former is 1:1. As shown in Figure 2, the periodic depths of the channels, which correspond to one of crystallographic axes, are 8.09 and 7.25 Å for the former and latter, respectively. These facts, together with the qualitative comparison of channel sizes for acetophenone molecules, indicate that the channel space formed by the CA molecules is much larger than that of DCA and also slightly larger than that of ACA. As shown also in Figure 2, the acetophenone molecules are accommodated in the channel of the host molecules so that their phenyl planes are parallel to the channel direction in DCA, whereas they are almost perpendicular to this direction in CA. This shows that the host–guest interaction in the CA channels is somewhat different from those of hitherto investigated DCA and ACA channels.

In conclusion, contrary to the long-accepted concept that it is a unique ability of DCA and ACA to form stable channel-type inclusion compounds,[4] the present study demonstrates that a new channel-type inclusion phenomenon which is different in the channel size and host–guest interaction character can be provided also by CA.

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Supplementary Material Available: Tables of fractional atomic coordinates and interatomic bond distances and angles (5 pages). Ordering information is given on any current masthead page.

Bis((pentamethylcyclopentadienyl)metal)pentalenes. A New Class of Highly Delocalized, Fused Metallocenes

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There is considerable interest in bridged metallocenes arising from the unusual properties of mixed-valence molecules[1] and the potential for new types of catalytic reactions involving multielectron transfer. However, a generally applicable, rational synthesis of such compounds has not yet been developed. With the exception of derivatives of fulvalene[2] and *as*-indacene,[3] most bridged ferrocenes have been obtained directly from $(\eta^5\text{-}C_5H_5)_2Fe$. Moreover, examples of binuclear metallocenes of other transition elements are limited to the fulvalene-bridged compounds reported by Smart and co-workers,[4] $(\eta^3\text{-}C_3H_5)Ni(\text{pentalenyl})Ni(\eta^3\text{-}C_3H_5)$,[5] bis(pentalenyl)dinickel,[6] and bis(pentalenyl)dicobalt.[7]

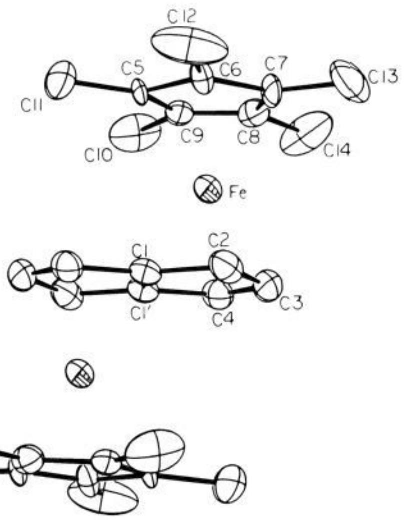


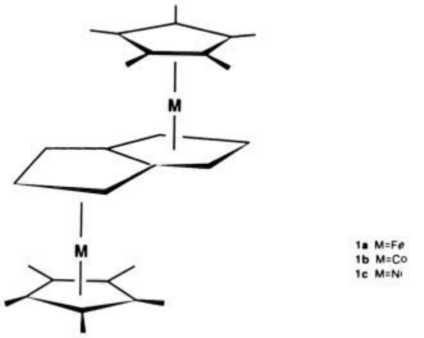
Figure 1. Molecular geometry and atom labeling scheme for **1a**. Selected bond distances (Å) are as follows: Fe–C(1) = 2.120 (4), Fe–C(1)' = 2.117 (3), Fe–C(2) = 2.025 (3), Fe–C(3) = 2.016 (4), Fe–C(4) = 2.023 (5), C(1)–C(1)' = 1.464 (5), C(1)–C(2) = 1.436 (4), C(2)–C(3) = 1.421 (7), C(3)–C(4) = 1.408 (5).

Table I. Cyclic Voltammetry Data[a]

compd	$E_{1/2}{}^b$	$E_{1/2}{}^c$	ΔE^d
1a	−0.665	0.335	1.011
1b	−1.545	−0.660	0.890
1c	−1.245	−0.405	0.830

[a] Supporting electrolyte is 0.1 M NBu_4ClO_4. All potentials in volts referenced to $Ag/AgNO_3$. Temperature 20 °C. Sweep rate 20 mv/s. Solvent CH_2Cl_2. [b] For the process M(II)/M(II) → M(II)/M(III) + e⁻. [c] For the process M(II)/M(III) → M(III)/M(III) + e⁻. [d] Obtained from differential-pulse voltammetry.

We recently reported the synthesis of (pentamethylcyclopentadienyl)acetylacetonate compounds of iron(II), cobalt(II), and nickel(II) and showed that they are convenient starting materials for the preparation of some mixed $(\eta^5\text{-}C_5Me_5)/(\eta^5\text{-}C_5H_5)$ derivatives.[8] We now report that they can also be used as starting materials in the synthesis of binuclear metallocenes of type **1**.



The only related compound which has been reported to date is $(\eta^5\text{-}C_5H_5)Fe(\textit{as}\text{-indacenyl})Fe(\eta^5\text{-}C_5H_5)$. This compound is obtained in 2% yield from a mixture of $FeCl_2\cdot THF$ (THF = tetrahydrofuran), dilithium *as*-indacenide, and excess lithium cyclopentadienide.[9]

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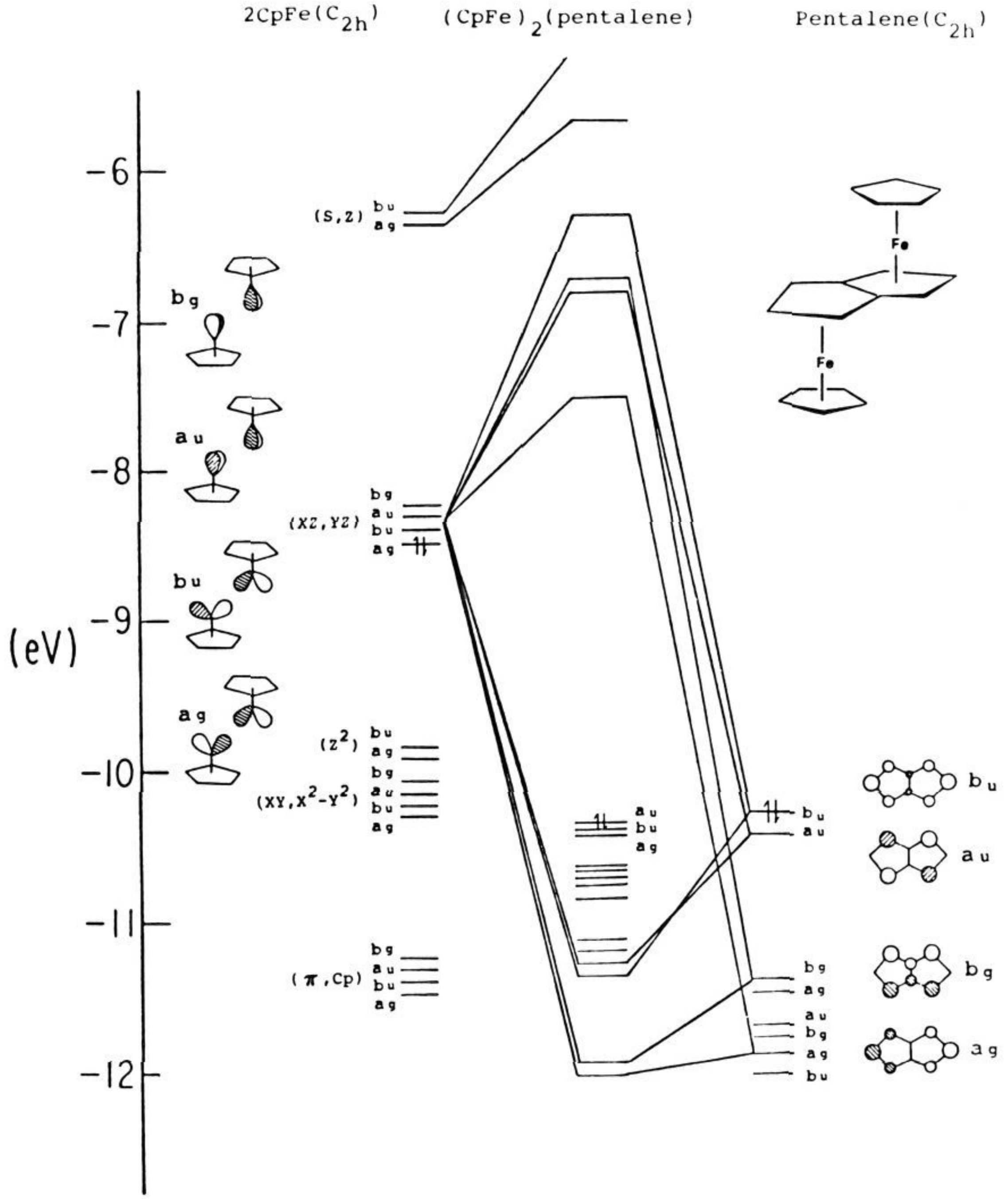

Figure 2. Extended Hückel molecular orbital diagram for $(CpFe)_2$(pentalene).

All compounds **1** are prepared by a straightforward "one-pot" procedure. The LiC_5Me_5 is added to $M(acac)_2$ (acac = acetylacetonate; M = Fe, Co, Ni) followed by addition of the dilithium pentalenide.[10] The air-sensitive product, **1a–c**, is isolated as nearly black crystals in yields of 48–70%.[11]

The molecular structure[12] of **1a** consists of two iron atoms in a trans conformation, each sandwiched between an η^5-pentamethylcyclopentadienyl ligand and one five-membered ring of the pentalene ligand (Figure 1). The iron atom is bonded symmetrically to the η^5-C_5Me_5 (Cp*) ligand (av Fe–C 2.04 (5) Å) analogous to the bonding displayed in Cp^*_2Fe (av Fe–C 2.050 Å).[13] The average C–C bond distance within the Cp* ligand is 1.41 (5) Å as expected.

The iron atom is more distant to the two carbon atoms at the pentalene bridgehead than the three remote carbon atoms resulting in deviation from C_{5v} symmetry for the Fe–C_5 pentalene ring moiety. This slipping distortion from regular η^5-coordination has

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(9) Iijima, S.; Motoyama, I.; Sano, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3180.

(10) Katz, T. J.; Rosenberger, M. *J. Am. Chem. Soc.* **1962**, *84*, 865.

(11) Satisfactory elemental analyses were obtained for **1a–c**. See Supplementary Material for analytical and spectroscopic data.

(12) Crystal data for $C_{28}H_{36}Fe_2$: space group C_i^1-$P1$, a = 8.455 (3) Å, b = 11.013 (3) Å, c = 7.918 (2) Å, α = 94.05 (2)°, β = 117.46 (2)°, γ = 68.36 (3)°, V = 603.7 Å^3, ρ(calcd) = 1.332 g cm^{-3}, Z = 1, T = 23 ± 1°, radiation Mo Kα. The structure was refined to R = 0.048 and R_w = 0.055 (226 variables) for 1862 independent reflections ($F_o^2 > 3\sigma(F_o^2)$) of 2911 unique reflections observed in the range $4.0° \le 2\theta \le 55.0°$. A complete description of structural details will be published later.

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been seen in metal–indenyl complexes where the M–bridgehead C distances are significantly longer than the other M–C distances.[14] This slipping of the Fe atom from η^5-coordination to the pentalene ring may be interpreted as maximization of the interaction of the Fe with π-electron density of the delocalized fused ring system. The longer C–C bond (1.464 (5) Å) between the two bridgehead carbon atoms supports this delocalization of π-electron density about the perimeter of the pentalene ligand with less electron density shared between the two bridgehead carbon atoms (Figure 1).

Strong coupling between the metal centers in these dinuclear compounds is evidenced by the diamagnetism of the compounds **1b** and **1c**[11] and by the large values of $\Delta E_{1/2}$ for their one- and two-electron oxidations (Table I).[15] Indeed, the $\Delta E_{1/2}$ values for **1a–c** are the largest yet observed for homodinuclear compounds.[16]

The anti conformation of the two iron atoms in **1a** and the large distance between them (3.98 Å), as confirmed by the X-ray structure determination, precludes the possibility that a metal-to-metal interaction is responsible for the diamagnetism of compounds **1b** and **1c**. We propose, instead, that the effect comes about because of a strong through-bond interaction facilitated by the bridging ligand. Extended Hückel molecular orbital calculations on $(CpFe)_2$(pentalene) support this assertion.[17] The MO diagram of this compound along with a fragment analysis based on an obvious partition of the molecule is shown in Figure 2. Owing to the large number of orbitals involved, the interaction diagram is simplified by focusing on the Cp–Fe frontier d-orbitals and the ligand π-orbitals. It is interesting to note that even though the destabilization of the d_{xz} and d_{yz} orbital combinations appears to be dominated by the interaction with the π-orbitals of pentalene, there is also a substantial contribution from the occupied σ-orbitals of the pentalene ligand (the effect of the orbitals, although not shown in the diagram, can be seen in the destabilization of the a_g (s, d_{z^2}) metal hybrid combination of the Cp–Fe units). The significant gap between the bonding and antibonding combinations, as depicted in Figure 2, represents the strength of the interaction between the Cp*Fe systems and the central pentalene ligand by which the electrons of the two Cp–Fe units are effectively coupled. This type of through-bond coupling provides a unique mechanism for delocalization in a mixed-valent system.

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Supplementary Material Available: A stereoview of the crystal packing of **1a**, table of analytical data and ^1H and ^{13}C NMR data for **1a–c**, tables of data collection and structure solution details, atomic positional parameters, thermal parameters, root-mean-square amplitudes of vibration, and bond distances and angles for **1a** (12 pages); a listing of observed and calculated structure factors for **1a** (5 pages). Ordering information is given on any current masthead page.

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3,4-Di-*tert*-butylthiophene 1,1-Dioxide, a Convenient Precursor of *o*-Di-*tert*-butylbenzene and Its Derivatives

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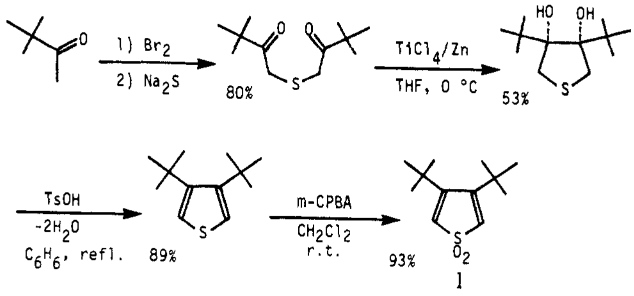
We have recently developed a surprisingly simple synthesis of 3,4-di-*tert*-butylthiophene and its oxidative conversion to 3,4-di-*tert*-butylthiophene 1,1-dioxide (**1**) in high yield (Scheme I).[1-3] This procedure allows the easy preparation of **1** in large quantities. Herein we report that the Diels–Alder reaction of **1**[4] with acetylenes and their synthetic equivalents provides a simple synthesis of *o*-di-*tert*-butylbenzene (**2a**) and its many derivatives having a variety of functional groups, which are otherwise very difficult to prepare.

Syntheses, reactivities, and structures of **2a** and related compounds have attracted much attention.[5] 1,2,4-Tri-*tert*-butylbenzene, the first compound to have *o*-*tert*-butyl groups, was obtained in 1961 from $Co_2(CO)_4(t\text{-BuC}{\equiv}CH)_3$ either by reaction with bromine or by thermolysis.[6] Parent compound **2a** was also obtained in low to moderate yields through cyclization of acetylene with $Co_2(CO)_6(t\text{-BuC}{\equiv}C\text{Bu-}t)$.[7,8] Although purely organic routes are also available, they are lengthy and suffer from low overall yields.[9,10] Introduction of a functional group to **2a** by electrophilic aromatic substitution is often accompanied by rearrangement of the *tert*-butyl group,[11] which makes it difficult to prepare functionalized derivatives of **2a**. A literature survey reveals that synthetic methods of **2a** and related compounds have scarcely developed thereafter,[12,13] though their physical and chemical properties have been a matter of extensive investigation.

The parent compound **2a** was cleanly obtained in 77% yield by heating **1** with phenyl vinyl sulfoxide (2.2 equiv) in refluxing *o*-chlorotoluene (Scheme II). Under the applied conditions, the initial adduct **3** extrudes sulfur dioxide and benzenesulfenic acid to give **2a**, thereby phenyl vinyl sulfoxide acting as an acetylene equivalent.[14]

A variety of acetylenes satisfactorily react with **1** to give the corresponding functionalized *o*-di-*tert*-butylbenzenes with elimination of sulfur dioxide from the initial Diels–Alder adducts (Scheme III). Acetylenes, activated by electron-withdrawing group(s) (dimethyl acetylenedicarboxylate, methyl propiolate, and 3-butyn-2-one) and acetylenes, activated by angle strain (benzyne

Scheme I



Scheme II