A Novel Isomerization of an Electron-Rich Alkene

Erica L. Weinberg, J. Thomas Burton, and Michael C. Baird
Department of Chemistry, Queen's University, Kingston, Canada K7L 3N6
Max Herberhold*
Anorganisch-chemisches Institut der Technischen Universität, D-8000 München
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Displacement of 2-methylpropene from \([\text{Fp(Me}_2\text{C}=\text{CH}_2])\text{BF}_4\) (see Eq. 1) by Z-1,2-dimethoxyethylene (Z-DME) gives \([\text{Fp}(\text{Z-DME})]\text{BF}_4\). 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 \(\text{C}==\text{C}\) 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 amino-alkene [3] complexes have been reported. In an effort to extend the former series of compounds, attempts were made to prepare cations of the type \([\text{Fp}(\text{methoxyalkene})]^{+}\) by treating \([\text{Fp}(\text{2-methylpropene})]\text{BF}_4\) 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 \([\text{Fp(Me}_2\text{C}=\text{CH}_2])\text{BF}_4\) with Z-DME led to the expected complex \([\text{Fp}(\text{Z-DME})]\text{BF}_4\). 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; CD\(_2\)NO\(_2\), CD\(_3\)CN, (CD\(_3\))\(_2\)CO). Reactions of \([\text{Fp}(\text{Me}_2\text{C}=\text{CH}_2])\text{BF}_4\) with E-DME (2-10 fold excess) at temperatures ranging from 20–50°C were monitored using both \(^1\)H and \(^13\)C 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 \([\text{Fp}(\text{Z-DME})]\text{BF}_4\), accompanied by smaller amounts of \([\text{Fp}(\text{CO})]\text{BF}_4\) (ν(CO) ~2130, ~2070 cm\(^{-1}\), δ(C\(_3\)H\(_5\)) ~6,1 ppm [9]) and \([\text{Fp}(\text{solvent})]\text{BF}_4\) (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 \(^1\)H and \(^13\)C 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];
neither situation pertains here. Isomerization of vinyl ethers of the type \( \text{RCH} = \text{CH(OR')} \), 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, \( \text{i.e.} \)

\[
\text{Pt} \quad \text{OR} \quad \text{H} \\
\text{H} \quad \text{R} \quad \text{OR}' \\
\text{H} \quad \text{R} \quad \text{OR}
\]

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(aminooalkenes of the type \( [:\text{CNR2CH2NR}]_2 \), which react with a wide variety of transition metal compounds to form complexes of the cyclic carbenes, \( :\text{CNR2CH2NR} \) [3]. While the mechanism of the carbone-forming reaction is not clear, a driving force would undoubtedly involve \( \pi \)-donation of the nitrogen lone pair electrons into the vacant \( p \pi \) orbital of the carbone 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 carbone complexes on coordination of the electron-rich alkenes E- and Z-DME to the \( \text{Fp}^+ \) 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 \( [\text{E-DME}]^+ \) [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 \( \eta^2 \)-cyclopentadienyl ring. Possibly because of the large cone angle of the \( \eta^2 \)-cyclopentadienyl ligand [24], the preferred conformations of substituted alkenes are those in which the substituents are directed away from the ring [23]. While \( \text{Fp}^+ \) 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 "carbone 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 \( [\text{Fp(2-methylpropene)}] \text{BF}_4 \) 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 (\( ^1H \)) and Bruker HX 60 (\( ^1H, ^{13}C \)) spectrometers.

The compound \( [\text{Fp(Z-DME)}] \text{BF}_4 \) was prepared by reaction of Z-DME with \( [\text{Fp(Me}_2\text{C} = \text{CH}_2)] \text{BF}_4 \) in 1,2-dichloroethane, following standard procedures [4, 5]. It was obtained as a yellow crystalline powder (70% yield).
Infrared spectrum: $\nu$(CO) 2068, 2028 cm$^{-1}$ (CH$_3$N0$_2$); $^1$H NMR: $\delta$ 5.52 (C$_5$H$_5$), $\delta$ 6.46 (=CH) and $\delta$ 4.03 (CH$_3$) (CD$_3$NO$_2$); $^{13}$C NMR: $\delta$ 89.1 (C$_5$H$_5$), $\delta$ 104.7 (=CH), $\delta$ 62.5 (CH$_3$) and $\delta$ 210.6 (CO) (CD$_3$NO$_2$).

$C_{11}H_{13}BF_4FeO_4$ (351.9)
  Caled 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(Me$_2$C=CH$_2$)]BF$_4$ 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 [(C$_5$H$_5$)Fe(CO)$_2$PPh$_3$]BF$_4$ 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.