

Dinuclear molybdenum complexes derived from diphenols: electrochemical interactions and reduced species

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Abstract—The new diphenolato complexes $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\text{Q}]$ where $\text{dmpz} = 3,5\text{-dimethylpyrazolyl}$ and $\text{Q} = \text{OC}_6\text{H}_4(\text{C}_6\text{H}_4)_n\text{C}_6\text{H}_4\text{O}$ ($n = 1$ or 2), $\text{OC}_6\text{H}_4\text{CR}=\text{CRC}_6\text{H}_4\text{O}$ ($\text{R} = \text{H}$ or Et), and $\text{OC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{O}$ have been prepared and their electrochemical properties (cyclic and differential pulse voltammetry) compared with previously reported analogues where $\text{Q} = \text{OC}_6\text{H}_4\text{O}$, $\text{OC}_6\text{H}_4\text{EC}_6\text{H}_4\text{O}$ ($\text{E} = \text{SO}_2$, CO and S), $\text{OC}_6\text{H}_4(\text{CO})\text{C}_6\text{H}_4\text{C}_6\text{H}_4(\text{CO})\text{C}_6\text{H}_4\text{O}$ and $1,5\text{-}$ and $2,7\text{-O}_2\text{C}_{10}\text{H}_6$. The electrochemical interaction between the redox centres in the new complexes is very weak, in contrast to that in the $1,4\text{-benzenediolato}$ and naphthalendiolato species. The EPR spectra of the reduced mixed-valence species $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\text{Q}]^-$ where $\text{Q} = 1,3\text{-}$ and $1,4\text{-OC}_6\text{H}_4\text{O}$ and $\text{OC}_6\text{H}_4\text{SC}_6\text{H}_4\text{O}$ shows that they are valence-trapped at room temperature, whereas those of the dianions $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\text{Q}]^{2-}$ where $\text{Q} = 1,4\text{-OC}_6\text{H}_4\text{O}$, $\text{OC}_6\text{H}_4\text{EC}_6\text{H}_4\text{O}$ ($\text{E} = \text{CO}$ or S) and $\text{OC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{O}$ shows that the unpaired spins on each molybdenum centre are strongly correlated (J , the spin exchange integral $\gg A_{\text{Mo}}$, the metal-hyperfine coupling constant). The electrochemical properties and the comproportionation constants for the reaction $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\text{Q}] + [\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\text{Q}]^{2-} \rightleftharpoons 2[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\text{Q}]^-$ where $\text{Q} = \text{diphenolato bridge}$, are compared with related compounds containing benzenediamido and dianilido bridges. © 1997 Elsevier Science Ltd

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Transition metal nitrosyl complexes very frequently undergo redox reactions, a facility which is largely associated with the versatile nature of the NO group [1], and addition of NO to a transition metal system usually enhances redox activity, if not conferring it *de novo* [2]. This is due to the ability of coordinated NO to absorb very substantial amounts of charge, *via* $d\pi-\pi^*$ interactions, without disruption of the N—O bond, and is one of the most remarkable features of this simple ligand.

Such a situation occurs in the now well-characterised molybdenum nitrosyl tris(pyrazolyl)borato system $[\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{XY}]$ where $\text{dmpz} = 3,5\text{-dimethylpyrazolyl}$ and X is a uninegative ligand (usually halide) and Y can be halide, alkoxide or alkyl-

amide, alkanethiolate, aryl-oxide or amide, or N-heterocycle [3,4]. All of these complexes are redox-active, undergoing a single one-electron reduction and, in certain cases, a one-electron oxidation [4]. The metal atom in $[\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{XY}]$ has a formal 16 valence electron (ve) configuration, and since it binds an electronegative halogen atom, the powerful π -acceptor NO, and cannot readily expand its coordination number because of the protective nature of the $\text{HB}(\text{dmpz})_3$ ligand, it is significantly 'electron deficient' [5]. One consequence is that the redox characteristics of the molybdenum centre are amplified, the electrochemical potential for the formation of $[\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{XY}]^-$ being substantially determined by the donor atoms X and Y, i.e. O, S or N (in amines or N-heterocycles) and their substituents, i.e. alkyl, aryl or substituted aryl. A further consequence is that the potentials for the

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redox process $[\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{XY}] + e^- \rightleftharpoons [\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{XY}]^-$ ranges from -0.35 to -2.55 V *vs* the ferrocene/ferrocenium couple [6,7], i.e. 2200 mV, an enormous and perhaps the largest recorded range in a single structurally discrete system.

We have observed that formation potentials for monoanionic phenolate species, $[\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{X}(\text{OAr})]^-$ are significantly more anodic than those of their anilido analogues $[\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{X}(\text{NHAr})]^-$, reflecting the electron donating/accepting properties of OAr *vs* NHAr [8]. We have recently carried out a thorough examination of dinuclear species derived from benzenediamides and dianilides [9], but there is less information on analogous phenol-based systems. This paper reports the augmentation of the data which have been reported, and we collate existing and new electrochemical data obtained from comparable dinuclear benzenediolato, diphenolato and naphthalenediolato complexes, $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{X}\}_2\text{Q}]$ where Q = I–IX (Fig. 1) [10–12]. We also report the EPR spectral characterisation of some reduced species derived from this group of compounds.

EXPERIMENTAL

Materials

All reactions were carried out under oxygen free, dry nitrogen atmosphere. Dry freshly distilled dichloromethane or toluene were used for all reactions. All other commercial reagents were used as received. The starting material $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}_2]$ was prepared following known procedures [4], and 4,4'-diphenol was used as purchased. The naphthalenediolato complexes $[\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\text{Q}]$ where Q = VII (1.5), VIII (1.6) and IX (2.7) were prepared as described previously [12]. New compounds were purified by column chromatography using silica gel 60 (70–230 mesh) and CH_2Cl_2 and $\text{CH}_2\text{Cl}_2/n$ -hexane mixtures as eluant; the bimetallic species were stable in solution and in the presence of air for short periods. IR spectra were recorded using either by PE357 or PE1600 FTIR spectrophotometers and ^1H NMR spectra were recorded using a JEOL JN MX 270 spectrometer. Cyclic voltammetric and differential pulse polarographic data were obtained using a Pt wire electrode with a PAR174 instrument in dry CH_2Cl_2 as solvent containing $[\text{NBu}_4][\text{PF}_6]$ (0.2 mol dm^{-3}) as supporting electrolyte. The data obtained were reproducible, the experimental error being ± 10 mV.

Synthetic methods

4,4'-MeOC₆H₄C₆H₄C₆H₄OMe. A THF solution (30 cm^3) of the Grignard reagent (4-MeOC₆H₄MgBr, prepared from 4-bromoanisole (4.40 g) and iodine-acti-

vated Mg turning (0.68 g), was added to a stirred, cooled (ice–water) solution of 4-bromobenzene (2.36 g) and $[\text{NiCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$ (0.32 g) in THF (40 cm^3). The solution turned dark brown, some precipitation occurred, and the mixture was left stirring overnight. It was then quenched with ethanol (15 cm^3) and conc. HCl (1.0 cm^3). The precipitate which formed was collected by filtration, washed with ethanol (*ca* 70 cm^3 50%). Found: C, 82.2; H, 5.8. C₂₀H₁₈O₂ requires C, 82.8; H, 6.2%.

4,4'-HOC₆H₄C₆H₄C₆H₄OH. To a hot (*ca* 140°C) solution of pyridine (14 cm^3) and conc HCl (13 cm^3) was added MeOC₆H₄C₆H₄C₆H₄OMe (0.87 g) and the mixture was heated at 190–220°C for 3 h. It was then cooled, water (*ca* 60 cm^3) was added, and after boiling the mixture, a white precipitate had formed. This was filtered off, washed with hot ethanol and recrystallised from THF affording the compound as a white solid (yield 0.58 g, 75%). Found: C, 79.9; H, 5.2. C₁₈H₁₄O₂ requires C, 82.4; H, 5.3%. NMR: ^1H (CDCl₃): δ 6.96 (d, 4H; 3,3',5,5'-C₆H₄); 7.52 (d, 4H; 2,2',6,6'-C₆H₄); 7.61 (s, 4H; 8,9,11,12-C₆H₄).

4,4'-MeOC₆H₄C₆H₄C₆H₄C₆H₄OMe. To a solution of 4-MeOC₆H₄MgBr, prepared from 4-bromoanisole (7.47 g) and Mg turnings (1.22 g) in THF (30 cm^3) was added, with stirring, a cooled solution of 4,4'-dibromodiphenyl (3.12 g) and catalytic amounts of $[\text{NiCl}_2(\text{PPh}_3)_2]$ in THF (30 cm^3). The reaction mixture turned dark brown and was left to stir overnight. It was then quenched with ethanol (50 cm^3) and conc. HCl (3 cm^3), the reaction mixture lightening in colour, affording an off-white precipitate. This was filtered off, washed with ethanol (50% aqueous; 80 cm^3) and dried in air affording the desired compound (yield 1.46 g, 40% based on 4,4'-bromodiphenyl). MS (EI): $m/z = 366$ (required 366). The compound was too insoluble to be characterised by ^1H NMR spectroscopy.

4,4'-HOC₆H₄C₆H₄C₆H₄C₆H₄OH. This compound was prepared in the same way as *trans*-(4-hydroxyphenyl)(3'-hydroxyphenyl)ethene, using pyridinium hydrochloride and 4-MeOC₆H₄C₆H₄C₆H₄C₆H₄OMe-4' (2.0 g). On cooling to 60°C, warm water (100 cm^3) was added, giving a turbid off-white solution. On filtration and drying the residue in air, the compound was obtained as an off-white solid (1.73 g, 94%), MS (EI): $m/z = 338$ (required 338).

Trans-4,4'-HOC₆H₄CH=CHC₆H₄OH. A mixture of technical grade pyridine (24 cm^3) and conc. HCl (26.4 cm^3) was heated with stirring to 220°C for 15 min, then cooled to 140°C and treated with *trans*-bis(4-methoxyphenyl)ethene (2.0 g). The mixture was then refluxed under nitrogen for 3 h at a temperature between 190 and 210°C. The mixture was then cooled and poured into distilled water (50 cm^3), the pH was adjusted with dilute HCl to 5–6, and the desired biphenol precipitated. It was filtered off, recrystallised from ethanol/water mixtures and again collected by filtration and air-dried, giving a white crystalline solid (1.2 g, 68%). NMR: ^1H (CDCl₃): δ 6.74 (d, 4H;

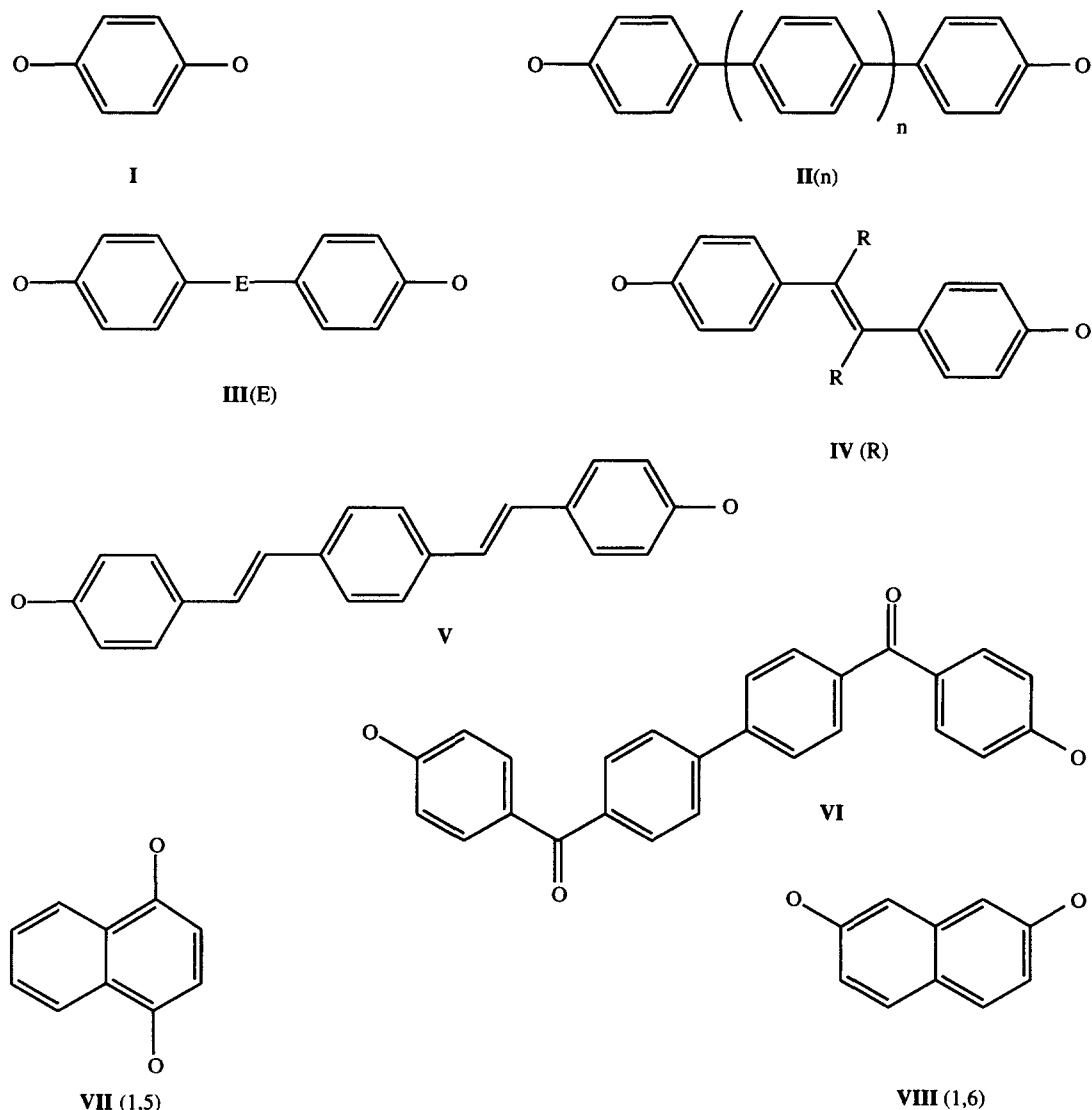


Fig. 1. Bridging ligands Q in $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\text{Q}]$.

3,3',5,5'- C_6H_4); 6.90 (s, 2H; 7,8- $\text{HC}=\text{CH}$); 7.35 (d, 2H; 2,2',6,6'- C_6H_4).

All-trans- $\text{MeOC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{OMe}$. A mixture of 4,4'-dibromobenzene (2.36 g), 4-methoxystyrene (3.35 g), triethylamine (2.53 g) and catalytic amounts of triphenylphosphine (0.11 g) and palladium(II) acetate (0.05 g) were heated in a sealed Schlenk tube at 100°C until it solidified (*ca* 1 week). The reaction mixture had become bright yellow, was removed from the tube, washed with water and dried in air overnight. The residue was recrystallised from toluene giving the desired compound as a yellow crystalline solid (1.28 g, 37%).

All-trans- $\text{HOC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{OH}$. This compound was obtained by demethylation of *all-trans*- $\text{MeOC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{OMe}$ using pyridinium hydrochloride in the same way as

trans-(4-hydroxyphenyl)(3'-hydroxyphenyl)ethene above, using $\text{MeOC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{OMe}$ (0.6 g). On cooling the reaction mixture to 60°C , warm water (100 cm^3) was added giving a turbid yellow/brown solution. Filtration afforded the desired compound as a light brown solid (0.4 g, 73%). Found: C, 82.9; H, 6.4. $\text{C}_{22}\text{H}_{18}\text{O}_2$ requires C, 84.1; H, 5.7%, m.wt (EI MS): 314 (calc. 314).

$[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{O}]$. A mixture of $[\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}_2]$ (0.17 g) and $\text{HOC}_6\text{H}_4\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{OH}$ (0.03 g) in toluene (40 cm^3) containing triethylamine (2 cm^3) was refluxed for 4 h during which time the yellow solution became first yellowish-green and then purple. The solvent was then evaporated *in vacuo* and the residue redissolved in the minimum volume of dichloromethane. The complex was purified by chromatography on silica gel using

dichloromethane as eluant, the major purple fraction being collected, the solvent evaporated *in vacuo* and the compound being recrystallised from dichloromethane/*n*-hexane mixtures. The complex was isolated as dark purple microcrystals (yield 0.09 g, 65%). Found: C, 49.3; H, 5.1; N, 16.8. $C_{48}H_{56}B_2Cl_2N_{14}O_4Mo_2$ requires C, 48.9; H, 4.8; N, 16.7%; m.wt (mass spectral): 1177 (calcd. 1177). IR (KBr disc): $\nu(NO)$ 1687 cm^{-1} . 1H NMR ($CDCl_3$): δ 7.40 (d, 4H, 3,3',5,5'- C_6H_4); 7.757 (d, 4H; 2,2',6,6'- C_6H_4); 7.761 (s, 4H; 8,9,11,12- C_6H_4).

$[Mo(NO)\{HB(dmpz)_3\}Cl(OC_6H_4C_6H_4C_6H_4OH)]$. A mixture of $[Mo(NO)\{HB(dmpz)_3\}Cl_2]$ (0.08 g) and $HOC_6H_4C_6H_4C_6H_4OH$ (0.06 g) in toluene (30 cm^3) containing triethylamine (2 cm^3) was refluxed for 4 h. The solvent was then evaporated *in vacuo* and the residue redissolved in the minimum volume of dichloromethane. The mixture was purified by chromatography on silica gel using dichloromethane as eluant, two purple fractions being collected. Both were worked-up as described above, the first being the bimetallic complex described above (yield 0.26 g, 10%) and the second the monometallic species (yield 0.18 g, 11%). Found: C, 56.9; H, 5.2; N, 12.4. Calc. for $[Mo(NO)\{HB(dmpz)_3\}Cl(OC_6H_4C_6H_4C_6H_4OH)] \cdot 1/2C_6H_{12}$, *viz.* $C_{36}H_{41}BClN_7O_3Mo$: C, 56.7; H, 5.5; N, 12.9%; m.wt (mass spectral): 719.5 (calculated 719.9). IR (KBr disc): $\nu(NO)$ 1684 cm^{-1} . 1H NMR ($CDCl_3$): δ 6.93 (m, 2H; 14,18- C_6H_4); 7.39 (m, 2H; 3,5- C_6H_4); 7.56 (m, 2H; 9,11- C_6H_4); 7.65 (d, 2H; 8,12- C_6H_4); 7.72 (d, 2H; 15,17- C_6H_4); 7.73 (d, 2H; 2,6- C_6H_4).

$[Mo(NO)\{HB(dmpz)_3\}Cl]_2OC_6H_4C_6H_4C_6H_4C_6H_4O$. A mixture of $[Mo(NO)\{HB(dmpz)_3\}Cl_2]$ (1.01 g) and 4- $HOC_6H_4C_6H_4C_6H_4OH-4'$ (0.34 g) in toluene (150 cm^3) was sonicated for 20 min, triethylamine (2.0 cm^3) was added, and the mixture refluxed overnight, during which time it changed in colour from green to deep purple. The mixture was cooled, the solvent evaporated *in vacuo*, and the residue chromatographed on silica gel. Using dichloromethane/*n*-hexane (50:50 v/v), a weak purple fraction was eluted and was discarded. Increasing the concentration of dichloromethane (75:25 v/v) caused elution of a strong purple fraction which was collected, the solvent evaporated *in vacuo* and the residue recrystallised from dichloromethane/diethylether, giving the compounds as dark purple microcrystals (0.09 g, 7%). Found: C, 51.5; H, 5.3; N, 15.8. $C_{54}H_{60}B_2Cl_2N_{14}O_4$: C, 51.7; H, 5.8; N, 15.6%; m.wt (mass spectral, FAB): 1253 (calculated 1253). IR (KBr disc): $\nu(BH)$ 2544; $\nu(NO)$ 1674 cm^{-1} . 1H NMR ($CDCl_3$): δ 7.75 (s, 8H; 2',3',5', 6',2'',3'',5'',6''-protons of C_6H_4); 7.74 (d, 4H; $J = 9.7$ Hz; 2,6,3'',5''-protons of C_6H_4); 7.44 (d, 4H; $J = 8.6$ Hz; 3,5,3'',5''-protons of C_6H_4); 5.77 (s, 2H), 5.96 (s, 2H), 5.89 (s, 2H), of $Me_2C_3HN_2$; 2.61 (s, 6H); 2.42 (s, 6H); 2.24 (s, 6H); 2.12 (s, 6H).

$[Mo(NO)\{HB(dmpz)_3\}Cl(OC_6H_4CH=CHC_6H_4OH)]$. A mixture of $[Mo(NO)\{HB(dmpz)_3\}Cl_2]$ (0.2 g) and *trans*-bis(4-hydroxyphenyl)ethene (0.10 g) was

refluxed for 2 h in dichloromethane (40 cm^3) containing a slight excess of NEt_3 (0.5 cm^3). The volume of the solution was reduced *in vacuo*, and the residue chromatographed on silica (30% *n*-hexane in dichloromethane as eluant). The first major purple fraction was identified as the dinuclear $[Mo(NO)\{HB(dmpz)_3\}Cl]_2(OC_6H_4CH=CHC_6H_4O)$ (see below), which could be isolated by evaporation of the eluant mixture and recrystallisation of the residue from *n*-hexane (yields 15–20%). The second major purple fraction, the desired monometallic species, was obtained by elution with pure dichloromethane, and was isolated following evaporation of the solvent and recrystallisation from *n*-hexane. It was isolated as purple microcrystals (yield 0.04 g, *ca* 25%). Found: C, 52.4; H, 5.0; N, 14.3. $C_{29}H_{33}BClN_7O_3Mo$ requires C, 52.0; H, 4.8; N, 14.6%. IR (KBr disc): 1681 (ν_{NO}); 2553 (ν_{BH}) cm^{-1} . 1H NMR ($CDCl_3$): 2.12 (s, 3H), 2.24 (s, 3H), 2.40 (s, 3H), 2.41 (s, 3H), 2.49 (s, 3H; $(CH_3)_2C_3HN_2$); 5.82 (s, 1H), 5.86 (s, 1H), 5.96 (1H; of $Me_2C_3HN_2$); 6.89 (d, 2H; 3',5'-H or C_6H_4); 7.02 (d, H8 of $CH=CH$); 7.15 (7H or $CH=CH$); 7.57 (d, 2H; 2,6-H of C_6H_4); 7.43 (d, 2H; 2',6'-H of C_6H_4); 7.18 (d, 2H; 3,5-H of C_6H_4).

$[Mo(NO)\{HB(dmpz)_3\}Cl]_2\{(4-OC_6H_4)CH=CH(C_6H_4O-4')\}$. The bimetallic species was obtained as described above, but using $[Mo(NO)\{HB(dmpz)_3\}Cl_2]$ (0.2 g) and 4,4'-dihydroxystilbene (0.043 g) in refluxing toluene (40 cm^3) containing a slight excess of NEt_3 (0.5 cm^3) over 3 h. The solvent was then removed *in vacuo* and the residue redissolved in dichloromethane. The work-up procedure was similar to that described above, using hexane/dichloromethane mixture (30% C_6H_{12}) as eluant. The bimetallic species was isolated as purple microcrystals (yield: 0.08 g, 40%). The monometallic species could also be obtained in yields of 15%. Found: C, 46.6; H, 4.9; N, 17.3. $C_{44}H_{54}B_2Cl_2N_{14}O_4Mo_2$ requires C, 46.9; H, 4.8; N, 17.4%. IR (KBr disc): 1680 (ν_{NO}); 2553 (ν_{BH}) cm^{-1} . 1H NMR ($CDCl_3$): 2.12 (s, 6H), 2.17 (s, 6H), 2.42 (s, 6H), 2.44 (s, 6H), 2.56 (s, 6H; $(CH_3)_2C_3HN_2$); 5.82 (s, 2H), 5.96 (s, 2H), 5.99 (s, 2H; $Me_2C_3HN_2$); 7.18 (s, 2H; $CH=CH$); 7.24 (d, 4H; 3,3',5,5' of C_6H_4 groups); 7.62 (d, 4H; 2,2',6,6' or C_6H_4).

$[Mo(NO)\{HB(dmpz)_3\}Cl\{(4-OC_6H_4)CET=CET(C_6H_4OH-4')\}]$ and $[Mo(NO)\{HB(dmpz)_3\}Cl\{(4-OC_6H_4)CET=CET(C_6H_4O-4')\}]$. These complexes were prepared in ways similar to those described above, both using $[Mo(NO)\{HB(dmpz)_3\}Cl_2]$ (0.2 g) and $HOC_6H_4CET=CETC_6H_4OH$. For the monometallic 0.129 g and for the bimetallic 0.054 g of the diphenol were used, giving yields of 20% (bimetallic) and 35% (monometallic) and of 43% (bimetallic) and 25% (monometallic), respectively, from each reaction. Analysis for $[Mo(NO)\{HB(dmpz)_3\}Cl(OC_6H_4CET=CETC_6H_4OH)]$: found: C, 54.9; H, 5.8; N, 13.3. $C_{33}H_{41}BClN_7O_3Mo$ requires C, 54.6; H, 5.7; N, 13.5%. IR (KBr disc): 1681 (ν_{NO}); 2553 (ν_{BH}) cm^{-1} .

$^1\text{H NMR}$ (CDCl_3): 2.19 (s, 3H), 2.37 (s, 3H), 2.38 (s, 3H), 2.39 (s, 3H), 2.40–2.42 (m, 16H; (CH_3) $_2\text{C}_3\text{HN}_2$) and C_2H_5); 5.82 (s, 1H), 5.91 (s, 1H), 5.96 (s, 1H; $\text{Me}_2\text{C}_3\text{HN}_2$); 6.80 (d, 2H; 3',5'-H of C_6H_4); 6.81 (d, 2H; 3,5-H of C_6H_4); 7.02 (d, 2H; 2',6'-H of C_6H_4); 7.08 (d, 2H; 2,6-H of C_6H_4). Anal. [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\text{OC}_6\text{H}_4\text{C}(\text{Et})=\text{C}(\text{Et})\text{C}_6\text{H}_4\text{O}\}$]: found: C, 49.1; H, 5.3; N, 16.2. $\text{C}_{48}\text{H}_{62}\text{B}_2\text{Cl}_2\text{N}_{14}\text{O}_4\text{Mo}_2$ requires C, 48.7; H, 5.3; N, 16.6%. IR (KBr discs): 1681 (ν_{NO}); 2553 (ν_{BH}) cm^{-1} . $^1\text{H NMR}$ (CDCl_3): 2.06 (s, 6H), 2.22 (s, 6H), 2.39 (s, 6H), 2.42–2.44 (m, 22H), 2.57 (s, 6H; (CH_3) $_2\text{C}_3\text{HN}_2$ and C_2H_5); 5.83 (s, 2H), 5.95 (s, 2H), 5.99 (s, 2H; $\text{Me}_2\text{C}_3\text{HN}_2$); 7.01 (d, 4H; 3,3',5,5'-H of C_6H_4); 7.12 (d, 4H; 2,2',6,6'-H of C_6H_4).

[$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{OC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{O})$]. A mixture of [$\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}_2$] (1.01 g) and $\text{HOC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{OH}$ (0.32 g) in toluene (150 cm^3) were sonicated for 20 min. Triethylamine was added and the mixture was refluxed overnight during which time it changed in colour from yellow/green to deep purple. The solvent was then evaporated *in vacuo* and the purple residue chromatographed on silica gel. Using dichloromethane as eluant, a strong blue-coloured fraction was eluted which afforded the desired compound. On addition of THF (5% by volume), further green [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\text{O}$] and purple [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}=\text{OC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{OH}\}$] were separated, and although the compounds were identified by mass spectrometry, their yields were too low to permit further characterisation. The deep blue eluate was evaporated *in vacuo*, and the residue recrystallised from dichloromethane/*n*-hexane affording the desired compound as a deep blue microcrystalline powder (yield 0.53 g, 44%). Found: C, 50.9; H, 5.2; N, 14.7. $\text{C}_{52}\text{H}_{60}\text{B}_2\text{Cl}_2\text{N}_{14}\text{O}_4\text{Mo}_2$: C, 50.8; H, 4.9; N, 15.9%; m.wt (FAB MS): 1229 (calc. 1229). IR (KBr): 2544 (ν_{BH}); 1679 (ν_{NO}) cm^{-1} . $^1\text{H NMR}$ (CDCl_3): δ 7.62 (d, 4H; $J = 8.8$ Hz; 2,6,2'',6''-protons of C_6H_4); 7.56 (s, 4H; 2',3',5'',6''-protons of C_6H_4); 7.31 (d, 4H; $J = 8.6$ Hz; 3,5,3''',5'''-protons of C_6H_4); 7.18 (d, 4H; $J = 11.0$ Hz; $\text{CH}=\text{CH}$); 5.83 (s, 2H), 6.01 (s, 2H), 5.93 (s, 2H) of $\text{Me}_2\text{C}_3\text{HN}_2$; 2.56 (s, 6H), 2.45 (s, 9H), 2.41 (s, 9H), 2.17 (s, 6H), 2.07 (s, 6H) of (CH_3) $_2\text{C}_3\text{HN}_2$.

[$\text{Co}(\text{C}_5\text{H}_5)_2$] $_2$ [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{OC}_6\text{H}_4\text{SC}_6\text{H}_4\text{O})$]. To a purple solution of [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{OC}_6\text{H}_4\text{SC}_6\text{H}_4\text{O})$] (0.03 g) in dry toluene (5 cm^3) was added cobaltocene (0.10 g) in toluene (20 cm^3) until the purple solution became green and a green precipitate was formed. The precipitate was collected under nitrogen and dried *in vacuo* overnight at 80°C (yield 0.02 g, 50%). Found: C, 50.4; H, 4.9; N, 12.7%. Calc. for [$\text{Co}(\text{C}_5\text{H}_5)_2$] $_2$ [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{OC}_6\text{H}_4\text{SC}_6\text{H}_4\text{O})$] · 1/2 $\text{C}_6\text{H}_5\text{Me}$, *viz.*, $\text{C}_{62}\text{H}_{72}\text{B}_2\text{Cl}_2\text{N}_{14}\text{O}_4\text{SCo}_2\text{Mo}_2$: C, 50.4; H, 4.9; N, 12.7%.

[$\text{Co}(\text{C}_5\text{H}_5)_2$] $_2$ [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{OC}_6\text{H}_4\text{COC}_6\text{H}_4\text{O})$]. This compound was prepared in the

same way as that above, using [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{OC}_6\text{H}_4\text{COC}_6\text{H}_4\text{O})$] (0.02 g), and a green-black precipitate was formed (0.013 g, 51%). Found: C, 53.4; H, 5.4; N, 11.6. Calc. for [$\text{Co}(\text{C}_5\text{H}_5)_2$] $_2$ [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{OC}_6\text{H}_4\text{COC}_6\text{H}_4\text{O})$] · 1.5 $\text{C}_6\text{H}_5\text{Me}$, *viz.*, $\text{C}_{73}\text{H}_{83}\text{B}_2\text{Cl}_2\text{N}_{14}\text{O}_5\text{Co}_2\text{Mo}_2$ requires C, 53.5; H, 5.1; N, 12.9%.

RESULTS

Synthesis and characterisation

The diphenols used in this work (Fig. 1) were prepared by conventional methods. They reacted with [$\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}_2$] in the presence of triethylamine giving mixtures of mono- and bimetalated species which were separated chromatographically. Five new dinuclear compounds, [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{\text{II}$ ($n = 1, 2$)], [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{\text{VI}$ ($\text{R} = \text{H}, \text{Et}$)}] and [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{V})$] were prepared. The characterisation of the monometallic species is reported in the Experimental Section and the compounds are not discussed further.

Reduction of [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{\text{III}$ ($\text{E} = \text{S}, \text{CO}$)}] with two mole equivalents of cobaltocene in toluene afforded the dianions [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{\text{III}$ ($\text{E} = \text{S}, \text{CO}$)}] $^{2-}$ which were isolated as cobaltocenium salts containing toluene of crystallisation. We were unable to isolate satisfactorily pure monoanionic species when the stoichiometry of reducing agent to complex was 1:1. The compounds [$\text{Co}(\text{C}_5\text{H}_5)_2$] $_2$ [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{\text{III}$ ($\text{E} = \text{S}, \text{CO}$)}] were stable as solids in air, but were too reactive in solution to permit effective recrystallisation.

The IR spectra contained ν_{BH} and other absorptions entirely typical of the $\text{HB}(\text{dmpz})_3$ ligand. The NO stretching frequencies of the neutral dinuclear species occurred at *ca* 1680 cm^{-1} , typical of phenolato complexes of this type [5,8,10], whereas those of the dianions [$\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{\text{III}$ ($\text{E} = \text{S}, \text{CO}$)}] $^{2-}$ occurred as a single absorption at 1600 cm^{-1} , a drop consistent with reduction of both metal centres. The $^1\text{H NMR}$ spectra (Experimental Section) are also in accordance with our formulations of these complexes but, as expected, the dianionic compounds are paramagnetic (for discussion of their EPR spectra, see below).

Electrochemical studies

The cyclic voltammograms of the new dimetallic complexes contain a broad reduction wave consistent with two sequential one-electron reductions (Table 1). The ideal peak-to-peak separation ($\Delta E_p = E_p^c - E_p^a$) for a thermodynamically reversible sequential two electron processes should be 118 mV, and only that

Table 1. Electrochemical data and comproportionation constants obtained from $[(\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}_2\text{Q})]$

Q	Electrode process	Cyclic voltammetry ^a		Square wave voltammetry			Differential pulse voltammetry ^b			Comproportionation constant data	
		$E_r(\Delta E_p)^c$	ΔE_r^d	E_r^e	E_{dp}^e	ΔE_{dp}^f	$E_{r,\text{calc.}}^g$	Ref.	$\log_{10} K_c^h$	K_c^i	
I	0 → -1	-0.72 (80)						[9]	7.8	59.8×10^6	
	-1 → -2	-1.18 (120)	460					[10]	1.86	72	
II, n = 0	0 → -2			-0.80	110	-0.74, -0.85		this work	1.10	12.6	
II, n = 1	0 → -2	-0.75 (131)		-0.77	65	-0.74, -0.80		this work	≤ 1.0	≤ 10	
II, n = 2	0 → -2	-0.79 (201)		-0.79				[10]	1.27	18	
III, E = SO ₂	0 → -2	-0.72 (147)		-0.71	75	-0.67, -0.73		[10]	1.44	27	
III, E = CO	0 → -2	-0.68 (130)		-0.68	85	-0.64, -0.72		[10]	2.33	215	
III, E = S	0 → -2	-0.78 (135)		-0.78	138	-0.71, -0.85		this work	≤ 1.0	≤ 10	
IV, R = H	0 → -2	-0.75 (237)		-0.70				this work	≤ 1.0	≤ 10	
IV, R = Et	0 → -2	-0.80 (228)		-0.79				this work	≤ 1.0	≤ 10	
V	0 → -2	-0.79 (190)		-0.82				this work	≤ 1.0	≤ 10	
VI	0 → -2	-0.64 (118)		-0.80				[10]	0.95	8.8	
VII (1, 5)	0 → -1	-0.78 (80)		-0.64	56	-0.60, -0.66					
	-1 → -2	-0.98 (75)	150					[13]	2.54	3.5×10^2	
IX (2, 7)	0 → -1	-0.81 (140)									
	-1 → -2	-0.94 (160)	150					[13]	2.54	3.5×10^2	

^aIn CH₂Cl₂ solution (10^{-3} M), [Bu₄N][PF₆] as base electrolyte (10^{-1} M); Pt bead electrode, scan rate 200 mV s⁻¹.

^bPulse potential 10 mV.

^cV ± 0.02 V, ($\Delta E_p = E_p^a - E_p^c$ mV), potential vs ferrocene/ferricinium couple (ΔE_p in range 70–89 mV).

^d $E_r^f - E_r^e$ where detectable.

^eDifferential pulse peak.

^fPeak to peak separation where measurable, or measured by graphical methods as described in Refs. [10] and [14].

^g E_r calculated as described in Ref. [10].

^h ΔE_{dp} (differential pulse potential)/59.

ⁱexp ($\Delta E_{dp}/25.69$).

for $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{\text{II} (n = 1)\}]$ comes close. The comparable ΔE_p -values for CVs of ferrocene/ferrocenium couple as internal reference ranged from 80 to 110 mV. This means that for the other new species described here, the electron transfer processes are quasi-reversible at best. Because of the impossibility of determining ΔE_f ($E_f^2 - E_f^1$) from the CVs, we employed differential pulse voltammetry and deconvoluted the peak by the graphical methods of Richardson and Taube [13]. We have used this method before, and record in Table 1 all the data available for dinuclear diphenolato species. Because of the lack of reversibility of the CV responses of the other new compounds, we felt that the data obtained by curve analysis of a differential pulse voltammogram would be unreliable. In any case, in all of these species, ΔE_f was expected to be less than 60 mV, leading to comproportionation constants of 1.0 or less.

Measurement of ΔE_f allowed us to calculate comproportionation constants K_c for the stability of the mono-reduced species in the equilibrium $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{X}\}_2\text{Q}] + [\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{X}\}_2\text{Q}]^{2-} \rightleftharpoons [\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{X}\}_2\text{Q}]^-$, which is a convenient way to express the extent of electrochemical interaction between the redox centres. The data are presented as $\log_{10} K_c$ and K_c for ease of comparison with data reported elsewhere [4,9].

Since the potential of the cobaltocene/ cobaltocenium couple is -1.34 V *vs* ferrocene/ ferrocenium, it is clear that as a reducing agent, the organocobalt derivative will convert all of the diphenolates to dianionic species. However, we were able to generate $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{\text{I}\}]^-$ ($\Delta E_f = 460$ mV) and $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{\text{III}(\text{E} = \text{S})\}]^-$ ($\Delta E_f = 138$ mV) by controlled potential electrolysis (for EPR spectral characterisation see below).

From the electrochemical and comproportionation data shown in Table 1 we can draw the following conclusions:

- (1) The first reduction potentials of the phenol-based complexes occur at *ca* -0.72 V *vs* the ferrocene/ferrocenium reference couple. The two species which deviate noticeably from this average contain keto groups, *viz.* **III** ($\text{E} = \text{CO}$) and **VI**, where the E_f -values are more anodic by *ca* 100 mV. This reflects the expected influence on the LUMO of the complex (the redox orbital) of an electron-withdrawing substituent at a *para* position on an aromatic ring.
- (2) The phenol-based complexes undergo their first reduction process at potentials on average 590 mV more positive than comparable benzenediamido and dianilido analogues. This is caused mainly by the higher electronegativity of the O atom *vs.* N and the consequent relative stabilisation of the LUMO.
- (3) The interaction between the two redox centres in the phenol-based systems decreases as the

distance between them increases, an effect which is well-established [4,9]. The order of decreasing ΔE_f in terms of Q is **I** > **VII**, **VIII** > **I** > the rest, and within the series **II**, the same effect is observed. Within the group with Q = **II**, the S atom increases the interaction by an order of magnitude, and this enhancing effect of S has been noticed before [14]. With that exception, incorporation of any group between the two rings in the diphenolato bridges virtually destroys the electrochemical communication between the molybdenum nitrosyl centres.

- (4) The comproportionation constants for the pairs $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{\text{I}\}]$ and $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(1,4\text{-NHC}_6\text{H}_4\text{NH})]$ [9] (59.8×10^6 and 4.0×10^{15}), $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(1,3\text{-OC}_6\text{H}_4\text{O})]$ [12] and $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(1,3\text{-NHC}_6\text{H}_4\text{NH})]$ [9] (2.5×10^4 and 2.8×10^6), and $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{\text{III}(\text{E} = \text{CO})\}]$ and $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{4,4'\text{-NHC}_6\text{H}_4(\text{CO})\text{C}_6\text{H}_4\text{NH}\}]$ [9] (27 and 1394) show that the interaction between the redox centres bridged by benzenediamido and dianilido ligands is substantially greater than that between those containing diphenolates.

EPR spectroscopic studies

In an earlier paper [10], we reported that cobaltocene reduction of $[\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}(\text{OC}_6\text{H}_4\text{OMe-}p)]$ afforded a paramagnetic monoanion (17 ve) which exhibited a characteristic 'singlet + sextet' EPR spectrum ^{95}Mo (15.9%) and ^{97}Mo (9.6%) have $I = 5/2$ with $g_{\text{iso}} = 1.968$, $A_{\text{Mo}} = 4.7$ mT [10]. We have obtained similar results from $[\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}(\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{OH})]^-$ ($g_{\text{iso}} = 1.969$, $A_{\text{Mo}} = 5.1$ mT) and these data are consistent with the unpaired spin being localised in a largely metal-based orbital (predominantly d_{xy}) [15].

The EPR spectrum of $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(1,4\text{-NHC}_6\text{H}_4\text{NH})]^-$ is a 'singlet + sextet + undecet' multiplet with $A_{\text{Mo}} = 2.5$ mT (the singlet arises from the $I = 0$, $I = 0$ nuclear spin combination, the 1:1:1:1:1:1 sextet from the $I = 5/2$, $I = 0$ combination, and the 1:2:3:4:5:6:5:4:3:2:1 undecet from the $I = 5/2$, $I = 5/2$ combination [9]. This shows that the unpaired spin in the benzenediamido monoanion is delocalised and the species exhibits, at room temperature, Class III mixed-valence behaviour on the EPR timescale [16]. In contrast, the EPR spectrum of electrochemically-generated $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{\text{I}\}]^-$ at room temperature is a 'singlet + sextet' with $g_{\text{iso}} = 1.97$ and $A_{\text{Mo}} = 5.0$ mT, analogous to that of $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(1,3\text{-OC}_6\text{H}_4\text{O})]^-$, both of which are valence-trapped under these conditions [10,11]. Cobaltocene reduction of $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2\{\text{I}\}]$ affords

a dianion, which has a 'singlet + sextet + undecet' spectrum, similar to those of dinuclear molybdenum nitrosyl 4,4'-dipyridyl complexes, indicating that the species has two unpaired electrons, one on each metal centre, which are strongly correlated, i.e. $J \gg A_{\text{Mo}}$, where J is the spin exchange integral. Identical EPR spectra are obtained following cobaltocene reduction of $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{II}) (n = 1)]$ and $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{III}) (E = \text{S}, \text{CO}, \text{SO}_2)]$ ($g_{\text{iso}} = 1.969$, $A_{\text{Mo}} = \approx 2.5$ mT), indicating that the dianionic species were formed, and we have confirmed this by isolation of $[\text{Co}(\text{C}_5\text{H}_5)_2][\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{III}) (E = \text{S}, \text{CO})]$, as described above.

However, we have reported that $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{VI})]^{2-}$ exhibits a *second-order* spectrum, where $J \approx A_{\text{Mo}}$ [11]. It is known that spin-correlation may be propagated through the σ - and the π -bonding framework in diradicals [17] attenuating very rapidly through the former but extended substantially through the latter, so the convergence of J and A_{Mo} could arise less because of the extended length of the bridging ligand but more because of the significant twist about the central C—C link between the C_6H_4 rings of the diphenylene moiety. In addressing this point, we have found that the EPR spectrum of the $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{V})]^{2-}$ is *first-order*, a 'singlet + sextet + undecet' with $A_{\text{Mo}} = 2.5$ mT. The bridging ligand is similar to VI although it has two fewer atoms (18 rather than 20) but, more importantly, it is essentially planar. The appearance of the EPR spectrum indicates that spin correlation in this class of dinuclear species is largely propagated through the π -orbitals of the bridging ligand, and is only diminished by twisting of aromatic rings which significantly reduces overlap.

The EPR spectrum of $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{Cl}\}_2(\text{III}) (E = \text{S})]^-$, generated by careful controlled potential electrolysis of the neutral precursor so that only one electron equivalent is passed, was a 'singlet + sextet' signal with $A_{\text{Mo}} = 4.9$ mT, indicating that the system is valence-trapped, as we expected.

DISCUSSION

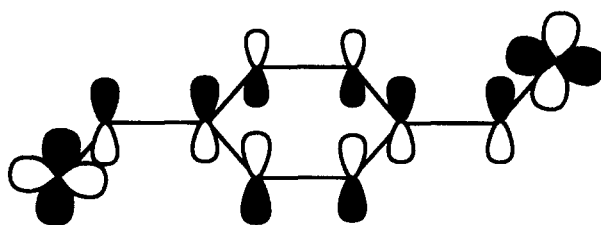
The dinuclear species $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{X}\}_2\text{Q}]$ where Q is based on phenolates, behave in much the same way as their benzenediamido, dianilido and 4,4'-dipyridyl analogues in that they undergo two one-electron reductions, the interaction between the $\{\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\}\text{X}\}$ redox centres being largely a function of the length of Q, decreasing rapidly with increasing distance. The phenolato-based species are more 'easy' to reduce, in that the formation potentials of the monoanions are substantially more anodic than their benzenediamido, dianilido and 4,4'-bipyridine analogues, mainly because of the electronegativity of the phenolic O atoms. In contrast,

however, the interaction between the two redox centres is substantially lower than in the benzenediamido, dianilido and 4,4'-dipyridyl analogues.

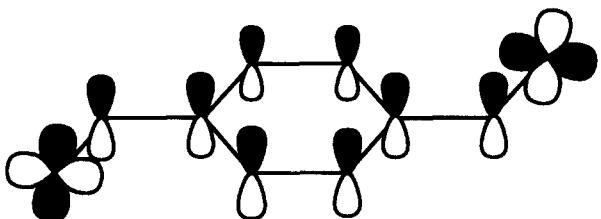
This can be explained as follows. In formal oxidation state terminology, assuming the nitrosyl group to be bound as NO^+ , reduction of the dinuclear 16/16 ve species to 16/17 and 17/17 ve anions means conversion of $\text{Mo}^{\text{II}} (d^4)$ to $\text{Mo}^{\text{I}} (d^5)$. Divalent molybdenum, particularly when associated with π -acid ligands like NO, is a potentially strong π -acceptor but monovalent molybdenum, while having reduced acceptor characteristics, may function as a π -donor. This means that the molybdenum nitrosyl system is very flexible, being capable of π -acceptor and π -donor behaviour depending on oxidation state. Why this is so 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 $\pi^*(\text{NO})$ orbitals leaving the d_{xy} orbital as the lowest unoccupied d orbital in species containing the $\text{Mo}(\text{NO})^{3+}$ core [1,15]. This orbital is ideally situated to interact with either the π -bonding or the π^* -orbitals of the bridging ligand (see Fig. 2). In the neutral 16 ve 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. When the d_{xy} orbital is partially filled, as in the 16/17 and 17/17 ve species, a low-energy LUMO of the bridge acts as a π -acceptor, thereby greatly facilitating electronic exchange.

The substantial difference in reduction potentials between the phenolato and diphenolato ligands and their benzenediamido and dianilido analogues arises because of the LUMO in the former group lies a higher energies relative to that in the latter. This is a consequence of 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. A further manifestation of the poorer overlap between the molybdenum d_{xy} orbital and the bridging ligand LUMO in the phenolates and their derivatives is that the mixed-valence species derived from compounds containing these ligands are valence-trapped at room temperature, in contrast to their benzenediamido and dianilido analogues. Such manipulation of the metal d_π , π and π^* orbitals of the bridging ligand in influencing the interactions between metal centres in dinuclear species has been described by others [18].

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



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

Fig. 2. Interaction between (a) empty molybdenum d_{xy} orbitals and a filled π -bonding orbital of a diphenolato bridging ligand and (b) partially filled molybdenum d_{xy} orbitals and a π^* orbital of the bridging ligand.

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