Transition-metal Derivatives of Arenediazonium Ions. Part 8.† The Reactions of Nitrosonium and Arenediazonium Ions with 2,2'-Bipyridyl and 1,10-Phenanthroline Derivatives of Group 6 Metal Carbonyls

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The reaction between [W(CO)$_4$(phen)] (phen = 1,10-phenanthroline) and [NO][PF$_6$] in methanol—toluene gives *mer*-[W(CO)$_3$(phen)(NO)][PF$_6$] (1) whereas [Mo(CO)$_4$(L–L)] [L–L = bipy (2,2'-bipyridyl) or phen] reacts with either [NO]$^+$ or [RN$_2$]$^+$ (R = aryl) in acetone to produce *fac*-[M(CO)$_3$(L–L)Z][BF$_4$] [Z = NO (2) or RN$_2$ (3)]. The complexes [Mo(CO)$_3$(L–L)(PPh$_3$)] and either [NO]$^+$ or [RN$_2$]$^+$ in acetone give [M(CO)$_2$(L–L)Z(PPh$_3$)]$^+$ [Z = NO (4) or RN$_2$ (5)] which may also be prepared form (1)—(3) and PPh$_3$. With an excess of PPh$_3$, (2) or (3) yield [Mo(CO)Z(L–L)(PPh$_3$)$_2$]$^+$ [Z = NO (6) or RN$_2$ (7)], and with halide ion (1)—(5) afford [MX(CO)$_2$(L–L)Z] [X = Cl, Br, or I; Z = NO (8) or RN$_2$ (9)]. Iodine or Br$_2$ reacts with (5) to give [{MoX$_3$(L–L)(N$_2$R)}$_n$] (10; X = I or Br). On refluxing (1) in acetone, rapid partial hydrolysis of he [PF$_6$]$^-$ anion, and carbonyl substitution, gives [W(CO)$_2$(phen)(NO)(O$_2$PF$_2$)] (11).

We have previously reported the reactions of nitrosonium [1-3] and arenediazonium [4-6] ions with a variety of transition-metal carbonyl complexes. We now describe the generation and subsequent reactions of a number of cationic nitrosyl and arenediazo-complexes derived from the Group 6 metal carbonyl substrates [M(CO)$_4$(L–L)] and [Mo(CO)$_3$(L–L)(PPh$_3$)] [M = Mo or W, L–L = 2,2'-bipyridyl (bipy) or 1,10-phenanthroline (phen)]. Comparisons may be made not only between analogous nitrosyl and arenediazo-complexes such as [M(CO)$_2$(L–L)Z(PPh$_3$)]$^+$ [Z = NO or RN$_2$ (R = aryl)] but also with known [1] closely related nitrosyls such as [M(CO)$_3$(NO)(dppe)]$^+$ (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$).

RESULTS AND DISCUSSION

The addition of [NO][PF$_6$] to solutions of [M(CO)$_4$(L–L)] (M = Mo or W, L–L = bipy or phen) in methanol–toluene mixtures resulted in the evolution of CO and the formation of orange solutions or precipitates. For M = W and L–L = phen, the orange solid formed may be fully characterised as the tricarbonylnitrosyl cation *mer*-[W(CO)$_3$(phen)(NO)][PF$_6$] (1) (Table). Under the same reaction conditions the other tricarbonyl cations, [M(CO)$_3$(L–L)(NO)]$^+$ (M = Mo, L–L = bipy or phen; M = W, L–L = bipy) are undoubtedly formed in solution but could not be isolated pure. Attempted isolation of these species invariably afforded solids which have i.r. spectra, in the carbonyl and nitrosyl regions, very similar to those of the halogenonitrosyl complexes (8) reported below, suggesting that the solids are of the type [MX(CO)$_2$(L–L)(NO)] where X is some unspecified monoanionic ligand deriving from the reaction mixture.

The reaction between [NO][BF$_4$] and [Mo(CO)$_4$(L–L)] (L–L = bipy or phen) in acetone at −78 °C again resulted in the formation of orange solutions from which red-brown solids (2) could be isolated after warming to room temperature. The solids, which slowly decompose in air or on attempted recrystallisation, show two carbonyl absorptions of equal intensity and one nitrosyl absorption in the i.r. spectrum. Although these spectra are superficially similar to those of the products of the reactions in methanol–toluene (see above), freshly prepared samples of (2) showed strong absorptions associated with the [BF$_4$]$^-$ anion, and the subsequent reactions of (2) with PPh$_3$ gave high yields of cationic complexes containing tetrafluoroborate as the counter anion. Elemental analysis (C, H, and N) for (2) gave results which are in good agreement with the formula [Mo(CO)$_3$(L–L)(NO)][BF$_4$] (L–L = bipy or phen), and careful measurement of the quantity of CO evolved on treating fresh samples of (2) with halide ion, X$^-$ {to give [MX(CO)$_2$(L–L)(NO)] (see below)}, showed that one carbonyl group is lost in the reaction, as would be anticipated from a tricarbonyl cation. By comparison of the i.r. spectra, in the carbonyl region, of (2) with that of (1) we therefore formulate (2) as the *fac*-tricarbonyl complex *fac*-[Mo(CO)$_3$(L–L)(NO)][BF$_4$].

The assignment of *mer* and *fac* geometries to (1) and (2) respectively is based on a consideration of the positions, and relative intensities, of the carbonyl absorptions in the i.r. spectra. It is not possible to assign geometry solely on the basis of the number of carbonyl bands observed since one would expect three i.r.-active absorptions for either *fac*- or *mer*-[M(CO)$_3$(L–L)(NO)]$^+$; neither complex strictly has the C_{3v} symmetry necessary for two i.r.-active carbonyl-stretching vibrations. Structural assignment may, however, be made on the basis of the shifts of certain of the carbonyl absorptions observed on changing the chelate ligand, L–L. In order to do this it is useful to consider the spectra, in the carbonyl-stretching region, of the neutral precursors [M(CO)$_4$(L–L)]. The ligand L–L will affect most strongly those vibrations associated with the CO groups *trans* to L–L while those associated with the *cis*-carbonyls will be more weakly influenced. Thus

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† Part 7 is ref. 12.

[1] N. G. Connelly, *J.C.S. Dalton*, 1973, 2183.

[2] N. G. Connelly and R. L. Kelly, *J.C.S. Dalton*, 1974, 2334.

[3] N. G. Connelly, Z. Demidowicz, and R. L. Kelly, *J.C.S. Dalton*, 1975, 2335.

[4] F. J. Lalor and P. L. Pauson, *J. Organometallic Chem.*, 1970, **25**, C51.

[5] W. E. Carroll and F. J. Lalor, *J. Organometallic Chem.*, 1973, **54**, C37.

[6] W. E. Carroll and F. J. Lalor, *J.C.S. Dalton*, 1973, 1954.

in the complex $[W(CO)_4(L–L)]$ the vibrations associated with the *trans*-carbonyl groups [assigned as A_1 CO$^{(1)}$ and B_2 CO$^{(1)}$ by Cotton and Kraihanzel[7,8]] occur at higher wavenumber for L–L = dppe (1 909 and 1 872 cm^{-1}, in CH_2Cl_2) than for L–L = bipy (1 869 and 1 825 cm^{-1}, in CH_2Cl_2). In contrast, the vibrations associated with the *cis*-carbonyl ligands [assigned[7,8] as A_1 CO$^{(2)}$ and B_1 CO$^{(2)}$] are essentially the same for L–L = dppe (2 009 and 1 897 cm^{-1}, in CH_2Cl_2) and L–L = bipy (2 005 and 1 893 cm^{-1}, in CH_2Cl_2). In the i.r. spectra of $[W(CO)_3(L–L)(NO)]^+$ we note that for L–L = dppe[1] there are two carbonyl bands, at 2 102m and 2 025vs cm^{-1}, whereas for L–L = phen there are three, at 2 111m, 2 033vs, and 1 997m cm^{-1}.

Microanalytical and i.r. data for nitrosyl and arenediazo-complexes of 2,2′-bipyridyl and 1,10-phenanthroline substituted Group 6 metal carbonyls

Complex	Analyses[a] (%)				I.r. data (cm^{-1})[b]		
	C	H	N	Other	$\bar{\nu}$(CO)[c]	$\bar{\nu}$(NO)	$\bar{\nu}$(NN)
fac-$[Mo(CO)_3(bipy)(NO)][BF_4]$	34.5 (34.5)	2.1 (1.8)	9.5 (9.3)		2 031, 1 948	1 668	
fac-$[Mo(CO)_3(phen)(NO)][BF_4]$	37.1 (37.8)	2.2 (1.7)	9.5 (8.8)		2 032, 1 949	1 668	
mer-$[W(CO)_3(phen)(NO)][PF_6]$	28.9 (28.9)	1.5 (1.3)	6.7 (6.8)		2 111w, 2 033vs, 1 997m	1 705s	
$[Mo(CO)_2(bipy)(NO)(PPh_3)][BF_4]$ Isomer (A)	52.3 (52.4)	3.8 (3.3)	6.2 (6.1)		2 044, 1 968	1 676	
$[Mo(CO)_2(bipy)(NO)(PPh_3)][BF_4]$ Isomer (B)	52.4 (52.4)	3.9 (3.3)	5.6 (6.1)		2 022, 1 939	1 665	
$[Mo(CO)_2(bipy)(NO)(PPh_3)][PF_6]$[d]	47.9 (48.4)	3.1 (3.1)	5.4 (5.6)				
$[Mo(CO)_2(phen)(NO)(PPh_3)][PF_6]$[d]	49.5 (50.0)	3.0 (3.0)	5.5 (5.5)		2 046, 2 030, 1 969, 1 944	1 677	
$[W(CO)_2(phen)(NO)(PPh_3)][PF_6]$	44.6 (44.8)	2.8 (2.7)	4.9 (4.9)		2 025, 1 941	1 663	
$[Mo(CO)(bipy)(NO)(PPh_3)_2][BF_4]$	61.1 (61.3)	4.4 (4.1)	4.5 (4.6)				
$[Mo(CO)(bipy)(NO)(PPh_3)_2][PF_6]$	57.2 (57.6)	4.1 (3.9)	4.5 (4.3)		1 929	1 632	
$[Mo(CO)(phen)(NO)(PPh_3)_2][PF_6]$	59.0 (58.7)	3.8 (3.8)	4.4 (4.2)		1 932	1 633	
$[MoCl(CO)_2(bipy)(NO)]$	38.7 (38.6)	2.3 (2.2)	11.0 (11.3)	Cl 9.2 (9.5)	2 020, 1 941	1 641	
$[MoBr(CO)_2(bipy)(NO)]$	34.6 (34.5)	2.2 (1.9)	9.9 (10.1)	Br 19.4 (19.1)	2 026, 1 940	1 643	
$[MoI(CO)_2(bipy)(NO)]$	30.9 (30.0)	1.8 (1.7)	9.0 (9.0)		2 023, 1 939	1 644	
$[MoCl(CO)_2(phen)(NO)]$	42.3 (42.2)	2.2 (2.0)	10.1 (10.6)	Cl 9.1 (8.9)	2 026, 1 941	1 642	
$[MoBr(CO)_2(phen)(NO)]$	37.9 (38.0)	2.0 (1.8)	9.0 (9.5)	Br 18.4 (18.1)	2 026, 1 944	1 641	
$[WCl(CO)_2(phen)(NO)]$	34.5 (34.6)	1.7 (1.7)	7.9 (8.7)		2 000, 1 903	1 637	
$[WBr(CO)_2(phen)(NO)]$	31.5 (31.7)	1.6 (1.5)	7.9 (7.9)		2 000, 1 907	1 637	
$[WI(CO)_2(phen)(NO)]$	29.4 (29.1)	1.5 (1.4)	7.3 (7.3)		1 992, 1 905	1 629	
$[W(CO)_2(phen)(NO)(O_2PF_2)]$	31.2 (32.1)	1.6 (1.6)	7.7 (8.0)		2 015, 1 923[e]	1 627	
fac-$[Mo(CO)_3(bipy)(N_2C_6H_4F\text{-}p)][BF_4]$	41.7 (41.8)	2.8 (2.2)	10.6 (10.3)		2 003, 1 921		1 622, 1 570[f]
$[Mo(CO)_2(bipy)(N_2Ph)(PPh_3)][BF_4]$	56.9 (56.8)	4.1 (3.7)	7.2 (7.4)		2 001, 1 918		1 632, 1 561[g]
$[Mo(CO)_2(bipy)(N_2C_6H_4Me\text{-}p)(PPh_3)][PF_6]$	53.1 (53.3)	4.2 (3.6)	6.8 (6.7)		2 002, 1 928		1 628, 1 565
$[Mo(CO)_2(bipy)(N_2C_6H_4F\text{-}p)(PPh_3)][BF_4]$	55.5 (55.4)	3.5 (3.5)	7.0 (7.2)		2 000, 1 921		1 621, 1 564
$[Mo(CO)_2(bipy)(N_2C_6H_4F\text{-}m)(PPh_3)][BF_4]$	55.1 (55.4)	4.0 (3.5)	6.9 (7.2)		2 001, 1 926		1 623, 1 560
$[Mo(CO)_2(phen)(N_2Ph)(PPh_3)][BF_4]$	57.9 (58.0)	3.6 (3.6)	6.7 (7.1)		2 006, 1 930		1 633, 1 561[h]
$[Mo(CO)_2(phen)(N_2C_6H_4Me\text{-}p)(PPh_3)][PF_6]$	54.9 (54.5)	4.0 (3.5)	6.5 (6.5)		2 004, 1 918		1 623, 1 562
$[Mo(CO)_2(phen)(N_2C_6H_4F\text{-}p)(PPh_3)][BF_4]$	56.6 (56.8)	3.7 (3.4)	6.9 (7.0)		2 002, 1 922		1 625, 1 567
$[Mo(CO)_2(phen)(N_2C_6H_4F\text{-}m)(PPh_3)][BF_4]$	56.2 (56.8)	3.5 (3.4)	6.7 (7.0)		2 004, 1 936		1 628, 1 656
$[Mo(CO)(bipy)(N_2C_6H_4Me\text{-}p)(PPh_3)_2][PF_6]$	60.4 (60.7)	4.6 (4.2)	5.1 (5.2)		1 880		1 534
$[Mo(CO)(phen)(N_2C_6H_4Me\text{-}p)(PPh_3)_2][PF_6]$	61.6 (61.6)	4.3 (4.1)	5.1 (5.1)		1 881		1 535
$[MoCl(CO)_2(bipy)(N_2C_6H_4Me\text{-}p)]$	49.7 (49.3)	3.6 (3.3)	11.9 (12.1)	Cl 7.7 (7.7)	1 999, 1 915		1 545
$[MoBr(CO)_2(bipy)(N_2C_6H_4Me\text{-}p)]$	45.5 (45.0)	3.2 (3.0)	11.1 (11.1)	Br 15.8 (15.8)	1 999, 1 916		1 546
$[MoCl(CO)_2(bipy)(N_2C_6H_4F\text{-}p)]$	45.8 (46.3)	2.7 (2.6)	12.0 (12.0)		2 008, 1 918		1 550
$[MoBr(CO)_2(bipy)(N_2C_6H_4F\text{-}p)]$	41.4 (42.3)	2.3 (2.3)	10.6 (11.0)		2 010, 1 918		1 553
$[MoI(CO)_2(bipy)(N_2C_6H_4F\text{-}p)]$	38.2 (38.7)	2.5 (2.2)	9.8 (10.0)		2 000, 1 918		1 553
$[MoCl(CO)_2(phen)(N_2C_6H_4Me\text{-}p)]$	51.5 (51.8)	3.0 (2.6)	11.1 (11.5)	Cl 7.4 (7.3)	2 001, 1 915		1 546
$[MoBr(CO)_2(phen)(N_2C_6H_4Me\text{-}p)]$	46.8 (47.5)	2.9 (2.9)	10.4 (10.6)	Br 14.6 (15.1)	2 001, 1 917		1 547
$[\{MoBr_3(bipy)(N_2C_6H_4Me\text{-}p)\}_n]$	34.1 (33.4)	2.8 (2.5)	8.6 (9.2)				1 408
$[\{MoI_3(bipy)(N_2C_6H_4Me\text{-}p)\}_n]$	27.2 (27.0)	2.2 (2.0)	6.9 (7.5)				1 407
$[\{MoBr_3(phen)(N_2Ph)\}_n]$	34.1 (34.8)	2.0 (2.1)	8.5 (9.0)				1 410[i]
$[\{MoBr_3(phen)(N_2C_6H_4Me\text{-}p)\}_n]$	36.1 (35.9)	2.7 (2.4)	8.3 (8.8)				1 414
$[\{MoI_3(phen)(N_2C_6H_4Me\text{-}p)\}_n]$	30.4 (29.4)	2.3 (2.0)	6.7 (7.2)				1 411

[a] Calculated values are given in parentheses. [b] In CH_2Cl_2 unless otherwise stated. [c] All the absorptions are strong unless otherwise stated (w = weak, vs = very strong, and m = medium). [d] Mixture of isomers (A) and (B) from method (*ii*) (see Experimental section). [e] In Nujol. [f] The presence of two bands associated with the co-ordinated arenediazo-ligand is discussed in the text. [g] $\nu(^{15}N^{14}N)$ at 1 618 and 1 549 cm^{-1}. [h] $\nu(^{15}N^{14}N)$ at 1 620 and 1 547 cm^{-1}. [i] $\nu(^{15}N^{14}N)$ at 1 390 cm^{-1}.

Applying the reasoning developed above for $[M(CO)_4(L–L)]$, the *fac*-tricarbonylnitrosyl cation [(*a*)] will show two CO bands whose positions are sensitive to the nature of L–L and one CO band which is essentially unaffected,

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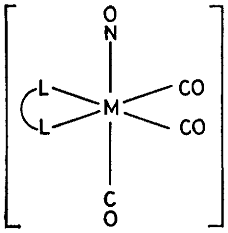
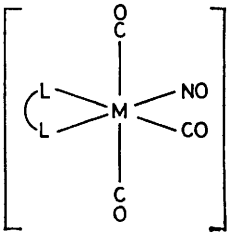
[7] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

[8] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, 1963, **2**, 533.

whereas the *mer*-tricarbonylnitrosyl cation [(*b*)] will show one carbonyl absorption which will be strongly affected by L–L and two which will be essentially invariant. The most reasonable interpretation of the spectra of $[W(CO)_3(L\text{–}L)(NO)]^+$ is that replacement of phen by dppe[1] shifts one carbonyl band from 1 997 cm^{-1} (L–L = phen) to *ca.* 2 025 cm^{-1} (L–L = dppe), while the other two peaks (at 2 111 and 2 033 cm^{-1} for L–L = phen, 2 102 and 2 025 cm^{-1} for L–L = dppe) are essentially unchanged in position. It is apparent that, since both structures (*a*) and (*b*) would give rise to three i.r. carbonyl absorptions, the variable peak for the dppe complex is shifted to coincide with one of the invariant peaks; the spectrum of $[W(CO)_3(NO)(dppe)]^+$ shows only two carbonyl bands. The i.r. spectra of $[W(CO)_3(L\text{–}L)(NO)]^+$ are therefore compatible with the *mer*-tricarbonylnitrosyl structure (*b*) rather than the *fac* structure (*a*). Confirmatory evidence for this assignment is provided by the observation that ν(NO) for the phen complex (1 705 cm^{-1}) is shifted (1 725 cm^{-1}) in the dppe analogue as would be expected for structure (*b*) in which NO is *trans* to L. The assignment of the *mer* geometry to (1) allows assignment of the *fac* geometry to (2). The observation of only two bands in the carbonyl region for (2) may be due to poor resolution of the low-frequency absorption in the polar solvent, CH_2Cl_2.*



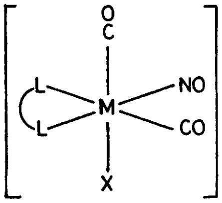
(*a*)



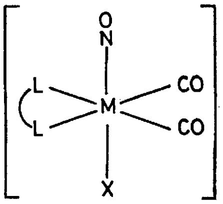
(*b*)

One would predict, on the basis of the *trans* effect, that the axial carbonyls of $[M(CO)_4(L\text{–}L)]$ would be more labile than the equatorial carbonyls since the π-acceptor ability of CO is greater than that of L–L. The reaction of $[NO]^+$ with $[M(CO)_4(L\text{–}L)]$ should thus lead to a *fac*-tricarbonyl complex with structure (*a*), as is observed for substitution by phosphine ligands.[9] However, substitution by $[NO]^+$ is likely to occur *via* an S_N2-type mechanism,[3] in which the nitrosonium ion behaves as a Lewis acid and the substrate as a base, to give the intermediate $[M(CO)_4(L\text{–}L)(NO)]^+$, and is unlikely to be controlled solely by the *trans* influence of the ligands attached to M. Thus it is not unreasonable that both *fac* and *mer* isomers of $[M(CO)_3(L\text{–}L)(NO)]^+$ are observed in the reaction between $[NO]^+$ and $[M(CO)_4(L\text{–}L)]$.

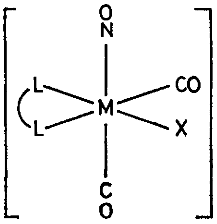
On treating (1) or (2) with PPh_3 the substituted derivatives $[M(CO)_2(L\text{–}L)(NO)(PPh_3)]^+$ (4; M = W, L–L = phen; M = Mo, L–L = bipy or phen) were formed. Although (1) and PPh_3 afforded only one isomer of $[W(CO)_2(phen)(NO)(PPh_3)][PF_6]$, the initial dicarbonylphosphine complex (A) formed from (2; M = Mo, L–L = bipy) and PPh_3 isomerised to a second complex, (B), on stirring in acetone overnight; the reaction of $[Mo(CO)_3(bipy)(PPh_3)]$ with $[NO]^+$ salts led directly to mixtures of the isomers (A) and (B). Prediction of the structures of the isomers of (4) is not possible on the basis of i.r. data alone. Although all the examples of (4) isolated show two carbonyl absorptions of equal intensity, indicating a *cis*-dicarbonyl arrangement in each case, no distinction between structures (*c*)—(*e*) can be made. If simple replacement of CO by PPh_3 occurs then the only *cis*-dicarbonyl complex which can be generated from (1) has structure (*c*), whereas the two isomers formed from (2) should have structures (*d*) and (*e*). However, since isomerisation of (A) to (B) occurs it is clear that rearrangement both during, and after, the reaction between (1) or (2) and PPh_3 can occur and therefore no assignment of the structures of the isomers of (4) can be made.



(*c*)



(*d*)



(*e*)

Although further substitution of the tungsten dicarbonylphosphine cation was not observed even in refluxing acetone, stirring the molybdenum analogues with an excess of PPh_3 at room temperature gave good yields of the monocarbonyl $[Mo(CO)(L\text{–}L)(NO)(PPh_3)_2]^+$ (6). Apparently only one isomer of this complex is formed.

The neutral halogeno-complexes $[MX(CO)_2(L\text{–}L)(NO)]$ (8; M = Mo, L–L = phen or bipy, X = Cl or Br; M = W, L–L = phen, X = Cl, Br, or I) may be prepared by addition of halide ion to (1), (2), or to either isomer of (4; M = Mo). In each case the formation of only one *cis*-dicarbonyl isomer was observed. A more exotic example of a complex of type (8) is $[W(CO)_2(phen)(NO)(O_2PF_2)]$ (11) which was formed when (1) was

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* *Note added in proof*: The structure proposed for *mer*-$[W(CO)_3(dppe)(NO)]^+$ has been verified by ^{31}P n.m.r. spectroscopy. This, and other studies on related complexes of the ligand $o\text{-}C_6H_4(AsMe_2)_2$ will be reported later (N. G. Connelly and C. Gardner, unpublished results).

[9] M. H. B. Stiddard, *J. Chem. Soc.*, 1963, 756.

heated under reflux in acetone.* The formation of (11) evidently involves carbonyl substitution by $[PF_2O_2]^-$ which is the product of partial hydrolysis of the $[PF_6]^-$ anion. Such hydrolysis is usually slow [10] and is therefore, in this case, probably catalysed by (1). The identity of (11) is confirmed by analytical data, and by its i.r. spectrum which not only shows the presence of two carbonyl absorptions and one nitrosyl absorption at positions similar to those for other complexes of type (8) but also bands at 1 320 and 1 128 cm^{-1} (symmetric and antisymmetric P–O stretches), and at 888 and 855 cm^{-1} [ν(PF)] due to the unidentate difluorophosphate ligand; the characteristic absorption of the anion $[PF_6]^-$ (at 835 cm^{-1}) is absent. Complexes (8; M = W, X = Cl, Br, or I) and (11) all show parent ions in the mass spectrum and peaks due to the sequential loss of two carbonyl groups. For the halogenonitrosyl species, competitive loss of NO or X then occurs with the ease of loss of the halogen following the order I > Br > Cl. In the case of (11) loss of the carbonyls is followed by loss of HF from the ion $[W(phen)(NO)(O_2PF_2)]^+$ to give $[W(C_{12}H_7N_2)(NO)(O_2PF)]^+$ (confirmed by the observation of a metastable ion at *m/e* 456).

The relative reactivities of the isostructural cations $[W(CO)_3(L–L)(NO)]^+$ (L–L = phen or dppe [1]) towards further substitution is of interest as one would predict, on the basis of the *trans* effect, that the dppe complex should be the more reactive; dppe is a better π acceptor than phen. The phen complex, however, reacted more rapidly with halide ions than the dppe analogue, and the latter, in contrast to the former, is not further substituted by phosphorus-donor ligands.[1] It is well known that nitrosyl complexes may undergo S_N2 substitution reactions whereas isoelectronic carbonyls generally react *via* S_N1 paths {*viz.* displacement of CO from $[Ni(CO)_4]$ and $[Co(CO)_3(NO)]$ by phosphines [11]}. The possibility of an associative path is the result of the ability of the co-ordinated nitrosyl ligand (bonded as a three-electron donor, in a linear fashion) to accept a pair of electrons from the metal and bend. On bending of the M–N–O group the metal becomes electron deficient with the co-ordinated nitrosyl acting as a one-electron donor. It is clear that the more basic the metal atom in a nitrosyl complex, the more likely is the bending of the M–N–O group and thus the more likely is an associative mechanism for a substitution reaction. Because dppe is a better π acceptor than phen, $[W(CO)_3(dppe)(NO)]^+$ is less likely to undergo substitution *via* an associative mechanism than $[W(CO)_3(phen)(NO)]^+$. While such a rationalisation of the relative reactivities of these species is attractive, it must be noted that other factors, particularly the different steric demands of dppe and phen, must also be considered.

In general the reactions of arenediazonium ions with $[Mo(CO)_4(L–L)]$ parallel those of the nitrosonium ion, described above. Addition of solid $[RN_2][BF_4]$ or $[RN_2][PF_6]$ (R = aryl) to acetone solutions or suspensions of the neutral tetracarbonyl complexes at −78 °C resulted in evolution of CO and formation of deep red solutions from which *fac*-$[Mo(CO)_3(L–L)(N_2R)]^+$ (3), analogous to the nitrosyls (2), were isolated. Addition of PPh_3 to solutions of (3) in acetone gave low yields of $[Mo(CO)_2(L–L)(N_2R)(PPh_3)]^+$ (5) which may also be prepared directly, and in good yields, from $[Mo(CO)_3(L–L)(PPh_3)]$ and the diazonium salt. Whereas the reaction between $[Mo(CO)_3(L–L)(PPh_3)]$ and $[NO]^+$ gives a pair of isomeric *cis*-dicarbonyl complexes (4), only one *cis*-arenediazodicarbonyl cation was formed. The i.r. spectra of the latter, however, not only show two carbonyl absorptions but also two bands associated with the RN_2 ligand. For example (5; M = Mo, L–L = bipy, R = Ph) shows bands at 1 632 and 1 561 cm^{-1}, which are shifted to 1 618 and 1 549 cm^{-1} on labelling (5) with ^{15}N (by the use of terminally labelled arenediazonium salts, $[R^{14}N^{15}N]^+$). This phenomenon is now well established as being due to vibrational interaction between the NN stretching mode and ring skeletal vibrations of the arene group.[12–14] An alternative explanation which would suggest the presence of two isomers of (5) may safely be rejected as only two carbonyl absorptions were observed in the i.r. spectrum.

The substitution reactions of (5) follow the pattern established for the analogous nitrosyls (4) described above. Triphenylphosphine in refluxing acetone displaced a second carbonyl group to give $[Mo(CO)(L–L)(N_2R)(PPh_3)_2]^+$ (7; L–L = bipy or phen, R = C_6H_4Me-*p*), and $[N(PPh_3)_2]X$ salts (X = Cl or Br) displaced the phosphine ligand to give $[MoX(CO)_2(L–L)(N_2R)]$ (9; L–L = bipy or phen, R = C_6H_4Me-*p*). In an alternative synthetic route the analogous iodo-complex (9; X = I, L–L = bipy, R = C_6H_4F-*p*) may be prepared *via* the reaction of the appropriate arenediazonium salt with the anion [15] $[Mo(CO)_3I(bipy)]^-$ in acetonitrile at −35 °C.

Reaction of (5) with bromine or iodine in CH_2Cl_2 at −78 °C afforded red-brown solids which analysed correctly for $[\{MoX_3(L–L)(N_2R)\}_n]$ (10; L–L = bipy, R = C_6H_4Me-*p*, X = Br or I; L–L = phen, R = Ph or C_6H_4Me-*p*, X = Br, R = C_6H_4Me-*p*, X = I). Unfortunately the low solubility of (10) prevented determination of *n*. These species are formally analogous to the chloronitrosyl $[MoCl_3(bipy)(NO)]$ reported by Davis *et al.*,[16] but the i.r. spectra of (10) suggest that the two species are not isostructural. The nitrosyl complex

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* Although the acetone was distilled from anhydrous calcium sulphate, sufficient water was probably present for hydrolysis of $[PF_6]^-$ to occur.

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[11] E. M. Thorsteinson and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 3929.

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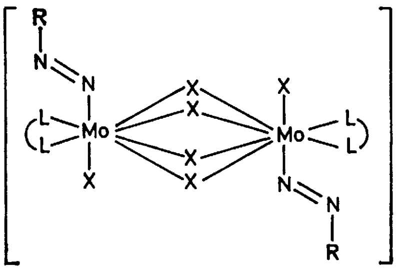
[14] B. L. Haymore, J. A. Ibers, and D. W. Meek, *Inorg. Chem.*, 1975, **14**, 541.

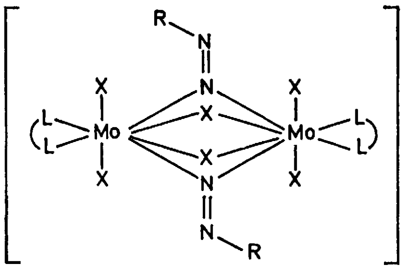
[15] B. J. Bridson and G. F. Griffin, *J. Organometallic Chem.*, 1974, **76**, C47.

[16] R. Davis, B. F. G. Johnson, and K. H. Al-Obaidi, *J.C.S. Dalton*, 1972, 508.

exhibits a strong i.r. band at 1 710 cm^{-1} which is probably due to a terminal nitrosyl ligand. In contrast, ^{15}N-labelling experiments on (10) demonstrate that the characteristic vibrations of the N_2 group occur in the range 1 408—1 411 cm^{-1}. Thus [{MoBr$_3$(bipy)(^{14}N^{14}NPh)}$_n$] exhibits a band at 1 410 cm^{-1} which is displaced to 1 390 cm^{-1} in [{MoBr$_3$(bipy)(^{15}N^{14}NPh)}$_n$]. Even allowing for the difficulties inherent in relating the mode of co-ordination of the arenediazo-group to the position of the NN stretching vibration,[12-14] this absorption is far outside the limits so far observed for the ' singly bent ' [RN$_2$]$^+$ ligand. Furthermore, if the co-ordination mode of the arenediazo-ligand remains unchanged on formation of (10) from (5), the oxidation state of the metal atom would be increased by two formal units and an increase in ν(NN), rather than the decrease observed, would be expected. Two possibilities therefore remain: a ' doubly bent ' [RN$_2$]$^-$ ligand as in (*f*) or the less well documented doubly bridging arenediazo-group as in (*g*). However, no firm conclusion can be reached on the basis of the available evidence. The NN stretching frequency for the complex [{Mo{BH(pz)$_3$}I(N$_2$Ph)}$_2$] (pz = pyrazolyl) [for which a μ_2-halogeno-bridged structure similar to (*f*) has been proposed[17]] occurs at 1 530 cm^{-1} whereas that of [{Mn(CO)$_4$(N$_2$Ph)}$_2$], the only fully authenticated[18] example of a complex containing a bridging arenediazo-ligand, is thought[19] to occur at 1 479 cm^{-1}. An *X*-ray structural study is necessary to distinguish between structures (*f*) and (*g*) for (10).



(*f*)



(*g*)

EXPERIMENTAL

The preparation and purification of the complexes described were carried out under an atmosphere of dry nitrogen. The compounds [N(PPh$_3$)$_2$]X (X = Cl or Br),[20] [RC$_6$H$_4$N$_2$] Y(R = H, *p*-F, *m*-F, Y = BF$_4$; R = *p*-Me, Y = PF$_6$),[21] [M(CO)$_4$(L–L)],[22,23] and [Mo(CO)$_3$(L–L)(PPh$_3$)][9] (M = Cr, Mo, or W; L–L = bipy or phen) were prepared by published procedures; [NO][PF$_6$] and [NO][BF$_4$] were purchased from Ozark Mahoning Co., Tulsa, Oklahoma, and Na[^{15}NO$_2$], from which ^{15}N-labelled diazonium salts were prepared, was purchased from Stohler Isotopes, Im Baumgarten, CH 3044, Innerberg, Switzerland. All the solvents were dried by standard methods and deoxygenated before use.

Infrared spectra were recorded on Perkin-Elmer PE 257 or PE 457 spectrophotometers and calibrated against the absorption of polystyrene at 1 601 cm^{-1}. Mass spectra were obtained on an A.E.I. MS9 instrument. Microanalyses were by the staffs of the Microanalytical Services of the School of Chemistry, Bristol, and of the Department of Chemistry, University College, Cork.

fac-*(2,2′-Bipyridyl)tricarbonylnitrosylmolybdenum Tetrafluoroborate*, *fac*-[Mo(CO)$_3$(bipy)(NO)][BF$_4$].—To a stirred solution of [Mo(CO)$_4$(bipy)] (1 g, 2.7 mmol) in acetone (50 cm^3) at −78 °C was added [NO][BF$_4$] (0.32 g, 2.7 mmol). The mixture was then allowed to warm to room temperature during which time gas was evolved. On concentration of the solution to *ca.* 15 cm^3 and addition of diethyl ether a red oil was precipitated which solidified on drying *in vacuo*. Recrystallisation from CH$_2$Cl$_2$–OEt$_2$ gave the *product* as a red-brown solid, yield 0.98 g (80%). The complex is moderately stable in air, and soluble in polar solvents such as CH$_2$Cl$_2$ and acetone to give orange-red solutions which slowly decompose in air. The *complex fac*-[Mo(CO)$_3$(phen)(NO)][BF$_4$] was prepared similarly in 87% yield.

mer-*Tricarbonylnitrosyl(1,10-phenanthroline)tungsten Hexafluorophosphate*, *mer*-[W(CO)$_3$(phen)(NO)][PF$_6$].—To a vigorously stirred solution of [W(CO)$_4$(phen)] (0.25 g, 0.5 mmol) in a mixture of toluene (15 cm^3) and methanol (3 cm^3) was added an excess of solid [NO][PF$_6$] (*ca.* 0.17 g, 1 mmol). The dark red solution became orange and CO gas was evolved. After 30—45 min, when all the [W(CO)$_4$(phen)] had reacted, the product was filtered from the solution. Recrystallisation from acetone–diethyl ether gave the *complex* as an orange solid, yield 0.19 g (46%). The complex is stable in air and dissolves in polar solvents such as acetone or CH$_2$Cl$_2$ to give orange air-stable solutions.

(2,2′-Bipyridyl)dicarbonylnitrosyl(triphenylphosphine)-molybdenum Tetrafluoroborate, [Mo(CO)$_2$(bipy)(NO)(PPh$_3$)][BF$_4$], *Method* (*i*).—A mixture of PPh$_3$ (0.57 g, 2.2 mmol) and *fac*-[Mo(CO)$_3$(bipy)(NO)][BF$_4$] (1.0 g, 2.4 mmol) was stirred in acetone (50 cm^3) for 90 min. After filtration, to remove small quantities of [Mo(CO)(bipy)(NO)(PPh$_3$)$_2$][BF$_4$], the solution was evaporated to dryness. Recrystallisation from CH$_2$Cl$_2$–OEt$_2$ gave the *complex* as brown crystals of isomer (A), yield 0.91 g (57%).

(2,2′-Bipyridyl)dicarbonylnitrosyl(triphenylphosphine)-molybdenum Hexafluorophosphate, [Mo(CO)$_2$(bipy)(NO)(PPh$_3$)][PF$_6$], *Method* (*ii*).—To a vigorously stirred solution of [Mo(CO)$_3$(bipy)(PPh$_3$)] (2 g, 3.3 mmol) in acetone (50 cm^3)

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[22] M. H. B. Stiddard, *J. Chem. Soc.*, 1962, 4712.

[23] J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Organometallic Chem.*, 1971, **29**, 105.

at −78 °C was added an excess of solid $[NO][PF_6]$ (0.62 g, 3.5 mmol). Carbon monoxide gas was evolved and the purple solution became orange. After allowing the mixture to reach room temperature slowly the solvent was removed *in vacuo*. Extraction of the residue with CH_2Cl_2 (*ca.* 15 cm^3) followed by filtration and addition of diethyl ether (*ca.* 40 cm^3) afforded the product as an orange-brown precipitate. Recrystallisation once from CH_2Cl_2–OEt_2 and twice from CH_2Cl_2–hexane gave orange-brown crystals of the *complex* as a mixture of isomers (A) and (B), yield 2.1 g (84%).

A mixture of isomers (A) and (B) of $[Mo(CO)_2(phen)(NO)(PPh_3)][PF_6]$ was prepared similarly, in 71% yield.

(2,2′-Bipyridyl)dicarbonylnitrosyl(triphenylphosphine)molybdenum Tetrafluoroborate, $[Mo(CO)_2(bipy)(NO)(PPh_3)][BF_4]$, *Isomer (B)*.—A mixture of isomers (A) and (B), prepared by method (*ii*) using $[NO][BF_4]$, was stirred overnight in acetone. On evaporation to dryness, extraction with CH_2Cl_2, and precipitation with OEt_2 the *complex* was isolated as isomer (B) in *ca.* 70% yield. Both isomers are moderately air-stable brown solids which are soluble in polar solvents such as CH_2Cl_2 and acetone to give deep orange, moderately air-stable solutions.

Conversion of isomer (A) to (B). A solution of isomer (A) (0.5 g, 0.73 mmol) in acetone (50 cm^3) was stirred for 3 h; monitoring the reaction by i.r. showed the decrease of peaks due to isomer (A) and development of those of (B). Evaporation to dryness and recrystallisation from CH_2Cl_2–OEt_2 gave isomer (B), yield 0.4 g (80%).

Dicarbonylnitrosyl(1,10-phenanthroline)(triphenylphosphine)tungsten Hexafluorophosphate, $[W(CO)_2(phen)(NO)(PPh_3)][PF_6]$.—A mixture of *mer*-$[W(CO)_3(phen)(NO)][PF_6]$ (0.35 g, 0.55 mmol) and PPh_3 (0.30 g, 1.15 mmol) was heated under reflux in acetone (50 cm^3) for 2 h. The resulting orange-brown solution was reduced in volume to *ca.* 20 cm^3 and diethyl ether (60 cm^3) was added. The precipitated product was collected by filtration and recrystallised from acetone–diethyl ether to give the *complex* as orange crystals, yield 0.28 g (57%). The complex is stable in air and soluble in polar solvents such as CH_2Cl_2 and acetone to give orange air-stable solutions.

(2,2′-Bipyridyl)carbonylnitrosylbis(triphenylphosphine)molybdenum Hexafluorophosphate, $[Mo(CO)(bipy)(NO)(PPh_3)_2][PF_6]$, *Method (i)*.—The complex $[Mo(CO)_2(bipy)(NO)(PPh_3)][PF_6]$ (1 g, 1.3 mmol) and PPh_3 (0.7 g, 2.6 mmol) were heated under reflux in acetone (50 cm^3) for 6 h. After cooling, the mixture was evaporated to dryness, washed with CH_2Cl_2, and recrystallised twice from acetone to give the *complex*, yield 0.9 g (69%). The complex is an air-stable orange-red solid, moderately soluble in polar solvents such as acetone to give orange air-stable solutions. The *complex* $[Mo(CO)(phen)(NO)(PPh_3)_2][PF_6]$ was prepared similarly in 63% yield.

(2,2′-Bipyridyl)carbonylnitrosylbis(triphenylphosphine)molybdenum Tetrafluoroborate, $[Mo(CO)(bipy)(NO)(PPh_3)_2][BF_4]$, *Method (ii)*.—Triphenylphosphine (0.18 g, 0.72 mmol) and *fac*-$[Mo(CO)_3(bipy)(NO)][BF_4]$ (0.11 g, 0.24 mmol) were stirred in acetone (10 cm^3) for 6 h. Recrystallisation of the precipitate from CH_2Cl_2–OEt_2 gave the *product* as a bright red solid, yield 0.12 g (80%).

(2,2′-Bipyridyl)dicarbonylchloronitrosylmolybdenum, $[MoCl(CO)_2(bipy)(NO)]$, *Method (i)*.—To a stirred solution of *fac*-$[Mo(CO)_3(bipy)(NO)][BF_4]$ (0.50 g, 1.2 mmol) in acetone (30 cm^3) was added LiCl (0.17 g, 4.0 mmol). After 2 h the solvent was removed *in vacuo* and the residue was extracted with CH_2Cl_2. On filtration, addition of OEt_2, concentration to small volume, and addition of hexane the *complex* was precipitated as yellow crystals, yield 0.2 g (43%). The *complexes* $[MoBr(CO)_2(bipy)(NO)]$ (orange) and $[MoI(CO)_2(bipy)(NO)]$ (brown) were prepared by the same method in 64 and 52% yield respectively.

Method (ii). To a stirred solution of $[Mo(CO)_2(bipy)(NO)(PPh_3)][PF_6]$ (0.74 g, 1 mmol) in acetone (15 cm^3) was added $[N(PPh_3)_2]Cl$ (0.57 g, 1 mmol). After 30 min the mixture was reduced in volume (10 cm^3) and tetrahydrofuran (thf) (50 cm^3) was added. The precipitate of $[N(PPh_3)_2][PF_6]$ was then removed by filtration and the solution was evaporated to dryness. Recrystallisation twice from thf–hexane gave the *product*, yield 0.19 g (51%). The complex is stable in air in the solid state and dissolves in solvents such as thf, acetone, and CH_2Cl_2 to give air-stable yellow solutions. The *complexes* $[MoCl(CO)_2(phen)(NO)]$ (yellow) and $[MoBr(CO)_2(bipy)(NO)]$ (orange) were prepared by the same method in 48 and 52% yield respectively.

Dicarbonylchloronitrosyl(1,10-phenanthroline)tungsten, $[WCl(CO)_2(phen)(NO)]$.—To a stirred solution of LiCl (24 mg, 0.55 mmol) in acetone (50 cm^3) was added *mer*-$[W(CO)_3(phen)(NO)][PF_6]$ (0.35 g, 0.55 mmol). Carbon monoxide was evolved and a red precipitate formed almost immediately. After stirring for 30 min, filtration yielded the *complex* as a red solid. Washing with diethyl ether and drying in air gave an analytically pure sample, yield 88 mg (32%). The air-stable complex is moderately soluble in CH_2Cl_2 and poorly so in acetone to give air-stable brown solutions.

The *complexes* $[WBr(CO)_2(phen)(NO)]$, from LiBr (dark red, 62% yield), and $[WI(CO)_2(phen)(NO)]$, from NaI (dark purple, 74% yield), were prepared similarly. They are less soluble than the chloro-complex; the iodo-complex is only barely soluble in CH_2Cl_2.

Dicarbonyl(difluorophosphato)nitrosyl(1,10-phenanthroline)tungsten, $[W(CO)_2(phen)(NO)(O_2PF_2)]$.—The complex *mer*-$[W(CO)_3(phen)(NO)][PF_6]$ (0.36 g, 0.55 mmol) was heated under reflux in acetone (55 cm^3) until only two carbonyl-stretching absorptions were visible in the i.r. spectrum (1 h). After cooling, the mixture was reduced in volume to *ca.* 20 cm^3 and diethyl ether (50 cm^3) was added. The cloudy orange solution was allowed to stand for 3 h and then more diethyl ether was added. After 48 h at 0 °C the solid product was removed by filtration and recrystallised from acetone–diethyl ether to give the *complex* as orange crystals, yield 83 mg (27%). The air-stable complex is sparingly soluble in acetone and in CH_2Cl_2 to give pale orange-yellow solutions.

fac-*(2,2′-Bipyridyl)tricarbonyl(*p*-fluorobenzenediazo)molybdenum Tetrafluoroborate*, *fac*-$[Mo(CO)_3(bipy)(N_2C_6H_4F\text{-}p)][BF_4]$.—To $[Mo(CO)_4(bipy)]$ (2.0 g, 5.5 mmol) in acetone (40 cm^3) at −78 °C was added solid $[p\text{-}FC_6H_4N_2][BF_4]$ (1.15 g, 5.5 mmol). After slowly warming to room temperature, the solution was concentrated and diethyl ether was added. The resulting solid was recrystallised from acetone–diethyl ether to give the complex as brown crystals, yield 1.8 g (63%).

*(2,2′-Bipyridyl)dicarbonyl(*p*-toluenediazo)(triphenylphosphine)molybdenum Hexafluorophosphate*, $[Mo(CO)_2(bipy)(N_2C_6H_4Me\text{-}p)(PPh_3)][PF_6]$.—A concentrated solution of $[p\text{-}MeC_6H_4N_2][PF_6]$ (1.32 g, 5 mmol) in acetone was added dropwise to $[Mo(CO)_3(bipy)(PPh_3)]$ (2.94 g, 5 mmol) in acetone (50 cm^3) at −78 °C. Carbon monoxide was

evolved and the resulting brown solution was allowed to warm slowly to room temperature. The solvent was then removed *in vacuo* and the residue was extracted with CH_2Cl_2 (25 cm^3). After filtration, addition of diethyl ether (100 cm^3) yielded an oil which was isolated by decantation of the supernatant liquid. Recrystallisation once from CH_2Cl_2–OEt_2 and twice from CH_2Cl_2–hexane gave the *complex* as a dark brown solid, yield 3.1 g (74%). The complex is stable in air and soluble in polar solvents such as CH_2Cl_2 to give moderately air-stable brown solutions. The *complexes* $[Mo(CO)_2(L\text{–}L)(N_2C_6H_4X)(PPh_3)][BF_4]$ (L–L = bipy or phen, X = H, *p*-F, or *m*-F) and $[Mo(CO)_2(phen)(N_2C_6H_4Me\text{-}p)(PPh_3)][PF_6]$ were prepared similarly in yields of *ca.* 70%.

(2,2'-*Bipyridyl*)*carbonyl*(p-*toluenediazo*)*bis*(*triphenylphosphine*)*molybdenum Hexafluorophosphate*, $[Mo(CO)(bipy)(N_2C_6H_4Me\text{-}p)(PPh_3)_2][PF_6]$.—A mixture of $[Mo(CO)_2(bipy)(N_2C_6H_4Me\text{-}p)(PPh_3)][PF_6]$ (2.1 g, 2.5 mmol) and PPh_3 (1.3 g, 5 mmol) was heated under reflux in acetone (60 cm^3) for 6 h. The resulting dark brown solution was cooled and then evaporated to dryness. Recrystallisation twice from CH_2Cl_2–OEt_2 and then from CH_2Cl_2–hexane gave the *complex* as a brown solid, yield 1.3 g (50%). The complex is stable in air and moderately soluble in solar solvents such as CH_2Cl_2 and acetone to give brown, moderately air-stable, solutions. The *complex* $[Mo(CO)(phen)(N_2C_6H_4Me\text{-}p)(PPh_3)_2][PF_6]$ (brown) was prepared similarly in 65% yield.

(2,2'-*Bipyridyl*)*dicarbonylchloro*(p-*fluorobenzenediazo*)-*molybdenum*, $[Mo(CO)_2Cl(bipy)(N_2C_6H_4F\text{-}p)]$.—This *complex*, and the bromo- and iodo-analogues, was prepared using method (*i*) for the preparation of $[MoCl(CO)_2(bipy)(NO)]$.

(2,2'-*Bipyridyl*)*dicarbonylchloro*(p-*toluenediazo*)*molybdenum*, $[MoCl(CO)_2(bipy)(N_2C_6H_4Me\text{-}p)]$.—To a stirred solution of $[Mo(CO)_2(bipy)(N_2C_6H_4Me\text{-}p)(PPh_3)][PF_6]$ (0.84 g, 1 mmol) in acetone (15 cm^3) was added $[N(PPh_3)_2]Cl$ (0.57 g, 1 mmol). After 0.5 h the resulting brown solution was evaporated to dryness. The residue was washed with CH_2Cl_2 (10 cm^3) and then recrystallised from thf–hexane to give the *complex* as a brown-orange crystalline solid, yield 0.24 g (53%). The air-stable complex is soluble in thf, CH_2Cl_2, and acetone giving stable brown solutions. The *complexes* $[MoCl(CO)_2(phen)(N_2C_6H_4Me\text{-}p)]$ (56%), $[MoBr(CO)_2(bipy)(N_2C_6H_4Me\text{-}p)]$ (49%), and $[MoBr(CO)_2(phen)(N_2C_6H_4Me\text{-}p)]$ (55%) were prepared similarly.

(2,2'-*Bipyridyl*)*tribromo*(p-*toluenediazo*)*molybdenum*, $[\{MoBr_3(bipy)(N_2C_6H_4Me\text{-}p)\}_2]$.—A solution of Br_2 (0.4 g, 2.5 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise to $[Mo(CO)_2(bipy)(N_2C_6H_4Me\text{-}p)(PPh_3)][PF_6]$ in CH_2Cl_2 (30 cm^3) at −78 °C. Carbon monoxide was evolved and, after allowing the solution to warm slowly to room temperature, the *complex* was isolated by filtration and washed with acetone (2 × 10 cm^3), yield 0.25 g (16%). The complex is a brown-red air-stable solid insoluble in most organic solvents. The complexes $[\{MoBr_3(phen)(N_2Ph)\}_2]$ (25%), $[\{MoBr_3(phen)(N_2C_6H_4Me\text{-}p)\}_2]$ (19%), $[\{MoI_3(bipy)(N_2C_6H_4Me\text{-}p)\}_2]$ (21%), and $[\{MoI_3(phen)(N_2C_6H_4Me\text{-}p)\}_2]$ (15%) were prepared similarly.

We thank the Department of Education of the Irish Republic for postgraduate maintenance awards (to M. E. D. and D. C.), and the University College, Cork, for the award of an Undergraduate Summer Research Grant to Tadg Begley who gave valuable assistance.

[6/1845 *Received*, 1*st October*, 1976]