Measurements of $\Delta H^{\ddagger}_{-1}$ for recombination of Ru(III) and alkyl radicals are not available, but the literature contains data on analogous Co(II) systems,[13,14] for which recombination occurs at nearly diffusion-controlled rates ($\Delta H^{\ddagger}_{-1}$ = ca. 2 kcal/mol). Assumption of a similar rate for the Ru(III) species **3** yields a bond dissociation energy of 21.7 ± 1.5 kcal/mol for **1**.

Thermochemical data are sparse for organometallic complexes[15] with the exception of the cobalt alkyls which have been of great interest due to metal–carbon bond homolysis in the vitamin B_{12} cofactor.[13,16] It is interesting to note that our value for the BDE in **1** lies within the 18–32 kcal/mol range found by Finke and Halpern for Co–C bond dissociation in cofactor B_{12} and its analogues.[13,14,16] However, the stability of **3** to further Ru–ethyl cleavage under our reaction conditions suggests that the BDE of **1** may be anomalously low, possibly due to the large trans effect of the second alkyl ligand.

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$[4_5]$(1,2,3,4,5)Ferrocenophane: Superferrocenophane

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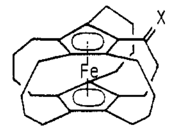
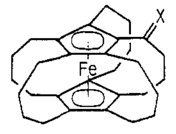
A large number of cage hydrocarbons have been synthesized in the last few decades.[1-5] These compounds do not have an atom or metal ion in the center of the molecule and their inner cavities are vacant. Some attempts have been made to entrap a metal ion or a small neutral molecule into the cavity of such cage hydrocarbons,[6,7] but the desired "core compounds" have not yet been reported.[8,9] Synthesis of intramolecularly pentabridged ferrocene, an analogue of superphane,[3] provides an example of this type of core compound. Much effort to synthesize such compounds[10] has been made by several groups.[11-14] However, compounds having four or five bridges have not been found until we recently synthesized some tetrabridged ferrocenophanes[15] and pentabridged $[4_4][3]$ferrocenophanes (**1**)[16] containing one trimethylene bridge. This paper describes the synthesis and characterization of symmetrical perbridged $[4_5]$ferrocenophane (**2b**),[17] the ultimate target compound.



1

a: X=O
b: X=H_2



2

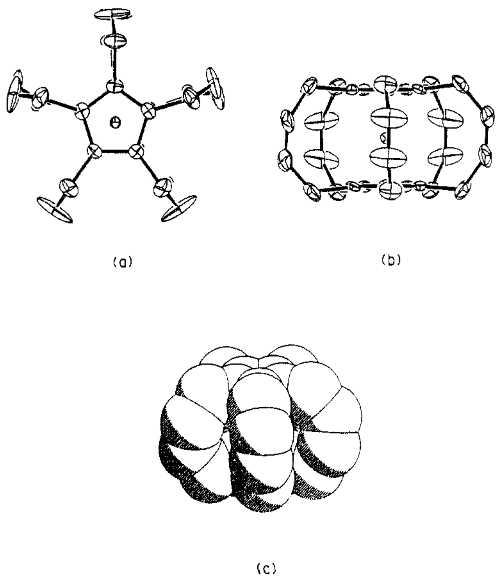


Figure 1. ORTEP drawings of **2b** projected on the Cp ring (a) and on the side of the molecule (b) and space-filling representation (c).

Insertion of a one-carbon unit into the oxotrimethylene bridge of the precursor ferrocenophane **1a**[16] was not successful by application of the reaction conditions which we had developed for the bridge enlargement of multibridged ferrocenophanes.[18] This

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difficulty was overcome by using an excess of reagents and running the reaction under strict control. To a solution of ketone **1a** in benzene was added an excess of $BF_3\cdot OEt_2$ (ca. 10 equiv to the substrate). The resulting dark violet solution was stirred for 30 min under a nitrogen atmosphere, and a large excess of diazomethane in ether, free from alcohols and moisture, was added to the solution of the aged complex. Chromatographic separation of the product yielded bridge-enlarged α-oxoferrocenophane **2a** (18%) as orange-yellow crystals: mp >300 °C; IR, 1655 cm^{-1} ($\nu_{C=O}$); high-resolution MS, *m/z* 470.2293 (calcd mol wt, 470.2270); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 24.2–44.3 (11 peaks, methylene C), 80.5–85.7 (six peaks, Cp C), 209.31 (C=O); absorption spectrum λ_{max} (THF), 425 nm (ϵ 313). Reduction of the ketone **2a** with $LiAlH_4/AlCl_3$ in ether quantitatively gave the target compound **2a**, as yellow needles: mp >300 °C; high-resolution MS, *m/z* 456.2470 (calcd mol wt, 456.2477); absorption spectrum λ_{max} (THF), 403 nm (ϵ 89). The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2b** showed two signals for the methylene resonances (δ 1.97, $W_{h/2}$ = 24.8 Hz, α-CH_2; δ 2.54, $W_{h/2}$ = 15.2 Hz, β-CH_2).[19] No other signal was present. The $^{13}C\{^1H\}$ NMR spectrum (25.1 MHz, $CDCl_3$), obtained under complete decoupling conditions, was dramatically simple as expected. Only three signals were observed at δ 84.46, 26.90, and 23.55, and these were assigned to the Cp rings and the β- and α-methylene carbons, respectively.[19] The NMR spectra thus indicate that the compound has D_{5d} or D_{5h} symmetric structure.

The crystal structure of **2b** was determined by X-ray diffraction.[20] Figure 1a,b shows the molecular structure in which each atom is drawn by a thermal ellipsoid of 30% probability. Whereas the thermal vibrations of the atoms of the ferrocene nucleus are small and almost isotropic, those of the β- and β'-carbon atoms on the bridges are large and remarkably anisotropic, their major axes being directed almost perpendicular to the C_β–$C_{\beta'}$ bonds. The distances between the β- and β'-carbons are unusually short (1.286 (17)–1.356 (13) Å), which may result from the anisotropic thermal motions and/or static disorders of the bridging carbons in the crystal. In fact, if one calculates the C_β–$C_{\beta'}$ distances by taking the positions of the C_β and $C_{\beta'}$ atoms, not at the center of the ellipsoid but shifted in the opposite direction to each other within their thermal ellipsoids, one can find the positions that give a normal C–C bond length. The Cp rings show a good planarity and the deviations of the Cp carbon atoms from their own least-squares planes are small (below 0.006 Å). On the other hand, all the α-carbon atoms linked to the Cp ring deviate by 0.127 (6)–0.160 (5) Å from this plane in the opposite direction to the iron atom. The Cp rings are almost stacked parallel to each other and are in an eclipsed conformation about the Cp–Fe–Cp axis. The distance between the Cp ring and iron atom is 1.622 (3) Å, which is slightly smaller than that found in the corresponding tetrabridged ferrocenophane (1.630 (2) Å).[21] The whole shape of the superferrocenophane[22] is nearly spherical as shown in Figure 1c.

Supplementary Material Available: Tables of atomic coordinates, temperature factors, bond lengths and angles, and deviations of atoms from the least-squares plane through the Cp ring (8 pages). Ordering information is given on any current masthead page.

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(19) The assignment of the proton and carbon signals was made by measurements of selective $^{13}C\{^1H\}$ decoupling and nondecoupling ^{13}C NMR spectra.

(20) Crystals grown from a 1,2-dichloroethane solution were transparent yellow thick plates. A small specimen with approximate dimensions 0.2 × 0.3 × 0.5 mm was cut from the crystal and used for the X-ray diffraction study. The lattice constants and intensity data were measured on a Phillips PW-1100 diffractometer using graphite monochromated Mo Kα radiation. Crystal data: $C_{30}H_{40}Fe$, MW = 456.5, tetragonal, space group $I\bar{4}2d$, a = 15.453 (8) Å, c = 18.968 (10) Å, V = 4529 Å^3; Z = 8, D_{calcd} = 1.334 g cm^{-3}, μ for Mo Kα = 6.79 cm^{-1}. Intensities of 2603 reflections were measured as above the $2\sigma(I)$ level out of 3193 within the 2θ range of 6–60° (involved in an octant of the reciprocal space). These data were processed to yield 1279 independent structure factors by averaging symmetry-equivalent reflections (*khl* vs. *hkl*) and by correcting for Lorentz and polarization factors. No correction for absorption was applied. The crystal structure was determined by the heavy-atom method and refined to an R factor of 0.065 by the block-diagonal matrix least-squares calculations. In the final stage of the refinement, the anomalous dispersion corrections were applied for iron atoms. (The space group, $I\bar{4}2d$ has a glide plane and nonenantiomorphic but has no center of symmetry.) Hydrogen atoms were not included. If the hydrogen atoms were placed at the calculated positions and refined with isotropic temperature factors, the R factor decreases to 0.053, but in view of the fact that the bridging carbon atoms have a pronounced temperature factor, all the hydrogen atoms are not shown in Figure 1.

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(22) The central metal ion of the superferrocenophane is bound to the two aromatic π-electron systems. Complete hydrogenation of the Cp rings may liberate a neutral iron atom from the bond. If the iron atom escapes from the molecule through small openings between the methylene chain, a cage hydrocarbon will be formed. If not, a novel cage compound keeping the neutral iron atom inside the hydrocarbon network will be generated from the superferrocenophane. Further experiments for testing these interesting questions are in progress.

New Methods for the Generation of Episulfonium Ions. An Application to the Synthesis of Carbocycles via Sulfenium Ion Promoted Arene–Alkene Cyclizations

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New synthetic operations which result in the annulation of carbocyclic derivatives with the *net incorporation* of latent functionality will exhibit great utility for the elaboration of natural products. In principle, the intramolecular interception of a highly reactive episulfonium ion by an appropriate carbon-centered nucleophile would constitute a powerful method for effecting cyclizations of this type. In this communication we report a novel and exceptionally versatile protocol for the generation of sulfenium ion equivalents and delineate the *first examples of cationic arene–alkene cyclizations* mediated by these species (Scheme I).

All of the previously reported procedures for the carbofunctionalization of alkenes via episulfonium ions require the use of sensitive silver salts[1–3] or result in the formation of the nucleophilic byproduct dimethyl sulfide.[4–6] These characteristics have imposed severe limitations on the application of episulfonium ion initiated cyclizations to carbocycle annulation. We have found that representative annulations of this type proceed efficiently in the presence of methyl benzenesulfenate (**4**)[7] and an appropriate Lewis acid.[8] Accordingly, exposure of the substrate **5a**[11] to 1.05 equiv

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