Formation of η^2-Aroyl, η^1-Halogenocarbyne or Sterically Crowded Aryldiazenide Ligands in the Reactions of Ring-substituted Tricarbonyl[hydrotris(pyrazolyl)borato]-molybdate and -tungstate Anions with Arenediazonium Cations and Related Oxidants †

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Although the hydrotris(pyrazolyl)borato complex $[Mo\{HB(pz)_3\}(CO)_3]^-$ reacted with 3- or 4-substituted arenediazonium cations $[R'N_2]^+$ yielding carbonyl-substitution (*i.e.* aryldiazenido) products $[Mo\{HB(pz)_3\}(CO)_2(N_2R')]$, reaction of the methyl-substituted analogue $[ML^*(CO)_3]^-$ [L* = tris(3,5-dimethylpyrazolyl)hydroborate; M = Mo or W] led, *via* oxidative formation of aryl radicals and $[ML^*(CO)_3]^{\bullet}$, to η^2-aroyl complexes $[ML^*(CO)_2(\eta^2\text{-}COR')]$ [R' = C_6H_4X-4 (X = NO_2, CN, COMe, CF_3, H, Me, OMe or NMe_2) or C_6H_4X-3 (X = NO_2 or OMe)] in acetonitrile or to the halogenocarbyne complexes $[ML^*(CO)_2(\equiv CX)]$ (X = Cl, Br or I) in the presence of the halogenoalkanes CH_2Cl_2 or CHX_3 (X = Br or I). The complex $[MoL^*(CO)_3]^-$ reacted similarly with diphenyliodonium or triphenylsulfonium cations, but in the latter case anion–cation redox is very slow in the dark but rapid upon irradiation with sunlight. Comparison of these results with those obtained for $[ML^*(CO)_3]^-$ analogues with different substituents in the pyrazolyl rings demonstrates that oxidation of the former by arenediazonium cations occurs in response to the steric rather than the electronic effect of the 3-methyl substituents. However further steric crowding in *either* the hydrotris(pyrazolyl)borate ligand *or* the diazonium cation promotes a reversion to the carbonyl-substitution pathway. A mechanism to account for these observations is proposed. Attempts to extend the chlorocarbyne synthesis to systems other than $[ML^*(CO)_3]^-$ met with only limited success. Spectroscopic data for the new complexes are reported and discussed. Two aryldiazenido complexes, $[MoL^*(CO)_2(N_2R')]$ (R' = 2,6-$Me_2C_6H_3$ or 2,3-dimethyl-5-oxo-1-phenyl-3-pyrazolin-4-yl) have been characterised by single-crystal X-ray diffraction studies and are found to differ in the manner in which the aryldiazenide ligand accommodates to steric crowding in the molybdenum co-ordination sphere.

The chemical similarity between related complexes containing the η-cyclopentadienide, $[\eta\text{-}C_5H_5]^-$, and η^3-poly(pyrazolyl)-borate ligands, $[RB(pz)_3]^-$ (R = H or pz, pz = pyrazol-1-yl), is illustrated by the reactions of their anionic tricarbonylmolybdenum complexes **1** and **3** with arenediazonium cations[1,2] to yield red neutral aryldiazenido complexes **2** and **4** (Scheme 1). However in 1971 Trofimenko[3] reported that the tricarbonylmolybdenum derivative of the hydrotris(3,5-dimethylpyrazolyl)borate anion, $[HB(dmpz)_3]^-$ (henceforth abbreviated as L*), $[MoL^*(CO)_3]^-$ **5** reacted with arenediazonium cations to yield products which were blue, rather than red, and which appeared to be seven-co-ordinate σ-aryl derivatives $[MoL^*(CO)_3(\sigma\text{-}R')]$ **6**. We now report the outcome of a study of this anomalous reaction. Some of the results described have been published in preliminary form.[4,5]

Results and Discussion

Product Characterisation and Outline Mechanism.—In Trofimenko's report[3] the reaction between the anion **5** and arenediazonium cations on a 0.1 molar scale at room temperature in either dimethylformamide (dmf) (250 cm^3) or dichloromethane (600 cm^3) produced the blue products in *ca.* 35% yield. Our attempts to repeat the reaction on a more economical scale (1.0 mmol **5** in *ca.* 10 cm^3 dmf) yielded only traces of the presumed σ-aryl complexes **6** and no other carbonyl-containing products. However small-scale reactions proceeded cleanly in acetonitrile at *ca.* −40 °C. Under these conditions the products described by Trofimenko (and a range of related compounds) were isolated in improved yields of up to 75%. An analogous tungsten complex $[WL^*(CO)_2(\eta^2\text{-}COPh)]$ **7** derived from $[WL^*(CO)_3]^-$ **8** was also prepared.

The new complexes are air-stable crystalline materials, varying from very intense blue-black with electron-withdrawing substituents in the diazonium cation (*e.g.* R' = 4-$O_2NC_6H_4$) through purple (R' = Ph) to red with electron-releasing substituents (*e.g.* R' = 4-$Me_2NC_6H_4$). Microanalytical data are collected in Table 1 and are compatible with the σ-aryl structure **6** proposed by Trofimenko.[3] However an X-ray crystallographic study[4] of the product of the reaction of **5** with toluene-4-diazonium cation revealed that the complexes actually adopt an isomeric η^2-aroyl structure $[MoL^*(CO)_2(\eta^2\text{-}COR')]$ **9**, *i.e.* that the reaction proceeds in outline as shown in equation (1). There is considerable current interest in the chemistry of η^2-acyl and -aroyl complexes.[6,7] The present reaction provides a useful extension to the known synthetic routes to complexes of this type, most of which lead to alkyl or

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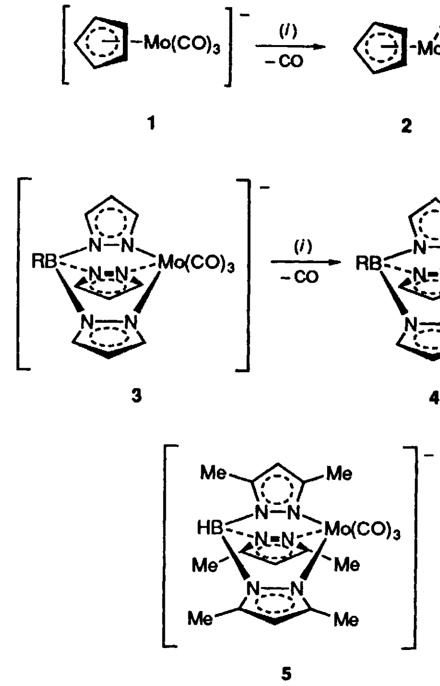
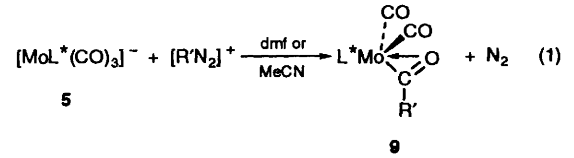
† Transition Metal Organometallic Complexes containing 3-Substituted Poly(pyrazolyl)borate Ligands. Part 1.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: D ≈ 3.33 × 10^{-30} C m, mmHg ≈ 133 Pa.



Scheme 1 R = H or pz. (*i*) $[R'N_2]^+$ (R' = aryl)



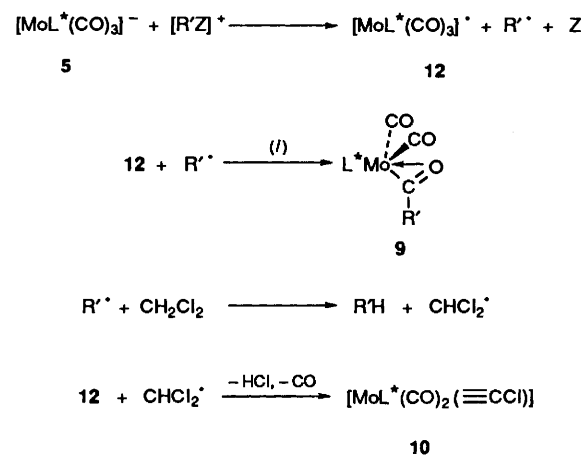
$$[MoL^*(CO)_3]^- + [R'N_2]^+ \xrightarrow[\text{MeCN}]{\text{dmf or}} L^*Mo(CO)_2(\eta^2\text{-}COR') + N_2 \quad (1)$$

substituted-alkyl derivatives. There are indications that our route can also be modified so as to yield η^2-acyl complexes (see below).

As in dmf solvent, only trace quantities of the η^2-aroyl complexes **9** were detected when **5** was treated with arenediazonium cations in dichloromethane on a 1.0 mmol scale. Here, however, a previously unreported yellow dicarbonyl complex was isolated in *ca.* 75% yield. An X-ray crystallographic study[5] revealed the latter to be $[MoL^*(CO)_2(\equiv CCl)]$ **10**, the first example of a complex containing an η^1-chlorocarbyne ligand. The analogous tungsten complex $[WL^*(CO)_2(\equiv CCl)]$ **11**, prepared in a similar fashion from the tungsten tricarbonyl anion **8**, and a number of analogous species to be described later are the only other known complexes containing this unusual and synthetically versatile[8,9] ligand.

Our intuitive feeling that the reactions described above involved oxidation of the anion by the arenediazonium cation was supported by the observation that the same products were formed using diphenyliodonium cation as reagent. Scheme 2 presents an outline mechanism for the formation of the η^2-aroyl and η^1-chlorocarbyne products from **5**. One-electron oxidation of **5** generates a neutral 17-electron tricarbonyl radical $[MoL^*(CO)_3]^{\bullet}$ **12** and an aryl radical, together with nitrogen or an aryl iodide depending on the oxidant.[10] In acetonitrile combination of the organometallic radical **12** with the aryl radical generates the η^2-aroyl complex **9**. In dichloromethane, radical transfer to the solvent generates a dichloromethyl radical which reacts with **12** to form the η^1-chlorocarbyne complex **10** together with CO and HCl.

Support for the general features of the mechanism outlined in Scheme 2 is available from several sources. The plausibility of the first step was confirmed by Shiu and Lee's subsequent isolation and characterisation of the 17-electron radical **12**[11] which we had proposed as the product of the initial redox



Scheme 2 Z = N_2 or IR'. (*i*) MeCN

process.[4,5] Additional verification of a radical mechanism was provided by our serendipitous discovery that using mixtures of acetonitrile or dichloromethane with cyclohexane as solvent led to formation of the η^2-hexahydrobenzoyl complex $[MoL^*(CO)_2(\eta^2\text{-}COC_6H_{11})]$ **13a** in up to 24–35% yield, together with the expected products **9** or **10**. Formation of **13a** (which has been characterised by X-ray crystallography[4]) is best explained by a process in which the initially formed aryl radical abstracts hydrogen from cyclohexane to generate a cyclohexyl radical which then couples with the tricarbonyl radical **12**. In an extension of this methodology, a 46% yield of the η^2-acetyl complex $[MoL^*(CO)_2(\eta^2\text{-}COMe)]$ **13b** was obtained after 45 min by oxidation of $[MoL^*(CO)_3]^-$ **5** with diphenyliodonium cation in neat methyl iodide at room temperature. In this case the aryl radical preferentially abstracts iodine from MeI to generate a methyl radical which then reacts with **12** to give **13b**. Prolonged reflux in tetrahydrofuran[12,13] is required to generate **13b** from **5** and MeI in the absence of the oxidant (presumably *via* an S_N2-type process[13]). The reaction of **5** with diphenyliodonium salts in the presence of an alkyl bromide or iodide thus provides a potentially useful alternative route to other η^2-acyl complexes.

The reaction of the tricarbonyl anion **5** with the triphenylsulfonium cation (unlike that with diazonium or iodonium salts) yielded a stable characterisable, but markedly photosensitive, salt $[SPh_3][MoL^*(CO)_3]$ **14a**. Exposure of **14a** to visible light, either in solution or in the solid state, induces anion–cation redox. Photolysis in the solid state (conveniently monitored by IR spectroscopy in a pressed KBr disc) or in acetonitrile yields $[MoL^*(CO)_2(\eta^2\text{-}COPh)]$ **9g**, while in dichloromethane the η^1-chlorocarbyne complex **10** is formed. An exploratory ^1H photo-CIDNP (chemically induced dynamic nuclear polarisation) experiment on **14a** in deuteriated dichloromethane revealed enhanced absorption in the spectrum of the starting material, indicating that, for this anion–cation combination at least, the initial electron-transfer step is reversible [equation (2)].† In view of the results obtained in

$$\underset{\mathbf{14a}}{[SPh_3][MoL^*(CO)_3]} \rightleftharpoons SPh_3^{\bullet} + \underset{\mathbf{12}}{[MoL^*(CO)_3]^{\bullet}} \quad (2)$$

dichloromethane, it is curious that we have not been able to detect any solvent-derived products when **5** is oxidised with $[R'N_2]^+$ or $[IPh_2]^+$ in acetonitrile. However the maximum yields of η^2-aroyl complexes under these conditions are *ca.* 75%. It is possible that radical transfer to acetonitrile accounts for

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† We are grateful to Professor D. J. Cardin of the Department of Chemistry, Dublin University, for this observation.

Table 1 Microanalytical and infrared spectroscopic data for complexes of the type [ML(CO)$_2$Z]

					Analysis[a] (%)			
Complex	L	M	Z	Colour	C	H	N	ν(CO)[b]/cm^{-1}
7	HB(dmpz)$_3$	W	η^2-COPh	Purple	44.95 (44.90)	4.40 (4.25)	13.15 (13.10)	1946m (br), 1853s
9a	HB(dmpz)$_3$	Mo	η^2-COC$_6$H$_4$NO$_2$-4	Blue-black	47.85 (48.10)	4.70 (4.35)	16.20 (16.35)	1964m (br), 1875s
9b	HB(dmpz)$_3$	Mo	η^2-COC$_6$H$_4$CN-4	Dark blue	52.15 (51.85)	4.65 (4.50)	17.25 (16.95)	1962m (br), 1872s
9c	HB(dmpz)$_3$	Mo	η^2-COC$_6$H$_4$COMe-4	Dark blue	52.65 (52.35)	4.95 (4.90)	14.35 (14.10)	1960m (br), 1869s
9d	HB(dmpz)$_3$	Mo	η^2-COC$_6$H$_4$NO$_2$-3	Blue-purple	48.20 (48.10)	4.65 (4.35)	15.90 (16.35)	1962m (br), 1872s
9e	HB(dmpz)$_3$	Mo	η^2-COC$_6$H$_4$CF$_3$-4	Blue-purple	48.25 (48.25)	4.30 (4.20)	13.65 (13.50)	1962m (br), 1871s
9f	HB(dmpz)$_3$	Mo	η^2-COC$_6$H$_4$OMe-3	Purple	51.70 (51.40)	5.00 (5.00)	14.05 (14.40)	1961m (br), 1871s
9g	HB(dmpz)$_3$	Mo	η^2-COPh	Purple	52.50 (52.00)	5.10 (4.90)	15.20 (15.15)	1958m (br), 1866s
9h	HB(dmpz)$_3$	Mo	η^2-COC$_6$H$_4$Me-4	Purple	52.65 (52.85)	5.05 (5.10)	14.85 (14.80)	1954m (br), 1863s
9i	HB(dmpz)$_3$	Mo	η^2-COC$_6$H$_4$OMe-4	Red	51.35 (51.40)	5.25 (5.00)	14.40 (14.40)	1953m (br), 1861s
9j	HB(dmpz)$_3$	Mo	η^2-COC$_6$H$_4$NMe$_2$-4	Red	52.70 (52.30)	5.65 (5.40)	16.20 (16.40)	1945m (br), 1852s
10	HB(dmpz)$_3$	Mo	η^1-CCl	Yellow	43.90 (43.55)	4.20 (4.45)	16.70 (16.95)	2005s, 1921s[c]
11	HB(dmpz)$_3$	W	η^1-CCl	Yellow	37.35 (37.00)	3.80 (3.80)	14.40 (14.65)	1991s, 1902s[d]
13a	HB(dmpz)$_3$	Mo	η^2-COC$_6$H$_{11}$	Red	51.75 (51.45)	6.10 (5.95)	14.90 (15.00)	1952m (br), 1858s
13b	HB(dmpz)$_3$	Mo	η^2-COMe	Red	46.70 (46.35)	5.60 (5.10)	17.55 (17.05)	1952m (br), 1857s
21	HB(dmpz)$_3$	Mo	η^1-CBr	Yellow	39.75 (39.95)	3.65 (4.10)	15.35 (15.55)	2008s, 1924s[e]
22	HB(dmpz)$_3$	W	η^1-CBr	Yellow	34.60 (34.35)	4.00 (3.55)	13.20 (13.35)	1994s, 1905s[f]
23	HB(dmpz)$_3$	Mo	η^1-CI	Yellow	*g*	*g*	*g*	2009s, 1927s
25	HB(mpz)$_3$	Mo	η^2-COC$_6$H$_4$OMe-4	Red	48.75 (48.75)	4.65 (4.30)	15.75 (15.50)	1959m (br), 1866s
26	HB(mpz)$_3$	Mo	η^1-CCl	Yellow	39.55 (39.65)	3.75 (3.55)	18.05 (18.50)	2006s, 1925s
27	HB(tmpz)$_3$	Mo	η^2-COC$_6$H$_4$Me-4	Purple	54.65 (55.10)	5.60 (5.80)	13.90 (13.75)	1952m (br), 1858s
28	HB(cmpz)$_3$	Mo	η^2-COC$_6$H$_4$Me-4	Purple	44.60 (44.70)	3.95 (3.90)	12.10 (12.50)	1960m (br), 1867s
29	HB(tmpz)$_3$	Mo	η^1-CCl	Yellow	46.70 (46.80)	5.20 (5.25)	15.85 (15.60)	2005s, 1920s
30	HB(cmpz)$_3$	Mo	η^1-CCl	Yellow	35.90 (36.05)	3.15 (3.20)	14.10 (14.00)	2010s, 1929s
31	HB(tmpz)$_3$	Mo	η^1-CBr	Yellow	43.70 (43.25)	5.15 (4.80)	14.50 (14.40)	2007s, 1923s
32a	HB(dmpz)$_3$	Mo	N$_2$C$_6$H$_4$NMe$_2$-4	Greenish red	50.25 (50.40)	5.40 (5.85)	21.10 (20.90)	1976s, 1860s[h,i]
32b	HB(dmpz)$_3$	Mo	N$_2$C$_6$H$_3$Cl-2-Me-6	Greenish red	48.00 (47.85)	4.95 (4.70)	18.15 (18.60)	1983s, 1881s[i,j]
32c	HB(dmpz)$_3$	Mo	N$_2$C$_6$H$_3$Me$_2$-2,6	Greenish red	51.75 (51.55)	5.00 (5.35)	19.30 (19.25)	1977s, 1872s[i,k]
32d	HB(dmpz)$_3$	Mo	N$_2$(dmpz)	Greenish red	46.25 (46.15)	5.00 (5.10)	24.50 (24.45)	1990s, 1879s[i,l]
32e	HB(dmpz)$_3$	Mo	N$_2$(ap)	Greenish red	50.55 (50.60)	5.50 (5.00)	20.90 (21.10)	1983s, 1878s[i,m]
34a	HB(tpz)$_3$	Mo	N$_2$Ph	Greenish brown	61.05 (61.65)	4.65 (4.50)	14.70 (15.15)	1990s, 1902s[i,n]
34b	HB(tpz)$_3$	Mo	N$_2$C$_6$H$_4$NMe$_2$-4	Green	61.00 (61.30)	5.20 (4.90)	15.95 (16.10)	1985s, 1890s[i,o]
34c	HB(tpz)$_3$	Mo	N$_2$(ap)	Green	60.50 (60.70)	4.65 (4.60)	15.95 (16.45)	2002s, 1894s[i,p]
35a	HB(tpz)$_3$	Mo	η^2-COPh	Purple	63.20 (63.25)	4.70 (4.50)	11.30 (11.35)	1966m (br), 1865s
36	HB(tpz)$_3$	Mo	η^1-CCl	Yellow	57.80 (58.05)	4.40 (4.15)	12.15 (12.30)	2003s, 1925s
37	B(tpz)$_4$	Mo	N$_2$C$_6$H$_4$NMe$_2$-4	Green	64.15 (63.90)	5.00 (4.95)	16.00 (16.40)	1984s, 1892s[i,q]
40	B(pz)$_4$	Mo	η^1-CCl	Yellow	37.85 (37.65)	2.80 (2.55)	23.20 (23.40)	2010s, 1929s
41	B(pz)$_4$	Mo	η^2-COPh	Reddish brown	47.40 (47.05)	3.70 (3.20)	20.75 (20.90)	1956m (br), 1870s

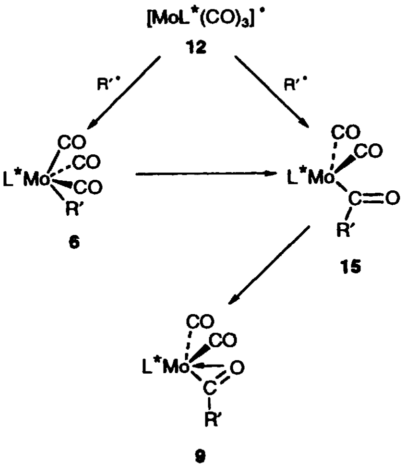
[a] Calculated values in parentheses. [b] All spectra recorded in cyclohexane solution except for those of complexes **32a**–**32e** (KBr discs) and **34a**–**37** (CH$_2$Cl$_2$); m = medium, br = broad, s = strong. [c] Very weak ν(^{13}CO) satellites at 1988 and 1896 cm^{-1}. [d] Very weak ν(^{13}CO) satellites at 1970 and 1871 cm^{-1}. [e] Very weak ν(^{13}CO) satellites at 1989 and 1897 cm^{-1}. [f] Very weak ν(^{13}CO) satellites at 1972 and 1876 cm^{-1}. [g] Not obtained, see Experimental section. [h] ν(NN) 1613 cm^{-1}. [i] Tentative assignment in the absence of ^{15}N labelling data. [j] ν(NN) 1604 cm^{-1}. [k] ν(NN) 1612 cm^{-1}. [l] ν(NN) 1599 cm^{-1}. [m] ν(NN) 1595 cm^{-1}. [n] ν(NN) 1630 cm^{-1}. [o] ν(NN) 1617 cm^{-1}. [p] ν(NN) 1574 cm^{-1}. [q] ν(NN) 1619 cm^{-1}.

some of the remaining 25% of starting material but that this reaction pathway does not lead to stable organometallic products. However, given the efficiency with which phenyl radicals abstract hydrogen from organic solvents (absolute rate constants of the order of 10^5 dm^3 mol^{-1} s^{-1} have been estimated by Lorand and co-workers[14]) the difference between their apparent behaviour in acetonitrile (a maximum of 25% hydrogen abstraction from the solvent, see above) and dichloromethane (a minimum of 75% hydrogen abstraction) is certainly striking.

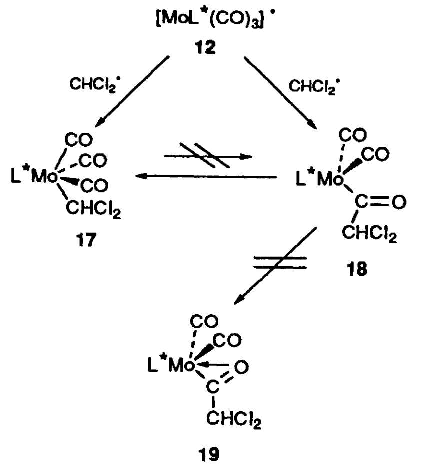
It is possible that these results simply reflect the greater polarity of the acetonitrile molecule *vis-à-vis* dichloromethane (dipole moments of 3.92 and 1.60 D respectively[15]) rather than any inherent lack of reactivity of the former towards hydrogen abstraction by phenyl radicals. Solvation of one or both ionic reactants by the polar acetonitrile may lead to the primary radical products being formed in a solvent cage which would promote combination of the phenyl radical with the cogenerated organometallic radical **12**. If the original reactants are less efficiently caged in dichloromethane, radical–solvent transfer would be promoted by easier diffusion of the primary radicals away from the initial site of reaction. It must also be noted, however, that the tetraethylammonium salt of **5** is reasonably soluble in acetonitrile but sparingly so in dichloromethane. It is conceivable that the oxidation of **5** under these conditions occurs largely at the solid–liquid interface and this, in turn, may favour reaction of the primary aryl radical with the dichloromethane solvent. Experiments aimed at clarifying this point are currently being carried out.

Mode of Formation of the η^2*-Aroyl and* η^1*-Halogenocarbyne Products.*—We can be less certain about the details of the reaction pathways which lead to the formation of η^2-aroyl or chlorocarbyne complexes from the primary radical products. The tricarbonyl radical **12** may initially react with aryl radicals at the metal centre to yield the seven-co-ordinate σ-aryl complex [MoL*(CO)$_3$(σ-R′)] **6** (Scheme 3). Migratory insertion of CO into the Mo–R′ σ bond, driven by steric crowding in **6**, could then yield a 16-electron η^1-aroyl complex [MoL*(CO)$_2$(η^1-COR′)] **15** and thence the 18-electron η^2-aroyl **9**. Alternatively, the 16-electron intermediate **15** may conceivably be formed by direct radical coupling at CO carbon in **12**.

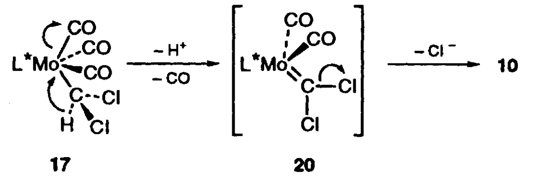
Evidence from the literature does not point clearly to one or other of these alternatives. Several recent studies of molybdenum complexes[7,16] indicate that a sterically crowded co-ordination sphere favours combination of adjacent CO and alkyl ligands to form more compact η^2-acyl structures but that



Scheme 3



Scheme 4



Scheme 5

electronic factors may also be significant. On the basis of theoretical and experimental studies Curtis *et al.*[17,18] concluded that both steric and electronic factors combine to disfavour the formation of seven-co-ordinate molybdenum σ-alkyl derivatives of the _unsubstituted_ hydrotris(pyrazolyl)borate ligand. They found no evidence for intervention of $[Mo\{HB(pz)_3\}(CO)_3Me]$ as a precursor of $[Mo\{HB(pz)_3\}(CO)_2(\eta^2\text{-COMe})]$ in the reaction of $[Mo\{RB(pz)_3\}(CO)_3]^-$ **3** (R = H) with MeI in boiling acetonitrile or with $[OMe_3]^+$ in dichloromethane at room temperature.[17] In contrast, Baird and co-workers[19] have isolated seven-co-ordinate $[Mo\{HB(pz)_3\}(CO)_3(\sigma\text{-}CH_2CN)]$ and characterised it by X-ray crystallography. In addition, Onyiriuka and Storr[20] observed that the anionic pyrazolylgallate complex $[Mo\{MeGa(pz)_3\}(CO)_3]^-$ reacts with alkyl halides in tetrahydrofuran (thf) at room temperature to yield a spectroscopically detectable methyl complex $[Mo\{MeGa(pz)_3\}(CO)_3Me]$ and an isolable ethyl derivative $[Mo\{MeGa(pz)_3\}(CO)_3Et]$. The former readily isomerises to the η2-acetyl complex $[Mo\{MeGa(pz)_3\}(CO)_2(\eta^2\text{-COMe})]$. The ethyl complex did not undergo a similar isomerisation but it is possible that an alternative β-elimination decomposition pathway intervenes in this case.[20]

The ligand L* exercises a significantly greater steric demand than does $[HB(pz)_3]^-$ (cone angles of 224 and 184° respectively[21]). Hence Curtis' results[17,18] imply that formation of the seven-co-ordinate σ-aryl intermediate **6** or the potentially still more congested complex $[MoL^*(CO)_3(C_6H_{11})]$ **16** will be even less favourable than in the hydrotris(pyrazolyl)borate system. However, in the light of the other evidence quoted above it is clear that we cannot eliminate the possibility that transient seven-co-ordinate σ-alkyl and -aryl intermediates are the kinetically favoured initial products of coupling of organic radicals with the tricarbonylmolybdenum radical **12** in our system. Indirect evidence for the intervention of such species will be presented later.

Following redox and radical transfer, we propose that the sequence of chemical events in dichloromethane (Scheme 4) parallels that in acetonitrile. The organometallic radical **12** and the dichloromethyl radical may couple at the metal atom to yield the seven-co-ordinate dichloromethyl complex $[MoL^*(CO)_3(CHCl_2)]$ **17** or at co-ordinated CO to form a 16-electron η1-dichloroacetyl complex $[MoL^*(CO)_2(\eta^1\text{-}COCHCl_2)]$ **18** and thence the η2-dichloroacetyl complex $[MoL^*(CO)_2(\eta^2\text{-}COCHCl_2)]$ **19**. A careful study of the reaction mixture revealed no evidence for the formation of **19**. {An attempt to effect an independent synthesis of **19** *via* the reaction of $[MoL^*(CO)_3]^-$ **5** with $CHCl_2COCl$ led to decomposition of the starting material.} Once formed, the 18-electron complex **19** would be expected to be stable enough to survive work-up and isolation. Hence we conclude that *either* the 16-electron η1-dichloroacetyl complex **18** is not formed in our reaction, *or* that it decarbonylates to form the 18-electron dichloromethyl compound **17** more rapidly than it can rearrange to the η2-dichloroacetyl complex **19**. Conversely, if **17** is the primary product of radical coupling its behaviour differs from the σ-aryl analogue **6** in that it does not undergo migratory insertion of CO to form complex **18**.

These conclusions are compatible with the known resistance to insertion of CO exhibited by alkyl ligands bearing electron-withdrawing substituents and the ease with which the corresponding acetyl complexes undergo decarbonylation,[22] an effect illustrated in the poly(pyrazolyl)boratomolybdenum system by the enhanced stability of the seven-co-ordinate cyanoalkyl complex $[Mo\{HB(pz)_3\}(CO)_3(\sigma\text{-}CH_2CN)]$.[19] Hence it seems probable that coupling of the dichloromethyl radical and the organometallic radical **12** leads to the seven-co-ordinate dichloromethyl compound **17**, irrespective of the initial site of reaction, and that **17** is a precursor of the chlorocarbyne complex **10**. Since complex **17** is likely to be even more sterically crowded than the related σ-aryl **6** we conclude that the latter, and presumably also the cyclohexyl analogue **16**, are likely, albeit highly transient, intermediates in the formation of the η2-aroyl complexes **9** and **13** and their analogues. There have been relatively few reports[23] of dichloroalkyl derivatives of the transition metals. We note that a radical mechanism similar to that proposed here and in our preliminary account of this work[5] has been invoked to explain the formation of complexes of the type $[(CNR)_n\{PPh(OEt)_2\}_{5-n}(CHCl_2)]^{+2}$ (n = 2 or 3) in the reaction of $[Co(CNR)_n\{PPh(OEt)_2\}_{5-n}]^+$ with arenediazonium cations and dichloromethane.[24]

We have suggested that relief of steric crowding underlies the formation of the η2-aroyl complexes **9** and believe that it is also the driving force behind conversion of the dichloromethyl complex **17** into the η1-chlorocarbyne complex **10**. Since rearrangement to the more compact η2-dichloroacetyl complex **19** is electronically disfavoured (see above) we propose that a less-crowded co-ordination sphere is achieved *via* simultaneous loss of a proton from the dichloromethyl group and expulsion of CO with formation of anionic $[MoL^*(CO)_2({=}CCl_2)]^-$ **20** containing a planar dichlorocarbene ligand (Scheme 5). Loss of chloride anion from the dichlorocarbene ligand in **20** would then lead directly to the even more compact linear η^1-chlorocarbyne ligand in **10**. This sequence is to be preferred to that proposed in our preliminary communication.[5]

Some other routes from $[\mathrm{MoL^*(CO)_3}]^-$ **5** to $[\mathrm{MoL^*(CO)_2(\equiv CCl)}]$ **10** were investigated briefly. The thallium(I) and benzyltriethylammonium salts of **5**, *i.e.* **14b** and **14c** respectively, both reacted with boiling chloroform (but not with dichloromethane) to yield **10** but with yields (20 and 40% respectively) much inferior to those obtainable using iodonium or diazonium salts in dichloromethane. It is not clear whether the reactions in chloroform are to be regarded as $\mathrm{S_N2}$-type substitutions [equation (3)] or involve an anion–solvent redox process

$$\underset{\mathbf{5}}{[\mathrm{MoL^*(CO)_3}]^-} + \mathrm{CHCl_3} \longrightarrow \underset{\mathbf{17}}{[\mathrm{MoL^*(CO)_3(CHCl_2)}]} + \mathrm{Cl^-} \quad (3)$$

(Scheme 6). Either pathway could lead to the dichloromethyl complex **17** and thence to the η^1-chlorocarbyne complex **10**.

The synthesis has also been extended to the bromo- and iodo-homologues of complex **10**. Since the order of reactivity of C–X bonds towards abstraction of X by an aryl radical is X = I > Br > H > Cl,[25] bromo- and iodo-form are the required precursors of the dibromo- and diiodo-methyl radicals respectively. Oxidation of $[\mathrm{MoL^*(CO)_3}]^-$ **5** or $[\mathrm{WL^*(CO)_3}]^-$ **8** with diphenyliodonium cation in bromoform gave the bromocarbyne complexes $[\mathrm{MoL^*(CO)_2(\equiv CBr)}]$ **21** and $[\mathrm{WL^*(CO)_2(\equiv CBr)}]$ **22** respectively in *ca.* 50% yield. Reaction of **5** with diphenyliodonium cation and an excess of iodoform in thf gave a low yield of the unstable iodocarbyne complex $[\mathrm{MoL^*(CO)_2(\equiv CI)}]$ **23**.

Redox versus *Carbonyl Substitution in the Reactions of Tricarbonyl[poly(pyrazolyl)borato]molybdenum Anions with Arenediazonium Cations.*—We turn now to the dramatic shift from substitution of CO in the reaction of arenediazonium cations with $[\mathrm{Mo\{RB(pz)_3\}(CO)_3}]^-$ **3** to the redox pathway observed with the ring-substituted analogue $[\mathrm{MoL^*(CO)_3}]^-$ **5**. Some insight into the origin of the effect was provided by a study of the behaviour of variously substituted analogues of **5**, *i.e.* complexes **24a**–**24c**. The 3-methylpyrazolyl (mpz) derivative **24a**[26] reacted with $[4\text{-}\mathrm{MeOC_6H_4N_2}]^+$ in acetonitrile to give $[\mathrm{Mo\{HB(mpz)_3\}(CO)_2(\eta^2\text{-}COC_6H_4OMe\text{-}4)}]$ **25** and with $[4\text{-}\mathrm{NO_2C_6H_4N_2}]^+$ in dichloromethane to give $[\mathrm{Mo\{HB(mpz)_3\}(CO)_2(\equiv CCl)}]$ **26**, both in *ca.* 60% yield, as the only carbonyl-containing products. Hence the observed change in reaction pathway with $[\mathrm{R'N_2}]^+$ from substitution with **3** to redox with **5** results from the introduction of the 3-methyl substituents in the latter. The 5-methyl groups have no function in this regard.

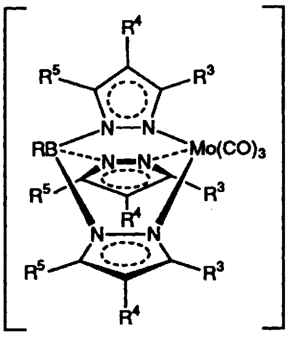
The results obtained with the 3,4,5-trimethyl- (tmpz) and 4-chloro-3,5-dimethyl-pyrazolyl (cmpz) analogues of **5**, *i.e.* $[\mathrm{Mo\{HB(tmpz)_3\}(CO)_3}]^-$ **24b** and $[\mathrm{Mo\{HB(cmpz)_3\}(CO)_3}]^-$ **24c** were particularly significant. The $\nu(\mathrm{CO})_{\mathrm{av}}$ and oxidation potential data summarised in Table 2 demonstrate that complex **24b** contains a more electron-rich molybdenum atom than does **5** while the electron density on the metal atom in **24c** is reduced compared to **5** and is similar to that in the *unsubstituted* $[\mathrm{Mo\{RB(pz)_3\}(CO)_3}]^-$ **3** (R = H or pz). Importantly, both complexes maintain the same degree of steric crowding around the $\mathrm{Mo(CO)_3}$ unit as in the dmpz analogue **5**.

$$\underset{\mathbf{5}}{[\mathrm{MoL^*(CO)_3}]^-} + \mathrm{CHCl_3} \longrightarrow \underset{\mathbf{12}}{[\mathrm{MoL^*(CO)_3}]^{\bullet}} + \mathrm{CHCl_3}^{\bullet -}$$

$$\mathrm{CHCl_3}^{\bullet -} \longrightarrow \mathrm{CHCl_2}^{\bullet} + \mathrm{Cl^-}$$

$$\mathbf{12} + \mathrm{CHCl_2}^{\bullet} \longrightarrow \underset{\mathbf{17}}{[\mathrm{MoL^*(CO)_3(CHCl_2)}]}$$

Scheme 6



24a $\mathrm{R^3 = Me, R^4 = R^5 = H}$
24b $\mathrm{R^3 = R^4 = R^5 = Me}$
24c $\mathrm{R^3 = R^5 = Me, R^4 = Cl}$

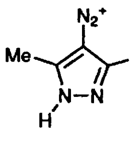
Table 2 The IR and oxidation potential data for tricarbonyl anions $[\mathrm{Mo\{RB(R^3R^4R^5\text{-}pz)_3\}(CO)_3}]^-$

Complex	$\nu(\mathrm{CO})_{\mathrm{av}}$ (cm^{-1})	$E^{\circ\,a}_{\frac{1}{2}}$/V
3 (R = H)	1829 [b]	−0.21
3 (R = pz)	1831 [b]	−0.18
5	1821 [b]	−0.31
24b	1816	—
24c	1828	−0.15

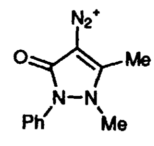
[a] Measured at a platinum electrode on the $[\mathrm{N(PPh_3)_2}]^+$ salts of the anion in $\mathrm{CH_2Cl_2}$ with $[\mathrm{NBu_4}]\mathrm{PF_6}$ as base electrolyte. Under the conditions used the E° value for the one-electron oxidation of ferrocene is 0.47 V. We are grateful to Dr. N. G. Connelly, School of Chemistry, University of Bristol, for these measurements. [b] Calculated from data in Ref. 27.

Reaction of complexes **24b** and **24c** with $[4\text{-}\mathrm{MeC_6H_4N_2}]^+$ in acetonitrile yielded the η^2-aroyl complexes $[\mathrm{Mo\{HB(tmpz)_3\}(CO)_2(\eta^2\text{-}COC_6H_4Me\text{-}4)}]$ **27** and $[\mathrm{Mo\{HB(cmpz)_3\}(CO)_2(\eta^2\text{-}COC_6H_4Me\text{-}4)}]$ **28**, both in *ca.* 50% yield, as the only carbonyl-containing products. In dichloromethane, reaction with $[4\text{-}\mathrm{NO_2C_6H_4N_2}]^+$ produced the η^1-chlorocarbyne complexes $[\mathrm{Mo\{HB(tmpz)_3(CO)_2(\equiv CCl)}]$ **29** and $[\mathrm{Mo\{HB(cmpz)_3(CO)_2(\equiv CCl)}]$ **30**, again in *ca.* 50% yield. There was no evidence for the formation of aryldiazenido complexes although we can show that, if formed, the latter should be sufficiently stable to allow isolation and characterisation (see below). A similar reaction of **24b** in bromoform produced the bromocarbyne complex $[\mathrm{Mo\{HB(tmpz)_3](CO)_2(\equiv CBr)}]$ **31** in 61% yield. These results conclusively demonstrate that the anomalous susceptibility of **5** and its analogues towards oxidation by arenediazonium cations is an artefact of steric crowding produced by the 3-methyl substituents and is not related to the electron-releasing power of these substituents.

The outcome of the reaction of $[\mathrm{MoL^*(CO)_3}]^-$ **5** with arenediazonium cations was also found to be sensitive to the nature of the diazonium cation. In acetonitrile nine of the ten 3- or 4-substituted arenediazonium cations investigated (see Table 1) produced an η^2-aroyl complex **9** in high yield as the only carbonyl-containing product detectable by careful thin-layer chromatography. However, the 4-dimethylaminobenzenediazonium cation gave, in addition to a 55% yield of the η^2-aroyl complex **9j**, *ca.* 3% of a carbonyl-containing complex identified as the CO-substitution (*i.e.* aryldiazenido) product $[\mathrm{MoL^*(CO)_2(N_2C_6H_4NMe_2\text{-}4)}]$ **32a**. Similar results were obtained from the reaction of **5** with $[4\text{-}\mathrm{Me_2NC_6H_4N_2}]^+$ in dichloromethane, where the major product $[\mathrm{MoL^*(CO)_2(\equiv CCl)}]$ **10** (75%) was accompanied by **32a** in *ca.* 3% yield. In dichloromethane the 2,6-disubstituted arenediazonium cations



I



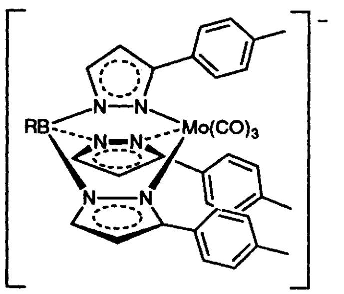
II

$[6\text{-Me-2-ClC}_6H_3N_2]^+$ and $[2,6\text{-Me}_2C_6H_3N_2]^+$ yielded aryldiazenido complexes $[MoL^*(CO)_2(N_2C_6H_3Cl\text{-2-Me-6})]$ **32b** and $[MoL^*(CO)_2(N_2C_6H_3Me_2\text{-2,6})]$ **32c** in *ca.* 5% yield, together with *ca.* 70% of the η^1-chlorocarbyne complex **10**. In acetonitrile reactions of **5** with the latter two arenediazonium cations gave no detectable quantities of the η^2-aroyl products but the aryldiazenido complexes **32b** and **32c** were isolated in increased yield (*ca.* 20%) as the sole carbonyl-containing products. The identity of **32c** was confirmed by an X-ray crystallographic determination (see below).

Formation of the η^1-chlorocarbyne complex **10** in high yields (*ca.* 67%) in the reaction of **5** with $[6\text{-Me-2-ClC}_6H_3N_2]^+$ and $[2,6\text{-Me}_2C_6H_3N_2]^+$ in dichloromethane demonstrates that this reaction must produce the aryl radicals $6\text{-Me-2-ClC}_6H_3{}^{\bullet}$ and $2,6\text{-Me}_2C_6H_3{}^{\bullet}$ in, at minimum, corresponding yields. Hence the failure to form η^2-aroyl complexes in acetonitrile presumably reflects the inability of these sterically hindered 2,6-disubstituted radicals to approach sufficiently close to the hindered metal atom to form the proposed σ-aryl intermediate $[MoL^*(CO)_3(\sigma\text{-R}')]$ **6**. This, in turn, may be taken as further (albeit indirect) evidence in favour of our proposal that those reactions which do lead to η^2-aroyl products proceed *via* initial radical coupling at the metal centre (see above). Radical coupling at carbonyl carbon would be expected to be significantly less sensitive to the bulk of the aryl radical.

Reaction of $[MoL^*(CO)_3]^-$ **5** with the 3,5-dimethylpyrazole-4-diazonium cation, $[(dmpz)N_2]^+$ **I** or the antipyrine-4-diazonium cation (2,3-dimethyl-5-oxo-1-phenyl-3-pyrazoline-4-diazonium cation), $[(ap)N_2]^+$ **II**, in acetonitrile gave even higher yields (*ca.* 90%) of the CO-substitution products $[MoL^*(CO)_2\{N_2(dmpz)\}]$ **32d** and $[MoL^*(CO)_2\{N_2(ap)\}]$ **32e**. There was no evidence for formation of η^2-aroyl products and this may be rationalised along the lines suggested above for the 2,6-disubstituted benzenediazonium analogues. In dichloromethane the yields of the organyldiazenido complexes **32d** and **32e** were slightly lower (*ca.* 80%) and the η^1-chlorocarbyne complex **10** was isolated in *ca.* 10% yield, demonstrating that a redox pathway does play a minor part in these reactions. The structure of **32e** has been verified by an X-ray diffraction study (see below).

In searching for the origins of these unexpected reversions to the carbonyl-substitution pathway we focus first on the 2,6-disubstituted benzenediazonium cations $[6\text{-Me-2-ClC}_6H_3N_2]^+$ and $[2,6\text{-Me}_2C_6H_3N_2]^+$. The contrasting electronic character of the pairs of 2,6-substituents suggests that the observed change in reaction pathway has its origin in the steric hindrance produced by having two non-hydrogen substituents flanking the diazonium functional group rather in a common electronic effect of the substituents themselves. Similar reactivity is thus to be expected for the heterocyclic diazonium cations **I** and **II** since these also contain diazonium groups flanked by a pair of non-hydrogen substituents. However the dramatic increase in yield of the carbonyl substitution products observed for their reactions with complex **5** suggests that an additional factor must also be operating. We believe that this is a strong conjugative electron release to the diazonium group from the attached heterocyclic nucleus. Elsewhere we have reported theoretical calculations and spectroscopic data which confirm that this effect is significant for the cations **I** and **II**[28] but it is, of course, lacking in $[2\text{-Cl-6-MeC}_6H_3N_2]^+$ and $[2,6\text{-Me}_2C_6H_3N_2]^+$, hence the lower yields of substitution with the latter. This suggestion is also supported by the fact that a low yield of the substitution product $[MoL^*(CO)_2(N_2C_6H_4NMe_2\text{-4})]$ **32a** is formed in the reaction of **5** with the sterically uncrowded, but conjugatively stabilised, $[4\text{-Me}_2NC_6H_4N_2]^+$ (see above).



33a R = H
33b R = tpz

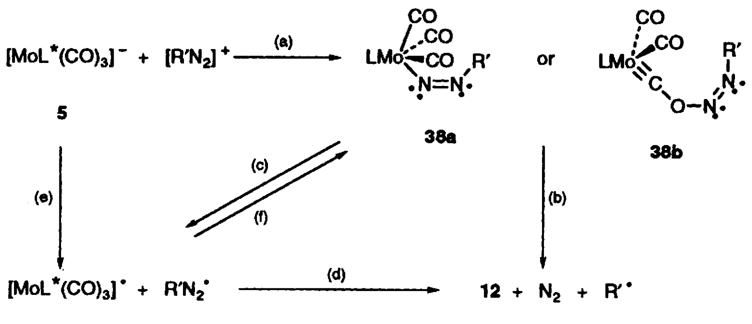
The attribution to steric effects of the re-emergence of the carbonyl-substitution pathway in the reaction of $[MoL^*(CO)_3]^-$ **5** with 2,6-disubstituted benzenediazonium cations requires further justification since we have shown above that steric crowding is responsible for the promotion of redox, rather than substitution, in the reaction of **5** with 4-substituted benzenediazonium cations. To test the hypothesis we investigated the reaction of tricarbonyl[poly{3-(4-tolyl)pyrazolyl}borato]-molybdenum complexes $[Mo\{HB(tpz)_3\}(CO)_3]^-$ **33a** and $[Mo\{B(tpz)_4\}(CO)_3]^-$ **33b** with unsubstituted and 4-substituted benzenediazonium cations. We reasoned that steric crowding in a reaction system involving tricarbonylmolybdenum anions containing these sterically demanding[29] ligands and *unhindered* arenediazonium cations might be close enough to that between **5** and bulky 2,6-disubstituted arenediazonium cations to force a reversion to the carbonyl-substitution pathway in the former system also. This prediction was justified by experiment.

Reaction of complex **33a** with benzenediazonium cation in acetonitrile yielded the carbonyl-substitution product $[Mo\{HB(tpz)_3\}(CO)_2(N_2Ph)]$ **34a** in 6% yield (*vs.* 0% with **5**) together with the η^2-aroyl compound $[Mo\{HB(tpz)_3\}(CO)_2(\eta^2\text{-COPh})]$ **35a** (21%) and a small quantity of a third, as yet uncharacterised, green complex (see Experimental section). Under similar conditions the analogous aryldiazenido complex $[Mo\{HB(tpz)_3\}(CO)_2(N_2C_6H_4NMe_2\text{-4})]$ **34b** was formed in 29% yield from $[4\text{-Me}_2NC_6H_4N_2]^+$ (*cf.* 3% from **5**) as the only significant carbonyl-containing product. As was the case with **5**, the highest yield of aryldiazenido complex (43% of $[Mo\{HB(tpz)_3\}(CO)_2\{N_2(ap)\}]$ **34c**) was obtained with cation **II**.

In dichloromethane reaction of $[4\text{-Me}_2NC_6H_4N_2]^+$ with complex **33a** yielded the aryldiazenido complex **34b** (18%) together with *ca.* 3% of the η^1-chlorocarbyne complex $[Mo\{HB(tpz)_3\}(CO)_2(\equiv CCl)]$ **36** and a trace of a complex tentatively identified as $[Mo\{HB(tpz)_3\}(CO)_2(\eta^2\text{-COC}_6H_4\text{-NMe}_2\text{-4})]$ **35b**. Complex **36** was also obtained in similar yield (along with 17% of the η^2-benzoyl complex **35a**) by oxidation of the anion **33a** with diphenyliodonium cation in dichloromethane.

Reaction of complex **33b** with $[4\text{-Me}_2NC_6H_4N_2]^+$ in acetonitrile yielded the aryldiazenido complex $[Mo\{B(tpz)_4\}(CO)_2(N_2C_6H_4NMe_2\text{-4})]$ **37** but in only 3% yield compared to the 29% obtained from **33a**. This is a puzzling result since the two 3-(4-tolyl)pyrazolylborate ligands would be expected to produce identical steric environments around the molybdenum atom and the ν(CO) values for the tricarbonyl anions **33a** and **33b** (Experimental section) suggest that the ligands likewise have very similar electronic properties.

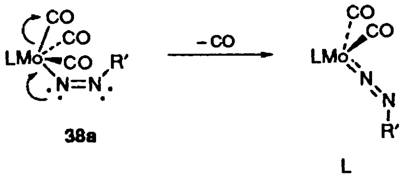
Although we do not yet have conclusive evidence for a mechanism accounting for all our observations we can propose a reasonable working hypothesis to serve as a basis for further



Scheme 7

study. (In what follows the term 'aryl' and the symbol 'R'' should be understood as including the heterocyclic dmpz and ap groups.) Generation of radicals from diazonium cations by reduction with transition-metal compounds is an important process for which both inner- and outer-sphere mechanisms have been suggested.[30] Scheme 7 outlines these possibilities as applied to the oxidation of $[MoL^*(CO)_3]^-$ **5** by diazonium cations. In the inner-sphere mechanism **5** and the diazonium cation combine to form a covalent intermediate [step (a), Scheme 7]. If the metal atom is the reactive site of **5** a seven-co-ordinate neutral σ-bonded 'doubly bent' aryldiazenido complex $[MoL(CO)_3(N_2R')]$ **38a** [L = HB(dmpz)$_3$] results.[31] Alternatively, Kochi's recent demonstration of contact ion pairing involving close approach of suitable cations to one carbonyl ligand of **5**[32] suggests the possibility of reaction at carbonyl oxygen to give the six-co-ordinate (aryldiazoato)carbyne complex **38b** [L = HB(dmpz)$_3$]. Homolytic fragmentation of either **38a** or **38b** [L = HB(dmpz)$_3$] to form the ultimate redox products, the tricarbonyl radical **12**, nitrogen and an aryl radical, may then occur in a concerted fashion [step (b)] or stepwise *e.g. via* the initial formation of **12** and an intermediate aryldiazenyl radical [step (c)]. The rate constant for decomposition of the latter to an aryl radical and nitrogen [step (d)] is estimated[30] to be of the order of 10^5 s^{-1}. An outer-sphere oxidation [step (e)] would simply involve transfer of an electron from the anion **5** to the diazonium cation followed by fragmentation of the resulting aryldiazenyl radical. It is possible for both inner- and outer-sphere mechanisms to contribute separately to an overall redox process.[33]

Some further general comments may be made on the basis of the results just described: of the two possible inner-sphere intermediates, the doubly bent aryldiazenido adduct **38a** is also the likely precursor of the 'singly bent' aryldiazenido complexes (*i.e.* the carbonyl-substitution products) **4**, **32a**–**32e**, **34a**–**34c** and **37** [equation (4)].[31] Isolation of the latter complexes is strong evidence, therefore, that an inner-sphere intermediate does form and that this is **38a** rather than **38b**.



(4)

	L
4	RB(pz)$_3$
32	HB(dmpz)$_3$
34	HB(tpz)$_3$
37	B(tpz)$_4$

Again, formation of the carbonyl-substitution products such as aryldiazenido complex **32** and its analogues *via* an outer-sphere redox pathway (Scheme 7) is only possible if recombination of the tricarbonyl radical **12** and related species and $R'N_2^•$ to form the doubly bent aryldiazenido complex of the general type **38a** can compete successfully with rapid decomposition[30] of the aryldiazenyl radical [step (d)]. Tentative evidence that this may be the case in certain circumstances is provided by our observation of a four-fold increase in yield of the 2,6-disubstituted aryldiazenido complexes **32b** and **32c** on changing the reaction solvent from dichloromethane to acetonitrile. A similar, though less dramatic, effect is observed in the analogous reactions of $[Mo\{HB(tpz)_3\}(CO)_3]^-$ **33a**. Earlier in this paper we rationalised the evident lack of radical transfer to acetonitrile solvent in the oxidation of the tricarbonyl **5** and its analogues by suggesting that reaction may take place within a solvent cage in acetonitrile but not in dichloromethane. In the case of arenediazonium as oxidant such a cage effect would also enhance the likelihood of combination of aryldiazenyl and organometallic radicals (whether generated by inner- or outer-sphere events) to form **38a** [step (f) of Scheme 7] and thus favour aryldiazenido products. Although it is possible that independent outer- and inner-sphere pathways are involved in the oxidation of **5** and related complexes with arenediazonium cations, formation of the aryldiazenido products must ultimately proceed *via* the inner-sphere intermediate **38a**.

Since the carbonyl-substitution products $[Mo\{RB(pz)_3\}(CO)_2(N_2R')]$ **4** are formed in up to 80% yield[2,34] in the reactions of $[Mo\{RB(pz)_3\}(CO)_3]^-$ with arenediazonium cations it follows that anion–cation combination to form the seven-co-ordinate σ-aryldiazenido inner-sphere complex **38a** [L = RB(pz)$_3$] is the dominant pathway for these reactants. As there is no evidence for redox products in this system[34] it must also be the case that **38a** [L = RB(pz)$_3$] persists long enough to undergo conversion to the 'singly bent' aryldiazenido complex **4** without any significant fragmentation to radical species. We have shown that the contrasting oxidation of the ring-substituted analogues **5** and **24** (and, by implication, **33**) with 4-substituted arenediazonium cations is a result of steric crowding. We may reasonably conclude that this is so *either* because intermolecular steric crowding inhibits the formation of the covalent inner-sphere adduct **38a** [L = HB(dmpz)$_3$, *etc.*], hence blocking the carbonyl-substitution pathway and favouring outer-sphere redox, *or* because the same inner-sphere intermediate is formed but is labilised towards homolysis *vis-à-vis* **38a** [L = RB(pz)$_3$] by increased intramolecular steric crowding across the nitrogen–nitrogen bond. We favour the latter (*i.e.* inner-sphere) alternative on the grounds that it accounts for both redox and carbonyl-substitution products within the framework of a single mechanism and also because it allows some further unexpected aspects of the reaction to be rationalised (see below).

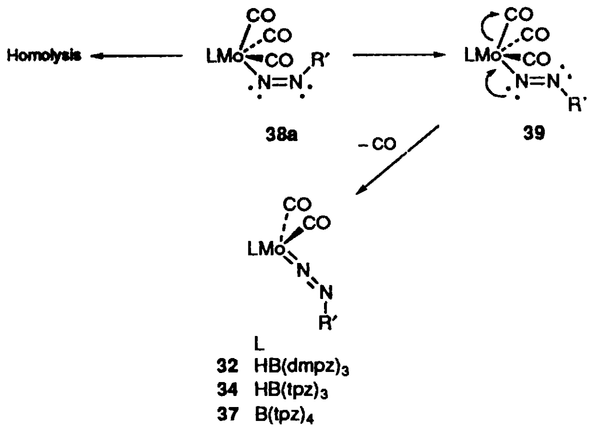
The simplest explanation for the surprising observation that a re-emergence of the carbonyl-substitution pathway is promoted by *further* steric hindrance in *either* the carbonyl anion (*i.e.* reaction of $[Mo\{HB(tpz)_3\}(CO)_3]^-$ **33a** and $[Mo\{B(tpz)_4\}$-

$(CO)_3]^-$ **33b** with unsubstituted or 4-substituted arenediazonium cations) *or* the arenediazonium cation {*i.e.* reaction of $[MoL^*(CO)_3]^-$ **5** with 2,6-disubstituted arenediazonium cations] is that this effect operates in an intermediate in which the anionic and cationic reactants are bound together, *i.e.* in the doubly bent aryldiazenido inner-sphere adduct $(OC)_3LMo-N{=}N-R'$ **38a** [L = $HB(dmpz)_3$, *etc.*]. The available evidence on the nature of the kinetically favoured adduct formed between arenediazonium cations and simple nucleophiles[35] would predict that **38a** should have a *cis* arrangement of $(OC)_3LMo$ and R′ groups about the nitrogen–nitrogen double bond and this geometry is also predicted for doubly bent aryldiazenido ligands on the basis of molecular orbital calculations.[36] The pyrazolyl 3-methyl substituents in $[MoL^*(CO)_3]^-$ **5**, would be expected to result in a severe increase in unfavourable non-bonded interactions across the nitrogen–nitrogen double bond in **38a** [L = $HB(dmpz)_3$] *vis-à-vis* **38a** [L = $HB(pz)_3$], thus facilitating homolytic fragmentation and the observed redox pathway. With 2,6-disubstituted arenediazonium cations or with bulkier pyrazolylborate ligands increased steric crowding will tend to destabilise the inner-sphere intermediate **38a** still further. It is our hypothesis that this destabilisation (*i.e.* increase in energy) is equivalent to a *lowering* in the effective barrier for *cis–trans* isomerisation of the doubly bent aryldiazenido ligand. As a result there are now two possible routes for the relief of steric crowding in **38a**, homolysis and isomerisation to the less crowded *trans* isomer **39** (Scheme 8). Since the less-crowded **39** is expected to be more stable than **38a** the former may now persist long enough to allow for conversion into the aryldiazenido complexes **32**, **34** or **37** to compete with homolysis, hence the apparently paradoxical observation that severe steric crowding effects a return to the carbonyl-substitution pathway.

We have also noted that the carbonyl-substitution route in these reactions is favoured by conjugative electron release to the diazonium functional group, *e.g.* for $[4\text{-}Me_2NC_6H_4N_2]^+$, $[(dmpz)N_2]^+$ and $[(ap)N_2]^+$. It has been established that electron-releasing substituents decrease the half-wave reduction potentials of arenediazonium cations[37] as well as significantly depressing the rate of outer-sphere reduction.[38] Hence formation of the inner-sphere adduct **38a** [L = $HB(dmpz)_3$, *etc.*] will be favoured for the cations under consideration. In addition it is possible that electron release from the aryl substituent also stabilises the covalent adduct **38a** *vis-à-vis* homolysis and thus inhibits the inner-sphere redox pathway.

Attempted Syntheses of η^1-*Chlorocarbyne Complexes from other Metal Tricarbonyl Substrates.*—Owing to their considerable synthetic utility[3,9] we have made considerable efforts to extend our route to η^1-halogenocarbyne complexes beyond $[MoL^*(CO)_3]^-$ **5** to other substrates of the general type $[ML(CO)_3]^{0,1-}$. Although $[Mo\{RB(pz)_3\}(CO)_3]^-$ **3** (R = pz), the ring-unsubstituted analogue of **5**, yields only carbonyl-substitution products $[Mo\{RB(pz)_3\}(CO)_2(N_2R')]$ **4** (R = pz)[2] with arenediazonium cations, oxidation with diphenyliodonium cation in dichloromethane produced a 24% yield of the new η^1-chlorocarbyne complex $[Mo\{B(pz)_4\}(CO)_2(\equiv CCl)]$ **40**, the structure of which has been established by an X-ray crystallographic study.[5] A similar reaction in acetonitrile at −40 °C gave the red η^2-benzoyl complex $[Mo\{B(pz)_4\}(CO)_2(\eta^2\text{-}COPh)]$ **41** in *ca.* 49% yield.

Less encouraging results were obtained with other substrates. Although $[CrL^*(CO)_3]^-$ **42** is a close analogue of **5**, reaction with $[4\text{-}Me_2NC_6H_4N_2]^+$ or $[(ap)N_2]^+$ in CH_2Cl_2 induced complete decomposition to carbonyl-free materials even at −70 °C. Neither was there any evidence for the formation of a chlorocarbyne product when the mono(thiocarbonyl) analogue of **5**, *i.e.* $[MoL^*(CO)_2(CS)]^-$ **43**[8] was treated with $[IPh_2]^+$ or arenediazonium cations in dichloromethane.[39] The anionic trifluoromethyl-substituted complex $[Mo\{HB(dtfpz)_3\}(CO)_3]^-$ **44** would be expected to be somewhat more sterically crowded than **5** but to have reduced susceptibility towards oxidation as a result of the electron-withdrawing effect of the CF_3 groups [$\nu(CO)_{av}$ 1864 cm^{-1} compared to 1821 cm^{-1} for **5**]. It reacted with $[4\text{-}FC_6H_4N_2]^+$ in CH_2Cl_2 to give the carbonyl-substitution product $[Mo\{HB(dtfpz)_3\}(CO)_2(N_2C_6H_4F\text{-}4)]$ **45** in *ca.* 43% yield contaminated with a small amount of the η^2-aroyl complex $[Mo\{HB(dtfpz)_3\}(CO)_2(\eta^2\text{-}COC_6H_4F\text{-}4)]$ **46** from which it could not be separated (see Experimental section). There was no evidence for formation of an η^1-chlorocarbyne complex or of any other carbonyl-containing product.



Scheme 8

The tris(3,5-dimethylpyrazolyl)methane molybdenum complex $[Mo\{HC(dmpz)_3\}(CO)_3]$ **47** and the manganese complex $[MnL(CO)_3]$ **48** are isoelectronic and isostructural, but neutral, analogues of the anionic **5**. The proposed mechanism for η^1-chlorocarbyne complex formation (Schemes 4 and 5 above) applied to the molybdenum complex **47** would imply formation of a neutral dichlorocarbene complex $[Mo\{HC(dmpz)_3\}(CO)_2(=CCl_2)]$ **49** which could then lose chloride anion to form the cationic η^1-chlorocarbyne complex $[Mo\{HC(dmpz)_3\}(CO)_2(\equiv CCl)]^+$ **50**. Since neutral $[MoL^*(CO)_2(\equiv CCl)]$ **10** readily *adds* anionic nucleophiles[8,9] and cationic **50** should do so even more readily it is probable that this reaction sequence would halt at the dichlorocarbene stage. With $[4\text{-}Me_2NC_6H_4N_2]^+$ in CH_2Cl_2 complex **47** gave a low yield (*ca.* 9%) of the carbonyl-substitution product $[Mo\{HC(dmpz)_3\}(CO)_2(N_2C_6H_4NMe_2\text{-}4)]^+$ **51**. A similar reaction with the heterocyclic diazonium cation $[(ap)N_2]^+$ gave $[Mo\{HC(dmpz)_3\}(CO)_2\{N_2(ap)\}]^+$ **52** in 89% yield. In neither case was there any evidence for the formation of redox products. Traces of an unstable material with ν(CO) 1980s and 1815s cm^{-1} were produced by the reaction of **47** with $[IPh_2]BF_4$ in CH_2Cl_2. This material decomposed rapidly and could not be characterised but comparison with ν(CO) for **47** itself (1900, 1760 cm^{-1})[40] suggested that it was an oxidation product of the latter. Surprisingly, in view of the reactivity shown by **47**, the closely related manganese complex **48** was found to be inert to reaction with arenediazonium or diphenyliodonium cations. Taken together the results described in this section suggest that the formation of **10** from **5** is the result of a subtle combination of steric and electronic effects which may be difficult or impossible to reproduce in other substrates.

Spectroscopic Studies.—(*i*) η^2-*Aroyl complexes.* Table 1 summarises the CO stretching-frequency data. The ν(CO) band at higher frequency is of medium intensity and broad, the lower band being strong and sharp. This pattern appears to be characteristic of the $[ML^*(CO)_2(\eta^2\text{-}COR')]$ system and is also observed in a variety of related complexes (R′ = alkyl, vinyl, *etc.*).[12] The ν(CO) bands of the η^2-aroyl complexes **9** are shifted to higher frequency with increasing electron-withdrawing character of the 4-substituent in the η^2-aroyl ligand. The

Table 3 Proton NMR data for selected complexes of the type $[MoL(CO)_2(\eta^2\text{-COR}')]$[a]

Complex	H(4)	3-Me	5-Me	R′
9b	5.89 (1) 5.78 (2)	2.31 (3) 1.98 (6)	2.41 (3) 2.36 (6)	8.81, 7.86 (dd), J = 8 (4)
9c	5.88 (1) 5.79 (2)	2.32 (3) 1.99 (6)	2.41 (3) 2.36 (6)	8.19 (4), 2.53 (3)
9d	5.91 (1) 5.81 (2)	2.37 (3) 2.02 (6)	2.45 (3) 2.40 (6)	8.85 (br) (1), 8.5 (br m), (2), 7.82 at, $J \approx 7.15$ (1)
9h	5.97 (1) 5.87 (2)	2.34 (3) 2.00 (6)	2.42 (3) 2.38 (6)	8.21, 7.55 (dd), J = 7.6 Hz (4) 2.49 (3)
9i	5.97 (1) 5.87 (2)	2.36 (3) 2.02 (6)	2.44 (3) 2.40 (6)	8.31, 7.25 (dd), J = 7.8 (4) 3.91 (3)
13a	5.82 (1) 5.77 (2)	2.21 (3) 2.04 (6)	2.38 (3) 2.35 (6)	1.65 (br m) (11)
13b	5.87 (1) 5.82 (2)	2.22 (3) 2.03 (6)	2.41 (3) 2.38 (6)	3.23 (3)
25[b]	6.12 (d), J = 3.2 (1) 6.02 (d), J = 2.4 (2)	2.37 (3) 2.03 (6)	—	8.23, 7.19 (dd), J = 9.0 (4) 3.90 (3)
27[c]	—	2.30 (3) 1.94 (6)	2.36 (3) 2.26 (6)	8.14, 7.44 (dd), J = 8.4 (4) 2.26 (3)
28	—	2.32 (3) 1.98 (6)	2.44 (3) 2.37 (6)	8.14, 7.51 (dd), J = 8.4 (4) 2.50 (3)
35a[d,e]	6.29 (d), J = 2.1 (2) 6.27 (d), J = 2.4 (1)			

[a] Recorded in $CDCl_3$ solution, δ in ppm downfield from $SiMe_4$ as internal standard, relative area in parentheses, J in Hz. Resonances are singlets unless indicated; d = doublet, dd = doublet of doublets, br m = broad multiplet, at = apparent triplet. [b] For H(5), δ 7.75 (d), J = 3.2 (1) and 7.52 (d), J = 2.4 (2). [c] For 4-Me, δ 1.83 (3) and 1.77 (6). [d] The resonances due to the aromatic protons of the η^2-COR′ ligand overlap with those of the 3-(4-tolyl) groups and cannot be separately identified: δ 7.28 (complex m) (13), 6.82 (d), J = 7.6 (4), 2.34 (3) and 2.06 (6). [e] For H(5), δ 7.93 (d), J = 2.4 (1) and 7.81 (d), J = 2.1 (2).

Table 4 Carbon-13 NMR data for complexes of the type $[MoL(CO)_2(\eta^2\text{-COR}')]$[a]

			Pyrazolyl carbons[b]				
Complex	η^2-COR′	CO	C(3)	C(4)	C(5)	Pyrazolyl methyl carbons[c]	R′
9a	233.25	231.31	152.36 151.32	107.47 106.69	146.51 144.43	15.33,[d] 13.38[e] 13.06,[d] 12.54[e]	149.11, 133.91, 132.32 124.49
9b	233.77	231.37	152.36 151.26	107.40 106.26	146.51 144.30	15.27,[d] 13.30[e] 13.06,[d] 12.48[e]	132.94, 131.70, 118.12 115.39, 65.82 (CN)
9c	234.75	231.83	152.30 151.32	107.36 106.56	146.32 144.24	15.33,[d] 13.38[e] 13.06,[d] 12.54[e]	197.39 (COMe), 139.30 133.20, 131.77, 129.04 26.76 (COMe)
9d	233.51	231.57	152.43 151.39	107.47 106.69	146.51 144.37	15.40,[d] 13.45[e] 13.12,[d] 12.60[e]	148.72, 137.36, 131.83 130.40, 126.70, 125.53
9g	235.65	232.53	152.39 151.39	107.14 106.43	146.25 144.11	15.33,[d] 13.12[f] 12.54	133.13, 132.03, 131.05 129.10
9h	234.81	232.79	152.17 151.17	107.14 106.42	146.12 144.06	15.33,[d] 13.38[e] 13.06,[d] 12.54[e]	144.17, 132.09, 129.75 128.78, 21.96 (Me)
9i	232.79	233.13	152.10 151.39	107.14 106.49	146.12 143.98	15.33,[d] 13.38[e] 13.12,[d] 12.54[e]	163.48, 134.50, 124.75 114.42, 55.68 (OMe)
13a	252.10	232.27	152.30 151.06	107.08 106.43	145.93 143.91	15.14,[d] 13.25[f] 12.48[e]	51.91, 29.30, 25.66
13b	251.53	231.87	152.30 151.06	107.45 106.43	147.17 145.05	15.35,[d] 13.48[f] 12.67[e]	28.18
25	233.25	232.73	153.21 152.43	106.04 105.58	135.41 134.58	15.20,[d] 13.12[d]	163.75, 137.68, 124.55, 114.48, 55.68 (OMe)
27	234.29	232.93	150.61 149.70	112.73 112.15	143.40 141.25	13.77,[d] 11.44[f] 10.85,[e] 8.32,[g] 7.99[g]	144.05, 132.16, 129.75 128.91, 21.90 (Me)
28	234.69	231.83	149.31 148.59	109.81 109.48	143.27 141.06	13.38,[d] 11.37[e] 11.05,[d] 10.66[e]	145.15, 132.42, 130.01 128.32, 22.03 (Me)
35a	235.18	232.11	158.14 158.24	107.44 107.09	138.44 135.88	*h*	137.94, 132.35, 131.30 129.97

[a] Recorded in $CDCl_3$ solution, δ in ppm downfield from $SiMe_4$ as internal standard. [b] With the exception of the C(3) resonances of complex **35a** the high-field line of each pair of ring carbon resonances is about twice as intense as the low-field line. [c] Other than in cases of accidental overlap, the high-field line of each pair of methyl resonances is about twice as intense as the low-field line. [d] 3-Me. [e] 5-Me. [f] 3- and 5-Me. [g] 4-Me. [h] 3-(4-tolyl) groups: δ 137.45, 135.88, 130.54, 129.34, 128.20, 128.04, 127.96, 21.28 and 21.06.

carbonyl stretching frequency of the η^2-COR′ moiety could not be identified and is evidently obscured by bands due to the ligand L*.

Representative ^1H NMR spectral data for η^2-aroyl complexes are summarised in Table 3 and ^{13}C NMR data for selected examples in Table 4. The 1 : 2 ratio of the pyrazolyl resonances in both spectra and the equivalence of the carbon monoxide ligands in the ^{13}C spectra demonstrate that the complexes have effective mirror symmetry in solution and, by analogy with related systems,[17] a stereochemically non-rigid

Table 5 Proton NMR data for complexes of the type $[ML(CO)_2(\equiv CX)]^a$

Complex	H(4)	H(5)	3-Me	4-Me	5-Me
10	5.83 (2)	—	2.42 (6)	—	2.31 (6)
	5.74 (1)		2.32 (3)		2.27 (3)
11	5.89 (2)	—	2.48 (6)	—	2.33 (6)
	5.78 (1)		2.39 (3)		2.29 (3)
21	5.85 (2)	—	2.48 (6)	—	2.33 (6)
	5.78 (1)		2.39 (3)		2.29 (3)
22	5.87 (2)	—	2.49 (6)	—	2.33 (6)
	5.76 (1)		2.40 (3)		2.29 (3)
26	6.06 (d), J = 2.3 (2)	7.53 (d), J = 2.3 (2)	2.48 (6)	—	—
	5.95 (d), J = 2.7 (1)	7.50 (d), J = 2.7 (1)	2.38 (3)		
29	—	—	2.44 (6)	1.89 (6)	2.30 (6)
			2.33 (3)	1.84 (3)	2.28 (3)
31	—	—	2.32 (6)	1.86 (6)	2.26 (6)
			2.29 (3)	1.80 (3)	2.23 (3)
36	6.25 (d), J = 2.2 (2)	7.68 (d), J = 2.2 (2)	b	—	—
	6.13 (d), J = 1.8 (1)	7.62 (d), J = 1.8 (1)			

[a] Recorded in $CDCl_3$ solution, δ in ppm downfield from $SiMe_4$ as internal standard, relative area in parentheses, J in Hz. Resonances are singlets unless the contrary is indicated. [b] Protons of 3-(4-tolyl) groups: δ 7.40 (d), J = 8.1 (4), 7.12 (m) (8) and 2.32 (9).

Table 6 Carbon-13 NMR data for selected complexes of the type $[MoL(CO)_2(\equiv CX)]^a$

			Pyrazolyl carbons[b]			
Complex	CO	CX	C(3)	C(4)	C(5)	Pyrazolyl methyl carbons
10	224.02	208.70	151.41	106.46	145.07	15.53, 14.75, 12.67
			151.24	106.23	144.44	
11	221.95	205.58	152.49	106.82	145.21	16.18, 15.27, 12.54
			152.17	106.29	144.43	
21	223.90	202.46	151.39	106.36	145.21	15.53, 14.75, 12.67
					144.56	
22	221.88	197.97	152.56	106.82	145.28	16.18, 15.33, 12.54
			152.23	106.56	144.43	
29	224.29	208.18	149.76	112.21	142.42	13.71, 13.12, 10.92, 8.25,[c] 8.06[d]
				112.02	141.77	
30	223.05	245.01	148.66	109.42	142.03	13.38, 12.67, 10.72
			148.59		141.45	
31	224.03	201.87	149.76	112.21	142.24	13.71, 13.06, 10.85, 8.25,[c] 7.99[d]
				112.02	141.71	

[a] Spectra were recorded in $CDCl_3$ and resonances are quoted in ppm downfield from tetramethylsilane. [b] The high-field line of each pair of ring carbon resonances is about twice as intense as the low-field line. [c] 4-Me *trans* to CO. [d] 4-Me *trans* to halogenocarbyne.

η^2-aroyl ligand. The resonance due to the carbonyl carbon of the η^2-COR′ ligand in **9** occurs at δ *ca.* 233–235 (*ca.* 20 ppm more shielded than for the analogous η^2-hexahydrobenzoyl complex **13a** or the η^2-acetyl complex **13b**[12]) and shows little sensitivity to the nature of the substituents in the aryl ring. The position of the carbonyl ligand resonance at δ *ca.* 232 is likewise scarcely affected by changes in the nature of the adjacent η^2-COR′ ligand. In both the proton and carbon spectra, the resonances of the unique pyrazolyl group *trans* to the η^2-aroyl ligand are deshielded with respect to those *trans* to the CO ligands. In the proton spectra the deshielding effect of the η^2-aroyl ligand is stronger at the more remote pyrazolyl H(5) protons (*i.e.* in compound **25**) than at H(4), while for the methyl groups the deshielding is in the order 3- > 4- ≈ 5-Me. A broadly similar deshielding pattern is observed in the ^{13}C NMR spectra: C(5) > C(3) > C(4) and 3- > 5- > 4-Me.

(*ii*) η^1-*Halogenocarbyne complexes.* The carbonyl stretching data are collected in Table 1. These complexes are characterised by a pair of very strong sharp bands at *ca.* 2004 and 1921 cm^{-1}, *i.e.* at significantly higher wavenumber than for either the η^2-aroyl or aryldiazenido complexes. The η^1-halogenocarbyne ligands are thus stronger π acceptors than are either η^2-COR′ or 'singly bent' aryldiazenide ligands and are broadly comparable to the nitrosyl ligand in $[MoL^*(CO)_2(NO)]$ [ν(CO) 2016, 1925 cm^{-1}].[2] In several cases very weak but sharp ν(^{13}CO) satellite peaks can also be detected (see Table 1). In the homologous series $[MoL^*(CO)_2(\equiv CX)]$ (X = Cl **10**, Br **21** or I **23**), $[WL^*(CO)_2(\equiv CX)]$ (X = Cl **11** or Br **22**) and $[Mo\{HB(tmpz)_3\}(CO)_2(\equiv CX)]$ (X = Cl **29** or Br **31**) the carbonyl stretching frequencies are observed to *decrease* in the order I > Br > Cl suggesting that π donation from the halogen makes an important contribution to the ground state of the complexed halogenocarbyne ligand: $M\equiv C{-}X \longleftrightarrow \overset{-}{M}{=}C{=}\overset{+}{X}$.

The ^1H NMR spectral data for the halogenocarbyne complexes are summarised in Table 5 and ^{13}C NMR data in Table 6 with the exception of that for compound **40** which is given in the Experimental section. Both sets of spectra exhibit resonances for the co-ordinated pyrazolyl groups in a *ca.* 1:2 ratio attesting to the C_{2v} symmetry of the complexes. Whereas the η^2-aroyl ligand is deshielding relative to CO in both the ^1H and ^{13}C spectra (see above), the halogenocarbyne ligands exert a shielding effect on the protons of the *trans*-pyrazolyl groups. The *trans* shielding is stronger at H(4) than at H(5) and for the ring methyl substituents varies in the order 3- > 4- > 5-Me. In contrast, the *trans* effect of the halogenocarbyne ligand on the pyrazolyl ring carbons in the ^{13}C NMR spectra is deshielding relative to CO, albeit significantly less so than for the η^2-COR′ ligands [*ca.* 0.7 *vs. ca.* 2.0 ppm for C(5)] and varies in the sequence C(5) > C(3) ≈ C(4). Accidental equivalence prevented a definite assignment of the 3- and 5-Me ^{13}C resonances, but the 4-Me resonances of complexes **29** and **31** were identified and here the effect of the *trans*-halogenocarbyne ligand is

Table 7 Proton NMR data for selected complexes of the type $[\mathrm{MoL(CO)_2(N_2R')}]$[a]

Complex	H(4)	H(5)	Pyrazolyl methyl groups	R′
32a	5.77 (2) 5.73 (1)	—	2.41 (3), 2.37 (12), 2.31 (3)	7.12, 6.66 (dd), J = 8.4 (4), 2.91 (6)
32b	5.78 (2) 5.72 (1)	—	2.23 (9), 2.21 (3), 2.16 (9)[b]	6.98 (m) (3)[b]
32c	5.78 (2) 5.73 (1)	—	2.31 (9), 2.21 (3), 2.13 (6) 2.08 (6)[b]	6.97 (3)[b]
32d	5.85 (2) 5.76 (1)	—	2.32 (br) (18), 2.18 (6)[b]	7.55 (br) (1)[b]
32e	5.82 (2) 5.73 (1)	—	2.42 (6), 2.32 (15), 2.26 (3)[b]	7.38 (5)[b]
34a	6.28 (d), J = 2.4 (2) 6.20 (d), J = 2.1 (1)	7.78 (d), J = 2.4 (2) 7.72 (d), J = 2.1 (1)	*c*	7.0 (m) (2), 6.94 (m) (1), 6.52 (m) (2)
34b	6.27 (d), J = 2.5 (2) 6.20 (d), J = 1.5 (1)	7.77 (d), J = 2.5 (2) 7.75 (d), J = 1.5 (1)	*d*	6.42 (4), 2.91 (6)
34c	6.29 (d), J = 2.3 (2) 6.18 (d), J = 2.2 (1)	7.78 (d), J = 2.3 (2) 7.72 (d), J = 2.2 (1)	*e*	7.45–7.20 (m) (5), 2.97 (3) 1.95 (3)
37	6.30 (d), J = 2.3 (2)[f] 6.22 (d), J = 2.6 (1)	7.97 (d), J = 2.3 (2)[g] 7.72 (d), J = 2.6 (1)	*h*	6.40 (br) (4), 2.91 (vbr) (6)

[a] Recorded in $CDCl_3$ solution, δ in ppm downfield from $SiMe_4$ as internal standard, relative area in parentheses, J in Hz. Resonances are singlets unless the contrary is indicated. [b] The methyl resonance(s) of the N_2R' ligand overlap with the pyrazolyl methyl resonances. [c] 3-(4-Tolyl) groups: δ 7.41, 6.91 (dd), J = 8.1 (8); 7.27, 7.20 (dd), J = 8.5 (4); 2.38 (3), 2.14 (6). [d] 3-(4-Tolyl) groups: δ 7.42, 6.95 (dd), J = 8.0 (8); 7.30, 7.19 (dd), J = 7.5 (4); 2.37 (3), 2.14 (6). [e] 3-(4-Tolyl) groups: δ 7.53, 7.07 (dd), J = 8.0 (8); 7.45–7.20 (m) (5); 7.25, 7.14 (dd), J = 8.0 (4); 2.34 (3); 2.25 (6). [f] H(4) of unco-ordinated pyrazole: δ 6.89 (d), J = 2.3. [g] H(5) of unco-ordinated pyrazole: δ 8.06 d, J = 2.3. [h] 3-(4-Tolyl) groups: δ 7.92, 7.26 (dd), J = 8.3 (4); 7.42, 6.94 (dd), J = 8.5 (8); 7.31, 7.19 (dd), J = 8.0 (4); 2.42 (3), 2.36 (3), 2.13 (6).

Table 8 Carbon-13 NMR data for selected complexes of the type $[\mathrm{MoL(CO)_2(N_2R')}]$[a]

		Pyrazolyl carbons[b]				
Complex	CO	C(3)	C(4)	C(5)	Pyrazolyl methyl carbons[c]	R′
32a	231.71	152.12 151.23	106.56 106.31	144.81 144.11	15.03, 12.59	148.95, 130.35, 122.39, 112.89, 40.61 (NMe_2)
32b	230.27	152.36 151.26	106.62 106.10	144.89 144.24	14.94, 12.67 14.42	140.21, 132.94, 128.71, 127.80, 127.48, 125.79, 18.52 (Me)
32c	230.85	152.43 151.26	106.56 106.04	144.76 144.11	14.94, 12.67 14.36	142.49, 130.40, 128.00, 124.40, 18.26 (Me)
32d	231.46	152.04 151.47	106.40	144.97 144.41	15.03, 12.67 14.70	137.26, 119.88, 10.88 (Me)
32e	230.13	152.23 151.78	106.49 106.23	144.76 144.17	14.94, 12.60 14.68	160.49 (CO), 135.35, 129.17, 126.70, 124.29, 111.76, 36.39 (NMe), 10.53 (Me)
34b	228.15	158.15 157.20	107.00 106.43	136.80 136.10	*d*	148.33, 138.40, 121.98, 112.70, 40.78 (NMe_2)
37	229.19	159.13[e] 157.98	107.47[f] 106.84	135.91[g] 136.67	*h*	148.48, 138.61, 122.08, 112.59, 40.66 (NMe_2)

[a] Recorded in $CDCl_3$ solution, δ in ppm downfield from $SiMe_4$ as internal standard. [b] With the exception of the C(3) and C(4) resonances of complexes **34b** and **37** (where the reverse is the case) the high-field line of each pair of ring carbon resonances is about twice as intense as the low-field line. [c] Other than in cases of accidental overlap, the high-field line of each pair of methyl resonances is more intense than is the low-field line. [d] 3-(4-Tolyl) groups: δ 137.46, 136.80, 130.84, 130.55, 129.72, 129.51, 128.66, 128.39 and 21.29. [e] C(3) of unco-ordinated pyrazolyl group, δ 154.13. [f] C(4) of unco-ordinated pyrazolyl group, δ 104.15. [g] C(5) of unco-ordinated pyrazolyl group, δ 138.04. [h] 3-(4-Tolyl) groups: δ 137.69, 137.66, 130.76, 130.58, 130.28, 129.75, 129.56, 129.36, 128.73, 128.41, 21.40 and 21.31.

shielding relative to CO. Significant broadening was noted for some of the pyrazolyl carbon resonances of $[\mathrm{Mo\{B(pz)_4\}(CO)_2(\equiv CCl)}]$ **40** (see Experimental section) suggesting that the molecule is stereochemically non-rigid in solution. The effect most likely has its origin in slow rotation of the tridentate pyrazolylborate ligand about the B···Mo axis and/or rotation of the unco-ordinated pyrazolyl group about the B–N bond.[41]

The resonance due to the CO ligands of the halogenocarbyne complexes occurs at δ *ca.* 223, *i.e. ca.* 9 ppm more shielded than for the η^2-aroyl complexes. With the single exception of the (4-chloro-3,5-dimethylpyrazolyl)hydroborate complex **30**, $\delta_{C(carbyne)}$ 245, the halogenocarbyne carbon resonance occurs in the region δ 213–197. This is at significantly higher field than previously reported for carbyne ligands (δ 401–235).[42] This result is unexpected since high-field carbyne resonances are normally associated with electron-releasing substituents on the carbyne carbon. It is tempting to relate the phenomenon to the π donation from the halogen suggested earlier to account for trends in the IR spectra of the complexes. However we note a consistent trend for the carbyne carbon in the bromocarbyne complexes to be *ca.* 7 ppm more shielded than in the η^1-chlorocarbyne analogues. The reverse trend would be expected if halogen to carbon π bonding were the determining factor.

(*iii*) *Aryldiazenido complexes.* Table 1 summarises ν(CO) and ν(NN) values for the new aryldiazenido complexes. An unexplained feature of the IR data is the fact that the $\nu(CO)_{av}$ values for the heteroaryldiazenido complexes **32d** and **32e** are as high or higher than those for the phenyldiazenido analogues **32a**–**32c**. Previous studies[26] have shown that the heteroaryldiazenido ligands are poorer π acceptors (or stronger net donors) than the phenyl derivatives and this would imply the opposite trend in ν(CO).

The NMR (^1H and ^{13}C) data for selected aryldiazenido complexes are in Tables 7 and 8. The aryldiazenido ligand has a net *trans*-shielding effect, *vis-à-vis* CO, on the protons of the pyrazolylborate ligand. The effect is stronger at the 4- than at the 5-position of the pyrazole groups and is noticeably greater for the 3,5-dimethylpyrazolyl- and antipyrin-4-yldiazenido ligands than for the phenyldiazenido analogues. In contrast, the overall *trans* effect of the aryldiazenido ligand in the ^{13}C NMR spectra is deshielding *vis-à-vis* CO for both the pyrazolyl ring carbons and the attached methyl groups. The deshielding varies in the sequence C(3) > C(5) > C(4) and R' > dmpz ≈ ap. Both the proton and carbon spectra exhibit resonances for the co-ordinated pyrazolyl groups in a *ca.* 1:2 ratio showing that the complexes have effective C_{2v} symmetry in solution.

Although the methyl substituents on the aryldiazenido ligand in $[MoL^*(CO)_2(N_2C_6H_3Me_2\text{-}2,6)]$ **32c** are not equivalent in the solid state (see below) they give rise to a single resonance in the ^{1}H and ^{13}C NMR spectra. Hence we conclude that rapid rotation of the aryl group about the N_β–C_{ipso} bond is taking place in solution. In the ^{1}H NMR spectrum of $[Mo\{B(tpz)_4\}(CO)_2(N_2C_6H_4NMe_2\text{-}4)]$ **37** {but not in the hydrotris[3-(4-tolyl)pyrazolyl]borato analogue **34b**} the resonances of the 4-$Me_2NC_6H_4$ moiety are significantly broadened suggesting the operation of a dynamic process involving this portion of the molecule which is slow on the ^{1}H NMR time-scale at room temperature.

Structural Studies.—The crystal and molecular structures of the η^2-aroyl compound $[MoL^*(CO)_2(\eta^2\text{-}COC_6H_4Me\text{-}4)]$ **9h**, the η^2-acyl analogue $[MoL^*(CO)_2(\eta^2\text{-}COC_6H_{11})]$ **13a** and of the halogenocarbyne complexes $[Mo\{HB(tmpz)_3\}(CO)_2(\equiv CCl)]$ **29** and $[Mo\{B(pz)_4\}(CO)_2(\equiv CCl)]$ **40** have already been discussed in other communications from these laboratories.[4,5,43] Aryldiazenido complexes derived from the sterically congested anion $[MoL^*(CO)_3]^-$ **5** had not been observed prior to this report. We have subjected two examples $[MoL^*(CO)_2(N_2C_6H_3Me_2\text{-}2,6)]$ **32c** and $[MoL^*(CO)_2\{N_2(ap)\}]$ **32e**, to an X-ray crystallographic investigation in order to clarify the effect of steric crowding on the molecular architecture. Views of the molecular structures of **32c** and **32e**, together with the crystallographic numbering schemes, are shown in Fig. 1. Crystal and refinement data for both complexes are collected in Table 9 while final fractional coordinates and details of the molecular geometry are summarised in Tables 10 and 11 for **32c** and in Tables 12 and 13 for **32e**.

The analysis confirms the proposed structure for both complexes. However the ratio of observations to parameters in the refinement of **32e** is much lower than we would have liked (2.6:1) so that the analysis, while serving to establish the connectivity unequivocally, does not allow of a detailed discussion of dimensions. In both complexes the co-ordination about molybdenum is octahedral with three adjacent sites occupied by the tridentate ligand L* and two by carbon monoxide. The remaining position contains a 'singly bent' 2,6-dimethylphenyldiazenide ligand in **32c** and a similarly angular antipyrin-4-yldiazenide ligand in **32e**. Bond lengths and angles within the MoL*(CO)$_2$ moieties of **32c** are unexceptional and the organodiazenide ligand does not exert a significant *trans* effect on the Mo–L* bonding. The two compounds differ primarily in the response of the organodiazenide ligands to steric crowding within the molybdenum co-ordination sphere.

The organodiazenide ligands adopt totally different orientations in the two complexes as measured by the torsion angles O(1)–Mo–N(2)–C(3) and O(2)–Mo–N(2)–C(3) (67.5 and 144.1 for **32c** and −98.0 and −20.4° for **32e**). The values for **32e** are close to the −118.6 and −36.0° which may be calculated from the structural data reported by Avitabile *et al.*[45] for the less-crowded $[Mo\{RB(pz)_3\}(CO)_2(N_2Ph)]$ **4** (R = H). In **32c** an over-congested co-ordination sphere is avoided by rotation of the 2,6-dimethylphenyl group about the N(2)–C(3) bond so that

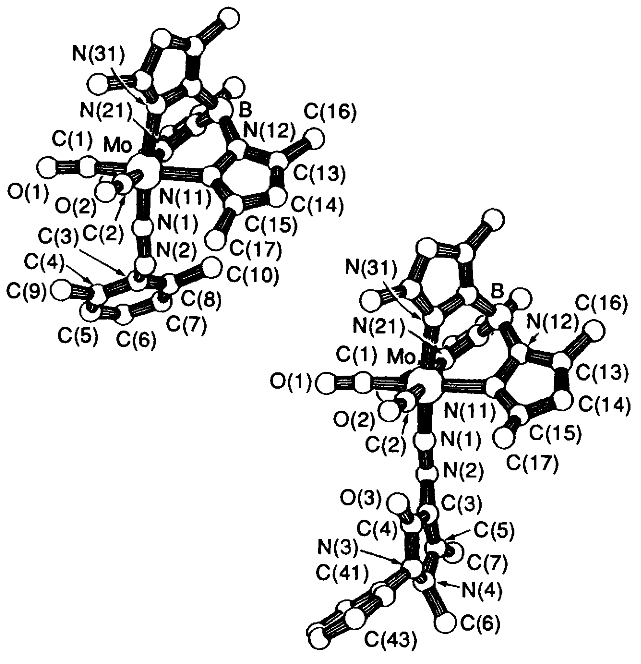


Fig. 1 Views of complexes **32c** (left) and **32e** (right) prepared with the aid of PLUTON[44] showing the molecular conformations and the numbering scheme. Hydrogen atoms are omitted for clarity

Table 9 Crystal and refinement data for complexes **32c** and **32e**

	32c	**32e**
Formula	$C_{25}H_{31}BMoN_8O_2$	$C_{28}H_{33}BMoN_{10}O_3$
M	582.3	664.4
Crystal class	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pn2_1a$
Crystal dimensions/mm	0.50 × 0.32 × 0.22	0.38 × 0.45 × 0.25
a/Å	8.086(2)	16.900(5)
b/Å	18.339(4)	10.462(3)
c/Å	19.286(4)	17.393(4)
β/°	100.14(2)	
U/Å^3	2815.6	3075.0
D_c/g cm^{-3}	1.37	1.43
Z	4	4
F(000)	1200	1368
μ/cm^{-1}	5.0	4.1
Total number of independent reflections	4944	1539
Number of reflections with $I > 3\sigma(I)$	4011	1123
$2\theta_{max}$/°	50	40
Final R	0.027	0.027
Final R'	0.037	0.029

Table 10 Final fractional coordinates for complex **32c** (× 10^5 for Mo, × 10^4 for others) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	11 303(2)	23 245(1)	23 944(1)	C(14)	−2 589(4)	1 043(2)	3 304(2)
C(1)	2 580(4)	2 807(2)	1 891(2)	C(15)	−2 180(3)	1 655(2)	2 951(2)
O(1)	3 320(3)	3 272(1)	1 572(1)	C(16)	−833(5)	−31(2)	3 932(2)
C(2)	313(4)	3 320(2)	2 574(2)	C(17)	−3 310(4)	2 253(2)	2 619(2)
O(2)	−69(4)	3 916(1)	2 622(2)	N(21)	2 370(3)	1 271(1)	2 229(1)
N(1)	−446(3)	2 275(1)	1 594(1)	N(22)	2 619(3)	761(1)	2 761(1)
N(2)	−1633(3)	2 219(2)	1 105(1)	C(23)	3 422(4)	172(2)	2 548(2)
C(3)	−1393(3)	1 824(2)	485(2)	C(24)	3 681(4)	313(2)	1 881(2)
C(4)	−962(4)	2 214(2)	−69(2)	C(25)	3 022(3)	994(2)	1 695(1)
C(5)	−795(5)	1 828(2)	−675(2)	C(26)	3 898(5)	−471(2)	3 009(2)
C(6)	−1 115(5)	1 098(3)	−716(2)	C(27)	3 002(4)	1 392(2)	1 016(2)
C(7)	−1 574(5)	733(2)	−166(2)	N(31)	2 795(3)	2 267(1)	3 439(1)
C(8)	−1 727(4)	1 081(2)	449(2)	N(32)	2 936(2)	1 608(1)	3 797(1)
C(9)	−553(6)	3 007(2)	−15(2)	C(33)	3 950(3)	1 693(2)	4 423(1)
C(10)	−2 170(6)	681(3)	1 074(3)	C(34)	4 460(4)	2 400(2)	4 483(2)
B	2 041(4)	922(2)	3 466(2)	C(35)	3 470(4)	2 744(1)	3 862(2)
N(11)	−512(3)	1 654(1)	2 959(1)	C(36)	4 369(5)	1 080(2)	4 937(2)
N(12)	119(3)	1 049(1)	3 322(1)	C(37)	3 898(5)	3 524(2)	3 655(2)
C(13)	−1 143(4)	670(2)	3 530(3)				

Table 11 Molecular dimensions (bond lengths in Å, angles in °) for [MoL(CO)$_2$(N$_2$C$_6$H$_3$Me$_2$-2,6)] **32c**

Mo–C(1)	1.964(3)	N(2)–C(3)	1.440(4)
Mo–C(2)	1.993(3)	C(3)–C(4)	1.392(4)
Mo–N(1)	1.824(2)	C(4)–C(5)	1.385(5)
Mo–N(11)	2.229(2)	C(5)–C(6)	1.363(6)
Mo–N(21)	2.226(2)	C(6)–C(7)	1.359(5)
Mo–N(31)	2.221(2)	C(7)–C(8)	1.372(5)
C(1)–O(1)	1.146(3)	C(8)–C(10)	1.506(5)
C(2)–O(2)	1.144(3)	C(3)–C(8)	1.389(4)
N(1)–N(2)	1.226(3)	C(4)–C(9)	1.485(5)

C(1)–Mo–C(2)	80.3(1)	N(22)–B–N(32)	109.2(3)
C(1)–Mo–N(1)	89.9(1)	Mo–C(1)–O(1)	174.9(2)
C(1)–Mo–N(11)	179.5(1)	Mo–C(2)–O(2)	172.8(3)
C(1)–Mo–N(21)	94.5(1)	Mo–N(1)–N(2)	172.6(2)
C(1)–Mo–N(31)	98.9(1)	N(1)–N(2)–C(3)	118.6(2)
C(2)–Mo–N(1)	89.4(1)	N(2)–C(3)–C(4)	118.3(3)
C(2)–Mo–N(11)	100.2(1)	N(2)–C(3)–C(8)	118.7(3)
C(2)–Mo–N(21)	172.7(1)	C(4)–C(3)–C(8)	122.9(3)
C(2)–Mo–N(31)	93.0(1)	C(3)–C(4)–C(5)	117.1(3)
N(1)–Mo–N(11)	89.9(1)	C(3)–C(4)–C(9)	121.9(3)
N(1)–Mo–N(21)	95.8(1)	C(5)–C(4)–C(9)	121.0(3)
N(1)–Mo–N(31)	171.2(1)	C(4)–C(5)–C(6)	120.6(3)
N(11)–Mo–N(21)	85.0(1)	C(5)–C(6)–C(7)	120.9(4)
N(11)–Mo–N(31)	81.3(1)	C(6)–C(7)–C(8)	121.6(4)
N(21)–Mo–N(31)	82.7(1)	C(3)–C(8)–C(7)	116.9(3)
N(12)–B–N(22)	108.7(2)	C(3)–C(8)–C(10)	120.6(3)
N(12)–B–N(32)	109.7(2)	C(7)–C(8)–C(10)	122.4(4)

	pyrazole with *i* = 1	*i* = 2	*i* = 3
B–N(*i*2)	1.547(3)	1.542(4)	1.533(3)
N(*i*1)–N(*i*2)	1.362(3)	1.376(3)	1.387(3)
N(*i*1)–C(*i*5)	1.346(3)	1.336(3)	1.340(3)
N(*i*2)–C(*i*3)	1.353(3)	1.361(3)	1.343(3)
C(*i*3)–C(*i*4)	1.358(4)	1.363(4)	1.358(4)
C(*i*3)–C(*i*6)	1.499(4)	1.487(4)	1.498(4)
C(*i*4)–C(*i*5)	1.383(4)	1.380(4)	1.387(4)
C(*i*5)–C(*i*7)	1.498(4)	1.497(4)	1.497(4)

	pyrazole with *i* = 1	*i* = 2	*i* = 3
Mo–N(*i*1)–N(*i*2)	119.9(1)	119.5(1)	118.5(1)
Mo–N(*i*1)–C(*i*5)	132.5(2)	133.6(2)	135.4(2)
N(*i*2)–N(*i*1)–C(*i*5)	106.9(2)	106.9(2)	106.1(2)
B–N(*i*2)–N(*i*1)	119.2(2)	120.1(2)	121.0(2)
B–N(*i*2)–C(*i*3)	131.0(2)	130.8(2)	129.7(2)
N(*i*1)–N(*i*2)–C(*i*3)	109.6(2)	109.2(2)	109.2(2)
N(*i*2)–C(*i*3)–C(*i*4)	107.4(3)	107.2(2)	108.5(2)
N(*i*2)–C(*i*3)–C(*i*6)	121.8(3)	122.4(3)	122.5(3)
C(*i*4)–C(*i*3)–C(*i*6)	130.8(3)	130.4(3)	129.0(3)
C(*i*3)–C(*i*4)–C(*i*5)	107.4(2)	107.5(2)	106.5(2)
N(*i*1)–C(*i*5)–C(*i*4)	108.6(3)	109.3(2)	109.7(2)
N(*i*1)–C(*i*5)–C(*i*7)	122.7(3)	122.9(2)	121.8(3)
C(*i*4)–C(*i*5)–C(*i*7)	128.6(3)	127.8(2)	128.5(3)

the torsion angle N(1)–N(2)–C(3)–C(4) is 90.7° and the plane of the arene ring no longer lies (as is normal, in the absence of other constraints) close to that containing the angular Mo–N(1)–N(2)–C(3) fragment. This rotation results in a closest non-bonded contact of 3.610 Å between methyl C(10) of the aryldiazenide ligand and methyl C(17) of the ligand L*. In its absence intramolecular crowding between these atoms would have been impossibly severe. In the relatively uncrowded **4** (R = H)[45] the corresponding torsion angle is 20°. There is no obvious effect of overcrowding on the bond lengths and angles within the angular Mo–N$_\alpha$–N$_\beta$–C fragment of the 2,6-dimethylphenyldiazenide ligand and these are very similar to those reported by Avitabile *et al.*[45] for **4** (R = H).

In the antipyrin-4-yldiazenide ligand the M–N$_\alpha$ and N$_\alpha$–N$_\beta$ bond lengths are essentially identical to the corresponding bond lengths in complex **32c**. Surprisingly, the antipyrinyl group is not rotated about the N(2)–C(3) in a similar fashion to the 2,6-dimethylphenyl group in **32c**. Instead the atoms of the Mo–N(1)–N(2)–C(3)–C(4)–O(3) skeleton of the antipyrin-4-yldiazenide ligand are almost coplanar. There is no evidence to suggest that the unusual orientation of the ligand is due to special electronic effects and we conclude that it results from a trade-off between crystal-packing effects and unfavourable non-bonded repulsions within the molecule.

Conclusion

The results described here demonstrate that the reaction between arenediazonium cations and 3-substituted tricarbonyl[poly(pyrazolyl)borato]molybdenum anions is of considerable complexity and leads to the formation of a variety of unusual products. While we have shown that the steric properties of the hydrotris(pyrazolyl)borate ligand are the most significant factors in determining the partitioning between carbonyl substitution and redox, it is clear that the manner in which the steric effects operate is far from straightforward and

Table 12 Final fractional coordinates for complex **32e** (× 10^5 for Mo, × 10^4 for others) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	22 352(4)	25 000	12 140(4)	C(17)	2 954(5)	4 267(9)	−478(5)
C(1)	2 285(5)	2 57(15)	2 344(5)	N(21)	2 357(4)	396(8)	1 131(4)
O(1)	2 339(4)	2 687(10)	2 990(4)	N(22)	1 975(4)	−168(8)	558(4)
C(2)	1 997(6)	4 338(10)	1 342(6)	C(23)	2 217(6)	−1 510(8)	588(5)
O(2)	1 875(5)	5 404(7)	1 503(5)	C(24)	2 757(6)	−1 633(9)	1 203(6)
N(1)	3 315(4)	2 776(6)	1 190(3)	C(25)	2 826(5)	−449(10)	1 510(5)
N(2)	4 036(4)	2 738(7)	1 144(4)	C(26)	1 899(6)	−2 480(11)	51(6)
N(3)	5 093(4)	5 710(7)	1 047(4)	C(27)	3 289(6)	−13(9)	2 212(6)
N(4)	5 669(3)	4 788(7)	948(4)	N(31)	958(4)	1 971(7)	1 126(4)
O(3)	3 743(3)	5 654(6)	1 317(4)	N(32)	736(4)	996(7)	616(4)
C(3)	4 536(5)	3 781(8)	1 005(5)	C(33)	−33(6)	726(9)	711(5)
C(4)	4 346(5)	5 117(9)	1 129(5)	C(34)	−322(6)	1 506(11)	1 306(5)
C(5)	5 312(5)	3 634(7)	874(5)	C(35)	315(5)	2 258(10)	1 513(4)
C(6)	6 368(5)	5 194(8)	507(5)	C(36)	−454(5)	−306(10)	298(6)
C(7)	5 782(4)	2 441(10)	710(4)	C(37)	301(6)	3 291(10)	2 113(6)
B	1 353(6)	403(10)	87(7)	C(41)	5 308(5)	6 824(8)	1 483(5)
N(11)	2 167(3)	2 407(10)	−68(4)	C(42)	4 991(7)	7 981(9)	1 278(6)
N(12)	1 733(4)	1 449(7)	−420(4)	C(43)	5 166(6)	9 051(11)	1 687(7)
C(13)	1 787(6)	1 594(10)	−1 214(5)	C(44)	5 670(7)	9 014(11)	2 330(7)
C(14)	2 340(5)	2 593(15)	−1 352(5)	C(45)	5 961(6)	7 863(10)	2 514(6)
C(15)	2 465(5)	3 140(9)	−623(5)	C(46)	5 790(6)	6 774(10)	2 114(5)
C(16)	1 354(7)	671(12)	−1 705(6)				

Table 13 Molecular dimensions (bond lengths in Å, angles in °) for complex **32e**

Mo–C(1)	1.969(9)	C(4)–O(3)	1.209(10)	C(14)–C(15)	1.442(13)	N(32)–C(33)	1.341(11)
Mo–C(2)	1.977(10)	N(3)–N(4)	1.381(11)	C(15)–C(17)	1.461(13)	N(32)–B	1.522(13)
Mo–N(1)	1.849(6)	N(3)–C(41)	1.437(11)	N(21)–N(22)	1.375(11)	C(33)–C(34)	1.406(13)
Mo–N(11)	2.235(6)	N(4)–C(5)	1.357(11)	N(21)–C(25)	1.358(12)	C(33)–C(36)	1.480(14)
Mo–N(21)	2.215(8)	N(4)–C(6)	1.470(11)	N(22)–C(23)	1.363(12)	C(34)–C(35)	1.381(13)
Mo–N(31)	2.233(7)	C(5)–C(7)	1.506(12)	N(22)–B	1.507(13)	C(35)–C(37)	1.503(14)
C(1)–O(1)	1.134(11)	N(11)–N(12)	1.384(11)	C(23)–C(24)	1.412(14)	C(41)–C(42)	1.371(13)
C(2)–O(2)	1.168(13)	N(11)–C(15)	1.331(12)	C(23)–C(26)	1.479(14)	C(41)–C(46)	1.369(13)
N(1)–N(2)	1.221(9)	N(12)–C(13)	1.393(11)	C(24)–C(25)	1.355(14)	C(42)–C(43)	1.359(15)
N(2)–C(3)	1.402(11)	N(12)–B	1.545(14)	C(25)–C(27)	1.521(13)	C(43)–C(44)	1.406(17)
C(3)–C(4)	1.450(13)	C(13)–C(14)	1.318(17)	N(31)–N(32)	1.404(10)	C(44)–C(45)	1.340(15)
C(3)–C(5)	1.338(12)	C(13)–C(16)	1.482(15)	N(31)–C(35)	1.314(10)	C(45)–C(46)	1.366(15)
C(4)–N(3)	1.414(11)						
C(1)–Mo–C(2)	81.8(5)	C(4)–C(3)–C(5)	110.7(7)	N(3)–C(41)–C(42)	118.7(8)	Mo–N(21)–C(25)	132.0(6)
C(1)–Mo–N(1)	88.5(3)	C(3)–C(4)–N(3)	102.1(7)	N(3)–C(41)–C(46)	122.9(8)	N(22)–N(21)–C(25)	107.3(8)
C(1)–Mo–N(11)	179.5(3)	C(3)–C(4)–O(3)	132.5(8)	C(42)–C(41)–C(46)	118.4(9)	N(21)–N(22)–C(23)	108.2(7)
C(1)–Mo–N(21)	95.8(5)	N(3)–C(4)–O(3)	125.1(8)	C(41)–C(42)–C(43)	120.4(10)	N(21)–N(22)–B	119.1(8)
C(1)–Mo–N(31)	96.9(3)	C(4)–N(3)–N(4)	109.6(7)	C(42)–C(43)–C(44)	121.7(11)	C(23)–N(22)–B	132.4(8)
C(2)–Mo–N(1)	93.0(4)	C(4)–N(3)–C(41)	121.9(7)	C(43)–C(44)–C(45)	115.9(11)	N(22)–C(23)–C(24)	108.0(8)
C(2)–Mo–N(11)	98.3(4)	N(4)–N(3)–C(41)	117.0(7)	C(44)–C(45)–C(46)	123.4(10)	N(22)–C(23)–C(26)	121.4(8)
C(2)–Mo–N(21)	173.0(4)	N(3)–N(4)–C(5)	108.7(7)	C(45)–C(46)–C(41)	120.2(10)	C(24)–C(23)–C(26)	130.5(8)
C(2)–Mo–N(31)	93.0(4)	N(3)–N(4)–C(6)	115.4(7)	Mo–N(11)–C(15)	132.7(7)	C(23)–C(24)–C(25)	105.7(8)
N(1)–Mo–N(11)	92.0(2)	C(5)–N(4)–C(6)	124.4(7)	N(12)–N(11)–C(15)	107.3(7)	C(24)–C(25)–N(21)	110.7(8)
N(1)–Mo–N(21)	93.6(3)	N(4)–C(5)–C(3)	108.5(7)	N(11)–N(12)–C(13)	109.0(7)	C(24)–C(25)–C(27)	129.5(9)
N(1)–Mo–N(31)	172.5(3)	Mo–N(11)–N(12)	120.0(6)	N(11)–N(12)–B	118.8(7)	N(21)–C(25)–C(27)	119.7(9)
N(11)–Mo–N(21)	84.1(3)	N(4)–C(5)–C(7)	121.4(7)	C(13)–N(12)–B	132.0(8)	Mo–N(31)–N(32)	118.8(5)
N(11)–Mo–N(31)	82.6(2)	C(3)–C(5)–C(7)	130.1(8)	N(12)–C(13)–C(14)	107.7(8)	Mo–N(31)–C(35)	135.1(6)
N(21)–Mo–N(31)	80.7(3)	C(33)–C(34)–C(35)	104.6(8)	N(12)–C(13)–C(16)	118.0(9)	N(32)–N(31)–C(35)	105.6(7)
Mo–C(1)–O(1)	175.9(12)	C(34)–C(35)–N(31)	112.4(8)	C(14)–C(13)–C(16)	134.3(9)	N(31)–N(32)–C(33)	109.5(7)
Mo–C(2)–O(2)	172.5(9)	C(34)–C(35)–C(37)	125.4(8)	C(13)–C(14)–C(15)	108.0(8)	N(31)–N(32)–B	119.7(7)
Mo–N(1)–N(2)	168.9(6)	N(31)–C(35)–C(37)	122.2(8)	C(14)–C(15)–N(11)	108.0(9)	C(33)–N(32)–B	130.8(8)
N(1)–N(2)–C(3)	126.1(7)	N(12)–B–N(22)	110.4(8)	C(14)–C(15)–C(17)	128.4(9)	N(32)–C(33)–C(34)	107.8(8)
N(2)–C(3)–C(4)	126.2(7)	N(12)–B–N(32)	109.9(8)	N(11)–C(15)–C(17)	123.6(8)	N(32)–C(33)–C(36)	124.0(8)
N(2)–C(3)–C(5)	122.0(8)	N(22)–B–N(32)	109.8(9)	Mo–N(21)–N(22)	120.4(6)	C(34)–C(33)–C(36)	127.9(9)

this problem is receiving further study. However, even at our present state of knowledge, it is also clear that the reactions described here are synthetically important, providing, as they do, simple high-yield routes to novel η^2-aroyl and -acyl complexes (a class of considerable current interest[6,7]) as well as the first (and still the only) synthesis of compounds containing halogenocarbyne ligands. The latter are particularly significant and our discovery of their unique ability to undergo nucleophilic displacement reactions at the carbyne carbon atom has been harnessed in these laboratories[8,9] and, more recently, by Templeton and co-workers[46] to provide access to a wide variety of novel organometallic structures. It is therefore disappointing to have to report only limited success in extending the synthesis of halogenocarbyne complexes to substrates other than [MoL*(CO)$_3$]$^-$ **5** but our investigations in this potentially important area are continuing.

Experimental

Literature procedures were employed for the synthesis of 3(5)-methylpyrazole,[47] 3,5-dimethylpyrazole,[48] 3,4,5-trimethylpyrazole,[49] 4-chloro-3,5-dimethylpyrazole,[50] 3,5-bis(trifluoromethyl)pyrazole,[51] 3(5)-(4-tolyl)pyrazole,[52] the potassium salts of the hydrotris(3-methylpyrazolyl)-,[53] tris(3,5-dimethylpyrazolyl)hydro- and hydrotris(3,4,5-trimethylpyrazolyl)-borate[54] anions, tris(3,5-dimethylpyrazolyl)methane,[55] substituted benzenediazonium tetrafluoroborates,[56] 3,5-dimethylpyrazole-4-diazonium chloride **I**,[26] antipyrine-4-diazonium tetrafluoroborate **II**,[57] diphenyliodonium chloride, tetrafluoroborate and hexafluorophosphate,[58] triphenylsulfonium tetrafluoroborate[58] and $[N(PPh_3)_2]Cl$[59] as well as for the following known transition-metal complexes: the tetraethylammonium salts of the anionic tricarbonyls **3** (R = pz), **5**, **8**,[27] **24a**,[26] **43**[8] and the neutral tricarbonyl[tris(3,5-dimethylpyrazolyl)methane]molybdenum **47** and tricarbonyl[hydrotris(3,5-dimethylpyrazolyl)borato]manganese **48**.[40]

All other reagents and solvents were commercial samples used as received. Preparations were carried out under an atmosphere of dry oxygen-free nitrogen but, except where the contrary is stated, work-up procedures were not generally protected from the air. Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer, ^1H NMR spectra using Perkin-Elmer Hitachi R20-A, JEOL PMX60si or JEOL GSX270 spectrometers and ^{13}C NMR spectra on JEOL FX60 or GSX270 instruments. Microanalyses were performed by the staff of the Microanalytical Laboratory of University College, Cork.

Synthesis of Poly(pyrazolyl)borates.—*Potassium tris(4-chloro-3,5-dimethylpyrazolyl)hydroborate.* A mixture of 4-chloro-3,5-dimethylpyrazole (9.79 g, 75 mmol) and KBH_4 (0.81 g, 15 mmol) was heated slowly to 240 °C until *ca.* 1.01 l of hydrogen (*ca.* 45 mmol) had been evolved (wet-test meter). The molten mixture was allowed to solidify, broken up, and unreacted pyrazole recovered by sublimation at *ca.* 1 mmHg. The yield of $K[HB(cmpz)_3]$ was 5.07 g, 77%; ν(BH) 2465 cm^{-1} (KBr disc). Entirely satisfactory microanalytical data could not be obtained but the product was sufficiently pure for use in the preparation of the tricarbonylmolybdenum complex **24c** (see below).

Salts of hydrotris[3-(4-tolyl)pyrazolyl]- and tetrakis[3-(4-tolyl)pyrazolyl)-borate. For hydrotris[3-(4-tolyl)pyrazolyl]-borate the procedure followed was essentially that described above employing 3(5)-(4-tolyl)pyrazole (35.2 g, 222.5 mmol) and KBH_4 (3.0 g, 55.6 mmol) and heating to 220 °C. When 3.8 l of hydrogen (*ca.* 167 mmol) had been evolved the melt was cooled to 100 °C under nitrogen and poured into toluene (100 cm^3). The resulting fine precipitate was filtered off, washed with toluene (2 × 100 cm^3) and hot light petroleum (b.p. 60–80 °C) (2 × 100 cm^3) and dried *in vacuo*. The crude product was dissolved in thf and the solution was slurried with Celite and filtered. Removal of the solvent *in vacuo* yielded pure $K[HB(tpz)_3]$, 14.48 g, 49.8%; ν(BH) 2420 cm^{-1} (KBr disc) (Found: C, 68.35; H, 5.30; N, 15.50. Calc. for $C_{30}H_{28}BKN_6$: C, 68.95; H, 5.40; N, 16.10%). Addition of an equimolar quantity of methanolic thallium(I) formate to a methanol solution of the potassium salt yielded $Tl[HB(tpz)_3]$ in *ca.* 60% yield. Microanalytically pure material was obtained by recrystallisation from a mixture of dichloromethane and light petroleum (Found: C, 52.45; H, 4.15; N, 12.20. Calc. for $C_{30}H_{28}BN_6Tl$: C, 52.40; H, 4.10; N, 12.20%). The crystal and molecular structures of the thallium(I) derivative have been determined.[60]

The sodium salt of tetrakis[3-(4-tolyl)pyrazolyl]borate was obtained in an analogous fashion from the pyrazole and $NaBH_4$ employing a reaction temperature of 250 °C. The yield was 65% (Found: C, 72.80; H, 5.75; N, 16.80. Calc. for $C_{40}H_{36}BN_8Na$: C, 72.50; H, 5.50; N, 16.90%). The thallium(I) salt, prepared as above, was obtained in 77% yield (Found: C, 56.95; H, 4.35; N, 13.35. Calc. for $C_{40}H_{36}BN_8Tl$: C, 56.95; H, 4.30; N, 13.35%).

Potassium and thallium(I) salts of hydrotris[3,5-bis(trifluoromethyl)pyrazolyl]borate. Crude $K[HB(dtfpz)_3]$ was prepared from 3,5-bis(trifluoromethyl)pyrazole (15.30 g, 75.0 mmol) as described above for the 4-chloro-3,5-dimethyl analogue. The yield was *ca.* 35%, ν(BH) 2610 cm^{-1} (KBr disc). This salt and its derivatives are characterised by very high solubility in organic solvents which renders purification difficult. Satisfactory microanalytical data could not be obtained and only slightly better results (see below) were obtained for the thallium(I) derivative although thallium(I) salts of poly(pyrazolyl)borates are usually highly crystalline and easy to purify. The borate was satisfactorily characterised in the form of its tricarbonylmolybdenum complex **44** (see below). The thallium(I) salt was prepared by addition of a methanolic solution of the potassium salt (0.70 g, 1.06 mmol) to thallium(I) formate (0.27 g, 1.06 mmol) in the same solvent. The crude salt was precipitated by addition of water and extracted into dichloromethane. The organic phase was washed several times with water, dried over anhydrous $MgSO_4$ and evaporated to give a white *solid* which was recrystallised from aqueous acetone to give $Tl[HB(dtfpz)_3]$ (0.33 g, 38%) (Found: C, 22.85; H, 0.75; N, 10.40. Calc. for $C_{15}H_4BF_{18}N_6Tl$: C, 21.85; H, 0.50; N, 10.20%).

Synthesis of the Tricarbonylmolybdenum Complexes.—The new complexes were prepared by reaction of the potassium salt of the corresponding borate and with $[Mo(CO)_6]$ in hot dmf as described by Trofimenko[27] for $[MoL(CO)_3]^-$ **5**.The products were isolated by addition of a salt of the appropriate cation to the cooled reaction mixture followed by precipitation with nitrogen-saturated water. With the exception of the thallium(I) salt of **5** (which was found to be analytically pure following washing with distilled water and ethanol) the crude salts were recrystallised by precipitation with diethyl ether from solutions in CH_2Cl_2.

$[N(PPh_3)_2]^+$ *Salts of* $[Mo\{RB(pz)_3\}(CO)_3]^-$ **3** (R = H *or* pz). Unlike the other $[N(PPh_3)_2]^+$ salts prepared in this work (see below) these materials are somewhat air sensitive and were stored *in vacuo*: **3** (R = H), yellow *crystals*, 94% yield (Found: C, 62.20; H, 4.65; N, 10.60. Calc. for $C_{48}H_{40}BMoN_7O_3P_2$: C, 61.90; H, 4.35; N, 10.50%); **3** (R = pz), yellow *crystals*, 96% yield (Found: C, 61.15; H, 4.35; N, 12.65. Calc. for $C_{51}H_{42}BMoN_9O_3P_2$: C, 61.40; H, 4.25; N, 12.65%).

$[SPh_3][MoL^*(CO)_3]$ **14a**. Since the salt is photosensitive (see text) the reaction mixture was protected from light subsequent to addition of $[SPh_3]BF_4$. Yellow *crystals*, 90% yield (Found: C, 58.40; H, 5.00; N, 11.35. Calc. for $C_{36}H_{37}BMoN_6O_3S$: C, 58.40; H, 5.05; N, 11.35%).

$Tl[MoL^*(CO)_3]$ **14b**. Orange *microcrystalline* powder, 80% yield (Found: C, 32.00; H, 3.00; N, 12.35. Calc. for $C_{18}H_{22}BMoN_6O_3Tl$: C, 31.70; H, 3.25; N, 12.35%). Even when stored *in vacuo* the salt slowly decomposes to a pale yellow carbonyl-free material which was not characterised.

$[NEt_3(CH_2Ph)][MoL^*(CO)_3]$ **14c**. Yellow *crystals*, 92% yield (Found: C, 55.65; H, 6.35; N, 14.60. Calc. for $C_{31}H_{44}BMoN_7O_3$: C, 55.60; H, 6.60; N, 14.65%).

$[N(PPh_3)_2][Mo\{HB(tmpz)_3\}(CO)_3]$ **24b**. Yellow *crystals*, 95% yield (Found: C, 64.40; H, 5.60; N, 9.35. Calc. for $C_{57}H_{58}BMoN_7O_3P_2$: C, 64.75; H, 5.55; N, 9.25%).

$[N(PPh_3)_2][Mo\{HB(cmpz)_3\}(CO)_3]$ **24c**. Yellow *crystals*, 96% yield (Found: C, 57.45; H, 4.60; N, 8.70. Calc. for $C_{54}H_{49}BCl_3MoN_7O_3P_2$: C, 57.95; H, 4.40; N, 8.75%).

$[NEt_3(CH_2Ph)][Mo\{HB(tpz)_3\}(CO)_3]$ **33a**. Orange-yellow *crystals*, 41% yield. Although stable in the solid state the complex appeared to undergo slight decomposition in solution (even under anaerobic conditions) and the presence of trace quantities of a complex presumed to be the 17-electron oxidation product [ν(CO) 2001s, 1870(br s) cm^{-1}] was detected by IR spectroscopy. Entirely satisfactory analytical data were not obtained (Found: C, 62.50; H, 5.80; N, 11.00. Calc. for $C_{46}H_{50}BMoN_7O_3$: C, 64.55; H, 5.90; N, 11.45%); IR: ν(CO) 1891s and 1765s cm^{-1} (thin film).

[NEt$_3$(CH$_2$Ph)][Mo{B(tpz)$_4$}(CO)$_3$] **33b**. Orange-yellow *crystals*, 61% yield (Found: C, 66.70; H, 6.30; N, 13.35. Calc. for $C_{56}H_{58}BMoN_9O_3$: C, 66.45; H, 5.80; N, 12.45%). IR: ν(CO) 1893s and 1765s cm^{-1} (thin film).

[N(PPh$_3$)$_2$][Mo{HB(dtfpz)$_3$}(CO)$_3$] **44**. Yellow *crystals*, 48% yield, extremely soluble in organic solvents. The salt was recrystallised by slow evaporation of a solution in a mixture of methanol and diethyl ether (Found: C, 48.90; H, 2.80; N, 7.70. Calc. for $C_{54}H_{34}BF_{18}MoN_7O_3P_2$: C, 48.40; H, 2.55; N, 7.30%). IR: ν(CO) 1924s and 1805s cm^{-1} (KBr disc).

Synthesis of η^2-*Aroyl Complexes*.—The following procedure is typical. A stirred suspension of the tetraethylammonium salt of the tricarbonyl anion [MoL*(CO)$_3$]$^-$ **5** (0.607 g, 1.0 mmol) in MeCN (10 cm^3) at −40 °C was treated portionwise with [4-O$_2$NC$_6$H$_4$N$_2$]BF$_4$ (0.237 g, 1.0 mmol). Addition of each aliquot was accompanied by gas evolution and darkening of the reaction mixture. When addition was complete the mixture was maintained at −40 °C for 10 min, allowed to come to room temperature spontaneously and stirred for 15 min. Removal of the solvent at reduced pressure yielded crude [MoL*(CO)$_2$(η^2-COC$_6$H$_4$NO$_2$-4)] **9a** which was subjected to preparative thin-layer chromatography on silica using 17% ether in light petroleum (b.p. 40–60 °C) as eluent. A dark blue band of R_f *ca.* 0.6 yielded the major product which was obtained as intensely blue-black *crystals* after recrystallisation from dichloromethane–ethanol. Yield *ca.* 70%. Similar results were obtained using [IPh$_2$]Cl or [IPh$_2$]BF$_4$ as oxidant. The η^2-hexahydrobenzoyl complex **13a** was prepared in 35% yield, together with *ca.* 30% of **9a**, by an analogous oxidation of **5** with [4-O$_2$NC$_6$H$_4$N$_2$]BF$_4$ using 3% acetonitrile in cyclohexane as solvent. Complexes **9h** and **13a** have been characterised by X-ray crystallographic methods.[4]

Solid-state photolysis of [SPh$_3$][MoL*(CO)$_3$] **14a**. A pressed KBr disc containing complex **14a** was exposed to normal sunlight and the progress of the reaction was monitored by IR spectroscopy. The presence of the η^2-aroyl complex **9g** was detectable in 1 h and after a total of 30 h of irradiation **14a** had been completely replaced by **9g**. A similar disc kept in the dark for 30 h showed no change.

Photolysis of complex **14a** *in acetonitrile*. A stirred solution of complex **14a** (0.74 g, 1.0 mmol) in acetonitrile (10 cm^3) was exposed to normal sunlight for 1 h during which time the yellow solution became purple. Work-up and purification by TLC as described above yielded SPh$_2$ (0.08 g, 43%, identified by comparison with authentic material) together with the η^2-benzoyl complex **9g** in 65% yield.

[MoL*(CO)$_2$(η^2-COMe)] **13b**. The tetraethylammonium salt of the tricarbonyl anion [MoL*(CO)$_3$]$^-$ **5** (0.607 g, 1.0 mmol) was suspended in MeI (10 cm^3) and [IPh$_2$]Cl (0.316 g, 1.0 mmol) was added in small portions with vigorous stirring. After 45 min the MeI was removed under reduced pressure and the residue was subjected to preparative thin-layer chromatography on silica using 5% ether in cyclohexane as eluent. An orange band (R_f *ca.* 0.32) yielded orange-red air-sensitive *microcrystalline* complex **13b** (0.228 g, 46%). A reddish purple band (R_f *ca.* 0.20) yielded *ca.* 2% of [MoL*(CO)$_2$(η^2-COPh)] **9g** which was identified by comparison with authentic material. Substituting [4-O$_2$NC$_6$H$_4$N$_2$]BF$_4$ for [IPh$_2$]Cl as oxidant lowered the yield of **13b** to 30% and **9a** was isolated in 10% yield.

[Mo{HB(tpz)$_3$}(CO)$_2$(η^2-COPh)] **35a**. The complex was isolated from the oxidation of [Mo{HB(tpz)$_3$}(CO)$_3$]$^-$ **33a** with [IPh$_2$]PF$_6$ in CH$_2$Cl$_2$ at −45 °C. The reaction mixture was passed down a short column of alumina before the solvent was removed and the residue purified by preparative thin-layer chromatography using 33% dichloromethane in light petroleum (b.p. 60–80 °C) as eluent. A purple band of $R_f \approx 0.32$ gave **35a** in 17% yield.

[Mo{B(pz)$_4$}(CO)$_2$(η^2-COPh)] **41**. Reddish brown *crystals* of complex **41** were prepared in 49% yield by oxidising the tetraethylammonium salt of [Mo{RB(pz)$_3$}(CO)$_3$]$^-$ **3** (R = pz) with [IPh$_2$]Cl in acetonitrile following the general procedure described above for **9**. IR: ν(CO) 1956br m and 1870s cm^{-1} (cyclohexane). NMR (CDCl$_3$, SiMe$_4$): ^{1}H, δ *ca.* 7.75 [complex m, 13 H, H(3) and H(5) of co-ordinated and unco-ordinated pz and COC$_6$H$_5$)], 6.78, 6.32 (triplets, *J* = *ca.* 2.25 Hz, 1 H and 3 H, H(4) of co-ordinated and unco-ordinated pz); ^{13}C δ 254.28 (η^2-*C*OC$_6$H$_5$), 239.34 (CO), 147.17 [C(3) of unco-ordinated pz], 143.92 [C(3) of co-ordinated pz *trans* to η^2-COPh], 142.21 [C(3) of co-ordinated pz *trans* to CO], 136.20 [C(5) of unco-ordinated pz], 135.65 [C(5) of co-ordinated pz *trans* to η^2-COPh], 134.66 [C(5) of co-ordinated pz *trans* to CO], 131.41, 129.54, 128.40 (η^2-CO*C*$_6$H$_5$), 107.21 [C(4) of unco-ordinated pz], 106.31 [C(4) of co-ordinated pz *trans* to η^2-COPh] and 105.91 [C(4) of co-ordinated pz *trans* to CO]. Similar results were obtained using the [N(PPh$_3$)$_2$]$^+$ salt of **3** (R = pz).

Synthesis of η^1-*Halogenocarbyne Complexes*.—The following procedure is typical. A vigorously stirred suspension of [MoL*(CO)$_3$]$^-$ **5** as its tetraethylammonium salt (0.607 g, 1.0 mmol) in CH$_2$Cl$_2$ (100 cm^3) at room temperature was treated portionwise with 1 equivalent of solid arenediazonium or diphenyliodonium tetrafluoroborate. Gas was evolved and the reaction mixture became greenish brown as the suspended material dissolved. When addition was complete the solution was stirred for 45 min, filtered, washed with water, dried over MgSO$_4$ and evaporated to dryness. The residue was purified by preparative thin-layer chromatography on silica gel using 5% ether in light petroleum (b.p. 40–60 °C) as eluent. A bright yellow band (R_f *ca.* 0.45) yielded yellow *crystalline* [MoL*(CO)$_2$(≡CCl)] **10** (0.387 g, 78%). A blue or purple band (R_f *ca.* 0.20) yielded *ca.* 3% of [MoL*(CO)$_2$(η^2-COR′)] **9** (R′ as in oxidant). Employing [4-Me$_2$NC$_6$H$_4$N$_2$]BF$_4$ as oxidant the reaction may be scaled up to produce up to 50 g of complex **10** without significant loss in yield. Before concentration, the crude reaction mixture was washed several times with *ca.* 18% aqueous HCl (to remove C$_6$H$_5$NMe$_2$ by-product), then with 10% aqueous Na$_2$CO$_3$ and finally with water. The crude residue was purified in *ca.* 20 g batches by dry-flash chromatography on silica gel using a column 6 cm high and 10 cm in diameter. The column was eluted with aliquots (50 cm^3) each of 1:10, 1:9 and 1:8 mixtures of CH$_2$Cl$_2$ and light petroleum (b.p. 30–40 °C) until a yellow band cleanly separated from the top of the column. This band was then removed by continued elution with CH$_2$Cl$_2$–light petroleum (b.p. 40–60 °C) (1:4). A combined yield of 48.7–50.6 g (77–80%) of **10** was obtained which is sufficiently pure for further reactions. A similar oxidation of **5** with [IPh$_2$]Cl using 5% CH$_2$Cl$_2$ in cyclohexane as solvent gave a 49% yield of **10** together with the η^2-aroyl complexes **9g** (3) and **13a** (24%). Complex **10** was also obtained by refluxing Tl[MoL*(CO)$_3$] **14b** or [NEt$_3$(CH$_2$Ph)][MoL*(CO)$_3$] **14c** (1 mmol) in chloroform (30 cm^3) under nitrogen for several hours. The reaction mixtures were filtered through Celite and evaporated to dryness *in vacuo*. Purification of the residue by preparative TLC yielded **10** in 20 and 40% yields respectively as the only carbonyl-containing product.

Photolysis of [SPh$_3$][MoL*(CO)$_3$] **14a** *in dichloromethane*. A stirred solution of **14a** (0.74 g, 1.0 mmol) in CH$_2$Cl$_2$ (100 cm^3) was exposed to normal sunlight for 1 h during which time the yellow solution gradually darkened. Work-up and purification by TLC as described above yielded SPh$_2$ (47%) together with the chlorocarbyne complex **10** (69%) and the η^2-aroyl complex **9g** (2%).

[MoL*(CO)$_2$(≡CBr)] **21** *and* [WL*(CO)$_2$(≡CBr)] **22**. The procedure was as described for the chloro-analogue, substituting freshly distilled bromoform for CH$_2$Cl$_2$ and removing the former at 2 mmHg and 30 °C to isolate the crude product.

[MoL*(CO)$_2$(≡CI)] **23**. The tetraethylammonium salt of [MoL*(CO)$_3$]$^-$ **5** (0.607 g, 1.0 mmol) was oxidised with [IPh$_2$]BF$_4$ (0.367 g, 1.0 mmol) in thf (100 cm^3) containing iodoform (3.9 g, 10 mmol). The solvent was removed under reduced pressure and the residue extracted with warm light petroleum (b.p. 40–60 °C). The extracts were concentrated to dryness and the residue was purified by preparative thin-layer chromatography as described above for complex **10**. A yellow band ($R_f \approx 0.95$) yielded unreacted iodoform. A second yellow band ($R_f \approx 0.5$) yielded **23** (0.065 g, 11% yield). Complex **23** is much less stable than its homologues and decomposes readily into a brown carbonyl-free material which was not characterised. Satisfactory microanalytical data were not obtained and the complex was identified by its characteristic IR spectrum.

[Mo{HB(tpz)$_3$}(CO)$_2$(≡CCl)] **36**. The reaction of [Mo{HB(tpz)$_3$}(CO)$_3$]$^-$ **33a** with [IPh$_2$]PF$_6$ in CH$_2$Cl$_2$ (described above for the synthesis of the η^2-aroyl complex **35a** yielded a second product ($R_f \approx 0.45$) in *ca.* 4% yield which was identified as the chlorocarbyne complex **36**.

[Mo{B(pz)$_4$}(CO)$_2$(≡CCl)] **40**. The tetraethylammonium salt of [Mo{RB(pz)$_3$}(CO)$_3$]$^-$ **3**, (R = pz) (5.89 g, 10 mmol) was oxidised with [IPh$_2$]Cl (3.16 g, 10 mmol) in CH$_2$Cl$_2$ (100 cm^3) at room temperature. After 45 min the solvent was removed *in vacuo* and the residue purified by preparative thin-layer chromatography as described for **10**. A reddish brown band ($R_f \approx 0.30$) yielded the η^2-benzoyl complex **41** (0.27 g, 5%). A yellow band ($R_f \approx 0.42$) gave a yellow crystalline solid identified as the η^1-chlorocarbyne complex **40** (1.13 g, 24% yield). NMR (CDCl$_3$, SiMe$_4$): ^{1}H, δ 7.90, 7.65 [overlapping multiplets, 5 H and 3 H, H(3) and H(5) of free and co-ordinated pyrazolyl groups], 6.64 (t, J = 1.5, 1 H) and 6.25 (t, J = 2.5 Hz, 3 H), [H(4) of free and co-ordinated pyrazolyl groups]; ^{13}C, δ 223.64 (CO), 213.50 (CCl), 145.08, 143.98, 142.16 [br, C(3) of free and co-ordinated pyrazolyl groups], 135.67 [vb, C(5) of free and co-ordinated pyrazolyl groups], 107.21, 105.65 [C(4) of free and co-ordinated pyrazolyl groups]. Similar results were obtained using the [N(PPh$_3$)$_2$]$^+$ salt of **3** (R = pz). Complex **40** has been characterised crystallographically.[5]

Synthesis of Aryldiazenido Complexes.—The general procedure involved reaction of the appropriate tricarbonyl anion and arenediazonium cation in acetonitrile or dichloromethane (as described earlier for the synthesis of the η^2-aroyl or η^1-chlorocarbyne complexes) and separation of the products by preparative thin-layer chromatography.

[MoL*(CO)$_2$(N$_2$C$_6$H$_4$NMe$_2$-4)] **32a**. Reaction of the anion [MoL*(CO)$_3$]$^-$ **5** with [4-Me$_2$NC$_6$H$_4$N$_2$]BF$_4$ (both 10 mmol) in MeCN at −40 °C and purification of the crude product by preparative thin-layer chromatography on silica gel, eluting with 17% ether in light petroleum (b.p. 40–60 °C), gave the η^2-aroyl complex **9j** (60%) and **32a** (3%). Using CH$_2$Cl$_2$ as solvent the major product (*ca.* 80%) was the η^1-chlorocarbyne complex **10** and only trace amounts of **32a** and **9j** were detected.

[MoL*(CO)$_2$(N$_2$C$_6$H$_3$Cl-2-Me-6)] **32b**. Reaction of complex **5** and [6-Me-2-ClC$_6$H$_3$N$_2$]BF$_4$ in MeCN as in the previous experiment gave **32b** in 17% yield. No other carbonyl-containing products were detected. In CH$_2$Cl$_2$ the η^1-chlorocarbyne complex **10** was formed in 65% yield and the yield of **32b** was 6%.

[MoL*(CO)$_2$(N$_2$C$_6$H$_3$Me$_2$-2,6)] **32c**. Reaction of complex **5** and [2,6-Me$_2$C$_6$H$_3$N$_2$]BF$_4$ in MeCN as in the previous experiment but eluting with 15% ether in cyclohexane gave complex **32c** in 20% yield as the only carbonyl-containing product. Reaction in CH$_2$Cl$_2$ gave **32c** (5) and **10** (67%).

[MoL*(CO)$_2${N$_2$(dmpz)}] **32d**. The crude product from the reaction of complex **5** with [(dmpz)N$_2$]$^+$ in MeCN was dissolved in CH$_2$Cl$_2$ and the solution was passed through a short column of grade III alumina, eluting with more CH$_2$Cl$_2$ until the washings were colourless. Removal of the solvent and recrystallisation of the residue from a mixture of CH$_2$Cl$_2$ and hexanes gave complex **32d** in 89% yield. Reaction in CH$_2$Cl$_2$ gave **32d** (72) and **10** (11%).

[MoL*(CO)$_2${N$_2$(ap)}] **32e**. Reaction of complex **5** and [(ap)N$_2$]$^+$ in MeCN as in the previous experiment produced complex **32e** in 91% yield. In CH$_2$Cl$_2$ **32e** was formed in 83% yield together with 5% of **10**.

Reaction of [Mo{HB(dtfpz)$_3$}(CO)$_3$]$^-$ **44** *with* [4-FC$_6$H$_4$N$_2$]$^+$ *in* CH$_2$Cl$_2$. The [N(PPh$_3$)$_2$]$^+$ salt of complex **44** (0.576 g, 0.43 mmol) in CH$_2$Cl$_2$ (30 cm^3) was treated portionwise with [4-FC$_6$H$_4$N$_2$]PF$_6$ (0.115 g, 0.43 mmol) at −70 °C and the mixture was allowed to warm slowly to room temperature. After removal of the solvent, preparative TLC on silica gel using 10% ether in hexane gave two overlapping bands at R_f *ca.* 0.6 which could not be completely separated even following multiple elutions. The products were identified by their IR spectra: [Mo{HB(dtfpz)$_3$}(CO)$_2$(N$_2$C$_6$H$_4$F-4)] **45**, *ca.* 43%, ν(CO) (cyclohexane) 2020s and 1947s; ν(NN) 1665m cm^{-1}; [Mo{HB(dtfpz)$_3$}(CO)$_2$(η^2-COC$_6$H$_4$F-4)] **46**, *ca.* 1%, ν(CO) (thin film) 1955m (br) and 1910s cm^{-1}. Further attempts at purification were not successful. No other carbonyl-containing products were detected.

[Mo{HB(tpz)$_3$}(CO)$_2$(N$_2$Ph)] **34a** *and related complexes.* The crude product from the reaction of [Mo{HB(tpz)$_3$}(CO)$_3$]$^-$ **33a** and benzenediazonium tetrafluoroborate (both 1.17 mmol) in MeCN at −40 °C was dissolved in dichloromethane and passed through a short column of silica gel. The solvent was removed *in vacuo* and the residue purified by preparative TLC, eluting with 20% CH$_2$Cl$_2$ in light petroleum (b.p. 60–80 °C). Apart from 21% of the η^2-benzoyl complex **35a** (see above) this gave the aryldiazenido complex **34a** ($R_f \approx 0.5$) in 6% yield and *ca.* 0.08 g of a green material [$R_f \approx 0.3$, ν(CO) 2024s and 1952s cm^{-1}] which has yet to be characterised. The complexes [Mo{HB(tpz)$_3$}(CO)$_2$(N$_2$C$_6$H$_4$NMe$_2$-4)] **34b**, [Mo{HB(tpz)$_3$}(CO)$_2${N$_2$(ap)}] **34c** and [Mo{B(tpz)$_4$}(CO)$_2$(N$_2$C$_6$H$_4$NMe$_2$-4)] **37** were prepared in similar fashion. In none of the latter reactions was there evidence for the formation of significant quantities of η^2-aroyl coproduct. Reaction of **33a** with [4-Me$_2$NC$_6$H$_4$N$_2$]BF$_4$ in CH$_2$Cl$_2$ gave the aryldiazenido complex **34b** in 18% yield together with 3% of the η^1-chlorocarbyne complex **36** (see above) and a trace of material with ν(CO) 1961m (br) and 1853s cm^{-1} tentatively identified as [Mo{HB(tpz)$_3$}(CO)$_2$(η^2-COC$_6$H$_4$NMe$_2$-4)] **35b**. Insufficient quantities of the latter were available for further characterisation.

[Mo{HC(dmpz)$_3$}(CO)$_2$(N$_2$R′)]$^+$ (R′ = C$_6$H$_4$NMe$_2$-4 **51** *or* ap **52**). A stirred suspension of [Mo{HC(dmpz)$_3$}(CO)$_3$] **47** (0.4 g, 0.84 mmol) in CH$_2$Cl$_2$ (40 cm^3) was treated with [4-Me$_2$NC$_6$H$_4$N$_2$]BF$_4$ (0.19 g, 0.84 mmol) at room temperature. After 4 h the cloudy yellow suspension had changed to a brown homogeneous solution. The solvent was removed and the residue purified by preparative TLC, eluting with 20% methanol in CH$_2$Cl$_2$. A brown band, $R_f \approx 0.46$, yielded the tetrafluoroborate salt of complex **51** (0.05 g, 9% yield) (Found: C, 45.20; H, 4.25; N, 17.95. C$_{26}$H$_{32}$BF$_4$MoN$_9$O$_2$ requires C, 45.55; H, 4.70; N, 18.40%). IR (CH$_2$Cl$_2$): ν(CO) 1988s, 1902s, ν(NN) 1722m cm^{-1}. Complex **52** was prepared similarly in 89% yield. The crude product was purified by precipitation with ether from solution in CH$_2$Cl$_2$ (Found: C, 45.20; H, 4.25; N, 17.95. C$_{26}$H$_{32}$BF$_4$MoN$_9$O$_2$ requires C, 45.55; H, 4.70; N, 18.40%). IR (CH$_2$Cl$_2$): ν(CO) 2000s, 1902s, ν(NN) 1678m, ν(CO) of antipyrine nucleus 1616 cm^{-1}. ^{13}C NMR (CDCl$_3$, SiMe$_4$): δ 227.64 (CO), 156.46 [C(3) of pz groups *trans* to CO], 156.03 [C(3) of pz groups *trans* to N$_2$(ap)], 143.74 [C(5) of pz groups *trans* to CO], 143.08 [C(5) of pz groups *trans* to N$_2$(ap)], 109.24 [C(4) of pz groups *trans* to CO], 109.06 [C(4) of pz groups *trans* to N$_2$(ap)], 68.64 [HC(dmpz)$_3$], 15.18, 12.79 [Me groups of HC(dmpz)$_3$ *trans* to CO], 14.72, 13.10 [Me groups of HC(dmpz)$_3$ *trans* to N$_2$(ap)]; 160.12 (CO of antipyrine nucleus), 144.58, 134.28 (alkene carbons of antipyrine nucleus), 129.49, 127.76, 125.41, 106.16 (phenyl carbons of antipyrine nucleus), 36.07 (NMe of antipyrine nucleus), 10.81 (CMe of antipyrine nucleus). In neither of these reactions was any other carbonyl-containing material observed.

Crystallography.—Crystals of complexes **32c** and **32e** were obtained by slow evaporation of saturated solutions in a mixture of dichloromethane and hexanes. Crystal data and details of the refinement for both complexes are summarised in Table 9. Accurate cell parameters were determined by least-squares refinement of the setting angles of 25 reflections measured on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatised Mo-Kα radiation. After corrections for Lorentz and polarisation effects (but not for absorption) the data with $I > 3\sigma(I)$ were regarded as observed and used in the subsequent structure solutions and refinements. The coordinates of the Mo atoms were obtained by an analysis of the three-dimensional Patterson function and the remaining non-hydrogen atoms were located in a heavy-atom-phased Fourier summation. Refinement[61] was by full-matrix least-squares calculations, initially with isotropic, then with anisotropic vibration parameters.

Difference maps were computed at intermediate stages in the refinement and revealed maxima in the positions expected for all the hydrogen atoms. The latter were then allowed for in geometrically idealised positions and included in the final rounds of calculations (C–H, B–H 0.95 Å, U_{iso} 0.10 for methyl hydrogens and 0.05 Å^2 for others) but were not refined. Scattering factors used in the structure-factor calculations were taken from the literature and allowance was made for anomalous dispersion.[62] Final difference maps were devoid of any significant features.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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