angles equal to 14 and 16° and 15 and 30°, respectively for the syn and anti isomer). Apart from steric considerations, this preference for an almost eclipsed O–*C–C–N conformation may result from a five-membered bent hydrogen bonding interaction;[25] thus, this fragment leads to more highly structured molecular architectures as well as to convergence of potential binding sites.

(e) The structural features provide an explanation for the marked differences between the physicochemical properties of the two isomers. For (*syn*-**2a**), the ring conformation resembles that of the cation complexes of the parent [18]-crown-6 itself;[26] the gauche and anti preferences of the CC and CO bonds, respectively,[27] are compatible with a ring conformation bringing the two carboxylate groups in close contact with the cation [see (b)]; the six ether oxygens form an almost planar hexagon (extreme deviations from 0.24 to –0.31 Å from the mean plane, from +0.20 to –0.20 Å for [18]-crown-6[26]) surrounding the complexed cation. The only conformational distorsions brought about by the tartaric acid residues involve the *C*C–OC bonds (dihedral angles of 133 and 145°) and the carbon framework ($g^+g^-g^+g^+g^-g^+$), leading to a lower pseudotwofold symmetry for the ring.

(f) In contrast, the structure of (*anti*-**2a**) shows a strained, sigmoïdal conformation for the macrocyclic ring. The electrostatic interaction of the complexed cation with the two anti carboxylate groups imposes two eclipsed CC-bond conformations (dihedral angles of 1 and 14°), and the six ether oxygen atoms are displaced from their mean plane by distances ranging from –0.86 to +0.55 Å. This may explain why the complexes of the anti isomers are ca. 100 times less stable than those of the syn isomers.[21] Furthermore, the carboxylate group above the ring in Figure 2 is shielded from its environment by the aromatic group located in front of it, a feature which may be related to the lower polarity of this isomer in the chromatographic separation. This view is strengthened by the structural study of a dimeric form as schematically depicted in Figure 1, which has been isolated for (*anti*-**2c**)Ca^{2+} after chromatography. Although the diffraction data were of poor quality, it appears that in the structure arrived at, a second molecule lies in a pseudocentrosymmetric way at the open side of the macrocycle (replacing the water molecules shown in Figure 2), thus shielding the polar sides of both macrocycles in an organic shell.

Both the *syn*-**2** and *anti*-**2** macrocycles possess attractive features. The syn species are synthesized selectively and have very interesting conformational and complexing properties; developments into the *macropolycyclic dimension* are being pursued. The laterally discriminated anti system may allow placing a complexed substrate in an electrostatic field between charged sites, a feature of much interest for developing "*charge-relay*"*-type catalytic systems.*

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[25] H···O distances with the calculated hydrogen position range from 2.20 to 2.26 Å.

[26] Dunitz, J. D.; Dobler, M.; Seiler, P.; Phizackerley, R. P. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2733–2738.

[27] Dale, J. *Tetrahedron* **1974**, *30*, 1683–1694.

Di-μ-oxo-(η^1:η^5-1,2,3,4-tetramethyl-5-methylene-1,3-cyclopentadiene-bis[(η-pentamethylcyclopentadienyl)titanium], $(\mu\text{-O})_2[\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5(CH_2)(CH_3)_4]][Ti[\eta^5\text{-}C_5(CH_3)_5]]_2$, a Complex Containing a Bridging Tetramethylmethylenecyclopentadienyl Ligand

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We wish to report the preparation and structure of $(\eta\text{-O})_2$-$[\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5(CH_2)(CH_3)_4]][Ti[\eta^5\text{-}C_5(CH_3)_5]]_2$ (I), the first structurally characterized complex containing a bridging $[\eta^1{:}\eta^5\text{-}C_5(CH_2)(CH_3)_4]$ ligand. It has been previously suggested that monomeric complexes containing the $[\eta^1{:}\eta^5\text{-}C_5(CH_2)(CH_3)_4]$ ligand occurred as reactive intermediates in the chemistry of $[\eta^5\text{-}C_5(CH_3)_5]_2Ti$, in particular during the perdeuteration of this complex.[1,2] Structural evidence is, however, lacking, and no dimeric species were involved. In complexes of the parent C_5H_5 ligand, $(\eta^1{:}\eta^5\text{-}C_5H_4)$ is known to bridge two Ti atoms.[3] The synthesis of I followed from our continuing investigation of the use of N_2O as a controlled source of oxygen atom oxidation for transition-metal complexes.[4,5]

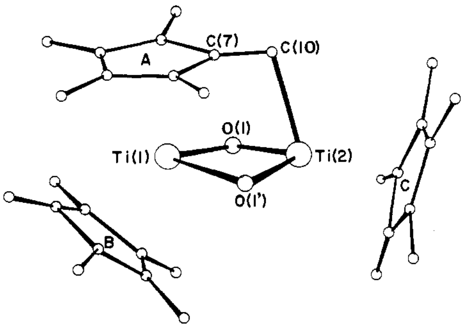

Figure 1. Structure of I. Hydrogen atoms have been omitted for clarity. There is a crystallographic mirror plane through atoms C(7), C(10), Ti(1), and Ti(2) and bisecting each of the three rings.

When N_2O reacted with a toluene solution of $Cp^*{}_2Ti^1$ (Cp^* = $[\eta^5\text{-}C_5(CH_3)_5]$) at 0 °C, there was a color change from orange to green-yellow and an immediate evolution of N_2. On reduction of the volume of the solution, precipitation of light green crystals, together with a small amount of an unknown brown, hexane-soluble material, occurred. The moderately air-stable green crystals had the apparent stoichiometry "$Cp^*{}_3Ti_2O_2$" but showed an ^1H NMR spectrum in the ring methyl region very similar to that of $C_{10}(CH_3)_9CH_2TiH$ (see Figure 1 of ref 1), indicating the presence of a cyclopentadienyl ring other than $[\eta^5\text{-}C_5(CH_3)_5]$. The structural analysis showed that the green compound has formula I, and the reaction can therefore be represented by

$$2Cp^*{}_2Ti + 2N_2O \rightarrow \underset{\mathbf{I}}{(\eta\text{-O})_2[\eta^1{:}\eta^5\text{-}C_5(CH_2)(CH_3)_4][Ti[\eta^5\text{-}C_5(CH_3)_5]]_2} + 2N_2 + C_5(CH_3)_5H$$

The complex (see Figure 1) has several very unusual structural features.[6,7] It is clear that one methyl group of a $C_5(CH_3)_5$ ring attached to one titanium has become a methylene bridge to the second titanium. The Ti(2)–CH_2 distance, 2.176 (6) Å, is similar to the 2.19 (2) Å found in $(\eta^5\text{-}C_5H_5)_2Ti\text{-}\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)\text{-}Ti(\eta^5\text{-}C_5H_5)$[3] and the 2.15 (1) and 2.09 (1) Å in $[(C_2H_5O)(C_6H_5CH_2)_2Ti]_2(\eta\text{-}C_2H_5O)_2$.[8] The CH_2–ring A distance [C(7)–C(10) in Figure 1] of 1.473 (9) Å is barely significantly different from the average CH_3–ring distance in the three rings, 1.501 (6) Å. The C–C ring distances in ring A do not differ significantly from those in ring B or C. These two facts coupled with the Ti(2)–C(7) distance of 2.872 (6) Å and the C(7)–C(10)–Ti(2) angle of 102.1 (4)° indicate that the Ti(2)–CH_2 bond

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[1] Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219–38.

[2] Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087–95.

[3] Pez, G. P. *J. Am. Chem. Soc.* **1976**, *98*, 8072–8.

[4] Bottomley, F.; White, P. S. *J. Chem. Soc., Chem. Commun.*, in press.

[5] Bottomley, F.; Lin, I. J. B.; Mukaida, M. *J. Am. Chem. Soc.* **1980**, *102*, 5238–42.

[6] The structure was determined by X-ray crystallography. Crystal data: $C_{30}H_{44}O_2Ti_2$, M = 532.5; orthorhombic, *Pnma*; a = 10.650 (5), b = 15.283 (3), c = 17.064 (8) Å; R = 0.041, R_w = 0.060 for 1120 observed reflections out of 1904 measured. Hydrogen atoms were refined isotropically, all other atoms anisotropically. Full details will be published elsewhere.

[7] We have considered the possibility that there is an additional hydrogen atom in the structure. However, attempts to place a hydrogen at various likely positions on the Ti, O, or C(7) atoms gave unrefinable structures. Also, the diamagnetism of the complex is not compatible with the presence of a hydrogen atom.

[8] Stoeckli-Evans, H. *Helv. Chim. Acta* **1975**, *58*, 373.

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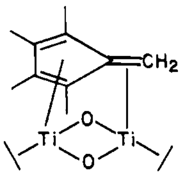
is essentially a single σ bond, without significant contribution from the olefinic structure



The Ti(1)-C(10) distance of 3.205 (6) Å and the normal Ti(1)-C(7) distance of 2.402 (6) Å indicate that there is no interaction between the methylene group and Ti(1). The ring A-Ti(1)-ring B angle of 140.6°[9] is close to the 145.8° and 145.6° observed in $(Cp^*{}_2Ti)_2N_2$.[10] The bridging CH_2 therefore produces little distortion of the $Cp^*{}_2Ti$ unit. However, the angle between the Ti(1)-O(1)-O(1′) and Ti(2)-O(1)-O(1′) planes is 158.8°, producing an extremely short Ti-Ti distance of 2.725 (2) Å [compare this to the 3.336 (4) Å in $(\eta^5\text{-}C_5H_5)_2Ti\text{-}\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)\text{-}Ti(\eta^5\text{-}C_5H_5)$ for which a single Ti-Ti bond is proposed,[3] or the shortest Ti-Ti distance previously observed, 2.891 (1) Å in $(C_5H_5)_6Ti_6O_8$].[11] However, there can be no Ti-Ti bond, since we are dealing formally with Ti(IV), d°. The folding is produced by the strong C(10)-Ti(2) bond.

If the usual electron counting rules are followed, Ti(1) has 16 electrons and Ti(2) only 12. The extreme electron deficiency of Ti(2) manifests itself in the highly unsymmetrical Ti-O distances to the bridging oxo ions: Ti(1)-O is 1.961 (3) Å whereas Ti(2)-O is only 1.789 (3) Å.

It is becoming apparent that N_2O functions as a source of a bridging O atom in its reactions with Cp_2M derivatives of the early transition metals. In addition to the present work, examples have now been found for Ti,[5] V,[4] and Mo and W.[12] These aspects as well as the reactivity of I are being further investigated.

Acknowledgment. We thank the National Sciences and Engineering Research Council of Canada and the University of New Brunswick Research Fund for financial support of this work.

Supplementary Material Available: Tables of fractional atomic coordinates, thermal parameters, and bond distances and structure of I (5 pages). Ordering information is given on any current masthead page.

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(9) The ring A-Ti(1)-ring B angle is defined by using the center of the rings A and B as terminus.

(10) Sanner, R. D.; Duggan, D. M.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8358-65.

(11) Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829-31.

(12) Cooper, N. J.; Green, M. L. H.; Couldwell, C.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1979**, 145-46.

Conformational Mobility in 1,4-Bridged Cyclooctanes. ^{13}C NMR Evidence for Facile Chirality Inversion

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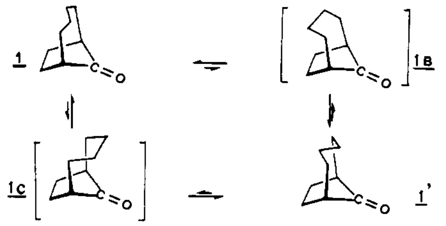
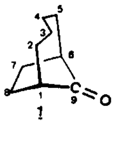
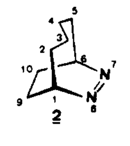
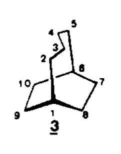
The family of cyclooctane conformers has been investigated both theoretically by means of semiempirical strain energy calculations[1] and experimentally by dynamic NMR (^1H, ^{19}F, and ^{13}C)[2] and X-ray diffraction.[3] Universal agreement exists concerning the cyclooctane minimum energy conformation, which has been shown to be the boat-chair (BC). 1,4-Bridged cyclooctanes **1-5** are expected to retain some of the flexibility of the cyclooctane system but are also expected to behave similarly to cyclohexenes[4] as far as the dynamics of the four-membered bridge is concerned.[5] In order to elucidate the structure and dynamics of 1,4-bridged cyclooctanes, we synthesized compounds **1**,[8] **2**,[9] **3**,[10] **4**,[11] and **5**[11] and investigated their 25.2-MHz ^{13}C NMR spectra (^1H noise decoupled) as a function of temperature.

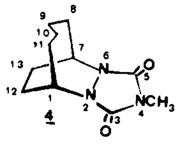
Scheme I

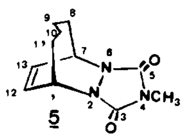












All compounds produced slow-exchange ^{13}C NMR spectra which are in agreement with 1:1 mixtures of the chiral structures **1-5** and their mirror images **1′-5′**. In the fourth column of Table I the change in the molecule's symmetry group during the exchange-producing process is given. In the fifth column the chemical shifts at two representative temperatures are displayed and exchanging signals are grouped together. Line-shape analyses were performed[12] by employing suitable exchanging sites, and with these calculated first-order rate constants, activation parameters were obtained which are given in Table II.

In Scheme I a probable reaction sequence for the conformational mobility of **1** is displayed. **1** has the choice of racemizing

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† The Technological Institute, Gregersensvej, DK2630, Tåstrup, Denmark.

(1) Anet, F. A. L. *Fortschr. Chem. Forsch.* **1974**, *45*, 169-220 and references cited therein.

(2) Anet, F. A. L.; Hartman, J. S. *J. Am. Chem. Soc.* **1963**, *85*, 1204-1205. Anet, F. A. L.; St. Jacques, M. *Ibid.* **1966**, *88*, 2585-2587. Anderson, J. E.; Glazer, E. S.; Griffith, D. L.; Knorr, R.; Roberts, J. D. *Ibid.* **1969**, *91*, 1386-1395. Anet, F. A. L.; Basus, V. J. *Ibid.* **1973**, *95*, 4424-4426.

(3) Dobler, M.; Dunitz, J. D.; Mugnoli, A. *Helv. Chim. Acta* **1966**, *49*, 2492-2502. Bürgi, H. B.; Dunitz, J. D. *Ibid.* **1968**, *51*, 1514-1526. Groth, P. *Acta Chem. Scand.* **1965**, *19*, 1497. *Ibid.* **1967**, *21*, 2695-2710.

(4) Bucourt, R. *Top. Stereochem.* **1974**, *8*, 183-187.

(5) It has been suggested[6] that the *N*-phenyl derivative of **5** should exist as a mixture of diastereomeric "boat" conformers which interconvert rapidly at room temperature. Lehn and Wagner,[7] on the other hand, argue that the $-(CH_2)_4-$ bridge in this system probably adopts a conformation in which H/H eclipsing is minimized but do not specify the structure.

(6) Chung, C. Y.-J.; Mackay, D.; Sauer, T. D. *Can. J. Chem.* **1972**, *50*, 3315-3321.

(7) Lehn, J. M.; Wagner, J. *Tetrahedron* **1969**, *25*, 677-689.

(8) Antkowiak, T. A.; Sanders, D. C.; Trimitsis, G. B.; Press, J. B.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 5366-5373.

(9) Heyman, M.; Bandurco, V. T.; Snyder, J. P. *J. Chem. Soc., Chem. Commun.* **1971**, 297-298.

(10) This compound was obtained by catalytic hydrogenation (PtO_2) of the [4 + 4] photoadduct of 1,3-butadiene and benzene. Bicyclo[4.2.2]deca-3,7,9-triene was obtained by using the procedure described by Löffler [Löffler, H. P. *Tetrahedron Lett.* **1974**, 786-788]. For a more tedious procedure, see: Pozdnikina, S. G.; Morozova, O. E.; Petrov, Al. A. *Neftekhimiya* **1973**, *13*, 21-26.

(11) Snyder, J. P.; Bandurco, V. T.; Darack, F.; Olsen, H. *J. Am. Chem. Soc.* **1974**, *96*, 5158-5166.

(12) The line-shape analyses were carried out by using the LSHKUBO program, written by Dr. J.-M. Gilles. For a description of the underlying algorithms, see: Oth, J. F. M.; Müllen, K.; Gilles, J.-M.; Schröder, G. *Helv. Chim. Acta* **1974**, *57*, 1415-1433 and references quoted therein.

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