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Transition metal derivatives of arenediazonium ions

XV *. The synthesis, chemistry and X-ray crystallographic characterisation of molybdenum(0) and tungsten(0) complexes containing the *cis*-$[M(NO)(N_2Ar)]^{2+}$ structural unit

M.E. Deane, F.J. Lalor **,

Department of Chemistry, University College, Cork (Ireland)

G. Ferguson **, **B.L. Ruhl and M. Parvez**

Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1 (Canada)

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Abstract

Synthetic procedures and preliminary chemical studies are described for four new types of Group VIa nitrosyl-arenediazo complex: $(\eta\text{-}C_5H_5)M(NO)(N_2Ar)Cl$ (VII), $(HBpz_3)M(NO)(N_2Ar)Cl$ (VIII), $[(HCpz_3)M(NO)(N_2Ar)Cl]^+$ (IX) and $[(\eta\text{-}C_5H_5)M(NO)(N_2Ar)(PPh_3)]^+$ (XIII). These complexes complete the homologous series containing the isoelectronic and quasi-isostructural fragments $[M(NO)_2]^{2+}$, $[M(NO)(N_2Ar)]^{2+}$ and $[M(N_2Ar)_2]^{2+}$ (M = Group VIa metal). IR spectroscopic studies of VII and VIII suggest that the hydrotris-(1-pyrazolyl)borato ligand in these complexes is a better π-acceptor than cyclopentadienide. Two of the new complexes have been characterised by X-ray crystallographic methods. Crystals of $(HBpz_3)Mo(NO)(N_2C_6H_4F\text{-}p)Cl$ (VIIIb) are triclinic, space group $P\bar{1}$ with four molecules in a unit cell of dimensions $a = 13.053(3)$, $b = 18.275(3)$, $c = 8.954(2)$ Å, $\alpha = 97.18(2)$, $\beta = 106.50(2)$, $\gamma = 88.53(2)°$. Crystals of $[(\eta\text{-}C_5H_5)Mo(NO)(N_2C_6H_4F\text{-}p)(PPh_3)]PF_6$, $[(XIIIc)]PF_6$, are also triclinic, space group $P\bar{1}$, with two formula units in a unit cell of dimensions $a = 11.526(1)$, $b = 13.875(2)$, $c = 10.873(2)$ Å, $\alpha = 108.37(2)$, $\beta = 105.82(10$, $\gamma = 103.00(1)°$. Both structures were determined by the heavy-atom method and refined to final R values of 0.030 (for 3812 observed reflections, VIIb) and 0.028 (for 3560 observed reflections $[(XIIIc)]PF_6$). There are two independent molecules of VIIIb in the asymmetric unit. Principal bond lengths

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* For part XIV see ref. 1.

** E mail address FJL STCH8002@IRUCCVAX
GF CHMFERG@UOGUELPH

are: VIIIb: Mo–N(nitrosyl) 1.767(4) and 1.789(4), Mo–N(arenediazo) 1.857(3) and 1.877(3), Mo–N(Pz) 2.158–2.200(4), Mo–Cl 2.424(1) and 2.428(1) Å; [(XIIIc)]PF_6: Mo–N(nitrosyl) 1.802(3), Mo–N(arenediazo) 1.876(3), Mo–P 2.487(1), Mo–C(C_5H_5) 2.318–2.371(4) Å.

Introduction

The *cis*-dinitrosyl fragment *cis*-$[M(NO)_2]^{2+}$ (M = Cr, Mo, W) is a prominent feature of Group VIa chemistry and complexes which contain this structure (particularly in combination with the cyclopentadienide anion) are known to have a rich and extensive chemistry [2]. *Cis*-$[M(NO)_2]^{2+}$ may be formally regarded as M^0 coordinated by two 2-electron donor nitrosonium cations. Since $[NO]^+$ and the arenediazonium cation, $[N_2Ar]^+$ are isoelectronic species [3], there exists a potentially homologous series of isoelectronic and quasi-isostructural (i.e. linear M–N–O, linear M–N–N) fragments *cis*-$[M(NO)_2 2]^{2+}$, *cis*-$[M(NO)(N_2Ar)]^{2+}$ and *cis*-$[M(N_2Ar)_2]^{2+}$. While Group VIa complexes containing the bis(arenediazo) fragment *cis*-$[M(N_2Ar)_2]^{2+}$ have been described by us [4] and by others [5], the only examples of Group VIa mixed nitrosyl-arenediazo complexes that we are aware of were described some years ago in a brief report from these laboratories [6]. In this paper we report in detail on the synthesis and preliminary chemical investigation of several Group VIa complexes containing this relatively rare * structural unit as well as the X-ray crystallographic characterisation of two of them.

Synthetic, spectroscopic and chemical studies

A simple and convenient strategy for the preparation of complexes of the desired type was suggested by the observation that nitrosyl chloride oxidatively displaces CO from the complexes (η-C_5H_5)$M(CO)_2(NO)$ (I, M = Cr, Mo, W) or ($RBpz_3$)$M(CO)_2(NO)$ (II, R = H, pz; M = Mo, W; pz ≡ 1-pyrazolyl) to yield the dinitrosyl complexes (η-C_5H_5)$M(NO)_2Cl$ (III) and ($RBpz_3$)$M(NO)_2Cl$ (IV) respectively [9,10]. We have found that the analogous arenediazo complexes (η-C_5H_5)$Mo(CO)_2(N_2Ar)$ (V) and ($HBpz_3$)$M(CO)_2(N_2Ar)$ (VI) (M = Mo, W) also react smoothly with NOCl to give new mixed nitrosyl-arenediazo complexes (η-C_5H_5)$Mo(NO)(N_2Ar)Cl$ (VII) and ($HBpz_3$)$M(NO)(N_2Ar)Cl$ (VIII) in excellent yield. A cationic analogue, $[(HCpz_3)Mo(NO)(N_2Ar)CL]^+$ (IX), was similarly prepared from $[(HCpz_3)Mo(CO)_2(N_2Ar)]^+$ (X) (Scheme 1).

The new complexes are orange-red crystalline solids which can be isolated in ca. 70% yield. They are unaffected by the laboratory atmosphere for extended periods of time either in the solid state or in polar organic solvents (in which they have good solubility). All complexes gave correct microanalytical data and produced well-resolved, correctly integrating, ^1H NMR spectra (Experimental section) indicative of the expected diamagnetism. The resonances of the protons at the 4-positions of the pyrazolyl rings in the hydrotris(1-pyrazolyl)borate and the tris(1-pyrazolyl)methane

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* A few complexes containing *cis*-$[M(NO)(N_2Ar)]^{n+}$ structural units are known for the later transition metals, e.g. $Mn(NO)(N_2Ar)(PPh_3)_2Cl$ ($n = 1$) [7] and $Fe(NO)(N_2Ar)(CO)(PPh_3)$ ($n = 0$) [8].

$$[LM(CO)_2(N_2Ar)]^{n+} \xrightarrow[CH_2Cl_2,\ -25\,^\circ C]{NOCL} [LM(NO)(N_2Ar)Cl]^{n+}$$

(V) (VII)

$L = \eta\text{-}C_5H_5$, $n = 0$
a, M = Mo; Ar = C_6H_5
b, M = Mo; Ar = C_6H_4F-*p*
c, M = Mo; Ar = C_6H_4F-*m*

(VI) (VIII)

$L = HBpz_3$, $n = 0$
a, M = Mo; Ar = C_6H_5
b, M = Mo; Ar = $C_{64}F$-*p*
c, M = Mo; Ar = C_6H_4F-*m*
d, M = W; Ar = C_6H_5

(X) (IX)

$L = HCpz_3$, $n = 1$
a, M = Mo; Ar = C_6H_5
b, M = Mo; Ar = C_6H_4F-*p*
c, M = Mo; Ar = C_6H_4F-*m*

Scheme 1

ligands of complexes VIII and IX respectively appear as three sharp well-separated apparent triplets in a 1/1/1 ratio. This attests to the asymmetry imposed by three non-identical *trans*-ligands in the formally octahedral coordination sphere and to the absence of rotation of $[HBpz_3]^-$ or $HCpz_3$ ligands about the HB $\cdots$ Mo or HC $\cdots$ Mo axes [11]. The pyrazolyl H(4) resonances of the cationic tris(1-pyrazolyl)methane complexes (IXa–c) all appear shifted by ca. 0.39 ppm to lower field compared to their neutral hydrotris(1-pyrazolyl)borate analogues (VIIIa–c). The resonance of the cyclopentadienyl protons in complexes (VIIa–c) occurs at ca. δ 6.24 ppm. The greater shielding observed for the cyclopentadienyl protons in the dinitrosyl analogue $(\eta\text{-}C_5H_5)Mo(NO)_2Cl$ (III) (δ 6.05 ppm [2]) may be understood in terms of increased effective π-electron withdrawal from the cyclopentadienide ring in the latter by the coordinated nitrosonium cation which is a more powerful π-acceptor than coordinated $[ArN_2]^+$ [12].

Solutions of complexes VII, VIII or IX in dichloromethane exhibit two strong IR bands and one band of variable intensity in the region 1735 to 1550 cm^{-1} (Table 1). Representative examples of each of the three classes of mixed nitrosyl-arenediazo complexes (i.e. VIIa, VIIIa and IXa) were prepared in which ^{15}N had been substituted for ^{14}N at the metal-bound nitrogen atom of the arenediazo ligand. Isotopic shifts of ca. 10–17 cm^{-1} were observed in the two lower-wavenumber bands in the 1735–1500 cm^{-1} region (i.e. ca. 1620, 1562 cm^{-1} for VII; ca. 1641, 1575 cm^{-1} for VIII (M = Mo); 1617, 1560 cm^{-1} for VIII (M = W) and ca. 1652, 1576 cm^{-1} for IX). These results show that both of these bands are associated with the arenediazo ligand and that there is kinematic coupling between ν(NN) and skeletal vibrations of the attached aromatic ring [12,13]. The band at highest wavenumber in the 1735–1530 cm^{-1} region (i.e. ca. 1673 cm^{-1} for VII; ca. 1713 for VIII (M = Mo); 1675 for VIII (M = W) and ca. 1729 cm^{-1} for IX is assigned to

Table 1

Infrared [a] and microanalytical data

Complex	ν(NO) (cm^{-1})	ν(NN) (cm^{-1})	Analysis (Found (calc) (%))			
			C	H	Cl	N
VIIa	1675s [b]	1623s, 1559m [b]	40.21 (39.84)	3.27 (3.04)	10.85 (10.69)	12.35 (12.67)
VIIb	1672s	1616s, 1567m	37.46 (37.79)	2.44 (2.59)	10.47 (10.14)	12.03 (12.02)
VIIc	1673s	1622s, 1560s	37.91 (37.79)	2.58 (2.59)	10.56 (10.14)	12.27 (12.02)
VIIIa	1711s [c]	1642s, 1573s [c]	37.81 (37.57)	3.42 (3.15)	7.51 (7.39)	26.69 (26.29)
VIIIb	1713s	1641s, 1572w	36.39 (36.21)	2.92 (2.84)	7.25 (7.13)	25.36 (25.34)
VIIIc	1715s	1641s, 1580s	36.48 (36.21)	2.97 (2.84)	6.99 (7.13)	25.73 (25.34)
VIIId	1675s	1617s, 1560s	32.08 (31.75)	2.44 (2.66)	6.04 (6.25)	22.65 (22.21)
IXa [d]	1727s [e]	1653s, 1567w [e]	30.84 (30.71)	2.91 (2.42)	5.37 (5.67)	20.08 (20.15)
IXb [f]	1729s	1652s, 1581w	32.43 (32.82)	2.46 (2.41)	6.26 (6.05)	21.37 (21.33)
IXc [f]	1730s	1652s, 1579m	32.67 (32.82)	2.53 (2.41)	6.54 (6.05)	21.80 (21.33)
XIIIa [d]	1705s [g]	1651s, 1563m [g]	49.47 (49.52)	4.00 (3.58)		5.82 (5.97)
XIIIb [d]	1708s	1654s, 1572w	49.93 (50.22)	4.11 (3.79)		5.75 (5.86)
XIIIc [f]	1707s	1650s, 1579s	52.17 (52.52)	3.83 (3.65)		6.54 (6.33)
XIIId [f]	1708s	1649s, 1575s	52.48 (52.52)	3.89 (3.65)		6.50 (6.33)

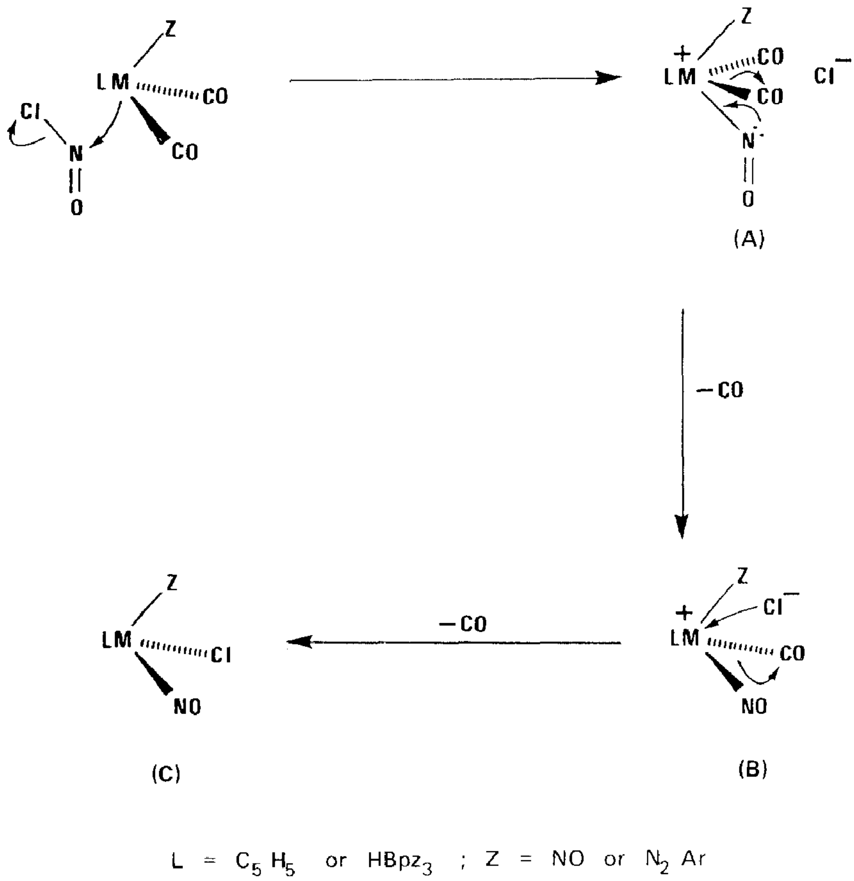
[a] Solution in CH_2Cl_2 s = strong, m = medium, w = weak. [b] On ^{15}N labelling (see text) these bands shift to 1671, 1610 and 1542 cm^{-1} respectively. [c] Shifted to 1706, 1627 and 1563 cm^{-1} on ^{15}N labelling. [d] PF_6^- salt. [e] Shifted to 1721, 1638 and 1561 on ^{15}N labelling. [f] BF_4^- salt. [g] Shifted to 1699, 1631 and 1558 on ^{15}N labelling.

ν(NO). Small shifts to lower wavenumber (ca. 4–5 cm^{-1}) in the ν(NO) bands of the species which had been isotopically labelled in the arenediazo ligand indicate that there is weak vibrational coupling between the adjacent nitrosyl and arenediazo ligands.

The cyclopentadienyl and hydrotris(1-pyrazolyl)borato nitrosylarenediazo complexes VII and VIII may be regarded as being derived from the dinitrosyl species (η-C_5H_5)Mo(NO)$_2$Cl (III) and (HBpz$_3$)Mo(NO)$_2$Cl (IV) by the formal replacement of one $[NO]^+$ ligand with an isoelectronic arenediazonium cation. In line with the poorer π-acceptor character of $[N_2Ar]^+$ vis-a-vis $[NO]^+$ this formal substitution process is accompanied by a decrease of ca. 29–40 cm^{-1} in ν(NO) of the arenediazo-nitrosyl complexes VII and VIII compared to $\nu(NO)_{av}$ in the dinitrosyl precursors [2,10]. For the related pairs of complexes (η-C_5H_5)Mo(NO)$_2$Cl (III) and (η-C_5H_5)Mo(NO)(N$_2$Ar)Cl (VIIa–c) (or (HBpz$_3$)Mo(NO)$_2$Cl (IV) and (HBpz$_3$)-Mo(NO)(N$_2$Ar)Cl (VIIIa–c)) we have observed that formal replacement of $[NO]^+$

by $[N_2Ar]^+$ consistently produced a smaller shift of $\nu(NO)$ to lower wavenumbers in the hydrotris(1-pyrazolyl)borate complexes than in their cyclopentadienyl analogous. This implies that the increased metal electron density in the fragment $[Mo(NO)(N_2Ar)]^{2+}$ – vis-a-vis the isoelectronic $[Mo(NO)_2]^{2+}$ – is more efficiently absorbed by the pyrazolylborate anion than by the cyclopentadienide ligand. For related pairs of cyclopentadienyl and pyrazolylborato carbonyl complexes $\nu(CO)$ invariably occurs to lower wavenumber in the latter. This would seem to indicate that the pyrazolylborate ligands are better net electron donors than cyclopentadienide. Indeed it has long been assumed that pyrazolylborate ligands bonded to transition metals exclusively as σ-donors [14]. More recently, however, Curtis and Shiu have presented theoretical calculations and some experimental evidence in favour of the argument that the hydrotris(1-pyrazolyl)borate anion is actually a slightly better π-acceptor than $[C_5H_5]^-$ [15]. The trends in $\nu(NO)$ discussed here support this conclusion which is further reinforced by the fact that formal substitution of $[\eta\text{-}C_5H_5]^-$ by $[HBpz_3]^-$ on the $[Mo(NO)_2Cl]^+$ fragment (i.e. complexes III and IV) or on the $[Mo(NO)(N_2Ar)Cl]^+$ fragment (i.e. complexes VII and VIII) produces an increase of 28 and ca. 40 cm^{-1} in $\nu(NO)_{av}$ and $\nu(NO)$ respectively. A similar, but smaller, increase is observed in the bands associated with the arenediazo ligands in VII and VIII. If – as these and other recent results [15] suggest – the $[HBpz_3]^-$ ligand is a more effective π-acceptor than the cyclopentadienide anion it remains to be explained why this phenomenon is not reflected in the observed trends in $\nu(CO)$. The $\nu(NO)$ and (to a lesser extent) the $\nu(NN)$ bands in the cationic tris(1-pyrazolyl)methane complexes (IXa–c) are, as anticipated, shifted to higher wavenumbers in comparison to the corresponding neutral hydrotris(1-pyrazolyl)borate compounds. The single tungsten complex studied, $(HBpz_3)W(NO)(N_2C_6H_5)$-Cl (VIIId), exhibits a $\nu(NO)$ band which is displaced 36 cm^{-1} to lower wavenumber with respect to the molybdenum analogue VIIIa. The two IR bands associated with $\nu(NN)$ are shifted in the same direction by 25 and 13 cm^{-1} respectively. These trends reflect the increased π-donor capacity of tungsten and are slightly greater than the shifts in $\nu(NO)_{av}$ observed for $(\eta\text{-}C_5H_5)M(NO)_2Cl$ (III, M = Mo, W) [2].

A plausible mechanism for the nitrosation of complexes of the type $LM(CO)_2(NO)$ and $LM(CO)_2(N_2Ar)$ ($L = [C_5H_5]^-$ or $[HBpz_3]^-$) by NOCl is illustrated in Scheme 2. We propose that electrophilic attack of NOCl on the substrate generates a cationic intermediate (A) which contains an angular nitrosyl ligand, formally $[NO]^-$. Conversion of $[NO]^-$ to $[NO]^+$ (with concommitant intramolecular transfer of a pair of electrons to the metal and expulsion of CO) produces a second cationic intermediate (**B**) in which the nitrosyl ligand is linear. Nucleophilic attack of the chloride counter-anion upon the cation **B** with displacement of a second CO ligand leads to the final neutral product (**C**). In an attempt to halt the reaction at an intermediate stage – and to detect or isolate the cationic species **A** or **B** – we have investigated the nitrosation of arenediazo complexes by nitrosonium salts such as $[NO]BF_4$ and $[NO]PF_6$ which contain weakly nucleophilic counteranions. All three of the substrates studied, i.e. $(\eta\text{-}C_5H_5)M(CO)_2(N_2Ar)$ (V), $(HBpz_3)Mo(CO)_2(N_2Ar)$ (VI) and $[(HCpz_3)Mo(CO)_2(N_2Ar)]^+$ (X) reacted vigorously with $NOPF_6$ at $-78\,^\circ C$ in CH_2Cl_2 but we were unable to isolate any characterisable products following work-up at room temperature. This is an unexpected result since cations of the type $[(\eta\text{-}C_5H_5)M(NO)_2(L')]^+$ (XI, M = Mo, W; L′ = CO, solvent, etc.) are known and isolable (albeit reactive) species [2]. The



Scheme 2

$[Mo(NO)(N_2Ar)]^{2+}$ fragment, being more electron-rich than $[Mo(NO)_2]^{2+}$, would be expected to stabilise the bonding to π-acceptor co-ligands such as carbon monoxide more efficiently than the latter. On the assumption that insufficient back-bonding to the carbonyl ligand in the hypothetical cations of type **B** (Scheme 2) was responsible for our failure to isolate these species we reasoned that replacement of CO by a ligand of predominantly σ-donor character should produce analogous cations of greater stability. In agreement with this prediction more successful results were obtained on nitrosation of the phosphine-substituted arenediazo complexes $(\eta\text{-}C_5H_5)Mo(PPh_3)(CO)(N_2Ar)$ (XII) which reacted with $NOBF_4$ or $NOPF_6$ in dry acetone at −78°C to yield orange air-stable salts of the cation $[(\eta\text{-}C_5H_5)Mo(PPh_3)(NO)(N_2Ar)]^+$ (XIII) in ca. 70% yield (Scheme 3). Complexes of type XIII (which may be regarded as phosphine-stabilised derivatives of the cationic intermediate **B** in Scheme 3) exhibit strong $\nu(NO)$ bands at ca. 1702 cm^{-1} as well as bands at ca. 1651 and 1572 cm^{-1} which were identified as arising from the coordinated arenediazo ligand by ^{15}N labelling experiments (Table 1). Isotopic labelling also showed evidence for the weak vibrational coupling between adjacent nitrosyl and arenediazo ligands which appears to be characteristic of the *cis*-$[M(NO)(N_2Ar)]^{2+}$ fragment. As would be anticipated, the $\nu(NO)$ and $\nu(NN)$ bands in the cationic XIII are displaced to higher wave-number compared to those of

$$\underset{\text{(XII)}}{(\eta\text{-}C_5H_5)Mo(CO)(N_2Ar)(PPh_3)} \xrightarrow[\text{Acetone, } -78\,^{\circ}\text{C}]{[NO]^+} \underset{\text{(XIII)}}{[(\eta\text{-}C_5H_5)Mo(NO)(N_2Ar)(PPh_3)]^+}$$

a, Ar = C_6H_5
b, Ar = $C_6H_4CH_3$-*p*
c, Ar = C_6H_4F-*p*
d, Ar = C_6H_4F-*m*

Scheme 3

(η-C_5H_5)Mo(NO)(N_2Ar)Cl (VII). The effect is more marked for ν(NO) (+34 cm^{-1}) and for the arenediazo band at ca. 1651 cm^{-1} (+31 cm^{-1}) than it is for the arenediazo band at ca. 1572 cm^{-1} (+10 cm^{-1}). However the nitrosyl stretching frequencies in complexes XIIIa–d are ca. 44 cm^{-1} lower than $\nu(NO)_{av}$ for the related dinitrosyl cation $[(\eta\text{-}C_5H_5)Mo(NO)_2(PPh_3)]^+$ (XIV) [2] again reflecting the reduced π-acceptor capacity of arenediazonium versus nitrosonium cations. The ^{1}H NMR spectra of compounds XIIIa–d (Experimental section) exhibit resonances for the cyclopentadienyl protons at ca. δ 6.00 ppm and these ring protons are therefore more shielded than the corresponding protons in the analogous dinitrosyl (XIV (δ 6.38 ppm [2]) which reverses the trend exhibited by the neutral chlorides III and VII (see above). Although coupling between the cyclopentadienide ring protons and the triphenylphosphine phosphorus atom was observed in the dinitrosyl complex XIV (^3J(PH) = 1.1 Hz) no such coupling was detected in the nitrosyl-arenediazo analogous XIIIa–d.

On the basis of the known chemical versatility of the dinitrosyl halides (η-C_5H_5)M$(NO)_2$Cl (III; M = Cr, Mo, W) [2,16] we anticipated that the coordinated chloride in $[LMo(NO)(N_2Ar)Cl]^{n+}$ (VII, L = η-C_5H_5, $n = 0$; VIII, L = $HBpz_3$, $n = 0$; IX, L = $HCpz_3$, $n = 1$) would be readily displaced by nucleophiles. However, VII and VIII were completely unaffected by refluxing with C_5H_5Tl or KCN in acetone and VIII was also recovered unchanged after treatment with PPh_3 or CF_3CO_2Ag under similar conditions. Complex VIII was equally unreactive towards CH_3MgI in boiling ether or towards CH_3CN and $AlCl_3$ in boiling benzene. Neither could any reaction be observed between the cationic tris(1-pyrazolyl)methane complex IX and KCN in boiling acetone or with either C_5H_5Tl or PPh_3 in refluxing tetrahydrofuran. The lack of reactivity shown by VII, VIII and IX is surprising. Stronger binding of the co-ligands by the relatively electron-rich $[M(NO)(N_2Ar)]^{2+}$ fragment together with (for VIII and IX) steric protection by the bulky hydrotris(1-pyrazolyl)borate and tris(1-pyrazolyl)methane ligands may be among the causative factors involved.

The cationic bis-nitrosyl complex $[(\eta\text{-}C_5H_5)M(NO)_2(L')]^+$ (XI, M = Mo, W; L′ = CO, solvent) has been shown by Stewart and co-workers [2] to undergo facile replacement of L by either neutral or anionic nucleophiles. We have found the analogous bis-arenediazo cation $[\eta\text{-}C_5H_5)M(N_2Ar)_2(PPh_3)]^+$ (XIV, M = Mo, W) to be even more labile. Both phosphine and cyclopentadienide ligands are cleaved off by nucleophiles and complexes of type XIV are effective reagents for introducing the *cis*-$[M(N_2Ar)_2]^{2+}$ fragment into a variety of coordination environments [4a]. The reactivity of the nitrosyl-arenediazo cation $[(\eta\text{-}C_5H_5)Mo(NO)(N_2Ar)(PPh_3)]^+$ (XIII) might be expected to be intermediate between that of XI and XIV but the results of our preliminary studies have not been entirely clear-cut. Rapid colour change from orange to reddish-brown was observed when acetone solutions of XIIIb (Ar = $C_6H_4CH_3$-*p*) were treated with either one equivalent of $[(C_6H_5)_3PNP(C_6H_5)_3]X$ (X = Cl, Br, CN) or with two equivalents of TlAcac. However no characterisable products could be isolated form the reaction mixtures. A similar colour change was noted when XIIIb was treated with two equivalents of the sodium salt of the 1,1-dicyanoethylene-2,2-dithiolate dianion ($[(CN)_2C{=}CS_2]^{2-}$ ≡ $dcdt^{2-}$) and from this reaction we were able to isolate the new dianionic nitrosyl-arenediazo complex $[Mo(NO)(N_2C_6H_4CH_3\text{-}p)(dcdt)_2]^{2-}$ (XIV) as its reddish-brown air-stable tetraphenylphosphonium salt. By analogy with the known bis-arenediazo analogues [4a] we assume that XIV has octahedral geometry with mutually *cis* nitrosyl and arenediazo ligands. The IR spectrum of $[(C_6H_5)_4P]_2[(XIV)]$ (Experimental section) shows a strong band at 1614 cm^{-1} (tentatively assigned to ν(NO)) and a number of medium-intensity bands in the region 1550–1680 cm^{-1}. Some or all of the latter may be associated with ν(NN) but in the absence of isotopic labelling studies a definite assignment is not possible. We conclude that complex XIII has at least limited potential as a source of the *cis*-$[Mo(NO)(N_2Ar]^{2+}$ fragment and our studies of this system are continuing.

Crystallographic studies

We have determined the structures of the neutral complex VIIIb by X-ray crystallographic methods. The results provide the first structural details of complexes containing the *cis*-$[Mo(NO)(N_2Ar)]^{2+}$ molecular fragment. Crystal and refinement data for the two complexes are summarised in Table 2. The unit cell of the hydrotris(1-pyrazolyl)borato complex $(HBpz_3)MO(NO)(N_2C_6H_4F\text{-}p)Cl$ (VIIIb) contains two independent molecules in the asymmetric unit. One of these, together with the crystallographic numbering scheme is shown in Fig. 1; the other molecule has a very similar conformation and differs from the first mainly in the orientation of the plane of the (arenediazo) *p*-substituted phenyl ring (torsion angles N(2)–N(3)–C(1)–C(2) 5.5′ in molecule 1, −12.9° in molecule 2). Presumably such small differences serve to minimize packing interactions. Bond lengths and angles for VIIIb are summarised in Table 3. The crystal structure of $[(\eta^5\text{-}C_5H_5)Mo(NO)(N_2C_6H_4F\text{-}p)(PPh_3)][PF_6]$ $[(XIIIc)]PF_6$ consists of discrete ions with two formula units in the unit cell. The nearest anion ··· cation approach (between F(6) and C(11)) is 3.207 Å. A view of the cation with the atom labelling scheme is presented in Fig. 2, and principal dimensions are given in Table 4. A complete list of dimensions for $[(XIIIc)]PF_6$ has been deposited.

The analysis confirms the structures proposed for complexes VIIIb and $[(XIIIc)]PF_6$. Both compounds contain *cis*-$[Mo(NO)(N_2C_6H_4F\text{-}p)]^{2+}$ molecular fragments in a formally octahedral coordination sphere, the remaining coordination positions of which are occupied by three nitrogen atoms of the $[HBpz_3]^-$ ligand and a covalently bound chloride moiety in VIIIb or the cyclopentadienide group and a triphenylphosphine ligand in $[(XIIIc)]PF_6$.

The arenediazo ligand has Mo–N–N angles of 170.7(4) and 163.4(3)° in VIIIb and 178.3(3)° in $[(XIIIc)]PF_6$ and N–N–C angles of 119.5(4) and 119.3(3) in VIIIb and 122.9(3)° in $[(XIIIc)]PF_6$ corresponding to an essentially "singly-bent" geometry for both complexes. There are no untoward inter- or intramolecular contacts in

(*continued on p. 223*)

Table 2

Crystal and refinement data for $(HBpz_3)Mo(NO)(N_2C_6H_4F\text{-}p)Cl$ (VIIIb) and $[(\eta\text{-}C_5H_5)Mo(NO)(N_2C_6H_4F\text{-}p)(PPh_3)]PF_6$ $[(XIIIc)]PF_6$

Formula	$C_{15}H_{14}BClMoN_9O$	$C_{29}H_{24}F_7MoN_3OP_2$
F.W.	478.5	721.4
Crystal class	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Crystal dimensions (mm)	0.15×0.18×0.27	0.12×0.16×0.25
a (Å)	13.053(3)	11.526(1)
b (Å)	18.275(3)	13.875(2)
c (Å)	8.954(2)	10.873(2)
α (°)	97.18(2)	108.37(2)
β (°)	106.50(2)	105.82(2)
γ (°)	88.53(2)	103.00(1)
V (Å^3)	2031.7	1492.8
D_c (g dm^{-3})	1.38	1.60
Z	4	2
$F(000)$	992	724
μ (cm^{-1})	7.2	5.4
Total number of independent reflections	4649	4662
Number of reflection with $I > 3\sigma(I)$	2812	3560
$2\theta_{max}$ (°)	40	48
Final R	0.030	0.028
Final R_w	0.042	0.031

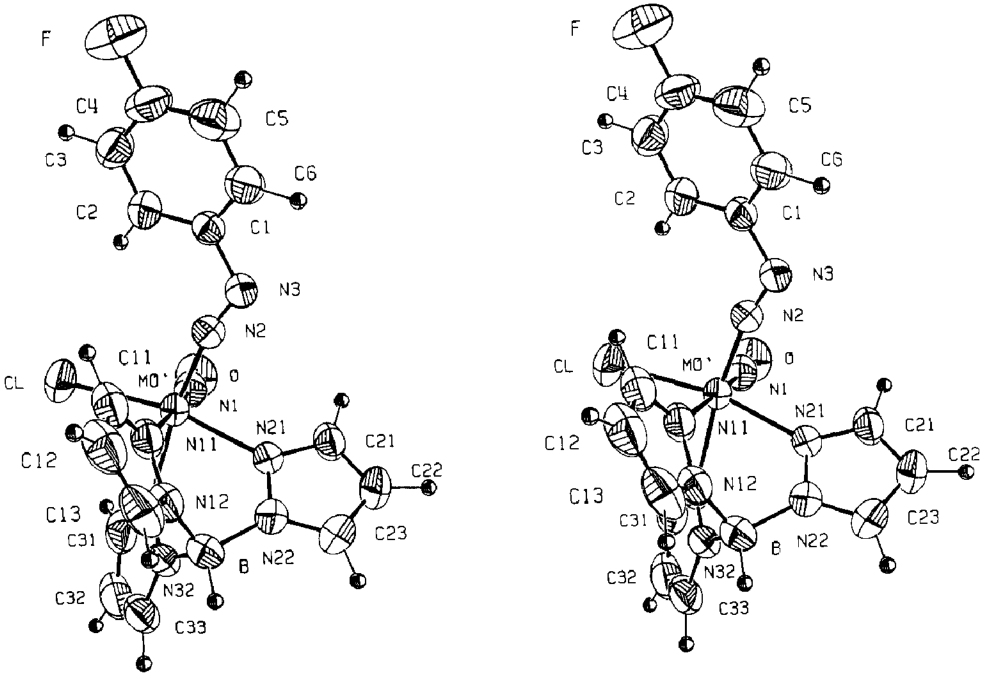


Fig. 1. A view of molecule VIIIb with the crystallographic numbering scheme; ellipsoids are at the 50% level.

Table 3

Bond lengths and bond angles in $(HBpz_3)Mo(NO)(N_2C_6H_4F\text{-}p)Cl$ (VIIIb)

	Molecule 1	Molecule 2
(a) Bond lengths (Å)		
Mo–Cl	2.428(1)	2.424(1)
Mo–N(1)	1.789(4)	1.767(4)
Mo–N(2)	1.857(3)	1.877(3)
Mo–N(11)	2.192(3)	2.200(4)
Mo–N(21)	2.158(3)	2.166(3)
Mo–N(31)	2.190(2)	2.184(3)
N(1)–O	1.171(6)	1.192(6)
N(2)–N(3)	1.206(5)	1.196(5)
N(3)–C(1)	1.422(5)	1.432(5)
C(1)–C(2)	1.380(7)	1.380(6)
C(1)–C(6)	1.391(6)	1.380(7)
C(2)–C(3)	1.367(6)	1.375(6)
C(3)–C(4)	1.378(7)	1.371(7)
C(4)–C(5)	1.363(11)	1.359(8)
C(4)–F	1.340(6)	1.356(5)
C(5)–C(6)	1.371(7)	1.379(6)
N(11)–N(12)	1.360(4)	1.358(4)
N(11)–C(11)	1.337(4)	1.332(6)
N(12)–C(13)	1.342(5)	1.350(7)
N(12)–B	1.527(5)	1.532(7)
C(11)–C(12)	1.386(7)	1.368(8)
C(12)–C(13)	1.362(5)	1.371(7)
N(21)–N(22)	1.368(5)	1.366(4)
N(21)–C(21)	1.338(6)	1.321(5)
N(22)–C(23)	1.346(6)	1.334(6)
N(22)–B	1.531(5)	1.541(6)
C(21)–C(22)	1.365(9)	1.383(6)
C(22)–C(23)	1.378(9)	1.373(6)
N(31)–N(32)	1.354(4)	1.366(6)
N(31)–C(31)	1.339(5)	1.332(7)
N(32)–C(33)	1.339(4)	1.338(6)
N(32)–B	1.535(6)	1.521(8)
C(31)–C(32)	1.373(5)	1.376(7)
C(32)–C(33)	1.370(6)	1.358(12)
(b) Bond angles (°)		
Cl–Mo–N(1)	94.3(1)	91.5(1)
Cl–Mo–N(2)	98.6(1)	100.2(1)
Cl–Mo–N(11)	86.6(1)	85.9(1)
Cl–Mo–N(21)	164.3(1)	165.7(1)
Cl–Mo–N(31)	86.6(1)	89.1(1)
N(1)–Mo–N(2)	92.2(2)	94.8(2)
N(1)–Mo–N(11)	178.6(1)	177.2(2)
N(1)–Mo–N(21)	96.2(2)	98.6(1)
N(1)–Mo–N(31)	96.0(1)	95.3(2)
N(2)–Mo–N(11)	88.7(1)	86.5(1)
N(2)–Mo–N(21)	92.6(1)	89.2(1)
N(2)–Mo–N(31)	170.0(1)	166.0(2)
N(11)–Mo–N(21)	82.7(1)	83.9(1)
N(11)–Mo–N(31)	83.0(1)	83.7(1)
N(21)–Mo–N(31)	80.8(1)	79.8(1)

Table 3 (continued)

	Molecule 1	Molecule 2
(b) Bond angles (°)		
Mo–N(1)–O	178.3(3)	175.8(3)
Mo–N(2)–N(3)	170.7(4)	163.4(3)
Mo–N(11)–N(12)	120.9(2)	121.4(3)
Mo–N(11)–C(11)	131.8(3)	131.7(3)
Mo–N(21)–N(22)	121.2(2)	120.6(2)
Mo–N(21)–C(21)	131.9(4)	132.5(3)
Mo–N(31)–N(32)	121.1(2)	119.8(3)
Mo–N(31)–C(31)	132.1(3)	132.7(3)
N(2)–N(3)–C(1)	119.5(4)	119.3(3)
N(3)–C(1)–C(2)	123.5(4)	122.5(4)
N(3)–C(1)–C(6)	115.4(5)	116.3(4)
C(2)–C(1)–C(6)	121.1(4)	121.2(4)
C(1)–C(2)–C(3)	120.0(4)	119.5(4)
C(2)–C(3)–C(4)	117.8(5)	117.8(4)
C(3)–C(4)–C(5)	123.3(5)	124.1(4)
C(3)–C(4)–F	118.1(6)	117.9(4)
C(5)–C(4)–F	118.6(5)	118.0(5)
C(4)–C(5)–C(6)	119.0(5)	117.8(5)
C(5)–C(6)–C(1)	118.7(6)	119.6(4)
C(11)–N(11)–N(12)	107.0(3)	107.0(4)
N(11)–N(12)–C(13)	108.8(3)	108.6(4)
N(11)–N(12)–B	120.5(3)	119.3(4)
C(13)–N(12)–B	130.3(3)	132.1(4)
N(11)–C(11)–C(12)	109.8(3)	108.5(4)
C(11)–C(12)–C(13)	105.2(4)	105.3(5)
C(12)–C(13)–N(12)	109.2(4)	110.5(4)
C(21)–N(21)–N(22)	106.9(4)	106.7(3)
N(21)–N(22)–C(23)	109.4(4)	108.6(3)
N(21)–N(22)–B	120.7(3)	120.5(3)
C(23)–N(22)–B	129.9(4)	130.8(4)
N(21)–C(21)–C(22)	109.6(5)	111.0(3)
C(21)–C(22)–C(23)	106.8(5)	104.1(4)
C(22)–C(23)–N(22)	107.3(5)	109.5(4)
C(31)–N(31)–N(32)	106.5(3)	107.4(3)
N(31)–N(32)–C(33)	109.5(3)	108.8(5)
N(31)–N(32)–B	120.4(3)	121.1(3)
C(33)–N(32)–B	130.0(3)	129.9(5)
N(31)–C(31)–C(32)	110.2(4)	108.8(6)
C(31)–C(32)–C(33)	105.4(3)	106.8(6)
C(32)–C(33)–N(32)	108.4(3)	108.3(5)
N(12)–B–N(22)	108.5(3)	108.1(4)
N(12)–B–N(32)	108.1(3)	109.6(4)

the molecules of VIIIb which could be held responsible for the noticeable deviation of the Mo–N–N angles of this complex from the 180° expected for an idealised singly-bent arenediazo ligand. The deviation from linearity may reflect an asymmetry in the interaction between the arenediazo $\pi^{\star}$ and molybdenum 4*d* orbitals and/or crystal-packing effects. Although the N–N–C(aryl) angles in both complexes are close to the ideal 120° it is interesting to note that the ligand with the more nearly linear Mo–N–N structure has also the largest N–N–C angle. Sutton

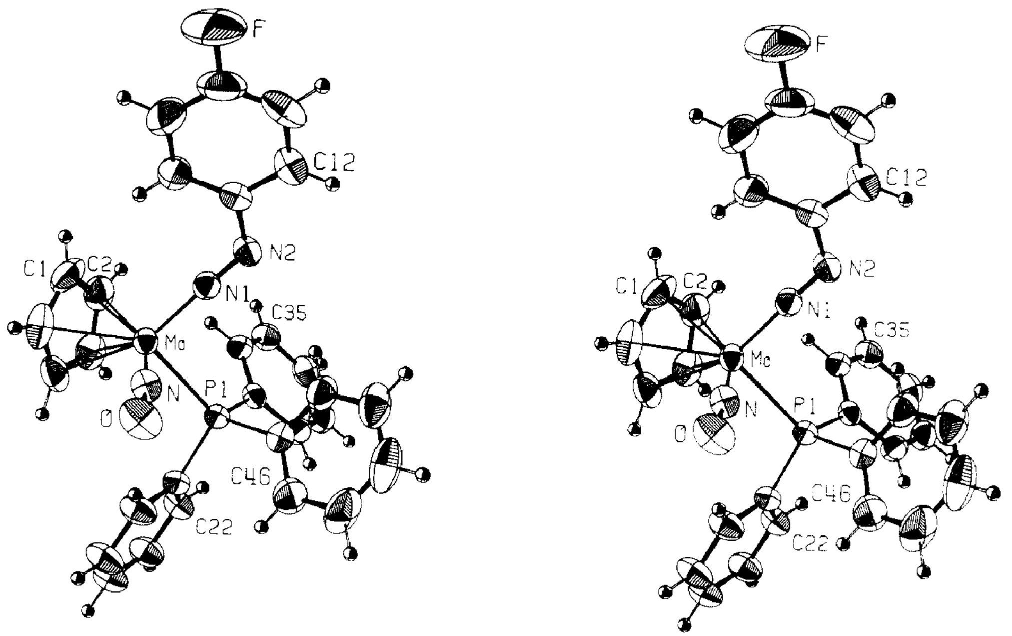


Fig. 2. A view of cation XIIIc with the crystallographic numbering scheme: ellipsoids are at the 50% level.

and co-workers [19] have proposed that the slight opening of this angle which has been observed in several singly-bent arenediazo complexes serves to minimize unfavourable non-bonded contacts between an *ortho*-hydrogen on the arenediazo aryl ring and the metal-bound nitrogen atom (N_α) of the M–N–N–Ar structure (Fig. 3). If such an effect is important in VIIIb and [(XIIIc)]PF_6 we would predict that, as observed, the latter would have the larger N–N–C(aryl) angle since the Mo–N–N bending in VIIIb is such as to minimise the *ortho*-H · · · N_α interaction. In this context we note that there is angle-bending at the diazo-bound carbon of the aryl ring in both VIIIb (N(3)–C(1)–C(2), 123.5(4), 122.5(4); N(3)–C(1)–C(6) 115.4(5), 116.3(4)°) and in[(XIIIc)]PF_6 (N(2)–C(11)–C(16), 122.9(3); N(2)–C(11)–C(12), 115.6(3°). In both cases the direction of the angle-bending is such as to minimise *ortho*-H · · · N_α interaction.

The Mo–N(diazo) distances of 1.857(3) and 1.877(3) Å in VIIIb and 1.876(3) Å in [(XIIIc)]PF_6 are significantly longer than the corresponding distances of 1.826(3) and 1.834(3) Å found in (η-$CH_3C_5H_4$)Mo($N_2C_6H_5F$-*p*)$_2$Cl (XV) [4b] or the 1.832(3) Å reported for ($HBpz_3$)Mo($N_2C_6H_4CH_3$-*p*)$_2$F (XVI) [17]. The decrease in Mo · · · N(diazo) bond-order in VIIIb and [(XIIIc)]PF_6 which may be inferred from

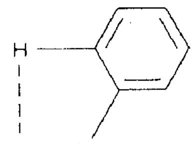


Fig. 3. A schematic diagram to show the unfavorable *ortho*-hydrogen to metal-bound nitrogen atom interaction.

Table 4

Principal dimensions for $[(\eta\text{-}C_5H_5)Mo(NO)(N_2C_6H_4F\text{-}p)(PPh_3)]PF_6$ $[(XIIIc)]PF_6$

(a) Bond lengths (Å)

Mo-P(1)	2.487(1)	N(1)-N(2)	1.198(4)
Mo-N	1.802(3)	N(2)-C(11)	1.435(4)
Mo-N(1)	1.876(3)	C(11)-C(12)	1.378(5)
Mo-C(1)	2.353(4)	C(11)-C(16)	1.365(5)
Mo-C(2)	2.371(4)	C(12)-C(13)	1.382(6)
Mo-C(3)	2.357(4)	C(13)-C(14)	1.341(7)
Mo-C(4)	2.333(4)	C(14)-C(15)	1.356(7)
Mo-C(5)	2.318(4)	C(15)-C(16)	1.381(6)
		F-C(14)	1.361(5)
C(1)-C(2)	1.418(6)		
C(1)-C(5)	1.410(6)		
C(2)-C(3)	1.389(6)	N-O	1.173(4)
C(3)-C(4)	1.402(6)		
C(4)-C(5)	1.385(6)		

(b) Bond angles (°)

P(1)-Mo-N	87.7(1)	N-Mo-C(2)	154.0(1)
P(1)-Mo-N(1)	96.7(1)	N-Mo-C(3)	131.5(1)
N-Mo-N(1)	95.2(1)	N-Mo-C(4)	99.8(1)
P(1)-Mo-C(1)	142.2(1)	N-Mo-C(5)	95.9(1)
P(1)-Mo-C(2)	108.1(1)	N(1)-Mo-C(1)	99.8(1)
P(1)-Mo-C(3)	87.0(1)	N(1)-Mo-C(2)	103.0(1)
P(1)-Mo-C(4)	100.6(1)	N(1)-Mo-C(3)	133.4(1)
P(1)-Mo-C(5)	135.1(1)	N(1)-Mo-C(4)	157.5(1)
N-Mo-C(1)	124.0(2)	N(1)-Mo-C(5)	127.2(2)
Mo-P(1)-C(21)	110.1(1)	N(2)-C(11)-C(12)	115.6(3)
Mo-P(1)-C(31)	118.4(1)	N(2)-C(11)-C(16)	122.9(3)
Mo-P(1)-C(41)	111.6(1)	C(12)-C(11)-C(16)	121.6(4)
Mo-N-O	173.1(3)	C(11)-C(12)-C(13)	118.5(4)
Mo-N(1)-N(2)	178.3(3)	C(12)-C(13)-C(14)	119.0(4)
Mo-C(1)-C(2)	73.2(2)	C(13)-C(14)-C(15)	123.4(4)
Mo-C(1)-C(5)	71.1(2)	F-C(14)-C(13)	118.5(5)
Mo-C(2)-C(1)	71.8(2)	F-C(14)-C(15)	118.0(5)
Mo-C(2)-C(3)	72.4(2)	C(14)-C(15)-C(16)	118.3(5)
Mo-C(3)-C(2)	73.5(2)	C(11)-C(16)-C(15)	119.2(4)
Mo-C(3)-C(4)	71.7(2)		
Mo-C(4)-C(3)	73.5(2)	C(1)-Mo-C(2)	34.9(1)
Mo-C(4)-C(5)	72.1(2)	C(1)-Mo-C(3)	57.3(2)
Mo-C(5)-C(1)	73.8(2)	C(1)-Mo-C(4)	57.8(2)
Mo-C(5)-C(4)	73.3(2)	C(1)-Mo-C(5)	35.1(2)
C(2)-C(1)-C(5)	107.6(4)	C(2)-Mo-C(3)	34.2(1)
C(1)-C(2)-C(3)	107.0(4)	C(2)-Mo-C(4)	57.8(1)
C(2)-C(3)-C(4)	109.3(4)	C(2)-Mo-C(5)	58.3(1)
C(3)-C(4)-C(5)	107.8(4)	C(3)-Mo-C(4)	34.8(1)
C(1)-C(5)-C(4)	108.3(4)	C(3)-Mo-C(5)	57.6(1)
N(1)-N(2)-C(11)	122.9(3)	C(4)-Mo-C(5)	34.7(1)

these results presumably reflects the inability of the arenediazo ligand to compete effectively with the strongly electron withdrawing $[NO]^+$ ligand for the available metal *d*-electron density. The NN bond lengths of the arenediazo groups (1.206(5), 1.196(5) in (VIIIb) and 1.198(4) Å in [(XIIIc)]PF_6) are within the range previously reported for this ligand [4b,17,18]. Clearly the NN bond length is not sensitive to the changes in the Mo · · · N (and hence N · · · N) bond order discussed above.

The Mo–N(nitrosyl) bond lengths (1.789(4), 1.767(4) (VIIIb); 1.802(3) Å [(XIIIc)]PF_6) lie within the range 1.70–1.80(2) Å reported for a variety of Mo-nitrosyl complexes. The Mo–N–O angles are essentially linear in VIIIb (178.3(3), 175.8(3)°); in [(XIIIc)]PF_6 the angle is 173.1° and is bent in such a direction as to minimize intramolecular interaction with an adjacent phenyl ring of the triphenylphosphine ligand. In VIIIb the Mo–Cl distances (2.428(1), 2.424(1) Å) are typical of Mo^{II} · · · Cl bond lengths (2.42–2.56 Å [20]) although longer than the 2.387(1) Å found in the bis(arenediazo) complex (η-$CH_3C_5H_4$)Mo($N_2C_6H_5F$-*p*)$_2$Cl (XV) [4b].

In the complex [(XIIIc)]PF_6 the Mo–P(phosphine) distance (2.487(1) Å) is in good agreement with those reported for related systems [21–24]. The Mo–C(cyclopentadienyl) distances are typical of the distances reported for a number of Mo complexes containing this ligand [4b, and references therein]. The dimensions within the triphenylphosphine ligand and in the $[PF_6]^-$ anion are as expected.

In the complex ($HBpz_3$)Mo(NO)($N_2C_6H_4F$-*p*)Cl (VIIIb) the coordination of hydrotris(1-pyrazolyl)borate ligand shows a pronounced *trans*-effect. The molybdenum-(pyrazolyl)nitrogen distances *trans* to the nitrosonium (2.192(3), 2.200(3) Å) and diazonium (2.190(2), 2.184(3) Å) ligands are similar and significantly longer than the molybdenum–(pyrazolyl)nitrogen bonds *trans* to chlorine (2.158(3), 2.166(3) Å). A similar lengthening of molybdenum-(pyrazolyl)nitrogen bonds *trans* to strongly π-electron withdrawing ligands has been observed in the complex ($HBpz_3$)Mo($N_2C_6H_4F$-*p*)$_2$F [17] and in the cation $[HB(Me_2pz)_3Mo(NO)(MeCN)_2]^+$ and has been ascribed to a diminution of the π-bonding from the metal atom to the affected *trans* pyrazolyl group [25]. The dimensions within the hydrotris(1-pyrazolyl)borato ligand are in accord with previous results [18].

Experimental

Published procedures were used to prepare the complexes V [26], VI [10], X [27] and XII [26]. The ^{15}N labelling experiments were carried out as described elsewhere [12]. Other reagents and solvents were commercial samples and were used as received unless stated otherwise. All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. IR spectra were recorded on a Perkin Elmer 257 spectrophotometer and ^1H NMR spectra were obtained using a Perkin Elmer Hitachi R20-A spectrometer operating at 60 MHz and 34°C. Microanalyses were carried out by staff of the Microanalytical Laboratory of University College Cork and are summarised in Table 1.

η-Cyclopentadienyl(nitrosyl)(benzenediazo)chloromolybdenum(0) (VIIa) and related compounds

Nitrosyl chloride (0.65 g, 10 mmol) was slowly bubbled into a solution of (η-C_5H_5)Mo(CO)$_2$($N_2C_6H_5$) (Va) (3.22 g, 10 mmol) in 100 ml of dry CH_2Cl_2 at −25°C. The reaction mixture was then allowed to warm slowly to room temperature and the solvent was removed in vacuo. The residue was chromatographed on alumina (activity III), eluting with benzene. The orange band was collected and concentrated to dryness on the rotary evaporator. The solid residue was taken up in

Table 5

Final fractional coordinates ($\times 10^5$ for Mo, Cl; $\times 10^4$ for others) with estimated standard deviations in parentheses for $(HBpz_3)Mo(NO)(N_2C_6H_4F\text{-}p)$ (VIIIb)

Atom	x	y	z
Molecule 1			
Mo	28968(2)	14751(2)	15061(3)
Cl	25190(8)	1859(6)	15548(12)
N(1)	2112(3)	1810(2)	2788(4)
N(2)	1806(3)	1641(2)	−264(4)
N(3)	1204(3)	1810(2)	−1461(4)
O	1578(3)	2017(3)	3606(5)
F	1819(2)	−92(2)	−5396(4)
N(11)	3890(2)	1082(2)	−29(3)
N(12)	4925(2)	1307(2)	316(3)
N(21)	3673(3)	2513(2)	1584(4)
N(22)	4736(3)	2549(2)	1681(4)
N(31)	4370(2)	1335(2)	3365(3)
N(32)	5335(2)	1509(2)	3216(3)
C(1)	436(3)	1288(3)	−2434(5)
C(2)	273(3)	605(3)	−2027(5)
C(3)	−485(4)	134(3)	−3023(6)
C(4)	−1074(4)	368(4)	−4414(6)
C(5)	−920(4)	1035(4)	−4852(6)
C(6)	−166(4)	1511(3)	−3848(5)
C(11)	3714(3)	570(2)	−1283(4)
C(12)	4641(4)	458(2)	−1740(5)
C(13)	5379(3)	928(2)	−708(4)
C(21)	3309(5)	3205(3)	1574(6)
C(22)	4123(6)	3678(3)	1668(7)
C(23)	5025(5)	3257(3)	1754(6)
C(31)	4560(3)	1030(2)	4701(4)
C(32)	5640(3)	1006(2)	5402(4)
C(33)	6108(3)	1318(2)	4442(4)
B	5415(3)	1851(2)	1771(5)
Molecule 2			
Mo	23557(3)	66023(2)	22292(4)
Cl	28107(10)	54661(6)	33926(15)
N(1)	2134(3)	7053(2)	3973(4)
N(2)	3725(3)	7010(2)	2612(4)
N(3)	4484(3)	7324(2)	2492(4)
O	1993(3)	7315(2)	5185(4)
F	8525(2)	6235(2)	4541(4)
N(11)	2623(3)	5988(2)	100(4)
N(12)	1904(3)	6002(2)	−1329(4)
N(21)	1715(2)	7434(2)	699(4)
N(22)	1133(3)	7236(2)	−822(4)
N(31)	718(3)	6192(2)	1204(5)
N(32)	276(3)	6128(2)	−385(5)
C(1)	5529(3)	7033(2)	3095(4)
C(2)	5727(3)	6490(2)	4079(5)
C(3)	6746(4)	6223(2)	4588(5)
C(4)	7525(3)	6508(3)	4067(5)
C(5)	7355(4)	7042(3)	3098(6)
C(6)	6336(3)	7315(2)	2612(5)

Table 5 (continued)

Atom	x	y	z
Molecule 2			
C(11)	3436(4)	5576(2)	−125(6)
C(12)	3254(4)	5317(3)	−1680(7)
C(13)	2282(5)	5595(3)	−2418(6)
C(21)	1825(3)	8159(2)	886(5)
C(22)	1315(4)	8450(2)	−485(6)
C(23)	895(4)	7844(3)	−1532(6)
C(31)	−3(4)	5948(2)	1823(7)
C(32)	−908(4)	5729(3)	623(10)
C(33)	−710(4)	5845(3)	−730(8)
B	856(4)	6419(3)	−1447(6)

a 6/1 mixture of ether and dichloromethane and filtered through a 2.5 × 20 cm column of activity II alumina. n-Hexane (50 ml) was added to the filtrate and the solution was slowly concentrated on the rotary evaporator to yield orange crystals of VIIa (2.29 g, 69%).

Complexes VIIb, VIIc, VIIIa–d and IXa–c were prepared in an essentially similar fashion except that recrystallisation of the crude product from CH_2Cl_2/Et_2O (rather than column chromatography) was employed to purify (IXa–c).

η-Cyclopentadienyl(nitrosyl)(benzenediazo)(triphenylphosphine)molybdenum(0) hexafluorophosphate (XIIIa) and related compounds

Solid $NOPF_6$ (0.87 g, 5 mmol) was added portionwise to a stirred solution of $(\eta\text{-}C_5H_5)Mo(PPh_3)(CO)(N_2C_6H_5)$, (XIIa), (2.78 g, 5 mmol) in dry acetone at −78 °C. The reaction mixture was then allowed to warm slowly to room temperature and reduced in volume to ca. 25 ml on the rotary evaporator. Slow addition of ether precipitated a brown solid which was recrystallised from acetone/ether and then from CH_2Cl_2/ether to yield pure XIIIa, 2.53 g, 72%.

Complexes XIIIb–d were prepared in a similar fashion.

Reaction of complex [(XIIIb)]PF_6 with disodium 1,1-dicyanoethylene-2,2-dithiolate

A stirred solution of [(XIIIb)]PF_6 (1.0 g, 1.39 mmol) in the minimum quantity of acetone was treated portionwise with $Na_2[S_2C{=}C(CN)_2]3H_2O$ (0.67 g, 2.79 mmol). After 15 min at room temperature $[(C_6H_5)_4P]Br$ (1.17 g, 2.79 mmol) was added and after a further 15 min the solution was concentrated to dryness in vacuo. The reddish-brown residue was washed several times with boiling water and the dried solid was further purified by recrystallisation from acetone/ether and CH_2Cl_2/ether to yield 0.87 g (52% yield) of $[(C_6H_5)_4P]_2[(XIV)]$. Found: C, 62.46; H, 4.04; N, 7.93. $C_{63}H_{47}MoN_7OP_2S_4$ calc.: C, 62.83; H, 3.93; N, 8.14%. IR (thin film) 2200s (ν(CN)), 1614s (ν(NO)), 1670, 1590, 1550, 1564m (ν(NN), tentative assignment).

^1H NMR spectra

VIIa. (Acetone-d_6, Me_4Si) δ 6.26 (s, 5H, C_5H_5) 7.43–7.65 (br, m, 5H, $N_2C_6H_5$) ppm. For the following compounds the measurement conditions and assignments are as for VIIa above: VIIb; δ 6.23 (s, 5H), 7.29–7.55 (br, m, 4H) ppm. VIIc; δ 6.22 (s, 5H), 7.32–7.57 (br, m, 4H).

Table 6

Final fractional coordinates ($\times 10^5$ for Mo, $\times 10^4$ for others) with estimated standard deviations in parentheses for $[(\eta\text{-}C_5H_5)Mo(NO)(N_2C_6H_4F\text{-}p)(PPh_3)]PF_3$ $[(XIIIc)]PF_6$

Atom	*x*	*y*	*z*
Mo	22700(3)	34600(2)	25479(3)
P(1)	3151(1)	1957(1)	2216(1)
P(2)	917(1)	3512(1)	7285(1)
F	4514(4)	8887(3)	1925(5)
F(1)	514(3)	4233(2)	6504(3)
F(2)	1299(3)	2771(3)	8036(4)
F(3)	2045(3)	3519(3)	6746(4)
F(4)	−279(3)	3443(3)	7717(4)
F(5)	35(3)	2468(2)	5910(3)
F(6)	1757(4)	4536(3)	8594(3)
O	4052(3)	4477(2)	5512(3)
N	3412(3)	4097(2)	4320(3)
N(1)	3281(3)	4238(2)	1854(3)
N(2)	3954(3)	4737(2)	1436(3)
C(1)	373(4)	3837(4)	1789(6)
C(2)	187(4)	2804(4)	810(4)
C(3)	217(3)	2126(3)	1515(4)
C(4)	434(3)	2714(4)	2916(4)
C(5)	539(4)	3767(4)	3089(5)
C(11)	4051(3)	5820(3)	1586(3)
C(12)	5064(4)	6365(3)	1344(4)
C(13)	5209(5)	7411(4)	1465(5)
C(14)	4361(5)	7856(4)	1807(6)
C(15)	3346(5)	7327(4)	2025(7)
C(16)	3193(4)	6285(4)	1922(5)
C(21)	2595(3)	1121(3)	3080(3)
C(22)	2024(3)	14(3)	2408(4)
C(23)	1559(4)	−585(3)	3080(4)
C(24)	1660(4)	−86(3)	4416(4)
C(25)	2225(4)	1017(3)	5107(4)
C(26)	2690(4)	1615(3)	4444(4)
C(31)	2792(3)	1026(2)	447(3)
C(32)	3421(3)	278(3)	227(4)
C(33)	3118(4)	−470(3)	−1105(4)
C(34)	2213(4)	−464(3)	−2218(4)
C(35)	1612(4)	287(3)	−2016(4)
C(36)	1896(3)	1030(3)	−694(3)
C(41)	4896(3)	2459(3)	2956(3)
C(42)	5536(4)	3051(3)	2392(5)
C(43)	6859(4)	3448(3)	2889(6)
C(44)	7545(4)	3254(4)	3964(6)
C(45)	6919(4)	2662(5)	4536(5)
C(46)	5598(4)	2264(4)	4039(4)

VIIIa. (Acetone-d_6, Me_4Si) δ 6.23, 6.39, 6.52 (apparent t, 1H, H(4) of pyrazolyl groups), 7.48–8.23 (br, m, 11H, H(3) and H(5) of pyrazolyl groups and $N_2C_6H_5$). For the following compounds the measurement conditions and assignments are as for VIIIa. VIIIb: δ 6.25, 6.40, 6.53 (apparent t, 1H), 7.50–8.21 (br, m, 10H) ppm. VIIIc; δ 6.23, 6.39, 6.53 (apparent t, 1H), 7.49–8.21 (br, m, 10H) ppm. VIIId: δ

6.23, 6.39, 6.51 (apparent t, 1H) 7.46–8.16 (br, m, 11H) ppm.

IXa. (Acetone-d_6, Me_4Si) δ 6.62, 6.78, 6.90 (apparent t, 1H, H(4) of pyrazolyl groups), 7.57–8.77 (br, m, 11 H, H(3) and H(5) of pyrazolyl groups and $N_2C_6H_5$), 9.88 (s, 1H, methine proton of tris(pyrazolyl)methane ligand) ppm. For the following compounds the measurement conditions and assignments are as for IXa. IXb: δ 6.64, 6.79, 6.90 (apparent t, 1H), 7.47–8.79 (br, m, 10H), 9.89 (s, 1H) ppm IXc: δ 6.63, 6.78, 6.89 (apparent t, 1H), 7.49–8.78 (br, m, 10H), 9.89 (s, 1H) ppm.

XIIIa. (CH_2Cl_2-d_2, Me_4Si) δ 5.98 (s, 5H, η-C_5H_5), 7.10–7.95 (br, m, 20H, $P(C_6H_5)_3$ and $N_2C_6H_5$) ppm. For the following compounds, except where stated otherwise, measurement conditions and assignments are as for XIIIa, XIIIb: δ 2.44 (s, 3H, $N_2C_6H_4CH_3$-*p*), 6.00 (s, 5H), 7.10–8.00 (br, m, 19H) ppm. XIIIc: δ 6.02 (s, 5H), 7.12–7.90 (br, m, 19H) ppm. XIIId: δ 6.01 (s, 5H), 7.10–7.92 (br, m, 19H) ppm.

Collection and reduction of X-ray data

Crystals of $(HBpz_3)Mo(NO)(N_2C_6H_4F$-*p*)Cl (VIIIb) and [(η-$C_5H_5$)Mo(NO)-($N_2C_6H_4F$-*p*)($PPh_3$)]$PF_6$ [(XIIIc)]PF_6 were grown by slow evaporation of saturated solutions in dichloromethane/40/60° petroleum and dichloromethane/ethanol respectively. Crystal data and details of refinement for VIIIb and [(XIIIc)]PF_6 are in Table 2. For both compounds, data were collected with monochromatized Mo-K_α radiation on a CAD4 diffractometer and were corrected for Lorentz and polarization factors, but not for absorption. The structures were solved via the heavy-atom method and refined by full-matrix least-squares calculations with anisotropic thermal parameters. In the final rounds of calculations, hydrogen atom contributions were allowed for but not refined. Final difference maps were devoid of chemically significant features. All calculations were performed with the SHELX76 program and weights in the least-squares calculations were derived from counting statistics. Final fractional coordinates for VIIIb and [(XIIIc)]PF_6 are listed in Tables 5 and 6 respectively. Listings of observed and calculated structure factors, the anisotropic thermal parameters and the calculated hydrogen coordinates for both compounds together with the least-squares planes and angles and a listing of short intermolecular contacts in [(XIIIc)]PF_6 have been deposited.

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