Dimerization of (2,4-Dimethylpentadienyl)iron Tricarbonyl: Isolation and Characterization of (2,4,7,9-Tetramethyl-1,3,7,9-decatetraene)diiron Hexacarbonyl Isomers

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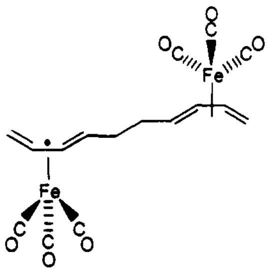
The reduction of the (2,4-C_7H_{11})Fe(CO)$_3$ (C_7H_{11} = dimethylpentadienyl) cation by zinc in THF leads to the formation of a dimer (μ-η^4, η^4-2,4,7,9-(CH$_3$)$_4$-1,3,7,9-$C_{10}H_{10}$)Fe$_2$(CO)$_6$, where $C_{10}H_{10}$ is decatetraene. Unlike the previously reported dimer of Co(2,4-C_7H_{11})$_2$, which was found to contain an isomerized bridging unit, (μ-η^4,η^4-2,4,7,9-(CH$_3$)$_4$-2,4,6,8-$C_{10}H_{10}$), the present complex was found spectroscopically not to have undergone such an isomerization, suggesting that the isomerization in the latter complex was induced by η^5–η^3 pentadienyl transformations, as previously suggested. An X-ray structural study of the dimer was carried out. The compound crystallizes in the monoclinic space group C_{2h}^5—$P2_1/n$ (No. 14), with a = 7.643 (2) Å, b = 12.068 (3) Å, c = 11.741 (2) Å, β = 97.700 (13)°, and V = 1073.14 Å^3 for Z = 2 dimeric units. Least-squares refinement of the structure led to agreement indices of R = 0.039 and R_w = 0.035 for the 1892 independent reflections judged to be above background ($I > 2.5\sigma(I)$). Each dimeric unit is situated on a crystallographic center of inversion, and the result confirms the unisomerized nature of the bridging unit. The overall structure about iron is similar to those of other (diene)Fe(CO)$_3$ compounds, and a number of comparisons are provided involving these and the above cobalt complexes.

A not uncommon reaction for pentadienyl ligands involves the coupling to another organic group, whether to another pentadienyl ligand,[2] or some other unsaturated molecule.[3] Not surprisingly, the intermolecular coupling between two pentadienyl ligands is especially favored in cases in which the starting monomers can be considered to possess 19-electron configurations. Thus, the reduction of (C_5H_7)Fe(CO)$_3^+$, or related species, leads to dimeric complexes such as I and II, apparently through the intermediacy of [(C_5H_7)Fe(CO)$_3$] "radicals".[4] More recently, attempts to prepare a bis(2,4-dimethylpentadienyl)cobalt complex, which could also be considered to be a 19-electron species, led, not unexpectedly, to a dimeric complex.[5] However, the isolated dimer had actually undergone an interesting isomerization from the expected bridging form III, involving a 1,3,7,9-decatetraene, to the observed form IV, with a more conjugated 2,4,6,8-decatetraene. It was believed that a key to this isomerization was the presence of an unaltered η^5-2,4-dimethylpentadienyl ligand on cobalt, which could lead to a reactive 16-electron cobalt site via η^5–η^3 isomerizations. One can note that in the iron dimers I and II, there are no pentadienyl ligands present to promote such an isomerization. However, it can also be noted that there exists a significant difference in the framework of the bridging di(pentadienyl) ligands, with I and II being composed of two sickle partners and III and IV being composed of two "U" partners. This difference could also be used to explain the lack of isomerization in (μ-η^4,η^4-1,3,7,9-$C_{10}H_{14}$)Fe$_2$(CO)$_6$, as the formation of a 2,4,6,8-decatetraene with two sickle partners would lead to *trans*-butadiene moieties coordinated to iron, which would clearly be unfavorable. Hence, it could be argued that isomerization in the iron system was prevented by a geometric, rather than an electronic, barrier. Since it is known that 2,4-dimethylpentadienyl ligands exhibit a preference for the "U" conformation,[6] one would expect



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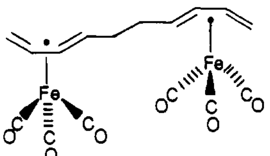

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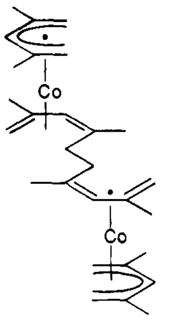

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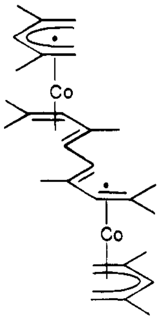

IV

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(1) (a) University of Utah. (b) Universität Heidelberg.

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that the reduction of $(2,4\text{-}C_7H_{11})Fe(CO)_3^+$ (C_7H_{11} = dimethylpentadienyl) would lead to a dimeric complex with a bridging unit identical to that in III. Such a complex would not be subject to any geometric barrier to the isomerization and would therefore allow a conclusion to be reached regarding whether or not a substantial electronic barrier actually exists for the isomerization of di(pentadienyl) bridging units in the iron complexes and thus provide a clearer comparison between the iron and cobalt systems regarding the relative tendencies toward the isomerization of their tetraene bridging units. One way or the other, this should also provide an indication about the likelihood of the proposed involvement of η^5–η^3 pentadienyl transformations in bringing about the isomerization observed in the (μ-2,4,7,9-tetramethyldecatetraene)$[Co(2,4\text{-}C_7H_{11})]_2$ system.

Experimental Section

All operations involving organometallics were carried out under a prepurified nitrogen atmosphere in Schlenk apparatus or in a glovebox. Nonaqueous solvents were thoroughly dried and deoxygenated in a manner appropriate to each and were distilled immediately before use. Elemental analyses were performed by MicAnal Laboratories (Tucson, AZ).

Spectroscopic Studies. Infrared spectra were recorded with a Perkin-Elmer 298 spectrophotometer. Mulls were prepared in a glovebox with dry, degassed Nujol. ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on Varian EM-300 and SC-300 spectrometers. Mass spectra were obtained with a Varian MAT 112 spectrometer at 70 or 20 eV. Except for the parent fragment, peaks are only quoted if their relative intensities are at least 10% of the intensity of the strongest peak.

(2,4-Dimethyl-1,3-pentadiene)iron Tricarbonyl. This compound has been previously reported,[7] and we have utilized a slight variation of the reported procedures for its isolation. A stirred mixture of 1.5 g (15.6 mmol) of 2,4-dimethylpentadiene, 7.7 g (21.2 mmol) of iron nonacarbonyl, and 80 mL of ether was refluxed overnight while being shielded from light. The green solution obtained was cooled to room temperature and filtered through Celite. After the ether was removed under reduced pressure, the residue was dissolved in 3–5 mL of pentane and purified by chromatography on silica gel using hexane as the solvent. The orange eluent, on removal of solvent in vacuo, gave 1.9 g of an orange-red oil (51%). An infrared spectrum of the product exhibited very strong carbonyl absorption peaks at 2046, 1967, and 1958 cm^{-1}. ^1H NMR (C_6D_6): δ 4.63 (s, br, 1 H, CH), 1.70 (s, 3 H, CH_3), 1.40 (m, 1 H, CH), 1.26 (s, 1 H, CH), 1.20 (s, 3 H, CH_3), 0.77 (s, 3 H, CH_3). ^{13}C NMR (CD_2Cl_2, 53.8 ppm): δ 103.5 (s), 93.4 (d, J = 163 Hz), 67.7 (s), 44.0 (t, J = 159 Hz), 33.6 (q, J = 127 Hz), 25.0 (q, J = 128 Hz), 20.7 (q, J = 128 Hz). Mass spectrum (70 eV): m/e relative (intensity) 42 (18), 44 (19), 56 (49), 73 (36), 96 (100), 110 (17), 112 (12), 152 (77), 180 (23), 208 (29), 236 (2.6).

(2,4-Dimethylpentadienyl)iron Tricarbonyl Fluoroborate. A solution of 1.10 g (4.6 mmol) of (2,4-dimethylpentadiene)iron tricarbonyl in 5 mL of dichloromethane was added dropwise to a stirred solution of 2.46 g (7.7 mmol) of triphenylmethyl fluoroborate in 15 mL of the same solvent at 0 °C. The solution was then warmed to room temperature and stirred overnight. Subsequently, 80 mL of ether was added to the dark red solution to precipitate the salt and decompose the excess triphenylmethyl fluoroborate. The suspension was stirred for 2 h, then filtered, and washed with 3 × 10 mL portions of ether. After the ether was removed in vacuo, 0.80 g of product was obtained (53%). The crude salt crystallized in yellow prisms from nitromethane–ether mixtures. An infrared spectrum of the salt showed very strong carbonyl absorption peaks at 2120, 2080, and 2041 cm^{-1}. ^1H NMR (CD_3NO_2): δ 6.93 (s, 1 H, CH), 3.58 (d, J = 4 Hz, 2 H, CH_2), 2.48 (s, 6 H, CH_3), 2.01 (d, J = 4 Hz, 2 H, CH_2). ^{13}C NMR (CD_3NO_2): δ 202.8, 127.0, 102.4, 66.8, 27.9. Anal. Calcd for $C_{10}H_{11}BF_4FeO_3$: C, 37.31; H, 3.45. Found: C, 37.33; H, 3.43.

(2,4,7,9-Tetramethyl-1,3,7,9-decatetraene)diiron Hexacarbonyl. A suspension of 2.05 g (31.4 mmol) of crude (2,4-dimethylpentadienyl)iron tricarbonyl fluoroborate and 2.25 g (34.4 mmol) of zinc dust in 60 mL of THF was stirred at room temperature for 3 days. The slurry was filtered through Celite and the solvent removed under reduced pressure. The residue was extracted with 2 × 30 mL of hexane and filtered through Celite. After reduction of the solution volume and cooling to −78 °C, a yield of 1.5 g (50%) of yellow crystalline solid, mp 85–125 °C, was obtained. The product was isolated as a mixture of two isomers through successive recrystallizations from pentane. The melting point of the less soluble isomer was 131.5–133 °C, while that for the more pentane-soluble isomer was 94–95.5 °C. An infrared spectrum of the dimer mixture showed very strong carbonyl absorption peaks at 2045, 1968, and 1962 cm^{-1}. ^1H NMR (C_6D_6): isomer I, δ 4.47 (s, 2 H, CH), 1.69 (s, 6 H, CH_3), 1.53 (q, 4 H, CH), 1.19 (s, 6 H, CH_3), 1.16 (s, 2 H, CH), 1.09 (s, 2 H, CH). ^{13}C NMR (C_6D_6): isomer I δ 212.49 (s), 103.06 (s), 91.55 (d, J = 163 Hz), 71.58 (s), 43.61 (t, J = 159 Hz), 37.07 (t, J = 130 Hz), 31.25 (q, J = 128 Hz), 23.96 (q, J = 128 Hz); isomer II, δ 212.56, 102.95, 91.72, 71.72, 43.70, 36.96, 30.68, 23.97. Mass spectrum (20 eV): m/e (relative intensity) 28 (56), 32 (12), 148 (38), 149 (10), 151 (14), 162 (22), 179 (27), 204 (48), 206 (25), 207 (16), 228 (14), 235 (16), 242 (59), 246 (35), 296 (22), 298 (12), 300 (59), 301 (11), 302 (100), 303 (76), 328 (13), 330 (74), 331 (15), 358 (28), 384 (16), 386 (100), 387 (28), 442 (31), 470 (2.1). Anal. Calcd for $C_{20}H_{22}Fe_2O_6$: C, 51.10; H, 4.72. Found: C, 51.14; H, 4.70.

X-ray Diffraction Study of (μ-η^4,η^4-2,4,7,9-$(CH_3)_4$-$C_{10}H_{10}$)-$Fe_2(CO)_6$. Single crystals of this compound were isolated by slowly cooling a concentrated solution in hexane. Unit cell data were determined from a combination of oscillation photographs and standard software programs for the Nicolet R3 autodiffractometer and confirmed by cell reduction. Accurate cell constants and their standard deviations were determined from a least-squares refinement of 25 centered reflections, leading to a = 7.643 (2) Å, b = 12.068 (3) Å, c = 11.741 (2) Å, β = 97.700 (13)°, V = 1073.14 $Å^3$ for Z = 2 dimetallic units. From the characteristic systematic absences, the space group was determined to be C_{2h}^5—$P2_1/n$ (No. 14). Data were collected out to 2θ = 60° on a yellow single crystal of approximate dimensions 0.2 × 0.25 × 0.25 mm using Mo Kα radiation (λ = 0.71069 Å) and θ–2θ scans. A total of 2113 unique reflections were collected, of which 1892 were judged to be above background ($I > 2.5\sigma(I)$). All calculations employed the SHELXTL program package 4.1 (August 1983). An empirical absorption correction was applied, based on six reflections in the 2θ range of 9.7–41.3°. The relative range in transmission factors was 0.786–1.000, and it can be noted that the value for the linear absorption coefficient is 13.81 cm^{-1}. The function minimized in least-squares calculations was $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F)$.

The iron atom position was located from a Patterson map, and the remaining non-hydrogen atoms were located from Fourier maps and subjected to anisotropic refinement. The hydrogen atoms were located on a difference Fourier map and were refined isotropically. Final refinement led to agreement indices of R = 0.039 and R_w = 0.035. A final difference Fourier map revealed no peaks greater than 0.55 e/$Å^3$. The positional parameters for the nonhydrogen atoms are listed in Table I, and pertinent bond distances and angles are included in Table II. Least-squares plane information may be found in Table III, while the anisotropic thermal parameters for the non-hydrogen atoms, and the hydrogen atom parameters, may be found in Tables IV (supplementary material) and V, respectively. The final values of $|F_o|$ and $|F_c|$ are available as supplementary material.

Results

(η^4-2,4-Dimethyl-1,3-pentadiene)iron tricarbonyl could be readily prepared from the reaction of the diene with an excess of $Fe_2(CO)_9$. Treatment of the oily compound with triphenylmethyl tetrafluoroborate in methylene

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Table I. Positional Parameters for the Non-Hydrogen Atoms of $(\mu\text{-}\eta^4,\eta^4\text{-}2,4,7,9\text{-}(CH_3)_4\text{-}1,3,7,9\text{-}C_{10}H_{10})Fe_2(CO)_6$

atom	*x*	*y*	*z*
Fe	0.15769 (5)	0.66240 (3)	0.81160 (4)
C(1)	0.2112 (4)	0.6926 (3)	0.6718 (3)
O(1)	0.2411 (3)	0.7102 (2)	0.5808 (2)
C(2)	0.0705 (4)	0.5262 (3)	0.7875 (3)
O(2)	0.0183 (3)	0.4381 (2)	0.7738 (2)
C(3)	−0.0338 (4)	0.7476 (3)	0.7877 (3)
O(3)	−0.1581 (3)	0.8015 (2)	0.7743 (2)
C(4)	0.1354 (5)	0.6642 (3)	0.9889 (3)
C(5)	0.2601 (4)	0.7421 (3)	0.9625 (3)
C(51)	0.2399 (7)	0.8640 (4)	0.9867 (4)
C(6)	0.3966 (4)	0.7062 (3)	0.9033 (3)
C(7)	0.4172 (3)	0.5944 (2)	0.8684 (2)
C(71)	0.5386 (4)	0.5787 (3)	0.7782 (3)
C(8)	0.4268 (4)	0.4936 (3)	0.9490 (3)

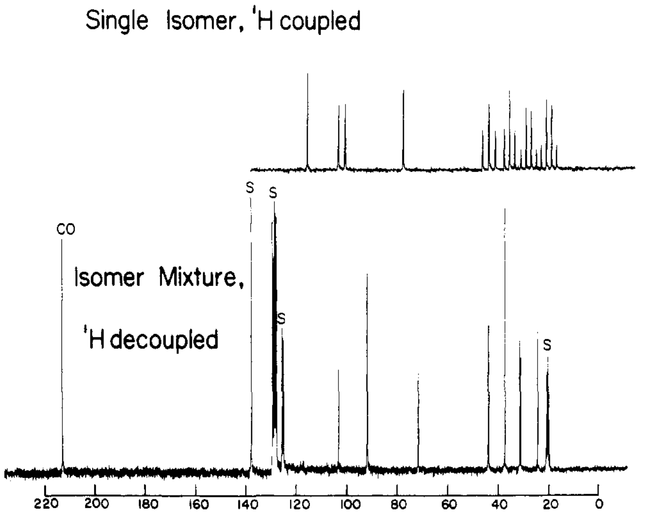
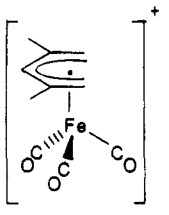


Figure 1. ^{13}C NMR spectra for the $(\mu\text{-}\eta^4,\eta^4\text{-}2,4,7,9\text{-}(CH_3)_4\text{-}1,3,7,9\text{-}C_{10}H_{10})Fe_2(CO)_6$ isomers in toluene-d_8. The lower spectrum was recorded on the mixture of isomers and consists of seven pairs of closely spaced resonances for the bridging ligands in the 20–110 ppm range. Each solvent peak is marked by an "S". The upper spectrum, recorded on a single isomer in benzene-d_6, is presented as an expansion of the 20–110 ppm region.



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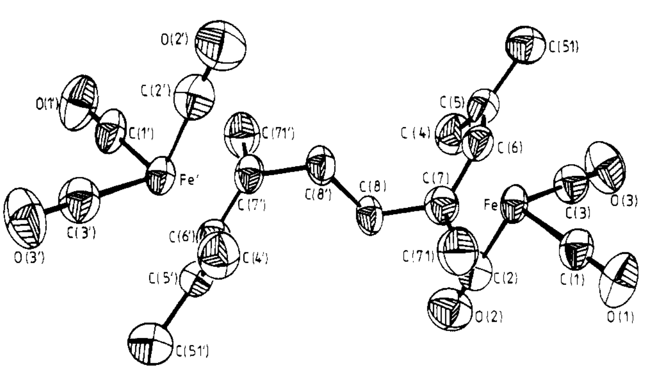
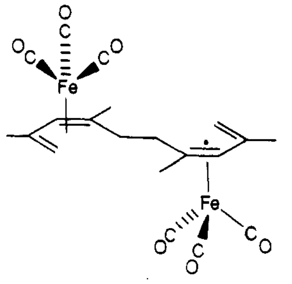


Figure 2. Perspective view and numbering scheme for the $(\mu\text{-}\eta^4,\eta^4\text{-}2,4,7,9\text{-}(CH_3)_4\text{-}1,3,7,9\text{-}C_{10}H_{10})Fe_2(CO)_6$ molecule. The molecule sits on an inversion center, so that the nonprimed atoms are related to the primed ones.

chloride led to abstraction of a hydride ion and formation of $(\eta^5\text{-}2,4\text{-}C_7H_{11})Fe(CO)_3{}^+BF_4{}^-$ (C_7H_{11} = dimethylpentadienyl, V), which was subsequently isolated in yields of ca. 53%. Analytical and spectroscopic (IR, NMR) data provided sufficient characterization of the product. Interestingly, the ^1H NMR resonances (in ppm) (δ 6.93 (1 H), 3.58 (2 H), 2.48 (6 H), 2.01 (2 H)) for the cationic complex are found substantially downfield from those of the analogous "open ferrocene", $Fe(2,4\text{-}C_7H_{11})_2$[8] (δ 4.40 (1 H), 2.68 (2 H), 1.85 (6 H), 0.26 (2 H)). A similar trend is observed in the ^{13}C NMR spectra (δ 127.0, 102.4, 66.8, and 27.9 ppm vs. 99.2, 93.4, 50.6, and 26.3 ppm, respectively). Reduction of the cation with zinc takes place readily at room temperature over a period of several days to yield the expected product of stoichiometry $[Fe(C_7H_{11})(CO)_3]$, whose dimeric nature was confirmed by mass spectroscopy. The material could be separated by recrystallization into a mixture of two isomers, which were present in nearly equal amounts and whose melting points differed considerably although their infrared and NMR spectra were nearly identical. Spectral characteristics for each isomer clearly indicated that no isomerization of the carbon–carbon double bonds has taken place; i.e., the bridging unit is 2,4,7,9-tetramethyl-1,3,7,9-decatetraene, as in III. Thus, each isomer possessed two methyl resonances in the ^1H NMR spectrum, rather than the three expected for IV. Similarly, for each isomer the ^{13}C NMR spectrum (Figure 1) contained two types of methyl carbon atoms, two types of CH_2 carbon atoms, and one type of CH carbon atom, as expected for the bridging unit in III, while the isomerized ligand would possess three types of methyl groups, no CH_2 groups, and two types of CH groups. Note that each isomer does possess two quaternary carbon atom environments. Therefore, the two isomers may be conveniently represented as VI and VII (below) with the more symmetric VI probably corresponding to the higher melting point isomer, as actually has been verified by the X-ray diffraction study (vide infra).[9] One should note, however, that the spectral data does not really demonstrate that the backbone of the bridging ligand still retains the former pentadienyl fragments in the "U" conformations,



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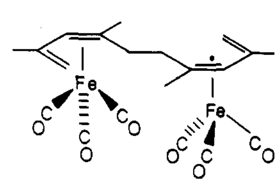

VII

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(9) Isomer VI is described as the more symmetric species in that the opposite placement of the two $Fe(CO)_3$ groups would lead to a dipole moment of zero. There could well be some rotation about the central carbon–carbon bond in VII, which would tend to orient the $Fe(CO)_3$ groups on opposite sides of the bridging ligand. However, in isomer VII there would still always be a dipole moment (unlike VI), regardless of orientation. A reviewer has questioned whether this second isomer might not have the two pentadienyl units joined in sickle shape, as has been observed in one *intramolecular* coupling reaction.[2d] While this cannot be absolutely established from speectroscopic data, one might expect a larger difference between the ^{13}C NMR resonances for the two isomers if this were true. In addition, one would also have to wonder why the U–U coupling and the S–S coupling processes only led to one isomer each (whereas previous couplings have led to two isomers[4b]) and why neither of the two potential U–S coupling products would be observed.

Table II. Selected Bond Distances (Å) and Angles (deg) for $(\mu,\eta^4,\eta^4\text{-}2,4,7,9\text{-}(CH_3)_4\text{-}1,3,7,9\text{-}C_{10}H_{10})Fe_2(CO)_6$

Bond Distances					
Fe–C(1)	1.782 (3)	Fe–C(4)	2.112 (3)	C(5)–C(6)	1.397 (5)
Fe–C(2)	1.782 (3)	Fe–C(5)	2.075 (3)	C(6)–C(7)	1.425 (4)
Fe–C(3)	1.780 (3)	Fe–C(6)	2.060 (3)	C(7)–C(71)	1.511 (4)
C(1)–O(1)	1.142 (4)	Fe–C(7)	2.167 (3)	C(7)–C(8)	1.537 (4)
C(2)–O(2)	1.139 (4)	C(4)–C(5)	1.403 (5)	C(8)–C(8′)	1.533 (6)
C(3)–O(3)	1.145 (4)	C(5)–C(51)	1.510 (5)		

Bond Angles					
C(1)–Fe–C(4)	164.8 (1)	C(1)–Fe–C(2)	99.7 (1)	Fe–C(1)–O(1)	178.0 (3)
C(1)–Fe–C(7)	92.7 (1)	C(1)–Fe–C(3)	91.3 (1)	Fe–C(2)–O(2)	178.3 (3)
C(2)–Fe–C(4)	95.1 (1)	C(2)–Fe–C(3)	103.0 (1)	Fe–C(3)–O(3)	178.6 (3)
C(2)–Fe–C(7)	90.4 (1)	C(4)–C(5)–C(51)	121.4 (3)	C(6)–C(7)–C(71)	114.9 (3)
C(3)–Fe–C(4)	88.6 (1)	C(4)–C(5)–C(6)	118.4 (3)	C(6)–C(7)–C(8)	124.8 (3)
C(3)–Fe–C(7)	165.2 (1)	C(6)–C(5)–C(51)	119.9 (3)	C(8)–C(7)–C(71)	110.5 (2)
C(4)–Fe–C(7)	83.8 (1)	C(5)–C(6)–C(7)	123.8 (3)	C(7)–C(8)–C(8′)	111.7 (3)

Table III. Deviations of Atoms from Best Least-Squares Planes Defined by Atoms C(4)–C(7)[a]

atom	dist	atom	dist
C(4)	−0.001	Fe	−1.590
C(5)	0.002	C(51)	−0.128
C(6)	−0.002	C(71)	−0.392
C(7)	0.001	C(8)	1.028
C(1)	−2.792	H(4A)	0.580
C(2)	−1.802	H(4B)	−0.190
C(3)	−2.678	H(6)	−0.152

[a] Equation (monoclinic coordinates): $3.463x - 2.320y + 9.416z = 8.241$.

Table V. Positional and Thermal Parameters for the Hydrogen Atoms in $(\mu\text{-}\eta^4,\eta^4\text{-}2,4,7,9\text{-}(CH_3)_4\text{-}1,3,7,9\text{-}C_{10}H_{10})Fe_2(CO)_6$

atom	x	y	z	U, Å^2
H(4A)	0.1685 (36)	0.5943 (24)	1.0211 (24)	0.053 (9)
H(4B)	0.0333 (43)	0.6888 (26)	1.0123 (28)	0.071 (11)
H(51A)	0.1237 (48)	0.8816 (32)	0.9849 (34)	0.095 (15)
H(51B)	0.3001 (44)	0.9109 (29)	0.9313 (32)	0.090 (13)
H(51C)	0.2890 (53)	0.8796 (32)	1.0547 (36)	0.103 (15)
H(6)	0.4615 (28)	0.7568 (18)	0.8759 (19)	0.034 (7)
H(71A)	0.6511 (37)	0.5615 (23)	0.8102 (25)	0.075 (9)
H(71B)	0.4985 (40)	0.5182 (25)	0.7258 (26)	0.080 (10)
H(71C)	0.5541 (35)	0.6441 (21)	0.7324 (24)	0.057 (8)
H(8A)	0.3114 (31)	0.4779 (21)	0.9810 (21)	0.055 (8)
H(8B)	0.4514 (38)	0.4266 (25)	0.9023 (26)	0.063 (10)

even though steric considerations (vide supra) would make this the most reasonable choice. To determine the actual backbone geometry, resort was made to X-ray diffraction.

The result of the single-crystal X-ray study is presented in Figure 2, along with the atom numbering scheme. Atomic coordinates are listed in Table I, while pertinent bond distances and angles are contained in Table II. Least-squares plane information is given in Table III, and atomic thermal parameters and hydrogen atom parameters are given in Tables IV (supplementary material) and V, respectively. It can be seen that the compound is indeed dimeric and has a crystallographically imposed center of inversion which relates the set of unprimed atoms to their primed counterparts. The structure was carried out on the higher melting isomer, which did indeed correspond to the "trans" form VI. In addition, it can be clearly seen that the former 2,4-dimethylpentadienyl ligands have retained their "U" shapes, and in agreement with spectroscopic results (vide supra), no isomerization of the butadiene groups has taken place. Since there is now no geometric barrier to the isomerization process, as there could have been for the $(C_5H_7)Fe(CO)_3$ dimers, it must be concluded that a substantial electronic barrier exists.

The coordination geometry about iron is similar to those in other (diene)$Fe(CO)_3$ complexes[10] and can be regarded as essentially square-pyramidal, with CO(2) and CO(2′) being the apical ligands. As one indication of this, one can note the angles formed between the "butadiene" least-squares plane perpendicular and the three M–C vectors for the carbonyl ligands. The value of 96.8° for CO(2) is clearly much less than the values of 132.4° and 127.6° for CO(1) and CO(3). One can also note that many of the angles around iron involving C(1), C(2), C(3), C(4), and C(7) are near 90° (Table III). The Fe–C and C–O bond distances for the three unique carbonyl ligands are virtually identical at 1.781 (2) and 1.142 (3) Å, respectively, despite their varying orientations. The carbonyl ligands are essentially linear, with an average value for Fe–C–O being 178.3 (2)°.[11] The Fe–C bond distances involving the terminal "butadiene" carbon atoms (2.112 (3) and 2.167 (3) Å) are longer than those to the internal carbon atoms (2.075 (3) and 2.060 (3) Å), the differences being ca. 0.07 Å, very similar to the average value of 0.08 Å found in similar (diene)$Fe(CO)_3$ complexes.[10] Interestingly, one bond distance in each pair is significantly shorter than the other, and in each case the shorter bond involves a less substituted carbon atom. The biggest difference, in fact, involves the external pair C(4) and C(7) for which the difference in the number of substitutions is greater than that for the other pair, C(5) and C(6). Either steric or electronic factors could contribute to this. In regard to the steric possibility, it can be noted that there are a significant number of intramolecular contacts which are less than the sum of the van der Waals radii for carbon (1.7 Å) or a methyl group (2.0 Å).[12] Several of these do, in fact, involve the three substituent atoms on the butadiene fragment, namely, C(2)···C(8) at 3.128 Å, C(3)···C(51) at 3.241 Å, and C(1)···C(71) at 2.979 Å.[13]

The carbon–carbon bond distances in the coordinated butadiene fragment are reasonable, being 1.403 (5), 1.397 (5), and 1.425 (4) Å for C(4)–C(5), C(5)–C(6), and C(6)–C(7), respectively. The two external C–C bonds appear to be slightly longer (by 0.017 Å) than the internal bond. This value is similar to the average value of 0.021 (2) Å quoted by Cotton et al. for similar structures.[10] Thus, the molecule appears to be quite normal when compared to other (diene)$Fe(CO)_3$ complexes. Finally, all carbon–carbon single bond distances are normal, and those in-

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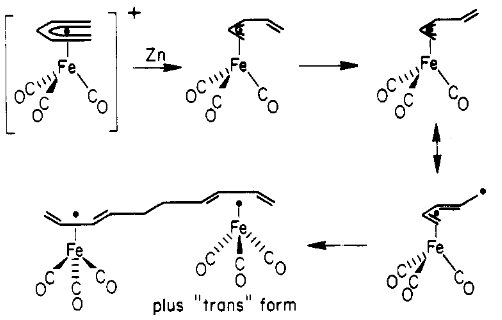
(10) Cotton, F. A.; Day, V. W.; Frenz, B. A.; Hardcastle, K. I.; Troup, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 4522.

(11) When average values are cited, the accompanying standard deviation is that of the mean value.

(12) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 7.

(13) Other possibly significant contacts are present between C(1) and C(2) (2.725 Å), C(1) and C(3) (2.546 Å), C(1) and C(6) (2.897 Å), C(1) and C(7) (2.870 Å), C(2) and C(3) (2.787 Å), C(2) and C(4) (2.880 Å), C(2) and C(7) (2.815 Å), C(3) and C(4) (2.729 Å), and C(3) and C(5) (2.833 Å).

Scheme I



volving the methyl groups appear to be shorter than those serving to bridge the two butadiene portions. With regard to the three substituents present on each butadiene ligand, the C(5)–C(51), vectors make angles of 4.9, 15.0, and 42.0°, respectively, with the butadiene plane, of which only the C(7)–C(8) vector is bent away from the iron atom. Quite analogous bendings have been observed in related allyl, butadiene, and pentadienyl complexes.[14] The hydrogen atom positions were refined, yielding C–H bond distances which averaged 0.946 (9) Å, a quite reasonable value given the normal apparent shortening of such bonds in an X-ray experiment.[15] The hydrogen atoms attached to C(4) and C(6) are bent significantly out of the butadiene plane by angles of 37.9, 12.0, and 10.0 degrees for H(4A), H(4B), and H(6), respectively. The bendings for H(4B) and H(6) occur in a direction toward the iron atom, while H(4A) is bent away from the iron atom, similar to the analogous C(8).

Discussion

Previous studies have demonstrated that the reduction of $(C_5H_7)Fe(CO)_3^+$ or related species leads to a pair of isomeric neutral complexes of the general formula (μ-η^4,η^4-1,3,7,9-$C_{10}H_{14})Fe_2(CO)_6$, e.g., I and II. The formation of these isomeric complexes may be readily understood by Scheme I.[4a] As noted earlier, the attempted preparation of $Co(2,4\text{-}C_7H_{11})_2$ also led to a dimeric complex in which a tetramethyldi(pentadienyl) fragment served to bridge two Co(η^5-2,4-C_7H_{11}) units.[5] However, there was a major difference in the constitution of this bridging unit in that an isomerization from a 1,3,7,9-decatetrene to a 2,4,6,8-decatetraene had taken place. While several considerations, especially electronic and steric,[5,8,14,16] tended to implicate an η^5–η^3 pentadienyl transformation in this isomerization process, another alternative could be considered. Conceivably an η^4–η^2 transformation of the coordinated butadiene fragment of the bridging unit could lead to the observed isomerization for the cobalt compound, while such a process would encounter a geometric barrier for the iron carbonyl compounds due to the prior conversion of the "U" pentadienyl group into an "S" (sickle) configuration, as shown in Scheme I. For a dimer such as I or II, isomerization to a 2,4,6,8-decatetraene (or even to a 1,3,5,7-decatetraene) would lead to trans-butadiene moieties bound to iron, which would clearly be unfavorable. For determination of whether a geometric barrier was preventing the isomerization in the iron carbonyl systems, resort was again made to the 2,4-dimethylpentadienyl ligand, which naturally tends to adopt the "U" conformation[6] and would provide for the best comparison between the two systems as the geometric and electronic natures of bridging units would be identical. Indeed, reduction of $(2,4\text{-}C_7H_{11})Fe(CO)_3^+$ with zinc dust led to an isomeric pair of dimers, each linked by a pair of former pentadienyl groups in the "U" conformation, i.e., VI and VII. Significantly, even in this system no isomerization to a conjugated tetraene was observed, even though isomerizations have been observed in other $(diene)Fe(CO)_3$ complexes (generally at much higher temperatures[17]). Hence, it can be concluded that a substantial electronic barrier exists for the isomerization of the bridging 1,3,7,9-decatetraene in the iron systems, which strongly implicates η^5–η^3 transformations in the isomerization process observed for the cobalt system. Certainly, however, one could maintain that the electronic influences exerted by $Fe(CO)_3$ and $Co(2,4\text{-}C_7H_{11})$ on the bridging decatetraene ligand would differ substantially, and hence a direct comparison could not be made with complete confidence. However, more recently the corresponding dimer with a 1,3,7,9-tetramethyldecatetraene group bridging two $Co(C_5H_5)$ units has been prepared,[18] and spectroscopic data indicate that no isomerization has taken place. Since the electronic effects exerted on a bridging decatetraene by Co(η^5-C_5H_5) and Co(η^5-2,4-C_7H_{11}) units should be reasonably similar, this would convincingly implicate the involvement of an η^5–η^3 pentadienyl transformation in the isomerization process, provided that the 1,4,7,9-tetramethyl-1,3,7,9-decatetraene has adopted the expected conformation, as in III. A structural study on this complex is underway and should provide conclusive evidence on the involvement of η^5–η^3 pentadienyl transformations in the "open cobaltocene" dimer.

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Registry No. V, 103533-90-0; VI, 103533-91-1; VII, 103617-41-0; $Fe_2(CO)_9$, 15321-51-4; (2,4-dimethyl-1,3-pentadiene)iron tricarbonyl, 12264-19-6; 2,4-dimethylpentadiene, 1000-86-8.

Supplementary Material Available: Listings of the anisotropic thermal parameters for the non-hydrogen atoms (Table IV) and complete bond distance and angle information (3 pages); a listing of structure factors (12 pages). Ordering information is given on any current masthead page.

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