

Magnetic Spin Exchange Interactions between Several Metal Centres in Paramagnetic Complexes with New Polynucleating Bridging Ligands

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The polynucleating bridging ligands L^1 and H_3L^2 were simply prepared *via* a Heck coupling of 4-vinylpyridine or 4-methoxystyrene with 1,3,5-tribromobenzene; in the trinuclear complexes of L^1 and L^2 with a paramagnetic $\{Mo(NO)\{BH(C_3HN_2Me_2-3,5)_3\}Cl\}$ moiety $[BH(C_3HN_2Me_2-3,5)_3 = \text{tris}(3,5\text{-dimethylpyrazol-1-yl) hydroborate}]$ at each binding site the EPR spectra demonstrate that all three unpaired electrons are in 'fast exchange' between all three metal centres

The availability of a wide range of ligands which can bridge two remote metal centres is of fundamental importance in coordination chemistry.¹⁻⁶ In contrast there are few ligands comprising three or more binding sites linked to a central spacer which can bind metal ions in a polygonal array.^{7,8} Such ligands would be of considerable interest in allowing examination of metal-metal interactions in symmetrical polynuclear complexes, and as a starting point for metal-containing arborols.⁷

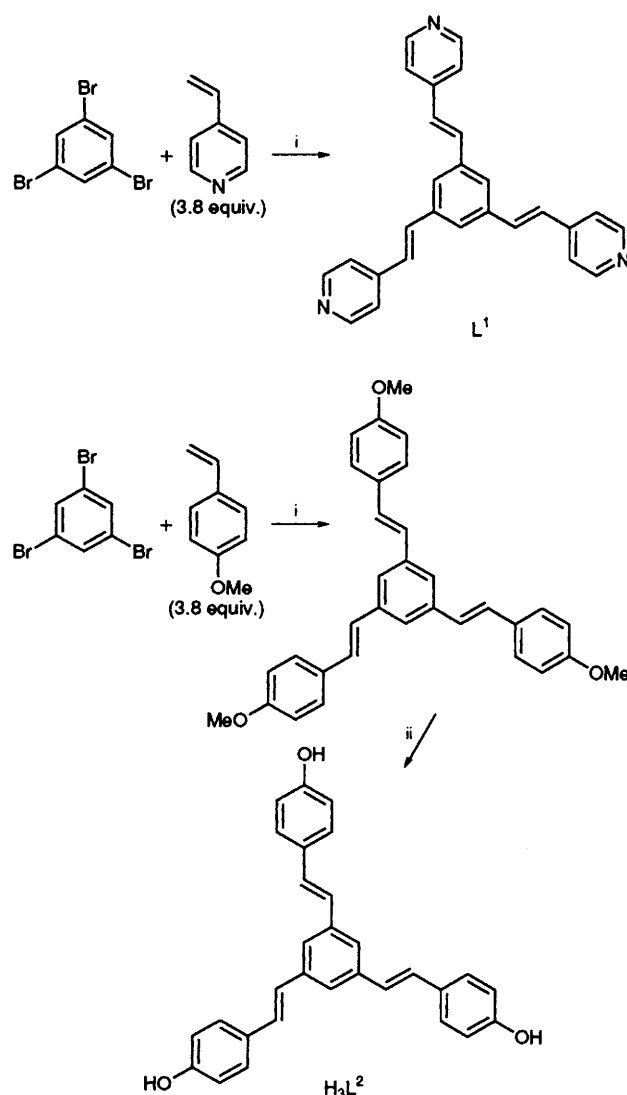
We describe here a simple synthesis of the new terdentate ligands L^1 and H_3L^2 containing respectively three 4-pyridyl and three 4-hydroxyphenyl binding sites linked *via* alkene bridges to a central phenyl spacer. As an example of their potential interest, we illustrate the detection of a three-way spin-exchange interaction in their trinuclear molybdenum complexes. The ligands were prepared in good yield using a standard Heck reaction (Scheme 1),⁹ which involved coupling of 3 equivalents of 4-vinylpyridine (for L^1) or 4-methoxystyrene (for H_3L^2) to 1,3,5-tribromobenzene, using a $Pd(O_2CMe)_2/PAr_3$ (Ar = phenyl or *o*-tolyl) catalyst.† L^1 was isolated directly from the reaction; preparation of H_3L^2 required removal of the protecting methoxy groups.¹⁰ This is a simple and potentially very powerful method for preparing new polynucleating ligands that is limited only by the availability of polybrominated aromatics as starting materials. To understand the potential utility of, for example, L^1 as a bridging ligand in polynuclear complexes, it is only necessary to consider the pivotal role of binucleating bridging ligands such as 4,4'-bipyridine and its relatives in recent coordination chemistry.

Reaction of L^1 with excess $[Mo\{BH(C_3HN_2Me_2-3,5)_3\}(NO)Cl_2]^{11}[BH(C_3HN_2Me_2-3,5)_3 = \text{tris}(3,5\text{-dimethylpyrazol-1-yl) hydroborate}]$ afforded a mixture of $\{[Mo\{BH(C_3HN_2Me_2-3,5)_3\}(NO)Cl]_nL^1\}$ ($1, n = 1; 2, n = 2; 3, n = 3$) in which one, two or three pyridyl sites of L^1 are coordinated to the paramagnetic 17-electron molybdenum groups. The mixture was readily separated by chromatography on silica with CH_2Cl_2 -thf using gradient elution. A similar reaction of H_3L^2 with 3 equivalents of $[Mo\{BH(C_3HN_2Me_2-3,5)_3\}(NO)Cl_2]$ afforded only the trinuclear complex $\{[Mo\{BH(C_3HN_2Me_2-3,5)_3\}(NO)Cl]_3L^2\}$ **4**, containing three 16-electron molybdenum centres bound to the phenolates.‡

The solution EPR spectra of **1-3** are depicted in Fig. 1. The spectrum of **1** is typical for an isolated molybdenum centre, with $g_{iso} = 1.979$ and a sextet pattern ($A_{Mo} = 5.0$ mT) due to hyperfine coupling to the isotopes with $I = 5/2$.¹ The spectrum of **2** is typical of many bridged binuclear molybdenum complexes we have examined recently, and shows that the two unpaired electrons are in 'fast exchange'; *i.e.* the modulus of the spin-spin interaction J is much greater than A_{Mo} (which is 140 MHz, or about 0.005 cm^{-1}) giving a spectrum in which both electrons are apparently coupled to both nuclei and the separation between hyperfine components is halved to 2.5 mT.¹ Complex **2** may be useful building block for complexes containing multiply interaction paramagnetic centres in geometrically well-defined arrays, *via* attachment of the pendant

pyridyl groups of **2** or more equivalents of **2** to the same metal centre.

In the spectrum of **3** it is apparent that all three electrons are in 'fast exchange' between all three metal centres; *i.e.* each unpaired electron is simultaneously involved in spin-exchange interactions with the other two, and for all three interactions $|J| \gg A_{Mo}$. All of the expected combinations for coupling to three equivalent nuclei are apparent. Since 25.2% of Mo nuclei have $I = 5/2$ (with similar nuclear magnetic moments) and 74.8% have $I = 0$, we would expect the following sets of signals: all three nuclei with $I = 0$ will give a singlet (42%); two nuclei with $I = 0$, one with $I = 5/2$, 1:1:1:1:1:1



Scheme 1 i, $Pd(OAc)_2$ - PPh_3 (1 mol%), NEt_3 , 100 °C, 3 d; ii, molten pyridinium chloride, 200 °C, 2 h

sextet (42%); one nucleus with $I = 0$, two with $I = 5/2$, 1:2:3:4:5:6:5:4:3:2:1 eleven-fold multiplet (14%) and all three nuclei with $I = 5/2$, 1:3:6:10:15:21:25:27:25:21:15:10:6:3:1 sixteen-fold multiplet (2%).

Despite considerable overlap at the centre of the spectrum, enough of the outlying components of each set of signals are resolved to confirm the presence of all of them. In addition, the separation between the hyperfine components is now 1.7 mT, one-third of the value in **1**. Similarly, treatment of **4** with excess cobaltocene in MeCN under N_2 afforded $[4]^{3-}$, in which each of the three 16-electron metal centres was reduced to a 17-electron configuration;² the EPR spectrum of this trianion was essentially identical to that of **3**, confirming that the exchange interaction is also occurring across the phenoxide substituents of the bridging ligand. In the absence of close contacts between the paramagnetic centres which would allow direct overlap of the magnetic orbitals, the mechanism of the exchange interaction is likely to be *via* spin-polarisation of the σ -core of the bridging ligand.¹² In neither case were double- or

triple-quantum transitions observed, doubtless due to the large metal-metal separation.

Although they have been the subject of theoretical investigations,^{12,13} there are only a handful of studies of exchange interactions in triangular multi-spin systems, most being organic triradicals.¹⁴ The only such inorganic systems are the oxo-centred trinuclear carboxylates,¹⁵ which were examined by low-temperature susceptibility studies but whose EPR properties have not been reported, and a vanadyl pyrophosphate trimer which gives a 22-line EPR spectrum but whose structure is uncertain.¹⁶ Complexes **1** and $[4]^{3-}$ are therefore the first examples of well-characterized triangular metal complexes where the onset of three-way fast exchange is apparent from the EPR spectrum. With larger ligands of this type *air-stable* polyradical systems of higher spin may be envisaged.

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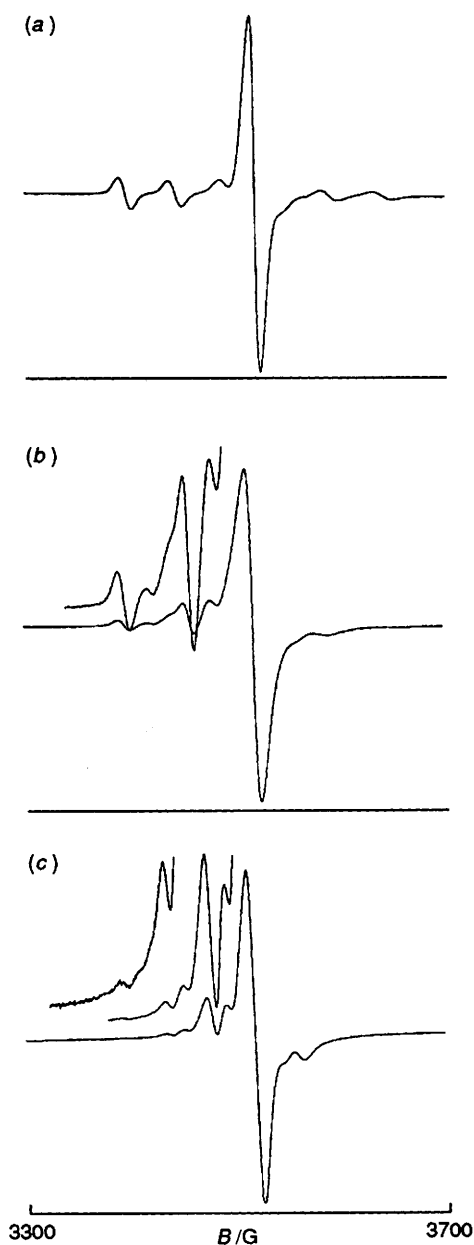


Fig. 1 Room temperature EPR spectra of (a) **1**, (b) **2** and (c) **3** in CH_2Cl_2 -thf (1:1)

Footnotes

† Preparation of L^1 : A mixture of 1,3,5-tribromobenzene (1.56 g, 5 mmol), 4-vinylpyridine (1.97 g, 18.8 mmol), triethylamine (1.90 g, 18.8 mmol), palladium acetate (34 mg, 0.15 mmol) and PPh_3 (79 mg, 0.3 mmol) was sealed in a Schlenk tube under N_2 , and heated to 100 °C for 3 d. The resulting solid mass was partitioned between CH_2Cl_2 and water. The organic layer was separated and evaporated to dryness, and the crude product was recrystallised from acetone to give L^1 in 60–70% yield. EI MS: m/z 387 (M^+). 1H NMR ($CDCl_3$), δ 8.63 (6 H, dd, $J = 4.7, 1.7$, pyridyl H^2/H^6), 7.42 (6 H, d, $J = 4.7, 1.7$ Hz, pyridyl H^3/H^5), 7.67 (3 H, s, phenyl), 7.37 (3 H, d, $J = 16.3$ Hz, $CH=CH$), 7.14 (3 H, d, $J = 16.3$ Hz, $CH=CH$).

Preparation of H_3L^2 : The above procedure was used but with 4-methoxystyrene as starting material. Crude $C_6H_3(CH=CHC_6H_4OMe-p)$ -1,3,5 was purified by chromatography on alumina (Brockman activity III) using CH_2Cl_2 . EI MS: m/z 474 (M^+). 1H NMR ($CDCl_3$), δ 7.49 (6 H, d, $J = 8.8$ Hz, phenyl H^2/H^6), 7.48 (3 H, s, central phenyl), 7.15 (3 H, d, $J = 16.5$ Hz, $CH=CH$), 7.01 (3 H, d, $J = 16.5$ Hz, $CH=CH$), 6.92 (6 H, d, $J = 8.8$ Hz, phenyl H^3/H^5), 3.84 (9 H, s, OCH_3). Demethylation was performed with pyridine-HCl according to a published method (ref. 10). After addition of water to the reaction mixture, H_3L^2 precipitated and was collected by filtration, washed with water and dried in *ca.* 40% yield overall. 1H NMR (CD_3OD), δ 7.45 (3 H, s, central phenyl), 7.40 (6 H, d, $J = 9$ Hz, phenyl H^2/H^6), 7.15 (3 H, d, $J = 16$ Hz, $CH=CH$), 6.95 (3 H, d, $J = 16$ Hz, $CH=CH$), 6.75 (6 H, d, $J = 9$ Hz, phenyl H^3/H^5). Satisfactory analyses were obtained.

‡ Preparations of **1–3**: A mixture of L^1 (50 mg, 0.13 mmol), $[Mo\{BH(C_3HN_2Me_2-3,5)_3\}(NO)Cl_2]$ (255 mg, 0.56 mmol) and dry NEt_3 (1 cm^3) was heated to reflux in dry toluene (100 cm^3) for 18 h. After evaporation of the solvent *in vacuo*, the residue was purified by chromatography on SiO_2 . Initial elution with CH_2Cl_2 removed some relatively non-polar impurities. The solvent polarity was smoothly increased by addition of increasing amounts thf to the CH_2Cl_2 eluent until the molybdenum complexes eluted in the order **3** (2% thf in CH_2Cl_2), **2** (thf- CH_2Cl_2 , 1:9) **1** (thf- CH_2Cl_2 1:1) as well-separated dark bands. The yield of **3** was typically 40%; those of **2** and **1** were typically 5–10% each but variable. FAB⁺ MS: m/z 851, 1304 and 1763 for **1**, **2** and **3** respectively (expected values: 847, 1305 and 1763). IR: ν_{BH} occurred at 2554 cm^{-1} and ν_{NO} at 1609 cm^{-1} in each case.

Complex **4** was prepared by reaction of H_3L^2 with $[Mo\{BH(C_3HN_2Me_2-3,5)_3\}(NO)Cl_2]$ in the same way and purified by chromatography on SiO_2 with CH_2Cl_2 in 50–60% yield. FAB⁺ MS: m/z 1806 (expected value 1805). 1H NMR (270 MHz, $CDCl_3$), δ 7.57 (6 H, d, $J = 8.6$, phenyl H^2/H^6), 7.51 (3 H, s, central phenyl ring), 7.30 (6 H, d, $J = 8.6$, phenyl H^3/H^5), 7.21 (3 H, d, $J = 16.1$, $CH=CH$), 7.09 (3 H, d, $J = 16.1$, $CH=CH$), 5.87, 5.84, 4.71 (all 3 H, s, pyrazolyl H^4), 2.53, 2.36, 2.35, 2.33, 2.15, 2.02 (all 9H, s, pyrazolyl Me groups). Satisfactory analyses (C, H, N) were obtained for all complexes.

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