Transition-metal Derivatives of Arenediazonium Ions. Part 12.[1] Complexes derived from Pyrazole-4-diazonium and 3-Pyrazolin-5-one-4-diazonium Cations. *X*-Ray Crystallographic Characterisation of a Sterically Distorted Organodiazenido-complex: Dicarbonyl(3,5-dimethylpyrazol-4-yl-diazenido)tris(pyrazol-1-yl)methanemolybdenum(II) Tetrafluoroborate–Diethyl ether (1/1) †

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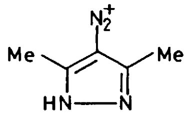
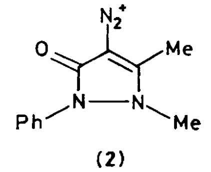
Reaction of the 3,5-dimethylpyrazole-4-diazonium cation, $[(3,5Me_2\text{-pz})N_2]^+$ (**1**), or the antipyrene-4-diazonium cation (2,3-dimethyl-1-phenyl-3-pyrazolin-5-one-4-diazonium), $[(ap)N_2]^+$ (**2**), with the appropriate transition-metal substrates yields the complexes $[Mo(CO)_2\{N_2(3,5Me_2\text{-pz})\}\{HC(pz)_3\}]BF_4\cdot Et_2O$ (**3**), $[Mo(CO)_2\{N_2(ap)\}\{HC(pz)_3\}]BF_4$, $[Mo(CO)_2\{N_2(3,5Me_2pz)\}\{HB(pz)_3\}]$, $[Mo(CO)_2\{N_2(ap)\}\{HB(pz)_3\}]$ (pz = pyrazol-1-yl), $[Mo(CO)_3\{N_2(ap)\}(bipy)]BF_4$, (bipy = 2,2′-bipyridyl), $[Mo(CO)_3\{N_2(ap)\}(phen)]BF_4$ (phen = 1,10-phenanthroline), and $[Fe(CO)_2\{N_2(ap)\}(PPh_3)_2]BF_4$, the first organodiazenido complexes derived from heterocyclic diazonium cations. Crystals of (**3**) are monoclinic, space group *C*2, with four formula units in a unit cell of dimensions a = 18.326(2), b = 9.185(2), c = 16.886(2) Å, and β = 91.387(6) Å. The structure was solved by the heavy-atom method and refined by least-squares calculations to R = 0.034 for 1 145 reflections with $I > 3\sigma(I)$. The molybdenum atom has a slightly distorted octahedral co-ordination with Mo–N(pz) 2.21(1)—2.28(2), Mo–C(CO) 1.92(2) and 1.95(2), Mo–N(organodiazenido) 1.84(1), and N–N(organodiazenido) 1.22(2) Å. Steric interaction between the organodiazenido ligand and the tris(pyrazol-1-yl)methane ligand causes the former to deviate significantly from the idealised 'singly-bent' geometry: Mo–N–N 164.5(8), N–N–C(pz) 124.4(10)°. The antipyrene-4-diazonium cation (**2**) degrades $[Ni(CO)_2(PPh_3)_2]$ with the formation of an azophosphonium salt $[PPh_3\{N_2(ap)\}]BF_4$ but reacts with $[Mn(CO)_2(thf)(\eta\text{-}C_5H_4Me)]$ (thf = tetrahydrofuran) at −50 °C to yield $[Mn(CO)_2\{N_2(ap)\}(\eta\text{-}C_5H_4Me)]BF_4$.

The diversity of structures shown by transition-metal complexed arenediazonium cations, $[RN_2]^+$, has attracted much interest.[2] It has recently become clear that complexed neutral diazo compounds, $R'N_2$, show even greater structural versatility.[3] A related, but hitherto uninvestigated, group of potential ligands comprises diazonium cations in which the diazonium functional group is attached to a five-membered heterocyclic ring system. If the heterocyclic nucleus bears an acidic hydrogen atom, as is the case for the 3,5-dimethylpyrazole-4-diazonium cation $[(3,5Me_2\text{-pz})N_2]^+$ (1),[4] a treatment with base generates neutral heterocyclic diazo compounds (isoelectronic with diazocyclopentadiene) which are useful synthetic intermediates.[5] Diazonium cations such as (1) thus offer the possibility of studying the structure and reactivity of closely related co-ordinated diazonium and diazo ligands. We have recently investigated the unusual stability of cation (1) *via* a combination of *X*-ray crystallography and an MNDO theoretical study.[6] In this paper we report the results of our initial exploration of the ligating ability of (1) and of a related pyrazolinone-based ligand, *i.e.* the 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one-4-diazonium cation {antipyrene-4-diazonium cation, $[(ap)N_2]^+$} (2),[7] which is reported to have a stability intermediate between (1) and typical arenediazonium cations.[8]

We also describe the crystal and molecular structure of a complex containing (1) as a ligand, *i.e.* dicarbonyl(3,5-dimethylpyrazol-4-yldiazenido)tris(pyrazol-1-yl)methanemolybdenum(II) tetrafluoroborate–diethyl ether, $[Mo(CO)_2\{N_2(3,5Me_2\text{-pz})\}\{HC(pz)_3\}]BF_4\cdot Et_2O$ (3).



(1)



(2)

Results and Discussion

We first examined some reactions of (1) and (2) with the Mo^0 substrates $[Mo(CO)_3\{HC(pz)_3\}]$, $[Mo(CO)_3\{HB(pz)_3\}]^-$, and $[Mo(CO)_4(L\text{-}L)]$ [L–L = 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen)] and the Fe^0 substrate $[Fe(CO)_3(PPh_3)_2]$, all of which are known to form stable complexes with $[RN_2]^+$ (R = arene),[9–12] From these reactions we were able to isolate the new organodiazenido complexes (3), $[Mo(CO)_2\{N_2(ap)\}\{HC(pz)_3\}]BF_4$ (4), $[Mo(CO)_2\{N_2(3,5\text{-}Me_2\text{-pz})\}\{HB(pz)_3\}]$ (5), $[Mo(CO)_2\{N_2(ap)\}\{HB(pz)_3\}]$ (6), $[Mo(CO)_3\{N_2(ap)\}(bipy)]BF_4$ (7), $[Mo(CO)_3\{N_2(ap)\}(phen)]BF_4$ (8), and $[Fe(CO)_2\{N_2(ap)\}(PPh_3)_2]BF_4$ (9) in *ca.* 60—80% yield. The new complexes are brown or orange air-stable solids which are soluble in polar organic solvents to give red solutions moderately stable in the absence of air. In view of the stability

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† *Supplementary data available* (No. SUP 56348, 5 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

of complexes (3)—(9) and their similarity to the known aryldiazenido analogues we conclude that, like the latter, they contain organodiazenido ligands in the 'singly-bent'[2] co-ordination mode. The ^{1}H n.m.r. spectrum of complex (3) was considerably broadened, possibly due to the presence of trace paramagnetic impurities, and complexes (7) and (8) were insufficiently stable in solution for satisfactory spectra to be recorded. Complex (9) was not sufficiently soluble in $CHCl_3$ or CH_2Cl_2 to yield a useful ^{1}H n.m.r. spectrum but spectra in accord with the proposed structures were obtained for complexes (4)—(6) (see Experimental section).

Complexes (3)—(9) exhibit CO stretching frequencies (Table 1) *ca.* 10—25 cm^{-1} to lower wavenumber than their aryldiazenido counterparts suggesting that diazonium cations (1) and (2) are somewhat weaker π-acceptors than $[RN_2]^+$. This finding correlates with the results of our crystallographic and theoretical study of (1) which reveals significant conjugative transfer of π-electron density from the pyrazole ring to a π^* orbital of the diazonium functional group.[6] If this effect persists in the complexed ligand it would be anticipated to reduce the capacity of co-ordinated (1) to accept metal *d*-electron density into the diazenido π^* orbitals. Complexes (3)—(6) show a single strong i.r. band in the region 1 596—1 619 cm^{-1} which is assigned to ν(NN) of the organodiazenido ligand. Complex (9) exhibits ν(NN) as a medium intensity band at *ca.* 1 715 cm^{-1}. The i.r. results for (3)—(6) contrast with the data for their aryldiazenido analogues where vibrational coupling between the complexed diazenido N_2 structure and the attached arene ring leads to the observation of two bands associated with ν(NN) in the 1 600 cm^{-1} region.[13] Complexes (7) and (8) show two i.r. bands in this region (*ca.* 1 595 and 1 572 cm^{-1}) but, in the absence of ^{15}N isotopic labelling studies, we have no means of deciding whether or not both of these bands are associated with the ν(NN) vibration.

Table 1. Microanalytical and i.r. data

	Analysis[a]			I.r. data (cm^{-1})[b]	
Compound	C	H	N	ν(CO)	ν(NN)[c]
(4)	41.00 (41.35)	3.25 (3.15)	20.60 (20.95)	1 996, 1 907[d]	1 617
(5)	39.40 (39.35)	3.50 (3.50)	28.50 (28.70)	1 980, 1 887[e]	1 605
(6)	45.50 (45.55)	3.60 (3.65)	24.20 (24.15)	1 988, 1 890[f]	1 596
(7)	45.20 (45.15)	2.95 (3.00)	13.20 (13.15)	1 990, 1 896[g,h]	1 600, 1 570[g]
(8)	47.05 (47.15)	2.90 (2.90)	12.50 (12.70)	1 985, 1 889[g,i]	1 590, 1 575[g]
(9)	62.95 (62.70)	4.35 (4.40)	6.20 (5.95)	2 019, 1 963[j]	1 715[k]

[a] Calculated values in parentheses. [b] Solutions in CH_2Cl_2 unless stated otherwise. [c] Strong band unless stated otherwise, assignment tentative in the absence of ^{15}N labelling. [d] Pyrazolinone CO at 1 670 cm^{-1}. [e] ν(NH) at 3 445 cm^{-1}. [f] Pyrazolinone CO at 1 668 cm^{-1}. [g] Thin film from CH_2Cl_2. [h] Pyrazolinone CO at 1 660 cm^{-1}. [i] Pyrazolinone CO at 1 655 cm^{-1}. [j] Pyrazolinone CO at 1 669 cm^{-1}. [k] Medium intensity band.

We have determined the structure of complex $[Mo(CO)_2\{N_2(3,5Me_2\text{-}pz)\}\{HC(pz)_3\}]BF_4\cdot Et_2O$ (3) by *X*-ray crystallographic methods and the results provide the first structural details of an organodiazenido ligand derived from a heterocyclic diazonium cation. A stereoscopic view of the molecular structure of the complex is shown in Figure 1 together with the crystallographic numbering scheme. A stereoview of the contents of the unit cell is shown in Figure 2. Final fractional co-ordinates are listed in Table 2 and details of the molecular geometry are summarised in Table 3. The crystals contain discrete anions and cations separated by normal van der Waals distances. The diethyl ether of solvation is linked to the pyrazolyldiazenido ligand *via* hydrogen bonding between the acidic ring NH group and the ether oxygen atom [N(44)–H···O(3), 2.89(2) Å]. The co-ordination around the molybdenum atom in (3) is slightly distorted octahedral and broadly resembles that found in the isoelectronic neutral phenyldiazenido complex $[Mo(CO)_2(N_2Ph)\{HB(pz)_3\}]$.[14] The N(pz)–Mo–N(pz) angles [mean 79.8(4)°] in (3) are slightly smaller than those in $[Mo(CO)_2(N_2Ph)\{HB(pz)_3\}]$ (82°) in accord with the shortness of the HC–N(pz) distances [1.38(2)—1.48(2) Å] in the former relative to the HB–N(pz) distances in the latter [1.53(1)—1.56(1) Å].[14] The organodiazenidomolybdenum structural unit is significantly distorted from the idealised 'singly-bent' geometry. The N(42)–N(41)–Mo bond angle [164.5(8)°] deviates considerably from linearity. This N–N–Mo bending is a response to unfavourable steric interaction between the methyl carbon [C(420)] of the pyrazolyldiazenido ligand and the neighbouring pyrazolylmethane

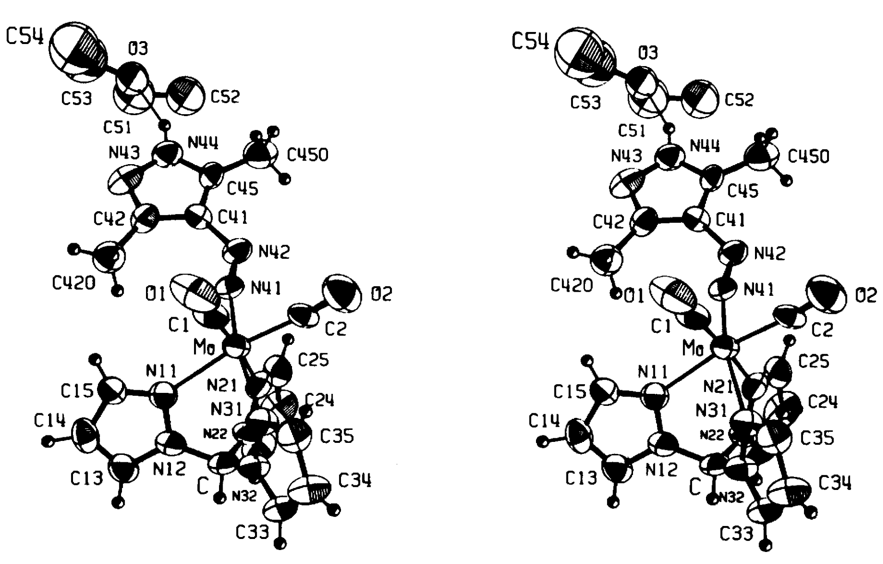


Figure 1. Stereoscopic view of the molecular structure of complex (3) with the crystallographic numbering scheme

Table 2. Final fractional co-ordinates (× 10^4) for $[Mo(CO)_2\{N_2(3,5Me_2\text{-}pz)\}\{HC(pz)_3\}]BF_4{\cdot}Et_2O$ (3) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	4 736(1)	2 500	2 235(1)	C(2)	5 215(9)	700(20)	2 495(10)
B	1 769(11)	3 449(18)	893(10)	C(13)	4 427(9)	6 726(17)	1 080(8)
F(1)	1 844(6)	4 332(16)	1 541(7)	C(14)	3 711(9)	6 421(18)	1 086(8)
F(2)	1 017(5)	3 344(9)	712(5)	C(15)	3 668(10)	5 105(18)	1 495(10)
F(3)	2 021(7)	2 142(15)	1 058(13)	C(23)	6 140(8)	6 218(18)	2 833(12)
F(4)	2 103(6)	4 084(18)	321(7)	C(24)	6 153(9)	5 678(24)	3 582(11)
O(1)	3 656(10)	405(17)	1 346(9)	C(25)	5 740(8)	4 423(19)	3 552(9)
O(2)	5 443(8)	−474(18)	2 617(8)	C(33)	6 336(8)	4 089(21)	575(8)
N(11)	4 301(8)	4 594(15)	1 697(7)	C(34)	6 373(8)	2 580(35)	346(8)
N(12)	4 780(6)	5 607(13)	1 450(6)	C(35)	5 826(8)	1 914(19)	773(9)
N(21)	5 496(7)	4 156(18)	2 825(8)	C(41)	3 511(7)	2 190(17)	4 259(7)
N(22)	5 755(7)	5 294(14)	2 394(8)	C(42)	2 885(7)	2 919(15)	3 998(7)
N(31)	5 494(6)	2 829(14)	1 253(6)	C(420)	2 712(8)	3 648(17)	3 210(7)
N(32)	5 807(6)	4 184(13)	1 123(6)	C(45)	3 402(7)	1 734(14)	5 027(8)
N(41)	4 308(4)	2 236(16)	3 201(6)	C(450)	3 854(7)	848(17)	5 594(8)
N(42)	4 193(5)	1 967(11)	3 891(7)	O(3)	3 218(5)	7 260(14)	3 469(5)
N(43)	2 388(6)	2 906(15)	4 566(7)	C(51)	3 026(12)	8 411(28)	2 866(14)
N(44)	2 722(6)	2 136(13)	5 181(7)	C(52)	2 323(10)	7 911(24)	2 476(10)
C	5 561(7)	5 369(16)	1 541(9)	C(53)	3 992(13)	7 314(47)	3 697(15)
C(1)	4 060(11)	1 205(22)	1 677(11)	C(54)	4 203(16)	6 578(39)	4 216(20)

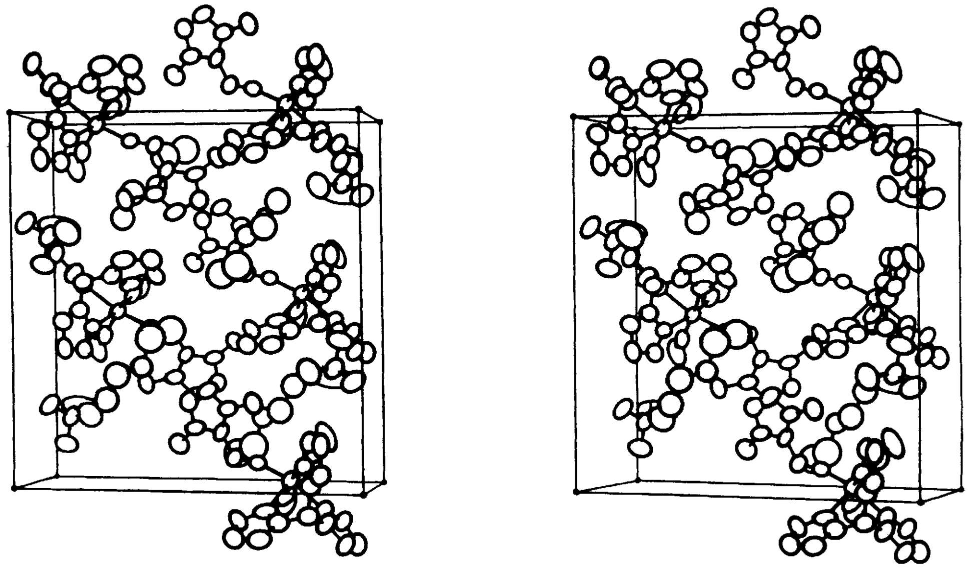


Figure 2. Stereoscopic view of the contents of the unit cell of complex (3)

carbon [C(15)] and may be compared to typical N–N–Mo angles of 170.8—176.5° found for uncrowded organodiazenido ligands in related complexes.[14–16] There is also concomitant angle bending at the diazenido-bound carbon atom of the pyrazolyldiazenido ligand; thus C(42)–C(41)–N(42) is 10.1° larger than C(45)–C(41)–N(42). The organodiazenido C–N–N angle in uncrowded aryldiazenido complexes is close to the expected 120° value. A larger N–N–C angle [C(41)–N(42)–N(41), 124.4(10)°] is found in (3) and this also helps to relieve steric strain. The effect of steric crowding can also be detected by a consideration of torsion and interplanar angles within the organodiazenido ligand and its immediate environment. The C(41)–N(42)–N(41)–Mo torsion angle is 175.5° and the angle between the C(41)–C(42)–N(43)–N(44)–C(45) plane of the pyrazolyldiazenido ligand and the C(41)–N(42)–N(41) plane is 8.7°. These small rotations both help to relieve steric interaction between C(420) and C(15). Furthermore, the plane of atoms N(42)–C(41)–C(42)–N(43)–N(44)–C(45) is inclined at 28.9° to the plane containing the molybdenum atom, the nitrogen atoms N(11) and N(21) of the *cis* and *trans* pyrazolyl rings of the $HC(pz)_3$ ligand, the *cis* carbonyl carbon C(2), and the organodiazenido nitrogen N(41). In the absence of steric constraints the angle between these two planes would be expected to be close to zero. The bond lengths within the immediate co-ordination sphere of the molybdenum atom of (3) are similar to those found in $[Mo(CO)_2(N_2Ph)\{HB(pz)_3\}]$; mean Mo–N(pz) 2.26(2) (2.22[14]), mean Mo–C(CO) 1.93(2) (1.99[14]) Å. The dimensions within the pyrazolyl rings of the tris(pyrazol-1-yl)methane ligand (mean C–C 1.38, mean C–N 1.33, mean N–N 1.37 Å) are comparable with those reported elsewhere for the hydrotris(pyrazol-1-yl)-borate ligand.[14–16]

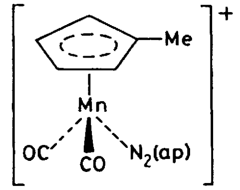
The structural details of the pyrazole fragment of the co-ordinated pyrazolediazenido ligand are broadly similar to those

Table 3. Interatomic distances (Å) and angles (°) in $[Mo(CO)_2\{N_2(3,5Me\text{-}pz)\}\{HC(pz)_3\}]BF_4\cdot Et_2O$ (**3**) with estimated standard deviations in parentheses

Mo–C(1)	1.945(23)	N(12)–N(11)	1.353(15)	C(35)–N(31)	1.326(17)	C(450)–C(45)	1.492(14)
Mo–C(2)	1.918(18)	C(15)–N(11)	1.290(19)	C(33)–N(32)	1.359(16)	F(1)–B	1.367(19)
Mo–N(11)	2.264(13)	C(13)–N(12)	1.359(16)	C(34)–C(33)	1.441(33)	F(2)–B	1.407(21)
Mo–N(21)	2.276(15)	C(14)–C(13)	1.341(19)	C(35)–C(34)	1.391(21)	F(3)–B	1.314(21)
Mo–N(31)	2.209(11)	C(15)–C(14)	1.395(22)	N(42)–N(41)	1.215(12)	F(4)–B	1.295(18)
Mo–N(41)	1.842(10)	N(22)–N(21)	1.366(18)	C(41)–N(42)	1.423(15)	C(51)–O(3)	1.504(24)
O(1)–C(1)	1.174(21)	C(25)–N(21)	1.319(18)	C(42)–C(41)	1.391(16)	C(53)–O(3)	1.462(24)
O(2)–C(2)	1.174(20)	C(23)–N(22)	1.320(19)	C(45)–C(41)	1.383(15)	C(52)–C(51)	1.503(26)
N(12)–C	1.451(16)	C(24)–C(23)	1.359(21)	C(420)–C(42)	1.517(14)	C(54)–C(53)	1.166(36)
N(22)–C	1.477(18)	C(25)–C(24)	1.380(21)	N(43)–C(42)	1.338(14)	O(3) · · · N(44)	2.89(2)
N(32)–C	1.379(17)	N(32)–N(31)	1.391(17)	N(44)–N(43)	1.387(14)	O(3) · · · H(44)	2.00
				C(45)–N(44)	1.331(15)		

C(1)–Mo–C(2)	82.3(7)	N(42)–N(41)–Mo	164.5(8)	C(35)–C(34)–C(33)	104.2(16)
N(11)–Mo–C(1)	96.4(7)	N(22)–C–N(12)	108.9(10)	C(34)–C(35)–N(31)	112.6(18)
N(11)–Mo–C(2)	168.2(6)	N(32)–C–N(i2)	113.5(12)	C(41)–N(42)–N(41)	124.4(10)
N(21)–Mo–C(1)	175.6(7)	N(32)–C–N(22)	112.8(11)	C(42)–C(41)–N(42)	131.1(11)
N(21)–Mo–C(2)	101.8(7)	C(15)–N(11)–N(12)	104.7(12)	C(45)–C(41)–N(42)	121.0(12)
N(11)–Mo–N(21)	79.3(5)	N(11)–N(12)–C	120.6(12)	C(45)–C(41)–C(42)	107.8(10)
N(31)–Mo–C(1)	97.2(6)	C(13)–N(12)–C	128.3(12)	C(420)–C(42)–C(41)	130.0(11)
N(31)–Mo–C(2)	89.8(5)	C(13)–N(12)–N(11)	110.8(11)	N(43)–C(42)–C(41)	109.9(10)
N(11)–Mo–N(31)	78.7(4)	C(14)–C(13)–N(12)	107.1(13)	N(43)–C(42)–C(420)	120.1(12)
N(21)–Mo–N(31)	81.3(4)	C(15)–C(14)–C(13)	104.6(14)	N(44)–N(43)–C(42)	104.2(10)
N(41)–Mo–C(1)	94.0(6)	C(14)–C(15)–N(11)	112.7(15)	C(45)–N(44)–N(43)	113.2(10)
N(41)–Mo–C(2)	83.5(6)	C(25)–N(21)–N(22)	103.9(14)	N(44)–C(45)–C(41)	104.9(10)
N(11)–Mo–N(41)	108.3(5)	N(21)–N(22)–C	118.5(13)	C(450)–C(45)–C(41)	132.6(12)
N(21)–Mo–N(41)	88.2(5)	C(23)–N(22)–C	129.1(14)	C(450)–C(45)–N(44)	122.2(12)
N(31)–Mo–N(41)	166.2(4)	C(23)–N(22)–N(21)	112.4(13)	F(2)–B–F(1)	107.0(13)
O(1)–C(1)–Mo	178.9(16)	C(24)–C(23)–N(22)	106.6(14)	F(3)–B–F(1)	110.1(17)
O(2)–C(2)–Mo	172.7(17)	C(25)–C(24)–C(23)	105.8(13)	F(3)–B–F(2)	108.7(14)
N(12)–N(11)–Mo	118.9(10)	C(24)–C(25)–N(21)	111.3(15)	F(4)–B–F(1)	106.9(15)
N(22)–N(21)–Mo	119.7(10)	C(35)–N(31)–N(32)	105.8(12)	F(4)–B–F(2)	110.4(14)
N(32)–N(31)–Mo	120.7(9)	N(31)–N(32)–C	118.9(10)	F(4)–B–F(3)	113.6(18)
C(15)–N(11)–Mo	136.2(11)	C(33)–N(32)–C	130.3(12)	C(53)–O(3)–C(51)	111.3(19)
C(25)–N(21)–Mo	136.2(12)	C(33)–N(32)–N(31)	110.8(12)	C(52)–C(51)–O(3)	105.4(17)
C(35)–N(31)–Mo	132.7(10)	C(34)–C(33)–N(32)	106.4(13)	C(54)–C(53)–O(3)	118.6(30)
				O(3) · · · H(44)–N(44)	154.8

found in the free cationic ligand.[6] However, the relatively large e.s.d.s in the bond length and angle data for (**3**) (see Experimental section) do not allow a meaningful comparison with the fine details of the structure of the latter. One obvious similarity between (**1**) and (**3**) is that the ring proton bound to N(44) (which was located from a difference map) is attached to the nitrogen atom with the greater endocyclic C–N–N angle [C(45)–N(44)–N(43) 113.2(10), N(44)–N(43)–C(42) 104.2(10)°].



(**11**)

We have also carried out some exploratory reactions in order to determine whether the increased stability of (**1**) and (**2**) *vis-a-vis* arenediazonium cations[6,8] could be exploited to prepare organodiazenido complexes from substrates which are decomposed by the latter. Both (**1**) and (**2**) react rapidly with $[Ni(CO)_2(PPh_3)_2]$ to give red ionic carbonyl-free solids. The product of the reaction with (**2**) proved to be $[PPh_3\{N_2(ap)\}]BF_4$ (**10**) which could also be prepared from the direct reaction of (**2**) with PPh_3. The product from the reaction of (**3**) with $[Ni(CO)_2(PPh_3)_2]$ or PPh_3 also appears to be an azophosphonium salt but it was much less stable than (**10**) and could not be fully purified. It appears that both diazonium cations degrade $[Ni(CO)_2(PPh_3)_2]$, the liberated PPh_3 then being captured by unreacted diazonium cations. No reaction could be detected between (**2**) and $[Mn(CO)_3(\eta\text{-}C_5H_4Me)]$. More encouraging results were obtained in the reaction of (**2**) with $[Mn(CO)_2(thf)(\eta\text{-}C_5H_4Me)]$ (thf = tetrahydrofuran). Although this complex is destroyed by $[RN_2]^+$ at -35 °C[17] it reacted smoothly with (**2**) at -50 °C to yield the new organodiazenido-complex $[Mn(CO)_2\{N_2(ap)\}(\eta\text{-}C_5H_4Me)]BF_4$ (**11**) in *ca.* 49% yield. Complex (**11**) is an olive-green solid which is moderately air-stable in the solid state but less so in solution in polar organic solvents. We were unable to record satisfactory ^1H n.m.r. spectra of (**11**), possibly due to the presence of traces of paramagnetic Mn^{II} products generated by competing oxidation of $[Mn(CO)_2(thf)(\eta\text{-}C_5H_4Me)]$ by the diazonium cation.[18] Its i.r. spectrum (KBr disc) shows two very strong ν(CO) bands at 2 059 and 2 010 cm^{-1} together with a strong band at 1 800 cm^{-1} which is assigned to ν(NN). While the ν(NN) stretching frequency in (**11**) lies close to the position of the ν(NN) band in a variety of aryldiazenido complexes of the type $[Mn(CO)_2(N_2R)(\eta\text{-}C_5H_4Me)]BF_4$ (*ca.* 1 792 cm^{-1}),[17] the latter exhibit two ν(CO) bands which are *ca.* 30 cm^{-1} higher than those in (**11**), attesting once again to the reduced π-acceptor capacity of (**2**) relative to $[RN_2]^+$. Our ability to record the i.r. spectrum of (**11**) in a pressed KBr disc without any evidence of decomposition contrasts interestingly with the reported behaviour of the analogous phenyldiazenido complexes. Under similar conditions the organodiazenido C–N bond of the latter is rapidly cleaved by bromide anion to give $[Mn(CO)_2(N_2)(\eta\text{-}C_5H_4Me)]$ and PhBr.[17] It is clear from this result that 'a positive charge on the metal atom and a high ν(NN) value of *ca.* 1 750 cm^{-1} or greater'[17] are not in themselves sufficient predictors of whether nucleophilic attack of halide at the R group in $[Mn(CO)_2(N_2R)(\eta\text{-}C_5H_5Me)]^+$ will take place or not. We suggest that the failure of (**11**) to react with Br^- may be a result of strengthening of the (diazenido)N–C bond by π-donation from the pyrazolinone ring (see above).

More recent work in these laboratories[19] has confirmed the synthetic potential of (**1**) and (**2**) and revealed further examples of reactions in which they may be employed for the synthesis of organodiazenido complexes which are not accessible using arenediazonium cations. Our research in this area is continuing.

Experimental

The compounds $[(3,5Me_2\text{-pz})N_2]Cl$,[4] $[(ap)N_2]BF_4$,[5] $[Mo(CO)_3\{HC(pz)_3\}]$,[9] $[NEt_4][Mo(CO)_3\{HB(pz)_3\}]$,[20] $[Mo(CO)_4(bipy)]$,[21] $[Mo(CO)_4(phen)]$,[21] and $[Fe(CO)_3(PPh_3)_2]$[22] were prepared by the literature procedures. All other reagents and solvents were commercial samples and were used without further purification. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer calibrated with a standard polystyrene film. Microanalyses were carried out by the staff of the Microanalytical Laboratory of University College, Cork.

Preparation of 3,5-*Dimethylpyrazole*-4-*diazonium Tetrafluoroborate*, $[(3,5Me_2\text{-pz})N_2]BF_4$.—A solution of $[(3,5Me_2\text{-pz})N_2]Cl$ (0.5 g, 3.15 mmol) in methanol (30 cm^3) was treated with $NaBF_4$ (1.0 g, 9.11 mmol) in the minimum quantity of the same solvent. The solution was concentrated to dryness *in vacuo* and the residue was extracted with acetone. Addition of diethyl ether to the extract precipitated a white crystalline solid which was recrystallised several times from acetone–diethyl ether to yield 0.59 g (89%) of pure $[(3,5Me_2\text{-pz})N_2]BF_4$ (Found: C, 28.60; H, 3.40; N, 26.70. $C_5H_7BF_4N_4$ requires C, 28.60; H, 3.35; N, 26.70%).

Preparation and X-*Ray Structure Determination of* $[Mo(CO)_2\{N_2(3,5Me_2\text{-pz})\}\{HC(pz)_3\}]BF_4\cdot Et_2O$ (**3**).—A stirred suspension of $[Mo(CO)_3\{HC(pz)_3\}]$ (0.74 g, 1.88 mmol) in dry, nitrogen-saturated *N,N*-dimethylformamide (10 cm^3) was treated portionwise under nitrogen with solid $[(3,5Me_2\text{-pz})N_2]Cl$ (0.40 g, 2.52 mmol). The molybdenum complex rapidly dissolved, the solution initially becoming green, then dark brown. After stirring the reaction mixture for 3 h at room temperature it was poured into water (200 cm^3) containing a large excess of $NaBF_4$. The brown precipitate was collected by filtration, washed with water, and dried *in vacuo* over P_2O_5. The crude product was dissolved in acetone and the solution diluted with a large volume of diethyl ether. A trace of greenish-yellowish precipitate was removed by filtration and the filtrate was set aside at 0 °C for several hours. Large reddish brown crystals of complex (**3**) were deposited (0.70 g, 57.3%), one of which was subsequently used for the *X*-ray analysis (Found: C, 39.25; H, 4.45; N, 21.90. $C_{21}H_{27}BF_4MoN_{10}O_3$ requires C, 38.80; H, 4.20; N, 21.55%). I.r. (KBr disc): ν(CO) at 1 982s, 1 892s cm^{-1}; ν(NN) at 1 619s cm^{-1}.

Crystal data for (**3**). $[Mo(CO)_2\{N_2(3,5Me_2\text{-pz})\}\{HC(pz)_3\}]BF_4\cdot Et_2O$, $C_{21}H_{27}BF_4MoN_{10}O_3$, $M = 650.2$, monoclinic, $a = 18.326(2)$, $b = 9.185(2)$, $c = 16.886(2)$ Å, $\beta = 91.387(6)°$, $U = 2\,841.5$ Å^3, $Z = 4$, $D_c = 1.52$ g cm^{-3}, $F(000) = 1\,320$, $\lambda(Mo\text{-}K_\alpha) = 0.710\,69$ Å, $\mu(Mo\text{-}K_\alpha) = 5.15$ cm^{-1}. Space group $C2$, Cm, or $C2/m$ from systematic absence hkl if $h + k = 2n + 1$, $C2$ established by analysis.

Three-dimensional PDP-8I data were collected as described elsewhere[23] on a PDP 8I-controlled Hilger and Watts four-circle diffractometer. The intensity data were corrected for Lorentz, polarisation, and absorption factors. The crystals were of poor quality and did not diffract well above $\theta(Mo\text{-}K_\alpha)$ of 20°; of the 1 394 independent reflections measured with $1 < \theta < 20°$, 1 145 with $I > 3\sigma(I)$ were labelled as observed and used in the structure solution and refinement.

Structure solution and refinement. The space group was initially assumed to be $C2$ and this has been confirmed by the analysis. The x and z co-ordinates of the Mo atom were obtained from a three-dimensional Patterson function and the y co-ordinate was arbitrarily fixed at 0.25. A heavy-atom phased Fourier summation was complicated by the inevitable pseudo-mirror symmetry, but by careful selection of peaks the structure of the complex could be discerned. Full-matrix refinement with isotropic thermal parameters lowered R to 0.117 and in a subsequent difference synthesis a set of five rather diffuse peaks in an almost zig-zag row was the main feature. These atoms were allowed for as a molecule of diethyl ether of solvation. With the diethyl ether atoms allowed isotropic motion and the atoms of the complex cation and BF_4^- anion allowed anisotropic motion, full-matrix refinement lowered R to 0.041 and $R'[= (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}]$ to 0.044. A difference synthesis computed at this stage showed maxima for all hydrogen atoms of the complex and evidence of marked anisotropy around the molecule of diethyl ether of solvation. In the final cycles of refinement the hydrogen atoms of the complex were positioned geometrically and only an overall isotropic thermal parameter was refined for them. Refinement converged with $R = 0.034$ and $R' = 0.035$. Scattering factors were taken from the literature[24,25] and allowance was made for anomalous dispersion.[26] In the calculations a weighting scheme of the form $w^{\frac{1}{2}} = 1/(\sigma F^2)^{\frac{1}{2}}$ was employed.

The structure of (**3**) is well established despite the fact that the crystal did not diffract well (undoubtedly due to the loosely bound diethyl ether of solvation) and did not give a plethora of observed data. Consequently the e.s.d.s of the bond lengths and bond angles are rather large (0.010—0.033 Å, 0.6—1.7°).

Preparation of Complexes (**4**)—(**9**).—These complexes were prepared employing either $[(3,5Me_2\text{-pz})N_2]BF_4$ or $[(ap)N_2]BF_4$ using the procedures described in the literature for the aryldiazenido analogues.[10–12] Microanalytical and i.r. data are summarised in Table 1. ^1H N.m.r.: $[Mo(CO)_2\{N_2(ap)\}\{HC(pz)_3\}]BF_4$ (**4**) (CD_2Cl_2, $SiMe_4$), δ 2.28 (s, 3 H, Me^3 of antipyrene nucleus), 3.24 (s, 3 H, Me^2 of antipyrene nucleus), 6.67 (s, br, 3 H, H^4 of pz groups), 7.44 (s, 5 H, Ph of antipyrene nucleus), 8.27, 8.50 (s, br, 1 H and 5 H, H^3 and H^5 of pz groups). The methine proton of the $HC(pz)_3$ ligand, which may give rise to a broad resonance,[9] was not observed. $[Mo(CO)_2\{N_2(3,5\text{-}Me_2\text{-pz})\}\{HB(pz)_3\}]$ (**5**) (CD_2Cl_2, $SiMe_4$), δ 2.4 (s, 6 H, Me^3 and Me^5 groups of pyrazolyldiazenido ligand), 6.2 (t, br, J 2.5 Hz, 3 H, H^4 of pz groups), 7.68 (m, br, 6 H, H^3 and H^5 of pz groups), 9.7 (s, vbr, 1 H, H^1 of pyrazolyldiazenido ligand) $[Mo(CO)_2\{N_2(ap)\}\{HB(pz)_3\}]$ (**6**) (CD_2Cl_2, $SiMe_4$), δ 2.2 (s, 3 H, Me^3 of antipyrene nucleus), 3.0 (s, 3 H, Me^2 of antipyrene nucleus), 6.2 (t, J 2.5 Hz, 3 H, H^4 of pz groups), 7.63, 8.05, 8.18 (apparent multiplet, 3 H; d, 2 H, J 2.5 Hz; d, 1 H, J 2.5 Hz; H^3 and H^5 of pz groups).

Preparation of 2,3-*Dimethyl*-1-*phenyl*-3-*pyrazolin*-5-*one*-4-*diazo*(*triphenyl*)*phosphonium Tetrafluoroborate*, $[PPh_3\{N_2(ap)\}]BF_4$ (**10**).—Triphenylphosphine (1.0 g, 3.81 mmol) was added to a solution of $[(ap)N_2]BF_4$ (1.15 g, 3.81 mmol) in acetone (*ca.* 30 cm^3). After 30 min the deep orange solution was concentrated to small volume and diluted with diethyl ether. The orange precipitate was recrystallised several times from acetone–diethyl ether to yield 1.3 g (60%) of pure (**10**) identical to the product isolated from the reaction of $[(ap)N_2]BF_4$ with $[Ni(CO)_2(PPh_3)_2]$ (see text) (Found: C, 61.75; H, 4.90; N, 10.00. $C_{29}H_{26}BF_4N_4OP$ requires C, 61.70; H, 4.60; N, 9.95%).

Preparation of $[Mn(CO)_2\{N_2(ap)\}(\eta\text{-}C_5H_4Me)]BF_4$ (**11**).—A stirred solution of $[Mn(CO)_3(\eta\text{-}C_5H_4Me)]$ (2.00 g, 9.2 mmol) in dry, N_2-saturated, thf (150 cm^3) was irradiated for 12 h using a Hanovia 100-W medium-pressure u.v. lamp with a quartz filter. The resulting solution of $[Mn(CO)_2(thf)(\eta\text{-}C_5H_4Me)]$[27] was cooled to −50 °C and solid $[(ap)N_2]BF_4$ (2.80 g, 9.3 mmol) was added slowly over *ca.* 30 min. The reaction mixture was allowed to warm slowly to room temperature and stirred for 6 h, after which the solvent was removed *in vacuo*. The residue was recrystallised from CH_2Cl_2–Et_2O to yield 2.22 g (49%) of the olive-green microcrystalline product (Found: C, 46.55; H, 4.05; N, 10.95. $C_{19}H_{18}BF_4MnN_4O_3$ requires C, 46.35; H, 3.70; N, 11.40%). I.r. (KBr disc): ν(CO) at 2 059vs, 2 010vs cm^{-1}; ν(NN) at 1 800s cm^{-1}; ν(CO, pyrazolinone) at 1 664m cm^{-1}.

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