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KINETIC STUDY OF NUCLEOPHILIC ADDITION TO THE CYCLOHEPTATRIENE RING IN $[(C_7H_8)Fe(Cp)]PF_6$

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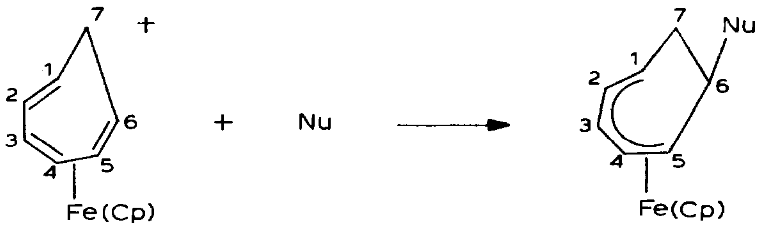
Summary

Tri-n-butylphosphine, tri-n-butylphosphite, and imidazole add to the cycloheptatriene ring in $(C_7H_8)Fe(Cp)^+$ (I) to give cycloheptadienyl adducts (II). The second order rate constants (M^{-1} s^{-1}) in acetone at 25°C are: $P(OBu)_3$, 0.50; PBu_3, 2250; HIm, 67. The relative nucleophilic reactivities are the same as that found with other coordinated cyclic π-hydrocarbons and with free carbocations. This further supports the recent suggestion [1] that a Ritchie type correlation holds for attack on all complexes of the form (ring)ML_n. The $Fe(Cp)^+$ moiety is 11,000 times weaker than $Mn(CO)_3{}^+$ in activating coordinated cycloheptatriene. $NaBH_4$, MeLi, and $NaCH(CO_2Et)_2$ also add to the ring in I, indicating that I may have synthetic utility.

Introduction

Nucleophilic addition to coordinated cyclic π-hydrocarbons is an important organometallic reaction that has found many synthetic applications and has provided a better understanding of the mechanistic aspects of electrophile-nucleophile combination [1]. Nucleophilic addition to coordinated cycloheptatriene has been reported for $(C_7H_8)Mn(CO)_2L^+$ ($L = CO, PPh_3$) [2–4] and $(C_7H_8)Ru(C_7H_9)^+$ [5]. The former complexes have been the subject of kinetic studies [3,4], which showed



(I) (II) (1)

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that $(C_7H_8)Mn(CO)_3^+$ is one of the most electrophilic systems known. Herein we report nucleophilic addition to $(C_7H_8)Fe(Cp)^+$ (eq. 1). The purpose of the study was to determine the relative abilities of the $Mn(CO)_3^+$ and $Fe(Cp)^+$ moieties to activate π-hydrocarbons, and to explore the potential synthetic uses of the readily available $(C_7H_8)Fe(Cp)^+$. Another purpose of this study was to further test the applicability of the Ritchie correlation, eq. 2, which so far seems to hold for nucleophilic additions to free carbocations and complexed π-hydrocarbons [1,6,7]. In eq. 2, k is the second order rate constant for the electrophile-nucleophile reaction, k_0 is the rate constant for a reference nucleophile, and N_M is a parameter dependent *only* on the nature of the nucleophile and the reaction conditions.

$$\log(k/k_0) = N_M \qquad (2)$$

Experimental section

$[(C_7H_8)Fe(Cp)]PF_6$ (I) was prepared according to the procedure of Mann et al. [8–11] and the ^1H NMR spectrum in acetone-d_6 matched that reported [8]. Coupling constants have not been published for I; we found that J(*endo*-H^7, *exo*-H^7) 13 Hz, J(*endo*-H^7,$H^{1,6}$) 9 Hz, and J(*exo*-H^7,$H^{1,6}$) 5 Hz. Complex I reacts readily with PBu_3, $P(OBu)_3$, and imidazole (HIm) to give ring adducts II. The adduct II (Nu = PBu_3) was synthesized by the following procedure: to a slight excess of PBu_3 in CH_2Cl_2 was added I as the PF_6^- salt. The reaction mixture became homogeneous within a few seconds and diethyl ether was then added until the solution turned cloudy. After cooling at −10°C for 12 h, the orange crystals were filtered and washed with ether. At this stage the yield was 60%, however additional product could be obtained by concentrating the CH_2Cl_2/ether filtrate and adding more ether. The addition of PBu_3 to I in situ was shown by ^1H NMR in acetone-d_6 to be quantitative. The isolated product is air stable and gave the following analysis (Galbraith Laboratories, Inc.): Found: C, 50.4; H, 7.0. calcd.: C, 51.4; H, 7.2%. Based on decoupling experiments, the ^1H NMR spectrum of II (Nu = PBu_3) in $CDCl_3$ was assigned as follows: δ 5.91 (t, J 6 Hz, H^3), 4.98 (m, J 7 Hz, H^2), 4.43 (s, Cp), 4.4 (m, J 7 Hz, H^4), 3.82 (m, $H^{1,5}$), 3.56 (qd, J 4.9 Hz, H^6), 1.87 (m, P–CH_2), 1.45 (m, P–CH_2*CH_2CH_2*CH_3), 0.95 (m, CH_3). The H^7 bands were obscured by the butyl resonances.

The adducts II with Nu = $P(OBu)_3$ and HIm were prepared in situ using excess nucleophile. ^1H NMR spectra confirmed that simple cycloheptadienyl adducts were formed. For Nu = HIm, ^1H NMR in acetone-d_6: δ 7.67, 6.93 (HIm), 5.99 (t, H^3), 5.32, 5.20 (m, $H^{2,4}$), 4.40 (s, Cp), 4.31, 4.09 (m, $H^{1,5}$), 3.17 (m, H^6), 180 (m, *endo*-H^7), −0.31 (m, *exo*-H^7). For Nu = $P(OBu)_3$, ^1H NMR in acetone-d_6: δ 6.06 (t, H^3), 5.03, 4.48 (m, $H^{2,4}$), 4.46 (Cp), also unassigned bands at 4.49, 4.01, 3.93, 1.76; other bands obscured by excess $P(OBu)_3$.

II (Nu = H^-) was synthesized by adding a slight excess of $NaBH_4$ to a suspension of I in 1,2-dimethoxyethane. After stirring for 30 min a homogeneous yellow-orange solution resulted. Water and then diethyl ether was added and after shaking, the ether layer was dried with $MgSO_4$ and evaporated to yield (70%) an air sensitive orange oil. ^1H NMR in $CDCl_3$: δ 5.80 (tt, J 6.1 Hz, H^3), 4.45 (dd, J 6.8 Hz, $H^{2,4}$), 4.24 (s, Cp), 3.82 (m, $H^{1,5}$), 1.95 (m, *endo*-$H^{6,7}$)· 0.77 (d, J 9 Hz, *exo*-$H^{6,7}$). II (Nu = $CH(CO_2Et)_2^-$) was made by adding a THF solution of $NaCH(CO_2Et)_2$ to a

THF suspension of I. After stirring for 1 h, the homogeneous solution was treated with NaCl saturated water and diethyl ether. After shaking, the ether layer was dried over $MgSO_4$ and evaporated to give a 65% yield of product, which was air and heat sensitive enough to preclude elemental analysis. Decomposition, as shown by discoloration, occurred in C_6D_6. However, ^1H NMR clearly indicated the proposed adduct: δ 5.47 (t, H^3), 3.96 (Cp), 3.95 (CH_2CH_3), 2.98 (d, J 9 Hz, $CH(CO_2Et)_2$), 1.00 (CH_3), with additional bands at 4.65, 4.55, and 3.20. Excess MeLi in diethyl ether was added to I in 1,2-dimethoxyethane. Workup as with the diethylmalonate analogue gave an air sensitive orange oil that decomposed too rapidly for characterization at room temperature. MeMgBr and PhMgBr and I in THF gave only decomposition products.

The kinetics of reaction 1 with Nu = PBu_3, $P(OBu)_3$, and HIm were followed at 390 nm using a Dionex stopped-flow instrument. Carefully purified and dried acetone was used as the solvent. Pseudo first order conditions were maintained by keeping the nucleophile concentration in at least a tenfold excess over the concentration of I, which was ca. 1×10^{-4} M. Pseudo first order rate constants, k_{obs}, were calculated several times at each of three or more different nucleophile concentrations.

Results and discussion

Nucleophilic addition to the ring in $(C_7H_8)Fe(Cp)^+$ occurs rapidly. The adducts II with PBu_3, $P(OBu)_3$, and HIm are stable in solution, whereas carbon donor nucleophiles give rather sensitive products. Nevertheless, $NaCH(CO_2Et)_2$ and MeLi (as well as $NaBH_4$) definitely add to the ring, and the adducts probably could be handled at low temperature without decomposition. It seems, therefore, that functionalization of the C_7H_8 ring in I with carbon donors is possible.

In this paper, more attention is focused on the mechanistic aspects of ring addition and on the quantitative estimation of the ability of the $FeCp^+$ moiety to activate the C_7H_8 ring. Kinetic studies with PBu_3 and $P(OBu)_3$ showed that the rate law $k_{obs} = k[Nu]$ is followed. With HIm, k_{obs} is more complicated because the overall reaction does not go to completion; nevertheless the value of the second order rate constant (k) for reaction 1 was readily obtained. At 25°C, k (M^{-1} s^{-1}) was found to dependent on the nucleophile as follows: $P(OBu)_3$, 0.50; PBu_3, 2250; HIm, 67.

Use of these rate constants to calculate N_M parameters from eq. 2 gives the following results with respect to $P(OBu)_3$ as the reference: $P(OBu)_3$, 0; HIm, 2.1; PBu_3, 3.6_5. These N_M values are within 0.2 of those calculated for a wide variety of (π-hydrocarbon)ML_n^+ systems [1]. This further confirms our assertion that relative nucleophilic reactivities for addition to coordinated cyclic π-hydrocarbons is electrophile independent. Stated another way, relative rates of nucleophilic addition to (π-hydrocarbon)ML_n^+ are independent of the nature of the π-hydrocarbon, the metal, and the nonreacting ligand L.

The extent of electrophilic activation of the coordinated hydrocarbon in (π-hydrocarbon)ML_n^+ depends greatly on the nature of the ML_n moiety. The present study in conjunction with previous work [3,4] with $(C_7H_8)Mn(CO)_3^+$ shows that $Mn(CO)_3^+$ is 11,000 times more effective than $Fe(Cp)^+$. Similarly, a coordinated arene is much more electrophilic in (arene)$Mn(CO)_3^+$ than in (arene)$Fe(Cp)^+$.

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