Substitution Reactions of *cis*-Bis(2,2′-bipyridine)dicarbonyl(solvent)-molybdenum(II) and *cis*-Bis(2,2′-bipyridine)dicarbonyltungsten(II) Salts with Uni-, Bi-, and Ter-dentate Tertiary Phosphines, Trimethyl Phosphite, Nitric Oxide, and 2,2′-Bipyridine

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Reaction of *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ (bipy = 2,2′-bipyridine) with PPh_3 and PBu^n_3 substitutes the solvent to produce $[Mo(CO)_2(bipy)_2(PR_3)][BF_4]_2$ (R = Ph or Bu^n) under mild conditions. Oxidation of *cis*-$[Mo(CO)_2(bipy)_2]$ with $Ag[BF_4]$ in trimethyl phosphite at room temperature gives $[Mo(CO)_2(bipy)_2\{P(OMe)_3\}][BF_4]_2$. Under similar conditions, further substitution of one carbonyl ligand, to give $[Mo(CO)(bipy)_2L_2][BF_4]_2$ [L = PEt_3 or $P(OMe)_3$], or both carbonyl ligands to give $[Mo(NO)_2(bipy)_2][BF_4]_2$ or $[Mo(bipy)_3][BF_4]_2$ may occur. Reaction of *cis*-$[W(CO)_2(bipy)_2][BF_4]_2$ with the same phosphorus donor ligands results in the substitution of bipy to form *cis*-$[W(CO)_2(bipy)L_2][BF_4]_2$[L = PPh_3 or $P(OMe)_3$]; reaction with bis(diphenylphosphino)methane (dppm) or 1,2-bis(diphenylphosphino)ethane (dppe) produces $[WF(CO)_2(bipy)(L\text{–}L)][BF_4]$ (L–L = dppm or dppe). Reaction of $[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ with dppe produces $[Mo(CO)(bipy)_2(dppe)][BF_4]_2$. With bis(2-diphenylphosphinoethyl)phenylphosphine (bdpp), *cis*-$[W(CO)_2(bipy)_2][BF_4]_2$ forms $[W(CO)_2(bipy)(bdpp)][BF_4]_2$ in high yield. The new complexes have been characterised by microanalysis, spectroscopy (i.r., ^1H, ^{13}C, ^{19}F, ^{31}P n.m.r., electronic absorption), and conductivity measurements. $[Mo(NO)_2(bipy)_2][BF_4]_2$ reacts with $Na[S_2CNEt_2]$ to give $[Mo(NO)_2(S_2CNEt_2)_2]$.

Reactions of neutral *cis*-$[M(CO)_2(bipy)_2]$ (M = Mo or W; bipy = 2,2′-bipyridine) complexes with simple neutral nucleophilic ligands, L, such as phosphines or isocyanides, lead to displacement of bipy producing *cis,trans*-$[M(CO)_2(bipy)L_2]$, *cis,cis*-$[M(CO)_2(bipy)L_2]$, or *cis*-$[M(CO)_2L_4]$ depending on the ligand, the metal, and the conditions (temperature, solvent) used. Only when L has a high π-acceptor/σ-donor ratio (for example, PF_3) is it possible to substitute CO in preference to bipy and obtain $[M(bipy)_2L_2]$.[1] The neutral metal(0) complexes can be oxidised [with silver(I)] in solution to give stable metal(I) and metal(II) complexes which have been isolated and characterised.[2] The molybdenum(II) complex incorporates a solvent molecule (S) in the seven-co-ordinate dicationic product, *cis*-$[Mo(CO)_2(bipy)_2(S)]^{2+}$, but the tungsten(II) dication is six-co-ordinate in *cis*-$[W(CO)_2(bipy)_2]^{2+}$.

The reaction of the molybdenum(II) complex, *cis*-$[Mo(CO)_2(bipy)_2(NCMe)[BF_4]_2$ with isocyanides, RNC, proceeds under mild conditions to displace CO and the solvent in preference to bipy giving $[Mo(bipy)_2(CNR)_3][BF_4]_2$ and, subsequently, $[Mo(bipy)(CNR)_5][BF_4]_2$ (R = Et or C_6H_4Me-*p*). Attempts to prepare or to observe the precursors to $[Mo(bipy)_2(CNR)_3]^{2+}$ were unsuccessful.[2]

We present here the results of an investigation of some substitution reactions of $[Mo(CO)_2(bipy)_2(NCMe)_2]^{2+}$ and $[W(CO)_2(bipy)_2]^{2+}$ with various simple nitrogen- and phosphorus-centred nucleophiles. We show that it is possible to isolate complexes in which partial substitution has occurred, and we present evidence for a distinction between molybdenum(II) and tungsten(II). The latter often prefers a six-co-ordinate environment and is a softer acid than molybdenum(II). We have identified examples in which the co-ordination number of the metal increases [tungsten(II), six- to seven-co-ordinate] and decreases [molybdenum(II), seven- to six-co-ordinate] as a result of substitution.

Results

Substitution by Phosphorus Donor Ligands.—Reaction of *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ with triphenylphosphine in acetone–diethyl ether (1:2 v/v) solution at room temperature resulted in the formation of a yellow-brown complex *cis*-$[Mo(CO)_2(bipy)_2(PPh_3)][BF_4]_2$ which is photosensitive in the solid state. The greater reducing power of a tertiary alkylphosphine relative to an arylphosphine is shown by the fact that excess tri-n-butylphosphine causes reductive substitution of *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ in acetonitrile–diethyl ether (1:1) at room temperature with formation of purple[1,3] *cis,trans*-$[Mo(CO)_2(bipy)(PBu^n_3)_2]$. When less than two equivalents of the phosphine are used both the molybdenum(0) complex and yellow *cis*-$[Mo(CO)_2(bipy)_2(PBu^n_3)][BF_4]_2$ are formed, suggesting that substitution precedes reduction. Even when the proportions of $[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2 : PBu^n_3 < 1$, both the purple molybdenum(0) and the yellow molybdenum(II) substitution products are still formed. The molybdenum(II) complex is sensitive to normal laboratory light and the yellow solid darkens to a dirty brown colour within 0.5 h. The process is more rapid in the solid state than in solution. The photoproduct has not been identified. Reaction of triethylphosphine with *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ in acetone–acetonitrile (1:2 v/v) at room temperature produces red-purple $[Mo(CO)(bipy)_2(PEt_3)_2][BF_4]_2$. A very small amount of a monosubstituted product *cis*-$[Mo(CO)_2(bipy)_2(PEt_3)][BF_4]_2$ was also detected by i.r. spectroscopy, but could not be isolated in a state of sufficient purity for complete characterisation. Even when excess triethylphosphine was used in the reaction, no molybdenum(0) product such as $[Mo(CO)_2(bipy)(PEt_3)_2]$ was formed. One of the triethylphosphine ligands in the molybdenum(II) complex is labile and can be displaced by a co-ordinating solvent; for example, recrystallisation of $[Mo(CO)(bipy)_2(PEt_3)_2]$-

$[BF_4]_2$ from acetone produces $[Mo(CO)(bipy)_2(PEt_3)(OCMe_2)][BF_4]_2$.

Oxidation of *cis*-$[Mo(CO)_2(bipy)_2]$ with $Ag[BF_4]$ in trimethyl phosphite solution gives $[Mo(CO)_2(bipy)_2\{P(OMe)_3\}][BF_4]_2$. The reaction between $[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ and trimethyl phosphite in acetonitrile solution, also at room temperature, produces an orange complex, $[Mo(CO)(bipy)_2\{P(OMe)_3\}_2][BF_4]_2$. Substitution of both the co-ordinated solvent and one CO ligand also occurs when a chelating ditertiary phosphine ligand, $Ph_2PCH_2CH_2PPh_2$ (dppe), is used; the product is a red-brown crystalline solid, $[Mo(CO)(bipy)_2(dppe)][BF_4]_2$.

These observations on substitution at molybdenum(II) are in contrast to those we have made in the case of reactions of *cis*-$[W(CO)_2(bipy)_2][BF_4]_2$. The tungsten(II) complex reacts with triphenylphosphine and with trimethyl phosphite in acetone solution to form *cis,trans*-$[W(CO)_2(bipy)L_2][BF_4]_2$ [L = PPh_3 or $P(OMe)_3$] at room temperature. The same tungsten(II) complex reacts with $Ph_2PCH_2PPh_2$ (dppm) and with dppe to form the seven-co-ordinate complexes $[WF(CO)_2(bipy)(L–L)][BF_4]$ (L–L = dppm or dppe). In all three cases, bipy is substituted in preference to CO.

Substitution by Nitrogen Donor Ligands.—Heating a solution containing *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ and bipy in acetonitrile at reflux produces purple-black $[Mo(bipy)_3][BF_4]_2$, which is very sensitive to oxygen both in the solid state and in solution. The i.r. absorption spectrum of the reagents stirred in solution at room temperature showed an intense new absorption at 1 860 cm^{-1}, which disappeared when the solution was warmed. Careful isolation of the purple product of this room temperature reaction led to its identification as $[Mo(CO)(bipy)_3][BF_4]_2$, which loses CO very easily. Attempts to prepare $[W(bipy)_3][BF_4]_2$ from the reaction between $[W(CO)_2(bipy)_2][BF_4]_2$ and bipy in refluxing acetonitrile were unsuccessful. Unreacted starting material was isolated.

When nitrogen monoxide gas is passed through $[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ in acetonitrile solution, a clear green solution is obtained after *ca.* 0.25 h at ambient temperature. An emerald green powder is isolated by careful evaporation of the solution. This green complex was shown to be *cis*-$[Mo(NO)_2(bipy)_2][BF_4]_2$. The same dinitrosyl cation is produced in the reaction between $[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ and $[NO][BF_4]$ in acetonitrile solution. The dinitrosyl complex reacts with $Na[S_2CNEt_2]$ in acetonitrile solution at room temperature to produce $[Mo(NO)_2(S_2CNEt_2)]$. The dithiocarbamate complex has been prepared previously[4] from the reaction of $[\{Mo(NO)_2Br_2\}_n]$ with $Na[S_2CNEt_2]$.

Discussion

The mild conditions of reaction which suffice to effect substitution of the metal(II) complexes at, or close to, ambient temperature are in contrast to the more severe conditions which are necessary[1,5] to effect substitution by the same nucleophiles in the metal(0) complexes. There is a significant difference in the behaviour of molybdenum(II) and tungsten(II). Phosphorus-centred nucleophiles PR_3 (R = Ph, Et, Bu^n, or OMe) react with *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ to give products in which seven-co-ordination is retained and the co-ordinated solvent (MeCN) and one of the CO ligands are displaced. The same nucleophiles react with *cis*-$[W(CO)_2(bipy)_2][BF_4]_2$ under similar conditions to displace a bipy ligand and to form *cis*-$[W(CO)_2(bipy)L_2][BF_4]_2$ in which the six-co-ordination is retained. However, when a bidentate phosphine ligand (dppm or dppe) is used, substitution at tungsten(II) is accompanied by fluoride ion abstraction from tetrafluoroborate ion producing the seven-co-ordinate $[WF(CO)_2(bipy)(L–L)][BF_4]$ (L–L = dppm or dppe). Examples of fluoride-ion abstraction from polyfluorometalate ions (especially from $[PF_6]^-$) by neutral $[M(CO)_2(dppe)_2]$ (M = Mo or W) are known[6] which result in formal oxidation of the metal. In the present instance the metal is not oxidised but the co-ordination number changes in circumstances where this might not have seemed necessary. When the tridentate phosphine ligand bis(2-diphenylphosphinoethyl)phenylphosphine (bdpp) reacts with *cis*-$[W(CO)_2(bipy)_2][BF_4]_2$ the product is $[W(CO)_2(bipy)(bdpp)][BF_4]_2$. This shows that when chelating phosphine ligands are present, the electrophilic character of tungsten(II) is enhanced so that it will accept a further donor atom, whether this is by fluoride-ion abstraction or by co-ordination of a neutral nucleophile which is present in a relatively high (local) concentration.

Table 1. Infrared wavenumbers (cm^{-1}; Nujol mull) of characteristic ligand vibrations

Complex	L	ν(CO)	
cis-$[Mo(CO)_2(bipy)_2L][BF_4]_2$	MeCN	1 985s	1 908s
	$P(OMe)_3$	1 980s	1 900s
	PPh_3	1 950s	1 882s
	PBu^n_3	1 920s	1 840s
	PEt_3	1 900s	1 820s
$[Mo(CO)(bipy)_2L_2][BF_4]_2$	$P(OMe)_3$	1 868s	
	0.5 (dppe)	1 864s	
	0.5 (bipy)	1 860s	
	PEt_3	1 850s	
cis-$[W(CO)_2(bipy)L_2][BF_4]_2$	0.5 bipy	1 982s	1 895s
	$P(OMe)_3$	1 978s	1 878s
	PPh_3	1 925s	1 820s
cis-$[W(CO)_2(bipy)(bdpp)][BF_4]_2$		1 969s	1 896s
cis-$[WF(CO)_2(bipy)(dppm)][BF_4]$		1 913s	1 835s
cis-$[WF(CO)_2(bipy)(dppe)][BF_4]$		1 905s	1 837s
cis-$[Mo(NO)_2(bipy)_2][BF_4]_2$		1 820s	1 720s
cis-$[Mo(CO)_2(bipy)_2]$		1 782s	1 711s

The ease with which substitution of *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ by bipy occurs *via* $[Mo(CO)(bipy)_3][BF_4]_2$ to form $[Mo(bipy)_3][BF_4]_2$ is in contrast to the observation that *cis*-$[Mo(CO)_2(bipy)_2]$ is inert to substitution by bipy at 520 K. Substitution of $[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ by NO occurs easily in solution. The metal is formally reduced to molybdenum(0) and the nitrogen monoxide is oxidised to NO^+. Consistent with this, the product, *cis*-$[Mo(NO)_2(bipy)_2][BF_4]_2$ did not react with CO or with phosphines, PR_3, to give a seven-co-ordinate complex. Substitution of the neutral *cis*-$[Mo(CO)_2(bipy)_2]$ by $[NO][PF_6]$ gives[2] $[Mo(CO)(NO)(bipy)_2][PF_6]$ but further substitution could not be achieved.

Spectroscopic Properties.—*Infrared spectra.* The ν(CO) absorption wavenumbers of both the $[Mo(CO)_2(bipy)_2L]^{2+}$ and $[Mo(CO)(bipy)_2L_2]^{2+}$ cations (Table 1) generally decrease as the donor strength of L increases in the order L = $P(OMe)_3 > PPh_3 > PBu^n_3 > PEt_3$, just as was observed in the neutral *cis*-$[Mo(CO)_2(bipy)L_2]$ complexes.[1] The range of variation, indicated by $\Delta = |\nu(CO)[L = P(OMe)_3] - \nu(CO)(L = PEt_3)|$, is much reduced in the molybdenum(II) complexes: Δ for $[Mo(CO)_2(bipy)L_2]$ is ~150 cm^{-1}, for $[Mo(CO)_2(bipy)_2L]^{2+}$, Δ is ~80 cm^{-1}. The change in co-ordination number and the introduction of a fluoride ion into the co-ordination sphere of the metal in $[WF(CO)_2(bipy)(dppe)]^+$ causes the two ν(CO) i.r. absorptions to move closer together (Δν 68 cm^{-1}) than in $[W(CO)_2(bipy)(PPh_3)_2]^{2+}$ (Δν 105 cm^{-1}).

Table 2. Proton n.m.r. spectra (δ/p.p.m.) of 2,2′-bipyridine complexes

Complex	H^3	H^4	H^5	H^6	Solvent
cis-$[Mo(CO)_2(bipy)_2]$	8.48	7.94	7.44	8.72	CD_3CN
cis-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$	8.75	8.37	7.66	8.62	CD_3CN
cis-$[Mo(CO)_2(bipy)_2(PPh_3)][BF_4]_2$	8.69	8.47	7.41	8.83	CD_3CN
cis-$[Mo(CO)_2(bipy)_2(PBu^n_3)][BF_4]_2$	8.84	8.54	7.68	8.95	CD_3CN
cis-$[Mo(CO)_2(bipy)_2\{P(OMe)_3\}][BF_4]_2$	8.44	8.25	7.84	8.94	CD_2Cl_2
$[Mo(CO)(bipy)_2(PEt_3)_2][BF_4]_2$	8.63	7.80	7.32	9.23	CD_2Cl_2
$[Mo(CO)(bipy)_2(PEt_3)(OCMe_2)][BF_4]_2$	8.57	8.00	7.30	9.17	CD_2Cl_2
cis-$[Mo(NO)_2(bipy)_2][BF_4]_2$	8.63	8.25	7.53	9.17	CD_3CN
$[Mo(bipy)_3][BF_4]_2$	8.77	8.49	7.96	9.01	$(CD_3)_2CO$
cis-$[W(CO)_2(bipy)(PPh_3)_2][BF_4]_2$	9.10	8.76		9.34	$(CD_3)_2SO$
cis-$[W(CO)_2(bipy)\{P(OMe)_3\}_2][BF_4]_2$	8.68	8.50	7.98	9.18	CD_3CN
cis-$[WF(CO)_2(bipy)(dppm)][BF_4]$	8.46	8.15		8.71	CD_3CN
cis-$[WF(CO)_2(bipy)(dppe)][BF_4]$	8.66	8.34	7.35	8.66	CD_3CN
cis-$[W(CO)_2(bipy)(bdpp)][BF_4]_2$	8.17	5.73	5.73	9.49	CD_3CN

A comparable reduction in the frequency difference (Δν 73 cm^{-1}) is observed in $[W(CO)_2(bipy)(bdpp)][BF_4]_2$, in which the metal atom is seven-co-ordinate in an environment of neutral ligands.

N.m.r. spectra. Previous work has shown that the bipy ring proton resonances can provide a sensitive indicator of electronic structure. In *cis*-$[Mo(CO)_2(bipy)L_2]$ complexes the ring proton resonances H^i (i = 3, 4, or 5) shift to lower field as the acceptor strength of L increases.[1] In *cis*-$[Mo(CO)_2(bipy)_2L]^{2+}$, the variation is less significant (Table 2).

The bipy ring proton resonances in *cis*-$[Mo(NO)_2(bipy)_2][BF_4]_2$ can be compared directly with those in *cis*-$[Mo(CO)_2(bipy)_2]$ because both are formally molybdenum(0) complexes. The chemical shift of each ring proton, $\delta(H^i)$, in the dinitrosyl complex is at lower field than its counterpart in the dicarbonyl complex. The simplicity of the ^1H n.m.r. spectrum of *cis*-$[Mo(NO)_2(bipy)_2][BF_4]_2$ is very like that[7] of *cis*-$[Mo(CO)_2(bipy)_2]$. The ^1H n.m.r. spectrum of $[Mo(bipy)_3][BF_4]_2$ shows that all the protons are strongly deshielded relative to free bipy as a consequence, presumably, of the donation of electron density to the molybdenum(II) centre. Comparison of the proton chemical shifts with those reported[8] for $[Ru(bipy)_3]^{2+}$ show that the metal atom exerts a significant influence, particularly on H^6. The ^1H n.m.r. spectrum of *cis*-$[W(CO)_2(bipy)(bdpp)][BF_4]_2$ is remarkable for the large difference in the chemical shift of H^6 (δ 9.49 p.p.m.) and H^4, H^5 (δ 5.73 p.p.m.). The reason for this is not apparent.

The ^{31}P n.m.r. spectra of some of the complexes have been observed. The spectrum of $[Mo(CO)(bipy)_2(PEt_3)_2][BF_4]_2$ shows a sharp resonance at +36.71 p.p.m. and a rather broader resonance at +22.54 p.p.m. Recrystallisation of the complex salt from acetone produces $[Mo(CO)(bipy)_2(PEt_3)(OCMe_2)][BF_4]_2$, the ^{31}P n.m.r. spectrum of which contains a signal at +36.78 p.p.m. The ^{31}P n.m.r. spectrum of $[Mo(CO)_2(bipy)_2\{P(OMe)_3\}][BF_4]_2$ shows a single resonance at +24.0 p.p.m. in CD_3CN, and that of $[Mo(CO)(bipy)_2\{P(OMe)_3\}_2][BF_4]_2$ in CD_3CN contains two sharp signals (+28.7 and +26.90 p.p.m.). The phosphite ligands do not exchange with donor solvent at room temperature. In the comparable tungsten(II) complex there is a single resonance [$\delta(^{31}P)$ +127.90 p.p.m.; $^1J(WP)$ 277 Hz] from the *trans*-phosphite ligands in *cis,trans*-$[W(CO)_2(bipy)\{P(OMe)_3\}_2][BF_4]_2$.

The ^{31}P n.m.r. spectrum of *cis*-$[W(CO)_2(bipy)(bdpp)][BF_4]_2$ contains three resonances, each of which shows splitting produced by both W–P and P–P coupling. This establishes that all three phosphorus atoms are bound to tungsten and that the two terminal phosphorus atoms are not equivalent. Analysis of the coupling pattern shows that each of the terminal phosphorus atoms couples to the central phosphorus atom differentially [$^3J(PP)$ 33.8, 13.5 Hz] and also to one another (1.6 Hz). These observations are consistent with a seven-co-ordinate structure for the cation in which one Ph_2P group is *trans* to CO and the other Ph_2P group is *trans* to nitrogen of the bipy ligand (Figure).

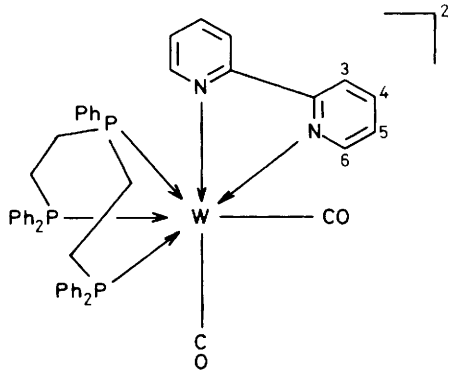

Figure. The seven-co-ordinate structure of *cis*-$[W(CO)_2(bipy)(bdpp)]^{2+}$

The structures of the complexes $[WF(CO)_2(bipy)(L\text{–}L)][BF_4]$ (L–L = dppm or dppe) are established by n.m.r. spectroscopy. The ^{31}P spectrum of the dppe complex comprises a single resonance [$\delta(^{31}P)$ +50.40 p.p.m.] with ^{183}W satellites [$^1J(WP)$ 203.6 Hz] which show coupling to fluorine [$^2J(PF)$ 33.2 Hz] giving a six-line spectrum with the expected intensity ratio (7.2:85.6:7.2). The corresponding results for the dppm complex are $\delta(^{31}P)$ −8.84 p.p.m., $^1J(WP)$ 162 Hz, and $^2J(PF)$ 33.2 Hz. The ^{19}F spectrum of the dppe complex shows a singlet (−151.71 p.p.m.) assigned to the tetrafluoroborate anion, and a triplet signal centred at δ −169.30 p.p.m. [$^1J(WF)$ 61.64 Hz], assigned to the tungsten-bonded fluoride.

Conclusions

The substitution chemistry of *cis*-$[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$ encompasses a variety of behaviour which is determined by the particular nucleophile. We have presented examples in which: (*a*) the co-ordinated solvent molecule alone is substituted by PPh_3 or by PBu^n_3, (*b*) the co-ordinated solvent molecule and one CO ligand are replaced by PEt_3, $P(OMe)_3$, and dppe, (*c*) the co-ordinated solvent molecule and both CO ligands are replaced by isocyanides with retention of seven-co-ordination,[2] and by bipy or NO with conversion to a six-co-ordinate product, and (*d*) further substitution by isocyanides which displaces bipy.[2] Clearly the ease of thermal substitution by neutral nucleophiles decreases in the order solvent (MeCN) > CO > bipy. This is the reverse of the order[1] in the molybdenum(0) complex, *cis*-[$Mo(CO)_2(bipy)_2$].

There is a clear difference between this and the chemistry of the tungsten(II) complex, *cis*-[$W(CO)_2(bipy)_2$][BF_4]$_2$. Nucleophilic attack on tungsten(II) results in substitution of bipy to form *cis*-[$W(CO)_2(bipy)L_2$][BF_4]$_2$. These results show that tungsten(II) is a softer acid than molybdenum(II) in a similar ligand environment.

Although substitution of bipy in [$W(CO)_2(bipy)_2$][BF_4]$_2$ by neutral unidentate nucleophiles conserves the co-ordination number of the metal atom in the product, this is not maintained when polydentate nucleophiles (dppm, dppe, or bdpp) are involved and seven-co-ordinate products are obtained in these cases.

Experimental

All preparations were carried out in an atmosphere of prepurified dinitrogen using standard techniques (Schlenk tubes, cannulae, vacuum manifold). Reactions involving the molybdenum complexes were carried out in a darkened fume hood, taking care to exclude direct light. All solvents were of reagent grade or better and were dried, deaerated, and distilled prior to use. 2,2′-Bipyridine (Aldrich) was recrystallised from light petroleum (b.p. 60—80 °C) often after initial sublimation (360—370 K, 13.33 Pa). The compounds [$Mo(CO)_6$] and [$W(CO)_6$] (Pressure Chemical Co.) were sublimed before use. [$Mo(CO)_2$-$(bipy)_2(NCMe)$][BF_4]$_2$ and [$W(CO)_2(bipy)_2$][BF_4]$_2$ were prepared by methods described in detail elsewhere.[2] Triphenylphosphine (Aldrich) was recrystallised from diethyl ether and checked for the absence of triphenylphosphine oxide by i.r. spectroscopy [ν(PO) at 1 140—1 100 cm^{-1}]. Trimethyl phosphite (BDH) was treated with sodium wire (24 h) and then distilled under an inert atmosphere onto activated molecular sieves. Triethyl- and tri-n-butyl-phosphine and 1,2-bis(diphenylphosphino)ethane (Aldrich) were used as received. Nitrogen monoxide (BDH) was taken directly from the cylinder in which it was received. Conductivity measurements were made with a Philips PR 9500 conductivity bridge 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, PE 683 and Pye-Unicam SP-200 spectrometers. N.m.r. spectra were recorded on Bruker WP80, WB-WS 200 and JEOL PS100 spectrometers. Electronic absorption spectra were measured on a Perkin-Elmer PE 402 spectrometer. Microanalyses were performed by Mr. M. Hart at Manchester, by Mr. A. Fassam at Canterbury, and by Mr. F. S. Frith at Runcorn.

Preparations.—*Bis*(2,2′-*bipyridine*)*dicarbonyl*(*tri-n-butylphosphine*)*molybdenum*(II) *bis*(*tetrafluoroborate*). Tri-n-butylphosphine (0.57 cm^3, 0.47 g, 2.31 mmol) in diethyl ether (20 cm^3) was added *via* a syringe to a stirred solution of *cis*-[$Mo(CO)_2(bipy)_2(NCMe)$][BF_4]$_2$ (1.03 g, 1.52 mmol) in acetonitrile (15 cm^3). The solution became purple on stirring for 2.5 h. A yellow powder precipitated from the solution on standing. This was removed by filtration. The filtrate contained *cis*-[$Mo(CO)_2(bipy)(PBu^n{}_3)_2$] [$\nu$(CO) 1 784, 1 717 cm^{-1}; $\lambda_{max.}$ 785, 516 nm in benzene, ref. 1]. The yellow powder was dissolved in acetone from which it was reprecipitated by addition of diethyl ether. The yellow solid (0.27 g, 21% yield), particularly sensitive to normal laboratory light, darkened to a dirty brown colour within 20 min. The yellow solid is soluble in polar organic solvents (Found: C, 47.9; H, 5.0; F, 17.3; Mo, 11.7; N, 6.4; P, 3.2. Calc. for $C_{34}H_{43}B_2F_8MoN_4O_2P$: C, 48.6; H, 5.1; F, 18.1; Mo, 11.4; N, 6.7; P, 3.7%). I.r. (Nujol): 1 600m, 1 470s, 1 375m, 1 058s br, 772s, 763s cm^{-1}; ^{1}H n.m.r. (CD_3CN): δ 0.69 (t, CH_3), 1.61, 1.08 (m, CH_2) p.p.m.

Bis(2,2′-*bipyridine*)*dicarbonyl*(*triphenylphosphine*)*molybdenum*(II) *bis*(*tetrafluoroborate*). A solution of triphenylphosphine (1.52 g, 5.81 mmol) in diethyl ether (30 cm^3) was added to a rapidly stirred solution of [$Mo(CO)_2(bipy)_2(NCMe)$][BF_4]$_2$ (1.31 g, 1.94 mmol) in acetone (15 cm^3). The mixture was stirred for 5 h at ambient temperature (*ca.* 295 K) after which a yellow-green precipitate was collected by filtration, washed with diethyl ether, and dried under vacuum. The crude product was dissolved in acetone and reprecipitated with diethyl ether. The dried purified product was a yellow-brown powder (0.59 g, 34% yield) (Found: C, 52.5; H, 3.4; F, 15.9; Mo, 11.0; N, 6.3; P, 3.4. Calc. for $C_{40}H_{31}B_2F_8MoN_4O_2P$: C, 53.3; H, 3.4; F, 16.9; Mo, 10.7; N, 6.2; P, 3.4%). I.r. (Nujol): 1 600m, 1 057br, 765m, 695m cm^{-1}; ^{1}H n.m.r. (CD_3CN): δ 7.2—7.5 (m, C_6H_5) p.p.m.

Bis(2,2′-*bipyridine*)*carbonylbis*(*triethylphosphine*)*molybdenum*(II) *bis*(*tetrafluoroborate*). A solution of triethylphosphine (0.44 g, 3.7 mmol) in acetone (10 cm^3) was added to a rapidly stirred solution of [$Mo(CO)_2(bipy)_2(NCMe)$][BF_4]$_2$ (0.86 g, 1.85 mmol) in acetonitrile (20 cm^3). The mixture became red-purple immediately. The reaction mixture was stirred for 1 h, and then evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane (25 cm^3) and the crude product quickly reprecipitated with diethyl ether. The pure product crystallised from dichloromethane and light petroleum (b.p. 40—60 °C) and was isolated as red-purple crystals (0.68 g, 45% yield) (Found: C, 46.5; H, 5.2; N, 6.5. Calc. for $C_{33}H_{46}B_2F_8MoN_4OP_2$: C, 46.8; H, 5.4; N, 6.6%). I.r. (Nujol): 1 600m, 1 500m, 1 320w, 1 060br, 765s cm^{-1}; ^{1}H n.m.r. (CD_2Cl_2): δ 1.00 (CH_3), 1.79 (CH_2) p.p.m.

Bis(2,2′-*bipyridine*)*carbonylbis*(*trimethyl phosphite*)*molybdenum*(II) *bis*(*tetrafluoroborate*). Pure trimethyl phosphite (0.5 cm^3, 0.521 g, 4.21 mmol) was added dropwise (syringe) to a stirred solution of *cis*-[$Mo(CO)_2(bipy)_2(NCMe)$][BF_4]$_2$ (0.949 g, 1.40 mmol) in acetonitrile (15 cm^3). The mixture became orange-red on stirring for 10 h (overnight). The mixture was subsequently evaporated to dryness under reduced pressure, the residue was extracted with acetone (2 × 10 cm^3), and the crude product rapidly reprecipitated with diethyl ether. The powdery precipitate was collected by filtration and redissolved in acetone from which it was recrystallised by the careful addition of diethyl ether. The product was isolated as orange crystals (0.17 g, 14% yield) (Found: C, 37.1; H, 3.7; F, 17.3; Mo, 12.1; N, 6.6; P, 7.4. Calc. for $C_{27}H_{34}B_2F_8MoN_4O_7P_2$: C, 37.9; H, 4.0; F, 17.8; Mo, 11.2; N, 6.3; P, 7.2%). I.r. (Nujol): 1 601m, 1 257w, 1 180m, 1 060br, 755br, 707s cm^{-1}; $\lambda_{max.}$ 473 nm in acetone.

Bis(2,2′-*bipyridine*)*dinitrosylmolybdenum*(0) *bis*(*tetrafluoroborate*). A slow stream of nitrogen monoxide gas was bubbled through a solution of *cis*-[$Mo(CO)_2(bipy)_2(NCMe)$][BF_4]$_2$ (1.56 g, 3.36 mmol) in acetonitrile (100 cm^3) until a clear green solution was obtained (0.25 h). The solution was concentrated by evaporation under reduced pressure. The emerald green powder which precipitated from the solution was collected by filtration, washed with diethyl ether, and dried under vacuum (1.3 g, 61% yield) (Found: C, 37.8; H, 2.3; N, 13.0. Calc. for $C_{20}H_{16}B_2F_8MoN_6O_2$: C, 37.4; H, 2.4; N, 13.1%). I.r. (Nujol): 1 600m, 1 320m, 1 260m, 1 180w, 1 055br, 920s, 785s cm^{-1}; $\lambda_{max.}$ 423 nm in acetonitrile. Conductivity (10^{-3} mol dm^{-3} in MeCN) = 245 S cm^2 mol^{-1}.

Tris(2,2′-*bipyridine*)*molybdenum*(II) *bis*(*tetrafluoroborate*). Solid 2,2′-bipyridine (0.168 g, 1.07 mmol) was added to a stirred solution of *cis*-[$Mo(CO)_2(bipy)_2(NCMe)$][BF_4]$_2$ (0.727 g, 1.07 mmol) in acetonitrile (20 cm^3). On warming the mixture (323

K) the dark yellow solution changed to purple quite quickly (0.3 h). The mixture was heated at reflux for 5 h, and then evaporated to dryness. The residue was dissolved in acetone, filtered, and then the filtrate was allowed to mix with diethyl ether by slow diffusion. Well formed purple-black crystals grew from the solution over a period of days. These crystals were isolated by filtration and washed with diethyl ether. The complex is air-sensitive both as a solid and, particularly, in solution (0.36 g, 46% yield) (Found: C, 48.5; H, 3.1; F, 20.1; Mo, 13.0; N, 10.8. Calc. for $C_{30}H_{24}B_2F_8MoN_6$: C, 48.8; H, 3.3; F, 20.6; Mo, 13.0; N, 11.4%); $\lambda_{max.}$ 580 nm (very broad) in acetone.

(2,2′-Bipyridine)dicarbonylbis(triphenylphosphine)tungsten(II) *bis(tetrafluoroborate)*. A solution of triphenylphosphine (0.82 g, 3.14 mmol) in diethyl ether (30 cm^3) was added to a rapidly stirred solution of $[W(CO)_2(bipy)_2][BF_4]_2$ (1.14 g, 1.57 mmol) in acetone (40 cm^3). The mixture became red-brown immediately. After 0.3 h a red-brown precipitate had formed but the mixture was allowed to continue stirring for 3 h to ensure completion of the reaction. The precipitate was collected by filtration, washed with diethyl ether, and dried under vacuum. The crude product was dissolved in acetonitrile and reprecipitated by the addition of diethyl ether. A red-brown powder (0.85 g, 49% yield) was isolated (Found: C, 51.5; H, 2.5; N, 2.7; P, 5.1; W, 19.2. Calc. for $C_{48}H_{38}B_2F_8N_2O_2P_2W$: C, 52.7; H, 3.5; N, 2.6; P, 5.7; W, 16.8%). I.r. (Nujol): 1 600m, 1 055br, 765m, 745m, 690m cm^{-1}; ^{1}H n.m.r. (CD_3CN): δ 8.14—7.76 [m, C_6H_5 and H^5 (bipy)] p.p.m.

(2,2′-Bipyridine)dicarbonylbis(trimethyl phosphite)tungsten(II) *bis(tetrafluoroborate)*. A solution of trimethyl phosphite (0.41 cm^3, 3.1 mmol) in diethyl ether (15 cm^3) was added dropwise to a rapidly stirred solution of $[W(CO)_2(bipy)_2][BF_4]_2$ (1.13 g, 1.56 mmol) in acetone (40 cm^3). The colour of the mixture darkened immediately. The reaction was stirred for 17 h (overnight) at ambient temperature and then evaporated to dryness under reduced pressure. The residue was extracted with acetone (20 cm^3) and the crude product rapidly reprecipitated with diethyl ether. The precipitate was collected by filtration and redissolved in acetone from which it was recrystallised by the careful addition of diethyl ether. The product was isolated as yellow-orange crystals (0.76 g, 59% yield) (Found: C, 26.6; H, 3.0; N, 2.7; P, 9.5; W, 18.5. Calc. for $C_{18}H_{26}B_2F_8N_2O_8P_2W$: C, 26.4; H, 3.2; N, 3.4; P, 7.6; W, 22.5%). I.r. (Nujol): 1 600m, 1 315w, 1 170m, 1 055br, 800m, 780m, 718m, 540m, 518m cm^{-1}; ^{1}H n.m.r. (CD_3CN): δ 3.84 (m, OCH_3) p.p.m.

(2,2′-Bipyridine)[1,2-bis(diphenylphosphino)ethane]dicarbonylfluorotungsten(II) *tetrafluoroborate*. Solid dppe (0.34 g, 0.854 mmol) was added to a stirred solution of $[W(CO)_2(bipy)_2][BF_4]_2$ (0.62 g, 0.854 mmol) in acetonitrile (40 cm^3). After 0.5 h all the dppe had dissolved. The reaction mixture was stirred at ambient temperature for 15 h (overnight) and then evaporated to dryness under reduced pressure. The residue was extracted with acetone and the crude product rapidly reprecipitated with diethyl ether. The orange-brown solid was isolated and redissolved in acetone from which it was recrystallised by the careful addition of diethyl ether. The product was isolated as orange-brown crystals (0.49 g, 64% yield) (Found: C, 50.0; H, 3.6; F, 10.8; N, 3.2; P, 6.5; W, 19.6. Calc. for $C_{38}H_{32}BF_5N_2O_2P_2W$: C, 50.7; H, 3.6; F, 10.5; N, 3.1; P, 6.9; W, 20.4%). I.r. (Nujol): 1 597m, 1 308m, 755m, 735m, 685m, 525m cm^{-1}; ^{1}H n.m.r. (CD_3CN): δ 7.75 (m, C_6H_5) p.p.m.

(2,2′-Bipyridine)[bis(2-diphenylphosphinoethyl)phenylphosphine]dicarbonyltungsten(II) *bis(tetrafluoroborate)*. Solid bdpp (0.66 g, 1.24 mmol) was added in small portions to a rapidly stirred solution of $[W(CO)_2(bipy)_2][BF_4]_2$ (0.90 g, 1.24 mmol) in acetonitrile (50 cm^3). After 0.25 h most of the bdpp had dissolved and the solution turned red. The mixture was stirred for 24 h at ambient temperature and then evaporated to dryness under reduced pressure. The residue was extracted with acetone (80 cm^3) and then concentrated under reduced pressure (20 cm^3). Addition of diethyl ether to the concentrated solution caused rapid precipitation of the crude product which was then purified by reprecipitation from acetone solution. The product was isolated as an orange powder (1.08 g, 79% yield) (Found: C, 49.0; H, 3.6; N, 2.4; P, 9.4; W, 20.9. Calc. for $C_{46}H_{41}B_2F_8N_2O_2P_3W$: C, 50.0; H, 3.7; N, 2.5; P, 8.4; W, 16.7%). I.r. (Nujol): 1 603m, 1 308w, 1 160m, 1 050br, 993w, 880m, 812m, 759m, 690m, 563m, 519m cm^{-1}; ^{1}H n.m.r. (CD_3CN): δ 7.87—7.71 (m, C_6H_5) p.p.m.

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