Stereoselectivity in the Formation of Metallomacrocycles from $[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}I_2]$ and Ditopic Proligands: The X-ray Crystal Structures of *anti*-$[[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}\{1,4\text{-}(OCH_2)_2C_6H_4\}]_2\cdot 4CHCl_3$, *syn*-$[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}\{1,4\text{-}(OCH_2)_2C_6H_4\}]_2\cdot 2CH_2Cl_2$, and *anti*-$[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}\{(4\text{-}OC_6H_4)_2CH_2\}]_2\cdot 2CHCl_3\cdot CH_2Cl_2$

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The reaction between the chelating ligand 1,2-$(HOCH_2)_2C_6H_4$ and $[Mo(NO)(tp^*)I_2]$ {tp* = $HB(3,5\text{-}Me_2C_3HN_2)_3$} in the presence of NEt_3 affords the monometallic complex $[Mo(NO)(tp^*)\{(OCH_2)_2C_6H_4\}]$, **1**. However, reactions involving the nonchelating ditopic proligands HE-EH {HE-EH = 1,4-$(HOCH_2)_2C_6H_4$, 1,3-$(HOCH_2)_2C_6H_4$, and 4,4′-$(HOC_6H_4)_2CH_2$} afford the binuclear metallocyclophanes $[Mo(NO)(tp^*)(E-E)]_2$ as mixtures of *syn*- and *anti*-isomers. These binuclear complexes are formed under kinetic control so that *syn*-$[Mo(NO)(tp^*)\{1,4\text{-}(OCH_2)_2C_6H_4\}]_2$, **2s**, forms more rapidly than *anti*-$[Mo(NO)(tp^*)\{1,4\text{-}(OCH_2)_2C_6H_4\}]_2$, **2a**, but in lower yield. Some kinetic control is also apparent in the formation of the *syn*- and *anti*-isomers of $[Mo(NO)(tp^*)\{4,4'\text{-}(OC_6H_4)_2\text{-}CH_2\}]_2$, **4**, and $[Mo(NO)(tp^*)\{1,3\text{-}(OCH_2)_2C_6H_4\}]_2$, **3**, but in these cases the reaction is less stereoselective. The X-ray crystal structures of three complexes were determined to establish their isomeric structures: *anti*-$[[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}\{1,4\text{-}(OCH_2)_2C_6H_4\}]_2\cdot 4CHCl_3$, $C_{46}H_{60}B_2Mo_2N_{14}O_6\cdot 4CHCl_3$, triclinic, space group $P\bar{1}$, $a = 11.967(3)$ Å, $b = 18.004(2)$ Å, $c = 8.740(2)$ Å, $\alpha = 102.31(1)°$, $\beta = 109.32(1)°$, $\gamma = 82.08(1)°$, $Z = 1$; *syn*-$[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}\{1,4\text{-}(OCH_2)_2C_6H_4\}]_2$, $C_{46}H_{60}B_2Mo_2N_{14}O_6\cdot 2CH_2Cl_2$, monolinic, space group $P2_1/a$, $a = 16.576(3)$ Å, $b = 20.844(2)$ Å, $c = 17.024(2)$ Å, $\beta = 109.32(1)°$, $Z = 4$; *anti*-$[Mo(NO)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}\{(4,4'\text{-}OC_6H_4)_2CH_2\}]_2$, $C_{56}H_{64}B_2Mo_2N_{14}O_6\cdot 2CHCl_3\cdot CH_2Cl_2$, triclinic, space group $P\bar{1}$, $a = 12.665(2)$ Å, $b = 13.013(2)$ Å, $c = 11.894(2)$ Å, $\alpha = 111.80(1)°$, $\beta = 95.48(1)°$, $\gamma = 94.78(2)°$, $Z = 1$. All three structures are characterized by short Mo−O bond distances indicative of some $Op_\pi \rightarrow Mod_\pi$ bonding. In the case of **2a** evidence for weak hydrogen bonds between solvating $CHCl_3$ molecules and the alkoxide oxygens was found.

Introduction

The reactions of appropriately selected ditopic proligands[1] with suitable transition metal complexes can lead to the formation of metallomacrocycles which can have the potential to act as host molecules.[2] One commonly used approach to the synthesis of such compounds involves the reaction of square planar, or tetrahedral, metal centers with bi- or polypyridyl ligands.[3,4] These reactions often involve labile metal centers so that the reaction products are formed under equilibrium control in self-assembly reactions. The product distribution obtained in such reactions reflects the geometric requirements of the metal center and the structural demands of the ditopic proligand. Thus the 90° angle between the *cis*-coordination sites on $\{Pd(en)\}^{2+}$ and the rigid linear arrangement of the donor atoms in the 4,4′-bipyridyl proligand leads to the formation of the cyclic tetramer $[\{Pd(en)(4,4'\text{-}C_5H_4N)_2\}_4]^{8+}$. In contrast, the more "flexible" proligand 1,2-bis(4′-pyridyl)ethane can accommodate the 90°angles at the metal center to form the cyclic dimer $[\{Pd(en)(4\text{-}NC_5H_4CH_2)_2\}_2]^{4+}$.[3b]

An alternative approach to the production of metallomacrocycles involves reactions in which the product distribution is controlled kinetically. Stephan has shown that $[Zr(\eta^5\text{-}C_5H_5)_2\text{-}\{1,3\text{-}(OCH_2)_2C_6H_4\}]_2$ may be obtained in 29% yield from the reaction between $[Zr(\eta^5\text{-}C_5H_5)_2(Me)_2]$ and 1,3-$(HOCH_2)_2C_6H_4$.[5] In this case $O \rightarrow Zr\ p_\pi \rightarrow d_\pi$ charge donation contributes to Zr−O bonding and enhances the stability of the product. In our laboratory we have been investigating the formation of metal-

(1) The term *ditopic* refers to a ligand containing two donor atom sites which are potentially able to coordinate to a metal centre, but does not imply that the ligand can act in a bidentate sense toward a single metal ion to form a chelate ring. Since, strictly speaking, a ligand only exists as a component of a metal complex, the term *proligand* is used to refer to a molecule that may become a ligand following reaction with a metal ion. This terminology avoids difficulty in cases involving the release of protons during complexation so that a proligand HE-EH can give rise to the ligand $E\text{-}E^{2-}$, which is a component in a binuclear metal complex; in such cases HE-EH is not the ligand.

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lomacrocycles from [M(A)(tp*)X_2] {tp*$^-$ = hydrotris(3,5-dimethylpyrazol-1-yl)borate; M = Mo, W; A = NO; X = I: M = Mo; A = O; X = Cl}[6,7] in reactions that involve proligands with two suitably disposed hydroxy, thiol, or amine donor groups. In the presence of NEt_3 phenols or alcohols, ROH, react with [Mo(tp*)(NO)I_2] to produce [Mo(tp*)(NO)$(OR)_2$].[8] This finding may be exploited in the development of rational syntheses of metallomacrocycles. Thus we have found that [Mo(tp*)(NO)I_2] reacts with poly(ethylene glycol)s in the presence of NEt_3 to produce the monometallomacrocycles [Mo(tp*)(NO){$OCH_2(CH_2OCH_2)_nCH_2O$}] (n = 2, 3, 4, 5), of which the compound with n = 3 has been characterized by an X-ray crystal structure.[9] These reactions proceed smoothly in yields of 47−68% without recourse to high dilution techniques. The Mo−O bonds in these complexes are augmented by $Op_\pi \rightarrow Mod_\pi$ interactions which stabilize the coordinatively unsaturated 16-electron Mo center.[8] A similar situation is found in [Mo(NO)(η^5-C_5H_5)$(SPh)_2$], where the coordinatively unsaturated 16-electron Mo center is stabilized by $Sp_\pi \rightarrow Mod_\pi$ interactions.[10]

Although there is some evidence that ligand exchange can occur between alcohols and [Mo(NO)(tp*)Cl(OR)],[11] reaction rates are slow in the absence of Brønsted acids. This suggests that, once formed, the Mo−O bonds in [Mo(NO)(tp*)$(OR)_2$] might be sufficiently kinetically stable to allow the formation of polynuclear metallomacrocycles under kinetic control. The presence of the Mo−O−R link in such compounds reduces the degree of structural control present during any macrocycle formation reaction as compared to the situation with [{Pd(en)(4,4′-$C_5H_4N)_2$}$_4$]$^{8+}$. However, the $Op_\pi \rightarrow Mod_\pi$ charge donation may be expected to restrict rotation about the O−Mo bond and impose some rigidity on the {Mo−O−R} link.[8] Furthermore, the steric demands of the tp* ligand may also promote the metallomacrocycle formation process as the pyrazolyl 3-methyl groups project toward the trigonal prismatic coordination sites of the metal, restricting the volume of space that can be explored by a bound ditopic ligand. As a consequence, macrocycle formation may be favored by the proximity of the second metal binding site and the restricted orientational freedom of the ditopic ligand. Once a metallomacrocycle is formed, it is likely to be kinetically trapped and isolable from the reaction mixture. Preliminary studies have confirmed these expectations and show that the nuclearity and isomer distribution in the mixtures of cyclic oligomers formed is highly dependent on the nature of the ditopic ligand involved.[7b,12] We have previously described the syntheses and crystal structures of the *syn*- and *anti*-isomers of [Mo(NO)(tp*)(2,7-$O_2C_{10}H_6$)]$_2$, which contain the rigid 2,7-$C_{10}H_6$ linking group and which do not interconvert thermally.[13] In this paper we describe the syntheses of metal-containing cyclophane[14]-like structures from the reactions of [Mo(NO)(tp*)I_2] with the symmetric "flexible" ligands HE-EH {HE-EH = 4,4′-$(HOC_6H_4)_2CH_2$, 1,2-$(HOCH_2)_2C_6H_4$, 1,3-$(HOCH_2)_2C_6H_4$, and 1,4-$(HOCH_2)_2C_6H_4$}.

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 molecular sieves (4 Å) and stored over activated alumina. The starting material [Mo(NO)(tp*)I_2]·$C_6H_5CH_3$ was prepared following known procedures.[15] 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. ^{1}H NMR spectra were recorded using a Bruker AMX-400 (400 MHz) spectrometer. Liquid secondary positive ion mass spectra {(+)-LSIMS} were obtained from a VG Zabspec mass spectrometer utilizing a *m*-nitrobenzyl alcohol matrix and scanning in the positive ion mode. Cyclic voltammetry was carried out using an EG & G model 174A polarographic analyzer, with ca. 10^{-3} mol dm^{-3} solutions of complex 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.

Microanalyses were performed by the Microanalytical Laboratories of the University of Birmingham and the Univrsity of North London on finely ground samples dried for several days in vacuo at 100 °C to remove solvent.

Preparation of [Mo(NO)(tp*){(1,2-$OCH_2)_2C_6H_4$}], 1. Triethylamine (1.0 cm^3) was added to a solution of [Mo(NO)(tp*)I_2]·$C_6H_5CH_3$ (334 mg, 0.43 mmol) and 1,2-$(HOCH_2)_2C_6H_4$ (69 mg, 0.50 mmol) in dry dichloromethane (80 cm^3). The mixture was heated under reflux for 2 h; the solution was allowed to cool to room temperature and filtered to remove $HNEt_3I$. The filtrate was evaporated to dryness in vacuo, the residue was redissolved in CH_2Cl_2, and the reaction products were separated by column chromatography on silica gel using a mixture of dichloromethane and *n*-hexane (7:3 v/v) as the eluent. The major blue fraction was collected and further purified by recrystallization from dichloromethane and *n*-hexane. Yield: 179 mg (74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (4H, m C_6H_4), 7.32, 6.29 (2H, d, ^2J 11, 2H, d, ^2J 11 Hz, CH_2), 6.04, 5.54 (2H, s, 1H, s, $Me_2C_3HN_2$), 2.48, 2.47, 2.36, 1.29 {6H, s, 6H, s, 3H, s, 3H, s ($CH_3)_2C_3HN_2$}. Anal. Found: C, 49.2; H, 5.70; N, 17.2. Calcd for $C_{23}H_{30}BN_7O_3Mo$: C, 49.4; H, 5.41; N, 17.5. (+)-LSIMS: *m*/*z* 561 (M$^+$). IR data (KBr disk): 2540w (ν_{BH}); 1635s (ν_{NO}) cm^{-1}.

Preparation of [Mo(NO)(tp*)(1,4-$OCH_2C_6H_4CH_2O$)]$_2$, 2. Triethylamine (1.0 cm^3) followed by 1,4-$(HOCH_2)_2C_6H_4$ (180 mg, 1.30 mmol) was added to a solution of [Mo(NO)(tp*)I_2]·$C_6H_5CH_3$ (1.00 g, 1.30 mmol) in dry toluene (100 cm^3). The mixture was heated under reflux for 18 h. The dark brown solution was allowed to cool to room temperature and filtered to remove $HNEt_3I$. The filtrate was evaporated to dryness in vacuo, the residue was redissolved in CH_2Cl_2, and the reaction products were separated by column chromatography on silica gel using a mixture of dichloromethane and *n*-hexane (8:2 v/v) as the

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eluent. The first two green bands to elute were discarded, and the major salmon pink fraction that followed was collected. This contained a mixture of the *anti*- and *syn*-isomers (**2a** and **2s**, respectively) of [Mo(NO)(tp*)(1,4-$OCH_2C_6H_4CH_2O$)]$_2$. Yield: 220 mg (30%) {*anti*-[Mo(NO)(tp*)(1,4-$OCH_2C_6H_4CH_2O$)]$_2$, **2a**, 23%**,** and *syn*-[Mo(NO)(tp*)(1,4-$OCH_2C_6H_4CH_2O$)]$_2$, **2s**, 7% by ^{1}H NMR}. ^{1}H NMR (400 MHz, $CDCl_3$): **2a**, δ 7.28 (8H, s C_6H_4), 5.87, 5.72 (4H, s, 2H, s, $Me_2C_3HN_2$), 6.61, 6.05 (4H, d, ^2J 11.3, 4H, d, ^2J 11.3 Hz, CH_2), 2.73, 2.37, 1.73 {12H, s, 18H, s, 6H, s $(CH_3)_2C_3HN_2$}. **2s** δ 7.13 (8H, s C_6H_4), 5.87, 5.71 (4H, s, 2H, s, $Me_2C_3HN_2$), 6.74, 6.10 (4H, d, ^2J 11.5, 4H, d, ^2J 11.5 Hz, CH_2), 2.75, 2.36, 2.34, 1.93 {12H, s, 12H, s, 6H, s, 6H, s $(CH_3)_2C_3HN_2$}. Anal. Found: C, 49.9; H, 5.60; N, 17.3. Calcd for $C_{46}H_{60}B_2N_{14}O_6Mo_2$: C, 49.4; H, 5.41; N, 17.5. (+)-LSIMS: *m*/*z* 1119 (M^+). IR data (KBr disk): 2541w (ν_{BH}); 1634s (ν_{NO}) cm^{-1}.

Further fractionation by repeated column chromatography afforded an isomerically pure sample of *anti*-[Mo(NO)(tp*)(1,4-$OCH_2C_6H_4CH_2O$)]$_2$, **2a**, but it was not possible to obtain a sample of *syn*-[Mo(NO)(tp*)(1,4-$OCH_2C_6H_4CH_2O$)]$_2$, **2s**, free of **2a**, although some single crystals of **2s** were physically separated and characterized by an X-ray diffraction study (vide infra).

The reaction was repeated using different heating times to give differing yields of **2a** and **2s** as follows: after 90 min **2a**, 14%; **2s**, 6%; after 54 h **2a**, 25%; **2s**, 5%, the relative proportions of **2a** and **2s** in the binuclear product fraction being determined by ^{1}H NMR spectroscopy.

Preparation of [Mo(NO)(tp*)(1,3-$OCH_2C_6H_4CH_2O$)]$_2$, 3. Triethylamine (1.0 cm^3) followed by 1,3-$(HOCH_2)_2C_6H_4$ (180 mg, 1.30 mmol) was added to a solution of [Mo(NO)(tp*)I_2]·$C_6H_5CH_3$ (1.00 g, 1.30 mmol) in dry toluene (100 cm^3). The mixture was heated under reflux for 18 h. The dark brown solution was allowed to cool to room temperature and filtered to remove $HNEt_3I$. The filtrate was evaporated to dryness in vacuo, the residue was redissolved in CH_2Cl_2, and the reaction products were separated by column chromatography on silica gel using a mixture of dichloromethane and *n*-hexane (7:3 v/v) as the eluent. The first two green bands to elute were discarded, and the major pink/brown fraction that followed was collected. Further fractionation by repeated column chromatography using dichloromethane and *n*-hexane (1:1 v/v) as the eluent afforded a pink isomer, **3i**, which is sparingly soluble in toluene, and a peach/brown colored isomer, **3ii**, which is soluble in toluene.

3i. Yield: 130 mg (18%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47, 7.28, 7.27, 7.19 (2H, t, ^4J 1.8. 2H, dd, ^3J 8.3, ^4J 1.8, 2H, d, ^3J 6.6, ^4J 1.8, 2H, dd, ^3J 8.3,^3J 6.6 Hz, C_6H_4), 5.83, 5.68 (4H, s, 2H, s, $Me_2C_3HN_2$), 6.12, 6.02 (4H, d, ^2J 12.1, 4H, d, ^2J 12.1 Hz, CH_2), 2.67, 2.32, 2.31, 2.14 {12H, s, 12H, s, 6H, s, 6H, s $(CH_3)_2C_3HN_2$}. Anal. Found: C, 49.4; H, 5.31; N, 17.4. Calcd for $C_{46}H_{60}B_2N_{14}O_6Mo_2$: C, 49.4; H, 5.41; N, 17.5. (+)-LSIMS: *m*/*z* 1119 (M^+). IR data (KBr disk): 2547w (ν_{BH}); 1647s (ν_{NO}) cm^{-1}.

3ii. Yield: 130 mg (18%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59, 7.20, 7.19 Hz), 7.10 (2H, t, ^4J 1.8, 2H, dd, ^3J 8.2, ^4J 1.8, 2H, d, ^3J 6.6, ^4J 1.8, 2H, dd, ^3J 8.2,^3J 6.6 Hz, C_6H_4), 5.85, 5.60 (4H, s, 2H, s, $Me_2C_3HN_2$), 6.47, 6.34 (4H, d, ^2J 12.6, 4H, d, ^2J 12.6 Hz, CH_2), 2.64, 2.36, 2.34 {6H, s, 24H, s, 6H, s $(CH_3)_2C_3HN_2$}. Anal. Found: C, 49.1; H, 5.25; N, 17.5. Calcd for $C_{46}H_{60}B_2N_{14}O_6Mo_2$: C, 49.4; H, 5.41; N, 17.5%). (+)-LSIMS: *m*/*z* 1119 (M^+). IR data (KBr disk): 2544w (ν_{BH}); 1644s (ν_{NO}) cm^{-1}.

The reaction was repeated using different heating times to give differing yields of **3i** and **3ii** as follows: after 50 min **3i**, 68 mg, 9%; **3ii** 97 mg, 13%; after 54 h **3i**, 135 mg, 19%; **3ii** 105 mg, 14%.

Preparation of [Mo(NO)(tp*){4,4′-$OC_6H_4)_2CH_2$}]$_2$, 4. Triethylamine (1.0 cm^3) followed by 4,4′-$(HOC_6H_4)_2CH_2$ (260 mg, 1.3 mmol) was added to a solution of [Mo(NO)(tp*)I_2]·$C_6H_5CH_3$ (1.00 g, 1.30 mmol) in dry toluene (100 cm^3). The mixture was heated under reflux for 18 h. The dark brown solution was allowed to cool to room temperature and filtered to remove $HNEt_3I$. The filtrate was evaporated to dryness in vacuo, the residue was redissolved in CH_2Cl_2, and the reaction products were separated by column chromatography on silica gel using a mixture of dichloromethane and *n*-hexane (1:1 v/v) as the eluent. The first two green bands to elute were discarded, and the major brown fraction that followed was collected. Further fractionation by repeated column chromatography using dichloromethane and *n*-hexane (1:1 v/v) as the eluent afforded a brown isomer, **4a** (R_f = 0.70), which is sparingly soluble in toluene, and a brown isomer, **4s** (R_f = 0.64), which is freely soluble in toluene.

4a. Yield: 282 mg (35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05, 7.20 (8H, d, ^3J 8, 8H, d, ^3J 8 Hz C_6H_4), 5.85, 5.81 (4H, s, 2H, s, $Me_2C_3HN_2$), 4.00 (4H, s CH_2), 2.41, 2.40, 2.33, 2.30 {6H, s, 12H, s, 12H, s, 6H, s $(CH_3)_2C_3HN_2$}. Anal. Found: C, 54.4; H, 5.40; N, 15.4. Calcd for $C_{56}H_{64}B_2N_{14}O_6Mo_2$: C, 54.1; H, 5.19; N, 15.8). (+)-LSIMS: *m*/*z* 1243 (M^+). IR data (KBr disk): 2543w (ν_{BH}); 1652s (ν_{NO}) cm^{-1}.

4s. Yield: 210 mg (26%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (16H, s, C_6H_4), 5.87, 5.75 (4H, s, 2H, s, $Me_2C_3HN_2$), 4.06, 3.79 (2H, d, ^3J 15, 2H, d, ^3J 15 Hz CH_2), 2.40, 2.39, 2.13 {12H, s, 18H, s, 6H, s $(CH_3)_2C_3HN_2$}. Anal. Found: C, 54.2; H, 5.20; N, 15.6. Calcd for $C_{56}H_{64}B_2N_{14}O_6Mo_2$: C, 54.1; H, 5.19; N, 15.8. (+)-LSIMS: *m*/*z* 1243 (M^+). IR data (KBr disk): 2543w (ν_{BH}); 1666s (ν_{NO}) cm^{-1}.

The reaction was repeated using different heating times to give differing yields of **4a** and **4s** as follows: after 15 min **4a**, 237 mg, 29%; **4s** 199 mg, 25%; after 54 h **4a**, 639 mg, 79%; **4s** 69 mg, 9%.

A cyclic trimer, [Mo(NO)(tp*){4,4′-$OC_6H_4)_2CH_2$}]$_3$, **5** (R_f = 0.83), could be isolated from the product mixture after reaction times of 15 min or 18 h but was not present in isolable amounts when a reaction time of 54 h was used.

5. Yield: 207 mg; 26% at 15 min reaction time; 160 mg, 20% at 18 h reaction time. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18−7.07 (24H, overlapping signals, C_6H_4), 5.81, 5.74, 5.73, 5.71 (6H, s, $^3/_4$H, s, $1^1/_2$H, s, $^3/_4$H, s $Me_2C_3HN_2$), 3.94 (6H, overlapping signals CH_2), 2.40, 2.39, 2.22, 2.21, 2.20, 2.19, 2.15, 2.12, 2.09 {9H,s, 18H, s, $4^1/_2$H, s, $4^1/_2$H, s,$4^1/_2$H, s,$4^1/_2$H, s, $2^1/_4$H, s, $4^1/_2$H, s, $2^1/_4$H, s $(CH_3)_2C_3HN_2$}. Anal. Found: C, 53.9; H, 5.42; N, 15.5. Calcd for $C_{28}H_{32}B_3N_{21}O_9Mo_3$: C, 54.2; H, 5.19; N, 15.8. (+)-LSIMS: *m*/*z* 1865 (M^+). IR data (KBr disk): 2542w (ν_{BH}); 1661s (ν_{NO}) cm^{-1}.

Structure Determinations.[16] Cell dimensions and intensity data (Table 1) for the three complexes, **2a**, **2s**, and **4a**, were measured on a Rigaku R-AXIS II area detector diffractometer. The structures were determined[16a] by direct methods and refined[16b] by least-squares on F^2 using anisotropic thermal parameters for non-hydrogen atoms, apart from the carbon atom of a disordered molecule of dichloromethane in **4a**, which was located from a difference map and included in the calculations with an isotropic thermal parameter. Hydrogen atoms were placed in calculated positions, but those of the disordered dichloromethane were omitted. Diagrams were drawn with ORTEP;[16c] thermal ellipsoids are at the 30% probability level.

Results and Discussion

The reaction between [Mo(NO)(tp*)I_2] and 1,2-$(HOCH_2)_2C_6H_4$ in the presence of NEt_3 affords, as the main reaction product, the chelate complex [Mo(NO)(tp*){1,2-$(HOCH_2)_2C_6H_4$}], **1** (Figure 1). The elemental analyses and IR and ^{1}H NMR spectra of **1** are in accord with its formulation as a 1:1 complex of {Mo(NO)(tp*)} with {1,2-$(HOCH_2)_2C_6H_4$}. The mass spectrum (LSIMS) contained a molecular ion at *m*/*z* 561 in accord with a monomeric formulation and contained no ions attributable to higher nuclearity cyclic oligomers. In contrast the reactions involving 1,4- and 1,3-$(HOCH_2)_2C_6H_4$, which are unable to form mononuclear chelate complexes, afforded crude reaction products with mass spectra that indicate the presence of both cyclic dimers and cyclic trimers.

The mass spectrum of the crude product isolated from the reaction involving [Mo(NO)(tp*)I_2] and 1,4-$(HOCH_2)_2C_6H_4$ contained a molecular ion at *m*/*z* 1118 corresponding with the cyclic dimer [Mo(NO)(tp*){1,4-$(HOCH_2)_2C_6H_4$}]$_2$ (**2**) together

(16) (a) *TeXsan*: Single-Crystal Analysis Software, version 1.6; Molecular Structure Corporation: The Woodlands, TX 77381, USA, 1993. (b) Sheldrick, G. M. *SHELXL-93*, Program for Crystal Structure Refinement; University of Gottingen, 1993. (c) Johnson, C. K. *ORTEP*, Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 1. Crystallographic Data

	2a	**2s**	**4a**
formula	$C_{46}H_{60}B_2N_{14}O_6Mo_2 \cdot 4CHCl_3$	$C_{46}H_{60}B_2N_{14}O_6Mo_2 \cdot 2CH_2Cl_2$	$C_{56}H_{64}B_2N_{14}O_6Mo_2 \cdot 2CHCl_3 \cdot CH_2Cl_2$
fw	1596.1	1288.4	1566.4
a, Å	11.967(3)	16.576(3)	12.665(2)
b, Å	18.004(2)	20.844(2)	13.013(2)
c, Å	8.740(2)	17.024(2)	11.894(2)
α, deg	102.31(1)	90	111.80(1)
β, deg	109.32(1)	94.87(2)	95.48(1)
γ, deg	82.08(1)	90	94.78(2)
V, Å^3	1732(1)	5861(2)	1797(1)
Z	1	4	1
space grp	$P\bar{1}$	$P2_1/a$	$P\bar{1}$
T, °C	21	21	21
λ, Å	0.7107	0.7107	0.7107
ρ_{calcd}	1.531	1.460	1.448
μ(Mo Kα), mm^{-1}	0.880	0.668	0.703
$R_w(F_o^2)$	0.1699	0.1115	0.1979
$R(F_o)$ for obsd rflns[a]	0.0522	0.0789	0.0648

[a] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. $R(F_o) = \sum(|F_o - F_c|)/\sum|F_o|$.

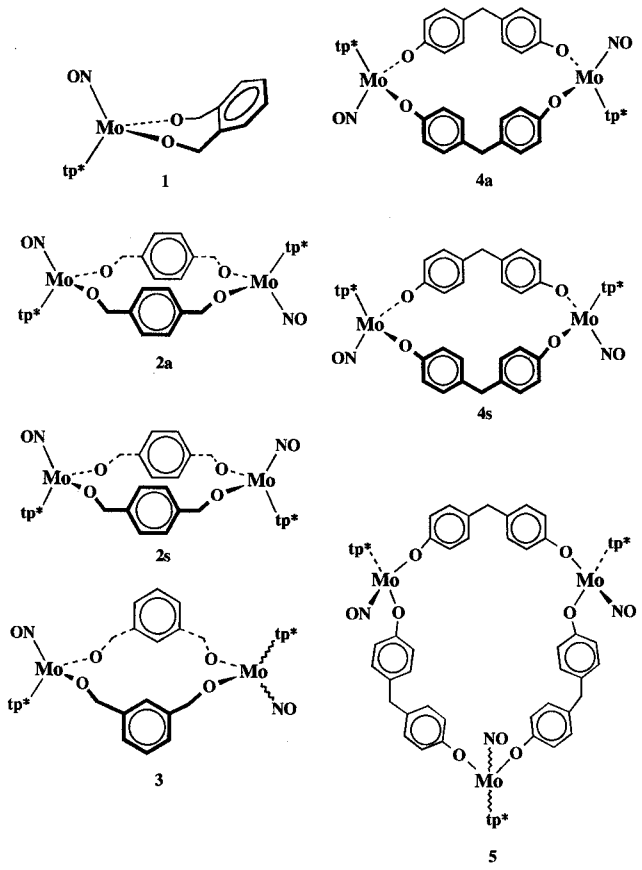

Figure 1. Structural formulas for compounds **1**−**5**.

with an ion at *m*/*z* 1677 attributable to the cyclic trimer with an intensity 3% that of the ion at *m*/*z* 1118. Chromatographic separation afforded a pure sample of **2** as a mixture of *syn*- and *anti*-isomers. These isomers could not be completely separated, but repeated chromatography afforded a sample of *anti*-[Mo(NO)(tp*){1,4-$(HOCH_2)_2C_6H_4$}]$_2$ (**2a**), which was isomerically pure and was characterized by an X-ray crystallographic study (vide infra). Attempts to obtain a sample of *syn*-[Mo(NO)(tp*){1,4-$(HOCH_2)_2C_6H_4$}]$_2$ (**2s**) free of the *anti*-isomer were unsuccessful, although single crystals of **2s** were separated from a mixed crystalline sample and used in an X-ray crystallographic study (vide infra). The mixture of isomers **2a** and **2s** was further characterized by LSIMS, IR, and ^{1}H NMR spectroscopy and by elemental analyses. The ^{1}H NMR spectra of the isomers **2a** and **2s** differ but do not distinguish between the *syn*- and *anti*-forms. However, the isomeric structures can be unambiguously assigned by reference to the X-ray studies. Thus in the ^{1}H NMR spectra of both **2a** and **2s** the signals due to the pyrazolyl C^4 protons appear in the area ratio 4:2 and those due to the pyrazolyl 3- and 5-methyl protons in the area ratios 12:12:6:6. The signals due to the methylene protons of the 1,4-$(OCH_2)_2C_6H_4$ ligands appear at low field due to their proximity to the formally 16-electron Mo center[17] and comprise two doublets associated with an AB system. In **2a** these signals appear at slightly lower field than in **2s**. The relative proportions of **2a** and **2s** in the isomer mixture may be determined from the ^{1}H NMR spectrum and were found to vary with reaction time. Thus the ratio of **2a**:**2s** was 14:6 after 90 min, 23:7 after 18 h, and 25:5 after 54 h, the total yield of **2a** and **2s** at these respective times being 20, 30, and 30%. Heating the 14:6 mixture of **2a** and **2s** under reflux in toluene solution for 2 days produced no change in the relative proportions of the isomers. These findings are consistent with the reaction proceeding under kinetic control with no significant changes in yield or isomer distribution occurring between 18 and 54 h. The small increase in the yield of **2a** and decrease in the yield of **2s** after 18 h may simply reflect experimental errors, or some slight decomposition of **2s** may occur with the extended reaction time. Overall the *anti*-isomer **2a** is formed in preference to the *syn*-isomer **2s** with a selectivity of ca. 4:1 in this reaction. The cyclic trimer could not be isolated in a pure form.

The mass spectrum of the crude product isolated from the reaction involving [Mo(NO)(tp*)I$_2$] and 1,3-$(HOCH_2)_2C_6H_4$ contained a molecular ion at *m*/*z* 1119 corresponding with the cyclic dimer [Mo(NO)(tp*){1,3-$(HOCH_2)_2C_6H_4$}]$_2$ (**3**) and an ion at *m*/*z* 1678 attributable to the cyclic trimer. After a reaction time of 50 min the intensity of the ion at *m*/*z* 1678 was 13% that of the ion at *m*/*z* 1119. Chromatographic separation afforded pure samples of two isomers, **3i** and **3ii**, of the binuclear compound. The ^{1} H NMR spectra of **3i** and **3ii** differ, but both contain signals consistent with the presence of a 1,3-substituted phenyl ring in addition to signals due to the tp* ligand and the methylene groups. In each case the relative areas of the signals are consistent with the presence of a mirror plane bisecting the tp* ligands and relating the two xylyl moieties. The relative areas are also consistent with the tp* and xylenediolate ligands

(17) 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.

being present in equimolar proportions. The ^{1}H NMR spectra do not reveal whether **3i** and **3ii** are *syn*- or *anti*-isomers. However, these isomers differ in solubility in that **3i** is sparingly soluble in toluene whereas **3ii** is freely soluble. Since we have found that **2a** and **4a** (vide infra) are less soluble in toluene than **2s** and **4s**, and that *anti*-[Mo(NO)(tp*)(2,7-$O_2C_{10}H_6$)]$_2$ is insoluble in toluene whereas *syn*-[Mo(NO)(tp*)(2,7-$O_2C_{10}H_6$)]$_2$ is soluble, the emerging trend is for the *anti*-isomers of these bimetallomacrocycles to have lower solubility in toluene than the *syn*-isomers. On this basis we tentatively assign the *anti*-structure to **3i** and the *syn*-structure to **3ii**. Once again the proportions of **3i** and **3ii** formed in the reaction vary with reaction time. Thus the yield ratio of **3i**:**3ii** was 9:13 after 90 min, 18:18 after 18 h, and 19:14 after 54 h, the total yields of **3i** and **3ii** at these respective times being 22, 36, and 33%. Heating **3i** or **3ii** under reflux in toluene solution for 2 days did not result in isomerization. As in the case of **2a** and **2s**, these findings are consistent with the reaction proceeding under kinetic control with **3ii** forming more rapidly than **3i** and both compounds reaching a maximum yield within about 18 h. If the assignment of the *syn*-structure to **3ii** is correct, then it is the *syn*-isomer that reaches its maximum yield most quickly as was found for 1,4-$(HOCH_2)_2C_6H_4$. However, the reaction with 1,3-$(HOCH_2)_2C_6H_4$ appears to be essentially nonselective after 18 h unlike that involving 1,4-$(HOCH_2)_2C_6H_4$. Attempts to isolate a pure sample of the cyclic trimer, observed in the mass spectrum of the crude product, were unsuccessful.

The mass spectrum of the crude product from the reaction between [Mo(NO)(tp*)I_2] and (4-$HOC_6H_4)_2CH_2$ contained a molecular ion at *m*/*z* 1243 corresponding with the cyclic dimer [Mo(NO)(tp*){(4-$OC_6H_4)_2CH_2$}]$_2$, **4**, together with an ion at *m*/*z* 1865 attributable to the cyclic trimer [Mo(NO)(tp*){(4-$OC_6H_4)_2CH_2$}]$_2$, **5**, and low intensity ion at *m*/*z* 2484 attributable to the cyclic tetramer. Compared to the reactions involving 1,3- or 1,4-$(HOCH_2)_2C_6H_4$, significantly larger proportions of the cyclic trimer were present, particularly after short reaction times. Chromatographic separation afforded pure samples of the two isomers, **4a** and **4s**, of the binuclear compound and of the trinuclear compound **5**. A small sample of a cyclic tetramer was also isolated. However, despite giving a mass spectrum free of ions due to other cyclic oligomers, this compound could not be obtained in a pure form as judged by ^{1}H NMR spectroscopy. One of the binuclear isomers, **4a**, was of low solubility in toluene and was assigned the *anti*-structure on the basis of the ^{1} H NMR spectral data since the methylene protons appear as a singlet. The other isomer, **4s**, was more freely soluble in toluene and was assigned the *syn*-structure, the methylene protons appearing as an AB system in the ^{1}H NMR spectrum.

The cyclic trimer can exist as the *anti*,*syn*-isomer and the *syn*,*syn*-isomer. In a nonselective reaction, the isomer ratio might be expected to be statistically determined with the isomers present in the respective relative proportions 3:1. The ^{1}H NMR spectrum of **5**, the product isolated, is in accord with this expectation.[12b,d] Although signal overlap obscures the relative areas of the signals due to the aryl or methylene protons, the signals due to the dimethylpyrazolyl C^4 and 3,5-methyl protons are sufficiently well resolved to show that neither the pure *anti*,*syn*-isomer nor the pure *syn*,*syn*-isomer has been isolated. The spectrum of a 3:1 mixture of isomers should give rise to seven signals due to the pyrazolyl C^4 protons. When normalized to a single [Mo(NO)(tp*){$OC_6H_4CH_2C_6H_4O$)]$_3$ molecule, these should appear in the area ratio $1^1/_2$:$1^1/_2$:$1^1/_2$:$1^1/_2$:$1^1/_2$:$^3/_4$:$^3/_4$.[12b,d] A similar analysis of the environments of the pyrazolyl methyl protons leads to the conclusion that a 3:1 mixture of isomers should give rise to a total of 14 singlets, of which 10 should be of relative area $4^1/_2$ and four of relative area $2^1/_4$. Despite some signal overlap the observed spectrum fits this model well, indicating that **5** contains a statistical mixture of isomers and that its formation is not stereoselective**.** Attempts to isolate a pure sample of the cyclic tetramer, observed in the mass spectrum of the crude product, were unsuccessful.

The variation with time in the proportions of **4a**, **4s**, and **5** formed in the reaction was investigated. After 15 min the ratio of **4a**:**4s** was 29:25, 35:26 after 18 h, and 79:9 after 54 h, the total yields of **4a** and **4s** at these respective times being 54, 61, and 88%. Heating **4a** under reflux in toluene solution for 3 days did not result in isomerization. However, under these conditions **4s** converted to a ca. 1:1 mixture of **4a** and **4s** together with some decomposition products. The yields of the cyclic trimer, **5**, isolated after 15 min and 18 h were 26 and 20%, but significant quantities of **5** could not be isolated after a reaction time of 54 h. Heating a sample of **5** under reflux in toluene for 54 h resulted in some decomposition, but under these conditions, no substantial conversion of **5** to **4a** or **4s** was observed**.** Since the yields of the *syn*-isomer **4s** and the cyclic trimer, **5**, decline with time while the yield of the *anti*-isomer **4a** continues to increase to 79%, it would appear that **4s** and **5** are kinetic products of the reaction between between [Mo(NO)(tp*)I_2] and (4-$HOC_6H_4)_2CH_2$ and that **4a** is the thermodynamic product. This represents the first identified example of isomer interconversion in these {Mo(NO)(tp*)}-containing metallomacrocycles and shows that such isomerizations can occur and that the extent to which kinetic or thermodynamic factors affect the outcome of the metallomacrocycle formation reaction is sensitive to the nature of the ditopic ligand used.

The stereoselective formation of **2a** over **2s** is an unexpected feature of these metallomacrocycle-forming reactions. Unfortunately the origin of this selectivity is hard to define, as three pathways are possible for the formation of the binuclear macrocycles from the achiral complex [Mo(NO)(tp*)I_2] and the achiral ditopic proligand HE-EH {HE-EH = 1,3-$(HOCH_2)_2C_6H_4$, 1,4-$(HOCH_2)_2C_6H_4$, (4-$HOC_6H_4)_2CH_2$}. All three pathways involve, as a first step, formation of the chiral monosubstituted derivative [Mo(NO)(tp*)(E-EH)I] as a racemic mixture. The final step in each pathway involves the ring closure,with HI elimination, of the racemic acyclic binuclear complex [{Mo(NO)(tp*)(E-EH)}(μ-E-E){Mo(NO)(tp*)I}], which is the cyclic dimer precursor. In the first of the three possible intermediate reaction pathways, two molecules of [Mo(NO)(tp*)(E-EH)I] react together to form the cyclic dimer precursor. In the second pathway addition of a further metal center to [Mo(NO)(tp*)(E-E)I] affords a mixture of *meso*- and *dl*-isomers of the bimetallic complex [{Mo(NO)(tp*)I}$_2$(E-E)]. Reaction of this complex with further HE-EH then affords the cyclic dimer precursor. In the third pathway the monosubstituted derivative [Mo(NO)(tp*)(E-EH)I] reacts with further HE-EH to give the achiral complex [Mo(NO)(tp*)(E-EH)$_2$]. This may then react with a molecule of [Mo(NO)(tp*)I_2] to give the cyclic dimer precursor. Not all of these pathways may be involved in the reaction, and the stereoselectivity of each may differ. Furthermore, since the substitution of the chiral ligand in a single diastereoisomer of [Mo(NO)(tp*)I{(−)-mentholate}] by the achiral ligand $HOC_6H_4NO_2$-4 affords a racemic product,[11] there are no grounds to suppose that chirality would be retained at the molybdenum center during the metallomacrocycle-forming reactions.

In an attempt to determine which of the possible intermediates might be involved in the metallomacrocycle formation process,

the reactions of the known[8b] complexes [Mo(NO)(tp*)I(E-EH)] and [{Mo(NO)(tp*)I}$_2$(E-E)] have been examined. Attempts to prepare [Mo(NO)(tp*)(E-EH)$_2$] have been unsuccessful since the conditions necessary to induce substitution of both iodides lead to metallomacrocycle formation, even in the presence of excess HE-EH. The self-reaction of [Mo(NO)(tp*)I(OCH$_2$C$_6$H$_4$-CH$_2$OH-4)] in the presence of NEt$_3$ and the reaction of [{Mo(NO)(tp*)I}$_2$\{1,4-(OCH$_2$)C$_6$H$_4$\}] with further 1,4-(HOCH$_2$)$_2$C$_6$H$_4$ and NEt$_3$ afforded no metallomacrocyclic products. In the cases of [Mo(NO)(tp*)I(OCH$_2$C$_6$H$_4$CH$_2$OH-3)] and [{Mo(NO)(tp*)I}$_2$-\{1,3-(OCH$_2$)C$_6$H$_4$\}] only low yields (<8%) of cyclic dimer were obtained, and reliable estimates of the *syn*/*anti*-isomer ratio could not be made. The self-reaction of [Mo(NO)(tp*)I(OC$_6$H$_4$-CH$_2$C$_6$H$_4$OH-4,4′)] in the presence of NEt$_3$ also afforded low yields of cyclic dimer compared to the direct reaction between [Mo(NO)(tp*)I$_2$] and (4-HOC$_6$H$_4$)$_2$CH$_2$, total yields of **4a** and **4s** being 3% after 105 min, 22% after 18 h, and 25% after 54 h. The reaction between the acyclic bimetallic complex [{Mo(NO)(tp*)I}$_2$\{(4-OC$_6$H$_4$)$_2$CH$_2$\}] and (4-HOC$_6$H$_4$)$_2$CH$_2$ in the presence of NEt$_3$ gave total yields of **4a** and **4s** of 8% after 45 min, 50% after 18 h, and 39% after 54 h. These findings would suggest that the pathway involving the bis-substituted intermediates [Mo(NO)(tp*)(E-EH)$_2$] may represent the more efficient route to the cyclic dimers, but we have been unable to confirm this by a direct experiment due to the synthetic inaccessibility of [Mo(NO)(tp*)(E-EH)$_2$].

Since the structures of the metallomacrocycles produced in this work resemble those of cyclophanes, which are known to act as host molecules,[14] attempts were made by ^{1}H NMR spectroscopy to detect evidence for host−guest interations between the new binuclear compounds and 1,2- or 1,4-dimethoxybenzene. However, no evidence for host−guest behavior was found, and in the cases of **2a** and **2s** at least, the crystallographic studies described below provide structural reasons for this negative result.

Structural Studies. Views of the complexes **2a** and **2s** and **4a** are shown in Figures 2−4, and selected geometric parameters are listed in Table 2. The two *anti* complexes are centrosymmetric (crystallographic C_i symmetry), whereas the *syn* complex, **2s**, has no crystallographic symmetry, but possesses approximate *mm*2 (C_{2v}) symmetry. The mirror symmetry along the Mo−Mo axis observed in the ^{1}H NMR spectra of the three complexes is found in the solid state only approximately in **2s**.

The coordination geometry at the molybdenum atoms is approximately octahedral in each case. The mean deviations from ideal octahedral range from 7.1° in **2a** to 7.8° at the "primed" molybdenum center of structure **2s**. As had been noted previously,[13] these deviations show a consistent pattern, and differences between corresponding angles at the four molybdenum centers are relatively small, mean differences being 0.6−1.2°. Comparison of these molybdenum centers with monomeric[18,19] and other binuclear[13] molybdenum complexes shows that the mean differences between corresponding angles are of similar magnitude.

The molybdenum−oxygen bonds fall into two categories. In **2a** and **2s**, where the oxygen links the molybdenum to an sp^3-hybridized carbon, the Mo−O bonds have lengths of 1.899−1.923 Å (mean 1.909(3) Å), whereas in **4a**, involving an Mo−O−C(sp^2) system, the Mo−O lengths are longer at 1.946(3) and 1.931(3) Å. Both categories of Mo−O bonds are relatively short. This implies pπ−dπ electron donation from the donor atom (O) to the coordinatively unsaturated metal. Large angles at oxygen and the small N(nitrosyl)−Mo−O−C torsion angles (<±20.6°) are consistent with this, although steric effects may also play a role in increasing the bond angle at oxygen. The longer Mo−O lengths and larger Mo−O−C angles in systems where the carbon atom is unsaturated may be the result of additional electron delocalization involving the aromatic rings, which compete with the oxygen-to-metal pπ−dπ donation. The phenyl rings are fairly close to coplanarity with their respective Mo−O−C planes [31.1(5)° and 3.6(7)° for rings C(16)−C(21) and C(23)−C(28), respectively], consistent with this model.

The overall conformation of complexes **2a** and **2**s can be described by reference to the 12-atom best plane through the four oxygen atoms bonded to molybdenum, the methylene carbon atoms bonded to these oxygen atoms, and the adjoining atoms of the phenyl rings. In the centrosymmetric complex **2a**, this grouping is coplanar to within ±0.53 Å, with the Mo atoms close to the plane (deviation ±0.18 Å) and the nitrosyl oxygen atoms displaced by 2.78 Å on opposite sides of this central plane. The corresponding 12-atom grouping in **2s** is less planar, with atomic deviations of up to to 0.87 Å and the Mo atoms displaced by 0.59 Å on the same side of this plane in accord with the approximate C_{2v} symmetry of complex **2s**. The nitrosyl oxygen atoms, O(1) and O(1)′, are displaced by 2.31 and 2.30 Å, respectively. However, when compared with the *anti* complexes **2a** and **4a**, and analogous *anti* and *syn* binuclear complexes,[13] the orientation of both the {Mo(NO)(tp*)} residues is rotated through 180° with respect to the linking ring system,

Table 2. Selected Structural Parameters for **2a**, **2s**, and **4a**[a,b]

		2s		
	2a	Mo	Mo′	**4a**
	Distances (Å)			
Mo−N(1)	1.756(5)	1.771(13)	1.745(13)	1.761(4)
Mo−N(2)	2.245(4)	2.253(11)	2.263(13)	2.251(4)
Mo−N(4)	2.241(4)	2.231(13)	2.237(14)	2.191(4)
Mo−N(6)	2.219(4)	2.236(12)	2.236(13)	2.190(4)
Mo−O(2)	1.907(3)	1.903(10)	1.912(10)	1.946(3)
Mo−O(3)	1.923(3)	1.908(10)	1.899(10)	1.931(3)
N(1)−O(1)	1.204(6)	1.204(13)	1.205(13)	1.206(5)
O(2)−C(16)	1.413(6)	1.428(13)	1.40(2)	1.354(5)
O(3)−C*	1.437(6)	1.41(2)	1.41(2)	1.365(5)
	Angles (deg)			
N(1)−Mo−N(2)	177.9(2)	177.7(5)	177.7(6)	177.4(2)
N(1)−Mo−N(4)	93.2(2)	94.0(5)	95.5(6)	95.4(2)
N(1)−Mo−N(6)	93.7(2)	93.4(5)	93.6(6)	93.3(2)
N(1)−Mo−O(2)	97.1(2)	97.7(5)	97.1(5)	97.1(2)
N(1)−Mo−O(3)	97.0(2)	98.3(5)	98.1(5)	99.1(2)
N(2)−Mo−N(4)	85.7(2)	85.1(5)	84.7(6)	84.6(2)
N(2)−Mo−N(6)	84.3(2)	84.3(5)	84.2(6)	84.2(2)
N(2)−Mo−O(2)	83.6(2)	82.7(4)	82.2(5)	82.5(2)
N(2)−Mo−O(3)	84.8(2)	83.8(4)	84.2(5)	83.5(2)
N(4)−Mo−N(6)	76.7(2)	77.3(5)	75.8(5)	79.0(2)
N(4)−Mo−O(2)	162.3(2)	161.8(5)	161.0(6)	163.4(2)
N(4)−Mo−O(3)	90.1(2)	89.4(4)	89.1(5)	88.7(2)
N(6)−Mo−O(2)	88.2(2)	88.2(4)	89.3(5)	89.5(2)
N(6)−Mo−O(3)	163.4(2)	162.8(4)	161.7(5)	163.3(2)
O(2)−Mo−O(3)	102.8(2)	102.5(4)	103.1(4)	100.0(2)
Mo−N(1)−O(1)	178.3(4)	177.6(12)	178.7(13)	178.2(4)
Mo−O(2)−C(16)	130.7(3)	131.3(10)	132.9(10)	133.7(3)
Mo−O(3)−C*	127.4(3)	129.4(10)	129.9(10)	141.5(3)
	Torsion Angles (deg)			
N(1)−Mo−O(2)−C(16)	9.6(4)	6.3(13)	−3.7(14)	20.6(4)
N(1)−Mo−O(3)−C*	3.3(4)	−6.0(14)	0.7(14)	−8.4(5)

[a] Values in parentheses are estimated standard deviations. [b] C* is C(23) in **2a** and **4a**, and C(20) in **2s**.

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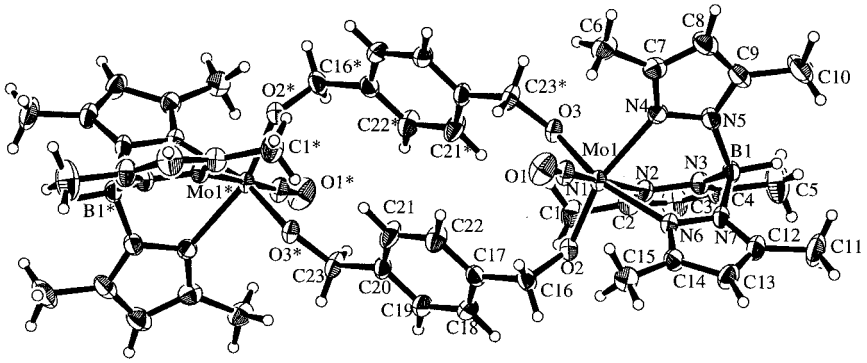

Figure 2. View of complex **2a**. Starred atoms are related to the corresponding unstarred atoms by an inversion center.

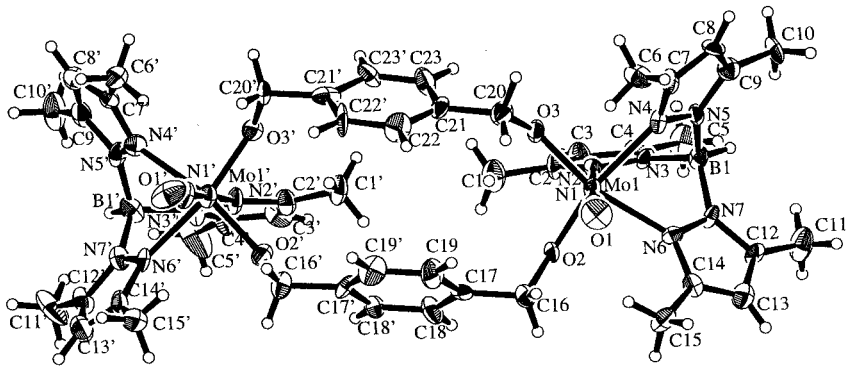

Figure 3. View of complex **2s**. Primed atoms are related to the corresponding unprimed atoms by an approximate (noncrystallographic) mirror plane.

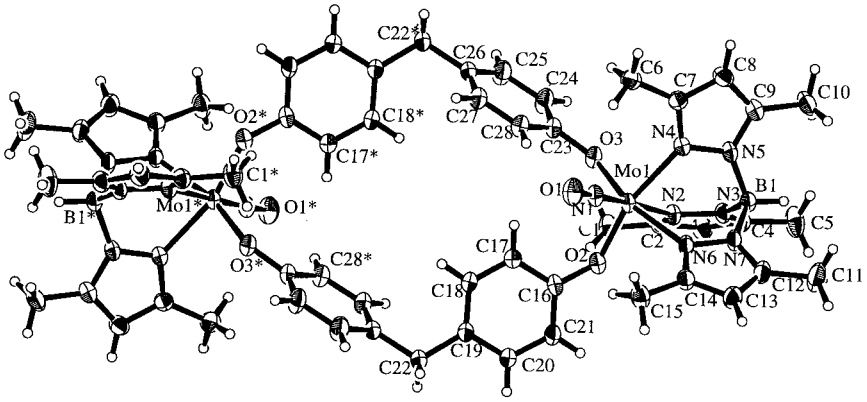

Figure 4. View of complex **4a**. Starred atoms are related to the corresponding unstarred atoms by an inversion center.

so that, effectively, the nitrosyl ligand and the (N(2), N(3), C(1)−C(5)) pyrazolyl ring have interchanged coordination sites, bringing the nitrosyl ligand closer to the central plane. The centrosymmetric complex **4a** can be described by reference to a 14-atom central plane, consisting of the seven atoms C(22), C(19), C(16), O(2), O(3), C(23), and C(26) and the symmetrically related atoms (starred in Figure 4). This atomic grouping is coplanar to within ±0.07 Å with the metal atoms displaced by ±0.88 Å. The nitrosyl oxygen atoms are at distances of 3.31 Å on opposite sides of the plane.

The capacity of cyclic complexes to bind guest molecules is limited by the size of the cavity formed. For complexes **2a** and **2s**, the central cavity is too small to bind even small guest molecules. Critical cross-ring interatomic distances in **2a** are C(21)···C(21)* 3.37 Å and C(21)···C(22)* [and C(21)*···C(22)] 3.50 Å, and in **2s**, C(19)′···C(22) 3.50 Å, C(19)···C(22) 3.61 Å, and C(19)′···C(22)′ 3.66 Å. The central cavity of **4a** is somewhat larger, with C(18)···C(18)* 5.44 Å and C(17)··· C(18)* [and C(17)*···C(18)] 5.62 Å.

All three complexes contain solvent of crystallization. In crystals of **2a**, two symmetry-related molecules of chloroform are hydrogen-bonded to ring oxygen atoms O(3) and O(3)*, with C···O 3.20 Å, H···O 2.27 Å, and angle C−H···O 159° (H atoms in calculated positions). The angles Mo−O(3)···H and C(23)−O(3)···H are 110° and 104°, respectively, so that the hydrogen atom appears to be in a suitable orientation for hydrogen bonding. Two other symmetry-related molecules of chloroform have their hydrogen atoms at 2.45 Å from ring oxygens O(2) and O(2)*, probably too far for significant hydrogen bonding.[20] In **2s**, two molecules of dichloromethane and, in **4a**, two molecules of chloroform and one molecule of disordered dichloromethane appear to act as space fillers and do not interact significantly with the complex molecules.

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Electrochemical Studies. The electrochemical properties of the new binuclear complexes were investigated using cyclic voltammetry. Each redox active {Mo(NO)} center should undergo electrochemical reduction at a potential that will depend on the nature of the bridging ligand.[21−23] In the binuclear complexes the extent to which the bridging ligand can communicate the presence of the other metal center will also affect the reduction potentials.[8b,24] Thus for *syn*-[Mo(tp*)(NO)(2,7-$O_2C_{10}H_6$)]$_2$ two reduction waves are observed at −0.633 and −0.807 V (CH_2Cl_2 SCE) separated by 174 mV due to the interaction between the two metal centers.[13] The longer bridging groups in the complexes described here might be expected to support smaller interactions,[8b] and this is in fact observed. Cyclic voltammetric investigation of **2a** revealed a single broad wave centered at −0.65 V (CH_2Cl_2 SCE) which did not appear fully reversible. This results from two overlapping electron-transfer processes with a separation, ΔE_f, estimated at 85 mV from the differential pulse voltammogram.[25] This is comparable to the electrochemical behavior of the binuclear acyclic complex [{Mo(tp*)(NO)Cl}$_2${1,4-$(OCH_2)_2C_6H_4$}], which also shows a broad wave at −0.60 V with an estimated ΔE_f of 85 mV.[8b] The solubilities of the complexes **3i** and **3ii** in solvents suitable for electrochemistry were insufficient to allow meaningful electrochemical study. However, in the cases of complexes **4a** and **4s**, well-formed, apparently reversible, waves appear at −0.72 V (CH_2Cl_2 SCE) with an estimated ΔE_f of 90 mV, there being no resolvable difference between the electrochemical behaviors of the two isomers. The binuclear acyclic complex [{Mo(tp*)(NO)Cl}$_2${4-$(OC_6H_4)_2CH_2$}] shows a well-formed wave at −0.35 V involving two unresolved processes with an estimated ΔE_f of 65 mV. The presence of a second phenoxide ligand in **4a** produces a negative shift in the reduction potential compared to the acyclic complex, an effect that has been observed previously.[23]

Conclusion

Metal-directed macrocycle formation reactions involving [Mo(NO)(tp*)I_2] and the flexible ditopic proligands HE-EH {HE-EH = 1,3-$(HOCH_2)_2C_6H_4$, 1,4-$(HOCH_2)_2C_6H_4$, (4-$HOC_6H_4)_2CH_2$} afford binuclear cyclophane-like molecules. Trinuclear cyclic oligomers also form, but in much lower yields. This finding may be contrasted with the reactions of [Mo(NO)(tp*)I_2] with the rigid "linear" ditopic proligands 1,4-$(HO)_2C_6H_4$[21] and 1,4-(4′-$HOC_6H_4)_2C_6H_4$,[12b] which afford cyclic trimers and tetramers as the predominant cyclic oligomer fractions. The reactions with the flexible ligands appear to proceed under kinetic control, with the *syn*-isomer of the cyclic dimer forming most rapidly. The outcome of the reaction is highly dependent on the nature of the ditopic proligand HE-EH. Thus with 1,2-$(HOCH_2)_2C_6H_4$ no cyclic dimers are isolated; instead only the mononuclear chelate complex **1** is obtained. In the case of 1,4-$(HOCH_2)_2C_6H_4$, the *anti*-isomer of the cyclic dimer is formed stereoselectively, but with 1,3-$(HOCH_2)_2C_6H_4$ or (4-$HOC_6H_4)_2CH_2$ the reaction appears essentially nonselective. Only in the case of (4-$HOC_6H_4)_2CH_2$ was evidence found for the conversion of one isomer of the cyclic dimer, **4s**, to another, **4a**. Although direct evidence is lacking, the relatively low yields of cyclic dimer obtained from reactions involving [Mo(NO)(tp*)(E-EH)I] or [{Mo(NO)(tp*)I_2(E-E)], and the high yield of **1** (74%), suggest that [Mo(NO)(tp*)(E-EH)$_2$] may be an important intermediate in cyclic dimer formation.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes *anti*-[[Mo(NO){HB(3,5-$Me_2C_3HN_2)_3$}{1,4-$(OCH_2)_2C_6H_4$}]$_2$·4$CHCl_3$ (**2a**), *syn*-[Mo(NO){HB(3,5-$Me_2C_3HN_2)_3$}{1,4-$(OCH_2)_2C_6H_4$}]$_2$·2CH_2Cl_2 (**2s**), and *anti*-[Mo(NO){HB(3,5-$Me_2C_3HN_2)_3$}{(4-$OC_6H_4)_2CH_2$}]$_2$·2$CHCl_3$·CH_2Cl_2 (**4a**). This material is available free of charge via the Internet at http://pubs.acs.org.

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