

Metallocene Analogues with Split (2 + 4)- π -Electron Ligands

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After reaction of the split (2 + 4)- π -electron ligands bicyclo[3.2.1]octa-2,6-dien-4-yl (BCOD), bicyclo[3.2.2]nona-2,6,8-trien-4-yl (BCNT), and tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-5-yl (DICP) anion with iron(II) and chromium(II) chloride the orange diamagnetic compounds (BCNT)₂Fe (5), (BCOD)₂Fe (11), (DICP)FeCp (16; Cp = cyclopentadienyl), and red paramagnetic (BCOD)₂Cr (13) have been isolated. When the reactions were carried out in the presence of CpNa, the mixed-ligand species (BCNT)FeCp (7) and (BCOD)FeCp (12) were obtained, while (BCNT)-SnMe₃ and (CO)₅MnBr gave (BCNT)Mn(CO)₃ (8) and (BCOD)K and Cp*Ni(acac) (Cp* = pentamethylcyclopentadienyl, acac = acetylacetonate) gave green diamagnetic (BCOD)NiCp* (14). The ¹H and ¹³C NMR data, including ⁵⁷Fe-¹³C and ¹³C-¹³C coupling constants for 16, were consistent with the bonding of both the olefin and the allyl part of BCOD, BCNT, and DICP to the metal, except for 14, which contains a Cp*Ni fragment bound in a η^3 fashion to the *exo* face of BCOD. Temperature-dependent magnetic measurements for 13 established two unpaired electrons per molecule and a close resemblance to chromocene. In cyclic voltammetry 5, 7, 11, and 16 underwent chemically reversible one-electron oxidations which occurred 0.23–0.26 or 0.53–0.56 V more negative than ferrocene, depending on whether one or both Cp's were replaced by split (2 + 4)- π -electron ligands. The Mössbauer spectrum of 16 showed an isomer shift and a quadrupole splitting which were smaller than previously known for ferrocenes. The X-ray crystal analysis of 11 confirmed the η^5 bonding of BCOD to iron and showed a gauche-eclipsed arrangement of the two ligands (orthorhombic, space group *Fddd*, *a* = 16.228(2) Å, *b* = 16.481(2) Å, *c* = 17.016(2) Å, *Z* = 16, *R_w* = 0.027 for 114 refined parameters and 951 unique structure factors). Comparison of the X-ray results of 11, 5, and 16 disclosed a strong, but similar, distortion of the split (2 + 4)- π -electron ligands: The two systems have moved together, the allyl plane is bent away from the metal up to 27°, and the olefinic and allylic protons are bent away from and toward the metal, respectively.

Introduction

Cyclopentadienyl (Cp) ligands are well-known to give predominantly η^5 transition-metal derivatives. The metal-Cp bonding is usually very stable, as reflected, for instance, in the dissociation energies or the kinetic stabilities of the metallocenes (Cp₂M).¹ Therefore, this bonding remains intact not only after substitution of the Cp but also, as shown for the ligands A, on the replacement of a CH fragment with heteroatoms E = N,² P,³ As,⁴ and Sb.⁵ The five Cp carbon atoms bound to the metal may be held together by an additional R₂C (ligand B⁶) or RP moiety

(ligand C⁷), and the ring may even be cut (ligand D). The last variant has led to a rich chemistry of pentadienyl complexes which has been explored systematically by the groups of Ernst and Blecke.⁸

In each of the ligands A–D the cyclic conjugation is interrupted once. It appeared to us that a further general and challenging step toward the stability limit (and thus toward high reactivity) of the metal-ligand bond should be a 2-fold interruption of the conjugated π system of Cp. When we confine ourselves to hydrocarbons, this means

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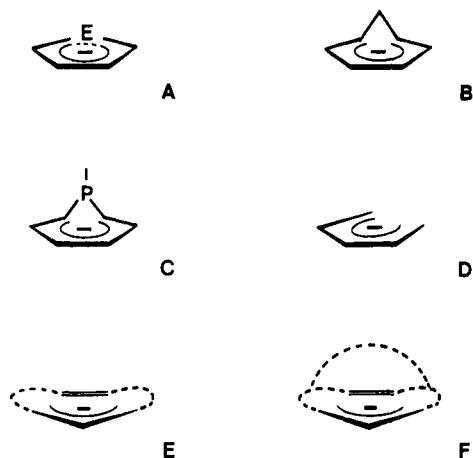
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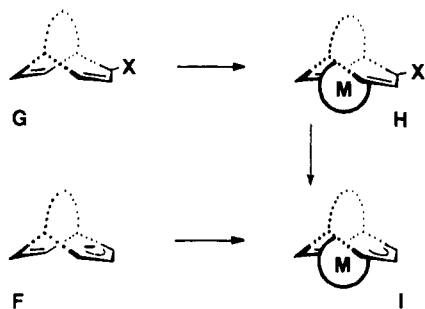
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a separation of the 6- π -electron system into an olefin and an allyl part, as shown in ligand E. Bond shifts are conceivable in E which lead back to A, where E is a (saturated hydrocarbon) chain. Therefore, we have selected ligands of type F where one or more bridges guarantee the separation of the π systems.

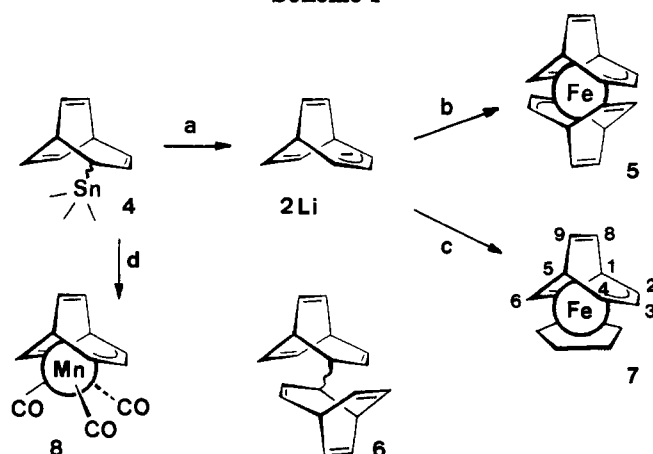
This relates our strategy to the problem of homoconjugation, and we may ask whether anions still bind to various transition metals when the conjugation of their π system is replaced by homoconjugation. We and others have addressed the fascinating problem of bonding in bicyclic anions previously.⁹

η^5 bonding of F was first realized indirectly: A suitable diene (G) was fixed in a fragment (H) which, after removal of X^- , was transformed to the fragment I.¹⁰ [8]Annulene



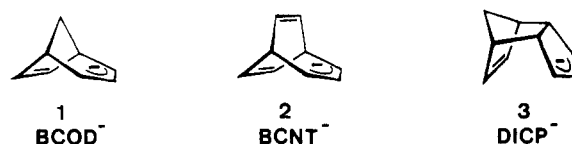
bound to iron could also be transformed to I.¹¹ These

Scheme I*



* Key: (a) MeLi; (b) $\text{FeCl}_2(\text{THF})_n$; (c) CpNa, $\text{FeCl}_2(\text{THF})_n$; (d) $(\text{CO})_5\text{MnBr}$.

reactions have in common that they yield exclusively cationic derivatives. Neutral molecules related to I (and species without a bridge) have been obtained by photochemically induced C-C coupling in the ligand sphere of manganese complexes.¹² In a different approach we wanted to get access to I by starting from carbanions of type F. This report describes our experiments with bicyclo[3.2.1]octa-2,6-dien-4-yl (BCOD, 1), bicyclo[3.2.2]nona-2,6,8-trien-4-yl (BCNT, 2), and tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-5-yl anion (DICP, 3). Preliminary reports on iron derivatives of 2 and 3 have previously been published.¹³



Results and Discussion

Synthesis. The anions 1 and 2 reacted rapidly with a variety of metal halides even at low temperature. In some cases these reactions were accompanied by color changes when the mixtures were warmed to ambient temperature, thus indicating secondary reactions which prevented the isolation of bis(ligand)metal species.

The most convenient precursors for the synthesis of the iron derivatives were bi- or tricyclic di- or trienes which had Me_3Sn groups in the allylic position. For instance, the stannylated bicyclo[3.2.2]nona-2,6,8-triene 4 was converted to the lithium salt of 2¹⁴ and reacted with solvated FeCl_2 to give $(\text{BCNT})_2\text{Fe}$ (5) (Scheme I). A major byproduct was hydrocarbon 6, which probably formed by transition-metal-mediated coupling of the ligand at the allylic carbon atom. 6 was identified by the ¹³C NMR spectrum, which showed two sets of signals with different intensity for the *meso* form and the racemate.¹⁵ Although

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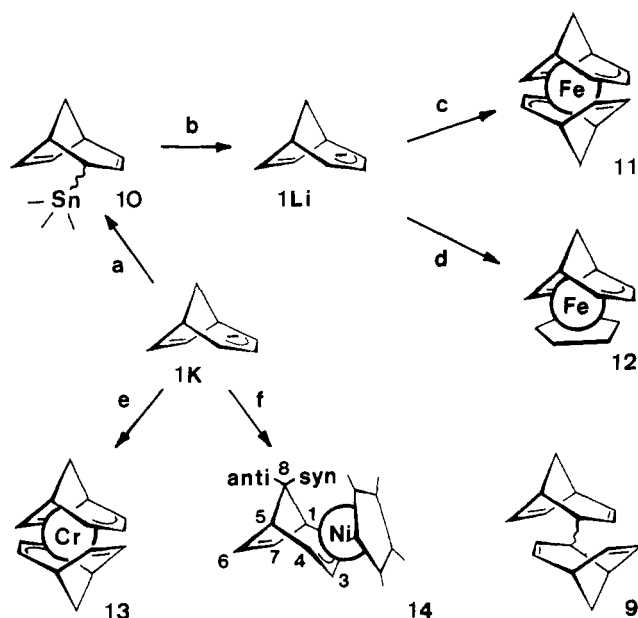
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(15) ¹³C NMR (C_6D_6): δ 36.8, 40.4, 42.8, 129.7, 131.4, 132.5, 138.3, 139.2, (major coupling product); δ 37.0, 40.2, 40.5, 128.5, 129.5, 130.6, 132.5, 139.7, 140.2 (minor coupling product). Cf. also: Grutzner, J. B.; Winstein, S. *J. Am. Chem. Soc.* 1972, 94, 2200.

Scheme II^a

^a Key: (a) Me_3SnCl ; (b) MeLi ; (c) (1) ZnCl_2 , (2) $\text{FeCl}_2(\text{THF})_n$; (d) CpNa , $\text{FeCl}_2(\text{THF})_n$; (e) $\text{CrCl}_2(\text{THF})_n$; (f) $\text{Cp}^*\text{Ni}(\text{acac})$.

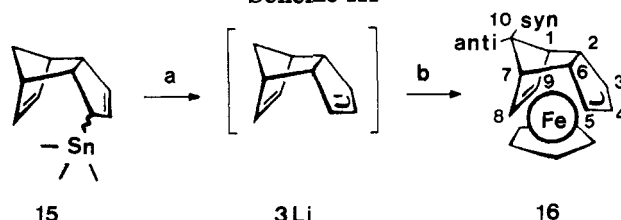
6 could be removed by chromatography subsequent crystallization gave the pure solid 5 only in low yield while most of the product remained in solution. The diamagnetic $(\text{BCNT})_2\text{Fe}$ forms orange crystals which are better soluble in ethers and hydrocarbons than is ferrocene; they are air-sensitive but stable in the presence of water, and they may be sublimed at $50^\circ\text{C}/0.1\text{ Pa}$, although the compounds decompose partly under these conditions.

When 2Li was reacted with solvated FeCl_2 in the presence of 1 equiv of CpNa , the mixed-ligand species $(\text{BCNT})\text{FeCp}$ (7) was obtained, in addition to ferrocene and a small amount of $(\text{BCNT})_2\text{Fe}$. Chromatography and repeated crystallization gave a 2/1 mixture of 7 and ferrocene, which allowed us to identify 7 unambiguously by its ^1H and ^{13}C NMR spectra.

The reaction of 2Li with $(\text{CO})_5\text{MnBr}$ or $(\text{CO})_3\text{Mn}(\text{pyridine})_2\text{Br}$ was not successful; the only manganese-containing product was $\text{Mn}_2(\text{CO})_{10}$. The desired cyanotrene analogue $(\text{BCNT})\text{Mn}(\text{CO})_3$ (8 in Scheme I) was finally obtained by heating a mixture of 4 and $(\text{CO})_5\text{MnBr}$. After removal of the main products $\text{Mn}_2(\text{CO})_{10}$ and 6 by chromatography and crystallization, 8 could be identified unambiguously by its ^1H and ^{13}C NMR spectra.

The bicyclo[3.2.1]octa-2,6-dien-4-yl anion 1 behaved differently. When its potassium salt 1K^{9e} was reacted with $\text{FeCl}_2(\text{THF})_n$ under various conditions, only the ligand coupling product 9¹⁶ and unidentified compounds were produced. The same is true for 1Li, which was synthesized^{9h} via the stannyl derivative 10,¹⁷ as shown in Scheme II. Eventually, addition of anhydrous zinc chloride to 1Li prior to reaction with iron(II) chloride gave orange crystals of $(\text{BCOD})_2\text{Fe}$ (11). As for 5, the isolation of 11 was accompanied by heavy losses of the product. The properties of 11 did not differ much from those described for 5.

Another parallel between the anions 1 and 2 is the formation of the mixed-ligand compound $(\text{BCOD})\text{FeCp}$

Scheme III^a

^a Key: (a) MeLi ; (b) $\text{FeCl}_2(\text{THF})_n$.

(12 in Scheme II). Although it could not be isolated, it was possible to identify 12 by NMR spectroscopy.

The extension to metals other than iron was successful for chromium and nickel. Dark red paramagnetic and air-sensitive $(\text{BCOD})_2\text{Cr}$ (13) was obtained from the reaction of 1K with solvated CrCl_2 . Like all iron derivatives described so far, it is highly soluble in inert solvents such as ethers and pentane, thus rendering its isolation difficult. For 13 as an example, we have tried to optimize crystallization. Cooling to -130°C in pentane gave a 35% yield of solid 13; the dark red color of the mother liquor points to a much higher overall yield.

While the reaction of 1K with solvated NiCl_2 gave no $(\text{BCOD})_2\text{Ni}$, dark green diamagnetic and air-sensitive $(\text{BCOD})\text{NiCp}^*$ (14) was isolated when $\text{Cp}^*\text{Ni}(\text{acac})$ ¹⁸ (Cp^* = pentamethylcyclopentadienyl, acac = acetylacetonate) was treated with 1K (Scheme II). A purple intermediate was observed below -40°C but could not be isolated. After workup at ambient temperature the pentane extract contained an unknown brown compound in addition to 14, which was purified by chromatography.

The chemistry of the tricyclic anion 3 is hampered by the unusually fast retro-Diels-Alder reaction, which produces Cp^- and dicyclopentadiene.¹⁹ However, when the temperature was kept low, the lifetime of 3Li, made in situ from the stannyl precursor 15 (Scheme III), was sufficient to allow the formation of $(\text{DICP})\text{FeCp}$ (16), which was isolated in 20% yield as red-brown crystals. 16 is slightly air sensitive, sublimable, and highly soluble in hydrocarbons and ethers; it may be heated in toluene to 160°C without decomposition, and it is not attacked by water. To our surprise no other iron-containing organometallic product, in particular no ferrocene, could be discovered. From this we conclude that the reaction of 3Li with FeCl_2 is much faster than its cleavage. No $(\text{DICP})_2\text{Fe}$ was found, presumably because, when a second DICP enters the coordination sphere of iron, steric strain causes cyclopentadiene to split off in a delayed retro-Diels-Alder reaction (see also X-ray results).

As mentioned before, the yield of the new compounds after purification suffered from their high solubility. However, the NMR spectra showed that the reactions were more efficient. The estimated crude yields are 80% for 16, 60% for 5, 7, and 13, 40% for 11 and 14, 20% for 12, and 10% for 8.

NMR Studies. The ^1H and ^{13}C NMR spectra were particularly helpful for the elucidation of the ligand bonding mode. In most cases the signal assignment was almost trivial. The signals of H1/5, H2/4, and H6/7 of the BCNT and BCOD derivatives were distinguished by their coupling pattern: a poorly resolved multiplet for H1/5, a

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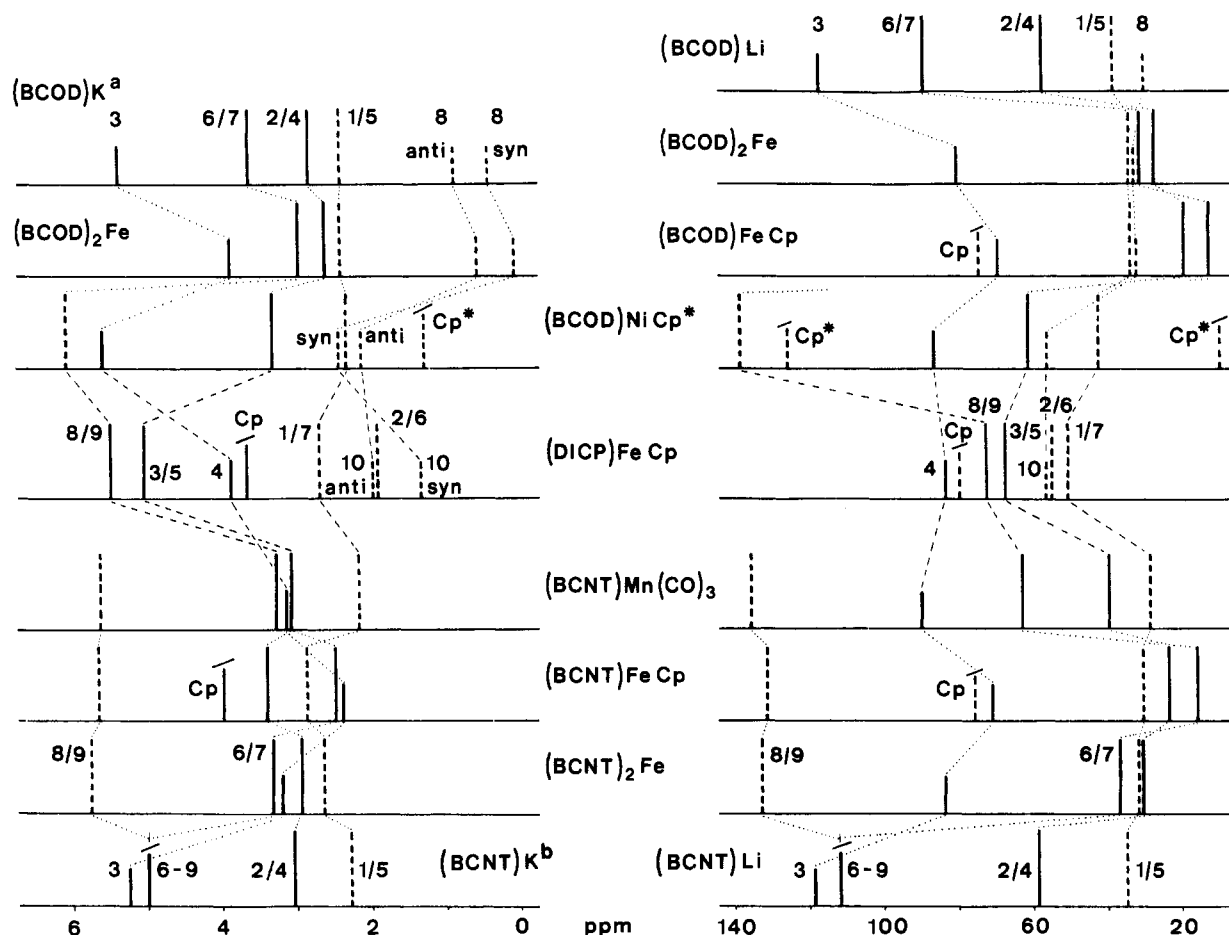


Figure 1. Comparison of the ^1H (left) and ^{13}C NMR (right) signal shifts of metal compounds with BCNT, BCOD, and DICP as ligands. Solid bars denote carbon atoms bound to the metal (except CO) or protons next to these carbon atoms. For the numbering, see Schemes I–III. Key: (a) from ref. 20; (b) from ref. 15.

pseudotriplet for H2/4, and a double doublet for H6/7. Homonuclear decoupling assured the correlation between H3 and H2/4 and thus the identity of the latter. Since the signals of C6/7 and C2/4 occasionally had similar shifts, the latter was identified by heteronuclear decoupling. C2/4 and C6/7 also differed in their signal pattern originating from the C–H couplings over more than one bond: all C2/4 atoms gave a triplet, whereas C6/7 nuclei gave a doublet of poorly resolved multiplets.

In Figure 1 the most important NMR signals of the transition-metal derivatives are compared to those of the alkali-metal salts of BCOD $^-$ and BCNT $^-$. The signals of carbon atoms which are susceptible to binding to the metal and those of their neighboring protons are given as solid bars and other signals as broken bars.

When BCNT $^-$ binds to a transition metal, the most striking change in the proton spectra is found for H3 and H6–9. The signal of H3 moves to low frequency, while that of H6–9 splits: the signal of H6/7 is strongly shifted to low frequency and that of H8/9 to high frequency. This indicates that C3 and one of the two double bonds (C6/7) is involved in bonding, whereas C8/9 must belong to a free double bond. Note that a decrease of the proton shielding as one passes from BCNT $^-$ to, e.g., (BCNT) $_2\text{Fe}$ is well in accord with a delocalization of negative charge from the allylic to the olefinic part of BCNT $^-$ and with an overall decrease of charge on BCNT $^-$ when it is bound to a transition metal. These trends are even more pronounced in the ^{13}C NMR spectra, which, in addition, indicate the metal bonding to C2/4 by a signal shift to low frequency.

BCOD $^-$ behaves in much the same way when it is bound to iron, except that the bridge (C8) is hardly affected. In particular, no change occurs for the signal sequence of H8 $_{\text{syn/anti}}$; both may be easily distinguished by the coupling between H1 and H8, which is greater for the *anti* protons (see Experimental Section). For (BCOD)NiCp* two striking spectral changes are observed: the signals of C6/7 and H6/7 are strongly shifted to high frequency and those of H8 $_{\text{syn/anti}}$ are inverted. From this it must be concluded that C6/7 does not bind to Ni (thus avoiding a 20-electron count) and that the Cp*Ni fragment prefers the *exo* face of BCOD. An analogous response of the signal shifts of H $_{\text{syn/anti}}$ to the change of a metal fragment from the *endo* to the *exo* face has been observed previously.²¹

(DICP)FeCp is an example which shows that ^1H NMR signal shifts may not allow us to decide whether a double bond is coordinated or not. The signal of H8/9 (δ 5.52) is in the same range as those for the free double bond of the BCNT derivatives 5, 7, and 8, whereas the ^{13}C NMR and X-ray results leave no doubt that C8/9 is bound to iron. The assignment of the ^1H and ^{13}C NMR signals of (DICP)FeCp was assured by homo- and heteronuclear decoupling and by analysis of the ^{13}C satellites. The one-bond C–C coupling constants and the isotope shifts are comparable to those found for dicyclopentadiene.¹⁹ Also visible in the ^{13}C satellite spectrum were the ^{57}Fe – ^{13}C coupling constants for C3/5 (5.2 Hz), C8/9 (6.0 Hz), and

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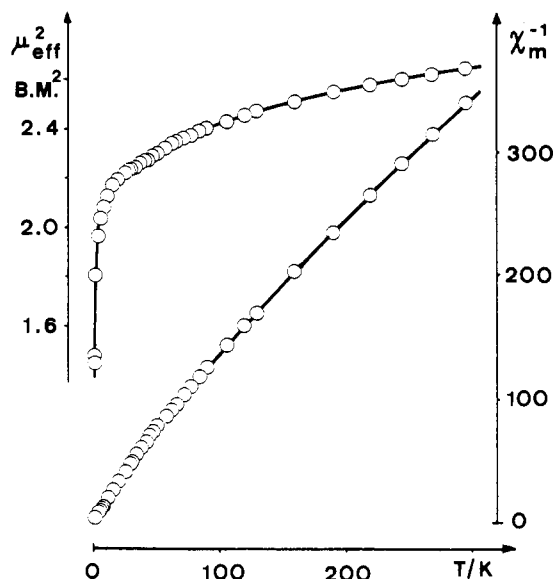


Figure 2. Temperature dependence of the inverse molar magnetic susceptibility χ_m^{-1} and of the squared effective magnetic moment μ_{eff}^2 for $(\text{BCOD})_2\text{Cr}$.

Cp (2.6 Hz); they are about 1.8 times smaller than the ^{103}Rh - ^{13}C coupling constants in $(\text{DICP})\text{RhCp}^*$.^{10c}

The ^{13}C NMR resonances of the Cp's of $(\text{BCOD})\text{FeCp}$, $(\text{BCNT})\text{FeCp}$, and $(\text{DICP})\text{FeCp}$ also deserve some comment. They all appear between 75 and 80 ppm, which means that their carbon atoms are much less shielded than those of ferrocene (δ 67.8). The high-frequency shift seems to be characteristic of a Cp group that is pushed away by a sterically demanding π ligand sitting opposite to it. This interpretation is suggested by the fact that the best plane through the η^5 carbon atoms of DICP in $(\text{DICP})\text{FeCp}$ is only 1.21 Å away from iron, whereas the Fe-Cp distance is 0.08 Å longer than in ferrocene^{13a} (see also Figure 6 below).

By analogy with chromocene $(\text{BCOD})_2\text{Cr}$ was expected to yield paramagnetically shifted signals. However, only one could be located definitively at 64 ppm (-66°C , half-width 4 kHz).

Magnetic Properties of $(\text{BCOD})_2\text{Cr}$. The magnetic behavior of $(\text{BCOD})_2\text{Cr}$ between 1.15 and 296.4 K is shown in Figure 2. From the slope of the inverse molar magnetic susceptibility χ_m^{-1} above 130 K an effective magnetic moment of $\mu_{\text{eff}} = 2.85 \mu_B$ is calculated. This is close to the spin-only value of two unpaired electrons and slightly smaller than what one of us has found for chromocenes.²² We take this as evidence that the two BCOD ligands are bound to chromium in a η^5 fashion as in $(\text{BCOD})_2\text{Fe}$. As can also be seen from Figure 2, the χ_m^{-1} curve deviates somewhat from linearity, which corresponds to a decrease of μ_{eff}^2 especially in the low-temperature range. A similar behavior, although with a drop of μ_{eff}^2 at lower temperature, has been observed for chromocenes and explained by the local anisotropy at chromium.²² It is conceivable that the stronger electronic and structural perturbation in $(\text{BCOD})_2\text{Cr}$ as compared to Cp_2Cr causes the slight difference (and the problems with ^1H NMR). Field-dependent measurements at seven temperatures between 1.15 and 20.45 K (supplementary material) showed no

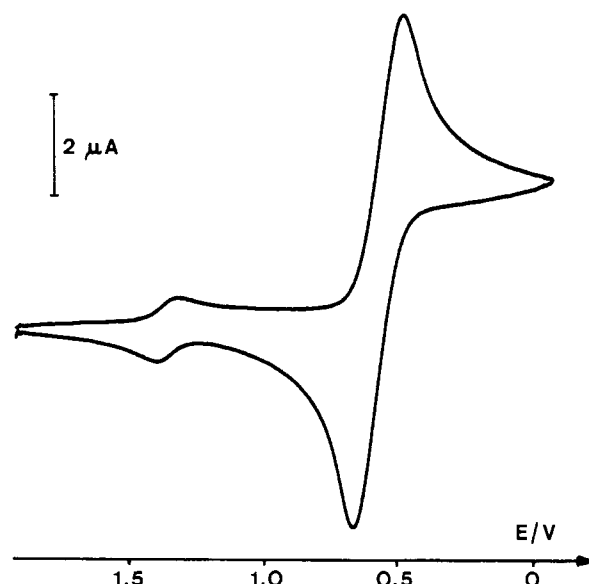


Figure 3. Cyclic voltammogram of $(\text{BCOD})_2\text{Fe}$ (right wave) and Cp_2Co in THF at room temperature (supporting electrolyte $n\text{Bu}_4\text{NPF}_6$ (0.1 M), scan rate 50 mV s^{-1} , potential relative to Cp_2Fe).

Table I. CV Data^a for Compounds 5, 7, 11, and 16

	$(\text{BCNT})_2\text{Fe}$ (5)	$(\text{BCNT})\text{FeCp}$ (7)	$(\text{BCOD})_2\text{Fe}$ (11)	$(\text{DICP})\text{FeCp}$ (16)
$E_{1/2}$ (V) ^b	-0.53	-0.23	-0.57	-0.26
ΔE_p (mV)	120	90	180	240
i_{pa}/i_{pc}	0.98	c	1.0	0.94
concn (mol L ⁻¹)	4×10^{-4}	1×10^{-3}	3×10^{-3}	1×10^{-3}

^a Conditions: In THF, 24°C , scan rate 50 mV s^{-1} , supporting electrolyte $0.1 \text{ mol L}^{-1} n\text{Bu}_4\text{NPF}_6$. ^b Relative to $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$. ^c Not determined.

anomaly. However, we cannot exclude the possibility that some intermolecular interaction contributes to the shape of the μ_{eff}^2 curve.

Electrochemical Studies. Cyclic voltammetry (CV) established that the iron derivatives 5, 7, 11, and 16 in THF undergo an oxidation at room temperature; a typical example is shown in Figure 3, while the data are listed in Table I. Due to some deposit on the platinum working electrode the separation of the oxidation and reduction wave, ΔE_p , was often much larger than the expected 60 mV. Furthermore, ΔE_p increased with the scan rate. We have tried to optimize the CV experiment for $(\text{BCNT})\text{FeCp}$. In any case, ΔE_p was similar to or much smaller than that of internal Cp_2Fe , and in the case of $(\text{BCNT})\text{FeCp}$ ΔE_p was as small as that of internal Cp_2Co . It follows that the reversibility of the oxidation of the compounds in Table I is at least as good as that of ferrocene.²³ In addition, the peak current ratios, i_{pa}/i_{pc} , were close to 1, indicating chemical reversibility on the CV time scale. The redox potentials $E_{1/2}$ were determined relative to internal Cp_2Fe and Cp_2Co (added as $\text{Cp}_2\text{Co}^+\text{PF}_6^-$); the latter confirmed the $E_{1/2}$ values when their separation from that of Cp_2Fe was less than 0.3 V. The standards were also used as a check for the one-electron charge transfer by comparing the concentrations and the corresponding redox waves.

The redox behavior of 5, 7, 11, and 16 resembles that of ferrocene. However, the $E_{1/2}$ values are shifted dras-

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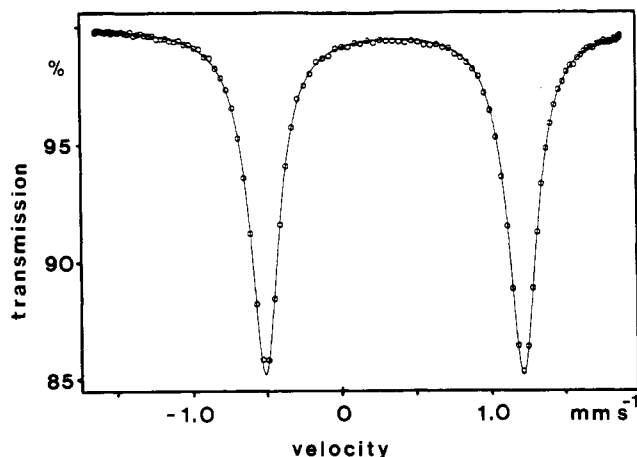


Figure 4. Mössbauer spectrum of (DICP)FeCp at room temperature (velocity relative to α -iron).

tically to more negative potentials. These shifts occur stepwise: for each Cp of ferrocene that is replaced by a new ligand, $E_{1/2}$ decreases by 0.23–0.29 V or about 0.26 V on the average. On the other hand, the shift of the potential, $\Delta E_{1/2}$, is influenced only marginally when we compare compounds 5 and 11 or 7 and 16, respectively. This strongly suggests that, although the CV experiments reflect the separation of the ligand π system into an allylic and an olefinic part, they hardly show whether ligand 1, 2, or 3 is present in a given type of compound.

Various types of ligand changes forced upon ferrocene have been investigated by cyclic voltammetry. For instance, methylation leads to a shift of $\Delta E_{1/2} = -0.05$ V per methyl group.²⁴ When a CH moiety of ferrocene is replaced by phosphorus, the oxidation is more difficult ($\Delta E_{1/2} = 0.19$ ²⁵), whereas it is easier when a CC moiety is replaced by BN ($\Delta E = -0.18$ V; we have corrected the literature data²⁶ for the effect of methyl groups). Finally, opening of Cp to pentadienyl yields $\Delta E_{1/2} = -0.1$ V.^{24c} In most of these cases the oxidation products undergo further reaction, especially in donor solvents. The ferrocene analogues of the present study differ from the previous ones in two remarkable points: $\Delta E_{1/2}$ is much greater and seems to indicate a stronger perturbation of the π ligand, and yet the oxidation products are more stable, at least in the CV experiment. Preliminary extended Hückel calculations show that the HOMO is raised stepwise in energy whenever a Cp of ferrocene is substituted for the ligands 2 and 3. This parallels the stepwise easier oxidation found experimentally (Table I).

Mössbauer Spectroscopy. (DICP)FeCp has also been studied by Mössbauer spectroscopy (Figure 4). The spectrum consists of a doublet with a signal half-width of 0.236 ± 0.002 mm/s, a quadrupole splitting $QS = 1.736 \pm 0.009$ mm/s, and an isomer shift $IS = 0.352 \pm 0.001$ mm/s. Although the pattern is typical for low-spin iron(II) species, the values are considerably smaller than those known for ferrocene derivatives ($QS = 2.0$ – 2.5 mm/s, $IS = 0.50$ – 0.55 mm/s).²⁷ The pioneering work of Ernst, Wilson, and

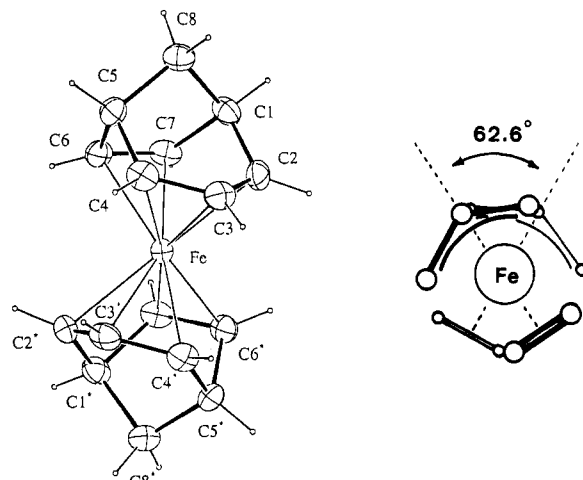


Figure 5. (Left) ORTEP representation of the molecular geometry of (BCOD)₂Fe (displacement ellipsoids at the 50% probability level; hydrogen atoms with arbitrary radii). (Right) Top view of the gauche-eclipsed arrangement of the BCOD ligands.

Herber²⁸ has shown that only a major perturbation of a ferrocene will result in comparable changes. For a series of bis(pentadienyl)iron compounds they have found $QS = 1.2$ – 1.5 mm/s and $IS = 0.46$ – 0.50 mm/s.

When judged from the quadrupole splitting, the present case of (DICP)FeCp is closer to the ferrocenes than to the pentadienyl complexes. This is understandable in terms of a symmetry-dependent mixture of d orbitals: In ferrocene the d orbitals are strictly separated into a filled ($xy, x^2 - y^2, z^2$) and an empty (xz, yz) set. The d-electron distribution at iron is therefore asymmetric and leads to large QS values. When the molecular symmetry is lowered by going from Cp₂Fe to (DICP)FeCp, d_{xz} and d_{yz} are mixed into the other d orbitals so that the d electrons are now distributed more symmetrically and, hence, the QS value decreases. The effect must, of course, depend on the ligand's d orbital mixing power and whether one or two Cp's of ferrocene are replaced. Because the quadrupole splitting of 1.736 mm/s for (DICP)FeCp lies between the values for ferrocenes and for pentadienyl complexes, the d orbital mixing power of the DICP ligand should be less pronounced than that of the pentadienyls.

In contrast to the quadrupole splitting the isomer shift of (DICP)FeCp deviates more strongly from the shift for ferrocenes than it does for pentadienyl complexes. In particular, the low IS value indicates a higher s-electron density at iron. However, with only one example at hand it is difficult to separate the various contributions to the change in s-electron density.

Crystal Structures. (BCOD)₂Fe, (BCNT)₂Fe, and (DICP)FeCp formed crystals upon cooling pentane solutions slowly to -30 °C. The structures of the last two compounds have been discussed briefly,¹³ while that of (BCOD)₂Fe is described in detail in this paper. Figure 5 represents the molecular structure, while Table II summarizes important structural parameters.

Both ligands are bound to iron through their allylic (C2, C3, C4) and olefinic (C6, C7) carbon atoms, i.e. in a η^5 fashion. This is similar to what we have found for (BCNT)₂Fe and (DICP)FeCp and what is expected from the electron count. The observed molecular structure is

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Table II. Selected Bond Distances (Å) and Angles (deg) for 11 with Esd's in Units of the Last Significant Figure in Parentheses

Fe-C2	2.176(2)	Fe-C3	2.059(2)
Fe-C4	2.128(2)	Fe-C6	2.139(2)
Fe-C7	2.162(2)	C1-C2	1.514(3)
C1-C7	1.517(3)	C1-C8	1.530(3)
C2-C3	1.397(3)	C3-C4	1.414(3)
C4-C5	1.521(3)	C5-C6	1.531(3)
C5-C8	1.530(3)	C6-C7	1.374(3)
C2-C1-C7	100.9(2)	C2-C1-C8	110.2(2)
C7-C1-C8	101.6(2)	C1-C2-C3	117.9(2)
C2-C3-C4	118.1(2)	C3-C4-C5	118.4(2)
C4-C5-C6	100.8(2)	C4-C5-C8	109.1(2)
C6-C5-C8	102.1(2)	C5-C6-C7	107.8(2)
C1-C7-C6	109.7(2)	C1-C8-C5	100.7(2)

entirely consistent with the NMR results. In the crystal the molecules are located on a crystallographic 2-fold axis which passes through the iron center and relates one of the BCOD ligands to the other. The two ligands are fixed relative to each other with a torsional angle of 62.6°, thus adopting the gauche-eclipsed arrangement (C_1 symmetry). This is in contrast to the very similar compound (BCNT)₂-Fe, for which we have found a perfectly antiparallel trans arrangement of the two ligands. Since we could not observe any change of the ¹³C NMR spectrum down to -95 °C, we conclude that both ligands rotate with a rather low barrier or that they oscillate. There do not seem to exist simple rules that allow us to predict the relative orientation of two negatively charged 6- π -electron ligands in sandwichlike compounds. Unsymmetric structures similar to that of (BCOD)₂Fe have been found for norbornene- and norbornene-annelated Cp's²⁹ and pentadienyls.³⁰ Apparently, the two ligands do not interfere sufficiently with each other to give rise to a pronounced rotational barrier, which also results in the seemingly erratic conformations observed in the solid state.

In any case, the peculiar conformation of (BCOD)₂Fe gives rise to noticeably different Fe-C bond lengths (Table II). Not only are Fe-C2/4, the bonds to the allylic part of BCOD, significantly different but also the Fe-C bonds to the olefinic part (Fe-C6/7) show conspicuous differences. A comparison with the structure of the (higher symmetric) compound (BCNT)₂Fe^{13b} is most informative in this respect. In the latter the (chemically) equivalent Fe-C bonds do not show significant differences and are similar to the chemically equivalent Fe-C bonds in (BCOD)₂Fe. Furthermore, the Fe-C bonds to the "internal" allylic C atom (C3) in (BCOD)₂Fe and (BCNT)₂Fe are virtually identical. As can be seen from the structural data in Table II, the double bond C6-C7 shows the typical lengthening after coordination.

The seemingly rigid bicyclic anion BCOD undergoes some more distortions upon bonding to iron. They are visualized in Figure 6, and after comparison with (BCNT)₂Fe and (DICP)FeCp, they turn out to be characteristic of ligands with split (2 + 4)- π -electron systems.

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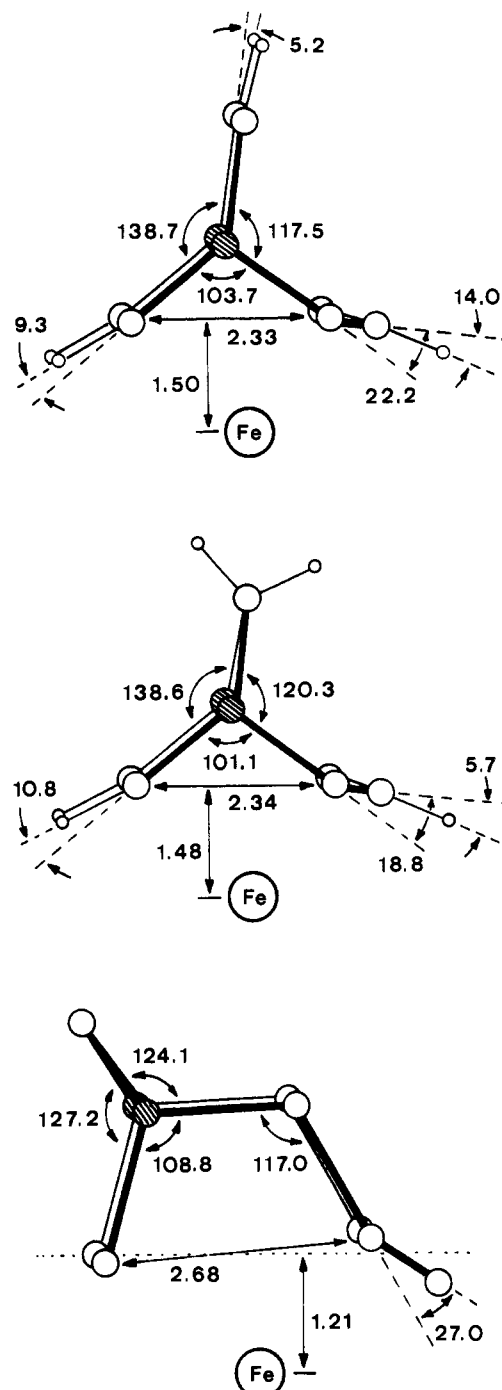


Figure 6. Side view of the ligand-iron fragments (BCNT)₂-Fe (top), (BCOD)₂Fe (middle), and (DICP)Fe (bottom) with selected interplanar angles (deg), bending (deg) of the hydrogen atoms (mean values are given for pairs of chemically equivalent hydrogen atoms of (BCNT)₂Fe and (BCOD)₂Fe), and distances (Å).

Of the angles between the three planes which all include the bridgehead carbon atoms C1/5 of (BCNT)₂Fe and (BCOD)₂Fe or C1/7 of (DICP)FeCp (the hatched circles in Figure 6), only one is close to the ideal value of 120°. The interplane angle facing iron has decreased to 101.1°, so that the olefinic and the terminal allylic carbon atoms are separated by only 2.34 Å (0.29 Å less than expected for a 120° angle), a value which might renew the speculation about some homoaromatic stabilization⁹ within the ligand. The bending of the allyl plane by 18.8° away from iron is much more pronounced than in (BCOD)Li-TMEDA,⁹ⁱ but it is still surpassed by that in (BCNT)₂Fe and (DICP)-

FeCp. There is no uniform behavior of the hydrogen atoms, which could all be refined: While the allylic hydrogen atoms are bent toward iron (H3 5.7° and, not shown in Figure 6, H2/4 7.1/3.8°), the olefinic hydrogen atoms point away (H6/7 10.3/11.4°). This bending pattern parallels that in (BCNT)₂Fe and must be a compromise between the optimal orientation of the ligand orbitals relative to the iron orbitals and the mutual steric interference of the two ligands. These steric problems are also evident from Figure 6 when the distances between the iron centers and the best plane through the five coordinated carbon atoms are considered. In all cases the distance is much smaller than found for ferrocene (1.65 Å³¹), and in the case of DICP⁻ as a ligand it reaches a minimum which has most probably prevented the isolation of (DICP)₂Fe.^{13a}

Conclusions

When the 6- π -electron system of a Cp is split into olefinic and allylic fragments, it is still possible to obtain stable transition-metal complexes. The compounds are analogous to the metallocenes as long as the electron count is 18 or smaller as for iron and chromium, whereas a η^3 nickel complex is formed rather than a nickelocene-like species, leaving the olefin part of the ligand uncoordinated.

The new compounds differ from the metallocenes in that their formation is less clean, the NMR signals of the iron derivatives spread out much beyond the range known for substituted ferrocenes, and the susceptibility for undergoing oxidation is much more pronounced. On the other hand, there are also some similarities, such as the colors (orange for all iron derivatives and red for (BCOD)₂Cr), the magnetism, and the structures, which represent metals sandwiched between two 6- π -electron ligands. When a ligand has a split (2 + 4)- π -electron system, its basketlike shape leads to steric interference with the second π ligand which may destabilize the bonding of the latter.

Experimental Section

All experiments were performed under purified inert gas by Schlenk techniques. Solvents were dried by standard methods, and oxygen was removed. The elemental analyses were carried out by the microanalytical laboratory of the Anorganisch-chemisches Institut.

1. **Bis((2,3,4,6,7- η^5)-bicyclo[3.2.2]nona-2,6,8-trien-4-yl)-iron, (BCNT)₂Fe (5).** A solution of 2 from 0.98 g (3.5 mmol) of 4-(trimethylstannyl)bicyclo[3.2.2]nona-2,6,8-triene (4)¹⁴ in 50 mL of THF and 2.2 mL of a 1.6 M solution of methyllithium in ether was cooled to -78 °C and treated with 0.39 g (1.7 mmol) of FeCl₂·1.35THF. From the dark reaction mixture, which formed during warming to 25 °C, the solvents were evaporated, the remainder was extracted with pentane, and the resulting solution was concentrated and chromatographed (silylated silica, Merck 60; pentane; column diameter/length 1/15 cm). The orange-brown phase was collected, and the solvent was partly evaporated. After the solution was cooled to -30 °C, a few orange crystals of 5 (yield 8 mg, 1.6%) formed while most of the product remained in solution together with coupled ligand (BCNT)₂ (NMR¹⁵). MS (*m/z* (%)): 290 (10), M⁺; 117 (55), C₈H₉⁺; 91 (100), C₇H₇⁺; 78 (9), C₆H₆⁺; 65 (14), C₅H₅⁺; 56 (20), Fe⁺. ¹H NMR (C₆D₆): δ 2.67 (m, 2H, H1/5), 2.94 (pt,³² 2H, H2/4), 3.17 (t, 1H, H3), 3.37 (dd, 2H,

H6/7), 5.75 (dd, 2H, H8/9); ³J_{1,2} = 7.5 Hz,³² ⁴J_{1,6} = 3.1 Hz,³³ ³J_{1,7} = 5.3 Hz, ³J_{1,8} = 4.6 Hz, ⁴J_{1,9} = 3.1 Hz, ³J_{2,3} = 7.0 Hz. ¹³C NMR (C₆D₆; δ /¹J_{CH} in Hz): 30.7/165.7 (d, C2/4), 31.6/139.7 (d, C1/5), 37.2/169.1 (d, C6/7), 83.9/161.9 (d, C3), 132.8/160.5 (d, C8/9); ²J_{C2H1} = 6.4 Hz (t), ²J_{C3H2/4} = 6.8 Hz (t), ²J_{C8H3} = 6.0 Hz (d). Anal. Calcd for C₁₈H₁₈Fe: C, 74.50; H, 6.25. Found: C, 74.49; H, 6.26.

2. **Reaction of 2 with Iron(II) Chloride in the Presence of Cp⁻.** A solution of 3.5 mmol of 2 in THF (see paragraph 1), 0.31 g (3.5 mmol) of CpNa, and 0.78 g (3.4 mmol) of FeCl₂·1.35THF were reacted and worked up similarly as described in section 1. Purification by chromatography with silylated silica gave a mixture of ferrocene and ((2,3,4,6,7- η^5)-bicyclo[3.2.2]nona-2,6,8-trien-4-yl)(η^5 -cyclopentadienyl)iron, (BCNT)FeCp (7), which could be enriched by repeated recrystallization. The best result was 26.4 mg of a material that contained a ratio of 7/Cp₂Fe = 2/1 (integration of the well-separated ¹³C NMR signals of Cp). NMR data for 7 is as follows. ¹H NMR (C₆D₆): δ 2.40 (t, 1H, H3), 2.50 (dd, 2H, H6/7), 2.87 (m, 2H, H1/5), 3.42 (pt,³² 2H, H2/4), 4.01 (s, 5H, Cp), 5.64 (dd, 2H, H8/9); ³J_{1,2} = 8.1 Hz,³² ⁴J_{1,6} = 3.2 Hz, ³J_{1,7} = 5.1 Hz, ³J_{1,8} = 4.6 Hz, ⁴J_{1,9} = 3.2 Hz, ³J_{2,3} = 6.8 Hz. ¹³C NMR (C₆D₆; δ /¹J_{CH} in Hz): 15.6/172.3 (d, C6/7), 23.8/165.0 (d, C2/4), 31.1/130.1 (d, C1/5), 70.9/interference with signal of Cp (C3), 75.8/174.1 (d, Cp), 132.4/159.9 (C8/9); ²J_{C2H1} $\approx$ ²J_{C2H3} = 6.6 Hz (t), ²J_{C8H1} = 6.0 Hz (d), ²J_{CpCH} $\approx$ ³J_{CpCH} = 6.6 Hz (quint). MS (*m/z* (%)): 238 (100), M⁺; 212 (3), M⁺ - C₂H₂; 172 (64), FeC₉H₈⁺; 147 (7), FeC₇H₆⁺; 134 (7), FeC₆H₅⁺; 121 (60), FeC₅H₄⁺; 117 (43), C₉H₈⁺; 91 (34), C₇H₇⁺; 65 (12), C₆H₆⁺.

3. **Reaction of 2 with Mn(CO)₅Br.** A solution of 0.26 g (0.90 mmol) of Mn(CO)₅Br and 0.27 g (0.96 mmol) of 4 in 80 mL of toluene was heated to 80 °C for 48 h. The reaction mixture was cooled to room temperature, the solvent was evaporated, and the solid was extracted with pentane. Filtering the yellow solution through Na₂SO₄ and cooling to -30 °C gave a yellow precipitate which contained a large excess of Mn₂(CO)₁₀ and, according to NMR spectroscopy, ((2,3,4,6,7- η^5)-bicyclo[3.2.2]nona-2,6,8-trien-4-yl)tricarbonylmanganese, (BCNT)Mn(CO)₃ (8), together with some organic impurities. Decomposition prevented purification by chromatography. The highly volatile Mn₂(CO)₁₀ prevented the collection of the mass data of 8. NMR data for 8 are as follows. ¹H NMR (C₆D₆): δ 2.18 (m, 2H, H1/5), 3.10 (pt,³² 2H, H2/4), 3.15 (t, 1H, H3), 3.31 (dd, 2H, H6/7), 5.66 (pt,³² 2H, H8/9); ³J_{1,2} = 7.6 Hz, ⁴J_{1,6} = 3.7 Hz, ³J_{1,7} = 4.9 Hz, ³J_{1,8} = 4.2 Hz, ⁴J_{1,9} = 3.4 Hz, ³J_{2,3} = 7.8 Hz. ¹³C NMR (C₆D₆; δ /¹J_{CH} in Hz): 29.5/135.0 (C1/5), 39.9/169.5 (C2/4), 62.8/171.4 (C6/7), 89.5/162.9 (C3), 135.8/165.6 (C8/9); ²J_{C2H1} $\approx$ ²J_{C2H3} = 5.9 Hz (t), ²J_{C8H1} = 6.8 Hz (d).

4. **Bis((2,3,4,6,7- η^5)-bicyclo[3.2.1]octa-2,6-dien-4-yl)iron, (BCOD)₂Fe (11).** A solution of 0.84 g (3.1 mmol) of 4-(trimethylstannyl)bicyclo[3.2.1]octa-2,6-diene¹⁷ (10) in 30 mL of THF was cooled to -78 °C. When an equimolar quantity of methyllithium in ether was added, the colorless mixture became lemon yellow, indicating the formation of 1. Adding 0.21 g (1.6 mmol) of ZnCl₂ (dried at 600 °C/10⁻² Pa), short warming to 0 °C, cooling to -78 °C again, and adding 0.37 g (1.6 mmol) of FeCl₂·1.35THF gave an orange solution which became brown to black upon warming to 25 °C. After all volatile components were stripped off, the remainder was extracted with pentane and the solution was filtered over Na₂SO₄ and chromatographed as described in section 1. When the resulting orange solution was concentrated and cooled to -30 °C, feather-shaped crystals of 11 (yield 10 mg, 2.4%) suitable for X-ray analysis formed. Most of the orange product remained in solution together with organic impurities. MS (*m/z* (%)): 266 (57), M⁺; 186 (30), M⁺ - C₆H₆; 160 (20), M⁺ - C₈H₁₀; 148 (8), M⁺ - C₉H₈; 134 (100), FeC₈H₆⁺; 121 (15), FeC₅H₄⁺; 105 (7), C₈H₉⁺; 78 (16), C₈H₈⁺; 56 (74), Fe⁺. ¹H NMR (C₆D₆): δ 0.12 (d, 1H, H8_{syn}), 0.60 (dt, 1H, H8_{anti}), 2.45 (m, 2H, H1/5), 2.64 (t, 2H, H2/4), 3.02 (dd, 2H, H6/7), 3.92 (t, 1H, H3); ³J_{1,2} = 5.9 Hz, ⁴J_{1,6} = 1.6 Hz, ³J_{1,7} = 2.7 Hz, ³J_{1,anti} = 4.9 Hz, ³J_{2,3} = 5.9 Hz, ²J_{8,3} = 9.3 Hz. ¹³C NMR (C₆D₆; δ /¹J_{CH} in Hz): 28.0/165.8 (d,

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(32) Nonresolved inner lines of a double doublet yield a pseudotriplet (pt). The separation of the two outer lines minus ³J_{2,3} (derived from the signal of H3) yields ³J_{1,2}. Similar arguments apply for 7, 8, and 14.

(33) The assignment of this coupling constant in ref 13b has been revised.

C2/4), 32.0/173.4 (d, C6/7), 34.5/131.6 and 133.5 (dd, C8), 34.7/145.3 (d, C1/5), 81.2/161.6 (d, C3). Anal. Calcd for $C_{16}H_{18}Fe$: C, 72.20; H, 6.82. Found: C, 72.48; H, 6.91.

5. Reaction of 1 with Iron(II) Chloride in the Presence of Cp⁻. A solution of 1 was prepared from 0.94 g (3.3 mmol) of 10 in THF and 2.19 mL of a 1.6 M solution of methylolithium in ether as described in section 4 and combined with 0.31 g (3.5 mmol) of CpNa. To the clear solution which resulted after stirring was added 0.78 g (3.4 mmol) of $FeCl_2 \cdot 1.35THF$ at $-78^\circ C$. Stirring for another 2 h at room temperature, removing the solvents, and extracting the residue with pentane gave an orange solution which according to the NMR spectra contained ferrocene and ((2,3,4,6,7- η^5)-bicyclo[3.2.1]octa-2,6-dien-4-yl)(η^5 -cyclopentadienyl)iron, (BCOD)FeCp (12). The low yield of 12 did not allow us to obtain it free from ferrocene after repeated recrystallization. Due to organic byproducts, we were unable to obtain the mass data for 12. ^{13}C NMR for 12 (C_6D_6 ; $\delta^{13}J_{CH}$ in Hz): 13.2/170.0 (d, C6/7), 20.2/164.1 (d, C2/4), 33.4/133.5 (br t, C8), 34.1/140.4 (d, C1/5), 70.3/159.9 (d, C3), 75.89/173.1 (d, Cp).

6. (exo-(2,3,4- η^3)-Bicyclo[3.2.1]octa-2,6-dien-4-yl)(η^5 -pentamethylcyclopentadienyl)nickel, (BCOD)NiCp* (14). A solution of 0.99 g (3.38 mmol) of $Cp^*Ni(acac)^{18}$ in 150 mL of THF was cooled to $-78^\circ C$. When 3.40 mmol of the potassium salt of 1^{9a} in 20 mL of THF was added, the color changed from red to purple. As the temperature was raised slowly to $25^\circ C$, the mixture turned brown above $-40^\circ C$. After the mixture was stirred for 3 h, the THF was replaced by 300 mL of pentane and the resulting suspension was filtered. The solution was reduced to 5 mL, whereupon dark microcrystals formed. Recrystallization from 2.5 mL of ether gave a mixture of brownish green and green microcrystals which were extremely soluble in ethers, benzene, and pentane. Chromatography (silylated silica Merck 60; pentane; $-35^\circ C$; column diameter/length 1/80 cm) gave a green band followed by a brown band. The green phase was collected, and pentane was evaporated until 1 mL was left. When this was kept at $-78^\circ C$, dark green microcrystals of 14 formed (yield 20 mg, 2.0%). MS (m/z (%)): 298 (66), M^+ ; 268 (4), $M^+ - C_2H_6$; 240 (7), $M^+ - 58$; 222 (6), $M^+ - C_6H_6$; 220 (15), $M^+ - C_6H_8$; 210 (3), $(C_6H_9)_2^+$; 192 (100), Cp^*Ni ; 178 (44), $NiC_5H_{10}^+$; 162 (10), $NiC_5H_8^+$; 135 (37), Cp^{*+} ; 134 (55), $C_{10}H_{14}^+$; 133 (36), $C_{10}H_{13}^+$; 119 (58), $C_9H_{11}^+$; 105 (76), $C_8H_9^+$; 91 (33), $C_7H_7^+$; 79 (28), $C_6H_7^+$; 78 (24), $C_6H_6^+$; 77 (28), $C_6H_5^+$; 58 (15), Ni^+ . 1H NMR (C_6D_6): δ 1.82 (s, 15H, Cp^*), 2.14 (dt, 1H, H_{8anti}), 2.37 (m, 2H, $H_{1/5}$), 2.46 (d, 1H, H_{8syn}), 3.35 (d pt, $^{32}J_{1,2} = 5.7$ Hz, $^{32}J_{1,anti} = 4.3$ Hz, $^{32}J_{2,3} = 5.6$ Hz, $^4J_{2,8} = 1.0$ Hz, $^2J_{8,8} = 8.6$ Hz. ^{13}C NMR (C_6D_6 ; $\delta^{13}J_{CH}$ in Hz): 10.4/125.7 (q, CH_3), 42.7/142.3 (d, C1/5), 57.2/132.2 (br t, C8), 62.3/158.0 (d, C2/4), 87.4/168.2 (d, C3), 97.8 (s, CCH_3), 139.2/167.2 (d, C6/7). Anal. Calcd for $C_{18}H_{24}Ni$: C, 72.57; H, 8.27. Found: C, 72.28; H, 8.27.

7. Bis((2,3,4,6,7- η^5)-bicyclo[3.2.1]octa-2,6-dien-4-yl)chromium, (BCOD) $_2Cr$ (13). A 0.80-g (3.36-mmol) amount of $CrCl_2 \cdot 0.8THF^{34}$ was suspended in 150 mL of THF and cooled to $-78^\circ C$. When 6.72 mmol of the potassium salt of 1^{9a} in 40 mL of THF was added, the light blue solution and the colorless solid gave a brown mixture which became red after stirring for 5 h and warming slowly to $25^\circ C$. Then, THF was stripped, the remaining solid was extracted with pentane, and the solution was concentrated. Cooling to $-130^\circ C$ gave dark red microcrystals which after recrystallization from toluene formed very small red needles of 13 (yield 0.31 g, 35%). MS (m/z (%)): 262 (5), M^+ ; 210 (2), $M^+ - 52$; 184 (1), $M^+ - C_2H_6$; 182 (1), $M^+ - C_6H_6$; 158 (3), $M^+ - C_8H_8$; 130 (9), $C_6H_6Cr^+$; 117 (3), $C_5H_5Cr^+$; 106 (16), $C_8H_{10}^+$; 105 (29), $C_8H_9^+$; 104 (11), $C_8H_8^+$; 103 (10), $C_8H_7^+$; 91 (29), $C_7H_7^+$; 79 (38), $C_6H_7^+$; 78 (100), $C_6H_6^+$; 77 (34), $C_6H_5^+$; 65 (6), $C_5H_5^+$; 52 (42), Cr^+ . Anal. Calcd for $C_{16}H_{18}Cr$: C, 73.26; H, 6.92. Found: C, 73.13; H, 6.96.

8. ((3,4,5,8,9- η^5)-Tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-5-yl)(η^5 -cyclopentadienyl)iron, (DICP)FeCp (16). A 1.98-g (6.7-mmol)

Table III. Summary of Crystallographic Data for 11

formula	$C_{16}H_{18}Fe$
M_r	266.169
cryst syst	orthorhombic
space group	$Fddd$ (No. 70)
a , Å	16.228(2)
b , Å	16.481(2)
c , Å	17.016(2)
V , Å ³	4551.0
Z	16
d_{calcd} , g/cm ³	1.554
μ (Mo $K\alpha$), cm ⁻¹	12.9
$F(000)$, e	2240
T , °C	-50
diffractometer	Syntex P2 ₁
radiation	Mo $K\alpha$, (λ = 0.710 69 Å)
monochromator	graphite
scan	ω
scan width (in ω), deg	0.8
$((\sin \theta)/\lambda)_{max}$, Å ⁻¹	0.617
hkl range	+20,+20,+20
no. of reflns (meas/unique)	1249/1127
no. of reflns obsd [$F_o \geq 4.0\sigma(F_o)$]	951
abs cor	empirical
rel. transmissn	0.71-1.00
H atoms (found/calcd)	9/-
no. of params ref	114
R^a	0.027
R_w^b	0.027
$\Delta\rho_{fin}(max/min)$, e/Å ³	+0.35/-0.27

^a $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. Function minimized: $\sum w(|F_o| - |F_c|)^2$.

amount of 4-(trimethylstannyl)tricyclo[5.2.1.0^{2,6}]deca-3,8-diene (15)¹⁹ was mixed with 100 mL of THF and cooled to $-78^\circ C$. When 4.1 mL of a 1.66 M solution of methylolithium in ether (6.8 mmol) was poured in, the color changed to yellow. The solution was stirred at $-78^\circ C$ for 4 min, and 0.79 g (3.4 mmol) of solid $FeCl_2 \cdot 1.5THF$ was added. A brown suspension was obtained, which darkened when it was warmed to ambient temperature. The solvent was evaporated, the residue was extracted with pentane, and the solution was filtered over Na_2SO_4 , reduced to a few milliliters, and chromatographed as described in section 1. Only one orange phase was eluted, and pentane was partly evaporated. After the solution was cooled to $-30^\circ C$, 0.17 g of red-brown brick-shaped crystals of 16 was collected (yield 20%). 16 could be sublimed at $50^\circ C$ and 7×10^{-2} Pa. MS (m/z (%)): 252 (43), M^+ ; 186 (100), $M^+ - C_5H_6$; 121 (65), $FeC_5H_5^+$; 56 (38), Fe^+ . 1H NMR (C_6D_6): δ 1.36 (dt, 1H, H_{10syn}), 1.96 (m, 2H, $H_2/6$), 1.98 (dt, 1H, H_{10anti}), 2.72 (m, 2H, $H_{1/7}$), 3.69 (s, 5H, Cp), 4.42 (t, 1H, H_4), 5.06 (m, 2H, $H_{3/5}$), 5.52 (m, 2H, $H_{8/9}$); $^3J_{1,10syn} \approx ^3J_{1,10anti} = 1.2$ Hz, $^3J_{3,4} = 3.4$ Hz, $^2J_{10,10} = 8.8$ Hz. ^{13}C NMR (C_6D_6 ; $\delta^{13}J_{CH}$ in Hz): 50.6/140.9 (C1/7), 55.7/127.9 (C2/6), 56.6/127.8 and 133.3 (C10), 68.0/163.1 (C3/5), 73.2/165.1 (C8/9), 79.9/174.6 (Cp), 84.6/167.5 (C4); $^2J_{C_3H_2} = 5.1$ Hz and $^2J_{C_3H_4} = 9.5$ Hz (dd), $^2J_{CpCH} \approx ^3J_{CpCH} = 6.6$ Hz (quint); $^1J_{CC}$ in Hz/isotope shift $^1\Delta$ -[$^{13}C_i(^{13}C_j)$] in ppb 35.1/14 (C1/7-C2/6), 36.8/11 (C1/7-C8/9), 31.1/11 (C1/7-C10), 35.1/11 (C2/6-C1/7), 41.0/9 (C2/6-C3/5), 41.0/9 (C3/5-C2/6), 41.7/18 (C3/5-C4), 41.7/14 (C4-C3/5), 36.8/18 (C8/9-C1/7), 31.1/12 (C10-C1/7).

9. Physical Measurements. The mass spectra were obtained in the electron impact mode (70 eV) with a Varian MAT 311A and a Finnigan MAT 90 instrument. A JEOL JNM-GX 270 and a Bruker CXP 200 spectrometer were used for the NMR spectra. The signal shifts were measured at $30^\circ C$ relative to solvent signals and calculated relative to TMS by using the data in ref 35. The ^{57}Fe Mössbauer spectrum was measured with both the source of ^{57}Co in Rh and the absorber at ambient temperature. The spectrum was recorded using an electromechanical velocity drive operated in a sinusoidal velocity scan mode³⁶ and least squares

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fitted with superpositions of Lorentzian lines.³⁷ The isomer shift has been calculated relative to α -iron, which has an isomer shift of -0.12 mm s^{-1} relative to the source of ^{57}Co in Rh. The electrochemical equipment used for cyclic voltammetry and the Faraday balance used for the magnetic measurements have also been described previously.^{38,39}

10. Crystal Structure Analysis of $(\text{BCOD})_2\text{Fe}$. Suitable single crystals of 11 were grown from pentane at -30°C and sealed at dry ice temperature under argon into thin-walled glass capillaries. All subsequent measurements were made directly on the diffractometer at -50°C . Table III contains the pertinent crystallographic data.

Diffractometer measurements yielded an orthorhombic unit cell with systematic extinctions pointing to space group $Fddd$ (No. 70). Reduced cell calculations did not indicate metric symmetry higher than orthorhombic. Exact cell dimensions were obtained by least-squares on the setting angles of 15 selected reflections from all parts of reciprocal space carefully centered on the diffractometer. The measured integrated intensities were corrected for L_p effects and empirically for those of absorption. For the latter ψ scans at 10° intervals around the diffraction vectors of nine reflections near $\kappa = 90^\circ$ served to determine the absorption profiles. Repeated measurement of three standard reflections (040, 400, 008) did not indicate significant crystal decay. The structure was solved by automated Patterson methods (SHELXS-86) and completed by standard Fourier techniques. After anisotropic refinement of the non-H atoms all H atoms could be located in difference Fourier syntheses. They were refined with isotropic displacement parameters in the final refinement cycles. All other atoms were refined with anisotropic displacement parameters. For the refinement all structure factors

Table IV. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 11^a

atom	x/a	y/b	z/c	$U(\text{eq})$
Fe	0.375	0.07419(2)	0.375	0.017
C1	0.3217(1)	0.1325(1)	0.5180(1)	0.027
C2	0.3874(1)	0.0693(1)	0.5022(1)	0.029
C3	0.3629(1)	-0.0041(1)	0.4686(1)	0.028
C4	0.2876(1)	-0.0059(1)	0.4267(1)	0.026
C5	0.2241(1)	0.0596(1)	0.4438(1)	0.026
C6	0.2572(1)	0.1293(1)	0.3933(1)	0.025
C7	0.3138(1)	0.1713(1)	0.4375(1)	0.025
C8	0.2375(1)	0.0918(1)	0.5271(1)	0.028

$$^a U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij}^* a_i a_j^* a_i a_j$$

with $F_o \geq 4.0\sigma(F_o)$ were used; one (755) was suppressed because of supposed extinction (SHELX-76). Refinement was terminated at a maximum ratio of shift over error of 0.001. A final difference synthesis was featureless.

Table II contains selected bond lengths and angles and Table IV the atomic parameters of the non-H atoms. See the paragraph regarding supplementary material at the end of the paper for additional crystal structure data.

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Supplementary Material Available: Temperature- and field-dependent magnetic measurements for $(\text{BCOD})_2\text{Cr}$ (Table V) and complete H atom coordinates, anisotropic displacement parameters, and H atom distances and angles for 11 (Tables VI–VIII) (5 pages). Ordering information is given on any current masthead page.

OM930344G

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