with no short contacts to the hexafluorophosphate counterions. The double-helical geometry is emphasized in the sketch of the molecule presented in Figure 1b. The two cadmium atoms are in irregular six-coordinate N_6 environments, with all Cd–N distances in the expected range 2.301 (6)–2.403 (6) Å. The intramolecular Cd(1)–Cd(1A) distance is 4.173 (4) Å and is dictated by the conformation of the ligand set. It is worthy of note that this metal–metal distance is actually shorter than that of 4.503 (2) Å observed in the complex $[Cu_2(L^1)_2(OAc)][PF_6]_3$ (L^1 = 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine)[3] and is dictated by the double-helical arrangement of the ligands. The double-helical geometry is achieved by a twist of 57.3° between rings C and D such that each ligand presents a terpyridyl donor set to each cadmium ion. Each terpyridyl moiety is approximately planar, with interplanar angles between adjacent rings in the range 2.0–13.2°. A stacking interaction is observed between terpyridyl fragments of the two ligands, with closest interplanar contacts between rings B and C′ (3.736 Å) and rings D and E′ (3.561 Å); all other interplanar contacts are greater than 4.0 Å. These structural features are seen in the space-filling representation of the cation presented in Figure 1c. We consider that the stacking interaction observed between the aromatic ligands is the most important feature in the formation of the double-helical geometry, and this interaction is emphasized in Figure 1d. This is the first example of a double-helical binuclear complex incorporating two near-octahedral six-coordinate metal ions coordinated to the helicate-forming ligand, although the binding of ancillary ligands in the case of nickel(II) and cobalt(II) complexes of quinquepyridine allows the formation of two six-coordinate sites. In contrast, the complex cation $[Pd_2(\text{quinquepy})_2]^{4+}$ contains two *five*-coordinate metal ions.[11] The ^1H NMR spectrum of the complex indicates 10 magnetically distinct proton resonances, strongly suggesting that the double-helical geometry (which results in local D_2 symmetry about each metal ion) is maintained in solution. The complex is electrochemically inert, merely exhibiting irreversible absorption processes at moderate negative potentials.

The crystal-structural analysis confirms our predictions that the sexidentate ligand L allows the preparation of binuclear double-helical complexes with second-row (and third-row) transition elements, and we are currently investigating the properties of the ruthenium(II) complexes.[12]

Acknowledgment. We thank the Science and Engineering Research Council for support.

Registry No. 1, 87007-78-1; 2, 51928-95-1; L, 124561-86-0; $[Cd_2L_2][PF_6]_4$·4MeCN, 124561-89-3.

Supplementary Material Available: Details of the crystal structure determination and tables of aromatic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, bond distances, and bond angles for $[Cd_2(C_{30}H_{20}N_6)_2][PF_6]_4\cdot 4CH_3CN$ (6 pages); listing of observed and calculated structure factors for $[Cd_2(C_{30}H_{20}N_6)_2][PF_6]_4\cdot 4CH_3CN$ (24 pages). Ordering information is given on any current masthead page.

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(8) Crystal data for $C_{68}H_{52}N_{16}F_{24}P_4Cd_2$: monoclinic, $C2/c$, a = 20.466 (8) Å, b = 18.872 (6) Å, c = 20.617 (5) Å, β = 111.98 (2)°, V = 7384 Å^3, Z = 4, D(calcd) = 1.71 g cm^{-3}, λ (Mo Kα) = 0.71073 Å (graphite monochromator), μ = 7.7 cm^{-1}. A Nicolet R3m/V diffractometer was used to collect 7732 reflections ($5° \le 2\theta \le 50°$) on a pale yellow crystal 0.28 × 0.26 × 0.70 mm. Of these, 6512 were independent and 3968 observed $[I \ge 3\sigma(I)]$. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The cadmium atom was located by direct methods. The remaining non-hydrogen atoms were located by iterative least-squares refinement and difference Fourier synthesis. All non-hydrogen atoms of the cations and anions were refined anisotropically. The hydrogen atoms of the cation were included in idealized positions. R = 0.0599, R' = 0.0634. All computations used SHELXTL-PLUS: Sheldrick, G., University of Göttingen, Federal Republic of Germany, 1986.

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$[2_2]$(1,5)Cyclooctatetraenophane

Leo A. Paquette* and Mark A. Kesselmayer

Evans Chemical Laboratories
The Ohio State University
Columbus, Ohio 43210

Received November 8, 1989

The view has long been held that $[2_n]$cyclophanes constructed of decks possessing $4n$ π-electrons or a combination of decks with $4n$ and $(4n + 2)$ π-electrons will differ intrinsically in chemical properties from structural counterparts where both decks have $(4n + 2)$ π-electrons.[1,2] The ability to alter cavity size reversibly by means of redox reactions holds particular fascination.[3,4] Unusual opportunities for metal complexation are also offered. For these and many other reasons, the parent cyclooctatetraenophanes constitute attractive synthetic targets.[5] Since they are unknown, we have sought to develop new and versatile synthetic technology for their acquisition. Herein we detail the successful preparation of the first member of this series, $[2_2]$(1,5)-cyclooctatetraenophane (**9**) and present an early glimpse at the properties inherent to this fascinating molecule.

The route to **9** began with the [6.3.3]propellenedione **1**, a tricyclic compound readily available[6] from *cis*-5-cyclooctene-1,2-dione.[7] Its conversion to acetonide **2**[8] was efficiently accomplished (83%) by dihydroxylation with catalytic (0.1 mol %) osmium tetraoxide and direct acetonide formation.[9] Lithium aluminum hydride reduction of **2**, subsequent 2-fold xanthate elimination to give **3**, and mild acidic hydrolysis provided the diol as a mixture of olefin isomers (56% overall). The formation of two regioisomeric dienes at this point is not of long-range consequence, since they converge to a single intermediate at a later stage.

Application of the Swern protocol to **3** gave **4** (69%) with minimal complication stemming from overoxidation or cleavage.[10] As shown in Scheme I, submission of **4** to the Cook–Weiss procedure[6] served admirably to generate the pivotal pentacyclic diketone **5** (85%). This highly crystalline solid was next subjected to the same two-step reduction–elimination sequence utilized previously on **3**. As anticipated, the resulting tetraene **6** (70%) could be allylically tetrabrominated when heated (20 min) with 4 equiv of *N*-bromosuccinimide and a catalytic quantity of AIBN in carbon tetrachloride solution. The unpurified product mixture was directly converted into the unusual bis(semibullvalene) **7′** ⇄ **7″** by coupling with nickel carbonyl (34% isolated).[11] The simplicity of the ^1H and ^{13}C NMR spectra of this hydrocarbon[12] attests to the highly fluxional character of both of its divinyl-

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(8) All of the illustrated compounds were obtained in analytically pure form and characterized satisfactorily by IR, 300-MHz ^1H NMR, ^{13}C NMR, MS, and combustion data.

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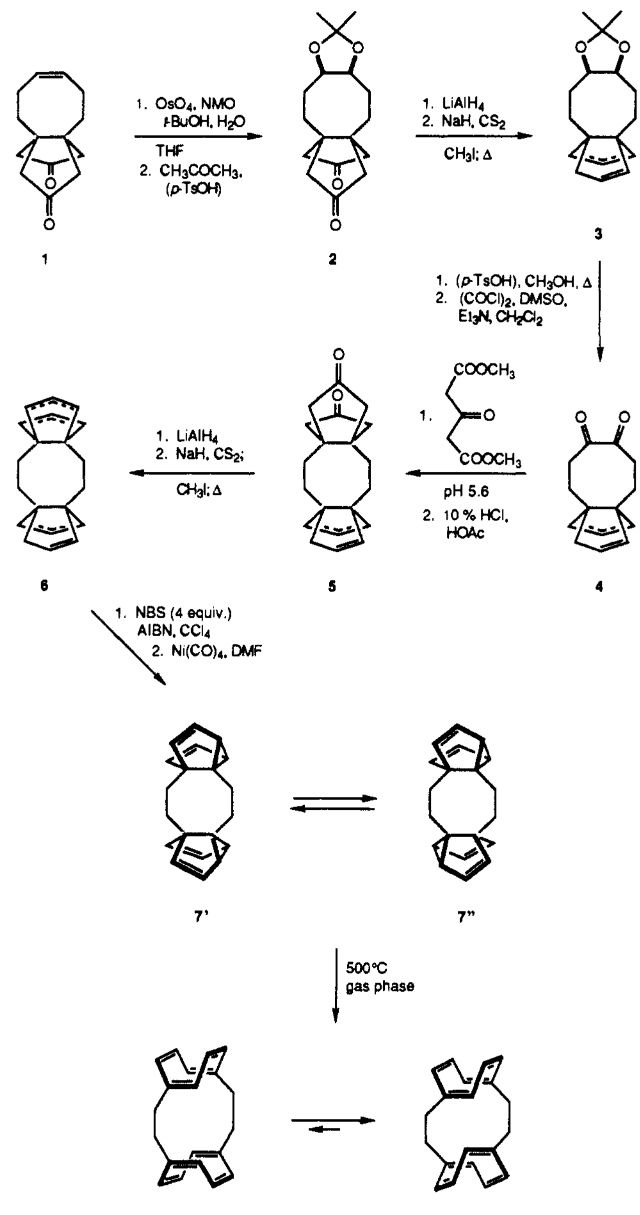
(12) ^1H NMR (300 MHz, $CDCl_3$): δ 5.16 (t, J = 3.8 Hz, 2 H), 4.99 (t, J = 3.8 Hz, 2 H), 4.18 (t, J = 3.8 Hz, 4 H), 4.09 (t, J = 3.8 Hz, 4 H), 1.60–1.40 (m, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): (ppm) 120.37, 118.62, 94.08, 91.55, 65.19, 26.75.

0002-7863/90/1512-1258$02.50/0

Scheme I



cyclopropane segments.[13] An X-ray analysis of **7** gave results quite similar to the other "averaged" structures reported previously for functionalized semibullvalenes.[14]

Thermal isomerization[15] of **7** at 500–510 °C by dropping an ethereal solution into a vertical quartz tube under nitrogen gave the (1,5)cyclooctatetraenophane as a waxy white solid (32%; 40% based on recovered **7**). The temperature-invariant ^{1}H and ^{13}C NMR spectra of the product[16] provide strong suggestion that one bond-shift isomer heavily dominates the *dl* ⇄ *dl* equilibrium. Important insight into this issue was gained by conducting a multiconformer search with the "statistical search" function of the MODEL (version KS 2.94) program.[17] All 124 conformers within 5 kcal/mol of the global minimum were examined for their MM2 energy and ultimately submitted to MMX analysis for final minimization. By this means, the *dl* isomer **9** was found to be 3.1 kcal/mol more stable than *dl*-**8**. The lack of accountability by this computer program of symmetry numbers is of no consequence in this case since either isomer is d_2-symmetric.[18]

Preliminary vacuum-line electrochemical studies on *dl*-**9** using previously developed techniques[19,20] have shown reduction in dry HMPA to give rise to three well-defined *irreversible* one-electron waves at scan rates of 100–600 mV/s. These appear at −2.65, −2.86, and −3.15 V. The difficulty in adding the first electron is quite striking.[21] While arrival at the tetraanion stage is clearly not achieved,[22] analysis of the precise details of the reduction process awaits completion of additional studies soon to be undertaken.

In our view, the synthetic pathway outlined herein should be amenable to modifications that allow for control of the length, chemical constitution, and location of the interconnective bridges. We hope to report on such developments and on the further chemical modification of **9** at a later date.

Acknowledgment. We thank the National Science Foundation for their financial support, Prof. Robin Rogers (Northern Illinois University) for the X-ray analysis of **7**, George Maynard and Eugene Hickey for assistance with the computer calculations, and Stephen D. House for performing the electrochemical measurements.

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[16] ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.89 (dd, J = 3.4, 11.3 Hz, 4 H), 5.66 (d, J = 11.3 Hz, 4 H), 5.43 (d, J = 3.4 Hz, 4 H), 2.13 (s, 8 H). ^{13}C NMR (75 MHz, CDCl$_3$): (ppm) 140.17, 133.19, 132.19, 129.67, 36.87.

[17] We thank Professor W. C. Still (Columbia University) for making this program available to us and Professor K. Steliou (University of Montreal) for updates to this software package.

[18] Furthermore, the existence of a 2-fold difference in symmetry number would translate into a free energy change of only 0.6 kcal/mol at 233 K.

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[22] Such behavior may be a result of homolytic cleavage of one of the ethano bridges. This question is under investigation.

Metalloradical Activation of Methane

Alan E. Sherry and Bradford B. Wayland*

Department of Chemistry, University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323

Received July 17, 1989

(Octaethylporphyrinato)rhodium(II) dimer, [(OEP)Rh]$_2$, which has a Rh–Rh bond energy of ~16 kcal mol^{-1},[1,2] is observed to react with benzylic C–H bonds ($D_{\text{C-H}} \sim 87$ kcal mol^{-1}) in alkyl aromatics[3,4] (eq 1) but not with unactivated alkanes ($D_{\text{C-H}} \sim$ 100–105 kcal mol^{-1}). Our approach to extending the range of C–H bond reactions for rhodium(II) porphyrin complexes has been to introduce ligand steric requirements that reduce the Rh$^{\text{II}}$–Rh$^{\text{II}}$ bond energy without seriously weakening the Rh–C bonding. (Tetramesitylporphyrinato)rhodium(II), (TMP)Rh$^\bullet$, constitutes a limiting case where ligand steric requirements completely exclude metal–metal bonding.[5] This article reports on the selective reaction of (TMP)Rh$^\bullet$ with methane in benzene solution and further describes aspects of the thermodynamic and kinetic–mechanistic features for this reaction.

$$[(\text{OEP})\text{Rh}]_2 + \text{CH}_3\text{C}_6\text{H}_5 \rightleftharpoons (\text{OEP})\text{Rh-CH}_2\text{C}_6\text{H}_5 + (\text{OEP})\text{Rh-H} \quad (1)$$

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