C_5H_5)\{C_7H_5(CO)_2O\}(NO)(\eta^2\text{-}S_2CNMe_2)]$ (8), respectively, were rapidly formed. However, no adducts could be obtained with $PhC{\equiv}CPh$. Treatment of (3) with $Na[S_2CNMe_2]$ readily afforded (5).

The i.r. spectra of the complexes derived from hexafluorobut-2-yne, *viz.* (3) and (5), are characterised by aliphatic C–H and C–F stretching modes, and by the occurrence of what may be ν(C=C) at 1 682 (3) and 1 675 cm^{-1} (5), respectively. These last bands are absent in the spectra of all the other adducts. The NO stretching frequency in (3) occurs 24 cm^{-1} higher than that in (5), suggesting that in the former complex an electron-withdrawing group may be bound to the metal.[*] In the spectra of (4) and (7), bands due to C≡N are present, and ν(NO) in the former is 60 cm^{-1} higher than that in the latter. The spectra of (6) and (8) contain absorptions due to the added molecule and, of course, species (5)—(8) exhibit bands characteristic of co-ordinated dithiocarbamate [*e.g.* ν(C–N) of the $S_2C\text{–}NMe_2$ group]; the NO stretching frequency in these complexes occurs at 1 620 cm^{-1}.

The ^1H n.m.r. spectrum of (3) exhibits three unresolved multiplets (appearing as broad singlets) at 3.00, 3.94, and 4.60 p.p.m. which must be due to the protons (H_A, H_B, and $H_{B'}$) attached to sp^3-hybridised C atoms. The singlet at 6.78 p.p.m. is clearly due to the η^5-C_5H_5 group and the remaining singlets, at 6.49 and 7.29 p.p.m., are therefore due to the olefinic protons (H_C and $H_{C'}$). This spectrum may be compared with that of (1b). In the species (1b; $R' = CF_3$, $R'' = H$), excluding the cyclopentadienyl proton resonance, there are three groups of signals (observed in $CFCl_3$), at 2.33 p.p.m. due to the proton on the carbon atom σ-bonded to the metal, at 3.83 p.p.m. due to the bridgehead protons, and at 6.70 p.p.m. due to the uncomplexed olefinic protons. Similar assignments were made for (1b; $R' = CO_2Me$, $R'' = H$), *viz.* 2.18 p.p.m. for the unique proton and 6.62 p.p.m. for the olefinic protons. Following these assignments, we may assume that in (3) the singlet at highest field is due to the proton attached to the C atom bound to Mo and that the two signals at 6.49 and 7.29 p.p.m. are due to the protons of an *uncomplexed* olefinic group. Substantiation of this view may be obtained from the spectra of (5) and (6). Except for the different substituents, the spectra of these two species are very similar, the signals at 3.72 ($R = CF_3$) and 3.83 p.p.m. (CO_2Me) being due to the proton on the metal-bound C atom, and those at 6.74 and 6.97 ($R = CF_3$) and 6.73 and 6.96 p.p.m. (CO_2Me), respectively, being due to the free olefinic group. (It is reasonably assumed that these species contain bidentate S_2CNMe_2 and consequently that the modified cyclopentadienyl ligand is bound to Mo only *via* the unique C atom.) Comparing the spectra of (5) and (6) with those of (3) and (1b), it seems very likely that (3) has the structure shown, *i.e.* analogous to (1b). This would also be consistent with the i.r. spectral data where ν(NO) is higher in (3) than in (5).

Species (4), (7), and (8) were too insoluble for ^1H n.m.r. spectral studies. It is possible that (4) has the structure shown, but in view of its insolubility alternative structures involving dimerisation *via* co-ordination at the metal of the olefinic or CN group of an adjacent molecule cannot be discounted.

Finally, it is tempting to speculate that a possible intermediate in the formation of (3) is $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(F_3CC{\equiv}CCF_3)I(NO)]$, in which the metal-bound acetylene functions as a two-electron donor. The proposed configuration of (3) would not be inconsistent with such an intermediate. It must be realised, however, that the formation of (3) need not necessarily occur *via* this intermediate, but its existence seems to suggest the presence of σ-cyclopentadienyl species in solution.

EXPERIMENTAL

The complexes $[Mo(C_5H_5)_2I(NO)]$ [8] and $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(NO)(\eta^2\text{-}S_2CNMe_2)]$ [2] were prepared as described earlier. The yields quoted are relative to the molydenum-containing starting material, the melting points are uncorrected, and, unless otherwise stated, all the reactions were carried out under nitrogen. Elemental analyses were by the Microanalytical Laboratory of this Department. Infrared spectra were obtained using Perkin-Elmer 457 and 180 spectrophotometers, and ^1H and ^{19}F n.m.r. spectra using Varian HA 100 and Jeol PFT-100 instruments.

Reaction between $[Mo(C_5H_5)_2I(NO)]$ *and* $F_3CC{\equiv}CCF_3$ *to give* $[Mo(\eta^5\text{-}C_5H_5)\{C_7H_5(CF_3)_2\}I(NO)]$ (3).—Hexafluorobut-2-yne (*ca.* 2 cm^3) was condensed into a Carius tube (−196 °C) containing $[Mo(C_5H_5)_2I(NO)]$ (1.0 g) dissolved in acetone (30 cm^3). The tube was sealed *in vacuo* and shaken at room temperature for 3 weeks. The tube was then opened, the yellow solution filtered, and the filtrate partially evaporated *in vacuo*. Addition of diethyl ether to the residue afforded yellow crystals of $[Mo(\eta^5\text{-}C_5H_5)\{C_7H_5(CF_3)_2\}I(NO)]$ (m.p. 160—162 °C) which were collected by filtration and dried *in vacuo* (0.8 g, 56%) (Found: C, 31.3; H, 2.1; I, 23.4; N, 2.6. $C_{14}H_{10}F_6IMoNO$ requires C, 30.9; H, 1.9; I, 23.3; N, 2.6%). Infrared spectrum in KBr discs ν(C–H) at 3 260vw, 3 110vw, 3 080w, 3 060w, 2 970vw; ν(C=C)(?) at 1 682m; ν(N–O) at 1 644s; ν(C–F) and others at 1 345m, 1 300s, 1 245s, 1 205w, 1 185s, 1 170m, 1 130s, and 1 120s cm^{-1}. Hydrogen-1 n.m.r. spectra in $CDCl_3$ ($SiMe_4$ as internal reference): 3.00 (1 H, br s), 3.94 (1 H, br s), 4.60 (1 H, br s), 6.78 (5 H, s, C_5H_5), 6.49 (1 H, br s), and 7.29 p.p.m. (1 H, br s). Fluorine-19 n.m.r. spectrum in $CDCl_3$ (relative to internal $C_6H_5CF_3$): 1.05 p.p.m. (A_3B_3 multiplet).

Reaction between $[Mo(C_5H_5)_2I(NO)]$ *and* $C_2(CN)_4$ *to give* $[Mo(\eta^5\text{-}C_5H_5)\{C_7H_5(CN)_4\}I(NO)]$ (4).—A mixture of $[Mo(C_5H_5)_2I(NO)]$ (0.5 g, 1.31 mmol) and tetracyanoethylene (0.17 g, 1.31 mmol) was stirred in diethyl ether (100 cm^3) for 4 h. The resulting orange-brown suspension was filtered off, and the complex $[Mo(\eta^5\text{-}C_5H_5)\{C_7H_5(CN)_4\}I(NO)]$ (m.p. >280 °C) was washed with dichloromethane and diethyl ether, and dried *in vacuo* (0.55 g, 82%) (Found: C, 37.4; H, 2.7; I, 24.6; N, 13.5. $C_{16}H_{10}IMoN_5O$ requires

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[*] The dithiocarbamate ligand, as in $[Mo(\eta^5\text{-}C_5H_5)\{C_7H_5(CF_3)_2\}(NO)(\eta^2\text{-}S_2CNMe_2)]$, is not regarded as a strong electron-releasing ligand; see F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, 1964, **3**, 1398.

[8] R. B. King, *Inorg. Chem.*, 1968, **7**, 90.

C, 37.7; H, 2.0; I, 24.9; N, 13.7%). Infrared spectrum in KBr discs: ν(C–H) at 3 110w, 3 090w(sh), 3 040w, 2 960vw, 2 920vw; ν(C≡N) at 2 225m, 2 150s; and ν(NO) at 1 680s cm^{-1}.

Reaction between [Mo(η^5-C$_5$H$_5$)(σ-C$_5$H$_5$)(NO)(η^2-S$_2$CNMe$_2$)] *and Selected Acetylenes and Olefins.*—(*a*) *Hexafluorobut*-2-*yne*. Hexafluorobut-2-yne (*ca.* 2 cm^3) was condensed into a Carius tube (−196 °C) containing [Mo(η^5-C$_5$H$_5$)(σ-C$_5$H$_5$)(NO)(η^2-S$_2$CNMe$_2$)] (1.0 g) dissolved in diethyl ether (30 cm^3). The tube was sealed and shaken at room temperature for 1 d. It was then opened and the yellow-orange solution filtered. Partial evaporation of the filtrate afforded the complex [Mo(η^5-C$_5$H$_5$){C$_7$H$_5$(CF$_3$)$_2$}(NO)(η^2-S$_2$CNMe$_2$)] (4) m.p. 178—180 °C, as yellow crystals. These were filtered off, washed with pentane, and dried *in vacuo* (1.0 g, 75%) Found: C, 38.3; H, 3.2; N, 5.3; S, 12.1. C$_{17}$H$_{16}$F$_6$MoN$_2$OS$_2$ requires C, 37.9; H, 3.0; N, 5.2; S, 11.9%). Infrared spectrum in KBr discs: ν(C–H) at 3 320w, 3 115vw, 3 075vw, 2 990vw, 2 940vw, 2 855w; ν(C=C) (?) at 1 675w; ν(NO) at 1 620s; ν(C–N) at 1 520m; ν(C–F) and others at 1 400m, 1 330m, 1 290s, 1 250w, 1 210w, 1 200w, 1 170s, 1 130s, and 1 090w cm^{-1}. Hydrogen-1 n.m.r. spectrum in CDCl$_3$ (relative to SiMe$_4$): 3.27 and 3.29 [6 H, singlets, N(CH$_3$)$_2$], 3.72 (1 H, s), 3.84 (1 H, br s), 4.29 (1 H, br s), 5.54 (5 H, s, C$_5$H$_5$), 6.74 (1 H, m), and 6.97 p.p.m. (1 H, m). Fluorine-19 spectrum in CDCl$_3$ (external CF$_3$CO$_2$H): 15.3 p.p.m. (A$_3$B$_3$ multiplet).

(*b*) *Dimethyl acetylenedicarboxylate*. A mixture of [Mo(η^5-C$_5$H$_5$)(σ-C$_5$H$_5$)(NO)(η^2-S$_2$CNMe$_2$)] (0.4 g, 1.06 mmol) and MeO$_2$CC≡CCO$_2$Me (1.0 g, 7.03 mmol) in acetone (20 cm^3) was stirred at room temperature for 4 h. The resulting yellow-orange solution was treated with active charcoal, the mixture was filtered, and the filtrate partially evaporated *in vacuo*. Addition of diethyl ether followed by further partial evaporation *in vacuo* afforded the complex [Mo(η^5-C$_5$H$_5$){C$_7$H$_5$(CO$_2$Me)$_2$}(NO)(η^2-S$_2$CNMe$_2$)] (6), m.p. 188—190 °C, as yellow crystals. These were filtered off, washed with diethyl ether, and dried *in vacuo* (0.3 g, 60%) (Found: C, 43.3; H, 4.6; N, 5.3; S, 12.7. C$_{19}$H$_{22}$MoN$_2$O$_5$S$_2$ requires C, 44.0; H, 4.3; N, 5.4; S, 12.4%). Infrared spectrum in KBr discs: ν(C–H) at 3 200vw, 3 110vw, 2 990w, 2 950w, 2 910vw, 2 850vw; ν(OCO) at 1 710s; ν(NO) at 1 620s; and ν(C–N) at 1 540m cm^{-1}. Hydrogen-1 n.m.r. spectrum in CDCl$_3$ (relative to SiMe$_4$): 3.27 and 3.28 [6 H, singlets, N(CH$_3$)$_2$], 3.75 and 3.76 (6 H, singlets, CO$_2$CH$_3$), 3.83 (1 H, s), 3.91 (1 H, m), 4.29 (1 H, m), 5.55 (5 H, s, C$_5$H$_5$), 6.73 (1 H, m), and 6.96 p.p.m. (1 H, m).

(*c*) *Tetracyanoethylene*. A mixture of [Mo(η^5-C$_5$H$_5$)(σ-C$_5$H$_5$)(NO)(η^2-S$_2$CNMe$_2$)] (0.5 g, 1.33 mmol) and C$_2$(CN)$_4$ (0.2 g, 1.56 mmol) in diethyl ether (30 cm^3) was stirred for 30 min. The resulting yellow precipitate of the complex [Mo(η^5-C$_5$H$_5$){C$_7$H$_5$(CN)$_4$}(NO)(η^2-S$_2$CNMe$_2$)] (7) was filtered off, washed with several portions of diethyl ether, and dried *in vacuo* (0.6 g, 90%) (Found: C, 45.3; H, 3.5; N, 16.4; S, 12.6. C$_{19}$H$_{16}$MoN$_6$OS$_2$ requires C, 45.2; H, 3.2; N, 16.7; S, 12.7%). Infrared spectrum in KBr discs: ν(C–H) at 3 075vw, 2 950w, 2 900vw, 2 850vw; ν(C≡N) at 2 250w, 2 200w, 2 130m; ν(NO) at 1 620s; and ν(C–N) at 1 540s cm^{-1}.

(*d*) *Maleic anhydride*. A mixture of [Mo(η^5-C$_5$H$_5$)(σ-C$_5$H$_5$)(NO)(η^2-S$_2$CNMe$_2$)] (0.6 g, 1.59 mmol) and maleic anhydride (0.2 g, 2.04 mmol) in diethyl ether (50 cm^3) was stirred for 12 h. The resulting yellow suspension was filtered off, washed with diethyl ether, and recrystallised from acetone–methanol affording yellow crystals of the complex [Mo(η^5-C$_5$H$_5$){C$_7$H$_5$(CO)$_2$O}(NO)(η^2-S$_2$CNMe$_2$)] (8), m.p. 138—140 °C. These were filtered off, washed with diethyl ether, and dried *in vacuo* (0.5 g, 65%) (Found: C, 43.3; H, 4.1; N, 5.8; S, 13.3. C$_{17}$H$_{16}$MoN$_2$O$_4$S$_2$ requires C, 43.0; H, 3.8; N, 5.9; S, 13.5%). Infrared spectrum in KBr discs: ν(C–H) at 3 100w, 3 050vw, 3 000w, 2 950vw, 2 875w; ν(OCO) at 1 843m, 1 772s; ν(NO) at 1 620s; and ν(C–N) at 1 583m cm^{-1}.

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