J. Am. Chem. Soc. **1987**, *109*, 5711-5719

The less than totally solvated form of complex **2**, i.e., $[Mn_3O(O_2CMe)_6(pyr)_3](pyr)_{0.7}$ (**6**), did not show a visible thermal effect in its DSC thermogram. It is likely that the defect concentration is appreciably greater in this nonstoichiometric compound **6**. Thermal effects associated with phase transitions could then become broad, eventually becoming so broad that they could not be distinguished from the background.

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Supplementary Material Available: Complete listings of atomic coordinates, anisotropic thermal parameters, bond distances, and angles for **2** and **4** and magnetic susceptibility data for **1–4** (21 pages); listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page. Complete copies of the MSC Structure Reports (85096 and 86033 for **2** and **4**, respectively) are available on request from the Indiana University Chemistry Library.

Conformational Analysis for the Pseudooctahedral Complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2R$ [R = Me, Et, *i*-Pr, *t*-Bu, $SiMe_3$, $(PMe_3)^+$, $(PPh_3)^+$, Mesityl, Ph, Vinyl, 1-Naphthyl]: X-ray Crystal Structures of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2R$ (R = Me, $SiMe_3$)

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Abstract: A conformational analysis for the ligands CH_2R attached to the pseudooctahedral chiral auxiliary $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ is presented. For the complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2R]$ (**1**) R = (a) Me, (b) Et, (c) *i*-Pr, (d) *t*-Bu, (e) $SiMe_3$, (f) $[PMe_3]^+$, and (g) $[PPh_3]^+$ ^1H NMR spectroscopic analysis, including variable temperature studies, indicates that only one conformation, that where the R group resides in the space between the cyclopentadienyl ligand and the CO ligand with one methylene hydrogen approximately antiperiplanar to the CO ligand, conformation I, is populated. This is confirmed by X-ray crystal structure analyses for the complexes **1a** (R = Me) and **1e** (R = $SiMe_3$) and NOE data for complexes **1d** (R = *t*-Bu), **1e** (R = $SiMe_3$), and **1f** (R = $[PMe_3]^+$). For complex **1h** (R = mesityl) conformation I is unattainable, because of the lateral bulk of the mesityl group, and it adopts a single conformation with R (mesityl) essentially eclipsing the cyclopentadienyl ligand such that a methylene hydrogen is approximately eclipsing the CO ligand, conformation IV. In contrast to the above, complexes **1**, R = (i) Ph, (j) vinyl, and (k) 1-naphthyl, where R is planar, do show significant variation with temperature of their $^3J_{PH}$ coupling constants for both methylene protons consistent with the two conformations I and IV being populated. These results are in complete agreement with a previously proposed theoretically based conformational analysis.

The chiral auxiliary $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ has been shown to exert powerful stereocontrol in a wide variety of reactions of attached ligands.[1,2] In order to rationalize this remarkable stereocontrol we recently proposed a conformational analysis for complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2R]$ based on extended Huckel calculations.[3,4] This analysis, which is at variance with the previous long standing model,[5-10] has come in for considerable criticism,[11,12] although recently it has been successfully employed not only by ourselves[13] but also by others to this same iron system[14] and to rationalize some stereoselective reactions of ligands attached to the analogous rhenium chiral auxiliary $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]$.[15] We describe here our experimental studies on the conformational properties of the complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2R]$ (**1**) where R is (a) Me, (b) Et, (c) *i*-Pr, (d) *t*-Bu, (e) $SiMe_3$, (f) $[PMe_3]^+$, (g) $[PPh_3]^+$, (h) mesityl, (i) Ph, (j) vinyl, and (k) 1-naphthyl.

The new conformational analysis for complexes **1** was based on a pseudooctahedral model which took into account the dominant steric properties of the triphenylphosphine ligand. It predicted that for **1** (R = alkyl) three stable conformations exist with the order of stability I ≫ II > III (Figure 1),[3,4] whereas previously it had been deduced that III > I > II.[5-10] In particular the new model predicted that even for complex **1a** (R = Me) only conformer I (R = Me) would be significantly populated. Criticisms of this model[11,12] have been levied on the basis of the observed

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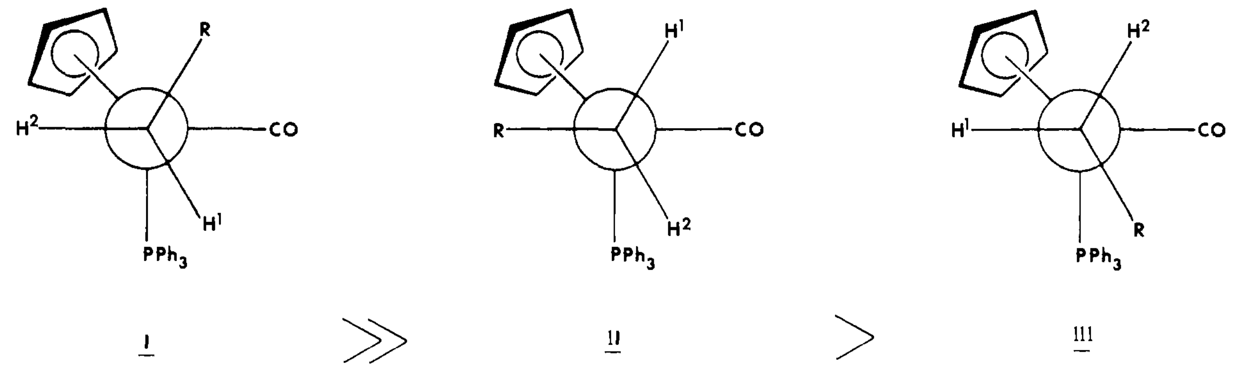
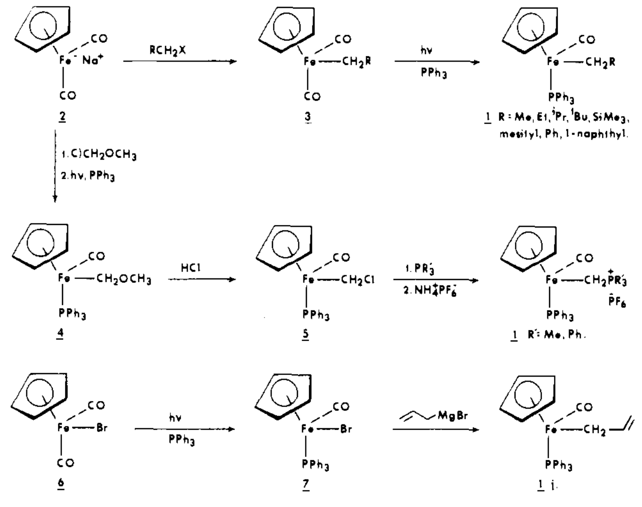


Figure 1. Calculated stable conformations for $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2R$.

Scheme I. Preparation of Complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2R]$ (1a-k)



variations with temperature of the $^3J_{PH}$ coupling constant for **1e** (R = $SiMe_3$) and **1h** (R = Ph)[7,8] which were assumed to indicate the population of several conformations, which must thus be close in energy, for all complexes **1**. Clear support for the new model has been provided by a recently reported NOE difference NMR study on complex **1e** (R = $SiMe_3$) which demonstrated that the lowest energy conformation for **1e** was close to I not III, although this experiment gave no information about the relative energies of other accessible conformations.[12]

Results

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+$ (**2**)[16] with the alkyl halides RCH_2X (R = Me, X = I; R = Et, *i*-Pr, *t*-Bu, Ph, X = Br; R = $SiMe_3$, mesityl, 1-naphthyl, X = Cl) generated complexes **3**. Photolysis of **3** in the presence of triphenylphosphine produced complexes **1a–e**, **1h**, **1i**, and **1k**. Similar alkylation of **2** with chloromethylmethyl ether and photolysis with triphenylphosphine gave **4** which on treatment with HCl gas gave the chloromethyl complex **5**.[17] Addition of trimethyl or triphenylphosphine to **5** produced the complexes **1f** and **1g**, respectively. Finally photolysis of the iron bromide **6** in the presence of triphenylphosphine generated **7**,[18] which on reaction with allylmagnesium bromide gave complex **1j** (Scheme I).[19]

A. $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2Me$ (1a).[20] In the 300 MHz ^1H NMR spectrum of **1a** the diastereotopic methylene protons appeared at δ 1.07 (H^1) and 1.87 (H^2) and exhibited coupling to the methyl protons (*J* = 7.4 Hz), the phosphorus of the triphenylphosphine ($^3J_{PH}$ = 12.1 and 2.0 Hz, respectively) as well

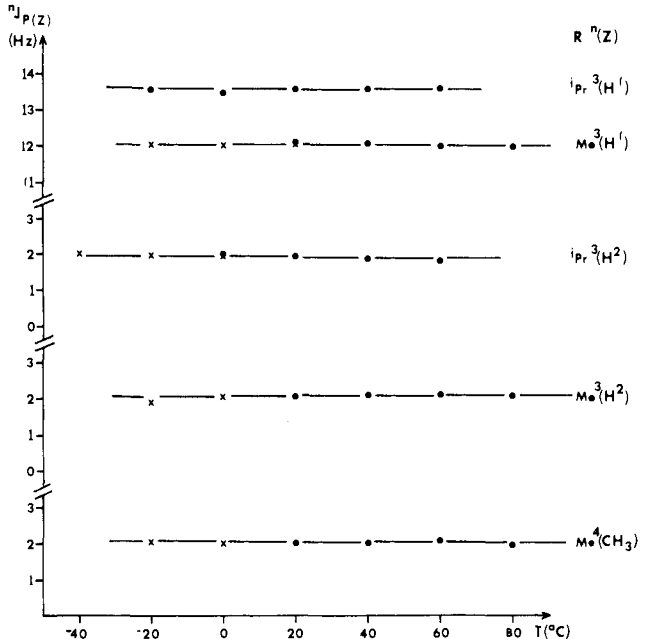


Figure 2. $^3J_{PH}$ and $^4J_{PH}$ vs. temperature for the complexes **1a** (R = Me) and **1c** (R = *i*-Pr): (●) = toluene-d_8 and (×) = dichloromethane-d_2.

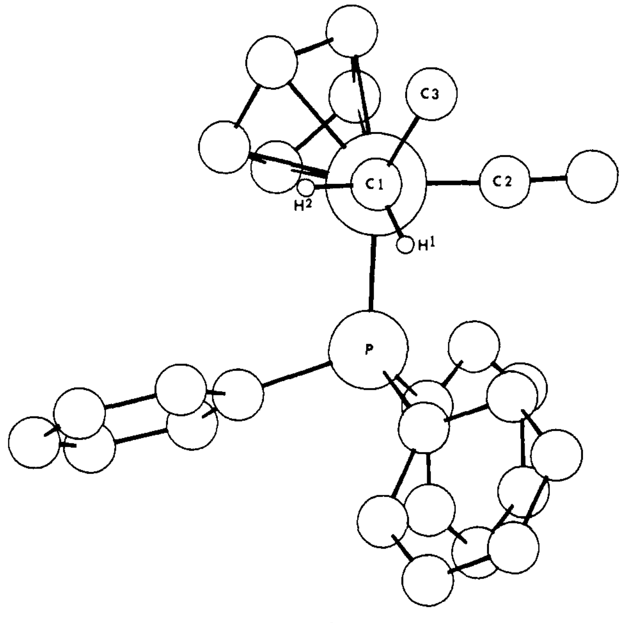


Figure 3. Molecular structure of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2CH_3]$ (**1a**).

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Table I. Final Atomic Positional Coordinates and Equivalent Isotropic Temperature Factors[a]

atom	*x/a*	*y/b*	*z/c*	*U*(iso)
Fe(1)	0.09562 (4)	−0.05926 (3)	−0.14225 (2)	0.0348
P(1)	−0.12252 (8)	−0.08224 (5)	−0.11634 (3)	0.0310
O(1)	0.1762 (3)	−0.2207 (2)	−0.1437 (1)	0.0569
C(1)	0.1709 (4)	−0.0406 (3)	−0.0708 (1)	0.0456
C(2)	0.1430 (3)	−0.1557 (2)	−0.1411 (1)	0.0380
C(3)	0.3275 (4)	−0.0610 (3)	−0.0632 (2)	0.0586
C(4)	0.2183 (5)	0.0407 (3)	−0.1602 (2)	0.0617
C(5)	0.0710 (4)	0.0563 (2)	−0.1685 (2)	0.0553
C(6)	0.0210 (4)	0.0034 (2)	−0.2050 (1)	0.0507
C(7)	0.1344 (4)	−0.0440 (2)	−0.2191 (1)	0.0517
C(8)	0.2573 (4)	−0.0209 (3)	−0.1911 (2)	0.0587
C(9)	−0.1550 (3)	−0.1250 (2)	−0.0544 (1)	0.0341
C(10)	−0.0597 (4)	−0.1800 (2)	−0.0355 (1)	0.0434
C(11)	−0.0837 (4)	−0.2141 (2)	0.0103 (1)	0.0544
C(12)	−0.2038 (5)	−0.1948 (2)	0.0378 (1)	0.0564
C(13)	−0.3000 (4)	−0.1419 (2)	0.0195 (1)	0.0516
C(14)	−0.2762 (4)	−0.1068 (2)	−0.0264 (1)	0.0462
C(15)	−0.2279 (3)	−0.1491 (2)	−0.1555 (1)	0.0337
C(16)	−0.1691 (3)	−0.1823 (2)	−0.1980 (1)	0.0402
C(17)	−0.2456 (4)	−0.2349 (2)	−0.2263 (1)	0.0470
C(18)	−0.3827 (4)	−0.2555 (2)	−0.2126 (1)	0.0501
C(19)	−0.4429 (4)	−0.2232 (2)	−0.1711 (2)	0.0513
C(20)	−0.3676 (3)	−0.1701 (2)	−0.1429 (1)	0.0464
C(21)	−0.2299 (3)	0.0066 (2)	−0.1142 (1)	0.0356
C(22)	−0.2024 (4)	0.0605 (2)	−0.0772 (1)	0.0475
C(23)	−0.2713 (4)	0.1314 (2)	−0.0769 (2)	0.0561
C(24)	−0.3678 (4)	0.1492 (2)	−0.1140 (2)	0.0534
C(25)	−0.3961 (4)	0.0971 (2)	−0.1514 (2)	0.0522
C(26)	−0.3277 (3)	0.0252 (2)	−0.1514 (1)	0.0446
H(1)	0.116 (4)	−0.069 (2)	−0.048 (1)	0.06 (1)
H(2)	0.153 (4)	0.014 (2)	−0.063 (2)	0.07 (1)

[a] esd's are found in parentheses.

Table II. Selected Bond and Torsional Angles for $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2CH_3$ (deg)

C(2)–Fe(1)–C(1)–H(1)	−65	P(1)–Fe(1)–C(1)–H(1)	+29
C(2)–Fe(1)–C(1)–H(2)	−179	P(1)–Fe(1)–C(1)–H(2)	−85
C(2)–Fe(1)–C(1)–C(3)	+57	P(1)–Fe(1)–C(1)–C(3)	+151
C(1)–Fe(1)–P(1)	92.9 (1)	C(2)–Fe(1)–C(1)	92.7 (2)
C(2)–Fe(1)–P(1)	93.4 (1)	Fe(1)–C(1)–C(3)	114.7 (3)

as to each other (J_{AB} = 9.3 Hz). Selective decouplings of the phosphorus and of the methyl group facilitated assignment of these coupling constants. The methyl protons as well as coupling to the two methylene protons (J = 7.5 Hz) exhibited a four bond coupling to phosphorus ($^4J_{PH}$ = 2.1 Hz). Monitoring the $^3J_{PH}$ and $^4J_{PH}$ coupling constants over the temperature range −20 to 80 °C showed (Figure 2), within experimental error, no variation. In differential NOE NMR experiments irradiation of the cyclopentadienyl protons showed enhancements to Me (2%) and H^2 (4%); irradiation of H^2 showed enhancements to the cyclopentadienyl protons (3%) and H^1 (30%); irradiation of H^1 showed enhancement to H^2 (30%).

An X-ray crystal structure analysis of **1a** is shown in Figure 3. Final atomic positional coordinates are listed in Table I, and selected bond lengths and bond angles are given in Table II.

B. $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2Et$ (1b). In the ^1H NMR spectrum of **1b** the diastereotopic α-methylene protons appeared at δ 0.98 (H^1) and 1.78 (H^2) with $^3J_{PH}$ of 11.8 and 2.0 Hz, respectively. Although a phosphorus decoupling experiment allowed unambiguous assignment of these couplings, the complexity of the spin system precluded a variable temperature study.

C. $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2\text{-}i\text{-}Pr$ (1c). The diastereotopic methylene protons appeared in the ^1H NMR spectrum at δ 0.93 (H^1) and 1.89 (H^2) with $^3J_{PH}$ of 13.5 and 2.0 Hz, respectively. These $^3J_{PH}$ coupling constants showed no variation with temperature over the range −40 to 80 °C (Figure 2).

D. $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2\text{-}t\text{-}Bu$ (1d). The diastereotopic methylene protons appeared in the ^1H NMR spectrum at δ 1.24 (H^1) and 2.30 (H^2) with $^3J_{PH}$ couplings of 15.6 and 0 Hz, respectively. These coupling constants remained invariant over the temperature range −40 to 80 °C (Figure 4). In differential NOE NMR experiments irradiation of the cyclopentadienyl protons showed enhancements to H^2 (5%), H^1 (−0.5%); irradiation of H^2 showed enhancements to the cyclopentadienyl protons (4%) and H^1 (26%); irradiation of H^1 showed enhancements to the cyclopentadienyl protons (−0.5%) and H^2 (26%).

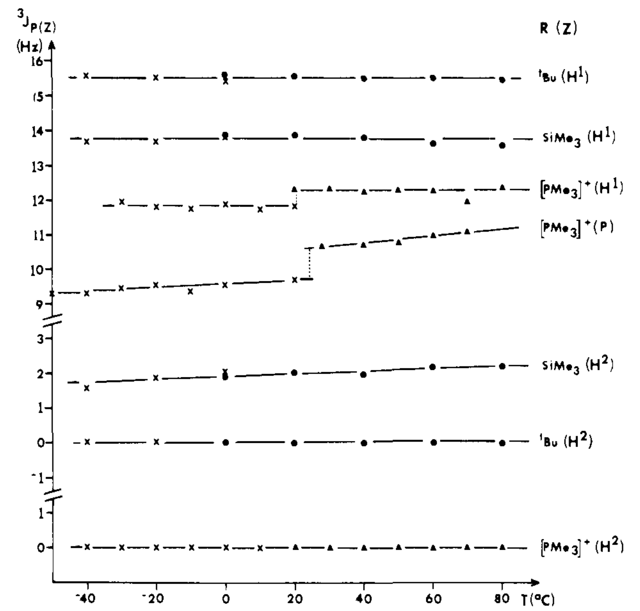

Figure 4. $^3J_{PH}$ and $^3J_{PP}$ vs. temperature for complexes **1d** (R = *t*-Bu), **1e** (R = $SiMe_3$), and **1f** (R = $[PMe_3]^+$): (●) = toluene-d_8, (×) = dichloromethane-d_2, (▲) = dimethyl sulfoxide-d_6.

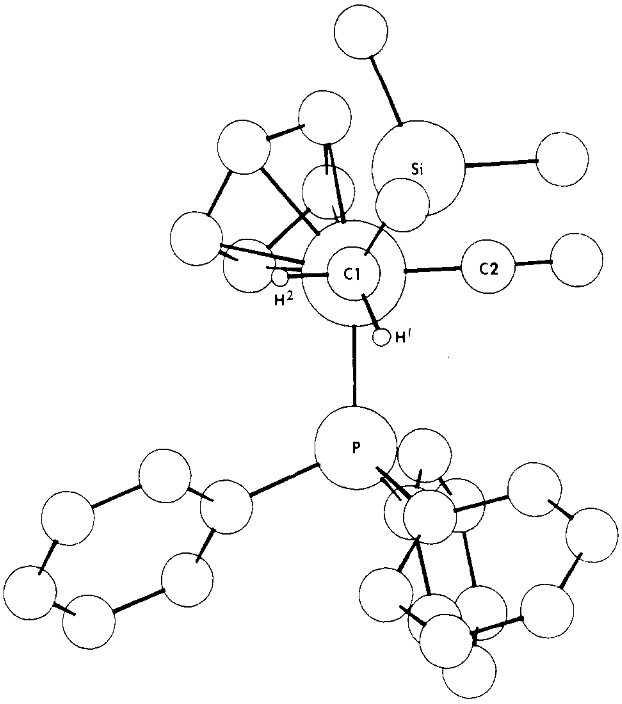

Figure 5. Molecular structure of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2SiMe_3]$ (**1e**).

E. $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2SiMe_3$ (1e). In the 300 MHz ^1H NMR spectrum of **1e** the diastereotopic methylene protons appeared at δ −0.89 (H^1) and −0.01 (H^2) with $^3J_{PH}$ couplings of 13.8 and 1.9 Hz, respectively. The larger coupling constant showed essentially no variation with temperature (Figure 4), whereas the smaller increased slightly with increasing temperature over the range −40 to 80 °C. In differential NOE NMR experiments irradiation of the cyclopentadienyl protons showed enhancements to $SiMe_3$ (2%), H^2 (5%), and H^1 (−0.7%); irradiation of H^2 showed enhancements to the cyclopentadienyl protons (5%) and H^1 (34%);

Table III. Final Atomic Positional Coordinates and Equivalent Isotropic Temperature Factors[a]

atom	x/a	y/b	z/c	U(iso)
Fe(1)	0.34158 (4)	0.31511 (2)	0.37543 (2)	0.0358
P(1)	0.47184 (7)	0.19945 (4)	0.34188 (3)	0.0351
SI(1)	0.3042 (1)	0.32068 (5)	0.53963 (3)	0.0480
O(1)	0.6532 (3)	0.4004 (2)	0.4080 (1)	0.0647
C(1)	0.3058 (4)	0.2584 (2)	0.4642 (1)	0.0428
C(2)	0.5296 (4)	0.3641 (2)	0.3973 (1)	0.0449
C(3)	0.1270 (5)	0.4000 (2)	0.5456 (2)	0.0713
C(4)	0.5063 (5)	0.3787 (3)	0.5564 (2)	0.0736
C(5)	0.2768 (5)	0.2420 (2)	0.6068 (1)	0.0685
C(6)	0.0908 (4)	0.3621 (2)	0.3822 (2)	0.0534
C(7)	0.1994 (4)	0.4296 (2)	0.3687 (2)	0.0552
C(8)	0.2776 (4)	0.4108 (2)	0.3089 (2)	0.0572
C(9)	0.2148 (4)	0.3314 (2)	0.2880 (1)	0.0526
C(10)	0.0987 (4)	0.3006 (2)	0.3335 (1)	0.0531
C(11)	0.6041 (3)	0.1395 (2)	0.3996 (1)	0.0438
C(12)	0.7279 (4)	0.1840 (2)	0.4336 (2)	0.0633
C(13)	0.8247 (5)	0.1433 (3)	0.4798 (2)	0.0762
C(14)	0.8011 (5)	0.0568 (3)	0.4918 (2)	0.0774
C(15)	0.6857 (5)	0.0120 (3)	0.4575 (2)	0.0772
C(16)	0.5850 (4)	0.0525 (2)	0.4111 (2)	0.0628
C(17)	0.3294 (3)	0.1161 (2)	0.3106 (1)	0.0404
C(18)	0.1999 (3)	0.0880 (2)	0.3504 (1)	0.0503
C(19)	0.0898 (4)	0.0247 (2)	0.3306 (2)	0.0595
C(20)	0.1062 (4)	−0.0114 (2)	0.2704 (2)	0.0600
C(21)	0.2299 (4)	0.0166 (2)	0.2305 (2)	0.0593
C(22)	0.3421 (4)	0.0802 (2)	0.2501 (1)	0.0509
C(23)	0.6227 (3)	0.2134 (2)	0.2766 (1)	0.0402
C(24)	0.7350 (4)	0.1486 (2)	0.2609 (1)	0.0534
C(25)	0.8396 (4)	0.1576 (2)	0.2083 (2)	0.0635
C(26)	0.8328 (4)	0.2312 (3)	0.1721 (2)	0.0627
C(27)	0.7246 (4)	0.2961 (2)	0.1880 (2)	0.0629
C(28)	0.6205 (4)	0.2874 (2)	0.2401 (1)	0.0551
H(1)	0.386 (4)	0.215 (2)	0.472 (1)	0.052 (8)
H(2)	0.198 (4)	0.225 (2)	0.462 (1)	0.050 (8)

[a] eds's are found in parentheses.

Table IV. Selected Bond and Torsional Angles for (η^5-C_5H_5)Fe(CO)(PPh_3)$CH_2Si(CH_3)_3$ (deg)

C(2)–Fe(1)–C(1)–H(1)	−69	P(1)–Fe(1)–C(1)–H(1)	+24
C(2)–Fe(1)–C(1)–H(2)	−180	P(1)–Fe(1)–C(1)–H(2)	−87
C(2)–Fe(1)–C(1)–Si(1)	+55	P(1)–Fe(1)–C(1)–Si(1)	+147
C(1)–Fe(1)–P(1)	90.5 (1)	C(2)–Fe(1)–C(1)	94.4 (2)
C(2)–Fe(1)–P(1)	92.1 (1)	Fe(1)–C(1)–Si(1)	122.8 (2)

irradiation of H^1 showed enhancement to H^2 (35%).

An X-ray crystal structure analysis of **1e** is shown in Figure 5. Final atomic positional coordinates are listed in Table III, and selected bond lengths and bond angles are given in Table IV.

F. [(η^5-C_5H_5)Fe(CO)(PPh_3)CH_2PMe_3]$^+$ (1f). The diastereotopic methylene protons appeared at δ −0.48 (H^1) and 1.38 (H^2) and exhibited $^3J_{PH}$ couplings of 11.8 and 0 Hz, respectively. Selective phosphorus decoupling experiments clearly distinguished the $^3J_{PH}$ from the $^2J_{PH}$ couplings. Whilst these couplings showed no variation with temperature, the $^3J_{PH}$ coupling (9.7 Hz at 20 °C) showed a slight change (Figure 4). In differential NOE NMR experiments irradiation of the cyclopentadienyl protons showed enhancements to [PMe_3]$^+$ (3%), H^2 (6%), and H^1 (−1%); irradiation of H^2 showed enhancements to the cyclopentadienyl protons (5%) and H^1 (25%); irradiation of H^1 showed enhancement to the cyclopentadienyl protons (−1%) and H^2 (35%).

G. [(η^5-C_5H_5)Fe(CO)(PPh_3)CH_2PPh_3]$^+$ (1g). The diastereotopic methylene protons appeared at δ 0.72 (H^1) and 2.04 (H^2) and showed $^3J_{PH}$ couplings of 9.7 and 1.9 Hz, respectively. These coupling constants did not vary, within experimental error, with temperature (Figure 6). In contrast however the $^3J_{PP}$ coupling constant (16.3 Hz at 20 °C) did vary significantly with temperature (Figure 6).

H. (η^5-C_5H_5)Fe(CO)(PPh_3)CH_2(mesityl) (1h). The diastereotopic protons for **1h** appeared at δ 1.75 (H^2) and 2.25 (H^1) with $^3J_{PH}$ coupling constants of 1.7 and 12.0 Hz, respectively. These couplings did not vary with temperature, within experimental error (Figure 7). At 60 °C the resonances due to the meta protons and ortho methyl protons appeared as sharp singlets at δ 7.75 and 2.33, respectively. Upon cooling these resonances broadened and eventually each became two singlets of equal intensity ($\Delta\upsilon$ 5.14 and 77.94 Hz, respectively). From the coalescence temperatures for the meta protons and for the methyl protons of 243 and 273 K, respectively, $\Delta G^{\ddagger}$ for rotation about the C_α–C_{ipso} bond was calculated in each case to be 54.2 ± 1.5 kJ mol^{-1} (12.95 ± 0.4 kcal mol^{-1}).[21]

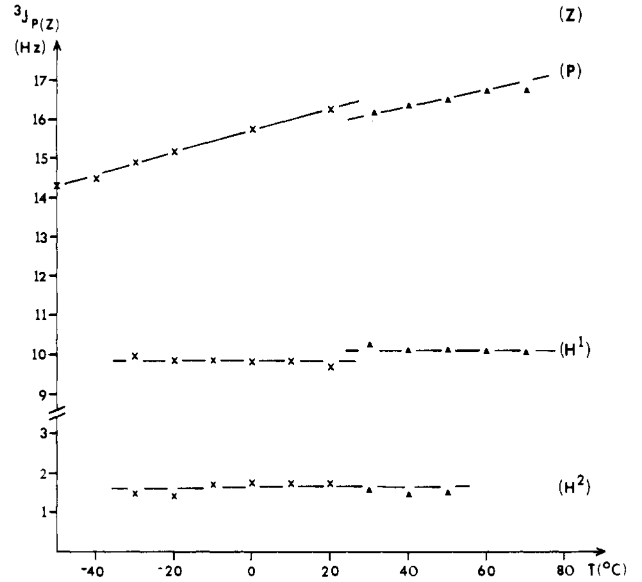

Figure 6. $^3J_{PH}$ and $^3J_{PP}$ vs. temperature for complex **1g** (R = [PPh_3]$^+$): (×) = dichloromethane-d_2 and (▲) = dimethyl sulfoxide-d_6.

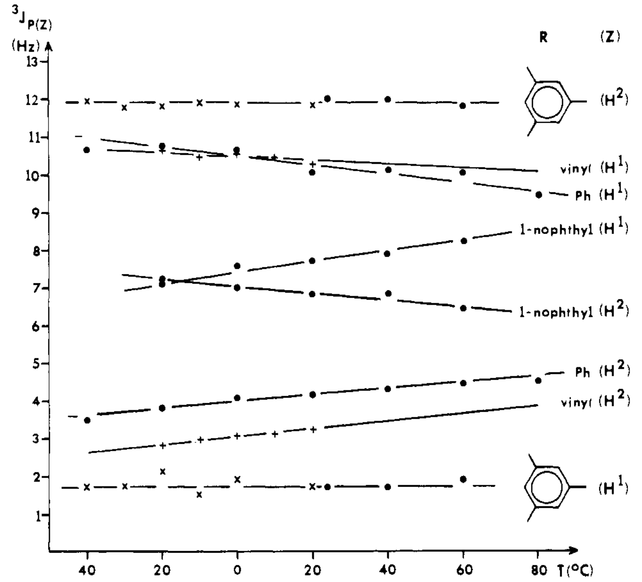

Figure 7. $^3J_{PH}$ vs. temperature for complexes **1h** (R = mesityl), **1i** (R = Ph), **1j** (R = vinyl), and **1k** (R = 1-naphthyl): (●) = toluene-d_8 and (×) and (+) = dichloromethane-d_2.

I. (η^5-C_5H_5)Fe(CO)(PPh_3)CH_2Ph (1i). The diastereotopic methylene protons for **1i** appeared at δ 2.29 (H^1) and 2.79 (H^2) with $^3J_{PH}$ coupling constants at 25 °C of 10.6 and 4.1 Hz, respectively. Both of these couplings varied significantly with temperature (Figure 7).

J. (η^5-C_5H_5)Fe(CO)(PPh_3)CH_2(vinyl) (1j). In the ^1H NMR spectrum of **1j** the diastereotopic α-methylene protons appeared at δ 1.30 (H^1) and 2.04 (H^2) with $^3J_{PH}$ couplings of 11.2 and 3.2 Hz, respectively. In addition allylic coupling ($^4J_{HH}$ = 1.2 Hz)

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(21) Binsch, G. *Top. Stereochem.* **1968**, *3*, 97. Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219.

Table V. Summary of Coupling Constants and Chemical Shifts at 20 °C

		H¹		H²		
no.	R	δ (ppm)	$^3J_{PH}{}^1$ (Hz)	δ (ppm)	$^3J_{PH}{}^2$ (Hz)	$^3J_{PP}$ (Hz)
1a	Me	1.07	12.1	1.87	2.0	
1b	Et	0.98	11.8	1.78	2.0	
1c	*i*-Pr	0.93	13.5	1.89	2.0	
1d	*t*-Bu	1.24	15.6	2.30	0	
1e	$SiMe_3$	−0.89	13.8	−0.01	1.9	
1f	$(PMe_3)^+$	−0.48	11.8	1.38	0	9.7
1g	$(PPh_3)^+$	0.72	9.7	2.04	1.9	16.3
1h	mesityl	1.75	1.7	2.25	12.0	
1i	Ph	2.29	10.6	2.79	4.1	
1j	vinyl	1.30	11.2	2.04	3.2	
1k	1-naphthyl	3.21	7.6	2.57	6.9	

to each of the α-methylene protons is observed. Selective decoupling of the phosphorus facilitated the assignment of coupling constants. Both of the $^3J_{PH}$ couplings varied appreciably with temperature (Figure 7).

K. $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2(1\text{-naphthyl})$ (1k). The ^1H NMR spectrum of **1k** showed the diastereotopic methylene protons at δ 2.57 (H^2) and 3.21 (H^1) with $^3J_{PH}$ couplings at 25 °C of 6.9 and 7.6 Hz, respectively. These coupling constants varied considerably with temperature having values of 7.2 and 7.1 Hz, respectively, at −20 °C and 6.5 and 8.2 Hz, respectively, at 50 °C (Figure 7).

Discussion

If complexes **1** exist in a single conformation which is close to I (Figure 1), then it is to be expected that in the ^1H NMR spectrum H^1 will be shifted upfield relative to H^2 since H^1 is shielded by the proximate phenyl group.[22] Furthermore in accordance with the Karplus equation the $^3J_{PH}$ coupling constant for H^2 will be small (dihedral angle close to 90°), whereas that for H^1 will be large (dihedral angle close to 30°).[23,24] If the single conformation is close to II (Figure 1), then H^2 would experience an upfield shift, and the $^3J_{PH}$ coupling constants would be large for both H^2 and H^1 (dihedral angles ca. 30° and ca. 150°, respectively). On the other hand if the single conformation is best described by III (Figure 1), then similar chemical shifts for H^1 and H^2 might be expected with the $^3J_{PH}$ coupling constant for H^1 being small and H^2 large. If only a single conformation is populated, then essentially no change with temperature in the $^3J_{PH}$ coupling constants to H^2 and H^1 would be observed. In this case it is not to be expected that they will remain completely invariant given the extremely asymmetric nature of the potential energy wells.

If complexes **1** exist in two degenerate (i.e., equally populated) conformations, then the observed values for $^3J_{PH}$ for H^2 and H^1 will be the average of those for H^2 and H^1 in the two individual conformations. Thus for I $\rightleftharpoons$ II H^2 would have a moderate $^3J_{PH}$ coupling constant whereas H^1 would be large; for I $\rightleftharpoons$ III the $^3J_{PH}$ coupling constants to both H^2 and H^1 would be moderate; for II $\rightleftharpoons$ III H^2 would be large, but H^1 would be moderate. For any two degenerate conformations then these $^3J_{PH}$ coupling constants would not vary significantly with temperature. For any two populated nondegenerate conformations then the $^3J_{PH}$ coupling constants would be expected to vary significantly, in fact approaching the values for the degenerate case above at infinite temperature and the values for the most stable conformation at low temperature.

Similar effects would apply if three (or more) conformations were populated.

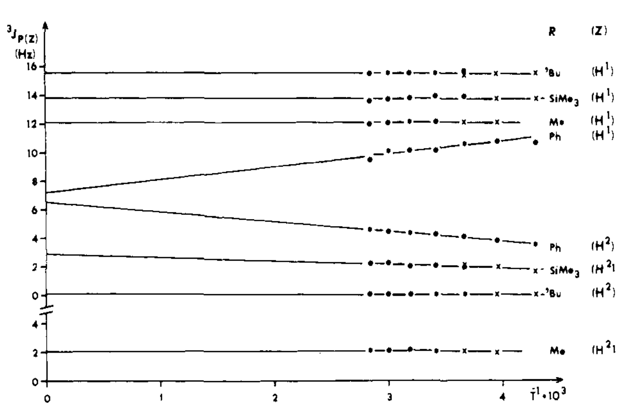

Figure 8. $^3J_{PH}$ vs. temperature^{-1} for complexes **1a** (R = Me), **1d** (R = *t*-Bu), **1e** (R = $SiMe_3$), and **1i** (R = Ph): (●) = toluene-d_8 and (×) = dichloromethane-d_2.

For complex **1a** (R = Me) the chemical shifts and $^3J_{PH}$ coupling constants observed for H^1 and H^2 (Table V) are consistent with conformation I. Of most significance however is the observation of a four bond coupling ($^4J_{PH}$ = 2.1 Hz) between the phosphorus and the methyl protons. Such long range couplings only occur between atoms in a "W" arrangement[25] which in this case is only achieved in conformations close to I. The lack of variation of the $^3J_{PH}$ coupling constants to H^1 and H^2 and the $^4J_{PH}$ coupling constant with temperature (Figure 2) is consistent with only conformation I being populated for complex **1a** (R = Me). The X-ray crystal structure analysis shows that conformation I is also adopted in the solid state.

Similarly the chemical shift and coupling constant data for complexes **1b** (R = Et) and **1c** (R = *i*-Pr) (Table V) together with the lack of variation of $^3J_{PH}$ coupling constants with temperature of **1c** (Figure 2) indicate that these complexes also exist in a single conformation close to I.

For complex **1d** (R = *t*-Bu) the negative NOE enhancement between the cyclopentadienyl protons and H^1 indicates that H^1, H^2, and the circle swept by the cyclopentadienyl protons must subtend an obtuse angle.[12,26] Such a situation only pertains in conformations close to I. The chemical shifts and coupling constants for H^1 and H^2 (Table V) are also consistent with conformation I, and furthermore the lack of variation in $^3J_{PH}$ for H^1 and H^2 (Figure 4) indicates that it is the only conformation populated.

Thus all the experimental evidence so far obtained for complexes **1** (R = alkyl) indicates that only a single stable conformation is populated and that conformation resembles I. This is in complete agreement with our previously calculated analysis for **1a** (R = Me) which predicted I to be by far the most stable conformation. Since all complexes **1** (R = alkyl) adopt approximately the same conformation, it might be expected that in differential NOE NMR experiments irradiation of the cyclopentadienyl protons would result in negative enhancement to H^1 for them all. However, for complexes where there are protons on C3 (e.g., **1a** (R = Me)) negative NOE's are not observed due to alternative relaxation pathways.[26]

Baird et al. have previously reported for complex **1e** (R = $SiMe_3$) that the $^3J_{PH}$ coupling constants to H^1 and H^2 vary with temperature[7,8] and that a negative NOE can be observed between the cyclopentadienyl protons and H^1.[12] We have confirmed the negative NOE result, and, as Baird states, this requires H^1, H^2, and the circle swept by the cyclopentadienyl protons subtend an obtuse angle,[12,26] i.e., the most stable conformation for **1e** must correspond to I. Monitoring the $^3J_{PH}$ coupling constants for **1e**

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(22) Waugh, J. S.; Fessenden, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 846.

(23) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.

(24) Gorenstein, D. G. *Phosphorus-31 NMR, Principles and Applications*; Academic Press: Orlando, 1984. Karplus relationships for $^3J_{PH}$ have been established for a range of phosphorus compounds and in all cases a minimum in the vicinal coupling constant vs. dihedral angle is found at ca. 90° though in some cases the curve is asymmetric about this point.

(25) Meinwald, J.; Meinwald, Y. C. *J. Am. Chem. Soc.* **1963**, *85*, 2514. Robinson, S. D.; Sahajpal, A. *Inorg. Chem.* **1977**, *16*, 2718, 2722. Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 1123. Davies, S. G.; Moon, S. D.; Simpson, S. J.; Thomas, S. E. *J. Chem. Soc., Dalton Trans.* **1983**, 1805.

(26) (a) Noggle, J. H.; Schirmer, R. E. *The Nuclear Overhauser Effect*; Academic Press: New York, 1971. (b) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon Press: Oxford, 1987.

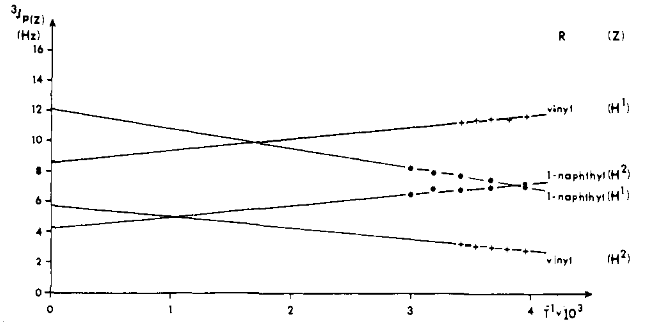


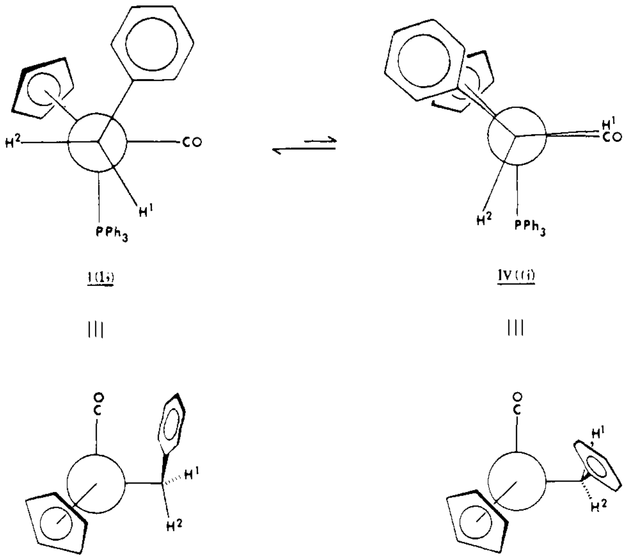
Figure 9. $^3J_{PH}$ vs. temperature^{-1} for complexes **1j** (R = vinyl) and **1k** (R = 1-naphthyl): (●) = toluene-d_8 and (+) = dichloromethane-d_2.

against temperature (Figure 4) we find little if any variation for H^1 and a slight variation for H^2. If this slight variation was due to the population of several stable conformations, as asserted by Baird in his criticism of our model,[11,12] then at high temperature for I ⇌ II $^3J_{PH}$ for H^1 would remain fairly constant but for H^2 would tend toward 8 Hz [(13.8 + 1.9) ÷ 2], whereas I ⇌ II ⇌ III both $^3J_{PH}$ for H^1 and H^2 should tend toward 10 Hz [((13.8 × 2) + 1.9) ÷ 3]. In order to provide a rough indication of the actual trend Figure 8 shows the extrapolation of the coupling constants to $T^{-1} = 0$ (i.e., infinite temperature when all equilibrating conformations should be equally populated). Figure 8 clearly shows that at $T^{-1} = 0$ $^3J_{PH}$ for H^2 is little changed. A much more reasonable explanation for the slight change in $^3J_{PH}$ for H^2 is that it is a result of the extremely asymmetric nature of the energy well corresponding to the single stable conformation I due to rotation of the $SiMe_3$ group toward the CO being extremely disfavorable. The effective size of a $SiMe_3$ group is much larger than that of a *t*-Bu group, and hence the asymmetry of the potential energy well would be more pronounced for the former. The X-ray crystal structure analysis (Figure 5) shows that conformation I is adopted in the solid state for **1e** (R = $SiMe_3$).

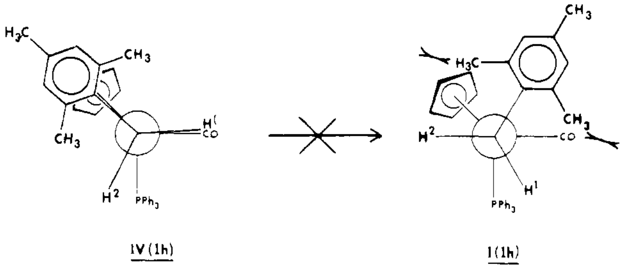
For the cationic complexes **1f** (R = $[PMe_3]^+$) and **1g** (R = $[PPh_3]^+$) the $^3J_{PH}$ coupling constants for H^1 and H^2 do not vary significantly with temperature whereas the $^3J_{PP}$ coupling constants do. For **1f** the negative NOE observed between the cyclopentadienyl protons and H^1 again indicates conformation I is the most stable. From the invariance of the $^3J_{PH}$ coupling constants we again conclude that only conformation I is populated with the variation in $^3J_{PP}$ coupling constants arising from changing the Fe–C_α–P angle with temperature. The X-ray crystal structure data for **1e** (Figure 5) indicate that the large $SiMe_3$ group is only accommodated by distorting the Fe–C_α–Si angle. The same would be true for the large $[PMe_3]^+$ and $[PPh_3]^+$, and this distortion would be expected to be aggravated by increasing temperature. Any change in the Fe–C_α–P angle would alter the $^3J_{PP}$ coupling constants but not the $^3J_{PH}$.[24] As can be seen in Figures 4 and 6, for the cationic complexes **1f** and **1g** changing the solvent from CD_2Cl_2 to DMSO-d_6 causes a small change in the magnitude of the $^3J_{PP}$ and $^3J_{PH}$ coupling constants. For the neutral complexes changing the solvent essentially has no effect. The change for the cations is presumably due to a small change in conformation of the PF_6^- salts with solvation.

In contrast to the complexes **1a–g** discussed above, for complexes **1i** (R = Ph), **1j** (R = vinyl), and **1k** (R = 1-naphthyl) significant variations in $^3J_{PH}$ coupling constants for both H^1 and H^2 with temperature are observed (Figure 7). This is in agreement with the earlier reports by Baird for complexes **1i** and **1k**.[7,8]

For complex **1i** (R = Ph) extrapolating the variable temperature data to infinite temperature ($T^{-1} = 0$, Figure 8) in order to get a rough estimate of the limiting value for these $^3J_{PH}$ shows that the $^3J_{PH}$ coupling constants for both H^1 and H^2 are approaching 7 Hz. This is consistent only with the two conformations I and IV being populated for **1i**. Furthermore the relative populations of I and IV at 20 °C can be estimated as approximately 75:25 which corresponds to an energy difference of ca. 2.5–3 kcal mol^{-1}. This value is in good agreement with the previously calculated value for this complex (ca. 5 kcal mol^{-1}). The planar nature of the phenyl group in **1i** allows it to eclipse the cyclopentadienyl group without producing any severe steric interactions; this is not the case (see above) for nonplanar R groups in complexes **1a–g**. Furthermore it is to be expected that the most favorable orientation of the phenyl ring in conformation IV will be with the phenyl ring orthogonal to the iron–cyclopentadienyl centroid axis. Such an optimized orientation was not considered in the original extended Huckel calculations but would reduce the calculated energy difference still closer to the observed one.

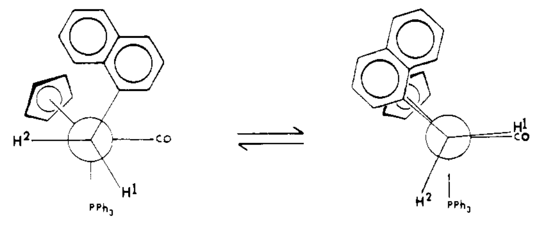


For complex **1h** (R = mesityl) calculations and examination of molecular models indicate that only conformation IV will be populated.[4] Consistent with this, the α-proton with the small $^3J_{PH}$ is upfield with respect to the α-proton with the large $^3J_{PH}$ (Table V) and no variation with temperature of these $^3J_{PH}$ coupling constants is observed (Figure 7). The preferred conformation IV for complex **1h** has the planar aromatic ring eclipsing the cyclopentadienyl ligand while at the same time places the two bulky ortho methyl groups in the most favorable positions, i.e., in the spaces between the cyclopentadienyl and the CO and PPh_3 ligands. Conformation I is unattainable for complex **1h** since it would result in severe steric interactions between the ortho methyl groups and the cyclopentadienyl and CO ligands. Rotation about the C_α–C_{ipso} bond would be expected to be very hindered as observed ($\Delta G^\ddagger$ = 12.95 kcal mol^{-1}). It did not prove possible to obtain a single crystal of **1h** of sufficient quality for X-ray analysis and so obtain confirmation that conformation IV is adopted in the solid state.



Predictably the variations in the two $^3J_{PH}$ coupling constants for complex **1j** (R = vinyl) parallel those for the R = phenyl case (Figure 7). Both $^3J_{PH}$ coupling constants tend toward 7 Hz at infinite temperature (Figure 9), and again the calculated populations for conformations I and IV at 20 °C are 75:25, respectively.

The variation of the two $^3J_{PH}$ coupling constants for complex **1k** (R = 1-naphthyl) with T^{-1} is shown in Figure 9. Extrapolation to $T^{-1} = 0$ indicates that one $^3J_{PH}$ tends toward a large value with increasing temperature while the other tends to a small value. The most reasonable explanation for this phenomenon is that two conformations are populated at room temperature, one of which becomes increasingly more favored relative to the other at higher temperatures. This unusual situation can arise when for two



I(1k) IV(1k)

conformations where ΔH° is small but ΔS° is large thus resulting at high temperatures in $T\Delta S^\circ$ becoming dominant in determining ΔG° ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$). The data obtained for complex **1k** are consistent with conformations I and IV being populated at room temperature. Molecular models indicate that rotation about the C_α–C_{ipso} bond is severely restricted in conformation IV but not in conformation I and suggest therefore that the latter will be favored at high temperatures.

Conclusions

The pseudooctahedral complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\text{-}CH_2R$, where R is nonplanar, generally exist in the single conformation which places the R group between the cyclopentadienyl and the CO ligands (conformation I). For complexes where R is planar (e.g., phenyl, vinyl) conformation I is still favored, but a second conformation (IV) with R essentially eclipsing the cyclopentadienyl is also significantly populated. These conformational features should also be manifest in analogous complexes of other transition metals such as $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\text{-}CH_2R$.[15,27] Indeed, coupling constant data are available for four rhenium complexes of the type $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)CH_2R]$ (**8**)[27] and correlate well with the corresponding data for the iron complexes **1** (Table VI). Furthermore, in the solid state the rhenium benzyl complex **8** (R = Ph) adopts conformation I.[27a] For complex **8** (R = mesityl) the reported variations in $^3J_{PH}$ coupling constants with temperature[27d] resemble those observed for **1i** (R = Ph) and suggest that the rhenium complexes are more conformationally flexible than the iron complexes. This is also reflected in the lower barrier to rotation about the C_α–C_{ipso} bond for **8** (R = mesityl), 12.0 kcal mol^{-1}, compared to **1h** (R = mesityl), 12.95 kcal mol^{-1}.

Experimental Section

General Remarks. All reactions and purifications were performed under a nitrogen atmosphere with use of standard vacuum line and Schlenk tube techniques.[28] Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled. Dichloromethane was distilled from calcium hydride. Infrared spectra were recorded in CH_2Cl_2 on a Perkin-Elmer 297 instrument. Proton NMR spectra were recorded on a Bruker WH 300 spectrometer at 300.13 MHz and referenced to residual protio-solvent, with chemical shifts being reported as δ ppm from $(CH_3)_4Si$. Proton differential NOE NMR experiments were conducted on a Bruker AM 500 spectrometer at 500.13 MHz (with presaturation greater than 5 × longest T_1) by using benzene-d_6 as solvent and internal standard. Carbon-13 NMR spectra were recorded on a Bruker AM 250 spectrometer at 62.90 MHz by using CD_2Cl_2 as solvent and internal standard and are reported as δ ppm from $(CH_3)_4Si$. Phosphorus-31 NMR spectra were recorded on a Bruker AM 250 spectrometer at 101.26 MHz and are reported as δ ppm from an external reference of trimethyl phosphate in D_2O. Mass spectra were recorded on a V.G. micromass ZAB 2F instrument with use of FD and FAB techniques. Elemental analyses were performed by the Dyson Perrins Laboratory Analytical Service (Oxford, U.K.).

Table VI. Comparison of Three Bond Coupling Constants (Hz)

	$(\eta^5\text{-}C_5H_5)Fe(CO)\text{-}(PPh_3)CH_2R$		$(\eta^5\text{-}C_5H_5)Re(NO)\text{-}(PPh_3)CH_2R$	
R	$^3J_{PH}{}^1$	$^3J_{PH}{}^2$	$^3J_{PH}{}^1$	$^3J_{PH}{}^2$
t-Bu	15.6	0	12.8	0[27c]
PAr_3	16.3 ($^3J_{PP}$, Ar = Ph)		17.9 ($^3J_{PP}$, Ar = *p*-MeC_6H_4)[27g]	
Ph	10.6	4.1	8.0	3.0[27b]
mesityl	1.7	12.0	1.5	8.9[27d]

General Procedure for Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CH_2R)$ (1a–e and 1h–j) (R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$, $Si(CH_3)_3$, Mesityl, Ph, 1-Naphthyl). Over a period of 15 min, a solution of alkyl halide (RCH_2X) (R = Me, X = I; R = Et, *i*-Pr, *t*-Bu, Ph, X = Br; R = $SiMe_3$, mesityl, 1-naphthyl, X = Cl) (45.0 mmol) in THF (10 mL) was added to a stirred solution of $[(\eta^5\text{-}C_5H_5)Fe(CO_2)]^-Na^+$ (**2**) (prepared from 8.00 g (22.6 mmol) of cyclopentadienyldicarbonyliron dimer[16a] by a standard procedure[16b]) in THF (100 mL) at 0 °C. After having been stirred at ambient temperature overnight, the solvent was removed under reduced pressure. The residue was taken up in dichloromethane and filtered through Celite, and the solvent was removed. Chromatography of the oil on alumina (grade I) upon elution with 0–50% ether–40/60 petroleum ether gave $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2R)$ as either an amber colored oil or crystalline solid in 18–94% yield. $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}(CH_2R)$ (10.0 mmol) and triphenylphosphine (3.90 g, 15.0 mmol) were dissolved in dichloromethane (120 mL) and irradiated in a quartz immersion apparatus by using a Hanovia 125-W medium-pressure mercury arc lamp. The reaction was monitored by IR (disappearance of carbonyl stretches at 2020 and 1970 cm^{-1} relative to the emergence of carbonyl stretch at 1900 cm^{-1}), and irradiation stopped after 4–6 h. The solvent was removed, and the residue was treated with chloroform (10 mL) for 15 min, in order to convert byproduct $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H)$ to the more readily separable $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(Cl)$.[29] Removal of solvent and chromatography on alumina (grade I) upon elution with 0–50% ether–40/60 petroleum ether followed by recrystallization from either dichloromethane–40/60 petroleum ether or acetone–water gave $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CH_2R)$ as a red crystalline solid in 36–90% yield (14–80% overall yield from cyclopentadienyldicarbonyliron dimer).

$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2Me$ (1a):[29] red crystalline solid (20%); IR ν (C≡O) 1900 cm^{-1}; ^1H NMR (C_6D_6, 297 K) δ 7.57–6.94 (15 H, m, Ph), 4.13 (5 H, d, $^3J_{PH}$ = 1.1 Hz, C_5H_5), 1.87 (1 H, ddq, $^3J_{PH}$ = 2.0 Hz, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 7.4 Hz, $FeCH^2$), 1.58 (3 H, dt, $^4J_{PH}$ = 2.1 Hz, $^3J_{HH}$ = 7.5 Hz, CH_3), 1.07 (1 H, ddq, $^3J_{PH}$ = 12.1 Hz, $^2J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 7.4 Hz, $FeCH^1$); $^{13}C\{^1H\}$ NMR δ 223.71 (d, $^2J_{PC}$ = 32.7 Hz, C≡O), 137.54 (d, $^1J_{PC}$ = 39.2 Hz, Ph C_{ipso}), 133.57 (d, $^2J_{PC}$ = 9.6 Hz, Ph C_{ortho}), 129.73 (s, Ph C_{para}), 128.36 (d, $^3J_{PC}$ = 9.1 Hz, Ph C_{meta}), 85.18 (s, C_5H_5), 23.19 (d, $^3J_{PC}$ = 3.7 Hz, CH_3), −2.45 (d, $^2J_{PC}$ = 18.6 Hz, CH_2); $^{31}P\{^1H\}$ NMR δ 81.4; MS, *m/z* 440 (M^+). Anal. Calcd for $C_{26}H_{25}FeOP$: C, 70.93; H, 5.72. Found: C, 71.29; H, 5.78%.

$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2Et$ (1b):[29] deep red crystalline solid (69%); IR ν (C≡O) 1905 cm^{-1}; ^1H NMR (C_6D_6, 297 K) δ 7.60–6.93 (15 H, m, Ph), 4.13 (5 H, d, $^3J_{PH}$ = 1.0 Hz, C_5H_5), 1.92 (1 H, m, $CHCH_3$), 1.78 (1 H, ddt, $^3J_{PH}$ = 2.0 Hz, $^2J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 6.7 Hz, $FeCH^2$), 1.65 (1 H, m, $CHCH_3$), 1.14 (3 H, t, $^3J_{HH}$ = 7.0 Hz, CH_3), 0.98 (1 H, ddt, $^3J_{PH}$ = 11.8 Hz, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 7.5 Hz, $FeCH^1$); $^{13}C\{^1H\}$ NMR δ 223.79 (d, $^2J_{PC}$ = 33.4 Hz, C≡O), 137.56 (d, $^1J_{PC}$ = 38.7 Hz, Ph C_{ipso}), 133.60 (d, $^2J_{PC}$ = 9.4 Hz, Ph C_{ortho}), 129.73 (s, Ph C_{para}), 128.34 (d, $^3J_{PC}$ = 10.0 Hz, Ph C_{meta}), 85.10 (s, C_5H_5), 32.75 (d, $^3J_{PC}$ = 3.5 Hz, CH_2CH_3), 20.12 (s, CH_3), 7.81 (d, $^2J_{PC}$ = 18.7 Hz, $FeCH_2$); $^{31}P\{^1H\}$ NMR δ 81.4; MS, *m/z* 454 (M^+). Anal. Calcd for $C_{27}H_{27}FeOP$: C, 71.38; H, 5.99. Found: C, 71.66; H, 5.94.

$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2\text{-}i\text{-}Pr$ (1c):[30] deep red crystalline solid (26%); IR ν (C≡O) 1895 cm^{-1}; ^1H NMR (C_6D_6, 297 K) δ 7.56–6.96 (15 H, m, Ph), 4.17 (5 H, d, $^3J_{PH}$ = 1.1 Hz, C_5H_5), 1.89 (1 H, ddd, $^3J_{PH}$ = 2.0 Hz, $^2J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 5.9 Hz, $FeCH^2$), 1.81 (1 H, m, $CHMe_2$), 1.23 (3 H, d, $^3J_{HH}$ = 6.4 Hz, CH_3), 1.18 (3 H, d, $^3J_{HH}$ = 6.4 Hz, CH_3), 0.93 (1 H, ddd, $^3J_{PH}$ = 13.5 Hz, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 6.4 Hz, $FeCH^1$); $^{13}C\{^1H\}$ NMR δ 224.32 (d, $^2J_{PC}$ = 34.5 Hz, C≡O), 137.40 (d, $^1J_{PC}$ = 39.8 Hz, Ph C_{ipso}), 133.65 (d, $^2J_{PC}$ = 9.3 Hz, Ph C_{ortho}), 129.80 (s, Ph C_{para}), 128.36 (d, $^3J_{PC}$ = 9.2 Hz, Ph C_{meta}), 85.18 (s, C_5H_5), 36.49 (s, $CHMe_2$), 27.31 (s, CH_3), 26.51 (s, CH_3), 14.31 (d, $^2J_{PC}$ = 18.4 Hz, $FeCH_2$); $^{31}P\{^1H\}$ NMR δ 81.0; MS, *m/z* 468 (M^+). Anal. Calcd for $C_{28}H_{29}FeOP$: C, 71.81; H, 6.24. Found: C, 71.87; H, 6.30.

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(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)CH$_2$-*t*-Bu (1d): dark red crystalline solid (14%); IR ν (C$\equiv$O) 1895 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 297 K) δ 7.60–6.95 (15 H, m, Ph), 4.22 (5 H, d, $^3J_{PH}$ = 1.2 Hz, C$_5$H$_5$), 2.30 (1 H, dd, $^3J_{PH}$ = OHz, $^2J_{HH}$ = 9.8 Hz, FeCH^2), 1.24 (1 H, dd, $^3J_{PH}$ = 15.6 Hz, $^2J_{HH}$ = 9.8 Hz, FeCH^1), 1.16 (9 H, s, C(CH$_3$)$_3$); ^{13}C{^{1}H} NMR δ 225.11 (d, $^2J_{PC}$ = 34.4 Hz, C$\equiv$O), 137.48 (d, $^1J_{PC}$ = 39.7 Hz, Ph C$_{ipso}$), 133.74 (d, $^2J_{PC}$ = 9.1 Hz, Ph C$_{ortho}$), 129.80 (s, Ph C$_{para}$), 128.33 (d, $^3J_{PC}$ = 9.0 Hz, Ph C$_{meta}$), 85.17 (s, C$_5$H$_5$), 36.77 (s, *C*(CH$_3$)$_3$), 33.92 (s, C(*C*H$_3$)$_3$), 18.89 (d, $^2J_{PC}$ = 17.6 Hz, CH$_2$); ^{31}P{^{1}H} NMR δ 80.7; MS, *m/z* 482 (M$^+$). Anal. Calcd for C$_{29}$H$_{31}$FeOP: C, 72.21; H, 6.48. Found: C, 72.28; H, 6.48.

(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)CH$_2$SiMe$_3$ (1e):[31] dark red blocks (46%); IR ν (C$\equiv$O) 1905 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 297 K) δ 7.58–6.95 (15 H, m, Ph), 4.15 (5 H, d, $^3J_{PH}$ = 1.0 Hz, C$_5$H$_5$), 0.31 (9 H, s, Si(CH$_3$)$_3$), –0.01 (1 H, dd, $^3J_{PH}$ = 1.9 Hz, $^2J_{HH}$ = 11.8 Hz, FeCH^2), –0.89 (1 H, dd, $^3J_{PH}$ = 13.8 Hz, $^2J_{HH}$ = 11.8 Hz, FeCH^1); ^{13}C{^{1}H} NMR δ 223.78 (d, $^2J_{PC}$ = 34.7 Hz, C$\equiv$O), 137.39 (d, $^1J_{PC}$ = 40.3 Hz, Ph C$_{ipso}$), 133.63 (d, $^2J_{PC}$ = 8.8 Hz, Ph C$_{ortho}$), 129.90 (s, Ph C$_{para}$), 128.42 (d, $^3J_{PC}$ = 8.2 Hz, Ph C$_{meta}$), 84.83 (s, C$_5$H$_5$), 2.74 (s, Si(CH$_3$)$_3$), –22.75 (d, $^2J_{PC}$ = 15.9 Hz, FeCH$_2$); ^{31}P{^{1}H} NMR δ 80.3; MS, *m/z* 498 (M$^+$). Anal. Calcd for C$_{28}$H$_{31}$FeOPSI: C, 67.47; H, 6.27. Found: C, 67.50; H, 6.50.

(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)CH$_2$(mesityl) (1h): red plates (86%); IR ν (C$\equiv$O) 1905 cm^{-1}; ^{1}H NMR (C$_7$D$_8$, 297 K) δ 7.60–6.97 (15 H, m, Ph), 6.78 (2 H, s, meta H), 3.85 (5 H, d, $^3J_{PH}$ = 0.9 Hz, C$_5$H$_5$), 2.37 (6 H, br s, ortho CH$_3$), 2.25 (1 H, dd, $^3J_{PH}$ = 12.0 Hz, $^2J_{HH}$ = 8.9 Hz, FeCH^2), 2.19 (3 H, s, meta CH$_3$), 1.75 (1 H, dd, $^3J_{PH}$ = 1.7 Hz, $^2J_{HH}$ = 8.7 Hz, FeCH^1); ^{13}C{^{1}H} NMR δ 224.42 (d, $^2J_{PC}$ = 35.1 Hz, C$\equiv$O), 151.57 (d, $^3J_{PC}$ = 3.5 Hz, mesityl C$_{ipso}$), 136.54 (d, $^1J_{PC}$ = 39.5 Hz, Ph C$_{ipso}$), 133.93 (s, mesityl C$_{ortho}$), 133.66 (d, $^2J_{PC}$ = 9.5 Hz, Ph C$_{ortho}$) 130.53 (s, mesityl C$_{para}$), 128.81 (s, mesityl C$_{meta}$), 128.53 (d, $^3J_{PC}$ = 9.6 Hz, Ph C$_{meta}$), 85.00 (s, C$_5$H$_5$), 21.49 (s, ortho CH$_3$), 20.90 (s, para CH$_3$), –3.34 (d, $^3J_{PC}$ = 15.3 Hz, FeCH$_2$); ^{31}P{^{1}H} NMR δ 77.33; MS, *m/z* 544 (M$^+$). Anal. Calcd for C$_{34}$H$_{33}$FeOP: C, 75.01; H, 6.11. Found: C, 75.09; H, 6.16.

(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)CH$_2$Ph (1i):[29] light red plates (14%); IR ν (C$\equiv$O) 1905 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 297 K), δ 7.63–6.97 (20 H, m, Ph), 4.04 (5 H, d, $^3J_{PH}$ = 0.9 Hz, C$_5$H$_5$), 2.79 (1 H, dd, $^3J_{PH}$ = 4.1 Hz, $^2J_{HH}$ = 8.2 Hz, FeCH^2), 2.29 (1 H, dd, $^3J_{PH}$ = 10.6 Hz, $^2J_{HH}$ = 8.2 Hz, FeCH^1); ^{13}C{^{1}H} NMR δ 223.53 (d, $^2J_{PC}$ = 32.9 Hz, C$\equiv$O), 158.05 (d, $^3J_{PC}$ = 3.6 Hz, Ph′ C$_{ipso}$), 136.91 (d, $^1J_{PC}$ = 40.3 Hz, Ph C$_{ipso}$), 133.70 (d, $^2J_{PC}$ = 10.1 Hz, Ph C$_{ortho}$), 130.01 (s, Ph C$_{para}$), 128.54 (d, $^3J_{PC}$ = 9.3 Hz, Ph C$_{meta}$), 127.88 (s), 127.32 (s) (Ph′ C$_{ortho}$ and C$_{meta}$), 121.85 (s, Ph′ C$_{para}$), 85.53 (s, C$_5$H$_5$), 6.79 (d, $^2J_{PC}$ = 16.4 Hz, FeCH$_2$); ^{31}P{^{1}H} NMR δ 79.1; MS, *m/z* 502 (M$^+$). Anal. Calcd for C$_{31}$H$_{27}$FeOP: C, 74.12; H, 5.42. Found: C, 73.75; H, 5.54.

(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)CH$_2$(1-naphthyl) (1k): red plates (34%); IR ν (C$\equiv$O) 1910 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 297 K) δ 8.37–6.98 (22 H, m, Ph and C$_{10}$H$_7$), 3.93 (5 H, d, $^3J_{PH}$ = 1.2 Hz, C$_5$H$_5$), 3.21 (1 H, dd, $^3J_{PH}$ = 7.6 Hz, $^2J_{HH}$ = 8.6 Hz, FeCH^1), 2.57 (1 H, dd, $^3J_{PH}$ = 6.9 Hz, $^2J_{HH}$ = 8.7 Hz, FeCH^2); ^{13}C{^{1}H} NMR δ 223.62 (d, $^2J_{PC}$ = 32.7 Hz, C$\equiv$O), 155.57 (d, $^3J_{PC}$ = 3.5 Hz, naphthyl C-1), 136.63 (d, $^1J_{PC}$ = 39.5 Hz, Ph C$_{ipso}$), 134.58 (s, naphthyl C), 133.78 (d, $^2J_{PC}$ = 9.6 Hz, Ph C$_{ortho}$), 131.64 (s, naphthyl C), 130.15 (s, Ph C$_{para}$), 128.75 (s, naphthyl C), 128.61 (d, $^3J_{PC}$ = 9.3 Hz, Ph C$_{meta}$), 126.03 (s), 125.90 (s), 125.18 (s), 124.49 (s), 124.17 (s), 122.32 (s) (naphthyl C's), 85.24 (s, C$_5$H$_5$), 1.37 (d, $^2J_{PC}$ = 15.6 Hz, FeCH$_2$); ^{31}P{^{1}H} NMR δ 77.5; MS, *m/z* 552 (M$^+$). Anal. Calcd for C$_{35}$H$_{29}$FeOP: C, 76.10; H, 5.29. Found: C, 76.35; H, 5.32.

Preparation of [(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)(CH$_2$PMe$_3$$^+$)]PF$_6$$^-$ (1f). A solution of trimethylphosphine (0.091 g, 1.2 mmol) in dichloromethane (2 mL) was added over 10 min to a stirred solution of (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)(CH$_2$Cl)[17] (0.500 g, 1.1 mmol) in dichloromethane (30 mL) at 0 °C. The color of the solution changed from orange to red. The mixture was stirred for 15 min at 0 °C, and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (5 mL) and transfered to the top of a column of alumina (grade V). Elution with ether gave a faint orange fraction, which was discarded; the intense red band remaining at the top of the column. Elution with a solution of ammonium hexafluorophosphate (1 g) in acetone (30 mL) followed by dichloromethane gave after crystallization from dichloromethane–40/60 petroleum ether [(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)(CH$_2$PMe$_3$$^+$)]PF$_6$$^-$ (0.690 g, 98% yield) as a red crystalline solid: IR ν (C$\equiv$O) 1920 cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, 297 K) δ 7.53–7.32 (15 H, m, Ph), 4.52 (5 H, d, $^3J_{PH}$ = 1.4 Hz, C$_5$H$_5$), 1.44 (9 H, d, $^2J_{PH}$ = 12.8 Hz, P(CH$_3$)$_3$), 1.38 (1 H, ddd, $^3J_{PH}$ = 0 Hz, $^2J_{PH}$ = 13.2 Hz, $^2J_{HH}$ = 13.2 Hz, FeCH^2), –0.48 (1 H, ddd, $^3J_{PH}$ = 11.8 Hz, $^2J_{PH}$ = 15.4 Hz, $^2J_{HH}$ = 13.0 Hz, FeCH^1); ^{13}C{^{1}H} NMR δ 222.65 (dd, $^3J_{PC}$ = 6.3 Hz, $^2J_{PC}$ = 32.5 Hz, C$\equiv$O), 134.62 (d, $^1J_{PC}$ = 43.4 Hz, Ph C$_{ipso}$), 133.58 (d, $^2J_{PC}$ = 8.8 Hz, Ph C$_{ortho}$), 131.06 (s, Ph C$_{para}$), 129.13 (d, $^3J_{PC}$ = 9.8 Hz, Ph C$_{meta}$), 84.89 (s, C$_5$H$_5$), 13.26 (d, $^1J_{PC}$ = 54.8 Hz, P(CH$_3$)$_3$), –17.01 (dd, $^2J_{PC}$ = 17.1 Hz, $^3J_{PC}$ = 34.6 Hz, FeCH$_2$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K) δ 74.5 (d, $^3J_{PP}$ = 9.7 Hz, PPh$_3$), 34.7 (d, $^3J_{PP}$ = 9.7 Hz, PMe$_3$$^+$), –147.2 (septet, $^1J_{FP}$ = 711.5 Hz, PF$_6$$^-$); MS, *m/z* 501 (M$^+$ for cation). Anal. Calcd for C$_{28}$H$_{31}$F$_6$FeOP$_3$: C, 52.04; H. 4.83. Found: C, 52.09; H, 4.87.

Preparation of [(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)(CH$_2$PPh$_3$$^+$)]PF$_6$ (1g).[32] In a similar manner to that described for the preparation of [(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)(CH$_2$PMe$_3$$^+$)]PF$_6$$^-$, triphenylphosphine (2.80 g, 11.0 mmol) was reacted with (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)(CH$_2$Cl)[4] (0.490 g, 1.1 mmol) in dichloromethane at ambient temperature for 48 h. Chromatography over alumina (grade V) on elution with ether removed excess phosphine. Treatment with a solution of ammonium hexafluorophosphate (1 g) in acetone (30 mL) and elution with dichloromethane gave after crystallization from acetone–40/60 petroleum ether [(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)(CH$_2$PPh$_3$$^+$)]PF$_6$$^-$ as a red crystalline solid (0.74 g, 78% yield): IR ν (C$\equiv$O) 1935 cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, 297 K) δ 7.73–7.32 (30 H, m, Ph), 4.04 (5 H, d, $^3J_{PH}$ = 1.5 Hz, C$_5$H$_5$), 2.04 (1 H, ddd, $^3J_{PH}$ = 1.9 Hz, $^2J_{PH}$ = 12.9 Hz, $^2J_{HH}$ = 12.9 Hz, FeCH^2), 0.72 (1 H, ddd, $^3J_{PH}$ = 9.7 Hz, $^2J_{PH}$ = 15.1 Hz, $^2J_{HH}$ = 12.8 Hz, FeCH^1); ^{13}C{^{1}H} NMR δ 220.81 (d, $^2J_{PC}$ = 30.5 Hz, C$\equiv$O; weak resonance), 134.62 (d, $^1J_{PC}$ = 43.6 Hz, Ph C$_{ipso}$), 134.09 (s, P$^+$Ph C$_{para}$), 133.76 (d, $^3J_{PC}$ = 9.3 Hz, P$^+$Ph C$_{meta}$), 133.44 (d, $^2J_{PC}$ = 8.7 Hz, Ph C$_{ortho}$), 131.20 (s, Ph C$_{para}$), 130.03 (d, $^2J_{PC}$ = 11.1 Hz, P$^+$Ph C$_{ortho}$), 129.32 (d, $^3J_{PC}$ = 8.9 Hz, Ph C$_{meta}$), 124.86 (d, $^1J_{PC}$ = 81.8 Hz, P$^+$Ph C$_{ipso}$), 84.27 (s, C$_5$H$_5$), –19.19 (dd, $^2J_{PC}$ = 14.1 Hz, $^1J_{PC}$ = 25.3 Hz, FeCH$_2$); ^{31}P{^{1}H} (CD$_2$Cl$_2$, 293 K) δ 72.0 (d, $^3J_{PP}$ = 16.3 Hz, FePPh$_3$), 37.4 (d, $^3J_{PP}$ = 16.2 Hz, CH$_2$PPh$_3$$^+$), –147.4 (septet, $^1J_{FP}$ = 712.0 Hz, PF$_6$$^-$); MS, *m/z* 687 (M$^+$ for cation). Anal. Calcd for C$_{43}$H$_{37}$F$_6$FeOP$_3$: C, 62.04; H, 4.48. Found: C, 62.17; H, 4.54.

Preparation of (η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)CH$_2$(vinyl) (1j).[19] Following the procedure reported by Aris and Brown,[19] solid **7** (2.0 g, 4.1 mmol), prepared by photolysis of **6** with triphenylphosphine,[18] was added in small portions to allylmagnesium bromide (12 mmol) in diethyl ether (30 mL) at 0 °C. The resulting red solution was stirred for 30 min, treated with dioxan (7 mL), and filtered through Celite. The filtrate was washed with degassed cold water (2 × 20 mL) and dried, and the solvent was evaporated to give a red oil (1.1 g, 65%), which was characterized without further purification due to its thermal instability: IR ν (C$\equiv$O) 1905 cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ 7.75–7.27 (15 H, m, Ph), 6.11 (1 H, ddt, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 16.9 Hz, C*H*=CH$_2$), 4.53 (1 H, ddt, $^4J_{HH}$ = 1.3 Hz, $^3J_{HH}$ = 16.6 Hz, $^2J_{HH}$ = 2.6 Hz, CH=C*H*H), 4.35 (1 H, dd, $^3J_{HH}$ = 9.8 Hz, $^2J_{HH}$ = 2.7 Hz, CH=CH*H*), 4.18 (5 H, d, $^3J_{PH}$ = 1.2 Hz, C$_5$H$_5$), 2.04 (1 H, dddd, $^3J_{PH}$ = 3.2 Hz, $^4J_{HH}$ = 1.3 Hz, $^3J_{HH}$ = 7.4 Hz, $^2J_{HH}$ = 8.7 Hz, FeCH^2), 1.30 (1 H, dddd, $^3J_{PH}$ = 11.2 Hz, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.6 Hz, $^2J_{HH}$ = 8.8 Hz, FeCH^1); ^{13}C{^{1}H} NMR δ 223.12 (d, $^2J_{PC}$ = 32.7 Hz, C$\equiv$O), 152.23 (d, $^3J_{PC}$ = 4.0 Hz, *C*H=CH$_2$), 137.08 (d, $^1J_{PC}$ = 39.4 Hz, Ph C$_{ipso}$), 133.63 (d, $^2J_{PC}$ = 10.5 Hz, Ph C$_{ortho}$), 129.92 (s, Ph C$_{para}$), 128.49 (d, $^3J_{PC}$ = 8.9 Hz, Ph C$_{meta}$), 102.05 (s, CH=*C*H$_2$), 85.72 (s, C$_5$H$_5$), 6.63 (d, $^2J_{PC}$ = 17.0 Hz, FeCH$_2$); ^{31}P{^{1}H} NMR δ 80.0.

X-ray Crystal Structure Analysis of (*RS*)-[(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)CH$_2$CH$_3$] (1a) and (*RS*)-[(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)CH$_2$Si(CH$_3$)$_3$] (1e). Cell parameters and reflection intensities were measured by using graphite monochromated Mo Kα radiation on an Enraf-Nonius CAD4-F diffractometer operating in the $\omega/2\theta$ mode. For both analyses the scan range (ω) was calculated from [1.00 + 0.347 tan θ], and the scan speed was varied from 0.9° to 5.6° min^{-1} depending upon intensity. Reflections were measured in the range $0 \leq \theta \leq 25°$. Three standard reflections measured every hour were used to scale the intensity data and correct for any crystal decay. The data were corrected for Lorentz polarization and absorption effects,[33] and equivalent reflections were merged to give unique data sets. Reflections with $I > 3\sigma(I)$ were considered to be observed and were used in the subsequent structure analyses. The structures were solved by Patterson function and electron density Fourier synthesis methods. Final full-matrix least-squares refinement included, in both cases, parameters for atomic positions, anisotropic temperature factors (for non-hydrogen atoms), an overall scale factor, and an extinction parameter.[34] All hydrogen atoms were located in difference Fourier syntheses, and all, except the α-methylene hydrogens which were refined isotropically, were placed in calculated positions and allowed to "ride" on their respective carbon atoms. Refinement was terminated when the rms (shift/σ) was less than 0.001σ. Weights for each reflection were calculated from a Chebyshev series of the form $w = [A_0t_0(X) +$

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$A_1t_1(X) + ... + A_nt_n(X)]$ where $X = F_{obsd}/F_{max}$.[35] In each case, final difference Fourier synthesis showed no significant residual electron density, and a detailed analysis failed to reveal any systematic errors. All calculations were performed by using the CRYSTALS package on the Chemical Crystallography Laboratory VAX 11/750 computer.

Crystal Data for (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)CH_2CH_3] (1a): $C_{26}H_{25}FeOP$, $M = 440.3$, orthorhombic, $a = 9.328$ (3) Å, $b = 17.218$ (5) Å, $c = 26.810$ (7) Å, $V = 4306$ Å^3, $Z = 8$, $D_{calcd} = 1.36$ Mg m^{-3}, μ (Mo Kα) = 7.86 cm^{-1}, space group *Pbca*, relative transmission factors 1.00–1.16, crystal dimensions 0.75 × 0.51 × 0.19 mm, number of reflections [$I > 3\sigma(I)$] 2326, Chebyshev weighting coefficients (A_n) 6.3658, −7.7926, 4.9203, −2.2966, $R = 0.035$, $R_w = 0.037$, GOF = 1.07.

Crystal Data for (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)$CH_2Si(CH_3)_3$] (1e): $C_{28}H_{31}FeOPSi$, $M = 498.5$, monoclinic, $a = 7.941$ (3) Å, $b = 15.552$ (5) Å, $c = 20.929$ (6) Å, $\beta = 90.69$ (2)°, $V = 2584.4$ Å^3, $Z = 4$, $D_{calcd} = 1.28$ Mg m^{-3}, μ (Mo Kα) = 7.06 cm^{-1}, space group $P2_1/c$, relative transmission factors 1.00–1.10, crystal dimensions 0.88 × 0.62 × 0.57 mm, number of reflections [$I > 3\sigma(I)$] 3012, Chebyshev weighting coefficients (A_n) 8.3764, −0.8804, 7.1499, $R = 0.032$, $R_w = 0.039$, GOF = 0.97.

Variable Temperature NMR. Spectra were recorded at the higher temperatures in toluene-d_8 or dimethyl sulfoxide-d_6, whilst at lower temperatures dichloromethane-d_2 was the solvent of choice. The coupling constants did not show any significant variation with different solvents, except for complexes **1f** and **1g**.

^{1}H NMR experiments were conducted on a Bruker WH 300 spectrometer at 300.13 MHz. Typically, a sweep width of 3500 Hz was used, and the FID was recorded and processed in 16K blocks of computer memory. Thus, the values obtained for coupling constants are accurate to ±0.2 Hz, whilst the temperature control was accurate to ±1 °C.

^{31}P NMR experiments were conducted on a Bruker AM 250 spectrometer at 101.26 MHz. A sweep width of 10000 Hz was used, and the FID was recorded and processed in 32K blocks of computer memory. Coupling constants are accurate to ±0.3 Hz and temperature control to ±1 °C.

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Optical Absorption Spectra of Tetraalkyl Olefin Cation Radicals

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Abstract: The cation radicals of five Bredt's rule protected olefins have been investigated by electrochemistry, optical spectroscopy, and MNDO semiempirical molecular orbital calculations. In all cases σ,π^+ transitions involving excitation of an electron from a C–C σ-bonding orbital to the singly occupied π orbital of the olefin cation radical are observed. A simple NCG method for calculating the wavelength of optical absorptions with MNDO, coupled with elementary calculations on the expected intensities, provides a useful tool in interpreting the spectra. Two types of σ,π^+ transitions, where the σ orbital has π^* symmetry, are observed. The first type, a hyperconjugation transition, is found at low energies for the bis-alkylidene cation radicals, where the nodal plane bisects the two alkylidene fragments. In the second type seen for the lowest energy bands of the sesquialkene cation radicals, the nodal plane contains the olefinic carbons and is perpendicular to the π-nodal plane. Through-bond effects are found in the spectra. The sesquihomoadamantene radical cation, 3^+, is kinetically extremely stable.

The current interest in electron-transfer phenomena has led to a rapid improvement in the technique available for the experimental investigation of cation radicals by ESR or optical spectroscopy in matrices[1,2] or in solution.[3,4] The data provided by such experiments are, however, often difficult to interpret or are subject to a variety of explanations. In these cases, molecular orbital calculations can be a valuable tool in resolving difficulties. However, "definitive" calculations can seldom be applied to large organic systems so that lower level ab initio or semiempirical calculations must be tested and adapted to the problems involved. The practical requirement is for computationally efficient but relatively accurate methods to calculate observable parameters reliably for large organic radical ions.

Unfortunately, the experimentally accessible quantities of ESR spectra, hyperfine coupling constants and g values, or optical spectra, λ_{max} and extinction coefficient data, are among those which can be calculated least reliably, even by the highest levels of theory. This paper attempts partly to remedy this situation by reporting experimental and calculated data for a series of large olefin cation radicals and by presenting a simple, effective method for the prediction of λ_{max} for radicals and radical ions.

Olefin cation radicals show hyperconjugation transitions[5] arising from promotion of electrons from σ-bonding orbitals to the π singly occupied molecular orbital (SOMO) of the radical cation. The wavelengths of such σ,π^+ transitions show large and not easily interpretable variations between related cation radicals, so that a method for predicting λ_{max} values is potentially of great value. In this work, we have used the MNDO[6] semiempirical molecular

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