Mixed-valence dinuclear molybdenum complexes with benzenediamido and dianilido bridges: comparison with related phenolato and dipyridyl species, and with their pentammineruthenium analogues†

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The monoanionic mixed-valence benzenediamido complexes *ortho*- and *para*-[{Mo(NO)[HB(dmpz)$_3$]X}$_2$-(Z$_2$C$_6$H$_4$)]$^-$ **A** [HB(dmpz)$_3$ = tris(3,5-dimethylpyrazolyl)hydroborate; Z = NH; X = Cl, Br or I] have been characterised by electronic, EPR and IR spectroscopic and electrochemical techniques. They are delocalised at room temperature on the EPR time-scale but valence-trapped on the IR time-scale, whereas the *meta* isomer exhibits valence-trapped behaviour according to both techniques. The electrochemical properties of these species and of related dianilido complexes [{Mo(NO)[HB(dmpz)$_3$]X}$_2$(ZC$_6$H$_4$EC$_6$H$_4$Z)] **B** [Z = NH; E = CH$_2$, O, SO$_2$, CO or OC$_6$H$_4$(SO$_2$)C$_6$H$_4$O] are dependent on X and E. These results are compared with those obtained from related diphenolato species **A** (Z = O) and **B** (Z = O) and dipyridyl analogues [{Mo(NO)[HB(dmpz)$_3$]X}$_2${(NC$_5$H$_4$)E′-(C$_5$H$_4$N)}] **C** (E′ = nothing, CH$_2$CH$_2$, CH=CH or dimethyldecapentene). Comproportionation constants and related data for the redox equilibria $\mathbf{A} + \mathbf{A}^{2-} \rightleftharpoons 2\mathbf{A}^-$, $\mathbf{B} + \mathbf{B}^{2-} \rightleftharpoons$; $2\mathbf{B}^-$ and $\mathbf{C} + \mathbf{C}^{2-} \rightleftharpoons 2\mathbf{C}^-$ show that interaction between the molybdenum-based redox centres increases significantly as the distance between them decreases and as a function of the group connecting the bridge to the molybdenum, in the order O < NH < N (pyridine). The data are generally consistent with those obtained from related dinuclear pentammineruthenium complexes [{Ru(NH$_3$)$_5$}$_2$Q]$^{n+}$ (Q = bridging group) but the interaction between the metal centres is much greater in the molybdenum species than in the ruthenium complexes, and a simple explanation for this behaviour is given.

The incorporation of redox-active metals in a highly polarisable molecular framework is an attractive design feature for the creation of new materials with potential applications as electronic devices.[1] Such metal centres can be activated by external stimuli (*e.g.* electro- or photo-chemical) and often have considerable thermal and oxidative stability. They can provide access to molecular architectures not easily available through more conventional carbon-based chemistry, and can be designed to have intrinsic variable magnetic or spectroscopic characteristics depending on the formal metal oxidation state.

Among the simplest model compounds which can be investigated for novel magnetic and electronic behaviour with potential switching capabilities are redox-active homodimetallic complexes in which the metal centres are linked by near-linear multiple-atom bridges. In such species, mixed-valence behaviour is a dominant characteristic,[2] and manipulation of this in a redox chemistry context is at the heart of much current activity in this sector of molecular electronics.

The understanding of the nature of the Creutz–Taube ion, [{Ru(NH$_3$)$_5$}$_2$(pyz)]$^{5+}$ (pyz = pyrazine), and its polypyridyl analogues has provided the essential foundation for the study of photochemically and electrochemically stimulated electron-transfer behaviour in di- and oligo-metallic systems.[3] The Creutz–Taube ion formally contains Ru$^{\mathrm{II}}$ (d^6) and Ru$^{\mathrm{III}}$ (d^5), but the unpaired electron is delocalised over the metals and bridging ligand framework and the oxidation-state formalism is unhelpful.[4] While the largest groups of redox-active homodimetallic compounds exhibiting mixed valency are based on ruthenium ammine or polypyridyl systems, there are other important groups of organometallic species based largely on η^5-cyclopentadienyl derivatives of iron,[5] manganese, rhenium[6] and Group VI metal carbonyls.[7] Generation of the mixed-valence compound is usually achieved by *oxidation* of the parent homovalent dinuclear species, *e.g.* [{Ru(NH$_3$)$_5$}$_2$Q]$^{4+}$ or [(η^5-C$_5$H$_5$)Fe(η^5:η^5-C$_5$H$_4$QC$_5$H$_4$)Fe(η^5-C$_5$H$_5$)}], where Q = linking group. In electronic terms, this means removal of an electron from a *bonding* orbital in the precursor, leading to a mixed-valence species which may exhibit Class II or Class III behaviour depending on the extent to which the unpaired electron is delocalised.[2a] From detailed physical and theoretical studies of the Creutz–Taube ion and its many analogues, it is clear that the classification of mixed-valence co-ordination and organometallic compounds is very largely dependent on the nature of the linking group Q.[4]

In contrast to the large number of mixed-valence species generated by oxidation of homodinuclear species, there are relatively few compounds formed by *reduction*. The added electron must be accommodated in the LUMO (lowest unoccupied molecular orbital) which could be non-bonding or antibonding, partly filled or empty. The EPR spectra of the dinuclear carbonyls [{M(CO)$_3$(PR$_3$)$_2$}$_2$Q]$^-$ (M = Mo or W; Q = pyrazine or related N-heterocyclic ligand) suggest that these compounds are best described as ligand radical anions stabilised by the two {M(CO)$_3$(PR$_3$)$_2$} fragments. While there is clear coupling between the unpaired electron and the metal nuclei, this system cannot be defined as a genuine mixed-valence species in the Creutz–Taube sense, since the metal-based orbitals are formally occupied [each metal centre has 18 valence electrons (v.e.s) prior to reduction] and the LUMO must be predominantly bridging ligand based.[7]

However, there is very large group of compounds which have the capability to exhibit mixed-valence behaviour on reduction: the dinuclear nitrosyl tris(3,5-dimethylpyrazol-1-yl)hydroborato halide complexes of molybdenum and tungsten, [{M(NO)[HB-(dmpz)$_3$]X}$_2$Q] (M = Mo or W; X = halide; Q = deprotonated dihydroxy- or diamino-aromatic ligand) (Scheme 1).[8–12] Electrochemical reduction of the isovalent neutral precursors (16 v.e.s per metal) occurs in two steps giving first a mixed-valence, paramagnetic (16/17 v.e.) monoanion [{M(NO)[HB-(dmpz)$_3$]X}$_2$Q]$^-$ (formation potential E_f^1) and then an isovalent (17/17 v.e.) dianion, [{M(NO)[HB(dmpz)$_3$]X}$_2$Q]$^{2-}$ (formation potential E_f^2). The latter are formally isoelectronic with the well characterised bipyridyl species, [{Mo(NO)[HB(dmpz)$_3$]X}$_2$(N-C$_5$H$_4$)E(C$_5$H$_4$N)}] **V** (E = oligoethene, phenylene, *etc.*).[11,12] In order to generate significant amounts of the monoanions syn-

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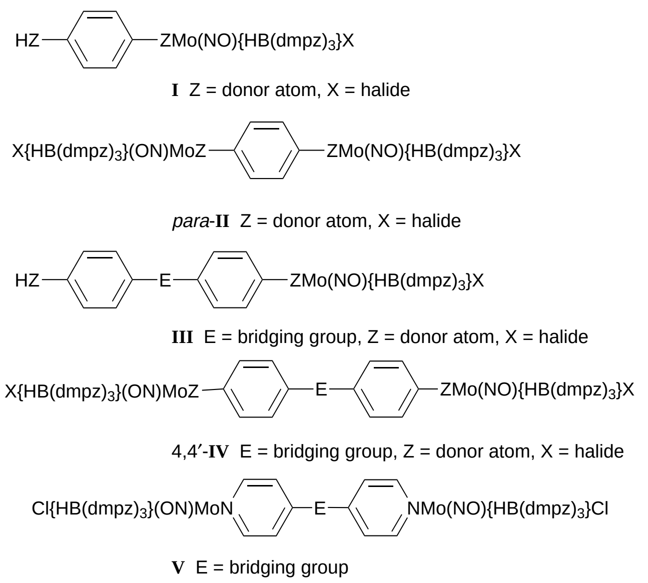
† Dedicated to the memory of Geoffrey Wilkinson: inspirational PhD supervisor, enthusiast, iconoclast, Yorkshireman and friend.



Scheme 1 Some benzenediamide (Z = N) and dianilino (Z = N) complexes and their benzenediolato (Z = O), diphenolato (Z = O) and dipyridyl analogues

thetically or electrochemically, free from the starting material or the derivative dianions, the separation between E_f^1 and E_f^2, *i.e.* ΔE_f, must be substantial (ideally >200 mV). Such a situation can be expected in compounds containing benzenediamido bridges, *e.g.* in $[\{Mo(NO)[HB(dmpz)_3]X\}_2\{(HN)_2C_6H_4\}]$ **II** (Z = NH, X = halide),[8,9,13] where the separation between the metal-based redox centres may be varied by choice of the geometric isomers of the $[(HN)_2C_6H_4]^{2-}$ bridge. The effect of the substitution pattern in aromatic bridges on the spectral properties of mixed-valence dinuclear complexes has received sparse attention. The most notable study has been that of Richardson and Taube,[14] who connected $\{Ru(NH_3)_5\}^{2+}$ fragments by sets of bridging ligands such as 1,2-, 1,3- and 1,4-dicyanobenzene, pyrazine and pyrimidine, and various isomers of dicyanonaphthalene. They observed that 1,3-substituted bridges such as pyrimidine and 1,3-dicyanobenzene significantly diminished the interactions between the metal centres relative to their 1,2 and/or 1,4 analogues, the mixed-valence complexes derived from them having smaller comproportionation constants (K_c) values and higher-energy, less-intense i.v.c.t. (intervalence charge transfer) absorptions.

The converse of the short bridge is, of course, the extended bridge, such as occurs in the dianilides $[\{Mo(NO)[HB(dmpz)_3]X\}_2(HNC_6H_4EC_6H_4NH)]$ **IV** (Z = NH; E = CO, O, SO_2 or CH_2CH_2; X = halide) (species with X = I have been reported earlier[11]). The interaction between the two molybdenum nitrosyl redox centres must be significantly diminished, ultimately reducing ΔE_f to the statistical value of 35.6 mV,[15] and it may no longer be possible to generate the mixed-valence anion free of the other oxidation states.

Our first and principal targets were therefore the monoanions $[\{Mo(NO)[HB(dmpz)_3]X\}_2Q]^-$, where $Q = (HN)_2C_6H_4$, *i.e.* **II**$^-$ (Z = NH, X = halide), and, while a preliminary report of our studies has been published,[16] we describe here a fuller spectroscopic characterisation of the mixed-valence behaviour of these species. Our second target was a further study of the effect of prolongation of the bridge in $[\{Mo(NO)[HB(dmpz)_3]X\}_2(HNC_6H_4EC_6H_4NH)]$ **IV** (Z = NH, X = halide) on the electrochemical properties of these molecules, and the generation of a fully reduced dianionic system in order to compare its electronic properties with those of related isoelectronic diphenolato and dipyridyl species.

These dinuclear molybdenum nitrosyl compounds have three particular advantages with respect to most other dinuclear species capable of mixed-valence behaviour. (1) Electrochemical, in that E_f can be significantly varied by choosing appropriate combinations of M, X, Z and E, giving easily managed control of synthesis of singly or doubly reduced species. Furthermore, comproportionation constants (K_c) related to the stability of mixed-valence species can be calculated from differential pulse data obtained from the three-membered electron-transfer chain (neutral, mono- and di-anionic species). (2) The proximity of metal-co-ordinated NO to the redox centres, where the position and number of ν_{NO} in mixed-valence species is very sensitive to electron-exchange parameters. Infrared techniques have been used in this context.[3,5,17,18] (3) The magnetic properties of the reduced species. Monoanionic paramagnets will exhibit EPR spectra with a characteristic molybdenum hyperfine coupling constant, A_{Mo} (molybdenum has two naturally occurring isotopes with $I = \frac{5}{2}$), which can reveal whether the unique electron is valence-trapped or interacts with both metal centres. The use of EPR spectroscopy to characterise mixed-valence systems is feasible.[7,17,18]

A disadvantage of this class of compound is, however, that assignment of the electronic spectra of transition-metal nitrosyls is difficult because possible intervalence charge transfers are obscured by intense ligand-to-metal and/or metal-to-ligand charge-transfer (l.m.c.t. and/or m.l.c.t.) bands. For this reason it is unproductive to carry out solvatochromism studies and extremely difficult to determine the value of V_{ab}, the electron-exchange parameter which quantifies mixed-valence behaviour.[2] However, the combination of IR and EPR methods provides a convenient time-scale reference for classifying mixed-valence behaviour, allowing at least some differentiation between Class I and Class III properties.

Experimental

The complexes $[Mo(NO)\{HB(dmpz)_3\}X_2]$ (X = Cl or I), $[Mo(NO)\{HB(dmpz)_3\}Cl\{o\text{-}(HN)C_6H_4(NH_2)\}]$ and $[\{Mo(NO)[HB(dmpz)_3]X\}_2(HNC_6H_4EC_6H_4NH)]$ (X = Cl or I) were prepared by reported methods with only small modifications,[8–10,19] and $[Mo(NO)\{HB(dmpz)_3\}Br_2]$ was made by reaction of $[Mo(CO)_2(NO)\{HB(dmpz)_3\}]$ with iodine and benzyl bromide in toluene.[20] Solvents were thoroughly dried (hydrocarbons and CH_2Cl_2 over CaH_2, toluene over Na) and degassed, all reactions were carried out under nitrogen, and yields are based on the starting molybdenum-containing compound. All complexes were stable enough to be purified using column chromatography using silica gel 60 (70–230 mesh) and dichloromethane (to remove dinuclears) or mixtures of dichloromethane and tetrahydrofuran (thf) (1:1 v/v; to remove mononuclears) as eluents.

Proton NMR spectra were recorded on a JEOL GX270 or GX300 instrument in CD_2Cl_2 solution, FAB mass spectra using a VG-Autospec with 3-nitrobenzyl alcohol as matrix and IR spectra in CH_2Cl_2 solutions using a PE1600 FTIR spectrophotometer. Microanalyses were determined by the Microanalytical Laboratory of the School of Chemistry, University of Bristol. Electrochemical measurements were made using an EG & PAR model 273A potentiostat, with dichloromethane, purified by distillation from CaH_2, as solvent and $[NBu^n_4][PF_6]$ or $[NBu^n_4][BF_4]$ (0.1 mol dm^{-3}) as base electrolyte. A standard three-electrode configuration was used, with a platinum-wire working and auxiliary electrodes and a saturated calomel electrode (SCE) as reference. Ferrocene was added at the end of each experiment as an internal standard; all potentials are quoted *vs.* the ferrocene–ferrocenium couple). The EPR spectra were recorded using a Bruker ESP-300E spectrometer.

Synthetic procedures for complexes derived from diaminobenzenes

***(a)* Mononuclear species.** These were obtained by reaction of $[\{Mo(NO)\{HB(dmpz)_3\}X_2]$ (X = Cl, Br or I) with 3 equivalents of $C_6H_4(NH_2)_2$ in the presence of hexamethylenetetramine in toluene.[8–10] The reaction mixtures were refluxed and stirred for 1.5–6 h, then cooled, filtered and the filtrate evaporated *in vacuo*. The residue was dissolved in dichloromethane and chromatographed, the main two fractions being collected (bi- and mononuclear benzenediamide species). With pure dichloromethane, the dinuclear species were eluted first, and using dichloromethane–thf the more polar mononuclear species could be separated. The respective fractions were evaporated to dryness *in vacuo* and the desired products crystallised from dichloromethane and hexane or pentane. After filtration, the microcrystalline solids were dried at 100 °C for 3 h.

[Mo(NO){HB(dmpz)$_3$}Cl{*o*-(HN)C$_6$H$_4$(NH$_2$)}] *ortho*-**I** (Z = NH, X = Cl): FAB mass spectrum *m/z* 567 (required 565.72) and 531; IR 2552 (ν_{BH}), 1662 cm^{-1} (ν_{NO}); ^{1}H NMR (300 Mz) δ 12.72 (1 H, br s, NH), 7.77–6.80 (4 H, m, C$_6$H$_4$), 5.88 (2s), 5.65 (1 H, Me$_2$C$_3$*H*N$_2$), 3.64 (2 H, br s, NH$_2$), 2.68 (3 H, s), 2.44 (3 H, s), 2.38 (6 H, s), 2.24 (3 H, s) and 2.08 [3 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[Mo(NO){HB(dmpz)$_3$}Br{*o*-(HN)C$_6$H$_4$(NH$_2$)}] *ortho*-**I** (Z = NH, X = Br) (Found: C, 42.3; H, 5.0; N, 20.6. C$_{21}$H$_{28}$BBrMoN$_9$O requires C, 41.3; H, 4.8; N, 20.7%): IR 2554 (ν_{BH}), 1663 cm^{-1} (ν_{NO}); ^{1}H NMR (300 Mz) δ 12.98 (1 H, br s, NH), 7.94 (1 H, d), 7.12 (1 H, t), 6.99 (1 H, t), 6.80 (1 H, d, C$_6$H$_4$), 5.92 (1 H, s), 5.91 (1 H, s), 5.82 (1 H, s, Me$_2$C$_3$*H*N$_2$), 3.52 (2 H, br s, NH$_2$), 2.64 (3 H, s), 2.45 (3 H, s), 2.40 (6 H, s), 2.38 (3 H, s) and 2.02 [3 H, (C*H*$_3$)$_2$C$_3$HN$_2$].

[Mo(NO){HB(dmpz)$_3$}I{*o*-(HN)C$_6$H$_4$(NH$_2$)}] *ortho*-**I** (Z = NH, X = I): IR 2556 (ν_{BH}), 1662 cm^{-1} (ν_{NO}); ^{1}H NMR (300 Mz) δ 13.27 (1 H, br s, NH), 8.17 (1 H, d), 7.20 (1 H, t), 6.99 (1 H, t), 6.78 (1 H, d, C$_6$H$_4$), 5.96 (1 H, s), 5.91 (1 H, s), 5.81 (1 H, s, Me$_2$C$_3$*H*N$_2$), 3.42 (2 H, br s, NH$_2$), 2.66 (3 H, s), 2.45 (3 H, s), 2.48 (3 H, s), 2.40 (3 H, s), 2.38 (3 H, s) and 1.96 [3 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[Mo(NO){HB(dmpz)$_3$}Cl{*m*-(HN)C$_6$H$_4$(NH$_2$)}] *meta*-**I** (Z = NH, X = Cl): IR 2554 (ν_{BH}), 1659 cm^{-1} (ν_{NO}); ^{1}H NMR (300 Mz) δ 10.19 (1 H, br s, NH), 7.38 (1 H, d), 6.88 (2 H, m), 6.74 (1 H, d, C$_6$H$_4$), 5.89 (1 H, s), 5.85 (1 H, s), 5.80 (1 H, s, Me$_2$C$_3$*H*N$_2$), 3.51 (2 H, br s, NH$_2$), 2.55 (3 H, s), 2.42 (3 H, s), 2.36 (3 H, s), 2.354 (3 H, s), 2.350 (3 H, s) and 2.09 [3 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[Mo(NO){HB(dmpz)$_3$}Br{*m*-(HN)C$_6$H$_4$(NH$_2$)}] *meta*-**I** (Z = NH, X = Br) (Found: C, 42.0; H, 4.9; N, 20.4. C$_{21}$H$_{28}$BBrMoN$_9$O reques C, 41.3; H, 4.8; N, 20.7%): IR 2554 (ν_{BH}), 1659 cm^{-1} (ν_{NO}); ^{1}H NMR (300 Mz) δ 13.15 (1 H, br s, NH), 7.12 (2 H, m), 6.73 (2 H, m, C$_6$H$_4$), 5.97 (1 H, s), 5.91 (1 H, s), 5.81 (1 H, s, Me$_2$C$_3$*H*N$_2$), 3.90 (2 H, br s, NH$_2$), 2.66 (3 H, s), 2.48 (3 H, s), 2.44 (3 H, s), 2.39 (3 H, s), 2.38 (3 H, s) and 2.00 [3 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[Mo(NO){HB(dmpz)$_3$}I{*m*-(HN)C$_6$H$_4$(NH$_2$)}] *meta*-**I** (Z = NH, X = I): IR 2555 (ν_{BH}), 1662 cm^{-1} (ν_{NO}); ^{1}H NMR (300 Mz) δ 12.92 (1 H, br s, NH), 7.15 (2 H, t), 7.02 (1 H, s), 6.69 (1 H, d), 6.59 (1 H, d, C$_6$H$_4$), 5.93 (1 H, s), 5.91 (1 H, s), 5.82 (1 H, s, Me$_2$C$_3$*H*N$_2$), 3.90 (2 H, s, NH$_2$), 2.65 (3 H, s), 2.45 (3 H, s), 2.39 (3 H, s), 2.38 (6 H, s) and 2.02 [3 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[Mo(NO){HB(dmpz)$_3$}Cl{*p*-(HN)C$_6$H$_4$(NH$_2$)}] *para*-**I** (Z = NH, X = Cl): ^{1}H NMR (270 Mz) δ 12.71 (1 H, br s, NH), 7.38 (2 H, d), 6.76 (2 H, d, C$_6$H$_4$), 5.90 (2 H, s), 5.82 (1 H, s, Me$_2$C$_3$*H*N$_2$), 4.04 (2 H, br s, NH$_2$), 2.63 (3 H, s), 2.43 (3 H, s), 2.39 (3 H, s), 2.37 (3 H, s), 2.35 (3 H, s) and 2.03 [3 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[Mo(NO){HB(dmpz)$_3$}Br{*p*-(HN)C$_6$H$_4$(NH$_2$)}] *para*-**I** (Z = NH, X = Br) (Found: C, 42.1; H, 5.1; N, 20.6. C$_{21}$H$_{28}$BBrMoN$_9$O requires C, 41.3; H, 4.8; N, 20.7%): IR 2553 (ν_{BH}), 1649 cm^{-1} (ν_{NO}); ^{1}H NMR (270 Mz) δ 12.96 (1 H, br s, NH), 7.38 (2 H, d), 6.70 (2 H, d, C$_6$H$_4$), 5.93 (1 H, s), 5.91 (1 H, s), 5.82 (1 H, s, Me$_2$C$_3$*H*N$_2$), 4.10 (2 H, br s, NH$_2$), 2.66 (3 H, s), 2.45 (3 H, s), 2.40 (3 H, s), 2.39 (3 H, s), 2.38 (3 H, s) and 2.02 [3 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[Mo(NO){HB(dmpz)$_3$}I{*p*-(HN)C$_6$H$_4$(NH$_2$)}] *para*-**I** (Z = NH, X = I): IR 2555 (ν_{BH}), 1650 cm^{-1} (ν_{NO}); ^{1}H NMR (270 Mz) δ 13.17 (1 H, br s, NH), 7.52 (2 H, d), 6.67 (2 H, d, C$_6$H$_4$), 5.95 (1 H, s), 5.90 (1 H, s), 5.78 (1 H, s, Me$_2$C$_3$*H*N$_2$), 4.10 (2 H, br s, NH$_2$), 2.67 (3 H, s), 2.46 (3 H, s), 2.43 (3 H, s), 2.39 (3 H, s), 2.37 (3 H, s) and 2.00 [3 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

***(b)* Dinuclear species.** The species [{Mo(NO)[HB(dmpz)$_3$]X}$_2$-{(HN)$_2$C$_6$H$_4$}] **II** (Z = NH, X = Cl, Br or I) could be obtained by reaction of 2 molar equivalents of [Mo(NO){HB(dmpz)$_3$}X$_2$] (X = Cl, Br or I) with one of the appropriate diamines in refluxing toluene in the presence of NEt$_3$.[8–10] The products were purified in the same way as that described above.

For [{Mo(NO)[HB(dmpz)$_3$]Br}$_2${1,3-(HN)$_2$C$_6$H$_4$}], [Mo(NO){HB(dmpz)$_3$}Br$_2$] (0.58 g), C$_6$H$_4$(NH$_2$)$_2$-1,3 (0.05 g) and NEt$_3$ (0.3 cm^3) in toluene (50 cm^3) refluxed for 2 h afforded the compound as a brown powder (0.53 g, 48%). Yields of other dinuclear compounds varied between 42 and 80%.

[{Mo(NO)[HB(dmpz)$_3$]Cl}$_2${1,2-(HN)$_2$C$_6$H$_4$}] *ortho*-**II** (Z = NH, X = Cl): IR 2556 (ν_{BH}), 1668 cm^{-1} (ν_{NO}); ^{1}H NMR (300 MHz) δ 12.10 (2 H, br s, NH), 8.19 (2 H, m), 7.40 (2 H, m, C$_6$H$_4$), 5.86 (2 H, s), 5.64, (2 H, s), 5.44 (2 H, s, Me$_2$C$_3$*H*N$_2$), 2.55 (6 H, s), 2.44 (6 H, s), 2.37 (6 H, s), 2.35 (6 H, s), 2.02 (6 H, s) and 1.79 [6 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[{Mo(NO)[HB(dmpz)$_3$]Br}$_2${1,2-(HN)$_2$C$_6$H$_4$}] *ortho*-**II** (Z = NH, X = Br) (Found: C, 39.1; H, 4.8; N, 19.2. C$_{36}$H$_{40}$B$_2$Br$_2$Mo$_2$N$_{14}$O$_2$ requires C, 38.9; H, 4.5; N, 20.1%): FAB mass spectrum *m/z* 1114 (requires 1112.20) and 1033; IR 2555 (ν_{BH}), 1667 cm^{-1} (ν_{NO}); ^{1}H NMR (300 MHz) δ 12.24 (2 H, br s, NH), 8.25 (2 H, m), 7.46 (2 H, m, C$_6$H$_4$), 5.87 (2 H, s), 5.85 (H, s), 5.38 (2 H, s, Me$_2$C$_3$*H*N$_2$), 2.57 (6 H, s), 2.43 (6 H, s), 2.40 (6 H, s), 2.35 (6 H, s), 1.96 (6 H, s) and 1.58 [6 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[{Mo(NO)[HB(dmpz)$_3$]I}$_2${1,2-(HN)$_2$C$_6$H$_4$}] *ortho*-**II** (Z = NH, X = I): FAB mass spectrum *m/z* 1205 (requires 1206.20); IR 2555 (ν_{BH}), 1669 cm^{-1} (ν_{NO}); ^{1}H NMR (300 MHz) δ 12.44 (1 H, s), 12.42 (1 H, s, NH), 8.37 (2 H, m), 7.51 (2 H, m, C$_6$H$_4$), 5.87 (1 H, s), 5.85 (2 H, s), 5.71 (1 H, s), 5.39 (1 H, s), 5.37 (1 H, s, Me$_2$C$_3$*H*N$_2$), 2.58 (6 H, s), 2.50 (3 H, s), 2.44 (6 H, s), 2.37 (3 H, s), 2.35 (3 H, s), 2.34 (3 H, s), 2.11 (3 H, s), 1.94 (3 H, s), 1.73 (3 H, s) and 1.55 [3 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[{Mo(NO)[HB(dmpz)$_3$]Cl}$_2${1,3-(HN)$_2$C$_6$H$_4$}] *meta*-**II** (Z = NH, X = Cl): FAB mass spectrum *m/z* 1024 (requires 1023.30); IR 2554 (ν_{BH}), 1664 cm^{-1} (ν_{NO}); ^{1}H NMR (300 MHz) δ 12.74 (1 H, br s), 12.71 (1 H, br s, NH), 7.55–7.30 (4 H, m, C$_6$H$_4$), 5.92 (4 H, s), 5.86, (1 H, s), 5.81 (1 H, s, Me$_2$C$_3$*H*N$_2$), 2.60 (6 H, s), 2.45 (6 H, s), 2.40 (9 H, s), 2.39 (3 H, s), 2.34 (3 H, s), 2.33 (3 H, s) and 2.04 [6 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[{Mo(NO)[HB(dmpz)$_3$]Br}$_2${1,3-(HN)$_2$C$_6$H$_4$}] *meta*-**II** (Z = NH, X = Br) (Found: C, 39.1; H, 4.8; N, 20.0. C$_{36}$H$_{40}$B$_2$Br$_2$Mo$_2$N$_{14}$O$_2$ requires C, 38.9; H, 4.5; N, 20.1%): FAB mass spectrum *m/z* 1112 (requires 1112.20); IR 2554 (ν_{BH}), 1665 cm^{-1} (ν_{NO}); ^{1}H NMR (300 MHz) δ 12.99 (1 H, br s), 12.97 (1 H, br s, NH), 7.48 (4 H, m, C$_6$H$_4$), 5.95 (1 H, s), 5.94 (1 H, s), 5.91 (2 H, s), 5.86 (1 H, s), 5.81 (1 H, s, Me$_2$C$_3$*H*N$_2$), 2.62 (3 H, s), 2.617 (3 H, s), 2.47 (6 H, s), 2.40 (9 H, s), 2.392 (3 H, s), 2.386 (3 H, s), 2.376 (3 H, s) and 2.02 [6 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[{Mo(NO)[HB(dmpz)$_3$]I}$_2${1,3-(HN)$_2$C$_6$H$_4$}] *meta*-**II** (Z = NH, X = I): FAB mass spectrum *m/z* 1206 (requires 1206.20) and 1079; IR 2555 (ν_{BH}), 1661 cm^{-1} (ν_{NO}); ^{1}H NMR (270 MHz) δ 13.22 (2 H, br s, NH), 7.68 (3 H, m), 7.45 (1 H, m, C$_6$H$_4$), 5.99 (1 H, s), 5.98, (1 H, s), 5.91 (2 H, s), 5.85 (1 H, s), 5.80 (1 H, s, Me$_2$C$_3$*H*N$_2$), 2.631 (3 H, s), 2.626 (3 H, s), 2.49 (6 H, s), 2.44 (3 H, s), 2.43 (3 H, s), 2.40 (12 H, s) and 1.99 [6 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[{Mo(NO)[HB(dmpz)$_3$]Cl}$_2${1,4-(HN)$_2$C$_6$H$_4$}] *para*-**II** (Z = NH, X = Cl): FAB mass spectrum *m/z* 1024 (requires 1023.30); IR 2554 (ν_{BH}), 1658 cm^{-1} (ν_{NO}); ^{1}H NMR (270 MHz) δ 12.61 (1 H, br s), 12.59 (1 H, br s, NH), 7.53 (4 H, m, C$_6$H$_4$), 5.93 (2 H, s), 5.92, (2 H, s), 5.88 (1 H, s), 5.85 (1 H, s, Me$_2$C$_3$*H*N$_2$), 2.64 (3 H, s), 2.63 (3 H, s), 2.45 (6 H, s), 2.40 (12 H, s), 2.39 (3 H, s), 2.37 (3 H, s), 2.07 (3 H, s) and 2.05 [3 H, s, (C*H*$_3$)$_2$C$_3$HN$_2$].

[{Mo(NO)[HB(dmpz)$_3$]Br}$_2${1,4-(HN)$_2$C$_6$H$_4$}] *para*-**II** (Z = NH, X = Br) (Found: C, 39.8; H, 4.7; N, 19.5. C$_{36}$H$_{40}$B$_2$Br$_2$Mo$_2$N$_{14}$O$_2$ requires C, 38.9; H, 4.5; N, 20.1%): FAB mass spectrum *m/z* 1113 (requires 1112.20); IR 2554 ($\nu_{\mathbf{BH}}$), 1660 cm^{-1} ($\nu_{\mathbf{NO}}$); ^{1}H NMR (300 MHz) δ 12.81 (1 H, br s), 12.78 (1 H, br s, NH), 7.57 (4 H, m, C_6H_4), 5.95 (2 H, s), 5.92 (2 H, s), 5.87 (1 H, s), 5.85 (1 H, s, $Me_2C_3HN_2$), 2.65 (6 H, s), 2.46 (6 H, s), 2.41 (3 H, s), 2.40 (12 H, s), 2.39 (3 H, s), 2.05 (3 H, s) and 2.03 [3 H, s, $(CH_3)_2C_3HN_2$].

[{Mo(NO)[HB(dmpz)$_3$]I}$_2${1,4-(HN)$_2C_6H_4$}] *para*-**II** (Z = NH, X = I): IR 3280 ($\nu_{\mathbf{NH}}$), 2555 ($\nu_{\mathbf{BH}}$) 1659 cm^{-1} ($\nu_{\mathbf{NO}}$); ^{1}H NMR (270 MHz) δ 9.7 (2 H, br s, NH), 7.62 (4 H, m, C_6H_4), 5.99 (2 H, s), 5.92, (2 H, s), 5.85 (1 H, s), 5.83 (1 H, s, $Me_2C_3HN_2$), 2.66 (6 H, s), 2.46 (6 H, s), 2.40 (12 H, s), 2.39 (6 H, s), 2.02 (3 H, s) and 2.00 [3 H, s, $(CH_3)_2C_3HN_2$].

Synthetic procedures for complexes derived from dianilines

(*a*) Mononuclear species. These complexes were obtained by reaction of 1 mol equivalent of [Mo(NO){HB(dmpz)$_3$}X$_2$] (X = Cl, Br or I, as appropriate) with 0.5 mol equivalent of the dianiline and triethylamine in refluxing toluene.[10] The reaction was mainly complete in 2 h, but after refluxing overnight all the starting dihalide had disappeared but significant quantities of the dinuclear species were also obtained. The reaction mixture was cooled, filtered to remove residual solids, and evaporated to dryness *in vacuo*. The residue was dissolved in the minimum volume of dichloromethane and chromatographed on silica gel. Dinuclear species were eluted first using pure CH_2Cl_2 but dilution of the eluent with thf (1:1 v/v) afforded the mononuclear species. Yields varied between 55 and 75%.

[Mo(NO){HB(dmpz)$_3$}Cl($HNC_6H_4CH_2C_6H_4NH_2$)] **III** (Z = NH, E = CH_2, X = Cl) (Found: C, 50.8; H, 5.7; N, 19.0. Calc. for $C_{28}H_{35}BClMoN_9O$: C, 51.3; H, 5.4; N, 19.2%): electron impact (EI) mass spectrum *m/z* 657 (requires 655.9); IR 3283 ($\nu_{\mathbf{NH}}$), 2553 ($\nu_{\mathbf{BH}}$), 1659 cm^{-1} ($\nu_{\mathbf{NO}}$); ^{1}H NMR (300 MHz) δ 12.74 (1 H, s, NH), 7.37 (2d), 7.23 (2 H, d), 6.99 (2 H, d), 6.61 (2 H, d, 2C_6H_4), 5.91 (2 H, s), 5.82 (1 H, s, $Me_2C_3HN_2$), 3.90 (2 H, s, CH_2), 2.63 (2 H, s, NH_2), 2.63 (3 H, s), 2.43 (3 H, s), 2.39 (3 H, s), 2.37 (3 H, s), 2.32 (3 H, s) and 1.99 [3 H, s, $(CH_3)_2C_3HN_2$].

[Mo(NO){HB(dmpz)$_3$}I($HNC_6H_4CH_2C_6H_4NH_2$)] **III** (Z = NH, E = CH_2, X = I) (Found: 44.7; H, 5.0; N, 16.9. Calc. for $C_{28}H_{35}BIMoN_9O$: C, 45.0; H, 4.7; N, 16.9%): EI mass spectrum *m/z* 749 (requires 747.3); IR 3281 ($\nu_{\mathbf{NH}}$), 2556 ($\nu_{\mathbf{BH}}$), 1661 cm^{-1} ($\nu_{\mathbf{NO}}$); ^{1}H NMR (270 MHz) δ 13.22 (1 H, s, NH), 7.52 (2 H, d), 7.20 (2 H, d), 7.00 (2 H, d), 6.22 (2 H, d, 2C_6H_4), 5.96 (1 H, s), 5.90 (1 H, s), 5.80 (1 H, s, $Me_2C_3HN_2$), 3.81 (2 H, s, CH_2), 3.63 (2 H, s, NH_2), 2.66 (3 H, s), 2.47 (3 H, s), 2.42 (3 H, s), 2.39 (3 H, s), 2.37 (3 H, s) and 1.96 [3 H, s, $(CH_3)_2C_3HN_2$].

[Mo(NO){HB(dmpz)$_3$}Cl(4,4′-$HNC_6H_4OC_6H_4NH_2$)] **III** (Z = NH, E = O, X = Cl) (Found C, 49.2; H, 5.1; N, 19.2. $C_{27}H_{33}BClMoN_9O_2$ requires C, 49.3; H, 5.1; N, 19.2%): EI mass spectrum *m/z* 659 (requires 657.8); IR 3286 (ν_{NH}), 2552 (ν_{BH}), 1654 cm^{-1} ($\nu_{\mathbf{NO}}$); ^{1}H NMR (270 MHz) δ 12.72 (1 H, s, NH), 7.40 (2 H, d), 6.93 (2 H, d), 6.92 (2 H, d), 6.69 (2 H, d, 2C_6H_4), 5.90 (2 H, s), 5.83 (1 H, s, $Me_2C_3HN_2$), 3.67 (2 H, s, NH_2), 2.62 (3 H, s), 2.43 (3 H, s), 2.33 (3 H, s), 2.38 (3 H, s), 2.34 (3 H, s) and 2.03 [3 H, s, $(CH_3)_2C_3HN_2$].

[Mo(NO){HB(dmpz)$_3$}I(4,4′-$HNC_6H_4OC_6H_4NH_2$)] **III** (Z = NH, E = O, X = I) (Found: C, 43.5; H, 4.9; N, 16.5. $C_{27}H_{33}BIMoN_9O_2$ requires C, 43.3; H, 4.4; N, 16.8%): EI mass spectrum *m/z* 751 (requires 749.3); IR 3281 (ν_{NH}), 2556 (ν_{BH}), 1659 cm^{-1} ($\nu_{\mathbf{NO}}$); ^{1}H NMR (270 MHz) δ 13.21 (1 H, s, NH), 7.56 (2 H, d), 6.91 (4 H, d), 6.70 (2 H, d, 2C_6H_4), 5.96 (1 H, s), 5.90 (1 H, s), 5.81 (1 H, s, $Me_2C_3HN_2$), 3.69 (2 H, s, NH_2), 2.65 (3 H, s), 2.47 (3 H, s), 2.44 (3 H, s), 2.39 (3 H, s), 2.38 (3 H, s) and 2.00 [3 H, s, $(CH_3)_2C_3HN_2$].

[Mo(NO){HB(dmpz)$_3$}Cl{4,4′-$HNC_6H_4(CO)C_6H_4NH_2$}] 4,4′-**III** (Z = NH, E = CO, X = Cl) (Found: C, 49.2; H, 5.1; N, 18.7. $C_{28}H_{33}BClMoN_9O_2$ requires C, 50.2; H, 5.0; N, 18.8%): EI mass spectrum *m/z* 671 (requires 669.8); IR 3286 (ν_{NH}), 2554 ($\nu_{\mathbf{BH}}$), 1667 cm^{-1} ($\nu_{\mathbf{NO}}$); ^{1}H NMR (300 MHz) 12.57 (1 H, s, NH), 7.80 (2 H, d), 7.71 (2 H, d), 7.52 (2 H, d), 6.71 (2 H, d, 2C_6H_4), 5.93 (2 H, s), 5.86 (1 H, s, $Me_2C_3HN_2$), 4.24 (2 H, s, NH_2), 2.64 (3 H, s), 2.45 (3 H, s), 2.40 (3 H, s), 2.395 (3 H, s), 2.36 (3 H, s) and 2.03 [3 H, s, $(CH_3)_2C_3HN_2$].

[Mo(NO){HB(dmpz)$_3$}I{4,4′-$HNC_6H_4(CO)C_6H_4NH_2$}] 4,4′-**III** (Z = NH, E = CO, X = I) (Found: C, 43.9; H, 5.0; N, 17.3. $C_{28}H_{33}BIMoN_9O_2$ requires C, 44.2; H, 4.4; N, 16.6%): EI mass spectrum *m/z* 763 (requires 761.3); IR 3284 ($\nu_{\mathbf{NH}}$) 2555 ($\nu_{\mathbf{BH}}$), 1668 cm^{-1} ($\nu_{\mathbf{NO}}$); ^{1}H NMR (270 MHz) δ 13.06 (1 H, s, NH), 7.93–6.69 (8 H, m, 2C_6H_4), 6.00 (1 H, s), 5.92 (1 H, s), 5.84 (1 H, s, $Me_2C_3HN_2$), 4.25 (2 H, s, NH_2), 2.66 (3 H, s), 2.49 (3 H, s), 2.46 (3 H, s), 2.40 (6 H, s) and 2.00 [3 H, s, $(CH_3)_2C_3HN_2$].

[Mo(NO){HB(dmpz)$_3$}Cl{3,3′-$HNC_6H_4(CO)C_6H_4NH_2$}] 3,3′-**III** (Z = NH, E = CO, X = Cl) (Found: C, 49.3; H, 5.7; N, 18.9. $C_{28}H_{33}BClMoN_9O_2$ requires C, 50.2; H, 5.0; N, 18.8%): EI mass spectrum *m/z* 671 (requires 669.8); IR 3282 ($\nu_{\mathbf{NH}}$), 2554 ($\nu_{\mathbf{BH}}$), 1665 cm^{-1} ($\nu_{\mathbf{NO}}$); ^{1}H NMR (300 MHz) δ 12.63 (1 H, s, NH), 7.90–6.80 (8 H, m, 2C_6H_4), 5.92 (2 H, s), 5.85 (1 H, s, $Me_2C_3HN_2$), 3.90 (2 H, s, NH_2), 2.62 (3 H, s), 2.44 (3 H, s), 2.39 (3 H, s), 2.38 (3 H, s), 2.34 (3 H, s) and 2.04 [3 H, s, $(CH_3)_2C_3HN_2$].

[Mo(NO){HB(dmpz)$_3$}I{3,3′-$HNC_6H_4(CO)C_6H_4NH_2$}] 3,3′-**III** (Z = NH, E = CO, X = I) (Found: C, 43.8; H, 4.5; N, 17.0. $C_{28}H_{33}BIMoN_9O_2$ requires C, 44.2; H, 4.4; N, 16.6%): EI mass spectrum *m/z* 763 (requires 761.3); IR 3283 ($\nu_{\mathbf{NH}}$), 2556 ($\nu_{\mathbf{BH}}$), 1665 cm^{-1} ($\nu_{\mathbf{NO}}$); ^{1}H NMR (270 MHz) δ 13.14 (1 H, s, NH), 8.01–6.89 (8 H, m, 2C_6H_4), 5.98 (1 H, s), 5.91 (1 H, s), 5.83 (1 H, s, $Me_2C_3HN_2$), 3.94 (2 H, s, NH_2), 2.64 (3 H, s), 2.48 (3 H, s), 2.45 (3 H, s), 2.39 (3 H, s), 2.38 (3 H, s) and 1.99 [3 H, s, $(CH_3)_2C_3HN_2$].

[Mo(NO){HB(dmpz)$_3$}Cl{$HNC_6H_4OC_6H_4(SO_2)C_6H_4OC_6H_4NH_2$}] **III** (Z = NH, E = $OC_6H_4(SO_2)C_6H_4O$, X = Cl] (Found: C, 53.1; H, 5.0; N, 13.7. $C_{39}H_{41}BClMoN_9O_5S$ requires C, 52.6; H, 4.6; N, 14.2%): EI mass spectrum *m/z* 891 (requires 890.1); IR 3289 ($\nu_{\mathbf{NH}}$), 2555 ($\nu_{\mathbf{BH}}$), 1666 cm^{-1} ($\nu_{\mathbf{NO}}$); ^{1}H NMR (270 MHz) δ 12.51 (1 H, s, NH), 7.90–6.30 (16 H, m, 4C_6H_4), 5.91 (2 H, s), 5.85 (1 H, s, $Me_2C_3HN_2$), 3.80 (2 H, s, NH_2), 2.57 (3 H, s), 2.43 (3 H, s), 2.39 (3 H, s), 2.38 (3 H, s), 2.33 (3 H, s) and 2.03 [3 H, s, $(CH_3)_2C_3HN_2$].

[Mo(NO){HB(dmpz)$_3$}I{$HNC_6H_4OC_6H_4(SO_2)C_6H_4OC_6H_4NH_2$}] **III** (Z = NH, E = $OC_6H_4(SO_2)C_6H_4O$, X = I] (Found: C, 47.2; H, 4.4; N, 12.7. $C_{39}H_{41}BIMoN_9O_5S$ requires C, 47.7; H, 4.2; N, 12.8%): EI mass spectrum *m/z* 855 ($M^+ - $ I; M^+ requires 981.5); IR 3283 ($\nu_{\mathbf{NH}}$) 2556 ($\nu_{\mathbf{BH}}$) 1667 cm^{-1} ($\nu_{\mathbf{NO}}$); ^{1}H NMR (270 MHz) δ 12.99 (1 H, s, NH) 7.90–6.33 (16 H, m, 4C_6H_4), 5.97 (1 H, s,), 5.90 (1 H, s), 5.85 (1 H, s, $Me_2C_3HN_2$), 3.79 (2 H, s, NH_2), 2.59 (3 H, s), 2.47 (3 H, s), 2.43 (3 H, s), 2.38 (3 H, s), 2.37 (3 H, s) and 1.99 [3 H, s, $(CH_3)_2C_3HN_2$].

(*b*) Dinuclear complexes. These complexes were prepared in the same way as the mononuclear species described above, but using a mole ratio of 1:1.5 precursor dihalide to dianiline, and an excess of hexamine as a deprotonating agent in place of triethylamine.[10] The mixture was refluxed and stirred from between 2 and 8 h, depending on the ligand, and the reaction was continuously monitored by thin-layer chromatography. Separation and purification was as for the mononuclear analogues. Yields varied between 15 and 30%.

[{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$($HNC_6H_4CH_2C_6H_4NH$)] **IV** (Z = NH, E = CH_2, X = Cl) (Found: C, 46.1; H, 5.2; N, 20.3. $C_{43}H_{56}B_2Cl_2Mo_2N_{16}O_2$ requires C, 46.4; H, 5.1; N, 20.1%): EI mass spectrum *m/z* 1113 (requires 1113.4); IR 3284 ($\nu_{\mathbf{NH}}$), 2554 ($\nu_{\mathbf{BH}}$), 1660 cm^{-1} ($\nu_{\mathbf{NO}}$); ^{1}H NMR (270 MHz) δ 12.74 (2 H, s, NH), 7.41 (4 H, d), 7.30 (4 H, d, 2C_6H_4), 5.91 (4 H, s), 5.83 (2 H, s, $Me_2C_3HN_2$), 4.09 (2 H, s, CH_2), 2.63 (6 H, s), 2.43 (6 H, s), 2.39 (6 H, s), 2.38 (6 H, s), 2.33 (6 H, s) and 2.01 [6 H, s, $(CH_3)_2C_3HN_2$].

[{Mo(NO)[HB(dmpz)$_3$]I}$_2$($HNC_6H_4CH_2C_6H_4NH$)] **IV** (Z = NH, E = CH_2, X = I) (Found: C, 40.2; H, 4.5; N, 17.1. $C_{43}H_{56}B_2I_2Mo_2N_{16}O_2$ requires C, 39.8; H, 4.4; N, 17.3%): EI mass spectrum *m/z* 1170 ($M^+ -$ I; M^+ requires 1296.3); IR 3281

(ν_{NH}), 2555 (ν_{BH}), 1662 cm^{-1} (ν_{NO}); ^{1}H NMR (270 MHz) δ 13.22 (2 H, s, NH), 7.57 (4 H, d), 7.27 (4 H, d, 2C_6H_4), 5.97 (2 H, s), 5.91 (2 H, s), 5.81 (2 H, s, $Me_2C_3\textit{H}N_2$), 3.92 (2 H, s, CH_2), 2.66 (6 H, s), 2.47 (6 H, s), 2.43 (3 H, s), 2.42 (3 H, s), 2.39 (6 H, s), 2.38 (6 H, s), 2.33 (6 H, s) and 1.98 [6 H, s, $(C\textit{H}_3)_2C_3HN_2$].

[{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$($HNC_6H_4OC_6H_4NH$)] **IV** (Z = NH, E = O, X = Cl) (Found: C, 44.8; H, 5.2; N, 19.5. $C_{42}H_{54}B_2Cl_2Mo_2N_{16}O_3$ requires C, 45.2; H, 4.9; N, 20.1%): mass spectrum *m/z* 1115 (requires 1115.4); IR 3286 (ν_{NH}), 2554 (ν_{BH}), 1660 cm^{-1} (ν_{NO}); ^{1}H NMR (270 MHz) δ 12.71 (2 H, s, NH), 7.47 (4 H, d), 7.12 (4 H, d, 2C_6H_4), 5.92 (4 H, s), 5.85 (2 H, s, $Me_2C_3\textit{H}N_2$), 2.63 (6 H, s), 2.44 (6 H, s), 2.40 (6 H, s), 2.39 (6 H, s), 2.38 (6 H, s) and 2.06 [6 H, s, $(C\textit{H}_3)_2C_3HN_2$].

[{Mo(NO)[HB(dmpz)$_3$]I}$_2$($HNC_6H_4OC_6H_4NH$)] **IV** (Z = NH, E = O, X = I) (Found: C, 39.0; H, 4.4; N, 17.3. $C_{42}H_{54}B_2I_2Mo_2N_{16}O_3$ requires C, 38.9; H, 4.2; N, 17.3%): EI mass spectrum *m/z* 1297 (requires 1298.3); IR 3282 (ν_{NH}), 2555 (ν_{BH}), 1662 cm^{-1} (ν_{NO}); ^{1}H NMR (270 MHz) δ 13.20 (2 H, s, NH), 7.64 (4 H, d), 7.09 (4 H, d, 2C_6H_4), 5.98 (2 H, s), 5.91 (2 H, s), 5.83 (2 H, s, $Me_2C_3\textit{H}N_2$), 2.66 (6 H, s), 2.48 (6 H, s), 2.46 (6 H, s), 2.40 (6 H, s), 2.39 (6 H, s) and 2.02 [6 H, s, $(C\textit{H}_3)_2C_3HN_2$].

[{Mo(NO)[HB(dmpz)$_3$]Cl}$_2${4,4′-$HNC_6H_4(CO)C_6H_4NH$}] 4,4′-**IV** (Z = NH, E = CO, X = Cl) (Found: C, 45.6; H, 4.7; N, 20.2. $C_{43}H_{54}B_2Cl_2Mo_2N_{16}O_3$ requires C, 45.8; H, 4.8; N, 19.9%): IR 3284 (ν_{NH}), 2556 (ν_{BH}), 1668 cm^{-1} (ν_{NO}); ^{1}H NMR (300 MHz) δ 12.51 (2 H, s, NH), 7.91 (4 H, d), 7.55 (4 H, d, 2C_6H_4), 5.93 (4 H, s), 5.87 (2 H, s, $Me_2C_3\textit{H}N_2$), 2.64 (6 H, s), 2.45 (6 H, s), 2.404 (6 H, s), 2.400 (6 H, s), 2.36 (6 H, s) and 2.04 [6 H, s, $(C\textit{H}_3)_2C_3HN_2$].

[{Mo(NO)[HB(dmpz)$_3$]Br}$_2${4,4′-$HNC_6H_4(CO)C_6H_4NH$}] 4,4′-**IV** (Z = NH, E = CO, X = Br) (Found: C, 42.8; H, 4.9; N, 19.1. $C_{43}H_{54}B_2Br_2Mo_2N_{16}O_3$ requires C, 42.5; H, 4.5; N, 18.4%): IR 3283 (ν_{NH}), 2554 (ν_{BH}), 1671 cm^{-1} (ν_{NO}); ^{1}H NMR (300 MHz) δ 12.76 (2 H, s, NH), 7.90 (4 H, d), 7.61 (4 H, d, 2C_6H_4), 5.96 (2 H, s), 5.93 (2 H, s), 5.86 (2 H, s, $Me_2C_3\textit{H}N_2$), 2.65 (6 H, s), 2.47 (6 H, s), 2.41 (18 H, s) and 2.02 [6 H, s, $(C\textit{H}_3)_2C_3HN_2$].

[{Mo(NO)[HB(dmpz)$_3$]I}$_2${4,4′-$HNC_6H_4(CO)C_6H_4NH$}] 4,4′-**IV** (Z = NH, E = CO, X = I) (Found: C, 39.6; H, 4.4; N, 16.8. $C_{43}H_{54}B_2I_2Mo_2N_{16}O_3$ requires C, 39.4; H, 4.2; N, 17.1%): EI mass spectrum 1309 (requires 1310); IR 3285 (ν_{NH}), 2556 (ν_{BH}), 1671 cm^{-1} (ν_{NO}); ^{1}H NMR (270 MHz) δ 13.00 (2 H, s, NH), 7.88 (4 H, d), 7.70 (4 H, d, 2C_6H_4), 6.00 (2 H, s), 5.93 (2 H, s), 5.85 (2 H, s, $Me_2C_3\textit{H}N_2$), 2.66 (6 H, s), 2.50 (6 H, s), 2.47 (6 H, s), 2.40 (12 H, s) and 2.00 [6 H, s, $(C\textit{H}_3)_2C_3HN_2$].

[{Mo(NO)[HB(dmpz)$_3$]Cl}$_2${3,3′-$HNC_6H_4(CO)C_6H_4NH$}] 3,3′-**IV** (Z = NH, E = CO, X = Cl) (Found: C, 45.7; H, 4.7; N, 19.5. $C_{43}H_{54}B_2Cl_2Mo_2N_{16}O_3$ requires C, 45.8; H, 4.8; N, 19.9%): EI mass spectrum *m/z* 1129 (requires 1127.4); IR 3286 (ν_{NH}), 2554 (ν_{BH}), 1666 cm^{-1} (ν_{NO}); ^{1}H NMR (300 MHz) δ 12.62 (2 H, s, NH); 8.00–7.65 (8 H, m, 2C_6H_4), 5.91 (4 H, s), 5.85 (1 H, s), 5.82 (1 H, s, $Me_2C_3\textit{H}N_2$), 2.61 (6 H, s), 2.44 (6 H, s), 2.39 (6 H, s), 2.38 (3 H, s), 2.37 (3 H, s), 2.353 (3 H, s), 2.349 (3 H, s), 2.01 (3 H, s) and 2.00 [6 H, s, $(C\textit{H}_3)_2C_3HN_2$].

[{Mo(NO)[HB(dmpz)$_3$]I}$_2${3,3′-$HNC_6H_4(CO)C_6H_4NH$}] 3,3′-**IV** (Z = NH, E = CO, X = I) (Found: C, 39.2; H, 4.2; N, 17.0. $C_{43}H_{54}B_2I_2Mo_2N_{16}O_3$ requires C, 39.4; H, 4.2; N, 17.1%): EI mass spectrum *m/z* 1309 (requires 1310.3); IR 3284 (ν_{NH}), 2554 (ν_{BH}), 1668 cm^{-1} (ν_{NO}); ^{1}H NMR (300 MHz) δ 13.12 (2 H, s, NH), 8.15 (2 H, d), 7.77 (4 H, d), 7.58 (2 H, t, 2C_6H_4), 5.98 (2 H, s), 5.91 (2 H, s), 5.82 (1 H, s), 5.80 (1 H, s, $Me_2C_3\textit{H}N_2$), 2.63 (6 H, s), 2.48 (6 H, s), 2.455 (3 H, s), 2.45 (3 H, s), 2.39 (6 H, s), 2.38 (3 H, s), 2.37 (3 H, s), 1.99 (3 H, s) and 1.97 [3 H, s, $(C\textit{H}_3)_2C_3HN_2$].

[{Mo(NO)[HB(dmpz)$_3$]Cl}$_2${$HNC_6H_4OC_6H_4(SO_2)C_6H_4OC_6H_4NH$}] **IV** [Z = NH, E = $OC_6H_4(SO_2)C_6H_4O$, X = Cl] (Found: C, 48.6; H, 5.0; N, 16.0. $C_{54}H_{62}B_2Cl_2Mo_2N_{16}O_6S$ requires C, 48.1; H, 4.6; N, 16.6%): EI mass spectrum *m/z* 1347 (requires 1347.7); IR 3288 (ν_{NH}), 2555 (ν_{BH}), 1667 cm^{-1} (ν_{NO}); ^{1}H NMR (300 MHz) δ 12.50 (2 H, s, NH), 7.88–6.86 (16 H, m, 4C_6H_4), 5.91 (4 H, s), 5.85 (2 H, s, $Me_2C_3\textit{H}N_2$), 2.58 (6 H, s), 2.43 (6 H, s), 2.39 (6 H, s), 2.33 (6 H, s) and 2.03 [6 H, s, $(C\textit{H}_3)_2C_3HN_2$].

[{Mo(NO)[HB(dmpz)$_3$]I}$_2${$HNC_6H_4OC_6H_4(SO_2)C_6H_4OC_6H_4NH$}] **IV** [Z = NH, E = $OC_6H_4(SO_2)C_6H_4O$, X = I] (Found: C, 42.5; H, 4.4; N, 14.5. $C_{54}H_{62}B_2I_2Mo_2N_{16}O_6S$ requires C, 42.4; H, 4.1; N, 14.6%): EI mass spectrum *m/z* 1533 (requires 1530.6); IR 3284 (ν_{NH}), 2556 (ν_{BH}), 1668 cm^{-1} (ν_{NO}); ^{1}H NMR (300 MHz) δ 12.99 (2 H, s, NH), 7.91–7.00 (16 H, m, 4C_6H_4), 5.97 (2 H, s), 5.90 (2 H, s), 5.83 (2 H, s, $Me_2C_3\textit{H}N_2$), 2.60 (6 H, s), 2.47 (6 H, s), 2.43 (6 H, s), 2.39 (6 H, s), 2.38 (6 H, s) and 1.99 [6 H, s, $(C\textit{H}_3)_2C_3HN_2$].

Results and Discussion

The full physical characterisation (elemental analyses for new compounds, mass spectra where available, IR and ^{1}H NMR spectra) of [{Mo(NO)[HB(dmpz)$_3$]X}$_2${$(HN)_2C_6H_4$}] **II** (Z = NH, X = halide) and [Mo(NO)[HB(dmpz)$_3$]X}$_2${$HNC_6H_4EC_6H_4NH$}] **IV** [Z = N, E = CH_2, O, CO (as 4,4′ and 3,3′ isomers), SO_2 or $OC_6H_4(SO_2)C_6H_4O$, X = halide] are reported in the Experimental section. The mononuclear species [Mo(NO){HB(dmpz)$_3$}X($HNC_6H_4NH_2$)] **I** (Z = NH, X = halide) and [Mo(NO){HB(dmpz)$_3$}X($HNC_6H_4EC_6H_4NH_2$)] **III** (Z = NH, X = halide) are also recorded for completeness and comparison with their dinuclear analogues. A number of these compounds are new, *viz*. **II** (Z = NH, X = Br), **IV** (Z = NH, X = Cl), 3,3′-**IV** (Z = NH, E = CO, X = Cl or I), **IV** [Z = NH, E = $OC_6H_4(SO_2)C_6H_4O$, X = Cl or I] and, of course, their mononuclear progenitors **I** (Z = NH, X = halide) and **III** (Z = NH, X = halide).

Since the value of ΔE_f, the separation in first and second reduction potentials, for the dinuclear benzenediamido species are particularly large (see below), it is possible to generate the monoanions **II**$^-$ (Z = NH, X = Cl, Br or I)] selectively and relatively easily by reducing the neutral precursor either using 1 mol equivalent of cobaltocene in dichloromethane, or by electrolysis at potentials close to but slightly more anodic than that of E_f^1 (see below) in acetonitrile. The dianion **IV**$^{2-}$ [Z = NH, E = $OC_6H_4(SO_2)C_6H_4O$, X = Cl] was also obtained by cobaltocene reduction of the neutral precursor in dichloromethane. None of the reduced species was isolated from solution, characterisation being effected by a combination of spectroscopic techniques (electronic, IR, EPR, as appropriate).

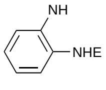
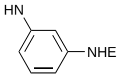
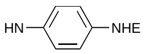
Complexes containing benzenediamido bridges

Electronic spectra. The electronic spectral data for compounds **I** (Z = NH, X = halide) and **II** (Z = NH, X = halide) in the visible region in dichloromethane are recorded in Table 1. There is a qualitative difference between the *ortho* and *para* complexes on the one hand, and their *meta* analogues on the other: the former group has strong, deep colours (purple-brown, purple or deep blue) while the latter is a paler orange-brown.

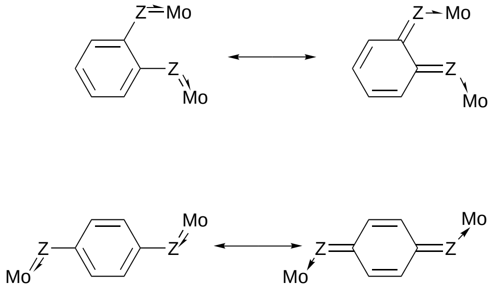
The mononuclear species **I** exhibit quite strong transitions in the range 430–520 nm, which we suggest are due to aryl NH→Mo charge transfer (l.m.c.t.), λ_{max} in the *meta* isomers occurring at 439–467 nm, significantly shorter than the comparable bands for the other two isomers (490–523 nm). The wavelength of this transition also increases, within each isomer set, as the electronegativity of X decreases. The aryl NH→Mo charge-transfer transitions of the dinuclear *ortho* and *para* isomers also move similarly to longer wavelengths as a function of X, with the appearance of an intense band between 535 and 560 nm (*ortho*) or two intense bands between 560 and 630 nm (*para*). While the intensities of the spectral absorptions of the *meta* isomers also increase for the dinuclear with respect to their mononuclear precursors, the position of the bands does not shift dramatically, although a new absorption, in the range 575–600 nm, appears as a shoulder on the band positioned near 460 nm.

On reduction of *ortho*-**II** (Z = NH, X = halide) the electronic

Table 1 Electronic spectral data obtained from [Mo(NO){HB(dmpz)$_3$}X(HNC$_6$H$_4$NH$_2$)] **I** (Z = NH, X = halide) and [{Mo(NO[HB(dmpz)$_3$]X}$_2$-(HNC$_6$H$_4$NH)], **II** (Z = NH, X = halide)

				Bimetallic {E = Mo(NO)[HB(dmpz)$_3$]X}		
		Monometallic (E = H)		Neutral		Reduced species[a]
Ligand	X	Colour[b]	λ_{max} (ε)[b]	Colour[b]	λ_{max} (ε)[b]	λ_{max} (ε)[b]
	Cl	Purple-brown	286 (7716), 490 (8405)	Deep purple	297 (11 181), 429 (10 590), 535 (18 374), 630 (sh)	530 (15 129), 863 (3968)
	Br		Not measured	Deep purple	330 (12 260), 435 (9657), 552 (18 964), 640 (sh)	535 (15 667), 844 (2381)
	I	Purple-brown	275 (6438), 369 (5873), 503 (9197)	Deep purple	326 (9387), 388 (12 232), 560 (17 173), 650 (sh)	538 (10 440), 866 (5136) 540 (11 032),[d] 914 (5104)[d]
	Cl	Orange-brown	289 (8354), 439 (9089)	Orange-brown	293 (11 417), 455 (19 754), 575 (sh)	442 (19 370), 564 (sh)
	Br	Orange-brown	303 (6781), 445 (8583)	Orange-brown	318 (13 064), 462 (21 272), 593 (sh)	518 (7641), 627 (sh), 880w (sh)
	I	Orange-brown	275 (6797), 377 (7408), 467 (9162)	Orange-brown	378 (14 557), 480 (20 241), 605 (sh)	475 (20 647), 608 (sh) 472 (21 000),[d] 620 (sh)[d]
	Cl	Deep purple	284 (9017), 323 (5868), 507 (13 155)	Deep blue	286 (10 139), 566 (22 900), 608 (20 389)	524 (14 500), 773 (br) (28 944)
	Br	Deep purple	282 (9434); 298 (9535); 516 (14 972)	Deep blue	330 (11 688), 451 (7140), 569 (22 209), 630 (19 256)	529 (15 326), 770 (31 047)
	I	Deep purple	300 (4917), 370 (3333), 523 (17 631)	Deep blue	283 (9045), 344 (7835), 394 (7326), 605 (br) (23 987)	539 (11 927), 756 (br) (36 425) 538 (11 621),[d] 737 (35 839),[d] 800 (32 236)[d]

[a] Formed by addition of 1 mol equivalent of cobaltocene in dichloromethane solution, generating [{Mo(NO)[HB(dmpz)$_3$]X}$_2$(HNC$_6$H$_4$NH)]$^-$. [b] In dichloromethane. [c] In nm (ε in dm^3 mol^{-1} cm^{-1}). [d] Spectrum recorded after 30 min.



Scheme 2 Quinonoidal forms derived from *ortho*- and *para*-substituted benzene-based bridging ligands

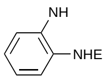
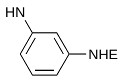
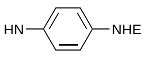
spectra alter dramatically, with the appearance of a very intense absorption in the range 840–870 nm. Similar changes are detected in the spectra of *para*-**II**$^-$ (Z = NH, X = halide), with a new strong absorption in the range 770–760 nm, perhaps a m.l.c.t. band. No other new absorptions were detected down to 1200 nm. However, in the spectra of the *meta*-**II**$^-$ (Z = NH, X = halide) no new strong absorptions appear. The spectra of the reduced iodo complexes were recorded immediately after addition of cobaltocene, and again 30 min later. Slight changes were observed, and since it is known that reduced iodo complexes of this general class of tris(pyrazolyl)hydroborato molybdenum nitrosyls are substitution labile, readily dissociating I$^-$,[21] this is not surprising, although the spectra of the aged reduced complexes were not greatly different to those of the freshly prepared monoanions.

In general, the electronic spectra of the complexes reflect the structures of the isomers, the strong interaction of the metal fragments with the bridging ligand being evident in the *ortho* and *para* isomers where ligand-to-metal charge transfer is facilitated by delocalisation *via* quinonoidal forms of the *ortho*- and *para*-(HN)$_2$C$_6$H$_4$ ligands (Scheme 2). Such delocalisation cannot occur in the 1,3-substituted bridging ligand, and so interaction between the two metal centres is greatly diminished. On reduction, the occurrence of very strong transitions between 770 and 870 nm for the *ortho* and *para* isomers, but not for the *meta* species, suggests but does not confirm that the reduced species exhibit either Class II or Class III mixed-valence behaviour, while the latter is probably valence-trapped (Class I). Owing to the method of synthesis of these monoanions, and their relative instability in air, we were not able to carry out solvatochromism studies which might have differentiated between Class II and III behaviour.

Electrochemical behaviour. The electrochemical behaviour of both mono- and bi-metallic complexes was measured in dichloromethane (Table 2). We have reported the cyclic voltammetric properties of some of these complexes before,[8–10] but have remeasured them under consistent and comparable conditions, and have also recorded differential pulse voltammetric data.

As expected, the *mononuclear* complexes **I** (Z = NH, X = halide) are reduced in the range -1.39 to -1.57 V *vs.* ferrocene–ferrocenium couple. This is a one-electron process, confirmed coulometrically using *para*-**I** (Z = NH, X = Br) and assumed for the remaining complexes on the basis of chemical comparability. Most of these complexes exhibit quasi-reversible electrode behaviour at best, as revealed by the small but significant departure of ΔE_p from ideality, *viz*. 59 mV in theory for a reversible one-electron-transfer process but averaging 89 mV for the well behaved ferrocene–ferrocenium couple added to the cell containing the molybdenum complexes. The reduction potentials for *ortho*- and *meta*-**II** (Z = NH, X = halide) became more negative in the order I < Br < Cl, implying that the energy of the LUMO, presumed to be the redox orbital, increases with increasing p_π-donor activity of X. The *para* isomer deviated slightly but not significantly from this. This is entirely consistent with the X→Mo $p_\pi \longrightarrow d_\pi$ donation revealed by the short Mo–X bonds, a response to the strong electronegativity of the {Mo(NO)[HB(dmpz)$_3$]X} group.[22] The difference between E_f values for each set of halide isomers was small (a maximum of 50 mV), but the trend of the potential becoming more negative

Table 2 Electrochemical data obtained from [Mo(NO){HB(dmpz)$_3$}X(NHC$_6$H$_4$NH$_2$)] **I** (Z = NH, X = halide) and [{Mo(NO[HB(dmpz)$_3$]X}$_2$-(HNC$_6$H$_4$NH)] **II** (Z = NH, X = halide) (cobaltocene reduction potential *vs.* ferrocene–ferrocenium couple = −1.34 V)

		Monometallic (E = H)			Bimetallic {E = Mo(NO)[HB(dmpz)$_3$]X}							
		CV[a]		DPV[b]	CV[a]					DPV[b]		
Ligand	X	E_f[c]	ΔE_p[d]	E_f[e]	E_f^{1}[c,f]	ΔE_p^{1}[d]	E_f^{2}[c,g]	ΔE_p^{2}[d]	ΔE_f[h]	E_f^{1}[c,f]	E_f^{2}[c,g]	ΔE_f[h]
	Cl	−1.46	108 (111)	−1.47	−1.14	84 (72)	−1.92	110 (72)	778	−1.14	−1.92	779
	Br	−1.44	126 (78)	−1.44	−1.09	87 (105)	−1.91	100 (105)	820	−1.09	−1.89	803
	I	−1.41	111 (93)	−1.40	−1.05	81 (72)	−1.92[i]	100[i] (72)	870[i]	−1.03	−1.88	852
	Cl	−1.43	148 (93)	−1.42	−1.35	174 (96)	−1.72	147 (96)	371	−1.34	−1.72	381
	Br	−1.40	165 (87)	−1.40	−1.30	96 (72)	−1.68	120 (72)	382	−1.29	−1.67	375
	I	−1.39	123 (72)	−1.37	−1.28	114 (90)	−1.67	111 (90)	386	−1.28	−1.64	354
	Cl	−1.57	114 (87)	−1.58	−1.12	105 (87)	−2.04	70 (87)	917	−1.11	−2.03	923
	Br	−1.53	120 (102)	−1.51	−1.10	147 (81)	−2.03	160 (81)	929	−1.07	−2.00	928
	I	−1.56	75 (78)	−1.52	−1.06	75 (83)	−2.17[j]		1076[k]	−1.05	−2.04	995

[a] Cyclic voltammetry using a platinum electrode. [b] Differential pulse voltammetry. [c] In V. [d] $E_\mathrm{p}^\mathrm{c} - E_\mathrm{p}^\mathrm{a}$, in mV (value for ferrocene oxidation). [e] Peak potential in V. [f] First reduction potential, $z = 0 \longrightarrow -1$. [g] Second reduction potential, $z = -1 \longrightarrow -2$. [h] $\Delta E_\mathrm{f} = E_\mathrm{f}^1 - E_\mathrm{f}^2$, in mV. [i] Irreversible process; $i^\mathrm{a}/i^\mathrm{b}$ not unity, values quoted not reliable. [j] Irreversible process, E_p^c given. [k] Estimate based on $E_\mathrm{p}^\mathrm{c1} - E_\mathrm{p}^\mathrm{c2}$, in mV.

in the order *meta* < *ortho* < *para* was consistent, indicating that the energy of the LUMO in the *meta* isomer was least influenced by the NH$_2$ substituent, as expected from simple inductive and mesomeric considerations.[23] None of these complexes was reduced by cobaltocene {E_f[Co(cp)$_2$–Co(cp)$_2^+$] (cp = η^5-C$_5$H$_5$) = −1.34 V *vs.* ferrocene–ferrocenium couple}.

The *dinuclear* species exhibited two one-electron reduction processes in dichloromethane which was confirmed coulometrically using *para*-**II** (Z = NH, X = Br). These reduction processes were mostly quasi-reversible, presumably as a result of gradual dissociation of X or slow electrode kinetics, as has been observed before in this type of complex.[24] In general, the first reduction potentials are *ca.* 300 mV more positive and the second *ca.* 500 mV more negative than those of the comparable mononuclear progenitors. The separation between the first and second reduction potentials, ΔE_f, for each of the three isomers increased in the order *meta* < *ortho* < *para*, *viz. ca.* 367, 811 and 949 mV, respectively, independent of X. However, there is evidence of dissociation of I$^-$ from *para*-**II** (Z = NH, X = I) on reduction, as expected,[21] so the absolute magnitude of ΔE_f for the iodo species should be treated with caution. However, the large values of ΔE_f for the *ortho* and *para* isomers in comparison to their *meta* analogues, measured by cyclic and differential pulse voltammetry (Table 2), is more evidence of the very significant interaction between the two metal redox centres in the former pair. This must be largely due to a combination of inductive and mesomeric effects in the former where quinonoidal forms can be envisaged (Scheme 2), relative to the latter where extensive delocalisation of metal d and bridging ligand π orbitals is impossible and quinonoid structures cannot be drawn. The electrochemical data are consistent with the electronic spectral results in highlighting the substantial differences between *ortho*- and *para*-**II** (Z = NH, X = halide) and their *meta* analogues and, clearly, there is a substantial difference between the stability of the monoanionic mixed-valence derivatives of the *ortho* and *para* isomers relative to that of the *meta* species, as shown by the comproportionation constants in Table 3. For Class II or III mixed-valence behaviour K_c must be very much larger than that for a Class I system.

EPR spectroscopic results. The paramagnetic mixed-valence (16/17 v.e.) species **II**$^-$ (Z = NH, X = halide) were generated either by reduction of the neutral precursor by cobaltocene in dichloromethane, or electrochemically by controlled-potential electrolysis at a potential slightly more anodic that E_f^1. Most of the results were recorded only at room temperature, and the data are summarised in Table 4. For compounds exhibiting Class I (valence-trapped) behaviour on the EPR time-scale the spectrum will be that of an isolated mononuclear molybdenum centre, namely a ‘singlet + sextet’ signal with a separation of *ca.* 50 G between the components of the sextet due to hyperfine coupling to those nuclei (*ca.* 25% natural abundance) with $I = \frac{5}{2}$. For compounds exhibiting Class III (fully delocalised) or strongly interacting Class II behaviour in which the thermal barrier between the two minima of the potential-energy curve is sufficiently small that thermal excitation is fast on the EPR time-scale (*ca.* 10^{-8} s), the single electron will couple equally to both metal centres to give superimposed components consisting of 1, 6 and 11 lines with a separation of *ca.* 25 G between each of the lines of the multiplet (the singlet arising from the $I = 0$, $I = 0$ nuclear spin combination, the 1:1:1:1:1:1 sextet from the $I = \frac{5}{2}$, $I = 0$ combination and the 1:2:3:4:5:6:5:4:3:2:1 undecet from the $I = \frac{5}{2}$, $I = \frac{5}{2}$ combination) (for typical examples see ref. 13).

The electrochemically generated species *ortho*-**II** (Z = NH, X = halide) showed a well resolved ‘singlet : sextet : undecet’ spectrum with $A_\mathrm{Mo} = 27.4$ G, confirming that this species must be Class III or strongly interacting Class II. The corresponding bromo and iodo monoanions behaved similarly, although there was evidence of decomposition of the iodo species on electrochemical reduction at 0.56 V over a period of 30 min.

The EPR spectra of compounds *para*-**II**$^-$ (Z = NH, X = halide) were generally similar to those of their *ortho* isomers, although the spectra at 77 K were broad and featureless. The reduction of the bromo derivative electrolytically at −1.23 V afforded a typical ‘delocalised’ spectrum, and on reduction at −2.34 V similar but slightly broader spectra were obtained. At this more negative potential it appears that the isovalent dianion *para*-**II**$^{2-}$ (Z = NH, X = Br) (17/17 v.e.s) is generated, and since this is isoelectronic with the well characterised 4,4′-bipyridyl species **V** (E = linking group) in which there is strong correlation between the spins on each metal we would expect a ‘singlet : sextet : undecet’ spectrum not substantially different to that of the mixed-valence species.

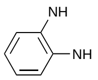
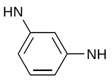
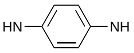
The EPR spectra of compounds *meta*-**II**$^-$ (Z = NH, X = halide) however differed significantly from their *ortho* and *para* isomers. Electrochemical reduction to generate the chloro derivative afforded a ‘singlet : sextet’ spectrum with $A_\mathrm{Mo} = 50.8$ G, typical of a valence-trapped species. Similar results were obtained from the bromide in solution. The EPR spectrum of *meta*-**II**$^-$ (Z = NH, X = Br) at 77 K revealed three *g* and three *A* values: $g_1 = 2.0082$, $g_2 = 1.9881$, $g_3 = 1.9380$ ($g_\mathrm{iso} = 1.9781$) and $A_1 = 34.7$, $A_2 = 36.3$, $A_3 = 72.5$ G ($A = 47.8$ G). Owing to extensive decomposition of the reduced iodo species it was not

Table 3 Comproportionation constants for the process $[\{Mo(NO)[HB(dmpz)_3]X\}_2Q] + [\{Mo(NO)[HB(dmpz)_3X]_2Q\}]^{2-} \rightleftharpoons 2[\{Mo(NO)[HB(dmpz)_3]X\}_2Q]^-$

Q	X	E_f^{1} [a]	ΔE_f [b]	$\log_{10} K_c$ [c]	K_c [d]
1,2-HNC_6H_4NH	Cl	−1.14	779	13.2	1.5×10^{13}
	Br	−1.09	803	13.6	3.8×10^{13}
	I	−1.03	852	14.4	25×10^{13}
1,3-HNC_6H_4NH	Cl	−1.34	381	6.5	2.8×10^{6}
	Br	−1.29	375	6.4	2.2×10^{6}
	I	−1.28	354	6.0	0.96×10^{6}
1,4-HNC_6H_4NH	Cl	−1.11	923	15.6	4.0×10^{15}
	Br	−1.07	928	15.7	4.9×10^{15}
	I	−1.05	995	16.9	66×10^{15}
1,3-OC_6H_4O [e]	Cl	−0.89 [f]	260	4.4	2.5×10^{4}
1,4-Pyrazine [g]	Br	−0.95	1440	24.4	2.2×10^{24}
$OC_6H_4C_6H_4O$ [h]	Cl	−0.84 [f]	110	1.9	72
	I	−0.80 [f]	80	1.4	23
4,4′-Bipyridyl [i]	Cl	−1.41	765	13.0	8.6×10^{12}
	I	−1.38	685	11.6	0.38×10^{12}
$HNC_6H_4CH_2C_6H_4NH$	Cl	−1.41	72	1.0	16.5
	I	−1.34 [f]	86	1.6	28.4
$HNC_6H_4OC_6H_4NH$	Cl	−1.40	123	2.1	120.0
	I	−1.33	135	2.3	191.5
$HNC_6H_4(SO_2)C_6H_4NH$ [e]	I	−1.03 [f]	135	2.3	191.5
4,4′-$HNC_6H_4(CO)C_6H_4NH$	I	−1.04	186	3.2	1394
4,4′-$OC_6H_4(CO)C_6H_4O$ [e]	Cl	−0.78	85	1.4	27.3
3,3′-$HNC_6H_4(CO)C_6H_4NH$	Cl	−1.29	81	1.4	23.4
	I	−1.23	81	1.4	23.4
$HNC_6H_4CH_2CH_2C_6H_4NH$ [e]	I	−1.40	45	0.76	5.8
Di-4-pyridylethane, $(NC_5H_4)CH_2CH_2(C_5H_4N)$ [i]	Cl	−2.00	105	1.8	59.6
Di-4-pyridylethene, $(NC_5H_4)CH{=}CH(C_5H_4N)$ [i]	Cl	−1.45	582	9.9	6.9×10^{9}
	I	−1.38	565	9.6	3.6×10^{9}
$HNC_6H_4OC_6H_4(SO_2)C_6H_4OC_6H_4NH$	Cl	−1.28 [f]	58	1.0	9.6
	I	−1.22 [f]	50	0.8	7.00
4,4′-$OC_6H_4(CO)C_6H_4C_6H_4(CO)C_6H_4O$ [j]	Cl	−0.74	56	0.95	8.8
1,10-bis(4-pyridyl)-3,8-dimethyldec-1,3,5,7,9-pentaene	Cl	−1.01 [f]	40	0.68	4.7

[a] First reduction (formation) potential, in V *vs.* ferrocene–ferrocenium couple. [b] $E_f^2 - E_f^1$, in mV. [c] $\log_{10} K_c$ from ΔE_f, ref. 11. [d] $K_c = \exp(\Delta E_f/25.69)$, ref. 15. [e] Ref. 8. [f] Calculated, $E_f^1 = E_{dpp} + [\Delta E_f + (E_{pul}/2)]$ where E_{dpp} = centre of differential pulse peak, shown as E_f in Table 3, and E_{pul} = pulse potential (10 mV). [g] Data from ref. 27. [h] Data from ref. 10. [i] Ref. 12. [j] Ref. 25.

Table 4 The EPR spectral data obtained from $[\{Mo(NO)[HB(dmpz)_3]X\}_2(HNC_6H_4NH)]^-$, **II**$^-$ (Z = NH, X = halide)

	X = Cl				X = Br				X = I			
	$[Co(cp)_2]$ [a]		*b*		$[Co(cp)_2]$ [a]		*b*		$[Co(cp)_2]$ [a]		*b*	
Bridging ligand	*g*	*A* [c]	*g*	*A* [c]	*g*	*A* [c]	*g*	*A* [c]	*g*	*A* [c]	*g*	*A* [c]
	1.968_3	25.0	1.968_3	27.4	1.978_2	26.7	1.978_1	26.8	1.992_2	25.0	1.9919	26.4
			1.974_1	50.8	1.978_1	47.8	1.985_6	48.5				
	1.969	27.9_6			1.979_3	27.2_7	1.979_3	27.7_9	1.993_8	26.3		

[a] Reduction by cobaltocene in dichloromethane. [b] Reduction electrochemically. [c] In Gauss (G = 10^{-4} T).

possible to obtain reliable spectral parameters, although the spectra of the initially generated mixed-valence species were generally similar to those of the chloro and bromo analogues.

The mixed-valence *meta* isomers therefore exhibit Class I behaviour whereas their *ortho* and *para* analogues are delocalised (Class III) on the EPR time-scale at room temperature. These conclusions are consistent with the electronic spectral data, and also reflect the significantly reduced electrochemical interaction between the metal redox centres in the *meta* species with respect to the other isomers. We also note that the EPR spectrum of the isoelectronic mixed-valence benzenediolate $[\{Mo(NO)[HB(dmpz)_3]Br\}_2(p\text{-}O_2C_6H_4)]^-$ is consistent with *valence-trapped* behaviour at room temperature,[25] revealing a subtle difference in the electron-exchange energy with this species in comparison with its benzenediamido analogue.

Infrared spectroscopic studies. Cobaltocene reduction of the compound *ortho*-**II** (Z = NH, X = Br) in dichloromethane caused ν_{NO} in the neutral species (1667 cm^{-1}) to be replaced by two bands (1631 and 1575 cm^{-1}, $\Delta\nu_{NO}$ = 56 cm^{-1}). Similar behaviour was observed with the *para* isomer, ν_{NO} in the neutral species (1660 cm^{-1}) being replaced by two absorptions at 1600 and 1569 cm^{-1} ($\Delta\nu_{NO}$ = 31 cm^{-1}). This shows that these reduced species are valence-trapped on the IR time-scale despite being delocalised on the EPR time-scale. The compound *meta*-**II** (Z = NH, X = Br) was different, both the neutral and mono-

Table 5 Electrochemical data obtained from mono- and di-metallic dianilido complexes $[Mo(NO)[HB(dmpz)_3]X(HNC_6H_4ZC_6H_4NHE)]$ {E = H and $Mo(NO)[HB(dmpz)_3]X$} **III** (Z = NH, E = linking group, X = halide) and **IV** (Z = NH, E = linking group, X = halide)

		Monometallic (E = H)			Bimetallic {E = $Mo(NO)[HB(dmpz)]_3X$}							
		CV[a]		DPV[b]	CV[a]					DPV[b]		
Bridging ligand	X	E_f[c]	ΔE_p[d]	E_f[e]	E_f^1[c,f]	ΔE_p^1[d]	E_f^2[c,g]	ΔE_p^2[d]	ΔE_f[h]	E_f^1[c,e,f]	E_f^2[c,e,g]	ΔE_f[h]
$HNC_6H_4CH_2C_6H_4NHE$	Cl	−1.44	153 (117)	−1.44	−1.46[i]	261 (96)	—	—	—	−1.413	−1.485	72
	I	−1.40	123 (102)	−1.40	−1.41[i]	183 (99)	—	—	—	−1.39[j]	—	86[k]
$HNC_6H_4OC_6H_4NHE$	Cl	−1.47	117 (96)	−1.46	−1.39	132 (111)	−1.54	150 (111)	147	−1.40	−1.52	123
	I	−1.41	181 (108)	−1.41	−1.34	135 (100)	−1.51	147 (100)	168	−1.33	−1.46	135
4,4′-$HNC_6H_4(CO)C_6H_4NHE$	Cl	−1.14	111 (99)	−1.17	n.m.[l]		n.m.[l]			n.m.[l]		
	I	−1.12	93 (93)	−1.12	−1.07	96 (64)	−1.25	108 (84)	174	−1.04	−1.23	186
3,3′-$NHC_6H_4(CO)C_6H_4NHE$	Cl	−1.32	129 (84)	−1.32	−1.33[i]	198 (84)				−1.29	−1.37	81
	I	−1.25	109 (90)	−1.25	−1.27[i]	189 (102)				−1.23	−1.31	81
$HNC_6H_4OC_6H_4(SO_2)C_6H_4OC_6H_4NHE$	Cl	−1.30	120 (120)	−1.30	−1.31[i]	138 (144)				−1.31[j]		58[k]
	I	−1.25	84 (87)	−1.25	−1.25[i]	126 (108)				−1.25[j]		50[k]

[a] Cyclic voltammetry using a platinum electrode. [b] Differential pulse voltammetry. [c] In V. [d] $E_p^c - E_p^a$, in mV (value for ferrocene oxidation). [e] Peak potential in V. [f] First reduction potential ($z = 0 \longrightarrow -1$). [g] Second reduction potential ($z = -1 \longrightarrow -2$). [h] $\Delta E_f = E_f^1 - E_f^2$, in mV. [i] Broad, two-electron wave. [j] Broad two-electron process analysed graphically. [k] Determined by methods described in ref. 15. [l] Not measured.

anionic species each exhibiting only *one* NO stretching frequency (1665 and 1560 cm^{-1}, respectively). The appearance of only *one* NO stretching frequency for *meta*-**II** (Z = N, X = Br) is not consistent with Class I properties: we would have expected to observe two ν_{NO} corresponding to the localised oxidised and reduced metal centres. However, since the reduction potentials for the *meta* isomer are close to that of cobaltocene (−1.34 V) and ΔE_f (375 mV) is relatively small, and we were obliged to use a large excess of reduction agent to guarantee spectral detection of a reduced species, we suspect that we have generated *meta*-$\mathbf{II}^{2-}$ (Z = NH, X = Br); indeed, the reaction solution was green rather than the expected deep brown or purple. The EPR spectrum of this species is very similar to that of the monoanion, with $g = 1.98$ and $A_{Mo} = 25$ G, behaviour entirely expected by analogy with the isoelectronic dipyridyl species **V**.[11,12] We were unable to characterise this species further.

Complexes derived from 4,4′-dianilino bridges

Our interest in anilino complexes **IV** [Z = NH, E = CH_2, O, CO or $OC_6H_4(SO_2)C_6H_4O$; X = halide] was primarily a more detailed look at the electrochemical properties of these species, to compare these with related diphenoxy and dipyridyl species, and to synthesize at least one example of a 17/17 v.e. dianion formally isoelectronic with the dipyridyl species **V** (E = linking group) referred to in the introduction.

Electrochemical properties. The mononuclear species **III** (Z = NH, E = linking group, X = halide) underwent a quasi-reversible or irreversible one-electron reduction in the range −1.12 to −1.47 V *vs.* the ferrocene–ferrocenium couple. These potentials are only slightly more anodic than those of their mononuclear benzenediamido analogues (Table 5). Again, there is a small but significant dependence of E_f on the halogen substituent X, in line with the benzenediamido species. The cyclic voltammograms of the dinuclear species, however, generally exhibit a broad two-electron wave, the exceptions being **IV** (Z = NH, E = O, X = Cl or I) and 4,4′-**IV** (Z = NH, E = CO, X = I) where two one-electron reduction processes were detected. These reduction processes appeared to be quasi-reversible, ΔE_p being only slightly more than twice that of that measured for the ferrocene–ferrocenium couple in the same cell but, of course, peak potential differences deviated significantly from their theoretical values (59 and 120 mV for one- and two-electron sequential electron-transfer processes, respectively). This is due, as mentioned above, to a combination of relatively slow electron-transfer kinetics and the nature of the electrochemical cell, factors we have regularly encountered before. We further analysed these electron-transfer processes by differential pulse voltammetry in order to extract ΔE_f and hence the comproportionation constant K_c for the equilibrium (1).

$$\mathbf{IV}^{2-}\ (Z = NH,\ E = \text{linking group},\ X = \text{halide}) + \mathbf{IV}\ (Z = NH,\ E,\ X = \text{halide}) \rightleftharpoons 2\,\mathbf{IV}^{-}\ (Z = N,\ E,\ X = \text{halide}) \qquad (1)$$

The values of ΔE_f for this group of complexes depends on the nature of E, as we have noted earlier, being very small with 'insulating' groups such as CH_2, but larger when E has p orbitals which can facilitate transmission of charge effects between the two halves of the molecule. The magnitude of ΔE_f (Tables 3 and 4) increases in the order $CH_2 < O \approx SO_2 < CO$. The size of ΔE_f also depends on the distance between the two redox centres, as can be seen most dramatically in the data obtained from *para*-**II** (Z = NH, X = halide) where ΔE_f averages 959 mV and from **IV** [Z = NH, E = $OC_6H_4(SO_2)C_6H_4O$, X = halide] where ΔE_f averages 54 mV, close to the statistical limit for two isolated redox centres. Similar effects have been detected in the redox behaviour of the dipyridyl derivatives $[\{Mo(NO)[HB(dmpz)_3]X\}_2\{(NC_5H_4)(CH{=}CH)_n(C_5H_4N)\}]$ **V** [E = $(CH{=}CH)_n$, $n = 0$–5] where ΔE_p ranges from 765 ($n = 0$) to 40 mV ($n = 5$).[11,12]

Infrared and EPR spectroscopic studies. Neutral compound **IV** [Z = NH, E = $OC_6H_4(SO_2)C_6H_4O$, X = Cl] has one NO stretching frequency at 1666 cm^{-1} which drops to 1584 cm^{-1} on reduction with cobaltocene. Since the metal-based redox centres are effectively isolated from each other (K_c *ca.* 10), we expected only one ν_{NO}. The frequency observed is very close to that for the species obtained by cobaltocene reduction of *meta*-**II** (Z = NH, X = Br) (1560 cm^{-1}), which we believe to be that of a 17/17 v.e. dianion. We also note that the NO stretching frequencies of the uncharged isoelectronic dipyridyl species **V** occur at *ca.* 1600 cm^{-1},[12] the lower value of the dianionic species presumably being due to the negative charge. The very low values of ν_{NO}, normally indicative of bridging NO groups, are a clear indication that it is the metal centres, and not the bridging ligands, which are reduced.

The EPR spectra of cobaltocene-reduced species of this class of compound, $\mathbf{IV}^{2-}$ (Z = NH, E, X = halide), are very similar to those of the isoelectronic dipyridyls **V** (E = bridging group). The *g* values average 1.98 and A_{Mo} is *ca.* 25 G, consistent with strong correlation between the unpaired spins on each metal.[11,12,25]

Comparison of dinuclear systems containing benzenediamido and dianilino bridges with related phenolato and dipyridyl systems

In Table 3 we summarise electrochemical and comproportionation constant data for the series of dinuclear complexes $[\{Mo(NO)[HB(dmpz)_3]X\}_2Q]$ where X = Cl, Br or I and Q = OC_6H_4O, $OC_6H_4EC_6H_4O$, NHC_6H_4NH, $NHC_6H_4EC_6H_4$-NH, pyrazine[26] or dipyridyls $(NC_5H_4)E(C_5H_4N)$. Several general points can be made.

(*a*) The first reduction potential for the compounds falls in the order benzenediolates/diphenolates (average $E_f = -0.81$ V) < benzenediamides/dianilides (average $E_f = -1.22$ V) < pyrazine/dipyridyls (average $E_f = -1.64$ V). These data reflect the interelectron repulsion energies inherent in reduction of a diamagnetic 16/16 v.e. to a 16/17 v.e. species in complexes containing dianion bridges (benzenediamides, diphenolates, *etc.*) *versus* reduction of the paramagnetic 17/17 to 17/18 v.e. species in the dipyridyl complexes. They first reflect the differences in electronic configurations of the benzene-diamido and -diolato species which contain 16/16 v.e. configurations prior to reduction with those in the dipyridyls (17/17 v.e.s). Secondly, the data are generally consistent with donation from relatively high-energy (π) orbitals on the dianionic ligands (benzenediamide, benzenediolate, *etc.*) to the empty d_{xy} orbital on the 16 v.e. molybdenum, whereas in the dipyridyl species a low-energy LUMO acts as a π acceptor from a partially filled metal d_{xy} orbital (see Fig. 1 and discussion later for a fuller explanation). The differences in potentials between the benzenediamido and dianilido species on the one hand and the benzenediolato and diphenolato species on the other is due to the greater spatial extension of the p_z on an sp^2-hybridised N atom compared to that on an O atom, for electronegativity reasons.

(*b*) The difference between first and second reduction potentials (ΔE_f) varies substantially depending on whether the bridging ligand is a benzenediamide, benzenediolate or N-heterocycle, which may be illustrated dramatically by a comparison of the related pair of 1,4-disubstituted benzene derivatives **II** (Z = NH, X = Cl), ΔE_f = 923 mV, and **II** (Z = O, X = Cl), ΔE_f = 460 mV, with the 1,4-pyrazine species $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2(pyz)]$, ΔE_f = 1440 mV.[26] The magnitude of ΔE_f, of course, determines the value of the comproportionation constant K_c which relates to the stability of the monoanionic mixed-valence species. Table 3 shows that the redox centres in relatively short bridging ligands derived from one benzene ring, 4,4′-bipyridyl or di-4-pyridylethene, are extremely strongly interacting, with $K_c > 10^9$. The extent of interaction between the redox centres is dependent on the length of the bridge and also on the relative position of these centres within an aromatic bridging ligand. It is clear that in **IV** [Z = NH, E = $OC_6H_4(SO_2)C_6H_4O$, X = Cl], **IV** [Z = O, E = $C(O)C_6H_4C_6H_4C(O)$, X = Cl][24] and **V** [E = $(CH{=}CH)_5$][12] (Table 3), where the bridging ligand has at least 18 atoms, the redox centres are isolated from each other since ΔE_f is in the range 40–60 mV ($K_c \approx$ 5–10) and the theoretical value for two non-interacting centres is 36 mV ($K_c = 4$). The species **IV** (Z = NH, E = CH_2CH_2, X = I) is similar and it appears that 'insulation' of the two $\{Mo(NO)[HB(dmpz)_3]X\}$ redox centres can be effected either by using a short saturated bridge between the two NHC_6H_4 fragments, or by introducing twists in the aromatic bridging chain by incorporating diphenyl groups. Replacement of a *para*- by a *meta*-substituted bridging ligand causes a reduction of between 40 and 56% in ΔE_f.

(*c*) The comproportionation constants for compounds *ortho*- and *para*-**II** (Z = NH, X = halide) (*ca.* 10^{13} and 10^{15}), *taken together with the spectroscopic data,* are consistent with Class III mixed-valence behaviour at room temperature, and we expect that the monoanionic 4,4′-bipyridyl derivative $\mathbf{V}^-$ (E = nothing) ($K_c \approx 10^{13}$) should also exhibit Class III properties. We have previously attempted to classify the mixed-valence behaviour of $\mathbf{V}^-$ (E = nothing) by UV/VIS spectroelectrochemical techniques, and while new low-energy absorptions in the near-IR region have been detected, we were unable unambiguously to assign intervalence charge-transfer transitions.[12] Electron paramagnetic resonance spectral studies of **V** (E = nothing) should be revealing and will be reported later. The huge value of K_c for $[\{Mo(NO)[HB(dmpz)_3]Br\}_2(pyz)]$ (10^{24}), probably the largest comproportionation constant so far reported in this medium, is also entirely consistent with Class III behaviour which has been confirmed by spectroscopic techniques.[25] In contrast, K_c for the valence-trapped *meta*-**II** (Z = NH, X = halide) is *ca.* 10^6. These data may be compared with results obtained from diruthenium complexes $[\{Ru(NH_3)_5\}_2Q]^{5+}$ where Q = *para*-HNC_6H_4NH ($K_c = 10^{10}$, Class III), 4,4′-bipyridyl (K_c = 20, Class II), and pyrazine ($K_c = 10^6$; the lower limit of Class III in the pentammineruthenium system).[4] The comproportionation constant data for the molybdenum complexes were obtained from electrochemical measurements in dichloromethane while those for the Creutz–Taube ion and its analogues were determined in aqueous media and so the magnitude of K_c must be treated with caution since it is dependent on solvent, base electrolyte, temperature, cyclovoltammetric voltage scan rate, *etc.* Nevertheless it is clear that the interactions between the metals in the dimolybdenum species are substantially greater than those in comparable diruthenium compounds.

Conclusion

We have shown by a combination of IR and EPR spectroscopic and electrochemical techniques that the benzenediamido complexes *ortho*- and *para*-**II** (Z = NH, X = halide) are delocalised on the EPR timescale but valence-trapped on the IR timescale. This places the electron exchange within the range 10^8 to 10^{13} per second. The *meta* isomer, however, is valence-trapped over the whole of this range. The monoanionic species $\mathbf{IV}^-$ (E, X = halide), which we have not prepared, should also be valence-trapped. The spectroscopic, electrochemical and comproportionation constant data are all broadly consistent with the empirical rules devised by Richardson and Taube[14] to explain the mediating effects of bridging ligands on metal–metal interaction. These interactions are greatly enhanced when the metal centres are close together and when there is extensive conjugation in the bridging ligands. Our results are entirely consistent with those obtained in dinuclear pentammineruthenium systems using the isomers pyrazine and pyrimidine,, the dinitriles 1,2-, 1,3- and 1,4-$(NC)_2C_6H_4$ and various dicyanonaphthalenes.[14]

However, we have drawn attention to a major difference between the dimolybdenum and the diruthenium systems, namely that the interaction between the metals in the former is much larger than that in the latter. Since we are not able to assign i.v.c.t. absorptions and so calculate the electronic coupling parameter V_{ab}‡ we are not yet able to make a quantifiable comparison. Nevertheless, it is possible to rationalise this dif-

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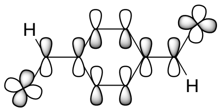
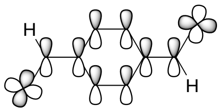
‡ The electronic coupling parameter is also referred to as $J = 2.05 \times 10^{-2} (\varepsilon\nu_{\frac{1}{2}}E)^{\frac{1}{2}}/r$, in cm^{-1}, where ε is the absorption coefficient for the i.v.c.t. band in $dm^3\ mol^{-1}\ cm^{-1}$, $\nu_{\frac{1}{2}}$ the width at half-height of the i.v.c.t. band in cm^{-1}, *E* the energy of the i.v.c.t. band in cm^{-1}, and *r* the metal–metal separation in Å.[27]



(*b*) Metal-to-ligand π-donor interaction in dinuclear molybdenum nitrosyls



(*a*) Ligand-to-metal π-donor interaction in dinuclear molybdenum nitrosyls

Fig. 1 Interaction between (*a*) empty molybdenum d_{xy} orbitals and a filled π-bonding orbital of a benzenediamide bridging ligand and (*b*) partially filled molybdenum d_{xy} orbitals and a π* orbital of the bridging ligand. Interactions in benzenediolate ligands, where NH is replaced by O, and in dipyridyls, where the NH group disappears, are similar

ference in behaviour by examining the electronic structure of the two metal centres in each system.

As explained in the introduction, generation of the mixed-valence species containing pentammineruthenium fragments requires *oxidation* by removal of electrons from the HOMO (highest occupied molecular orbital) of the complex. Formally, this can be regarded as oxidation of low-spin Ru^{2+} (d^6) to low-spin Ru^{3+} (d^5), converting a very good π-donor ion into a less good one which, at the same time, may act as a very weak π acceptor. The mixed-valence molybdenum nitrosyls are prepared by *reduction*, that is addition of an electron to the LUMO of the dinuclear species. In formal oxidation-state terminology, assuming the nitrosyl group to be bound as NO^+, this means reduction of Mo^{II} (d^4) to Mo^{I} (d^5). Divalent molybdenum, particularly when associated with π-acid ligands like NO, is a potentially strong π acceptor. However, monovalent molybdenum, while having reduced acceptor characteristics, may function as a π donor. What this implies is that the molybdenum nitrosyl system is more flexible, being capable of π-acceptor *and* π-donor behaviour depending on oxidation state, whereas the ruthenium pentammine system acts primarily as a π donor.

The reason that the molybdenum nitrosyls have this remarkable property may be clarified if we assume that the Mo–N–O bond system defines the *z* axis in the molybdenum complexes and the remaining donor atoms lie on the other axes. It follows that the d_{xz} and d_{yz} orbitals are stabilised by interaction with the π*(NO) orbitals leaving the d_{xy} orbital as the lowest unoccupied d orbital in species containing the $Mo(NO)^{3+}$ core.[28,29] This orbital is ideally situated to interact with either the π bonding or the π* orbitals of the bridging ligand (see Fig. 1). In the neutral 16 v.e. species where d_{xy} is empty the metal acts as an acceptor with respect to the relatively high-energy π-bonding orbitals of the dianionic bridging ligands. This is consistent with the occurrence of l.m.c.t. abosrptions in the dinuclear 16/16 v.e. molybdenum nitrosyls. When the d_{xy} orbital is partially filled, as in the 16/17 and 17/17 v.e. species, a low-energy LUMO of the bridge acts as a π acceptor, thereby greatly facilitating electronic exchange, and we see m.l.c.t. absorptions.

Richardson and Taube[14] have commented that the comproportionation constants of the dinuclear pentammineruthenium species were a function of, among other things, electronic delocalisation effects and electrostatic interactions. In their opinion, the latter were much more significant than the former. However, given that in the equilibrium $[M_2Q]^n + [M_2Q]^{n-2} \rightleftharpoons 2[M_2Q]^{n-1}$ the change in electrostatic units is the same for the pentammineruthenium system ($n = 2+$) as it is in the molybdenum nitrosyls ($n = 0$), it is our view that the influence of delocalisation effects on K_c in the molybdenum nitrosyls is very significant.

We have reported that the reduction potentials for benzenediamido, dianilido and dipyridyl species are relatively cathodic with respect to those of the benzenediolates and diphenolates. These differences in potentials are due to the greater spatial extension of the p_z orbital on an sp^2-hybridised N atom compared to that on an O atom, because of electronegativity. However, a more thorough description of the dinuclear molybdenum nitrosyl system must await molecular orbital calculations which are in progress.[28]

Finally, we must comment on the methods of classification which we have applied to these flexible dinuclear molybdenum complexes. The techniques that we have used to define their mixed-valence behaviour are *time-scale and temperature dependent*. For the reasons explained above we are not able, at the moment, to assign i.v.c.t. absorptions for the partially reduced complexes, and this prevents us from calculating the electron-coupling parameter V_{ab} which is the most reliable *temperature-independent* test of mixed-valence classification. It is quite possible that those of our mixed-valence compounds which exhibit 'localised' EPR spectra (*i.e.* $A_{Mo} = 50$ G) actually have weak Class II characteristics. Perhaps a deconvolution of the absorptions occurring in the near-IR spectra of these species will afford useful data concerning i.v.c.t. transitions, and we hope to report on this in due course.[28]

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