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# Kinetics and Mechanism of Cyclopropanation of Cyclooctene by [Fe($\eta^5$-$C_5H_5$)$(CO)_2CH_2SPh_2$]$BF_4$

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The kinetics of reaction of [Fe($\eta^5$-$C_5H_5$)$(CO)_2CH_2SPh_2$]$BF_4$ with cyclooctene in $CH_2Cl_2$ solution have been studied under pseudo-first-order conditions at room temperature. The variation of $k_{obs}$ is nonlinear in both cyclooctene and added $Ph_2S$. The results are interpreted in terms of a two-step reaction in which the cation [Fe($\eta^5$-$C_5H_5$)$(CO)_2CH_2SPh_2$]$^+$ undergoes reversible, dissociative loss of $Ph_2S$ followed by competitive capture of the methyleneiron complex by cyclooctene to produce bicyclo[6.1.0]nonane. The methyleneiron intermediate is 4−5 times more reactive toward diphenylsulfide than cyclooctene. In the absence of added $Ph_2S$, millimolar solutions of the iron complex react with cyclooctene at room temperature with a half-life of about 36 min to give >85% yields of bicyclo[6.1.0]nonane after 3 h, and it is thus more reactive than the dimethyl- and methylphenylsulfonium salt analogues.

## Introduction

A variety of molecular complexes have been utilized as reagents for conversion of alkenes to cyclopropanes. One class of reagents developed by Helquist for this purpose are salts of the cations {Fe($\eta^5$-$C_5H_5$)$(CO)_2$[CH($R^1$)$SR^2R^3$]}$^+$.[1] The salt [FeCp$(CO)_2CH_2S(CH_3)_2$]$BF_4$ has been most extensively studied.[2] It is readily prepared in excellent yield from inexpensive starting materials, has an extensive shelf life, and under appropriate conditions, converts olefins to cyclopropanes in moderate to good yields with high stereoselectivity. Unlike related cyclopropanating reagents, such as those generated by induced α-ionization of {Fe($\eta^5$-$C_5H_5$)(CO)(L)[C(X)RR′]}[3] or protonation of [Fe($\eta^5$-$C_5H_5$)(CO)(L)C(R)═$CR_2$],[4] for which there is good evidence that a metal−carbene complex is generated in at least some instances,[5] there is no direct evidence currently available concerning the pathway followed by the sulfonium salts.[6] Two limiting pathways can be envisioned: an $S_N1$ pathway in which dissociation of sulfide produces a carbene, or an $S_N2$ pathway in which the sulfide is displaced by the olefin. In principle, the latter pathway might allow the use of a chiral sulfonium salt as a means of directing the stereochemistry of cyclopropanation of a prochiral substrate[7,8] whereas the former would not.

In connection with our investigation of thallium(I)-promoted substitution of chloride in chloromethyl alkyl complexes by neutral nucleophiles[9] we generated several new [CpFe$(CO)_2CH_2SR_2$]$^+$ salts including [CpFe$(CO)_2CH_2SPh_2$]$BF_4$. Not unexpectedly, the diphenylsulfonium salt proved to be considerably more reactive for cyclopropanation of olefins than either the dimethyl- or methylphenylsulfonium salts studied by Helquist.[1] The complex reacted with 1 equiv of $C_8H_{14}$ in methylene chloride (0.1 M) at room temperature ($t_{1/2}$ ∼36 min) to give >85% of bicyclo[6.1.0]nonane after 3 h. The convenient time scale of this reaction led us to perform a detailed kinetics study, which is the primary subject

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(1) An exhaustive review of Helquist's work on these reagents and of other methods of cyclopropanation of alkenes up to 1987 is given in: O'Connor, E. J.; Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1987**, *109*, 3739.

(2) This compound is currently available from Aldrich Chemical Co., and its preparation and procedures for cyclopropanation have appeared in: *Organic Syntheses*; Mattson, M. N.; O'Connor, E. J.; Helquist, P. *Org. Synth.* **1992**, *70*, 177.

(3) Such reactions include: (1) $Ag^+$ ion induced ionization of $CpFe(CO)_2CH_2Cl$ (a) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044, (b) Bodnar, T. W.; Cutler, A. R. *Organometallics* **1985**, *4*, 1558. (2) $H^+$ reaction with CpFe(CO)(L)C(OR)R′R″; ref 3a; (c) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099, (d) Green, M. L. H.; Ishag, M.; Whiteley, R. N. *J. Chem. Soc., A* **1967**, 1508. (3) $Ph_3C^+$ abstraction of $RO^-$ from CpFe(CO)(L)C(OR)R′R″, ref 3c (this is not a general reaction). (4) TMSOTf silylation of CpFe(CO)(L)C(OR)R′R″, R = alkyl: (e) Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. *J. Am. Chem. Soc.* **1980**, *102*, 7802, R = $Me_3Si$, (f) R. M.; Theys, R. D.; Hossain, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 777.

(4) (a) Casey, C. P.; Miles, W. H.; Tuikada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761. (b) Kremer, K. A. M.; Kuo, G. H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 9. (c) Kuo, G. H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806. (d) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924.

(5) Evidence for the formation of "free" metal−carbenes and a discussion of their reactions is given in: (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411, and (b) Petz, W. *Iron-Carbene Complexes*; Springer-Verlag: Berlin, 1993. [CpFe$(CO)_2CH_2$]$^+$ has never been spectroscopically detected. When generated in the absence of a trapping agent, the ion undergoes disproportionation to give [CpFe$(CO)_2(C_2H_4)$]$^+$ and "[CpFe$(CO)_2$]$^+$" (ref 3b and references cited).

(6) A bimolecular process was initially suggested for the reaction of olefins with {Fe(Cp)$(CO)_2$[CH$(CH_3)S(CH_3)$Ph]}$^+$ (Kremer, K. A. M.; Helquist, P. *J. Organomet. Chem.* **1985**, *285*, 231), but see ref 1 for alternative mechanistic considerations.

(7) The efficiency of such a process would likely be limited, although the extent of bond breaking in the transition state would be very important. It would also be inefficient in that the chiral center would be lost upon displacement of the sulfide.

(8) A highly enantioselective cyclopropane synthesis has been accomplished using chiral forms of [CpFe(CO)$(PR_3)$═$CHCH_3$]$^+$: Brookhart, M.; Liu, Y.; Goldman, E. W.; Timmers, D. A.; Williams, G. D. *J. Am. Chem. Soc.* **1991**, *113*, 927. References to earlier less successful attempts at enantioselective cyclopropane synthesis using chiral [CpFe(CO)$(PR_3)$═$CH_2$]$^+$ are cited.

(9) Barefield, E. K.; McCarten, P.; Hillhouse, M. C. *Organometallics* **1985**, *4*, 1682.

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of this report. Also reported are some qualitative investigations of the reactivity of the diphenylsulfonium complex toward a number of olefins with substituents that were either more or less electron donating than alkyl.

## Experimental Section

All synthetic operations and manipulations of solutions of organometallics were conducted under a nitrogen atmosphere. Methylene chloride and hexane were purified by standard methods.[10] Diphenylsulfide (Aldrich Chemical Co.) was distilled from sodium under vacuum. Cyclooctene (Aldrich Chemical Co.) was passed through a column of alumina and distilled from calcium hydride. All other olefinic substrates (all from Aldrich Chemical Co.) were used as received. Infrared spectra were recorded using 0.1 mm NaCl cells and a Beckman 4240 spectrophotometer. Gas chromatographic analyses were performed at 140 °C using a 10% OV-101 on Chromosorb G (1 m × 1/8 in.) column and a thermal conductivity detector.

**Preparation of [$CpFe(CO)_2CH_2SPh_2$]$BF_4$.** A solution of 4.0 mL of $Ph_2S$ (4.5 g, 24 mmol) and 1.20 g (5.3 mmol) of $CpFe(CO)_2CH_2Cl$ in 40 mL of $CH_2Cl_2$, which was prepared and maintained under a nitrogen atmosphere, was combined with 2.70 g (10.0 mmol) of $TlBF_4$, and the resulting slurry was stirred for 20 h. The insoluble thallium salts were removed by filtration and washed with $CH_2Cl_2$. The combined methylene chloride solutions were concentrated to a small volume (ca. 15 mL), and hexane was added to complete precipitation of the yellow-orange product. The solid was redissolved in a minimum amount of methylene chloride and crystallized by slow addition of hexane. The product was collected by filtration and dried under vacuum to give a nearly quantitative yield of product (2.4 g). Anal. Calcd for $C_{20}H_{17}BF_4FeO_2$: C, 51.76; H, 3.69. Found: C, 51.92; H, 3.76. IR ($CH_2Cl_2$): $\nu_{CO}$ 2034, 1990 $cm^{-1}$. NMR (acetone-$\boldsymbol{d}_6$): $\delta$ 5.31 (s, 5H, $C_5H_5$), 3.53 (s, 2H, $CH_2$), 7.52−7.75 (m, 6H, *m*,*p*-$C_6H_5$), 7.93−8.17 (m, 4H, *o*-$C_6H_5$).

**Cyclopropanation of Cyclooctene by [$CpFe(CO)_2CH_2SPh_2$]$BF_4$.** To a solution of 0.250 g of [$CpFe(CO)_2CH_2SPh_2$]$BF_4$ (0.539 mmol) in 5 mL of methylene chloride was added 0.0594 g (0.540 mmol) of $C_8H_{14}$ and 0.0791 g (0.468 mmol) of diphenylmethane as an internal standard for gas chromatography. The mixture was stirred at room temperature for 3 h, at which time an infrared spectrum of the CO stretching region indicated that the peaks due to starting material (2034, 1990 $cm^{-1}$) had been replaced by new absorptions at 2069 and 2027 $cm^{-1}$ (due to $[CpFe(CO)_2(SPh_2)]^+$, vide infra). The inorganic material was precipitated by the addition of hexane, and the supernatant was concentrated and analyzed by gas−liquid chromatography. Bicyclo[6.1.0]nonane (80% yield based on iron) and 1-methylcyclooctene (15%) were the only products detected.[11] Washing of the supernatant with aqueous sodium bicarbonate and drying over sodium sulfate prior to concentration as suggested by Brookhart[12] gave increased yields of bicyclononane (up to 92%) and smaller amounts of 1-methylcyclooctene (as low as 3%). Survey experiments indicated that the rate of disappearance of the iron complex increased at higher concentrations of $C_8H_{14}$, but decreased sharply when $Ph_2S$ was added to the reaction mixture.

**Table 1. Yields and Half-Lives for Cyclopropanation of Various Olefins by [$CpFe(CO)_2CH_2SPh_2$]$BF_4$ at Room Temperature**

| olefin | cyclopropane/yield, % | $t_{1/2}$,[a] h |
|---|---|---|
| cyclooctene | bicyclo[6.1.0]nonane/92 | 0.6 |
| styrene | cyclopropylbenzene[18]/82 | 1 |
| *trans*-stilbene | *trans*-1,2-diphenylcyclopropane[19]/98 | 4 |
| 2,3-dihydropyran | 1-oxabicyclo[4.1.0]heptane[20]/75 | 0.25 |
| methyl acrylate | no reaction | |
| trichlorethene | no reaction | |

[a] Approximate half-life for disappearance of iron complex; based upon infrared monitoring of the reaction mixture.

**Cyclopropanation of Other Olefins with [$CpFe(CO)_2CH_2SPh_2$]$BF_4$.** Reactions were done by combining 1.0 mmol of the olefin with 1.0 mmol of the iron complex in 5 mL of methylene chloride at room temperature. After the iron starting material had disappeared (determined by infrared spectroscopy), 2 g of alumina (Brockman Activity 1) was added to the reaction mixture, the solvent was evaporated, and the alumina was transferred to the top of a 20 cm × 2 cm alumina column. The organic products were isolated by elution with 100 mL of 2-methylbutane. The elutant was evaporated, the residue was weighed, and the products were identified by comparison of their NMR spectra with data recorded in the literature. The olefins tested, approximate half-lives for reaction, and yield of cyclopropanation product are given in Table 1.

**Kinetics of the Reaction of [$CpFe(CO)_2CH_2SPh_2$]$BF_4$ with Cyclooctene.** The infrared spectrum of a solution of 0.0374 g (0.081 mmol) of [$CpFe(CO)_2CH_2SPh_2$]$BF_4$ in 1.00 mL of methylene chloride gave an absorbance of 0.73 for the CO stretch at 1990 $cm^{-1}$, which decreased linearly with concentration as the sample was diluted. The CO absorptions slowly decreased in intensity as solutions aged, but this was completely inhibited by the addition of small amounts of $Ph_2S$. For kinetic runs samples of [$CpFe(CO)_2CH_2SPh_2$]$BF_4$ were weighed into Schlenk vessels, which were then flushed with nitrogen and further charged with measured amounts of methylene chloride and a standard solution of diphenylsulfide. The vessel was capped with a septum and placed in a constant-temperature bath (22.4 ± 0.2 °C). A measured amount of a standard solution of $C_8H_{14}$ in methylene chloride thermostated to the same temperature was added, and the disappearance of the 1990 $cm^{-1}$ carbonyl absorption monitored on samples taken at intervals from the reaction vessel. The final concentration of the iron complex was 0.0434 M after addition of the cyclooctene solution. Three trials were run at five concentrations of $C_8H_{14}$ (10, 15, 20, 30, 40 equiv relative to complex), each in the presence of 10 equiv of added $Ph_2S$.[13] Two trials were run at four additional concentrations of $Ph_2S$ (7.5, 15, 20, 30 equiv relative to complex), each in the presence of 20 equiv of $C_8H_{14}$.

Plots of $\ln(A_t - A_\infty)$ vs t were linear for at least 3 half-lives for each reaction. $A_\infty$ was determined after 16 h. Values of $k_{obs}$ were obtained from the slopes of these plots; $k_{obs}$ values from duplicate runs were averaged[14] to prepare Figures 1 and 2.

**Identification of Iron-Containing Products of Cyclopropanation Reactions.** The observation of a high-frequency pair of carbonyl absorptions (ca. 2060 and 2030 $cm^{-1}$) for some spent reaction mixtures suggested that a cationic $[CpFe(CO)_2L]^+$ species was formed during the cyclopropanation reaction. A yellow crystalline solid precipitated from the reaction of 40 equiv of $C_8H_{14}$ with [$CpFe(CO)_2CH_2SPh_2$]$BF_4$

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[10] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press Ltd: Oxford, 1966.

[11] Identified by comparison of their $^1H$ NMR spectra with those of authentic materials. Bicyclo[6.1.0]nonane, prepared according to the procedure given by Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. *Org. React.* **1973**, *20*, 1, was provided by James G. Davidson. 1-Methylcyclooctene was obtained from Aldrich Chemical Co.

[12] Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.

[13] The actual concentrations of diphenylsulfide are less than the number of equivalents indicated by a factor of 0.424/0.434. The correct molar concentrations were used in all calculations of rate constants.

[14] The rate constants (units of $s^{-1} \times 10^4$) used in constructing Figures 1 and 2 are 0.89 ± 0.09, 1.21 ± 0.09, 1.25 ± 0.07, 1.58 ± 0.02, 1.66 ± 0.04, 2.03 ± 0.12, 2.50 ± 0.01, 2.93 ± 0.17, and 3.35 ± 0.09.

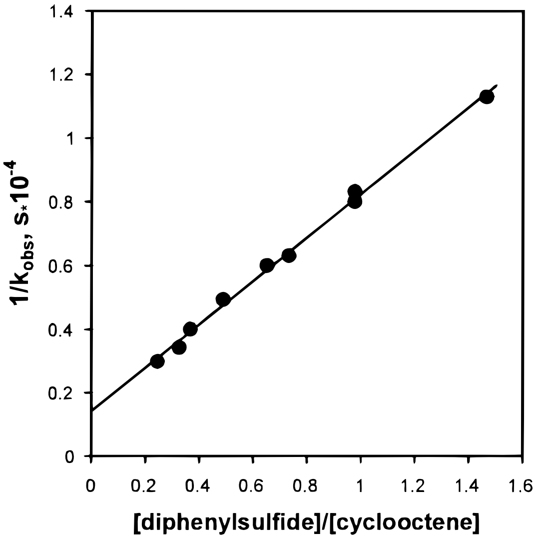

**Figure 1.** Plots of $1/k_{obs}$ vs [diphenylsulfide]/[cyclooctene] where $1/k_{obs} = k_{-1}[Ph_2S]/k_1k_2[C_8H_{14}] + 1/k_1$. The intercept is $1/k_1$, and the slope is proportional to $k_{-1}/k_2$.

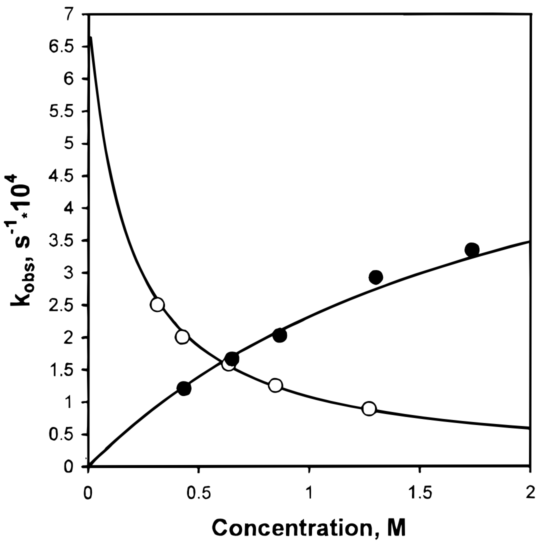

**Figure 2.** Plot of $k_{obs}$ for cyclopropanation of cyclooctene by $[Fe(\eta^5\text{-}C_5H_5)(CO)_2CH_2SPh_2]^+$ in the presence of added diphenylsulfide: (●) as a function of $[C_8H_{14}]$ in the presence of 10 equiv of added $Ph_2S$; (○) as a function of $[Ph_2S]$ in the presence of 20 equiv of $C_8H_{14}$. The value of $k_{obs}$ of 2.03 is common to both plots. The lines are curves calculated using the expression for $k_{obs}$ and the rate constants determined in Figure 1.

in the presence of 10 equiv of $Ph_2S$ after allowing the reaction mixture to stand for 24 h. This compound was filtered, washed with 2-methylbutane, and dried in vacuo. It was identified as $[CpFe(CO)_2(cyclooctene)]BF_4$ by comparison of its infrared spectrum (CO = 2060, 2035 $cm^{-1}$) and $^1H$ NMR spectra with the literature values.[15] A yellow crystalline solid precipitated from the reaction of 20 equiv of $C_8H_{14}$ with $[CpFe(CO)_2CH_2SPh_2]BF_4$, in the presence of 30 equiv of $Ph_2S$ after 48 h. This solid was filtered, washed with 2-methylbutane, and dried in vacuo. The product was formulated as $[CpFe(CO)_2(SPh_2)]BF_4$ on the basis of its $^1H$ NMR spectrum: $^1H$ NMR (acetone-$d_6$) $\delta$ 7.48−7.65 (m, 10H, $Ph_2S$), 5.80 (s, 5H, $\eta^5\text{-}C_5H_5$). The CO stretching absorptions ($CH_2Cl_2$ solution) were at 2069 and 2027 $cm^{-1}$.

## Results

**Preliminary Cyclopropanation Studies.** $[CpFe(CO)_2(SPh_2)]BF_4$ reacted with 1 equiv of $C_8H_{14}$ (ca. 0.1 M in methylene chloride) with a half-life of about 36 min to give up to 92% bicyclo[6.1.0]nonane and a small amount of 1-methylcyclooctene after suitable workup. $[CpFe(CO)_2(SPh_2)]^+$ was the major iron-containing product. Survey experiments indicated that the rate of disappearance of the iron complex increased at higher cyclooctene/complex ratios, but decreased markedly when $Ph_2S$ was added to the reaction mixture.

**Kinetics of Cyclopropanation of Cyclooctene by $[CpFe(CO)_2CH_2SPh_2]BF_4$.** The observations described above suggest the following reaction sequence:

$$[CpFe(CO)_2CH_2SPh_2]^{1+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [CpFe(CO)_2CH_2]^{1+} + SPh_2 \quad (1)$$

$$[CpFe(CO)_2CH_2]^{1+} + C_8H_{14} \xrightarrow{k_2} [CpFe(CO)_2]^{1+} + C_9H_{16} \quad (2)$$

$$[CpFe(CO)_2]^{1+} + L \xrightarrow{\text{fast}} [CpFe(CO)_2L]^{1+} \quad (3)$$

where L in the third step is either diphenylsulfide or cyclooctene. If it is assumed that reaction 2 is irreversible, that reaction 3 is fast compared to 1 and 2, and that the steady-state approximation holds for the concentration of $[CpFe(CO)_2CH_2]^{1+}$, then the rate law for the reaction is:

$$\frac{-d[\text{complex}]}{dt} = \frac{k_1k_2[\text{complex}][C_8H_{14}]}{k_{-1}[Ph_2S] + k_2[C_8H_{14}]}$$

In this expression complex refers to $[CpFe(CO)_2CH_2SPh_2]^{1+}$. Defining $k_{obs} = k_1k_2[C_8H_{14}]/(k_{-1}[Ph_2S] + k_2[C_8H_{14}])$ allows for the extraction of values for both $k_1$ and $k_{-1}/k_2$ by plotting $1/k_{obs}$ vs the ratio $[Ph_2S]/[C_8H_{14}]$ when the reaction is examined under pseudo-first-order conditions varying either olefin or sulfide while holding the other constant (both $C_8H_{14}$ and $Ph_2S$ in excess). Figure 1 shows the dependence of $1/k_{obs}$ on the ratio $[Ph_2S]/[C_8H_{14}]$. The value of $k_1$ obtained from the intercept is $7.0 \pm 0.6 \times 10^{-4}$ $s^{-1}$, and the value of $k_{-1}/k_2$ obtained from the slope is $4.8 \pm 0.5$.[16] When $k_{-1}[Ph_2S] \approx k_2[C_8H_{14}]$, the dependence of the rate on $[C_8H_{14}]$ is nonlinear and added diphenylsulfide will retard the reaction. Figure 2 shows the effect on $k_{obs}$ of increasing the concentration of either cyclooctene (in the presence of 10 equiv of diphenylsulfide) or diphenylsulfide (in the presence of 20 equiv of cyclooctene).

In the iron product $[CpFe(CO)_2L]^+$ L is either cyclooctene or $Ph_2S$.[17] $[CpFe(CO)_2(C_8H_{14})]BF_4$[15] was isolated from the reaction with 40 equiv of $C_8H_{14}$ in the presence of 10 equiv of $Ph_2S$, whereas $[CpFe(CO)_2(SPh_2)]BF_4$ was isolated from the reaction with 20 equiv

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[15] Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495.

[16] Errors in $k_1$ and $k_{-1}/k_2$ are derived from the estimated standard errors of the intercept and slope from regression analysis (SigmaPlot). The value for $k_{-1}/k_2$ is dimensionless, as it is the ratio of second-order rate constants.

[17] Helquist reports isolation of $[CpFe(CO)_2SMe_2]^+$ from spent cyclopropanation reactions involving $[CpFe(CO)_2CH_2SMe_2]^+$; see reference 1.

of $C_8H_{14}$ and 30 equiv of $Ph_2S$. Infrared spectra of reaction mixtures suggest that both of these complexes are formed in some cases, but no effort was made to establish the relative stabilities of these two complexes or to determine their relative solubilities.

**Survey of Reactivity of [CpFe(CO)$_2$CH$_2$SPh$_2$]BF$_4$ in Cyclopropanation of Olefins.** The reactivity of the iron complex was surveyed in a qualitative fashion for cyclopropanation of some other olefins besides cyclooctene. Half-lives and yields of cyclopropanation products for the olefins surveyed are given in Table 1. The reactivity pattern is similar to that observed by Helquist and co-workers for their sulfonium salts.[1] None of the olefins chosen for our studies provide information concerning the stereoselectivity of addition of the methylene to the double bond. One item of interest is the reasonable yield of the cyclopropanation product derived from 2,3-dihydropyran. Although it is not clear if dihydropyran was examined in earlier studies with other sulfonium salts, it has been reported that whereas their reactivity is high toward electron-rich olefins, the anticipated cyclopropanes were generally not observed.[1]

## Discussion

As expected, based upon Helquist's results with the $[CpFe(CO)_2CH_2S(Me)R]^+$ salts (R = Me, Ph),[1] the diphenylsulfonium analogue is more reactive toward nucleophiles than either of these salts. Although equally good yields of cyclopropanation products can be obtained with any one of the three reagents, the dimethyl derivative requires reflux temperatures,[21] whereas the diphenyl derivative reacts at room temperature. Unfortunately, as long as $[CpFe(CO)_2CH_2Cl]$ is required as an intermediate in the preparation of the diphenyl derivative, it is not likely to see much application except possibly in cyclopropanation of thermally sensitive substrates. The kinetics of the reaction of $[CpFe(CO)_2CH_2SPh_2]^+$ with cyclooctene are entirely consistent with a two-step mechanism, with reversible dissociative loss of $Ph_2S$ occurring in the first step. Most likely the other sulfonium salts react in a similar fashion. Helquist's observation that addition of $[Cu(NCCH_3)_4]^+$ increased the rate of reaction of $[CpFe(CO)_2CH_2SMe_2]^+$ with $Ph_2C{=}CH_2$[1] is most likely a result of trapping of dissociated $Me_2S$ and thus eliminating its competition for the carbene.

Assuming that it is the free iron methylene carbene that reacts with the olefin for all of the sulfonium salts, their similar reactivity pattern toward substituted olefins is predictable. The fact that these sulfonium salt reagents can be used to prepare cyclopropanes in high yields without competitive formation of the disproportionation products $[CpFe(CO)_2C_2H_4]^+$ and $[CpFe(CO)_2L]^+$, which occurs when the methylene complex is generated rapidly by other methods, is surely because the disproportionation reaction is second order.[22] Thus when the rate of formation of the methylene species is low and a suitable trapping agent is present, its concentration never builds up sufficiently for disproportionation to become a competitive process.

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(18) Adams, W.; Birke, A.; Cadiz, C.; Diaz, S.; Rodriquez, A. *J. Org. Chem.* **1978**, *43*, 1154.

(19) Casey, C. P.; Polichnowski, S. W.; Schusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.

(20) Friedrich, E. C.; Domek, J. M.; Pong, R. Y. *J. Org. Chem.* **1985**, *50*, 4640.

(21) The best solvent for synthetic applications of $[CpFe(CO)_2CH_2SMe_2]BF_4$ appears to be nitromethane; see ref 1 and also Bäckvall, J.-E.; Löfström, C.; Juntunen, S. K.; Mattson, M. *Tetrahedron Lett.* **1993**, *34*, 2007.

(22) The kinetics of disproportionation of $[CpFe(CO)_2CH_2]^+$ have not been studied. However, the disproportionation of $[CpRe(PPh_3)(NO)CH_2]^+$ is second order: Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.