Organometallics **1999,** *18,* 115−122

Articles

Diels−Alder Reactions of 3-Ferrocenyl-2,4,5-triphenylcyclopentadienone: Syntheses and Structures of the Sterically Crowded Systems C_6Ph_5Fc, C_7Ph_6FcH, and $[C_7Ph_6FcH][SbCl_6]$

Hari K. Gupta, Stacey Brydges, and Michael J. McGlinchey*

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

Received July 29, 1998

Diels−Alder addition of diphenylacetylene or of 1,2,3-triphenylcyclopropene to 3-ferrocenyl-2,4,5-triphenylcyclopentadienone yields, upon thermolysis, C_6Ph_5Fc (**5**) or C_7Ph_6FcH (**8**), respectively. Subsequent treatment of **8** with triethyloxonium hexachloroantimonate results in the formation of the ferricinium complex $[C_7Ph_6FcH]^+[SbCl_6]^-$ (**13**), rather than the anticipated tropylium cation $[C_7Ph_6Fc]^+$. The substituted ferrocene derivatives **5**, **8**, and **13** have been characterized by X-ray crystallography. From the solid-state structure of **5** it is evident that the peripheral aryl substituents do not adopt a regular propeller type conformation, but instead exhibit an incremental progression of twist angles relative to the central ring. The dynamics of peripheral ring rotations in **5** and **8** have been studied by variable-temperature NMR.

Introduction

Sterically crowded molecules, with their attendant opportunities for correlated molecular motions,[1] their suggested roles as micromachines,[2] and their consequent relevance to nanotechnology,[3] continue to attract much interest. Typical examples include Kelly's recent reports of "molecular brakes and ratchets"[4] and Moore's "molecular turnstile".[5]

Germane to the aforementioned theme are molecular propellers, a broad class of compounds comprising two or more substituents arranged in a helical (chiral) conformation about a central core.[6] Such a molecular model combines structure with dynamic function, introducing the possibility of correlated rotation and complex stereoisomerization phenomena. This concept is intricately tied to the time scale of observation and is rendered more likely when the internal rotors (such as aryl groups) of the propeller framework are tightly intermeshed.[1]

Whereas propellers of 2- or 3-fold symmetry (C_2, C_3 or D_2, D_3) have been studied in considerable detail,[7] less attention has been given to higher order systems. Not only do molecular paddle-wheels of the type $C_nAr_n^{\pm}$ present a synthetic and structural challenge[8] but a comprehensive probe of the stereochemistry of such species, under static and dynamic conditions, may ultimately allow one to extend the scope of the topological analysis of isomerism and isomerization developed by Gust and Mislow for triaryl and diaryl systems.[7] To date, our own contributions to the diverse collection of molecular paddle-wheels and their organometallic derivatives have included such species as $(C_5Ph_5)Fe(CO)(HC{=}O)PR_3$, **1**,[9] $(C_6Ph_6)Cr(CO)_3$, **2**,[10] and the novel seven-bladed propeller $[C_7Ph_7]^+$, **3**.[11] Relevant to our long-term goal of preparing molecular machines possessing bulky organometallic fragments, we now describe the syntheses, structures, and molecular dynamics of a series of polyphenylated systems incorporating the ferrocenyl moiety.

---

* E-mail: mcglinc@mcmaster.ca. Phone: (905)-525-9140 ext 24504. Fax: (905)-522-2509.

[1] Iwamura, H.; Mislow, K. *Acc. Chem. Res.* **1988**, *21*, 175.

[2] Mislow, K. *Chemtracts: Org. Chem.* **1989**, *2*, 151.

[3] Rouhi, A. M. *Chem. Eng. News* **1998**, *76*, 6(16), 57−62 (April 20).

[4] (a) Kelly, T. R.; Bowyer, M. C.; Bhaskar, K. V.; Bebbington, D.; Garcia, A.; Lang, F.; Kim, M. H.; Jette, M. P. *J. Am. Chem. Soc.* **1994**, *116*, 3657. (b) Kelly, T. R.; Tellitu, I.; Sestelo, J. P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1866. (c) Kelly, T. R.; Sestelo, J. P.; Tellitu, I., *J. Org. Chem.* **1998**, *63*, 3655.

[5] Bedard, T. C.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 10662.

[6] For a review of molecular propellers, refer to: Meurer, K. P.; Vögtle, F. *Top. Curr. Chem.* **1985**, *127*, 3−75.

[7] (a) Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535, and references therein. (b) Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 3198. (c) Mislow, K.; Gust, D.; Finocchiaro, P.; Boettcher, R. *Top. Curr. Chem.* **1974**, *47*, 1. (d) Finocchiaro, P. *Gazz. Chim. Ital.* **1975**, *105*, 149. (e) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26. (f) Glaser, R.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 2777. (g) Willem, R.; Gielen, M.; Hoogzand, C.; Pepermans, H. *Adv. Dyn. Stereochem.* **1985**, *1*, 207.

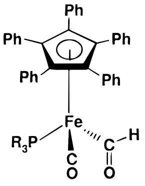
[8] For examples of $C_nAr_n^{\pm}$ systems, see: Olah, G. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1430.

[9] Li, L.; Decken, A.; Sayer, B. G.; McGlinchey, M. J.; Brégaint, P.; Thépot, J.-Y.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1994**, *13*, 682.

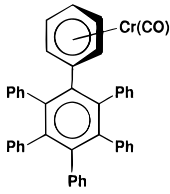
[10] Mailvaganam, B.; Sayer, B. G.; McGlinchey, M. J. *J. Organomet. Chem.* **1990**, *395*, 177.

[11] Brydges, S.; Gupta, H. K.; Chao, L. C. F.; Pole, D. L.; Britten, J. F.; McGlinchey, M. J. *Chem. Eur. J.* **1998**, *7*, 1199.

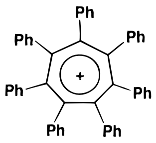
10.1021/om980645w CCC: $18.00
Publication on Web 12/24/1998



1



2



3

Results and Discussion

$(C_6Ar_5)ML_x$ Complexes, $ML_x = (C_5H_4)Fe(C_5H_5)$. The pioneering papers by Gust et al. on the mechanisms of aryl rotations in C_6Ar_6 systems, and their associated barriers, established (i) that peripheral aryl ring rotations are uncorrelated and (ii) that the incorporation of *ortho*-methoxy or *meta*-methyl or methoxy substituents give rise to rotational barriers of 33 and 17 kcal mol^{-1}, respectively.[12] These experiments have subsequently been extended to complexes of the type $(C_nPh_n)ML_x$ whereby the π-bonded organometallic fragment(s) render inequivalent the *faces* rather than the *edges* of the aryl rings.[13]

Accordingly, a dynamic NMR spectroscopic analysis of $(C_6Ph_6)Cr(CO)_3$, in which the tricarbonylchromium moiety is complexed to a peripheral ring, yielded a $\Delta G^{\ddagger}$ value of 12.2 kcal mol^{-1} for the independent rotation of the substituted ring relative to the central plane.[10] Although not detectable under the experimental conditions, a concomitant isomerization process involving a low-energy oscillation which inverts the handedness of the enantiomerically related chiral propellers was proposed. Thus, $(C_6Ph_6)Cr(CO)_3$ exists in two stereoisomeric forms, a *d*,*l* pair having C_1 symmetry, which may only be observed as a NMR time-averaged C_s isomer at low temperature (193 K) and as an effective C_{2v} conformation at 300 K.

In the quest to obtain a system that could be locked as a chiral propeller, perhaps even at ambient temperature, it was thus of considerable appeal to construct another $C_6Ph_5ML_n$ molecule possessing a different sterically demanding organometallic fragment. The ferrocenyl analogue of **2**, i.e., C_6Ph_5Fc, **5**, was prepared by Rausch and Siegel in 1978, but no structural or dynamic data were reported.[14] The original synthesis involved the Diels–Alder addition of ferrocenylphenylacetylene to tetraphenylcyclopentadienone (commonly referred to as tetracyclone), followed by decarbonylation of the intermediate bicyclic ketone to yield **5**. Our somewhat complementary approach required the prior preparation of 3-ferrocenyl-2,4,5-triphenylcyclopentadienone, **4**,[15] as depicted in Scheme 1. This latter methodology has the advantage of also providing a route to the seven-membered ring system C_7Ph_6FcH, **8**, a consideration that is discussed below. It is important to recognize that the versatility of tetraarylcyclopentadienones as Diels–Alder reagents has recently been exploited in the preparation of spherical polyphenylene dendrimers[16] and polyphenyl polycyclic aromatic hydrocarbons.[17,18]

The X-ray crystal structure of C_6Ph_5Fc, **5**, appears as Figure 1, and crystallographic refinement parameters and selected structural data are provided in Tables 1 and 2, respectively. In the solid state **5** exhibits several intriguing features and may be contrasted with the structure of C_6Ph_6, which adopts a propeller configuration with interplanar angles of approximately 67(75)° between the phenyl groups and the central ring.[19a,b,20] Steric requirements undoubtedly influence the geometry of C_6Ph_5Fc, as evinced by the severe twisting of the peripheral phenyls out of the central plane. However, the dihedral angles made by the ferrocenyl and phenyl substituents relative to the central ring follow a curious progression, as illustrated in Figure 2. The ferrocenyl ring bonded to C(1) is oriented at 51° to the central plane, and the phenyls attached to C(2) through C(6) exhibit dihedral angles of 64°, 70°, 81°, 89°, and 120°, respectively. The net effect is to provide a series of peripheral rings each displaced slightly more than its immediately preceding neighbor. One is tempted to postulate that rotation of the ferrocenyl moiety would induce a domino effect such that all the phenyls turn in a synchronous fashion. Verification of such an assertion would require extensive labeling studies, and we make no definitive claims at this time.

Perhaps surprisingly, the 500 MHz ^1H and 125 MHz ^{13}C data on **5** indicate that both fluxional processes previously detailed for $(C_6Ph_6)Cr(CO)_3$ are fast on the NMR time scale. Even at 188 K, the ^{13}C spectrum of the phenyl rings remains essentially unchanged from its appearance at room temperature; apparently, the overall effect of replacing a $(C_6H_5)Cr(CO)_3$ substituent by a ferrocenyl fragment is to lower substantially the barriers to fluxionality, thus rendering more difficult the generation of a chiral propeller. In retrospect, the typical cone volume of a $Cr(CO)_3$ moiety (~21 Å^3) is somewhat greater than that of its ferrocenyl counterpart (~17 Å^3), on account of the spatial extension engendered by the carbonyl ligands.[21] To achieve hindered rotation

---

(12) (a) Gust, D. *J. Am. Chem. Soc.* **1977**, *99*, 6980. (b) Gust, D.; Patton, J. *J. Am. Chem. Soc.* **1978**, *100*, 8175.

(13) (a) Mailvaganam, B.; McCarry, B. E.; Sayer, B. G.; Perrier, R. E.; Faggiani, R.; McGlinchey, M. J. *J. Organomet. Chem.* **1987**, *335*, 213. (b) Malisza, K. L.; Chao, L. C. F.; Britten, J. F.; Sayer, B. G.; Jaouen, G.; Top, S.; Decken, A.; McGlinchey, M. J. *Organometallics* **1993**, *12*, 2462.

(14) Siegel, A.; Rausch, M. D. *Synth. React. Inorg. Met.-Org. Chem.* **1978**, *8* (3), 209.

(15) For details of the synthesis, refer to: Rausch, M. D.; Siegel, A. *J. Org. Chem.* **1968**, *33*, 4545.

(16) (a) Morgenroth, F.; Reuther, E.; Müllen, K. *Angew. Chem.* **1997**, *109*, 1067. (b) Morgenroth, F.; Reuther, E.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 361. (c) Morgenroth, F.; Kübel, C.; Müllen, K. *J. Mater. Chem.* **1997**, *7*, 1207. (d) Morgenroth, F.; Berresheim, A. J.; Wagner, M.; Müllen, K. *Chem. Commun.* **1998**, 1139.

(17) (a) Qiao, X.; Padula, M. A.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 741. (b) Qiao, X.; Ho, D. M.; Pascal, R. A., Jr. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1531. (c) Tong, L.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *Tetrahedron Lett.* **1997**, *38*, 7. (d) Tong, L.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1997**, *119*, 7291. (e) Tong, L.; Lau, H.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1998**, *120*, 6000.

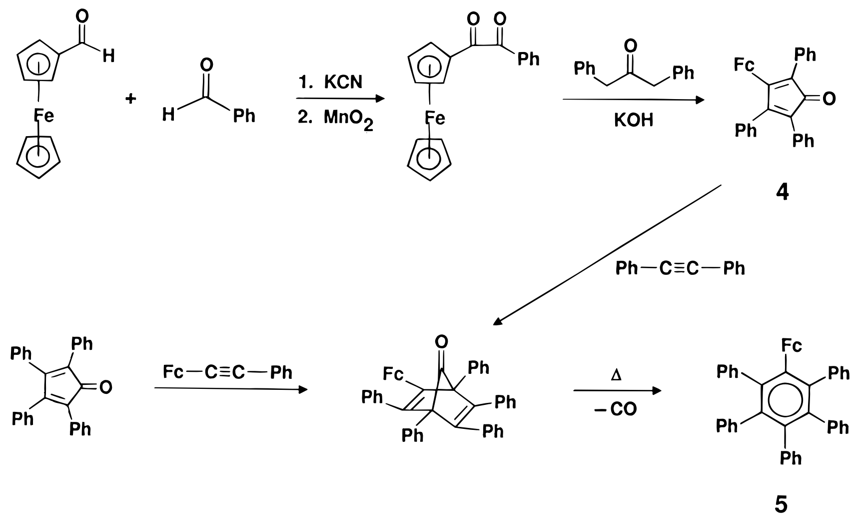
(18) (a) Iyer, V. S.; Wehmeier, M.; Brand, J. D.; Keegstra, M. A.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1604. (b) Müller, M.; Iyer, V. S.; Kübel, C.; Enkelmann, V.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1607.

(19) (a) Bart, J. C. J. *Acta Crystallogr.* **1968**, *B24*, 1277. (b) Larson, E. M.; Von Dreele, R. B.; Hanson, P.; Gust, J. D. *Acta Crystallogr.* **1990**, *C46*, 784.

(20) Early electron diffraction studies of hexaphenylbenzene vapor found that the peripheral phenyl rings oscillate at ±10° from the orthogonal form. Almenningen, A.; Bastiansen, O.; Skancke, P. N. *Acta Chem. Scand.* **1958**, *12*, 1215.

(21) Ligand cone volumes ($\pi r^2 h/3$) were estimated from the structural data of several organometallic complexes, utilizing the dimensions defined by the ligand base (r) and the centroid of the C_nH_n ring to the centroid of the ligand base (h).

Scheme 1. Synthetic Routes to C_6Ph_5Fc, 5



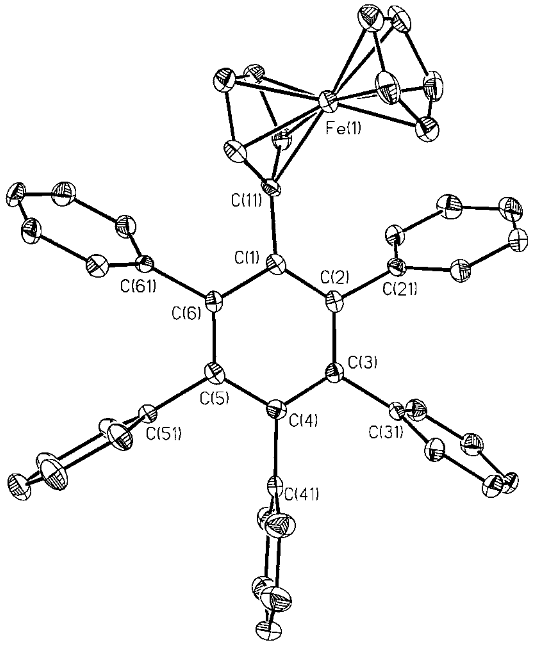


Figure 1. Top view of the molecular structure of C_6Ph_5-Fc, **5** (30% thermal ellipsoids), with hydrogen atoms omitted for clarity.

Table 1. Crystal Data and Structure Refinement for 5, 8, and 13

	5	**8**	**13**
empirical formula	$C_{46}H_{34}Fe$	$C_{53}H_{40}Fe$	$C_{53}H_{40}Cl_6FeSb$
molecular weight	642.58	732.70	1067.15
description	red plate	red-orange prism	dark blue prism
dimens, mm	0.05 × 0.15 × 0.30	0.20 × 0.18 × 0.10	0.09 × 0.10 × 0.12
temp, K	213(2)	267(2)	210(2)
wavelength, Å	(Mo Kα) 0.710 73	(Mo Kα) 0.710 73	(Mo Kα) 0.710 73
cryst syst	orthorhombic	triclinic	monoclinic
space group	Pccn	$P(\bar{1})$	$P2_1/n$
a, Å	45.1814(1)	9.7962(1)	10.8063(0)
b, Å	11.6417(2)	11.0580(0)	11.9269(1)
c, Å	12.2057(2)	18.8717(2)	39.0821(3)
α, deg	90.000(0)	87.795(1)	90.000(0)
β, deg	90.000(0)	89.927(1)	96.256(1)
γ, deg	90.000(0)	69.973(1)	90.000(0)
volume, Å^3	6420.1(2)	1919.18(3)	5007.13(6)
Z	8	2	4
calcd density, g/cm^3	1.330	1.268	1.416
abs coeff, mm^{-1}	0.503	0.430	1.183
F(000)	2688	768	2148
θ-range for collection, deg	0.90−23.00	1.08−22.50	1.05−22.50
transmission (min)	0.629	0.850	0.592
transmission (max)	0.941	0.977	0.914
index ranges	$-56 \leq h \leq 56$ $-14 \leq k \leq 11$ $-15 \leq l \leq 15$	$-8 \leq h \leq 12$ $-13 \leq k \leq 13$ $-23 \leq l \leq 23$	$-12 \leq h \leq 13$ $-14 \leq k \leq 14$ $-48 \leq l \leq 48$
no. reflns collected	36 391	11 499	20 633
no. ind reflns	4472	4906	6520
R(int)	0.1962	0.0273	0.1034
refinement method	full-matrix least-squares on F^2		
no. data/restraints/ params	4448/0/424	4887/0/488	6520/0/551
goodness-of-fit on F^2	1.101	1.054	0.784
final R indices ($I > 2\sigma(I)$)*	R1 = 0.0734	0.0354	0.0365
	wR2 = 0.1110	0.0793	0.0759
R indices (all data)[a]	R1 = 0.1340	0.0492	0.0620
	wR2 = 0.1316	0.0865	0.0807
largest diff peak, e/Å^3	0.288	0.289	0.565
largest diff hole, e/Å^3	−0.337	−0.245	−0.516

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR2 = [\Sigma[\omega(F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]]^{0.5}$.

about the single bond joining the central and peripheral aryl groups, the steric influence imparted by an organometallic fragment must be reflected in both of its dimensions.

Synthesis and Structure of C_7Ph_6FcH. As noted above, 3-ferrocenyl-2,4,5-triphenylcyclopentadienone, **4**, is an effective diene in the Diels−Alder reaction and, when treated with diphenylacetylene, gives **5** after extrusion of carbon monoxide. We have previously reported the synthesis, structure, and molecular dynamics of C_7Ph_7H, **7**, which is readily prepared by decarbonylation of the Diels−Alder adduct of tetracyclone with 1,2,3-triphenylcyclopropene (Scheme 2).[22,23]

It was also emphasized that the initial decarbonylation product, **6**, in which the unique hydrogen is *endo*, undergoes facile [1,5]-suprafacial sigmatropic hydrogen shifts to generate a mixture of isomeric products from suitably labeled precursors.[23] This product distribution is frozen after an irreversible ring inversion which places the unique hydrogen in the favored *exo*-site, as in compound **7**.

---

(22) (a) Battiste, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 4101. (b) Battiste, M. A. *Chem. Ind.* **1961**, 550.

(23) Chao, L. C. F.; Gupta, H. K.; Hughes, D. W.; Britten, J. F.; Rigby, S. S.; Bain, A. D.; McGlinchey, M. J. *Organometallics* **1995**, *14*, 1139.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 5, 8, and 13

	5	8	13
Bond Lengths			
C(1)−C(2)	1.412(7)	1.353(3)	1.369(5)
C(2)−C(3)	1.403(7)	1.478(3)	1.479(6)
C(3)−C(4)	1.406(7)	1.360(3)	1.362(6)
C(4)−C(5)	1.403(7)	1.487(3)	1.475(5)
C(5)−C(6)	1.396(7)	1.355(3)	1.360(4)
C(6)−C(1)	1.434(7)		
C(6)−C(7)		1.527(3)	1.523(5)
C(7)−C(1)		1.526(3)	1.502(7)
C(1)−C(11)	1.493(7)	1.486(3)	1.487(6)
Fe−C_5H_4R (avg)	2.052	2.044	2.089
Fe−C_5H_5 (avg)	2.053	2.037	2.072
Bond Angles			
C(1)−C(2)−C(3)	119.9(5)	122.8(2)	122.1(5)
C(2)−C(3)−C(4)	121.1(5)	124.9(2)	124.5(3)
C(3)−C(4)−C(5)	119.3(5)	124.7(2)	125.6(3)
C(4)−C(5)−C(6)	120.3(5)	122.7(2)	124.1(3)
C(5)−C(6)−C(1)	120.6(5)		
C(6)−C(1)−C(2)	118.3(5)		
C(5)−C(6)−C(7)		120.6(2)	119.6(3)
C(6)−C(7)−C(1)		107.5(2)	107.7(4)
C(7)−C(1)−C(2)		121.1(2)	121.8(4)

Treatment of **4** with triphenylcyclopropene, and subsequent decarbonylation, resulted in the corresponding polyphenylated species, C_7Ph_6FcH, in an acceptable yield. Despite the complexity of the ^1H and ^{13}C NMR spectra, only one of several possible isomers (as depicted in Scheme 2) appeared to be present, and the identification of this product was realized by X-ray crystallography. From the two views of the molecular structure of **8** that are provided in Figure 3, it is evident that the ferrocenyl substituent is positioned at C(1), adjacent to the sp^3-hybridized carbon of the CHPh unit.

Clearly, such an isomer must have arisen as the result of a [1,5]-hydrogen shift after decarbonylation but prior to inversion of the cycloheptatriene ring. Comparison of the structure of **8** with that of C_7Ph_7H reveals that the ferrocenyl unit is located in the sterically least demanding site. In C_7Ph_7H itself, variable-temperature ^1H and ^{13}C NMR data disclosed that the phenyls at C(2)/C(5) have relatively high rotational barriers (11.0 ± 0.5 kcal mol^{-1}) relative to the phenyls positioned at C(1)/C(6) and C(3)/C(4) and presumably reside in the most hindered locale.[23]

Consistent with the solid-state geometries of other C_n-Ar_n systems,[24] the peripheral aryl substitutents are oriented in a twisted fashion relative to the central ring in C_7Ph_6FcH, **8**, affording dihedral angles of 56°, 82°, 81°, 68°, 55°, 132°, and 142° with the plane defined by the attached central ring carbons C(1) to C(7), respectively, and neighboring ring atoms. Moreover, the seven-membered ring in **8** adopts a boat conformation that is distinguished by the planes containing C(6)−C(7)−C(1) [plane 1], C(1)−C(2)−C(5)−C(6), [plane 2], and C(2)−C(3)-C(4)−C(5) [plane 3]. The interplanar angles of 54° ([plane 1]/[plane 2]) and 34° ([plane 2]/[plane 3]) are consonant with the values that we have previously reported for other cycloheptatrienes bearing very bulky substituents: in C_7Ph_7H (C_7Cl_8) the corresponding angles for ([plane 1])/[plane 2]) and for ([plane 2]/[plane 3]) are 55° (52°) and 35° (32°), respectively.[23,25]

As a complement to these crystallographic studies, the conformational flexibility of C_7Ph_6FcH, **8**, in solution was probed by variable-temperature NMR spectroscopy. The room-temperature 500 MHz ^1H and ^{13}C NMR spectra of **8** were completely assigned (with the exception of phenyl rings 3 and 4, which cannot be differentiated) by means of ^1H−^1H COSY and ^1H−^{13}C shift-correlated experiments. In its perphenylated analogue, C_7Ph_7H, **7**, the rotation of phenyl 7 could not be monitored because the mirror plane renders its *ortho* and *meta* protons equivalent at any temperature. This symmetry is disrupted in C_7Ph_6FcH, and on warming the sample, the pair of doublets (at 7.71 and 8.08 ppm) attributable to the *ortho* protons of phenyl 7 (H72/H76) broaden and converge to give a doublet at 7.97 ppm. These coalescence data, obtained at 202 K, yield a rotational barrier of 9.3 (±0.5) kcal/mol. Likewise, the *ortho* protons of phenyl 4 (H42/H46), which at 193 K resonate at 5.59 and 6.16 ppm, exhibited coalescence at 223 K, corresponding to a free energy of activation of 10.1 (±0.5) kcal/mol for the analogous process. Rotation of the other phenyls in **8** is also clearly slowed on the NMR time scale (refer to Figure 4), but overlapping resonances leave the assignments less certain.

One of our aims in preparing C_7Ph_6FcH, **8**, was to attempt the isolation of the corresponding cation $[C_7Ph_6Fc]^+$, **9**, to compare its geometry with that of $[C_7Ph_7]^+$, **3**,[11] and with other ferrocenyl cations.[26] The ability of the ferrocenyl moiety, in addition to other cluster-based organometallic units, to alleviate electron deficiency at a neighboring carbocationic center has been well-established.[27,28] This is generally accomplished by allowing the positively charged site to bend toward the metal so as to optimize the orbital overlap between the vacant p orbital on carbon and a filled d orbital on iron.[29] In the extreme, one may view the resulting structure as a fulvene coordinated to a $[(C_5H_5)Fe]^+$ unit, as in **10**. On the contrary, if the carbocation does not require anchimeric assistance from the electron-rich metal center, it is reasonable to infer that the organometallic fragment will effect minimal geometric distortions in the adjacent cationic center. For instance, it has been shown crystallographically that Hückel-type aromatic cationic systems, which are stable in the absence of a metal, retain their planarity even when an organometallic moiety is present. Examples include the tropylium and pyrylium complexes **11** and **12**,

---

[24] For examples, refer to: (a) C_3Ph_3: Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 833. (b) C_4Ph_4: Iyoda, M.; Sultana, F.; Sasaki, S.; Butenschön, H. *Tetrahedron Lett.* **1995**, *36*, 579. (c) C_5Ph_5: Schumann, H.; Lentz, A.; Weimann, R.; Pickardt, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1731. (d) C_6Ph_6: Biagini, P.; Funaioli, T.; Fachinetti, G.; Laschi, F.; Zanazzi, P. F. *J. Chem. Soc., Chem. Commun.* **1989**, 405.

[25] Dunn, J. A.; Gupta, H. K.; Bain, A. D.; McGlinchey, M. J. *Can. J. Chem.* **1996**, *74*, 2258.

[26] For examples, see: (a) Lupon, S.; Kapon, M.; Cais, M.; Herbstein, F. H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1025. (b) Behrens, U. *J. Organomet. Chem.* **1979**, *182*, 89.

[27] (a) Hill, E. A.; Wiesner, R. *J. Am. Chem. Soc.* **1969**, *91*, 510. (b) Gleiter, R.; Seeger, R.; Binder, H.; Fluck, E.; Cais, M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1028. (c) Dannenberg, J. J.; Levenberg, M. K.; Richards, J. H. *Tetrahedron* **1973**, *29*, 1575.

[28] (a) Caffyn, A. J. M.; Nicholas, K. M. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, Chapter 7.1, pp 685−702. (b) El Amouri, H.; Gruselle, M. *Chem. Rev.* **1996**, *96*, 1077. (c) McGlinchey, M. J.; Girard, L.; Ruffolo, R. *Coord. Chem. Rev.* **1995**, *143*, 331.

[29] Albright, T.; Hoffmann, R.; Hofmann, P. *Chem. Ber.* **1978**, *111*, 1591.

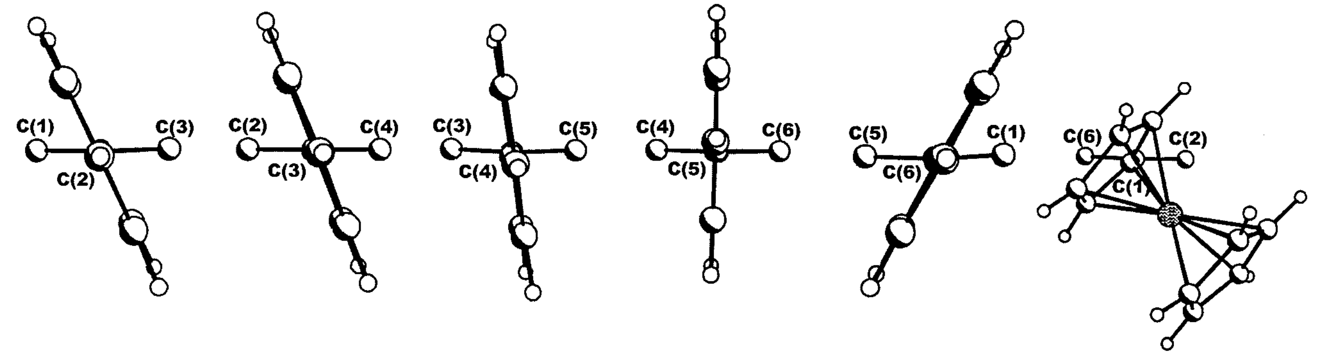
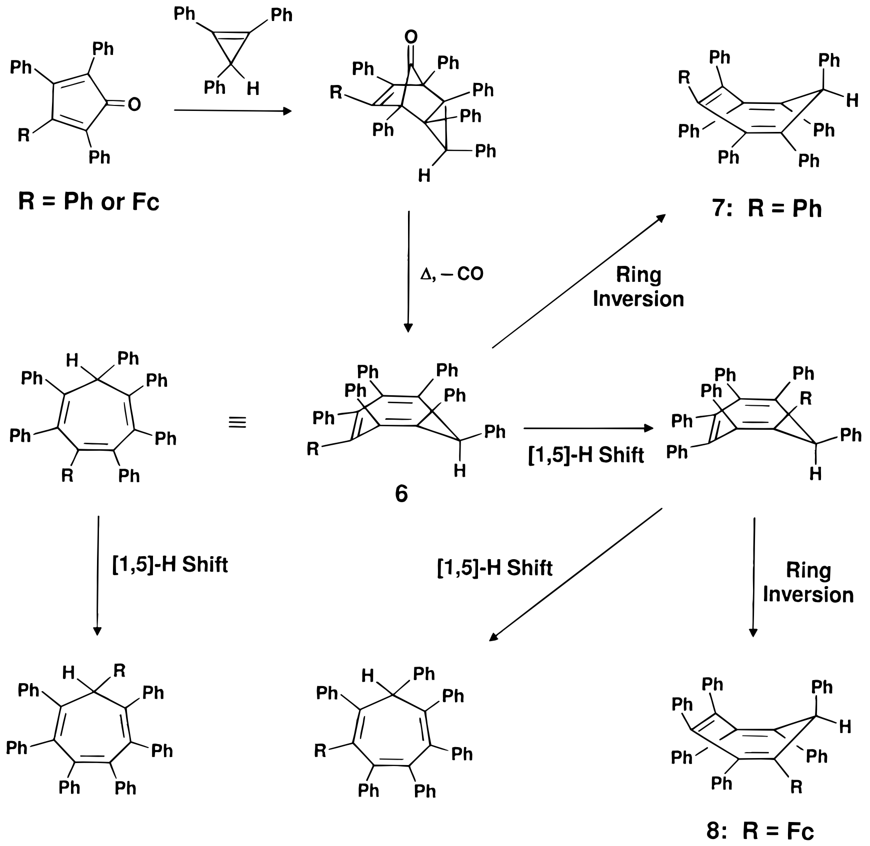


Figure 2. Views along successive peripheral ring–central ring axes in C_6Ph_5Fc, **5**, showing the gradual change in phenyl ring orientations.

Scheme 2. Preparation of and Isomerization Processes in C_7Ar_6RH Systems



respectively.[30,31] In our efforts to generate the cation $[C_7Ph_6Fc]^+$ from C_7Ph_6FcH, several approaches were considered: attempted removal of the unique hydrogen by use of the trityl cation or via successive replacement of this hydrogen by bromine and methoxy substituents (as was done with C_7Ph_7H) proved fruitless. Finally, treatment of C_7Ph_6FcH with triethyloxonium hexachloroantimonate, $[Et_3O]^+$ $[SbCl_6]^-$, which is known to be an excellent reagent for hydride abstractions,[32] yielded deep blue crystals, which were analyzed by use of X-ray diffraction techniques; the resulting structure appears as Figure 5. The product is not the anticipated ferrocenylhexaphenyltropylium cation but rather $[C_7Ph_6FcH]^+[SbCl_6]^-$, **13**, the ferricinium salt of the starting material (Scheme 3). The characteristic boat conformation of the seven-membered ring is maintained, and the unique hydrogen attached to the sp^3-carbon was also readily located. The major differences between **8** and **13**, apart from the presence of the hexachloroantimonate counteranion, are found in the ferrocenyl unit, where the average Fe–C distance has lengthened from 2.04 Å to 2.08 Å, a value that is typical for ferricinium systems.[33] Given the success of the aforementioned reactions with C_7Ph_7H, it is plausible that the steric bulk of the ferrocenyl unit in C_7Ph_6FcH, **8**, hinders the approach of any reagent that might abstract hydride, such that an electron-transfer process intervenes.

---

(30) Brownstein, S. K.; Gabe, E. J.; Hynes, R. C. *Can. J. Chem.* **1992**, *70*, 1011.

(31) Malisza, K. L.; Top, S.; Vaissermann, J.; Caro, B.; Sénéchal-Tocquer, M.-C.; Sénéchal, D.; Saillard, J.-Y.; Triki, S.; Kahlal, S.; Britten, J. F.; McGlinchey, M. J.; Jaouen, G. *Organometallics* **1995**, *14*, 5273.

(32) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley: New York, 1993; p 131.

(33) Deeming, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 4, Chapter 31.3, pp 479–481.

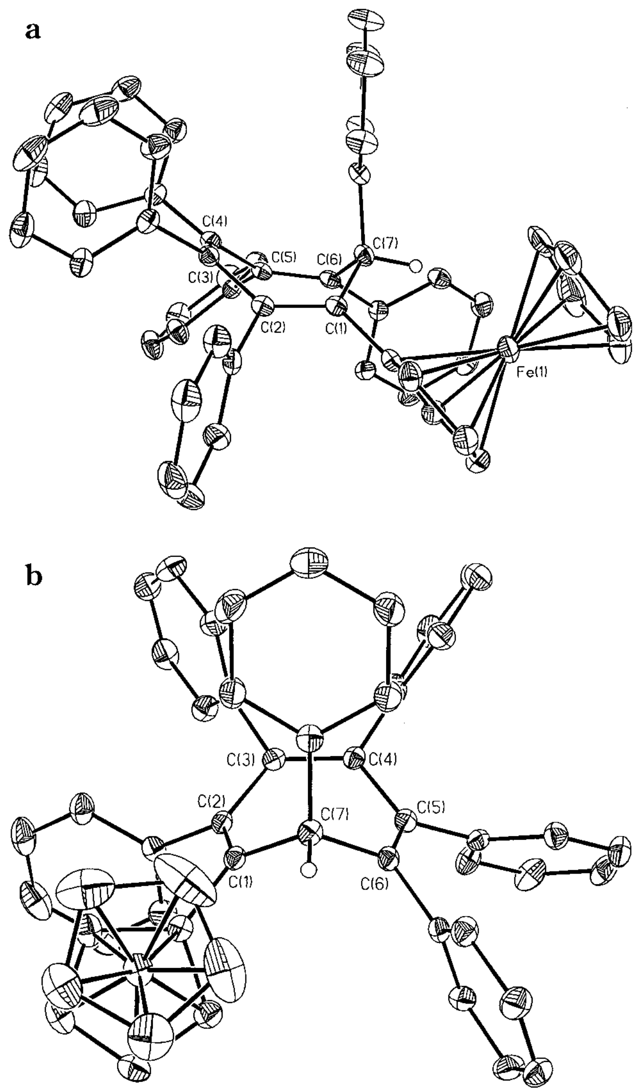
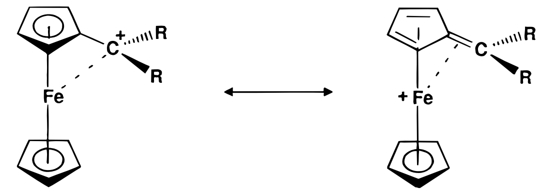
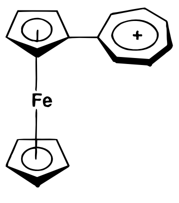


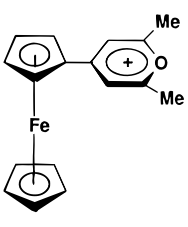
Figure 3. (a) Side view of the molecular structure of C_7Ph_6FcH, **8** (30% thermal ellipsoids), depicting the atom-numbering scheme. (b) "Bow" to "stern" view of the molecular structure of C_7Ph_6FcH, **8** (30% thermal ellipsoids).



10



11



12

Concluding Remarks

The incorporation of a ferrocenyl substituent, rather than π-bonded addenda such as the $Cr(CO)_3$ moiety, into a perphenylated ring system lowers the barriers to a variety of fluxional processes and does not permit the observation of chiral propellers on the NMR time scale at room temperature. As conformationally flexible species, C_nAr_n molecular paddle-wheels are extremely attractive, albeit challenging, synthetic and structural targets. The studies described herein have afforded insight into the steric demands of specific molecular fragments and will serve as important calibration points for the further construction of organometallic architectures which may exhibit restricted rotations. Our ongoing efforts to develop sterically encumbered C_nAr_n systems will be the subject of future reports.

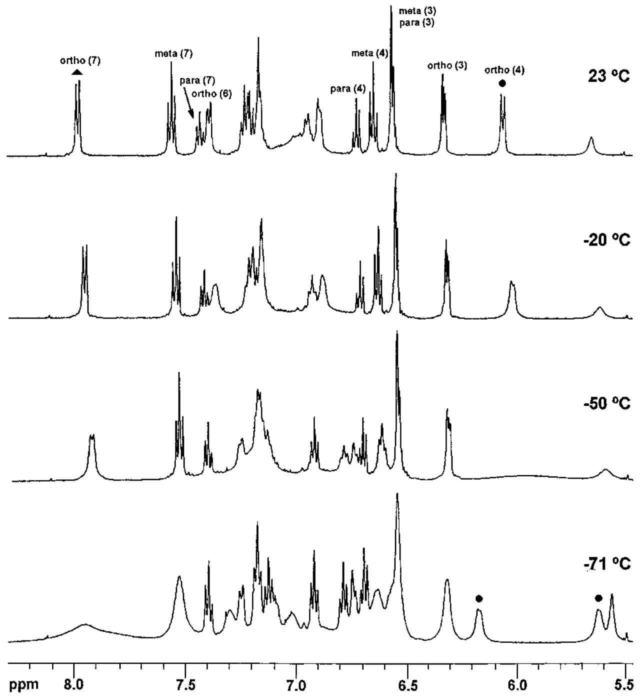


Figure 4. Variable-temperature 500 MHz ^1H NMR spectra of C_7Ph_6FcH, **8**.

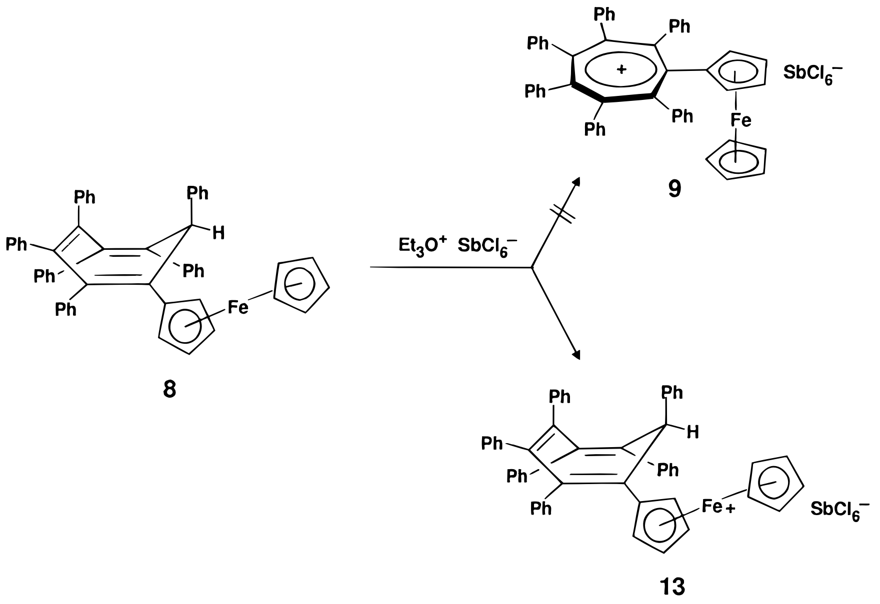
Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry nitrogen utilizing conventional benchtop and glovebag techniques. Solvents were dried and distilled according to standard procedures.[34] Formylferrocene, triethyloxonium hexachloroantimonate, dibenzyl ketone, and diphenylacetylene were purchased from Aldrich Chemical Co., Inc., and used as received. NMR spectra were recorded on a Bruker Avance DRX-500 spectrometer (^1H, 500.13 MHz; ^{13}C, 125.76 MHz) equipped with an 11.74 T superconducting magnet, a Bruker B-VT 2000 temperature controller, and a 5 mm broad-band inverse probe with triple axis gradient capability. One-dimensional ^1H and ^{13}C NMR spectra, as well as two-dimensional $^1H-^1H$ COSY, $^1H-^{13}C$ shift correlated, and long range $^1H-^{13}C$ shift-correlated spectra were recorded on spinning samples (except during the acquisition of 2-D spectra), locked to a solvent signal. NMR resonances were referenced to a residual proton signal of the solvent or to a ^{13}C solvent signal. Mass spectra were collected on a VG analytical ZAB-E spectrometer by direct electron impact and direct chemical ionization (NH_3) methods. Melting points (uncorrected) were determined on a Thomas-Hoover melting point apparatus.

---

[34] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.

Scheme 3. Generation of $[C_7Ph_6FcH]^+$ $[SbCl_6]^-$, 13



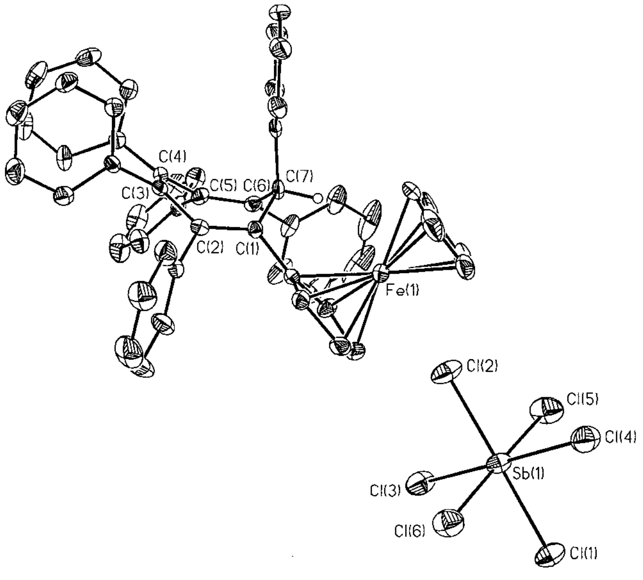


Figure 5. Side view of $[C_7Ph_6FcH]^+[SbCl6]^-$, **13** (30% thermal ellipsoids), depicting the atom-numbering scheme.

$(C_6Ph_5\text{-}C_5H_4)Fe(C_5H_5)$, 5. 3-Ferrocenyl-2,4,5-triphenylcyclopentadienone, **4**, was prepared according to the literature procedure,[15] from the reaction of ferrocenylphenylglyoxal[35] and dibenzyl ketone in refluxing ethanolic potassium hydroxide. In a modification of the synthesis published by Siegel and Rausch,[14] **4** (0.492 g, 1.0 mmol) and diphenylacetylene (0.018 g, 1.0 mmol) were sealed under vacuum in a glass tube and heated at 200 °C for 48 h. The reaction mixture was subsequently cooled to room temperature, the tube broken carefully, and the residue extracted from CH_2Cl_2 (~50 mL) and filtered. The addition of hexane (~50 mL) to the filtrate facilitated the precipitation of a dark solid. After removal of the solvent the recovered material was subjected to flash chromatography on silica gel. Elution with hexane/CH_2Cl_2 (50:50, 25:75, 0:100) afforded a orange-yellow band, which was collected and evaporated to give **5** as an orange-yellow solid, mp > 265 °C (0.215 g, 0.335 mmol, 34%): ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C) $\delta = 7.07$ (m, 10H, H(*aromatic*)), 6.81 (m, 15H, H(*aromatic*)), 3.85 (m, 2H, C_5H_4), 3.75 (m, 2H, C_5H_4), 3.71 (s, 5H, C_5H_5); ^{13}C NMR (CD_2Cl_2, 125 MHz, 25 °C) $\delta = 132.6$ (4C), 131.7 (4C), 131.5 (2C), 127.0 (4C), 126.7 (2C), 126.6 (4C), 126.1 (2C), 125.4 (1C), 125.3 (2C), 69.0 (2C, C_5H_4), 68.5 (5C, C_5H_5), 68.0 (2C, C_5H_4); LRMS (DEI) m/z (%) = 642 (64) [M$^+$], 577 (74) $[M - C_5H_5]^+$, 120 (100) $[M - C_6Ph_5(C_5H_5)]^+$, 55 (88); LRMS (DCI) m/z (%) = 643 (100) $[M + H]^+$, 577 (25). A sample suitable for structural determination by single-crystal X-ray diffraction was obtained by recrystallization from hexane/CH_2Cl_2.

$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4C_7Ph_6H)$, 8. 3-Ferrocenyl-2,4,5-triphenylcyclopentadienone, **4**, (0.049 g, 0.1 mmol) and 1,2,3-triphenylcyclopropene (0.027 g, 0.1 mmol) were combined in 5 mL of dry xylene. The reaction mixture was refluxed at approximately 170 °C in an atmosphere of N_2 for 48 h and then cooled to room temperature. Thereafter, the reaction flask was stored at −20 °C for 72 h, yielding red-orange crystals of **8**, which were isolated by filtration, washed with hexane (~5 mL), and dried in vacuo, mp >265 °C (0.045 g, 0.062 mmol, 62%): ^{1}H NMR (CD_2Cl_2, 500 MHz) $\delta = 7.97$ (d, 2H, $^3J = 8.2$ Hz, H(72A) and H(76A) (*ortho*)), 7.54 (t, 2H, $^3J = 8.0$ Hz, H(73A) and H(75A) (*meta*)), 7.43 (t, 1H, $^3J = 7.1$ Hz, H(74A) (*para*)), 7.39 (d, 2H, $^3J = 6.4$ Hz, H(62A) and H(66A) (*ortho*)), 7.20 (m, 3H, H(63A), H(65A) (*meta*) and H(64A) (*para*)), 7.15 (m, 3H, H(23A), H(25A) (*meta*) and H(24A) (*para*)), 6.90−7.10 (m, 5H, H(52A), H(56A) (*ortho*), H(53A), H(55A) (*meta*) and H(54A) (*para*)), 6.88 (m, 2H, H(22A) and H(26A) (*ortho*)), 6.71 (t, 1H, $^3J = 7.3$ Hz, H(44A) (*para*)), 6.64 (t, 2H, $^3J = 7.9$ Hz, H(43A) and H(45A) (*meta*), 6.55 (m, 3H, H(33A), H(35A) (*meta*) and H(34A) (*para*)), 6.31 (m, 2H, H(32A) and H(36A) (*ortho*)), 6.05 (d, 2H, $^3J = 7.3$ Hz, H(42A) and H(46A) (*ortho*)), 5.64 (s, 1H, sp^3-H (H(7A))), 3.88 (s, 5H, η^5-C_5H_5 (H(16A), H(17A), H(18A), H(19A), H(20A))), 3.90 (s, 1H, η^5-C_5H_4), 3.82 (s, 1H, η^5-C_5H_4), 3.78 (s, 1H, η^5-C_5H_4), 3.22 (s, 1H, η^5-C_5H_4); ^{13}C NMR (CD_2Cl_2, 125 MHz) $\delta = 144.2$, 143.7, 143.4, 141.4, 141.2, 140.8, 136.5 (C-*ipso* and C_7-ring), 131.7, 131.1, 131.0, 130.8, 130.7, 128.1, 127.7, 127.3, 127.2, 127.0, 126.6, 126.1, 125.8, 124.9, 124.6 (C-*ortho*, C-*meta*, C-*para*), 68.5 (η^5-C_5H_5, C(16-C(20)), 68.9, 68.5, 67.9, 67.8 (η^5-C_5H_4, C(11)−C(15)), 56.3 (sp^3-C, C(7));* LRMS (DEI) m/z (%) = 732 (75) [M$^+$]; LRMS (DCI) m/z (%) = 733 (100) $[M + H]^+$, 141 (86). Anal. Calcd for $C_{53}H_{40}Fe$ (732.70): C, 86.88; H, 5.50. Found: C, 87.00; H, 5.76. Single crystals suitable for X-ray diffraction studies were selected directly from the xylene solution. (**Note:* Definitive NMR assignment of phenyl rings 3 and 4 was not possible; it should be recognized that the chemical shift assignments could be interchanged.)

$[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4\text{-}C_7Ph_6H]^+[SbCl_6]^-$ 13. (η^5-C_5H_5)Fe-

---

(35) Prepared according to the procedure outlined in: Broadhead, G. D.; Osgerby, J. M.; Pauson, P. L. *J. Chem. Soc.* **1958**, 650.

(η^5-C_5H_4−C_7Ph_6H), **8** (0.073 g, 0.1 mmol), and triethyloxonium hexachloroantimonate (0.044 g, 0.1 mmol) were dissolved in freshly distilled CH_2Cl_2 (∼5 mL) and stirred under an atmosphere of N_2 at ambient temperature for 24 h. The reaction mixture was filtered, and from the filtrate dark blue-green crystals of **13** were isolated after several days of slow solvent evaporation at reduced temperatures; **13** decomposes on heating (0.026 g, 0.062 mmol, 24%). Crystals suitable for structural determination by single-crystal X-ray diffraction were carefully selected.

Crystallographic Data for (C_6Ph_5-C_5H_4)Fe(C_5H_5), (η^5-C_5H_5)Fe(η^5-C_5H_4-C_7Ph_6H, and [(η^5-C_5H_5)Fe(η^5-C_5H_4-C_7Ph_6H]$^+$[$SbCl_6$]$^-$. X-ray crystallographic data for **5**, **8**, and **13** were obtained from single-crystal samples, which were mounted on glass fibers. Data were collected using a P4 Siemens diffractometer, equipped with a Siemens SMART 1K charge-coupled device (CCD) area detector (employing the program SMART[36]) and a rotating anode utilizing graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The crystal-to-detector distance was 3.991 cm, and the data collection was carried out in 512 × 512 pixel mode, employing 2 × 2 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular settings of the strong reflections, collected by 4.5° scans in 15 frames over three different parts of reciprocal space (45 frames total). One complete hemisphere of data was collected, to better than 0.8 Å resolution. Upon completion of the data collection, the first 50 frames were re-collected in order to improve the decay analysis. Processing was carried out by use of the program SAINT,[37] which applied Lorentz and polarization corrections to three dimensionally integrated diffraction spots. The program SADABS[38] was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The structures were solved by use of the direct method (procedure outlined in the Siemens SHELXTL program library[39]) followed by full-matrix least-squares refinement on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the atoms to which they were bonded. (For cell parameters and intensity collection refer to Table 1).

Acknowledgment. Financial support from NSERC Canada and from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. S.B. thanks the Government of Ontario and the NSERC for graduate fellowships.

Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **5**, **8**, and **13** (25 pages). Ordering information is given on any current masthead page.

OM980645W

---

(36) *SMART, Release 4.05*; Siemens Energy and Automation Inc., Madison, WI 53719, 1996.

(37) *SAINT, Release 4.05*; Siemens Energy and Automation Inc., Madison, WI 53719, 1996.

(38) Sheldrick, G. M. *SADABS (Siemens Area Detector Absorption Corrections)*; Siemens Energy and Automation, Madison, WI, 1996.

(39) Sheldrick, G. M. *SHELXTL, Version 5.03;* Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.