Λ-β_2-[Co(*R*-ala)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73493-91-1; Λ-β_2-[Co(*S*-val)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73453-01-7; Λ-β_2-[Co(*R*-val)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73493-89-7; Λ-β_2-[Co(*S*-phe)(3-(*S*),9(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73452-99-0; Λ-β_2-[Co(*R*-phe)(3(*S*),9-(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73493-87-5; Λ-β_2-[Co(*S*-ala)(*SS*-pyht)]$^{2+}$, 64387-61-7; Λ-β_2-[Co(*R*-ala)(*SS*-pyht)]$^{2+}$, 64439-78-7; *trans*-[$CoCl_2$(3(*S*),8(*S*)-Me_2trien)]ClO_4, 60872-59-5; *trans*-[$CoCl_2$(2-(*S*),10(*S*)-Me_2-2,3,2-tet)]ClO_4, 60801-67-4; *trans*-[$CoCl_2$(3(*S*),9-(*S*)-Me_2-2,3,2-tet)]ClO_4, 73396-02-8; *trans*-[$CoCl_2$(*SS*-pyht)]ClO_4, 59202-14-1.

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Mechanism of Halide Abstraction from $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ by $AgBF_4$

BRUCE M. MATTSON and WILLIAM A. G. GRAHAM*

Received August 27, 1980

The mechanism of halide abstraction from $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with $AgBF_4$ was investigated by ^1H NMR ($CDCl_3$ solvent) and infrared (CH_2Cl_2 and $CHCl_3$ solvents) spectroscopic methods. $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ initially forms a silver(I) adduct formulated as $(\eta^5\text{-}C_5H_5)Fe(CO)_2IAg^+$, which decomposes to yield AgI and, in the presence of excess $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, the iodine-bridged species $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2IBF_4$. This material then reacts with a second 0.5 equiv of $AgBF_4$ to yield $(\eta^5\text{-}C_5H_5)Fe(CO)_2BF_4$, in which tetrafluoroborate is coordinated.

Introduction

Substitution reactions involving the abstraction of halide ion from $(\eta^5\text{-}C_5H_5)Fe(CO)(L)X$, (L = CO, PR_3, $P(OR)_3$; X = Cl, Br, I) and replacement by a two-electron donor such as PR_3, olefin, alkyne, ketone, H_2O, THF, or CO have been extensively utilized over the past few years.[1-6] In particular, cationic olefin complexes of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-olefin})^+$ have been quite thoroughly investigated because of their applications in stoichiometric organic synthesis.[7] In many of the reported syntheses of η^2-olefin complexes, a two-step preparation is utilized: the halide is initially quantitatively abstracted by silver ion, and the resulting solution is then treated with an excess of olefin. The "16-electron" intermediate produced in the halide abstraction step has frequently been postulated to be solvent coordinated, and for reactions done in THF,[6] H_2O,[4,8] or other donor solvents, this is undoubtedly true. For halide abstractions done in CH_2Cl_2, the intermediate has been proposed by several authors,[3,5,9,10] with a degree of speculation, to be the solvent-coordinated $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2Cl_2)^+$.

In our hands, the synthesis of η^2-olefin complexes in CH_2Cl_2 by the literature method[5] always yielded a fairly large amount of the known iodine-bridged species $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2I^+$.[11] If excess Ag(I) were used, the amount of this iodine-bridged cationic species could be reduced. However, the resulting excess $AgBF_4$ in solution complicated the next step in which the olefin is added. In order to determine the role of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2I^+$ in the halide abstraction reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with $AgBF_4$ and because of our general interest in weakly coordinated species[12] such as $CpFe(CO)_2BF_4$, we have undertaken a thorough investigation of the mechanism of halide abstraction with Ag^+ from $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ in $CHCl_3$ and CH_2Cl_2 solvents. The results of this investigation are reported here.

Experimental Section

All operations were carried out under Ar or dried N_2. Solvents were distilled and purified by established techniques and degassed prior to use. $CDCl_3$ and $CHCl_3$ solvents were passed through a column of Kieselgel 60G silica gel (30 mL of solvent required a 10 cm × 2 cm plug of silica gel) and then degassed. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer, and ^1H NMR spectra were recorded on a Bruker WH 200-MHz spectrometer.

Reagents. $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, purchased from Strem Chemicals Inc., was used without further purification. $AgBF_4$, purchased from Ozark-Mahoning Co., was dried at room temperature and 0.005 torr for 1 week prior to use.

$(\eta^5\text{-}C_5H_5)Fe(CO)_2BF_4$. A foil-wrapped 100-mL flask with side arm was charged with 0.213 g (0.70 mmol) of $CpFe(CO)_2I$ and 0.146 g (0.74 mmol) of $AgBF_4$. The dry mixture was evacuated to 0.005 torr for 1 h to remove any water absorbed by $AgBF_4$ during transfer. Dichloromethane (20 mL) was then added and the mixture stirred in the dark for 45 min. An infrared spectrum obtained at this point featured broad bands at 2076 (s) with 2065 (sh), 2053 (w), and 2031 (s) with 2020 (sh) cm^{-1} due to $CpFe(CO)_2BF_4$ and $[CpFe(CO)_2]_2IBF_4$. The reaction mixture was cooled to −78 °C and stirred for 30 min. The solution was allowed to settle and was then filtered at −78 °C to remove $AgBF_4$ and $[CpFe(CO)_2]_2IBF_4$. The resulting burgundy-colored CH_2Cl_2 solution was pumped to dryness and dried in vacuo for 1 h. The product, formulated as $CpFe(CO)_2BF_4$, could be stored for short periods of time as a solid microcrystalline material; after a 3-h period only ca. 70% of the material would redissolve in CH_2Cl_2. The solid product is extremely hygroscopic and brief exposure to air caused conversion to the orange $CpFe(CO)_2(OH_2)BF_4$. Data for $CpFe(CO)_2BF_4$: IR (CH_2Cl_2) 2078 (s), 2032 (s) cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 5.26$ (s); yield 0.154 g (83%). Anal. Calcd: C, 31.88; H, 1.91. Found: C, 30.71; H, 2.22.

$[\eta^5\text{-}C_5H_5Fe(CO)_2]_2IBF_4$. $CpFe(CO)_2I$ (0.681 g, 2.25 mmol) and $AgBF_4$ (0.327 g, 1.69 mmol) were placed in a 100-mL side-armed

---

(1) Fischer, E. O.; Fichtel, K. *Chem. Ber.* **1962**, *94*, 1200.

(2) (a) Foxman, B. M.; Klemarczyk, P. T.; Liptrot, R. E.; Rosenblum, M. *J. Organomet. Chem.* **1980**, *187*, 253. (b) Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3155. (c) Davison, A.; Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3172.

(3) Green, M. L. H.; Whiteley, R. N. *J. Chem. Soc. A* **1971**, 1943.

(4) Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165.

(5) Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73.

(6) Reger, D. L.; Coleman, C. J. *J. Organomet. Chem.* **1977**, *131*, 153.

(7) Lennon, P.; Rosen, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8476 and references therein. See also: Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122.

(8) Dombek, B. D.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, *7*, 345.

(9) (a) Ferguson, J. A.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 1025. (b) Boyle, P. F.; Nicholas, K. M. *J. Organomet. Chem.* **1976**, *114*, 307.

(10) A solvent adduct of $CpFe(CO)_2^+$ was proposed as the product of the reaction between $CpFe(CO)_2CH_3$ and HSO_3F in CH_2Cl_2-SO_2ClF: Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099.

(11) This halogen-bridged cation has been reported by others to be a by-product of this reaction.

(12) J. R. Sweet and W. A. G. Graham, research in progress on $[(\eta^5\text{-}C_5H_5)(ON)(OC)Re(Ph_3CH)]^+$ and related compounds.

0020-1669/81/1320-3186\$01.25/0

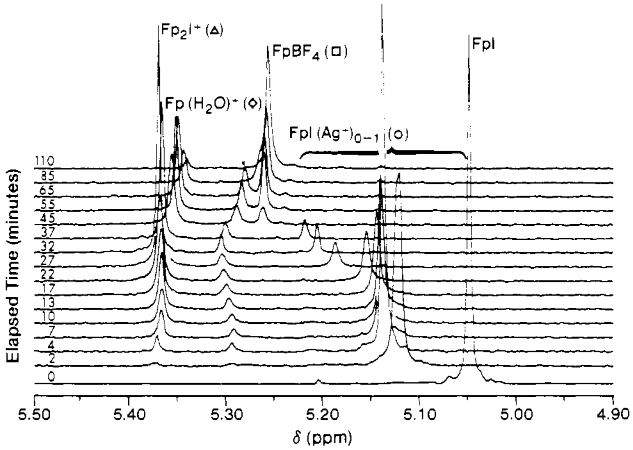

Figure 1. Change with time of ^{1}H NMR spectra of the η^5-cyclopentadienyl region through the course of the reaction between CpFe(CO)$_2$I and AgBF$_4$ in CDCl$_3$ solvent. Species are labeled with the symbols used in Figure 2 (Fp ≡ η-C_5H_5Fe(CO)$_2$).

flask and dried in vacuo for 1 h. Dichloromethane (60 mL) was added and the solution stirred for 45 min. Solvent volume was then reduced to 20 mL; the mixture was filtered and product precipitated with Et$_2$O. The golden crystals were washed with 2 × 10 mL of ether. Rapid recrystallization from CH$_2$Cl$_2$/ether and subsequent ether washings were repeated twice. Data for [CpFe(CO)$_2$]$_2$IBF$_4$: IR (CH$_2$Cl$_2$) 2064 (s), 2053 (s), 2020 (s, b) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 5.38 (s); yield 0.290 g (46%). Anal. Calcd: C, 29.62; H, 1.78. Found: C, 29.71; H, 1.76.

Reaction Mechanism Studies. CpFe(CO)$_2$BF$_4$ was prepared as above with the following modifications.

^{1}H NMR Studies. CpFe(CO)$_2$I (0.21 g, 0.70 mmol) was reacted with AgBF$_4$ (0.42 g, 2.2 mmol) in 30 mL of CDCl$_3$. AgBF$_4$ is not very soluble in CDCl$_3$, and the reaction was slower than in CH$_2$Cl$_2$ solvent. The solution was periodically allowed to settle, and an aliquot was removed for ^{1}H NMR spectral analysis. The results of one ^{1}H NMR-monitored reaction sequence are given in Figure 1. The time labels in the figure have only relative significance; since the reaction is heterogeneous because of poor AgBF$_4$ solubility, no quantitative kinetic study was possible. The rate of the overall reaction varied between experiments and seemed to be affected by the nature of the AgBF$_4$ used and the rate of stirring of the heterogeneous reaction mixture.

Infrared Studies. Reaction conditions were duplicated from the ^{1}H NMR study. The reaction was monitored in CH$_2$Cl$_2$ as well as in CHCl$_3$ and was thus shown to proceed qualitatively by the same route in both solvents. In CH$_2$Cl$_2$ the bands due to CpFe(CO)$_2$I (2043 (s) and 1998 (s) cm^{-1}) decreased while bands attributable to [CpFe(CO)$_2$]$_2$IBF$_4$ grew in intensity. These latter bands then slowly decreased with the simultaneous formation of bands due to CpFe(CO)$_2$BF$_4$.

Results and Discussion

The reaction between AgBF$_4$ and (η^5-C_5H_5)Fe(CO)$_2$I, henceforth referred to as FpI (where Fp ≡ (η^5-C_5H_5)Fe(CO)$_2$), in CH$_2$Cl$_2$ is reported to yield an unexpectedly stable compound that has been suggested to be the solvent-coordinated Fp(CH$_2$Cl$_2$)$^+$.[3,5,9,10] Previous attemps at its isolation have been unsuccessful although the material is reported to be stable in solution for several hours.[5]

In the time-monitored ^{1}H NMR analysis of the reaction between FpI and excess AgBF$_4$ in CDCl$_3$ (Figure 1) several aspects of the reaction mechanism can be discerned.[13] The t = 0 min spectrum was taken without AgBF$_4$ present and shows a single resonance due to FpI at δ = 5.05. After addition of AgBF, this resonance makes a progressive downfield shift which continues for the first 40 min of the reaction with a simultaneous decrease in intensity with time. Since AgBF$_4$ dissolves only very slowly in CDCl$_3$, we propose that the substantial and progressive downfield shift for the FpI resonance (δ = 5.05 → 5.22) is actually due to the rapid exchange of Ag$^+$ between free FpI and the silver(I) adduct FpIAg$^+$. It is reasonable to suppose that adduct formation between Ag$^+$ and the electron-rich soft base FpI would occur.[14] Thus the initial steps of the reaction are likely to be as shown in eq 1–3.

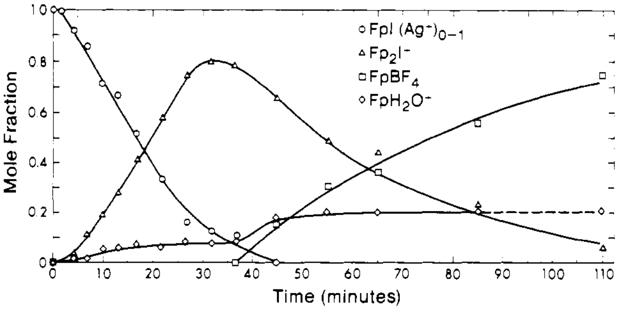

Figure 2. Plot of mole fraction of FpI, Fp$_2$I$^+$, FpBF$_4$, and Fp(H$_2$O)$^+$ for the reaction between FpI and excess AgBF$_4$ in CDCl$_3$ solvent as a function of time.[17] Data plotted were obtained for the experiment shown in Figure 1. The point for FpH$_2$O$^+$ at 110 min could not be obtained directly owing to peak overlap but has been placed by extrapolation.

$$\mathrm{AgBF_4(s)} \xrightarrow[\text{slow}]{\mathrm{CDCl_3}} \mathrm{AgBF_4(soln)} \tag{1}$$

$$\mathrm{FpI} + \mathrm{AgBF_4(soln)} \xrightarrow{\text{fast}} \mathrm{FpIAg^+BF_4^-} \tag{2}$$

$$\mathrm{FpIAg^+} + \mathrm{Fp'I} \xrightleftharpoons{\text{rapid exchange}} \mathrm{FpI} + \mathrm{Fp'IAg^+} \tag{3}$$

The exact averaged chemical shift of the resonance due to FpI(Ag$^+$)$_{0-1}$ is dependent on the mole fraction of each component, FpI and FpIAg$^+$. In order to substantiate this assignment, we reacted FpI with 0.3 equiv of AgBF$_4$. The resonance initially due to FpI was observed to move progressively from δ = 5.05 to δ = 5.13 during the first 20–30 min of the reaction. This resonance then slowly but progressively *returned* to the high-field position assignable to free FpI as the silver(I)-containing species FpIAg$^+$ slowly decomposed to AgI(ppt) and Fp$_2$I$^+$.[15]

At the same time as the C$_5$H$_5$ resonance due to FpI(Ag$^+$)$_{0-1}$ shifts to lower field, a new product is observed to form stoichiometrically with a concomitant decrease in the amount of FpI(Ag$^+$)$_{0-1}$. The new product has a C$_5$H$_5$ resonance at δ = 5.37 and is the known compound Fp$_2$I$^+$BF$_4^-$.[16] The mole fractions of FpI(Ag$^+$)$_{0-1}$ and Fp$_2$I$^+$ are plotted as a function of time in Figure 2. During the first 30 min of the reaction, the mole fraction of FpI(Ag$^+$)$_{0-1}$ is observed to decrease with the resultant, virtually stoichiometric production of Fp$_2$I$^+$. A byproduct with a C$_5$H$_5$ resonance at δ = 5.29 is also formed in a small amount. This material has been confirmed to be the known[8] compound Fp(H$_2$O)$^+$ and is the exclusive final product if wet CDCl$_3$ and/or AgBF$_4$ are used. Commercially available AgBF$_4$ is hygroscopic enough that if the material is not redried in vacuo after each handling, appreciable amounts of Fp(H$_2$O)$^+$ are observed in subsequent experiments.

---

(13) CD$_2$Cl$_2$ could not be used for the ^{1}H NMR study because the CD*H*Cl$_2$ resonance overlaps with the Cp region of interest in the reaction sequence.

(14) For simplicity we have formulated the silver adduct complex as FpIAg$^+$ but other formulations including the two-coordinate species (FpI)$_2$Ag$^+$ and FpIAgFBF$_3$ are plausible.

(15) Fp$_2$I$^+$ is formed from the reaction between Fp$^+$ and FpI (see footnote 19). The overall reaction in this experiment is theoretically balanced as FpI + 0.3AgBF$_4$ → 0.4FpI + 0.3AgI + 0.3Fp$_2$I$^+$.

(16) Fischer, E. O.; Moser, E. *Z. Anorg. Allg. Chem.* **1966**, *342*, 156.

(17) Slight decomposition to Cp-free or insoluble products occurs throughout the reaction so the mole fractions plotted in Figure 2 are normalized such that their sum is 1.00.

Several authors have pointed out that this aquo complex is quite stable and generally cannot be displaced by weak ligands, including olefins.[4,8]

Thus, the first half of the overall reaction involves adduct formation between FpI and Ag^+ with the subsequent formation of Fp_2I^+. The latter reaction probably involves the steps 4 and 5. The Fp^+ produced in eq 4 would be coordinatively unsaturated and probably immediately becomes solvated or, alternatively, BF_4^- coordinated.[18] Regardless of the formulation of this intermediate, in the presence of FpI the final product is Fp_2I^+, suggesting that the iodine of FpI is a comparatively better nucleophile.[19] $Fp^+(Solv/BF_4^-)$ would be expected to be susceptable to aquo complex formation if any H_2O were present.

$$FpIAg^+ \xrightarrow{\text{slow}} Fp^+ + AgI\downarrow \qquad (4)$$

$$Fp^+ \xrightarrow[\text{or } BF_4^-]{\text{solvent}} Fp(Solv)^+ \text{ or } FpBF_4 \xrightarrow{FpI} Fp_2I^+ \qquad (5)$$

The first half of the overall reaction is over once all of the FpI initially present has been converted to Fp_2I^+; in the experiment shown in Figures 1 and 2 this took about 35 min. The Fp_2I^+ produced can be isolated, if desired (see Experimental Section) and as a preparative route to Fp_2I^+, this method is much cleaner and simpler than the original synthesis.[16] The relationship between Fp_2I^+, FpI, and $FpBF_4$ is that of an equilibrium (eq 6). FpI reacts immediately with $FpBF_4$ in $CDCl_3$ to yield cleanly Fp_2I^+. However, $CDCl_3$ (or CH_2Cl_2) solutions of Fp_2I^+ decompose over relatively short periods of time (ca. 5–7% in 1.5 h, 30–50% in 20 h) to yield primarily FpI. Some $Fp(H_2O)^+$ is also observed, and $CDCl_3$-insoluble materials are produced.

$$Fp_2I^+BF_4^- \rightleftharpoons FpI + FpBF_4 \qquad (6)$$

In an attempt to set an upper limit to the equilibrium constant for eq 6, we triply recrystallized a sample of Fp_2I^+ from CH_2Cl_2/hexane, extracted with $CDCl_3$, and immediately measured the ^1H NMR spectrum. Peaks due to Fp_2I^+, FpI, and $Fp(H_2O)^+$ could be observed; however, no peak attributable to $FpBF_4$ could be detected in three separate attempts.[20] Thus a value for the equilibrium constant, K, for eq 6 could not be obtained. However, the upper limit of K was estimated to be 1.6×10^{-3} by assuming $[FpBF_4] = [FpI]$. The actual value of K is undoubtedly much smaller.

During the second half of the overall reaction, Fp_2I^+ is converted to $FpBF_4$. This process does not become operative until all of the FpI has been converted into Fp_2I^+. The Fp_2I^+ equilibrium (eq 6) likely plays an integral role in the conversion of Fp_2I^+ into $FpBF_4$: Although the Ag^+ could attack the bridging iodine in Fp_2I^+, it seems plausible, in view of the above equilibrium, that the Ag^+ attacks iodine in the FpI produced via eq 6. Thus, FpI produced in the second half of the reaction is rapidly consumed via eq 2 and 4, while the relative amounts of Fp_2I^+ and $FpBF_4$ decrease and increase, respectively (Figure 2). The final steps in the overall halogen abstraction are summarized as eq 7–9.

$$Fp_2I^+ \rightleftharpoons Fp^+ + FpI \quad K < 1.6 \times 10^{-3} \qquad (7)$$

$$FpI + AgBF_4(\text{soln}) \longrightarrow FpIAg^+BF_4^- \qquad (8)$$

$$Fp^+ + BF_4^- \longrightarrow FpBF_4 \qquad (9)$$

Either eq 7 or eq 8 could be the slow step during the second half of the overall reaction. Although eq 8 is formally identical to step 2, the concentration of FpI during the second half of the overall reaction is at least 200 times smaller than that during the first half, and unless excess $AgBF_4$ is in solution, reaction to completion takes an inordinate amount of time.[21]

Isolated samples of Fp_2IBF_4 were also found to yield $FpBF_4$ when treated with $AgBF_4$ in a manner analogous to that observed for in situ Fp_2IBF_4.

The identity of the 2-electron donor that fills the coordination site in the 16-electron Fp^+ cation is not exactly known. Several authors have speculatively proposed[3,5,9,10] that the species is solvated with CH_2Cl_2 but have presented no spectroscopic or other evidence in support of this notion. Beck and Schloter have reported[18] that, in the highly analogous molybdenum and tungsten systems, $(\eta^5\text{-}C_5H_5)M(CO)_3BF_4$ (M = Mo, W), the BF_4^- is coordinated to the metal in CH_2Cl_2 solutions. We submit several observations in support of a BF_4^--coordinated species, $Fp \leftarrow FBF_3$, being the observed product in the FpI + $AgBF_4$ reaction in CH_2Cl_2 or $CHCl_3$: (1) $FpBF_4$ is unexpectedly soluble. Whereas $Fp(H_2O)^+$ is almost insoluble in CH_2Cl_2 and Fp_2I^+ is virtually insoluble in CH_2Cl_2 at −78 °C, $FpBF_4$ behaves more like a neutral species and is quite soluble in CH_2Cl_2 at −78 °C. (2) The Cp resonance in $FpBF_4$ would be expected at lower fields than the corresponding signal for Fp_2I^+ if a full positive charge existed on a species such as Fp^+ or $Fp(CH_2Cl_2)^+$. The observed chemical shift indicates that $FpBF_4$ is in fact more shielded than $Fp(H_2O)^+$ and Fp_2I^+ and is just slightly less shielded than $FpI(Ag^+)_{\sim 1}$. (3) The ^{11}B NMR spectrum was obtained for each of $FpBF_4$, $AgBF_4$, and NBu_4BF_4 in chloroform (30% $CDCl_3$). Both $AgBF_4$ and $FpBF_4$ had resonances shifted from free BF_4^- (in the form of NBu_4BF_4), suggesting a strong interaction between cation and anion in both cases. While the ^{11}B resonance in NBu_4BF_4 showed B–F coupling ($J_{BF} = 1.2$ Hz), the loss of T_d symmetry in a coordinated BF_4^- would result in the loss of coupling for a quadrupolar nucleus.[22] In fact, no B–F coupling was observed for either $AgBF_4$ or $FpBF_4$. The ^{11}B chemical shifts found relative to solution of $BF_3 \cdot OEt_2$ (ca. 2% in chloroform (30% $CDCl_3$)) are 1.08, 1.19, and 1.85 ppm, for NBu_4BF_4, $AgBF_4$, and $FpBF_4$, respectively.[23] In solutions containing both $AgBF_4$ and $FpBF_4$, unique resonances were observed for both species, indicating that BF_4^- exchange was slow on the NMR time scale. Treating the $FpBF_4$ sample with NBu_4I resulted in the loss of a ^{11}B resonance for $FpBF_4$, and a new resonance, assignable to NBu_4BF_4, was observed. (4) The elemental analysis is inconsistent with a CH_2Cl_2-solvated species.

The reaction between $FpBF_4$ and NBu_4I in chloroform solvent was also studied by ^1H NMR and infrared spectroscopic methods. The reaction is instantaneous and follows the reverse path of halide abstraction: $FpBF_4$ is quantitatively converted into Fp_2I^+, which is then converted into FpI. In using NMR to monitor the titration of $FpBF_4$ with NBu_4I, we observed that in the step involving conversion of Fp_2I^+ to FpI, the Cp resonance due to the latter grew in unshifted from free FpI. This substantiates our assignment of the migrating resonance in the halide-abstraction reaction as the result of Ag^+ adduct formation with FpI. If excess $AgBF_4$ is present in solutions of $FpBF_4$, treatment with NBu_4I will quantitatively

---

(18) Beck, W.; Schloter, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33*, 1214.

(19) In support of this we have found that the reaction between FpI and ca. 1 equiv of $FpBF_4$ yields Fp_2I^+ within minutes as monitored by ^1H NMR and IR.

(20) Fp_2I^+ is only sparingly soluble in $CDCl_3$, and the resonances due to FpI and $FpBF_4$ would be expected to be considerably smaller than that of Fp_2I^+. Thus, it was necessary to pulse for >30 min during which time $FpBF_4$ could decompose or react with any H_2O present. The resonance due to FpI would be artifically large relative to Fp_2I^+. The ratio of FpI:Fp_2I^+ doubled when one sample was aged 1 h in $CDCl_3$.

(21) Since a precise equilibrium measurement could not be made for eq 7, we cannot rule out the establishment of eq 7 as the slow step during the second half of the reaction.

(22) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. "High Resolution Nuclear Magnetic Resonance"; McGraw-Hill: New York, 1959; p 102.

(23) These chemical shifts are all to high field of $BF_3 \cdot OEt_2$.

remove it as a cream-colored AgI precipitate prior to reacting with $FpBF_4$.

Conclusions

^1H NMR and infrared data have established that halide abstraction from FpI by $AgBF_4$ in $CHCl_3$ or CH_2Cl_2 initially yields Fp_2I^+, which then reacts with additional $AgBF_4$ to yield $FpBF_4$. The overall reaction consists of two parts; complete conversion of FpI into Fp_2I^+ occurs before any $FpBF_4$ is detected.

Although evidence is presented suggesting that BF_4^- is metal coordinated in the complex $FpBF_4$, such may not be the case with other anions. Beck and Schloter[18] found that the coordinating ability of various anions and solvents decreased in the order acetone > BF_4^- > CH_2Cl_2 > PF_6^- for the highly analogous complexes $CpM(CO)_3^+$ (M = Mo, W).

The preparative method for $FpBF_4$ outlined in the Experimental Section has an important implication in synthesizing olefinic complexes of the formula $Fp(olefin)^+$. When the reaction mixture is cooled as described in the Experimental Section, samples of $FpBF_4$ free of Fp_2I^+ and $Fp(H_2O)^+$ can be obtained. This would greatly simplify the purification of the desired olefin complex, especially in the case of less stable complexes.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support. We also thank Glen Bigam for obtaining the NMR spectra and for helpful discussions.

Note Added in Proof. It has come to our attention that the crystal structure of Fp_2IBF_4, obtained from the reaction of FpI with $AgBF_4$ in dry benzene, has been reported: Cotton, F. A.; Frenz, B. A.; White, A. J. *J. Organomet. Chem.* **1973**, *60*, 147.

Registry No. $FpBF_4$, 76391-69-0; $Fp_2I^+BF_4^-$, 12212-41-8; FpI, 12078-28-3; $AgBF_4$, 14104-20-2; $Fp(H_2O)^+$, 62077-07-0; $FpIAg^+$, 76391-70-3.

Contribution from the Departments of Chemistry, Wayne State University, Detroit, Michigan 48202,
and the University of Wisconsin—Eau Claire, Eau Claire, Wisconsin 54701

Macrocyclic, Ring Size, and Anion Effects As Manifested in the Equilibrium Constants and Thermodynamic Parameters of Copper(II)-Cyclic Polythia Ether Complexes

LUCIA S. W. L. SOKOL,[1a] L. A. OCHRYMOWYCZ,[1b] and D. B. RORABACHER*[1a]

Received September 29, 1980

The equilibrium constants for Cu(II) reacting with two open-chain tetrathia ethers, five cyclic tetrathia ethers, and a cyclic pentathia ether (i.e., Me_2- and Et_2-2,3,2-S_4; 12-, 13-, 14-, 15-, and 16-ane-S_4; and 15-ane-S_5) have been determined spectrophotometrically in aqueous solution at 5, 15, 25, and 35 °C in a medium of 0.10 M $HClO_4$. In this medium the 25 °C stability constants range from 94 M^{-1} for the Me_2-2,3,2-S_4 complex to a maximum of 2.2×10^4 M^{-1} for the 14-ane-S_4 complex. As the ring size increases, the apparent $\Delta S°$ value exhibits a steady decrease from +15.9 eu for the complex formed with the smallest cyclic ligand, 12-ane-S_4, to −5.4 eu for infinite ring size as represented by the open-chain ligand Me_2-2,3,2-S_4. The corresponding apparent $\Delta H°$ values progress from 0 kcal mol^{-1} for 12-ane-S_4 through a minimum value of −4.2 kcal mol^{-1} for 14-ane-S_4 to −1.4 kcal mol^{-1} for 16-ane-S_4, decreasing once again for the open-chain ligand complexes. As the concentration of perchlorate ion is increased at constant temperature, the apparent stability constants also increase for all of these complexes. This phenomenon has been quantitatively investigated for the 14-ane-S_4 system and has been shown to fit a model in which perchlorate ion combines to form either a tight ion pair or a ternary complex which markedly enhances the apparent stability of the copper–polythia ether complex. The activity-corrected equilibrium constant and thermodynamic parameters for the perchlorate association with Cu^{II}(14-ane-S_4) are as follows: K(25 °C), 24.1 ± 0.5 M^{-1}; $\Delta H°$, −2.1 ± 0.3 kcal mol^{-1}; $\Delta S°$, −0.7 ± 1.1 eu.

Introduction

One of the unique properties observed for macrocyclic multidentate ligands is their ability to form more stable metal ion complexes than do their open-chain analogues. In studies on Cu^{II}–tetraamine complexes, Cabbiness and Margerum[2] originally attributed this *macrocyclic effect* to a combination of the restricted configuration (an entropic effect) and the diminished solvation (primarily an enthalpic effect) of the *free* macrocyclic ligands relative to their open-chain analogues. Subsequently, Hinz and Margerum[3] concluded that ligand solvation was by far the more important effect in the case of hydrogen-bonding ligands such as the tetraamines when operating in aqueous solution.

In expressing a contrasting point of view, Paoletti, Fabbrizzi, and Lever[4] as well as Kodama and Kimura[5] concluded that the macrocyclic effect manifested in the Cu^{II}–tetraamine complexes is dominated by an entropy effect. Although this view was later modified,[6] the relative importance of the enthalpic and entropic contributions to the macrocyclic effect was not clarified.

Recently, Clay, Paoletti, and co-workers[7] have reported the results of direct measurements on the solvation enthalpies of the 14-membered cyclic tetraamine ligand (14-ane-N_4 or cyclam), which exhibits the maximum macrocyclic effect with Ni(II) and Cu(II), and an open-chain analogue (2,3,2-N_4 or 2,3,2-tet). As measured in 0.5 M NaOH (to prevent ligand protonation), the aqueous heats of solution for these two ligands are −2.5 and −15.8 kcal mol^{-1}, respectively.[7] With the assumption that the metal complexes with these two ligands show little difference in solvation, these results appear to corroborate Hinz and Margerum's contention that free ligand solvation enthalpy is, indeed, the primary contributor to the macrocyclic effect *as manifested by the polyamine ligands in aqueous solution.*

As a result of the dominance of the ligand solvation term, other contributions to the macrocyclic effect cannot be quantitatively assessed from data gathered on the tetraamine

---

(1) (a) Wayne State University. (b) University of Wisconsin—Eau Claire.
(2) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 6540.
(3) Hinz, F. P.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2941; *J. Am. Chem. Soc.* **1974**, *96*, 4993.
(4) Fabbrizzi, L.; Paoletti, P.; Lever, A. B. P. *Inorg. Chem.* **1976**, *15*, 1502.
(5) Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1976**, 116, 1720; *J. Chem. Soc., Chem. Commun.* **1975**, 326, 891.
(6) Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *Inorg. Chim. Acta* **1977**, *22*, L25.
(7) Clay, R. M.; Micheloni, M.; Paoletti, P.; Steele, W. V. *J. Am. Chem. Soc.* **1979**, *101*, 4119.