Oxidation and Reduction of *cis*-Bis(2,2′-bipyridine)dicarbonylmolybdenum(0) and -tungsten(0). Preparation of Bis(2,2′-bipyridine)dicarbonyl(solvent)molybdenum(II) Bis(tetrafluoroborate) Salts and their Reaction with Isocyanides †

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Oxidation of *cis*-$[\mathrm{M(CO)_2(bipy)_2}]$ (M = Mo or W; bipy = 2,2′-bipyridine) with silver(I) tetrafluoroborate in solution produces red-brown, diamagnetic $[\mathrm{Mo_2(CO)_4(bipy)_4}][\mathrm{BF_4}]_2$ or orange *cis*-$[\mathrm{W(CO)_2(bipy)_2}][\mathrm{BF_4}]$. $[\mathrm{Mo_2(CO)_4(bipy)_4}][\mathrm{BF_4}]_2$ dissociates in acetone solution to form green, paramagnetic *trans*-$[\mathrm{Mo(CO)_2(bipy)_2}][\mathrm{BF_4}]$. Addition of one equivalent of silver(I) ion to the metal(I) cations in solution produces *cis*-$[\mathrm{Mo(CO)_2(bipy)_2(solvent)}][\mathrm{BF_4}]_2$ (solvent = MeCN, $\mathrm{Me_2CO}$, or $\mathrm{H_2O}$) or *cis*-$[\mathrm{W(CO)_2(bipy)_2}][\mathrm{BF_4}]_2$. Oxidation of *cis*-$[\mathrm{Mo(CO)_2(phen)_2}]$ (phen = 1,10-phenanthroline) with $\mathrm{Ag[BF_4]}$ (two equivalents) in acetonitrile produces *cis*-$[\mathrm{Mo(CO)_2(phen)_2(NCMe)}][\mathrm{BF_4}]_2$. *cis*-$[\mathrm{Mo(CO)_2(bipy)_2}]$ reacts with $[\mathrm{NO}][\mathrm{PF_6}]$ to form $[\mathrm{Mo(CO)(NO)(bipy)_2}][\mathrm{PF_6}]$. Addition of isocyanides, RNC (R = Et or $\mathrm{C_6H_4Me}$-*p*), to *cis*-$[\mathrm{Mo(CO)_2(bipy)_2(NCMe)}][\mathrm{BF_4}]_2$ in acetonitrile solution at room temperature produces, successively, $[\mathrm{Mo(CNR)_3(bipy)_2}][\mathrm{BF_4}]_2$ and $[\mathrm{Mo(CNR)_5(bipy)}][\mathrm{BF_4}]_2$. The new complexes have been characterised by microanalysis, spectroscopy [i.r., ^{1}H, and ^{13}C n.m.r., mass (fast atom bombardment), electronic absorption], conductivity measurements, and electrochemistry in solution. Reduction of *cis*-$[\mathrm{Mo(CO)_2(bipy)_2}]$ with sodium amalgam in tetrahydrofuran solution produces paramagnetic *cis*-$[\mathrm{Mo(CO)_2(bipy)_2}]^{\cdot -}$. Reaction of CNEt with $[\{\mathrm{Mo(CO)_4Cl_2}\}_2]$ in dichloromethane, followed by anion exchange with $[\mathrm{NH_4}][\mathrm{PF_6}]$ produces $[\mathrm{Mo(CNEt)_7}][\mathrm{PF_6}]_2$.

The oxidation of ditertiary phosphine complexes of the Group 6 metals of the general type *cis*-$[\mathrm{M(CO)_2(P{-}P)_2}]$ [P–P = $\mathrm{CH_2(PPh_2)_2}$ (dppm), M = Cr, Mo, or W; [1] P–P = $\mathrm{(CH_2PPh_2)_2}$ (dppe), M = Mo or W; [2] P–P = $\mathrm{(CH_2PMe_2)_2}$ (dmpe), M = Cr or Mo [3]] with various agents ($\mathrm{Ag^I}$ ion, $\mathrm{I_2}$, $[\mathrm{NO}][\mathrm{PF_6}]$) has drawn attention to the isomerisation processes which occur. The stereochemistry of the carbonyl ligands changes on successive one-electron oxidations, thus: *cis* $\mathrm{M^0} \longrightarrow$ *trans* $\mathrm{M^I} \longrightarrow$ *cis* $\mathrm{M^{II}}$. Similar observations have been made using electrochemistry which show that rapid isomerisation follows electron transfer.[4] Redox isomerisation reactions have also been observed [5] in related complexes of manganese(I), $[\mathrm{Mn(CO)_3X(P{-}P)}]$ (X = Cl or Br). Other studies have shown [6] that a contrasting *trans* $\mathrm{M^0} \longrightarrow$ *cis* $\mathrm{M^I} \longrightarrow$ *trans* $\mathrm{M^{II}}$ redox series exists for $[\mathrm{MoL_2(P{-}P)_2}]$ (L = $\mathrm{N_2}$, CNR, or $\mathrm{C_2H_4}$) complexes. An explanation has been proposed [7] on the basis of extended Hückel molecular orbital calculations, which suggest that the stereochemical changes depend on the number of valence electrons and, in a complementary fashion, on whether the ligands are π-donors or π-acceptors.

In order to observe the influence on redox behaviour of a major change in the character of the non-carbonyl ligands we have studied the redox chemistry of *cis*-$[\mathrm{M(CO)_2(bipy)_2}]$ (bipy = 2,2′-bipyridine). The presence of bipy ligands is expected to favour outer-sphere electron-transfer reactions. We hoped that these ligands, which have a higher donor : acceptor ratio than the ditertiary phosphine ligands, P–P, and in which the acceptor character is (*d*–π*)π rather than (*d*–*d*)π, would produce a decrease in the oxidation potentials which would serve to stabilise the intermediate metal(I) complex and that it might be possible to isolate a dication, such as $[\mathrm{M(CO)_2(bipy)_2}]^{2+}$ or $[\mathrm{M(CO)_2(bipy)_2(solvent)}]^{2+}$, which is not accessible in the bis(ditertiary phosphine) complexes. Previous work has shown that, like the *cis*-$[\mathrm{Mo(CO)_2(P{-}P)_2}]$ complexes which react with $\mathrm{I_2}$ to form *cis*-$[\mathrm{MoI(CO)_2(P{-}P)_2}]\mathrm{I}$, the complex *cis*-$[\mathrm{MoI(CO)_2(bipy)_2}]\mathrm{I}$ is formed [8a] from *cis*-$[\mathrm{Mo(CO)_2(bipy)_2}]$.

We report the redox chemistry of *cis*-$[\mathrm{M(CO)_2(bipy)_2}]$ (M = Mo or W) which has led to the preparation and characterisation of *cis*-$[\mathrm{Mo(CO)_2(bipy)_2(solvent)}]^{2+}$ (solvent = MeCN, $\mathrm{Me_2CO}$, or $\mathrm{H_2O}$) and *cis*-$[\mathrm{W(CO)_2(bipy)_2}]^{2+}$ as stable species. Some chemical reactions of *cis*-$[\mathrm{Mo(CO)_2(bipy)_2(NCMe)}][\mathrm{BF_4}]_2$ with isocyanides are described.[8b]

Results

Careful addition of solid silver(I) tetrafluoroborate (1 mol equiv.) to a solution/slurry of *cis*-$[\mathrm{Mo(CO)_2(bipy)_2}]$ in acetonitrile which was stirred rapidly at room temperature resulted in the formation of the red-brown complex $[\mathrm{Mo_2(CO)_4(bipy)_4}][\mathrm{BF_4}]_2$. This diamagnetic solid dissolves in warm acetone to give a green solution from which green, paramagnetic ($g_{\mathrm{av.}} = 1.980$ in solution) *trans*-$[\mathrm{Mo(CO)_2(bipy)_2}][\mathrm{BF_4}]$ was isolated. Addition of 1 mol equiv. of silver(I) tetrafluoroborate to either red-brown $[\mathrm{Mo_2(CO)_4(bipy)_4}][\mathrm{BF_4}]_2$ or green *trans*-$[\mathrm{Mo(CO)_2(bipy)_2}][\mathrm{BF_4}]$ in acetonitrile produces a yellow-brown complex *cis*-$[\mathrm{Mo(CO)_2(bipy)_2(NCMe)}][\mathrm{BF_4}]_2$. The same product is obtained when 2 mol equiv. of silver(I) tetrafluoroborate are added directly to the solution/slurry of *cis*-$[\mathrm{Mo(CO)_2(bipy)_2}]$ in acetonitrile at room temperature.

Reaction of *cis*-$[\mathrm{Mo(CO)_2(bipy)_2(NCMe)}][\mathrm{BF_4}]_2$ with either sodium dihydronaphthylide in tetrahydrofuran (thf) or sodium amalgam in the same solvent causes reduction first, and rapidly, to $[\mathrm{Mo_2(CO)_4(bipy)_4}][\mathrm{BF_4}]_2$ and then more slowly to *cis*-$[\mathrm{Mo(CO)_2(bipy)_2}]$. The molybdenum(0) complex can be reduced further in a slower reaction to give a paramagnetic species *cis*-$[\mathrm{Mo(CO)_2(bipy)_2}]^{\cdot -}$ which was not isolated as an analytically pure solid, but was characterised by spectroscopy [ν(CO) 1 770, 1 680 cm^{-1}; $g_{\mathrm{av.}} = 1.981$].

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† *Non-S.I. units employed:* 1 eV ≈ 1.60 × 10^{-19} J; 1 mmHg = 13.6 × 9.8 Pa.

Oxidation of *cis*-$[Mo(CO)_2(bipy)_2]$ with silver(I) tetrafluoroborate (2 mol equiv.) in water produces the yellow aqua-salt *cis*-$[Mo(CO)_2(bipy)_2(OH_2)][BF_4]_2$ [ν(OH) 3 260 cm^{-1}], which is converted to *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ on dissolution in acetonitrile. Oxidation of *cis*-$[Mo(CO)_2(bipy)_2]$ with silver(I) hexafluorophosphate in acetone produces the orange-yellow salt *cis*-$[Mo(CO)_2(bipy)_2(OCMe_2)][PF_6]_2$: the acetone is displaced on stirring the salt in acetonitrile solution to produce *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][PF_6]_2$.

A solution of *cis*-$[Mo(CO)_2(phen)_2]$ (phen = 1,10-phenanthroline) in dichloromethane can be oxidised by the addition of a solution of silver(I) tetrafluoroborate (2 mol equiv.) in acetonitrile giving *cis*-$[Mo(CO)_2(phen)_2(NCMe)][BF_4]_2$. This reaction has the advantage of being homogeneous throughout.

The tungsten complex *cis*-$[W(CO)_2(bipy)_2]$ reacts with silver(I) tetrafluoroborate (1 mol equiv.) in acetonitrile–dichloromethane (*ca.* 1 : 1 v/v) to give the bright orange tungsten(I) complex *cis*-$[W(CO)_2(bipy)_2][BF_4]$; with a further mol equiv. of silver(I) tetrafluoroborate, oxidation to a six-co-ordinate tungsten(II) salt, *cis*-$[W(CO)_2(bipy)_2][BF_4]_2$, occurs. These reactions in a mixed solvent are homogeneous: in acetonitrile alone the reaction is heterogeneous, but the product is the same.

The neutral complex *cis*-$[Mo(CO)_2(bipy)_2]$ reacts rapidly with nitrosyl hexafluorophosphate (1 mol equiv.) in acetonitrile to give a green, diamagnetic solution from which crystals of $[Mo(CO)(NO)(bipy)_2][PF_6]$ were isolated. Addition of further $[NO][PF_6]$ to this solution produced only intractable oily materials. As expected, *cis*-$[Mo(CO)_2(bipy)_2]$ reacts rapidly with hydrogen chloride and with carbon tetrachloride at or below room temperature, to give molybdenum(II) dicarbonyl complexes in which the bipy ligands have been partially chlorinated, as indicated by i.r. and ^1H n.m.r. spectra. It is important to note that the ^1H n.m.r. spectrum of the product of the reaction between HCl and *cis*-$[Mo(CO)_2(bipy)_2]$ contains *no evidence* which might suggest that protonation had occurred at the metal giving a hydrido-metal complex.

Reaction between *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ and ethyl- or *p*-tolyl-isocyanide in acetonitrile solution at room temperature or below proceeds rapidly, causing evolution of carbon monoxide. Addition of 3 mol equiv. of isocyanide, RNC (R = Et or C_6H_4Me-*p*), to *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ gives $[Mo(CNR)_3(bipy)_2][BF_4]_2$ as purple (R = Et) or red (R = C_6H_4Me-*p*) crystalline solids. The addition of excess isocyanide to *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ produces $[Mo(CNR)_5(bipy)][BF_4]_2$ as red (R = Et) or deep orange (R = C_6H_4Me-*p*) crystalline solids. Further substitution to give $[Mo(CNR)_7][BF_4]_2$ could not be achieved, even under forcing conditions: however, this homoleptic seven-co-ordinate cation was prepared quite simply from the reaction between $[\{Mo(CO)_4Cl_2\}_2]$ and ethyl isocyanide in dichloromethane solution.

Discussion

Careful experiments using electrochemistry [4] and ^{31}P n.m.r. spectroscopy [9] have shown that the isomerisation which accompanies one-electron oxidation of *cis*-$[Mo(CO)_2(P\text{-}P)_2]$ (P-P = dppm, dppe, dmpe, and other ditertiary phosphines) to *trans*-$[Mo(CO)_2(P\text{-}P)_2]^+$ involves a non-dissociative distortion (twist) of the chelating ligands through a trigonal-biprismatic intermediate, rather than a dissociative process.[10] The results of the present investigation are in agreement with these findings and indicate that the greater rigidity of the bipy ligand in *cis*-$[M(CO)_2(bipy)_2]$ may either impede the isomerisation (M = Mo) or inhibit it completely (M = W).

Oxidation of *cis*-$[Mo(CO)_2(bipy)_2]$ to give the dimeric dication $[Mo_2(CO)_4(bipy)_4]^{2+}$ can also be effected by silver(I) hexafluorophosphate and by aluminium trichloride in dichloromethane.[11] The characterisation of the molybdenum(I) dinuclear dication is based on the following evidence from physicochemical measurements. Conductivity measurements on the tetrafluoroborate salt as a function of concentration in solution are consistent [12] with a 1 : 2 ($CaCl_2$ type) electrolyte. The complex does not give an e.s.r. spectrum at room temperature in solution. A complex but unshifted and well resolved ^1H n.m.r. spectrum is observed, which contrasts with the (deceptively) simple spectrum of *cis*-$[Mo(CO)_2(bipy)_2]$ [13] and of *cis*-$[Mo(CO)_2(bipy)_2(solvent)]^{2+}$ salts discussed below. We have not been able to assign this spectrum completely but it is consistent with diamagnetism. The fast atom bombardment (f.a.b.) mass spectrum of the tetrafluoroborate salt shows a group of ions around *m/e* 1 101 (based on ^{96}Mo) corresponding to the [(formula mass) − 1]$^+$ ion in $[Mo_2(CO)_4(bipy)_4][BF_4]_2$. The i.r. spectrum of the solid in the region 2 000—1 600 cm^{-1} shows two strong, widely separated absorptions (1 901, 1 761 cm^{-1}) which we assign to terminal and (semi-)bridging carbonyl ligands respectively. These observations are consistent with a structure written as $[\{Mo(CO)(bipy)_2\}_2(\mu\text{-}CO)_2][BF_4]_2$. We have been unable to prepare a satisfactorily crystalline sample of the salt for determination of the structure by *X*-ray diffraction. Disruption of the dinuclear cation occurred on warming the salt in acetone, producing green *trans*-$[Mo(CO)_2(bipy)_2][BF_4]$. This material is paramagnetic, and its i.r. spectrum shows a single strong absorption (1 860 cm^{-1}) in the region 2 000—1 600 cm^{-1}. In solution the solid behaves as a 1 : 1 (NaCl type) electrolyte. A [formula mass]$^+$ ion (*m/e* 551) is observed in the f.a.b. mass spectrum of the solid complex.

Oxidation of *cis*-$[W(CO)_2(bipy)_2]$ by $Ag[BF_4]$ in acetonitrile under conditions which were identical to those used for the molybdenum analogue produced *no evidence* for either a dinuclear dicationic tungsten(I) complex or a mononuclear *trans*-dicarbonyl cation. The orange photosensitive product was characterised as *cis*-$[W(CO)_2(bipy)_2][BF_4]$ on the evidence of microanalysis and two strong absorptions (1 895, 1 815 cm^{-1}) in the i.r. spectrum. The i.r. spectrum of this complex did not show an absorption in the region around 3 400 cm^{-1} which might be attributed to ν(OH). The complex did not give an e.s.r. spectrum at room temperature in solution; a well resolved, unshifted ^1H n.m.r. spectrum is observed. The oxidation of *cis*-$[W(CO)_2(bipy)_2]$ by silver(I) is remarkable because both the *cis* disposition of the carbonyl ligands and the six-co-ordinate character of the metal atom are maintained throughout. This provides a rare example of the influence of oxidation on physical properties which will be referred to later.

Whereas *cis*-$[Mo(CO)_2(dppe)_2]$ [14] and *cis*-$[Mo(CO)_2(dmpe)_2]$ [15] are oxidised by $[NO][PF_6]$ to give *cis*-$[MoF(CO)_2(dppe)_2][PF_6]$ (in CH_2Cl_2), *cis*-$[Mo(NCMe)(CO)_2(dppe)_2][PF_6]_2$ (in MeCN), and *trans*-$[MoH(CO)_2(dmpe)_2][PF_6]$ (in either solvent) respectively, *cis*-$[Mo(CO)_2(bipy)_2]$ undergoes simple substitution by $[NO][PF_6]$ at ambient temperature to give $[Mo(CO)(NO)(bipy)_2][PF_6]$ [ν(CO) 1 880, ν(NO) 1 590 cm^{-1} (Nujol)]. The dppe analogue $[Mo(CO)(NO)(dppe)_2][PF_6]$ [ν(CO) 1 940, ν(NO) 1 640 cm^{-1} (Nujol)] is prepared [14] from the reaction between $[Mo(CO)_3(NO)(dppe)][PF_6]$ and dppe in acetone. The ease with which substitution occurs in *cis*-$[Mo(CO)_2(bipy)_2]$ is reminiscent of the substitution by trifluorophosphine in the same complex at ambient temperature which produces [16] *cis*-$[Mo(PF_3)_2(bipy)_2]$. We have also prepared [17] *cis*-$[Mo(NO)_2(bipy)_2][BF_4]_2$, the product of reaction between nitric oxide and $[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$, to be described in detail elsewhere.

The ensemble of these chemical observations are in agreement with the results of electrochemical measurements which

Table 1. Cyclic voltammetry ($E_{\frac{1}{2}}$/V) of *cis*-$[M(CO)_2(bipy)_2]$ in acetonitrile solution

	M = Mo		M = W	
$M^0 \rightarrow M^{-1}$	-1.64	reversible	not observed	
$M^0 \rightarrow M^{I}$	-0.54	reversible	-0.44	reversible
$M^{I} \rightarrow M^{II}$	$+0.30$	irreversible	$+0.3$	irreversible

have been made on *cis*-$[M(CO)_2(bipy)_2]$ (M = Mo or W) in acetonitrile solution (Table 1). When the solvent was changed from acetonitrile to dichloromethane, in which *cis*-$[W(CO)_2(bipy)_2]$ is more soluble, the half-wave potentials increase to -0.35 (reversible) and $+0.80$ V respectively. The greatly increased potential of the second, irreversible oxidation in dichloromethane suggests that reaction with the solvent occurs, perhaps by abstraction of chloride ion. Similar behaviour has been observed [18] for *cis*-$[Mo(CO)_2(dmpe)_2]$ and $[Mo(CNR)_6]$ (R = aryl). We were surprised to find that *cis*-$[W(CO)_2(bipy)_2]$ showed no reduction wave above -2.0 V.

These observations of the electrochemistry of *cis*-$[M(CO)_2(bipy)_2]$ indicate that the tungsten complex is more difficult both to oxidise and to reduce by one electron than its molybdenum analogue. The reversibility of the first one-electron oxidation and the irreversibility of the second one-electron oxidation of *cis*-$[M(CO)_2(bipy)_2]$ is typical of other Group 6A metal complexes, such as those containing ditertiary phosphines which have the general form $[ML_2(P\text{-}P)_2]$. The remarkably low value of the first one-electron oxidation potential of *cis*-$[Mo(CO)_2(bipy)_2]$ (-0.54 V) compared with those [19] for *cis*-$[Mo(CO)_2(dmpe)_2]$ (-0.23 V) and *cis*-$[Mo(CO)_2(dppe)_2]$ (-0.02 V) when similar data for *cis*-$[Mo(CO)_4(L\text{-}L)]$ [L-L = bipy (0.62 V), dmpe (0.61 V), or dppe (0.68 V)] are taken into account, provides eloquent testimony for the influence of the *second* bipy ligand on the properties of the metal complex.

Pure ethyl isocyanide reacts so rapidly with *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ at room temperature that the reaction vessel becomes hot, there is rapid evolution of carbon monoxide, and significant decomposition is observed. When the reaction is moderated by a solvent (acetonitrile) the complexes $[Mo(CNEt)_3(bipy)_2][BF_4]_2$ (dark blue-purple rhombic crystals) and $[Mo(CNEt)_5(bipy)][BF_4]_2$ (red-purple needle crystals) can be isolated on addition of exactly 3 and at least 5 mol equiv. of ethyl isocyanide respectively. If less than 3 mol equiv. of ethyl isocyanide are added to *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ in acetonitrile solution an orange-red oil is obtained. No crystalline product could be isolated from this oily material even when the reaction was carried out at 240 K. Spectroscopic (i.r., ^{1}H n.m.r.) investigations of the product suggest that it is a mixture of compounds, which may include $[Mo(CO)_2(CNEt)(bipy)_2][BF_4]_2$ and $[Mo(CO)(CNEt)_2(bipy)_2][BF_4]_2$, neither of which was isolated. Similar results were obtained at each stage with *p*-tolyl isocyanide.

Refluxing a solution containing *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ and a large excess of ethyl isocyanide in acetonitrile failed to effect substitution beyond $[Mo(CNEt)_5(bipy)][BF_4]_2$ to form $[Mo(CNEt)_7][BF_4]_2$. However, we were able to prepare this complex very easily, as the hexafluorophosphate salt, as the product of reaction between $[\{Mo(CO)_4Cl_2\}_2]$ and ethyl isocyanide in dichloromethane solution at room temperature followed by metathesis with $[NH_4][PF_6]$. Other homoleptic isocyanide complexes $[Mo(CNR)_7][PF_6]_2$ (R = Me or Bu^t) have been reported [20] recently. We find that $[Mo(CNEt)_7][PF_6]_2$ reacts with bipy in acetonitrile solution at room temperature to give $[Mo(CNEt)_5(bipy)][PF_6]_2$. The reasons for the particular stability of the $[Mo(CNEt)_5(bipy)]^{2+}$ ion are not apparent.

Table 2. Infrared wavenumbers (ν/cm^{-1}; Nujol mull) of characteristic CX (X = O or NR) ligand absorptions

Complex	ν(C≡X)		X
cis-$[Mo(CO)_2(bipy)_2]$	1 782s	1 711s	O
$[Mo_2(CO)_4(bipy)_4][BF_4]_2$	1 901s	1 761s	O
trans-$[Mo(CO)_2(bipy)_2][BF_4]$	1 860		O
cis-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$	1 985s	1 908s	O
cis-$[Mo(CO)_2(bipy)_2(OH_2)][BF_4]_2$	1 982s	1 896s	O
cis-$[Mo(CO)_2(bipy)_2(OCMe_2)][BF_4]_2$	1 992s	1 917s	O
cis-$[Mo(CO)_2(phen)_2]$	1 780s	1 710s	O
cis-$[Mo(CO)_2(phen)_2(NCMe)][BF_4]_2$	1 988s	1 898s	O
$[Mo(CO)(NO)(bipy)_2][PF_6]$	1 880		O
$[Mo(CNEt)_3(bipy)_2][BF_4]_2$	2 140s	2 100s	NR
$[Mo(CNC_6H_4Me\text{-}p)_3(bipy)_2][BF_4]_2$	2 110 (sh)	2 050br	NR
$[Mo(CNEt)_5(bipy)][BF_4]_2$	2 176s	2 128s	NR
$[Mo(CNC_6H_4Me\text{-}p)_5(bipy)][BF_4]_2$	2 136 (sh)	2 090s	NR
$[Mo(CNEt)_7][PF_6]_2$	2 156s	2 130 (sh)	NR
cis-$[W(CO)_2(bipy)_2]$	1 778s	1 708s	O
cis-$[W(CO)_2(bipy)_2][BF_4]$	1 895s	1 815s	O
cis-$[W(CO)_2(bipy)_2][BF_4]_2$	1 982s	1 895s	O

The crystal structure * of $[Mo(CNEt)_5(bipy)][BF_4]_2$ shows that the cation geometry approximates to a capped trigonal prism with a distorted isocyanide ligand in the capping position and the bipy ligand co-ordinated at one of the longer edges of the capped face. The crystal structure † of $[Mo(CNEt)_3(bipy)_2][BF_4]_2$ shows that the cation geometry approximates to capped octahedral with a slightly distorted isocyanide ligand in the capping position.

Comparison of the reactivity towards isocyanides of the molybdenum(0) complex, *cis*-$[Mo(CO)_2(bipy)_2]$, which results [16] in substitution of the bipy ligands and formation of *cis,cis*-$[Mo(CO)_2(CNR)_2(bipy)]$ (R = Et) and *cis*-$[Mo(CO)_2(CNR)_4]$ (R = C_6H_4Me-*p*), and of the molybdenum(II) complex *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ which results in preferential substitution of the CO ligands with formation of $[Mo(CNR)_3(bipy)_2][BF_4]_2$ and, subsequently, $[Mo(CNR)_5(bipy)][BF_4]_2$ (R = Et or C_6H_4Me-*p*), shows how the binding strengths of the CO and bipy ligands are reversed on oxidation of the metal atom.

Spectroscopic Properties.—Infrared spectra. The ν(CO) absorption wavenumbers of the various bipy complexes of molybdenum and tungsten are very useful as a means of identification. The formal oxidation state has a significant influence on these values and this is most apparent in the oxidation of *cis*-$[W(CO)_2(bipy)_2]$ when the *cis* geometry is maintained throughout (Table 2). The carbonyl ligand absorptions move to higher wavenumbers by *ca.* 95 cm^{-1} per unit charge as the formal charge on the metal complex increases, reflecting a decrease in the π back-donation to the CO π* molecular orbitals. The first oxidation causes a larger change in ν(CO) (*ca.* 110 cm^{-1}) than the second oxidation (*ca.* 80 cm^{-1}).

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* $[Mo(CNEt)_5(bipy)][BF_4]_2$ crystallises in the space group *Pbca* (orthorhombic), with $a = 17.650(4)$, $b = 17.690(7)$, $c = 20.950(7)$ Å, $\alpha = \beta = \gamma = 90°$; $R = 0.1094$ from 1 751 reflections (O. S. Mills, Manchester University, unpublished work).

† $[Mo(CNEt)_3(bipy)_2][BF_4]_2$ crystallises in the space group $P2_1/a$ (monoclinic), with $a = 14.584(5)$, $b = 14.072(5)$, $c = 17.281(5)$ Å, $\beta = 113.35°$; $R = 0.0834$ from 2 685 reflections (M. B. Hursthouse, Queen Mary College, unpublished work).

Table 3. Hydrogen-1 n.m.r. spectra (δ/p.p.m.) of 2,2′-bipyridine and 1,10-phenanthroline complexes (q = quartet)

Compound	H^3	H^4	H^5	H^6	Solvent
cis-$[Mo(CO)_2(bipy)_2]$	8.44 (d)	8.01 (t)	7.50 (t)	8.66 (d)	$(CD_3)_2SO$
cis-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$	8.75 (dq)	8.37 (td)	7.66 (ddd)	8.62 (dq)	CD_3CN
cis-$[Mo(CO)_2(bipy)_2(OH_2)][BF_4]_2$	8.72 (d)	8.31 (td)	7.89 (td)	9.13 (d)	D_2O
cis-$[Mo(CO)_2(bipy)_2(OCMe_2)][BF_4]_2$	8.96 (d)	8.42 (td)	7.78 (td)	9.06 (d)	$[^2H_6]$acetone
$[Mo(CNEt)_3(bipy)_2][BF_4]_2$	8.56 (dt)	8.14 (td)	7.53 (td)	8.22 (dq)	CD_3CN
$[Mo(CNC_6H_4Me\text{-}p)_3(bipy)_2][BF_4]_2$	8.46 (dt)	7.91 (td)	7.62 (td)	8.88 (dt)	CD_3CN
$[Mo(CNEt)_5(bipy)][BF_4]_2$	8.57 (dt)	8.26 (td)	7.74 (td)	9.00 (dq)	CD_3CN
$[Mo(CNC_6H_4Me\text{-}p)_5(bipy)][BF_4]_2$	8.66 (dt)	8.39 (td)	7.83 (td)	9.32 (d)	CD_3CN
cis-$[W(CO)_2(bipy)_2]$	8.72 (d)	8.24 (td)	7.53 (td)	9.10 (d)	$(CD_3)_2SO$
cis-$[W(CO)_2(bipy)_2][BF_4]$	8.79 (dd)	8.36 (td)	7.65 (td)	8.66 (d)	CD_3CN
cis-$[W(CO)_2(bipy)_2][BF_4]_2$	8.52 (dd)	8.16 (td)	7.55 (td)	8.52 (d)	CD_3CN
	H^2	H^3	H^4	H^5	
phen	8.95 (dd)	7.38 (dd)	7.99 (dd)	7.49 (s)	CD_2Cl_2
cis-$[Mo(CO)_2(phen)_2]$	9.15 (d)	7.76 (q)	8.36 (d)	7.94 (s)	CD_3CN
$[Mo(CO)_2(phen)_2(NCMe)][BF_4]_2$	8.92 (d)	7.93 (dd)	8.92 (d)	8.38 (s)	CD_3CN

Table 4. Carbon-13 n.m.r. chemical shifts of $[Mo(CNEt)_x(bipy)_y]^{2+}$ complex ions in solution

Compound	C^2	C^3	C^4	C^5	C^6	CH_2	CH_3	Solvent
bipy	156.7	124.2	137.4	121.3	149.6			CD_2Cl_2
cis-$[Mo(CO)_4(bipy)]$	155.5	125.8	138.0	122.7	153.7			CD_2Cl_2
$[Mo(CNEt)_3(bipy)_2][BF_4]_2$	154.9	127.6	140.2	125.4	152.7	42.5	16.3	$(CD_3)_2CO$
$[Mo(CNEt)_5(bipy)][BF_4]_2$	155.5	128.1	140.9	125.2	154.8	41.8	15.8	$(CD_3)_2CO$
$[Mo(CNEt)_7][PF_6]_2$						40.8	15.9	$(CD_3)_2CO$
CNEt						36.2	14.7	CD_3CN

Oxidation also causes an increase in ν(CN) indicated by the comparison of *cis,cis*-$[Mo(CO)_2(CNEt)_2(bipy)]$ [16] with $[Mo(CNEt)_5(bipy)][BF_4]_2$, but in this case there is a change in co-ordination number and consequently in geometry. Substitution of ethyl isocyanide in $[Mo(CNEt)_5(bipy)][BF_4]_2$ by bipy to produce $[Mo(CNEt)_3(bipy)_2][BF_4]_2$ results in a decrease in ν(CN), reflecting the improved donor : acceptor ratio of the bipy ligand. Similar comparisons can be drawn between $[Mo(CO)_2(CNC_6H_4Me\text{-}p)_4]$ [16] and $[Mo(CNC_6H_4Me\text{-}p)_x(bipy)_y][BF_4]_2$ ($x = 3$, $y = 2$; $x = 5$, $y = 1$). The presence of bipy ligands in these complexes is easily recognised by absorptions of variable intensity in the region 1 600, 930, and 750 cm^{-1}, but no clear pattern of change as a result of oxidation could be discerned.

N.m.r. spectra. The ^1H n.m.r. spectra of all the bipy complexes with the exceptions of the paramagnetic *trans*-$[Mo(CO)_2(bipy)_2][BF_4]$ and the dimeric $[Mo_2(CO)_4(bipy)_4][BF_4]_2$ are simple and completely assignable. These assignments (Table 3) are assisted by the use of coupling constant measurements [$^3J(H^3H^4)$ = *ca.* 8, $^3J(H^5H^6)$ = *ca.* 5.5 Hz]. Oxidation of *cis*-$[Mo(CO)_2(bipy)_2]$ to the molybdenum(II) solvent-complex cation, *cis*-$[Mo(CO)_2(bipy)_2(solvent)][BF_4]_2$ (solvent = MeCN, Me_2CO, or H_2O), causes a general shift to low field of the bipy ring proton reasonances which is consistent with the drift of electron density from the bipy ligand towards the more electropositive metal atom. The influence of the co-ordinated solvent molecule on this shift is significant, as may be judged from a comparison of the values of the ring proton chemical shifts of the seven-co-ordinate molybdenum(II) complexes with the six-co-ordinate tungsten(II) complex which does not contain co-ordinated solvent and in which the bipy ring proton resonances are generally to higher field. The role of the greater diffuse character of the 5*d* orbitals in the observation is unclear. The proton resonance of the co-ordinated solvent molecule is indistinguishable from bulk solvent at room temperature which indicates that exchange is rapid.

Comparison of ring proton chemical shifts of *cis,cis*-$[Mo(CO)_2(CNEt)_2(bipy)]$ [16] with those of $[Mo(CNEt)_3(bipy)_2][BF_4]_2$ indicates that they are determined both by the electron density at the metal and by their position in the heterocyclic ring. The protons of the ethyl groups are significantly deshielded as a result of oxidation which is consistent with a reduction in electron density at the metal. Unusually, the bipy ring proton resonance H^3 (δ 8.56 p.p.m., ^3J = 8.0 Hz) in $[Mo(CNEt)_3(bipy)_2][BF_4]_2$ is observed at lower field than H^6 (δ 8.22 p.p.m., ^3J = 5.7 Hz). The normal pattern [$\delta(H^6) > \delta(H^3)$] is observed in most other bipy complexes considered here. The bipy ring protons in the *p*-tolyl isocyanide complexes are slightly deshielded compared to their ethyl isocyanide analogues. This is consistent with the superior π-acceptor ability of the aryl isocyanide. The chemical shifts of the bipy protons in the $[Mo(CNR)_3(bipy)_2][BF_4]_2$ complexes are individually at higher fields than in the analogous $[Mo(CNR)_5(bipy)][BF_4]_2$ (R = Et or C_6H_4Me-*p*) complexes. This confirms the superior π-acidity of isocyanides in competition with bipy ligands. The same interpretation can be made of the variation in the ν(C≡NR) wavenumbers between the two groups. Consistent with this spectroscopic evidence are the qualitative observations that the $[Mo(CNR)_3(bipy)_2]^{2+}$ complexes are much more air-sensitive than their $[Mo(CNR)_5(bipy)]^{2+}$ analogues, and within each group the ethyl isocyanide complex is more readily oxidised than its *p*-tolyl isocyanide analogue.

The solubility of the molybdenum(II) isocyanide complexes in polar solvents is sufficiently good to enable their ^{13}C n.m.r. spectra to be recorded. The results are shown in Table 4 with those for $[Mo(CO)_4(bipy)]$, bipy, and CNEt for comparison. The resonance(s) of the co-ordinated isocyanide carbon atoms could not be detected, even when $[Cr(acac)_3]$ (acac = acetylacetonate) was added to the solutions in an attempt to decrease the relaxation time. It is possible that this resonance may be obscured by the envelope of the bipy ring carbon resonances C^2 and C^6. All of the isocyanide complexes are

Table 5. Low-energy ($\lambda_{max.} > 400$ nm) absorption maxima in solution

Complex	$\lambda_{max.}$/nm [a]	Solvent
cis-$[Mo(CO)_4(bipy)]$	440 (3.41)	*b*
cis-$[Mo(CO)_2(bipy)_2]$	414 (3.50), 500 (3.6), 720 (3.2)	*c*
cis-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$	420 (3.60)	*b*
cis-$[Mo(CO)_2(bipy)_2(OH_2)][BF_4]_2$	434 (3.56)	*d*
cis-$[Mo(CO)_4(phen)]$	400 (3.8), 437 (3.51)	*b*
cis-$[Mo(CO)_2(phen)_2]$	468 (3.6), 578 (3.9), 716 (3.8)	*e*
cis-$[Mo(CO)_2(phen)_2(NCMe)][BF_4]_2$	440 (3.70)	*b*
cis-$[W(CO)_2(bipy)_2]$	485 (3.61)	*c*
cis-$[W(CO)_2(bipy)_2][BF_4]$	501 (3.42)	*b*
cis-$[W(CO)_2(bipy)_2][BF_4]_2$	540 (3.83)	*b*
$[Mo(CNEt)_3(bipy)_2][BF_4]_2$	543 (3.97), 581 (3.99)	*b*
$[Mo(CNC_6H_4Me\text{-}p)_3(bipy)_2][BF_4]_2$	476 (3.71)	*b*
$[Mo(CNEt)_5(bipy)][BF_4]_2$	504 (3.66)	*b*
$[Mo(CNC_6H_4Me\text{-}p)_5(bipy)][BF_4]_2$	472 (3.86)	*b*

[a] Log_{10} (ε/dm^3 mol^{-1} cm^{-1}) in parentheses. [b] MeCN. [c] Me_2SO. [d] H_2O. [e] CH_2Cl_2.

fluxional down to 200 K; the complex $[Mo(CNBu^t)_7]^{2+}$ is known [21] to be fluxional at 140 K. The combined influence of oxidation of the molybdenum and substitution of CO by CNEt, an inferior acceptor, causes a slight shift (*ca.* 1.5 p.p.m.) of the ring carbon resonances to lower field. Substitution of CNEt by bipy causes an even less significant shift (*ca.* 0.5 p.p.m.) of the ring carbon resonances to higher field. The variations of the ethyl carbon resonances of the co-ordinated CNEt ligands are more readily interpretable; the shift to lower field of the methylene carbon resonance on co-ordination of CNEt to molybdenum(II) is increased slightly by substitution of CNEt by bipy which may reflect the weaker acceptor ability of bipy compared with ethyl isocyanide. Similar but less significant changes occur for the methyl carbon resonances.

Electronic absorption spectra. The highly coloured isocyanide complexes $[Mo(CNR)_x(bipy)_y][BF_4]_2$ (R = Et or C_6H_4-Me-*p*; $x = 5, y = 1$; $x = 3, y = 2$) all show intense ($\varepsilon > 1\,000$ dm^3 mol^{-1} cm^{-1}) low-energy electronic transitions (Table 5). The bis-bipy isocyanide complexes ($x = 3$, $y = 2$) have lower-energy absorptions than the mono-bipy ($x = 5$, $y = 1$) isocyanide complexes. The complexes $[Mo(CNR)_7][PF_6]_2$ (R = Me, cyclohexyl, Bu^t, or Ph), $[Mo(CNR)_6X][PF_6]$ (R = Bu^t or Ph; X = Cl, Br, or I), $[Mo(CNR)_6(PR'_3)][PF_6]_2$ (R,R' = alkyl) and $[Mo(CNR)_5\{R'_2P(CH_2)_nPR'_2\}][PF_6]_2$ (R = Me or Bu^t, R' = Ph, $n = 1$ or 2) all show [22] electronic absorptions in the regions 432—392 (ε = 400—900) and 375—330 nm (ε = 1 200—2 200 dm^3 mol^{-1} cm^{-1}). These results suggest that the low-energy visible absorptions observed in $[Mo(CNR)_x(bipy)_y][BF_4]_2$ complexes are the result of $Mo(4d) \longrightarrow$ bipy(π^*) charge-transfer transitions. The shift of this absorption to lower energy compared to that observed in $[Mo(CO)_2(bipy)_2(solvent)][BF_4]_2$ (solvent = MeCN or H_2O) is consistent with the diminished acceptor capability of the isocyanide ligands compared to carbon monoxide.

Conclusions

Comparison of *cis*-$[M(CO)_2(P\text{–}P)_2]$ with *cis*-$[M(CO)_2(N\text{–}N)_2]$ (N–N = ditertiary amine) indicates how the higher donor : acceptor ratio of the N–N type ligands is able to influence the chemistry of the metal complexes in a highly significant manner, permitting access to *cis*-$[M(CO)_2(N\text{–}N)_2]^{2+}$ {or *cis*-$[M(CO)_2(N\text{–}N)_2(solvent)]^{2+}$} which does not have a stable P–P analogue. Nucleophilic substitution of *cis*-$[M(CO)_2(N\text{–}N)_2]$ generally results in displacement of the N–N ligand: the enhanced electrophilicity of the metal in *cis*-$[M(CO)_2(N\text{–}N)_2]^{2+}$ results in displacement of CO in substitution by the same nucleophile.

Experimental

Preparations were all carried out in an atmosphere of prepurified dinitrogen using standard techniques (Schlenk tubes, cannulae, vacuum manifold). All solvents were dried (calcium hydride, sodium, or molecular sieves), deaerated and distilled prior to use. Reactions were carried out in a darkened fume hood to exclude light. 2,2'-Bipyridine (Aldrich) was recrystallised from light petroleum (b.p. 60—80 °C), often after initial sublimation (360—370 K, 0.1 mmHg). The metal hexacarbonyls (Pressure Chemical Co.) were sublimed before use. Silver(I) tetrafluoroborate and silver(I) hexafluorophosphate (Aldrich) were used as received. Ethyl isocyanide was prepared by the modified Hofmann carbylamine method, using $[N(CH_2Ph)Et_3]Cl$ as a phase-transfer catalyst.[23] *p*-Tolyl isocyanide was prepared by dehydrating the formamidine of *p*-toluidine, $HCONHC_6H_4Me$-*p*, with PPh_3 and CCl_4.[24] *cis*-$[M(CO)_2(bipy)_2]$ (M = Mo or W) were prepared by our modification [13] of the published method.[8] Conductivity measurements were made with a Philips conductivity bridge PR 9500 at 1 kHz; the cell constant of the glass conductivity probe was calculated using standardised 0.01 mol dm^{-3} potassium chloride solution. I.r. spectra were recorded on Perkin-Elmer PE 257, PE 577, and Pye-Unicam SP3-200 spectrometers. N.m.r. spectra were recorded on Brucker WP80, JEOL PS100, and Varian SC300 spectrometers. Electronic absorption spectra were measured on a Perkin-Elmer PE402 spectrometer. The electrochemical apparatus has been described elsewhere.[25] Microanalyses were performed by Mr. M. Hart and his staff at Manchester and by Mr. A. Fassam at Canterbury.

Preparations.—Tetrakis(*2,2'-bipyridine*)*tetracarbonyldimolybdenum*(I) *bis*(*tetrafluoroborate*). *cis*-$[Mo(CO)_2(bipy)_2]$ [13] (1.27 g, 2.7 mmol) was stirred with acetonitrile (60 cm^3) at room temperature for 15 min. A solution of silver(I) tetrafluoroborate (0.53 g, 2.7 mmol) in acetonitrile (50 cm^3) was added dropwise from a syringe to the dark solution/slurry of the complex over a period of 45 min, and the reaction mixture was stirred for a further 30 min. The fine deposit of silver which formed during the reaction was removed by filtration through Celite. The dark red-brown filtrate was concentrated to *ca.* 20 cm^3 by evaporation under reduced pressure. The product $[Mo_2(CO)_4(bipy)_4][BF_4]_2$ can be precipitated from this solution by the addition of acetone–diethyl ether (1 : 1 v/v) or dichloromethane–thf (1 : 1 v/v) mixtures. The dark red powdery solid could not be recrystallised and so was washed with water, benzene, then pentane and finally dried *in vacuo*. The air-sensitive solid is soluble in acetonitrile, nitromethane, acetone, and dichloromethane; it is insoluble in thf and benzene. Magenta coloured solutions of the complex turn green immediately on exposure to air (Found: C, 46.8; H, 2.9; F, 12.4; Mo, 16.5; N, 10.2. Calc. for $C_{22}H_{16}BF_4MoN_4O_2$: C, 47.9; H, 2.9; F, 13.8; Mo, 17.4; N, 10.2%). Mass spectrum: *m/e* 1 101 $(M - 1)^+$, 1 073 $(M - CO)^+$, based on ^{96}Mo. Conductivity 241 S cm^2 mol^{-1} (5.61×10^{-3} mol dm^{-3} in $MeNO_2$).

cis-*Acetonitrilebis*(*2,2'-bipyridine*)*dicarbonylmolybdenum*(II) *bis*(*tetrafluoroborate*). Solid *cis*-$[Mo(CO)_2(bipy)_2]$ (1.68 g, 3.6 mmol) was stirred rapidly in acetonitrile (100 cm^3) for

15 min. Silver(I) tetrafluoroborate (1.41 g, 7.2 mmol) dissolved in acetonitrile (60 cm^3) was added dropwise from a syringe to the stirred solution/slurry of *cis*-[Mo(CO)$_2$(bipy)$_2$] during approximately 45 min, after which the mixture was stirred for a further 1 h. The fine deposit of silver formed during the reaction was removed by filtration through Celite. The yellow-brown solution was concentrated by evaporation under reduced pressure. The concentrated solution was added to rapidly stirred diethyl ether giving a fine yellow-brown powder which was isolated by filtration and dried *in vacuo*. The salt *cis*-[Mo(CO)$_2$(bipy)$_2$(NCMe)][BF$_4$]$_2$ is soluble in MeCN and acetone, is slightly soluble in dichloromethane and thf, and is insoluble in diethyl ether, benzene, and pentane. The solid is not particularly air-sensitive (Found: C, 42.2; H, 2.9; F, 21.6; Mo, 14.8; N, 9.9. Calc. for $C_{24}H_{19}B_2F_8MoN_5O_2$: C, 42.4; H, 2.8; F, 22.4; Mo, 14.1; N, 10.3%). Mass spectrum: m/e 678 $(M-1)^+$, 651 $(M-\mathrm{CO})^+$, 610 $(M-\mathrm{CO}-\mathrm{CH_3CN})^+$, 426 $(M-2\mathrm{CO}-\mathrm{CH_3CN}-\mathrm{bipy})^+$, 408 $(M-2\mathrm{CO}-\mathrm{CH_3CN}-2\mathrm{BF_4})^+$, based on ^{96}Mo. Conductivity 261 S cm^2 mol^{-1} (10.03×10^{-3} mol dm^{-3} in MeCN). The acetonitrile complex dissolves in acetone from which *cis*-[Mo(CO)$_2$(bipy)$_2$(OCMe$_2$)][BF$_4$]$_2$ is obtained as a yellow crystalline solid by the slow diffusion of diethyl ether (Found: C, 42.3; H, 2.9; Mo, 13.9; N, 8.6. Calc. for $C_{25}H_{22}B_2F_8MoN_4O_3$: C, 43.1; H, 3.2; Mo, 13.1; N, 8.0%). I.r. (Nujol): 1 670w, 1 605m, 1 470m, 1 315m, 1 245m, 1 085br, and 775s cm^{-1}. *cis*-[Mo(CO)$_2$(phen)$_2$(NCMe)][BF$_4$]$_2$ was prepared in a very similar manner by oxidation of *cis*-[Mo(CO)$_2$(phen)$_2$] with Ag[BF$_4$]. The khaki-yellow powdery solid complex is soluble in MeCN, MeNO$_2$, Me$_2$SO, and other polar solvents (Found: C, 45.9; H, 2.6; Mo, 13.2; N, 9.3. Calc. for $C_{28}H_{19}B_2F_8MoN_5O_2$: C, 46.2; H, 2.6; Mo, 13.2; N, 9.6%).

cis-[W(CO)$_2$(bipy)$_2$][BF$_4$] and *cis*-[W(CO)$_2$(bipy)$_2$][BF$_4$]$_2$ were prepared from *cis*-[W(CO)$_2$(bipy)$_2$] by methods very similar to those described above for their molybdenum(I) and molybdenum(II) analogues. *cis*-[W(CO)$_2$(bipy)$_2$][BF$_4$] was dissolved in acetone, filtered and reprecipitated with diethyl ether. The orange-red, light-sensitive solid complex was washed with diethyl ether and dried *in vacuo*; it is soluble in acetone, acetonitrile and Me$_2$SO, but is insoluble in solvents of low polarity (Found: C, 40.2; H, 2.5; F, 11.4; N, 8.4; W, 29.3. Calc. for $C_{22}H_{16}BF_4N_4O_2W$: C, 41.3; H, 2.5; F, 11.9; N, 8.8; W, 28.8%). *cis*-[W(CO)$_2$(bipy)$_2$][BF$_4$]$_2$ is a *brown* powder which can be precipitated from acetone solution by diethyl ether. It is very soluble in acetone and acetonitrile, slightly soluble in CH$_2$Cl$_2$ and thf, and insoluble in solvents of lower polarity (Found: C, 35.6; H, 2.5; F, 19.5; N, 7.9; W, 26.4. Calc. for $C_{22}H_{16}B_2F_8N_4O_2W$: C, 36.4; H, 2.2; F, 20.9; N, 7.7; W, 25.3%).

Bis(*2,2′-bipyridine*)*tris*(*ethyl isocyanide*)*molybdenum*(II) *bis*(*tetrafluoroborate*). *cis*-[Mo(CO)$_2$(bipy)$_2$(NCMe)][BF$_4$]$_2$ (1.003 g, 1.48 mmol) was dissolved in acetonitrile (30 cm^3). A solution of ethyl isocyanide (0.244 g, 4.44 mmol) in acetonitrile (15 cm^3) was added dropwise to the rapidly stirred solution of the metal complex. The solution gradually became blue-purple in colour. The mixture was stirred at room temperature (4 h) during which time the reaction vessel was occasionally vented to release the positive pressure of gaseous carbon monoxide which developed as the reaction proceeded. The solvent was evaporated under reduced pressure and the deep purple residue was extracted with acetone (2 × 20 cm^3). The extracts were combined and filtered (cannula) before diethyl ether was very carefully placed above the acetone solution (syringe). The mixture was left undisturbed in the dark at ambient temperature for several days. Large, dark purple cubic crystals were isolated. A further quantity of crystals was isolated from the mother-liquor at 250 K after a further period of storage. The combined crystalline material was redissolved in acetone and recrystallised by addition of diethyl ether. Large, diamond-shaped deep purple crystals were isolated by filtration, washed with cold diethyl ether and dried in a good vacuum (0.48 g, 43% yield) (Found: C, 46.3; H, 4.1; F, 20.4; Mo, 12.5; N, 12.9. Calc. for $C_{29}H_{31}B_2F_8MoN_7$: C, 46.6; H, 4.2; F, 20.3; Mo, 12.8; N, 13.1%). I.r.: 1 600m, 1 338w, 1 312w, 1 055br, 957m, and 761m cm^{-1} (Nujol); ν(CN) 2 140vs cm^{-1} (MeCN). ^{1}H N.m.r. (CD$_3$CN): δ 1.34 (t, CH$_3$), 4.04 p.p.m. (q, CH$_2$). The solid complex slowly turns into a brown amorphous powder on exposure to air. In solution the purple colour is immediately discharged on contact with air.

(*2,2′-Bipyridine*)*pentakis*(*ethyl isocyanide*)*molybdenum*(II) *bis*(*tetrafluoroborate*). Excess ethyl isocyanide (0.500 g, 9.09 mmol) in acetonitrile (20 cm^3) was added rapidly (syringe) to a stirred solution of *cis*-[Mo(CO)$_2$(bipy)$_2$(NCMe)][BF$_4$]$_2$ (1.010 g, 1.51 mmol) in acetonitrile (30 cm^3). On mixing, the reaction mixture became red, then purple and, finally, burgundy red in colour. Evolution of a colourless gas (presumed to be carbon monoxide) proceeded rapidly. The reaction mixture was stirred at room temperature (4 h) and then evaporated to dryness under reduced pressure. The dark red residue was dissolved in acetone, filtered (cannula) and diethyl ether was carefully placed above the acetone solution. Dark burgundy red needles were formed on storing the mixture undisturbed for several days. A further quantity of crystals was isolated from the mother-liquor at 250 K after a further period of storage (0.72 g, 68% yield) (Found: C, 42.5; H, 4.5; F, 21.5; Mo, 14.1; N, 13.6. Calc. for $C_{25}H_{33}B_2F_8MoN_7$: C, 42.8; H, 4.7; F, 21.7; Mo, 13.7; N, 14.0%). I.r.: 1 605w, 1 341m, 1 054br, and 775w cm^{-1} (Nujol); ν(CN) 2 134vs cm^{-1} (MeCN). ^{1}H N.m.r. (CD$_3$CN); δ 1.44 (t, CH$_3$), 3.96 p.p.m. (q, CH$_2$). The shiny deep red crystals of [Mo(CNEt)$_5$(bipy)][BF$_4$]$_2$ are only slightly air-sensitive. In solution, the complex is significantly more sensitive to oxidation by air.

The *p*-tolyl isocyanide complexes [Mo(CNC$_6$H$_4$Me-*p*)$_x$(bipy)$_y$][BF$_4$]$_2$ [$x = 3$, $y = 2$ (red); $x = 5$, $y = 1$ (deep orange)] are prepared in a very similar manner to their ethyl isocyanide analogues described above. The *p*-tolyl isocyanide complexes have a tendency to form oils when recrystallisation is attempted but this can be overcome and highly crystalline samples can be prepared by slow evaporation of an acetone–diethyl ether (2 : 1 v/v) solution. Both of the *p*-tolyl isocyanide complexes are less air-sensitive than their ethyl isocyanide analogues. For [Mo(CNC$_6$H$_4$Me-*p*)$_3$(bipy)$_2$][BF$_4$]: yield 44% (Found: C, 56.3; H, 4.2; F, 17.4; Mo, 10.7; N, 9.7. Calc. for $C_{44}H_{37}B_2F_8MoN_7$: C, 56.6; H, 4.0; F, 16.3; Mo, 10.3; N, 10.5%). I.r.: 1 600 w, 1 495m, 1 050br, 812m, 763m, 720m cm^{-1} (Nujol); ν(CN) 2 100vs cm^{-1} (MeCN). ^{1}H N.m.r. (CD$_3$CN): δ 2.42 (d,CH$_3$), 7.1—7.45 p.p.m. (m,C$_6$H$_4$). For [Mo(CNC$_6$H$_4$Me-*p*)$_5$(bipy)][BF$_4$]$_2$: yield 72% (Found: C, 59.1; H, 4.3; F, 15.6; Mo, 9.7; N, 9.5. Calc. for $C_{50}H_{43}B_2F_8MoN_7$: C, 59.3; H, 4.3; F, 15.0; Mo, 9.5; N, 9.7%). I.r.: 1 605w, 1 500m, 1 050br, 814m, 773m, and 718m cm^{-1} (Nujol); ν(CN) 2 140vs, 2 103vs cm^{-1} (MeCN). ^{1}H N.m.r. (CD$_3$CN): δ 2.44(d,CH$_3$), 7.1—7.45 p.p.m. (m, C$_6$H$_4$).

Heptakis(*ethyl isocyanide*)*molybdenum*(II) *bis*(*hexafluorophosphate*). A solution of ethyl isocyanide (2.00 g, 36.4 mmol) in dichloromethane (20 cm^3) was added (syringe) to a stirred solution of [{Mo(CO)$_4$Cl$_2$}$_2$] [26] (1.00 g, 1.8 mmol) in dichloromethane (25 cm^3). Rapid evolution of a gas presumed to be carbon monoxide was observed. The yellow solution was stirred (4 h) at room temperature to ensure complete reaction. The mixture was then evaporated to dryness under reduced pressure. The residue was redissolved in anhydrous methanol (10 cm^3). Ammonium hexafluorophosphate (0.7 g, 4.29 mmol) was added to the stirred methanolic solution. A yellow precipitate formed immediately and was isolated by filtration. The solid was redissolved in acetone and crystallised by slow diffusion of diethyl ether. Large yellow cubic crystals of the complex were isolated by filtration (cannula), washed with diethyl ether and dried in a good vacuum. The complex $[Mo(CNEt)_7][PF_6]_2$ (1.36 g, 47% yield) is only slightly sensitive to dry oxygen, but it is extremely hygroscopic (Found: C, 33.2; H, 5.0; F, 29.4; Mo, 12.5; N, 13.2; P, 7.9. Calc. for $C_{21}H_{35}F_{12}MoN_7P_2$: C, 32.7; H, 4.5; F, 29.6; Mo, 12.5; N, 12.7; P, 8.0%). I.r.(Nujol): 1 345s, 1 092m, and 838s cm^{-1}. ^1H N.m.r. (CD_3CN): δ 1.44(t,CH_3), 3.93 p.p.m. (q, CH_2).

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