# Nucleophilic Attack on the Cyclohexadienyl Ligand: From Mono- to Heterobifunctional (Cyclohexadiene)iron Complexes and the Role of the Electron-Transfer Pathway in Hydride Abstraction

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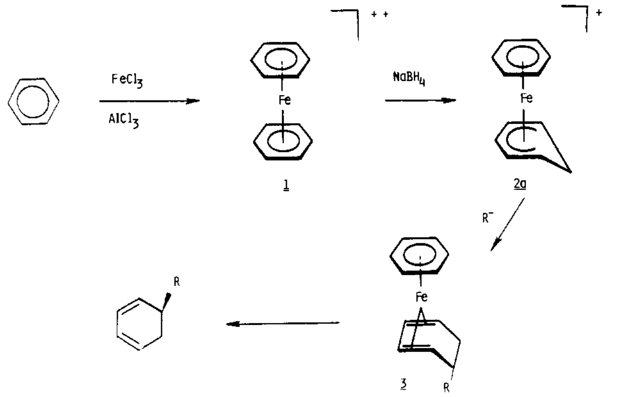
*Received March 13, 1989*

With the aim of synthesizing heterobifunctional *cis*-1,2-cyclohexadienes from benzene, we have investigated hydride abstraction from exo-substituted complexes $[\mathrm{Fe(C_6H_6)(\eta^4\text{-}C_6H_7R)}]$ (**3**) and the second addition of a functional nucleophile to the functional complexes $[\mathrm{Fe(C_6H_6)(\eta^5\text{-}C_6H_6R)}]^+$ (**2**). Although hydride abstraction by $[\mathrm{Ph_3C}]^+$ from $[\mathrm{Fe(\eta^5\text{-}C_6H_6R)(CO)_3}]$ (R ≠ H) was known to be sterically inhibited, we first attempted to remove a hydride from the known complexes **3** (R = $\mathrm{CH_2Ph}$ (**3b**), $\overline{\mathrm{CHS(CH_2)_3S}}$ (**3c**), $\mathrm{CH(CO_2Et)_2}$ (**3d**), CN (**3e**)) according to an electron-transfer (ET) pathway. The ET between **3b** and $[\mathrm{Ph_3C}]^+$ is exergonic ($\Delta G° = -5.5$ kcal/mol$^{-1}$) and proceeds at −50 °C, giving $\mathrm{Ph_3C^\bullet}$ and the 17e Fe$^{\mathrm{I}}$ complexes **3b**$^+$, both characterized by ESR spectroscopy. The species **3**$^+$ are stable at −50 °C for R = $\mathrm{CH_2Ph}$ or $\overline{\mathrm{CHS(CH_2)_3S}}$, and slow H atom transfer to $\mathrm{Ph_3C^\bullet}$ occurs between −50 and −40 °C to give the desired cations $[\mathrm{Fe(C_6H_6)(\eta^5\text{-}C_6H_6R)}]^+$ (**2**) in high yields. However, the 17e Fe$^{\mathrm{I}}$ complex is not stable at −50 °C with R = $\mathrm{CH(CO_2Et)_2}$ and decomposes to R$^\bullet$ and $[\mathrm{Fe(C_6H_6)(\eta^5\text{-}C_6H_7)}]^+$ (**2a**) in 70% yield. Above −40 °C, **3b**$^+$ and **3c**$^+$ also decompose to R$^\bullet$ and **2a** faster than H atom transfer occurs. Addition of KCN to **2b** and **2c** in acetone at 20 °C gives the heterobifunctional (*cis*-1,2-cyclohexadiene)iron(0) complexes **4b** and **4c**. The X-ray crystal structure of **4b** has been reported and its decomplexation using $\mathrm{FeCl_3}$ gives *cis*-1,2-$\mathrm{PhCH_2CNC_6H_4}$ (**5**) free of any rearomatized product (the latter is easily formed thermally).

## Introduction

The modification of reactivity of aromatic compounds by coordination to a transition-metal moiety has led to facile nucleophilic substitutions and additions, enhanced acidity of the benzylic protons, and easier reduction of side chain.[1,2] Whereas all these types of possibilities have been currently used, the double nucleophilic addition[2-11] with functional carbanions[5-8] has attracted attention more recently, especially with $[\mathrm{Mn(CO)_3}]^+$, $[\mathrm{Co(Cp)}]^{2+}$, and $[\mathrm{Fe(C_6H_6)_2}]^{2+}$ as activating groups. In the Mn series,[6] the substituted complex $[\mathrm{Mn(\eta^5\text{-}cyclohexadienyl)(CO)_3}]$ obtained after the first attack needs to be reactivated by exchanging a CO ligand by $\mathrm{NO^+}$. In the Co[5] and Fe[8] dicationic series, the successive addition of two distinct carbanions should provide heterobifunctional cyclohexadienyl complexes. This has indeed been achieved by Vollhardt by addition of $\mathrm{CH_3O^-}$ and $\mathrm{C_5H_5^-}$ to the benzene ligand in $[\mathrm{Co(C_6H_6)Cp}]^{2+}$.[5] With the complex $[\mathrm{Fe(C_6H_6)_2}]^{2+}$, the first addition of a carbanion leads to electron transfer and not to the formation of a C–C bond.[12] On the other hand, $\mathrm{NaBH_4}$ reacts cleanly with $[\mathrm{Fe(C_6H_6)_2}]^{2+}(\mathrm{PF_6^-})_2$ (**1**), to give the cyclohexadienyl complex $[\mathrm{Fe(C_6H_6)(\eta^5\text{-}C_6H_7)}]^+$ (**2a**).[8-10,13] A variety of carbanions were shown to give the monosubstituted cyclohexadiene complexes $[\mathrm{Fe(C_6H_6)(\eta^4\text{-}\mathit{exo}\text{-}RC_6H_7)}]$ (**3**) by a regio- and stereospecific orbital-controlled reaction.[9,10] A series of substituted cyclohexadienes[9,10] could be obtained in this way after oxidation of the Fe$^0$ complex by $\mathrm{FeCl_3}$ (Scheme I).

**Scheme I**



However, an even more interesting challenge was to open the route to heterodisubstituted cyclohexadienes. For this purpose we attempted to remove a hydride from **3** and add a carbanion to the resulting monocation. Especially challenging was the hydride removal from **3** since a hydride could not be removed (for steric reasons) from exo-substituted ($\eta^5$-cyclohexadiene)iron tricarbonyl[14] (eq 1). These

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(1) (a) Jaouen, G. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 59. (b) Semmelhack, M. F. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 36. (c) Abd-El-Aziz, A. S.; Lee, C. C.; Piorko, A.; Sutherland, R. G. *J. Organomet. Chem.* **1988**, *348*, 95; *J. Organomet. Chem. Libr.* **1976**, *1*, 361.

(2) Astruc, D. In *The Chemistry of the Metal-Carbon Bond*; Patai, S., Hartley, F. R., Eds.; Wiley: London, 1987; Vol. IV, Chapter 7, p 625. Astruc, D. Tetrahedron Report 157. *Tetrahedron* **1983**, *39*, 4027; *Acc. Chem. Res.* **1986**, *103*, 377.

(3) For a double hydride attack and an hydride + methide attack on $[\mathrm{Mn(C_6H_8)(CO)_3}]^+$ and for a review on nucleophilic attacks on arenes in cationic complexes, see: Lamana, W.; Brookhart, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 989.

(4) (a) Brookhart, M.; Lamana, W.; Pinkas, A. P. *Organometallics* **1983**, *2*, 638. (b) Brookhart, M.; Lukacs, A. *J. Am. Chem. Soc.* **1984**, *106*, 4161. (c) Brookhart, M.; Lamana, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117.

(5) Lai, Y.-L.; Tam, W.; Vollhardt, K. P. L. *J. Organomet. Chem.* **1981**, *216*, 97.

(6) (a) Chung, Y. K.; Khoi, H. S.; Sweigart, D. A.; Connelly, N. G. *J. Am. Chem. Soc.* **1982**, *10*, 4245. (b) Chung, Y. K.; Sweigart, D. A.; Connelly, N. G.; Sheridan, J. B. *J. Am. Chem. Soc.* **1985**, *107*, 2388.

(7) (a) Pearson, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 488. (b) Pearson, A. J.; Ong Chi Wi *J. Org. Chem.* **1982**, *47*, 3780.

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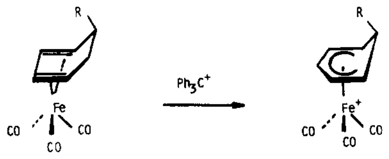
studies have been the subject of a preliminary communication[8] and are detailed here.



(1)

## Experimental Section

**General Data.** All reactions were performed under an argon atmosphere by Schlenk techniques or in a nitrogen-filled Vacuum Atmosphere drylab. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl under argon just before use. Aromatic impurities from pentane and hexane were removed by treatment with a sulfonitric mixture; pentane and hexane were first distilled under argon on potassium hydroxide and then distilled on sodium benzophenone ketyl just before use. Benzene was distilled and stored under argon. Acetonitrile and dichloromethane were dried on $P_2O_5$, distilled from sodium carbonate, and stored under argon. Aluminum trichloride was trisublimed. Sodium borohydride and potassium cyanide were dried by standing 15 h at 100 °C and stored under argon. All other chemicals were used as received. The complexes of the series $[Fe(C_6H_6)(\text{cyclohexadiene})]$ (**3**) were synthesized as previously described.[10] $^1H$ NMR spectra were obtained with a Varian 360 instrument (60 MHz) (FT 80 MHz $^1H$, 20.115 Hz); $^{13}C$ spectra were recorded with a Brucker WP 80 FT spectrometer by Dr. S. Sinbandhit (Centre de Mesures Physiques de l'Ouest, Rennes). All chemical shifts are reported in parts per million ($\delta$, ppm) with reference to tetramethylsilane ($Me_4Si$) and were measured relative to the solvent or $Me_4Si$. Mass spectra were recorded by using a Varian MAT 311 (70 eV) instrument by Dr. P. Guênot (CMPO, Rennes). Gas chromatographic (GC) analyses were obtained with a Delsi GC 121 chromatograph equipped with a Helwett-Packard 3390 integrator by using a glass column (length 1.4 m, i.d. 3 mm) packed with Apiezon L (15%) on Chromosorb WAW. Infrared spectra were recorded with a Pye-Unicam SP 1100 photospectrometer that was calibrated with polystyrene film. Elemental analyses were performed by the Centre of microanalyses of the CNRS at Lyon-Villeurbane.

**Reaction of $[Ph_3C]^+PF_6^-$ with the Complexes $[Fe(C_6H_6)(\eta^4\text{-}C_6H_7R)]$ (3; R = $CH_2Ph$ (3b), $\overline{CHS(CH_2)_3S}$ (3c), and $CH(CO_2Et)_2$ (3d)). (1) Increase of the Reaction Temperature from −80 to 20 °C.** Complex **3** (1 mmol) was solubilized under argon in 20 mL of $CH_2Cl_2$. This solution was cooled down to −90 °C, and $[Ph_3C]^+PF_6^-$ (390 mg, 1 mmol) was added under argon and vigourous stirring. The mixture was then greenish black, and the temperature was allowed to rise to −50 °C. At this temperature, the reaction mixture became lighter and orange-red. The temperature was raised to 20 °C for 1 more hour. Addition of ether allowed the salt $[Fe(C_6H_6)(\eta^5\text{-}C_6H_7)]^+PF_6^-$ to precipitate as **2a** in 20% yield, leading to a dark brown solution.

**(2) Low-Temperature Reaction.** For complex **3b** or **3c**, the greenish black reaction mixture, prepared as above, was allowed to warm to −50 °C where a color change to orange-red occurred; but then it was kept between −50 and −40 °C for 2 h before being warmed up for 2 more hours to 20 °C. The solvent was evaporated in vacuo and the residue dissolved in acetonitrile. This solution was then filtered under argon and concentrated. Slow addition of ether allowed the salt to precipitate as red microcrystals that were filtered, then washed, and dried with ether.

**R = $CH_2Ph$**: 0.42 g of **2b** (94% yield); $^1H$ NMR ($CD_3CN$) $\delta$ 1.59 (d, 2 H, $^1J_{H-H}$ = 7.3 Hz, $CH_2Ph$), 2.81 (m, 1 H, endo), 3.62 (m, 2 H, o-C*H*), 4.77 (m, 2 H, m-C*H*), 6.16 (s, 6 H, $C_6H_6$), 6.85, 7.20 (2m, 6 H, p-C*H*, Ph); $^{13}C$ NMR ($CD_2Cl_2$) $\delta$ 36.9 (*C*HR ipso), 46.9 (*C*h$_2$Ph), 48.5 (ortho dienyl), 84.1 (meta dienyl), 85.3 (para dienyl), 90.8 ($C_6H_6$), 126.8, 128.8, 129.4, 136.6 ($C_6H_5$). Anal. Calcd for $C_{19}H_{19}FePF_6$: C, 50.89; H, 4.24. Found: C, 50.61; H, 4.30.

**R = $\overline{CHS(CH_2)_3S}$**: 0.45 g of **2c** (95% yield); $^1H$ NMR ($CD_3CN$) $\delta$ 1.76–3.15 (m, 8 H, dithiane, H endo), 3.92 (m, 2 H, ortho C*H*), 4.84 (m, 2 H, meta C*H*), 6.24 (s, 6 H, $C_6H_6$), 6.66 (m, 1 H, para C*H*); $^{13}C$ NMR ($CD_3CN$) $\delta$ 26.8 ($CH_2$, dithiane), 27.1 (s, $CH_2$, dithiane), 37.1 (*C*HR ipso), 47.9 (ortho dienyl), 52.5 (H$CS_2$ dithiane), 84.2 (meta dienyl), 86.1 (para dienyl), 91.8 ($C_6H_6$); infrared (KBr) $\nu_{C-S}$ = 905 cm$^{-1}$. Anal. Calcd for $C_{16}H_{19}FePF_6S_2$: C, 40.33; H, 3.99. Found: C, 40.44; H, 3.99.

**Preparation of the ESR Sample.** The complex $[Fe(C_6H_6)(\eta^4\text{-}C_6H_7CH_2Ph)]$ (**3b**) (1 mmol) and $[Ph_3C]^+PF_6^-$ (1 mmol) were dissolved in 10 mL of dichloromethane at −70 °C under argon. Part of this solution was transferred into an ESR tube and warmed up until the solution began to change color; then the ESR tube was cooled down in liquid nitrogen and stored until the spectra were recorded at 140 K. This operation was repeated four times.

**Reaction of KCN with $[Fe(C_6H_6)(\eta^5\text{-}C_6H_6R)]^+PF_6^-$ (2; R = $CH_2Ph$ (2b) and $\overline{CHS(CH_2)_3S}$ (2c)). (1) R = $CH_2Ph$.** Dry KCN (200 mg, excess) was added under argon at 20 °C to an acetone solution of $[Fe(C_6H_6)(\eta^5\text{-}C_6H_6CH_2Ph)]^+PF_6^-$ (150 mg, 0.33 mmol), and the mixture was stirred for 3 days. The solvent was removed in vacuo, the yellow solid was extracted with ether, and the ether solution was filtered and concentrated. After the addition of pentane, the crystalline orange neutral complex **4b** was formed and separated (95 mg, 87%). The crystals were found suitable for X-ray crystal structure determination. They were air-sensitive, becoming black in air within a few hours. The solution decomposed in air within a few minutes. If the reaction time was reduced to 1 day, only lower yields were obtained: $^1H$ NMR ($C_6D_6$) $\delta$ 2.24 (m, 2 H, endo), 2.97 (m, 2 H, C*H*$_2$Ph), 4.22 (m, 2 H, $\alpha$ C*H* diene), 4.50 (m, 2 H, $\beta$ C*H* diene), 4.54 (s, 6 H, $C_6H_6$), 7.16 (m, 5 H, $C_6H_5$); $^{13}C$ NMR ($CD_2Cl_2$) $\delta$ 32.6 (*C*HCH$_2$ diene), 43.0 (*C*H$_2$Ph), 45.3, 46.3 (C sp$^2$, $\alpha$ diene), 83.6 ($C_6H_6$), 121.7 (*C*N), 126.1, 128.5, 129.5, 141.0 ($C_6H_5$); infrared (KBr) $\nu_{C\equiv N}$ = 2240, $\nu_{C=C}$ = 1610 cm$^{-1}$.

**(2) R = $\overline{CHS(CH_2)_3S}$.** Dry KCN (200 mg, excess) was added under argon at 20 °C to an acetone solution of $[Fe(C_6H_6)\{\eta^5\text{-}C_6H_6\overline{CHS(CH_2)_3S}\}]^+PF_6^-$ (250 mg, 0.52 mmol), and the mixture was stirred for 1 week. The solvent was removed in vacuo, the residue was dissolved in ether, and the pale yellow solution was filtered. This did not yield microcrystals, but an oily residue of **4c** was obtained (80 mg, after washing with pentane, 45% yield): $^1H$ NMR ($C_6D_6$) $\delta$ 1.56 (para C*H*$_2$ dithiane, 2 H exo), 2.38 (m, 5 H, SCH$_2$, dithiane), 4.30, 4.50 (m, 4 H, diene), 4.52 (s, 6 H, $C_6H_6$); infrared (KBr) $\nu_{C\equiv N}$ = 2240 cm$^{-1}$.

## Results and Discussion

**Syntheses of Functional Monocations.** The complexes $[Fe(C_6H_6)(\eta^4\text{-}C_6H_7R)]$ (R = $CH_2Ph$ (**3b**), $\overline{CHS(CH_2)_3S}$ (**3c**), $CH(CO_2Et)_2$ (**3d**), and CN (**3e**))[10] were reacted with $[Ph_3C]^+PF_6^-$ in order to abstract $H^-$ and obtain the corresponding functional monocations. The reactions do not occur at −80 °C but only start at −50 °C, as indicated by the color change from greenish black to orange. However, when the reaction temperature was allowed to increase regularly from −90 to 20 °C, various amounts of the

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(8) Mandon, D.; Toupet, L.; Astruc, D. *J. Am. Chem. Soc.* **1986**, *108*, 1320.

(9) Madonik, A. M.; Mandon, D.; Michaud, P.; Lapinte, C.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 3381.

(10) Astruc, D.; Michaud, P.; Madonik, A. M.; Saillard, J.-Y.; Hoffmann, R. *Nouv. J. Chim.* **1985**, *9*, 41.

(11) For early reports on double hydride attack on coordinated benzene, see: (a) Jones, D.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4458. (b) Jones, D.; Wilkinson, G. *J. Chem. Soc.* **1971**, 3807. (c) Grundy, S. L.; Maitlis, P. M. *J. Chem. Soc.* **1982**, 379.

(12) (a) Madonik, A. M.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 2437. (b) See, however, the recent reaction of $AlEt_3$ with $[Fe(C_6H_6)_2]^{2+}$ giving $[Fe(C_6H_6)(\eta^5\text{-}C_6H_6Et)]^+$: Cameron, T. S.; Clerk, M. D.; Linden, A.; Sturge, K. C.; Zaworotko, M. J. *Organometallics* **1988**, *7*, 2571.

(13) (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N.; Polkovnikova, L. S. *Dokl. Akad. Nauk SSSR* **1977**, *236*, 1130. (b) $NaBH_4$ reacts further to give a second hydride attack that provides $[Fe(C_6H_8)(\eta^4\text{-}C_6H_8)]$.[9,10]

(14) (a) Fischer, E. O.; Fischer, R. D. *Angew. Chem.* **1960**, *72*, 919. (b) Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463; *Transition Met. Chem.* (*Weinheim, Ger.*) 1981, *6*, 67.

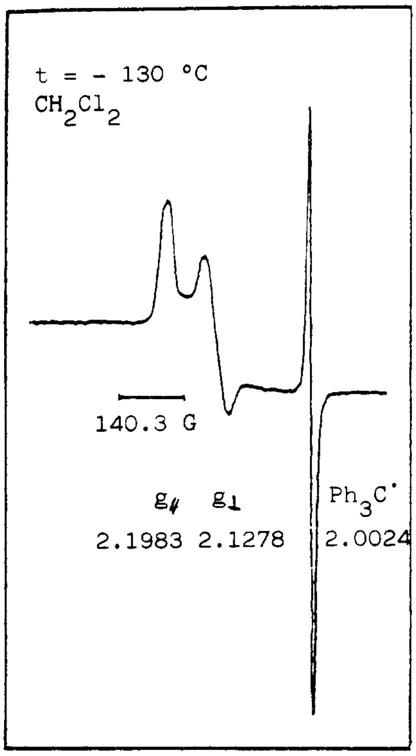


**Figure 1.** Monitoring the reaction of $[Ph_3C]^+$ with $[Fe(C_6H_6)(\eta^4\text{-}C_6H_7CH_2Ph)]$ by ESR spectroscopy at −130 °C.

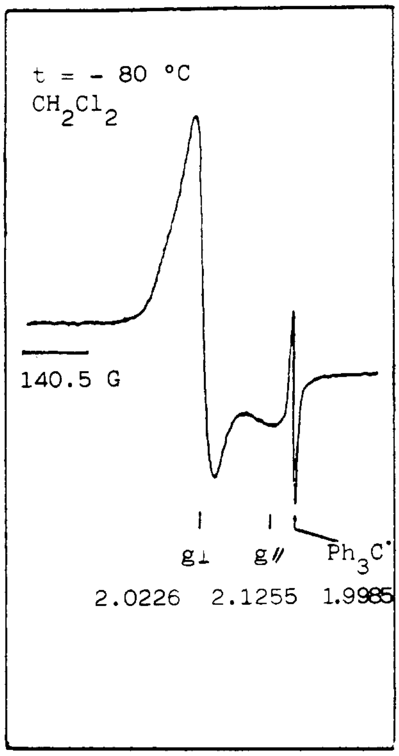


**Figure 2.** Monitoring the reaction of $[Ph_3C]^+$ with $[Fe(C_6H_6)(\eta^4\text{-}C_6H_7CH_2Ph)]$ by ESR spectroscopy at −80 °C.

*nonfunctional* cation $[Fe(C_6H_6)(\eta^5\text{-}C_6H_7)]^+$ (**2a**)[13] were obtained as the only tractable organoiron product. However, if the reaction mixture was kept at −50 to −40 °C for 2 h, then the complexes **3b** and **3c** led to the pure hydride abstraction products **2b** and **2c** in 90–95% yields. However, the complexes **3d** and **3e** did not give the satisfactory product. In the case of **3d**, the unsubstituted cation **2a** was obtained in 70% yield whereas the reaction with **3e** seemingly led to decomposition.

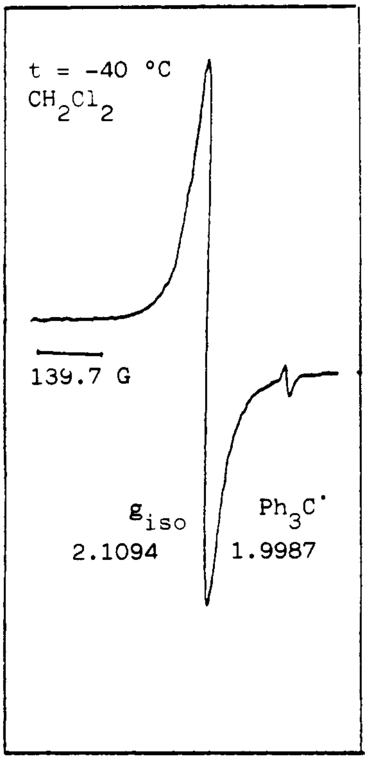


**Figure 3.** Monitoring the reaction of $[Ph_3C]^+$ with $[Fe(C_6H_6)(\eta^4\text{-}C_6H_7CH_2Ph)]$ by ESR spectroscopy at −40 °C.

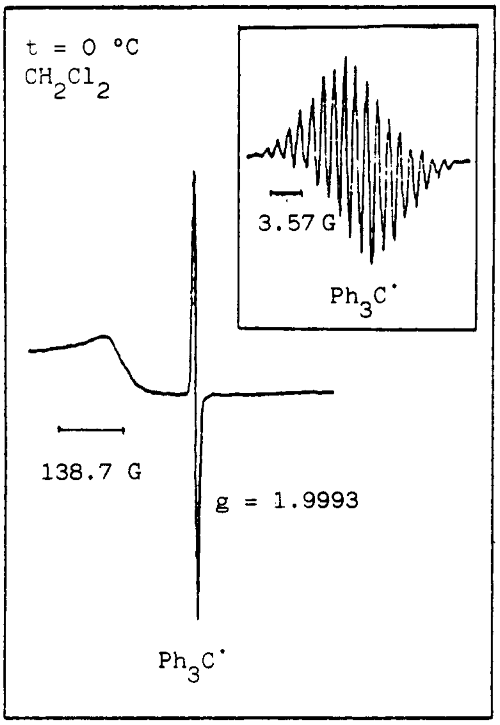


**Figure 4.** Monitoring the reaction of $[Ph_3C]^+$ with $[Fe(C_6H_6)(\eta^4\text{-}C_6H_7CH_2Ph)]$ by ESR spectroscopy at 0 °C.

**ESR Studies of the Intermediates in the $H^-$ Abstraction.** The reaction of **3b** with $[Ph_3C]^+PF_6^-$ was monitored by ESR since the intermediacy of paramagnetic species was strongly suspected. The ESR spectra were recorded at −140 °C for samples with changed color at −50 °C and were immediately frozen down to −196 °C. Indeed paramagnetic species were observed as shown in Figures 1–5.

1. At −130 °C in frozen solutions, two radicals were observed: one showed a large signal characteristic of an

iron centered radical ($g_{\parallel} = 2.198$, $g_{\perp} = 2.128$),[15] the other was a sharp singlet, typical of an organic radical, $g = 2.002$ (Figure 1).

2. At −80 °C, the solution was viscous and both radicals were still observed. The intensity of the signal of the iron radical ($g_{\parallel} = 2.125$, $g_{\perp} = 2.022$) was larger than that of the organic radical, $g = 1.998$ (Figure 2).

3. At −40 °C, the sample was perfectly liquid and the medium was isotropic. Both radicals were still observed, and the signal of the iron radical ($g_{\text{iso}} = 2.108$) was much more intense than that of the organic radical, $g = 1.998$ (Figure 3).

4. At 0 °C, the signal of the iron radical disappeared and was replaced by a weak signal due to the decomposition product of the iron radical. An intense signal presenting a fine structure was observed: 16 lines centered on $g = 1.999$ for $Ph_3C^{\bullet}$ (Figure 4).[16]

5. When this sample was cooled down to −120 °C, the spectrum was the same as that observed at 0 °C except that no fine structure for $Ph_3C^{\bullet}$ was seen (the electron was "frozen" on the carbon center $Ph_3C^{\bullet}$).

**Mechanism of the Hydride Abstraction from 3.** The hydride abstraction reaction by $[Ph_3C]^+$ is well-known and has been largely used in organometallic chemistry.[17] It was observed in the case of $[Fe(\eta^4\text{-}C_6H_8)(CO)_3]$.[14a] If the cyclohexadiene ligand bears an exo substituent, it was found impossible to realize[14] except when the $SiMe_3$ group in β-position[18] was present. Similarly, Faller et al.[19] and Green et al.[20] have shown the versatility of this reaction in molybdenum chemistry. An ET mechanism was disclosed by Cooper in the hydride abstraction of a tungsten–methyl complex.[20] The trityl cation is also known as a good oxidizing agent as the potential $E°$ of the reversible couple $[Ph_3C]^+/Ph_3C^{\bullet}$ is 0.2 V vs SCE.[22]

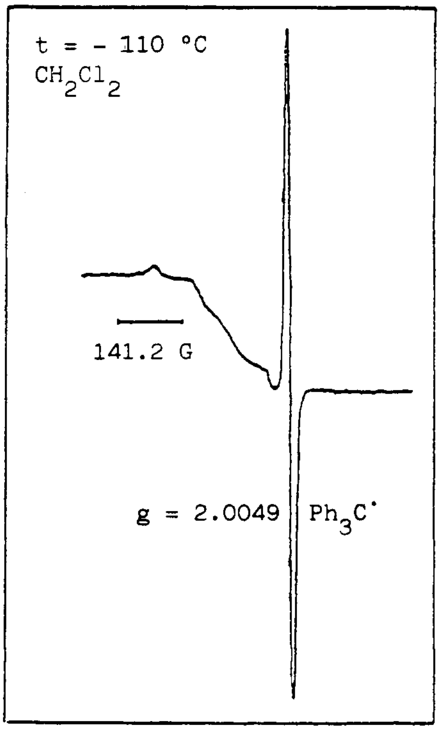
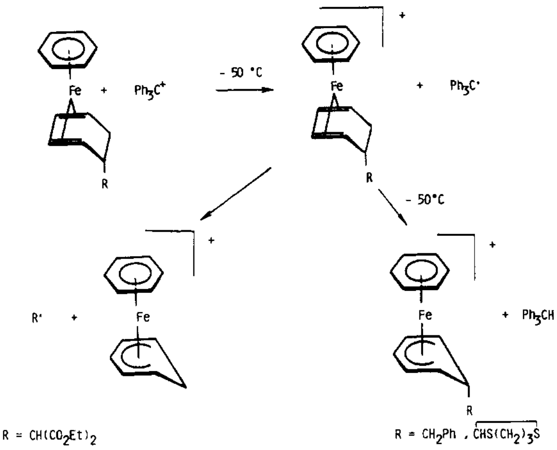


**Figure 5.** Monitoring the reaction of $[Ph_3C]^+$ with $[Fe(C_6H_6)(\eta^4\text{-}C_6H_7CH_2Ph)]$ by ESR spectroscopy at −110 °C.

**Scheme II**



We reasoned that, if hydride transfer from an exo-substituted cyclohexadiene complex to $[Ph_3C]^+$ is sterically inhibited, the ET pathway could be a valuable alternative. A driving force for the ET pathway is provided if the redox potential of the cyclohexadiene complex is lower than 0.2 V, i.e. negative. This is indeed the case when the neutral organometallic complex does not bear carbonyls or other strong π-acid ligands. The thermodynamic redox potential of the system **3b**/**3b**$^+$ (18e $Fe^0$/17e $Fe^I$) is $E° = -0.04$ V vs SCE. The ET according to eq 2 is exergonic and thus is fast according to the Marcus theory.[23] The lack of a free coordination site and the bulk prevent inner-sphere ET).

$$Fe^0 + Ph_3C^+ \rightarrow Fe^I + Ph_3C^{\bullet} \qquad (2)$$

The ESR observations show the presence of both the $Fe^I$ and the trityl radicals in the orange solution. As indicated by the cyclic voltammetry of **3b**, the $Fe^I$ radical is stable at −40 °C and unstable at 20 °C. Above −40 °C, the decomposition of the 17e $Fe^I$ radical is faster than the H atom transfer to $Ph_3C^{\bullet}$.

If the reaction temperature is kept between −50 and −40 °C, the $Fe^I$ radical is thermodynamically stable and the slow H atom transfer step can take place. Note that the H atom transfer has a much lower kinetic barrier than hydride ion transfer in the present situation because of the bulk. The H atom transfer step starts with two interacting radicals and ends up with two closed-shell compounds; it

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(15) For discussions of ESR spectra of other organo $Fe^I$ radicals, see: (a) Rajasekharan, M. V.; Giezynski, S.; Ammeter, J. H.; Ostwald, P.; Michaud, P.; Hamon, J.-R.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 2400. (b) Brintzinger, H.; Palmer, G.; Sands, R. H. *J. Am. Chem. Soc.* **1966**, *88*, 623.

(16) (a) McBride, J. M. *Tetrahedron* **1974**, *30*, 2009. (b) March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; p 173.

(17) (a) Green, M. L. H.; Nagy, P. L. *J. Organomet. Chem.* **1963**, *1*, 58. (b) Rosan, A.; Rosenblum, M.; Trancrede, J. *J. Am. Chem. Soc.* **1973**, *95*, 3062. (c) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (d) Fischer, E. O.; Fischer, R. D. *Angew. Chem.* **1960**, *72*, 919. (e) Birch, A. J.; Cross, P. E.; Lewis, J.; White, D. A.; Wild, S. B. *J. Chem. Soc. A* **1968**, 332. (f) Birch, A. J.; Haas, M. A. *J. Chem. Soc. C* **1971**, 2465. (g) Sander, A.; Cohen, L.; Giering, W. P.; Kennedy, D.; Magatti, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 5430. (h) Cohen, L.; Giering, W. P.; Kennedy, D.; Magatti, C. V.; Sander, A. *J. Organomet. Chem.* **1974**, *65*, C57. (i) Laycock, D. E.; Hartgerink, J.; Baird, M. C. *J. Org. Chem.* **1980**, *45*, 291. (j) Kiel, W. A.; Lin, G.-Y.; Gladysz, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3299. (k) Birch, A. J.; Jenkins, I. D. In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976; Chapter 1, p 1. (l) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858.

(18) Pasquette, L. A.; Daniels, R. G. *Organometallics* **1984**, *3*, 560.

(19) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858.

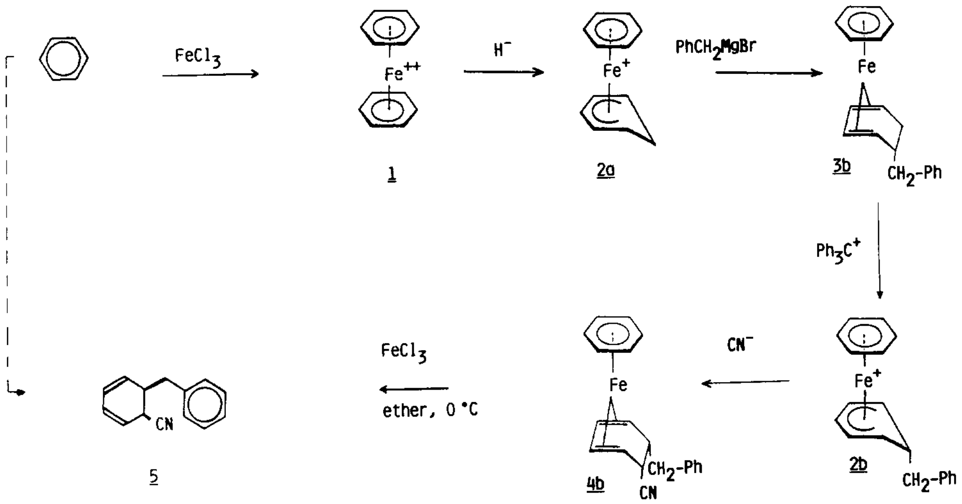
(20) Green, M.; Greensfield, S.; Kersting, M. *J. Chem. Soc., Chem. Commun.* **1985**, 18.

(21) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570.

(22) (a) Volz, H.; Lotsch, W. *Tetrahedron Lett.* **1969**, 2275. (b) Kothe, G.; Söumermann, W.; Baumgartel, H.; Zimmermann, H. *Tetrahedron Lett.* **1969**, 2185. (c) Asaro, M. F.; Bodner, G. S.; Gladysz, J. A.; Cooper, S. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1020.

(23) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: 1987; Berlin, p 27.

**Scheme III**



is therefore extremely favored. Thus, H atom transfer between the Fe$^I$ species and Ph$_3$C$^\bullet$ occurs at a larger distance between the two radicals than hydride transfer usually does because of this driving force.

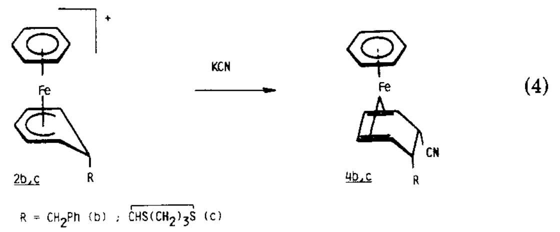
$$\underset{17e}{Fe^{I}} + \underset{7e}{Ph_3C^\bullet} \xrightarrow[\text{slow}]{-40\ °C} \underset{18e}{Fe^{II}} + \underset{8e}{Ph_3CH} \qquad (3)$$

The trityl radical, fortunately, does not decompose and is in equilibrium with its dimer. This dimerization equilibrium is displaced toward the monomer as the temperature increases and the concentration of the latter reaches 1% at 20 °C (Figures 1–5).

The decomposition of the 17e Fe$^I$ radicals $3^+$ was not thoroughly investigated, but the parent complex 2 was always found as the only characterized decomposition product, sometimes in good yields. It appears that the cleavage of the radical R$^\bullet$ in this 17e Fe$^I$ radical [Fe(C$_6$H$_6$)($\eta^4$-C$_6$H$_7$R)]$^+$ is its favored mode of decomposition. Indeed it produces a closed-shell (18e) cation 2 and a stabilized radical R$^\bullet$. When R = CH$_2$Ph$^\bullet$ or $\overline{CHS(CH_2)_3S}^\bullet$, the 17e Fe$^I$ radical is stable enough between −50 and −40 °C, but when R = CH(CO$_2$Et)$_2^\bullet$, it is not and decomposes faster than the desired H atom transfer (Scheme II).

**Reaction of KCN with the Exo-Substituted Cyclohexadienyl Complexes 2b and 2c.** The reaction of various carbanions with the parent complex **2a** is known to give exo-substituted cyclohexadiene Fe$^0$ complexes **3** in high yields.[9,10] The reaction of KCN with **2c** needs 1 week to proceed to completion. The oily neutral complex obtained corresponds to the expected heterodisubstituted cyclohexadiene complex **4c**, as indicated by the $^1$H NMR and infrared data. However, the $^1$H NMR also shows the presence of some phenyldithiane, and recrystallization was not possible (the same reaction, after only 1 day, gives the microcrystalline complex, but in very much lower yields).

The reaction of KCN with **2b** gives a good yield of the crystalline heterodisubstituted complex **4b** (eq 4), the conversion being complete after 3 days of reaction at 20 °C in acetone (90% of isolated orange crystalline air-sensitive product). The coordinated benzene ligand has a remarkably low-field resonance at δ = 4.54 ppm in the $^1$H NMR spectrum (C$_6$D$_6$). The complexation of the diene ligand shifts its C resonance toward high fields. The $^{13}$C NMR spectrum also indicates that the reaction is very clean.



(4)

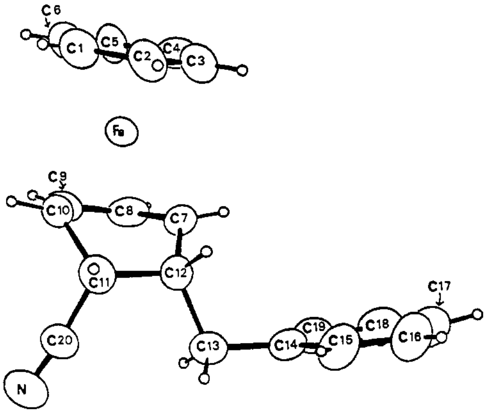
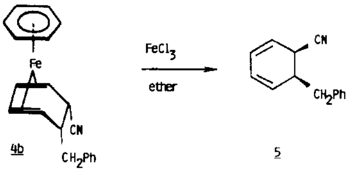


**Figure 6.** ORTEP diagram of the X-ray crystal structure of **4b** (reprinted from ref 8; copyright 1986 American Chemical Society).

The X-ray crystal structure of **4b** was recorded and fully reported in a preliminary communication (see Figure 6).

The decomplexation of **4b** (eq 5) by anhydrous FeCl$_3$ in ether is clean and instantaneous. The purity of the free cyclohexadiene derivative **5** and the absence of rearomatization were controlled by $^{13}$C NMR and mass spectra. However, some aromatization already appears when **5** is heated to 35 °C (from the mass spectrum). The rearomatization proceeds by loss of two H atoms, giving the ortho-difunctional benzene derivative.



(5)

## Concluding Remarks

The heterobifunctional cyclohexadiene derivative *cis*-1,2-PhCH$_2$CNC$_6$H$_6$ was synthesized in six steps from benzene according to Scheme III. Since carbanions react with [Fe(C$_6$H$_6$)$_2$]$^{2+}$ by ET, protection by a hydride is necessary (Scheme III).

The crucial step in Scheme III is the deprotection (removal of the hydride). A strategy using an exergonic ET from the monosubstituted cyclohexadiene $Fe^0$ complexes **3** to $[Ph_3C]^+$ has been developed. The intermediacy of the 17e $Fe^I$ cation $\mathbf{3}^+$ has been shown by ESR, and its stability between −50 and −40 °C allows further slow H atom abstraction in the case of **3b** and **3b**. Decomposition of $\mathbf{3}^+$ is faster than H atom transfer above −40 °C for **3b** and **3c** and above −50 °C for **3d**. Note that addition of hydride to [Fe(arene)(cyclohexadienyl)]$^+$ cations often also proceeds via ET.[24]

The limits of the present strategy are (i) electrophilic reactivity of $[Ph_3C]^+$ toward some functions such as cyano in **3e**, (ii) the decomposition of the radical to **2** and $R^\bullet$ in some cases as shown here for **3d** at −50 °C. A further investigation of oxidizing **3** more rapidly and selectively with a better oxidant such as $[FeCp_2]^+$ at −80 °C is needed in order to overcome these limits.

Contrary to the rules announced by Davies et al.[25] (based on charge control), the nucleophiles always attack the odd cyclohexadienyl ligand rather than the even benzene ligand in the mixed cation $[Fe(C_6H_6)(\eta^5\text{-}C_6H_6R)]^+$ (**2**). This was previously demonstrated in the case of the parent complex **2a**, where orbital control is predominant.[10] Remarkably, it is now also true even when the cyclohexadienyl ligand is substituted in the exo position by bulky substituents in **2**. In the present work, we have never found traces of bicyclohexadienyl-type complexes even in $^1H$ NMR and $^{13}C$ NMR spectra of crude reaction products. Extension and applications of the present strategy are thus awaited.[27]

**Acknowledgment.** We are grateful to Drs. P. Guênot and S. Sinbandhit (CMPO, Rennes), and F. Le Floch (Brest) for helpful experimental assistance and to Dr. L. Toupet (University of Rennes) for his collaboration concerning the X-ray crystal structure of **4a**. We also thank Dr. J.-R. Hamon (University of Rennes) for stimulating discussions and the CNRS for a thesis grant to D.M.

**Registry No.** **2a**, 65296-91-5; **2b**, 100681-69-4; **2c**, 100681-71-8; **3a**, 71265-76-4; **3b**, 90064-38-3; **3c**, 90064-39-4; **4b**, 100681-72-9; **4c**, 122382-87-0.

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(24) Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755.

(25) (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. Tetrahedron Report 57. *Tetrahedron* **1978**, *34*, 3047. (b) These authors justified their theory by referring to the reactions of carbanions with [Fe(mesitylene)$_2$]$^{2+}$ which indeed give [Fe(cyclohexadienyl)$_2$] derivatives. The bulk of the methyl groups inhibits the nucleophilic attack at the substituted arene carbon. Thus, in the second nucleophilic reaction, Helling[26] has shown that the carbanions attack the arene ligand rather than the cyclohexadienyl one. Our work[9,10] has indicated that this preference is only due to the presence of the methyl substituents in 1-, 3-, and 5-positions, not to charge control.

(26) (a) Helling, J. F.; Braitsch, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 7207 and 7209. (b) Helling, J. F.; Cash, C. G. *J. Organomet. Chem.* **1974**, *73*, C10.

(27) (a) Organometallic Electron Reservoirs. 39. For part 38, see: Hamon, J. R.; Astruc, D. *Organometallics* **1989**, *8*, 000. (b) This paper overlaps with the State Thesis of D.M. (Rennes, 1985).

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# Electrochemical Synthesis of "Costa-Type" Cobalt Complexes

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*Received March 10, 1989*

Due to the difficulty encountered in chemical preparations, [LCo((DO)(DOH)pn)R]X species [where L = neutral ligand, R = alkyl group, (DO)(DOH)pn = $N^2,N^{2'}$-propanediylbis(2,3-butanedione 2-imine 3-oxime)] have been prepared previously with only a limited range of alkyl ligands in comparison to other model systems. In this connection, the feasibility of electrochemical methods in the synthesis of these organocobalt Costa-type $B_{12}$ model complexes was examined. The Co(I) species produced from cathodic reduction of Co((DO)(DOH)pn)Br$_2$ at ca. −0.8 to −0.9 V (versus SCE) in acetonitrile at 25 °C reacted quickly with methyl iodide and more slowly with 2,2-bis(ethoxycarbonyl)propyl bromide ($C_2H_5O_2CC(CH_3)(CH_2Br)CO_2C_2H_5$, diester bromide). Although the product of the reaction with the diester bromide could be reduced at only slightly more negative potentials, we were able to prepare [H$_2$OCo((DO)(DOH)pn)-diester]ClO$_4$, a useful synthon, by controlled potential electrolysis of Co((DO)(DOH)pn)Br$_2$ at −0.8 V. This aqua complex, which we could not prepare by NaBH$_4$ reduction, was isolated and characterized. The electrochemical results are consistent with the view that both reduction of the organocobalt product and the slowness of the alkylation of the Co(I) species are responsible for previously observed difficulties in standard chemical preparations. The 1,5,6-trimethylbenzimidazole (Me$_3$Bzm) and pyridine (py) adducts were prepared by ligand substitution of the aqua complex and were characterized by NMR spectroscopy and elemental analysis. Rates of ligand dissociation of these adducts were found to be ~10 times faster than for the corresponding Me$_3$Bzm and py complexes in which R = methyl. In contrast, the $\gamma$-$^{13}C$ py shifts of the two py derivatives were similar. These results can be rationalized if the alkyl ligands are electronically similar but sterically different, with the more bulky diester group favoring L dissociation.

## Introduction

Preparation of organocorrinoid compounds, particularly 5′-deoxyadenosylcobalamin (coenzyme $B_{12}$) and other alkylcobalamins as well as of organocobalt $B_{12}$ models is most conveniently carried out in aqueous or in aqueous alcoholic basic NaBH$_4$ solutions via the well-known reduction of Co(III) to Co(I), which is readily alkylated by alkylating agents such as alkyl halides.[1] However, poor yields are

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(1) Toscano, P. J.; Marzilli, L. G. *Prog. Inorg. Chem.* **1984**, *31*, 105 and references therein.

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