

Thermodynamics of C–H Activation in Multiple Oxidation States:
Comparison of Benzylic C–H Acidities and C–H Bond Dissociation
Energies in the Isostructural 16–20-Electron Complexes
[Fe^x(η⁵-C₅R₅)(η⁶-arene)]ⁿ, x = 0–IV, R = H or Me, n = –1 to +3

Hernando A. Trujillo, Carmen M. Casado, Jaime Ruiz, and Didier Astruc*

Contribution from the Groupe de Chimie Supramoléculaire des Métaux de Transition, LCOO,
UMR CNRS 5802, Université Bordeaux I, 33405 Talence Cédex, France

Received November 30, 1998

Abstract: The pK_a of the 18-electron complexes [Fe(η⁵-C₅R₅)(η⁶-C₆Me₆)]PF₆ {**1a**[PF₆] (R = H) and **1b**[PF₆] (R = Me)} and [Fe(η⁵-C₅R₅)(η⁶-C₆H₅CHPh₂)]PF₆ {**1c**[PF₆]} have been determined by the direct method in DMSO using bases with known pK_a values and found to be 12–14 pK_a units lower than the pK_a of the free arenes, illustrating the electron-withdrawing character of the CpFe⁺ and Cp*Fe⁺ groups. Access to the pK_a values for 16-, 17-, 19-, and 20-electron iron-sandwich complexes of this type with various arene structures was available by means of thermodynamic diagrams using the standard redox potentials of the oxidation and reduction of the 18-electron cations **1**⁺ and the deprotonated complexes **2**. For instance, the pK_a of the 19-electron iron complex **1a** (43.5) is about the same as that of free C₆Me₆ (43–44) whereas that of **1b** is even slightly higher (46.4). The pK_as of the anionic 20-electron complexes **1a**[–] and **1b**[–] are 7 and 12 units, respectively, higher than that of C₆Me₆. The pK_as of **1**²⁺ are around –10, whereas those of **1a**³⁺ were estimated to be around –50. In summary, the pK_as were determined for the five isostructural oxidation states Fe^{IV} to Fe⁰, those of Fe^{IV} being more than 110 pK_a units lower than those of Fe⁰. The benzylic C–H bond dissociation energies (BDEs) of the 18-electron complexes have been determined by means of a thermodynamic cycle using the pK_a values and standard oxidation potentials of the deprotonated forms measured in DMSO. These BDE values are between 81 and 86 kcal/mol, i.e. approximately the same as that of the free arene. The benzylic C–H BDEs in the 19- and 20-electron complexes **1** and **1**[–] have been determined using other thermodynamic diagrams and are 20 kcal/mol lower than in the 18-electron complexes, indicating the ease of these H-atom abstraction reactions. This trend is well taken into account by the fact that the valence shells of the metals are one unit closer to 18 in the products resulting from H-atom abstraction than in the starting paramagnetic complexes. For the 17-electron complexes, the BDEs were estimated to be only between 47 and 51 kcal/mol. We propose this stabilization of the corresponding dicationic C–H activated species to be due to coordination of the exocyclic double bond reminiscent of the structure of ferrocenyl carbonium cations.

Introduction

Transition-metal-centered odd-electron species play a major role in organometallic mechanisms,¹ for instance in oxidative addition,² insertion,³ ligand substitution,⁴ carbenic polymeriza-

tion,⁵ redox catalysis,⁶ and electrocatalysis^{4d,7} and in materials science⁸ and biochemistry (co-enzyme B12 processes and models).⁹ One of the most important and thoroughly studied organometallic processes is the activation of C–H bonds.¹⁰ These reactions most often use 18-electron precursor complexes,¹⁰ although open-shell metal species in this field are currently found on the biological side.¹¹ With a few excep-

(1) (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978, p 1. (b) *Paramagnetic Species in Activation, Selectivity, Catalysis*; Chanon, M., Juliard, M., Poite, J.-C., Eds; Kluwer: Dordrecht, The Netherlands, 1989. (c) *Organometallic Radical Processes*; *J. Organomet. Chem. Library*; Trogler, W. C., Ed.; Elsevier: New York, 1990. (d) Kochi, J. K.; Bockman, T. M. *Adv. Organomet. Chem.* **1991**, *33*, 51. (e) Tyler, D. R. *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1988; Vol. 36, p 125. (f) Astruc, D. *Electron Transfer and Radical Processes in Transition Metal Chemistry*; VCH: New York, 1995.

(2) Osborn, J. A. In *Organotransition-Metal Chemistry*; Ishii, Y., Tsutsui, M., Eds.; Plenum: New York, 1978; p 69.

(3) (a) Magnuson, R. H.; Zulu, S. J.; Tsai, W. M.; Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6887. (b) Richeson, D. S.; Mitchel, J. F.; Theopold, K. H. *J. Am. Chem. Soc.* **1987**, *109*, 5868. (c) Donovan, B. T.; Geiger, W. E. *Organometallics* **1990**, *9*, 865. (d) Reference 1f, Chapters 5 and 6.

(4) (a) Taube, H. *Electron-Transfer Reactions of Complex Ions in Solution*; Academic Press: New York, 1970. (b) Feldberg, S. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1969; Vol. 3, p 199. (c) Pöe, A. J. *Pure Appl. Chem.* **1988**, *60*, 1209. (d) Kochi, J. K. *J. Organomet. Chem.* **1986**, *302*, 389. (e) Reference 1f, Chapters 5 and 6.

(5) (a) Delville, M.-H.; Astruc, D. *New J. Chem.* **1989**, *13*, 595. (b) Astruc, D. *Acc. Chem. Res.* **1991**, *24*, 36.

(6) (a) Savéant, J.-M. *Acc. Chem. Res.* **1980**, *13*, 323; **1993**, *26*, 455. (b) Andrieux, C. P.; Hapiot, P.; Savéant, J. M. *Chem. Rev.* **1990**, *90*, 323. (c) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135. (d) Steckhan, E. *Top. Curr. Chem.* **1987**, *142*, 1. (e) Collman, J. P.; Wagenknecht, P. S.; Hutchinson, J. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1620. (f) Reference 1f, Chapter 7.

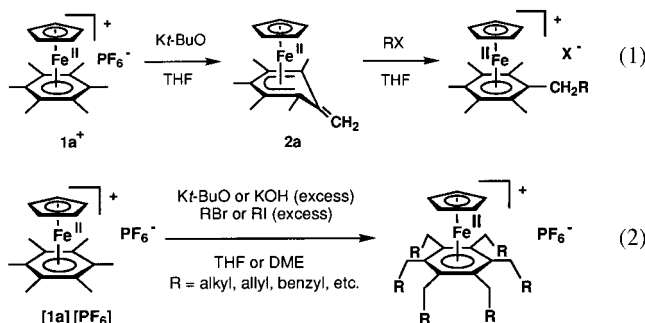
(7) (a) Chanon, M. *Acc. Chem. Res.* **1987**, *20*, 214. (b) Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 643. (c) Reference 1f, Chapter 6.

(8) (a) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993. (b) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201; *Acc. Chem. Res.* **1988**, *21*, 114; *Science* **1988**, *240*, 40.

(9) (a) Whitesides, T. H.; Shelly, J. H. *J. Organomet. Chem.* **1975**, *92*, 215. (b) Babior, B. M. *Acc. Chem. Res.* **1975**, *8*, 376. (c) Halpern, J. *Science* **1985**, *227*, 869. (d) Finke, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4820. (e) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley: New York, 1994; Chapter 16.

tions,^{10a,12} there is a remarkable paucity of data concerning the thermodynamic aspects of organometallic reactions in general and C–H activation reactions in particular.^{12c}

The benzylic C–H bonds can be easily activated by bases in the 18-electron complexes $[\text{Fe}^{\text{II}}\text{Cp}(\eta^6\text{-arene})][\text{PF}_6^-]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) and $[\text{Fe}^{\text{II}}\text{Cp}^*(\eta^6\text{-arene})][\text{PF}_6^-]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) or simply by contact with O_2 in the isostructural neutral 19-electron Fe^{I} complexes.^{13a} These C–H activation reactions are of great synthetic interest because they allow the formation of many C–element bonds by smooth reactions of a variety of electrophiles with the deprotonated species (eq 1). In particular, it is possible to synthesize useful dendritic cores in one pot by reactions with a base such as KOH or *Kt*-BuO and a carbon electrophile in excess as, for example, in eq 2.



The knowledge of thermodynamic data such as standard redox potentials, $\text{p}K_a$, and bond dissociation energy (BDE) values is of primary importance in the context of molecular engineering. For instance, high-yield syntheses of dendrons are required from functional organoiron complexes involving many steps in one-pot reactions. Moreover, the need for these data is not restricted to the classical Fe^{II} , 18-electron d^6 state but is extended to other oxidation states since the paramagnetic species involved have been shown to be intermediates in simple nucleophilic or electrophilic reactions of the 18-electron sandwich organoiron cations.^{13b}

A minority of 18-electron organometallic complexes such as ferrocene can give rise to more or less stable 17-electron species which can often be spectroscopically characterized, at least at

(10) (a) Bergman, R. G. *Science* **1995**, *270*, 1970. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (c) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006. (d) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (e) Stahl, S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961. (f) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987. (g) Lin, M.; Hogan, T.; Sen, A. *J. Am. Chem. Soc.* **1997**, *119*, 6048. (h) Shilov, A. E.; Shulpin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

(11) (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981; Chapter 8 (Biological Oxidations). (b) Shilov, A. E. *Metal Complexes in Biomimetic Chemical Reactions*; CRC Press: New York, 1996; Chapter 2. (c) Mansuy, D.; Battioni, P. In *Bioinorganic Catalysis*; Reedijk, J., Ed.; Dekker: New York, 1993; Chapter 12. (d) Que, L. *Prog. Inorg. Chem.* **1990**, *38*, 97.

(12) For pioneering thermodynamic aspects of organometallic chemistry, see: (a) Shriver, D. S. *Acc. Chem. Res.* **1970**, *3*, 231. (b) Connors, J. A. *Top. Curr. Chem.* **1977**, *71*, 71. (c) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (d) Marks, T. J. *Bonding Energetics in Organometallic Compounds*; ACS Symposium Series; American Chemical Society: Washington, DC, 1990; p 428. (e) Martinho Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

(13) (a) Astruc, D. *Top. Curr. Chem.* **1991**, *160*, 47; *New J. Chem.* **1992**, *16*, 305. (b) Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755. Michaud, P.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1982**, *104*, 3755. Michaud, P.; Lapinte, C.; Astruc, D. *Ann. N. Y. Acad. Sci.* **1983**, *415*, 97. Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 817. Madonik, A. M.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 2437. Madonik, A. M.; Mandon, D.; Michaud, P.; Lapinte, C.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 3381. Mandon, D.; Toupet, L.; Astruc, D. *J. Am. Chem. Soc.* **1986**, *108*, 1320. Review: Astruc, D. *Synlett* **1991**, 369.

low temperature.^{1e,f,14} On the other hand, true 19-electron species, i.e. with a metal-centered SOMO, are very rare.^{1e,f,15} In 1979, we reported the first thermally stable 19-electron complexes of these series, the key to thermal stability being the use of hexaalkylarene ligands. These complexes were named electron reservoirs^{16a,b} because the 19-electron complexes are very electron-rich (actually the most electron-rich neutral molecules known based on the very low values of their ionization potentials)^{16c} and the 18–19 electron interchange allows a variety of clean and efficient stoichiometric, redox catalytic, and electrocatalytic electron-transfer processes without decomposition of any form of the redox systems.^{13b,16b,17}

Since we have recently been able to also isolate the 17-electron complexes of this family (the most oxidizing thermally stable organometallic complexes known based on their redox potential values), the first triads of isostructural 17–18–19 electron complexes are available as stable (although very reactive) compounds in the $[\text{FeCp}^*(\eta^6\text{-arene})]^n$ series (arene = C_6Me_6 or $\text{C}_6\text{Me}_5\text{H}$, $n = -1$ to 2).¹⁸ The redox cascades of a large number of 18-electron iron compounds of this type and of their deprotonation products now allow the search for more thermodynamic data such as the BDEs spanning over four isostructural oxidation states from Fe^{III} to Fe^0 and the $\text{p}K_a$ s spanning over five oxidation states from Fe^{IV} to Fe^0 .

The first goal is the experimental determination of the standard redox potentials and the $\text{p}K_a$ s. Cyclic voltammetry¹⁹ is currently the ideal technique for the former, while $\text{p}K_a$ s have been determined by various methods. The direct method, which we have chosen, was first used by Norton to investigate the acidity of transition-metal hydride complexes,²⁰ then by Tilset,²¹ Theopold,²² and Bruno.²³ It consists of the addition of a known quantity of a base with strength similar to that of the compound under investigation to a solution of this compound, and the position of the equilibrium is spectroscopically determined. Knowing the position of the equilibrium, one may calculate the $\text{p}K_a$ of the analyte from the known $\text{p}K_a$ of the base used (Scheme 1).

(14) (a) Connelly, N.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 1. (b) Connelly, N. G. *Chem. Soc. Rev.* **1989**, *18*, 153. (c) Baird, M. *Chem. Rev.* **1988**, *88*, 1217.

(15) (a) Tyler, D. *Comments Inorg. Chem.* **1986**, *5*, 215. (b) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189.

(16) Astruc, D.; Hamon, J.-R.; Althoff, G.; Román, E.; Batail, P.; Michaud, P.; Mariot, J.-P.; Varret, F.; Cozak, D. *J. Am. Chem. Soc.* **1979**, *101*, 5445. (b) Astruc, D. *Acc. Chem. Res.* **1986**, *19*, 377. (c) Green, J. C.; Kelly, M. R.; Payne, M. P.; Seddon, E. A.; Astruc, D.; Hamon, J. R.; Michaud, P. *Organometallics* **1983**, *2*, 211.

(17) (a) Ruiz, J.; Lacoste, M.; Astruc, D. *J. Am. Chem. Soc.* **1990**, *112*, 5471. (b) Brown, D. S.; Delville, M.-H.; Vollhardt, K. P. C.; Astruc, D. *Organometallics* **1996**, *15*, 2360. (c) Alonso, E.; Ruiz, J.; Astruc, D. *J. Clust. Sci.* **1998**, *9*, 271. (d) Rigaut, S.; Delville, M.-H.; Astruc, D. *J. Am. Chem. Soc.* **1997**, *119*, 11132. (e) Rigaut, S.; Delville, M.-H.; Losada, J.; Astruc, D. To be published.

(18) (a) Ruiz, J.; Oligaro, F.; Saillard, J.-Y.; Hallet, J.-F.; Varret, F.; Astruc, D. *J. Am. Chem. Soc.* **1998**, *120*, 11693. (b) Oligaro, F. Ph.D. Thesis, University of Rennes 1, 1997.

(19) (a) Bard, A. J.; Faulkner, R. L. *Electrochemical Methods*; Wiley: New York, 1980. (b) Geiger, W. E. *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1985; Vol. 33, p 275. (c) Heinze, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 831; **1993**, *32*, 1268. (d) Reference 1f, Chapter 2.

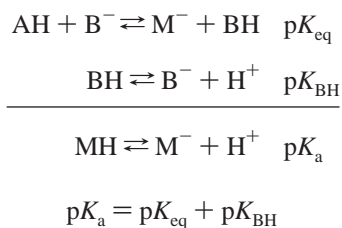
(20) (a) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (b) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257. (c) Kristjanddottir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983.

(21) Skagestad, V.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 5077.

(22) Protasiewicz, J. D.; Theopold, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 5559.

(23) Fermin, M. C.; Thiyagarajan, B.; Bruno, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 975.

Scheme 1



Hehre²⁴ calculated the C–H acidities of the complexes [Cr(η^6 -C₆F₆)(η^6 -C₆H_{6-n}Me_n)] by cyclotron resonance spectroscopy and deduced an enhancement of 16 pK_a units of the arenes in the gas phase upon coordination to the 12-electron Cr(η^6 -C₆F₆) fragment. The acidities of coordinated pyrroles have been calculated by conventional aqueous titration.²⁵ The ratio between the forward and backward rate constants of proton exchange has been used by several authors to calculate the pK_a.^{26–29} In particular, these kinetic data of proton exchange have been measured by Terrier et al.²⁸ in the case of mono- and binuclear metal complexes of diphenylmethane (including CpFe⁺-complexes) for DMSO/water and DMSO/methanol solvent mixtures. This technique allowed the determination by Terrier et al. of pK_a values between 20.12 and 20.56, indicating a 12 pK_a unit acidity enhancement on coordination of diphenylmethane to CpFe⁺ in [FeCp(η^6 -C₆H₅CH₂Ph)][PF₆] {**1d**[PF₆]}. These latter results are of interest in the context of our work³⁰ even if **1d**[PF₆] is considerably more acidic than the hexamethylbenzene complexes.

Direct measurement of BDEs is impractical, although Griller³¹ has calculated relative BDE values by determination of the equilibrium constants of “radical buffers” by double integration of EPR signals. Breslow’s seminal thermodynamic cycles were first used in the late 1960s to calculate the pK_a of triphenylenecyclopropene by comparison with triphenylmethane.³¹ They have been successfully followed by others, in particular by Arnett,³² Bordwell,³³ Griller,³⁴ and Parker³⁵ in organic chemistry and by Parker,³⁶ Tilset,³⁶ Morris,^{37a,b} Angelici,^{37c} Theopold,²² and Bruno^{37d} in inorganic and organometallic

(24) Hehre, W. J.; Bartmess, J. E.; Caldwell, G. *Organometallics* **1984**, *3*, 1740.

(25) Myers, W. H.; Koontz, J. I.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 5684.

(26) (a) Bernasconi, C. F. *Tetrahedron* **1985**, *41*, 3219. (b) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301; *Pure Appl. Chem.* **1982**, *54*, 2335.

(27) (a) Terrier, F.; Farrel, P. G.; Lelièvre, J.; Top, S.; Jaouen, G. *Organometallics* **1985**, *4*, 1291. (b) Bernasconi, C. F.; Terrier, F. *J. Am. Chem. Soc.* **1987**, *109*, 7115. (c) Bernasconi, C. F.; Bunnell, R. D.; Terrier, F. *J. Am. Chem. Soc.* **1988**, *110*, 6514.

(28) Terrier, F.; Vichard, D.; Chatrousse, A. P.; Top, S.; McGlinchey, M. J. *Organometallics* **1994**, *13*, 690.

(29) Editin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945.

(30) Trujillo, H. A.; Casado, C. M.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1995**, 7.

(31) (a) Breslow, R.; Balasubramanian, K. *J. Am. Chem. Soc.* **1969**, *91*, 5182. (b) Breslow, R.; Chu, W. *J. Am. Chem. Soc.* **1970**, *92*, 2165; **1973**, *95*, 411. (c) Breslow, R.; Mazur, S. *J. Am. Chem. Soc.* **1973**, *95*, 584. (d) Juan, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741 and references therein.

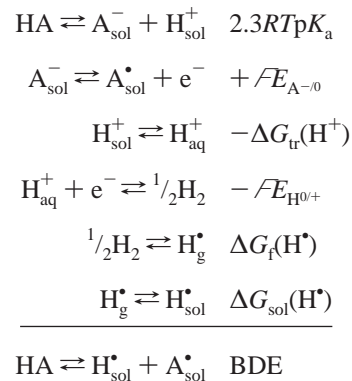
(32) (a) Arnett, D. M.; Harvey, N. G.; Amarnath, K.; Cheng, J.-P. *J. Am. Chem. Soc.* **1989**, *111*, 4143. (b) Arnett, E. M.; Flowers, R. A.; Ludwig, R. T.; Meckhof, A.; Walek, S. *Pure Appl. Chem.* **1995**, *67*, 729.

(33) (a) Bordwell, F. G.; Baush, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979. (b) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1989**, *111*, 1792. (c) Bordwell, F. G.; Cheng, J.-P.; Baush, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 2867 and 2872. (d) Bordwell, F. G.; Satish, A. V.; Zhang, S.; Zhang, X.-M. *Pure Appl. Chem.* **1995**, *67*, 735.

(34) (a) Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635. (b) Griller, D.; Simoes, J. A. M.; Mulder, P.; Sim, B. A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 7872.

chemistry. The calculation of the element-hydrogen BDEs has been achieved using such cycles which required measurement of the pK_a of the acid AH and the oxidation potential of the conjugated base A⁻ and estimation of the solvation, transfer, and formation energies of the hydrogen radical and the proton (Scheme 2).

Scheme 2



$$\begin{aligned} \text{BDE} &= 2.3RTpK_{\text{a}} - \mathcal{F}(E_{\text{H}^{0+}} - E_{\text{A}^{-0}}) - \Delta G_{\text{tr}}(\text{H}^+) + \\ &\quad \Delta G_{\text{f}}(\text{H}^{\bullet}) + \Delta G_{\text{sol}}(\text{H}^{\bullet}) \\ &= 2.3RTpK_{\text{a}} + \mathcal{F}E_{\text{A}^{-0}} + C \end{aligned}$$

A value of 73.5 ± 1 kcal/mol (307 ± 4 kJ/mol) for the constant C has been determined by Parker et al.^{35a} and we will use this value. Parker et al.^{35a} have introduced cycles based on isodesmic reactions, and the BDEs of metal–hydrogen bonds in 18-electron transition metal hydrides have been measured by Parker^{35,36} and Tilset^{36,37} using this technique. Zhang and Bordwell³⁸ have reported the determination of pK_as and BDEs of 18-electron complexes of fluorene coordinated to Cr(CO)₃, CpFe⁺, and Mn(CO)₃⁺, a study of which was simultaneous to our work.³⁰ The pK_a of [FeCp(η^6 -fluorene)][PF₆] {**1c**[PF₆]}. was found to be 14.6, a value 8.0 pK_a units lower than that of free fluorene, and the BDEs (80–81 kcal/mol; 334.4–338.6 kJ/mol) were independent of the organic or organometallic substituent.³⁷

A second class of thermodynamic cycle has been used to relate the pK_a or BDE for stable, neutral compounds with the same physical property of the radical cation (Schemes 3 and 4).

(35) (a) Parker, V.; Handoo, K. L.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 7493. (b) Parker, V. D.; Tilset, M.; Hammerich, O. *J. Am. Chem. Soc.* **1987**, *109*, 7905. (c) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1988**, *110*, 1649. (d) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287.

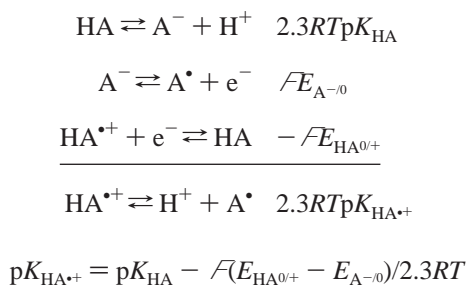
(36) (a) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711. (b) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2843. (c) Ryan, O.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618. (d) Ryan, O.; Tilset, M.; Parker, V. *Organometallics* **1991**, *10*, 298. (e) Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 9554. (f) Tilset, M. *J. Am. Chem. Soc.* **1992**, *114*, 2740. (g) Skagestad, V.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 5077. (h) Tilset, M.; Hamon, J.-R.; Hamon, P. *Chem. Commun.* **1998**, 765.

(37) (a) Capellani, E. P.; Drouin, S. D.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 3375. (b) Schlaf, M.; Lough, A. J.; Maltby, P. A.; Morris, M. H.; Morris, R. H. *Organometallics* **1996**, *15*, 2270. (c) Wang, D.; Angelici, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 936. (d) Kerr, M. E.; Zhang, X. M.; Bruno, J. W. *Organometallics* **1997**, *16*, 3249.

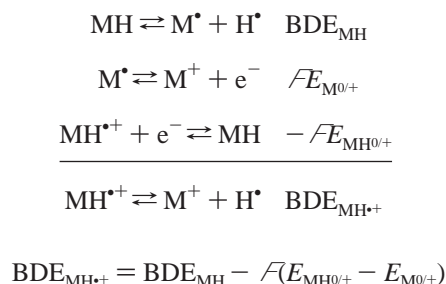
(38) (a) Zhang, X.-M.; Bordwell, F. G. *Organometallics* **1994**, *13*, 4251. (b) These authors used the “overlapping indicator method”, see: Bordwell, F. G.; Branca, J. C.; Hughes, D. L.; Olmstead, W. N. *J. Org. Chem.* **1980**, *45*, 3305.

(39) (a) Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165. (b) Okamoto, A.; Snow, M. S.; Arnold, D. R. *Tetrahedron* **1986**, *22*, 6175.

Scheme 3



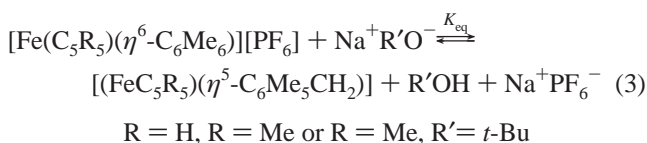
Scheme 4



First suggested by Arnold,³⁹ this method was used to obtain the pK_a values of the radical cations of several phenothiazine and fluorene derivatives. A related cycle was used by Parker and Tilstet^{35c} to link the pK_a s of dications to those of their cation radicals. Similarly, Tilstet^{37b} has obtained the BDEs of numerous transition-metal hydride radical cations from those of their neutral counterparts by a related cycle. Since we are searching the thermodynamic data in several oxidation states, we will take advantage of this type of cycle which does not need a constant.

Results

pK_a Studies of 18-Electron Complexes. The pK_a s of the complexes $[\text{Fe}(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-C}_6\text{Me}_6)][\text{PF}_6]$ **1a** [PF_6] (R = H), **1b** [PF_6] (R = Me) and $[\text{FeCp}(\eta^6\text{-C}_6\text{H}_5\text{CHPh}_2)][\text{PF}_6]$ **1c** [PF_6] were determined by direct observation of equilibrium 3



in DMSO by ¹H NMR or UV–vis spectroscopy. To make sure that the measurements were obtained at equilibrium, experiments were carried out by starting either from the compounds at the left or at the right of equilibrium 3, and identical values were obtained. To calculate the investigated pK_a (see Scheme 1), the pK_{eq} obtained from equilibrium 3 (see the Experimental Section) was added to the known pK_a values of R'OH and imidazole reported by Bordwell⁴¹ ($pK_a(\text{DMSO}) = 29.0$ for R' = Me, 32.2 for R' = *t*-Bu, and 18.6 for imidazole) and the results are presented in Table 1 together with those of the $E_{1/2}$ and BDE values.

Standard Redox Potentials. The standard redox potentials E° 's (noted E in the schemes) are determined by cyclic voltammetry and are considered to be equal to the $E_{1/2}$ values,

(40) (a) Astruc, D.; Hamon, J. R.; Roman, E.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 7502. (b) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758. (c) Solodovnikov, S. P.; Vol'kenau, N. A.; Kotova, L. S. *J. Organomet. Chem.* **1982**, *231*, 45.

(41) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

i.e. the average between the cathodic and anodic peaks potentials for reversible or partly reversible waves. Data are given in Table 1. For irreversible reductions or oxidations, we have found that the variation of the potential with scan rate is 30 mV for a 10-fold increase of scan rate, consistent with EC_{irrev} -type processes (not E_{irrev}). In these cases, the peak potential shifts vs E° have been analyzed by Parker et al.^{35a} (vide infra), who calculated the maximum error. In some other cases of extreme oxidation states, the E° value has been estimated by comparison with a closely related compound whose orbital diagram has been shown to be the same as that of the discussed compound and for which the desired E° value is known. This is the case of the influence of methyl groups on a ring, for instance, and this procedure by analogy has been shown to be correct using other cases where the E° values are known for two compared complexes. The estimated maximum error value has been considered to be larger in those cases, however (up to 100 mV). Details, also including the problem of solvents and references, are discussed below.

Reduction of the Complexes $[\text{FeCp}(\eta^6\text{-arene})][\text{PF}_6]$ and $[\text{FeCp}^*(\eta^6\text{-C}_6\text{Me}_6)][\text{PF}_6]$ **1b [PF_6].** Standard redox potentials have been measured for the first and second cathodic mono-electronic reductions of various salts of the 18-electron complexes of the $[\text{FeCp}(\eta^6\text{-arene})]^+$ family⁴⁷ and, in particular, for **1a** [PF_6] and **1b** [PF_6].^{16c,40a} However, no value was available in DMSO. Thus all the necessary $E_{1/2}$ values have been recorded by cyclic voltammetry again now using this solvent and ferrocene as the internal reference (see below, however, concerning this reference). When ferrocene was used as the internal reference, it could be verified that the following relationship holds true (eq 4):

$$E_{1/2}(\text{DMSO}) = E_{1/2}(\text{DMF}) + (-34 \pm 4 \text{ mV}) \quad (4)$$

The second reduction potential of **1b** has been calculated from that of **1a**, using the same shift (0.23 V) caused by the five methyl groups of Cp* on the two reduction potentials which involve the same e^* orbitals. All the data are reported in Table 1.

Oxidation of the Complexes $[\text{FeCp}(\eta^6\text{-C}_6\text{Me}_6)][\text{PF}_6]$ and $[\text{FeCp}^*(\eta^6\text{-C}_6\text{Me}_6)][\text{PF}_6]$ **1b [PF_6].** The oxidation potentials of the electrochemically and chemically reversible mono-electronic oxidations of **1a** [PF_6] and **1b** [PF_6] are now available in CH_2Cl_2 , MeCN, and SO_2 . These potentials are very positive, however, and measurements in DMSO would not be possible because DMSO is much more easily oxidized than these complexes. Thus, **1b** [SbCl_6]₂, which has been isolated as a pink crystalline solid, would oxidize DMSO. Nevertheless, the redox potentials determined in other solvents are not too different from one solvent to another. The difference between the redox

(42) (a) Deprotonation of **1b** [PF_6]^{40b,43} (as that of the ruthenium analogue)⁴⁴ occurs selectively on the arene ligand since this ligand, being even, is more acidic than the odd Cp* ligand. Nevertheless, deuteration of **1b** [PF_6] occurs completely on both rings upon refluxing **3b** (i.e., **3b**⁺, OD⁻) in D₂O.⁴⁵ Similarly, a crossover experiment between **3b** and **3b-d**₃₂ catalyzed by traces of **1b** [PF_6] gives complete scrambling on both rings⁴⁵ and deprotonation/alkylation of the Cp* ring, although minor, can also occur under forced conditions.⁴⁶

(43) Hamon, J.-R.; Astruc, D.; Román, E.; Batail, P.; Mayerle, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 2431.

(44) (a) Casado, C. M.; Wagner, T.; Astruc, D. *J. Organomet. Chem.* **1995**, *502*, 143. (b) Ruiz, J.; Astruc, D. Unpublished results.

(45) Hamon, J.-R.; Hamon, P.; Sinbandhit, S.; Guénot, P.; Astruc, D. *J. Organomet. Chem.* **1991**, *413*, 243.

(46) Hamon, J.-R.; Saillard, J.-Y.; Le Beuze, A.; McGlinchey, M. J.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 7549.

(47) (a) The first UV–vis spectra of $[\text{FeCp}(\text{arene})]^+$ salts were published by Hendrickson,^{43b} and UV–vis spectra of **1a** [PF_6], **1b** [PF_6], and **3a** in dimethoxyethane are also known.^{40a,b} (b) Morrison, W. J.; Ho, E. Y.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 500.

Table 1. Table of pK_a , $E_{1/2}$, and Benzylic C–H BDE Values (DMSO) Determined for the 16–20-Electron $[\text{Fe}(\text{C}_5\text{R}_5)(\text{arene})]$ Complexes **1**³⁺ to **1**[–] (Fe^{IV} to Fe^0), $E_{1/2}$ Values for the Deprotonated Fe^{II} Complexes **2**, and Comparison of the pK_a and BDE Values to Literature Values for the Free Arenes (Four Bottom Entries)

	$pK_a(\text{DMSO})^a$	$E_{1/2}(\text{reduction}) (\text{V vs Fc})^{a,b}$	$E_{1/2}(\text{oxidation}) (\text{V vs Fc})^{a,b}$	BDE ^{a,c} (C–H)
$[\text{Fe}^{\text{II}}\text{Cp}(\eta^6\text{-C}_6\text{Me}_6)]^+\text{PF}_6^-$ (1a ⁺) ^d	29.2 ± 0.2	–1.99 ± 0.01	+1.25 ± 0.03	86.5 ± 1.5 (362 ± 6)
$[\text{Fe}^{\text{II}}\text{Cp}^*(\eta^6\text{-C}_6\text{Me}_6)]^+\text{PF}_6^-$ (1b ⁺) ^d	31.4 ± 0.4	–2.22 ± 0.01	+1.03 ± 0.03	85.5 ± 2 (347 ± 8)
$[\text{Fe}^{\text{II}}\text{Cp}(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5)]^+\text{PF}_6^-$ (1b ⁺) ^f	20.0 ^g	–1.80 ± 0.01	+1.61 ± 0.03	84 ± 2 (347 ± 8)
$[\text{Fe}^{\text{II}}\text{Cp}(\eta^6\text{-C}_6\text{H}_5\text{CHPh}_2)]^+\text{PF}_6^-$ (1c ⁺)	18.2 ± 0.3	–1.74 ± 0.01	+1.61 ± 0.03	82.6 ± 2 (345 ± 8)
$[\text{Fe}^{\text{II}}\text{Cp}(\eta^6\text{-fluorene})]^+\text{PF}_6^-$ (1e ⁺) ^g	14.6 ^g	–1.77 ± 0.01	+1.49 ± 0.03	81 ± 2 (335 ± 8) ^g
$[\text{Fe}^{\text{II}}\text{Cp}(\eta^6\text{-C}_6\text{Me}_6)]$ (1a) ^d	43.5 ± 2.5	–2.77 ± 0.03	–1.99 ± 0.01	67.5 ± 1.5 (282 ± 6)
$[\text{Fe}^{\text{II}}\text{Cp}^*(\eta^6\text{-C}_6\text{Me}_6)]$, (1b) ^d	46.4 ± 2.5	–3.00 ± 0.05 ^k	–2.22 ± 0.01	65.1 ± 2 (272 ± 8)
$[\text{Fe}^{\text{I}}\text{Cp}(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5)]$ (1d)	32.9 ± 2.5	–2.55 ± 0.05	–1.80 ± 0.01	59.4 ± 1.5 (248 ± 6)
$[\text{Fe}^{\text{I}}\text{Cp}(\eta^6\text{-C}_6\text{H}_5\text{CHPh}_2)]$ (1c)	32.5 ± 2.5	–2.56 ± 0.05 ^e	–1.74 ± 0.01	58 ± 1.5 (242 ± 6)
$[\text{Fe}^{\text{I}}\text{Cp}(\eta^6\text{-fluorene})]$ (1e)	23.9 ± 2.5	–2.69 ± 0.05	–1.77 ± 0.01	52.6 ± 1.5 (220 ± 6)
$[\text{Fe}^0\text{Cp}(\eta^6\text{-C}_6\text{Me}_6)]^-$ (1a [–])	61.4 ± 4		–2.77 ± 0.03	68.2 ± 2 (285 ± 8)
$[\text{Fe}^0\text{Cp}^*(\eta^6\text{-C}_6\text{Me}_6)]^-$ (1b [–])	61.4 ± 4		–3.00 ± 0.05	67.5 ± 2 (282 ± 8)
$[\text{Fe}^0\text{Cp}(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5)]^-$ (1d [–])	46.2 ± 4		–2.55 ± 0.05	59.6 ± 2 (249 ± 8)
$[\text{Fe}^0\text{Cp}(\eta^6\text{-C}_6\text{H}_5\text{CHPh}_2)]^-$ (1c [–])	46.5 ± 3		–2.56 ± 0.05	59.3 ± 2 (248 ± 8)
$[\text{Fe}^0\text{Cp}(\eta^6\text{-fluorene})]^-$ (1e [–])	32.8 ± 4		–2.69 ± 0.05	44.1 ± 2 (184 ± 8)
$[\text{Fe}^{\text{III}}\text{Cp}(\eta^6\text{-C}_6\text{Me}_6)]^2$ (1a ²⁺)	–11.6 ± 3	+1.25 ± 0.03	+2.83 ± 0.10 ^l	48.2 ± 3 (202 ± 12) ⁿ
$[\text{Fe}^{\text{III}}\text{Cp}^*(\eta^6\text{-C}_6\text{Me}_6)]^2$ (1b ²⁺)	–8.5 ± 3	+1.03 ± 0.03	+2.61 ± 0.10 ^l	48.1 ± 3 (201 ± 12) ⁿ
$[\text{Fe}^{\text{III}}\text{Cp}(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5)]^2$ (1d ²⁺)	–18.5 ± 3	+1.61 ± 0.03	+3.19 ± 0.10 ^l	48.5 ± 3 (203 ± 12) ⁿ
$[\text{Fe}^{\text{III}}\text{Cp}(\eta^6\text{-C}_6\text{H}_5\text{CHPh}_2)]^2$ (1c ²⁺)	–19.1 ± 3	+1.61 ± 0.03	+3.19 ± 0.10 ^l	47 ± 3 (197 ± 12) ⁿ
$[\text{Fe}^{\text{III}}\text{Cp}(\eta^6\text{-fluorene})]^2$ (1e ²⁺)	–20.0 ± 3	+1.49 ± 0.01	+3.07 ± 0.10 ^l	51 ± 3 (213 ± 12) ⁿ
$[\text{Fe}^{\text{IV}}\text{Cp}(\eta^6\text{-C}_6\text{Me}_6)]^3$ (1a ³⁺)	–53.7 ± 4	+2.83 ± 0.10 ^l		
$[\text{Fe}^{\text{IV}}\text{Cp}^*(\eta^6\text{-C}_6\text{Me}_6)]^3$ (1b ³⁺)	–50.5 ± 4	+2.61 ± 0.10 ^l		
$[\text{Fe}^{\text{IV}}\text{Cp}(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{Ph})]^3$ (1d ³⁺)	–71.5 ± 4	+3.19 ± 0.10 ^l		
$[\text{Fe}^{\text{IV}}\text{Cp}(\eta^6\text{-C}_6\text{H}_5\text{CHPh}_2)]^3$ (1c ³⁺)	–72 ± 4	+3.19 ± 0.10 ^l		
$[\text{Fe}^{\text{IV}}\text{Cp}(\eta^6\text{-fluorene})]^3$ (1e ³⁺)	–68.6 ± 4	3.07 ± 0.10 ^l		
$[\text{Fe}^{\text{II}}\text{Cp}(\eta^5\text{-C}_6\text{Me}_5\text{CH}_2)]$ (2a) ^d		–2.80 ± 0.05	–1.16 ± 0.01 ^e	
		–3.58 ± 0.15 ^o	–0.41 ± 0.10 ^m	
$[\text{Fe}^{\text{II}}\text{Cp}^*(\eta^5\text{-C}_6\text{Me}_5\text{CH}_2)]$ (2b) ^d		–3.11 ± 0.05	–1.34 ± 0.10 ^e	
		–3.89 ± 0.15 ^o	–0.59 ± 0.10 ^m	
$[\text{Fe}^{\text{II}}\text{Cp}(\eta^5\text{-C}_6\text{H}_5\text{CHC}_6\text{H}_5)]$ (2d)		–2.56 ± 0.05 ^e	–0.67 ± 0.10 ^e	
		–3.31 ± 0.15 ^o	+0.05 ± 0.10 ^m	
$[\text{Fe}^{\text{II}}\text{Cp}(\eta^5\text{-C}_6\text{H}_5\text{CPh}_2)]$ (2c)		–2.61 ± 0.05 ^e	–0.68 ± 0.01	
		–3.43 ± 0.15 ^o	+0.07 ± 0.10 ^m	
$[\text{Fe}^{\text{II}}\text{Cp}(\text{fluorenyl})]$ (2e)		–2.32 ± 0.05 ^e	–0.56 ± 0.01 ^{e,g}	
		–3.24 ± 0.15 ^o	+0.19 ± 0.10 ^m	
$\text{C}_6\text{H}_5\text{CH}_3$	43 ^h			87–90 (364–376) ⁱ
$\text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5$	32.25 ^h			84 ± 2 (351 ± 8) ^j
$(\text{C}_6\text{H}_5)_3\text{CH}$	30.6 ^h			81 ^j
fluorene	22.6 ^h			80 (335) ^g

^a All the measurements were done at 20 °C in DMSO; in this solvent, the pK_a values of imidazole, MeOH, *t*-BuOH, MeCN, and DMSO are respectively 18.6, 29.0, 32.2, 31.3, and 33.5, from ref 41. ^b $E_{1/2}$ values of reversible waves (closely approximating the thermodynamic potential E°) were determined versus the ferrocene–ferricinium redox potential as the average of the anodic and cathodic peaks of the cyclic voltammograms in DMSO + [*n*-Bu₄N][PF₆] 0.1 M/Pt. Unless otherwise noted, ^c the waves are reversible, thus the uncertainty on E° is very weak (± 0.01 V). ^d BDE in kcal mol^{–1} (kJ mol^{–1}). ^e For $E_{1/2}$ in other solvents, see refs 16c and 40b. ^f Peak potential of an irreversible wave ($E_{\text{peak}} \neq E^\circ$); to minimize the error in the determination of E° in the calculation of the BDE, a 0.10 V correction ($\Delta E = E_{\text{peak}} - E^\circ$) was applied to the recorded E_{peak} to give the estimated E° value. This correction corresponds to a kinetic peak potential shift for an EC mechanism with a pseudo-first-order reaction between the solvent and the radical substrate with a rate constant equal to 10⁴ s^{–1}. For discussion of the uncertainties related to such follow-up reactions, see text and ref 35a. ^g Reference 28. ^h Lit. 80, see ref 38a. ⁱ Reference 41. ^j Reference 60 and Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1994**, *116*, 4251. ^k Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 1229. ^l Calculated from the value for **1** and the difference between the reduction potentials of **1**⁺ and **1**²⁺. ^m Calculated from the oxidation potentials of **1**⁺ by adding 1.58 V, i.e. the difference between the first and second oxidation potentials of [FeCp*₂]: Sharp, P. R.; Bard, A. J. *Inorg. Chem.* **1983**, *22*, 2689. Bard, A. J.; Garcia, E.; Kukhareenko, S.; Strelets, V. V. *Inorg. Chem.* **1993**, *32*, 3528. ⁿ Calculated by adding the difference between the first and second oxidation potential of **2c** (0.75 V) to the first oxidation potential of **2**. ^o Estimated value using the second oxidation potential of **1** and **2** calculated according to *l* and *m*. ^p Estimated value obtained by addition of the difference between the two reduction potentials of **1**⁺ to the first reduction potential of **2**.

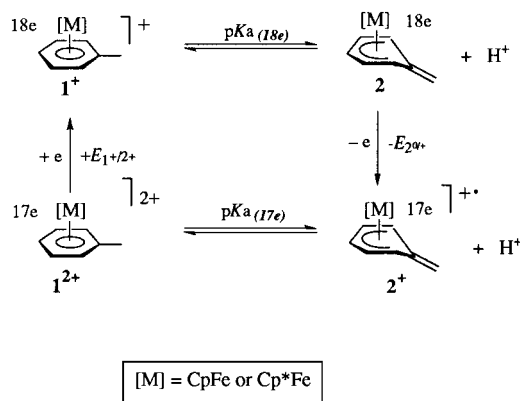
potentials in different solvents arises because ferrocene was the reference, and the interaction energies of various solvents with ferricinium are significantly different from one another. In other words, ferrocene is not a very good reference if one wishes to be accurate, because the cationic iron center is not well-protected from the solvent molecules in ferricinium. Recently, we have shown that solvent influences were much weaker in permethylated transition-metal sandwiches such as **1b**[PF₆] than in ferrocene because the metal center is well-protected by the shell of methyl groups. In fact, the redox potentials of **1b**[PF₆] are

(48) (a) Dessy, R. E.; Sary, F. E.; King, R. B.; Waldrop, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 471. (b) Nesmeyanov, A. N.; Denisovitch, L. I.; Gubin, S. P.; Vol'kenau, N. A.; Sirotkina, F. I.; Bolesova, I. N. *J. Organomet. Chem.* **1969**, *20*, 169. (c) For a review, see ref 14b.

independent of the solvent if decamethylferrocene or decamethylcobaltocene is taken as a reference.⁴⁹ We conclude that the redox potentials of **1b**[PF₆] may be recorded and further used without correction for thermodynamic calculations in any solvents (we will use values recorded in MeCN) and that the redox potentials of **1a**[PF₆] can be used in the same way in a relatively good approximation. The oxidation potentials of **1c**[PF₆] and of the CpFe⁺ complexes of diphenylmethane and fluorene have now also been recorded in SO₂ and are used without correction. Solvent effects, weak in SO₂, would have been more significant in DMSO for the fluorene and diphenylmethane complexes (although not larger than with ferrocene).

(49) Ruiz, J.; Astruc, D. *C. R. Acad. Sci., Ser. II: Chim.* **1998**, *1*, 21.

Scheme 5



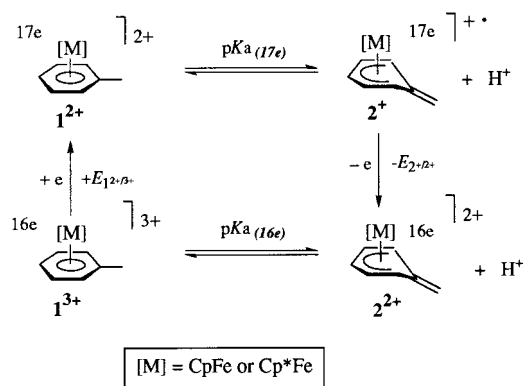
$$\begin{aligned} pK_a(\mathbf{1a}^{2+}) &= pK_a(\mathbf{1a}^+) - \mathcal{F}(E_{\mathbf{1a}^{1+/2+}}^\circ - E_{\mathbf{2a}^{0/+}}^\circ)/2.303RT \\ &= pK_a(\mathbf{1a}^+) - 16.89(E_{\mathbf{1a}^{1+/2+}}^\circ - E_{\mathbf{2a}^{0/+}}^\circ) = \\ &\quad 29.2 - 16.89(1.165 + 1.250) = -11.6 \\ pK_a(\mathbf{1b}^{2+}) &= pK_a(\mathbf{1b}^+) - 16.89(E_{\mathbf{1b}^{1+/2+}}^\circ - E_{\mathbf{2b}^{0/+}}^\circ) = \\ &\quad 31.4 - 16.89(1.03 + 1.34) = -8.46 \end{aligned}$$

The second oxidation potentials of the complexes $\mathbf{1}^+$ are not directly accessible experimentally, but Bard's group has measured the second oxidation potentials of ferrocene and decamethylferrocene, which are isoelectronic to $\mathbf{1}^+$. That the same orbitals are involved for the oxidation of $\mathbf{1}^+$ and ferrocene or decamethylferrocene has been confirmed recently by accurate DFT calculations.¹⁸ Thus, it is possible to obtain a fairly good estimation of the second oxidation potential of $\mathbf{1}^+$ from the second oxidation potentials of ferrocene or decamethylferrocene measured by Bard et al. The difference in the oxidation potentials of $\mathbf{1a}^+$, $\mathbf{1b}^+$, $[\text{FeCp}_2]$, and $[\text{FeCp}^*_2]$ is only due to the electrostatic factor and to the number of methyl groups. We can assume that the differences among the oxidation potentials of these four complexes are the same for the first and second oxidation potentials. This assumption leads to second oxidation potentials of $E_{\mathbf{1a}^{2+/3+}}^\circ = 2.83 \pm 0.10$ V vs FeCp_2 and $E_{\mathbf{1b}^{2+/3+}}^\circ = 2.63 \pm 0.10$ V vs FeCp_2 .

[FeCp($\eta^5\text{-C}_6\text{Me}_5\text{=CH}_2$)] (2a) and [FeCp*($\eta^5\text{-C}_6\text{Me}_5\text{=CH}_2$)] (2b). The oxidation and reduction potentials of the deprotonated complexes **2a,b** were also recorded. Both the oxidation on Pt anode and the reduction on Hg or Pt cathodes are chemically totally irreversible in various solvents even at -40 °C. The standard redox potential is different from the potential of an irreversible wave measured by cyclic voltammetry. This potential shift depends on the mechanism and the reaction rate of the chemical reaction following the primary heterogeneous electron transfer. For a pseudo-first-order reaction between the solvent and the generated radical anion, Parker et al.^{35a} calculated a shift of 50 mV for a reaction rate of 10^2 s⁻¹. Since an EPR spectrum of the radical anion of **3a** could be recorded,^{40c} we assume that the follow-up reaction is not exceedingly fast and, as an approximation, we use this correction of 0.05 V for values measured in DMSO.⁵⁰

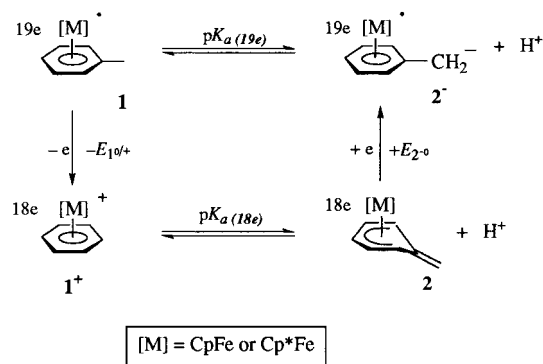
The lack of reversibility of the anodic oxidation of the deprotonated complexes prevented us from measuring a reliable second oxidation potential. Therefore we examined **2c** in which the triphenylmethane ligand was susceptible to sterically stabilize

Scheme 6



$$\begin{aligned} pK_a(\mathbf{1a}^{3+}) &= pK_a(\mathbf{1a}^{2+}) - \mathcal{F}(E_{\mathbf{1a}^{2+/3+}}^\circ - E_{\mathbf{2a}^{1+/2+}}^\circ)/2.303RT \\ &= -11.6 - 16.89(2.83 - 0.34) = -53.7 \\ pK_a(\mathbf{1b}^{3+}) &= pK_a(\mathbf{1b}^{2+}) - \mathcal{F}(E_{\mathbf{1b}^{2+/3+}}^\circ - E_{\mathbf{2b}^{1+/2+}}^\circ)/2.303RT \\ &= -8.46 - 16.89(2.61 - 0.12) = -50.5 \end{aligned}$$

Scheme 7



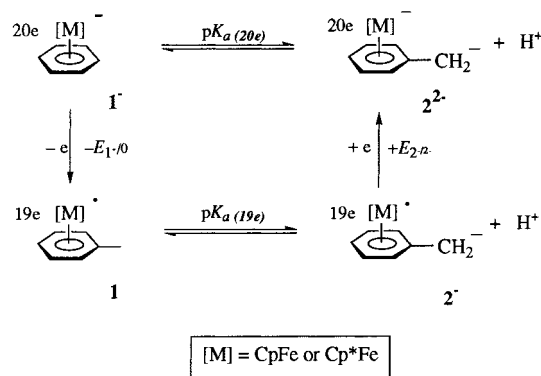
$$\begin{aligned} pK_a(\mathbf{1a}) &= pK_a(\mathbf{1a}^+) + \mathcal{F}(E_{\mathbf{1a}^{1+/0}}^\circ - E_{\mathbf{2a}^{0/-}}^\circ)/2.303RT \\ &= pK_a(\mathbf{1a}^+) + 16.89(E_{\mathbf{1a}^{1+/0}}^\circ - E_{\mathbf{2a}^{0/-}}^\circ) = \\ &\quad 29.2 - 16.89(-1.99 + 2.80) = 43.5 \\ pK_a(\mathbf{1b}) &= pK_a(\mathbf{1b}^+) + 16.89(E_{\mathbf{1b}^{1+/0}}^\circ - E_{\mathbf{2b}^{0/-}}^\circ) = \\ &\quad 31.4 - 16.89(-2.22 + 3.11) = 46.4 \end{aligned}$$

the mono-oxidized deprotonated complex. Indeed, whereas the anodic oxidation of the deprotonated fluorene and diphenylmethane on Pt complexes is fully irreversible at -40 °C in $\text{CH}_2\text{-Cl}_2$, THF, and DMF, the analogous oxidation of **2c** is reversible at $E_{1/2} = -0.650$ V vs FeCp_2 in DMF on Pt at 20 °C ($i_c/i_a = 1$ at a scan rate of 800 mV/s and 0.56 at 100 mV/s). Thus, at a scan rate of 800 mV/s, it is possible to confidently observe the oxidation of **2c** at a higher oxidation potential. Indeed, the irreversible anodic oxidation of **2c** is observed at $E_{\text{irr}} = +0.050$ V vs FeCp_2 . The influence of temperature on the potential is taken as negligible compared to the maximum error attributed here to the data.

Determination of pK_a s of the 16–20-Electron Complexes Using Thermodynamic Cycles. The pK_a s of the 16–20-electron complexes can be calculated using thermodynamic cycles. Applied to the complexes $\mathbf{1}^+$, these cycles are represented in Schemes 5–8 using the pK_a values of the 17–20-electron complexes and the difference between their oxidation and reduction potentials, respectively, and those of their deprotonated

(50) The largest shift that can occur is 0.287 V, involving a diffusion-controlled first-order reaction (EC mechanism, $k = 10^{10}$ s⁻¹). This corresponds to a shift of 6.6 kcal/mol for the estimation of the BDE value.^{35a}

Scheme 8



forms. Calculations are found below the Schemes for **1a,b**, and these and other data are summarized in Table 1.

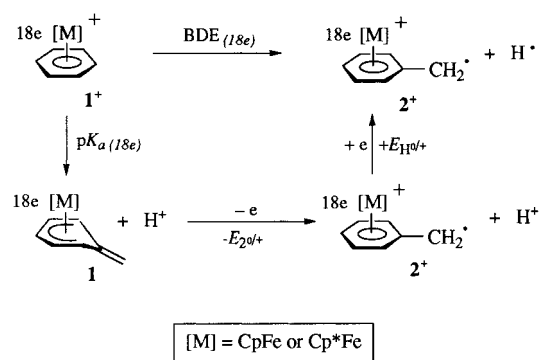
The determination of $pK_a(1^-)$ requires the knowledge of the second reduction potential of **3**. This is not experimentally directly accessible but can be reasonably estimated by adding to the first potential the constant value of 0.78 ± 0.10 V separating the first and second reduction potentials of $[\text{FeCp}(\text{arene})]^+$ complexes with various substituents on the rings (the carbanion $-\text{CH}_2^-$ is considered as a simple substituent; see the Discussion). The maximum uncertainty is estimated to be 0.10 V. Values of the potentials of the reversible reduction waves of **1a,b** were recorded in DMF and are adapted to DMSO with the approximation mentioned in the preceding section.

$$pK_a(1a^-) = pK_a(1a) + \mathcal{F}(E_{1a^{0/-}}^\circ - E_{2a^{1-/2-}}^\circ)/2.303RT = 43.5 + 16.89(-2.77 + 3.58) = 57.2$$

$$pK_a(1b^-) = pK_a(1b) + \mathcal{F}(E_{1b^{0/-}}^\circ - E_{2b^{1-/2-}}^\circ)/2.303T = 46.4 + 16.89(-3.00 + 3.89) = 61.4$$

Calculations of the BDEs Using the Thermodynamic Diagrams. Application of Scheme 2 leads to the BDE of the benzylic C–H bonds in the 18-electron complexes **1⁺** using their pK_a , the oxidation potentials of their deprotonated forms and the constant (Scheme 9).

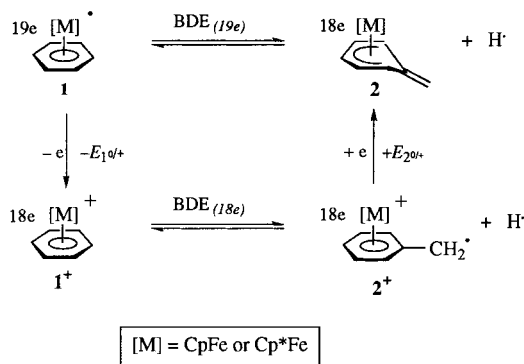
Scheme 9



$$\begin{aligned} \text{BDE}(1a^+) &= 2.3RTpK_a + \mathcal{F}E_{A-0}^\circ + C = 1.365pK_a(1a^+) + 23.06E_{2a^{0/+}}^\circ + 73.5 \text{ kcal/mol} \\ &= 1.365(29.2) + 23.06(-1.165) + 73.5 = 86.5 \text{ kcal/mol} \end{aligned}$$

$$\begin{aligned} \text{BDE}(1b^+) &= 1.365(31.4) + 23.06(-1.34) + 73.5 = 85.5 \text{ kcal/mol} \end{aligned}$$

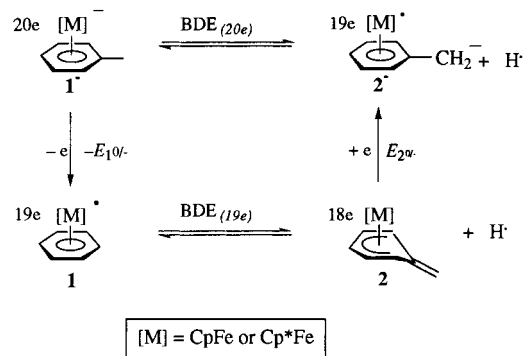
Scheme 10



$$\begin{aligned} \text{BDE}(1a) &= \text{BDE}(1a^+) - 23.06(E_{2a^{0/+}}^\circ - E_{1a^{+/0}}^\circ) \\ &= 86.5 - 23.06(-1.165 + 1.99) = 67.5 \text{ kcal/mol} \end{aligned}$$

$$\begin{aligned} \text{BDE}(1b) &= \text{BDE}(1b^+) - 23.06(E_{2b^{0/+}}^\circ - E_{1b^{+/0}}^\circ) \\ &= 85.5 - 23.06(-1.34 + 2.22) = 65.0 \text{ kcal/mol} \end{aligned}$$

Scheme 11



$$\begin{aligned} \text{BDE}(1a^-) &= \text{BDE}(1a) - 23.06(E_{2a^{0/-}}^\circ - E_{1a^{0/-}}^\circ) \\ &= 67.5 - 23.06(-2.80 + 2.77) = 68.2 \text{ kcal/mol} \end{aligned}$$

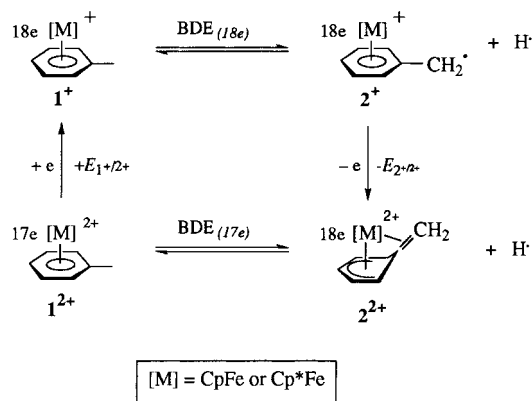
$$\begin{aligned} \text{BDE}(1b^-) &= \text{BDE}(1b) - 23.06(E_{2b^{0/-}}^\circ - E_{1b^{0/-}}^\circ) \\ &= 65.0 - 23.06(-3.11 + 3.00) = 67.5 \text{ kcal/mol} \end{aligned}$$

Application of Scheme 4 allows calculation of the BDE of another oxidation state from the BDE of the 18-electron complex (calculated above) if the appropriate redox potentials of the complex and its deprotonated forms are known. Thus, the access to the BDE in the 19- and 20-electron complexes requires the knowledge of the oxidation and reduction potentials of the deprotonated form, respectively (Schemes 9 and 10), while access to the BDE in the 17-electron complexes requires the knowledge of the second oxidation potential of the deprotonated form (Schemes 11 and 12, see the Discussion).

Discussion

As can be seen from the data in Table 1, there is a huge change in the acidities and BDEs upon changing the oxidation state in this first family of stable isostructural triad of 17–18–19-electron iron complexes of C_6Me_6 and among the 16–20-electron redox series with various arene ligands. Despite the well-known ability of transition metals to change oxidation state to a great extent, they usually only do so together with structural transformation of the coordination sphere. Addition or removal of a single electron from organic, inorganic, and organometallic

Scheme 12



$$\begin{aligned} \text{BDE}(\mathbf{1a}^{2+}) &= \text{BDE}(\mathbf{1a}^+) - 23.06(E_{\mathbf{1a}^{1+}/\mathbf{2+}}^{\circ} - E_{\mathbf{2a}^{1+}/\mathbf{2+}}^{\circ}) \\ &= 86.5 - 23.06(1.25 - 0.34) = 65.5 \text{ kcal/mol} \end{aligned}$$

$$\begin{aligned} \text{BDE}(\mathbf{1b}^{2+}) &= \text{BDE}(\mathbf{1b}^+) - 23.06(E_{\mathbf{1b}^{1+}/\mathbf{2+}}^{\circ} - E_{\mathbf{2b}^{1+}/\mathbf{2+}}^{\circ}) \\ &= 85.5 - 23.06(1.03 - 0.12) = 64.5 \text{ kcal/mol} \end{aligned}$$

molecules often changes their reactivity by kinetic factors of the order of 10^{10} , which provides the kinetic basis for chain reactions.⁵¹ Let us first discuss the features of the 18-electron complexes before analyzing the consequences of the changes in oxidation state.

pK_as of 18-Electron Cationic Fe^{II} Complexes. In these complexes, the benzylic hydrogens are not overly acidic. The pK_a values of 29.2 for **1a**⁺ and 31.4 for **1b**⁺ are high, but a methyl proton can be removed by NaOMe in THF for **1a**⁺ and *Kt*-BuO for **1b**⁺ (but not by NaOMe); **1a**⁺ can be deprotonated in MeCN only in the presence of excess base. These 18-electron cations are much less acidic than the numerous 18-electron transition-metal hydrides studied by Norton, Tilset, and Theopold, which cluster between pK_a values of 10 and 20 in MeCN (values in MeCN can be converted to approximate DMSO acidities by subtracting 10 pK_a units).⁵² The electron density increase at the metal center incurred on permethylation of the Cp ring of the iron-sandwich complexes raises the pK_a by 2.2 units. The observation by Norton^{20c} of similar but larger differences between the Cp and Cp* ligands of [Mo(η^5 -C₅R₅)(CO)₃H] (Δ pK_a = 3 units) and [Fe(η^5 -C₅R₅)(CO)₃H] (Δ pK_a = 7 units) reflects the more direct interaction between the metal center and the “proton” in these hydride complexes than in the hexamethylbenzene sandwich complexes.

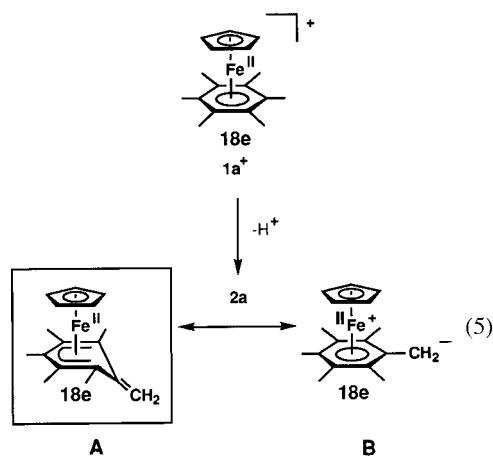
The niobium–acyl complexes investigated by Bruno, with pK_a values in the range 2–7, are much more acidic than **1a**⁺ and **1b**⁺ although an analogous iron compound, [FeCp(CO)-(PPh₃)(COCHMe₂)], does have a pK_a > 35 in DMSO.²³

Although the pK_a of C₆Me₆ is not available in the literature, it is expected not to be substantially higher than that of toluene. Gau has shown that ortho and meta methyl groups add roughly 0.1 pK_a unit of basicity, while a para methyl adds roughly 1 unit, although his results in diamine-containing hydrocarbon solvents are not directly applicable to the present case involving strongly polar solvents.⁵³ Likewise, Hehre has observed gas-

phase energy differences which correspond to an increase of 0.1 and 0.7 pK_a units, respectively, for *p*-xylene and *m*-xylene, compared to toluene.²⁴

Since **1a**⁺ and **1b**⁺ are respectively 13.8 and 11.6 pK_a units more acidic than toluene, coordination of C₆Me₆ to CpFe⁺ and Cp*Fe⁺ fragments can thus be estimated to enhance the acidity of the benzylic hydrogens by slightly greater than 14 and 12 pK_a units, respectively. This enhancement accords with the results obtained by Terrier et al., who found that coordination of one CpFe⁺ fragment to diphenylmethane leads, in DMSO/water or DMSO/methanol mixtures, to a 12 pK_a unit acidity increase, and coordination of a second fragment, to a further gain of 4 units.²⁸ On the other hand, with fluorene, the decrease of pK_a upon coordination to CpFe⁺ is only 8 pK_a units, as shown by Bordwell et al., due to the electronic delocalization between the coordinated and noncoordinated parts of this ligand.

The factors that favor the deprotonation of the complexes **1**⁺ are (i) the positive charge which is redistributed onto an even ligand to a larger extent than onto an odd ligand in a cationic complex such as **1**⁺ which contain both types of ligands⁵⁴ and (ii) the stabilization of the η^5 -cyclohexadienyl ligand in the deprotonated arene which gives the neutral ferrocene-like structure **A** (two pentahapto ligands, Fe^{II} oxidation state) of the complexes **3**, confirmed by X-ray data. This resonance form has considerably more weight than the zwitterionic *hexahapto* structure **B** bearing the classical carbanion (eq 5). This later form is dominant in the fluorene complexes, explaining why the influence of the metal moieties is weaker in those cases.



pK_as of Neutral 19-Electron Fe^I Complexes. The above advantages are lost in the 19-electron complexes **1** because they do not bear a charge and have an antibonding SOMO. Their acidities are equal or slightly inferior to that of the free arene ligand. Note the sensitivity of the acidity enhancement to the electron density on the metal: single-electron reduction of **1a**⁺ to **1a** virtually negates the acidity increase gained on coordination, bringing the reduced compound's pK_a in line with that of uncoordinated toluene. Coordination of C₆Me₆ to Cp*Fe even provokes a decrease in the acidity of the benzylic hydrogen atoms by about 3 pK_a units. The lack of benefit from the coordination in the 19-electron structure **C** arises because there is now no stabilization by a 19-electron cyclohexadienyl structure **D** in which the negative charge would be located on the metal center (eq 6); the latter would be of too high energy

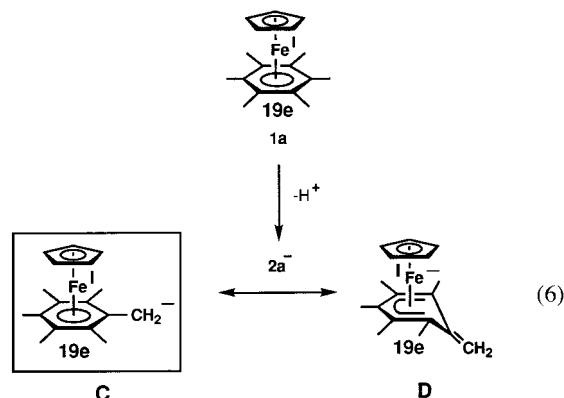
(51) For chain reactions in transition-metal chemistry, see Chapter 6 of ref 1f and the following: Chanon, M. *Bull. Soc. Chim. Fr.* **1982**, II-197; **1985**, 209.

(52) (a) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132. (b) Kolthoff, I. M.; Chantooni, M. K.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23.

(53) Gau, G.; Marques, S. *J. Am. Chem. Soc.* **1976**, *98*, 1538.

(54) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 20.

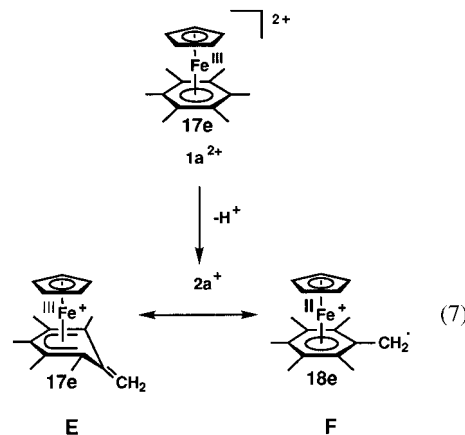
(for instance, a potential as negative as -3.5 V vs $\text{Cp}_2\text{Fe}^{0/+}$ is required to reduce ferrocene to its 19-electron radical anion).⁵⁵



pK_as of Anionic 20-Electron Fe^I Complexes. This species has only been observed by a chemically and electrochemically reversible cyclic voltammetry wave for a variety of [FeCp(arene)] complexes,⁵⁶ but not spectroscopically. It is isoelectronic with nickelocene^{57a} and [Fe(η^6 -C₆Me₆)₂],^{57b} which have a sandwich structure with two unpaired electrons in the doubly degenerate e*₁ orbital. The fact that no decoordination occurs in the 20-electron complexes [Fe⁰Cp(arene)]⁻ is shown by the full electrochemical reversibility of the Fe^I/Fe⁰ wave observed in cyclic voltammetry and by the absence of anodic shift of this wave and was recently confirmed by accurate DFT calculation.^{18b,58} Since the pK_a of **1a**, remarkably, is not influenced by the coordination to CpFe, we deduce that the structure of the carbanion C₆Me₅CH₂⁻ is the same in the free state and as a ligand coordinated to Fe^ICp in **3a**⁻. In other words, the -CH₂⁻ substituent does not interfere with the Fe^I center, so that the single-electron reduction of **2a**⁻ to **2a**²⁻, whose potential is required for the thermodynamic cycle leading to the calculation of the pK_a of **2a**⁻ can be regarded as involving only the iron e*₁ orbital. Whereas this potential is not experimentally accessible, we can calculate it with a good approximation since the difference between the first and second reduction potentials of the family of [FeCp(arene)]⁺ complexes with various substituents on the rings is constant. The resulting pK_as of the anions **2**⁻ are consistently 14–15 pK_a units higher than those of the neutral complexes and the free arene, which is due to the electrostatic factor.

pK_as of Dicationic 17-Electron Complexes. Tilset has reported an acidity enhancement of 23–26 pK_a units for the hydrogen atom attached to the metal upon oxidizing neutral 18-electron transition metal hydrides to their cationic 17-electron counterparts.^{37c} The effect of single-electron oxidation of the 18-electron cationic complexes on the acidity of the benzylic hydrogen atoms of our iron-sandwich complexes is more dramatic, provoking a drop of about 40 pK_a units in both Cp and Cp* complexes, which leads to negative pK_a values for the

17-electron complexes **1**²⁺. These values are only virtual in DMSO because **1a**⁺ and **1b**⁺ cannot be oxidized to the 17-electron complexes in DMSO, but only in solvents such as MeCN, CH₂Cl₂, and SO₂ in which their anodic oxidation is reversible. This large increase of acidity from **1**⁺ to **1**²⁺ is directly connected (in the thermodynamic cycle) to the enormous difference of standard potential (about 2.4 V) between the oxidation of **2** (the deprotonated form of **1**) and the oxidation of **1**⁺. Indeed, the oxidation of **1**⁺ occurs at very positive potentials (at more than 1 V vs Cp₂Fe^{0/+}), so that, for instance, **1b**²⁺ is the most oxidizing thermally stable organometallic complex known. The complexes **2**⁺ which form by virtual deprotonation of the very strong oxidants **1**²⁺ (eq 7) are very easily generated by mild oxidation of **2**.



Thus, the complexes **2**⁺ are thermodynamically relatively stable, being Fe^{III} compounds which resemble ferricinium. In fact, the complex **1b**[SbCl₆]₂ is such a strong oxidant that it oxidizes all the bases. Altogether, the isostructural 17-electron Fe^{III} and 19-electron Fe^I complexes are separated by 3.25 V in both Cp and Cp* series, which also results in a pK_a drop of about 55 units from the neutral Fe^I complexes to the dicationic Fe^{III} complexes. The isostructural Fe⁰ and Fe^{III} complexes are separated by a 4.1 V and about 70 pK_a units. Even though this gap seems enormous, it is less important than the gap that is involved when C₆Me₆ is not coordinated. The difference of pK_a between free C₆Me₆ and C₆Me₆^{•+} is given by

$$\text{p}K_{\text{a}}(\text{C}_6\text{Me}_6^{\bullet+}) - \text{p}K_{\text{a}}(\text{C}_6\text{Me}_6) = 16.89 (E^\circ\{\text{C}_6\text{Me}_6^{0/+}\} - E^\circ\{\text{C}_6\text{Me}_5\text{CH}_2^{0/-}\})$$

C₆Me₆ is oxidized at 1.6 V vs [FeCp₂],⁵⁹ i.e. at a potential 0.4 V more positive than its CpFe⁺ complex **1a**⁺ and 0.6 V more positive than its Cp*Fe⁺ complex **1b**⁺. The value of E^o{C₆Me₅-CH₂^{0/-}} is unknown, but this species must be reduced at an extremely negative (inaccessible) potential, i.e. beyond 3.5 V vs Cp₂Fe^{0/+}, so that the difference of pK_a above is presumably larger than 80 pK_a units. The reduction of this difference upon coordination is due to the fact that the orbitals involved in the redox processes of **1**⁺ are not ligand orbitals, but essentially metal d orbitals with some covalency: the SOMO of the 19-electron complexes **1**, of e*₁ symmetry (d_{xy} and d_{yz}), has about 20% ligand character, and the orbital involved in the oxidation of **1**⁺, of e₂ symmetry (d_{x²-y²}, d_{xy}), has a similar amount of covalency.¹⁸

pK_as of Tricationic 16-Electron Complexes. The increase of acidity from the Fe(III) dications to the Fe(IV) trication is

(59) Lehmann, R. E.; Kochi, J. K. *J. Am. Chem. Soc.* **1991**, *113*, 501.

(55) Mugnier, Y.; Moise, C.; Tirouflet, J.; Laviron, E. *J. Organomet. Chem.* **1980**, *186*, C49.

(56) (a) Desbois, M.-H.; Mariot, J.-P.; Varret, F.; Astruc, D. *J. Chem. Soc. Chem. Commun.* **1985**, 447. (b) Desbois, M.-H.; Astruc, D. *Organometallics* **1989**, *8*, 1841.

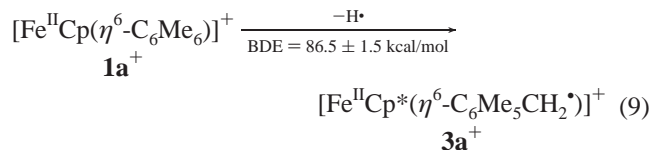
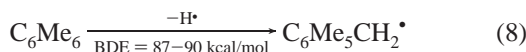
(57) (a) Ammeter, J. H.; Swallen, J. D. *J. Chem. Phys.* **1972**, *57*, 678.

(b) Michaud, P.; Mariot, J.-P.; Varret, F.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1982**, 1383.

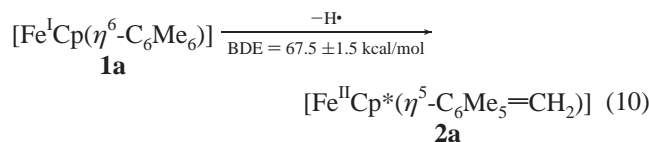
(58) (a) Decoordination upon electron transfer is currently observed in cyclic voltammetry by the low (measurable) rate of heterogeneous electron transfer and perturbed thermodynamics.^{56b,58b} (b) See Chapter 2 of ref 1d and the following: Geiger, W. E. *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1985; Vol. 33, p 275.

on the order of 50 pK_a units, *i.e.* much larger than from the Fe(II) monocations to the Fe(III) dications. Again, this huge increase of acidity is connected to the huge difference between the standard oxidation potentials of **1**²⁺ (around 3 V) and the second oxidation potential of **2** (around 0 V). This second oxidation potential, experimentally accessible only in the case of **2c**, is low probably because of the stabilization of **2**²⁺ by coordination of the exocyclic bond to iron in order to keep the 18-electron count. The 18-electron rule is indeed the basis of a strong driving force for this type of compound. The values obtained for the pK_as of **1**³⁺ are as low as –60, thus completely virtual in DMSO.

Bond Dissociation Energies. Let us first try to compare the BDE of the benzylic C–H bonds in the 18-electron complexes with those of free polymethylbenzenes. The BDE of C₆Me₆ is not known, but calculations by Gilliom⁶⁰ have found that the benzylic C–H bond energies for toluene, *m*-xylene, and *p*-xylene are identical (87–90 kcal/mol). If this observation can be extended to C₆Me₆ (eq 8), comparison with toluene or xylenes in lieu of C₆Me₆ shows that almost no change in BDEs is found upon coordination in the 18-electron complexes **1**⁺, a remarkable feature (eq 9). Thus, the situation is reversed in comparison with the acidities.

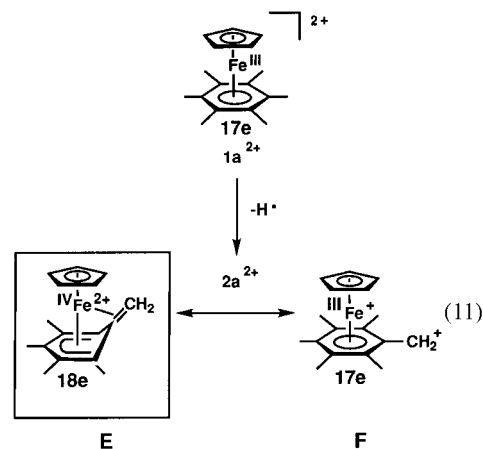


Whereas the acidities of the 19-electron complexes **1** are about the same as those of the free arene, an important drop (of the order of 20 kcal/mol) of BDE is now observed for this class of 19-electron complexes in comparison with the free arene. This is taken into account by the fact that, in breaking the benzylic C–H bond, one starts from the 19-electron complexes **1**, with an electron in an antibonding orbital, to form the very stable 18-electron complex **2** (eq 10).



The process is so easy that it has been experimentally carried out by simple contact with dioxygen or air at –80 °C.^{40a} These thermodynamic data indicate that a direct H-atom abstraction from **1** to **2** would be an easy process, although it has not yet been experimentally observed (the reaction with O₂ proceeds by electron transfer from **1** to O₂ followed by proton transfer from **1**⁺ to O₂^{•–}).^{40a} Hydrogen-atom abstractors which are not easily reduced such as Bu₃Sn[•] or [FeCp(PR₃)₂]^{17a} should be good candidates for a direct H-atom abstraction from **1** to give **2**. The BDEs of the 20-electron complexes are remarkably analogous to those of the 19-electron complexes, which is well taken into account by the decrease of one unit of the number of valence electrons from numbers above 18 in both cases. The energy gain in breaking a benzylic C–H bond is about the same because this electron is removed from the same antibonding e*₁ orbital in both cases.

The BDEs of the benzylic C–H bonds in the 17-electron complexes **1**²⁺ are even lower by 20 kcal/mol than those of the 19- and 20-electron electron complexes **1** and **1**[–]. We believe that these very low BDE value arise because of the tremendous stabilization obtained by coordination of the exocyclic double bond to the iron center in order to complete the 18-electron valence shell of the metal (eq 11) as in ferrocenylcarbonium cations.⁶¹



Concluding Remarks

Through direct measurements in DMSO and thermodynamic cycles, whose type has been established by Breslow,³¹ Arnett,³² Bordwell,³³ Griller,³⁴ Arnold,³⁹ Parker,^{35,36} and Tilset^{36,37} by combining pK_a values and electrochemical potentials, the acidities of the benzylic hydrogens in five oxidation states of the complexes [Fe^x(η⁵-C₅R₅)(η⁶-C₆Me₆)]ⁿ⁺ (x = 0–IV, R = H or Me, n = –1 to 3) and [Fe^x(η⁵-C₅R₅)(η⁶-arene)]ⁿ⁺ (arene = di- and triphenylmethane and fluorene) have been calculated for DMSO solutions. For the 16-electron species, the pK_a values were estimated using the values of the oxidation potentials of the 17-electron complexes available by adding the difference between the two oxidation potentials of decamethylferrocene to the first oxidation potential of these complexes measured in SO₂. Coordination of the arene by the Fe^x(η⁵-C₅R₅) fragment (R = H and Me, respectively) increases its acidity in the 18-electron complexes (x = 1) by roughly 12–14 pK_a units (except for fluorene). These data have been compared with those previously obtained by various techniques by Norton,²⁰ Tilset,^{36,37} Parker,^{35,36} Theopold,²² and Bruno²³ on transition-metal hydrides and Terrier³¹ and Bordwell,³⁸ respectively, on diphenylmethane and fluorene coordinated to CpFe⁺ in the 18-electron complexes **1d**[PF₆] and **1e**[PF₆].

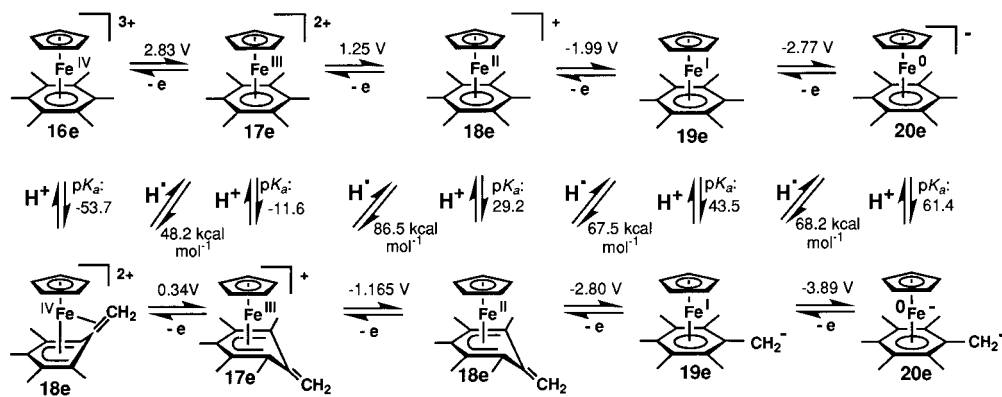
In the 17-electron complexes (x = 2), the pK_a of C₆Me₆ drops upon coordination by roughly 54 and 51 pK_a units with R = H and Me, respectively. In the 16-electron complexes (x = 3), the pK_a drop reaches more than 100 units. In the neutral 19-electron complexes (x = 0), the acidity of C₆Me₆ is either unchanged (R = H) or slightly decreased (R = Me). In the anionic 20-electron complexes (x = –1), the acidity drops by 14 and 12 pK_a units with R = H and Me, respectively.

Using other thermodynamic diagrams of related type, the BDE of the benzylic C–H bonds have been determined in the 17–20-electron complexes. Contrary to the acidity, these BDEs are not changed by complexation to the monocationic fragments Fe(η⁵-C₅R₅)⁺ in the 18-electron complexes. On the other hand, whereas the acidity is not significantly changed upon complexation of C₆Me₆ to the neutral fragments Fe(η⁵-C₅R₅), the

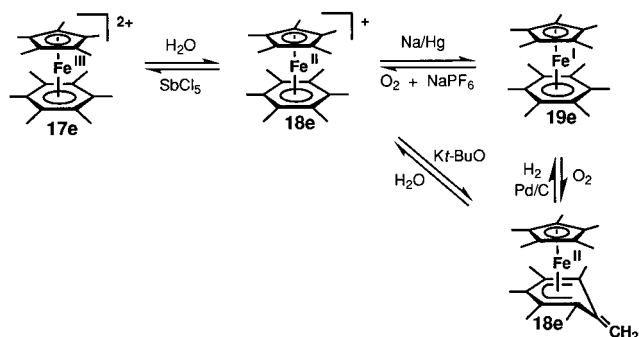
(60) Gilliom, R. D. *J. Mol. Struct. (THEOCHEM)* **1986**, *138*, 157.

(61) Watts, W. E. *J. Organomet. Chem. Libr.* **1979**, *7*, 399.

Scheme 13



Scheme 14



homolytic C–H cleavage reflected by the BDEs requires about 20–30 kcal/mol (85–125 kJ/mol) less energy in the 17-, 19-, and 20-electron complexes than in the 18-electron complexes or the free arene. This is due to the removal of one electron from an antibonding e^*_1 orbital upon benzylic C–H cleavage in both the 19- and 20-electron complexes, which show the same energy gain in this process. The experimental determination of the second oxidation potential of the deprotonated triphenylmethane complex **2c** led to reasonable estimations of the analogous values for the other complexes of this type. In this way, the approximated BDEs are available in the dicationic 17-electron complexes and their values are even lower than those found in the 19- and 20-electron complexes. This is best taken into account by a very strong stabilization of the deprotonated 16-electron species by coordination of the exo-cyclic double bond to the metal in the same fashion as ferrocenylcarbonium cations, which brings their valence electron count back to 18. These overall results, which are the first ones spanning over more than two oxidation states, are summarized in Table 1 and, as an example for the $[\text{FeCp}^*(\eta^6\text{-C}_6\text{Me}_6)]$ series, in Scheme 13. The relevance of these thermodynamic data to the chemistry of these complexes is illustrated in Scheme 14, which summarizes the known reactions relating the stable components of the family in the $[\text{FeCp}^*(\eta^6\text{-C}_6\text{Me}_6)]$ series. In particular, the richness of oxidation states and of electron-, proton-, and H-atom transfer reactions known together with the present study highlights the electron, proton, and H-atom reservoir properties of the families of iron-sandwich complexes permethylated on either one or both rings (cf. also the Introduction and eqs 1 and 2).

Experimental Section

General Procedures. All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of argon which had been dried by passage over 3 Å molecular sieves activated at 200 °C under vacuum. ^1H NMR spectra (90 MHz) were

obtained on a Bruker WH-90 spectrometer at 25 °C and are reported as parts per million downfield of TMS, referenced to the solvent. ^{13}C - $\{^1\text{H}\}$ NMR spectra (62.9 MHz) were likewise obtained on a Bruker WM-250 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1420 IR spectrophotometer; visible spectra were recorded on a Varian Cary 219 spectrophotometer (350–500 nm, 1 cm path length). The complexes **1a** $[\text{PF}_6]$,^{40b,62} **1b** $[\text{PF}_6]$,^{40b} **1c** $[\text{PF}_6]$,⁶³ **1d** $[\text{PF}_6]$,⁶³ **1e** $[\text{PF}_6]$,⁶⁴ **2a**,^{40a,62} **2b**,^{40a} **2c**,⁶³ **2d**,⁶³ and **2e**⁶⁵ were prepared by literature routes. $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ was prepared by metathesis of $[n\text{-Bu}_4\text{N}][\text{HSO}_4]$ and NaBF_4 . Potassium hydride (20% suspension in oil) and potassium *tert*-butoxide were purchased from Janssen; the latter was sublimed before use. AlCl_3 was purchased from Merck, and hexamethylbenzene, from Lancaster.

Solvent Purification. Hydrocarbon and ethereal reaction solvents were purified by distillation from sodium/benzophenone ketyl under argon. After predrying over NaOH and vacuum distillation, DMSO was vacuum distilled from CaH_2 . The distillate was collected after an initial forerun (10%). DMF was predried over CaO, then distilled at ambient pressure from CaH_2 immediately before use. The material which distilled above 149 °C was collected. DMSO- d_6 was allowed to stand over molecular sieves (3 Å, activated at 200 °C under vacuum) for 2 weeks before use.

Preparation of Bases. Sodium Methoxide. Methanol was dried by distillation followed by refluxing over Mg turnings and a catalytic amount of I_2 . The solvent was then distilled and treated with metallic sodium (~1:10 w/v). The mixture was refluxed briefly after H_2 evolution ceased, evaporated, and dried at 120 °C under vacuum. Titration (HCl/bromocresol green) showed that the white powder contained no entrained methanol.

Sodium Methoxide/DMSO- d_6 Suspension. Sodium methoxide (13.7 mg, 0.253 mmol) was ground in a small Schlenk tube. DMSO- d_6 (0.961 g, 0.808 mL) was added, and the mixture was sonicated 15 min, then allowed to stand several hours at room temperature to give a homogeneous suspension 0.313 M in NaOMe.

Sodium Phenoxide was prepared by treatment of phenol in dry methanol with metallic sodium, as described by Berny,⁶⁶ and was titrated (HCl/bromocresol green) to verify the lack of phenoxide/phenol/methanol agglomerates.

Potassium Imidazolate. Imidazole (1 equiv) and KH (1 equiv) were stirred in diethyl ether. After evolution of hydrogen ceased, the solvent was removed by filtration; the white precipitate was rinsed four times with diethyl ether and dried under vacuum. The ^1H NMR spectrum (DMSO- d_6 : δ_{ppm} = 6.96, 1H; 6.58, 2H) of this white powder showed only the signals corresponding to potassium imidazolate (compare for imidazole: δ_{ppm} = 12.04, 1H; 7.64, 1H; 7.01, 2H).

(62) Astruc, D.; Hamon, J. R.; Lacoste, M.; Desbois, M.-H.; Román, E. In *Organomet. Synthesis*; King, R. B., Ed.; Elsevier: Amsterdam, 1988; Vol. IV, pp 172–187.

(63) Helling, J. F.; Hendrickson, W. A. *J. Organomet. Chem.* **1977**, *141*, 99.

(64) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Dokl. Akad. Nauk, SSSR* **1966**, *166*, 607.

(65) Johnson, J. W.; Treichel, P. M. *J. Chem. Soc., Chem. Commun.* **1972**, 688; *J. Am. Chem. Soc.* **1977**, *99*, 1427.

(66) Berny, M. F.; Perrin, R. *Bull. Chim. Soc. Fr.* **1967**, 1013.

pK_a Studies of 18-Electron Complexes. [FeCp(η^6 -C₆Me₆)](PF₆) (1a⁺). The UV–vis spectrum of 1a[PF₆] and its deprotonated complex [FeCp(η^5 -C₆Me₅CH₂)] (2a) are easily manipulated through Beer's law, but 2a absorbs 10–20 times more strongly than 1a⁺ for all points within the transmission window of solvents in which both are soluble.⁴⁰ Thus, ¹H NMR appeared to be the best method to observe the position of equilibrium, despite the limitation of its time scale and the imprecision of its integration. In DMSO-*d*₆, clean singlets are observed for the Cp protons of 1a[PF₆] and 2a. The methyl and methylene peaks of 2a are unobservable, however, presumably due to fast equilibrium 3 on the NMR time scale (in contrast, they are sharp in C₆D₆). Likewise, the methoxide peak is broadened in DMSO-*d*₆ and represents an average signal for the methanol and sodium methoxide present. To permit direct comparison with the metal hydrides studied by Norton, Tilset, and Theopold, the use of acetonitrile as a solvent would have been desirable. However, acetonitrile solutions of 2a are unstable, suggesting that 2a is sufficiently basic to deprotonate acetonitrile. Indeed, the pK_a of acetonitrile, 31.3 in DMSO, is relatively close to that of 1a[PF₆]; the deprotonation of acetonitrile by 1a[PF₆] may be shifted by the reaction of the anion of acetonitrile. DMSO has the same desirable solvent characteristics as acetonitrile²³ and is less acidic than it (pK_a = 35.1), and a vast collection of pK_as has been amassed by Bordwell.⁴¹ The choice of base was governed by the acidity of the compound, as the limitations of NMR integration required that the protonated base and the analyte be of similar strength. Deprotonation was complete with potassium *tert*-butoxide (pK_a = 32.2 in DMSO)⁴¹ and partial with sodium methoxide (pK_a = 29.0).⁴¹ Sodium phenoxide (pK_a = 18.0)⁴¹ did not deprotonate 1a[PF₆] but caused a yellow solution of 1a[PF₆] to become green, presumably because single-electron reduction of 1a[PF₆] was shifted by the reactivity of the phenoxy radical.

[FeCp*(η^6 -C₆Me₆)](PF₆) {1b[PF₆]}. Deprotonation has already been achieved with various bases.^{42–46} Attempts to assay the equilibrium acidity of 1b[PF₆] by the ¹H NMR method used with 1a[PF₆] showed that this technique was unsuitable with 1b[PF₆]: while 1b[PF₆] alone provides a proper ¹H NMR spectrum in DMSO, all the signals broaden and disappear into the baseline when traces of *Kt*-BuO are added. This effect is worsened by the growth of the solvent peaks, due to washing of protons from 1b[PF₆] into the DMSO-*d*₆ through the low concentration of dimesyl ion MeS(O)CH₂[−] generated by *Kt*-BuO. This loss of deuterium is confirmed by changes in the solvent multiplicity and by peak-area comparison with TMS added as an internal concentration standard. Similarly, although deprotonated 2b, whose methylenecyclohexadienyl ligand has the same structure as in 2a,^{40c,42} gives clean ¹H and ¹³C NMR spectra in C₆D₆, only the proton-enriched solvent peaks are observed in DMSO. To circumvent this problem, UV–vis spectroscopy, which has a faster inherent time scale, was employed to ascertain the position of the equilibrium 3 for the 1b⁺/2b system, despite drawbacks analogous to those discussed above for the 1a⁺/2a system. The most promising wavelength pair of the visible spectra of 1b[PF₆] and 2b was that of 423 and 544 nm,⁴⁷ which combines relatively flat regions in the spectrum of 1b[PF₆] with local maxima and minima in that of 2b. However, neither simple dissolution of 2b in DMSO nor treatment of a DMSO solution of 1b[PF₆] with an excess of NaH led to reproducible results. The use of 100-fold excess of KH, a base capable of irreversibly deprotonating DMSO, gave reproducible results that agreed with those obtained when a 50-fold excess of *Kt*-BuO was used.^{40c} The excess of the strong base KH is apparently needed to generate sufficient dimesyl anion to ensure that the equilibrium 4 lies far to the left:



[FeCp(η^6 -C₆H₅CHPh₂)](PF₆) {1c[PF₆]}. Since the pK_as of di- and triphenylmethane (respectively 32.2 and 30.6) and that of [FeCp(η^6 -PhCH₂Ph)]⁺ (20.0) were known in DMSO from Bordwell's and Terrier's works, it was possible to anticipate an approximate pK_a value of 18.4 for 1c[PF₆] assuming that the CpFe⁺ activating group lowers

the pK_a value of these two closely related arenes by the same number of pK_a units. Thus, for the measurement by the direct method of the pK_a of 1c[PF₆], we selected imidazole, whose pK_a (18.6) was reported by Bordwell to be very close to that value. Indeed sodium imidazolate deprotonates 1c[PF₆] to a certain extent as indicated by immediate color change from yellow to red. The equilibrium constant of the equilibrium analogous to (3) was determined by ¹H NMR in DMSO-*d*₆ by starting from equimolar amounts of 1c[PF₆] and sodium imidazolate or imidazole and 2c, the deprotonated form of 1c[PF₆]. An average value of −0.05 was obtained for the pK_c of this equilibrium, which gave a pK_a value of 18.55 for 1c[PF₆].

Deprotonation Experiments. NMR Method. A solution of [FeCp-(C₆Me₆)](PF₆) (1a[PF₆], 40 mg, 94 μ mol) in DMSO-*d*₆ (0.8 mL) was prepared and divided equally into four NMR tubes. The samples were frozen, and between 0.5 and 2 equiv of NaOMe/DMSO-*d*₆ suspension was added to each tube, rinsed to the bottom of the tube with more DMSO-*d*₆, then frozen above the layer of 1a[PF₆], to give a final sample volume of ≈ 0.35 mL ([Fe] ≈ 0.13 M). The frozen samples were evacuated, sealed, and maintained frozen until immediately before insertion into the NMR probe, at which time the solutions were thawed and mixed. A similar experiment was carried out starting from a solution of [FeCp(η^5 -C₆Me₅=CH₂)] (2a) and a NaOH/DMSO-*d*₆ suspension. The integration values for the proton NMR peaks due to methoxide and to the Cp rings of 1a[PF₆], and 2 were obtained and used in the calculations section. Identical integration values were found in these two experiments. An analogous procedure was used with 1c[PF₆] and imidazole.

UV–Visible Method. In a typical experiment, [FeCp*(C₆Me₆)](PF₆) (1b[PF₆], 8.3 mg, 16.3 μ mol) was dissolved in DMSO (25.0 mL) to give a spectroscopically convenient concentration (6.6×10^{-4} M). Between 0.5 and 5 equiv of *Kt*-BuO was added as a DMSO stock solution (0.0424 M, 320 μ L, 13.6 μ mol). The visible spectrum of an aliquot (10.6 mL) from the resulting mixture was recorded; the reaction mixture was then treated with additional base (237 μ L, 1.86 equiv of total base), and the visible spectrum of the resulting solution was also recorded. The absorptions at 423 and 455 nm were used to determine the relative concentrations of 1b[PF₆] and 2b as described in the calculations section.

Determination of the Molar Absorption Constant of 2b. Schlenk tubes were charged with 1b[PF₆] (≈ 10 mg each), followed by a large excess of KH (≈ 100 mg), which had previously been washed with pentane and dried. DMSO (≈ 40 mL) was added to each Schlenk at a rate slow enough to control the effervescence. The resulting mixtures were stirred for 5 min, over which time a red color developed, and were then allowed to stand 15 min. Visible spectra were recorded for the samples and for a similarly prepared blank. Visible absorptions in DMSO are as follows: λ/nm (ϵ , L cm^{−1} mol^{−1}). 2b: 393 (λ_{max} , 2450), 423 (λ_{min} , 1890), 455 (λ_{max} , 2220). 1b[PF₆]: 406 (λ_{max} , 105), 450 (λ_{max} , sh, 88.6), 423 (99.8), 455 (88.7); 2a: 398 (λ_{max} , 5000), 500 (λ_{max} , 3000). 1a[PF₆]: 398 (λ_{max} , 200), 455 (λ_{max} , sh, 150).

Cyclic Voltammetry Studies. Cyclic voltammetry studies of the complexes [FeCp(arene)](PF₆) (1[PF₆]) with arene = C₆Me₆, fluorene, diphenylmethane, and triphenylmethane and [FeCp*(η^6 -C₆Me₆)](PF₆) (1b[PF₆]) and their deprotonated forms ([FeCp(η^5 -C₆Me₅=CH₂)] (2) and other homologues) were performed under argon at room temperature in DMSO and at room temperature or −35 °C in DMF, purified as described above, using a PAR 273 potentiostat equipped with a HMDE or Pt disk working electrode, a Pt counter electrode, and an SCE reference electrode, at sweep rates between 40 and 800 mV/s. Data were recorded on a Sefram TGV 164 plotter. Solutions were typically 4×10^{-3} M in analyte and 0.1 M in [*n*-Bu₄N][BF₄]. Ferrocene or decamethylferrocene was the internal reference ($E_{1/2}(\text{FcP}_2^{0/+}) = 0.435$ V vs SCE in DMSO and 0.470 V vs SCE in DMF at 20 °C; see text and ref 49 for the reference problem). Results are reported in Table 1.

Calculations of the pK_as of the 18-Electron Complexes. (1) pK_a Values from NMR Results. The integration ratios obtained for the cyclopentadienyl peaks of 1a[PF₆] or 1c[PF₆] and 2a or 2c and for the methoxide or imidazolate peak(s) (representing the total base, B) were

substituted into eq 13, after conversion-to-molar ratios.



$$K_{\text{eq}} = \frac{[2a][BH]}{[1aPF_6][B]} = \frac{[2a]^2}{[1aPF_6][B_t[2a]]} \quad (13)$$

This direct substitution assumes that **1a**[PF₆] is the only source of protons in the system and that proton exchange between the solvent and both bases present (NaOMe or potassium imidazolite and deprotonated **2**) are minimal. To verify this assumption, calculation of the MeOH concentration in DMSO under similar conditions, from the known acidity constants for DMSO and methanol (pK_a 35.1⁶⁷ and 29.0,⁴¹ respectively), showed that <1% of the NaOMe would be protonated by the solvent (eq 14). In the present case involving DMSO-*d*₆, an equilibrium isotope effect would predict an even smaller interaction. The resulting values of K_{eq} were then added to pK_{BH} (Scheme 1) to obtain the pK_a value for **1a**[PF₆]. Although no data for homo-hydrogen bonding (eq 15) was available for MeONa (or *t*-BuOK) in DMSO, the low concentration of the protonated base and high hydrogen-bond acceptor ability of DMSO⁶⁸ imply that this factor may be safely neglected.



(2) pK_a Values from Visible Spectra. For a mixture containing two absorbing species, a and b, the absorption at a given λ is the sum of two Beer's law terms:

$$A_\lambda = \epsilon_a c_a l + \epsilon_b c_b l \quad (16)$$

Knowing the total absorption at two points, λ_1 and λ_2 , one may solve the resulting pair of eq 16 to obtain

$$c_a = \frac{A_1/\epsilon_{1b} - A_2/\epsilon_{2b}}{l(\epsilon_{1a}/\epsilon_{1b} - \epsilon_{2a}/\epsilon_{2b})}$$

$$c_b = \frac{A_1/\epsilon_{1a} - A_2/\epsilon_{2a}}{l(\epsilon_{1b}/\epsilon_{1a} - \epsilon_{2b}/\epsilon_{2a})} \quad (17)$$

where the subscripts 1 and 2 refer to λ_1 and λ_2 , and subscripts a and b, to compounds a and b. In the case of Cp* compound **1b**⁺ and deprotonated **2b** (and similarly for Cp compounds **1a**⁺ and **2a**), unfortunately, the ϵ values for the conjugate base are roughly 20-fold those for the conjugate acid at most wavelengths observable in DMSO. Hence, while correct values are calculated for the more intensely absorbing conjugate base, **2b**, the calculated concentrations of weakly absorbing **1b**⁺ stray from those predicted by mass balance, especially

(67) Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 4251.

(68) (a) Kolthoff, I. M.; Chantooni, M. K.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23. (b) Kolthoff, I. M.; Chantooni, M. K. *J. Phys. Chem.* **1972**, *76*, 2024. (c) Matthews, W. S.; Bares, J. E.; Batmess, J. E.; Bordwell, F. G.; Cornforth, F. G.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.

when $[2b] > [1a^+]$. The concentration calculated by mass balance was therefore used in further calculations in the cases where this discrepancy was >10%.

In the deprotonation of **1a**[PF₆], two factors conspire to drive equilibrium 14 to the right, precluding the simplification that the deprotonation of the solvent is negligible, as had been assumed for the NMR experiments involving NaOMe in DMSO-*d*₆. In the present case, calculation of the *K**t*-BuO/DMSO interactions in the absence of the analyte shows that >97% of the *Kt*-BuO is protonated by the solvent. This high level of deprotonation may be ascribed both to the fact that the pK_a of the base (32.2 in DMSO)⁴¹ approaches that of the solvent (35.1)⁶⁴ and to the low concentrations of base and analyte ($\approx 5 \times 10^{-4}$ M) necessitated by the spectroscopic technique, compared to the concentration of the pure solvent (14.09 M). The concentrations in the system, therefore, were determined by assuming (i) complete protonation of the base by the solvent followed by equilibration "from the other side" and (ii) that primarily the thus-formed dimesyl ion deprotonates **1a**⁺ to give **2a**. These assumptions transform the equilibrium constant for eq 14 into

$$\frac{K_{\text{DMSO}}}{K_{t\text{-BuOH}}} = \frac{10^{-35.1}}{10^{-32.2}} = \frac{[BH][\text{dimesyl}^-]}{[B^-][\text{DMSO}]} = \frac{(B_t - [B])(B_t - [B] - [2b])}{[B^-][\text{DMSO}]} \quad (18)$$

where B_t represents the concentration of base initially added. Solving eq 18 for $[B^-]$ gives

$$[B^-] = \alpha - (a^2 B_t + B_t [2b])^{1/2} \quad (19)$$

$$\alpha = B_t - [2b]/2 + K_{\text{DMSO}}[\text{DMSO}]/(2K_{t\text{-BuOH}})$$

$$= B_t - [2b]/2 + 8.862 \times 10^{-3} \text{ M}$$

The base concentration thus obtained allows the calculation of the equilibrium constant K_{eq} by eq 20 (or by eq 21 when the concentration of **1b**[PF₆] calculated by eq 17 differs from the concentration obtained by mass balance, C_{Fe} being the total concentration of iron species):

$$K_{\text{eq}} = \frac{[2b][BH^-]}{[1bPF_6][B^-]} = \frac{[2b](B_t - [B^-])}{[1bPF_6][B^-]} = \frac{[2b](B_t - [B^-])}{(C_{\text{Fe}} - [2b])[B^-]} \quad (20)$$

The average of the resulting pK_{eq} values was then added to $pK_{t\text{-BuOH}}$ to obtain the pK_a value for **1b**[PF₆] (Scheme 1).

Acknowledgment. This paper is dedicated to Professor Henri Bouas-Laurent at the occasion of his 65th birthday. Financial support from the Institut Universitaire de France (D.A.), University Bordeaux I, the Centre National de la Recherche Scientifique, NSF (Post-doctoral Grant CHE-9203570 to H.A.T.), and Ministerio de Educación y Ciencia (C.M.C., Spain) is gratefully acknowledged.

Supporting Information Available: Tables giving values of the peak potentials for the cathodic reduction and anodic oxidation of **2a–e** at 100 and 1000 mV/s and a discussion of the shifts of peak potentials in the context of the EC_{irrev} mechanism (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA984101X