Conformational Energy of the (η^5-Cyclopentadienyl) Iron(II) Dicarbonyl Group

Nhu Y T. Stessman,[†] Mario Ordóñez,[‡] Eusebio Juaristi,*[,‡] and Richard S. Glass*[,†]

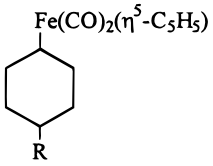
Contribution from the Department of Chemistry, The University of Arizona, Tucson, Arizona 85721, and Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, 07000 México, D.F., México

Received June 22, 1998

The conformational energy of the (η^5-cyclopentadienyl) iron(II) dicarbonyl group was determined by variable-temperature ^{1}H NMR spectroscopic studies on *cis*-4-phenyl-1-(η^5-cyclopentadienyl) iron-(II) dicarbonyl cyclohexane. This is the first determination of the *A*-value of a group with a transition metal directly attached to a cyclohexane ring. The stereospecific synthesis of *cis*- and *trans*-4-phenyl-1-(η^5-cyclopentadienyl) iron(II) dicarbonyl cyclohexane and *cis*- and *trans*-4-*tert*-butyl-1-(η^5-cyclopentadienyl) iron(II) dicarbonyl cyclohexane and the X-ray crystal structure of *cis*-4-*tert*-butyl-1-(η^5-cyclopentadienyl) iron(II) dicarbonyl cyclohexane are reported.

Introduction

A standard method to ascertain the inherent conformational parameters of a substituent is to determine the free energy difference between axial and equatorial isomers in a monosubstituted cyclohexane ring (*A*-value).[1] Although the *A*-values for a large number of substituents including main group metals have been determined, no such values have been reported for substituents in which a transition metal is directly attached to the cyclohexane ring.[1] This gap in knowledge is undoubtedly due, in large part, to the instability of such compounds owing to facile β-elimination. However, cyclohexyl η^5-cyclopentadienyl iron dicarbonyl **1a** (cyclohexylFp) is stable.[2] On the basis of NMR spectroscopic analysis,[2] it was concluded that the Fp group occupies an equatorial position. Furthermore



1a, R=H
b, R=t-Bu
c, R=Ph

it was suggested,[2] on the basis of analysis of space-filling molecular models, that the Fp group is at least as bulky as is the *tert*-butyl group, although an *A*-value was not determined. This paper presents the experimental determination of the *A*-value for the Fp group by counterpoising this group with a phenyl group.[3,4] This is the first reported *A*-value for a substituent with a transition metal directly bonded to the cyclohexyl ring.

Results and Discussion

The Fp anion is known to be an excellent nucleophile in S_N2 displacement reactions.[5] Consequently, *cis*- and *trans*-**1b** and **1c** were stereospecifically synthesized by reaction of Fp^- with *trans*- and *cis*-4-*tert*-butyl cyclohexyl *p*-toluenesulfonate and *trans*- and *cis*-4-phenyl cyclohexyl *p*-toluenesulfonate, respectively. All of the compounds were obtained pure, and their structures, including stereochemistry, were determined by spectroscopic analysis. In addition, the structure of *cis*-**1b** was unequivocally established by single-crystal X-ray crystallographic analysis. An ORTEP drawing of this molecule is shown in Figure 1. As seen from the drawing, the cyclohexane ring adopts a chair conformation with an equatorial *t*-Bu and axial Fp group (**2**). The chair is flattened around the Fp

2

group as seen by the C5−C6−C1−C2 and C6−C1−C2−C3 dihedral angles of −49.81° and 49.62°, respectively. (The C1−C2−C3−C4, C2−C3−C4−C5, C3−C4−C5−C6, and C4−C5−C6−C1 dihedral angles are −54.53°, 54.79°, −55.54°, and 55.64°, respectively, which are close to the C−C−C−C dihedral angle of 55.26[6] in the chair conformation of cyclohexane.) It can also be seen that the axial C−Fe bond is tilted away from the axial hydrogen atoms at C3 and C5, resulting in Fe−C1−C2−C3 and Fe−C1−C6−C5 dihedral angles of −82.99° and 85.29°, respectively. However, the angle between the C−Fe bond and the C2−C1−C6 plane is 49.9°, which is a little larger than the range of 31.6°−45.9° found for the seven other reported crystal structures[7−13] having an Fe−C(C)C

[†] The University of Arizona.
[‡] Instituto Politécnico Nacional.

(1) Bushweller, C. H. In *Confomational Behavior of Six-Membered Rings*; Juaristi, E., Ed.; VCH Publishers: New York, 1995; Chapter 2.
(2) Cameron, A. D.; Laycock, D. E.; Smith, V. H., Jr.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1987**, 2857.
(3) Juaristi, E. *Introduction to Stereochemistry and Conformational Analysis*; Wiley: New York, 1991.
(4) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994.
(5) Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541.
(6) Dommen, J.; Brupbacher, Th.; Grassi, G.; Bander, A. *J. Am. Chem. Soc.* **1990**, *112*, 953.
(7) Bennett, M. J., Jr.; Cotton, F. A.; Davison, A.; Faller, J. W.; Lippard, S. J.; Morehouse, S. M. *J. Am. Chem. Soc.* **1966**, *88*, 4371.

10.1021/jo981198x CCC: $15.00
Published on Web 11/05/1998

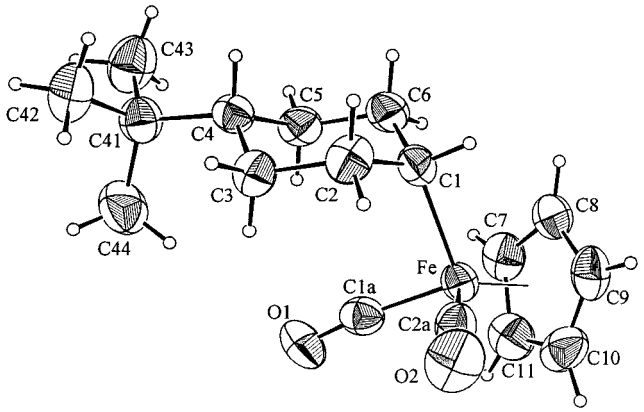


Figure 1. ORTEP view of *cis*-**1b**.

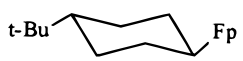
Table 1. ^{1}H NMR Spectroscopic Parameters for *cis*-1b, *trans*-1b, *cis*-1c, and *trans*-1c at Room Temperature

	H1[a]		H1[b]	
cmpd	δ[c] (ppm)	J (Hz)	δ[e] (ppm)	J (Hz)
cis-**1b**	3.35	4.6	3.36	4.6
trans-**1b**	2.50	3.6, 12.2	2.49	3.6, 12.2
cis-**1c**	2.90		2.75	
trans-**1c**	2.56[d]	3.4, 12	2.51	

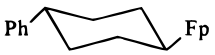
[a] The solvent is CD_2Cl_2. [b] The solvent is d_{14}-methylcyclohexane. [c] The chemical shifts are relative to residual protic solvent peak. [d] This peak assignment is tentative and may be reversed with that at 2.61 ppm assigned to H4. [e] Relative to internal TMS.

fragment. The Fe−C1 bond length of 2.112 Å is at the high end of the reported range of 2.060−2.110 Å for the Fe−C(sp^3) bond length.

The H1 chemical shifts and coupling constants for **1b** and **1c** are given in Table 1. The signal for H1 in *cis*-**1b** is an apparent quintet, which is consistent with its being equatorial with the same coupling constant with the adjacent axial and equatorial C2, C6 protons. The signal for H4 is also a triplet of triplets with a large coupling constant to the axial C3, C5 protons (10.8 Hz) and a smaller coupling constant with the equatorial protons (4.4 Hz). Thus, the solution ^{1}H NMR spectrum and X-ray crystal structure show that the predominant conformation of *cis*-**1b** is **2**. Furthermore, the spectrum of *cis*-**1b** shows no change on cooling in either CD_2Cl_2 or d_{14}-methylcyclohexane. Similarly, the data in Table 1 was used to assign the conformations of *trans*-**1b** and *trans*-**1c** as **3** and **4**, respectively. The ^{1}H NMR spectra of these



3



4

compounds also show no change on cooling. The H1 signal in *cis*-**1c** contrasted with that for *cis*-**1b**. There is a 0.6 ppm chemical shift difference between these two signals, whereas the H1 signals for *trans*-**1b** and *trans*-**1c** differ by only 0.1 ppm. The coupling constants for H1 in *cis*-**1c** could not be discerned. Furthermore, in contrast to *cis*-**1b**, *trans*-**1b**, and *trans*-**1c**, this signal is temperature-dependent. On cooling the sample of *cis*-**1c**, the spectrum changed. These changes are better seen in d_{14}-methylcyclohexane as solvent rather than CD_2Cl_2. Therefore, the H1 chemical shifts for all of the compounds were determined in this solvent and are recorded in Table 1. The signal for H4 of *cis*-**1c** in d_{14}-methylcyclohexane occurs at 2.96 ppm at room temperature, which may be compared with that for *trans*-**1c** at 2.61 ppm. The changes in the ^{1}H NMR spectrum of *cis*-**1c** on cooling can be seen in Figure 2. This suggests ring inversion as shown in eq 1. The assignments for H1 and H4 for **5** and **6** at −100 °C are shown in Table 2 and were made as follows. The chemical shifts for the equatorial and axial H1 are 3.36 and 2.49 ppm in *cis*-**1b** and *trans*-**1b**, respectively. The chemical shift for axial H4 in *trans*-**1c** is 2.61 ppm in d_{14}-methylcyclohexane. It should be noted that axial H4 and axial H1 are very close in chemical shifts in this solvent. Comparable overlap appears to occur for axial H4 in **5** and axial H1 in **6**. The signal for equatorial H1 in *cis*-**1b** at 3.36 ppm supports the assignment of equatorial H1 in **5** to the peak at 3.57 ppm. The assignments were confirmed by HMQC spectroscopy correlating the known ^{13}C chemical shifts with the ^{1}H chemical shifts. The ^{13}C chemical shift for the carbon attached to the phenyl group in phenylcyclohexane is 44.6 ppm and for that attached to the Fp group in cyclohexyl Fp is 28.2 ppm.

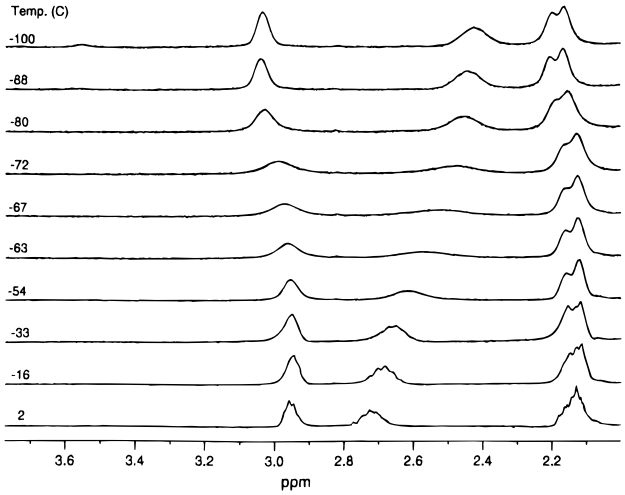
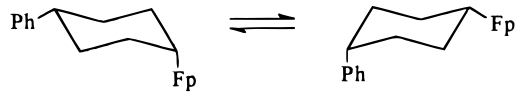


Figure 2. Variable-temperature ^{1}H NMR spectra of *cis*-**1c** in d_{14}-methylcyclohexane.

Table 2. ^{1}H NMR Spectroscopic Parameters for *cis*-1c at −100 °C

	H1		H4	
	δ[a] (ppm)	integral	δ[a] (ppm)	integral
5	3.57	0.07	2.44[b]	0.07
6	2.44[b]	0.82	3.05	0.79

[a] In d_{14}-methylcyclohexane versus tetramethylsilane as the internal reference. [b] Overlapping peaks.



5 **6**

(8) Churchill, M. R.; Ni Chang, S. W.-Y. *J. Am. Chem. Soc.* **1973**, *95*, 5931.
(9) Gompper, R.; Bartmann, E.; Nöth, H. *Chem. Ber.* **1979**, *112*, 218.
(10) Wright, M. E. *Organometallics* **1983**, *2*, 558.
(11) Kolobova, N. E.; Rozantseva, T. V.; Struchkov, Yu. T.; Batsanov, A. S.; Bakhmutov, V. I. *J. Organomet. Chem.* **1985**, *292*, 247.
(12) Bruce, M. I.; Duffy, D. N.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *310*, C33.
(13) Leung, T. W.; Christoph, G. G.; Gallucci, J.; Wojcicki, A. *Organometallics* **1986**, *5*, 846.

Using the integrated areas shown in Table 2, the equilibrium constant for eq 1 is 11.4, which corresponds to $-\Delta G° = 0.8$ kcal/mol. Using the reported $-\Delta G°$ value for an equatorial and axial phenyl group (2.9 kcal/mol)[14] and assuming additivity, $-\Delta G° = 3.7$ kcal/mol for the Fp group. Furthermore, from the observed coalescence temperatures (T_c) for H1 and H4 and the two rate constants (k_c) of the exchange for each of these protons, the free energy of activation for the ring inversion can be calculated. The rate constant was determined by the difference in chemical shifts of the two signals in each conformer in the absence of exchange. Using the Eyring equation,[15] $-\Delta G_c^{\ddagger} = 9.4$ kcal/mol. Although this energy of activation for ring inversion is significantly lower than that for cyclohexane (10.3 kcal/mol),[3,4] it is only slightly higher than that for phenylcyclohexane (8.8 kcal/mol).[16]

In conclusion, the *A* value for the Fp group has been determined to be 3.7 kcal/mol using the counterpoise method. Consequently, it is conformationally more demanding than the phenyl group but less demanding than the *tert*-butyl group when attached to a cyclohexane ring.

Experimental Section

All reactions were carried out by using standard Schlenk techniques under an atmosphere of argon. Solvents were purified by distillation under nitrogen from standard drying agents. Chemical shifts are reported in parts per million relative to the residual proton solvent peak except for the low-temperature ^{1}H NMR chemical shifts, which are reported relative to TMS. Low-temperature ^{1}H NMR spectra were measured using deuterated methylcyclohexane as solvent. Microanalysis was performed by Desert Analytics, Tucson, AZ. Mass spectrometry was performed at The University of Arizona Mass Spectrometry Facility.

***cis*-4-*tert*-ButylcyclohexylFp (*cis*-1b).** Sodium metal (1.10 g, 0.048 mol) was placed under an argon atmosphere in a three-necked round-bottom flask equipped with a stir bar and an addition funnel that contained mercury (7.2 mL). The mercury was added slowly into the flask to generate 1% sodium amalgam,[17] and the sodium amalgam mixture was stirred for about 30 min until it cooled to room temperature. Cyclopentadienyliron dicarbonyl dimer purchased from Aldrich Chemical Co., Milwaukee, WI (1.08 g, 3.0 mmol) dissolved in anhydrous THF (15 mL) was transferred into the sodium amalgam mixture either by syringe or by cannulation. The mixture was stirred for about 2 h at room temperature. The Fp anion in THF was separated from the excess sodium amalgam and transferred to a clean 50-mL flask equipped with a magnetic stir bar and a water condenser. In another flask, *trans*-4-*tert*-butylcyclohexyl *p*-toluenesulfonate[18,19] (1.0 g, 3.0 mmol) was dissolved in DMF (5 mL). This solution was then added dropwise into the Fp anion solution, and additional THF (5 mL) used to rinse the flask was also added into the reaction mixture. The reaction was stirred for 24 h at 65 °C. The solvent was removed under reduced pressure. The brown residue was taken up with anhydrous diethyl ether (50 mL). The solution was filtered through Celite. The solvent was again removed under reduced pressure. The residue was purified by column chromatography on alumina (grade III), eluting with hexanes. Collection of the first yellow band gave 404 mg (43%) of crude *cis*-**1b**. Recrystallization from cold pentane under a nitrogen atmosphere gave yellow needles: mp 82−84 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.83 (s, 9H, *t*-Bu), 1.05 (tt, 1H, J = 4.4, 10.8 Hz, H4), 1.30−1.52 (m, 4H, H3,5), 1.74 (m, 4H, H2,6), 3.34 (quintet, 1H, J = 4.72 Hz, H1), 4.70 (s, 5H, C_5H_5); ^{13}C NMR (300 MHz, CD_2Cl_2) δ 24.39 (C1), 26.02 (C3,5), 27.96 (CMe_3), 33.10 (CMe_3), 40.23 (C2,6), 47.12 (C4), 87.02 (C_5H_5); FT-IR (CH_2Cl_2) ν 1932, 1991 cm^{-1} (CO). Anal. Calcd for $C_{17}H_{24}FeO_2$: C, 64.57; H, 7.65. Found: C, 64.28; H, 7.55.

***cis*-4-PhenylcyclohexylFp (*cis*-1c).** The Fp anion was generated as described above from Fp_2 (1.08 g, 3.00 mmol) and 1% Na·Hg in THF (15 mL). After the Fp anion was transferred from the excess Na·Hg, *trans*-4-phenylcyclohexyl *p*-toluenesulfonate[19,20] (0.5 g, 1.5 mmol) dissolved in THF (5 mL) was added dropwise at room temperature into the Fp anion solution using a syringe. The reaction was stirred for 48 h at 65 °C. The solvent was removed under vacuum. The brown residue was taken up with anhydrous ether and filtered through Celite. The solvent was again removed under reduced pressure. The residue was purified by column chromatography on alumina (grade III), eluting with hexanes. The first orange yellow band consisted of ferrocene and olefin byproducts (NMR yield, 42%), and the second yellow band gave 135 mg (32%) of *cis*-**1c** as a brown oil: ^{1}H NMR (250 MHz, CD_2Cl_2) δ 1.79−2.17 (m, 8H, H2,3,5,6) 2.90 (m, 1H, H1), 3.01 (m, 1H, H4) 4.70 (s, 5H, C_5H_5) 7.19 (t, 1H, J = 7.5 Hz, ArH_p), 7.33 (t, 2H, J = 7.5 Hz, ArH_m), 7.39 (d, 1H, J = 7.5, ArH_o); ^{13}C NMR (250 MHz, CD_2Cl_2) δ 27.29 (C1), 34.69 (C3,5), 39.11 (C4), 39.28 (C2,6), 86.47 (C_5H_5), 125.55 (C_p), 128.09 (C_m), 128.43 (C_o), 146.48 (C_{ipso}), 218.90 (CO); FT-IR (CH_2Cl_2) ν 1932, 2000 cm^{-1} (CO); HRMS (EI) calcd for $^{12}C_{19}{}^1H_{20}{}^{16}O_2{}^{56}Fe$ 336.0813, found 336.0812.

***trans*-4-*tert*-ButylcyclohexylFp (*trans*-1b).** This compound was prepared according to the procedure described for *cis*-**1c** using *cis*-4-*tert*-butylcyclohexyl *p*-toluenesulfonate.[18,19] The residue was purified by column chromatography on alumina (grade III), eluting with hexanes, and sublimation of the residue yielded (NMR yield, 14%) *cis*-**1c** as a yellow solid: mp 74−76 °C; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 0.79 (s, 9H), 1.02−2.02 (m, 9H), 2.49 (tt, 1H, J = 12, 3.6 Hz, H1), 4.71 (s, 5H, C_5H_5); ^{13}C NMR (250 Hz, CD_2Cl_2) δ 23.25, 27.64, 32.78, 44.49, 49.03, 51.70, 86.28; FT-IR (CH_2Cl_2) 1932, 1991 cm^{-1} (CO); HRMS (EI) calcd for $^{12}C_{17}{}^1H_{24}{}^{16}O_2{}^{56}Fe$ 316.1126, found 316.1132.

***trans*-4-PhenylcyclohexylFp (*trans*-1c).** This compound was prepared according to the described procedure for *cis*-**1c** using *cis*-4-phenylcyclohexyl *p*-toluenesulfonate.[19] The residue was purified by column chromatography on alumina (grade III), eluting with hexanes. Collection of the first orange yellow band gave ferrocene and olefin byproducts (NMR yield, 58%), and the second yellow band gave *trans*-**1c** as a yellow solid (21%). For further purification, the material was recrystallized from cold pentane under inert gas: mp 90−92 °C; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 1.49−2.10 (m, 8H, H2,3,5,6), 2.56 (tt, 1H, J = 3.4, 12 Hz, H1), 2.62 (tt, J = 3.6, 12 Hz, H4), 4.76 (s, 5H, C_5H_5), 7.13−7.29 (m, 5H, ArH); ^{13}C NMR (250 MHz, CD_2Cl_2) δ 26.74 (C1), 39.32 (C3,5) 44.01 (C2,6), 44.37 (C4), 86.29 (C_5H_5), 125.96 (C_p), 127.17 (C_m), 128.54 (C_o), 148.33 (C_{ipso}), 218.73 (CO); FT-IR (CH_2Cl_2) ν 1932, 2000 cm^{-1} (CO); HRMS (EI) calcd for $^{12}C_{19}{}^1H_{20}{}^{16}O_2{}^{56}Fe$ 336.0813, found 336.0820.

Acknowledgment. Financial support by the U.S. National Science Foundation (grant INT-9602925) and Consejo Nacional de Ciencia y Tecnología is gratefully acknowledged. The X-ray crystal structure study reported in the paper was done at the Molecular Structure Laboratory of The University of Arizona.

Supporting Information Available: ^{1}H NMR spectra for *cis*-**1c**, *trans*-**1b**, and *trans*-**1c** and tables of X-ray crystal data, bond lengths and angles, atomic coordinates, and anisotropic thermal parameters for *cis*-**1b** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO981198X

(14) Eliel, E. L.; Manoharan, M. *J. Org. Chem.* **1981**, *46*, 1959.
(15) Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Compounds*; VCH Publishers: New York, 1985.
(16) Squillacote, M.; Neth, J. N. *J. Am. Chem. Soc.* **1987**, *109*, 198.
(17) Knobs, C.; Helquist, P. *Organomet. Synth.* **1988**, *4*, 205.
(18) Winstein, S.; Holness, N. J. *J. Am. Chem. Soc.* **1955**, *77*, 5562.
(19) Eliel, E. L.; Ro, R. S. *J. Am. Chem. Soc.* **1957**, *79*, 5995.
(20) Ungnade, H. E. *J. Org. Chem.* **1948**, *13*, 361.