The Oxidation of Alkyne-bridged Dimolybdenum Complexes

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The complexes $[Mo_2(CO)_3L^1(\mu\text{-}R^1C{\equiv}CR^2)(\eta^5\text{-}L^2)_2]$ (**1**: $L^2 = C_5H_5$, $L^1 = CO$, $R^1 = R^2 = CO_2Me$; $L^2 = C_5Me_5$, $L^1 = CO$, $R^1 = R^2 = CO_2Me$ or Me, $R^1 = H$, $R^2 = Ph$; $L^1 = CNBu^t$ or $CNC_6H_3Me_2\text{-}2,6$, $R^1 = R^2 = CO_2Me$; L^2 = indenyl, $L^1 = CO$, $R^1 = R^2 = Me$) undergo two sequential one-electron oxidations at a platinum bead electrode in CH_2Cl_2. Electrolytic oxidation of $[Mo_2(CO)_4(\mu\text{-}MeC{\equiv}CMe)(\eta\text{-}C_5Me_5)_2]$ gives $[Mo_2(CO)_4(\mu\text{-}MeC{\equiv}CMe)(\eta\text{-}C_5Me_5)_2]^+$; $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ oxidation of $[Mo_2(CO)_3(CNBu^t)(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)(\eta\text{-}C_5Me_5)_2]$ yields the paramagnetic salt $[Mo_2(CO)_3(CNBu^t)(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)(\eta\text{-}C_5Me_5)_2][PF_6]$.

We have recently reported on the redox activation of μ-alkylidene [1] and μ_3-ethylidyne [2] ligands at di- and tri-ruthenium centres respectively, and of the metallacyclononatetraene ring in $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$.[3] In each case, the reaction involves proton loss from the bridging hydrocarbon after the second of two sequential one-electron oxidations.

In seeking to use this 'double-oxidation/deprotonation' process in the activation of other hydrocarbons, we have begun to study the redox properties of alkyne- and polyalkyne-bridged complexes, particularly of molybdenum. Here we show (*i*) that the complexes $[Mo_2(CO)_3L^1(\mu\text{-}R^1C{\equiv}CR^2)(\eta^5\text{-}L^2)_2]$ (L^2 = cyclopentadienyl derivative) undergo double oxidation, (*ii*) that the unstable paramagnetic monocations can be spectroscopically characterised and in one case isolated {*viz.* $[Mo_2(CO)_3(CNBu^t)(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)(\eta\text{-}C_5Me_5)_2][PF_6]$}, but (*iii*) that electron transfer is followed by bridge cleavage rather than hydrocarbon ligand activation.

Results and Discussion

The complexes $[Mo_2(CO)_3L^1(\mu\text{-}R^1C{\equiv}CR^2)(\eta^5\text{-}L^2)_2]$ (**1**: $L^1 = CO$, $L^2 = C_5H_5$, $R^1 = R^2 = CO_2Me$; $L^2 = C_5Me_5$, $R^1 = R^2 = CO_2Me$ or Me, $R^1 = H$, $R^2 = Ph$) were prepared by published methods[4,5] and $[Mo_2(CO)_4(\mu\text{-}MeC{\equiv}CMe)(\eta^5\text{-}C_9H_7)_2]$ (C_9H_7 = indenyl) was kindly donated by Professor M. Green (King's College, University of London). The dark red crystalline isocyanide derivatives $[Mo_2(CO)_3L^1(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)(\eta\text{-}C_5Me_5)_2]$ (L = $CNBu^t$ or $CNC_6H_3Me_2\text{-}2,6$) (Table 1) were readily made by heating the tetracarbonyl $[Mo_2(CO)_4(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)(\eta\text{-}C_5Me_5)_2]$ with the appropriate isocyanide in toluene under reflux for 2 h.

In n-hexane, the i.r. spectra of $[Mo_2(CO)_3L^1(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)(\eta\text{-}C_5Me_5)_2]$ ($L^1 = CNBu^t$ or $CNC_6H_3Me_2\text{-}2,6$), in the metal carbonyl region [*e.g.* $L^1 = CNBu^t$, $\tilde{\nu}(CO)$ = 1 957mw, 1 938s (sh), 1 925vs, and 1 798s; $L^1 = CNC_6H_3Me_2\text{-}2,6$, $\tilde{\nu}(CO)$ = 1 963mw, 1 956m, 1 935s (sh), 1 927vs, and 1 796m cm^{-1}] show more than the three peaks expected for the structure shown in the Figure {*i.e.* that adopted by $[Mo_2(CO)_3(PPh_3)(\mu\text{-}HC{\equiv}CH)(\eta\text{-}C_5H_5)_2]$[6] and derived from that established[4] for $[Mo_2(CO)_4(\mu\text{-}RC{\equiv}CR)(\eta\text{-}C_5H_5)_2]$ (R = H, Et, or Ph) by *X*-ray crystallography}. However, the ^1H n.m.r. spectra are in agreement with that structure. The presence of only one set of proton resonances suggests that the additional i.r. carbony peaks result from rotamerism [due to the possibility of variable conformation about Mo(1) (Figure)] rather than from a more fundamental difference involving a distribution of the ligand L^1 between the two metals.

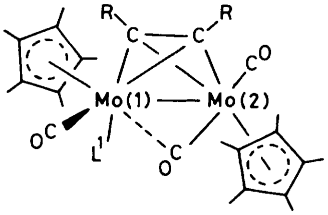

Figure. The proposed structure of $[Mo_2(CO)_3L^1(\mu\text{-}RC{\equiv}CR)(\eta\text{-}C_5Me_5)_2]$ (L^1 = isocyanide, R = CO_2Me)

Table 1. Analytical, i.r., and ^1H n.m.r. spectroscopic data for $[Mo_2(CO)_3(CNR)(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)(\eta\text{-}C_5Me_5)_2]^{z}$

R	Z	Yield (%)	Analysis[a]/% C	Analysis[a]/% H	Analysis[a]/% N	I.r.[b]/cm^{-1} $\tilde{\nu}(CO)$	I.r.[b]/cm^{-1} $\tilde{\nu}(CN)$	$^1H(\delta)$[c]
Bu^t	0	71	53.1 (52.9)	6.0 (5.8)	1.8 (1.8)	1 913vs, 1 788m, 1 681m[d]	2 141m	1.45 (9 H, s, Bu^t), 1.88 (15 H, s, C_5Me_5), 1.90 (15 H, s, C_5Me_5), 3.64 (3 H, s, CO_2Me), 3.72 (3 H, s, CO_2Me)
$C_6H_3Me_2\text{-}2,6$	0	66	55.2 (55.7)	5.6 (5.5)	1.7 (1.7)	1 917vs, 1 788m, 1 683m[d]	2 095m	1.85 (15 H, s, C_5Me_5), 1.95 (15 H, s, C_5Me_5), 2.44 (6 H, s, $C_6H_3\mathit{Me}_2$), 3.68 (6 H, s, CO_2Me), 7.1 (3 H, m, $C_6\mathit{H}_3Me_2$)
Bu^t	1	34	45.6 (44.6)	5.5 (4.9)	1.4 (1.5)[e]	2 012m, 1 986vs, 1 864m, 1 699m[d]	2 170m	

[a] Calculated values in parentheses. [b] In CH_2Cl_2; vs = very strong and m = medium. [c] In $CDCl_3$. [d] $\tilde{\nu}(CO)$ for ketonic carbonyl of CO_2Me groups. [e] Elemental analysis carried out at 0 °C

Table 2. Cyclic voltammetric data[a] for the oxidation of $[Mo_2(CO)_3L^1(\mu-R^1C\equiv CR^2)(\eta^5-L^2)_2]$

L^1	L^2	R^1	R^2	E_1^0/V	E_2^0/V	Δ/V[b]
CO	C_5H_5	CO_2Me	CO_2Me	0.62	1.03[c]	0.54[d]
CO	C_5Me_5	CO_2Me	CO_2Me	0.38	0.90[e]	0.52
CO	C_5Me_5	H	Ph	0.15	0.48	0.33
CO	C_5Me_5	Me	Me	−0.03	0.53	0.56
CO	C_9H_7	Me	Me	0.25	0.82[c]	0.53[d]
$CNBu^t$	C_5Me_5	CO_2Me	CO_2Me	0.05	0.67	0.62
$CNC_6H_3Me_2$-2,6	C_5Me_5	CO_2Me	CO_2Me	0.09	0.74	0.65

[a] Potentials are *versus* the aqueous saturated calomel electrode, measured at a platinum bead in CH_2Cl_2 with 0.1 mol dm^{-3} $[NBu^n{}_4][PF_6]$ as supporting electrolyte. Under these conditions the E^0 values for the complexes $[Fe(\eta-C_5H_5)_2]^+$–$[Fe(\eta-C_5H_5)_2]$ and $[Fe(\eta-C_5Me_5)_2]^+$–$[Fe(\eta-C_5Me_5)_2]$ are 0.47 and −0.07 V respectively. Unless otherwise stated, the oxidation processes are reversible. Where the process is irreversible, the oxidation peak potential, $(E_p)_{ox}$, at a scan rate, ν, of 100 mV s^{-1} is given. [b] $\Delta = E_2^0 - E_1^0$. Where the second process is irreversible, Δ is approximate; the peak potential $(E_p)_{ox}$ varies with scan rate and cannot be equated with E_2^0. [c] Completely irreversible oxidation; no return peak observed. [d] Δ is the difference, in volts, between the oxidation peak potentials for the two waves. [e] Incompletely reversible wave, E_2^0 estimated from $[(E_p)_{ox} + (E_p)_{red}]/2$ where $(E_p)_{ox}$ = oxidation peak potential.

Electrochemical Studies.—Cyclic voltammetry shows that each of the complexes $[Mo_2(CO)_3L^1(\mu-R^1C\equiv CR^2)(\eta^5-L^2)_2]$ (**1**) undergoes two sequential, diffusion-controlled ($i_{ox}/\nu^{\frac{1}{2}}$ = constant for scan rates $100 \leqslant \nu \leqslant 1\,000$ mV s^{-1}) one-electron oxidations at a platinum bead electrode in CH_2Cl_2 (Table 2). In all cases, the first oxidation is fully reversible (i_{red}/i_{ox} = 1.0 for scan rates $100 \leqslant \nu \leqslant 1\,000$ mV s^{-1}) and corresponds, at least on the cyclic voltammetric time-scale (see below), to the formation of the stable monocation ($\mathbf{1}^+$). By contrast, the reversibility of the second wave is variable, depending on L^1, L^2, *etc.* In most cases it is fully reversible implying some stability for the dication ($\mathbf{1}^{2+}$). For $[Mo_2(CO)_4(\mu-MeCO_2C\equiv CCO_2Me)(\eta-C_5Me_5)_2]$ however, full reversibility was only observed for $\nu \geqslant 1$ V s^{-1} (at ν = 50 mV s^{-1}, for example, i_{red}/i_{ox} = 0.74), and for $[Mo_2(CO)_4(\mu-MeCO_2C\equiv CCO_2Me)(\eta^5-C_9H_7)_2]$ the wave was irreversible at all scan rates used.

A comparison of the potentials for the first oxidation step (E_1^0/V) (Table 2) shows the expected trends in that E_1^0 becomes more negative (oxidation is easier) (*i*) as CO is replaced by isocyanide (by *ca.* 0.3—0.4 V), and (*ii*) with a decrease in the electron-withdrawing properties of the alkyne and η^5-ring substituents. Overall, the variation of L^1, L^2, R^1, and R^2 leads to E_1^0 values ranging from −0.03 to 0.62 V.

Where comparisons can be made, the same trends are shown by E_2^0. The difference between E_2^0 and E_1^0 (Δ/V) is nearly constant (*ca.* 0.5—0.6 V) apart from that for the complex $[Mo_2(CO)_4(\mu-PhC\equiv CH)(\eta-C_5Me_5)_2]$ where the two oxidation waves are much more closely spaced (Δ = 0.33 V).

The low values of E_1^0 and the reversibility of the first oxidation wave suggested that the monocations ($\mathbf{1}^+$) might be readily prepared by electrochemical or chemical oxidation. Accordingly $[Mo_2(CO)_4(\mu-MeC\equiv CMe)(\eta-C_5Me_5)_2]$, having the most negative E_1^0 value, was electrolysed at 0.1 V at a platinum basket electrode in CH_2Cl_2. After 20 min, and the passage of 0.9 F mol^{-1} of current, a deep violet solution had been produced, showing one oxidation wave and one reduction wave at potentials identical to those for the oxidations of $[Mo_2(CO)_4(\mu-MeC\equiv CMe)(\eta-C_5Me_5)_2]$. Further electrolysis at 0.7 V, a potential more positive than that of the second oxidation wave of $[Mo_2(CO)_4(\mu-MeC\equiv CMe)(\eta-C_5Me_5)_2]$ again resulted in the passage of *ca.* 0.9 F mol^{-1} of current, and a darkening of the solution to near black. However, the cyclic voltammogram of the product showed no waves which could be attributed to either the dication or to other identifiable species. Thus, the electrolytic study implies that $[Mo_2(CO)_4(\mu-MeC\equiv CMe)(\eta-C_5Me_5)_2]^+$ is stable at least on the time-scale of the experiment but that further oxidation leads to destruction of the complex.

Chemical Oxidation of (**1**).—The addition of $[Fe(\eta-C_5H_5)_2][PF_6]$ or $[N_2C_6H_4F$-*p*$][PF_6]$ to $[Mo_2(CO)_4(\mu-R^1C\equiv CR^2)(\eta-C_5Me_5)_2]$ ($R^1 = R^2$ = Me or CO_2Me, R^1 = H, R^2 = Ph) in CH_2Cl_2 gave in all cases a deep violet solution showing i.r. carbonyl absorptions shifted to higher wavenumber by 55—80 cm^{-1} [*e.g.* $R^1 = R^2$ = Me, $\tilde{\nu}(CO)$ = 2 020m, 1 966s, and 1 886m cm^{-1}; *cf.* (**1**), $L^2 = C_5Me_5$, L^1 = CO, $R^1 = R^2$ = Me, $\tilde{\nu}(CO)$ = 1 965m, 1 892s, and 1 807m cm^{-1}], as expected for the formation of ($\mathbf{1}^+$). However, despite the electrochemical results described above, which implied prolonged stability for the monocation, the i.r. spectra of the deep violet solutions soon showed new terminal carbonyl bands due to unidentified decomposition products.

Although the cations ($\mathbf{1}^+$) slowly decompose at room temperature, the e.s.r. spectrum of $[Mo_2(CO)_4(\mu-MeC\equiv CMe)(\eta-C_5Me_5)_2]^+$ was obtained by generating the sample *in situ*. Thus, the addition of CH_2Cl_2 to a solid mixture of $[Mo_2(CO)_4(\mu-MeC\equiv CMe)(\eta-C_5Me_5)_2]$ and $[Fe(\eta-C_5H_5)_2][PF_6]$ resulted in an intense single-line signal (g = 2.04), flanked by satellites due to molybdenum hyperfine coupling [$A(^{95,97}Mo)$ = 12.5 G, $I = \frac{5}{2}$], which slowly decayed as ($\mathbf{1}^+$) decomposed.

Although the tetracarbonyl cations have been only partially characterised, the paramagnetic salt $[Mo_2(CO)_3(CNBu^t)(\mu-MeCO_2C\equiv CCO_2Me)(\eta-C_5Me_5)_2][PF_6]$ has been prepared by $[Fe(\eta-C_5H_5)_2][PF_6]$ oxidation of $[Mo_2(CO)_3(CNBu^t)(\mu-MeCO_2C\equiv CCO_2Me)(\eta-C_5Me_5)_2]$ in CH_2Cl_2 at 0 °C. The violet complex is thermally unstable (it may be kept overnight at −20 °C under nitrogen) so that all spectroscopic studies were carried out rapidly (i.r.) or at low temperature (e.s.r.); the elemental analysis (Table 1) was also carried out at 0 °C.

The i.r. spectrum of the salt (Table 1), in the region 2 200—1 600 cm^{-1}, is almost identical to that of $[Mo_2(CO)_3(CNBu^t)(\mu-MeCO_2C\equiv CCO_2Me)(\eta-C_5Me_5)_2]$ in terms of the relative intensities and separations of the absorption bands. However, the frequencies are shifted to higher wavenumber, by *ca.* 30 cm^{-1} for $\tilde{\nu}(CN)$, by 75 cm^{-1} for both the terminal and semibridging carbonyl ligands, and by 18 cm^{-1} for the ketonic carbonyl group of the alkyne. This undoubtedly shows that there is no major structural change on oxidation, and the retention of the semibridging carbonyl group also perhaps suggests that there is little alteration in the metal–metal bond length. The anisotropic e.s.r. spectrum of $[Mo_2(CO)_3(CNBu^t)(\mu-Me_2CO_2C\equiv CCO_2Me)(\eta-C_5Me_5)_2]^+$ in frozen CH_2Cl_2 at −140 °C, shows three g values at 2.098, 2.011, and 1.999, the average value of which (2.036) is in excellent agreement with g_{av} for $[Mo_2(CO)_4(\mu-MeC\equiv CMe)(\eta-C_5Me_5)_2]^+$ at room temperature.

The salt $[Mo_2(CO)_3(CNBu^t)(\mu-MeCO_2C\equiv CCO_2Me)(\eta-C_5Me_5)_2][PF_6]$ decomposes at room temperature, slowly (hours) in the solid state but more rapidly in CH_2Cl_2, resulting in the appearance of new carbonyl and isocyanide bands in the i.r. spectrum. That only terminal absorptions are observed {*e.g.* for $[Mo_2(CO)_3(CNBu^t)(\mu-MeCO_2C\equiv CCO_2Me)(\eta-C_5Me_5)_2]^+$, $\tilde{\nu}(CN)$ = 2 178s, $\tilde{\nu}(CO)$ = 2 044s, and 1 992s cm^{-1}} suggests bridge cleavage of the paramagnetic cations to mononuclear products.

In summary, the binuclear complexes (**1**) do undergo two sequential one-electron oxidations, but subsequently ligand deprotonation does not occur, even from PhC≡CH. As in the case of $[Pd_2(\mu\text{-}PhC{\equiv}CPh)(\eta\text{-}C_5Ph_5)_2]$,[7] alkyne-bridge cleavage can follow the loss of either one or two electrons from the binuclear unit.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. The compounds $[Mo_2(CO)_3L^1(\mu\text{-}R^1C{\equiv}CR^2)(\eta^5\text{-}L^2)_2]$ (L^2 = C_5H_5, L^1 = CO, $R^1 = R^2 = CO_2Me$; $L^2 = C_5Me_5$, L^1 = CO, $R^1 = R^2$ = Me or CO_2Me, R^1 = H, R^2 = Ph)[4,5] and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$[8] were prepared by published methods.

Infrared spectra were recorded on a Perkin-Elmer 1710 IFTS instrument. Hydrogen-1 n.m.r. spectra were recorded on a JEOL JNM GX-270 spectrometer and calibrated against $SiMe_4$ as internal reference. *X*-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 instrument and were calibrated against a solid sample of the diphenylpicrylhydrazyl radical.

Electrochemical studies were carried out as described previously.[9] Solutions were 0.5×10^{-3} mol dm^{-3} and 1.0×10^{-3} mol dm^{-3} in complex for voltammetry and controlled potential electrolysis respectively; in both cases the solutions were 0.1 mol dm^{-3} in $[NBu^n_4][PF_6]$ as supporting electrolyte. Under these conditions, the E^0 values for the couples $[Fe(\eta\text{-}C_5H_5)_2]^+\text{–}[Fe(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5Me_5)_2]^+\text{–}[Fe(\eta\text{-}C_5Me_5)_2]$ are 0.47 and −0.07 V respectively. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Tricarbonyl(μ-*dimethylacetylenedicarboxylate*)*bis*(η-*pentamethylcyclopentadienyl*)(*t-butyl isocyanide*)*dimolybdenum*, $[Mo_2(CO)_3(CNBu^t)(MeCO_2C{\equiv}CCO_2Me)(\eta\text{-}C_5Me_5)_2]$.—A mixture of $[Mo_2(CO)_4(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)(\eta\text{-}C_5Me_5)_2]$ (0.50 g, 0.70 mmol) and $CNBu^t$ (0.2 cm^3, 2.4 mmol) was heated under reflux in toluene (30 cm^3) for 2 h. After cooling to room temperature, the red mixture was evaporated to dryness. The residue was then dissolved in a minimum volume of CH_2Cl_2 and added to an n-hexane–alumina chromatography column. Elution of the red band with CH_2Cl_2–n-hexane (2:1), evaporation of the eluate to dryness, and crystallisation from n-hexane at 0 °C gave the product as red crystals, yield 0.39 g (71%).

The complex $[Mo_2(CO)_3(CNC_6H_3Me_2\text{-}2,6)(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)(\eta\text{-}C_5Me_5)_2]$ was prepared similarly except that elution from the chromatography column required a 1:3 mixture of CH_2Cl_2–n-hexane.

Both of the complexes dissolved in common organic solvents to give red solutions which slowly decompose in air.

Tricarbonyl(μ-*dimethylacetylenedicarboxylate*)*bis*(η-*pentamethylcyclopentadienyl*)(*t-butyl isocyanide*)*dimolybdenum Hexafluorophosphate*, $[Mo_2(CO)_3(CNBu^t)(\mu\text{-}MeCO_2C{\equiv}CCO_2Me)(\eta\text{-}C_5Me_5)_2][PF_6]$.—To a cooled (0 °C) solution of $[Mo_2(CO)_3(CNBu^t)(\mu\text{-}MeCO_2{\equiv}CCO_2Me)(\eta\text{-}C_5Me_5)_2]$ (0.10 g, 0.13 mmol) in CH_2Cl_2 (25 cm^3) was added $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (43 mg, 0.13 mmol). After 10 min, pre-cooled n-hexane (50 cm^3) was added to the deep violet solution. Evaporation to low volume *in vacuo* gave the product which was recrystallised from CH_2Cl_2–n-hexane at 0 °C to give a violet-black solid, yield 0.04 g (34%).

The solid complex may be stored at −20 °C overnight under nitrogen but rapidly decomposes at room temperature. The complex dissolves in polar solvents such as CH_2Cl_2 and thf to give deep violet solutions which very rapidly decompose.

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