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COMMUNICATION

METAL-DIRECTED SELF ASSEMBLY OF REDOX ACTIVE BIMETALLOMACROCYCLES CONTAINING SIX-COORDINATE METAL CENTRES INCORPORATED INTO 16-, 18- AND 24-MEMBERED RINGS

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Abstract—The reaction between [Mo(NO)Tp*I$_2$] [Tp* = HB(3,5-Me$_2$C$_3$HN$_2$)$_3$] and the bifunctional ligands BLH$_2$ (BL = 4,4′-OC$_6$H$_4$CH$_2$C$_6$H$_4$O, 4,4′-OCH$_2$C$_6$H$_4$CH$_2$O and 2,7-O$_2$C$_{10}$H$_6$) in the presence of NEt$_3$ affords the redox active metallomacrocycles [Mo(NO)Tp*(BL)]$_2$ which have been isolated as *syn*- and *anti*-isomers, except where BL = 4,4′-OCH$_2$C$_6$H$_4$CH$_2$O, and characterized by spectroscopic and electrochemical methods.

Cyclophanes represent an important class of synthetic molecular receptor and are the subject of intense current research activity.[1] The incorporation of transition metal atoms into such compounds allows new properties such as Lewis acidity, magnetism or redox activity to be included into the receptor structure. However, although the incorporation of transition metal atoms at ring vertices in macrocyclic molecules is well established,[2] and work has been carried out on appending redox active metal centres to the periphery of cyclophane structures,[3] there have been relatively few reports of cyclophanes in which two or more metal ions are present at ring vertices. The use of flexible bridging ligands can lead to the formation of bimetallocyclophanes such as [Zr(η^5-C$_5$H$_5$)$_2$(OCH$_2$C$_6$H$_4$CH$_2$O-3)]$_2$,[4] [Pd(en)(NC$_5$H$_4$CH$_2$CH$_2$C$_5$H$_4$N)]$_2^{4+}$ and [Pd(en)(NC$_5$H$_4$CH$_2$C$_6$F$_4$CH$_2$C$_5$H$_4$N)]$_2^{4+}$.[5] When inflexible bridging ligands are used, higher cyclic oligomers may be obtained and cyclic trimers[6] and tetramers,[7,8] which contain metal atom vertices linked by rigid bifunctional ligands, have been reported. The redox properties of the metal centres in these systems have not been explored, although a macrocyclic tetra-palladium compound has been produced by oxidative coupling of [PdCl$_2$(*o*-C$_6$H$_4$-C(Me)=N-NPh){P(OMe)$_3$}]$_2$.[9] Furthermore, none of these examples contain six-coordinate metal centres, although these would seem to be suitable candidates for forming metallocyclophane structures through binding bridging ligands at mutually *cis* coordination sites.

Previously we have shown that, in reactions with suitable flexible bifunctional chelating ligands, the {Mo(NO)Tp*}$^{2+}$ moiety can be incorporated into redox active mono-metallomacrocycles.[10] By using

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bifunctional ligands that are insufficiently flexible to chelate to a single metal ion, but have sufficient flexibility to form a bimetallomacrocyclic structure, we have now obtained redox active bimetallocyclophane derivatives containing six-coordinate metal centres. In these compounds the structural features of the $\{Mo(NO)Tp^*\}^{2+}$ unit can lead to the formation of isomerically related products. This type of behaviour is not possible with the square planar palladium derivatives or the pseudotetrahedral zirconium derivative reported previously. Furthermore, in bimetallic complexes, the redox active 16-electron $\{Mo(NO)Tp^*X\}^+$ [$Tp^* = HB(3,5\text{-}Me_2C_3HN_2)_3$; X = I, Cl] moieties exhibit electrochemically detectable metal–metal interactions over considerable distances through bridging ligands, offering the possibility that interactions across metallocyclophane rings may be studied electrochemically.[11]

The reaction between 4,4′-$HOC_6H_4CH_2C_6H_4OH$ and [$Mo(NO)Tp^*I_2$] in toluene containing NEt_3 affords two macrocyclic products, **1** (27% yield) and **2** (18% yield), separable through their differing solubilities in toluene. Elemental analyses are consistent with the formulation [$Mo(NO)Tp^*$(4,4′-$OC_6H_4CH_2C_6H_4O$)]$_n$ for both compounds and their FAB mass spectra contain molecular ion clusters at $m/z = 1243$ consistent with a value of $n = 2$. The IR spectra of the complexes contain ν_{max}(NO) at 1653 (**1**) and 1657 cm^{-1} (**2**) in accord with the presence of the $\{Mo(NO)Tp^*O_2\}$ moiety.[12] The ^1H NMR spectra of **1** and **2** contain signals attributable to the presence of the Tp* ligand attached to an $\{Mo(NO)\}$ group lying in a plane of molecular symmetry. Thus in both cases the pyrazolyl H^4 protons appear in the region $\delta_{TMS} = 5.8$–5.9 ppm as two signals in the area ratio 4 : 2, but with differing chemical shifts for the two compounds. The pyrazolyl methyl protons appear in the region 2.1–2.4 ppm, notionally as four signals in the area ratio 12 : 6 : 12 : 6 but signal overlap leads to the observation of only three clearly resolved signals. Signals of total area 8 attributable to the aryl protons of the 4,4′-$OC_6H_4CH_2C_6H_4O$ ligands are also present; in the case of **1** these appear as two doublets comprising an AA′BB′ system ($J_{HH} = 8.4$ Hz) but in the case of **2** a singlet is observed. The most significant difference between the spectra of the two compounds appears in the signal from the methylene protons in the 4,4′-$OC_6H_4CH_2C_6H_4O$ ligands. This is observed as a singlet at $\delta_{TMS}(CDCl_3) = 4.00$ ppm for **1** but as two doublets at 3.79 and 4.06 ppm comprising an AB system ($J_{HH} = 14.6$ Hz) for **2**. These findings are consistent with the formulation of **1** as an *anti*-isomer (Fig. 1) in which the protons on each methylene (H_a) are equivalent, being related by a C_2 axis, and the formulation of **2** as a *syn*-isomer in which the methylene protons (H_a and H_b) are inequivalent.

A similar reaction between [$Mo(NO)Tp^*I_2$] and 4,4′-$HOCH_2C_6H_4CH_2OH$ affords a macrocyclic product, **3**, in 18% yield. The elemental analyses, IR spectrum [ν_{max}(NO) at 1634 cm^{-1}] and mass spectrum ($m/z = 1118$) of this compound are consistent with the formulation [$Mo(NO)Tp^*$(4,4′-$OCH_2C_6H_4CH_2O$)]$_2$. The ^1H NMR spectrum of **3** again contains signals attributable to Tp* ligands containing a plane of molecular symmetry. The methylene groups of the 4,4′-$OCH_2C_6H_4CH_2O$ ligands in **3** give rise to a singlet of relative area 4 at $\delta_{TMS}(CDCl_3) = 7.25$ ppm and the aryl protons appear as two doublets, each of relative area 2, at 6.59 and 6.04 ppm with $J_{HH} = 11.3$ Hz. [$Mo(NO)Tp^*$(4,4′-$OCH_2C_6H_4CH_2O$)]$_2$ should exist as the *syn*- and *anti*-isomers **3a** and **3b** (Fig. 2) but, as yet, only one isomer has been obtained and a definitive structural assignment for this isomer awaits an X-ray diffraction study.*

Reactions between [$Mo(NO)Tp^*I_2$] and the more rigid di-hydroxy ligand 2,7-$(HO)_2C_{10}H_6$ afford two products, **4** (47% yield) and **5** (27% yield), formulated as [$Mo(NO)Tp^*(O_2C_{10}H_6)$]$_2$ on the basis of elemental analyses, IR spectra [ν_{max}(NO) at 1630 cm^{-1}] and FAB mass spectra (m/z 1163). As found for **1** and **2**, **4** and **5** exhibit differing solubility properties with **4** being soluble in most common polar solvents whereas **5** exhibits very low solubility in common solvents other than chloroform. The two compounds give quite different ^1H NMR spectra, although both contain signals attributable to Tp* ligands containing a plane of symmetry. In both cases the signals due to the naphthyl protons of the bridging ligand appear as a doublet of doublets ($^3J_{HH}$ 8.8 and 2.3 Hz) and a doublet ($^3J_{HH}$ 8.8 Hz) due, respectively, to the two pairs of protons in positions 3 and 6 and in positions 4 and 5, along with a doublet ($^3J_{HH}$ 2.3 Hz) due to the protons in positions 1 and 8. The isolation of two compounds of formula [$Mo(NO)Tp^*(O_2C_{10}H_6)$]$_2$ can, again, be attributed to the formation of *syn*- and *anti*-isomers. However, the equivalence of the protons in positions 1 and 8 on the naphthyl ring in both compounds precludes a definitive assignment of *syn*- or *anti*- structures to **4** and **5** (Fig. 3) and indicates that reorientation of the naphthyl groups is rapid on the ^1H NMR time-scale at room temperature. In an attempt to assign structures to **4** and **5**, ^1H NMR spectra were recorded at −90°C but these

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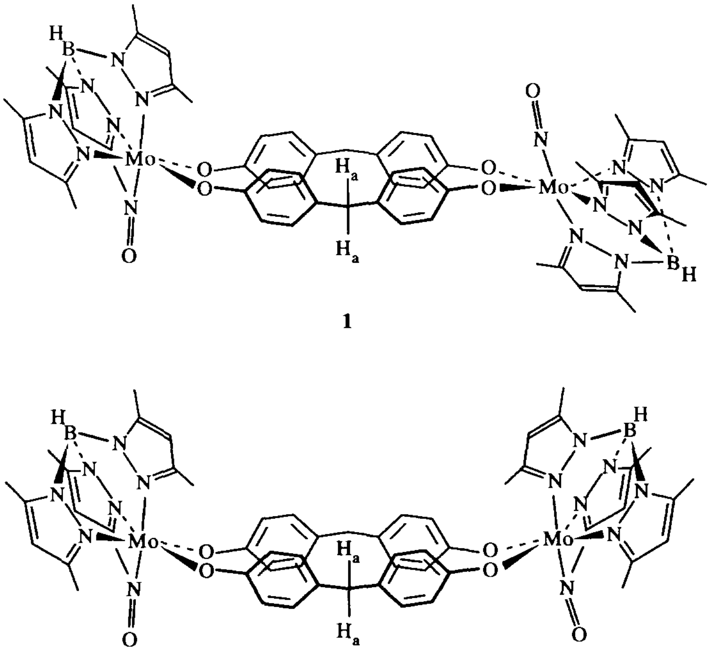
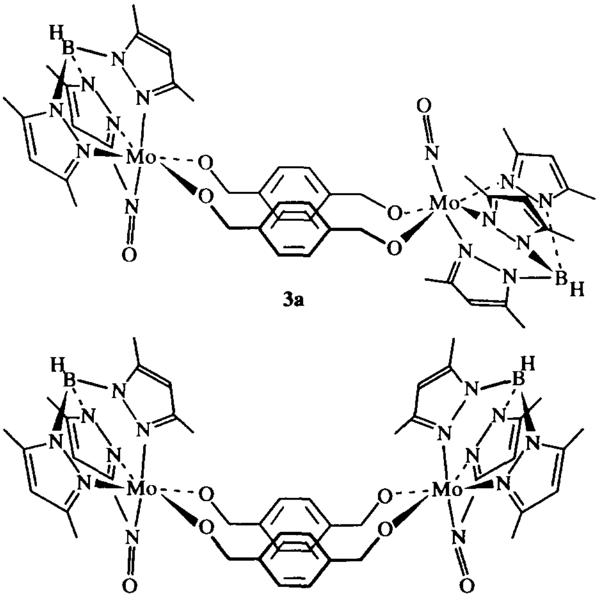
* *Note added in proof*: X-ray structural studies have now confirmed the structures of **1**, **3a** and **4** as shown.



1

2

Fig. 1. The proposed isomeric structures of **1** and **2**.*



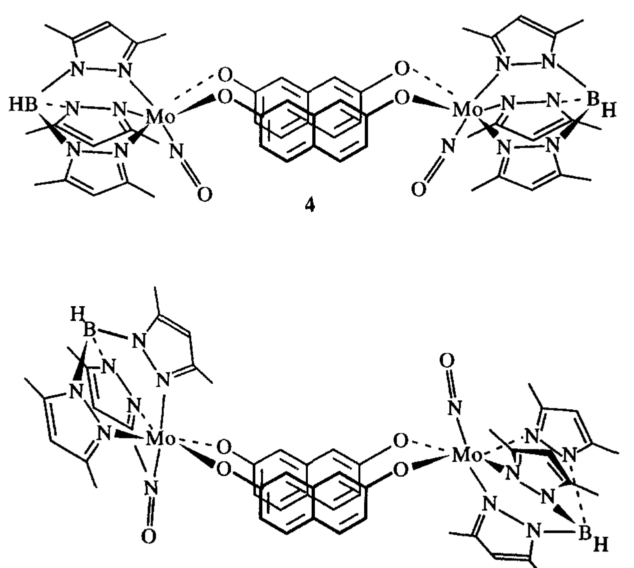
3a

3b

Fig. 2. Possible isomeric structures for **3**.*

show no significant differences from the room temperature spectra.

The electron withdrawing capacity of the $\{Mo(NO)\}^{3+}$ centre in these macrocycles might be expected to induce binding of electron rich guests within the cavity. However, ^1H NMR experiments have thus far provided no evidence for inclusion phenomena with potential guest molecules such as 1,4-$\{HOCH_2(CH_2OCH_2)_2CH_2O\}C_6H_4$. Models indicate that one pyrazolyl 3-methyl or the NO



4

5

Fig. 3. Proposed isomeric structures for **4** and **5**.*

group on each {Mo(NO)Tp*} moiety project over the cavity formed by these bimetallomacrocycles. Thus although **1** and **2**, for example, are structurally similar to a calix[4]arene, they do not offer a similarly accessible cavity to potential guests.

Electrochemical studies of these metallocyclophanes confirm that the molybdenum centres can be reduced at potentials of *ca* -0.7 V in accord with expectation.[13] These studies also reveal that two reduction processes are present and the separations between them, ΔE_f, have been measured using differential pulse voltammetry.[14] The values obtained [$\Delta E_f = 85$ (**1** and **2**), 90 (**3**) and 185 mV (**4**)]† indicate that there are weak interactions between the molybdenum centres in the macrocyclic structure. The synthesis of these new redox active metallocyclophanes containing six-coordinate metal centres has, for the first time, allowed an electrochemical study of isomerically related metallocyclophane structures and reveals that, in the case of the two isomers **1** and **2**, there is no detectable difference between their electrochemical properties.

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†The low solubility of **5** in solvents other than $CHCl_3$, which has proven unsuitable for electrochemical studies, has precluded a meaningful measurement of ΔE_f for **5**.

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