A Novel Isomerization of an Electron-Rich Alkene

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Displacement of 2-methylpropene from [Fp(Me2C=CH2)]BF4 (Fp = \( \phi^5-C_5H_5 \)Fe(CO)5) by Z-1,2-dimethoxyethylene (Z-DME) gives [Fp(Z-DME)]BF4. Displacement by E-1,2-dimethoxyethylene (E-DME), in contrast, does not give the expected complex of E-DME, but rather the complex of the Z-alkene. A mechanism involving scission of the C=C bond of the coordinated alkene to give a bis-carbene intermediate is proposed.

While a wide variety of complexes of electrophilic alkenes is known [1], until recent years few reactions of transition metal complexes with electron-rich alkenes had been described. Now, however, a number of methoxy- [2] and aminoalkene [3] complexes have been reported. In an effort to extend the former series of compounds, attempts were made to prepare cations of the type [Fp(methoxyalkene)]+ by treating [Fp(2-methylpropene)]BF4 [4, 5] with E- and Z-1,2-dimethoxyethylene (DME). To our surprise, both reactions gave the same complex of the Z-alkene, an unprecedented example of alkene isomerization which is reported herein.

Results and Discussion

As shown in the experimental section, reaction of [Fp(Me2C=CH2)]BF4 with Z-DME led to the expected complex [Fp(Z-DME)]BF4. Its spectroscopic properties are characteristic of compounds in this class [6, 7].

Surprisingly, the analogous reaction with E-DME gave also a complex with the spectroscopic properties of the complex of the Z-alkene. Confirmation of the identity of the product was obtained by displacing the olefin with excess triphenylphosphine.

In an effort to detect a presumed E-alkene intermediate, a series of NMR experiments was carried out in a number of solvents (1,2-dichloroethane; CD3NO2, CD3CN, (CD3)2CO). Reactions of [Fp(Me2C=CH2)]BF4 with E-DME (2-10 fold excess) at temperatures ranging from 20–50 °C were monitored using both 1H and 13C NMR spectroscopy. Interestingly, while similar substitution reactions of the Z-alkene proceeded smoothly and essentially to completion at 45 °C in about two hours [8], reactions of the E-alkene required a temperature of at least 50 °C for appreciable rates to be obtained. Under these conditions, the major iron complex formed was [Fp(Z-DME)]BF4, accompanied by smaller amounts of [Fp(CO)]BF4 ([Co(CO)5] ~ 2130, ~2070 cm⁻¹, δ(C6H5) ~ 6.1 ppm [9]) and [Fp(solvent)]BF4 (for reactions in acetone and acetonitrile [10, 11]). The recovered E-alkene had partially decomposed, as shown by a multiplicity of resonances in the methoxy regions of the 1H and 13C NMR spectra; the alkene is stable under these conditions in the absence of iron compound. The observed conversion of E-DME to Z-DME is not catalytic.

The conversion of E- to Z-DME was unexpected, as alkene isomerization catalyzed by transition metal compounds normally involves either metal hydrides or alkenes with allylic hydrogen atoms [12].

Abbreviations:

Fp = \( \phi^5-C_5H_5 \)Fe(CO)5;  
DME = 1,2-dimethoxyethylene;  
R = alkyl;  
Me = methyl.

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neither situation pertains here. Isomerization of vinyl ethers of the type \( RCH=CH(OR') \), however, has been reported to be catalyzed by compounds of platinum(II) [13]. It was suggested that the reaction might involve a \( \pi \leftrightarrow \sigma \) interconversion of the coordinated dipolar alkene, i.e.

\[
\text{Pt} - OR' \quad \longleftrightarrow \quad \text{Pt} - OR
\]

The \( \sigma \) intermediate would be stabilized by \( \pi \)-donation from the oxygen atom to the carbenium carbon atom, as occurs with platinum(II) complexes of 1,1-dimethoxyethylene [14] and vinyl alcohol [15].

Such a mechanism, however, does not seem likely for an olefin which is electron-rich at both ends. Instead, we assume a closer similarity to the chemistry of the tetrakis(amino)alkenes of the type

\[
[\text{CNRCH}_2\text{CH}_2\text{NR}]_2
\]

which react with a wide variety of transition metal compounds to form complexes of the cyclic carbenes, \( \text{CNRCH}_2\text{CH}_2\text{NR} \) [3]. While the mechanism of the carbene-forming reaction is not clear, a driving force would undoubtedly involve \( \pi \)-donation of the nitrogen lone pair electrons into the vacant \( \pi \) orbital of the carbenic carbon atom. This effect would probably be accentuated in the case of a complex of a metal atom in a higher oxidation state.

Formation of similar carbene complexes on coordination of the electron-rich alkenes E- and Z-DME to the Fp+ moiety might readily explain the observed isomerization process. The reaction would possibly involve either a 20 electron intermediate of the type \([\text{Fp(carbene)}]_2^+ [16]\), or an allylic species of the type \([\eta^5\text{-C}_5\text{H}_5]\text{Fe(OC)O}_2(\text{carbene})_2^+ \). While carbene stabilization from \( \pi \)-overlap with the oxygen lone pairs would not normally be as significant as in the cases of the aminoalkene mentioned above, the electron-withdrawing power of the cationic \([\eta^5\text{-C}_5\text{H}_5]\text{Fe(OC)O}_2 \) fragment may well be a significant factor. We note that the isoelectronic complex, \([\eta^5\text{-C}_5\text{H}_5]\text{Mn(OC)O}_2(\text{E-DME}) [17] \), is stable with respect to isomerization; in addition, it has been reported that alkoide substituents can weaken carbon-carbon bonds [18].

A number of carbene complexes of the type \([\text{Fp(carbene)}]^+ \) have been reported [19–21]; they exhibit exceedingly low field \( ^{13}\text{C} \) NMR carbene carbon chemical shifts (\( \sim 340 \) ppm). Monitoring the \( ^{13}\text{C} \) NMR spectrum in the region 200–440 ppm during the reaction of \([\text{Fp(Me_2C=CH}_2]BF_4 \) with E-DME at 50 \( ^\circ \)C revealed no new resonances (except for CO), however, showing that carbene complexes are not present in appreciable amounts in the solution under these conditions.

The actual isomerization process would involve coordination of the E-alkene, carbon-carbon bond scission, and rotation about the iron-carbon bonds prior to carbon-carbon bond reformation, i.e.

\[
\begin{array}{c}
\text{CH}_2 = \text{CHOR} + \text{Fe}^+ \text{OCH}_3 \text{CH} = \text{CHOR} \\
\text{CO ligands omitted for clarity.}
\end{array}
\]

As noted previously for complexes of this type [17, 22], and justified theoretically [23], the stable conformation of the alkene is that in which the C=C axis is parallel to the plane of the \( \eta^5 \)-cyclopentadienyl ring. Possibly because of the large cone angle of the \( \eta^5 \)-cyclopentadienyl ligand [24], the preferred conformations of substituted alkenes are those in which the substituents are directed away from the ring [23]. While Fp+ complexes of both E- and Z-but-2-ene are known, the former appears to be the more labile [22], and it is reasonable to expect that \([\text{Fp(Z-DME)}]^+ \) is for steric reasons more stable than \([\text{Fp(E-DME)}]^+ \).

It is tempting to suggest that a similar "carbene mechanism" may apply to the above-mentioned platinum(II)-catalyzed isomerization of vinyl ethers [13], as again the metal is in a relatively high (for alkene complexes) oxidation state.

Experimental
The complex \([\text{Fp(2-methylpropene)}]BF_4 \) was prepared as in the literature [4], while E- and Z-DME were gifts from Dynamit Nobel AG, Lülsdorf. All reactions were carried out under nitrogen in dried, purified solvents.

Infrared spectra were recorded on a Beckman IR 4240 spectrometer, NMR spectra on Varian EM 360 (\( ^1\text{H} \)) and Bruker HX 60 (\( ^1\text{H}, ^{13}\text{C} \)) spectrometers.

The compound \([\text{Fp(Z-DME)}]BF_4 \) was prepared by reaction of Z-DME with \([\text{Fp(Me_2C=CH}_2]BF_4 \) in 1,2-dichloroethane, following standard procedures [4, 5]. It was obtained as a yellow crystalline powder (70% yield).
Infrared spectrum: v(CO) 2068, 2028 cm⁻¹ (CH₃NO₂);
¹H NMR: δ 5.52 (C₅H₅), δ 6.46 (=CH) and δ 4.03 (CH₃)(CD₃NO₂);
¹³C NMR: δ 80.1 (C₅H₅), δ 104.7 (=CH), δ 62.5 (CH₃) and δ 210.6 (CO) (CD₃NO₂).

C₁₁H₁₃BF₄FeO₄ (351.9)
Calcd C 37.55 H 3.72 Fe 15.87,
Found C 37.29 H 3.77 Fe 15.69.

Reaction of E-DME with [Fp(Me₂C═CH₂)]BF₄ in 1,2-dichloroethane was somewhat slower and tended to give mixtures. However, on one occasion, there was obtained in low yield a single homogeneous product which had spectroscopic properties identical with those listed above (Found: C 37.85, H 3.87, Fe 16.00). Reaction of this compound with triphenylphosphine in acetone yielded [(η²-C₅H₅)Fe(CO)₂PPh₃]BF₄ and Z-DME.

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[8] In acetone, displacement of 2-methylpropene by solvent occurred more rapidly than did reaction with alkene. However, the acetone complex was also eventually converted to alkene complex, as well.