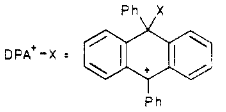
Scheme I

$$\begin{array}{lcr} & \Delta G^{\circ} & \\ A^{+\bullet} \rightleftharpoons A^{2+} + e^- & FE_1^{\circ} & (1) \\ A^{+}\text{–}Nu^{+} + e^- \rightleftharpoons A^{\bullet}\text{–}Nu^{+} & -FE_2^{\circ} & (2) \\ \hline A^{2+} + Nu \rightleftharpoons A^{+}\text{–}Nu^{+} & -RT \ln K(DC) & (3) \\ A^{\bullet}\text{–}Nu^{+} \rightleftharpoons A^{+\bullet} + Nu & RT \ln K(CR) & (4) \\ \hline \multicolumn{2}{l}{\log K(DC) - \log K(CR) = F(E_1^{\circ} - E_2^{\circ})/2.30RT} & (5) \end{array}$$

Table I. Electrode Potential and Equilibrium Data for Reactions of the Cation Radical and Dication of 9,10-Diphenylanthracene

quantity	X in DPA^+–X^b CF_3COO	 HO
$E_1^0 - E_2^0$/mV^a	1130	1230
log K(DC) – log K(CR)	19	21

^{a}Difference in reversible potentials estimated from cyclic voltammetry data in ref 11. ^{b}See structure below:



$DPA^{\bullet}$–Nu^+, the cation radical/nucleophile adduct formed in eq 4, but E^{rev} can be estimated with an accuracy of about 0.1 V giving rise to a maximum error in log K(DC) – log K(CR) of 2 units or less.

Pertinent electrode potential data for the application of the thermodynamic cycle for the equilibria of cation radicals and dications of 9,10-disubstituted anthracenes with a number of nucleophiles were published some time ago.[11] Data for 9,10-diphenylanthracene dications in dichloromethane–trifluoroacetic acid reacting with trifluoroacetic acid and water as nucleophiles are summarized in Table I. The analysis resulted in log K(DC)–log K(CR) of 19 and 21 for the two nucleophiles. The rate constant for the reaction of DPA^{2+} in acetonitrile at 273 K was determined by derivative cyclic voltammetry (DCV)[12] to be 900 s^{-1}, corresponding to $k(DC) = 9 \times 10^4$ M^{-1} s^{-1} for the reaction with water ($[H_2O]$ = 10 mM). The rate constant for the reaction of $DPA^{\bullet+}$ with water under similar conditions has been reported to be equal to 0.083 M^{-1} s^{-1}.[13] In dichloromethane (273 K) second-order rate constants of 0.035 and 1.25×10^5 M^{-1} s^{-1} were obtained by DCV for the reactions of $DPA^{\bullet+}$ and DPA^{2+}, respectively, with methanol.

The intrinsic reactivity of cation radicals as compared to the more reactive dications and carbenium ions has been assessed to be unusually low.[3,4] On the basis of our relative equilibrium constants, $K(DC)/K(CR) = 10^{20}$, we predict that the dication should react faster than the cation radical with nucleophiles. The relative rate constants observed, $k(DC)/k(CR) = 10^6$, are in the expected direction but very much smaller than the equilibrium constant ratio. Since Ritchie has found that rate and equilibrium constants for the reactions of carbenium ions with nucleophiles do not correlate,[14] it is not justified to conclude that it is the dications rather than the cation radicals that react unusually slowly. A possible reason for the fact that our rate and equilibrium constants do not correlate is that rate–equilibrium relationships break down when K becomes too far removed from unity.[15] Our data do suggest that it is not justified to conclude that cation radicals react unusually slowly when compared to the reactions of the corresponding dications. A change from a singly charged ion to a doubly charged ion is a very big perturbation and is expected to have a large effect on reactivity.

Table II. Acidity Constants of Triarylmethanes and the Corresponding Cation Radicals and Dications

triarylamine	pK_{HA}^{a}	$pK_{HA^{+}}$^{b}	$pK_{HA^{2+}}$^{c}
p-methoxyphenyldiphenylmethane	32.5	–19	–57 (–60)
triphenylmethane	31.5	–24	–72 (–76)

^{a}In dimethylsulfoxide, from ref 16. ^{b}Estimated from cyclic voltammetry data by using the procedure in ref 9. Oxidation potentials of carbanions were those reported in ref 16. ^{c}Application of the thermodynamic cycle in Scheme I; values in parentheses include a 200-mV kinetic shift correction for the oxidation potential of the triarylmethane cation radicals in dichloromethane

A variation of the thermodynamic cycle (Scheme I) can be applied to show the super acid properties of dications containing acidic hydrogen. Data for triarylmethanes (HA) are summarized in Table II. The pK_{HA} are those reported by Breslow,[16] and the $pK_{HA^{\bullet+}}$ were estimated by the method developed by Bordwell.[9] The most interesting feature of the data is the very large negative $pK_{HA^{2+}}$ values estimated (Table II) for the dications of *p*-methoxyphenyldiphenylmethane (–56) and triphenylmethane (–76).

The application of the thermodynamic cycle (Scheme I) has provided the first equilibrium data for the reactions of the highly reactive organic dications. The rate constants reported here are the first to be measured for the reactions of aromatic hydrocarbon dications. The pK_a value estimated for triphenylmethane dication is of the order of 50 units more negative than any previously reported values.

Acknowledgment. We gratefully acknowledge helpful comments by Professor John I. Brauman. The work was supported by a grant from the Norwegian Research Council for Science and the Humanities.

Registry No. DPa^{2+}, 70470-09-6; $DPA^{\bullet+}$, 34480-04-1; DPA^+-OC(O)CF_3, 112460-82-9; DPA^+-OH, 112460-83-0; H_2O, 7732-18-5; CF_3CO_2H, 76-05-1; *p*-$MeOC_6H_4CHPh_2$, 13865-56-0; *p*-$MeOC_6H_4CHPh_2^{\bullet+}$, 112481-57-9; *p*-$MeOC_6H_4CHPh_2^{2+}$, 112460-84-1; Ph_3CH, 519-73-3; $Ph_3CH^{\bullet+}$, 88424-77-5; Ph_3CH^{2+}, 112460-85-2.

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[12] Ahlberg, E.; Parker, V. D. *J. Electroanal. Chem.* **1981**, *121*, 57, 73. Parker, V. D. *Electroanal. Chem.* **1986**, *14*, 1.

[13] Sioda, R. E. *J. Phys. Chem.* **1968**, *72*, 2322.

[14] Ritchie, C. D.; Kubisty, C.; Ting, G. Y. *J. Am. Chem. Soc.* **1983**, *105*, 279.

[15] We are indebted to a referee for pointing out the pitfalls of attempting to use rate–equilibrium relationships in cases where K is very far removed from unity.

[16] Breslow, R.; Chu, W. *J. Am. Chem. Soc.* **1973**, *95*, 411.

[17] The values of pK_{HA} and $pK_{HA^{\bullet+}}$ refer to DMSO as solvent while $pK_{HA^{2+}} - pK_{HA^{\bullet+}}$ obtained by using eq 5 refer to CH_2Cl_2. The $pK_{HA^{2+}}$ in Table II assume that $E_{ox}^{\circ}(Ar_3CH) - E_{red}^{\circ}(Ar_3C^+)$ are the same in CH_2Cl_2 as in DMSO, within the limits of error (±100 mV) of the method.

Intermediacy of Paramagnetic Metal–Hydrocarbyl Species in Organometallic Reactions. Detection and Characterization of a Novel Paramagnetic Iron(II)–Benzyl Compound in the Coupling of Benzyl Halides[1]

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Paramagnetic metal–hydrocarbyl species have been postulated as intermediates in several organometallic reaction sequences.[3] In the preponderance of these reactions the paramagnetic intermediate has been detected by ESR spectroscopy. In other cases

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[2] Alfred P. Sloan Research Fellow, 1984–1988.

[3] Specific examples: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978. Examples relating to coupling of hydrocarbyl groups: (c) Reference 3a, Chapters 5 and 14. (d) Reference 3b, Chapter 14. (e) Fukuzumi, S.; Ishikawa, K.; Tanaka, T. *Organometallics* **1987**, *6*, 358. (f) Hegedus, L. S.; Thompson, D. H. P. *J. Am. Chem. Soc.* **1985**, *107*, 5663, (g) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547, 6319.

0002-7863/88/1510-1650$01.50/0

Table I. ^2H NMR Resonances[a] (Integrals) in the Following Reaction: $\mathbf{1} + RX \rightarrow \mathbf{2} + Cp_2Fe$ in Benzene at 20 °C

reactants	benzyl	*m*-phenyl	*o*-phenyl	*p*-phenyl	Cp
1-Cp-h_5 + benzyl-d_7 chloride	947 (2D)	30.5 (2D)	−42.3 (2D)	−64.5 (1D)	
1-Cp-h_5 + benzyl-α,α-d_2 bromide	947				
1-Cp-h_5 + benzyl-α-d_1 bromide	947				
1-Cp-h_5 + benzyl-*2,3,4,5,6*-d_5 chloride		30.5 (2D)	−42.3 (2D)	−64.5 (1D)	
1-Cp-h_5 + benzyl-*3*-d_1 chloride		30.5			
1-Cp-d_5 + benzyl-d_7 chloride	947 (2D)	30.5 (2D)	−42.3 (2D)	−64.5 (1D)	4.0 (5D)

[a] Chemical shifts in ppm.

these species have been implicated by the observation of CIDNP as a result of the formation of an accompanying organic radical. Unfortunately, the more direct characterization of these intermediates by NMR spectroscopy based upon chemical shifts and resonance intensities has, thus far, been hindered by severe line broadening.[4] Herein, we report the detection and characterization by NMR spectroscopy of a novel paramagnetic Fe(II)–benzyl compound $(TMEDA)Fe(CH_2Ph)_2$, **2**, which is the key intermediate in the coupling of benzyl halides by [CpFe(COD)][Li(TMEDA)], **1**[5] (Cp = $C_5H_5^-$, COD = 1,5-cyclooctadiene, TMEDA = $Me_2N(CH_2)_2NMe_2$).

The addition of an excess of $PhCH_2X$ (X = Cl, Br) to **1** in benzene or toluene at 25 °C resulted in the formation of $PhCH_2CH_2Ph$ (81% yield relative **1**) within a few minutes. The addition of 1 equiv of $PhCH_2X$ to **1** in benzene or toluene at 25 °C resulted in the change in solution color from yellow to red. At 20 °C, the ^1H NMR spectrum of this solution exhibited broad singlets at +947, +30.5, −42.3, and −64.5 ppm in the intensity ratio of 2:2:2:1 and two very broad resonances at +111.7 and +95.6 ppm in the intensity ratio of 3:1. By using ^2H NMR spectroscopy and selectively labeled compounds as outlined in Table I, the first four resonances were assigned to the benzylic, meta, ortho, and para hydrogens, respectively, of a paramagnetically shifted benzyl group. The two broad resonances at +111.7 and +95.6 ppm were assigned to the methyl and methylene groups, respectively, of coordinated TMEDA, based on the following observations. The coordination of COD was ruled out because the position of the vinylic resonance (5.5 ppm) corresponded to that of free COD. Furthermore, the removal of volatiles from the reaction mixture resulted in the quantitative removal of COD. When the residue was redissolved, the paramagnetically shifted NMR resonances were found to be unaffected. There was no coordination of the solvent (arene) since the above resonances were also observed when the reaction was carried out in THF, COD, and pentane. Finally, NMR spectroscopy revealed that the Cp ligand was present in the form of Cp_2Fe. In addition to the NMR resonances described thus far, there were broad overlapping resonances between 2.3–1.8 ppm as a result of allylic COD hydrogens and 0.5 equiv of uncoordinated TMEDA (relative to **1**).

In summary, the NMR spectroscopic data indicated that a paramagnetic complex **2** was formed through the reaction of **1** with $PhCH_2X$ and that **2** contained 0.5 equiv of TMEDA and 1 equiv of CH_2Ph relative to **1**. Furthermore, the simultaneous formation of 0.5 equiv of Cp_2Fe indicated that 0.5 equiv of Fe (relative to **1**) was present in **2**. Thus, **2** contains Fe, TMEDA, and CH_2Ph fragments in the ratio of 1:1:2, i.e., its formula is $(TMEDA)Fe(CH_2Ph)_2$ (eq 1). The equivalence of the hydrogens

$$\underset{\mathbf{1}}{[CpFe(COD)][Li(TMEDA)]} + PhCH_2X \rightarrow$$

$$\underset{\mathbf{2}}{0.5(TMEDA)Fe(CH_2Ph)_2} + 0.5Cp_2Fe + LiX + COD + 0.5TMEDA \quad (1)$$

on the two benzyl groups necessitates a structure with an S_n axis and this can be accommodated by postulating a (distorted) tetrahedral structure for **2**. In this context, we note that a similar paramagnetic, tetrahedral, Fe(II) complex, $(phosphine)_2FeR_2$, has been reported recently.[6]

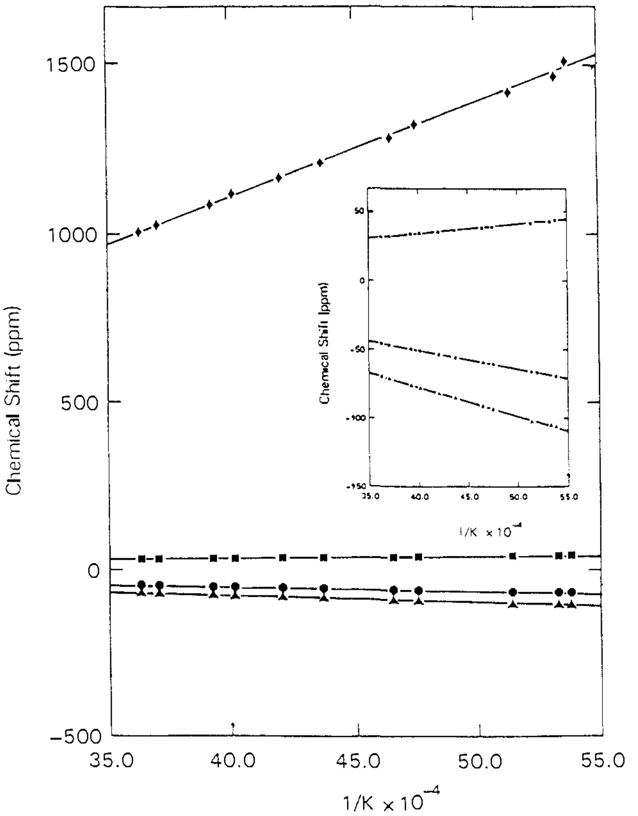

Figure 1. Plot of chemical shift versus 1/temperature for the benzylic (♦), meta (■), ortho (●), and para (▲) ^2H NMR resonances of $(TMEDA)Fe(benzyl\text{-}d_7)_2$. Inset: 50 to −150 ppm range expanded.

A linear relationship between the isotropic shift and the reciprocal of the absolute temperature was observed for the hydrogens of the benzyl group of **2**, as is expected of a paramagnetic compound (Figure 1). At 186 K, in toluene, the resonances due to the benzylic, meta, ortho, and para hydrogens of the benzyl group of **2** were at +1508(!), +43.8, −69.2, and −106.4 ppm, respectively. Note that the observation of only one resonance each for the four positions of the benzyl group, even at low temperatures, supports η^1- rather than η^3-coordination of the benzyl group to Fe. The structure of **2** was further confirmed by its independent synthesis from $(TMEDA)_xFeCl_2$[7] and $PhCH_2Li$[8] in THF and benzene.

In order to probe for intermediates in the conversion of **1** to **2**, the reaction of **1** with $PhCH_2X$ was examined in the presence of DIPHOS (= $Ph_2P(CH_2)_2PPh_2$). By itself, **1** did not react with DIPHOS presumably because the replacement of COD by the stronger donor, DIPHOS, would result in further increase in electron density at the already electron-rich Fe(0) center. The addition of 1 equiv of $PhCH_2X$ to an equimolar solution of **1** and DIPHOS in benzene at 25 °C led to the quantitative formation of the diamagnetic compound, $CpFe(DIPHOS)(CH_2Ph)$, **3** (eq 2). The structure of **3** was established by ^1H NMR[9] and ^{31}P NMR

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[4] La Mar, G. N.; Horrocks, W. DeW.; Holm, R. H. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

[5] Jonas, K.; Schieferstein, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 549.

[6] Hermes, A. R.; Girolami, G. S. *Organometallics* **1987**, *6*, 763.

[7] Hill, D. H.; Sen, A., unpublished results.

[8] Seyferth, D.; Suzuki, R.; Murphy, C. J.; Sabet, C. R. *J. Organomet. Chem.* **1964**, *2*, 431.

spectroscopy in solution and by an X-ray crystal structure determination in the solid state.[7] 3 has an unexceptional 3-legged piano-stool structure with normal bond lengths and bond angles.

$$\underset{\mathbf{1}}{[\mathrm{CpFe(COD)}][\mathrm{Li(TMEDA)}]} + \mathrm{PhCH_2X} \xrightarrow[-\mathrm{TMEDA}]{-\mathrm{LiX}}$$

$$\underset{\mathbf{4}}{[\mathrm{CpFe(COD)(CH_2Ph)}]} \xrightarrow[-\mathrm{COD}]{\mathrm{DIPHOS}} \underset{\mathbf{3}}{\mathrm{CpFe(DIPHOS)(CH_2Ph)}} \quad (2)$$

As shown in eq 2, the formation of **3** appears to indicate that the *initial* species formed in the reaction of **1** with $\mathrm{PhCH_2X}$ was $\mathrm{CpFe(COD)(CH_2Ph)}$, **4**. In the presence of DIPHOS, **3** was formed from **4** by ligand replacement. However, in the absence of a strongly coordinating ligand, **4** underwent disproportionation and reacted with TMEDA to form **2** and $\mathrm{Cp_2Fe}$ (eq 1).

Finally, the coupling product, $\mathrm{PhCH_2CH_2Ph}$, was formed in minutes upon the addition of excess $\mathrm{PhCH_2X}$ to a solution of **2** at 25 °C. This clearly established the intermediacy of **2** in the coupling of benzyl halides by **1**.

Registry No. **1**, 69393-63-1; **1**-Cp-d_5, 112440-11-6; **2**, 112440-07-0; **3**, 64827-29-8; $\mathrm{(TMEDA)_xFeCl_2}$, 112440-08-1; $\mathrm{PhCH_2Cl}$, 100-44-7; $\mathrm{PhCH_2Br}$, 100-39-0; $\mathrm{PhCH_2Li}$, 766-04-1; $\mathrm{PhCH_2CH_2Ph}$, 103-29-7; benzyl-d_7 chloride, 59502-05-5; benzyl-α,α-d_2 bromide, 51271-29-5; benzyl-α-d_1 bromide, 66343-88-2; benzyl-*2,3,4,5,6*-d_5 chloride, 68661-11-0; benzyl-*3*-d_1 chloride, 112440-09-2.

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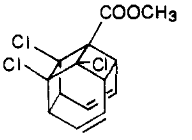
(9) Felkin, H.; Knowles, P. J.; Meunier, B. *J. Organomet. Chem.* **1978**, *146*, 151.

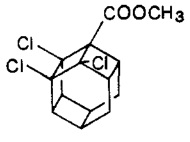
Additions and Corrections

Secohexaprismane [*J. Am. Chem. Soc.* **1987**, *109*, 2212–2213]. GOVERDHAN MEHTA* and S. PADMA

Page 2213: Structures **15** and **21** are missing one Cl atom each and the correct structures are as follows:



15



21

Page 2213, Scheme II, footnotes: Reagents and yields: (q) $\mathrm{HgO{-}CH_2Cl_2}$ should read $\mathrm{HgO{-}CH_2Br_2}$.

Computer Software Reviews

FORTRAN Package 2. Lektor, Inc.: P.O. Box 6713, Kennewick, WA. 77-page manual.

Lektor FORTRAN Package 2 is a collection of FORTRAN subroutines for a variety of numerical methods. The software is intended to run on an IBM PC or compatible with at least 256Kb of memory and two disk drives. A math co-processor is recommended. The software requires a FORTRAN compiler. Lektor suggests the IBM FORTRAN compiler, Version 2, or the IBM Professional FORTRAN compiler. These compilers require DOS, Version 2.00 or higher. The software is not copy protected; backing up the package is recommended by the vendor. The software consists of 34 source subroutines, as well as associated support routines and libraries.

The specific routines comprising the system perform the following functions: solutions to linear and nonlinear simultaneous and differential equations; numerical integration; interpolation; random number generation; special functions such as the error and γ functions and the exponential integral; the discrete Fourier transform; and an implementation of the Simplex algorithm. Since the software is distributed in source as well as object code, verification of the proper coding of the various algorithms can be accomplished by those wishing to do so.

The software is quite easy to use, as simple FORTRAN function calls are used, as

```
CALL SIMPS(N,FUN,A,B,ANS)
```

The limitation, of course, is for those who do not program in the FORTRAN language.

Various functions of the software were tested and found to operate properly. Although this package does not address particular chemical applications, it is a tool kit that can be readily applied to a number of problems of both industrial and academic interest. As with all numeric software, Lektor's caveat applies: "Because of the great variety of problems to which these service routines can be applied, no guarantee can be made... to the accuracy of any routine or its suitability for any particular application." For those in need of such FORTRAN software, this seems a complete and worthwhile package.

Brian J. McGrattan, *The Perkin-Elmer Corporation*

StatWorks. Cricket Software: 3508 Market St., Suite 206, Philadelphia, PA 19104. Retail price $125.00.

StatWorks is a software package designed for the Macintosh personal computer to provide an easy-to-use statistical analysis. Although the range of statistical procedures found in StatWorks is not as wide as that in a main frame environment, the procedures available are more than adequate for any statistical analysis or graphical representation which I have found necessary in my work as a chemist.

It is quite true, as is claimed in the Introduction to StatWorks, that statistical analysis on a personal computer often required wending one's way through a sea of often cryptic documentation or learning new higher level languages. This package contrasts dramatically from such procedures in that it can be easily addressed by anyone familiar with the simplest programs designed for the Macintosh (e.g., MacWrite or MacPaint). The philosophical goal of automatically taking the user through several stages to a complete statistical analysis without the requirement of creation of dummy variables is surely achieved.

The options for graphical representation of the data handled by StatWorks are the easiest methods I have seen for generation of tabular