Organometallics 1994, 13, 690–697

Ionization of (η^6-Diphenylmethane)(η^5-cyclopentadienyl)iron Cations in H_2O–Me_2SO and Methanol–Me_2SO Mixtures: A Kinetic, NMR, and EHMO Study

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Received July 29, 1993[⊗]

Rates of proton abstraction from the diphenylmethanes $[(PhCH_2Ph)FeCp]^+$, **8**, and $[(PhCH_2Ph)(FeCp)_2]^{2+}$, **9**, by OH^- and CH_3O^- and of reprotonation of the conjugate carbon bases (C-**8**, C-**9**) by the solvent have been measured at 25 °C in various aqueous and methanolic dimethyl sulfoxide solutions. From these data, the pK_a values of **8** and **9** in these mixtures have been determined. Comparison of the results obtained with those for 4-nitro- and (4,4′-dinitrodiphenyl)methanes (**5** and **6**) shows that the thermodynamic acidifying influence of a $FeCp^+$ moiety is similar to that of a p-NO_2 group. The kinetic effects of the two substituents are different, however, the $FeCp^+$ compounds having greater rates of proton abstraction but the nitro compounds giving carbanions with a lower susceptibility to reprotonation by the solvent. This indicates that the $FeCp^+$ group exerts a greater –I effect but a lower –M effect than the NO_2 group. A determination of the intrinsic reactivities of the various compounds confirms this conclusion, but it also shows clearly that the resonance effect of a $FeCp^+$ moiety is very substantial. ^1H and ^{13}C NMR data for the ionization of **8** and **9** provide additional evidence for this proposal, which is also supported by molecular orbital calculations at the extended Hückel level.

Introduction

π-Complexation with organotransition metal units is very commonly used to increase the electrophilic character of arenes which are not capable of reacting with basic reagents under normal conditions.[2–5] Activation by groups like $Cr(CO)_3$, $Mn(CO)_3^+$, (η^5-C_5H_5)Fe^+, or (η^5-C_5H_5)Ru^+ thus allows one to readily achieve nucleophilic aromatic displacements on unactivated aryl halides and related derivatives.[2–11] These groups have also proved to be very efficient in enhancing the acidity of benzylic hydrogen atoms, favoring the generation of carbanionic-type intermediates which can then react in situ as nucleophiles with various substrates to give a wide range of synthetic applications.[2–5,12–22]

So far, very few comprehensive studies have been carried out to quantify the activating effect of most transition metal–ligand residues used to increase the reactivity of otherwise inert arenes and heteroarenes.[2–5] Rate studies of a few S_NAr reactions have been reported which showed that the activation increases through the series: $Cr(CO)_3 < Mo(CO)_3 \ll \eta^5$-$C_5H_5Fe^+ < Mn(CO)_3^+$, with the effect of the $Cr(CO)_3$ group being comparable to that of a p-nitro group.[4,7] Recently, two kinetic and thermodynamic studies of the acidifying effect of the $Cr(CO)_3$ group upon the benzylic hydrogens of di- and triphenylmethanes **1**–**4** have been made.[23,24] These studies proved to be very informative concerning the mode of action of this π-bonded

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[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1993.

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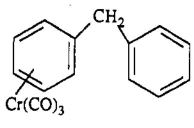

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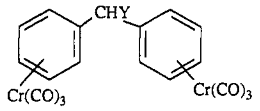
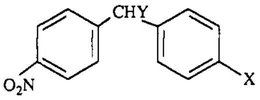




2 Y=H

3 Y=C_6H_5

4 Y=CN

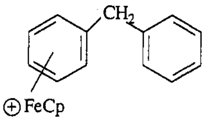
5 X=Y=H

6 X=NO_2, Y=H

7 X=NO_2, Y=C_6H_5

residue, especially because the intrinsic rate constants for the ionization of **1**–**4** could be estimated and compared to those for the ionization of the *p*-nitro substituted analogues **5**–**7**. It thus appeared that the activating influence of the $Cr(CO)_3$ group is the result of a combination of a strong inductive effect and a substantial resonance effect.

Despite its widespread use in the activation of arenes for synthetic purposes, the capability of the $FeCp^+$ group to promote proton transfers has not been quantitatively studied. In connection with our interest in the elucidation of the factors affecting carbon acid strengths and to provide direct comparisons with available data for compounds **1**–**7**,[25–28] we have measured the rates of proton abstraction from the two (η^6-diphenylmethane)(η^5-cyclopentadienyl)iron cations, **8** and **9**, by OH^- or CH_3O^- ions in some H_2O–Me_2SO and methanol–Me_2SO mixtures.[29] Where possible, measurements of the rates of reprotonation of the conjugate carbon bases by the solvent have also been made, allowing us to obtain both the kinetic and thermodynamic acidities of the substrates. Our results provide strong evidence that the $FeCp^+$ residue exerts a very strong inductive –I effect as well as a notable resonance effect. ^1H and ^{13}C NMR data pertaining to the ionization of **8** and **9** support this conclusion, which is also confirmed by molecular orbital calculations at the extended Hückel level.



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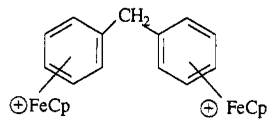

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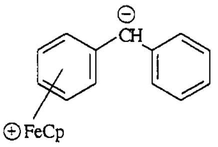
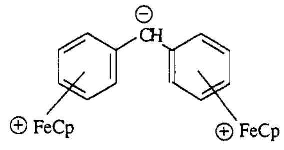


C-8



C-9

Results

Kinetic Studies. Rates of ionization of **8** and **9** by hydroxide or methoxide ions were measured in various aqueous or methanolic dimethyl sulfoxide solutions by monitoring spectrophotometrically the appearance of the absorption of the conjugated yellow or blue carbon bases **C-8** and **C-9** at or near λ_{max} = 375 nm, ϵ = 10 200 L mol^{-1} cm^{-1} for **C-8** in 10:90 (v/v) MeOH–Me_2SO and λ_{max} = 585 nm, ϵ = 6500 L mol^{-1} cm^{-1} for **C-9** in 15:85 (v/v) MeOH–Me_2SO. Experiments were carried out in a stopped flow apparatus, the rates being determined under pseudo-first-order conditions with a large excess of the base reagents (5×10^{-4} to 0.1 M) over the diphenylmethane concentration ($\approx 3 \times 10^{-5}$ M). Under these experimental conditions, the observed rate constant, k_{obsd}, for the approach to equilibrium according to eq 1 is simply given by eq 2.

$$\mathbf{8}\ (\text{or } \mathbf{9}) + RO^- \underset{k_{-p}^{ROH}}{\overset{k_p^{RO}}{\rightleftarrows}} \mathbf{C\text{-}8}\ (\text{or } \mathbf{C\text{-}9}) + ROH \qquad (1)$$

$$k_{obsd} = k_p^{RO}[RO^-] + k_{-p}^{ROH} \qquad (2)$$

In accordance with eq 2, plots of the measured k_{obsd} values versus the OH^- or CH_3O^- concentration were linear and, from the slopes, the values of the rate constants k_p^{RO} for deprotonation of **8** and **9** were readily determined in all solvent mixtures studied. Only when the intercepts had measurable values could the constants k_{-p}^{ROH} for reprotonation of the carbon bases **C-8** and **C-9** also be obtained. These rate constants are summarized in Table 1, together with the derived equilibrium constants, $K_p = k_p^{RO}/k_{-p}^{ROH}$, for the formation of **C-8** and **C-9**. Also given are the pK_a values for the ionization of **8** and **9** that we have calculated from the known autoprotolysis constants (pK_s) of the solvent mixtures by means of eq 3.[30]

$$pK_a = pK_s - \log K_p \qquad (3)$$

Table 1 includes some data for the ionization of the dideuterated cation **8** in 10:90 (v/v) and 5:95 (v/v) MeOH–DMSO mixtures. Assuming a secondary isotope effect of $\approx$1.15,[31] the results afford values of 13.32 and 8.64 for the primary isotope effects in 10:90 (v/v) and 5:95 (v/v) MeOH–DMSO mixtures, respectively. Such high values are common in the ionization of carbon acids,[32] confirming that our kinetic measurements refer to the proton abstraction processes.

In agreement with previous observations,[19] the carbon bases **C-8** and **C-9** are not stable species under aerobic conditions in solution. However, suitable experimental conditions could be found at low temperatures in THF and acetonitrile to carry out a structural study of the ionization of **8** and **9** by ^1H and ^{13}C NMR (see Experimental

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Table 1. Rate and Equilibrium Data for Proton Abstraction from the (η^6-Diphenylmethane)(η^5-cyclopentadienyl)iron Cations 8 and 9 in Aqueous and Methanolic Me_2SO Solution[a]

	cation **8**				cation **9**			
solvent composition (v/v)	k_p^{RO}, L mol^{-1} s^{-1}	k_{-p}^{ROH}, s^{-1}	K_p, L mol^{-1}	pK_a	k_p^{RO}, L mol^{-1} s^{-1}	k_{-p}^{ROH}, s^{-1}	K_p, L mol^{-1}	pK_a
30% H_2O–70% Me_2SO					550	74	7.43	17.15
20% H_2O–80% Me_2SO					2990	14	214	17.84
15% H_2O–85% Me_2SO					17000	8	2125	
10% H_2O–90% Me_2SO	81	1.3	62.3	20.56	1.2×10^5		$>5 \times 10^4$	<17.66
5% H_2O–95% Me_2SO	760	0.5	1520					
40% MeOH–60% Me_2SO					653	110	5.93	17.49
30% MeOH–70% Me_2SO					3300	53	62.5	17.14
20% MeOH–80% Me_2SO					17800	14	1272	16.73
15% MeOH–85% Me_2SO					84200	5	16840	16.29
10% MeOH–90% Me_2SO	141 (9.2)[b]	12.9	11	20.25	2.2×10^5		$>2 \times 10^5$	<16
5% MeOH–95% Me_2SO	924 (93)[b]	2.3	402	20.12				
2% MeOH–98% Me_2SO	7700	0.11	7000					

[a] t = 25 °C; no constant ionic strength. [b] k_p^{RO} for proton abstraction from **8**-d_2.

Table 2. ^{1}H NMR Data for the Diphenylmethanes 8 and 9 and the Related Cyclohexadienyl Derivatives C-8 and C-9

compd	complexed ring protons	uncomplexed ring protons	C_p	H_α
8[a]	6.36 (s)	7.22 (m, 5H)	5.10 (s, 5H)	4.09 (s, 2H)
	6.29 (m)			
C-8[a]	5.91 (t, 1H, *para*)	7.10 (m, 4H)	4.32 (s, 5H)	4.71 (s, 1H)
	4.95 (t, 1H, *meta*)	6.78 (t, 1H)		
	4.78 (t, 1H, *meta*)			
	4.37 (d, 1H, *ortho*)			
	3.81 (d, 1H, *ortho*)			
9[b]	6.24 (s, 10H)		5.05 (s, 10H)	4.14 (s, 2H)
C-9[b]	5.82 (t, 2H, *para*)		4.61 (s, 10H)	4.18 (s, 1H)
	5.67 (t, 4H, *meta*)			
	5.43 (d, 4H, *ortho*)			

[a] THF-d_8 solution, t = 20 °C. [b] CD_3CN solution, t = 0 °C.

Table 3. ^{13}C NMR Data for the Diphenylmethanes 8 and 9 and the Related Cyclohexadienyl Derivatives C-8 and C-9

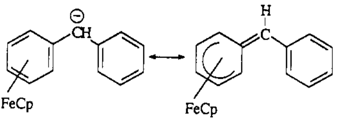
compd	complexed ring carbons	uncomplexed ring carbons	C_p	C_α
8[a]	108.79 (*ipso*)	141.73 (*ipso*)	79.79	42.73
	90.99 (*meta*)	131.47		
	90.55 (*ortho*)	131.42		
	89.55 (*para*)	129.57		
C-8[a]	130.22 (*ipso*)	142.25 (*ipso*)	73.37	97.01
	81.79 (*meta*)	128.39		
	81.33 (*meta*)	126.37		
	55.11 (*ortho*)	122.59		
	54.69 (*ortho*)			
	74.79 (*para*)			
9[b]	103.80 (*ipso*)		77.92	39.51
	88.87 (*ortho*)			
	88.75 (*meta*)			
	88.16 (*para*)			
C-9[b]	85.72 (*meta*)		75.78	82.55
	71.23 (*ortho*)			
	78.83 (*para*)			

[a] THF-d_8 solution, t = 20 °C. [b] CD_3CN solution, t = 0 °C.

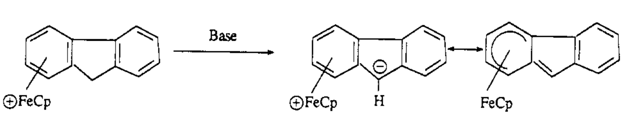
Section). The most pertinent data are summarized in Tables 2 and 3, respectively.

Discussion

Structure of the Carbon Bases C-8 and C-9. As can be seen in Tables 2 and 3, the resonances of the exocyclic atoms of the cation 8 suffer large downfield shifts upon ionization. The $\Delta\delta(H_\alpha)$ and $\Delta\delta(C_\alpha)$ values are 0.62 and 54.28 ppm, respectively; i.e. they are considerably larger than those reported for ionization of diphenylmethane ($\Delta\delta(H_\alpha)$ = 0.25; $\Delta\delta(C_\alpha)$ = 39 ppm).[33] Although such $\Delta\delta$ values are mainly the result of two opposing effects, namely a high-field shift caused by increased electron density at C_α and a low-field shift caused by the sp^3 → sp^2 rehybridization of this carbon,[34] the importance of the downfield variations suggests that the rehybridization factor is predominant. This implies a concomitant and important delocalization of the negative charge through the complexed ring and, therefore, an important contribution of the limiting cyclohexadienyl representation **R-8** to the structure of **C-8**. The finding of a $J_{C_\alpha H_\alpha}$ coupling constant of 153 Hz is entirely consistent with the olefin nature of C_α in **C-8**.[34] Similar extensive delocalization of a negative charge through activated phenyl rings was observed in studies of the ionization of various nitro-substituted and $Cr(CO)_3$-complexed diphenylmethanes[18,35] as well as in the ionization of the (η^5-cyclopentadienyl)(η^6-fluorenyl)iron cation **10**.[19a] In the latter case, Treichel and Johnson have reported $\Delta\delta(H_\alpha)$ and $\Delta\delta(C_\alpha)$ values of 1.7 and 49 ppm, respectively, upon formation of **C-10** from **10**.[19a]



C-8 R-8



10 C-10 R-10

That the canonical form **R-8** is important is further supported by the following observations: (1) with the exception of that for the *ipso* carbon, the resonances of the carbons of the coordinated ring move noticeably to high field upon ionization of 8 and the $\Delta\delta$(C) values are approximately 36, 15, and 9 ppm for the *ortho*, *para*, and *meta* carbons, respectively; (2) there is a concomitant upfield shift of the resonances of the protons of this ring ($\Delta\delta$(H) = 0.4–2.4) as well as of the proton and carbon resonances of the cyclopentadienyl ring ($\Delta\delta$(H) = 0.78; $\Delta\delta$(C) = 6.42); (3) there is a nonequivalence of the *ortho*, as well as of the *meta*, protons and carbons of the

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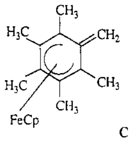
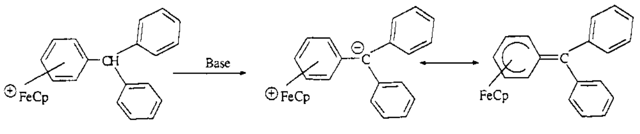
complexed ring of **C-8**. This last finding is clearly consistent with high double bond character of the C_{ipso}–C_α bond, as shown in structure **R-8**. In this regard, it is interesting to note that Astruc et al. have reported an X-ray structure of the benzylic species CpFe(η^5-C_6Me_5-CH_2) and found a C_{ipso}–C_α bond length of 1.376 Å, consistent with the olefin character of this linkage (structure **C-11**).[21] On the other hand, the absorption patterns mentioned above are similar to those for the formation of various π-cyclohexadienyl complexes which have been described previously. In particular, Helling and Hendrickson have studied the ionization of the triphenylmethane cation **12** and concluded that there is an especially high contribution of the limiting cyclohexadienyl form **R-12** to the structure of the conjugate species **C-12**.[20]

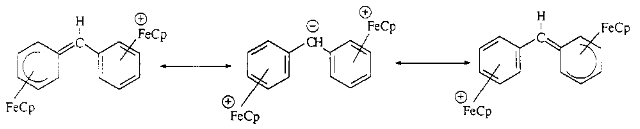


C-11



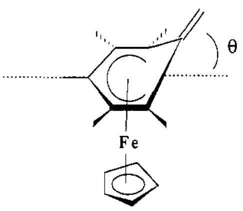
12   C-12   R-12

The ionization of the dication **9** results in somewhat different NMR absorption patterns, causing only a small downfield shift of the H_α resonance ($\Delta\delta(H_\alpha)$ = 0.04). Concomitantly, the move to low field of the C_α resonance is less than that observed upon ionization of **8**, but it remains typical for a marked $sp^3 \rightarrow sp^2$ rehybridization of this carbon ($\Delta\delta(C_\alpha)$ = 43.04). It is also noteworthy that the shieldings of the proton and carbon resonances of the arene and cyclopentadiene rings are reduced compared to the situation in the monocoordinated system. These results, together with the fact that both the ^1H and ^{13}C NMR spectra recorded at 0 °C indicate the equivalence of these rings in **C-9** suggest that the two limiting cyclohexadienyl representations **R-9** and **R-9′** contribute similarly to the delocalization of the negative charge but that the zwitterionic structure is by no means negligible. Statistically speaking, one can understand that the symmetrical repartition of the negative charge over the whole skeleton is consistent with an increased average electron density at the C_α carbon, accounting for the observation of a rather small downfield shift of the H_α resonance.

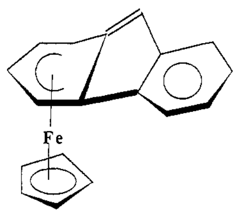


R-9   C-9   R-9′

Extended Hückel Molecular Orbital Studies. These NMR and kinetic data have been supplemented by molecular orbital calculations at the extended Hückel level. Initially, the neutral benzyl complex, $(C_5H_5)Fe$-$(C_6H_5{=}CH_2)$, was studied to ascertain the electronically most favorable geometry. Taking as our starting point the structural parameters reported by Astruc for the pentamethyl derivative $(C_5H_5)Fe(C_6Me_5{=}CH_2)$, **13**,[21] the planar vinylidene fragment was allowed to swivel out of the plane of the remaining five ring carbons.



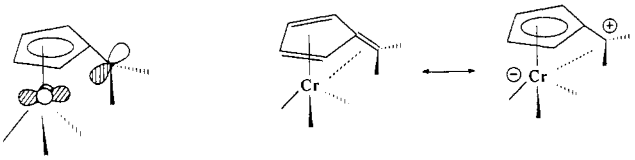
1 3



R-1 0

The minimum energy conformation is found when the CpFe unit is displaced by 0.15 Å toward the *para* carbon, and the dihedral angle, θ, made by the $C{=}CH_2$ moiety with the ring plane is 10°, a value in close accord with the X-ray crystallographic results obtained by Johnson and Treichel for the $CpFe^+$ and $Mn(CO)_3{}^+$ complexes of the fluorenide ligand.[19] One might suspect that the degree of bending in fluorenyl complexes might be constrained by the presence of the tricyclic system; in fact, the noncomplexed five- and six-membered rings essentially maintain their coplanarity as the molecule folds about the C(1)···C(4′) vector. In contrast, the angle θ reported by Astruc for $(C_5H_5)Fe(C_6Me_5{=}CH_2)$ is 32°.[21] We surmise, however, that there must be a considerable steric component since substitution of the phenyl ring hydrogens by methyls leads to an EHMO energy-minimized structure in which θ is 26°.

The electronic origin of this deformation is apparent and may be contrasted with the ferrocenylmethyl or Cr-$(CO)_3$-stabilized benzyl cations in which the vacant p_z orbital on the α-carbon interacts with a filled d orbital on the metal.[36] In these cases, the α-CH_2 group optimizes the orbital overlap by leaning toward the organometallic fragment by as much as 20°.[37] Similarly, in (fulvene)-$Cr(CO)_3$ systems, **14**, the exocyclic double bonded fragment bends markedly toward the metal.[38]



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However, in the (benzyl)FeCp systems discussed here, the p_z orbital at C_α is occupied and so the interaction with the filled orbital on the metal is destabilizing; hence, the methylene fragment folds *exo* to the organometallic group. Interestingly, we note that the X-ray crystal structure of $(C_6H_5NEt_2)Cr(CO)_3$, which is isoelectronic with the anion $[(C_6H_5CH_2)Cr(CO)_3]^-$, the cation $[(C_6H_5CH_2)Fe(CO)_3]^+$, or the neutral species $(C_6H_5CH_2)$FeCp, reveals not only that the diethylamino group is planar at nitrogen but also

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(36) (a) Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598. (b) Albright, T. A.; Hoffmann, R.; Hofmann, P. *Chem. Ber.* **1978**, *111*, 1591.

(37) (a) Downton, P. A.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1992**, *11*, 3281. (b) Acampore, M.; Ceccon, A.; Dal Farra, M.; Giacometti, G.; Rigatti, G. *J. Chem. Soc., Perkin Trans. 2* **1977**, 483. (c) Lupon, S.; Kapon, M.; Cais, M.; Herbstein, F. H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1025. (d) Behrens, U. *J. Organomet. Chem.* **1979**, *182*, 89.

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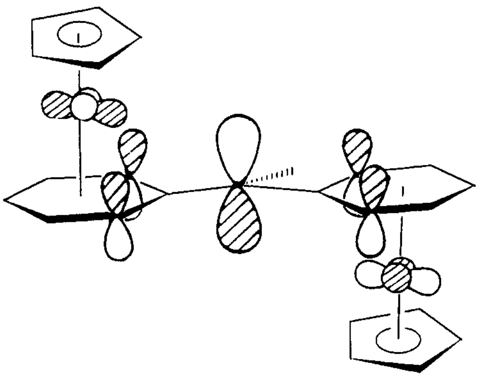

Figure 1. HOMO of $[(PhCH_2Ph)(FeCp)_2]^{2+}$, **9**, showing the out-of-phase character of the orbitals at the iron centers with that at C_α.

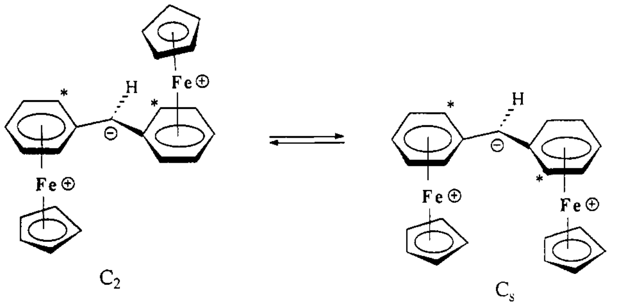

Figure 2. C_2 and C_s isomers of $[(PhCH_2Ph)(FeCp)_2]^{2+}$, **9**.

that the $C{=}NR_2$ is folded *exo* by 8.3°.[39] It is important to realize that delocalization of the negative charge at the α-position cannot occur by direct overlap with a metal orbital; rather there must be an interaction with a vacant orbital of the π-manifold of the carbocyclic ring.

Replacement of one benzylic hydrogen by a phenyl ring provides a model for structure **R-8**, and the EHMO approach finds an energy-minimized angle, θ, of 8°. Finally, incorporation of a second $CpFe^+$ moiety yields the cation **C-9**. In this latter case, the electronically favored structure is one in which the CpFe units are both folded away from the central carbon by 8°. The HOMO for **C-9**, shown in Figure 1, demonstrates clearly the out-of-phase character of p_z on the central carbon with the slightly reoriented $d_{x^2-y^2}$ orbitals on the iron atoms. Nevertheless, it is particularly noteworthy that only $\approx$2 kcal mol^{-1} is required for **C-9** to attain the conformation in which the anionic diphenylmethyl ligand is planar. Moreover, rotation of a complexed ring so as to interconvert the C_2 and C_s isomers of **C-9** (see Figure 2) has a calculated activation energy of $\approx$10 kcal mol^{-1}.

These values are directly relevant to the observed NMR spectra which exhibit only a single *ortho* or *meta* resonance in either the ^1H or ^{13}C domain. Clearly, on the NMR time scale, the molecule has an effective C_{2v} symmetry, suggesting that there is no strong multiple bond character in the C_α–C_{ipso} linkages. Overall, the molecular orbital picture of the cation $[CpFe(C_6H_5)]_2CH^+$, **C-9**, is one in which the charge is somewhat delocalized over both phenyl rings and is also transmitted via the iron atoms onto the cyclopentadienyl rings. To the extent that we choose to believe the charge distribution given by the EHMO calculations, the values found are +0.41 on each iron and −0.52 on the α-carbon atom.

This contrasts markedly with the neutral molecule **C-8** in which the diphenylmethyl anion is coordinated to a single $CpFe^+$ moiety. In this case, the Fe bears a positive charge of 0.39 while the α-carbon is negative to the tune of −0.48. Clearly, charge delocalization from the central carbon onto the single CpFe moiety is more pronounced than is the case for the analogous bis(CpFe) complex. The C_α–C_{ipso} linkage in **C-8** has considerable double bond character, and the barrier to rotation of the $(CpFe)C_6H_5$ unit about this bond is substantial. This view is buttressed by the NMR data which exhibit two *ortho* and two *meta* carbon resonances for the complexed ring, even at ambient temperature. In the absence of peak coalescence even between the *meta* carbons (at 81.79 and 81.33 ppm), the Gutowsky–Holm approximation[40] tells us that the rotation barrier about the C_α–C_{ipso} bond is at least 15 kcal mol^{-1} at 300 K, and probably much more! The EHMO-calculated charge on the cyclopentadienyl ring in **C-8** is +0.07; this compares with the value of +0.08 found for each Cp ring in $[CpFe(C_6H_5)]_2CH^+$, **C-9**. As mentioned already, the ^{13}C NMR shifts for the cyclopentadienyl rings in the mono(CpFe) complex, **8** (δ 79.79), and in its conjugate base, **C-8** (δ 73.37), differ by more than 6 ppm; in contrast, in the bis(cation), **9** (δ 77.92), and the corresponding monocationic system, **C-9** (δ 75.78), the shifts change much less upon deprotonation. These data may be correlated with the diminished charge delocalization onto each ring of the bis(Fe) system. Moreover, these observations are in accord with a study of a series of chromium sandwich compounds $(C_6F_nH_{6-n})Cr(C_6H_6)$ whereby the ^{13}C NMR shift of the C_6H_6 ring exhibited a linear progression to higher frequency (lower field) as one increased the number of electron-withdrawing fluoro substituents in the other ring.[41]

Kinetic and Thermodynamic Acidities of 8 and 9. Increasing the Me_2SO content of aqueous and methanolic solutions causes a large increase in the equilibrium constants K_p for the ionization of the carbon acids $[(PhCH_2Ph)FeCp]^+$, **8**, and $[(PhCH_2Ph)(FeCp)_2]^{2+}$, **9**, as in eq 1. This reflects both an increase in the rates of proton abstraction (k_p^{RO}) and a decrease in the rates of reprotonation of the conjugate basic species **C-8** and **C-9** by the solvent (k_{-p}^{ROH}). The increase in the k_p^{RO} values is similar to the one commonly found in the ionization of many carbon acids,[25,26,42] in accord with the idea that it results primarily from the progressive destabilization of OH^- and CH_3O^- ions by the dipolar aprotic solvent. The solvent effect on the reprotonation rates of **C-8** and **C-9** also appears to be comparable to that observed in the reprotonation of a number of negatively charged resonance stabilized carbon bases, including diphenylmethane carbanions. This result is noteworthy in view of the neutral and monocationic nature of the carbon bases **C-8** and **C-9**, respectively; however, it cannot be commented on further since solvent activity coefficients for the transfer of the various species from aqueous or methanolic solutions to DMSO rich solvents are not known.

The pK_a value for ionization of diphenylmethane has been only measured in Me_2SO,[43] but it has been noted

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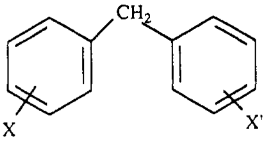
Table 4. Comparison of the Effects of the 4-NO_2, $Cr(CO)_3$, and $FeCp^+$ Substituents upon Diphenylmethane Reactivity[a]



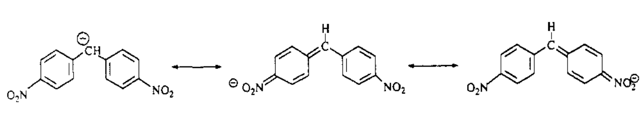
entry	solvent (v/v)	compd	X	X′	k_p, L mol^{-1} s^{-1}	k_{-p}^{ROH}, s^{-1}	K_p, L mol^{-1}	ref
1	5:95 H_2O–Me_2SO	**5**	4-NO_2		34.3	0.02	1715	*b*
2		**8**	$FeCp^+$		760	0.50	1520	*b*
3	5:95 MeOH–Me_2SO	**5**	4-NO_2		39.1	0.06	652	*b*
4		**8**	$FeCp^+$		924	2.30	402	*b*
5	2:98 MeOH–Me_2SO	**8**	$FeCp^+$		7700	0.11	7×10^4	*b*
6		**1**	$Cr(CO)_3$		810	1.2	675	*c*
7	30:70 H_2O–Me_2SO	**6**	4-NO_2	4′-NO_2	7.3	3.6×10^{-3}	2028	*d*
8		**9**	$FeCp^+$	$FeCp^+$	550	74	7.43	*b*
9	30:70 MeOH–Me_2SO	**6**	4-NO_2	4′-NO_2	33.1	0.13	255	*d*
10		**9**	$FeCp^+$	$FeCp^+$	3300	53	62.5	*b*
11	5:95 MeOH–Me_2SO	**6**	4-NO_2	4′-NO_2	3800			*d*
12		**9**	$FeCp^+$	$FeCp^+$	$\approx 10^6$	<1	$>10^6$	*b*
13		**2**	$Cr(CO)_3$	$Cr(CO)_3$	104.8	9.85	10.5	*c*

[a] t = 25 °C. [b] This work. [c] Reference 23. [d] References 25 and 26.

that the equilibrium acidity of nonactivated carbon acids with delocalized conjugate bases suffer relatively small variations on transfer from a dipolar aprotic to a protic solvent.[44] This makes it possible to use the pK_a value of 32, measured in Me_2SO by Bordwell,[43] as a reference to estimate the activating effect of the $FeCp^+$ group from the pK_a values measured for the ionization of 8 in 5% aqueous or methanolic solutions. Table 1 shows that the complexation of one phenyl ring by the cyclopentadienyliron moiety increases the thermodynamic acidity of diphenylmethane by about 12 pK units. Interestingly, this large acidifying effect is the same as that exerted by a *p*-nitro group but 100 times greater than that of a $Cr(CO)_3$ group.[23] Complexation of the second phenyl ring further increases the acidity ($\Delta pK_a \approx$ 3–4) but to a lesser extent than does a second *p*-nitro group ($\Delta pK_a \approx 5$).

An important result is that the similarity of the effects of the first $FeCp^+$ and *p*-NO_2 groups on the thermodynamic acidity of diphenylmethane is not the reflection of a similar influence of the two substituents on the rate parameters for the ionization of the CH_2 group. Table 4 (entries 1 and 2, or 3 and 4) actually shows that the rate of deprotonation of 8 by OH^- and CH_3O^- ions is 23-fold higher than that of the similarly acidic 4-nitro analogue **5**, indicating that the $FeCp^+$ group exerts a greater kinetic acidifying effect than the NO_2 group. This rate enhancing effect of $FeCp^+$ on k_p^{RO} is also seen in the rate constant k_{-p}^{ROH}: the reprotonation of the neutral species **C-8** is 25-fold and 38-fold more rapid than that of the (4-nitrophenyl)phenylmethyl carbanion **C-5** in aqueous and methanolic solutions, respectively. This suggests that the $FeCp^+$ group exerts a greater –I effect but that the *p*-nitro group has a greater capability to absorb the negative charge resulting from the breaking of the C–H bond. Comparison of the increases in the thermodynamic and kinetic acidities brought about by the introduction of a second $FeCp^+$ or *p*-NO_2 substituent further supports this idea. Entries 7 and 8, as well as 9 and 10, in Table 4 show that the rates of proton abstraction from the bis(CpFe) cation, **9**, are 75–100-fold higher than those for the bis(nitro) compound, **6**. In contrast, the (4,4′-dinitrodiphenyl)methyl carbanion, **C-6**, is 20 000 times less sensitive to reprotonation by the solvent than is the carbon base **C-9** in 30:70 (v/v) H_2O–Me_2SO.

Intrinsic Reactivities of 8 and 9. In the last decade, the notion of intrinsic reactivity in the Marcus sense[45] has proved to be very useful to assess and compare the reactivity of carbon acids, as well as to delineate the importance of resonance effects in ensuring the delocalization of the negative charge of the conjugate carbon bases.[24–28,46–53] This latter factor determines the extent of the structural and solvational reorganization associated with the ionization process and therefore governs the intrinsic reactivity of the carbon acid.[46,47] The greater is the importance of the resonance stabilization, the lower is the intrinsic reactivity. In this respect, it is of special interest that the strong capability of a NO_2 group to absorb a negative charge through its –M effect is responsible for the finding of especially low intrinsic reactivities for nitro-activated carbon acids.[47] The log values of the intrinsic rate constant k_0 (see definition below) are in most cases ≤2, including compounds with remote NO_2 groups which are suitably located for resonance delocalization of the negative charge in the carbanion. As a matter of fact, diphenylmethanes substituted by NO_2 groups in the *ortho* and *para* positions of the phenyl rings are representative examples of the latter category, in accord with the large potential for delocalization of the negative charge in carbanions such as **C-6**.[26–28,53]



C-6 R-6 R-6'

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For a reaction of a carbon acid (CH) with forward and reverse rate constants k_p^B, k_{-p}^{BH}, according to eq 4, the intrinsic rate constant (in the Marcus sense) is generally

$$\mathrm{CH} + \mathrm{B} \underset{k_{-p}^{BH}}{\overset{k_p^B}{\rightleftarrows}} \mathrm{C}^- + \mathrm{BH}^+ \qquad (4)$$

defined as $k_o = k_p^B = k_{-p}^{BH}$ for $\Delta G° = 0$ ($K_p = 1$) and determined by linear interpolation or extrapolation of Brønsted plots obtained from a study of the deprotonation of the acid by various bases B.[46,47] Thus, the relationship of eq 5 holds between k_o and any point on the Brønsted

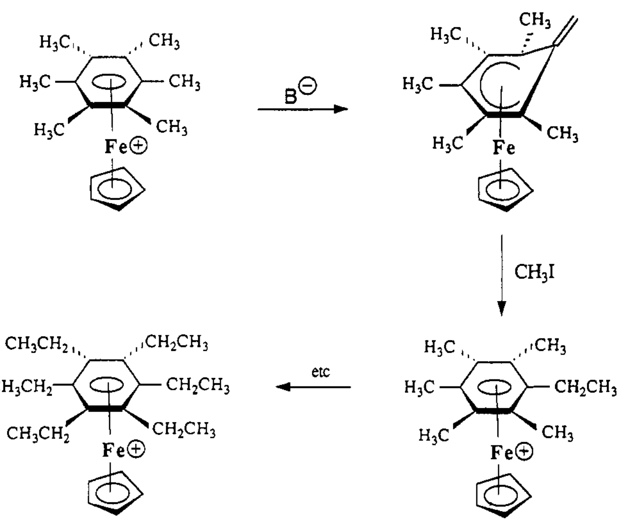
$$\log k_o = \log k_p^B - \beta_B \log K_p = \log k_{-p}^{BH} + \alpha_{BH} \log K_p \quad (5)$$

plot. In aqueous or methanolic solutions, structurally similar amines or weakly basic oxyanions are the commonly employed base catalysts to measure k_o values. In contrast, the use of strongly basic oxyanions like OH^- or CH_3O^- is not recommended because strong solvation considerably reduces their reactivity.[47] This situation is diagnosed by the observation that, in general, the points for these bases lie below the Brønsted lines drawn for other catalysts, with the deviations often being of the order of 2 log k units.[26-28,46,47,52]

In the present study, only the ionization of **8** and **9** by OH^- and CH_3O^- could be studied so that the requirements for an accurate determination of the intrinsic reactivities of these compounds are not met. It turns out, however, that the data of Table 4 can be appropriately manipulated out to provide interesting information on the k_o values of **8** and **9**. First, we note that the equilibrium constants for ionization of **8** and its p-nitro analogue **5** are essentially the same in 5:95 (v/v) H_2O–Me_2SO and MeOH–Me_2SO mixtures. Since there is considerable evidence that the β_B values for deprotonation of structurally related carbon acids of similar pK_a's are similar,[46,47] the difference in the log k_p values for the two compounds ($\Delta \log k_p \approx 1.30$) must give a fairly accurate measure of the difference in their intrinsic reactivities. It thus appears that the $FeCp^+$ derivative is about 20 times intrinsically more reactive than the nitro compound. Indeed, such a difference is not large, and it necessarily implies that the $FeCp^+$ substituent exerts an appreciable −M effect in addition to its −I effect.

Taking into account that most β_B values measured for the ionization of benzyl-type substrates in aqueous or methanolic Me_2SO solutions lie in the range 0.4–0.6,[26-28,54-56] one can proceed further by using a β_B value of 0.5 as a reference to correct for the thermodynamic driving force of the ionization reactions of **5** and **8**; thus one can estimate the log k_o values by means of eq 5. One thus obtains the following: log $k_o^5 = -0.07$, log $k_o^8 = 1.29$ in 5:95 (v/v) H_2O–Me_2SO; log $k_o^5 = 0.19$, log $k_o^8 = 1.66$ in 5:95 (v/v) MeOH–Me_2SO. In order to allow a comparison of these k_o values to those obtained with amines or weakly basic oxyanions they should be increased by ~2 log units to compensate for the reduced reactivity of OH^- and CH_3O^- mentioned above. Even after this correction the log k_o values remain in the range (log $k_o \leq 4$) typical for reactions that involve substantial structural–electronic–solvational reorganization. There is therefore no doubt that the $FeCp^+$ group exerts a substantial resonance effect.

Scheme 1. Successive Deprotonations and Methylations of $[(C_6Me_6)FeCp]^+$ To Give $[(C_6Et_6)FeCp]^+$



A similar treatment of the data for the ionization of **6** and **9** by OH^- and CH_3O^- affords the following estimates of the intrinsic rate constants: log $k_o^6 = -0.79$, log $k_o^9 = 2.30$ in 30:70 (v/v) H_2O–Me_2SO; log $k_o^6 = 0.32$, log $k_o^9 = 2.61$ in 30:70 (v/v) MeOH–Me_2SO. Again, such values can only be understood if the conjugated carbon bases are subject to some resonance stabilization. However, the higher k_o value for **9** compared to **6** confirms that the resonance effect of a $FeCp^+$ group is lower than that of a NO_2 group. Regarding the dinitro compound, it is worth noting that the estimated log k_o value is <1.3 (i.e. −0.79 + 2) in 30:70 (v/v) H_2O–Me_2SO. Such a value appears to be fairly consistent with our previous findings of log k_o values of 0 and 0.5 for ionization of (2,4,4′-trinitro- and (2,2′,4,4′-tetranitrodiphenyl)methanes by phenoxide ions, respectively, in 50:50 (v/v) H_2O–Me_2SO.[25,26] This consistency gives support to our previously mentioned comparison of the reactivities of **5** and **8**, or **6** and **9**.

Conclusions

The observation that the presence of a $CpFe^+$ substituent enhances the thermodynamic and kinetic acidities of benzyl protons, while yielding carbanions which are more susceptible to electrophilic attack than nitro-substituted carbanions, can be turned to synthetic advantage. Typically, as shown in Scheme 1, the preparation of $[(C_6Et_6)FeCp]^+$ from $[(C_6Me_6)FeCp]^+$ involves successive deprotonation of the series of $[(C_6Me_xEt_{6-x})FeCp]^+$ intermediates and rapid methylation of the intervening $[(C_6Me_yEt_{5-y}CH_2)FeCp]$ neutral species.[57]

Experimental Section

Materials. Samples of the cations **8** and **9** as hexafluorophosphate salts were kindly provided by Professor Sutherland.[27] Owing to their low stability under aerobic conditions and in basic

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media, the conjugated bases were prepared in situ for the NMR experiments, as follows.

C-8: **8** (0.129 g, 0.3 mmol) and potassium *tert*-butoxide (0.034 g, 0.3 mmol) were introduced in a Schlenk tube. The tube was purged with argon and cooled to −30 °C before 1 mL of THF-d_8 was added. The red solution of the base **C-8** thus obtained was filtered under argon in a NMR tube, and the tube was then sealed. Under these experimental conditions, the stability of **C-8** was sufficient to allow the recording of well-resolved ^{1}H and proton-decoupled ^{13}C spectra over the temperature range −50 to + 30 °C. In contrast, proton-coupled ^{13}C spectra which require longer acquisition times could be recorded only at −30 °C (Tables 2 and 3).

C-9: This purple base was generated from 0.140 g (0.2 mmol) of **9** and (0.028 g, 0.25 mmol) of ^{t}BuOK in the same way as its analogue **C-8**, except that acetonitrile-d_3 was used as the solvent. ^{1}H and proton-decoupled ^{13}C spectra were recorded up to 0 °C but, owing to the greater tendency of **C-9** than **C-8** toward decomposition in basic media, proton-coupled ^{13}C spectra could not be obtained (Tables 2 and 3).

(η^5-Cyclopentadienyl)(η^6-α,α-dideuteriodiphenylmethane)iron Hexafluorophosphate (8-d_2). Potassium *tert*-butoxide (0.284 g, 2.5 mmol) was added to a solution of 0.215 g (0.5 mmol) of **8** in 15 mL of THF under an argon atmosphere. After stirring for 30 min, D_2O (1 mL) was introduced into the solution. The stirring was maintained for 2 h until the solution began to turn yellow, at which point the solution was filtered and the solvent removed under vacuum. The resulting solid was washed with water and dissolved in acetone. After drying over magnesium sulfate, the solvent was evaporated to yield a yellow residue which was copiously washed with diethyl ether to yield $[(CpFe)PhCD_2Ph]^+[PF_6]^-$, (**8**-$d_2$) (0.20 g; 93%). ^{1}H NMR (250 MHz, acetone-d_6): δ 7.40 (s, Ph), 6.45 (s, Ph–Fe), 5.23 (s, Cp); n.b. there was no signal at 4.27 (CH_2). Mass spectrum (EI, 30 eV): m/z = 436 ($[M]^+$), 398 ($[M - 2F]^+$).

NMR and UV–Visible Measurements. NMR spectra were recorded on a Bruker AM 250 spectrometer equipped with an ASPECT 3000 computer. All chemical shifts are expressed in parts per million downfield from internal Me_4Si. UV–visible spectra were recorded in the various H_2O–Me_2SO and MeOH–Me_2SO mixtures studied by using concentrations of the parent diphenylmethanes and related carbon bases in the range (3–5) × 10^{-5} mol L^{-1}. A conventional Kontron-Uvikon spectrophotometer was used for the cations **8** and **9** while a Durrum stopped-flow spectrophotometer was employed for the unstable species **C-8** and **C-9**.

Kinetic Measurements. Stopped-flow determinations were performed on a Durrum stopped-flow spectrophotometer, the cell compartment of which was maintained at 25 ± 0.3 °C. All kinetic runs were carried out in triplicate under pseudo-first-order conditions with a substrate (**8** or **9**) concentration of approximately 3 × 10^{-5} mol L^{-1} and tetramethylammonium hydroxide or potassium methoxide concentrations in the range 5 × 10^{-4} to 0.1 mol L^{-1}. In any given experiment, the rates were found to be reproducible to ±2–3%.

Molecular orbital calculations were performed via the extended Hückel method using weighted H_{ij}'s;[58] calculations were carried out by use of the program CACAO.[59]

Acknowledgment. We are particularly pleased to thank Professor R. G. Sutherland (University of Saskatchewan, Canada) for his generous gift of the diphenylmethane derivatives. Financial support from the CNRS is gratefully acknowledged. M.J.M. thanks the University of Versailles for a Visiting Professorship.

OM930521D

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