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Redox-mediation of electron–electron spin–spin exchange interactions, |*J*|, in paramagnetic trinuclear molybdenum complexes: an example of a '*J* switch'

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A series of trinuclear molybdenum nitrosyl complexes has been prepared using the dinucleating ligands 4-(4-hydroxyphenyl)pyridine (HL^1), 1-(4-pyridyl)-2-(4-hydroxyphenyl)-ethene (HL^2) and -ethane (HL^3), and the trinucleating ligands 3,5-bis(4-hydroxyphenyl)pyridine (H_2L^4) and 2,6-bis(4-ethenylpyridyl)-4-hydroxytoluene (HL^5). These complexes are of the type $[\underline{\mathbf{Mo}}\{OC_6H_4Epy\underline{\mathbf{Mo}}Cl\}_2]$ ($\underline{\mathbf{Mo}}$ = Mo(NO)$Tp^{Me,Me}$, $Tp^{Me,Me}$ = tris(3,5-dimethylpyrazolyl)borate; E = nothing, CH=CH and CH_2CH_2; py = C_5H_4N or C_5H_3N; from HL^1, HL^2 and HL^3), $[\{Cl\underline{\mathbf{Mo}}(OC_6H_4)\}_2py\underline{\mathbf{Mo}}Cl]$ (from H_2L^4), and $[Cl\underline{\mathbf{Mo}}\{OC_6H_3Me[CH{=}CHpy\underline{\mathbf{Mo}}Cl]_2\}]$ (from HL^5). The species $[\underline{\mathbf{Mo}}\{OC_6H_4Epy\underline{\mathbf{Mo}}Cl\}_2]$ contains one 16 valence electron (ve) ($[\underline{\mathbf{Mo}}\{OC_6H_4–\}_2]$) and two 17 ve centres ($[(–py)\underline{\mathbf{Mo}}Cl]$), $[\{Cl\underline{\mathbf{Mo}}(OC_6H_4)\}_2py\underline{\mathbf{Mo}}Cl]$ has two 16 ($[Cl\underline{\mathbf{Mo}}\{OC_6H_4–\}]$) and one 17 ($[(–py)\underline{\mathbf{Mo}}Cl]$) ve centres and $[Cl\underline{\mathbf{Mo}}\{OC_6H_3Me[CH{=}CHpy\underline{\mathbf{Mo}}Cl]_2\}]$ one 16 and two 17 ve centres. Reduction of these species by cobaltocene in tetrahydrofuran/dichloromethane mixtures affords complexes having three 17 ve centres with one unpaired electron per metal centre. The interaction between these unpaired electrons in solution is determined by the relationship between $|J|$, the electron spin–spin exchange interaction, and A_{Mo}, the molybdenum hyperfine coupling constant, which was detected by EPR spectroscopy. In $[\underline{\mathbf{Mo}}\{OC_6H_4Epy\underline{\mathbf{Mo}}Cl\}_2]$, the interaction was dependent on ligand conformation, $|J| \approx A_{Mo}$ when E = nothing, $|J| \gg A_{Mo}$ when E = CH=CH and $|J| \ll A_{Mo}$ when E = CH_2CH_2. Reduction of $[\underline{\mathbf{Mo}}\{OC_6H_4Epy\underline{\mathbf{Mo}}Cl\}_2]$ to $[\underline{\mathbf{Mo}}\{OC_6H_4Epy\underline{\mathbf{Mo}}Cl\}_2]^-$ resulted in exchange between all three spins irrespective of ligand conformation, and the EPR spectra of $[\{Cl\underline{\mathbf{Mo}}(OC_6H_4)\}_2py\underline{\mathbf{Mo}}Cl]^{2-}$ and $[Cl\underline{\mathbf{Mo}}\{OC_6H_3Me[CH{=}CHpy\underline{\mathbf{Mo}}Cl]_2\}]^-$ were similar to that of $[\underline{\mathbf{Mo}}\{OC_6H_4Epy\underline{\mathbf{Mo}}Cl\}_2]^-$. Oxidation reconstitutes the original EPR spectra of $[\underline{\mathbf{Mo}}\{OC_6H_4Epy\underline{\mathbf{Mo}}Cl\}_2]$, $[\{Cl\underline{\mathbf{Mo}}(OC_6H_4)\}_2py\underline{\mathbf{Mo}}Cl]$ and $[Cl\underline{\mathbf{Mo}}\{OC_6H_3Me[CH{=}CHpy\underline{\mathbf{Mo}}Cl]_2\}]$. This behaviour is consistent with full three centre interaction being 'switched on' when the 17 : 16 : 17 or 16 : 17 : 16 ve systems are reduced to a 17 : 17 : 17 ve system, and 'switched off' on reoxidation.

The construction of stable multi-centre high-spin organic molecules which exhibit ferromagnetic behaviour is a major objective of the molecular magnetic community.[1] The synthesis and stabilisation of such polyradicals remains, however, a difficult synthetic challenge and while interesting magnetic behaviour has been detected,[2] it is as yet unclear how such species can be incorporated in magnetic materials. However, molecular magnets may also be derived from oligonuclear transition metal complexes containing at least two, and preferably more, paramagnetic transition metal centres.[3] Such oligomeric coordination and/or organometallic compounds are likely to have several advantages over organic polyradicals, such as the possibility of higher spin density, chemical stability, and redox activity for switching purposes. It is this last possibility which has attracted our attention.

Of course, the electronic interactions between metals in such oligonuclear species are critically dependent on the type of connection between the constituent metal ions,[3] and the control and manipulation of these interactions is a major objective of contemporary inorganic and related materials chemistry. If the metal orbitals are close enough to overlap directly, the nature of the magnetic interaction (ferro- or antiferro-magnetic) depends on their relative symmetry, as formalised by the Goodenough–Kanamori rules,[4] and this has been exploited in the preparation of complexes with predictable magnetic properties.[4,5] However if the relevant orbitals are too far apart to overlap directly then there may be no electron–electron spin–spin exchange (henceforth referred to as exchange (J) interactions), but if such exchange does occur, then coupling may only occur *via* the participation of the bridging ligand orbitals.

The mediating effect of bridging ligands on the exchange coupling between metals in oligonuclear complexes has received relatively little systematic attention, in contrast to the extensive investigations of the effects of structure and topology on the properties of organic polyradicals.[1,6] The identification of suitable paramagnetic transition metal components which can be easily linked within a rigid predominantly carbon-based architectural framework and which may couple magnetically is now an important goal in the design and assembly of 'molecular magnets'. At the heart of this type of work is the control of the sign and magnitude of the exchange interaction, J, which depends substantially on the nature of the pathway linking the interacting spins.

The magnetic behaviour of organic polyradicals and some oligonuclear transition metal complexes is also amenable to study by EPR spectroscopy,[6–8] and it is now well-established that an EPR spectrum for any compound depends on the magnitude of J compared to A, the hyperfine coupling constant.[9] When $|J| \ll A$, exchange is negligibly small but when $|J| \gg A$ it is detectable by EPR spectroscopy even though it may be too small to detect by conventional susceptibility measurements. In neither condition is it possible to easily extract the sign or magnitude of J. However, when $|J| \approx A$ more complex second-order EPR spectra result, and a value for J can be computed by spectral simulation.[10]

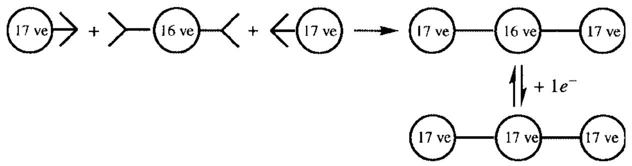
The EPR spectra of Mo(I) nitrosyl complexes of the type described in this paper are characteristic, as we have described elsewhere,[8,11] the electron–nuclei coupling constant A_{Mo} being *ca.* 5.0 mT for single or isolated paramagnetic *mono*-molybdenum nitrosyl centres.[12–14] However, in a *dinuclear* species with one unpaired spin on each Mo centre, the observed hyperfine splitting is *ca.* 2.5 mT, *i.e.* $A_{Mo}/2$, provided $|J| \gg A$.[12–14] Such a complex set of multiplets is observed in the EPR spectrum of $[Cl\underline{\mathbf{Mo}}\{py(CH{=}CH)_4py\}\underline{\mathbf{Mo}}Cl]$ ($\underline{\mathbf{Mo}}$ = Mo(NO)Tp^{Me,Me}, Tp^{Me,Me} = tris(3,5-dimethylpyrazolyl)borate, py = C_5H_4N or C_5H_3N)[13] and is characteristic of the situation where $J \gg A_{Mo}$.[9,15] It has long been known that such exchange coupled spectra are shown by nitroxide diradicals.[9] In trinuclear species such as the centrosymmetric $[1,3,5\text{-}\{\underline{\mathbf{Mo}}Cl(pyC{\equiv}C)\}_3C_6H_3]$ the observed hyperfine coupling is 1.6 mT ($A_{Mo}/3$),[11] and similar behaviour is observed in nitroxide triradicals.[16]

The asymmetric dinuclear complex $[Cl\underline{\mathbf{Mo}}(pyCH{=}CHC_6H_4O\underline{\mathbf{Mo}}Cl)]$, which contains a diamagnetic 16- (phenoxide) and a paramagnetic 17-valence electron (ve) (pyridine) metal centre,[14] has a 'singlet+sextet' multiplet EPR spectrum,† with $A_{Mo} = 5.0$ mT, consistent with the expected valence-trapped behaviour, no hyperfine coupling being observed between the unpaired electron and the adjacent diamagnetic Mo centre. However, reduction to the isovalent monoanion $[Cl\underline{\mathbf{Mo}}(pyCH{=}CHC_6H_4O\underline{\mathbf{Mo}}Cl)]^-$ (two 17 ve centres) caused the EPR spectrum to change to a 'singlet + sextet + undecet' multiplet,† with an observed hyperfine splitting of 2.5 mT ($A_{Mo}/2$): a situation consistent with $|J| \gg A_{Mo}$ and both electrons coupling equally to both nuclei despite the asymmetry of the complex. This monoanion is isoelectronic with $[Cl\underline{\mathbf{Mo}}(4,4'\text{-}pyCH{=}CHpy)\underline{\mathbf{Mo}}Cl]$ which has an observed hyperfine splitting of 2.5 mT, with $J = -18$ cm^{-1}, determined from susceptibility measurements.[17] The exchange interaction between the two molybdenum centres in $[Cl\underline{\mathbf{Mo}}(pyCH{=}CHC_6H_4O\underline{\mathbf{Mo}}Cl)]$ is 'switched on' by reversible reduction of the molybdenum phenolate terminus from a 16 ve to a 17 ve configuration. Re-oxidation caused the EPR spectrum to revert to its original 17/16 ve state prior to reduction ($A_{Mo} = 5.0$ mT).

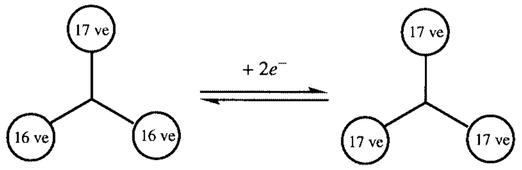
It was this 'switching' effect which has prompted our search for similar behaviour in more complex oligonuclear species. For example, could we make a trinuclear complex containing one diamagnetic and two paramagnetic centres which, on reduction, would be converted to a system where full exchange occurred between all three paramagnetic centres? If this behaviour was electrochemically reversible, the system would constitute a 'J switch'.

Synthetically, this objective could be achieved by three routes, all of which exploit the reversible redox couple $\{Mo(NO)\}^{3+}/\{Mo(NO)\}^{2+}$:

(a) by attaching two 17 ve metal centres *via* a bridging ligand to a central reducible 16 ve metal centre, forming an acyclic or chain-like molecule;

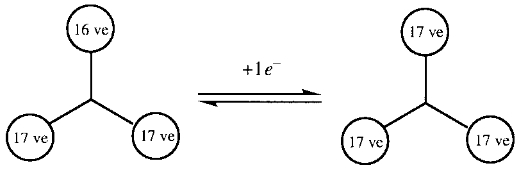


(b) constructing a bridge incorporating three binding sites capable of binding one 17 ve and two reducible 16 ve metal centres,



or

(c) making a similar type of ligand binding two 17 ve and one reducible 16 ve metal groups.



Route (a) could be realised using ligands HL^1–HL^3, Fig. 1, by preparing a 16 ve bis(phenolato) complex, *e.g.* $[\underline{\mathbf{Mo}}(OC_6H_4py)_2]$, and then attaching 17 ve molybdenum nitrosyl groups to the pyridyl residues giving $[\underline{\mathbf{Mo}}\{OC_6H_4py\underline{\mathbf{Mo}}Cl\}_2]$. Ligands H_2L^4 could afford entry to route (b) and HL^5 to route (c). Some preliminary results have been reported,[18] and this paper describes in full the outcome of our search for switchable three-centre paramagnets.

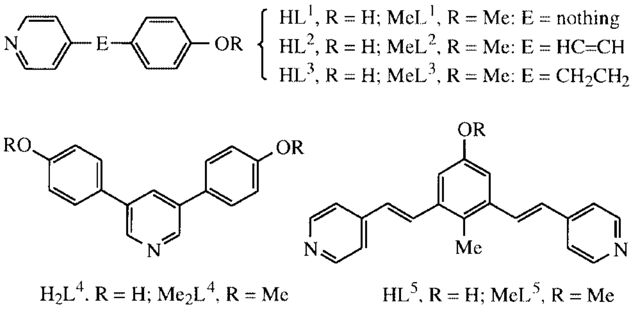


Fig. 1 Ligands.

Results and discussion

The ligands we have used in developing our synthetic strategies were prepared by relatively simple routes. We have described RL^1 and RL^2 (R = H or Me) before[14] and hydrogenation of MeL^2 gave MeL^3. Trifunctional Me$_2$L^4 was obtained *via* a coupling reaction involving 3,5-dichloropyridine and two equivalents of the Grignard reagent of 4-bromoanisole. The dipyridine MeL^5 was prepared using the Heck reaction, coupling 2,6-dibromo-4-methoxytoluene to two equivalents of 4-vinylpyridine. Demethylation of MeL^3, MeL^4 and MeL^5 using molten pyridinium chloride gave good yields of HL^3, H$_2$L^4 and HL^5. The ligands all contain two different types of reaction centre: at least one phenolic OH group and at least one pyridine N atom (Fig. 1).

The desired complexes were prepared by standard procedures which we have described in detail before,[11,19] and were characterised initially by their elemental analyses and FAB mass spectra. We used three 4-pyridylphenols HL^1, HL^2 and HL^3 to assemble trinuclear species *via* route (a), as shown in Scheme 1. The NO stretching frequencies of the monometallic **1**–**3** (Fig. 2) and trimetallic **4**–**6** were typical and consistent with our formulations.[11,14,20] Specifically, ν_{NO} in the mononuclear species occurred at *ca.* 1654 cm^{-1}, somewhat lower than the same centre in the trinuclear **4**–**6** because of the electronegativity of the $\{(\text{–}py)\underline{\mathbf{Mo}}Cl\}$ group, and much lower than that in mono-

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† The isotopes ^{92}Mo, ^{94}Mo, ^{96}Mo, ^{98}Mo and ^{100}Mo have $I = 0$, with relative abundance *ca.* 75%; ^{95}Mo, relative abundance 15.9%, nuclear magnetic moment $-0.914\ \mu_N$ and ^{97}Mo, relative abundance 9.6%, nuclear magnetic moment $-0.934\ \mu_N$ have $I = 5/2$. The EPR spectra of isolated paramagnetic monomolybdenum nitrosyl centres appear as a singlet (75% of total signal intensity) overlapped by a sextet (25% of total intensity). In dinuclear species with one unpaired spin on each Mo centre, the spectrum appears as a superimposed singlet ($I = 0$, $I = 0$; 56% probability), sextet ($I = 0$, $I = 5/2$; 38%) and 1:2:3:4:5:6:5:4:3:2:1 undecet ($I = 5/2$, $I = 5/2$; 6%). In trinuclear species with one unpaired electron per Mo, the EPR spectra appear as a superimposition of a singlet ($I = 0$, $I = 0$, $I = 0$; 42% probability), sextet ($I = 0$, $I = 0$, $I = 5/2$; 42%), undecet ($I = 0$, $I = 5/2$, $I = 5/2$; 14%) and 16-fold multiplet, ($I = 5/2$, $I = 5/2$, $I = 5/2$, 2%) with relative intensities. 1:3:6:10:15:21:25:27:27:25:21:15:10:6:3:1.

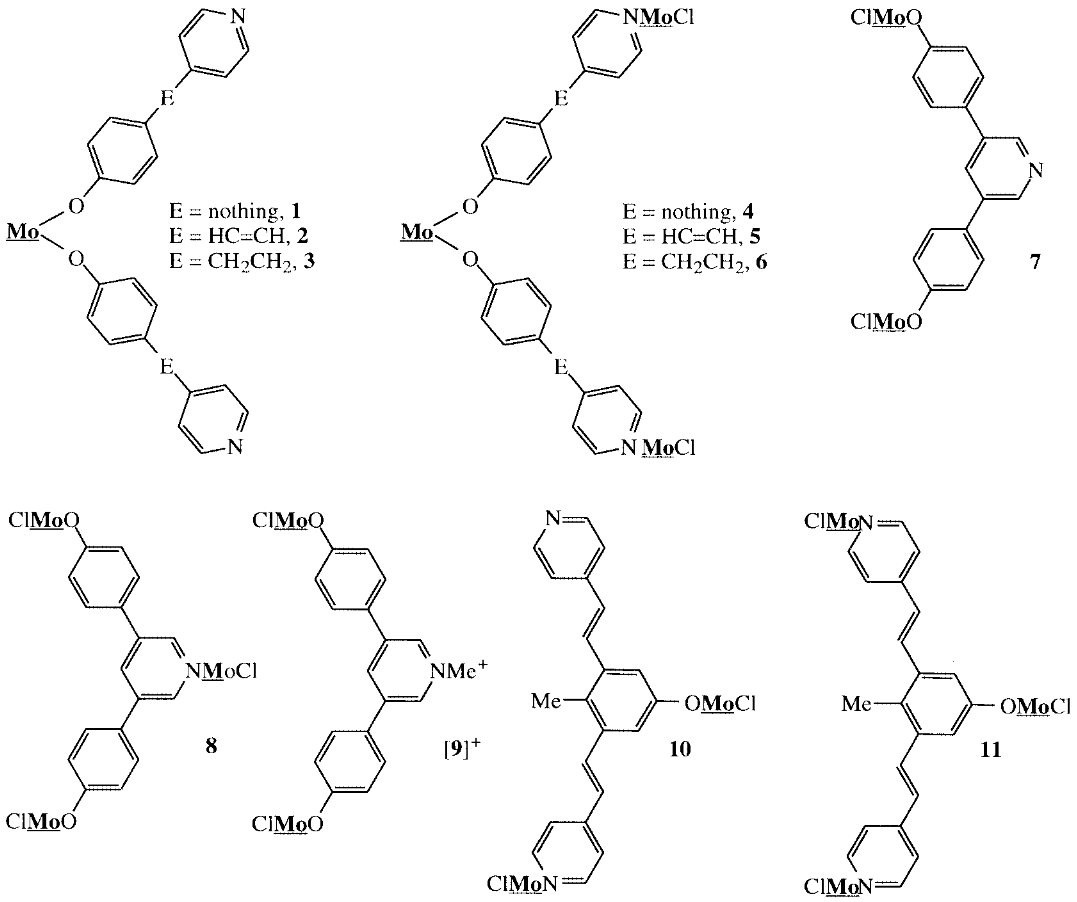
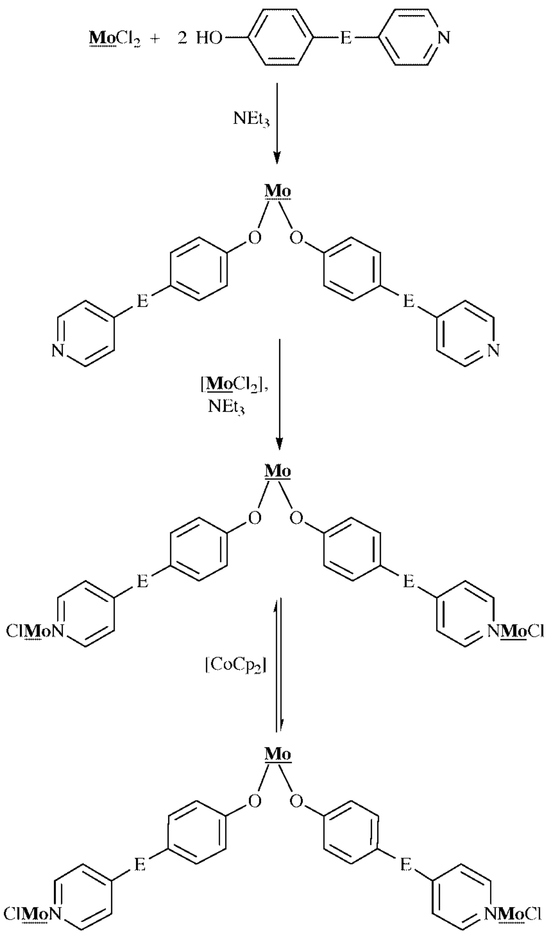


Fig. 2 Mono-, di- and tri-nuclear molybdenum complexes: Mo = Mo(NO)$Tp^{Me,Me}$.



Scheme 1

phenoxide species such as [ClMo(pyCH=CHC_6H_4OMoCl)] (*ca.* 1685 cm^{-1}) because two phenoxide groups are more effective electron donors than one. Reduction of **5** to $[\mathbf{5}]^-$ in tetrahydrofuran/dichloromethane by addition of one mole equivalent of cobaltocene caused the colour of the solution to change from red to pale brown and the NO stretching frequency of the {$Mo(OAr)_2$} group to decrease by 48 cm^{-1}, bringing ν_{NO} into the range characteristic of a 17 ve molybdenum(I) nitrosyl centre.[8]

Reaction of [MoCl_2] with H_2L^4 using a 2:1 mole ratio gave dinuclear **7** and trinuclear **8** *via* route (b). We were also able to quaternise the uncoordinated pyridine group in **7** using MeI, giving cationic $[\mathbf{9}]^+$, isolated as its PF_6^- salt. The NO stretching frequencies are again consistent with our formulations, but we did not detect a significant shift to higher frequencies in the conversion of **7** to $[\mathbf{9}]^+$, perhaps because the molybdenum nitrosyl fragments are too far away from the site of the positive charge. We were also able to make trimolybdenum complexes directly using HL^5 (route (c)). A mixture of dinuclear **10** and trinuclear **11** was prepared by the reaction of the ligand with a fourfold excess of [MoCl_2] in the presence of NEt_3. The FAB MS spectra and NO stretching frequencies of these compounds were as expected and selected data are listed in the Experimental section.

Electrochemical behaviour

The cyclic voltammograms (CVs) in dichloromethane obtained from most of the complexes described in this paper exhibited quasi-reversible behaviour at best (potential data are given in the Experimental section). While the CV curves were symmetric, with equal cathodic and anodic peak currents, the peak-to-peak separations in the CVs were larger than the theoretical ideal, in some cases being up to 230 mV. However, from several spectroelectrochemical studies on complexes of this type we

Table 1 EPR spectral data obtained from paramagnetic molybdenum and tungsten complexes, subdivided by ligand type according to bridging ligands

Complex[a]	g_{iso}[b]	A_{Mo}[c]	Complex[a]	g_{iso}[b]	A_{Mo}[c]	Complex[a]	g_{iso}[b]	A_{Mo}[c]
	17 ve phenolato centres			17 ve pyridyl centres			17 : 17 ve mixed centres	
Ligands L^1–L^3								
$[\mathbf{1}]^-$	1.963	5.1	**4**	1.978	[d]	$[\mathbf{4}]^-$	1.974	1.6
$[\mathbf{2}]^-$	1.964	5.1	**5**	1.977	2.4	$[\mathbf{5}]^-$	1.976	1.7
$[\mathbf{3}]^-$	1.963	5.1	**6**	1.977	4.9	$[\mathbf{6}]^-$	1.973	1.7
Ligand L^4								
$[\mathbf{7}]^{2-}$	1.969	2.6	**8**	1.979	4.9	$[\mathbf{8}]^{2-}$	1.971	1.7
$[\mathbf{9}]^-$	1.969	2.6						
Ligand L^5								
			10	1.978	4.8	$[\mathbf{10}]^-$	1.973	2.4
			11	1.978	2.4	$[\mathbf{11}]^-$	1.975	1.8

[a] Anionic complexes generated by addition of cobaltocene to the precursor complex in CH$_2$Cl$_2$/THF (1 : 1 v/v). [b] In CH$_2$Cl$_2$ except for anionic species, at 293 K. [c] Metal-hyperfine coupling (^{95}Mo, ^{97}Mo; $I = 5/2$), in mT. [d] Second order spectrum.

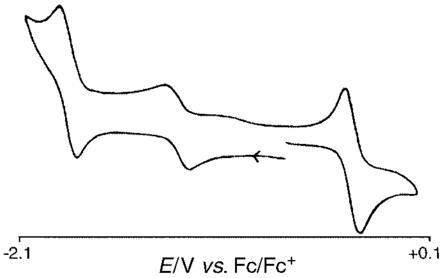


Fig. 3 Cyclic voltammogram of $[\underline{\mathrm{Mo}}\{\mathrm{OC_6H_4py}\underline{\mathrm{Mo}}\mathrm{Cl}\}_2]$, **4**, showing, from left to right, the 17/18 ve reductions of the two pyridinyl-molybdenum centres, the 16/17 ve reduction of the single phenolato-molybdenum fragment, and the 17/16 ve oxidation of the two pyridinyl-molybdenum centres.

have confirmed that the majority of the couples $\{\mathrm{Mo(NO)}\}^{3+}/\{\mathrm{Mo(NO)}\}^{2+}$ and $\{\mathrm{Mo(NO)}\}^{2+}/\{\mathrm{Mo(NO)}\}^{+}$ were chemically reversible.[13] Our electrochemical investigations were supplemented by square-wave voltammetry (SWV). We estimated whether each electrode process was a one- or two-electron transfer either from the relative intensities of the CV responses or from the relative areas under each peak in the appropriate SWVs. We know from previous studies of dinuclear and trinuclear species that, when there is no significant Coulombic interaction between the redox centres, the reductions or oxidations will appear as a synchronous two- or three-electron process.[11,14,21] Theoretically, the electron transfer must occur statistically in separate steps but the effect of this is not normally resolved by conventional CV or SWV techniques, and we did not attempt to analyse our electrochemical data with this in mind. A typical CV of a trinuclear species, **4**, in dichloromethane is shown in Fig. 3.

Generally, complexes containing the $[\underline{\mathrm{Mo}}\mathrm{Cl(OC_6H_4}–)]$ group reduce in a one-electron step with formation potentials in the range −0.74 to −0.91 V *vs.* the Fc$^+$/Fc couple, and the corresponding bis(phenoxides) reduce more cathodically. This is expected because phenoxides are stronger π-donors than chloride, as we have observed previously.[22] The $[\underline{\mathrm{Mo}}\mathrm{Cl(OC_6H_4}–)]$ group does not exhibit oxidation behaviour between 0 and +1.00 V. The complexes containing the $[\underline{\mathrm{Mo}}\mathrm{Cl(py}–)]$ fragment undergo a one-electron reduction between −1.70 and −2.50 V, a process which is largely determined by the nature of the pyridyl ligand but is irreversible when close to the medium decomposition at very negative potentials. This group also undergoes a one-electron oxidation at *ca.* +0.06 V which is largely metal-based and independent of the bridging ligand.[11–14]

Because the potential for the $[\mathrm{Co(C_5H_5)_2}]^+/[\mathrm{Co(C_5H_5)_2}]$ couple is −1.34 V with respect to the ferrocenium/ferrocene couple in dichloromethane, we were able to effect an electron transfer to all those complexes having a reduction potential equal to or less negative than −1.30 V, this process being associated exclusively with a molybdenum mono- or bis-phenolato fragment. Use of cobaltocene as a reducing agent in this system is particularly convenient because of its solubility in solvents compatible with the di- and tri-nuclear species being investigated, and because its oxidation product, $[\mathrm{Co(C_5H_5)_2}]^+$, is relatively kinetically stable.‡

EPR spectral behaviour

The EPR spectrum of the reduced mononuclear bis(phenolato) complexes $[\mathbf{1}]^-$ (Fig. 4a), $[\mathbf{2}]^-$ and $[\mathbf{3}]^-$ in THF are typical of their class, $g_{\mathrm{iso}} = 1.963$ and $A_{\mathrm{Mo}} = 5.1$ mT (Table 1).[8] The trimetallic complex **4** is unusual, however, in that it exhibits a "second-order" spectrum (Fig. 4b; $g_{\mathrm{iso}} = 1.978$)§ indicating that $|J| \approx A_{\mathrm{Mo}}$ (see later). In contrast, **5** (Fig. 4c) has a normal 'singlet + sextet + undecet' spectrum, the hyperfine splitting being 2.4 mT, indicating that $|J| \gg A_{\mathrm{Mo}}$, while **6** (Fig. 4d) has a 'singlet + sextet' spectrum, $A_{\mathrm{Mo}} = 4.9$ mT, consistent with two non-interacting spins, *i.e.* $|J| \ll A_{\mathrm{Mo}}$. These variations in the relationship between J and A_{Mo} are presumably a function of the bridging ligand where, in **4**, the two rings are relatively free to rotate in solution leading to some loss of delocalisation and therefore also of electron–electron spin–spin exchange across the bridge. The inter-ring torsion angle in such ligands in the solid state would be expected to fall in the range 30–40°. In **5** the bridging ligand is constrained to be essentially planar because of the ethene link which facilitates a high degree of delocalisation, but in **6** both the insulating effect and the rotational flexibility of the CH$_2$CH$_2$ group will substantially reduce delocalisation and hence the effectiveness of exchange. So in **6** the electron spins on each metal centre are effectively isolated.

Exchange coupling between pairs of 17 ve molybdenum nitrosyl fragments *via* another diamagnetic metal atom centre is not unprecedented. We have obtained second order EPR spectra from ruthenium(II) porphyrin adducts, $[trans\text{-}\{\mathrm{Cl}\underline{\mathrm{Mo}}\}\text{-}(4,4'\text{-bipy})[\mathrm{Ru(TPP)}](4,4'\text{-bipy})\{\underline{\mathrm{Mo}}\mathrm{Cl}\}]$ {TPP = *meso*-5,10,

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‡ Neither $[\mathrm{Co(C_5H_5)_2}]$ nor $[\mathrm{Co(C_5H_5)_2}]^+$ exhibit EPR spectra under the conditions described here.

§ The "second order" effects described here arise from the fact that J and A_{Mo} are of comparable magnitude and should be independent of the spectrometer frequency; here X-band. However, there will be an additional second order effect from the spin nuclei and adjacent separations are unlikely to be identical at X- and Q-band frequencies.

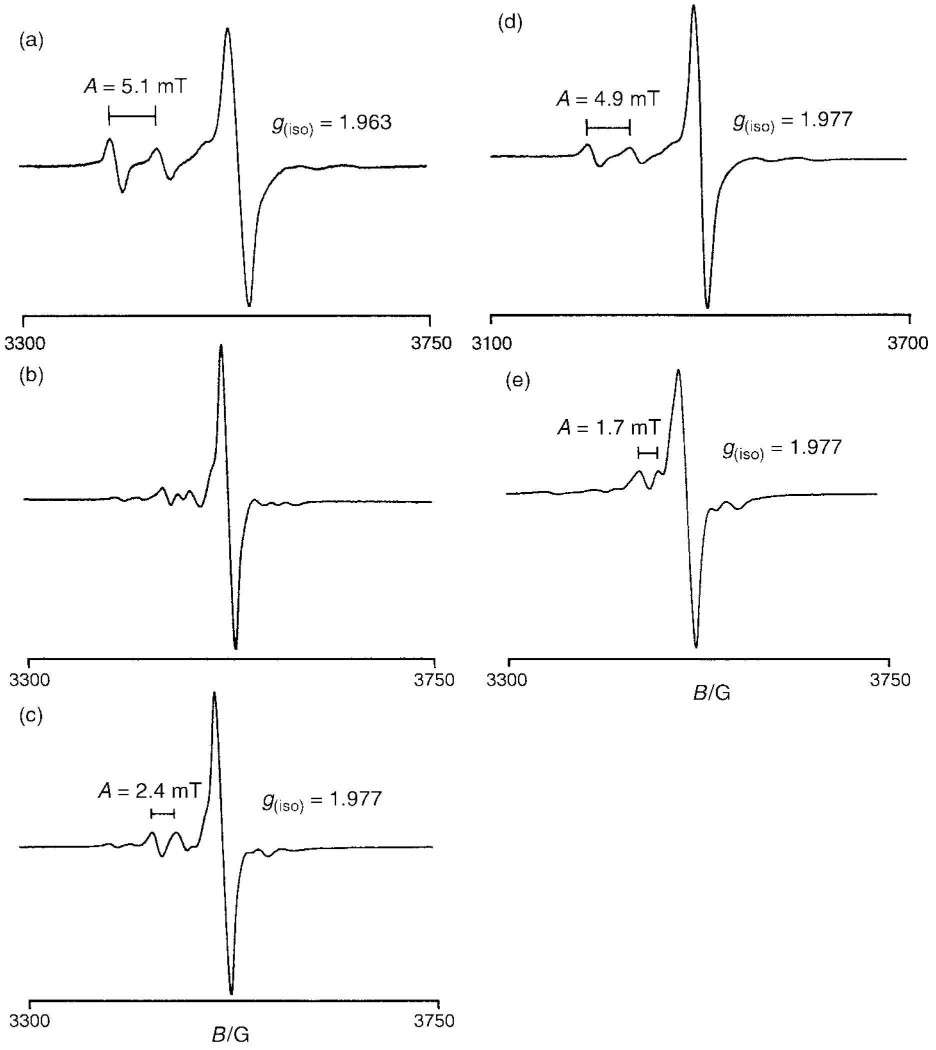

Fig. 4 EPR spectrum of (a) a reduced 17 ve bis(phenolato) complex, **[1]**$^-$; (b) **4** (17 : 16 : 17 ve), $J \approx A_{Mo}$ (second order spectrum); (c) **5**, $J \gg A_{Mo}$; (d) **6**, $J \ll A_{Mo}$; and (e) **[6]**$^-$ (17 : 17 : 17 ve).

15,20-tetraphenylporphyrinate(2−)},[23] where the two spins are interacting *via* a 17 atom pathway which incorporates the Ru atom (18 ve). In **4** and **5**, the central diamagnetic 16 ve Mo centre does not appear to inhibit in any obvious way the exchange coupling process. However, when the connecting metal group is paramagnetic, as in trinuclear oxomolybdenum(v) complexes which contain diphenolato bridges between the MoO^{3+} centres, the exchange coupling is significantly reduced.[24]

On reduction of **4**, **5** and **6**, the spectra appear as ‘singlet + sextet + undecet + 16-fold’ multiplets, although only the outer components are visible, on the low-field side of the spectra. These components are very weak, but their relative intensities are as expected, with $g_{iso} \approx 1.974$ and a hyperfine splitting reduced to 1.7 mT ($A_{Mo}/3$). This means that there is exchange coupling between the three spins. What is remarkable is the relationship between the spectra of **6** and **[6]**$^-$. In the former (17 : 16 : 17 ve) we could not detect any interaction between the two spins at the complex termini, but in the latter (17 : 17 : 17 ve) apparent full three-centre exchange occurs (Fig. 4e) with *all three electrons coupled to all three Mo nuclei* according to the EPR spectrum. This behaviour is reversible: reoxidation of **[4]**$^-$, **[5]**$^-$ and **[6]**$^-$ by iodine causes the EPR spectra to revert to those observed for unreduced **4**, **5** and **6**. Thus the terminal unpaired spins in **6** are electronically isolated but on reduction of the metal ion between them, they undergo exchange with each other as well as with the adjacent (central) spin.

The EPR spectra of the fully reduced dinuclear species **[7]**$^{2-}$ and **[9]**$^-$, which contain two {<u>Mo</u>Cl(OC_6H_4–)} groups, have hyperfine splittings of 2.6 mT, while that of trinuclear **8** is typical of a single 17 ve {<u>Mo</u>Cl(py–)} fragment ($A_{Mo} = 4.9$ mT). The dianion **[8]**$^{2-}$ contains three 17 ve centres and reveals full three-centre exchange, with an observed line splitting of 1.7 mT, just like that in the trinuclear **[4]**$^-$, **[5]**$^-$ and **[6]**$^-$.

The spectrum of **10**, like that of **8**, is typical of an isolated 17 ve mono-molybdenum centre, while those of **11** and **[10]**$^-$ are similar to those of two interacting 17 ve molybdenum paramagnets.

Our earlier descriptions of how the sign and magnitude of the exchange interaction between two {Mo(NO)}$^{2+}$ (17 ve) fragments may be controlled by bridging ligand topology and conformation are based qualitatively on the spin-polarisation principle as we have described elsewhere.[8,17,25] Propagation of the polarisation across the bridging ligand is obviously greatly facilitated by π-orbitals, but when these are not available, spin polarisation must occur through the σ-bonding system and the effect attenuates very rapidly. Provided that the magnitude of J is relatively large, this simple approach allows us to predict the sign of J, and our predictions were confirmed by susceptibility studies in the solid state.[8,17,24,25] The effect of this spin polarisation is implicit in contact-shifted NMR spectra of Ni(ii) aminotroponiminato complexes, where spin density alternates along conjugated groups attached to the ligand framework.[26]

Dealing first with the complexes derived from [L^4]$^-$ and [L^5]$^-$, the exchange interaction behaviour of **[7]**$^{2-}$ and **[9]**$^-$ is normal and consistent with that we have observed in most other reduced dinuclear phenolato complexes where $|J| \gg A_{Mo}$.[27]

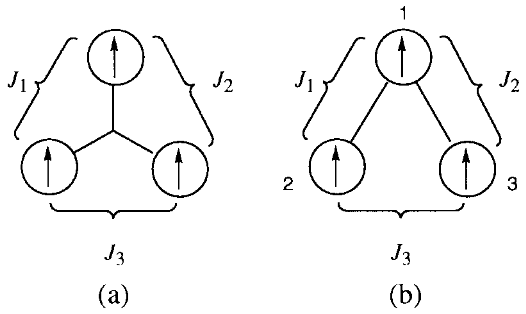

Fig. 5 Magnetic coupling between (a) an equilateral triangle and (b) an acyclic arrangement of three unpaired spins 1, 2 and 3 (the representation of the spin orientation is for illustration only and has no implications for the sign of *J*).

Exchange coupling here occurs *via* a 13-atom delocalised bridging ligand. The EPR spectra of the 17 : 17 : 17 ve species $[\mathbf{8}]^{2-}$ and $[\mathbf{11}]^{-}$ are extremely similar to those of [1,3,5-{MoCl(pyE)}$_3$C$_6$H$_3$], where E = CH=CH or C≡C.[14] In this last species we envisage that the couplings $|J_1|$, $|J_2|$ and $|J_3|$ (Fig. 5a) are all equal and substantially greater than A_{Mo}, the exchange being propagated *via* the bridging ligand, each pathway involving 15 atoms. The couplings in $[\mathbf{8}]^{2-}$ and $[\mathbf{11}]^{-}$ may also be regarded as pairwise interactions, although the path lengths are different. For $[\mathbf{8}]^{2-}$ there will be two couplings *via* 8 atoms and one *via* 13 atoms, while in $[\mathbf{11}]^{-}$ there are two 10-atom and one 15-atom pathways. The important point is that exchange must involve primarily the bridging ligand atoms (see below).

In the acyclic species **4**, **5** and **6**, spin-polarisation must involve the molybdenum d orbitals. The effect of this is implied in Fig. 5b, the symmetry of the three molecules requiring that $|J_1| = |J_2|$. We consider that $|J_3|$ is negligible if, indeed, there is any 'through space' or solvent-mediated exchange coupling between the terminal paramagnetic centres. In order to explore this possibility, and in the absence of suitable crystals for X-ray studies, we constructed the energy-minimised structures of **4**, **5** and **6** using the CAChe suite of programs (see Experimental section).[28] These calculations estimated the distances between the terminal metal centres to be 30.3 in **4**, 36.0 in **5** and 36.7 Å in **6**, probably too far to permit significant through-space or solvent-mediated exchange coupling in solution. We presume that the exchange between the three spins in solution is accounted for by two pairwise interactions, expressed as J_1 and J_2 (Fig. 5b). This would be consistent with the solid state magnetic behaviour of [MoO(Tp$^{\mathrm{Me,Me}}$)Cl(OC$_6$H$_4$O){MoO(Tp$^{\mathrm{Me,Me}}$)}(OC$_6$H$_4$O)MoO(Tp$^{\mathrm{Me,Me}}$)Cl], where the global value of *J* is derived from consideration of the pairwise interaction represented by the exchange spin Hamiltonian $H = -J(\boldsymbol{S}_1\boldsymbol{S}_2 + \boldsymbol{S}_1\boldsymbol{S}_3)$ and the interaction between the terminal spins, *i.e.* the $J(\boldsymbol{S}_2\boldsymbol{S}_3)$ term (2 and 3, Fig. 5), J_3, is negligible.[24] Broadly similar behaviour has been observed in chain-like organic tri-radicals, although the EPR spectral information is less informative because of the low abundance of nuclei with $I = 1/2$.[29]

Assuming that $|J_3|$ is negligible or non-existent, the subtle relationships between J_1, J_2 and A_{Mo} are determined by the bridging ligand structure and transmitted through the central {Mo} group. In **5**, $|J|$ must be very small (it is -6 cm^{-1} from solid-state susceptibility measurements of [ClMo{py(CH=CH)$_4$py}MoCl][30]) but it is obviously significantly larger than A_{Mo}, the coupling being transmitted through the {Mo} centre *via* two relatively planar bridges involving a 23-atom pathway. The bridge in **4** is shorter (19 atoms) but, as we mentioned above, there is rotational flexibility about the inter-ring bonds and so delocalisation could be significantly reduced but not totally eliminated, leading to a situation where $|J| \gg A_{\mathrm{Mo}}$. Complex **6** contains two saturated CH$_2$CH$_2$ links in the bridges and although the pathway contains the same number of atoms as **5**, this saturation and the rotational flexibility of the molecule are clearly sufficient to effectively isolate the two spins, so $|J| \ll A_{\mathrm{Mo}}$. Reduction of **6** to $[\mathbf{6}]^{-}$ reduces the pathway between the individual spins from 23 atoms (end-to-end) to 11 atoms (end-to-centre), and pairwise exchange coupling is obviously possible, and is consistent with our observations of similar coupling in [ClMo(pyCH$_2$CH$_2$py)MoCl] (A_{Mo} = 2.5 mT) which has a 10-atom bridge.[13]

The presence of a reduced 17 ve metal atom in these trinuclear species appears to diminish significantly exchange coupling between the paramagnetic centres, an observation we have made previously in connection with di- and tri-nuclear oxomolybdenum(V) complexes.[28]

Conclusions

Our results show quite conclusively that we can create simple '*J* switches', either by assembling two 17 ve and one 16 ve molybdenum centre and reversibly reducing the latter or, alternatively, connecting one 17 ve metal centre to two 16 ve centres and again reducing the latter. The switching phenomenon is demonstrated by the molybdenum hyperfine splitting, which is 2.4–2.6 mT in a exchange-coupled *two*-spin system and *ca.* 1.6 mT in an exchange-coupled *three*-spin system.

The most dramatic result is obtained from **6** whose EPR spectrum shows that the two spins on the 17 ve pyridinomolybdenum termini are effectively isolated ($|J| < 10$ MHz = 0.33×10^{-3} cm^{-1}) but on reduction to $[\mathbf{6}]^{-}$ full three-spin exchange is 'switched on'. The effect is reversed on oxidation.

Finally, while we have demonstrated that '*J* switching' effects are dependent on the oxidation states of the three metal centres, we note that their energies are far too small to be detected by solid-state magnetic susceptibility methods. However, under special conditions, particularly when $|J| \approx A_{\mathrm{Mo}}$, a good estimate of $|J|$ can be extracted by EPR spectral simulation. By this method,[10] we obtained a value of *ca.* 1400 MHz for $|J|$ in **4**, which corresponds to 5.0 mT (*ca.* 0.05 cm^{-1}). It remains to be seen whether oligonuclear metal systems having higher spin multiplicities and substantially stronger magnetic and electronic interactions can be made to function similarly.

Experimental

General

The starting materials [MoCl$_2$],[31] HOC$_6$H$_4$py and HOC$_6$H$_4$-CH=CHpy[14] were prepared by standard procedures. Solvents for reactions and electrochemistry were carefully pre-dried, and all reactions were carried out under dinitrogen. The new compounds were usually purified by column or plate chromatography using silica gel 60 (70–230 mesh) with CH$_2$Cl$_2$ alone or mixed with either n-hexane or THF as eluent. Chemical reduction was achieved using freshly prepared cobaltocene in a mixture of tetrahydrofuran and dichloromethane, and oxidation was carried out by using dilute solutions of iodine in the same solvent mixture.

The following instruments were used for routine spectroscopic work: ^{1}H NMR spectroscopy, JEOL GX-270 or λ-300 spectrometer (in CDCl$_3$ unless otherwise stated, *J* in Hz); electron-impact and fast-atom bombardment (FAB) mass spectrometry, VG-Autospec; EPR spectrometry, Bruker ESP-300E; UV-VIS spectrophotometry, Perkin-Elmer Lambda 2; FT-IR spectrometry, Perkin-Elmer 1600.

Electrochemical measurements (cyclic and/or square wave voltammetry) were made using a PC-controlled EC&G PAR model 273A potentiostat, with platinum wire working and counter electrodes, a saturated calomel electrode as reference, pre-dried CH$_2$Cl$_2$ as solvent and [NBu$^n_4$][PF$_6$] (*ca.* 0.1 M) as base electrolyte. Metal complexes for electrochemical examination were *ca.* 10^{-3} M. Ferrocene was added as internal standard, and all potentials are quoted relative to the ferrocenium/ferrocene couple.

For the modelling of **4**, **5** and **6**, each complex was drawn in the CAChe Editor and the energy of the structure was subsequently minimised in the molecular mechanics component of the suite. The program attempts to minimise the overall energy of the structure by an iterative process, using Allinger's standard MM2 molecular mechanics force field,[32] continuing until the change in energy for a structure refinement is less than 0.004 kJ mol^{-1}, but we are aware that this final value does not necessarily represent a global energy minimum, since the local minimum can be highly dependent on the starting geometry.

Ligands

1-(4-Methoxyphenyl)-2-(4-pyridyl)ethane (MeL^3). A suspension of *trans*-1-(4-methoxyphenyl)-2-(4-pyridyl)ethene (MeL^2; 1 g, 4.7 mmol),[14] 0.1 g of catalyst (Pd on activated carbon) and ethanol (100 cm^3) was stirred under H$_2$ overnight. The solution was then filtered through Celite to remove the catalyst and any unreacted starting material. The solvent was then evaporated *in vacuo* leaving 1-(4-methoxyphenyl)-2-(4-pyridyl)ethane as a white powder (0.63 g, 63%) (Found: C, 78.2; H, 7.5; N, 6.6. $C_{14}H_{15}NO$ requires: C, 78.8; H 7.1; N, 6.6%); EI mass spectrum *m*/*z* 213 [M$^+$] (requires 213); ^{1}H NMR δ 2.88 [4H, br s; *H*5, *H*5′, *H*6, *H*6′], 3.79 [3H, s; OC(*H*)$_3$], 6.81 [2H, d, *J* = 8.8; phenyl *H*3, *H*3′], 7.04 [2H, d, *J* = 8.8; phenyl *H*4, *H*4′], 7.06 [2H, d, *J* = 6.0; pyridyl *H*2, *H*2′], 8.47 [2H, d, *J* = 6.0; pyridyl *H*1, *H*1′].

3,5-Bis(4-methoxyphenyl)pyridine (Me$_2$L^4). To a stirred solution of 3,5-dichloropyridine (1 g; 6.75 mmol) and [NiBr$_2$(PPh$_3$)$_2$] (0.150 g) in THF (50 cm^3) was added dropwise a solution of the Grignard reagent prepared from 4-bromoanisole (3.5 g; 18.7 mmol) and Mg turnings (0.50 g; 20.6 mmol) in dry THF (20 cm^3). Stirring was continued overnight and, following hydrolysis with aqueous NaHCO$_3$, the organic solvent was evaporated *in vacuo*. The residue containing Me$_2$L^4 was extracted with several portions of dichloromethane, the fractions combined and the solvent reduced to low bulk *in vacuo*. Ethanol was added giving a white precipitate of Me$_2$L^4 which was filtered off and washed several times with ethanol affording the ligand as a white crystalline solid (0.63 g, 86%) (Found: C, 77.9; H, 5.9; N, 5.1. $C_{19}H_{17}NO_2$ requires C, 78.3; H 5.9; N, 4.8%); EI mass spectrum *m*/*z* 291 [M$^+$] (requires 292); ^{1}H NMR δ 3.87 [6H, s; 2 × OMe], 7.03 [4H, d, *J* = 8.8; phenyl *H*3, *H*3′, *H*5, *H*5′], 7.57 [4H, d, *J* = 8.8; phenyl *H*4, *H*4′, *H*6, *H*6′], 7.96 [1H, s; pyridyl *H*2], 8.73 [2H, s; pyridyl *H*1, *H*1′].

2,6-Bis(4-ethenylpyridyl)-4-methoxytoluene (MeL^5). A mixture of 2,6-dibromo-4-methoxytoluene (2.2 g, 7.85 mmol), 4-vinylpyridine (2.9 g, 28 mmol), triethylamine (3.8 g, 37.6 mmol), palladium acetate (45 mg, 0.20 mmol) and triphenylphosphine (105 mg, 0.40 mmol) was heated and stirred in a Schlenk tube under nitrogen at 100 °C (*ca.* 5 d). The solid mass which had formed was dissolved in CH$_2$Cl$_2$ (100 cm^3) and extracted with water (200 cm^3). The organic layer was collected, dried with magnesium sulfate, filtered and evaporated *in vacuo*. The desired compound was crystallised from acetone and dried *in vacuo* giving an off-white powder (1.91 g) (Found: C, 80.2; H, 6.1; N, 8.6. $C_{22}H_{20}N_2O$ requires C, 80.5; H, 6.1; N, 8.5%); EI mass spectrum *m*/*z* 328 [M$^+$] (requires 328).

1-(4-Hydroxyphenyl)-2-(4-pyridyl)ethane (HL^3). This was prepared in the same way as HL^2,[14] but using *trans*-1-(4-methoxyphenyl)-2-(4-pyridyl)ethane (MeL^3) (0.65 g, 3.2 mmol) as starting material. Removal of the solvent at the final stage of the reaction yielded the compound as a white powder (0.55 g, 85%) (Found: C, 78.0; H, 6.9; N, 7.4. $C_{13}H_{13}NO$ requires C, 78.4; H, 6.6; N, 7.1%). EI mass spectrum *m*/*z* 199 [M$^+$] (requires 199); ^{1}H NMR δ 2.87 [4H, br s; *H*5, *H*5′, *H*6, *H*6′], 6.73 [2H, d, *J* = 8.6; phenyl *H*3, *H*3′], 6.94 [2H, d, *J* = 8.6; phenyl *H*4, *H*4′], 7.06 [2H, d, *J* = 6.1; pyridyl *H*2, *H*2′], 8.45 [2H, d, *J* = 6.1; pyridyl *H*1, *H*1′].

3,5-Bis(4-hydroxyphenyl)pyridine (H$_2$L^4). This was prepared by demethylation of MeL^4 using pyridinium chloride at 200 °C for 3 h according to a published procedure.[9] After the reaction mixture was cooled to 140 °C and water added, the organic impurities were extracted with CH$_2$Cl$_2$ and the pH of the solution was adjusted to *ca.* 6 by adding aqueous NaOH. The resulting precipitate was filtered off and crystallised from aqueous methanol giving the ligand as a white crystalline solid (84%) (Found: C, 77.3; H, 4.9; N, 5.4. $C_{17}H_{13}NO_2$ requires C, 77.5; H, 5.0; N, 5.3%); EI mass spectrum *m*/*z* 263 [M$^+$] (requires 263); ^{1}H NMR δ 7.00 [4H, d, *J* = 8.8; phenyl *H*3, *H*3′, *H*5, *H*5′], 7.75 [4H, d, *J* = 8.8; phenyl *H*4, *H*4′, *H*6, *H*6′], 7.90 [1H, s; pyridyl *H*2], 8.92 [2H, s; pyridyl *H*1, *H*1′].

2,6-Bis(4-ethenylpyridyl)-4-hydroxytoluene (HL^5). The conversion of 2,6-bis(4-ethenylpyridyl)-4-methoxytoluene (1.0 g) to the corresponding phenol was achieved using molten pyridinium chloride according to a published procedure.[33] A tan product was obtained (0.81 g) (Found: C, 80.3; H, 5.8; N, 8.8. $C_{21}H_{18}N_2O$ requires C, 80.2; H, 5.8; N, 8.9%); EI mass spectrum *m*/*z* 314 [M$^+$] (requires 314).

Metal complexes

Complexes of 4-(4-hydroxyphenyl)pyridine, 1-(4-pyridyl)-2-(4-hydroxyphenyl)-ethene and -ethane. $[\underline{\mathrm{Mo}}(OC_6H_4py)_2]$, *1*, $[\underline{\mathrm{Mo}}(OC_6H_4CH{=}CHpy)_2]$, *2, and* $[\underline{\mathrm{Mo}}(OC_6H_4CH_2CH_2py)_2]$, *3*. A mixture of the appropriate ligand (HL^2, HL^3 or HL^4; 2.8 mmol), NEt$_3$ (1 cm^3) and $[\underline{\mathrm{Mo}}\mathrm{Cl_2}]$ (0.593 g; 1.2 mmol) was refluxed overnight in toluene (50 cm^3). The solvent was evaporated *in vacuo*, the residue redissolved in a minimum amount of CH$_2$Cl$_2$ and the solution chromatographed on a preparative TLC plate (20 cm × 20 cm) using CH$_2$Cl$_2$/THF (9 : 1 v/v) as eluent. The major brown band was collected each time and filtered through Celite to remove the silica gel. Each fraction was then evaporated *in vacuo* to *ca.* 5 cm^3 and the complexes were precipitated, as brown microcrystalline powders, by addition of n-pentane and collected by filtration, yielding the monometallic complexes **1**, **2** and **3**, respectively.

$[\underline{\mathrm{Mo}}(\mathrm{OC_6H_4py})_2]$, **1** (Found: C, 59.4; H, 5.5; N, 15.4. $C_{37}H_{38}N_9BO_3Mo$ requires C, 59.6; H, 5.6; N, 15.6%): FAB mass spectrum 764 (requires 764); IR 1654 cm^{-1} (ν_{NO}); λ_{max}/nm (ε/10^{-3} M^{-1} cm^{-1}) 280 (26), 433 (6.0); $E_f = -1.10$ V.

$[\underline{\mathrm{Mo}}(\mathrm{OC_6H_4CH{=}CHpy})_2]$, **2** (Found: C, 61.4; H, 5.6; N, 14.4. $C_{41}H_{42}N_9BO_3Mo$ requires C, 61.5; H, 5.7; N, 14.7%): FAB mass spectrum 817 (requires 816); IR 1655 cm^{-1} (ν_{NO}); λ_{max}/nm (ε/10^{-3} M^{-1} cm^{-1}) 331 (51), 465 (15); $E_f = -1.14$ V.

$[\underline{\mathrm{Mo}}(\mathrm{OC_6H_4CH_2CH_2py})_2]$, **3** (Found: C, 61.1; H, 6.0; N, 14.5. $C_{41}H_{46}N_9BO_3Mo$ requires C, 61.3; H, 6.2; N, 14.6%): FAB mass spectrum 822 (requires 820); IR 1651 cm^{-1} (ν_{NO}); λ_{max}/nm (ε/10^{-3} M^{-1} cm^{-1}) 274 (sh), 425 (7.5); $E_f = -1.31$ V.

$[\underline{\mathrm{Mo}}\{OC_6H_4py\underline{\mathrm{Mo}}Cl\}_2]$, *4*, $[\underline{\mathrm{Mo}}\{OC_6H_4CH{=}CHpy\underline{\mathrm{Mo}}Cl\}_2]$, *5, and* $[\underline{\mathrm{Mo}}\{OC_6H_4CH_2CH_2py\underline{\mathrm{Mo}}Cl\}_2]$, *6*. A mixture of the appropriate mononuclear complexes **1**, **2** or **3** (0.30 mmol), NEt$_3$ (1 cm^3), and $[\underline{\mathrm{Mo}}\mathrm{Cl_2}]$ (0.45 g; 0.9 mmol), was refluxed in toluene (40 cm^3) for 2 d. The solvent was evaporated *in vacuo*, the residue dissolved in CH$_2$Cl$_2$ and the solution chromatographed on silica gel. Initial elution with CH$_2$Cl$_2$/hexane (9 : 1 v/v) gave unreacted $[\underline{\mathrm{Mo}}\mathrm{Cl_2}]$ and the green by-product $[\{\underline{\mathrm{Mo}}\mathrm{Cl}\}_2(\mu\text{-O})]$. Pure CH$_2Cl_2$ was then used to elute first small amounts of binuclear complexes, which were discarded, and later the relatively non-polar trimetallic complexes. Recrystallisation from concentrated CH$_2$Cl$_2$ solutions by the addition of pentane afforded the desired products **4**, **5** or **6**, respectively, as brown powders.

$[\underline{\mathrm{Mo}}\{\mathrm{OC_6H_4py}\underline{\mathrm{Mo}}\mathrm{Cl}\}_2]$, **4** (Found: C, 47.7; H, 5.2; N, 18.9. $C_{67}H_{82}N_{23}B_3Cl_2O_5Mo_3$ requires C, 46.9; H, 4.9; N, 19.2%): FAB mass spectrum 1681 (requires 1681); IR 1670, 1616 cm^{-1} (ν_{NO}); λ_{max}/nm (ε/10^{-3} M^{-1} cm^{-1}) 286(30), 325(38), 383(19), 428(18); $E_f = -2.11, -1.05, +0.03$ V.

[**Mo**{OC$_6$H$_4$CH=CHpy**Mo**Cl}$_2$], **5** (Found: C, 44.8; H, 4.7; N, 16.4. $C_{71}H_{86}N_{23}B_3Cl_2O_5Mo_3$ requires C, 44.7; H, 4.7; N, 16.2%): FAB mass spectrum 1732 (requires 1733); IR 1670, 1611 cm^{-1} (ν_{NO}); λ_{max}/nm (ε/10^{-3} M^{-1} cm^{-1}) 281(27), 369(53), 426(26), 489 (sh); $E_f = -1.99, -1.06, +0.04$ V.

[**Mo**{OC$_6$H$_4$CH$_2$CH$_2$py**Mo**Cl}$_2$], **6** (Found: C, 44.8; H, 5.6; N, 16.3. $C_{71}H_{90}N_{23}B_3Cl_2O_5Mo_3$ requires C, 44.6; H, 4.6; N, 16.2%): FAB mass spectrum 1737 (requires 1737); IR 1655, 1617 cm^{-1} (ν_{NO}); λ_{max}/nm (ε/10^{-3} M^{-1} cm^{-1}) 276(29), 314 (sh), 417(12), 467 (sh); $E_f = -2.12, -1.30, +0.05$ V.

Complexes of 3,5-bis(4-hydroxyphenyl)pyridine. *[{**Mo**Cl(OC$_6$H$_4$)}$_2$py}], 7, and [{**Mo**Cl(OC$_6$H$_4$)}$_2$py**Mo**Cl], 8.* A mixture of H$_2$L^5 (0.08 g; 0.29 mmol), [**Mo**Cl$_2$] (0.30 g; 0.6 mmol) and NEt$_3$ (1 cm^3) in dry toluene (40 cm^3) was refluxed for 8 h. After cooling and evaporating the solvent *in vacuo*, the residue was chromatographed on silica gel. Initial elution with CH$_2$Cl$_2$/hexane (9 : 1 v/v) gave unreacted [**Mo**Cl$_2$] and the green by-product [{**Mo**Cl}$_2$(μ-O)]. Pure CH$_2$Cl$_2$ was then used to separate the desired trinuclear complex **8**. The solvent polarity was then increased by adding THF (up to 2.5% v/v) and the first major purple fraction contained the binuclear complex **7**. Each fraction was concentrated *in vacuo* to *ca.* 5 cm^3 and complexes **7** and **8** were precipitated by addition of n-pentane.

[{**Mo**Cl(OC$_6$H$_4$)}$_2$py], **7** (Found: C, 42.8; H, 5.1; N. 17.5. $C_{47}H_{44}N_{15}B_2Cl_2O_4Mo_2$ requires C, 48.5; H, 4.9; N, 17.3%): FAB mass spectrum 1179 (requires 1179); IR 1683 cm^{-1} (ν_{NO}); λ_{max}/nm (ε/10^{-3} M^{-1} cm^{-1}) 275 (sh), 306(26), 502(16); $E_f = -0.87$ V.

[{**Mo**Cl(OC$_6$H$_4$)}$_2$py**Mo**Cl], **8** (Found: C, 45.3; H, 5.0; N, 18.9. $C_{62}H_{77}N_{22}B_3Cl_3O_5Mo_3$ requires C, 45.5; H, 4.7; N, 18.8%): FAB mass spectrum 1635 (requires 1637); IR 1685, 1616 cm^{-1} (ν_{NO}); λ_{max}/nm (ε/10^{-3} M^{-1} cm^{-1}) 279(40), 316 (sh), 492(17); $E_f = -2.20, -0.83, +0.09$ V.

[{Mo Cl(OC$_6$H$_4$)}$_2$pyMe][PF$_6$], 9[PF$_6$]. A mixture of the starting complex **7** (0.10 g; 0.085 mmol) and methyl iodide (1 cm^3) was refluxed in CH$_2$Cl$_2$ (20 cm^3) for 18 h. After removal of the solvent *in vacuo* the solution was chromatographed on a short (12 cm long) column of alumina (Brockmann activity IV) using MeCN (99%)/aqueous KPF$_6$ (1%) as eluent. Small amounts of by-products eluted first before the major product. To the major brown fraction containing the pure product was added 5 cm^3 of saturated aqueous KPF$_6$. After evaporation to dryness the solid was extracted from the excess KPF$_6$ by partitioning between water and CH$_2$Cl$_2$. The product (**9**$^+$) was precipitated from the dried (MgSO$_4$), concentrated CH$_2$Cl$_2$ solutions by addition of pentane. [{**Mo**Cl(OC$_6$H$_4$)}$_2$pyMe][PF$_6$], **9**[PF$_6$] (Found: C, 43.9; H, 4.5; N, 15.2. $C_{48}H_{58}N_{15}B_2Cl_2F_6O_4Mo_2P$ requires C, 4.44; H, 4.7; N, 15.2%): FAB mass spectrum 554 (requires 553); IR 1685 cm^{-1} (ν_{NO}); λ_{max}/nm (ε/10^{-3} M^{-1} cm^{-1}) 316(30), 389(17), 456 (sh); $E_f = -1.55$ (reduction of quaternary site), -0.74 V.

Complexes of 2,6-bis(4-ethenylpyridyl)-4-hydroxytoluene. *[**Mo**Cl{OC$_6$H$_3$Me[CH=CHpy**Mo**Cl]}$_2$], 11, and [**Mo**Cl{OC$_6$H$_3$Me[CH=CHpy**Mo**Cl](CH=CHpy)}], 10.* A mixture of HL^7 (0.25 g, 0.8 mmol), [**Mo**Cl$_2$] (1.57 g, 3.2 mmol) and NEt$_3$ (2 cm^3) was stirred and refluxed in toluene (60 cm^3) for 24 h. The solvent was then removed *in vacuo* and the residue was purified chromatographically over silica using CH$_2$Cl$_2$ containing THF (2% v/v). The trinuclear complex **11** separated first, and was isolated, after solvent removal, as a microcrystalline black powder (0.59 g, 43%). Dinuclear **10** was eluted after **11** had been removed, by increasing the THF content (to 5%) of the CH$_2$Cl$_2$. It was isolated as a microcrystalline black powder (0.18 g, 18%).

[**Mo**Cl{OC$_6$H$_3$Me[CH=CHpy**Mo**Cl](CH=CHpy)}], **10** (Found: C, 50.3; H, 5.6; N, 18.2. $C_{47}H_{61}N_{16}B_2Cl_2O_3Mo_2$ requires C, 49.7; H, 5.1; N, 18.2%): FAB mass spectrum 1231 (requires 1231); IR 1676, 1607 cm^{-1} (ν_{NO}); λ_{max}/nm (ε/10^{-3} M^{-1} cm^{-1}) 280 (sh), 311(34), 489(7); $E_f = -1.92, -0.91, +0.03$ V.

[**Mo**Cl{OC$_6$H$_3$Me[CH=CHpy**Mo**Cl]}$_2$], **11** (Found: C, 46.8; H, 5.5; N, 18.7. $C_{66}H_{83}N_{23}B_3Cl_3O_4Mo_3$ requires C, 46.9; H, 5.5; N, 19.1%): FAB mass spectrum 1689 (requires 1689); IR 1676, 1609 cm^{-1} (ν_{NO}); λ_{max}/nm (ε/10^{-3} M^{-1} cm^{-1}) 285 (sh), 327(35), 415 (sh), 487(9); $E_f = -1.93, -0.88, +0.03$ V.

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