^{13}C NMR ($CDCl_3$) δ 142.0 ($_1J^{H-^{13}C}$ = 189.0 Hz), 96.7 ($_1J^{H-^{13}C}$ = 161.5, $_2J^{H-^{13}C}$ = 150.0, $J^{^{13}C-^{13}C}$ = 82.8 Hz).

Vinyl-*1,2*-$^{13}C_2$ acetate (4 g) and cyclopentadiene (4.5 mL) are placed in a sealed tube and heated to 200 °C for 14 h. The contents are distilled and, in addition to recovering about half of the starting acetate, 5-norbornenyl-*2,3*-$^{13}C_2$ acetate (1.8 g) is produced, bp 82–83 °C at 17 torr: ^{13}C NMR ($CDCl_3$) δ 74.8 ($_1J^{H-^{13}C}$ = 158.5 Hz), 34.8 ($_1J^{H-^{13}C}$ = 134.5, $J^{^{13}C-^{13}C}$ = 44.1 Hz).

5-Norbornenyl-*2,3*-$^{13}C_2$ acetate is converted to 5-norbornen-*2,3*-$^{13}C_2$-2-ol by Na/methanol hydrolysis in 72% yield: ^{13}C NMR (methanol-d_1) δ 19.4 ($_1J^{H-^{13}C}$ = 132.9 Hz), 55.03 ($_1J^{H-^{13}C}$ = 148.5, $J^{^{13}C-^{13}C}$ = 43.6 Hz). 5-Norbornen-*2,3*-$^{13}C_2$-2-ol is tranformed into 5-norbornen-2-yl-*2,3*-$^{13}C_2$ chloride and nortricycl-5-yl-*2,3*-$^{13}C_2$ chloride by PPh_3/CCl_4, as previously outlined. 5-Norbornen-2-yl-*2,3*-$^{13}C_2$ chloride and nortricycl-5-yl-*2,3*-$^{13}C_2$ chloride can be separated by preparative GC with a UV-101 column at 145 °C: ^{13}C NMR ($CDCl_3$) norbornenyl chloride δ 58.4 ($_1J^{H-^{13}C}$ = 161.8 Hz), 38.2 ($_1J^{H-^{13}C}$ = 137.7, $J^{^{13}C-^{13}C}$ = 42.7 Hz), *endo/exo*-nortricyclyl chloride 30.1, 11.1; 31.5, 13.7, ($J^{^{13}C-^{13}C}$ = 39.5 Hz).

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$(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2S^+(CH_3)_2\,BF_4^-$: A Methylene Transfer Reagent for the Direct Cyclopropanation of Alkenes[1]

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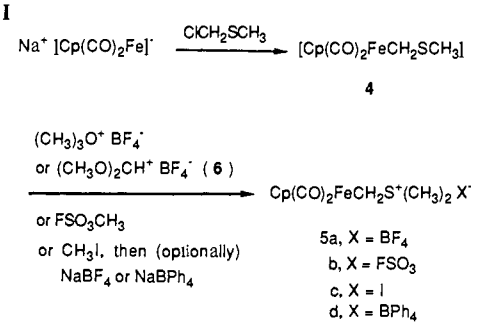
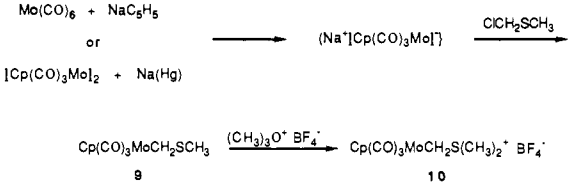
Abstract: $Cp(CO)_2FeCH_2S^+(CH_3)_2\,BF_4^-$ (**5a**, Cp = η^5-cyclopentadienyl) is readily prepared by the reaction of the ferrate $Na^+[Cp(CO)_2Fe]^-$ with chloromethyl methyl sulfide to give the alkylation product $Cp(CO)_2FeCH_2SCH_3$ (**4**) as an intermediate that need not be isolated but which is treated directly with various methylating agents (e.g. $(CH_3)_3O^+BF_4^-$, $(CH_3O)_2CH^+BF_4^-$, FSO_3CH_3, etc.) to give **5a**. This salt is an exceptionally stable organometallic reagent that has been characterized spectroscopically as well as by X-ray diffraction. Complex **5a** undergoes direct reaction with a wide range of alkenes to give cyclopropanes in a synthetically useful manner. Several aspects of this cyclopropanation procedure have been probed in order to gain a more detailed understanding of this reaction.

The cyclopropane ring system is seen as an important structural feature among many classes of naturally occurring compounds.[3] Also, because of various cleavage reactions and rearrangements in which they participate, cyclopropanes frequently serve as valuable synthetic intermediates leading to other ring systems or acyclic products. Consequently, a large number of methods have been developed for the synthesis of cyclopropanes. The vast majority of these methods may be placed in either of two broad categories: (1) addition of carbenes, carbenoids, or related species to alkenes and (2) intramolecular coupling or alkylation reactions. Certain aspects of these approaches are shared with a number of reagents that undergo nucleophilic addition to suitably activated alkenes followed by intramolecular alkylation, either with or without site equilibration of the initially formed carbanionic intermediates. Included in this description are the use of sulfonium ylides[4] among many other species.[5]

Scheme I



Scheme II



(1) Taken in part from the Ph.D. Dissertations of (a) S.B. (1979) and (b) E.J.O. (1984), State University of New York at Stony Brook.

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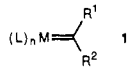
With respect to the addition of carbenes and related species, the use of diazo compounds is a classical method that is continuing to undergo further development, especially in the study of new metal catalysts to promote the reactions of these compounds.[3f,o] Also very important is the well-known Simmons–Smith[3b] reaction and its modifications.[6] However, when considering carbenes nowadays, one can hardly avoid including transition-metal carbene, or alkylidene, complexes. These compounds, having the general structure **1** (M = transition metal, L = ligand), were first studied



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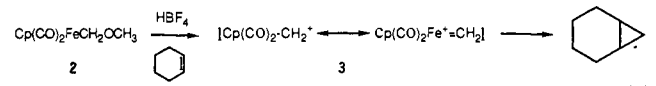
extensively by E. O. Fischer[7] and have continued to be studied very thoroughly by Fischer as well as by several others.[8] The use of carbene complexes in cyclopropanation reactions is an obvious possibility,[7b,9] and indeed, these complexes are believed to serve as intermediates in transition-metal-catalyzed reactions of diazo compounds.[3o,9j] For the most part, however, relatively few carbene complexes undergo useful cyclopropanation reactions, but they have instead been found to undergo many other types of reactions, some of which have seen beautiful applications in organic synthesis.[8]

An especially important exception to this commonly encountered lack of cyclopropanation reactivity is seen in an important class of organoiron compounds in the $CpFe(CO)_2$ series (Cp = η^5-cyclopentadienyl). The key observations, initially reported by Pettit[10] and by Green[11] approximately 20 years ago, were centered around the methoxymethyl derivative **2**. When treated with acid, **2** apparently undergoes cleavage to the cationic methylene complex **3** as evidenced, for example, by the formation of norcarane when the cleavage is done in the presence of cyclohexene (eq 1).



2 **3** (1)

Relatively little was done in this area for a number of years, but more recently, further general studies of **3** and related compounds have been reported by Brookhart,[12] Cutler,[13] Casey,[14] our group,[15] and many others.[16] Much of this work has shown that **3** is a

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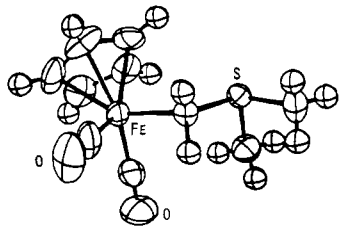

Figure 1. ORTEP drawing of **5** as determined by X-ray diffraction.[15c]

highly reactive intermediate having a very short lifetime. It has not been observed directly in solution, although Beauchamp has detected it in the gas phase with ion cyclotron resonance,[16e] and Hoffmann has done calculations to probe the bonding and conformational properties of **3**.[16i] More stable derivatives have been prepared in which (1) the two carbonyl groups are replaced by the 1,2-bis(diphenylphosphino)ethane (diphos or dppe) ligand,[12b] (2) the Cp group is replaced by the pentamethylcyclopentadienyl ligand,[16x,aa] (3) the simple methylene group is replaced, for example, by benzylidene,[12a,c] cycloheptatrienylidene,[16k,p] benzocyclobutenylidene,[16d] allylidene,[14c,15e,16h] isopropylidene,[14a,c,15d] and cyclopropylmethylidene[12g] groups, and (4) the carbene carbon bears various electron-donating substituents (e.g. alkoxy, alkylthio, etc.).[11b,12d,e,13a,b,d,14,16a,g,h,l,n,o,q,r,t-w]

Starting with this background information from earlier organometallic studies, our initial goal was to develop a cyclopropanation reagent that would be truly useful in synthetic organic chemistry. Our plan was to study compounds of the general formula $Cp(CO)_2FeCH_2Z$ that upon loss of the group Z would serve to generate (or that would at least be functionally equivalent to) the methylene complex **3** in the presence of alkenes. Ideally, these reagents should be relatively easily prepared and should be relatively stable. There are, however, a number of conceivable choices for the leaving group Z based upon functional groups containing oxygen, nitrogen, phosphorous, sulfur, selenium, etc.[17] Our first (and very fortunate) choice was to employ sulfonium derivatives of the structure $Cp(CO)_2FeCH_2SR_2^+$ in which a neutral dialkyl sulfide would serve as the leaving group. These compounds may be regarded as metal-bonded sulfonium ylides, of which many examples are known containing various transition metals.[18] In this paper, we now wish to report the details of our studies of alkene cyclopropanations using one of these iron complexes.[19]

Results and Discussion

Preparation of Reagents. Our first preparation involved a two-step pathway in which sodium cyclopentadienyldicarbonylferrate, generated in the standard manner from bis(cyclopentadienyldicarbonyliron)[20] and sodium amalgam, was alkylated with chloromethyl methyl sulfide to give the [(methylthio)methyl]iron derivative **4** in 93% yield after crystallization.[21] The isolated **4** was then subjected to alkylation with trimethyloxonium tetrafluoroborate[22] to give the desired sulfonium salt **5a** in 82% yield (Scheme I). Although this procedure is efficient, we have sought various means of streamlining the preparation of the salts **5**. We no longer actually isolate the sulfide **4**, but instead we simply withdraw the solution of **4** from the mercury remaining from the sodium amalgam, we remove inorganic salts by filtration, and then we treat the filtrate directly with the methylating agent. Any of several methylating agents may be used, the simplest being methyl iodide. However, because of subsequent reactivity considerations, the counterion in **5** must be relatively nonnucleophilic in order to obtain a reagent having good cyclopropanation ability (vide infra). Therefore, we have also studied various anion exchanges. For example, the iodide **5c** undergoes exchange with aqueous sodium tetrafluoroborate to give **5a**, and either the fluorosulfonate **5b** or the iodide **5c** undergoes exchange with aqueous sodium tetraphenylborate to give **5d**. However, our present method of choice for the methylation of intermediate **4** is to employ Borch's dimethoxycarbenium tetrafluoroborate (**6**), which is very easily generated in situ from trimethyl orthoformate and boron trifluoride etherate.[23] In this manner, the tetrafluoroborate salt **5a**, the most useful of the various salts that we have studied, is obtained directly without the need for using the less convenient trimethyloxonium reagent. Using this optimized procedure, we have prepared single batches of up to 90 g of **5a** in an 8-h period starting from bis(cyclopentadienyldicarbonyliron).

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(17) For a thorough compilation of references to complexes of this type see footnote 1 in ref 16z. See also: Barefield, E. K.; Sepelak, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 6542.

(18) For some other examples of sulfonium ylide complexes see: (a) Kilbourn, B. T.; Felix, D. *J. Chem. Soc. A* **1969**, 163. (b) Sato, T.; Higuchi, J. *Tetrahedron Lett.* **1972**, 407. (c) Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62. (d) Weleski, E. T.; Silver, J. L.; Jansson, M. D.; Burmeister, J. L. *J. Organomet. Chem.* **1975**, *102*, 365. (e) Koezuka, H.; Matsubayashi, G.; Tanaka, T. *Inorg. Chem.* **1976**, *15*, 417. (f) Bravo, P.; Fronza, G.; Ticozzi, C. *J. Organomet. Chem.* **1976**, *118*, C78. (g) Seno, M.; Tsuchiya, S. *J. Chem. Soc., Dalton Trans.* **1977**, 751. (h) Yoshida, G.; Kurosawa, H.; Okawara, R. *J. Organomet. Chem.* **1977**, *131*, 309. (i) Matsubayashi, G.; Kondo, Y.; Tanaka, T.; Nishigaki, S.; Nakatsu, K. *Chem. Lett.* **1979**, 375. (j) Nishiyama, H. *J. Organomet. Chem.* **1979**, *165*, 407. (k) Stein, J.; Fackler, J. P.; Paparizos, C.; Chen, H.-W. *J. Am. Chem. Soc.* **1981**, *103*, 2192. (l) McCormick, F. B.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, *218*, C57. (m) Puddephatt, R. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, pp 797–798. (n) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. *Ibid.* Vol. 6, pp 299–303. (o) Hartley, F. R. *Ibid.* Vol. 6, pp 511–513. (p) Weber, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 516. (q) Fischer, H.; Weber, L. *Chem. Ber.* **1984**, *117*, 3340. (r) Touchard, D.; Dixneuf, P. H.; Adams, R. D.; Segmüller, B. E. *Organometallics* **1984**, *3*, 640. (s) Davidson, J. G.; Barefield, E. K.; Van Derveer, D. G. *Ibid.* **1985**, *4*, 1178. (t) Weber, L.; Wewers, D.; Lücke, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 968. (u) Roper, W. R. *J. Organomet. Chem.* **1986**, *300*, 167. (v) McCormick, F. B.; Gleason, W. B.; Zhao, X.; Heah, P. C.; Gladysz, J. A. *Organometallics* **1986**, *5*, 1778. (w) Weber, L.; Lücke, E. *Organometallics* **1986**, *5*, 2114. For another review, see: Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1.

(19) For a preliminary communication of this work see ref 15a.

(20) $[Cp(CO)_2Fe]_2$ is commercially available (Alfa; Aldrich), but we also prepare it very straightforwardly from iron pentacarbonyl and cyclopentadiene dimer according to the procedure described in: King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 110. However, rather than the 38% yield reported therein, we routinely obtain yields of 80–90%.

(21) We follow the procedure reported in: King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1965**, *4*, 486. These earlier workers reported a yield of **4** of 25%.

(22) (a) Meerwein, H. *Organic Syntheses*; Wiley: New York, 1973; Coll. Vol. V, p 1096. (b) Curphey, T. J. *Org. Synth.* **1971**, *51*, 142.

(23) Borch, R. F. *J. Org. Chem.* **1969**, *34*, 627.

(24) Creary, X.; Mehrsheikh-Mohammadi, M., University of Notre Dame, personal communication, 1986.

(25) Curtin, D. Y.; Gruen, H.; Shoulders, B. A. *Chem. Ind.* (*London*) **1958**, 1205.

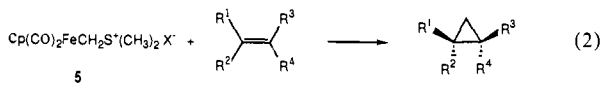
(26) Iyer, R. S. Ph.D. Dissertation, State University of New York at Stony Brook, 1985.

(27) Wender, P. A.; Eck, S. L. *Tetrahedron Lett.* **1982**, *23*, 1871.

The physical properties and unique stability of the salts **5** are deserving of separate discussion before we describe their reactions. As initially obtained from the procedures above, these salts are in the form of yellow powders that are quite acceptably pure for subsequent reactions. However, very simple recrystallization from various solvents (e.g. nitromethane) gives a high recovery of **5** as large, beautiful, amber-colored crystals. Most remarkable, however, is the exceptionally high stability of **5**, especially in comparison with other, sometimes notoriously unstable organometallic reagents. We have found that **5** is not only air-stable, but it is also stable to water. The best indication of this stability is that the anion exchanges mentioned above are done in flasks open to the air and using water as the solvent at 90 °C! We store **5** as an ordinary laboratory reagent in regular screw-cap or stoppered bottles exposed to the air. No noticeable deterioration has been seen in a sample of **5a** stored in this fashion for 4 years and occasionally checked by ^{1}H NMR and by using it in standard cyclopropanation reactions. Furthermore, the reactions of **5** may be performed in flasks open to the air.

Characterization. The sulfonium salts **5** have been characterized spectroscopically by a combination of IR, ^{1}H NMR, ^{13}C NMR, and MS. Of special interest is that the fast atom bombardment (FAB) mass spectrum shows, among other ions, peaks of masses corresponding to the cation of **5** *and* the methylene complex **3**. This observation parallels Beauchamp's use of ion cyclotron resonance to study the sequence shown in eq 1.[16e] The structure of **5** has been determined most definitively by X-ray diffraction as described in detail earlier (Figure 1).[15c]

Reactions. In preliminary experiments, we found that sulfonium salts **5** do indeed undergo direct reaction with alkenes to give cyclopropanes (eq 2). We then proceeded to study the effects



(2)

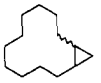
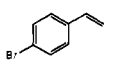
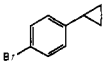
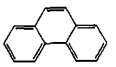
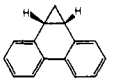
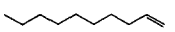
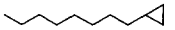
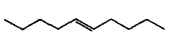
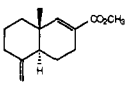
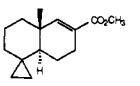
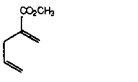
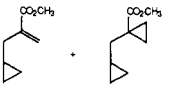
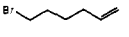
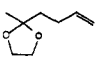
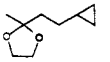
of various parameters. With *cis*-cyclooctene (1 mmol) as a test case, the following salts (1 mmol) in refluxing 1,4-dioxane (0.5 mL, 102 °C) give the indicated percent conversion to bicyclo[6.1.0]nonane over a 12-h period: **5a** (X = BF_4), 95%; **5b** (X = FSO_3), 72%; **5c** (X = I), 38%; **5d** (X = BPh_4), 0%. Very little (<10%) or no conversion of *cis*-cyclooctene occurs when methylene chloride (40 °C), THF (65 °C), 1,2-dimethoxyethane (85 °C), hexamethylphosphoric triamide (95 °C), or acetone (56 °C) is used as the reaction solvent at the indicated temperature, modest conversion (15–35%) occurs in 1,2-dichloroethane (93 °C) and dimethyl sulfoxide (120 °C), and high conversion (>70%) occurs in 1,4-dioxane (102 °C), dimethylformamide (120 °C), and ethanol (78 °C). Rather late in our investigations, we observed the highest conversion (95–100%) in nitromethane (104 °C). Our optimized stoichiometry and concentration is 1 mmol of alkene and 2 mmol of sulfonium salt in 0.5 mL of solvent. A typical reaction time is 12 h in most solvents but only 3 h in nitromethane. We have also found that modest conversion occurs (40–50%) when the reaction mixtures, under nominally ambient conditions, are placed in a Rayonet Srinivasan–Griffin photochemical reactor (350-nm lamps) for 12 h or in a laboratory ultrasonic cleaning bath for 22 h. Of course, we cannot easily distinguish photochemical or sonication effects from simple thermal effects.

Product isolation is generally quite simple. A nonpolar solvent such as pentane is added to the reaction mixture at the completion of the reaction; the metal-containing species thus precipitate from the mixture, and the cyclopropane product remains in the solvent phase. Subsequent filtration and removal of solvent from the filtrate provide the cyclopropane that may then be purified as desired by the usual procedures.

We have summarized the reactions of **5a** with several alkenes in Table I. The yields of cyclopropanes are modest to high for a wide range of alkene substrates. The general pattern that has emerged is that the reaction proceeds most reliably for mono- and disubstituted alkenes and that aryl-substituted alkenes are generally quite good substrates (see especially entries 3–5). Also, the reaction proceeds with very high stereospecificity in that the configurations of the starting alkenes are retained in the cyclopropane products (see entries 9 and 10).

Various limitations in this reaction have become apparent. The salt **5a** is sensitive to steric effects in that trisubstituted alkenes

Table I. Cyclopropanation of Alkenes with $Cp(CO)_2FeCH_2S^+(CH_3)_2BF_4^-$ (**5a**; eq 3)[a]

Entry	Alkene	Cyclopropane(s)	Conversion of Alkene (%)[b]	Yield of Cyclopropane (%)[c]
1			100	92, 76[d]
2			100	90[e]
3			100	99, 88[d]
4			100	>90[d,f,g]
5			100	64
6			62	64[h]
7			38	82
8			81	70[d]
9			59	87
10			49	67
11			90	26
12			--	--[i]
13			100	86[d,j]
14			99	62 + 5
15			100	60[k]
16			100	55
17			100	22

[a] Unless otherwise indicated, these reactions were run under a standard set of conditions employing 2 molar equiv of **5a** and a 2 M solution of alkene in dioxane at reflux for 12 h. [b] Conversion of alkene indicates the amount of alkene consumed in the reaction as determined by measuring the amount of unreacted alkene by GLPC using an internal standard. [c] Unless otherwise specified, the yields of cyclopropanes were determined by GLPC using an internal standard and a sample of pure, isolated product for calibration and are corrected for the amount of unreacted alkene. [d] Yield of pure, isolated product. [e] Both the starting cyclododecene and the product were ca. 1:1 mixtures of cis and trans isomers. [f] The reaction solvent was nitromethane. [g] Reference 24. [h] The stereochemistry of the product was determined by ^{1}H NMR as reported in ref 25. [i] Reference 15f and 26. This reaction was performed primarily for the purpose of a structure proof; the yield of the product was not determined. [j] Reference 27. These workers reported the use of 3 molar equiv of **5a**. [k] $PhSCH_3$ comprised the remaining 40% of the product mixture.

undergo low conversion to cyclopropanes, cis-disubstituted alkenes are better substrates than their trans isomers, and norbornene fails to react with **5a**. Cyclohexenes are surprisingly troublesome substrates; cyclohexene itself and 1-methylcyclohexene are both nearly completely consumed under our standard conditions, but each of them gives a complex mixture of products containing two compounds corresponding in molecular weight (MS) to the transfer of one methylene group and two products resulting from transfer of two methylene groups. In the case of 1-methylcyclohexene (entry 11), two products that we have actually identified are the expected 1-methylnorcarane (26%) and, surprisingly, 1,6-dimethylnorcarane. Attempts to obtain more synthetically useful results under various conditions have not been successful, and these product mixtures have not been characterized further. Substrates containing exocyclic double bonds (e.g. 6-methylenenorbornene, methylenecycloheptane) also give complex mixtures. 4-Vinylcyclohexene gives a mixture of at least four cyclopropane-containing products due to reaction of both double bonds of the substrate. Interestingly, our ethylidene transfer reagent, $Cp(CO)_2FeCH(SPh)CH_3$, reacts cleanly with only the monosubstituted double bond of 4-vinylcyclohexene.[15g] Rearrangements of cyclopropane products may also arise as a complication in some cases. One example is the case of phenanthrene (entry 7) wherein the indicated cyclopropane is accompanied by ca. 10% of 9-methylphenanthrene, which is known to arise from rearrangement of the cyclopropane.[28]

Functionalized alkenes give widely differing results. Useful reactions occur with alkenes containing halide (entries 4 and 16), ester (entries 13 and 14), and thioether groups (entry 15), although the last of these groups undergoes partial cleavage, apparently due to an equilibration of sulfonium salts that leads to formation of thioanisole as a side product. A ketal-containing substrate gives only a low yield of cyclopropane (entry 17). Substrates that fail to give cyclopropanes in detectable quantities include all unsaturated alcohols that we have studied, 5-hexen-2-one, and the allylic compounds 2-cyclohexenol, 3-bromocyclohexene, and 3-(phenylthio)cyclohexene. The latter substrate, in contrast to the case of allyl phenyl sulfide (entry 15), gives thioanisole as the only isolated product.

Not surprisingly, **5a** is not a useful reagent for the cyclopropanation of electron-deficient alkenes as indicated by the observations that simple alkene moieties undergo chemoselective cyclopropanation in the presence of α,β-unsaturated esters (entries 13 and 14), ethyl crotonate gives only 10–15% yield of cyclopropane, and α,β-unsaturated ketones fail to undergo cyclopropanation to any detectable extent. On the other hand, especially electron-rich alkenes such as enamines, enol ethers, and vinyl sulfides show very high reactivity toward **5a**, but if cyclopropanation actually occurs in these cases ((phenylthio)cyclopropane has been isolated but in only ca. 10% yield), the resulting heterosubstituted cyclopropanes are apparently very reactive toward the electrophilic organometallic byproducts (i.e. $Cp(CO)_2Fe(L)^+$ species) and undergo further, rapid transformations to give product mixtures that we have not been able to characterize.

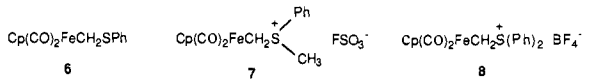
Among other methods for alkene cyclopropanation, comparison of our reagent with the Simmons–Smith reaction[3b,6] is most appropriate. For the simpler types of alkenes shown in Table I, the two methods give comparable yields of cyclopropanes, although the Simmons–Smith reaction is also useful with cyclohexenes in contrast to our findings discussed above. However, for some aryl-substituted alkenes, the Simmons–Smith reaction gives lower yields apparently due to alkene polymerization. We also wish to note that in connection with other work,[15f] we were unsuccessful in employing the Simmons–Smith reaction with the octalin shown in entry 12. A major advantage of the Simmons–Smith reaction, however, is its usefulness with many functionalized alkenes that do not serve as good substrates for **5a**. Examples include unsaturated alcohols, some α,β-unsaturated carbonyl compounds, enol derivatives, and, to a certain extent, enamines.[3b] Exceptions, however, include certain sulfur-containing compounds; Simmons–Smith reactions fail, for example, in cases of vinylic and allylic sulfides, the latter undergoing rearrangement to homoallylic sulfides rather than undergoing cyclopropanation (see, however, our entry 15). Furthermore, the Simmons–Smith reaction fails if a simple organic sulfide is added to a reaction mixture containing an alkene that normally undergoes cyclopropanation successfully. Presumably, carbenoid transfer to sulfur occurs, thus resulting in generation of a sulfonium ylide.[29]

With respect to the use of 2 molar equiv of **5a** under our standard conditions, we note that the Simmons–Smith reaction is often performed with a several-fold excess of zinc reagent.[3b] Also, the very commonly employed cyclopropanation reaction of diazo compounds is often done with large excesses of alkenes.[30]

The greatest advantage of employing **5a** is clearly that once the reagent is on hand, it is extremely convenient to use because of its stability and long shelf-life as discussed above. In contrast to Simmons–Smith reagents, there is no need to activate **5a** in some manner before it is used, but rather it is used directly. Also, there is no need to handle hazardous or sensitive materials such as diazomethane (or diethylzinc, as in a modification of the Simmons–Smith reaction[6]). The reactions of **5a** are therefore very easy to perform, and the isolation of products is very straightforward.

Modification of Reagents. The reagent **5a** is employed under conditions that are not altogether harsh, but we nonetheless chose to study modifications of our reagents that would permit the use of milder conditions. One approach is to employ thiophilic metal salts that may promote loss of dimethyl sulfide from **5a**. Indeed, when equimolar amounts of **5a**, 1,1-diphenylethylene, and $Cu(CH_3CN)_4^+BF_4^-$ are allowed to react in nitromethane at 25 °C, 50% conversion to 1,1-diphenylcyclopropane occurs within 2 h, but no further increase of product formation is seen after 20 h.

We have also directed efforts toward modification of the sulfonium groups. By a procedure analogous to Scheme I, the [(phenylthio)methyl]iron derivative **6** is obtained as a golden yellow, crystalline solid that may be handled in the air for at least an hour and that is stable for at least 3 years when stored at 25 °C under nitrogen. Alkylation of **6** with trimethyloxonium tetrafluoroborate affords the sulfonium salt **7**, obtained as a solid that is stable for at least 16 h at 25 °C. The crude salt reacts with *cis*-cyclooctene in methylene chloride at 25 °C to give a 20–30% yield of the corresponding cyclopropane within 12 h. After the completion of this work,[1b] Barefield reported a convenient route to not only the tetrafluoroborate derivative of **7**, but also, and more interestingly, the diphenylsulfonium derivative **8**, which is not available by the routes that we have employed for **5** and **7**. As expected, Barefield's compound **8** is even more reactive than our reagents as indicated by the use of **8** to convert *cis*-cyclooctene to the cyclopropane in 85% yield in only 3 h at 22 °C.[16z]



6 **7** **8**

We have also been interested in the possibility of employing metals[18] other than iron in our reagents. A tantalizing suggestion from the original work of Pettit[10] is to employ molybdenum, a lead that has also been pursued by Brookhart[31] and by Cutler.[13d]

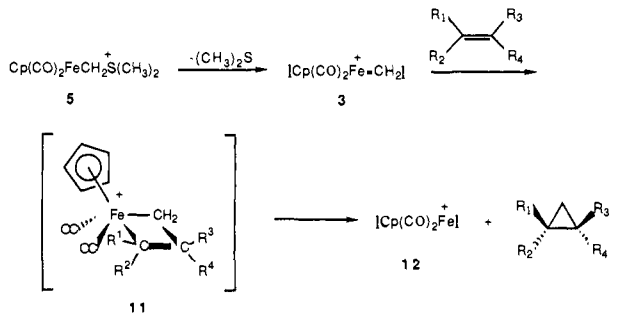
(28) Müller, E.; Kessler, H.; Suhr, H. *Tetrahedron Lett.* **1965**, 423. We have not ruled out the possibility, however, that the 9-methylphenanthrene arises from an electrophilic aromatic substitution pathway not involving the cyclopropane as an intermediate.

(29) Other workers have observed that Simmons–Smith reactions fail for allylic and vinylic sulfides. Furthermore, the Simmons–Smith reaction fails if a simple organic sulfide is added to a reaction mixture containing an alkene that normally undergoes cyclopropanation successfully. Presumably, carbenoid transfer to sulfur occurs, thus resulting in generation of a sulfonium ylide. See: (a) Kosarych, Z.; Cohen, T. *Tetrahedron Lett.* **1982**, *23*, 3019. (b) Liebowitz, S. M.; Johnson, H. J. *Synth. Commun.* **1986**, *16*, 1255.

(30) For a discussion of this problem and its solution based upon slow addition of diazo compounds see: Doyle, M. P.; van Leusen, D.; Tamblyn, W. H. *Synthesis* **1981**, 787. See also ref 3o and 9m.

(31) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760.

Scheme III



Again in analogy with our preparation of the iron reagents **5** (Scheme I), we have prepared the [(methylthio)methyl]molybdenum derivative **9** and the dimethylsulfonium salt **10** (Scheme II). However, **10** appears to be much less stable than the iron reagents **5**, and furthermore, **10** has not proven to be a useful cyclopropanation reagent in that only very low conversions occur with 1,1-diphenylethylene and *cis*-cyclooctene as test cases. Barefield has reported similar findings for Ni-containing analogues of our reagent.[18s]

Other Observations. We have not done mechanistic studies of the reaction of our iron-containing sulfonium salts with alkenes, but we can at least discuss some possible reaction pathways and some further observations that may bear upon these pathways. Keeping in mind the earlier work of Casey,[9b,14c] Brookhart,[12c-f] and Doyle[9j] among others[8] concerned with cyclopropane-forming reactions of various metal carbene species, we can first consider a pathway involving unimolecular dissociation of the sulfonium salt **5** to give the methylene complex **3** (Scheme III). We then show reaction of **3** with the alkene substrate to generate the metallacyclobutane **11** which undergoes fragmentation to the cyclopropane product and the unstable, coordinatively unsaturated cyclopentadienyldicarbonyliron cation (**12**), which would undergo disproportionation or trapping by an available ligand. We realize, however, that the metallacyclobutane is not a mandatory intermedate.

In order to avoid the intermediacy of the highly reactive methylene complex **3**, we could consider an alternative pathway involving direct, bimolecular reaction of the alkene with the sulfonium salt **5**. However, because of the low nucleophilicity of simple alkenes, direct displacement of dimethyl sulfide from the methylene center by the incoming alkene would appear to be difficult. Also, because of the coordinative saturation of iron and the low thermal lability of the carbonyl ligands, interaction of the alkene with the iron center of **5** is not expected, unless cyclopentadienyl slippage were to occur.[32] Many variations of these pathways may be envisioned, including metal-assisted loss of dimethyl sulfide, possibly involving a second metal center as suggested by our analysis of reaction byproducts (vide infra) and by the effect of copper(I) (vide supra).

The bulk of the precedents in the literature favor the pathway in Scheme III. Barefield has reported that $Cp(CO)_2FeCH_2S^+Ph_2\,BF_4^-$ undergoes alkene cyclopropanation by a dissociative mechanism,[16z] Gladysz has reported that $Cp(NO)(PPh_3)ReCH_2S^+(CH_3)_2\,PF_6^-$ undergoes reversible dissociation of dimethyl sulfide,[18l,v] and Fischer and Weber have reported irreversible dissociation of dimethyl sulfoxide from $(CO)_5CrCH_2S(O)(CH_3)_2$.[18q] Related dissociations have also been proposed in other systems by Weber,[18w] Roper,[33] and Dixneuf.[18r]

Among our observations is that the methylene transfer reagent **5a** undergoes loss of dimethyl sulfide under conditions of FAB mass spectrometry (vide supra) to give a peak corresponding to the methylene complex **3**. In solution, **5a** undergoes exchange reactions with dialkyl sulfides to give new sulfonium salts **13** (eq 3). Similar exchange reactions are also observed under cyclo-

$$\underset{\mathbf{5a}}{Cp(CO)_2FeCH_2S^+(CH_3)_2\,BF_4^-} + CH_3CH_2SR \longrightarrow \underset{\mathbf{13}\ (R = CH_3, CH_2CH_3)}{Cp(CO)_2FeCH_2S^+(R)CH_2CH_3\,BF_4^-} \quad (3)$$

propanation conditions. These results are closely akin to Gladysz's study of related rhenium compounds (see preceding paragraph)[18l,v] and to Cutler's finding that the methylene complex **3**, when generated by independent means, may be trapped by dimethyl sulfide to give our sulfonium derivative.[13d]

Some other observations are somewhat more difficult to rationalize in the context of a simple unimolecular dissociation mechanism. First of all, in cases in which cyclopropanations have failed to go to completion after extended reaction times, we have recovered both unreacted sulfonium salt **5a** and unreacted alkene substrate. Why unreacted **5a** should be recovered from reactions with some alkenes but not with others is not clear. The next point is that when the methylene complex **3** has been formed at low temperature (−80 °C) by other means by other workers, very rapid disproportionation has been observed to give $Cp(CO)_2Fe(CH_2{=}CH_2)^+BF_4^-$ and $Cp(CO)_2FeCH_3$.[10,13d] However, we do not observe these products, at least not in any significant quantities, despite the fact that if the dissociative mechanism were operative, the methylene complex **3** would be generated at much higher temperature (ca. +100 °C) under our typical cyclopropanation conditions. One might therefore expect rapid disproportionation to be competitive with our cyclopropanation reaction, unless, of course, the low concentration of **3** that may be present at any given time leads to a very slow rate of bimolecular disproportionation.[34] Rather than disproportionation products being observed under our reaction conditions, the principal iron-containing byproduct is the dimethyl sulfide complex $Cp(CO)_2Fe[S(CH_3)_2]^+BF_4^-$,[15d,35] which we isolate in approximately 50% yield after recrystallization, although the actual yield as indicated by NMR examination of our reaction mixtures appears to be much higher. Clearly, dimethyl sulfide, despite its high volatility under our reaction conditions, is not serving simply as a leaving group that is immediately lost from the reaction system, and therefore, the possibility arises of metal-assisted loss of dimethyl sulfide from **5a** (vide supra). We also note that, as in the work of others with carbene complexes of the $Cp(CO)_2Fe$ series, we do not observe alkene metathesis products.

There are obviously many unanswered questions pertaining to the actual pathway(s) of our cyclopropanation reactions. Detailed mechanistic studies, based most likely upon kinetic and spectro-

(32) For leading references pertaining to cyclopentadienyl slippage and related coordination changes, see: (a) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657. (b) Calderon, J. L.; Cotton, F. A.; Legzdins, P. *Ibid.* **1969**, *91*, 2528. (c) Hart-Davis, A. J.; White, C.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 441. (d) Cramer, R.; Seiwell, L. P. *J. Organomet. Chem.* **1975**, *92*, 245. (e) Kowala, C.; Wunderlich, J. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 820. (f) Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Friedrich, P.; Bejenke, V.; Neugebauer, D. *J. Organomet. Chem.* **1978**, *145*, 329. (g) Nesmeyanov, A. N.; Ustynyuk, N. A.; Makarova, L. G.; Andrianov, V. G.; Struchkov, Yu. T.; Andrae, S.; Ustynyuk, Yu. A.; Malyugina, S. G. *Ibid.* **1978**, *159*, 189. (h) Honan, M. B.; Atwood, J. L.; Bernal, I.; Herrmann, W. A. *Ibid.* **1979**, *179*, 403. (i) Werner, H.; Kühn, A.; Burschka, C. *Chem. Ber.* **1980**, *113*, 2291. (j) Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* **1980**, *102*, 6154. (k) Goel, A. B.; Goel, S.; VanDerVeer, D.; Clark, H. C. *Inorg. Chim. Acta* **1981**, *53*, L117. (l) Nakasuji, K.; Yamaguchi, M.; Murata, I.; Tatsumi, K.; Nakamura, A. *Organometallics* **1984**, *3*, 1257. (m) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 1241. (n) Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Dalton Trans.* **1985**, 1365. (o) Yang, G. K.; Bergman, R. G. *Organometallics* **1985**, *4*, 129. (p) Casey, C. P.; O'Connor, J. M. *Ibid.* **1985**, *4*, 384. (q) Faller, J. W.; Crabtree, R. H.; Habib, A. *Ibid.* **1985**, *4*, 929. (r) Merola, J. S.; Kacmarcik, R. T.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 329. (s) Kowaleski, R. M.; Rheingold, A. L.; Trogler, W. C.; Basolo, F. *Ibid.* **1986**, *108*, 2460. (t) Boese, R.; Tolman, W. B.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 582. (u) Belmont, J. A.; Wrighton, M. S. *Ibid.* **1986**, *5*, 1421. For a review, see: O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

(33) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1983**, *244*, C53.

(34) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811. An alternative explanation for the absence of these disproportionation products in our reactions is that in the earlier work (ref 10, 13d), formation of at least $Cp(CO)_2FeCH_3$ is due to reaction of the methylene complex $Cp(CO)_2Fe^+{=}CH_2$ (**3**) with the remaining precursor $Cp(CO)_2FeCH_2OCH_3$ (**2**) or $Cp(CO)_2FeCH_2Cl$ whereas our supposed precursors $Cp(CO)_2FeCH_2S^+(CH_3)_2X^-$ (**5**) may not be amenable to the corresponding reaction with the methylene complex **3**.

(35) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1965**, *4*, 482.

scopic measurements, are clearly needed in this area.

Conclusion

We have developed the sulfonium salts $Cp(CO)_2FeCH_2S^+(CH_3)_2X^-$ (**5**) as easily prepared, unusually stable organometallic reagents for the direct, high-yield cyclopropanation of alkenes. The utility of these reagents is at least comparable in many respects to other procedures such as the Simmons–Smith reaction, but we find the handling and use of **5** to be much more convenient than the earlier procedures. We hope that our findings will stimulate further mechanistic work with these compounds.

Experimental Section

General Procedures and Materials. All reactions involving air- and moisture-sensitive compounds were performed under a nitrogen atmosphere by using double manifold techniques in flame-dried glassware. Solutions were transferred with either hypodermic syringes or cannulas (stainless steel, double-ended needles).

The air-free, anhydrous solvents used in this work were freshly distilled under nitrogen from dark blue or purple solutions of sodium benzophenone radical anion or dianion, respectively, in the cases of tetrahydrofuran, diethyl ether, benzene, and 1,4-dioxane. Pentane was distilled from sodium, and methylene chloride and nitromethane were distilled from phosphorus pentoxide. Trimethyloxonium[22b] and dimethoxycarbenium[23] tetrafluoroborate were prepared according to published procedures. Most commercially obtained reagents were distilled or recrystallized prior to use, with the exception of iron pentacarbonyl, molybdenum hexacarbonyl, and sodium. All alkenes used as substrates in cyclopropanation reactions were commercially available unless otherwise specified. Organolithium and organomagnesium reagents were stored under nitrogen and titrated prior to use.[36]

Infrared spectra were obtained with a Pye-Unicam Model SP-1000 spectrophotometer as KBr wafers or in solution cells and were calibrated with a polystyrene standard. The ^1H NMR spectra were recorded at 80 MHz with a Varian HFT-80 or at 300 MHz with a Nicolet NT-300 spectrometer. The ^{13}C NMR spectra were recorded at 75 MHz on the Nicolet NT-300. The chemical shifts are reported in parts per million downfield (δ) from internal tetramethylsilane. Multiplicities of carbon peaks were determined by using the attached proton test when necessary. Mass spectra were recorded with Hewlett-Packard Model 5982A and AEI Model MS-30 mass spectrometers using electron-impact ionization at 70 eV. Analytical GLPC was performed with a Hewlett-Packard Model 5911 or a Varian Aerograph Series 1400 chromatograph equipped with a flame ionization detector, a linear temperature programmer, a Hewlett-Packard Model 3380A electronic reporting integrator, and a 6-ft $\times$ $^1/_8$-in. 5% OV-1 column. Product yields determined by GLPC were measured by using internal standards calibrated against pure samples of products isolated by preparative GLPC. Whenever indicated, the product yields are corrected for the amount of unreacted starting material. The percent conversions indicated in our tabulation of reaction data are based upon the amount of recovered starting materials (measured by GLPC) according to the following formula: percent conversion = (amount of starting alkene consumed/initial amount of starting material) $\times$ 100%. Preparative GLPC was performed with a Varian Aerograph Model 900 chromatograph using a 6-ft $\times$ $^1/_2$-in. 5% OV-1 column. Separations involving the use of medium-pressure liquid chromatography were performed by the flash chromatography procedure of Still[37] or, in the cases of air-sensitive materials, by the modified flash chromatography procedure of Kremer.[38]

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and are reported only when they agree with the calculated values within $\pm$0.3%. In all other required cases, the homogeneity of compounds was demonstrated by GLPC, and molecular formulas were determined by high-resolution mass spectrometry.

(η^2-Cyclopentadienyl)dicarbonyl[(dimethylsulfonio)methyl]iron Tetrafluoroborate (5a). The first stage of this preparation should be done behind a safety shield, and the apparatus should be placed over an appropriate tray to contain any mercury spills. Mercury (1300 g) was added in ca. 5-mL portions from an addition funnel to a 2-L round-bottom flask containing freshly pressed sodium wire or ribbon (13 g, 0.56 mol) and equipped with a large magnetic stirring bar and a three-way stopcock connected to a nitrogen source and a pressure-relief mercury bubbler. After the initial, somewhat violent formation of the amalgam (*Caution*: sudden pressure and temperature increase in the apparatus), and after the reaction flask cooled somewhat, the rest of the mercury was added rapidly. Tetrahydrofuran (800 mL) was added to the flask followed by solid bis[(η^5-cyclopentadienyl)dicarbonyliron][20] (80.0 g, 0.23 mol), and the mixture was stirred at 25 °C for 3 h. The flask was then cooled in an ice-water bath, and chloromethyl methyl sulfide (38 mL, 0.45 mol) was added dropwise over 15 min. After the addition was complete, the flask was removed from the bath, methylene chloride (500 mL) was added, stirring was stopped, the contents of the flask were allowed to settle for 1 h, and the resulting uppermost phase consisting mainly of a dark yellow-brown solution was transferred with a cannula to a Schlenk filter tube containing a layer of sand above a layer of neutral alumina (ca. 100 g). Slight vacuum was applied to a receiver flask attached to the filter tube, and after the filtration was complete, as much of the next phase (a solution floating above the mercury in the original reaction flask and containing suspended solid) as possible was transferred to the filter tube and was filtered. After this filtration was complete, additional methylene chloride (ca. 100 mL) was passed through the filtration apparatus. The combined filtrates contained the intermediate [(methylthio)methyl]iron derivative **4**. For the present preparation of **5a**, there is no need to isolate this compound, but optional evaporation of the solvent and recrystallization by the published procedure gives a 93% yield of **4**.[21]

During the 1–2 h required for the above filtration procedure, dimethoxycarbenium tetrafluoroborate[23] was generated separately by adding a 25 °C solution of boron trifluoride etherate (118 mL, 0.96 mol) and methylene chloride (100 mL) over 5 min to a 500-mL flask containing a magnetic stirring bar and trimethyl orthoformate (94 mL, 0.86 mol) at −30 °C. The mixture was warmed to 0 °C, stirred for 15 min, and recooled to −30 °C. The liquid phase was removed with a cannula, the white solid was washed at −30 °C with two 25-mL portions of methylene chloride, additional methylene chloride (50 mL) was added, and the mixture was warmed to 25 °C. The salt melted at ca. −20 °C, but it did not dissolve completely.

The mixture was stirred vigorously to suspend the salt while the mixture was added over 5 min with a cannula to the flask containing the filtered solution of **4** at 25 °C under nitrogen. The mixture was stirred for 2 h after which the resulting yellow solid was isolated by ordinary suction filtration in the air using a large Buchner funnel followed by washing with several small portions of cold (ca. 0 °C) methylene chloride (300 mL total). The solid was dried under vacuum at 25 °C, leaving 85 g (55% overall) of **5a** as a yellow powder. Although this solid was of sufficient purity for further use, it could be recrystallized by dissolution in nitromethane at 25 °C in the air and by cooling the solution slowly to −70 °C. Filtration afforded a high recovery (ca. 90%) of **5a** as large amber-colored crystals: mp 129–130 °C; decomp pt ca. 170 °C; IR (KBr) 3120, 3035, 2040, 1955, 1417, 1328, 1280, 1055 (br), 852 cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.34 (s, C_5H_5), 3.00 (s, $S(CH_3)_2$), 2.72 (s, $FeCH_2S$); ^{13}C NMR (CD_3NO_2) 215.56 (*C*O), 87.88 (C_5H_5), 31.20 ($S(CH_3)_2$), 13.35 ppm ($FeCH_2S$).

(η^5-Cyclopentadienyl)dicarbonyl[(dimethylsulfonio)methyl]iron Fluorosulfonate (5b). The procedure for **5a** was followed except for the replacement of dimethoxycarbenium tetrafluoroborate by methyl fluorosulfonate (1.0 molar equiv). Isolation of the final product by suction filtration afforded a 58% overall yield of **5b** as small yellow plates: mp 110–116 °C; ^1H NMR (acetone-d_6) δ 5.37 (s, C_5H_5), 2.99 (s, $S(CH_3)_2$), 2.73 (s, $FeCH_2S$). Simple recrystallization from acetone in the air gave material that was used in our earlier X-ray structure determination.[15c]

(η^5-Cyclopentadienyl)dicarbonyl[(dimethylsulfonio)methyl]iron Iodide (5c). The procedure for **5a** was followed except for the replacement of dimethoxycarbenium tetrafluoroborate by methyl iodide (1.0 molar equiv). Isolation of the final product by suction filtration gave a 59% overall yield of **5c** as pale yellow flakes: IR (KBr) 3080, 2985, 2920, 2030, 1940, 1417, 1385, 1322, 856 cm^{-1}; ^1H NMR (acetone-d_6) δ 5.46 (s, C_5H_5), 3.10 (s, $S(CH_3)_2$), 2.91 (s, $FeCH_2S$).

Anion Exchange of the Iodide 5c To Give (η^5-Cyclopentadienyl)dicarbonyl[(dimethylsulfonio)methyl]iron Tetrafluoroborate (5a). Into a 500-mL round-bottom flask were placed water (75 mL) and **5c** (8.0 g, 21 mmol). The mixture was heated to 90 °C in the air, and a hot filtration was performed to remove insoluble impurities. The filtrate was maintained at 90 °C while a concentrated aqueous solution (75 mL) of sodium tetrafluoroborate was added quickly. Amber-colored crystals began to form immediately. The mixture was cooled slowly to 25 °C and was placed in a −10 °C freezer for 1 h. The mixture was then subjected to suction filtration with a Buchner funnel, and the solid was dried first in the air and then under vacuum at 25 °C to give 5.50 g (77%) of **5a** as amber-colored plates. The IR and ^1H NMR spectra were identical with those obtained for **5a** prepared according to the procedure above.

Anion Exchange of the Iodide 5c To Give (η^5-Cyclopentadienyl)dicarbonyl[(dimethylsulfonio)methyl]iron Tetraphenylborate (5d). The

(36) (a) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165. (b) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.
(37) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(38) Kremer, K. A. M.; Helquist, P. *Organometallics* **1984**, *3*, 1743.

preceding procedure was employed but with sodium tetraphenylborate in place of sodium tetrafluoroborate. Obtained was a 44% yield of **5d** as a pale yellow solid: mp 164.5–165.5 °C; ^{1}H NMR (acetone-d_6) δ 7.35–7.63 and 6.85–7.27 (m, B(C_6H_5)$_4$), 5.33 (s, C_5H_5), 2.95 (s, S(CH_3)$_2$), 2.65 (s, FeCH_2S).

General Procedure for Cyclopropanation of Alkenes with the Sulfonium Salts 5a–d. 1,1-Diphenylcyclopropane. The unrecrystallized **5a** (35 g, 100 mmol) as a yellow powder was placed into a 200-mL round-bottom flask equipped with a magnetic stirring bar. 1,1-Diphenylethylene (9.3 g, 9.1 mL, 52 mmol) and 1,4-dioxane (25 mL) were added, the flask was equipped with a reflux condenser, and the mixture was stirred while it was heated at reflux for 12–14 h under a nitrogen atmosphere (performing the reaction in the air gives only slightly diminished yields). After the brown mixture was cooled somewhat, hexane (75 mL) was added, and the mixture was stirred in the air as it cooled to 25 °C. The mixture was filtered, and the retained solid was washed with additional hexane. The combined filtrates were concentrated by rotary evaporation, and the crude product was purified by flash chromatography (siliga gel, hexane) to give 1,1-diphenylcyclopropane (86% yield).

Alternatively, a specially developed workup procedure may be used that serves to remove by convenient, nonchromatographic means the small, varying amounts of ferrocene (seen as a fast-moving yellow band in the chromatographic purification above) that are produced as a reaction side product. The combined filtrates were concentrated by rotary evaporation, the residual dark brown oil was dissolved in methanol (200 mL) at 25 °C to give an orange-brown solution, solid ferric chloride (7 g) was added to destroy the ferrocene, the resulting dark green solution was stirred for 15 min and concentrated by rotary evaporation, the residual dark green oil was extracted with two 200-mL portions of hexane, and the combined extracts were filtered through a pad of silica gel and concentrated by rotary evaporation. The remaining colorless oil was distilled through a short-path apparatus to give 8.76 g (88%) of the cyclopropane as a clear, colorless liquid: bp 89 °C (0.8 torr); ^{1}H NMR ($CDCl_3$, 300 MHz, lit. ref 40) δ 7.12–7.40 (m, C(C_6H_5)$_2$), 0.275 (s, CH_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8 (ipso *C*), 128.4 and 128.2 (ortho and meta *C*), 125.9 (para *C*), 29.97 (quaternary cyclopropyl *C*), 16.33 (cyclopropyl CH_2CH_2); MS, *m/z* (relative intensity) 194 (M^+, 86), 193 (100), 178 (64), 115 (9).

The cyclopropanes that follow were prepared according to this same procedure from the indicated alkenes.

Bicyclo[6.1.0]nonane. Prepared from *cis*-cyclooctene and purified by column chromatography (silica gel, hexane) to give a 76% yield (92% yield by GLPC analysis of the crude product) of the cyclopropane as a clear, colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz, lit. ref 41) δ 1.20–2.25 (m, (CH_2)$_6$), 0.48–0.77 (m, cyclopropyl *CHCH*, exo *HCH*), −0.305 (m, endo cyclopropyl *HCH*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.99, 27.35, and 26.81 ((CH_2)$_6$), 15.59 (cyclopropyl *CHCH*), 9.86 (cyclopropyl CH_2); MS, *m/z* (relative intensity) 124 (M^+), 96 (M − C_2H_4, 100), 81 (99.9), 67 (76).

Bicyclo[10.1.0]tridecane. Prepared from a mixture of *cis*- and *trans*-cyclododecene in 100% conversion and in 90% yield (GLPC): ^{1}H NMR ($CDCl_3$, 300 MHz, lit. ref 41) δ 0.82–1.80 (m, (CH_2)$_{10}$), 0.46–0.76 (m, 3 cyclopropyl *H*), −0.29 to −0.40 (m, 1 cyclopropyl *H*); ^{13}C NMR ($CDCl_3$, 75 MHz) 28.58, 27.55, 26.96, 25.92, and 22.66 ((CH_2)$_{10}$), 16.78 (cyclopropyl *CHCH*), 10.15 (cyclopropyl CH_2); MS, *m/z* (relative intensity) 180 (M^+), 96.2 (84), 81.2 (100).

1-Methyl-1-phenylcyclopropane. Prepared from α-methylstyrene in 64% yield (GLPC): ^{1}H NMR ($CDCl_3$, 80 MHz, lit. ref 42) δ 7.28 (m, C_6H_5), 1.40 (s, CH_3), 0.82 (br d, *J* = 8 Hz, cyclopropyl CH_2CH_2); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 147.0 (ipso *C*), 128.1 and 126.7 (ortho and meta *C*), 125.4 (para *C*), 25.74 (*C*H_3), 19.73 (quaternary cyclopropyl *C*), 15.63 (cyclopropyl CH_2CH_2); MS, *m/z* (relative intensity) 132 (M^+, 17), 117 (M − CH_3, 100), 91 (22), 77.

***trans*-1,2-Diphenylcyclopropane.** Prepared from *trans*-stilbene in 62% conversion and 64% corrected yield (GLPC): ^{1}H NMR ($CDCl_3$, 300 MHz, lit. ref 9b) δ 7.20–7.85 (m, 2 C_6H_5), 2.30 (m, cyclopropyl *CHCH*), 1.62 (m, cyclopropyl CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.5, 128.3, and 125.7 (2 C_6H_5), 28.00 (cyclopropyl *CHCH*), 18.19 (cyclopropyl CH_2); MS, *m/z* (relative intensity) 194 (M^+, 100), 179 (68), 115 (89).

9,10-Methanophenanthrene. Prepared from phenanthrene in 38% conversion and 82% corrected yield (GLPC): ^{1}H NMR ($CDCl_3$, 80 MHz, lit. ref 28) δ 7.20–8.10 (m, 8 Ar*H*), 2.30 (dd, *J* = 8.5, 4.5 Hz, cyclopropyl *CHCH*), 1.60 (dt, *J* = 8.5, 4.6 Hz, exo cyclopropyl *HCH*), −0.02 (dt, *J* = 4.6, 4.5 Hz, endo cyclopropyl *HCH*); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 136.3, 129.1, 127.6, 126.1, and 123.1 (aromatic *C*), 19.60 (cyclopropyl *CHCH*), 12.70 (cyclopropyl CH_2); MS, *m/z* (relative intensity) 192 (M^+, 100), 191 (85), 178 (M − CH_2).

***n*-Octylcyclopropane.** Prepared from 1-decene and isolated by column chromatography (silica gel, hexane) in 70% yield: ^{1}H NMR ($CDCl_3$, 300 MHz, lit. ref 43) δ 1.28 (br s, (CH_2)$_6$), 1.20 (q, *J* = 7.0 Hz, CH_2-*c*-C_3H_5), 0.89 (t, *J* = 7.0 Hz, CH_3), 0.68 (m, cyclopropyl *CH*), 0.40 (m, cyclopropyl *HCH*–*HCH* trans to C_8H_{17}), −0.13 (m, cyclopropyl HC*H*–HC*H* cis to C_8H_{17}); ^{13}C NMR ($CDCl_3$, 75 MHz) 34.86, 32.26, 29.60, 29.58, 29.48, 29.27, and 22.96 ((CH_2)$_7$), 14.24 (CH_3), 11.09 (cyclopropyl *C*H), 4.54 (cyclopropyl CH_2CH_2); MS, *m/z* (relative intensity) 154 (M^+, 0.7), 126 (M − C_2H_4, 11), 97 (89), 83.1 (100).

***cis*-1,2-Di-*n*-butylcyclopropane.** Prepared from *cis*-5-decene in 59% conversion and 87% corrected yield (GLPC): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10–1.50 (br m, 2 (CH_2)$_3$), 0.89 (t, *J* = 7 Hz, 2 CH_3), 0.53–0.78 (cyclopropyl *CHCHCH*), −0.25 to −0.38 (m, cyclopropyl *HCH* cis to 2 C_4H_9); ^{13}C NMR ($CDCl_3$, 75 MHz) 32.49, 28.43, and 22.69 (2 (CH_2)$_3$), 15.84 (cyclopropyl *CHCH*), 14.10 (2 CH_3), 10.99 ppm (cyclopropyl CH_2); MS, *m/z* (relative intensity) 154 (M^+), 97 (61), 84 (88), 69 (100). Anal. Calcd for $C_{11}H_{22}$: C, 85.63; H, 14.37. Found: C, 85.76; H, 14.37.

***trans*-1,2-Di-*n*-butylcyclopropane.** Prepared from *trans*-5-decene in 49% conversion and 67% corrected yield (GLPC): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.34 (br m, 2 (CH_2)$_3$), 0.89 (t, *J* = 7 Hz, 2 CH_3), 0.32–0.55 (m, cyclopropyl *CHCH*), 0.11–0.32 (m, cyclopropyl CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 34.09, 31.93, and 22.58 (2 (CH_2)$_3$), 18.84 (cyclopropyl *CHCH*), 14.10 (2 CH_3), 11.84 (cyclopropyl CH_2); MS, *m/z* (relative intensity) 154 (M^+, 12), 126 (M − C_2H_4), 97 (50), 83 (50), 69 (100). Anal. Calcd for $C_{11}H_{22}$: C, 85.63; H, 14.37. Found: C, 85.46; H, 14.53.

1-Methylbicyclo[4.1.0]heptane (1-Methylnorcarane). Prepared from 1-methylcyclohexene in 90% conversion and 26% corrected yield (GLPC): ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.10–2.15 (m, (CH_2)$_4$), 1.20 (s, CH_3), 0.50–0.75 (m, cyclopropyl *CH*), 0.15–0.48 (m, cyclopropyl CH_2); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 30.90 (cyclohexyl CH_2), 27.98 (CH_3), 24.35, 21.95, and 21.75 (cyclohexyl (CH_2)$_3$), 18.80, 18.35, and 15.22 (3 cyclopropyl *C*); MS, *m/z* (relative intensity) 110 (M^+, 56), 95 (M − CH_3, 100), 81 (85).

Methyl 2-(Cyclopropylmethyl)propenoate. Prepared from methyl 2-(2′-propenyl)propenoate[44] in 99% conversion and 62% corrected yield (GLPC): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.16 (m, *cis*-*HC*=CCO_2CH_3), 5.71 (m, *trans*-*HC*=CCO_2CH_3), 3.75 (s, CO_2CH_3), 2.18–2.21 (d, *J* = 6.9 Hz, C=CCH_2), 0.80–0.95 (m, cyclopropyl *CH*), 0.42–0.60 (m, cyclopropyl *CHCH* trans to CH_2C=C), 0.080–0.14 (m, cyclopropyl *CHCH* cis to CH_2C=C); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.8 (CO_2CH_3), 140.6 (*C*=CH_2), 124.3 (C=*C*H_2), 51.62 (CO_2CH_3), 36.40, (C=*C*CH_2), 9.49 (cyclopropyl *C*H), 4.54 (cyclopropyl CH_2CH_2); MS, *m/z* (relative intensity) 140.1 (M^+, 0.9), 125 (M − CH_3, 100), 81 (M − CO_2CH_3, 67). Exact mass calcd for $C_8H_{12}O_2$: 140.0837. Found: 140.0822. This product was accompanied by a trace amount (5%) of a compound having a mass of 154 (MS) and assumed to be the biscyclopropanation product.

[(Phenylthio)methyl]cyclopropane. Prepared from allyl phenyl sulfide in 65% conversion and 85% corrected yield (GLPC): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.10–7.58 (m, SC_6H_5), 2.86 (d, *J* = 7.0 Hz, SCH_2), 1.035 (m, cyclopropyl *CH*), 0.59 (m, cyclopropyl *CHCH* trans to CH_2SPh), 0.27 (m, cyclopropyl *CHCH* cis to CH_2SPh); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.2 (ipso *C*), 129.6 and 128.7 (meta and ortho *C*), 125.8 (para *C*), 39.96 (SCH_2), 10.83 (cyclopropyl *CH*), 5.83 (cyclopropyl CH_2CH_2); MS, *m/z* (relative intensity) 166 (M + 2, 2.0), 165 (M + 1, 5.4), 164 (M^+, 49), 123 ($PhSCH_2^+$, 100). Anal. Calcd for $C_{10}H_{12}S$: C, 73.12; H, 7.36; S, 19.52. Found: C, 72.90; H, 7.52; S, 19.27.

(4-Bromobutyl)cyclopropane. Prepared from 6-bromohexene in 100% conversion and 55% corrected yield (GLPC): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.41 (t, *J* = 6.9 Hz, CH_2Br), 1.89 (m, (CH_2)$_3$), 0.656 (m, cyclopropyl *CH*), 0.42 (m, cyclopropyl *CHCH* trans to (CH_2)$_3$Br), 0.15 (m, cyclopropyl *CHCH* cis to (CH_2)$_3$Br); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 33.85 (CH_2Br), 34.04, 32.67, and 28.28 ((CH_2)$_3$), 10.68 (cyclopropyl *C*H), 4.43 (cyclopropyl CH_2CH_2); MS, *m/z* (relative intensity) 150 (65), 148 (61), 97 (M − Br), 69.2 (100), 55.2 (82). Anal. Calcd for $C_7H_{13}Br$: C, 47.48; H, 7.40. Found: C, 47.24; H, 7.15.

2-(2-Cyclopropylethyl)-2-methyl-1,3-dioxolane. Prepared from 2-(3-butenyl)-2-methyl-1,3-dioxolane (5-hexen-2-one ethylene ketal) in 100% conversion and 22% corrected yield (GLPC): ^{1}H NMR ($CDCl_3$, 300

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MHz) δ 3.85 (m, OCH_2CH_2O), 1.60–1.82 (m, CH_2CH_2-*c*-C_3H_5), 1.29 (s, CH_3), 0.59–0.75 (m, cyclopropyl *CH*), 0.30–0.42 (m, cyclopropyl *CHCH* trans to $(CH_2)_2$), −0.10 to +0.21 (m, cyclopropyl *CHCH* cis to $(CH_2)_2$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 110.1 (*OCO*), 64.61 (OCH_2CH_2), 39.07 (CH_2CH_2-*c*-C_3H_5), 29.25 (CH_2CH_2-*c*-C_3H_5), 23.81 (CH_3), 11.08 (cyclopropyl *CH*), 4.46 (cyclopropyl CH_2CH_2); MS, *m/z* (relative intensity) 141 (M − CH_3, 4.3), 86.9 (2-methyl-1,3-dioxalanyl, 100). Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.33; H, 10.15.

***trans*-1-Carbethoxy-2-methylcyclopropane.** Prepared from ethyl *trans*-2-butenoate (ethyl crotonate) in 19% conversion and 80% corrected yield (GLPC): ^1H NMR ($CDCl_3$, 300 MHz) δ 4.08 (q, J = 7.1 Hz, OCH_2CH_3), 1.26 (t, J = 7.1 Hz, OCH_2CH_3), 1.10 (d, *c*-$C_3H_4CH_3$), 0.76–1.58 (m, cyclopropyl $CHCO_2CH_2CH_3$, $CHCH_3$, *HCH*), 0.62–0.75 (m, cyclopropyl *HCH*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 60.28 (OCH_2CH_3), 21.34 (cyclopropyl $CHCO_2CH_2CH_3$), 17.88 (cyclopropyl CH_2), 17.16 (OCH_2CH_3), 16.71 (cyclopropyl $CHCH_3$), 14.30 (*c*-$C_3H_4CH_3$); MS, *m/z* (relative intensity) 128 (M^+, 2.7), 100 (100), 73 (M − $CO_2CH_2CH_3$), 83 (93), 55 (34). Exact mass calcd for $C_7H_{12}O_2$: 128.0837. Found: 128.0838.

Chloromethyl Phenyl Sulfide.[39a] Into a 500-mL round-bottom flask containing a magnetic stirring bar were placed sequentially finely ground potassium hydroxide (6.28 g, 97.4 mmol), bromochloromethane (300 mL), benzenethiol (10.0 mL, 97.4 mmol), and benzyltriethylammonium chloride (0.13 g, 0.55 mmol). The white suspension was stirred for 2 h at 25 °C and then filtered. The filtrate was concentrated by rotary evaporation, with the excess bromochloromethane being recovered by using a dry ice–acetone bath. The concentrated product mixture, which was a clear yellow solution, was diluted with ether (100 mL), and the solution was dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporation, leaving a yellow liquid which was subjected to bulb-to-bulb distillation at 42 °C (0.12 torr) [(lit.[39b] bp 103–104 °C (12 torr)] to give 8.16 g (53%) of chloromethyl phenyl sulfide as a clear, colorless liquid: ^1H NMR ($CDCl_3$) δ 6.85–7.53 (m, C_6H_5), 4.90 (s, CH_2Cl).

(η⁵-Cyclopentadienyl)dicarbonyl[(phenylthio)methyl]iron (6). The same procedure as for the [(methylthio)methyl]iron derivative **4**[21] was employed with sodium (1.18 g, 51.4 mmol), mercury (10.2 g), bis[(η⁵-cyclopentadienyl)dicarbonyliron][20] (9.11 g, 25.7 mmol), tetrahydrofuran (125 mL), and chloromethyl phenyl sulfide (8.16 g, 51.5 mmol). The reaction mixture was concentrated in vacuo, the remaining brown oil was extracted with two 50-mL portions of methylene chloride, and the resulting mixtures were filtered through diatomaceous earth. The combined filtrates were concentrated in vacuo, and the residual brown oil was purified by modified flash chromatography[38] (silica gel, hexane/methylene chloride, 1.4:1). A brown band, a yellow band, and an orange band eluted in order from the column. Concentration of the yellow band afforded **6** (60%) as golden yellow crystals: ^1H NMR ($CDCl_3$) δ 7.25 (m, C_6H_5), 4.93 (s, C_5H_5), 2.60 (s, CH_2); IR (KBr) 2000 (CO), 1940 (CO), 1580 (Ph), 1477 (Ph) cm^{-1}.

Cyclopropanation of *cis*-Cyclooctene with 6. Into a 50-mL Schlenk flask equipped with a magnetic stirring bar was placed **6** (1.05 g, 3.50 mmol) which was then dissolved in methylene chloride (10 mL) at 25 °C. The clear yellow-gold solution was cooled to 0 °C, and trimethyloxonium tetrafluoroborate (0.52 g, 3.5 mmol) was added all at once, at which point the solution became dark yellow-green. After the solution was stirred for 3.5 h at 0 °C, pentane (10 mL) was added, and a dark oil precipitated. The solvent mixture was removed with a cannula, and the residue was placed under vacuum, leaving 1.39 g (99%) of dark brown solid assumed to be the sulfonium salt **7**: ^1H NMR (Me_2SO-d_6) δ 8.06–8.15 (m, Ph, 2 H), 7.60–7.74 (m, Ph, 3 H), 5.32 (s, C_5H_5), 3.19 (s, SCH_3), 3.00 (d, J = 20.5 Hz, diastereotopic FeC*H*HS), 2.86 (d, J = 20.6 Hz, diastereotopic CH*H*S). Into a 5-mL flask were placed a portion of this solid (0.12 g, 0.30 mmol), methylene chloride 1 mL), and *cis*-cyclooctene (0.011 mL, 0.085 mmol). The golden yellow solution was stirred at 25 °C for 12 h, at which time GLPC analysis indicated 20–30% conversion of cyclooctene to bicyclo[6.1.0]nonane.

(η⁵-Cyclopentadienyl)tricarbonyl[(methylthio)methyl]molybdenum (9). Method A. Sodium amalgam was formed as above (see the preparation of **5**) from sodium (0.115 g, 5.0 mmol) and mercury (11.5 g) in a 25-mL round-bottom flask. After the amalgam cooled, tetrahydrofuran (15 mL) and then bis[(η⁵-cyclopentadienyl)tricarbonylmolybdenum] (1.00 g, 2.04 mmol) were added, and the initially dark maroon-colored solution was stirred at 25 °C. Within 1 h, the solution became yellow-green, and after 12 h, chloromethyl methyl sulfide (0.34 mL, 4.0 mmol) was added dropwise. After the mixture was stirred at 25 °C for 24 h, the solvent was removed in vacuo, the brown residue was extracted with three 2-mL portions of methylene chloride, the combined extracts were filtered through diatomaceous earth, the filtrate was concentrated in vacuo, the residue was extracted with pentane (10 mL), the extract was filtered through diatomaceous earth, the filtrate was slowly cooled to −78 °C, the mother liquor was removed with a cannula, and the remaining solid was dried under vacuum to give 0.50 g (41%) of **9** as a yellow powder.

Method B.[45] Into a nitrogen-filled 100-mL round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and three-way stopcock were placed sodium cyclopentadienide (4.0 g, 46 mmol), molybdenum hexacarbonyl (10 g, 46 mmol), and tetrahydrofuran (70 mL) at 25 °C. After the mixture was heated at reflux for 12 h and cooled to 0 °C, chloromethyl methyl sulfide (2.52 mL, 30 mmol) was added dropwise, and the mixture was stirred at 25 °C for 12 h. The resulting orange-brown solution was concentrated in vacuo, the remaining orange-brown oil was dissolved in methylene chloride (20 mL), the solution was filtered through basic alumina (20 g) which was then washed with additional methylene chloride (20 mL), and the combined filtrates were concentrated in vacuo to give **9** (ca. 50% yield) as a yellow-orange crystalline solid: ^1H NMR ($CDCl_3$, 80 MHz) δ 5.43 (s, C_5H_5), 2.44 (s, $MoCH_2S$), 2.22 (s, SCH_3).

(η⁵-Cyclopentadienyl)tricarbonyl[(dimethylsulfonio)methyl]molybdenum Tetrafluoroborate (10). Into a 25-mL Schlenk reaction flask were placed a magnetic stirring bar, **9** (0.500 g, 1.63 mmol), and trimethyloxonium tetrafluoroborate (0.242 g, 1.63 mmol). After a nitrogen atmosphere was established within the flask, methylene chloride (2.5 mL) was added at 25 °C, and the mixture was stirred. The initially yellow-orange solution became dark brown within 15 min, and after 4 h, the mixture was concentrated in vacuo, leaving **10** as a light brown solid: ^1H NMR (acetone-d_6, 80 MHz) δ 5.86 (s, C_5H_5), 3.02 (s, $S(CH_3)_2$), 2.88 (s, $MoCH_2S$). An attempt to purify this compound by recrystallization from methanol did initially afford amber-colored crystals similar in appearance to **5a**, but the molybdenum derivative rapidly turned blue and decomposed while being dried in vacuo.

Cyclopropanation of 1,1-Diphenylethylene Using the Molybdenum Complex 10. For this attempt at cyclopropanation, the sulfonium salt **10** was generated in situ from the [(methylthio)methyl]molybdenum derivative **9**. Into a 5-mL pear-shaped flask were placed a magnetic stirring bar, trimethyloxonium tetrafluoroborate (0.087 g, 0.58 mmol), **9** (0.18 g, 0.58 mmol), and 1,1-diphenylethylene (0.105 g, 0.58 mmol). The flask was equipped with a three-way stopcock, a nitrogen atmosphere was established within the flask, and methylene chloride (2 mL) was added at 25 °C. The mixture was stirred for 12 h, and pentane (1 mL) was added. GLPC and GC–MS analysis of the solution phase indicated only a 5% conversion of the alkene to 1,1-diphenylcyclopropane. Similarly unpromising results were obtained with *cis*-cyclooctene as the substrate.

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