Molybdenum(I) Mononitrosyl Complexes: Syntheses, Electrochemistry, Electron Paramagnetic Resonance Spectra and Magnetism of Complexes with N_6 and N_5I First-co-ordination Spheres and the Crystal Structures of [Mo{HB(dmpz)$_3$}(NO)(NC$_5$H$_4$Ph-4)$_2$]I and [Mo{HB(dmpz)$_3$}(NO)(NC$_9$H$_7$)$_2$]BPh$_4$ (dmpz = 3,5-dimethylpyrazol-1-yl)†

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The 17-electron, formally d^5 molybdenum(I), complexes [Mo{HB(dmpz)$_3$}(NO)I(L)]({HB(dmpz)$_3$} = hydrotris-3,5-dimethylpyrazol-1-ylborate; L = pyridine, 4-phenylpyridine, phenanthridine or isoquinoline) and [Mo{HB(dmpz)$_3$}(NO)(L)$_2$]Z (L = 4-phenylpyridine, Z = I; L = isoquinoline, Z = I_3 or BPh$_4$) have been prepared and exhibit varied magnetic behaviour. The magnetic moments of [Mo{HB(dmpz)$_3$}(NO)I(L)] (L = pyridine or isoquinoline) and [Mo{HB(dmpz)$_3$}(NO)(NC$_9$H$_7$)$_2$]BPh$_4$ are close to the spin-only value for one unpaired electron and do not vary significantly with temperature. The remaining complexes exhibit magnetic moments which increase from near the spin-only value at 6 K to substantially higher values at 300 K. The cationic complexes are reduced to 18-electron species at potentials which are almost invariant and *ca.* 400 mV more anodic than those of their neutral monoiodo counterparts, the reduction potentials of which vary over a range of *ca.* 150 mV in accord with the change in pK_a values of the heterocyclic ligands. The molecular structure of [Mo{HB(dmpz)$_3$}(NO)(NC$_5$H$_4$Ph-4)$_2$]I reveals dihedral angles of 41.0 and 29.9° between the aryl rings of the NC$_5$H$_4$Ph-4 ligands whilst the structure of [Mo{HB(dmpz)$_3$}(NO)(NC$_9$H$_7$)$_2$]BPh$_4$ reveals that, in the solid state at least, the two isoquinoline ligands do not form a 'cleft' which might act as a site for weak binding of an aryl group from the BPh$_4^-$ ion.

Transition-metal ions are of considerable importance as functional centres in new molecular materials.[1] They can be used to form polar sites in larger molecular species and may offer opportunities to incorporate redox activity or magnetic properties into molecular materials. A particular example is provided by the redox active[2] [Mo{HB(dmpz)$_3$}(NO)X]$^+$ [X = halide, HB(dmpz)$_3$ = hydrotris-3,5-dimethylpyrazol-1-ylborate] moiety[3] which has been incorporated into materials which show second-order non-linear optical effects.[4] Bimetallic complexes [{Mo{HB(dmpz)$_3$}(NO)X}$_2$L] (X = Cl or I, L = a bipyridyl ligand), containing the 17-electron counterpart of this group, are also redox active[5] but their electrochemical behaviour is quite different from that found for related systems containing the more extensively studied {Ru(NH$_3$)$_5$}$^{2+/3+}$ redox couple.[6] Consequently, such low-oxidation state early d-block metal complexes are of particular interest in the search for new molecular materials with unusual optical or electronic properties.

The chemistry of the lower oxidation states of molybdenum (−II to II) is dominated by carbonyl and organometallic species[7] and there are relatively few examples of stable compounds containing Mo^I, but of these many are nitrosyl derivatives containing halide, nitrogen or phosphorus based ligands.[8] In these species, the nitrosyl ligand is formally represented as NO$^+$, acting as a three-electron donor to the metal by provision of the σ lone pair electrons on the N atom and the π^* electron of NO. According to this formalism, species containing {Mo(NO)}$^{2+}$ can be regarded as derived from d^5 Mo^I bonded to an NO$^+$ group. Derivatives of the [Mo{HB(dmpz)$_3$}(NO)]$^+$ moiety provide a particular group of such complexes in which the effects of varying co-ligand sets on the properties of the Mo^I centre may be examined. Complexes of the general formula [Mo{HB(dmpz)$_3$}(NO)(L)$_2$]$^+$ (L = acetonitrile, pyridine or *N*-methylimidazole)[9] have been reported previously and recently examples of neutral monosubstituted chloro complexes [Mo{HB(dmpz)$_3$}(NO)Cl(L)] have been obtained from reactions involving [Mo{HB(dmpz)$_3$}(NO)Cl$_2$]$^-$.[5,10] Since in such systems the substitution of iodide is generally more easily effected than the substitution of chloride, the monoiodo compounds [Mo{HB(dmpz)$_3$}(NO)I(L)] are of interest as synthetic precursors to asymmetrically substituted complexes of the form [Mo{HB(dmpz)$_3$}(NO)(L)(Y)]. Accordingly we have now developed a reliable synthetic method for producing the monoiodo derivatives [Mo{HB(dmpz)$_3$}(NO)I(L)] (L = pyridine, 4-phenylpyridine, isoquinoline and phenanthridine). The cationic bis-substituted complexes [Mo{HB(dmpz)$_3$}(NO)(L)$_2$]$^+$ were also obtained, except in the case where L = phenanthridine.

A further point of interest in this work is the twist angle between the phenyl and pyridyl groups in complexes containing the phenylpyridine ligand. A recent structural study of [Mo{HB(dmpz)$_3$}(NO)Cl(NC$_5$H$_4$C$_6$H$_4$OMe-4)] has shown that, in the solid state at least, the pyridyl and C$_6$H$_4$OMe-4 rings are almost coplanar (inter-planar angle 4.9°).[11] This

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Electronic spectra

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})[a]			
[Mo{HB(dmpz)$_3$}(NO)I(py)]	458 (1 000)	378 (3 250)	272 (8 000)	228 (23 250)
[Mo{HB(dmpz)$_3$}(NO)I(NC$_5$H$_4$Ph-4)]	520 (2 050)	340 (sh) (6 250)	274 (23 250)	229 (30 000)
[Mo{HB(dmpz)$_3$}(NO)I(NC$_9$H$_7$)]	520 (1 520)	315 (8 000)	270 (13 500)	230 (49 750)
[Mo{HB(dmpz)$_3$}(NO)I(NC$_{13}$H$_9$)]	550 (1 300)	340 (6 350)	242 (47 000)	230 (sh)
[Mo{HB(dmpz)$_3$}(NO)(NC$_5$H$_4$Ph-4)$_2$]I·H$_2$O	462 (2 400)	368 (10 250)	295 (sh) (24 250)	248 (49 000)
[Mo{HB(dmpz)$_3$}(NO)(NC$_9$H$_7$)$_2$]I$_3$	495[b] (1 990)	362 (24 500)	292 (45 500)	230 (64 000)
[Mo{HB(dmpz)$_3$}(NO)(NC$_9$H$_7$)$_2$]BPh$_4$	480 (1 550)	390 (3 950)	312 (9 900)	232 (58 000)

[a] Recorded from solutions in dichloromethane. [b] Estimated value for a poorly resolved band lacking a well defined maximum.

finding was rationalised in terms of the planar structure optimising strong π-donation from OMe to {Mo(NO)}. It was of interest, therefore, to determine whether a coplanar geometry might be adopted by the aryl groups in a 4-phenylpyridine ligand which did not contain a suitably positioned π-donor substituent. Unfortunately, crystals of [Mo{HB(dmpz)$_3$}(NO)I(NC$_5$H$_4$Ph-4)] suitable for X-ray studies were not obtained. However, a crystal structure of the bis-substituted cationic complex [Mo{HB(dmpz)$_3$}(NO)(NC$_5$H$_4$Ph-4)$_2$]I was obtained, allowing the phenyl–pyridyl ring twist angles to be determined in this case at least.

Results and Discussion

Synthetic and Spectroscopic Studies.—The finding that the reduced complex [Mo{HB(dmpz)$_3$}(NO)Cl$_2$]$^-$ reacts with pyridine derivatives, L, to give[5,10] the monosubstituted complexes [Mo{HB(dmpz)$_3$}(NO)Cl(L)] prompted us to examine whether a similar approach might offer a route to the previously unavailable[9b] iodo–pyridine complex [Mo{HB(dmpz)$_3$}(NO)I(py)]. Since triethylamine is known[12] to produce paramagnetic 17-electron species from [Mo{HB(dmpz)$_3$}(NO)I$_2$] the reaction of the diiodide with an excess of pyridine (py) was carried out in the presence of NEt$_3$. The product of this reaction was found to be the green complex [Mo{HB(dmpz)$_3$}(NO)I(py)]. Similar reactions with 4-phenylpyridine also afforded the monosubstituted product in the presence of NEt$_3$ but, in the absence of NEt$_3$, the bis-substituted cation [Mo{HB(dmpz)$_3$}(NO)(NC$_5$H$_4$Ph-4)$_2$]I was obtained. In order to determine whether altering the steric size of the nitrogen heterocycle might provide an alternative means of restricting the extent of iodide substitution the reactions with isoquinoline and phenanthridine were investigated. In the case of isoquinoline bis-substitution occurred in the absence of NEt$_3$ and it was necessary to add NEt$_3$ in order to obtain the mono-substituted product. However, the more sterically demanding phenanthridine ligand afforded only the mono-substituted product, even in the absence of NEt$_3$, suggesting that, in this case, the steric size of the ligand is leading to mono-substitution.

The new compounds gave satisfactory elemental analyses and all exhibited molecular ions in their FAB mass spectra. Their IR spectra contained bands attributable to the presence of the {HB(dmpz)$_3$} ligand together with a strong nitrosyl band in the region 1610–1625 cm^{-1} in accord with their formulation as 17-electron species.[5,9–11] Solution conductivities for acetonitrile solutions of the new compounds were consistent with the formulations of [Mo{HB(dmpz)$_3$}(NO)I(L)] (L = pyridine, 4-phenylpyridine, phenanthridine or isoquinoline) as neutral complexes and the formulation of [Mo{HB(dmpz)$_3$}(NO)(L)$_2$]Z (L = 4-phenylpyridine, Z = I; L = isoquinoline, Z = I$_3$ or BPh$_4$) as 1 : 1 electrolytes.

The UV/VIS spectra of the new complexes are summarised in Table 1 and all contain a band at *ca.* 230 nm which is also present in the spectrum of HB(dmpz)$_3^-$ and may be attributed to a $\pi \longrightarrow \pi^*$ transition in this ligand. The spectrum of [Mo{HB(dmpz)$_3$}(NO)I(py)] also contains bands at 458, 378 and 272 nm. Since the spectrum of free pyridine contains bands in the region 250 to 285 nm, the absorption at 272 nm may be associated with an intraligand transition in the pyridine ligand. The other two bands correspond with those observed at 468 and 410 nm in the spectrum of [Mo{HB(dmpz)$_3$}(NO)Cl(py)].[10] Solvatochromism studies of [{Mo[HB(dmpz)$_3$](NO)Cl}$_x${NC$_5$H$_4$[(CH=CH)$_4$C$_5$H$_4$N-4′]-4}] (x = 1 or 2) have shown that, in these complexes, an absorption band in the region 540–600 nm is attributable to a metal-to-ligand charge transfer (m.l.c.t.) process.[13] Since the π^* orbitals of pyridine are at higher energy than those in the bipyridyl polyene ligands,[14] it seems reasonable to assume that such an m.l.c.t. process would occur at higher energy in the pyridine complexes. Thus the band at 458 nm might also be assigned to an m.l.c.t. transition. In accord with this proposal the spectra of [Mo{HB(dmpz)$_3$}(NO)I(NC$_5$H$_4$Ph-4)] and [Mo{HB(dmpz)$_3$}(NO)I(NC$_9$H$_7$)] contain bands at 520 nm, which would correspond to an m.l.c.t. transition intermediate in energy between those of the pyridine and bipyridyl polyene complexes, whilst [Mo{HB(dmpz)$_3$}(NO)I(NC$_{13}$H$_9$)] shows a further bathochromic shift to give a band at 550 nm. The electronic spectrum of the cationic complex [Mo{HB(dmpz)$_3$}(NO)(py)$_2$]BPh$_4$ contains a weak band at 450 nm (ε = 145 dm^{-3} mol^{-1} cm^{-1}) which has been assigned[9b] to a d–d transition. The spectra of [Mo{HB(dmpz)$_3$}(NO)(L)$_2$]$^+$ (L = NC$_5$H$_4$Ph-4, NC$_9$H$_7$, NC$_{13}$H$_9$) also contain a band in this region but this has a higher absorption coefficient than, and is bathochromically shifted with respect to, the band in the spectrum of [Mo{HB(dmpz)$_3$}(NO)(py)$_2$]$^+$. Both the cationic and neutral complexes exhibit an absorption band in the region 300 to 400 nm with molar absorption coefficients in the range 3000–10 000 dm^{-3} mol^{-1} cm^{-1} indicating that a charge-transfer process is involved. Since free isoquinoline absorbs at *ca.* 320 nm the spectra of the isoquinoline complexes may contain an intraligand band in this region. However, bands in the region 350 to 400 nm are a common feature in the spectra of 17-electron complexes containing the {Mo{HB(dmpz)$_3$}(NO)} moiety. Furthermore the position of this band does not change significantly when the chloride ligand in [Mo{HB(dmpz)$_3$}(NO)Cl{NC$_4$H$_4$[(CH=CH)$_n$C$_5$H$_4$N-4]}] is replaced by iodide.[5c] Thus, since [Mo{HB(dmpz)$_3$}(NO)Cl$_2$]$^-$ exhibits a band at 382 nm,[10] it seems probable that this band is

Table 2 Electrochemical, EPR and magnetic measurements

			μ_{eff}/μ_B					
Compound	$E_f{}^a$/V	$\Delta E_p{}^b$/mV	6 K	300 K^c	NMR^d	θ^e/K	g_{iso}	$10^4 A_{iso}{}^f$/cm^{-1}
[Mo{HB(dmpz)$_3$}(NO)I(NC$_5$H$_5$)]	−1.895	130	1.6	1.8 ±0.1		−2	2.006	45.2
[Mo{HB(dmpz)$_3$}(NO)I(NC$_5$H$_4$Ph-4)]	−1.772	70	1.8	3.5 ±0.2	2.27	0	2.006	45.0
[Mo{HB(dmpz)$_3$}(NO)I(NC$_9$H$_7$)]	−1.790	70	1.6	1.7 ±0.2		0	2.006	45.1
[Mo{HB(dmpz)$_3$}(NO)I(NC$_{13}$H$_9$)]	−1.741	60	1.6	2.9 ±0.2	2.49	−3	2.007	45.7
[Mo{HB(dmpz)$_3$}(NO)(NC$_5$H$_5$)$_2$]BPh$_4$	−1.435	68	2.1	3.8 ±0.3	2.89	0	1.977	43.8^g
[Mo{HB(dmpz)$_3$}(NO)(NC$_5$H$_4$Ph-4)$_2$]I·H$_2$O	−1.391	63	1.3	2.6 ±0.3	1.97	−3	1.997	46.9
[Mo{HB(dmpz)$_3$}(NO)(NC$_9$H$_7$)$_2$]I$_3$	−1.385	63	2.1	3.0 ±0.3	2.73	−2	1.997	46.9
[Mo{HB(dmpz)$_3$}(NO)(NC$_9$H$_7$)$_2$]BPh$_4$	−1.376	69	1.8	2.2 ±0.3		−4	1.997	47.2

^{a} Measured from 10^{-3} mol dm^{-3} solutions of complex in CH_2Cl_2 containing 0.2 mol dm^{-3} [NBu$_4$]BF$_4$ as base electrolyte, values are quoted *vs.* ferrocene used as an internal standard where $E_f\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\} = +0.545 \pm 0.010$ V *vs.* SCE. ^{b} Anodic and cathodic peak separation; $\Delta E_p\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\} = 70 \pm 10$ mV. ^{c} Magnetic moments calculated from solid-state susceptibility data obtained over the temperature range 6–300 K using a SQUID magnetometer, ± errors apply to the values for 300 K. ^{d} Magnetic moments measured from CH_2Cl_2 solutions by NMR spectroscopy at 400 MHz and 301 ± 3K. ^{e} Weiss constant obtained from the temperature intercept of a plot of inverse molar susceptibility against temperature. ^{f} Obtained at X-band frequency from solutions in CH_2Cl_2. ^{g} Data from ref. 9.

due to an l.m.c.t. process within the {Mo{HB(dmpz)$_3$}(NO)} fragment which does not involve the halide ligand.

The EPR spectral parameters of the new compounds were obtained from dichloromethane solutions and are summarised in Table 2. The isotropic hyperfine coupling constant values for the mono-substituted complexes lie in the range $A_{iso} = 45.0$–45.7×10^{-4} cm^{-1} and are comparable with the value $A_{iso} = 45.7 \times 10^{-4}$ cm^{-1} found for [Mo{HB(dmpz)$_3$}(NO)Cl(py)].[10] However, the isotropic *g* values of the mono-iodo compounds were somewhat higher than the value of *ca.* 1.977 found for [Mo{HB(dmpz)$_3$}(NO)Cl(py)], lying in the range $g_{iso} = 2.006$–2.007. The cationic complexes shows slightly lower g_{iso} values and slightly higher A_{iso} values than their neutral counterparts. However, as in previous studies, no hyperfine coupling to the neutral heterocyclic ligands was detected.[9,10]

Bulk magnetic measurements were carried out on solid samples over the temperature range 6–300 K using a SQUID magnetometer. Plots of the reciprocal of the molar susceptibility ($1/\chi_m$) against temperature (*T*) showed intercepts with the temperature axis, θ, close to 0 K (Table 2). None of the plots was linear, the line deviating towards the temperature axis at higher temperatures. For [Mo{HB(dmpz)$_3$}(NO)I(L)] (L = py or C_9H_7N) these deviations were small and the plot was essentially linear from 6 K to *ca.* 150 K, but in the other compounds pronounced curvature was apparent. Magnetic moments were calculated from the susceptibility data at 6 and 300 K (Table 2). In the cases of [Mo{HB(dmpz)$_3$}(NO)I(L)] (L = py or C_9H_7N) these were almost independent of temperature over the range 6–300 K. However, the magnetic moments of the other complexes exhibited significant temperature dependence. In order to obtain a measure of the room-temperature magnetic moments under more magnetically dilute conditions, the magnetic moments of these compounds were also determined by NMR from solutions at *ca.* 300 K (Table 2). This method gave lower values than those obtained using the SQUID measurements but confirmed that, at 300 K, the magnetic moments are significantly in excess of the spin-only value for one unpaired electron. In some cases the differences are barely significant when the errors in the measurements are taken into account. However, in the cases of [Mo{HB(dmpz)$_3$}(NO)(py)$_2$]BPh$_4$ and [Mo{HB(dmpz)$_3$}(NO)I(NC$_5$H$_4$Ph-4)] in particular they are substantially larger than the sum of the expected measurement errors.

The magnetic moments observed at 6 K are generally consistent with the presence of low-spin d^5 molybdenum(I) centres in the complexes. In a strictly octahedral environment this would give rise to a $^2T_{2g}$ ground term but the EPR spectra of [Mo{HB(dmpz)$_3$}(NO)(L)$_2$]$^+$ (L = py or N-methylimidazole)[9b] are consistent with axial symmetry. This suggests that the electronic state of these systems may be approximately described as arising from a tetragonally distorted octahedral structure, although the actual molecular symmetry is lower than this. A tetragonal structure would give rise to a $^2B_{2g}$ ground term which, in the absence of thermally accessible degenerate excited terms, could give rise to the magnetic behaviour found for [Mo{HB(dmpz)$_3$}(NO)I(L)] (L = py or C_9H_7N).[15] A more complex situation is found with the other complexes reported here and we are aware of no other magnetic studies of d^5 molybdenum(I) complexes of this type which would assist in the interpretation of their behaviour. The sensitivity of the magnetic properties to the nature of the co-ligand may result from significant interactions between the singly occupied orbital on the metal centre and π* orbital of the co-ligand which varies from compound to compound. However, no hyperfine interactions are apparent in the EPR spectra to provide evidence for the delocalisation of charge from the metal to the ligand. Thus the magnetic behaviour of these d^5 compounds does not appear amenable to a simple rationalisation and further theoretical analysis will be required to provide an unequivocal explanation of their properties.

Electrochemical Studies.—The electrochemistry of dichloromethane solutions of the new compounds was investigated using cyclic voltammetry and the Condecon 310 system which allows data collection and processing to be computer assisted. Thus, apart from the usual electrochemical parameters obtained from cyclic voltammetry and differential pulse voltammetry, information on mechanism and kinetics can be obtained through the use of convolutions, kinetic convolutions and deconvolutions.[16] As with [Mo{HB(dmpz)$_3$}(NO)Cl(py)] these compounds showed irreversible oxidation processes, although these were obscured by the oxidation of free I$^-$ or I$_3{}^-$ in the iodide salts. However, the reduction behaviour (Table 2) was chemically reversible despite being subject to some kinetic control. The reduction potentials of the cationic complexes [Mo{HB(dmpz)$_3$}(NO)(L)$_2$]$^+$ (L = pyridine, 4-phenylpyridine or isoquinoline) were essentially the same and some 400 mV more anodic than those of their neutral mono-substituted counterparts. This finding reflects the higher electron affinity of the cationic molybdenum centre in these complexes compared to their neutral counterparts. The potentials for the reduction of the mono-substituted complexes showed an increasing anodic shift with the number of fused aromatic rings present. Thus an anodic shift of 105 mV arises in going from [Mo{HB(dmpz)$_3$}-$^{(}\rangle \approx ^{)} \leqslant ^{(py)}$] to [Mo{HB(dmpz)$_3$}(NO)I(NC$_9H_7$)] followed by a further shift of 49 mV in going to [Mo{HB(dmpz)$_3$}(NO)I-(NC$_{13}$H$_9$)]. The changes in these reduction potentials correspond well with the variation in K_a values for the heterocyclic bases present as L. However, the higher *g* values found for the isoquinoline and phenanthridine ligands would be in accord with a greater delocalisation of charge from the metal onto the polyaromatic ligand. This could also account for the observed anodic shift in reduction potential and it is not possible to separate σ and π effects on the basis of these measurements alone. The cationic complexes exhibit a near constant reduction potential despite the variations in ligand K_a. In these cases it seems that the residual charge at the metal centre is the dominant factor leading to a virtually constant reduction potential in spite of changes in the co-ligand L.

Structural Studies.—The structures of the complex cations $[Mo\{HB(dmpz)_3\}(NO)(NC_5H_4Ph\text{-}4)_2]^+$ **1** and $[Mo\{HB(dmpz)_3\}(NO)(NC_9H_7)_2]^+$ **2** are illustrated in Fig. 1 and 2. The crystal structure of **1** also contains an iodide counter ion and a rather ill defined molecule of pentane with 0.42(2) site occupancy, while **2** contains BPh_4^- as counter ion. Atomic coordinates are listed in Tables 3 and 4, and selected bond lengths and angles in Table 5.

Apart from the phenyl residues of the phenylpyridine ligands in **1** and the fused benzo moieties of the isoquinoline ligands in **2**, the molecules have approximate mirror (C_s) symmetry, the pseudo plane passing through the N(2), N(3), C(2)–C(4) pyrazolyl ring, the Mo–N–O grouping and the boron atom, these nine atoms being co-planar to within ± 0.06(1) Å in **1** and ± 0.12(1) Å in **2**. The N(4), N(5), C(7)–C(9) and N(6), N(7), C(12)–C(14) pyrazolyl rings are inclined at angles * of 121.0 and 117.1° to this plane in **1**, and 116.5 and 118.2° in **2**, respectively. In **1** the two pyridyl rings are also oriented symmetrically to it, at angles of 50.8 [N(8), C(16)–C(20) ring] and 52.4° [N(9), C(27)–C(31) ring]. The phenyl rings differ to a greater extent in their inclination to the pseudo-mirror plane (dihedral angles of 77.1 and 66.0° respectively). In **2**, the isoquinoline ligands are oriented at angles of 65.4° [N(8), C(25)–C(32)] and 61.8° [N(9), C(16)–C(24)] to the central plane. However, they differ in that they are rotated through an angle of 180° with respect to each other, so that the orientations of the benzo moieties are different (see Fig. 2).

The co-ordination about the central molybdenum is essentially octahedral in both structures. The maximum angular deviation from ideal octahedral is 10.1° in **1** [angle N(6)–Mo–N(9), 169.9(3)°] and 11.5° in **2** [angle N(4)–Mo–N(8) 168.5(3)°]; mean deviations are 4.5° (**1**) and 5.5° (**2**). Corresponding angles in the two cations **1** and **2**, however, agree well, maximum difference 4.1°, mean difference 1.6°.

The Mo–N bond distances fall into four categories. By far the shortest of these is the Mo–N(nitrosyl) bond at 1.760(7) and 1.719(9) Å in **1** and **2**, respectively, similar to lengths found previously for this bond, 1.75(2),[17] and 1.751(3) Å.[18] The Mo–N(pyridyl) distances, 2.207(8) and 2.204(7) Å, and the Mo–N(isoquinolinyl) distances, 2.212(9) and 2.234(9) Å, are characteristic of Mo–N(amine) bonds.

The Mo–N(pyrazolyl) bond lengths reflect the nature of the *trans*-bonding. The bond Mo–N(2), *trans* to the nitrosyl group [2.252(7) Å in **1**, 2.233(9) Å in **2**] is the longest of these and compares with values in the range 2.235–2.302 Å in analogous complexes.[8,17–19] The *trans* bond lengthening effect of the nitrosyl group in this class of compound has been noted previously.[20] The bonds *trans* to the Mo–N(amine) bonds are relatively short [2.146(9)–2.171(11) Å], and reflect the lack of π character of Mo–N(amine) bonds. Similar Mo–N(pyrazolyl) bond lengths *trans* to amino ligands have been found previously.[8,19] In contrast, Mo–N(pyrazolyl) bonds *trans* to amido ligands, where considerable p_π–d_π donation appears to occur from the ligand to the metal, are typically[17–20] some 0.05–0.10 Å longer.

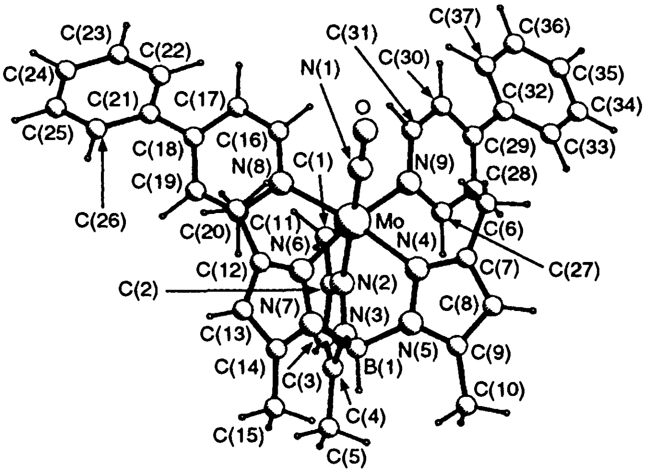

Fig. 1 View of the cation $[Mo\{HB(dmpz)_3\}(NO)(NC_5H_4Ph\text{-}4)_2]^+$ **1** showing the atom numbering

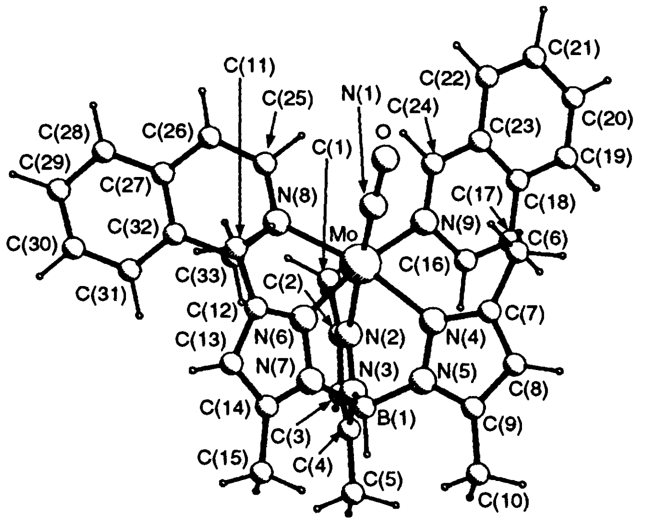

Fig. 2 View of the cation $[Mo\{HB(dmpz)_3\}(NO)(NC_9H_7)_2]^+$ **2** showing the atom numbering

In **1** the phenyl rings, C(21)–C(26) and C(32)–C(37) make angles of 41.0 and 29.9° respectively with their bonded pyridyl ring, thus breaking the approximate mirror symmetry of the cation noted above. These interplanar angles relieve steric interactions between the *ortho*-hydrogens of the aryl ring and are typical of biaryl structures (but not of biphenyl itself).[21] However, they contrast with the situation found[11] in $[Mo\{HB(dmpz)_3\}(NO)Cl\{NC_5H_4(C_6H_4OMe\text{-}4')\text{-}4\}]$ where the inter-ring torsion angle is only 5°. In another phenyl pyridine complex, $[Ti(OC_6H_3Pr^i{}_2\text{-}2,6)_2(NC_5H_4Ph\text{-}4)_3]$,[22] two of the phenyl pyridine ligands adopt 'normal' structures[22] in which the phenyl-pyridine C–C bond is 1.478(7) Å and the twist angle between the aryl rings along this bond is 35°. However, the third phenylpyridine ligand is formulated as $[NC_5H_4Ph]^-$ since it exhibits a short inter aryl C–C bond [1.38(1) Å] and a small twist angle of 5°. It would appear that, in these molybdenum(I) mononitrosyl complexes, the molybdenum can act as a π acceptor towards the pyridyl ligand but, in the absence of a suitably located π-donor group, it is the steric interaction between the *ortho*-hydrogens on the aryl rings which determines the structure of the biaryl moiety. These structural results provide further support for the view that the near co-planarity of the aryl rings in $[Mo\{HB(dmpz)_3\}(NO)Cl\{NC_5H_4(C_6H_4OMe\text{-}4')\text{-}4\}]$ arises from the stabilisation of the $\{Mo(NO)\}^{2+}$ centre by π donation from the methoxy group of the substituted pyridine ligand. Thus, although there appears to be little π contribution to Mo–N(pyridyl) bonding from the phenylpyridine complex, the

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* E.s.d.s for dihedral angles are approximately 0.4° in both structures.

Table 3 Fractional atomic coordinates (× 10^5 for I and Mo; × 10^4 for other atoms) with estimated standard deviations (e.s.d.s) in parentheses for complex **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
I	6 360(8)	6 156(9)	15 158(3)	C(16)	2 908(9)	3 565(9)	1 426(2)
Mo	50 429(7)	30 237(8)	9 263(2)	C(17)	2 283(10)	4 154(9)	1 684(3)
N(1)	3 586(8)	2 302(7)	730(2)	C(18)	2 643(9)	5 424(9)	1 795(3)
N(2)	6 867(7)	3 906(7)	1 209(2)	C(19)	3 631(10)	6 002(9)	1 621(2)
N(3)	7 764(7)	4 455(8)	1 005(2)	C(20)	4 239(10)	5 346(9)	1 384(2)
N(4)	6 388(7)	2 209(7)	594(2)	C(21)	2 006(9)	6 083(10)	2 054(3)
N(5)	7 445(7)	2 955(8)	515(2)	C(22)	1 727(10)	5 390(12)	2 346(2)
N(6)	5 063(7)	4 726(7)	611(2)	C(23)	1 163(12)	6 021(15)	2 598(3)
N(7)	6 260(7)	5 113(7)	504(2)	C(24)	851(12)	7 334(16)	2 569(4)
N(8)	3 913(7)	4 104(7)	1 286(2)	C(25)	1 131(12)	8 008(13)	2 291(4)
N(9)	5 404(7)	1 333(7)	1 265(2)	C(26)	1 692(10)	7 404(10)	2 038(3)
O	2 568(7)	1 788(8)	619(2)	C(27)	6 660(9)	935(9)	1 367(2)
B	7 544(11)	4 382(11)	617(3)	C(28)	6 927(9)	−53(9)	1 606(3)
C(1)	6 602(12)	3 664(11)	1 818(3)	C(29)	5 907(9)	−641(8)	1 750(2)
C(2)	7 300(10)	4 125(9)	1 529(2)	C(30)	4 619(9)	−273(9)	1 632(2)
C(3)	8 489(10)	4 838(11)	1 543(3)	C(31)	4 421(9)	668(9)	1 388(3)
C(4)	8 750(9)	5 036(11)	1 225(3)	C(32)	6 163(9)	−1 620(8)	2 029(2)
C(5)	9 839(11)	5 805(14)	1 080(4)	C(33)	7 296(10)	−2 388(10)	2 049(3)
C(6)	5 511(14)	−13(11)	495(3)	C(34)	7 561(12)	−3 258(10)	2 318(3)
C(7)	6 493(11)	1 034(10)	456(3)	C(35)	6 703(14)	−3 387(11)	2 549(3)
C(8)	7 635(11)	1 018(13)	278(3)	C(36)	5 575(14)	−2 670(12)	2 535(4)
C(9)	8 220(10)	2 225(11)	332(3)	C(37)	5 297(11)	−1 767(10)	2 275(3)
C(10)	9 479(11)	2 700(13)	196(3)	C(50)*	11 467(178)	1 539(159)	8 930(48)
C(11)	2 711(10)	5 466(11)	534(3)	C(51)*	10 515(110)	857(84)	9 264(25)
C(12)	4 138(9)	5 553(9)	473(2)	C(52)*	9 262(55)	732(42)	9 372(11)
C(13)	4 742(10)	6 486(9)	290(3)	C(53)*	8 455(62)	1 181(55)	9 304(15)
C(14)	6 089(10)	6 181(9)	314(2)	C(54)*	7 902(69)	1 357(64)	9 069(20)
C(15)	7 170(12)	6 890(10)	165(3)				

* Pentane molecule; site occupancy = 0.42(2).

Table 4 Fractional atomic coordinates (× 10^4) with e.s.d.s in parentheses for complex **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	0	1179(1)	0	C(24)	654(13)	−463(6)	−296(6)
N(1)	−1197(8)	763(5)	−333(4)	C(25)	−1081(11)	213(7)	898(7)
N(2)	1638(8)	1623(4)	422(4)	C(26)	−1498(12)	26(7)	1404(7)
N(3)	1935(7)	2318(4)	318(3)	C(27)	−1098(12)	420(7)	1904(7)
N(4)	481(8)	1771(5)	−737(5)	C(28)	−1493(14)	283(9)	2445(7)
N(5)	880(8)	2468(5)	−663(4)	C(29)	−1079(16)	706(9)	2923(7)
N(6)	−695(8)	2211(5)	235(4)	C(30)	−238(19)	1224(8)	2875(7)
N(7)	−48(8)	2849(5)	200(4)	C(31)	127(15)	1373(7)	2360(6)
N(8)	−345(8)	771(4)	849(4)	C(32)	−299(12)	986(6)	1871(6)
N(9)	1011(9)	220(4)	−249(4)	C(33)	22(12)	1148(6)	1317(5)
O	−1964(9)	360(7)	−561(6)	B(2)	4457(11)	986(7)	7703(5)
B(1)	1066(13)	2806(6)	−83(6)	C(34)	4492(9)	1092(5)	8402(5)
C(1)	2567(13)	572(7)	1026(6)	C(35)	5275(9)	684(6)	8783(5)
C(2)	2542(10)	1336(6)	766(5)	C(36)	5366(10)	787(7)	9353(5)
C(3)	3372(9)	1875(7)	857(5)	C(37)	4666(13)	1283(9)	9562(6)
C(4)	2986(10)	2488(6)	572(5)	C(38)	3921(11)	1663(7)	9250(5)
C(5)	3486(12)	3210(7)	523(7)	C(39)	3838(10)	1579(6)	8670(5)
C(6)	−10(14)	917(7)	−1561(6)	C(40)	3289(9)	1314(5)	7372(5)
C(7)	409(11)	1624(6)	−1306(5)	C(41)	2377(11)	885(8)	7124(6)
C(8)	793(12)	2213(8)	−1580(5)	C(42)	1415(14)	1198(9)	6835(6)
C(9)	1097(11)	2735(7)	−1179(6)	C(43)	1294(13)	1945(11)	6789(6)
C(10)	1540(15)	3503(9)	−1260(9)	C(44)	2165(14)	2395(8)	7033(6)
C(11)	−2562(12)	1886(7)	555(7)	C(45)	3149(11)	2071(6)	7307(6)
C(12)	−1623(9)	2402(6)	475(5)	C(46)	5550(10)	1415(6)	7481(4)
C(13)	−1557(10)	3158(7)	607(5)	C(47)	5521(10)	1620(6)	6917(5)
C(14)	−570(10)	3402(5)	429(5)	C(48)	6435(11)	1929(7)	6691(6)
C(15)	−93(13)	4162(6)	461(6)	C(49)	7430(12)	2067(7)	7047(6)
C(16)	2058(11)	388(7)	−458(6)	C(50)	7478(11)	1895(7)	7620(6)
C(17)	2703(11)	−125(7)	−676(5)	C(51)	6563(10)	1580(6)	7828(5)
C(18)	2309(11)	−836(6)	−715(5)	C(52)	4580(10)	108(6)	7543(5)
C(19)	2986(13)	−1410(7)	−950(7)	C(53)	3913(13)	−431(6)	7800(6)
C(20)	2588(13)	−2106(7)	−987(6)	C(54)	3922(15)	−1161(7)	7655(7)
C(21)	1498(14)	−2279(7)	−817(7)	C(55)	4667(14)	−1402(7)	7315(5)
C(22)	857(13)	−1770(6)	−571(7)	C(56)	5354(12)	−927(7)	7049(7)
C(23)	1285(10)	−1018(6)	−532(5)	C(57)	5300(10)	−170(7)	7205(5)

presence of a π-donor substituent produces a significant structural change to facilitate π interactions with Mo.

The closest contact between the iodide ion and the complex cation involves the hydrogen atom bonded to C(16) in its calculated position at 2.98 Å. The closest contact involving a non-hydrogen atom is I • • • C(16), 3.835(8) Å. Noteworthy is an apparently rather short intramolecular contact distance of 2.00 Å between the calculated positions of the hydrogen atoms bonded to C(16) and C(31). The crystal structure of **2** does not appear to contain any abnormally short intermolecular contact distances. The packing arrangements are illustrated in Figs. 3 and 4 for structures **1** and **2**, respectively. These provide no evidence for strong anion–cation interactions and, in particular, there is no evidence that the phenyl rings of the BPh_4^- anion in **2** interact with the V-shaped cleft formed by the isoquinoline ligands next to the cationic Mo centre. This is not, perhaps, surprising since the two isoquinoline ligands are oriented so as not to be capable of producing a stacking interaction with a guest anion.

Experimental

All commercial reagents were used as supplied; $[Mo\{HB(dmpz)_3\}(NO)I_2]$ was prepared as its toluene solvate according to the previously described method and used in this form.[23] Toluene and tetrahydrofuran (thf) used as reaction media were dried and freed of dioxygen before use by distillation from sodium/benzophenone under dinitrogen. Reactions were carried out under dinitrogen but purification procedures were carried out in air. Silica gel 60 (70–230 mesh) was used as the stationary phase for column chromatography. Elemental analyses were carried out by the Microanalytical Laboratories in the School of Chemistry at the University of Birmingham.

Infrared spectra were recorded using using KBr pellets and a Perkin-Elmer PE297 spectrometer, 270 MHz ^1H NMR spectra were obtained from solutions in $CDCl_3$ using a JEOL GX 270 spectrometer and FAB mass spectra were recorded from *m*-nitrobenzyl alcohol matrix using a Kratos MS80 spectrometer. Solution conductivities were determined from 10^{-3} mol dm^{-3} solutions in acetonitrile. Cyclic voltammetric measurements were made using a Pt bead electrode with a PAR 174A polarograph and 10^{-3} mol dm^{-3} solutions of complex in dichloromethane containing 0.2 mol dm^{-3} $[NBu_4]BF_4$ as base electrolyte. Values are referred to ferrocene used as an internal standard and, under these conditions, $E_f\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\} = +0.545 \pm 0.010$ V *vs.* saturated calomel electrode (SCE) with $\Delta E_p = 70 \pm 10$ mV. EPR spectra were recorded on a Bruker ESP-300E spectrometer at room temperature. Magnetic susceptibilities were obtained from solid samples using a Cryogenic S100 SQUID magnetometer in the School of Physics of the University of Birmingham. Because of the small sample volume which could be used in the SQUID, along with the comparatively weak magnetism of these complexes, there was significant scatter in the data obtained at the higher temperatures. Thus the magnetic moment values quoted for 300 K are subject to estimated errors of up to $\pm 0.3\mu_B$, compared to $\pm 0.05\mu_B$ for the values at 6 K. Magnetic

Table 5 Selected bond lengths (Å) and bond angles (°) for the cations of **1** and **2**

	1	2
Mo-N(1)	1.760(7)	1.719(9)
Mo-N(2)	2.252(7)	2.233(9)
Mo-N(4)	2.150(8)	2.171(11)
Mo-N(6)	2.151(7)	2.146(9)
Mo-N(8)	2.207(8)	2.212(9)
Mo-N(9)	2.204(7)	2.234(9)
N(1)-O	1.202(11)	1.241(15)
C(18)-C(21)	1.430(15)	
C(29)-C(32)	1.497(13)	
N(1)-Mo-N(2)	176.4(3)	174.7(4)
N(1)-Mo-N(4)	96.7(3)	97.8(4)
N(2)-Mo-N(4)	85.8(3)	83.0(3)
N(1)-Mo-N(6)	98.0(3)	100.2(4)
N(2)-Mo-N(6)	84.8(3)	85.1(3)
N(4)-Mo-N(6)	85.3(3)	85.4(4)
N(1)-Mo-N(8)	92.0(3)	91.8(4)
N(2)-Mo-N(8)	85.7(3)	88.0(3)
N(4)-Mo-N(8)	170.7(3)	168.5(3)
N(6)-Mo-N(8)	90.1(3)	86.7(3)
N(1)-Mo-N(9)	91.2(3)	88.9(4)
N(2)-Mo-N(9)	86.2(3)	85.9(3)
N(4)-Mo-N(9)	89.5(3)	88.6(3)
N(6)-Mo-N(9)	169.9(3)	169.7(4)
N(8)-Mo-N(9)	93.8(3)	97.9(3)
Mo(1)-N(1)-O	175.4(8)	169.9(9)

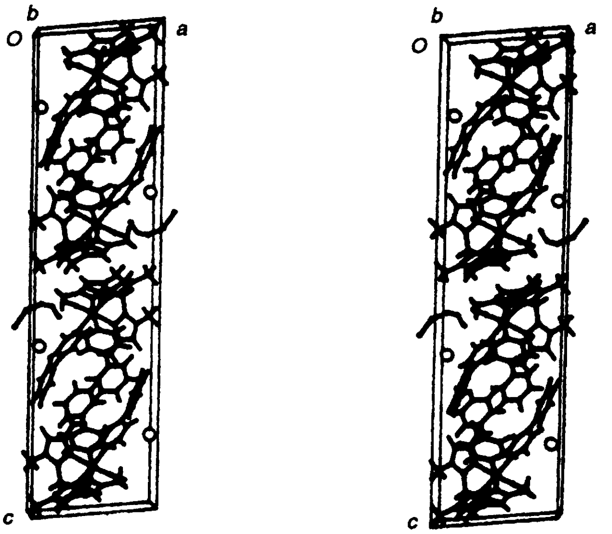

Fig. 3 Stereoscopic view of the crystal structure of **1**. Iodide ions are shown as open circles

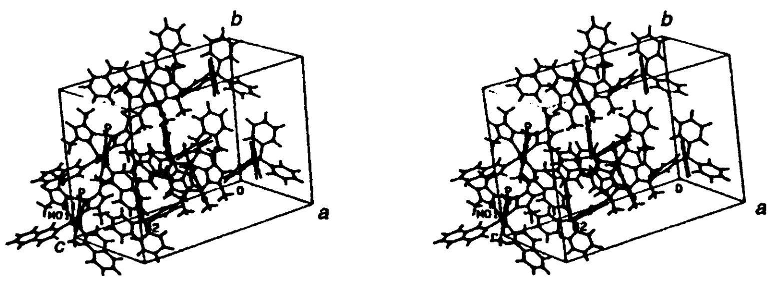

Fig. 4 Stereoscopic view of the crystal structure of **2**

moments in dichloromethane solutions were measured using the Evans NMR method.[24] Molar susceptibilities were corrected for the diamagnetic contribution of ligands using Pascal's constants.[25]

Synthetic Studies.—[Mo{HB(dmpz)$_3$}(NO)(py)I]. The complex [Mo{HB(dmpz)$_3$}(NO)I$_2$]·C$_6$H$_5$Me (500 mg, 0.65 mmol) and pyridine (600 mg; 7.58 mmol) were added to dry toluene (70 cm^3) containing a few drops of triethylamine. The mixture was heated under reflux for 70 h after which time the mixture was cooled, filtered and the solvent removed from the filtrate by evaporation under reduced pressure. The residue was purified by column chromatography on silica gel using dichloromethane as the eluent. The major green band contained the product (yield 273 mg, 59%) (Found: C, 38.4; H, 4.2; N, 18.2. $C_{20}H_{27}BIMoN_8O$ requires C,38.2; H, 4.3; N, 17.8%); ν_{max} 2547 (BH), 1625 (NO) cm^{-1}; Λ 2 ohm^{-1} cm^2 mol^{-1}.

[Mo{HB(dmpz)$_3$}(NO)(NC$_5$H$_4$Ph-4)I]. This compound was prepared by the preceding method using 4-phenylpyridine (500 mg; 3.22 mmol) in toluene (40 cm^3) and a reaction time of 24 h. The major cherry-red band from the chromatography column contained the product (yield 330 mg, 63%) (Found: C, 44.7; H, 4.5; N, 15.9. $C_{26}H_{31}BIMoN_8O$ requires C, 44.4; H, 4.4; N, 15.9%); ν_{max} 2544 (BH), 1618 (NO) cm^{-1}; Λ 0 ohm^{-1} cm^2 mol^{-1}.

[Mo{HB(dmpz)$_3$}(NO)(NC$_{13}$H$_9$)I]. This compound was prepared by the preceding method using phenanthridine (500 mg; 2.8 mmol) in toluene (80 cm^3). The major maroon band from the chromatography column contained the product (yield 120mg, 24%) (Found: C, 46.3; H, 4.2; N, 15.6. $C_{28}H_{31}BIMoN_8O$ requires C, 46.1; H, 4.3; N, 15.4%); ν_{max} 2550 (BH), 1628 (NO) cm^{-1}; Λ 1 ohm^{-1} cm^2 mol^{-1}.

[Mo{HB(dmpz)$_3$}(NO)(NC$_9$H$_7$)I]. This compound was prepared by the preceding method using [Mo{HB(dmpz)$_3$}(NO)I$_2$]·C$_6$H$_5$Me (300 mg, 0.39 mmol) and isoquinoline (300 mg; 2.32 mmol) in toluene (50 cm^3). The major maroon band from the chromatography column contained the product (yield 137 mg, 52%) (Found: C, 42.7; H, 4.3; N, 16.3. $C_{24}H_{29}BIMoN_8O$ requires C, 42.4; H, 4.3; N, 16.5%); ν_{max} 2550 (BH), 1622 (NO) cm^{-1}; Λ 1 ohm^{-1} cm^2 mol^{-1}.

[Mo{HB(dmpz)$_3$}(NO)(NC$_5$H$_4$Ph-4)$_2$]I·H$_2$O **1**. The complex [Mo{HB(dmpz)$_3$}(NO)I$_2$]·C$_6$H$_5$Me (300 mg, 0.39 mmol) and 4-phenylpyridine (300 mg; 1.93 mmol) were added to dry toluene (30 cm^3). The mixture was heated under reflux for 24 h after which time the mixture was cooled, filtered and the solvent removed from the filtrate by evaporation under reduced pressure. The residue was purified by column chromatography on silica gel using dichloromethane–tetrahydrofuran (97:3) as the eluent. The major orange-brown band contained the product (yield 74 mg, 19%) (Found: C, 50.2; H, 4.6; N, 14.2. $C_{37}H_{40}BIMoN_9O \cdot H_2O$ requires C, 50.6; H, 4.8; N, 14.4%); ν_{max} 2550 (BH), 1625, 1610 (NO) cm^{-1}; Λ 105 ohm^{-1} cm^2 mol^{-1}.

[Mo{HB(dmpz)$_3$}(NO)(NC$_9$H$_7$)$_2$]I$_3$. This compound was prepared by the preceding method using [Mo{HB(dmpz)$_3$}(NO)I$_2$]·C$_6$H$_5$Me (500 mg, 0.65 mmol) and isoquinoline (500 mg; 0.39 mmol) in toluene (70 cm^3). The major orange-brown band eluted with dichloromethane contained the product (yield 300 mg, 43%) (Found: C, 37.4; H, 3.4; N, 11.9. $C_{33}H_{36}BI_3MoN_9O$ requires C, 37.3; H, 3.4; N, 11.9%); ν_{max} 2546 (BH), 1606, 1628 (NO) cm^{-1}; Λ 87 ohm^{-1} cm^2 mol^{-1}.

[Mo{HB(dmpz)$_3$}(NO)(NC$_9$H$_7$)$_2$]BPh$_4$ **2**. To a solution of [Mo{HB(dmpz)$_3$}(NO)(NC$_9$H$_7$)$_2$] (70 mg, 0.07 mmol) in dichloromethane (20 cm^3) was added a solution of sodium tetraphenylborate (200 mg, 0.6 mmol) in ethanol (10 cm^3). The resulting mixture was then stirred at room temperature for 30 min. The solvents were removed under reduced pressure and the residue redissolved in dichloromethane (20 cm^3) and excess sodium tetraphenylborate was removed by filtration. The product was isolated as brown needles (45.6 mg, 69%) by recrystallisation from ethanol (Found: C, 68.0; H, 5.7; N, 12.5. $C_{57}H_{56}B_2MoN_9O$ requires C, 68.4; H, 5.6; N, 12.6%); ν_{max} 2547 (BH), 1619 (NO) cm^{-1}; Λ 119 ohm^{-1} cm^2 mol^{-1}.

Structural Studies.—Crystal data. Crystals of [Mo(NO){HB(dmpz)$_3$(NC$_5$H$_4$Ph-4)$_2$]I, $C_{37}H_{40}BIMoN_9O \cdot 0.42C_5H_{12}$ **1**, were grown from CH$_2$Cl$_2$–pentane, $M_r = 890.7$, monoclinic, space group $P2_1/c$, $a = 10.098(2)$, $b = 10.262(3)$, $c = 39.662(11)$ Å, $\beta = 95.49(3)°$, $U = 4091$ Å^3, $Z = 4$, $D_c = 1.446$ g cm^{-3}, $F(000) = 1802.6$, μ(Mo-Kα) = 1.11 mm^{-1}, $\lambda = 0.710\,69$ Å. Crystals of [Mo(NO){HB(dmpz)$_3$(NC$_9$H$_7$)$_2$]BPh$_4$, $C_{57}H_{56}B_2MoN_9O$ **2**, were grown from CH$_2$Cl$_2$–ethanol, $M_r = 1000.7$, monoclinic, space group Cc, $a = 11.908(10)$, $b = 18.165(5)$, $c = 23.50(4)$ Å, $\beta = 96.71(9)°$, $U = 5048$ Å^3, $Z = 4$, $D_c = 1.317$ g cm^{-3}, $F(000) = 2084$, μ(Mo-Kα) = 0.300 mm^{-1} $\lambda = 0.710\,69$ Å. The crystals [0.5 × 0.3 × 0.2 mm (**1**), 0.6 × 0.4 × 0.2 mm (**2**)] were mounted on an Enraf-Nonius CAD4 diffractometer; cell-dimensions and intensities were measured by ω–2θ scans with graphite-monochromated Mo-Kα radiation. 7606 (**1**) and 5134 (**2**) unique reflections were scanned in the range $2 < \theta < 25°$, and of these 5221 (**1**) and 4179 (**2**) having $I > 2.5\sigma(I)$ were considered observed and used in the analyses. Three standard reflections were measured every 2 h to monitor the stability of the system. No absorption corrections were applied. The structures were solved by Patterson and Fourier methods and refined by least squares, minimising $\Sigma w(|F_o| - |F_o|)^2$ and using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed in calculated positions riding on their respective bonded atoms with fixed isotropic thermal parameters [$U = 0.1$ Å^2 (**1**) 0.15 Å^2 (**2**)]. A cluster of residual electron density peaks in **1** was considered to indicate the presence of a molecule of pentane. For this molecule carbon-atom coordinates and isotropic thermal parameters and the site occupation factor were refined. Weights $w = 1/[\sigma^2(F) + gF^2]$, with $g = 0.0003$ (**1**) and 0.002 (**2**), were used in the least-squares refinements. The calculations were terminated when all shift/e.s.d. ratios were <0.05 and $R = \Sigma||F_o| - |F_o||/\Sigma|F_o| = 0.0656$, $R^1 = [\Sigma w(|F_o| - |F_o|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.1017$ (**1**) and 0.0679, 0.0982 (**2**) for observed reflections. The residual electron density in the final difference maps were within the ranges ±0.89 e Å^{-3} for **1** and ±1.04 e Å^{-3} for **2**. Extinction corrections were not considered to be necessary.

Complex neutral atom scattering factors were employed. Computations were carried out on the University of Birmingham IBM 3090 computer and on the Amdahl 5890 at Manchester Computing Centre with the SHELX 86[26] and SHELX 76[27] packages. The molecular diagrams were drawn using PLUTO.[28]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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