Figure 1. PLUTON drawing of 2. Selected bond distances (Å) and angles (deg): Mg-C(17), 2.189 (5); Mg-C(23), 2.190 (5); Mg-O(2), 2.204 (3); Mg-O(3), 2.222 (4); Mg-O(1), 2.516 (4); Mg-O(4), 2.520 (4); C(17)-Mg-C(23), 163.8 (2); C(17)-Mg-O(2), 96.9 (2); C(17)-Mg-O(3), 96.9 (2); C(23)-Mg-O(2), 96.1 (2); C(23)-Mg-O(3), 95.9 (2); O(2)-Mg-O(3), 74.6 (1).

X-ray structure of 2 (Figure 1) is its rotaxane character: the diphenylmagnesium is almost linear and rod-shaped with bulky oxygens and sticks through the cavity of the coordinating crown ether groups and stands through the cavity of the coordinating crown ether ring of ligand 3.

The magnesium shows an unusual type of hexacoordination: besides to the two apical carbons in the nearly sp-hybridized, coordinative Ph-Mg-Ph unit (angle C(17)-Mg-C(23) = 163.8 (2)°), the dihedral angle between the two phenyl rings: 66.2 (2)° magnesium is rather tightly bound to O(2) and O(3), and less so to O(1) and O(4); O(1)-O(4) = 4.038 (3) Å, a quasi-equatorial plane, and O(5) is clearly not participating in the coordination (d(Mg-O(5)) = 4.038 (3) Å). The aromatic ring of the ligand makes an oblique angle with the plane of the ligand.

Another interesting feature of 2 concerns the probable mode of its formation. The cavity of the ligand 3 is too small to permit direct penetration of a phenyl ring of diphenylmagnesium. Complex formation must therefore occur by dissociation of a phenyl anion, complexation of the PhMg⁺ cation, and recombinant formation of the Ph-Mg-Ph unit (angle C(17)-Mg-C(23), 163.8 (2)°); C(17)-Mg-0(2), 96.9 (2); C(17)-Mg-0(3), 96.9 (2); C(23)-Mg-0(2), 96.1 (2); C(23)-Mg-0(3), 95.9 (2); O(2)-Mg-0(3), 74.6 (1). Two clearly distinguishable complexes (4a: 4b = 3:1), while uncomplexed diphenylmagnesium and 3 (cf. ref 2d) are absent. We assume that 4a has the rotaxane structure of 2, because the resonance of H(2) (δ = 9.02 ppm) is strongly shifted downfield relative to the corresponding signal of 3 (δ = 8.16 ppm) or of 4b (δ = 8.24 ppm), presumably due to steric congestion. The close similarity between the resonances of 3 and 4b diphenylmagnesium is externally coordinated to some of the oxygens of 3. It is remarkable that the two complexes differ so little in stability; in THF-d₈ solution, 2 is completely dissociated into its components.

Acknowledgment. We thank A.J.M. Duijsebrouck for collecting the X-ray data. The investigations were supported in part (P.R.M., W.J.J.S., and J.J.L.S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advancement of Pure Research (ZWO); we also thank ZWO for a visiting scholarship (T.N.).

Registry No. 2, 114691-81-5; 3, 53914-83-3; PPh₃Mg, 555-54-4.

Supplementary Material Available: Tables of fractional atomic coordinates, anisotropic thermal parameters, all bond distances and angles and Figure 2 (ORTEP drawing of 2) (6 pages); listings of observed and calculated structure factors (22 pages).

Ordering information is given on any current masthead page.

(9) H NMR of a solution of pure 2 in toluene-d₄ (250 MHz, δ-H of THF-d₈ = 1.75 ppm) as internal standard. diphenylmagnesium (6 6.90 (tt, J₁ = 7 Hz, J₂ = 1 Hz, 2 H, xylyl-H(1)), 7.02 (tt, J₁ = 7 Hz, J₂ = 1 Hz, 2 H, xylyl-H(2)); 4b 3.31-3.35 (m, 9 A, 8 H, C₂H₅), 3.18-3.22 and 3.34-3.38 (m, 9 A, 8 H, C₂H₄), 4.54 (s, 4 H, xylyl-CH₃), 0.96 (dd, J₁ = 7 Hz, J₂ = 1 Hz, 2 H, xylyl-H(1)); 4a 7.66 (dd, J₁ = 8 Hz, J₂ = 8 Hz, 2 H, phenyl-H(2a)), 7.25 (dd, J₁ = 8 Hz, J₂ = 8 Hz, 2 H, phenyl-H(2a)) 7.21 (d, J = 7 Hz, 1 H, xylyl-H(5)), 7.76 (m, 1 H, xylyl-H(2)). The resonances of the protons xylyl-H(5) of 4a and 4b could not be assigned; probably, they coincide with other signals of 4a or toluene-d₄. (10) Ackman, L. M.; Sternhell, S. Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd ed.; Pergamon Press: Oxford, 1969, p 71. (b) Sato, T.; Takemura, T.; Kainosho, M. Tetrahedron Lett. 1977, 3, 3656. (c) Grutzner, J. B.; Winstein, S. Ibid. 1967, 89, 3656.

Bis(2,3,4,6,7-π6-bicyclo[3.2.2]nona-2,6,8-trien-4-yl)iron, a Ferrocene Analog with Separated Allyl and Olefin Systems

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It is a longstanding question in organic chemistry whether carbocations like bicyclo[3.2.2]nona-2,6,8-trien-4-yl)iron (BCNT) anion 2 or the congener 5 (cf. Scheme 1) experience some extra stabilization by homoaromatic interaction of the allyl and the olefin parts of the molecule. It dates back to early studies and even the most recent calculations find arguments


pro and contra homoeomarity although the counterion is now accepted to play an important role in the stabilization of 5. From a more practical and organometallic point of view we have simplified the problem by asking the following question: How similar are the cyclopentadienyl anion (Cp-) and 2 or 5? Here we report on a new short access to the anion 2 and on the prototype 4 of a metallicene-like derivative.

2a was prepared from cyclopentadiene in nine steps.16 When 1,1,3,3-tetramethylcyclopentadiene,4 is treated with n-BuLi/t-BuOK 2a is produced in more than 77% yield as shown by stannylamine to 3.5 Transmetallation leads to 2b in quantitative yield. Its 13C data differ somewhat from those in ref 3a and 7 due to experimental details which we have found to seriously affect the NMR spectra of the analogous anion.5 Additional of iron(II) chloride to 2b in THF provides a brown solution, and after replacing the ether by the slower evaporation and cooling to -30°C gives orange crystals of 4.

The molecular geometry of 4 is the solid state is presented in Figure 1.7. Two BCNT ligands are bound to iron in a π-fasion. Complex 4 is strictly centrosymmetric, implying opposite orientation of the two BCNT ligands with respect to each other. One of the two BCNT double bonds (C6-C7 1.365(3) Å) is bound to iron; it is significantly longer than the other one (C8-C9 1.320(3) Å). A typical metal-alkyl bond forms between C2, C3, C4, and iron with Fe-C3 being ca. 0.1 Å shorter than the other iron-carbon bonds. A “separate” allyl system is further suggested by the fact that its plane is inclined by 22.2° relative to the neighboring plane A (cf. Figure 1). Thus C3 is bent away from Fe similarly as is C3 from Li in 5-TMEDA.3d The interplanar angles A/B, A/C, and B/C reorganize on bonding to the metal so that A/B (103.7°) becomes rather small and hence the allyl and one olefinic part (C6/7) of BCNT move closer. This is manifested in C2X7 and C4-C6 distances of 2.32 A5 while 2.14 Å respectively in THF provides a brown solution, and after replacing the ether by pentane slow evaporation and cooling to -30°C gives orange crystals of 4.

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...1.125 Å, V = 613.5 Å3, dcalc = 1.571 g/cm3 for Z = 2, a(Fe-KO) = 12.11 Å, F(000) = 204. 2112 reflections were measured up to sin(θ/2)max = 0.638 Å−1 (+0.4, +0.6, or −0.4, or 0.6, or 0.0). The data were corrected for Lp effects and empirically for absorption (relative transmission: 0.83−1.00). Merging of equivalent data yielded 1237 unique structure factors (RF = 0.021), 1222 of which had 2Fobs ≥ 4σ(Fobs). The structure was solved by Patterson methods. All hydrogen atoms were localized in difference syntheses and refined isotropically. All other atoms were treated anisotropically.

The structure factors were refined for a refined set of parameters and all unique reflections (SHLXL-76): δ(2Fobs(max)/min) = 0.39/0.40 e/Å2. See note at the end of the paper for Supplementary Material Available.
of a coupling between the olefinic protons. \(^1\)\((JC(6/7-H6/7))\) increases on bonding to iron whereas it decreases on bonding to lithium in \(^2\)\(2b\), which means that charge transfer to and rehybridization at C6/7 do not dominate the coupling.

The isolation of 4 shows that even if the \(π\)-system of Cp anions is broken down into olefinic and allylic systems bonding to transition metals is still possible. "Opening" Cp ligands once as realized in metal-pentadienyl chemistry\(^{14}\) is not the ultimate perturbation that \(π\)-complexes tolerate.

Acknowledgment is made to the Fonds der Chemischen Industrie for a scholarship (J.B.) and support of this research.

Supplementary Material Available: NMR data\(^1\) of 1, 2a, and 3 and complete tables of atomic coordinates and displacement parameters for 4 (7 pages); listing of observed and calculated structure factors for 4 (8 pages). Ordering information is given on any current masthead page.

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(14) Recent contributions: (a) Kralik, M. S.; Rheingold, A. L.; Ernst, R. D. Organometallics 1988, 6, 2612. (b) Bleekie, J. R.; Rauscher, D. J.; Moore, D. A. Ibid. 1988, 6, 2614.

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Modification of Photochemical Reactivity by Zeolites: Norrish Type I and Type II Reactions of Benzoin Derivatives

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Selectivity in organic phototransformations continues to be one of the major topics of current interest.\(^1\) Of the various approaches use of constrained and ordered media has shown considerable promise.\(^2\) By the utilization of the cage effect\(^3\) and conformational control we illustrate below that one can induce molecules included in zeolites to follow reaction pathways that are improbable in isotropic solvents.

The photochemical behavior of benzoin alkyl ethers (1a) and alkyl deoxy benzoin (2a) in solution are fairly well understood.\(^4\) In benzene, the former prefers the Norrish type II pathway while the latter gives the Norrish type I products in high yields (Scheme I). Photolyses of alkyl benzoin ethers and alkyl deoxy benzoin in zeolites\(^5\) show a dramatic difference in behavior when compared to that in benzene (Table I). Results on benzoin methyl ether and propyl deoxy benzoin in faujasite zeolite (M-X type)\(^1\) alone

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* Contribution No. 4643.

(1) Ramamurthy, V. Tetrahedron 1986, 42, 5753.


(6) Benzoin ethers and deoxy benzoin were included in zeolites by stirring known amounts of the guest and the host in trimethylpentane for 10 h. The complex was filtered and washed with ether under dry nitrogen atmosphere. Known amount of the complex was degassed (10\(^{-4}\) Torr) and irradiated under sealed conditions. Products were extracted by stirring the irradiated complex in 10 mL of ether for 12 h. For comparison the products were also extracted by dissolving the zeolite with HCl. Material balance was ~90\% in all cases. Amounts of the guest included were estimated by elemental analysis of the zeolite and by GC analysis of the reextracted material.

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(7) Zeolite 13X (Na-X) and LZVY52 (Na-Y) were obtained from Linde. The cation of interest was exchanged into these powders by contacting the material with the appropriate nitrate solution at 90 °C. For each gram of zeolite, 10 mL of a 10\% nitrate solution was used. This was repeated a number of times. The samples were then thoroughly washed with water and dried. Exchange loadings were typically between 40 and 90\%. Prior to the use the samples were heated in air at 1 deg/min to 500 °C and held at 550 °C for 7 h. The samples were removed at 100 °C and stored under anhydrous conditions.

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Figure I are highlighted in Table I. Similar behavior was observed in M-Y zeolites. Identical behavior was found for other alkyl substituted benzoin ethers (1bc) and deoxy benzoin (2bc).

With 1a the amount of the type II products is considerably increased over that observed in benzene. Even more importantly, the rearrangement product, benzoylbenzyl alkyl ether (5), was not observed.

Table I. Product Distribution upon Photolysis of Benzoin Methyl Ether and Propyl Deoxy Benzoin in Zeolites

<table>
<thead>
<tr>
<th>medium</th>
<th>percentage of products</th>
<th>ratio of products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>benzene</td>
<td>26</td>
<td>66</td>
</tr>
<tr>
<td>Li-X (dry)</td>
<td>3</td>
<td>76</td>
</tr>
<tr>
<td>Li-X (wet)</td>
<td>18</td>
<td>40</td>
</tr>
<tr>
<td>Na-X (dry)</td>
<td>4</td>
<td>72</td>
</tr>
<tr>
<td>Na-X (wet)</td>
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<td>47</td>
</tr>
<tr>
<td>K-X (dry)</td>
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<td>44</td>
</tr>
<tr>
<td>Rb-X (dry)</td>
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<td>46</td>
</tr>
<tr>
<td>Cs-X (dry)</td>
<td>31</td>
<td>34</td>
</tr>
</tbody>
</table>

(a) Benzoin Methyl Ether

(b) Propyl Deoxy Benzoin