

Chemistry of *cis*-Bis(2,2'-bipyridine)dicarbonyl-molybdenum(0) and -tungsten(0). Substitution Reactions with Phosphorus Donor Ligands and with Isocyanides ‡

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Nucleophilic substitution reactions of *cis*-[M(CO)₂(bipy)₂] (M = Mo or W; bipy = 2,2'-bipyridine) by various unidentate (PR₃; R = Ph, Buⁿ, or OMe) and bidentate (Ph₂PCH₂CH₂PPh₂ = dppe) phosphorus and carbon (CNR; R = Et or *p*-tolyl) donor ligands, L, result in displacement of bipy to produce *cis,trans*-[Mo(CO)₂L₂(bipy)] (L = PR₃), *cis,cis*-[M(CO)₂L₂(bipy)] [M = Mo, L₂ = (CNEt)₂ or dppe; M = W, L = CNEt], *cis*-[M(CO)₂L₄] (M = Mo or W; L = CNC₆H₄Me-*p*), and *fac*-[Mo(CO)₃L(bipy)] (L = PPh₃) depending on the ligand L, temperature, and solvent. Trifluorophosphine reacts with *cis*-[Mo(CO)₂(bipy)₂] to displace CO and form *cis*-[Mo(PF₃)₂(bipy)₂]. Substitution in [M(CO)₄(bipy)] by isocyanides gives *fac*-[M(CO)₃(CNR)(bipy)] (M = Cr; R = Et or *p*-tolyl; M = Mo, R = Et) or *cis*-[Mo(CO)₄(CNR)₂] (R = *p*-tolyl). The products are characterised by microanalysis and by i.r., ¹H and ³¹P n.m.r., electronic, and mass spectroscopy. It is suggested that the formation of *cis,trans*-[Mo(CO)₂L₂(bipy)] may involve a trigonal bipyramidal intermediate structure which allows reorganisation to occur simply. The acceptor strength of L in [Mo(CO)₂L₂(bipy)] indicated by i.r. [ν(CO)], ¹H n.m.r. (bipy ring chemical shifts), and visible (Mo → bipy *dπ**) spectra, decreases in the order CO > P(OMe)₃ > CNEt > PBU₃ > bipy, which does not reflect geometrical differences in the disposition of these ligands.

The deep purple crystalline complexes *cis*-[M(CO)₂(bipy)₂] (M = Mo or W; bipy = 2,2'-bipyridine) might have been expected to attract attention since they were first reported,¹ because of their unusual colour which should presage an interesting photochemistry, their analogy to ruthenium(II) and osmium(II) complexes such as *cis*-[Ru(CO)₂(bipy)₂]²⁺ (ref. 2) and *cis*-[OsL₂(bipy)₂]²⁺ (L = unidentate ligand) (ref. 3), and especially because these Group 6 metal complexes might be expected to show interesting redox and substitution reactivity for comparison with the much-studied tertiary phosphine complexes [ML₂(PR₃)₄] (L = CO,⁴ N₂,⁵ CNR,⁶ or C₂H₄⁷). However, until now these expectations have remained unfulfilled.

We present the results of an investigation of ligand substitution reactions of *cis*-[M(CO)₂(bipy)₂] (M = Mo or W). Comparisons are made with *cis*-[M(CO)₄(bipy)] (M = Cr, Mo, or W), where this is appropriate. Some of the complexes have been prepared by others using different methods; in several instances, we are able to provide a more complete characterisation of these complexes. We show that, when care is taken to exclude or minimise the influence of light on the reactions, there is a remarkable spectrum of substitution reactivity in the chemistry of *cis*-[M(CO)₂(bipy)₂], leading to a rich variety of new, coloured complexes of the *d*⁶ metals.

Results

Substitution by Phosphorus Donor Ligands.—Reaction of *cis*-[Mo(CO)₂(bipy)₂] with unidentate tertiary phosphines, PR₃ (R = Ph or Buⁿ) in tetralin solution at 420 K produces the complexes *cis,trans*-[Mo(CO)₂(PR₃)₂(bipy)] (R = Ph, green powder; R = Buⁿ, purple crystals), which have been reported previously as the products of reaction between *cis,trans*-[Mo(CO)₂(PR₃)₂(NCMe)₂] and 2,2'-bipyridine in acetone.^{8,9} When *cis*-[Mo(CO)₂(bipy)₂] is heated (380 K)

with triphenylphosphine in a mixture of acetonitrile and tetralin the product is *fac*-[Mo(CO)₃(PPh₃)(bipy)] which is much more soluble in acetonitrile than is *cis,trans*-[Mo(CO)₂(PPh₃)₂(bipy)]. The product of the reaction between *cis*-[Mo(CO)₂(bipy)₂] and 1,2-bis(diphenylphosphino)ethane (dppe) is determined by the conditions. Heating equimolar quantities of the reactants in acetonitrile at reflux (355 K) produces *cis*-[Mo(CO)₂(dppe)(bipy)], isolated as green crystals [λ_{max}, 605 nm (CH₂Cl₂)]. Changing the solvent to tetralin and raising the temperature (400 K) results in the formation of *cis*-[Mo(CO)₂(dppe)₂]⁴ from a stoichiometric reaction. These observations are in contrast to the fact that we have been unable to detect any reaction between *cis*-[Mo(CO)₂(bipy)₂] and 1,2-bis(dimethylphosphino)ethane, even under more forcing conditions (tetralin, 420 K).

Heating *cis*-[Mo(CO)₂(bipy)₂] in pure trimethyl phosphite at reflux produces a Prussian blue coloured solution from which *cis,trans*-[Mo(CO)₂{P(OMe)₃}₂(bipy)] can be isolated as a purple crystalline solid. This complex has been reported previously¹⁰ as the product of reaction between trimethyl phosphite and [Mo(CO)₄(bipy)]. Heating *cis,trans*-[Mo(CO)₂{P(OMe)₃}₂(bipy)] with ethyl isocyanide in acetonitrile results in displacement of bipy and formation of *cis*-[Mo(CO)₂{P(OMe)₃}₂(CNEt)₂].

These observations of reactions requiring heat (350–420 K) to effect substitution of the bipy ligand(s) are in contrast to the rapid substitution reaction which occurs at room temperature when gaseous trifluorophosphine is passed through a solution-slurry of *cis*-[Mo(CO)₂(bipy)₂] in acetonitrile. The product of the reaction, *cis*-[Mo(PF₃)₂(bipy)₂], is isolated as a dark red crystalline solid.

Substitution by Isocyanides.—Addition of a solution of *p*-tolyl isocyanide in benzene to a solution-slurry of *cis*-[Mo(CO)₂(bipy)₂] in acetonitrile at room temperature results in a rapid reaction as indicated by the change in the colour of the mixture. The product of the reaction is *cis*-[Mo(CO)₂(CNC₆H₄Me-*p*)₄], a yellow crystalline solid. The tungsten analogue *cis*-[W(CO)₂(CNC₆H₄Me-*p*)₄] is obtained from the reaction between *cis*-[W(CO)₂(bipy)₂] and CNC₆H₄Me-*p*.

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‡ Non-S.I. units employed: 1 eV ≈ 1.60 × 10⁻¹⁹ J; 1 mmHg = 13.6 × 9.8 Pa.

The rapid and complete substitution of the bipy ligands by an aryl isocyanide is in marked contrast to the reaction with an alkyl isocyanide. Addition of excess pure ethyl isocyanide to cis -[Mo(CO)₂(bipy)₂] at room temperature results in a relatively slower reaction to produce cis,cis -[Mo(CO)₂(CNEt)₂(bipy)] which is isolated as a dark green crystalline solid. Heating this complex in pure ethyl isocyanide at reflux (*ca.* 350 K) for 20 h failed to induce further substitution. The substitution of cis -[W(CO)₂(bipy)₂] by ethyl isocyanide proceeds similarly to give cis,cis -[W(CO)₂(CNEt)₂(bipy)].

Reaction between [Cr(CO)₄(bipy)] and either *p*-tolyl isocyanide or ethyl isocyanide in excess in refluxing dichloromethane solution produces the dark green-black complexes fac -[Cr(CO)₃(CNR)(bipy)] in both cases. However, *p*-tolyl isocyanide reacts with [Mo(CO)₄(bipy)] in refluxing benzene to produce yellow cis -[Mo(CO)₄(CNC₆H₄Me-*p*)₂],¹¹ whereas ethyl isocyanide and [Mo(CO)₄(bipy)] react in refluxing chloroform to produce purple fac -[Mo(CO)₃(CNEt)(bipy)] as the only isolable product. The tungsten complex [W(CO)₄(bipy)] was recovered unchanged after refluxing in benzene with excess ethyl isocyanide for 10 h.

Discussion

It is perhaps important to reiterate that these reactions were carried out in well shrouded vessels, protected from direct light which, experience had shown, could lead to unreliable results in these systems. As far as possible, therefore, we are concerned with the examination of truly thermal reactions which may be compared directly with the reactions of analogous complexes such as cis -[Mo(CO)₂(dppe)₂].

The results presented indicate that the phosphorus donor ligands PR₃ require substantial thermal activation before they will react with cis -[Mo(CO)₂(bipy)₂]. No reaction could be detected between cis -[Mo(CO)₂(bipy)₂] and PR₃ (R = Ph, Buⁿ, or OMe) on refluxing in a polar solvent (acetonitrile) after 24 h. The complexes $cis,trans$ -[Mo(CO)₂(PR₃)₂(bipy)] (R = Ph, Buⁿ, or OMe) are remarkably stable once formed; for example, $cis,trans$ -[Mo(CO)₂(PBuⁿ)₂(bipy)] was recovered unchanged after being heated in refluxing tri-*n*-butylphosphine (425 K) for 8 h.

The formation of fac -[Mo(CO)₃(PPh₃)(bipy)] from cis -[Mo(CO)₂(bipy)₂] and PPh₃ in the presence of acetonitrile can be compared with formation of the same product in the reaction between $cis,trans,cis$ -[Mo(CO)₂(PPh₃)₂(NCMe)₂] and bipy in acetone solution.⁸ Reaction between fac -[Mo(CO)₃(NCMe)₃] and diolefin (cyclo-octa-1,5-diene, bicyclo[2.2.1]-hepta-2,4-diene) also results¹¹ in an increase in the number of CO ligands in the product, cis -[Mo(CO)₄(diolefin)].

The relatively milder conditions for the formation of cis -[Mo(CO)₂(dppe)(bipy)] in the reaction between dppe and cis -[Mo(CO)₂(bipy)₂] suggests that when the disubstitution is constrained to *cis* positions in a pseudo-octahedron, reaction proceeds more easily. In a less polar, non-donor, neutral solvent, substitution proceeds to give cis -[Mo(CO)₂(dppe)₂] even if less than two equivalents of dppe are added.

The only example of CO substitution in cis -[Mo(CO)₂(bipy)₂] is observed when PF₃, a ligand with a better acceptor: donor ratio than CO {as indicated by the i.r. spectra¹² of [Ni(CO)₃L]}, reacts to form cis -[Mo(PF₃)₂(bipy)₂]. The passage of CO gas through a solution-slurry of cis -[Mo(CO)₂(bipy)₂] did not produce cis -[Mo(CO)₄(bipy)].

The difficulty experienced in effecting thermal substitution of bipy in cis -[Mo(CO)₂(bipy)₂] with phosphorus donor ligands is in contrast to the much faster, easier substitution with isocyanides, particularly aryl isocyanides. The reaction between cis -[Mo(CO)₂(bipy)₂] and four or more equivalents of

p-tolyl isocyanide is complete in approximately 0.3 h at room temperature. If less than four equivalents of *p*-tolyl isocyanide are added, some cis -[Mo(CO)₂(bipy)₂] can be recovered unchanged. The formation of [Mo(CO)₂(CNC₆H₄Me-*p*)₂(bipy)] could not be observed (by i.r. spectra) even if the reaction was cooled to 250 K. Ethyl isocyanide reacts more slowly with cis -[Mo(CO)₂(bipy)₂] than does *p*-tolyl isocyanide, taking several hours to produce cis,cis -[Mo(CO)₂(CNEt)₂(bipy)] at room temperature. Further substitution to give cis -[Mo(CO)₂(CNEt)₄] could not be achieved. This is in contrast to the relative ease of substitution of bipy in $cis,trans$ -[Mo(CO)₂-{P(OMe)₃}₂(bipy)] with ethyl isocyanide to form $cis,trans,cis$ -[Mo(CO)₂{P(OMe)₃}₂(CNEt)₂]. In the group of cis -[M(CO)₄(bipy)] complexes, reaction with isocyanide results either in CO substitution to give fac -[M(CO)₃(CNR)(bipy)] (M = Cr, R = Et or *p*-tolyl; M = Mo, R = Et) or substitution of bipy to give cis -[M(CO)₄(CNR)₂] (M = Mo, R = *p*-tolyl).

The reactions of cis -[Mo(CO)₂(bipy)₂] with unidentate neutral ligands most probably proceed by a dissociative or dissociative-concerted mechanism¹² following thermal rupture of a Mo-N bond. From the structure of cis -[Mo(CO)₂(bipy)₂] in the solid state,¹³ it seems likely that the shorter Mo-N bond [2.155(6), 2.143(6) Å], *trans* to another bipy nitrogen atom, may be stronger than the Mo-N bond *trans* to a CO ligand [2.220(5), 2.239(5) Å] and consequently less likely to rupture. Following the first substitution which produces [Mo(CO)₂L(bipy)₂] in which one bipy ligand is unidentate, it is apparent that either of two products, cis,cis - and $cis,trans$ -[Mo(CO)₂L₂(bipy)], can be formed in the second substitution step. It is interesting to note that we have no evidence for mixtures of both isomers being produced, and that products having cis,cis stereochemistry are formed at much lower temperatures than those having $cis,trans$ stereochemistry. Occam's razor leads us to propose that the intermediate [Mo(CO)₂L(bipy)₂] adopts a trigonal bipyramidal structure from which both cis,cis - and $cis,trans$ -[Mo(CO)₂L₂(bipy)] can be derived without, for example, requiring that the second bipy ligand should also become unidentate. A well established example of *cis*→*trans* isomerisation *via* a trigonal bipyramidal intermediate is provided by the interconversion¹⁴ of the carbene complexes *cis*- and *trans*-[M(CO)₄(PR₃)(C(OR)²R³)]. We are unable to explain why unidentate phosphorus donor ligands produce only $cis,trans$ -[Mo(CO)₂(PR₃)₂(bipy)], or why they react much more slowly than isocyanides. Even if an associative mechanism is assumed to be more important for isocyanide substitution (which might be justified by the low steric demands of the C≡N-C moiety), it is difficult to account for the very much faster (*ca.* × 10⁴) reaction. Studies of the substitution reactions of $cis,trans$ -[Mo(CO)₂(PR₃)₂(NCMe)₂] (R = Ph or Buⁿ) have suggested that a tricarbonyl intermediate [Mo(CO)₃(PR₃)₂L] is involved, even when a dicarbonyl product is formed, and in some cases this has been isolated.⁸ If it is recalled that reaction between cis -[Mo(CO)₂(bipy)₂] and PPh₃ in an acetonitrile-tetralin mixture produces fac -[Mo(CO)₃(PPh₃)(bipy)] at a lower temperature than that required to form $cis,trans$ -[Mo(CO)₂(PPh₃)₂(bipy)] in the absence of acetonitrile, it would seem necessary to postulate a mechanism which involves a carbonyl-bridged binuclear intermediate.

Spectra.—The solid state (mull) i.r. spectra in the 2 200–1 700 cm⁻¹ region of the complexes are presented in Table 1. From the frequency of the ν(CO) absorption, the order of decreasing acceptor strength of the ligands, L, in complexes [Mo(CO)₂L₂(bipy)] is L = CO > P(OMe)₃ > CNEt > dppe > PPh₃ > PBuⁿ > bipy. The disposition of L (whether they are mutually *cis* or *trans* to one another) seems to have very little effect on the values of ν(CO) in the complexes.

Table 1. Infrared absorptions in the 2 200—1 700 cm⁻¹ region *

	$\nu(\text{CO})/\text{cm}^{-1}$	$\nu(\text{CN})/\text{cm}^{-1}$
<i>fac</i> -[Cr(CO) ₃ (CNEt)(bipy)]	1 910s, 1 805s, 1 782s	2 140s
<i>fac</i> -[Cr(CO) ₃ (CNC ₆ H ₄ Me- <i>p</i>)(bipy)]	1 905s, 1 828s, 1 797s	2 075s
<i>cis</i> -[Mo(CO) ₂ (bipy) ₂]	1 782s, 1 711s	
<i>cis,trans</i> -[Mo(CO) ₂ (PBU ₃) ₂ (bipy)]	1 784s, 1 717s	
<i>cis,trans</i> -[Mo(CO) ₂ (PPh ₃) ₂ (bipy)]	1 796s, 1 732s	
<i>cis,cis</i> -[Mo(CO) ₂ (dppe)(bipy)]	1 805s, 1 736s	
<i>cis,cis</i> -[Mo(CO) ₂ (CNEt) ₂ (bipy)]	1 820s, 1 754s	2 080s, 2 006s
<i>cis,trans</i> -[Mo(CO) ₂ {P(OMe) ₃ } ₂ (bipy)]	1 936s, 1 860s	
<i>cis</i> -[Mo(CO) ₄ (bipy)]	2 012s, 2 000s, 1 872s, 1 812s	
<i>fac</i> -[Mo(CO) ₃ (PPh ₃)(bipy)]	1 910s, 1 826s, 1 785s	
<i>fac</i> -[Mo(CO) ₃ (CNEt)(bipy)]	1 910s, 1 805s, 1 780s	2 140s
<i>cis,trans</i> -[Mo(CO) ₂ {P(OMe) ₃ } ₂ (CNEt) ₂]	1 920s, 1 878s	2 158s, 2 031s
<i>cis</i> -[Mo(CO) ₂ (CNC ₆ H ₄ Me- <i>p</i>) ₄]	1 879s, 1 858s	2 127s, 2 058s, 1 983s, 1 937s
<i>cis</i> -[Mo(CO) ₄ (CNC ₆ H ₄ Me- <i>p</i>) ₂]	2 005s, 1 870br	2 130s, 2 077s
<i>cis,cis</i> -[W(CO) ₂ (CNEt) ₂ (bipy)]	1 814s, 1 755s	2 078s, 1 998s, 1 976s
<i>cis</i> -[W(CO) ₂ (CNC ₆ H ₄ Me- <i>p</i>) ₄]	1 865s, 1 847s	2 119s, 2 048s

*All spectra recorded on solid mulls in Nujol.

Table 2. Proton n.m.r. spectra ($\delta/\text{p.p.m.}$) of 2,2'-bipyridine complexes ^a

Complex	H ³	H ⁴	H ⁵	H ⁶	Solvent ^b
<i>cis</i> -[Mo(CO) ₄ (bipy)]	8.16 (d)	7.95 (t)	7.39 (t)	9.12 (d)	CD ₂ Cl ₂
<i>cis</i> -[Mo(CO) ₄ (bipy)]	8.65 (d)	8.19 (t)	7.64 (t)	8.98 (d)	[² H ₆]dmsO
<i>cis,cis</i> -[Mo(CO) ₂ (CNEt) ₂ (bipy)]	7.98 (d)	7.66 (td)	7.16 (td)	9.26 (d)	CD ₂ Cl ₂
<i>fac</i> -[Mo(CO) ₃ (CNEt)(bipy)]	8.03 (d)	7.81 (td)	7.26 (t)	9.19 (d)	CD ₂ Cl ₂
<i>cis,trans</i> -[Mo(CO) ₂ {P(OMe) ₃ } ₂ (bipy)]	8.05 (dt)	7.79 (td)	7.23 (td)	9.23 (dt)	CD ₂ Cl ₂
<i>fac</i> -[Mo(CO) ₃ (PPh ₃)(bipy)]	8.09 (d)	7.64 (t)	c	8.80 (d)	CD ₂ Cl ₂
<i>cis,trans</i> -[Mo(CO) ₂ (PBU ₃) ₂ (bipy)]	7.95 (d)	7.26 (t)	7.02 (t)	9.14 (d)	CDCl ₃
<i>cis</i> -[Mo(PF ₃) ₂ (bipy) ₂]	8.49 (d)	7.93 (td)	7.42 (t)	8.67 (d)	CDCl ₃
<i>cis</i> -[Mo(CO) ₂ (bipy) ₂]	8.39 (d)	7.91 (td)	7.41 (t)	8.68 (d)	[² H ₆]dmsO
<i>cis</i> -[Mo(CO) ₂ (bipy) ₂]	8.48 (d)	7.94 (td)	7.44 (t)	8.72 (d)	CD ₃ CN
<i>cis</i> -[W(CO) ₄ (bipy)]	8.19 (d)	7.88 (t)	7.41 (t)	9.24 (d)	CD ₂ Cl ₂
<i>cis,cis</i> -[W(CO) ₂ (CNEt) ₂ (bipy)]	8.30 (dt)	7.94 (td)	7.37 (td)	9.24 (dt)	CD ₃ CN
<i>cis</i> -[W(CO) ₂ (bipy) ₂]	8.72 (d)	8.24 (td)	7.53 (td)	9.10 (d)	[² H ₆]dmsO
<i>fac</i> -[Cr(CO) ₃ (CNEt)(bipy)]	7.95 (d)	7.70 (t)	7.30 (t)	9.37 (d)	CDCl ₃
<i>fac</i> -[Cr(CO) ₃ (CNC ₆ H ₄ Me- <i>p</i>)(bipy)]	7.97 (d)	7.77 (t)	7.23 (t)	9.36 (d)	CDCl ₃

^a d = Doublet, t = triplet, dt = doublet of triplets, td = triplet of doublets. ^b dmsO = Dimethyl sulphoxide. ^c Obscured by resonances of -C₅H₅.

The proton chemical shifts measured from ¹H n.m.r. spectra of the bipy ring protons are listed in Table 2. The assignment was assisted by comparison with the free ligand and the simple complex, [Mo(CO)₄(bipy)]. The values of the coupling constants, $J_{i,j}$ ($i, j = 3-6$), are fairly insensitive to environment and together with the characteristic first-order coupling pattern usually permit a complete assignment of the spectra. The ¹H n.m.r. spectra of complexes containing bipy are often sensitive to solvent polarity, so that strict comparison can be made only when the solvents are the same. The chemical shifts of the ring protons H³, H⁴, and H⁵, which are not subject to the possible steric interactions as H⁶ may be, show the electronic influence of the acceptor strength of the ligands L in the complexes *cis*-[Mo(CO)₂L₂(bipy)] in shifting to lower field in the order L = CO > P(OMe)₃ > PBU₃ for strictly comparable solvents. This order is the same as that indicated by $\nu(\text{CO})$ absorptions in the i.r. spectra of these complexes.

In general, complexes having similar structural features have very similar ring proton chemical shifts {e.g. *cis*-[MoL₂(bipy)₂], L = CO or PF₃}. The ring proton chemical shifts in the series [Mo(CO)_{4-x}(CNEt)_x(bipy)] ($x = 0-2$) show a monotonic shift to high field for H³, H⁴, and H⁵ as x increases, whereas H⁶ moves progressively to lower field as the number

of isocyanide ligands increases. The coupling $^2J(^{14}\text{N}-^1\text{H})$ observed in pure ethyl isocyanide is not detected in these complexes. The proton n.m.r. spectrum of *cis*-[Mo(CO)₂(CNC₆H₄Me-*p*)₄] recorded at 300 MHz shows two different methyl groups (δ 3.30, 3.28 p.p.m.) which may be assigned to the ligands *trans* to CO and *trans* to isocyanide.

Poor solubility prevented the recording of ³¹P n.m.r. spectra of all but three of the phosphorus donor ligand complexes. The proton-decoupled spectrum of *cis*-[Mo(PF₃)₂(bipy)₂] shows the expected pattern of signals which gives $\delta(^{31}\text{P}) - 5.82$ p.p.m. [with reference to H₃PO₄; $^1J(\text{PF})$ 965 Hz]. Both the chemical shift and the coupling constant of PF₃ in this complex show large changes from their values in *cis*-[Mo(CO)₄(PF₃)₂] [$\delta(^{31}\text{P})$ 148.0 p.p.m.; $^1J(\text{PF})$ 1 305 Hz]. The completely decoupled ³¹P spectrum of *cis,trans*-[Mo(CO)₂{P(OMe)₃}₂(bipy)] contains a single resonance at $\delta - 24.38$ p.p.m. which can be compared with *trans*-[Mo(CO)₄{P(OMe)₃}₂] for which $\delta + 174.2$ p.p.m. is observed.¹⁵ The partially decoupled spectrum of *cis,trans*-[Mo(CO)₂{P(OMe)₃}₂(bipy)] provides a measure of $^3J(\text{PH})$ 5.8 Hz, which is less than that (11.6 Hz) in [Mo(CO)₅{P(OMe)₃}. There is a single resonance (δ 37.62 p.p.m.) in the ³¹P n.m.r. spectrum of *fac*-[Mo(CO)₃(PPh₃)(bipy)].

Consistent with the conclusion, drawn from i.r. and ^1H n.m.r. measurements mentioned above, concerning the influence of the acceptor strength of ligand L on the properties of *cis*-[Mo(CO)₂L₂(bipy)] complexes, the energy of the (Mo $4d \rightarrow \pi^*$ bipy) charge-transfer transition decreases as the acceptor strength of L decreases thus, in dichloromethane, L = CO (469) > P(OMe)₃ (567) > CNEt (647) > PBu₃ (710 nm). The effect is cumulative: for instance in *fac*-[Mo(CO)₃(CNEt)(bipy)] the metal-to-ligand charge-transfer absorption is observed at 529 nm.

Mass spectra of complexes of these bipy complexes are difficult to obtain because of their poor volatility. The electron impact mass spectrum (e.i.m.s.) of very pure samples of *cis*-[Mo(CO)₂(CNC₆H₄Me-*p*)₂] contains ions which derive from the complexes [Mo(CO)_{6-x}(CNC₆H₄Me-*p*)_x] ($x = 1-5$), which indicates that under the conditions of the measurement (70 eV, 520 K) the isocyanide and CO ligands undergo redistribution. This intermolecular ligand exchange principle has been used¹⁶ for the synthesis of *cis*-[Cr(CO)₂(CNPh)₄] and [Cr(CO)(CNPh)₅] from stoichiometric reactions between [Cr(CNPh)₆] and [Cr(CO)₆]. The fast atom bombardment mass spectrum (f.a.b.m.s.) has been recorded for *cis,trans*-[Mo(CO)₂(PBu₃)₂(bipy)]: comparison with the e.i.m.s. of *cis,trans*-[Mo(CO)₂{P(OMe)₃}(bipy)] indicates that the f.a.b.m.s. produces ions in which hydrogen is lost [($M - 1$)⁺, ($M - L - 1$)⁺], whereas e.i.m.s. produces M^+ and ($M - L$)⁺ ions.

Conclusions

The thermal substitution chemistry of *cis*-[M(CO)₂(bipy)₂] (M = Mo or W) by nucleophiles is shown to encompass a variety of products and relative rates of reaction. Whereas PF₃ reacts rapidly under mild conditions to displace CO and form *cis*-[Mo(PF₃)₂(bipy)₂], PBu₃ requires much higher temperature and longer reaction time to displace bipy and form *cis,trans*-[Mo(CO)₂(PBu₃)₂(bipy)] as a result of a major reorganisation which may proceed through a trigonal bipyramidal intermediate. Although *p*-tolyl isocyanide displaces both bipy ligands rapidly at room temperature, ethyl isocyanide will only substitute one of these ligands, to give *cis,trans*-[M(CO)₂(CNEt)₂(bipy)] (M = Mo or W).

The spectroscopic properties of the highly coloured *cis* dicarbonyl complexes *cis*-[Mo(CO)₂L₂(bipy)] indicate that the acceptor strength of L decreases in the order CO > P(OMe)₃ > CNEt > PBu₃. This order is the same as that of the $\nu(\text{CO})$ (A_1) absorption wavenumbers^{12,17} in [Ni(CO)₃L] which is generally accepted as a measure of the acceptor properties of L. This order of acceptor strength suggests that the geometric disposition of the ligands L, whether *cis* or *trans* to one another, does not play a significant role in determining the electron-density distribution in the other ligands (CO or bipy) bound to the metal.

Experimental

Preparations were all carried out in an atmosphere of pre-purified dinitrogen using standard techniques (Schlenk tubes, cannulae, vacuum manifold). Reactions were carried out in a darkened fume hood, taking care to exclude direct 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. Triphenylphosphine was recrystallised from diethyl ether and checked for the absence of triphenylphosphine oxide by i.r. spectroscopy [$\nu(\text{PO})$ 1140–1100 cm⁻¹]. Trimethyl phosphite and tetralin were treated with sodium wire and then distilled from fresh

sodium wire onto activated molecular sieves. Ethyl- and *p*-tolyl-isocyanide were prepared by the modified Hofmann carbylamine method, using [N(CH₂Ph)Et₃]Cl as a phase transfer catalyst.¹⁸ The complexes [M(CO)₄(bipy)] (M = Cr, Mo, or W) were prepared by the method of Stiddard.¹⁹ The complexes *cis*-[M(CO)₂(bipy)₂] (M = Mo or W) were prepared by our modification¹³ of the published method.¹

Preparations.—*cis*-2,2'-Bipyridinedicarbonylbis(trimethyl phosphite)molybdenum. Solid *cis*-[Mo(CO)₂(bipy)₂] (1.447 g, 3.12 mmol) was added to trimethyl phosphite (13 cm³, 13.68 g, 110 mmol) and the mixture heated at reflux for 24 h during which time the colour of the solution became deep blue. Most of the excess trimethyl phosphite was removed by distillation under reduced pressure and bipy was removed by sublimation from the reaction residue. The remainder was extracted with methylene chloride. The product was crystallised by slow diffusion of light petroleum (b.p. 40–60 °C) into the extract to give large purple cubic crystals (0.42 g, 24% yield) which are soluble in chloroform and more polar solvents (Found: C, 38.8; H, 4.5; Mo, 16.8; N, 4.7; P, 11.4. Calc. for C₁₈H₂₆MoN₂O₈P₂: C, 38.8; H, 4.7; Mo, 17.3; N, 5.0; P, 11.2%). I.r. 1580m, 1252w, 1179m, 1035br, 755br, 702s cm⁻¹; ^1H n.m.r.: δ 3.25 p.p.m. (t, CH₃) (CD₂Cl₂); m/e (I) 558 (1.2), M^+ , 530 (0.7), 434 (1.4), 402 (0.2), 378 (2.1), 254 (0.7); λ_{max} . 366, 567 nm (MeCN).

The complexes *cis*-[Mo(CO)₂(PPh₃)₂(bipy)] and *cis*-[Mo(CO)₂(PBu₃)₂(bipy)] were prepared from *cis*-[Mo(CO)₂(bipy)₂] in a similar manner using tetralin as solvent at 420 K. (i) *cis*-[Mo(CO)₂(PPh₃)₂(bipy)] green solid, yield 52%. (Found: C, 68.5; H, 4.5; Mo, 10.9; N, 3.3; P, 7.1. Calc. for C₄₈H₃₈MoN₂O₂P₄: C, 69.2; H, 4.6; Mo, 11.5; N, 3.4; P, 7.5%). This complex is insoluble even in polar solvents such as acetone and acetonitrile. (ii) *cis*-[Mo(CO)₂(PBu₃)₂(bipy)], purple platelets, yield 25%; λ_{max} . 516, 785 nm (benzene) (Found: C, 60.0; H, 8.4; Mo, 13.8; N, 4.1; P, 8.6. Calc. for C₃₄H₆₂MoN₂O₂P₂: C, 60.7; H, 8.7; Mo, 13.5; N, 3.9; P, 8.7%). This complex is slightly soluble in benzene and more polar solvents. ^1H N.m.r.: δ 0.67 (t), 1.08 (m) (CDCl₃) p.p.m.; m/e 713 ($M^+ - 1$), 511, 503.

fac-(2,2'-Bipyridine)tricarbonyl(triphenylphosphine)molybdenum. Triphenylphosphine (0.816 g, 3.11 mmol) and tetralin (20 cm³) were added to an acetonitrile solution-slurry of *cis*-[Mo(CO)₂(bipy)₂] (0.803 g, 1.73 mmol in 25 cm³). The stirred reaction mixture was warmed over a period of 3 h to 373 K and held at this temperature for a further 5 h, after which the green-purple solution was concentrated by evaporation under reduced pressure. Pentane (150 cm³) was added to precipitate the product which was filtered (cannula). The green solid residue was extracted with dichloromethane (2 × 30 cm³), the solution filtered, and light petroleum (b.p. 40–60 °C) added to effect crystallisation. After several days, large green crystals with a purple reflectance were isolated by filtration. Yield 0.38 g, 37% (Found: C, 61.8; H, 3.9; Mo, 16.8; N, 4.9; P, 5.0. Calc. for C₃₁H₂₅MoN₂O₃P: C, 62.2; H, 4.2; Mo, 16.1; N, 4.7; P, 5.2%). This complex is soluble in dichloromethane and more polar solvents. It is not very oxygen-sensitive as a solid, but is very much more so in solution.

cis-(2,2'-Bipyridine)[1,2-bis(diphenylphosphino)ethane]-dicarbonylmolybdenum. Solid 1,2-bis(diphenylphosphino)ethane (1.00 g, 2.51 mmol) was added to a solution-slurry of *cis*-[Mo(CO)₂(bipy)₂] in acetonitrile (1.23 g, 2.65 mmol in 25 cm³). No reaction was apparent at room temperature, consequently the mixture was heated at reflux for 8 h during which the solution became very dark green. The solvent was evaporated under reduced pressure and the residue recrystallised from dichloromethane-light petroleum (b.p. 40–60 °C) to

give small, well formed dark green platelets. Yield 0.33 g, 18% (Found: C, 64.1; H, 3.95; Mo, 13.2; N, 4.2; P, 8.9. Calc. for $C_{38}H_{32}MoN_2O_2P_2$: C, 64.6; H, 4.5; Mo, 13.6; N, 4.0; P, 8.8%). The complex is soluble in chloroform and more polar solvents; λ_{max} . 605 nm (CH_2Cl_2).

cis-Dicarbonyltetrakis(p-tolyl isocyanide)molybdenum. A benzene solution of *p*-tolyl isocyanide (0.9 g, 7.69 mmol in 20 cm³) was added to a stirred solution-slurry of *cis*-[Mo(CO)₂(bipy)] (0.793 g, 1.71 mmol) in acetonitrile (25 cm³) at room temperature. The reaction mixture soon (0.5 h) became green-yellow. After 2 h the mixture was transferred to a sublimation apparatus, the solvent was evaporated under reduced pressure, and the brown residue heated (330–340 K) under a dynamic vacuum (~0.1 mmHg). Over a period of 3 h, an off-white crystalline solid, shown to be 2,2'-bipyridine (u.v.-visible), sublimed onto the water-cooled probe. The residue was extracted with dichloromethane (4 × 15 cm³), this solution was filtered and concentrated (ca. 50% by volume) under reduced pressure. Addition of pentane precipitated a yellow-orange solid which was recrystallised from dichloromethane-light petroleum (b.p. 40–60 °C) to give yellow crystals. Yield 0.39 g, 37% (Found: C, 65.5; H, 4.5; Mo, 15.4; N, 9.0. Calc. for $C_{34}H_{28}MoN_4O_2$: C, 65.8; H, 4.5; Mo, 15.5; N, 9.0%). T.l.c. on silica showed R_f 0.64 (light petroleum-Et₂O, 5 : 1), 0.29 (light petroleum-C₆H₆, 4 : 1). The complex is soluble in most common organic solvents with the exception of light petroleum. The solid complex is not noticeably air sensitive over several days and in solution it is only slowly decomposed by aerial oxidation. I.r.: 1 502s, 812s, 717s cm⁻¹ (Nujol); ¹H n.m.r., δ 3.28, 3.30, 7.06–7.31 p.p.m. (CD_2Cl_2); *m/e* (*I*, %) 711 (2), 683 (1.5), 622 (5) *M*⁺, 594 (7), 566 (12), 533 (14), 505 (18), 477 (7), 444 (30), 416 (23), 388 (34). The tungsten analogue was prepared in a similar manner to the molybdenum compound; *cis*-[W(CO)₂(CNC₆H₄Me-*p*)₄] is isolated as a yellow powder (yield 28%) (Found: C, 57.0; H, 3.7; N, 7.5; W, 25.4. Calc. for $C_{34}H_{28}N_4O_2W$: C, 57.6; H, 3.9; N, 7.9; W, 26.0%); ¹H n.m.r., δ 2.36 (d), 7.15–7.35 p.p.m. (m) (CD_3CN); *m/e* (*I*, %) 708 (0.6) *M*⁺, 680 (0.3), 652 (0.8), 619 (7.4), 591 (8.2), 563 (8.3), 535 (9.8), 530 (25.1), 502 (25.3), 474 (31.3).

cis-(2,2'-Bipyridine)dicarbonylbis(ethyl isocyanide)molybdenum. Degassed ethyl isocyanide (0.84 cm³, 0.622 g, 11.3 mmol) was added dropwise to a stirred solution-slurry of *cis*-[Mo(CO)₂(bipy)₂] (1.41 g, 3.04 mmol) in acetonitrile (25 cm³). The mixture was stirred at room temperature for 6 h during which the colour of the solution became green-blue. The mixture was evaporated to dryness under reduced pressure. Dichloromethane (35 cm³) was added to the residue and the resulting green solution was filtered. Careful addition of light petroleum (b.p. 40–60 °C) to the filtrate produced green platelet crystals over a period of 4 d. The green crystalline product was isolated by filtration. Yield 0.72 g, 57% (Found: C, 51.2; H, 4.2; Mo, 22.5; N, 13.4. Calc. for $C_{18}H_{18}MoN_4O_2$: C, 51.7; H, 4.3; Mo, 23.0; N, 13.4%); ¹H n.m.r., δ 1.09 (t) (CH_3), 3.38 (q) (CH_2) p.p.m. (CD_2Cl_2); λ_{max} . 411, 647 nm (CH_2Cl_2).

The complex *cis*-[W(CO)₂(bipy)₂] reacts with ethyl isocyanide more rapidly (2 h) than does its molybdenum analogue to give, after recrystallisation, green diamond-shaped crystals. Yield 64% (Found: C, 41.9; H, 3.3; N, 10.4; W, 36.3. Calc. for $C_{18}H_{18}N_4O_2W$: C, 42.7; H, 3.6; N, 11.1; W, 36.4%); ¹H n.m.r., δ 1.12 (t) (CH_3), 3.46 p.p.m. (q) (CH_2) (CD_3CN); λ_{max} . 416, 670 nm (CH_2Cl_2). Both of the complexes *cis*, *cis*-[M(CO)₂(CNEt)₂(bipy)] are slightly soluble in more polar organic solvents (e.g. dichloromethane, acetone, or acetonitrile). The solid complexes are not affected by brief contact with air, but in solution they are much more sensitive to oxidation.

fac-(2,2'-Bipyridine)tricarbonyl(ethyl isocyanide)molybde-

num. Solid *cis*-[Mo(CO)₄(bipy)] (0.60 g, 1.62 mmol) was added to a solution of ethyl isocyanide (0.27 cm³, 0.200 g, 3.63 mmol) in dichloromethane (20 cm³). The mixture was heated at reflux for 7 h, the solution becoming red-purple. Evaporation of the solvent under reduced pressure left a sticky residue which was dissolved in chloroform and precipitated by the addition of light petroleum (b.p. 40–60 °C) as a purple solid. Yield 0.19 g, 30% (Found: C, 48.6; H, 3.1; Mo, 23.9; N, 10.5. Calc. for $C_{16}H_{13}MoN_3O_3$: C, 49.1; H, 3.3; Mo, 24.6; N, 10.7%); ¹H n.m.r., δ 1.13 (t) (CH_3), 2.32 p.p.m. (q) (CH_2) (CD_2Cl_2); λ_{max} . 529 nm (CH_2Cl_2).

The complexes *fac*-[Cr(CO)₃(CNR)(bipy)] (R = Et or *p*-tolyl) were prepared in a similar way. They were isolated as very dark green microcrystalline solids. (i) *fac*-[Cr(CO)₃(CNEt)(bipy)], yield 59% (Found: C, 54.8; H, 3.7; Cr, 15.1; N, 11.9. Calc. for $C_{16}H_{13}CrN_3O_3$: C, 55.3; H, 3.8; Cr, 15.0; N, 12.1%); λ_{max} . 553 nm (MeCN). (ii) *fac*-[Cr(CO)₃(CNC₆H₄Me-*p*)(bipy)], yield 65% (Found: C, 60.9; H, 3.9; Cr, 12.3; N, 10.1. Calc. for $C_{21}H_{15}CrN_3O_3$: C, 61.6; H, 3.7; Cr, 12.7; N, 10.3%); λ_{max} . 544 nm (MeCN).

cis-Bis(2,2'-bipyridine)bis(trifluorophosphine)molybdenum. Gaseous trifluorophosphine (Ozark Mahoning) was passed down a short column of activated molecular sieves and then bubbled slowly from a Pasteur pipette into a vigorously stirred solution-slurry of *cis*-[Mo(CO)₂(bipy)₂] (0.807 g, 1.74 mmol) in acetonitrile (25 cm³). After 15 min the black solid complex had all dissolved, forming a dark red solution. Passage of the gas was stopped and the reaction vessel (Schlenk tube) was sealed. The reaction mixture was stirred for a further 1.5 h, after which the solvent was removed by distillation under reduced pressure. The residue was extracted with dichloromethane (2 × 20 cm³). The deep purple solution of the extract was covered with a layer of light petroleum (b.p. 40–60 °C fraction). Small, well formed red-black crystals of *cis*-[Mo(PF₃)₂(bipy)₂] were isolated. Yield 0.345 g, 34% (Found: C, 41.0; H, 3.1; F, 18.9; Mo, 16.6; N, 9.0; P, 10.5. Calc. for $C_{20}H_{16}F_6MoN_4P_2$: C, 41.1; H, 2.7; F, 19.5; Mo, 16.6; N, 9.0; P, 10.5%); λ_{max} . 442, 648 nm (MeCN); i.r., 1 600m, 1 248m, 1 165w, 987m, 783vs, 770s cm⁻¹ (Nujol). This air-sensitive complex is much more soluble than *cis*-[Mo(CO)₂(bipy)₂] in solvents such as tetrahydrofuran, CH_2Cl_2 , acetone, or acetonitrile.

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