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Bi-, Tri-, and Tetranuclear Metallomacrocycles Constructed by Metal-Directed Reactions Involving Resorcinol or Hydroquinone or by Addition of Octahedral Metal Centers to Tetrahexylcalix[4]resorcinarene: X-ray Crystal Structure of *syn*,*syn*-[Mo{HB(3,5-$Me_2C_3HN_2$)$_3$}(NO)(1,4-$O_2C_6H_4$)]$_3$

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The reaction between [Mo(NO)(Tp)I_2] [Tp^- = hydrotris(pyrazol-1-yl)borate] and tetrahexylcalix[4]resorcinarene (resH_8) affords a mixture of metalated macrocycles from which [{Mo(NO)(Tp)}$_2$(resH_4)], [{Mo(NO)(Tp)}$_3$(resH_2)], and [{Mo(NO)(Tp)}$_4$(res)] can be isolated. In the solid state the tetrametalated compound can act as a host for CH_2Cl_2 which forms a weak hydrogen bond to the oxygen of a coordinated nitric oxide: H···O1 2.47 Å, angle C−H···O1 161°. Direct reaction of [Mo(NO)(Tp*)I_2] [Tp*$^-$ = hydrotris(3,5-dimethylpyrazol-1-yl)borate] with resorcinol itself offers a route to the related resorcinol-based tetrametallomacrocycle [Mo(NO)(Tp)(1,3-$O_2C_6H_4$)]$_4$. This reaction also produces the cyclic trimer [Mo(NO)(Tp)(1,3-$O_2C_6H_4$)]$_3$ together with some cyclic dimer. A similar reaction involving 1,4-dihydroxybenzene and [M(NO)(Tp*)I_2] (M = Mo, W) also affords cyclic trimers and cyclic tetramers, but in this case, cyclic dimers are not formed. It has been possible to separate the single isomers *syn*,*syn*-[Mo(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_3$, *anti*,*syn*-[M(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_3$ (M = Mo, W), *anti*,*syn*-[Mo(NO)(Tp*)(1,3-$O_2C_6H_4$)]$_3$, and *anti*,*syn*,*syn*-[Mo(NO)(Tp*)(1,3-$O_2C_6H_4$)]$_4$. The crystal structure of *syn*,*syn*-[Mo(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_3$ has been determined: $C_{63}H_{78}B_3Mo_3N_{21}O_9$; monoclinic space group $P2_1/a$; a = 16.269(10), b = 35.31(3), c = 16.056(10) Å; β = 97.59(2)°; Z = 4. The coordination geometry at the molybdenum atoms is essentially octahedral. The trimer does not show 3-fold symmetry, the triangle of molybdenum atoms having two long edges, 8.485(3) and 8.703(3) Å, and one short edge of 7.886(3) Å. These distances are paralleled by the corresponding distances between the nitrosyl oxygen atoms, 6.177(12), 6.526(12), and 3.729(12) Å, respectively. The electrochemical properties of the metallomacrocycles reveal differing patterns of redox potentials depending upon the number and geometric arrangement of metal centers in the macrocyclic structure.

Introduction

Cyclophanes have played a central role in the development of supramolecular chemistry,[1] an area which is having a major impact on current chemical research and which will continue to do so into the foreseeable future. Particular examples are provided by their applications in synthesis,[2] in the development of molecular sensors,[3] and their possible applications in catalysis, as exemplified by the development of a "molecular reaction vessel".[4] Recently it has been recognized that the synthetic approaches to macrocyclic molecules may be greatly extended by the incorporation of transition metal atoms.[5−7] Apart from their particular structural features, which can aid synthesis, transition metal vertexes can introduce functional properties such as Lewis acidity,[8] luminescence,[9] magnetism[10,11]or redox activity[12] into the macrocycle structure. Self-assembly reactions

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involving kinetically labile cationic four-coordinate metal centers and neutral polypyridyl ligands have provided a widely used route to new metallomacrocyle derivatives. However, other metal-directed approaches to metallomacrocyle synthesis are possible as demonstrated by the preparation of the neutral compound $[Zr(\eta^5\text{-}C_5H_5)_2\{1,3\text{-}(OCH_2)_2C_6H_4\}]_2$ by Stephan.[13] Calculations support the proposal that, in such compounds, the Zr–O bonds are strengthened by $O \rightarrow Zr\ p_\pi \rightarrow d_\pi$ charge donation, lending stability to the structure. In our laboratory we have been developing metal-directed syntheses of metallomacrocyles containing the redox-active $\{M(A)(Tp^*)\}^{2+}$ [Tp^{*-} = hydrotris(3,5-dimethylpyrazol-1-yl)borate; M = Mo, A = NO, O; M = W, A = NO) moieties. Bi-, tri-, and tetranuclear complexes have been obtained which contain either the diamagnetic d^4 $\{Mo(NO)\}^{3+}$ center[12,14] or the paramagnetic d^1 $\{Mo(=O)\}^{3+}$ center.[11,15] These compounds are formed in reactions which are subject to kinetic control and, unlike many of the reactions involving polypyridyl ligands, do not constitute self-assembly in the strict sense. However, the differing nature of the bridging ligands and the metal centers offers access to a complementary group of neutral metallomacrocyles which are redox active.

An alternative synthetic approach to metallomacrocyles is provided by the ligand-directed reaction of a preformed functionalized cyclophane with a metal complex. Thus the reaction between tetrahexylcalix[4]resorcinarene and $[Zr(\eta^5\text{-}C_5H_5)_2Me_2]$ affords $[Zr(\eta^5\text{-}C_5H_5)_2\{1,3\text{-}O_2C_6H_2\text{-}4\text{-}CH_2\text{-}\}]_4$.[10] It is also possible to bind metal ions to the periphery of cyclophanes, although in these cases the metal ions are appended to rather than being an integral part of the macrocyclic framework. Thus calixarenes have been found to form complexes with a variety of d- and f-block metal ions.[3b,16] In another approach Puddephatt and co-workers have introduced phosphinate groups into the rim of a calix[4]resorcinarene and then used these donor sites to bind metal ions to the rim to create a cyclophane host with metal-based anion binding sites.[17]

In a similar manner it has proven possible to synthesize redox-active bi-, tri-, and tetranuclear metallomacrocyles from the reaction between $[Mo(NO)(Tp)I_2]$ [Tp^- = hydrotris(pyrazol-1-yl)borate] and the preformed cyclophane tetrahexylcalix[4]-resorcinarene. A preliminary report of this work has appeared elsewhere.[18] In this paper we describe in full the syntheses and characterization of some tri- and tetranuclear metallomacrocyles containing the redox-active $\{Mo(NO)\}^{3+}$ center and synthesized from resorcinol, hydroquinone, or tetrahexylcalix[4]resorcinarene ($resH_8$) proligands. Electrochemical studies of these compounds reveal that the reduction behavior of the macrocycles depends on the number and the geometric arrangement of the redox centers present.

Experimental Section

General Details. All reactions were carried out under an oxygen-free, dry nitrogen atmosphere. Dry, freshly distilled dichloromethane or toluene was used for all reactions. Triethylamine was dried over 4A molecular sieves and activated alumina. The starting materials $[Mo(NO)(Tp)I_2]$ and $[Mo(NO)(Tp^*)I_2]\cdot C_6H_5CH_3$ were prepared by following known procedures.[19] The new compounds were purified by column chromatography using silica gel (Merck; Kiesel gel 60, 70–230 mesh). IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrophotometer from KBr disks. ^1H NMR spectra were recorded using Bruker AC-300 (300 MHz) or AMX-400 (400 MHz) spectrometers. Liquid secondary ion mass spectra (LSIMS) were obtained from a VG Zabspec mass spectrometer utilizing a *m*-nitrobenzyl alcohol matrix.

Cyclic voltammetry was carried out using an EG & G model 174A polarographic analyzer, with ca. 10^{-3} mol·dm^{-3} solutions under dry N_2 in dry solvents. A Pt bead working electrode was used, with 0.2 mol·dm^{-3} $[Bu^n{}_4N][BF_4]$ as supporting electrolyte and a scan rate of 200 mV s^{-1}. Potentials were recorded vs a saturated calomel reference electrode, and ferrocene was added as an internal standard. The data obtained were reproducible, the experimental error being ±10 mV.

Microanalyses were performed by the Microanalytical Laboratory of the University of North London.

Reaction of Tetrahexylcalix[4]resorcinarene with 4 equiv of [Mo(NO)(Tp)I$_2$]. Tetrahexylcalix[4]resorcinarene ($resH_8$) (0.14 g, 0.2 mmol) was added to a round-bottom flask containing toluene (100 mL). Triethylamine (1 cm^3, excess) was added and the mixture heated with stirring until all the resorcinarene had dissolved. $[Mo(NO)(Tp)I_2]$ (0.5 g, 0.74 mmol) was added to this solution and the mixture heated under reflux for 12 h. The reaction mixture was then allowed to cool to room temperature and filtered. Both the solid residue and the filtrate were retained. The solid residue contained the tetrametalated resorcinarene $[\{Mo(NO)(Tp)\}_4(res)]$ together with triethylammonium salts. This material was purified by repeated column chromatography on silica gel using dichloromethane as the eluent. The filtrate was evaporated to dryness in vacuo to give a second crude solid containing the $[\{Mo(NO)(Tp)\}_4(res)]$, $[\{Mo(NO)(Tp)\}_3(resH_2)]$, and $[\{Mo(NO)(Tp)\}_2(resH_4)]$. These were separated by column chromatography on silica gel. The tetranuclear complex, $[\{Mo(NO)(Tp)\}_4(res)]$, was eluted using dichloromethane; the trinuclear complex, $[\{Mo(NO)(Tp)\}_3(resH_2)]$, was then eluted using 5% (v/v) tetrahydrofuran in dichloromethane. Finally the binuclear complex, $[\{Mo(NO)(Tp)\}_2(resH_4)]$, was eluted using 10% (v/v) tetrahydrofuran in dichloromethane.

$[\{Mo(NO)(Tp)\}_4(res)]$: yield 193 mg (42%); 300 MHz ^1H NMR ($CDCl_3$) δ 8.11 (d, 4H, $J = 1.8$ Hz), $C_3N_2H_3$) 8.07 (d, 8H, $J = 1.8$ Hz, $C_3N_2H_3$), 7.9 (s, 4H, C_6H_2), 7.72 (12H, $C_3N_2H_3$), 6.5 (s, 4H, C_6H_2), 6.31 (t, 4H, $J = 1.8$ Hz, $C_3N_2H_3$), 6.21 (t, 8H, $J = 1.8$ Hz, $C_3N_2H_3$), 4.9 (t, 4H, $J = 8$ Hz, CH) 2.4 (multiplet, 8H, $CHCH_2$), 1.3 (32H, CH_2 overlaid), 0.9 (t, 12H, $J = 8$ Hz, CH_3). Anal. Found: C, 48.6; H, 4.89; N, 18.0. Calcd for $C_{88}H_{104}O_{12}B_4Mo_4N_{28}$: C, 48.6; H, 4.8; N, 18.1. (+) LSIMS: *m/z* 2173 (M^+). IR data (KBr disk): 2488 (ν_{BH}), 1708, 1684 (ν_{NO}) cm^{-1}.

$[\{Mo(NO)(Tp)\}_3(resH_2)]$: yield 31 mg (6%); 300 MHz ^1H NMR ($CDCl_3$) δ 8.10 (d, 1H, $J = 1.8$ Hz, $C_3N_2H_3$), 8.08 (d, 2H, $J = 1.8$ Hz, $C_3N_2H_3$), 8.05 (d, 2H, $J = 1.8$ Hz, $C_3N_2H_3$), 8.04 (d, 2H, $J = 1.8$ Hz, $C_3N_2H_3$), 7.87 (s, 2H, C_6H_2), 7.79 (d, 1H, $J = 1.8$ Hz, $C_3N_2H_3$), 7.76

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(s, 2H, C_6H_2), 7.74 (8H, $C_3N_2H_3$ overlaid), 7.65 (d, 2H, $J = 1.8$ Hz, $C_3N_2H_3$), 6.42 (s, 2H, C_6H_2), 6.37 (s, 2H, C_6H_2), 6.30 (t, 4H, $J = 1.8$ Hz, $C_3N_2H_3$), 6.27 (t, 2H, 1.8 Hz, $C_3N_2H_3$), 6.21 (t, 2H, 1.8 Hz, $C_3N_2H_3$), 6.18 (t, 1H 1.8 Hz, $C_3N_2H_3$,), 4.80 (t, 3H, $J = 8$ Hz, C*H*), 4.5 (t, 1H, $J = 8$ Hz, C*H*), 2.4 (8H, CHC*H*$_2$ overlaid), 1.3 (32H, C*H*$_2$ overlaid), 0.9 (12H, C*H*$_3$ overlaid); 300 MHz ^{1}H NMR (acetone-*d*$_6$) δ 8.12−7.92 (22H, $C_3N_2H_3$ and C_6H_2 overlaid), 6.52−6.39 (13H, $C_3N_2H_3$ and C_6H_2 overlaid), 4.94 (t, 1H, $J = 8$ Hz, C*H*), 4.84 (t, 2H, $J = 8$ Hz, C*H*), 4.53 (t, 1H, $J = 8$ Hz, C*H*), 2.8 (8H, HCC*H*$_2$ overlaid), 1.3 (32H, C*H*$_2$ overlaid), 0.9 (12H, C*H*$_3$ overlaid). Anal. Found: C, 51.8; H, 5.44; N, 15.9. Calcd for $C_{79}H_{96}O_{11}B_3Mo_3N_{21}$: C, 51.7; H, 5.27; N, 16.0. (+) LSIMS: *m/z* 1837 (M$^+$). IR data (KBr disk): 2490 (ν_{BH}), 1699, 1683 (ν_{NO}) cm^{-1}.

[{Mo(NO)(Tp)}$_2$(resH$_4$)]: yield 8 mg (2%); 300 MHz ^{1}H NMR (CDCl$_3$) δ 8.05 (d, 4H, $J = 1.8$ Hz, $C_3N_2H_3$), 8.00 (d, 2H, $J = 1.8$ Hz, $C_3N_2H_3$), 7.80 (d, 2H, $J = 1.8$ Hz, $C_3N_2H_3$), 7.76 (d, 4H, $J = 1.8$ Hz, $C_3N_2H_3$), 7.58 (s, 1H, C_6H_2), 7.50 (s, 2H, C_6H_2), 7.44 (s, 1H, C_6H_2), 6.57 (s, 3H, C_6H_2) 6.46 (s, 1H, C_6H_2), 6.35 (t, 2H $J = 1.8$ Hz, $C_3N_2H_3$,), 6.32 (t, 2H, $J = 1.8$ Hz, $C_3N_2H_3$), 6.27 (t, 2H, $J = 1.8$ Hz, $C_3N_2H_3$), 4.75 (t, 2H, $J = 8$ Hz, C*H*), 4.32 (t, 2H, $J = 8$ Hz, C*H*), 2.30 (8H, CHC*H*$_2$ overlaid), 1.35 (32H, C*H*$_2$ overlaid), 0.8 (12H, C*H*$_3$ overlaid); 300 MHz ^{1}H NMR (acetone-*d*$_6$) δ 8.11 (d, 2H, $J = 1.8$ Hz, $C_3N_2H_3$), 8.10 (pseudo triplet, 4H, $C_3N_2H_3$), 8.07 (d, 2H, $J = 1.8$ Hz, $C_3N_2H_3$), 8.02 (d, 2H, $J = 1.8$ Hz, $C_3N_2H_3$) 7.97 (3H, $C_3N_2H_3$ and C_6H_2 overlaid), 7.94 (s, 2H, C_6H_2), 7.90 (s, 1H, C_6H_2), 6.58 (t, 2H, $J = 1.8$ Hz, $C_3N_2H_3$), 6.49 (4H, $C_3N_2H_3$ and C_6H_2 overlaid), 6.44 (3H, $C_3N_2H_3$ and C_6H_2 overlaid), 6.25 (s, 1H, C_6H_2), 4.80 (t, 2H, $J = 8$ Hz, C*H*), 4.46 (t, 2H, $J = 8$ Hz, C*H*), 2.40 (8H, CHC*H*$_2$ overlaid), 1.3 (32H, C*H*$_2$ overlaid), 0.9 (12H, C*H*$_3$ overlaid). Anal. Found: C, 55.9; H, 6.06; N, 13.0. Calcd for $C_{70}H_{88}O_{10}B_2Mo_2N_{14}$: C, 56.1; H, 5.92; N, 13.1. (+) LSIMS: *m/z* 1499 (M$^+$). IR data (KBr disk): 2492 (ν_{BH}), 1691, 1678 (ν_{NO}) cm^{-1}.

Preparation of *anti,syn*-[Mo(NO)(Tp*)(1,3-O$_2$C$_6$H$_4$)]$_3$ and *anti,syn,syn*-[Mo(NO)(Tp*)(1,3-O$_2$C$_6$H$_4$)]$_4$. To a solution of [{Mo(NO)(Tp*)I}$_2$(1,3-O$_2$C$_6$H$_4$)] (1.00 g, 0.828 mmol) in dry toluene (100 cm^3) was added NEt$_3$ (1.0 cm^3) and 1,3-dihydroxybenzene (96 mg, 0.828 mmol) and the mixture heated under reflux for 18 h. The dark brown solution was allowed to cool to room temperature and filtered, and the filtrate was evaporated to dryness in vacuo. The residue was purified by column chromatography on silica gel using a mixture of dichloromethane and *n*-hexane (4:1 v/v) as the initial eluant. The first dark brown fraction ($R_f = 0.76$) to elute was collected and found to contain the cyclic tetramer, *anti,syn,syn*-[Mo(NO)(Tp*)(1,3-O$_2$C$_6$H$_4$)]$_4$. Further elution using a mixture of dichloromethane and *n*-hexane (5:1 v/v) afforded a second major dark red/brown fraction ($R_f = 0.20$) which was found to contain the cyclic trimer, *anti,syn*-[Mo(NO)(Tp*)(1,3-O$_2$C$_6$H$_4$)]$_3$.

***anti,syn*-[Mo(NO)(Tp*)(1,3-O$_2$C$_6$H$_4$)]$_3$** (169 mg, 38%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34, 7.18, 6.77, 6.64, 6.02, 6.00, 5.24 (1H, t, $^4J = 2$; 2H, t, $^4J = 2$; 1H, t, $^3J = 8$; 2H, t, $^3J = 8$; 2H, dd, $^3J = 8$, $^4J = 2$; 2H, dd, $^3J = 8$, $^4J = 2$; 2H, dd, $^3J = 8$, $^4J = 2$ Hz, $C_6H_4O_2$), 5.79, 5.77, 5.70, 5.62, 5.50 (2H, s; 2H, s; 2H, s; 1H, s; 2H, s Me$_2$C$_3$*H*N$_2$), 2.40, 2.38, 2.34, 2.33, 2.32, 2.19, 2.14, 1.95 [6H, s; 6H, s; 6H, s; 15H, s; 6H, s; 3H, s; 6H, s; 6H, s (C*H*$_3$)$_2$C$_3$HN$_2$]. Anal. Found: C, 47.5; H, 5.03; N, 18.8. Calcd for $C_{63}H_{78}B_3N_{21}O_9Mo_3$: C, 47.5; H, 4.93; N, 18.5. (+) LSIMS: *m/z* 1595 (M$^+$). IR data (KBr disk): 2545 w (ν_{BH}), 1665 s (ν_{NO}) cm^{-1}.

***anti,syn,syn*-[Mo(NO)(Tp*)(1,3-O$_2$C$_6$H$_4$)]$_4$** (75 mg, 9%): ^{1}H NMR (400 MHz, CDCl$_3$ 298 K) δ 7.02, 6.92, 6.85, 6.70, 6.62, 6.38, 6.15 (2H, br; 2H, s; 2H, t, $J = 8$; 4H, br; 2H, t, $J = 8$; 2H, d, $J = 7$ Hz; 2H, br $C_6H_4O_2$), 5.83, 5.80, 5.77, 5.67, 5.62, 5.60 (2H, s; 4H, s; 2H, s; 1H, s; 2H, s; 1H, s Me$_2$C$_3$*H*N$_2$), 2.39, 2.38, 2.37, 2.35, 2.34, 2.33, 2.24, 2.19, 2.09, 2.03 [24H, s; 15H, s; 6H, s; 3H, s; 6H, s; 6H, s; 6H, s; 3H, s; 3H, s; 6H, s (C*H*$_3$)$_2$C$_3$HN$_2$]. Anal. Found: C, 49.5; H, 5.5; N, 18.1. Calcd for $C_{84}H_{104}B_2N_{28}O_{12}Mo_4.C_6H_{14}$: C, 48.9; H, 5.34; N, 17.7. LSIMS: *m/z* 2126 (M$^+$). IR data (KBr disk): 2543 w (ν_{BH}), 1663 s (ν_{NO}) cm^{-1}.

Preparation of [Mo(NO)(Tp*)(1,4-O$_2$C$_6$H$_4$)]$_3$ and [Mo(NO)(Tp*)(1,4-O$_2$C$_6$H$_4$)]$_4$. To a solution of [Mo(NO)(Tp*)I$_2$]$\cdot$C$_6$H$_5$CH$_3$ (1.00 g, 1.30 mmol) in dry toluene (100 cm^3) was added NEt$_3$ (1.0 cm^3) and 1,4-dihydroxybenzene (114 mg, 1.31 mmol) and the mixture heated under reflux for 18 h. The dark brown solution was allowed to cool to room temperature and filtered to remove HNEt$_3$I. The filtrate was evaporated to dryness in vacuo and the residue purified by column chromatography on silica gel using a mixture of dichloromethane and *n*-hexane (1:1 v/v) as the eluant. The first major purple fraction to elute was collected and found to contain a mixture of cyclic trimer and cyclic tetramer (160 mg; approximate ratio 3:2 trimer/tetramer). Further repeated column chromatography afforded samples of two isomers of the cyclic trimer eluted with dichloromethane and *n*-hexane 1:1 v/v [$R_f = 0.32$ (*syn, syn*) and 0.08 (*anti*, *syn*)] and of an isomer of the cyclic tetramer eluted with dichloromethane and *n*-hexane 3:2 v/v ($R_f = 0.27$). These compounds were further purified by recrystallization from dichloromethane/*n*-hexane.

***syn,syn*-[Mo(NO)(Tp*)(1,4-O$_2$C$_6$H$_4$)]$_3$:** yield 330 mg (48%); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 306 K) δ 7.56 (12H, s), 5.90, 5.81 (2H, s; 1H, s Me$_2$C$_3$*H*N$_2$), 2.40, 2.41, 2.28 (27H, s; 18H, s; 9H, s (C*H*$_3$)$_2$C$_3$HN$_2$}. Anal. Found: C, 47.4; H, 4.91; N, 18.3. Calcd for $C_{63}H_{78}B_3N_{21}O_9Mo_3$: C, 47.5; H, 4.93; N, 18.5. (+) LSIMS: *m/z* 1594 (M$^+$). IR data (KBr disk): 2544 w (ν_{BH}); 1657 s (ν_{NO}) cm^{-1}.

***anti,syn*-[Mo(NO)(Tp*)(1,4-O$_2$C$_6$H$_4$)]$_3$:** yield 15 mg (2%); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) δ 7.34, 7.15, 7.00 (4H, s, 4H, d, $^3J = 9$; 4H, d, $^3J = 9$ Hz $C_6H_4O_2$), 5.97, 5.86, 5.85, 5.84, 5.82 (2H, s; 2H, s; 2H, s; 1H, s; 2H, s Me$_2$C$_3$*H*N$_2$), 2.53, 2.44, 2.42, 2.40, 2.39, 2.34, 2.27, 2.25, 2.20 {6H, s; 9H, s; 6H, s; 6H, s; 6H, s; 3H, s; 6H, s; 6H, s, 6H, s (C*H*$_3$)$_2$C$_3$HN$_2$}. Anal. Found: C, 47.7; H, 5.05; N, 18.2. Calcd for $C_{63}H_{78}B_3N_{21}O_9Mo_3$: C, 47.5; H, 4.93; N, 18.5. (+) LSIMS: *m/z* 1593 (M$^+$ − 1). IR data (KBr disk): 2549 w (ν_{BH}); 1665 s, 1652 s (ν_{NO}) cm^{-1}.

[Mo(NO)(Tp*)(1,4-O$_2$C$_6$H$_4$)]$_4$: yield 130 mg (19%); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$ 298 K) δ 7.35 (16H, s), 5.87, 5.80 (8H, s; 4H, s Me$_2$C$_3$*H*N$_2$), 2.44, 2.40, 2.21, 2.19 (12H, s; 24H, s; 12H, s, 24H, s (C*H*$_3$)$_2$C$_3$HN$_2$}. Anal. Found: C, 47.8; H, 4.64; N, 18.6. Calcd for $C_{84}H_{104}B_2N_{28}O_{12}Mo_4$: C, 47.5; H, 4.93; N, 18.5. LSIMS: *m/z* 2126 (M$^+$). IR data (KBr disk): 2543 w (ν_{BH}); 1662 s (ν_{NO}) cm^{-1}.

Preparation of *anti,syn*-[W(NO)(Tp*)(1,4-O$_2$C$_6$H$_4$)]$_3$. To a solution of [W(NO)(Tp*)I$_2$] (1.00 g, 1.31 mmol) in dry toluene (100 cm^3) was added NEt$_3$ (1.0 cm^3) and 1,4-dihydroxybenzene (114 mg, 1.31 mmol) and the mixture heated under reflux for 18 h. The dark brown solution was allowed to cool to room temperature and filtered to remove a dark brown solid byproduct. The filtrate was evaporated to dryness in vacuo and the residue purified by column chromatography on silica gel using a mixture of dichloromethane and *n*-hexane (4:1 v/v) as the eluant. The first major dark brown fraction ($R_f = 0.47$) to elute was collected, the solvent was removed in vacuo, and the product was obtained as dark brown crystals by recrystallization from dichloromethane/*n*-hexane: yield 86 mg (11%); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 193 K) δ 7.96, 7.01, 6.85, 6.68 (2H, s; 4H, d, $^3J = 8$; 4H, d, $^3J = 8$ Hz; 2H, s C_6H_4), 5.98, 5.91, 5.89, 5.86, 5,85 (2H, s; 1H, s; 2H, s; 2H, s; 2H, s Me$_2$C*H*N$_2$) 2.52, 2.35, 2.30, 2.29, 2.25, 2.23 [6H, s; 15H, s; 15H, s; 6H, s; 6H, s; 6H, s;(C*H*$_3$)$_2$C$_3$HN$_2$]. Anal. Found: C, 40.7; H, 4.29; N, 15.5. Calcd for $C_{63}H_{78}B_3N_{21}O_9W_3$: C, 40.7; H, 4.23; N, 15.3. (+) LSIMS: *m/z* 1857 (M$^+$). IR data (KBr disk): 2551 w (ν_{BH}); 1629 s (ν_{NO}) cm^{-1}.

Structure Determination. X-ray data were collected on a Rigaku R-axis II area-detector diffractometer at 293(2) K using graphite-monochromated Mo Kα radiation. Owing to the poor diffracting power of the crystal, only relatively low-angle data could be obtained. The structure was determined by direct methods[20] and refined[21] on F^2 by full-matrix least squares with anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters. Crystallographic and refinement data are listed in Table 1. Figures depicting the structure were prepared using ORTEP,[22] the thermal ellipsoids being drawn at the 30% probability level.

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(20) *TeXsan. Single-Crystal Structure Analysis Software*, version 1.6; Molecular Structure Corp.: 3200 Research Forest Drive, TX 77381, 1993.

(21) Sheldrick, G. M. *SHELXL-93, Program for Crystal Structure Refinement*; University of Gottingen: Gottingen, Germany, 1993.

(22) Johnson, C. K. *ORTEP*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 1. Crystallographic Data

formula	$C_{63}H_{78}N_{21}B_3Mo_3O_9$	fw	1593.7
a, Å	16.269(10)	ρ_{calc}, g cm^{-3}	1.158
b, Å	35.31(3)	μ(Mo Kα), cm^{-1}	4.59
c, Å	16.056(10)	θ range for data, deg	1.4−19.4
β, deg	97.59(2)	unique reflcns	7490
V, Å^3	9143	obsd refls [$I > 2\sigma(I)$]	4638
Z	4	$R(F_o)^a$ (obsd refls)	0.0743
λ, Å	0.710	$R_w(F_o)^{b,c}$ (all data)	0.2307
space grp	$P2_1/a$	lgst diff peak, e Å^{-3}	0.768
T, °C	20	lgst diff hole, e Å^{-3}	−0.348

[a] $R(F_o) = \Sigma(|F_o - F_c|)/\Sigma F_o$. [b] $R_w(F_o) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (0.127P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

Atomic coordinates and displacement parameters and full listings of bond lengths and angles have been deposited at the Cambridge Crystallographic Datacenter.

Results and Discussion

Synthetic Studies. The reaction between [Mo(NO)(Tp*)I_2] and the preformed cyclophane template tetrahexylcalix[4]-resorcinarene (resH_8) in the presence of triethylamine affords a mixture containing tetra-, tri-, bi-, and monometalated derivatives which were identified by LSIMS measurements on the crude reaction product. ^{1}H NMR studies showed signals attributable to these compunds but attempts to purify the crude product mixture by column chromatography were unsuccessful as the complexes decompose rapidly on contact with silica gel or other stationary phases. Since the Tp* ligand is sterically demanding in the region occupied by the coordinated resorcinarene ligand, and this may contribute to the low stability of the products obtained, reactions involving the less sterically demanding ligands C_5H_5 and Tp were investigated. The reaction of resH_8 with [Mo(NO)(η^5-C_5H_5)I_2]$_2$ afforded only insoluble products, the mass spectra of which contained no ions attributable to metallocyclophanes. However, reactions with [Mo(NO)(Tp)I_2] were more successful and the mass spectra of the crude reaction products again indicated the presence of the mono-, bi-, tri-, and tetrametalated resorcinarenes (Figure 1). In this case the products proved sufficiently stable to allow separation by repeated column chromatography and the bi-, tri-, and tetrametalated resorcinarenes were obtained in respective yields of 2%, 6%, and 42%. It has not been possible to isolate the monometalated resorcinarene in pure form. The structure of [{Mo(NO)(Tp)}$_4$(res)], in the form of its dichloromethane solvate, has been confirmed by a single-crystal X-ray diffraction study, which has been described in an earlier communication.[18] Attempts were made to improve the yields of the various products by altering the stoichiometry of the reaction, the base/halogen abstractor, and the reaction temperature, but the yields and distribution of the products showed little change.

The LSIMS mass spectrum of [{Mo(NO)(Tp)}$_4$(res)] contains a molecular ion based at m/z 2173, and an accurate mass determination confirmed the elemental composition for this formulation. A second ion at m/z 2305 is also observed and may be assigned to {[{Mo(NO)(Tp)}$_4$(res)]Cs}$^+$, the Cs arising from the atom beam used in the mass spectrometer. Attempts to demonstrate Cs$^+$ inclusion in [{Mo(NO)(Tp)}$_4$(res)] by ^{1}H NMR studies have been unsuccessful, but after treatment with K$^+$ salts, the LSIMS spectrum of [{Mo(NO)(Tp)}$_4$(res)] contains an ion at m/z 2205 attributable to {[{Mo(NO)(Tp)}$_4$(res)]K}$^+$, suggesting that the metallocyclophane has some capacity to bind alkali metal ions. However, single-crystal X-ray studies of [{Mo(NO)(Tp)}$_4$(res)] crystallized in the presence of a potassium salt indicated that the K$^+$ ions were not included in the cavity of the metallomacrocycle and further attempts to demonstrate the inclusion of metal ions have proved unsuccessful.

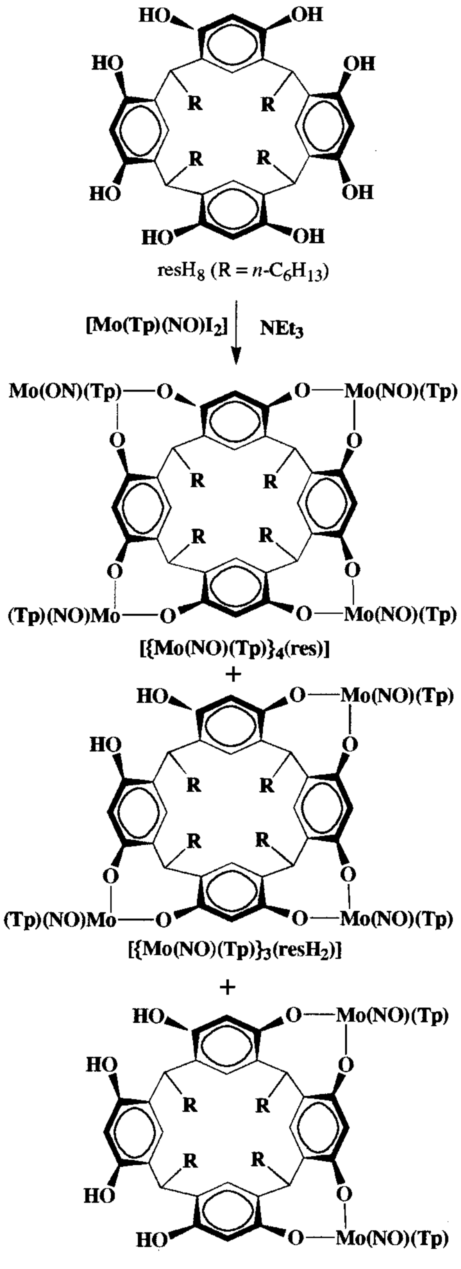

Figure 1. Formation of metallocyclophanes from [Mo(NO)(Tp)I_2] and resH_8.

The solid-state (KBr disk) IR spectrum of unsolvated [{Mo(NO)(Tp)}$_4$(res)] contains two nitrosyl stretching vibrations at 1708 and 1684 cm^{-1}. This is consistent with the findings of a crystallographic study[18] which shows that two of the nitrosyl groups point into the cavity of the resorcinarene and the other two point out of the cavity. The unsually high values of nitrosyl stretching vibrations, compared to [Mo(NO)(Tp*)(OPh)$_2$], for which ν_{NO} = 1655 cm^{-1},[23] may be attributable to poor orbital overlap between the {Mo(NO)(Tp)}$^{2+}$ centers and the filled p-orbitals on the oxygen donor atoms of the resorcinarene ligand.

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(23) (a) AlObaidi, N.; Chaudhury, M.; Clague, D.; Jones, C. J.; Pearson, J. C.; McCleverty, J. A.; Salam, S. S. *J. Chem. Soc., Dalton Trans.* **1987**, 1733−1736. (b) Jones, C. J.; McCleverty, J. A. Neaves, B. D.; Reynolds, S. J.; Adams, H.; Bailey, N. A.; Denti, G. *J. Chem. Soc., Dalton Trans.* **1986**, 733−741.

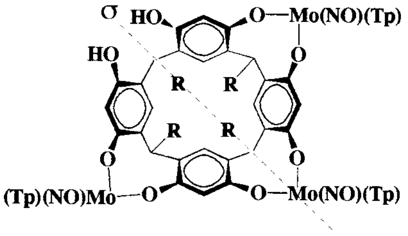
If the (O)N$-$Mo$-$O$-$C(res) torsion angle does not allow optimum overlap between the empty d_{xy} orbital on Mo and the filled p-orbitals of the coordinated oxygen $Op_\pi \rightarrow Mod_\pi$ donation will be restricted.[24] This will reduce electron density on Mo and result in a hypsochromic shift in ν_{NO} compared to the situation in [Mo(NO)(Tp*)(OPh)$_2$], where the orientations of the aryl groups are not constrained by their being part of a macrocyclic ring.

The 4-fold symmetry of the resorcinarene ligand renders the four {Mo(NO)(Tp)}$^{2+}$ centers in [{Mo(NO)(Tp)}$_4$(res)] equivalent in solution on the NMR time scale, although this symmetry is not retained in the solid state. Thus the pyrazole C^4 protons appear as two triplets of relative area 8:4 and the pyrazole C^3 and C^{5}protons should appear as four doublets of relative areas 4:8:4:8 but signal overlap leads to a 12:4:8 pattern. The resorcinarene protons give rise to signals similar in appearance to those of free resH$_8$ but with some small changes in chemical shifts.

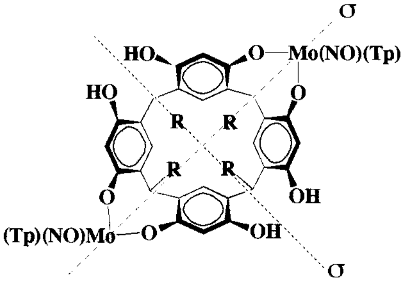
The LSIMS spectrum of the trinuclear complex [{Mo(NO)(Tp)}$_3$(resH$_2$)] contains a molecular ion at *m*/*z* 1837, and as found with the tetranuclear complex, an ion assigned to the Cs$^+$ adduct is present, in this case at *m*/*z* 1967. The IR spectrum contains bands at 1699 and 1683 cm^{-1} attributable to ν_{max}(NO), indicating the presence of two nitrosyl environments in the molecule. The small bathochromic shift of the nitrosyl stretching frequencies with respect to those of [{Mo(NO)(Tp)}$_4$(res)] may indicate some improvement in orbital overlap between the {Mo(NO)(Tp)}$^{2+}$ centers and the oxygen atoms of the resorcinarene, in keeping with the macrocycle becoming more flexible in the absence of one {Mo(NO)(Tp)}$^{2+}$ unit.

The ^{1}H NMR spectrum of [{Mo(NO)(Tp)}$_3$(resH$_2$)] is more complex than that of its tetranuclear counterpart due to its lower symmetry. The central {Mo(NO)(Tp)} moiety is bisected by a plane of symmetry whereas the outer two {Mo(NO)(Tp)} moieties do not contain a plane of symmetry but are related by one (Figure 2). Thus for the tri-metallic species the signals due to the pyrazole C^3 and C^5 protons should appear as 10 doublets of relative areas 2:2:2:2:2:2:2:2:1:1 and those due to the pyrazole C^4 protons should comprise five pseudotriplets of relative areas 2:2:2:2:1. The aryl protons of the resorcinarene ligand should appear as four singlets of relative areas 2:2:2:2 and the methylene bridge protons as three triplets of relative areas 2:1:1. The observed 300 MHz ^{1}H NMR (CDCl$_3$) is in accord with these expectations although there is some signal overlap. The ^{1}H NMR spectrum of an acetone-d_6 solution of [{Mo(NO)(Tp)}$_3$(resH$_2$)] shows significant shifting of both the pyrazole and the resorcinarene aryl proton signals compared to the spectrum obtained in CDCl$_3$. Thus two groups of overlapping signals are observed in the regions 8.12$-$7.97 and 6.52$-$6.39 ppm, which correspond to the pyrazolyl protons and to the resorcinarene aryl protons. The methylene bridge protons become resolved to give three triplets of relative area 1:2:1, but the remaining resorcinarene signals are essentially unshifted.

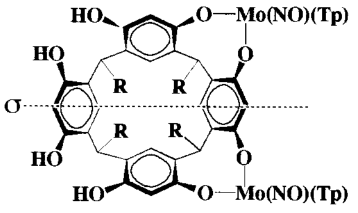
The LSIMS spectrum of the binuclear complex [{Mo(NO)(Tp)}$_2$(resH$_4$)] contains a molecular ion based at *m*/*z* 1499, and as with the other complexes, an ion due to a Cs$^+$ adduct is seen at *m*/*z* 1631. Two nitrosyl stretching frequencies are observed in the solid-state IR spectrum of this compound, indicating the presence of two NO environments, and both frequencies are bathochromically shifted with respect to the tri- and tetranuclear species. There are two possible isomers of [{Mo(NO)(Tp)}$_2$(resH$_4$)] depending on the relative positions of the {Mo(NO)(Tp)}$^{2+}$ groups within the resorcinarene ring (Figure 2). The metal centers can occupy adjacent (cis) or opposed (trans) sites within the resorcinarene ring. If the metal atoms were in "trans" positions only one NO environment would be expected. However, on the basis of the solid-state structure of [{Mo(NO)(Tp)}$_4$(res)], a cis-arrangement should lead to two NO environments as adjacent Mo centers are not equivalent.



[{Mo(NO)(Tp)}$_3$(resH$_2$)]



***trans*-[{Mo(NO)(Tp)}$_2$(resH$_4$)]**



***cis*-[{Mo(NO)(Tp)}$_2$(resH$_4$)]**

Figure 2. Symmetry planes in [{Mo(NO)(Tp)}$_3$(resH$_2$)] and [{Mo(NO)(Tp)}$_2$(resH$_4$)].)

The formulation of [{Mo(NO)(Tp)}$_2$(resH$_4$)] as the cis-isomer is in accord with the observed ^{1}H NMR spectrum. If the two metal atoms are in cis-positions the two {Mo(NO)(Tp)}$^{2+}$ groups are related by a plane of symmetry, but neither contains a plane of symmetry. Thus the pyrazolyl C^4 protons should appear as three triplets of relative areas 2:2:2 and the pyrazolyl C^3 and C^5 protons should appear as six doublets of relative areas 2:2:2:2:2:2. The resorcinarene aryl protons should appear as six singlets of relative areas 1:2:1:1:2:1, and the methylene protons would appear as two triplets of relative areas 2:2 (Figure 2). If the two metal atoms are in trans-positions the two {Mo(NO)(Tp)}$^{2+}$ groups are again related by a plane of symmetry, but in this case, both also contain a plane of symmetry. Thus the pyrazolyl C^4 protons should appear as two triplets of relative areas 2:4 and the pyrazolyl C^3 and C^5 protons should appear as four doublets of relative areas 2:2:4:4. The resorcinarene aryl protons should appear as two singlets of relative areas 4:4, and the methylene protons would appear as two triplets of relative areas 2:2. The spectrum measured fron a CDCl$_3$ solution contains three triplets of relative areas 2:2:2 attributable to the pyrazolyl C^4 protons and in accord with the cis-structure. The pyrazolyl C^3 and C^5 protons give rise to four doublets of relative areas 4:2:2:4 due to signal overlap. The resorcinarene signals

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(24) Ashby, M. T.; Enemark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 730$-$733.

appear as expected except for the upper rim aryl protons which overlap to give two singlets of relative areas 3:1. In acetone-d_6 the pyrazole and resorcinarene aryl protons are shifted and signal overlap reduced. Thus the pyrazolyl proton signals become more clearly resolved and the pyrazolyl C^3 and C^5 protons protons give rise to five signals comprising three doublets of relative area 2, two partially overlapped doublets of relative area 4, and one further signal comprising a doublet overlaid with one of the resorcinarene singlets to give a signal of total relative area 3. Two further signals of relative areas 2:1 arise from the three remaining lower rim aryl resorcinarene protons. The pyrazolyl C^4 protons give rise to three signals, but only one of these is fully resolved as the other two overlap with resorcinarene protons. The remaining resorcinarene protons appear as expected for the cis-isomer.

Macrocycles containing resorcinol units can also be constructed by metal-directed synthesis reactions involving [Mo(NO)(Tp*)I_2] and resorcinol itself. Thus the direct reaction between [Mo(NO)(Tp*)I_2] and resorcinol affords a mixture of cyclic oligomers of formula [Mo(NO)(Tp*)(1,3-$O_2C_6H_4$)]$_n$ ($n = 2-4$). The cyclic dimer ($n = 2$) will be described in detail elsewhere, and the synthetic procedure described here offers an improved route to the cyclic trimer and tetramer by using the binuclear precursor [{Mo(NO)(Tp*)I}$_2$(1,3-$O_2C_6H_4$)] in place of the mononuclear diiodide complex. This reaction again affords a mixture of cyclic oligomers, but fewer byproducts are formed and separation of the cyclic trimer and tetramer by repeated column chromatography is facilitated (Figure 3). It is notable that a similar reaction involving the sterically less demanding Tp ligand in place of Tp* failed to produce any metallomacrocycles. This may be attributed to the need to stabilize the coordinatively unsaturated formally 16-electron Mo center in the {Mo(NO)(Tp*)(OAr)$_2$} group. While Tp* is effective in this respect, Tp apparently is not unless another sterically demanding coligand, such as the resorcinarene, is present.[25] Two isomers of the cyclic trimer are possible (Figure 4), and on statistical grounds, it might be expected that *syn,anti*-[Mo(NO)(Tp*)(1,3-$O_2C_6H_4$)]$_3$ would form in 3-fold excess over *syn,syn*-[Mo(NO)(Tp*)(1,3-$O_2C_6H_4$)]$_3$ if the reaction is nonstereoselective. In the case of the cyclic tetramer four isomers are possible (Figure 4) and, again assuming no stereoselectivity, the *syn,syn,syn*-, *syn,syn,anti*-, *anti,syn,anti*- and *anti,anti,anti*-isomers might be expected to form in the respective ratio 1:4:4:1. Chromatographic separation of the reaction products afforded a single isomer of the cyclic trimer and a single isomer of the cyclic tetramer. The other isomers may be present in the product mixture but could not be separated from other products and isolated in a pure form.

The LSIMS spectrum of the purified trinuclear complex, Mo(NO)(Tp*)(1,3-$O_2C_6H_4$)]$_3$, contains a molecular ion based at *m*/*z* 1595 with no significant ion intensity present at *m*/*z* values associated with the cyclic dimer or tetramer. Weak ions (ca. 5% relative intensity; *cf. m*/*z* 1595) are also present at *m*/*z* 1565, $(M - NO)^+$, and 1499, $(M - Me_2C_3HN_2H)^+$. The IR spectrum (KBr disk) of this compound contains a single strong broad absorption attributable to ν_{NO} at 1665 cm^{-1}. The ^{1}H NMR spectrum allows the isomeric structure of the compound to be defined (Figures 4 and 5). In *syn,syn*-[Mo(NO)(Tp*)(1,3-$O_2C_6H_4$)]$_3$ the three{Mo(NO)(Tp*)}$^{2+}$ groups are equivalent and each is bisected by a plane of symmetry so that the pyrazolyl C^4 protons should give rise to two signals in the area ratio 3:6. Similarly the pyrazolyl methyl protons should appear as four signals in the area ratio 9:9:18:18. The observed spectrum is more complex than this indicating that the *anti,syn*-isomer has been isolated. In this case only one of the {Mo(NO)(Tp*)}$^{2+}$ groups is bisected by the plane of symmetry in the molecule so that its pyrazolyl C^4 protons should give rise to two signals in the area ratio 2:1. The other two {Mo(NO)(Tp*)}$^{2+}$ groups are related by the plane of symmetry, and as the three pyrazolyl C^4 protons in each are not symmetry related, three signals of relative area 2:2:2 should arise. Thus overall the pyrazolyl C^4 protons of the *anti,syn*-isomer should give rise to five signals in the area ratio 2:2:2:2:1 as actually observed. Similar reasoning suggests that the pyrazolyl C^3 and C^5 methyl protons should give rise to 10 signals in the area ratio 3:3:6:6:6:6:6:6:6:6. Again this pattern is present although there is some signal overlap. The aryl protons of the resorcinol bridging ligands also conform to the expected pattern for the *anti,syn*-isomer.

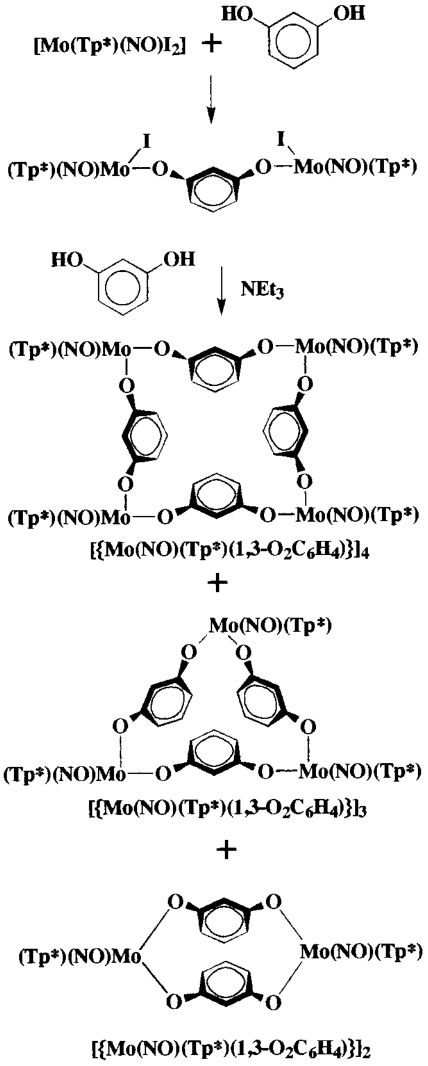

Figure 3. Formation of metallocyclophanes from [Mo(NO)(Tp*)I_2] and 1,3-$(HO)_2C_6H_4$.

The LSIMS spectrum of the purified tetranuclear complex, [Mo(NO)(Tp*)(1,3-$O_2C_6H_4$)]$_4$, contains a molecular ion based at *m*/*z* 2126 together with weak ions (ca. 8% relative intensity; *cf. m*/*z* 2126) at *m*/*z* 2096 and 2030 attributable to $(M - NO)^+$ and $(M - Me_2C_3HN_2H)^+$, respectively. Ion intensity at *m*/*z* 1995 associated with the cyclic trimer was 5% or less of that at *m*/*z* 2126, and there is no detectable ion intensity attributable to the cyclic dimer. The IR spectrum (KBr disk) of this compound contains a single strong broad absorption attributable to ν_{NO} at 1663 cm^{-1}. Once again the ^{1}H NMR spectrum may

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(25) Jones, H. A.; Jones C. J. Unpublished results.

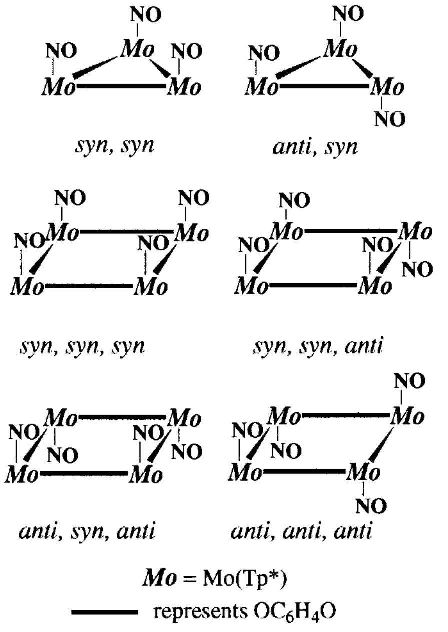

Figure 4. Schematic illustration of the isomers of [Mo(NO)(Tp*)-$(O_2C_6H_4)]_n$ ($n = 3, 4$).

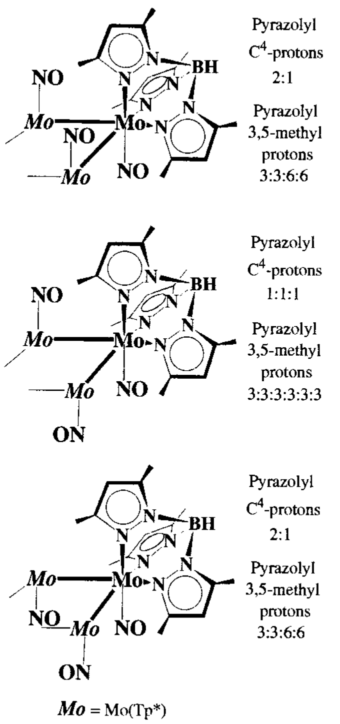

Figure 5. Schematic view of the local environment of the Tp* ligand in $[Mo(NO)(Tp^*)(O_2C_6H_4)]_n$ ($n = 3, 4$) to show effect of isomerism on the ^1H NMR signals of the Tp* protons.

be used to determine the isomeric structure of the compound. In *syn,syn,syn*-$[Mo(NO)(Tp^*)(1,3\text{-}O_2C_6H_4)]_4$ and in *anti,anti, anti*-$[Mo(NO)(Tp^*)(1,3\text{-}O_2C_6H_4)]_4$ the four $\{Mo(NO)(Tp^*)\}^{2+}$ groups are equivalent and each is bisected by a plane of symmetry (Figures 4 and 5) so that the pyrazolyl C^4 protons should give rise to two signals in the area ratio 4:8. The pyrazolyl methyl protons should appear as four signals in the area ratio 12:12:24:24. In *anti,syn,anti*-$[Mo(NO)(Tp^*)(1,3\text{-}O_2C_6H_4)]_4$ the four $\{Mo(NO)(Tp^*)\}^{2+}$ groups are also equivalent, but in this case they are not bisected by a plane of symmetry (Figure 4) so that the pyrazolyl C^4 protons should give rise to three signals in the area ratio 4:4:4. The pyrazolyl methyl protons should appear as six signals in the area ratio 12:12:12:12:12:12. The observed spectrum is not in accord with any of these expectations but suggests a structure of lower symmetry as present in *anti,syn,syn*-$[Mo(NO)(Tp^*)(1,3\text{-}O_2C_6H_4)]_4$. In this isomer two $\{Mo(NO)(Tp^*)\}^{2+}$ groups are equivalent and related by a plane of symmetry (Figure 4) but are not bisected by a plane of symmetry so that the pyrazolyl C^4 protons should give rise to three signals in the area ratio 2:2:2. The pyrazolyl methyl protons should appear as six signals in the area ratio 6:6:6:6:6:6. The remaining two $\{Mo(NO)(Tp^*)\}^{2+}$ groups are inequivalent, but each is bisected by a plane of symmetry so that the pyrazolyl C^4 protons should give rise to four signals in the area ratio 2:1:2:1 and the pyrazolyl methyl protons should give rise to eight signals in the area ratio 3:3:6:6:3:3:6:6. Taken overall, the ^1H NMR spectrum should thus contain 7 signals in the area ratio 2:2:2:2:2:1:1 due to the pyrazolyl C^4 protons and 14 signals in the area ratio 6:6:6:6:6:6:6:6:6:6:3:3:3:3 due to the pyrazolyl methyl protons. The observed spectrum conforms to this this pattern although there is some signal overlap, most particularly in the methyl region. On this basis the cyclic tetramer obtained in an isomerically pure form is assigned the structure *anti,syn,syn*-$[Mo(NO)(Tp^*)(1,3\text{-}O_2C_6H_4)]_4$. The structure is dynamic on the NMR time scale, and although the resonances due to the Tp* ligands are well resolved, the resonances due to the aryl protons are broadened and not fully resolved. Unfortunately, due to solubility and solvent property limitations, an activation energy barrier could not be reliably measured.

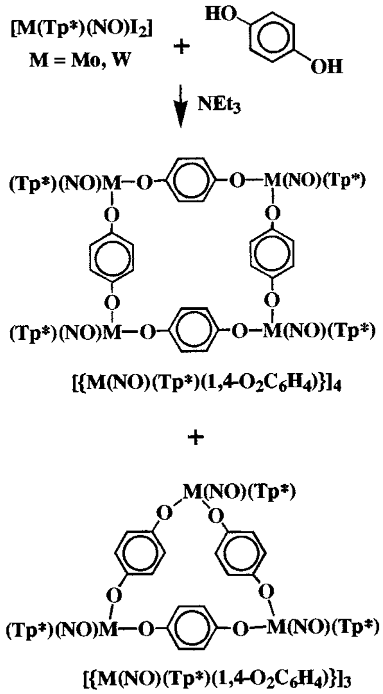

Figure 6. Formation of metallocyclophanes from $[Mo(NO)(Tp^*)I_2]$ and $1,4\text{-}(HO)_2C_6H_4$.

Metallocyclophanes can also be constructed in reactions involving $[M(NO)(Tp^*)I_2]$ (M = Mo, W) and 1,4-dihydroxybenzene. LSIMS measurements indicate that, in this case, cyclic dimers are not significant reaction products but cyclic trimers and tetramers of formula $[M(NO)(Tp^*)(1,4\text{-}O_2C_6H_4)]_n$ ($n = 3$, 4) are present (Figure 6). Repeated column chromatography allowed pure single isomers of the cyclic trimers *syn,syn*-$[Mo(NO)(Tp^*)(1,4\text{-}O_2C_6H_4)]_3$ and *anti,syn*-$[M(NO)(Tp^*)(1,4\text{-}O_2C_6H_4)]_3$ (M = Mo, W) to be obtained. Cyclic tetramers were also present but, with the exception of one isomerically pure sample of $[Mo(NO)(Tp^*)(1,4\text{-}O_2C_6H_4)]_4$, pure tetramer isomers could not be fully separated from the other products and cyclic trimer. The reaction between $[W(NO)(Tp^*)I_2]$ and 1,4-dihydroxybenzene also produced toluene-insoluble byproducts. The LSIMS spectra of these materials contained ions at *m*/*z* 1348, 1967, 1984, and 2586 attributed respectively to the presence of the acyclic polynuclear species $[\{W(NO)(Tp^*)(1,4\text{-}OC_6H_4OH)\}_2(\mu\text{-}1,4\text{-}O_2C_6H_4)]$, $[\{W(NO)(Tp^*)(1,4\text{-}OC_6H_4OH)(\mu\text{-}1,4\text{-}O_2C_6H_4)\}_2W]$, and $[\{W(NO)(Tp^*)(1,4\text{-}OC_6H_4OH)(\mu\text{-}1,4\text{-}O_2C_6H_4O)W(NO)(Tp^*)\}_2(\mu\text{-}1,4\text{-}O_2C_6H_4)]$. In each case ions attributable to $\{M - 1,4\text{-}OC_6H_4OH\}^+$ were also present. In addition to ions due to the cyclic trimer and tetramer the LSIMS spectrum of the toluene-soluble fraction of the reaction mixture contained ions at *m*/*z* 1167, 1366, 1984, and 2605 attributed respectively to the presence of $[\{W(NO)(Tp^*)(OH)\}_2(\mu\text{-}1,4\text{-}O_2C_6H_4)]$, $[\{W(NO)(Tp^*)(1,4\text{-}OC_6H_4OH)\}(\mu\text{-}1,4\text{-}O_2C_6H_4)\{W(NO)(Tp^*)I\}]$, $[\{W(NO)(Tp^*)(1,4\text{-}OC_6H_4OH)\}\{(\mu\text{-}1,4\text{-}O_2C_6H_4)_2W(NO)(Tp^*)\}\{W(NO)(Tp^*)I\}]$, and $[\{W(NO)(Tp^*)(1,4\text{-}OC_6H_4OH)\}\{(\mu\text{-}1,4\text{-}O_2C_6H_4)W(NO)(Tp^*)\}_3I\}]$. These acyclic polynuclear complexes are potential precursors to the cyclic oligomers, and their appearance in the reaction involving tungsten may reflect the differing reactivities of the molybdenum and tungsten diiodide precursors. These byproducts have not been investigated further, but it is possible that kinetically slower substitution reactions at tungsten, as compared to molybdenum, lead to their presence in the product mixture.

The LSIMS spectrum of the *syn*,*syn*-isomer of the trinuclear complex, $[Mo(NO)(Tp^*)(1,4\text{-}O_2C_6H_4)]_3$, contains a molecular ion based at *m*/*z* 1594 with no significant ion intensity present at *m*/*z* values associated with the cyclic dimer or tetramer. The IR spectrum (KBr disk) contains a single absorption attributable to ν_{NO} at 1657 cm^{-1}, and the ^1H NMR spectrum allows the isomeric structure of the compound to be defined as described previously for the metallocyclophanes derived from resorcinol. The pyrazolyl C^4 protons give rise to two singlets in the area ratio 6:3 at 5.90 and 5.81 ppm indicating that each Mo center lies on a plane of symmetry which also contains the NO ligand and one of the 3,5-dimethylpyrazole rings. In accord with this the pyrazolyl methyl protons give rise to three signals in the area ratio 27:18:9 at 2.40, 2.41, and 2.28 ppm. The simplicity of this spectrum indicates that only the *syn*,*syn*-isomer is present. At 298 K the 400 MHz ^1H NMR spectrum also contained a singlet of relative area 12 at 7.56 ppm which, on cooling to 193 K, collapsed and reappeared as two broad singlets at 6.47 and 8.55 ppm. These signals are assigned to the protons of the three equivalent bridging 1,4-disubstituted aryl groups which undergo hindered rotation with an activation energy of ca. 40 kJ mol^{-1}. The formulation of this isomer as *syn*,*syn*-$[Mo(NO)(Tp^*)(1,4\text{-}O_2C_6H_4)]_3$ was confirmed by the single-crystal X-ray diffraction study described below. The LSIMS spectrum of *anti*,*syn*-$[Mo(NO)(Tp^*)(1,4\text{-}O_2C_6H_4)]_3$ contains a molecular ion based at *m*/*z* 1594 with no significant ion intensity present at *m*/*z* values associated with the cyclic dimer or tetramer. The IR spectrum (KBr disk) contains two absorption attributable to ν_{NO} at 1664 and 1652 cm^{-1}, and the ^1H NMR spectrum contains five signals in the area ratio 2:2:2:1:2 at 5.97, 5.86, 5.85, 5.84, and 5.82 ppm due to the pyrazolyl C^4 protons, indicating that the *anti*,*syn*-isomer has been isolated.

If the two isomers of $[Mo(NO)(Tp^*)(1,4\text{-}O_2C_6H_4)]_3$ were formed quite randomly the *anti*,*syn*-isomer should predominate over the *syn*,*syn*-isomer in the ratio 3:1 leading to a maximum expected yield of 25% for the *syn*,*syn*-isomer. The yields quoted for the two isomers of $[Mo(NO)(Tp^*)(1,4\text{-}O_2C_6H_4)]_3$ relate to the material recovered after purification. The complex nature of the reaction product mixture and purification procedures employed have prevented any meaningful measurement of the proportions of the isomers initially present in the product mixture. However, the observed yield of 48% for the *syn*,*syn*-isomer is substantially higher than the 25% expected for a nonselective synthesis suggesting that the reaction is in fact stereoselective. Attempts were made to thermally isomerize *syn*,*syn*-$[Mo(NO)(Tp^*)(1,4\text{-}O_2C_6H_4)]_3$, but this isomer was recovered unchanged after heating to 100 °C for 4 weeks in the solid phase. After heating of the compound under reflux in toluene for 2 weeks some decomposition was observed, but again, no evidence was found for the formation of the *anti*,*syn*-isomer. Similar results were obtained on heating the *anti*,*syn*-isomer, which was stable to isomerization for at least 60 h in refluxing toluene. Thus the isomers of $[Mo(NO)(Tp^*)(1,4\text{-}O_2C_6H_4)]_3$ do not interconvert under the conditions in which they form indicating that the reaction is subject to kinetic control.

A single isomer of a cyclic tetramer was also isolated from the reaction involving $1,4\text{-}(HO)_2C_6H_4)$ and $[Mo(NO)(Tp^*)I_2]$. The LSIMS spectrum of this compound, $[Mo(NO)(Tp^*)(1,4\text{-}O_2C_6H_4)]_4$, contains a molecular ion based at *m*/*z* 2126 with ion intensity at *m*/*z* 1594 attributable to the cyclic trimer being ca. 3% that of the ion at *m*/*z* 2126. The IR spectrum (KBr disk) contains a single absorption attributable to ν_{NO} at 1662 cm^{-1}. The simplicity of the ^1H NMR spectrum of the complex indicates the presence of a single isomer of high symmetry but does not distinguish between two possibilities. The spectrum contains only two signals in the area ratio 8:4 at 5.87 and 5.80 ppm due to the pyrazolyl C^4 protons, indicating that the *anti*,*syn*,*syn*- or *anti*,*syn*,*anti*-isomers are not present as these should give rise to intensity ratios of 2:2:2:2:2:1:1 or 8:8:8, respectively. The signals due to the pyrazolyl methyl groups also reflect the high symmetry appearing at 2.44, 2.40, 2.21, and 2.19 ppm with relative areas of 12:24:12:24. At 298 K the aryl protons appear as a singlet of relative area 16 at 7.35 ppm, but on cooling of the sample to 193 K, this singlet collapses and a much more complex signal pattern appears as a result of the reduced dynamic behavior and limiting spectra could not be obtained. The observed intensity patterns in the ^1H NMR spectrum could arise from either the *syn*,*syn*,*syn*- or *anti*,*anti*,*anti*-isomer as, in each, all of the $\{Mo(NO)(Tp^*)\}$ centers are equivalent and bisected by a plane of symmetry. These isomers are expected to be minor components of the cyclic tetramer isomer mixture, but it is not possible to ascribe any stereoselectivity to the reaction as it is likely that the separation procedures used simply failed to afford pure samples of the major isomers.

The LSIMS spectrum of *anti*,*syn*-$[W(NO)(Tp^*)(1,4\text{-}O_2C_6H_4)]_3$, obtained from the reaction between $[W(NO)(Tp^*)I_2]$ and $1,4\text{-}(HO)_2C_6H_4$, contains a molecular ion based at *m*/*z* 1858 with no significant ion intensity present at *m*/*z* values associated with the cyclic dimer or tetramer. The IR spectrum (KBr disk) contains a single absorption attributable to ν_{NO} at 1629 cm^{-1}. The isomeric structure of this compound has been confirmed by a single-crystal X-ray diffraction study, which has been reported in an earlier communication.[12b] At 298 K the 400 MHz ^1H NMR spectrum contains, in addition to resonances due to the Tp* ligand, two doublets of total relative area 8 at 7.01 and 6.85 ppm ($^3J_{HH} = 8$ Hz) which arise from the AA′BB′ systems present in the two aryl groups bounded by an *anti*-arrangement of NO ligands. On cooling of the sample to 193 K, signals attributable to the third aryl ring appeared as two broad singlets at 7.96 and 6.68 ppm. This indicates that rotation of the aryl group bounded by the *syn*-oriented NO ligands is more sterically hindered than rotation of the aryl groups bounded by the *anti*-oriented NO ligands. The barrier to rotation of the unique aryl ring is ca. 45 kJ mol^{-1}, similar to the value obtained for *syn,syn*-[Mo(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_3$. The energy barrier to rotation of the aryl rings between the *anti*-oriented nitrosyl groups could not be determined accurately due to solvent physical property and complex solubilty limitations. The *syn,syn*-isomer of [W(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_3$ could not be isolated from the reaction mixture. However, this cannot be taken as evidence of stereoselectivity since the failure to isolate this isomer may merely reflect the complex nature of the reaction products and the limitations of the purification procedures used.

Electrochemical Studies. It has been shown previously that [Mo(NO)(Tp*)(OPh)$_2$] undergoes a one-electron reduction process at −0.74 V (MeCN, vs SCE)[23] so that metallomacrocycles containing {Mo(NO)(Tp*)(OAr$_2$} (Ar = aryl) groups would be expected to undergo reductions at similar potentials. Thus, the cyclic trimers and tetramers obtained from the synthetic studies provide an opportunity to investigate patterns of redox activity within metallomacrocycle rings. The reduction behavior of these compounds should reflect the pattern of interactions between the metal centers since the reductions of complexes containing the [Mo(NO)(Tp*)}$^{2+}$ moiety have been shown to be largely metal-centered.[23b,26,27] Furthermore, the bridging ligands are formally present in their reduced forms, $C_6H_4O_2^{2-}$, and so should not undergo reductions at moderate potentials. Significant ligand involvement in redox processes would only be expected in the case of oxidations where semiquinone formation is possible. In cases where adjacent metal centers are sufficiently close to show an interaction in their electrochemistry, the trimers and tetramers should exhibit differing reduction behavior. In the cyclic trimer, addition of the first electron would be expected to lead to a negative shift in the reduction potential of the remaining two metal centers (Figure 7). Addition of a second electron then leads to a further negative shift in the reduction potential of the third metal center. Thus, three separate one electron reductions should be observed at increasingly negative potentials. In the case of the cyclic tetramer, a different situation exists. Addition of the first electron will cause a negative shift in the reduction potentials of the two adjacent metal centers. However, the fourth, diagonally opposed, metal center is more remote and may be little affected by the reduction of the first metal center. Thus two electrons should be added to the molecule at similar potentials. Addition of the third electron will take place at a more negative potential because each remaining unreduced metal center is flanked by anionic reduced {M(NO)(Tp*)(OAr)$_2$}$^-$ groups. However, since the two unreduced metal centers are well separated, both should reduce at similar potentials so that the cyclic voltammogram of the molecule as a whole might be expected to resolve two two-electron processes rather than four one-electron processes.

These expectations are realized in the electrochemical results obtained for the cyclic oligomers and summarized in Table 2. The poor solubilities of *anti,syn*-[Mo(NO)(Tp*)$_2$(1,4-$O_2C_6H_4$)]$_3$ and [Mo(NO)(Tp*)$_2$(1,4-$O_2C_6H_4$)]$_4$ have precluded meaningful electrochemical studies of these compounds. However, the cyclic voltammograms of *syn,syn*-[Mo(NO)(Tp*)$_2$(1,4-$O_2C_6H_4$)]$_3$ and *anti,syn*-[W(NO)(Tp*)$_2$(1,4-$O_2C_6H_4$)]$_3$ each contain three well-resolved chemically reversible reduction processes (Figure 8). The more negative reduction potentials and smaller separations in reduction potential (ΔE_f) in the tungsten, as compared to the molybdenum, complexes are in accord with earlier findings for acyclic bimetallic complexes.[19,23,27] Similar results are obtained for *anti,syn*-[Mo(NO)(Tp*)$_2$(1,3-$O_2C_6H_4$)]$_3$, and three waves are again observed (Table 2, Figure 8) except that the ΔE_f values are smaller than for the complex containing the 1,4-$O_2C_6H_4$ bridge. Again, this effect has been observed previously in related acyclic complexes and reflects the removal of the mesomeric link between the ligating oxygen atoms on going from the 1,4- to the 1,3-aryl substitution pattern.[27] A different pattern is observed for *anti,syn,syn*-[Mo(NO)(Tp*)$_2$-(1,3-$O_2C_6H_4$)]$_4$, and only two reduction processes are fully resolved. Each should correspond with the reduction of two diagonally opposed metal centers within the cyclic tetramer. The metal centers within each diagonal pair are expected to be effectively noninteracting, but as the first reduction wave appears to consist of two unresolved processes (Figure 8), it seems that there may be some weak transannular interaction in this system. The ΔE_f value for the cyclic tetramer is larger than that observed in the corresponding cyclic trimer in accord with the presence of two reduced metal centers, one on each side of the remaining unreduced center, following the first reduction process. These observations demonstrate a new “closed circuit” motif for interactions between metal ions separated by polyatomic bridging ligands, the pattern of redox potentials reflecting the geometric arrangement of the metal centers.

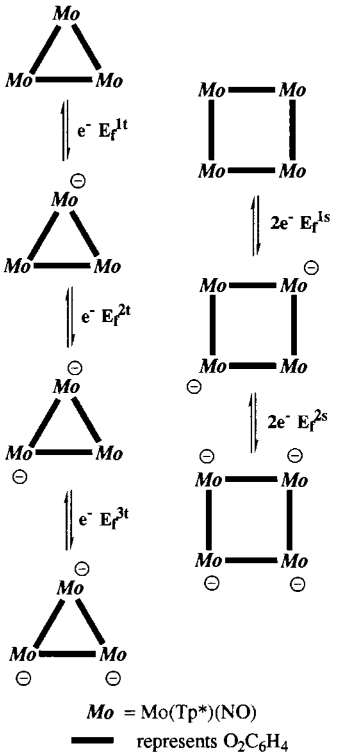

Figure 7. Patterns of electron addition to [Mo(NO)(Tp*)($O_2C_6H_4$]$_n$ (n = 3, 4).

For [{Mo(NO)(Tp)}$_4$(res)] two reduction processes are observed at −1.33 and −1.47 V (CH_2Cl_2 vs Fc/Fc$^+$) (Table 2) rather than four consecutive one-electron transfers. This finding may be rationalized in a manner similar to the electrochemistry of [Mo(NO)(Tp*)(1,3-$O_2C_6H_4$)]$_4$. In the case of [{Mo(NO)-

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[26] Briggs, T. N.; Colquhoun, H.; El Murr, N.; Jones, C. J.; McCleverty, J. A.; Neaves, B. D.; Adams, H.; Bailey, N. A. *J. Chem. Soc., Dalton Trans.* **l985**, l249−1254.

[27] Charsley, S. M.; Jones, C. J.; McCleverty, J. A.; Neaves, B. D.; Reynolds, S. J.; Denti, G. *J. Chem. Soc., Dalton Trans.* **1988**, 293−299.

Table 2. Electrochemical Data

compd	E_f (V)[a]	ΔE_p (mV)[b]	ΔE_p(Fc/Fc$^+$) (mV)[c]	ΔE_f (mV)[d]
[Mo(NO)(Tp*)(OC_6H_5)$_2$]	−1.211	156	78	
anti,syn-[Mo(NO)(Tp*)(1,3-$O_2C_6H_4$)]$_3$	−1.266	116	74	
	−1.516	81		250
	−1.722	110		206
anti,syn,syn-[Mo(NO)(Tp*)(1,3-$O_2C_6H_4$)]$_4$	−1.326	199	64	
	−1.744	220		418
syn,syn-[Mo(NO)(Tp(1,4-$O_2C_6H_4$)]$_3$	−1.169	88	78	
	−1.587	101		418
	−1.908	140		321
anti,syn-[[W(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_3$	−1.861	100	79	
	−2.136	110		275
	−2.400	150		264
[{Mo(NO)(Tp)}$_4$(res)]	−1.330	100	67	
	−1.470			140
[{Mo(NO)Tp}$_3$($resH_2$)]	−1.370[e,f]	158	94	60[f]
[{Mo(NO)Tp}$_2$($resH_4$)]	−1.240[e]	162	47	<50[f]

[a] Formal electrode potential from cyclic voltammograms obtained under an inert atmosphere at a Pt bead electrode from ca. 10^{-3} mole dm^{-3} solutions in dry CH_2Cl_2 containing 0.2 mol dm^{-3} [Bu_4N][BF_4] as the supporting electrolyte. Potentials were measured *vs* ferrocene (Fc) added as an internal standard. Under these conditions E_f (Fc/Fc$^+$) = 0.54(±0.02) V *vs* SCE. [b] Separation between the potentials corresponding to the peak cathodic and anodic currents for the *complex*. [c] Separation between the potentials corresponding to the peak cathodic and anodic currents for ferrocene at a similar peak diffusion current. [d] Separation between reduction potentials for successive reduction processes. [e] Value estimated from the first derivative of the cyclic voltammogram.[26b] [f] Wave presumed to involve unresolved reduction processes associated with weakly interacting metal centers.

(Tp)}$_3$($resH_2$)] the central molybdenum atom should be reduced initially as this is influenced by two adjacent 16-electron metal centers. The remaining two molybdenum atoms are adjacent to only one 16-electron metal center and are equivalent so that they should be simultaneously reduced at a more negative potential. The cyclic voltammogram of [{Mo(NO)(Tp)}$_3$($resH_2$)] contains only one broad wave, but the first and second derivative plots suggest the presence of two reduction processes with an estimated separation of 60 mV. This is less than the value of 140 mV obtained for [{Mo(NO)(Tp)}$_4$(res)] and is consistent with the second reduction potential being subject to only one reduced molybdenum center rather than two as in the case of [{Mo(NO)(Tp)}$_4$(res)]. If the proposed structure of [{Mo(NO)(Tp)}$_2$($resH_4$)], in which the metals are adjacent, is correct, two sequential reduction processes would be expected, reduction of the first metal center negatively shifting the reduction potential of the second. However, the observed cyclic voltammogram shows only one wave at −1.24 V (vs Fc/Fc$^+$) suggesting that interaction between the adjacent metal centers is too small to resolve by cyclic voltammetry. In this case the first derivative plot also failed to resolve two waves. Electrochemical studies of $resH_8$ itself show no electrochemical processes in the region being studied, suggesting that the processes are metal centered as has been reported previously for complexes of this type.[26a]

Structural Studies. The structures of *anti,syn*-[W(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_3$[12b] and [{Mo(NO)(Tp)}$_4$(res)][18] have been described elsewhere in preliminary communications and are not discussed in detail here. The structure of *syn,syn*-[Mo(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_3$ has since been determined and is reported here in full.

A view of the molecule of *syn,syn*-[Mo(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_3$ is shown in Figure 9, and selected geometrical parameters are listed in Tables 3 and 4. The three molybdenum atoms form an almost isosceles triangle, Mo(1)⋯Mo(2) 8.485(3) Å, Mo(1)⋯Mo(3) 8.703(3) Å, and Mo(2)⋯Mo(3) 7.886(3) Å. The coordination geometry at the molybdenum atoms is essentially octahedral, with mean angular deviations from ideal octahedral of 7.5, 7.5, and 7.0° at Mo(1), Mo(2), and Mo(3), respectively. These deviations from octahedral angles are similar to those commonly observed in monomeric {Mo(NO)(Tp*)} species, e.g. 7.1° in [Mo(NO)(Tp*)(NHC_6H_4N-2)$_2$][28] and also 6.9−7.8° in the dimeric *anti*- and *syn*-[Mo(NO)(Tp*)(2,7-O2C$_{10}$H$_6$)]$_2$ complexes.[29] As was noted previously,[28,29] these deviations from ideal octahedral show a consistent pattern. Thus the N(n)−Mo−N(t) angle (see Table 3) is always within 4° of 180°, whereas the other two trans angles deviate by 14−21° from ideality.[28,29] Also noteworthy is the very small N(c)−Mo−N(c) angle of 76−79°. Mean deviations between corresponding angles at the three molybdenum centers are quite small, 0.8−0.9°. Comparison with the monomeric [Mo(NO)(Tp*)(NHC_6H_4N-2)$_2$][28] indicates that the mean differences between corresponding angle types at Mo are only slightly larger, 1.3−1.5°, and comparison with the analogous trimeric tungsten complex,[12b] *anti,syn*-[W(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_3$, again shows the same pattern of angular variation, mean differences between the coordination angles at the Mo and W centers, 0.4−1.5°.

Also characteristic of {Mo(NO)(Tp*)} complexes are the near-linear metal−nitrosyl moieties, with mean Mo−N(n)−O(n) angle 176.9(6)°, short metal−NO bonds, mean Mo−N(n) 1.754(14) Å, and long metal−N(pyrazolyl) bonds trans to these, mean Mo−N(t) 2.261(12) Å. The other Mo−N(pyrazolyl) bonds, Mo−N(c) in Table 3, average 2.193(6) Å. The Mo−O bonds are relatively short, mean 1.939(8) Å, with large valence angles at oxygen, 127.5−142.3°, mean 135.6(22)° (see Table 3). This is consistent with the occurrence of $p\pi - d\pi$ electron donation from oxygen to the coordinatively unsaturated metal. Near-planarity of the nitrosyl−Mo−O−C moieties [see N(n)−Mo−O−C torsion angles in Table 4] is also consistent with this. Further, there appears to be an (inverse) correlation between the magnitude of the Mo−O−C angle and the angle between the adjoining phenyl ring and the nitrosyl−Mo−O residue. In two analogous dimeric oxido complexes,[29] Mo−O distances average 1.949(4) Å and Mo−O−C angles average 134.7(16)°, and in *anti,syn*-[W(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_3$,[12b] the corresponding lengths and angles average 1.949(12) Å and 134(4)°, respectively, indicating similar degrees of electron delocalization.

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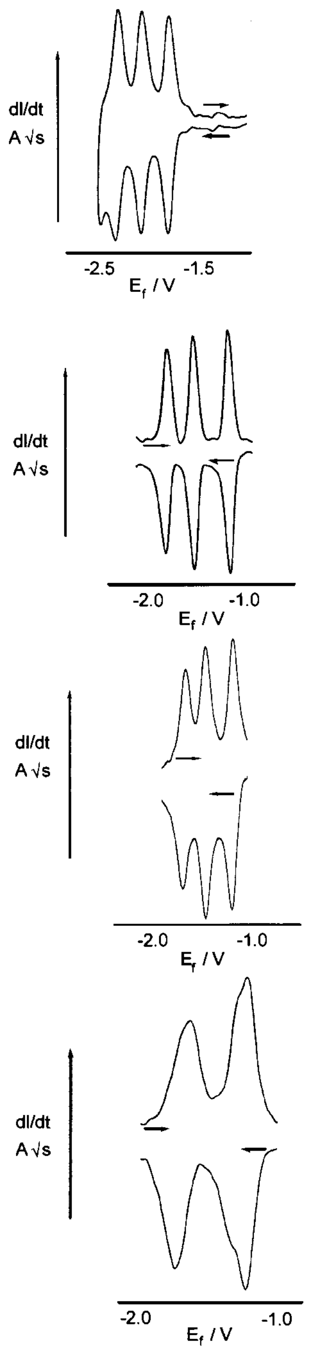

Figure 8. First derivative plots of the cyclic voltammograms of (a) *anti,syn*-[W(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_4$; (b) *syn,syn*-[Mo(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_3$, (c) *anti,syn*-[Mo(NO)(Tp*)(1,3-$O_2C_6H_4$)]$_3$, and (d) *anti, syn,syn*-[Mo(NO)(Tp*)(1,3-$O_2C_6H_4$)]$_4$.

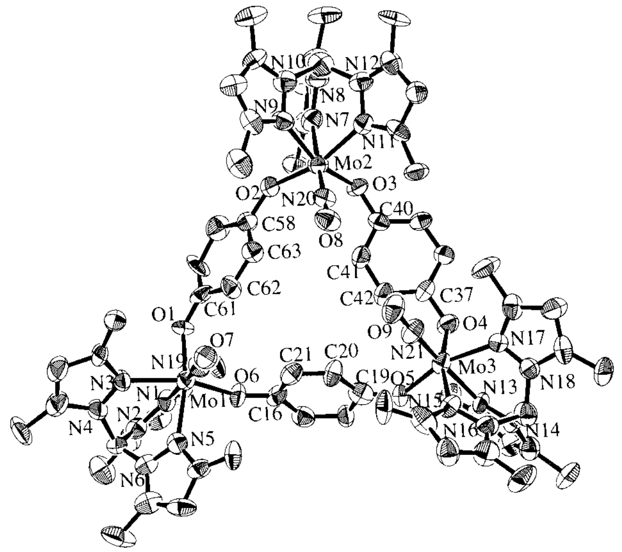

Figure 9. View of the complex *syn,syn*-[Mo(NO)Tp*(1,4-$O_2C_6H_4$)]$_3$.

Table 3. Bond Lengths (Å) and Angles (deg) at the Molybdenum Atoms[a]

	Mo(1)	Mo(2)	Mo(3)
Mo−N(n)	1.730(12)	1.752(13)	1.779(13)
Mo−N(t)	2.279(11)	2.237(11)	2.267(11)
Mo−N(c)	2.193(21)	2.199(8)	2.189(10)[b]
Mo−O	1.929(10)	1.939(4)	1.949(26)[b]
N(n)−O(n)	1.231(12)	1.200(12)	1.214(12)
N(n)−Mo−N(t)	176.5(5)	176.9(5)	177.7(5)
N(n)−Mo−N(c)	93.9(2)	94.0(18)	93.6(10)[b]
N(n)−Mo−O	98.7(5)	98.0(9)	98.2(24)[b]
N(t)−Mo−N(c)	83.5(2)	84.3(4)	84.8(16)[b]
N(t)−Mo−O	83.6(9)	83.5(9)	83.1(17)[b]
N(c)−Mo−N(c)	79.0(4)	76.6(5)	78.2(5)
N(c)−Mo−O trans angle	163.5(20)	162.7(15)	163.9(19)[b]
N(c)−Mo−O cis angle	89.5(24)	90.0(8)	90.6(9)[b]
O−Mo−O	99.1(4)	100.8(4)	98.3(4)
Mo−N(n)−O(n)	175.9(10)	177.0(11)	177.8(11)

[a] N(n) denotes the nitrosyl nitrogen atoms, N(t) denotes the pyrazolyl nitrogen atom trans to N(n), N(c) denotes the pyrazolyl nitrogen atoms cis to N(n), and O(n) denotes the nitrosyl oxygen atoms. [b] Mean of two measurements; estimated standard deviation calculated as $(|x1 - x2|)/2$.

The overall conformation of the complex can be described and compared with that of *anti,syn*-[W(NO)(Tp*)(1,4-$O_2C_6H_4$)]$_3$,[12b] by reference to a central near-planar 12-atom grouping consisting of the six oxygen atoms and the six adjoining carbon atoms of the 1,4-dihydroxybenzene residues [atoms O(1), C(61), C(58), O(2), O(3), C(40), C(37), O(4), O(5), C(19), C(16), O(6) in the molybdenum complex]. Rms atomic deviations from the mean plane are 0.29 Å, in the Mo complex, and 0.04 Å, in the W complex. The molybdenum atoms are displaced on the same side of this plane by 0.390(7), 1.091(6), and 1.249(6) Å, respectively for Mo(1)−Mo(3), whereas, in the tungsten complex, the corresponding displacements have a smaller range, 0.930(14) Å for the unique tungsten atom and 1.041(9) Å on the opposite side of the plane for the two mirror-related tungsten atoms.[12b] In both complexes the nitrosyl ligands are displaced by similar amounts and in the same direction as their bonded metal atom, range 3.18−3.34 Å for oxygen-to-plane distances. The phenyl rings C(16)−C(21), C(37)−C(42), and C(58)−C(63) are inclined to the central plane by 58.9(3), 12.2(6), and 49.1(3)°, respectively. Thus as can be seen from Figure 9, the complex possesses a very approximate mirror symmetry plane, passing through Mo(1), its nitrosyl group, and the pyrazolyl ring trans to the nitrosyl ligand and bisecting the C(37)−C(42) phenyl ring. In the tungsten complex, a similar plane passing through W(2) is an exact crystallographic mirror plane.

Of note are the large differences in the distances between the nitrosyl ligands in the molybdenum complex; those involving the Mo(1) nitrosyl oxygen, O(7), are 6.177(12) Å to O(8) and 6.526(12) Å to O(9), whereas the O(8)···O(9) distance is much shorter at 3.729(12) Å. This appears to be due to Mo(1) rotating outward and toward the central plane, relative to the positions of the other two metal atoms, which results in a quite large movement of the nitrosyl atoms [especially O(7)] rotating them outward, away from the other two nitrosyl ligands and from the adjacent steeply inclined phenyl rings, thus avoiding steric

Table 4. Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) at the Oxido Oxygen Atoms

	Mo−O	Mo−O−C	N(n)−Mo−O−C	Mo−O−C−C
N(19)−Mo(1)−O(6)−C(16)−C(21)	1.938(8)	142.3(9)	−5.2(14)	−14.4(22)
N(19)−Mo(1)−O(1)−C(61)−C(62)	1.919(19)	133.4(9)	30.6(12)	−0.5(22)
N(20)−Mo(2)−O(2)−C(58)−C(63)	1.943(9)	140.4(9)	−16.1(13)	12.5(20)
N(20)−Mo(2)−O(3)−C(40)−C(41)	1.935(8)	132.6(8)	7.2(12)	49.8(17)
N(21)−Mo(3)−O(4)−C(37)−C(42)	1.974(9)	127.5(8)	−17.5(11)	−43.3(17)
N(21)−Mo(3)−O(5)−C(19)−C(20)	1.923(9)	137.3(9)	17.5(13)	−27.3(21)

crowding. In the tungsten complex the *syn* NO···ON internitrosyl distance is 5.56(3) Å, intermediate between the extreme "long" and "short" distances in the molybdenum structure.

Short cross-ring distances include C(21)···C(62), C(41)···C(63), and C(20)···C(42), 3.62(2), 3.88(2), and 3.56(2) Å, respectively. The corresponding distances in the tungsten complex are similar, 3.79, 3.44, and (mirror-related) 3.44 Å. Unlike the tungsten complex, the present structure does not contain any solvent of crystallization.

Inclusion Behavior. The tetra-, tri-, and bimetalated resorcinarenes described here provide a series of novel potential host molecules. Despite the cavity of the resorcinarene fragment in [{Mo(NO)(Tp)}$_4$(res)] being obstructed by the NO ligands, as shown by the crystal structure,[18] the Tp ligands form a secondary cavity. The tri- and bimetalated resorcinarenes [{Mo(NO)(Tp)}$_3$(resH$_2$)] and [{Mo(NO)(Tp)}$_2$(resH$_4$)] should have a more open structure which may provide more unhindered access to the central molecular cavity and so facilitate possible host−guest interactions. The boron atoms in each of the Tp ligands carry a putative negative charge so forming a polar guest environment, and it was hoped that cations might be incorporated into the cavity of the metallocyclophane. Evidence for the formation of complexes with Cs$^+$ was found in the LSIMS spectra of [{Mo(NO)(Tp)}$_4$(res)], [{Mo(NO)(Tp)}$_3$(resH$_2$)], and [{Mo(NO)(Tp)}$_2$(resH$_4$)], but attempts to isolate well-defined complexes with this cation were unsuccessful. Definitive evidence for interactions with these complexes and positively charged organic salts was similarly elusive, and ^{1}H NMR studies revealed no significant host/guest interactions between diquat, or other cationic organic species, and any of the metalated resorcinarenes. However, the ^{1}H NMR spectra do show significant changes (differences in shift of between 0.2 and 0.4 ppm in some but not all signals) in their pyrazole and aryl proton shifts when the solvent is changed from CDCl$_3$ to (CD$_3$)$_2$CO. It has been shown previously that hydrogen bond donor solvents interact with coordinated nitric oxide in compounds of the type [{Mo(NO)(Tp*)X}$_n$(NC$_5$H$_4$(CH=CH)$_4$H$_4$C$_5$N-4,4′)] ($n = 1, 2$; X = Cl, I),[30] and in the case of [{Mo(NO)(Tp)}$_4$(res)], single-crystal X-ray studies have shown a significant interaction between a dichloromethane molecule acting as a hydrogen bond donor and one of the nitric oxide ligands (H···O1 2.47 Å, angle C−H···O1 161°). Such solvation effects could account for the solvent dependence of the ^{1}H NMR spectra of the metalated resorcinarenes.

The ^{1}H NMR spectra of [Mo(NO)(Tp*)(1,3-O$_2$C$_6$H$_4$)]$_n$ (n = 2, 3) are also sensitive to solvent, and spectra recorded in CDCl$_3$, CH$_2$Cl$_2$, and (CD$_3$)$_2$CO again reveal changes of up to 0.2 ppm in the shifts of some aryl and pyrazolyl protons. However, the solid-state structures of [M(NO)(Tp*)(1,3-O$_2$C$_6$H$_4$)]$_3$ ({M(NO)}$_3$ = *syn*,*syn*-{Mo(NO)}$_3$, *anti*,*syn*-{W(NO)}$_3$) which have been obtained so far provide no definitive evidence for specific interactions with solvent molecules although such interactions have been observed with [Mo(NO)(Tp*)(2,7-O$_2$C$_{10}$H$_6$)]$_2$[29] and [Mo(NO)(Tp*){1,4-(OCH$_2$)$_2$C$_6$H$_4$)]$_2$.[31] Furthermore, ^{1}H NMR studies have provided no evidence of inclusion behavior for [Mo(NO)(Tp*)(1,3-O$_2$C$_6$H$_4$)]$_n$ (n = 2, 3) with potential guests such as dimethoxybenzene, and this may reflect the absence of a sufficiently large host cavity within the molecules as illustrated by the crystal structures of *syn*,*syn*-[Mo(NO)(Tp*)(1,3-O$_2$C$_6$H$_4$)]$_3$ and *anti*,*syn*-[W(NO)(Tp*)(1,3-O$_2$C$_6$H$_4$)]$_3$.[12b]

Conclusion

The results described here demonstrate that metallocyclophanes may be synthesized both by adding metal centers to a preformed calix[4]resorcinarene template and by the direct reaction of a dihydroxybenzene with a suitable metal containing precursor. The steric demands of the coligand on the metal center play an important part in stabilizing the metallomacrocycles formed. Where the rigid preformed cyclophane template resH$_8$ is used as a ligand, stable metallocyclophanes are obtained only with the sterically less demanding coligand Tp. However, when the metallocyclophanes are synthesied in metal-directed reactions with resorcinol itself, stable products are only obtained when the more sterically demanding coligand Tp* is present. In the former case the requirement is to reduce steric interactions between the res ligand and the pyrazolylborate coligand. In the latter case stabilization of the formally 16-electron metal center is more important due to the lower rigidity and steric protection afforded by the metallomacrocycle structure. No definitive evidence of inclusion properties was found for the new metallocyclophanes, but evidence for hydrogen- bonding interactions with solvent is seen in the ^{1}H NMR spectra of the complexes. Electrochemical studies reveal differing patterns of interaction beteween metal-based redox centers in the metallocyclophanes depending upon the macrocyclic structure. These novel compounds extend the structural types and levels of functionality available in cyclophane chemistry.

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Supporting Information Available: Listings of X-ray parameters, positional parameters, thermal parameters, hydrogen atom coordinates and selected distances and angles (13 pages). Ordering information is given on any current masthead page.

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