

stitution product of **4** when, instead of CO, trimethylphosphite is used as ligand. One trimethylphosphite ligand is bonded to each of the ring iron atoms in the resulting product of type **4**.^[10]

Elimination of the Fe(CO)₄ group of **4** produces **5**, which contains a conjugated cyclic 4π system that is stabilized by the coordination to a Fe(CO)₃ group.^[11]

Complex **5** reacts with an excess of Fe₂(CO)₉ at 25°C, undergoing formal insertion of an Fe(CO)₄ fragment into the ring P-Fe bond, to give **4** once again. Complex **4**, in turn, undergoes rapid decarbonylation to give **2**. At 60°C, **5**, as well as **3**, reacts with Fe₂(CO)₉ to give the triple-decker complex **6**.^[10]

The closed sequence of reactions described here, in which the opening and formation of Fe-Fe, P-Fe, C-Fe, and P-C bonds occur alternately and sequentially, implies very similar enthalpies for these bonds. Overall, the observed pattern of reactions is strongly reminiscent of the chemistry of carboranes.^[12]

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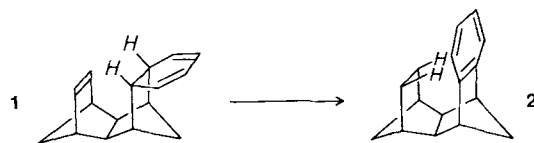
1, 97913-15-0; 2, 104779-83-1; 3, 104779-84-2; 4, 104779-85-3; 5, 104779-86-4; 6, 104779-87-5.

- [1] G. Huttner, J. Schneider, H.-D. Müller, G. Mohr, J. von Seyerl, L. Wohlfahrt, *Angew. Chem.* 91 (1979) 82; *Angew. Chem. Int. Ed. Engl.* 18 (1979) 76; J. Schneider, G. Huttner, *Chem. Ber.* 116 (1983) 917.
- [2] K. Knoll, G. Huttner, L. Zsolnai, I. Jibril, M. Wasiucioneck, *J. Organomet. Chem.* 294 (1985) 91.
- [3] J. Schneider, M. Minelli, G. Huttner, *J. Organomet. Chem.* 294 (1985) 75.
- [4] K. Knoll, G. Huttner, M. Wasiucioneck, L. Zsolnai, *Angew. Chem.* 96 (1984) 708; *Angew. Chem. Int. Ed. Engl.* 23 (1984) 739; K. Knoll, G. Huttner, L. Zsolnai, O. Orama, M. Wasiucioneck, *J. Organomet. Chem.* 310 (1986) 225; cf. G. D. Williams, G. L. Geoffroy, R. R. Whittle, *J. Am. Chem. Soc.* 107 (1985) 729.
- [5] a) K. Knoll, O. Orama, G. Huttner, *Angew. Chem.* 96 (1984) 989; *Angew. Chem. Int. Ed. Engl.* 23 (1984) 976; K. Knoll, G. Huttner, L. Zsolnai, *J. Organomet. Chem.* 312 (1986) C57; b) cf. J. Lunness, S. A. MacLaughlin, N. J. Taylor, A. J. Carty, *Organometallics* 4 (1985) 2066; T. Jaeger, H. Vahrenkamp, *Z. Naturforsch. B41* (1986) 789; J. S. Field, R. J. Haines, E. Minshall, D. N. Smit, *J. Organomet. Chem.* 310 (1986) C69.
- [6] K. Knoll, G. Huttner, L. Zsolnai, *J. Organomet. Chem.* 307 (1986) 237.
- [7] H. Lang, L. Zsolnai, G. Huttner, *J. Organomet. Chem.* 282 (1985) 23.
- [8] **2**: C₇H₁₀Fe₂O₃P, monoclinic, P2₁/c, a = 1416(1), b = 1107.2(8), c = 1710(1) pm, β = 97.50(8)°, Z = 4, V = 2658 × 10⁶ pm³, 2614 unique reflections (I > 2σ), R₁ = 0.048, ω scan (Δω = 1°, 2.0 ≤ ω ≤ 29.3° min⁻¹, 2° ≤ 2θ ≤ 44°), T = 198 K. Structure solution: direct methods (SHELXTL).—**3**: C₂₆H₁₉Fe₂O₃P, monoclinic, P2₁/c, a = 827.4(5), b = 1619(1), c = 2019(1) pm, β = 111.15(5)°, Z = 4, V = 2521 × 10⁶ pm³, 2115 unique reflections (I > 2σ), R₁ = 0.067, ω scan (Δω = 1°, 1.6 ≤ ω ≤ 29.0° min⁻¹, 2° ≤ 2θ ≤ 44°), T = 233 K. Structure solution: direct methods (SHELXTL). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-52085, the names of the authors, and the journal citation.
- [9] **2-6**: IR (n-pentane): ¹H-NMR (CDCl₃, TMS int., 25°C); ³¹P-NMR (toluene, 85% H₃PO₄ ext., 0°C).—**2**: IR: ν̄ = 2068 s, 2027 vs, 2017 s, 2002 s, 1989 w, 1971 m, 1953 vw cm⁻¹ (CO); ¹H-NMR: δ = 1.43 (d, 9H, J(PH) = 18.0 Hz), 7.10–7.48 (m, 10H); ³¹P-NMR: δ = 155.3.—**3**: IR: ν̄ = 2066 w, 2033 vs, 2012 s, 2003 m, 1990 vw, 1982 vw, 1957 w cm⁻¹ (CO); ¹H-NMR: δ = 2.18 (d, 9H, J(PH) = 19.0 Hz), 7.05–7.29 (m, 10H); ³¹P-NMR: δ = 409.2.—**4**: IR: ν̄ = 2087 m, 2047 vs, 2044 sh, 2022 vs, 2014 s, 1992 w, 1978 w, 1965 vw, 1956 vw cm⁻¹ (CO).—**5**: IR: ν̄ = 2065 s, 2025 vs, 2024 sh, 1998 s, 1983 s, 1978 s, 1965 w cm⁻¹ (CO); ¹H-NMR: δ = 1.39 (d, 9H, J(PH) = 19.0 Hz), 7.02–7.17 (m, 10H); ³¹P-NMR: δ = 129.7.—**6**: IR: ν̄ = 2069 w, 2050 vw, 2037 s, 2016 vw, 2012 sh, 2004 m, 1995 w, 1986 m, 1975 w, 1970 w, 1883 vw, 1943 m cm⁻¹ (CO); ¹H-NMR: δ = 1.09 (d, 9H, J(PH) = 19.0 Hz), 6.28–6.39 (m, 4H), 6.77–6.94 (m, 6H); ³¹P-NMR: δ = 362.2.
- [10] K. Knoll, G. Huttner, unpublished results.
- [11] H. Lang, L. Zsolnai, G. Huttner, *Chem. Ber.* 118 (1985) 4426.
- [12] Review: R. N. Grimes, *Adv. Inorg. Chem. Radiochem.* 26 (1983) 55.

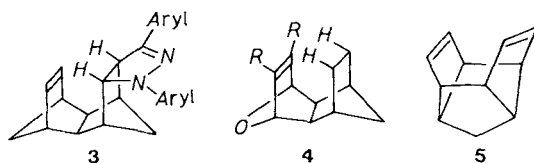
Dyotropic Hydrogen Migration in Pentacyclo[7.6.0.0^{2,13}.0^{3,8}.0^{10,14}]pentadeca-4,6,11-triene

By Tahsin J. Chow* and Mei-Fang Ding

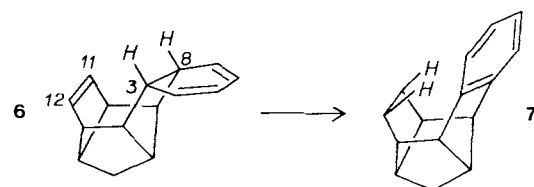
Nonbonding interactions between the two closely spaced ethylene bridges on an isodrin skeleton (cf. **11**) have been extensively analyzed. One of the most interesting phenomena is the dyotropic migration of two hydrogens from one bridge to the other.^[1] Primary and secondary orbital effects of such transformations have been ana-



lyzed by Reetz.^[2] Refluxing a toluene solution of **1** induces its smooth transformation to **2**. Two other derivatives, **3** (for example, Aryl = C₆H₅ or *p*-Me-C₆H₄)^[3] and **4** (R = COOMe)^[4], have also been shown to react in a similar fashion, and their thermodynamic parameters have been calculated. The energy of aromatization in **1** and **3** contributes part of the driving force, but the degree of orbital overlap between the *endo*-H atoms of the ethane bridge and the C atoms of the ethylene bridge also plays a determining role in these processes. The carbon-to-carbon dis-



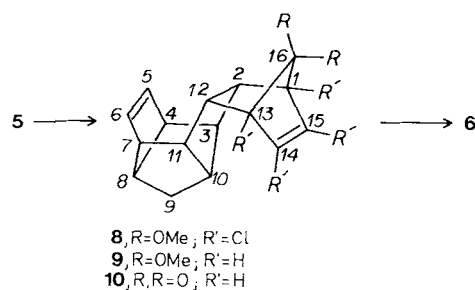
tance between the ethylene bridges of homohyprostone, **5**,^[5,6] is very close to that of isodrin,^[7] but the two compounds have different directional angles between the π lobes and the C-H bonds of the opposite bridge.



A derivative of **5**, the title compound **6**, has now been prepared by us. Gas-phase flash pyrolysis of **6** at 400°C through a Vycor tube packed with glass beads was examined and shown to produce a high yield (ca. 70%) of **7**.^[8] The presence of an aromatic ring in **7** was obvious since the ¹H-NMR spectrum showed a multiplet at δ = 7.0 (4H) and two upfield-shifted protons at δ = 0.9 for H-11 and H-12 due to a strong shielding effect from the proximately

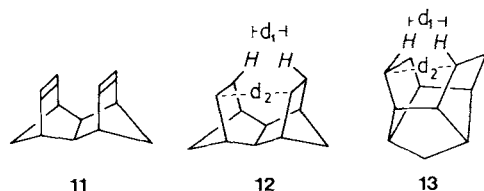
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located aromatic ring. The reaction **6**→**7** is thus a rare example of an intramolecular dyotropic hydrogen migration between two nonconjugated ethylene moieties.



Scheme 1.

The synthesis of **6**^[8] is outlined in Scheme 1. Refluxing a xylene solution of **5** and 2,3,4,5-tetrachloro-1,1-dimethoxycyclopentadiene (molar ratio 1:1) for 24 h produced the [4+2] adduct **8**^[8] in 50% yield. Dechlorination of **8** was effectively carried out in sodium/ethanol to give **9** in 60% yield. In the 200-MHz ¹H-NMR spectrum of **9**, H-2 and H-12 appear as a doublet of doublets at $\delta=1.9$, which is 0.5 ppm more upfield than the signals of H-3 and H-11 ($\delta=2.4$). The shift is believed to be due to the shielding caused by the ethylene bridge (C-5, C-6). Acidic hydrolysis of **9** (10% H₂SO₄, 20°C, 2 h) gave **10**^[8] quantitatively, which was then decarbonylated to form **6** by heating it in a sealed tube at 125°C (2 h in CCl₄, quantitative yield). The triene **6** is a colorless solid (m.p.=50–51°C) with the vinylic protons appearing as three multiplets at $\delta=5.5$, 5.7, and 6.1 (2H each).



The distance between the two ethylene bridges of dichlorinated isodrin, **11**, is ca. 2.8 Å.^[9] The corresponding distance for homohypostrophene, **5**, is also about 2.8 Å.^[5] However, since the double bonds of **11** are nearly parallel to each other, the through-space interaction is maximized to produce a 1.26-eV energy gap between *IP*₁ (8.08 eV) and *IP*₂ (9.34 eV) in its photoelectron spectrum.^[10] In **5**, the π lobes are not parallel but instead form an angle bending outward. The small difference between its *IP*₁ (8.6 eV) and *IP*₂ (8.8 eV) indicates a very weak interaction.^[11] Moreover, a comparison based on the hydrogenated products **12** and **13** is also revealing. The ethane bridges of **12** and **13** are pushed apart by steric repulsions between the *endo* hydrogens but to different extents. The distance between the *endo* hydrogens (*d*₁) is 1.85 Å for **12**^[12] and 2.14 Å for **13**.^[6] However, the carbon-to-carbon distance (*d*₂) between the bridges increases by 0.4 Å to a value of 3.2 Å^[12] in going from **11** to **12**, and by only 0.2 Å to a value of 3.0 Å in going from **5** to **13**.^[6] These data clearly show that introduction of *endo* hydrogens induces a more severe distortion in **12** than in **13**. The same criterion can be equally applied to **1** and **6** (i.e., nonbonding interactions of **6** should be much weaker than those of **1**). The transannular

strain of **1** has been calculated as ca. 0.3 eV,^[13] thus, the corresponding value in **6** is expected to be much smaller. Nevertheless, our observation of double hydrogen migration suggests that orbital interactions across the bridges of **6** are still of significance.

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- [1] a) K. Mackenzie, *J. Chem. Soc.* 1965, 4646; b) *ibid.* C1969, 1784; c) C. H. M. Adams, K. Mackenzie, *ibid.* C1969, 480.
 [2] a) M. T. Reetz, *Tetrahedron* 29 (1973) 2189; b) *Angew. Chem.* 84 (1972) 161, 163; *Angew. Chem. Int. Ed. Engl.* 11 (1972) 129, 130.
 [3] K. Mackenzie, G. J. Proctor, D. J. Woodnutt, *Tetrahedron Lett.* 25 (1984) 977.
 [4] J.-P. Hagenbuch, B. Stampfli, P. Vogel, *J. Am. Chem. Soc.* 103 (1981) 3934.
 [5] W. Schmidt, B. T. Wilkins, *Tetrahedron* 28 (1972) 5649.
 [6] E. Osawa, *J. Am. Chem. Soc.* 101 (1979) 5523.
 [7] B. Alber, W. Berning, C. Burschka, S. Hünig, H.-D. Martin, F. Prokschy, *Chem. Ber.* 114 (1981) 423.
 [8] **6**: ¹H-NMR (CDCl₃): $\delta=1.5$ (s, 2H), 2.0 (dd, *J*=4 Hz, 9 Hz, 2H), 2.3 (m, 1H), 2.5 (m, 4H), 2.75 (m, 1H), 5.5, 5.7, 6.1 (3m, 2H each); MS (70 eV): *m/z* (rel. int.) 196 (*M*⁺, 19), 167 (43), 129 (100), 128 (48), 116 (91), 114 (52), 81 (24), 67 (24).—**7**: ¹H-NMR (CDCl₃): $\delta=0.9$ (d, *J*=10 Hz, 2H), 1.5 (dm, *J*=10 Hz, 2H), 1.7 (s, 2H), 2.3 (m, 2H), 2.5 (m, 1H), 2.9 (dd, *J*=4 Hz, 10 Hz, 2H), 3.1 (m, 1H), 7.0 (m, 4H); MS (70 eV): *m/z* (relat. int.) 196 (*M*⁺, 13), 155 (21), 154 (100), 153 (29), 152 (38), 129 (40), 116 (24), 115 (34), 114 (24), 77 (21).—**8**: ¹H-NMR (CCl₄): $\delta=1.4$ (br. s, 2H), 2.1 (m, 1H), 2.2 and 2.5 (2m, 2H each), 2.6 (m, 1H), 2.75 (m, 2H), 3.5 and 3.55 (2s, 3H each), 6.1 (m, 2H); MS (70 eV): *m/z* 406 (*M*⁺ for Cl=35), 371 (*M*⁺—Cl).—**9**: ¹H-NMR (CDCl₃): $\delta=1.3$ (br. s, 2H), 1.9 (dd, *J*=2 Hz, 9 Hz, 2H), 2.4 (dm, *J*=9 Hz, 2H), 2.5 (m, 2H), 2.65 (m, 1H), 2.7 (m, 2H), 2.95 (m, 1H), 3.1 and 3.2 (2s, 3H each), 6.1 and 6.2 (2m, 2H each); MS (70 eV): *m/z* 270 (*M*⁺), 255 (*M*⁺—CH₃), 239 (*M*⁺—OCH₃), 223; correct elemental analysis.—**10**: ¹H-NMR (CDCl₃): $\delta=1.3$ (br. s, 2H), 2.0–2.1 (m, 2H), 2.4 (m, 4H), 2.6 (m, 2H), 2.9 (m, 2H), 6.1 and 6.4 (2m, 2H each); IR (CHCl₃): $\tilde{\nu}$ (C=O)=1760 cm⁻¹; MS (70 eV): *m/z* (rel. int.) 196 (*M*⁺—CO, 40), 129 (100), 116 (80).
 [9] O. Ermer, C.-D. Bödecker, H. Preut, *Angew. Chem.* 96 (1984) 57; *Angew. Chem. Int. Ed. Engl.* 23 (1984) 55.
 [10] H.-D. Martin, R. Schwesinger, *Chem. Ber.* 107 (1974) 3143.
 [11] H.-D. Martin, S. Kagabu, R. Schwesinger, *Chem. Ber.* 107 (1974) 3130.
 [12] O. Ermer, *Angew. Chem.* 89 (1977) 833; *Angew. Chem. Int. Ed. Engl.* 16 (1977) 798.
 [13] H. Prinzbach, G. Sedelmeier, H.-D. Martin, *Angew. Chem.* 89 (1977) 111; *Angew. Chem. Int. Ed. Engl.* 16 (1977) 103.

Large Molecular Cavities for Small Ions— Double Bridging of Three Bipyridine Units**

By Smaragda Grammenudi and Fritz Vögtle*

We recently reported on a Fe³⁺-selective ligand of the siderophore-type, in which three pyrocatechol units are bridged symmetrically.^[1] With the synthesis of the macrobicyclic ligand **10**, we have now been able to achieve for the first time an analogous bridging of three bipyridine units via two 1,3,5-substituted benzene rings as spacers. Compared to cryptands with two-membered chains between the donor centers and the coordinating bridgehead nitrogen atoms,^[2] **10** has the great advantage that complexation and decomplexation are less sterically hindered because of the size of its cavity, which is of importance in chemical and biological applications.^[3]

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