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THE REACTION OF NUCLEOPHILES WITH [DICARBONYL(h^5-CYCLOPENTADIENYL)(h^2-ACENAPHTHYLENE)(IRON)]$^+$[TETRAFLUOROBORATE]$^-$

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Summary

The reactions between (h^5-C_5H_5)$Fe(CO)_2$(h^2-acenaphthylene)$^+$ BF_4^- (I) and the nucleophiles methoxide, triphenylphosphine, trimethylamine, iodide, tert-butyl mercaptide and isobutyraldehyde pyrollidine enamine give products resulting from (*1*) nucleophilic addition to coordinated acenaphthylene and (2) displacement of acenaphthylene. The addition process occurs stereospecifically to produce *trans* adducts II. Mechanistic aspects of the reactions are discussed.

Introduction

Nucleophilic addition to coordinated olefins is a characteristic reaction of mercury(II)[1], palladium(II)[2], platinum(II)[3] and certain iron(II)[4,5] complexes. The synthetic potential of these reactions has partly been realized in the solvomercuration reaction and the Wacker process. Recently, attention has been drawn to the cationic iron complexes, (h^5-C_5H_5)$Fe(CO)_2$(olefin)$^+$$BF_4^-$ which react with a variety of nucleophiles including methoxide, primary amines, phosphines[4] and perhaps most notably carbon nucleophiles such as malonates, some Grignard reagents, enamines and (C_5H_5)$Fe(CO)_2$(h^1-allyl)[5].

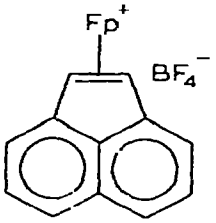
Considerable interest has centered around the stereochemistry of this process. *Anti* addition (relative to the metal) of nucleophiles has been generally observed for Hg^{II} [1], Pt^{II} [6], and Pd^{II} [7] olefin and diene complexes presumably the result of intermolecular backside attack. *Syn* addition, however, has been noted in a few instances for Hg^{II} [8] and Pd^{II} [9]; this mode of addition has been explained in terms of attack on a short-lived free carbonnium ion (for Hg) or internal delivery of coordinated nucleophile (for Pd).

On the other hand, stereochemical information on nucleophilic additions

to the $(h^5\text{-}C_5H_5)Fe(CO)_2(olefin)^+$complexes is sparse*. As these complexes appear to have a promising future in synthesis, we sought to establish the stereochemistry of the addition reaction by examining the interaction of various nucleophiles with the acenaphthylene complex I. Compound I appeared to be an attractive model system since the stereochemistry of 1,2-substituted acenaphthene derivatives (e.g., II) is readily determined from the magnitude of the vicinal coupling constant $J(H_1—H_2)$ [11]; J_{trans} = 0-3, J_{cis} = 6-8 Hz. Additionally, the planar acenapthylene ligand should have a minimal steric effect on the reactions.

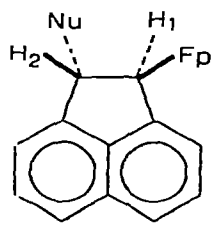
Results and discussion

Complex I, an orange-yellow air stable solid, was conveniently prepared in 85-90% yield by the exchange reaction between acenaphthylene and Fp-(isobutylene)$^+$ BF_4^- [12]. Satisfactory spectral and analytical data were obtained in support of the assigned structure. The reactions of I with nucleophilic reagents generally were carried out in acetonitrile solution and their progress monitored by observing disappearance of the carbonyl absorption of I (2040, 2005 cm^{-1}) in the infrared spectrum.



(I)

Fp = $(h^5\text{-}C_5H_5)Fe(CO)_2$



(II)

Two overall reactions occur when I reacts with nucleophiles: *(1)* addition to coordinated acenaphthylene and *(2)* ligand substitution (displacement) of acenaphthylene. Thus treatment of I with CH_3OH/Na_2CO_3, PPh_3, and NaI gave acenaphthylene as well as $[(C_5H_5)Fe(CO)_2]_2$ (with MeO^-) or $(C_5H_5)Fe(CO)_2Nu$ (with PPh_3 and NaI). Good yields of the addition products IIa (Nu = —$SCMe_3$) and IIb (Nu = —CMe_2CHO), however, were obtained from the interaction of I with $Me_3CSH/NaHCO_3$ and isobutyraldehyde pyrollidine enamine (after hydrolysis) respectively. The proton NMR data for these adducts are summarized in Table 1.

The most important feature of the NMR data is the appearance of absorptions due to H_1 and H_2 as broad singlets (width at half-height, 2.5 Hz, IIb) or weakly coupled doublets (J = 1 Hz, IIa). In light of the published coupling constants for 1,2-substituted acenaphthenes [11], these results clearly in-

* While this manuscript was in preparation, W.P. Giering and coworkers [10] reported *trans* addition of some nucleophiles to $(h^5\text{-}C_5H_5)Fe(CO)_2(h^2\text{-}benzocyclobutadiene)^+PF_6^-$.

TABLE 1

^{1}H NMR DATA FOR IIa, b (τ)

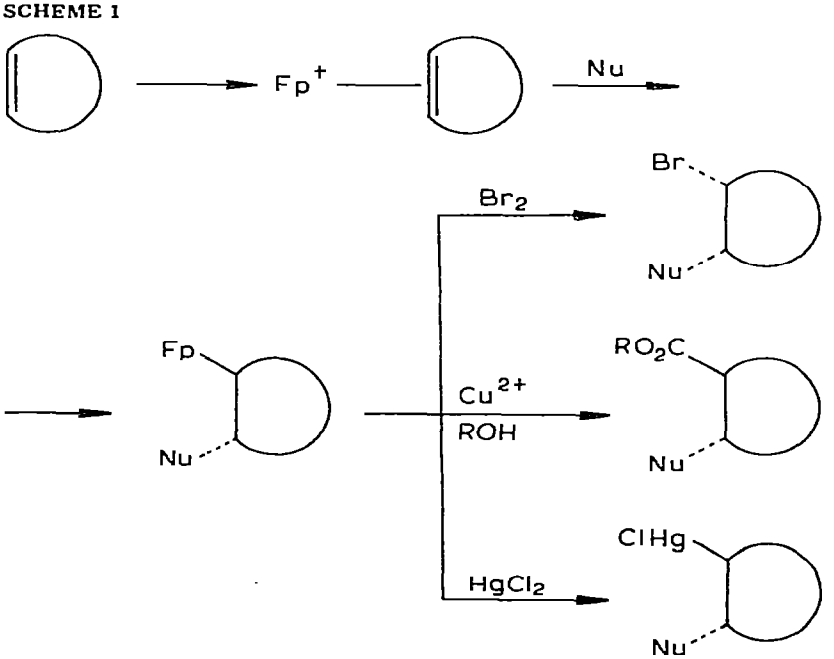
	Aromatic	C_5H_5	H_1	H_2	Other
IIa[a] (Nu = —$SCMe_3$)	2.3—2.9 (m)	5.40 (s)	5.85 (d, J = 1 Hz)	5.30 (d, J = 1 Hz)	8.50 [s,—$C(CH_3)_3$]
IIb[b] (Nu = —CMe_2CHO)	2.3—3.0 (m)	5.85 (s)	6.10 (bs)	6.30 (bs)	0.50 (s,—CHO) 9.1, 9.2 (s,—CH_3)[c]

[a] CD_3COCD_3 solvent. [b] CS_2 solvent. [c] Diastereotopic.

dicate a *trans* relationship between H_1 and H_2 and hence demonstrate *anti* attack by nucleophile. None of the isomeric *cis* complexes were detected chromatographically or spectroscopically suggesting a high degree of stereoselectivity for this addition process. These findings concur with those of Giering et al. [10] for the analogous benzocyclobutadiene complex.

The preferred *anti* attack by nucleophiles on I is understandable in terms of approach at the least hindered face of the coordinated olefin, i.e., that opposite the bulky organometallic moiety. The specificity of these additions coupled with the stereospecificity of the demetalation reactions of the Fp-(alkyl) complexes [13] and the ready availability of the Fp(olefin)$^+$ complexes [12,14] provides a selective route to vicinally substituted compounds from olefins. This scheme is outlined below for a generalized cyclic olefin (Scheme 1).

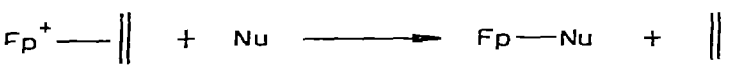
SCHEME 1



Starting with acyclic alkenes *erythro* or *threo* derivatives could be obtained.

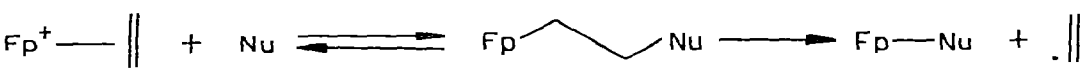
For the displacement reaction two different mechanisms should be considered: *(a)* direct nucleophilic attack at iron (S_N1 or S_N2, Scheme 2) or

SCHEME 2



(b) a sequence (Scheme 3) involving primary reversible attack on the coordinated olefin followed by elimination of Fp—Nu or reversion to the starting complex and irreversible displacement according to Scheme 2. That initial attack occurs on coordinated acenaphthylene for PPh_3 and NMe_3 was demonstrated by detection of the intermediate adducts spectroscopically during the reaction of I with these nucleophiles. Thus treatment of a CD_3CN solution of I with one equivalent of PPh_3 resulted in rapid disappearance of the NMR absorptions of I with concurrent appearance of cyclopentadienyl resonances at τ 4.7 (d, J = 2 Hz) and τ 5.3 (s) assigned to Fp $(PPh_3)^+BF_4^-$ and IIc (Nu = PPh_3) respectively. Also present were absorptions due to free acenaphthylene. Within 20 min the absorptions of IIc had completely disappeared with the final spectrum exhibiting absorptions arising only from $Fp(PPh_3)^+BF_4^-$ and acenaphthylene . The reaction of I with PPh_3 and NMe_3 could also be monitored in the IR; carbonyl absorptions appeared at 1995 and 1960 cm^{-1} for IIc and 1990 and 1960 cm^{-1} for IId (Nu = NMe_3). Attempted isolation of these adducts was unsuccessful. Analogous intermediates were not detected by IR for the reactions of I with iodide or methoxide. This result suggests that their collapse must be very rapid or that attack occurs directly at iron (Scheme 2).

SCHEME 3



The acenaphthylene complex I appears more prone to displacement of coordinated olefin than many of the simpler Fp(olefin)$^+$ complexes. For example, treatment of $Fp(ethylene)^+BF_4^-$ or $Fp(propene)^+BF_4^-$ with MeOH/Na_2CO_3, PPh_3 or NMe_3 gives isolable addition products although there is some evidence that the reactions with PPh_3 are reversible [15]. The factors which affect the stability and lability of these complexes are presently undetermined and require additional study.

Experimental

$(C_5H_5)Fe(CO)_2(isobutylene)^+BF_4^-$ was prepared as described by Giering and Rosenblum [12]. Isobutyraldehyde enamine was prepared by the standard method [16]. All other materials were obtained commercially. Acenaphthylene was recrystallized from 95% ethanol. Solvents were degassed prior to use and a nitrogen atmosphere was maintained during all reactions and operations. NMR spectra were recorded at 60 MHz on a Perkin—Elmer R24 or Varian A60 spectrometer. Infrared spectra were obtained on Perkin—Elmer 137 or Beckman IR 10 spectrometers. Elemental analysis were performed by Galbraith Laboratories, Knoxville, Tenn.

$(C_5H_5)Fe(CO)_2$(acenaphthylene)$^+BF_4^-$ (I)

Acenaphthylene (6.0 g, 39 mmol), $(C_5H_5)Fe(CO)_2$(isobutylene)$^+BF_4^-$ (1.0 g, 3.1 mmol) and 40 ml of 1,2-dichloroethane were placed in an Erlenmeyer flask. A rubber septum fitted with a syringe needle and thermometer was secured to the flask and the mixture heated at 65° for 10 min. After cooling, the resulting yellow-orange precipitate (1.2 g, 91%) was collected and washed with ether. IR(CH_3CN): 2040, 2005 cm^{-1}(C≡O); NMR (CD_3NO_2) τ: 1.7-2.5 (m, 6H), 3.1 (s, 2H) and 4.25 (s, 5H) ppm. (Found: C, 54.6; H, 3.3. $C_{19}H_{13}BF_4FeO_2$ calcd.: C, 54.8; H, 3.1%.)

Reaction of I with $Me_3CSH/NaHCO_3$

A solution of I (0.416 g, 1.00 mmol) in acetonitrile (10 ml) containing 1.0 ml of tert-butyl thiol and 0.5 g of sodium bicarbonate was stirred at room temperature for 5 h. During this time the mixture turned from orange to yellow. The solvent and excess thiol were evaporated and the resulting residue extracted with a few small portions of ether. The combined extracts were concentrated and chromatographed on basic alumina (activity III). Development with pentane gave acenaphthylene (0.021 g, 14%); development with 1/9 ether/pentane gave the thiol adduct as a yellow oil (0.32 g, 76%). An analytical sample was obtained by re-chromatography over basic alumina (act. III). IR (CH_3CN); 1995, 1960 cm^{-1} (C≡O). (Found: C, 66.3; H, 5.4; S, 7.9. $C_{23}H_{22}FeO_2S$ calcd.: C, 66.0; H, 5.3; S, 7.7%.)

Development with 1/4 ether/pentane gave a small amount of $[(C_5H_5)Fe(CO)_2]_2$ identified by its IR spectrum.

Reaction of I with $Me_2C{=}CH\overline{N(CH_2)_3CH_2}$ and hydrolysis

Isobutyraldehyde pyrollidene enamine (0.095 g, 0.75 mmol) in 3 ml of acetonitrile was added dropwise to a stirred solution of I (0.33 g, 0.80 mmol) in acetonitrile (5 ml). After 15 min the reaction mixture was poured into 30 ml of water and extracted with three 20 ml portions of ether. The combined extracts were dried, concentrated and the resulting residue chromatographed on neutral alumina (act. III). Development with hexane gave a small quantity of acenaphthylene (ca 5%); development with 1/9 ether/hexane eluted a yellow band which left the product as a yellow oil after solvent evaporation (0.24g, 83%). IR ($CHCl_3$): 1990, 1960 (M—C≡O), 1725 cm^{-1} (C≡O). The complex was converted to the corresponding 2,4-dinitrophenylhydrazone in the standard fashion. (Found: C, 60.5; H, 4.7; N, 9.2. $C_{29}H_{24}FeN_4O_6$ calcd.: C, 60.0; H, 4.2; N, 9.6%.)

Reaction of I with PPh_3

Triphenylphosphine (0.026 g, 0.10 mmol), I (0.0416 g, 0.10 mmol) and 0.30 ml of CD_3CN containing two drops of TMS were placed in an NMR tube. After centrifuging the sample spectra were recorded periodically over 30 min.

The above reaction carried out on a 0.50 mmol scale afforded 0.45 mmol of $(C_5H_5)Fe(CO)_2PPh_3^+BF_4^-$ upon addition of the reaction mixture to a large volume of ether.

Reaction of I with NMe_3

An excess of trimethylamine was added to a solution of I (0.21 g, 0.50

mmol) in acetonitrile (5ml). After 15 min the spectrum of an aliquot indicated complete disappearance of I with new carbonyl absorptions at 1990 and 1960 cm^{-1}. The yellow solution was added to a large volume of ether causing a yellow solid to separate. The solid redissolved within minutes producing a yellow-orange solution which contained only acenaphthylene and $[(C_5H_5)Fe(CO)_2]_2$ as characterizable products.

Reaction of I with NaI

An excess of sodium iodide was added to a solution of I (0.10 g, 0.24 mmol) in acetone (10 ml). After stirring for 2 h the dark green solution was concentrated and the resulting residue extracted with three small portions of hexane. The combined extracts were chromatographed on alumina to give 0.029 g (80%) of acenaphthylene. Extraction of the hexane-washed reaction residue with dichloromethane gave $(C_5H_5)Fe(CO)_2I$ (82%).

Reaction of I with MeOH/Na_2CO_3

The complex I (0.21 g, 0.50 mmol) was suspended in 5 ml of methanol containing 0.3 g of sodium carbonate and the mixture stirred for 1 h. The solvent was evaporated, the residue extracted with hexane, and the combined extracts were chromatographed over basic alumina (act. III). Development with hexane gave acenaphthylene (0.065 g, 86%); development with 1/9 ether/hexane eluted a small yellow band which upon solvent evaporation left 0.005 g of an orange solid (IR: 1990, 1960 cm^{-1}) which was not further characterized; development with 1/4 ether/hexane gave 0.10 g (57%) of $[(C_5H_5)Fe(CO)_2]_2$.

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References

1 N.S. Zefirov, Russ. Chem. Rev., 34 (1965) 527. W. Kitching, Organometal. Chem. Rev., 3 (1968) 61.
2 P.M. Maitlis, The Organic Chemistry of Palladium, Vol. 1, Academic Press, New York, N.Y., 1971.
3 J. Tsuji, Accounts Chem. Res., 2 (1969) 144; M.H. Chisolm, H.C. Clark and L.E. Manzer, J. Amer. Chem. Soc., 94 (1972) 1532.
4 M. Graziani, L. Busetto and A. Palazzi, J. Organometal. Chem., 25 (1970) 207; M. Rosenblum, Accounts Chem. Res., 7 (1974) 122.
5 A. Rosan, M. Rosenblum and J. Tancrede, J. Amer. Chem. Soc., 95 (1973) 3062.
6 A. Panunzi, A. DeRenzi and G. Paiaro, J. Amer. Chem. Soc., 92 (1970) 3489 and refs. therein.
7 J.K. Stille and R.H. Morgan, J. Amer. Chem. Soc., 88 (1966) 5135; M. Green and R.I. Hancock, J. Chem. Soc. A, (1967) 2054; L.F. Dahl and W.E. Oberhansli, Inorg. Chem., 4 (1965) 629.
8 H.C. Brown and J.H. Kawakami, J. Amer. Chem. Soc., 95 (1973) 8665.
9 P.M. Henry, J. Org. Chem., 37 (1972) 2443.
10 A. Sanders, C.V. Magatti and W.P. Giering, J. Amer. Chem. Soc., 96 (1974) 1610.
11 M.J.S. Dewar and R.C. Fahey, J. Amer. Chem. Soc., 85 (1963) 2705; W.H. Mueller and P.E. Butler, ibid, 88 (1966) 2866; R.F. Merrit and F.A. Johnson, J. Org. Chem., 31 (1966) 1859.
12 W.P. Giering and M. Rosenblum, Chem. Commun., (1971) 441.
13 G.M. Whitesides and D.J. Boschetto, J. Amer. Chem. Soc., 93 (1971) 1529; K.M. Nicholas and M. Rosenblum, ibid., 95 (1973) 4449.
14 E.O. Fischer and K. Fichtel, Chem. Ber., 94 (1961) 1200; M.L.H. Green and P.L.I. Nagy, J. Organometal. Chem., 1 (1963) 58; W.P. Giering, M. Rosenblum and J. Tancrede, J. Amer. Chem. Soc., 94 (1972) 7170.
15 A. Rosan and M. Rosenblum, personal communication.
16 C. Mannich and H. Davidsen, Ber., 69 (1936) 2106.