Notes

Open-shell Molybdenum Carbonyl Complexes and the Binding of π-Acid Ligands to Higher-oxidation-state Molybdenum Sites

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Molybdenum sites which have a mixed-ligand tertiary phosphine and dithiocarbamate environment bind carbon monoxide at three oxidation levels, Mo^{II} and open-shell Mo^{III} and Mo^{IV}. The complex $[Mo^{III}(CO)(S_2CNEt_2)_2(Ph_2PCH_2CH_2PPh_2)]^+$ is stable in tetrahydrofuran at 0 °C and may be prepared by low-temperature controlled-potential electrolysis. The open-shell Mo^{III}–CO and Mo^{IV}–CO complexes are new; their significance to the binding of π-acid ligands to higher-oxidation-state molybdenum sites in the nitrogenase system is briefly discussed.

ELECTRON-DEFICIENT open-shell molybdenum carbonyl complexes (*i.e.* complexes with less than an 18-electron valence-orbital complement) are relatively rare and generally unstable: those which are also in a high formal oxidation state of Mo such as III are exceptional,[1a] whilst seven-co-ordinate Mo^{IV}–CO species have not hitherto been reported.

We are interested in defining the coligand environment necessary to stabilise the binding of π-acid ligands such as CO and N_2 to such higher-oxidation-state open-shell molybdenum centres.[1b] Both CO and N_2 are believed to bind to a molybdenum site in the enzyme nitrogenase, although the highest oxidation level of Mo with which these substrates can first interact is unknown. A simple question which we consider here is whether it is chemically feasible for open-shell molybdenum-(III) or -(IV) intermediates with CO or N_2 to be involved in the (reductive) interactions of nitrogenase with CO or N_2.

Our approach has been to synthesise electron-rich closed-shell monocarbonylmolybdenum(II) precursors in which we take advantage of the electron releasing properties of tertiary phosphine ligands and the ability of dithiocarbamato-coligands to stabilise seven-co-ordinate Mo in the higher oxidation states. The properties of these complexes, which are of the type $[Mo(CO)(S_2CNEt_2)_2L_2]$ and $[Mo(CO)(S_2CNEt_2)_2(dppe)]$ (L = PMe_2Ph or $PMePh_2$; dppe = $Ph_2PCH_2CH_2PPh_2$) and which may be synthesised according to reactions (1) or (2) (see Experimental section), are listed in the Table. Each complex has a relatively low ν(CO) and oxidises at a low potential consistent with its being electron-rich.[2,3] Although dicarbonyl complexes of the type $[Mo(CO)_2(S_2CNEt_2)_2L_2]$ have been reported these represent the first monocarbonyls in this series.[4]

$$[Mo(CO)_4Cl_2] \xrightarrow{S_2CNEt_2^-} [Mo(CO)_3(S_2CNEt_2)_2] \xrightarrow{dppe} [Mo(CO)(S_2CNEt_2)_2(dppe)] \quad (1)$$

$$[MoCl_2(CO)_2(PPh_3)_2] \xrightarrow{L} [MoCl_2(CO)_2L_2] \xrightarrow{Na[S_2CNEt_2]} [Mo(CO)(S_2CNEt_2)_2L_2] \quad (2)$$

Cyclic voltammetry at a platinum electrode in acetonitrile or tetrahydrofuran containing 0.2 mol dm^{-3} $[NBu_4][BF_4]$ shows that these molybdenum(II) complexes undergo two successive one-electron oxidations. In each case, the primary oxidation is electrochemically reversible in the scan rate range 0.01—0.3 V s^{-1}, whereas electrochemical reversibility for the secondary oxidation process is only observed for the dppe complex at scan rates in excess of 10 V s^{-1}. Thus these complexes oxidise to Mo^{III}–CO and Mo^{IV}–CO open-shell species according to reaction (3). From the cyclic voltammetry experiments it is clear that the molybdenum(III) species are stable for at least several seconds whereas the molybdenum(IV) species are only stable on the ms time scale. Product reduction waves observed during cyclic voltammetry are consistent with the loss of CO, anation, and formation of the stable molybdenum(IV) complexes [reaction (3)] as the decomposition pathway of the Mo^{IV}–CO species.[5]

Analytical, i.r., and redox data

Complex	Analysis (%) [a]			M.p. (θ_c/°C)	I.r. bands (cm^{-1}) [b]		Oxidation step [c]	
	C	H	N		ν(CO)	ν(CN)	I $E_{\frac{1}{2}}^{ox}$/V [d]	II E_p^{ox}/V [e]
$[Mo(CO)(S_2CNEt_2)_2(PMe_2Ph)_2]$	46.4 (46.4)	6.1 (6.3)	4.0 (4.0)	109—111	1 750	1 495	0.09	0.99
$[Mo(CO)(S_2CNEt_2)_2(PMePh_2)_2]$	54.1 (54.1)	5.9 (5.6)	3.5 (3.4)	108—109	1 755	1 490	0.18	1.20
$[Mo(CO)(S_2CNEt_2)_2(dppe)]$	53.9 (54.3)	5.9 (5.6)	3.4 (3.4)	119—121	1 790	1 495	0.24	1.03
			Range:	±1	±2.5	±2.5	±0.01	±0.01

[a] Calculated values are given in parentheses. [b] Nujol mulls. [c] Stoicheiometry of electrode reaction, $n = 1$; $i_p v^{-\frac{1}{2}}$ [complex]$^{-1}$/$i_p v^{-\frac{1}{2}}[Fe(\eta\text{-}C_5H_5)_2]^{-1}$ = *ca.* 0.7—0.8 where $i_p/v^{\frac{1}{2}}[Fe(\eta\text{-}C_5H_5)_2]$ = 2.3 dm^3 s$^{\frac{1}{2}}$ A^{-3} V$^{-\frac{1}{2}}$ mol^{-1} at the platinum electrode. [d] *Versus* the s.c.e. in tetrahydrofuran–0.2 mol dm^{-3} $[NBu_4][BF_4]$. The value for the $[Fe(\eta\text{-}C_5H_5)_2]$–$[Fe(\eta\text{-}C_5H_5)_2]^+$ couple is 0.55 V *versus* s.c.e. in this system. [e] Peak potential at 0.3 V s^{-1}.

The electrochemical behaviour of these mixed-ligand molybdenum(II) complexes is in contrast to that of

$$\underset{\text{18-electron Mo}^{\text{II}}}{[Mo(CO)(S_2CNEt_2)_2(L_2 \text{ or dppe})]} \underset{+e}{\overset{-e}{\rightleftharpoons}} \underset{\text{17-electron Mo}^{\text{III}}}{[Mo(CO)(S_2CNEt_2)_2(L_2 \text{ or dppe})]^+}$$

$$\underset{+e}{\overset{-e}{\rightleftharpoons}} \underset{\substack{\text{16-electron Mo}^{\text{IV}} \\ \text{(unstable)}}}{[Mo(CO)(S_2CNEt_2)_2(L_2 \text{ or dppe})]^{2+}} \underset{-CO}{\overset{BF_4^-}{\rightleftharpoons}} \underset{\text{Mo}^{\text{IV}}}{[MoF(S_2CNEt_2)_2(L_2 \text{ or dppe})]^+} \quad (3)$$

$[Mo(CO)_6]$, $[Mo(CO)_2(S_2CNEt_2)_2(PPh_3)]$, or $[MoX_2(CO)_3(PPh_3)_2]$ (X = Cl, Br, or I) which oxidise irreversibly or are inaccessible to electrochemical oxidation.[6,7] They more closely parallel that of the molybdenum(0) species *trans*-$[Mo(CO)_2(dppe)_2]$ which oxidises reversibly (albeit with *cis–trans* isomerisation) at a relatively negative potential of −0.11 V *versus* the saturated calomel electrode (s.c.e.).[2,8]

A solution of the molybdenum(III) carbonyl, which is indefinitely stable at 0 °C, may be prepared by controlled-potential electrolysis of $[Mo(CO)(S_2CNEt_2)_2(dppe)]$ in tetrahydrofuran–0.2 mol dm^{-3} $[NBu_4][BF_4]$ at a platinum electrode. Thus, at −10 °C the orange solution of the molybdenum(II) precursor may be oxidised in this medium at +0.3 V *vs.* s.c.e. to give a dark red solution of the Mo^{III}–CO complex. Plots of current *versus* charge passed show that 1 F per mol of complex is consumed, whilst *in situ* cyclic voltammetry before and after electrolysis establishes the simple overall one-electron oxidation. In addition, monitoring the electrolysis by low-temperature i.r. spectroscopy reveals that the ν(CO) band at 1 790 cm^{-1} is replaced by a new band at 1 930 cm^{-1}, and, at the *end* of electrolysis, this band is of comparable intensity to that at 1 790 cm^{-1} *before* oxidation of the complex. These results unambiguously define the nature of the oxidised product as $[Mo(CO)(S_2CNEt_2)_2(dppe)]^+$.

In related work,[5] we have shown that an electrochemically generated molybdenum(III) site, $[Mo(S_2CNEt_2)_2(dppe)]^+$, reacts rapidly with CO to give the Mo^{III}–CO species whereas, under the same conditions, N_2 does not react. Clearly, CO could bind at a higher oxidation level than N_2 in the nitrogenase system, and binding to open-shell molybdenum-(III) or -(IV) sites is chemically feasible for this substrate. This in turn suggests that it may well be possible to detect stable higher-oxidation-state (III or IV) Mo–CO species during redox transformations of the enzyme under CO.

EXPERIMENTAL

Unless otherwise stated, experiments were carried out under an atmosphere of dinitrogen using conventional Schlenk-tube techniques. Infrared spectra were recorded as Nujol mulls using a Pye-Unicam SP 2000 spectrophotometer, ^{1}H n.m.r. spectra on a JEOL PS 100 spectrometer in solution using $SiMe_4$ as internal standard. Carbon, hydrogen, nitrogen, and halogen analyses were performed by Mr. and Mrs. A. Olney of the University of Sussex.

The complexes $[MoCl_2(CO)_4]$,[9] $[Mo(CO)_3(S_2CNEt_2)_2]$,[10] and $[MoCl_2(CO)_2(PMe_2Ph)_3]\cdot MeOH$ [11] were prepared by literature methods. The mono-and di-tertiary phosphines were prepared by standard procedures and all other chemicals were used as purchased.

Carbonylbis(dimethyldithiocarbamato)bis(dimethylphenylphosphine)molybdenum.—The complex $[MoCl_2(CO)_2(PMe_2Ph)_3]\cdot MeOH$ (0.5 g) and sodium diethyldithiocarbamate (0.5 g) in methanol (40 cm^3) were heated under reflux for 0.5 h. The resultant red-orange solution was reduced to *ca.* 5 cm^3 *in vacuo*, giving an orange-red microcrystalline product which was recrystallised as red prisms from dichloromethane–methanol (66%). The complex $[Mo(CO)(S_2CNEt_2)_2(PMePh_2)_2]$ was prepared similarly from $[MoCl_2(CO)_2(PMePh_2)_2]$ and $Na[S_2CNEt_2]$.

[1,2-Bis(diphenylphosphino)ethane]carbonylbis(diethyldithiocarbamato)molybdenum.—The complex $[Mo(CO)_3(S_2CNEt_2)_2]$ (0.7 g) and 1,2-bis(diphenylphosphino)ethane (0.7 g) were heated in methanol (40 cm^3) under reflux for 0.5 h. The resultant orange solid was crystallised as orange plates from CH_2Cl_2–MeOH (80%).

Electrochemical Studies.—The following instrumentation was employed: Hi-Tek Instruments potentiostat, type DT 2101; Chemical Electronics waveform generators, types RB1 or 01; Bryans XY recorder, type 26000 A 3; Hewlett Packard storage oscilloscope, type 1201 A; and Chemical Electronics integrator. Cyclic voltammetry was carried out in dry dinitrogen-saturated acetonitrile or tetrahydrofuran with 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$ as supporting electrolyte. Controlled-potential electrolyses were performed in dry tetrahydrofuran–0.2 mol dm^{-3} $[NBu_4][BF_4]$. The cells used have been described elsewhere.[6]

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