Organometallics **1998,** *17,* 1333−1339

A Method for the Synthesis of Carbene Precursors from Aldehydes and the Metalates $(\eta^5\text{-}C_5H_5)(CO)_2Fe^-$ and $(\eta^5\text{-}C_9H_7)(CO)_2Fe^-$

Ronald D. Theys, Roy M. Vargas, Qinwei Wang, and M. Mahmun Hossain*

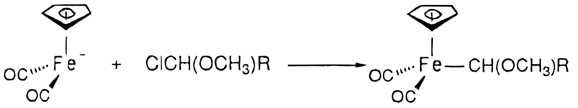
Department of Chemistry, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201

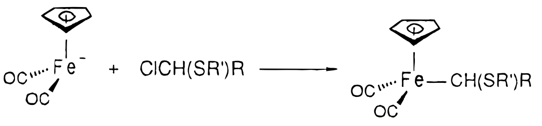
Received August 11, 1997

Nucleophilic addition of the metalate $Cp(CO)_2Fe^-M^+$ ($M = Na, K$) to aldehydes RCHO (R = Ph, CH_3, *p*-OCH_3Ph, *p*-ClPh, *p*-CH_3Ph, *p*-CF_3Ph, *o*-OCH_3Ph, and $CH{=}C(CH_3)_2$) and subsequent capture with $ClSi(CH_3)_3$ provided the (α-siloxyalkyl)iron complexes $Cp(CO)_2FeCH(OSiMe_3)R$ in 42−79% yield. This new reaction was extended to the indenyl-ligated metalate $In(CO)_2Fe^-Na^+$ with several aldehydes RCHO (R = Ph, CH_3, *p*-OCH_3Ph). Treatment of the (α-siloxyalkyl)iron complexes with trimethylsilyl triflate at between −25 and −78 °C, in the presence of alkenes, gave cyclopropanes through iron carbene complexes.

Introduction

Electrophilic iron carbene complexes have been and continue to be of interest as highly reactive intermediates or potential intermediates for both stoichiometric[1] and metal-catalyzed[2] cyclopropanation reactions. Among these iron carbenes, the complexes $(\eta^5\text{-}C_5H_5)(CO)(L)\text{-}Fe^+{=}CHR$ ($L = CO, PR_3$) have been found to be the most effective in transferring their carbene ligands to alkenes, forming cyclopropanes.[1k] Transfer frequently occurs with nearly exclusive formation of the sterically more crowded, thermodynamically less stable isomers of cyclopropane. This, coupled with the relatively lower cost of iron-type complexes, makes iron carbene complexes attractive in cyclopropanation reactions. Due to their lability, these carbene complexes are often generated in situ from their corresponding precursors by treatment with Bronsted or Lewis acids. Synthesis of these precursors to date has required use of the highly nucleophilic $(\eta^5\text{-}C_5H_5)(CO)_2Fe$ anion, commonly designated as Fp^-, via S_N2 substitution reactions with organohalides. The earliest reaction utilized the toxic and often difficult to prepare α-chloroalkyl methyl ethers $ClCH(OCH_3)R$ (R = H, Ph; eq 1).[1a,b,c] A variation of this reaction uses α-chloroalkylmethyl/phenyl thioethers $ClCH(SR')R$ ($R = H$, $R' = CH_3$, Ph; $R = CH_3$, CH_2CH_3, $R' =$ Ph) to produce more stable precursors (eq 2).[1h,j,l] Both of these reactions have inherent limitations.


(1)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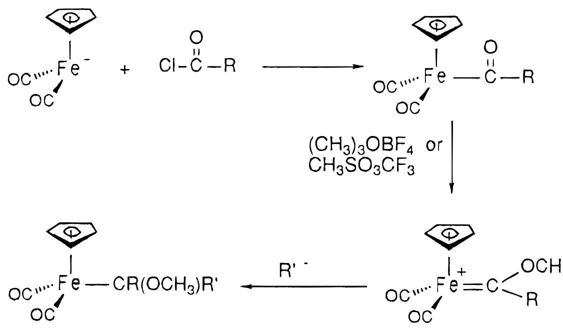
A more general reaction has been devised involving hydride or alkyl anion reduction of a Fischer carbene (eq 3).[1d,f,i] This procedure is lengthier than the previous two.



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Recently, we reported[3] that the Fp anion acts as a nucleophile in reactions with aldehydes RCHO to form the alkoxides $FpCH(O^-)R$, which were trapped with chlorotrimethylsilane to provide the α-siloxyalkyliron complexes $FpCH(OSiMe_3)R$. These reactions represent a simple and efficient method for synthesizing electrophilic iron carbene precursors from readily available starting materials. The new precursors were found to be efficient reagents for stereoselective cyclopropanation, presumably through in-situ-generated carbene complexes. We wish to report on extension of this new

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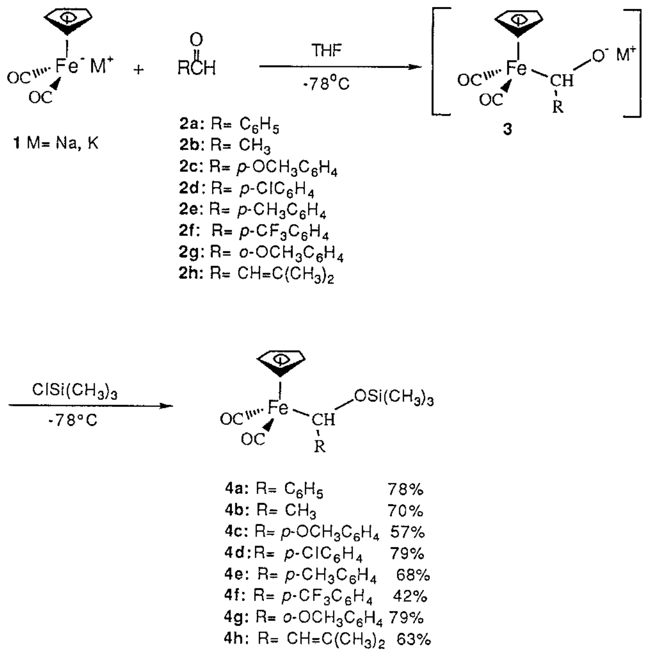
(1) (a) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. (b) Brookhart, M.; Nelson, G. O. *Ibid.* **1977**, *99*, 6099. (c) Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. *Ibid.* **1980**, *102*, 7802. (d) Brookhart, M.; Tucker, J. R.; Husk, G. R. *Ibid.* **1981**, *103*, 979. (e) Kremer, K. A. M.; Kuo, G. H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *Ibid.* **1982**, *104*, 6119. (f) Brookhart, M.; Tucker, J. R.; Husk, G. R. *Ibid.* **1983**, *105*, 258. (g) Casey, C. P.; Miles, W. H. *Organometallics* **1984**, *3*, 808. (h) Kremer, K. A. M.; Helquist, P. *J. Organomet. Chem.* **1985**, *285*, 231. (i) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924. (j) O'Connor, E. J.; Brandt, S.; Helquist, P. *Ibid.* **1987**, *109*, 3739. (k) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (l) Helquist, P. *Adv. Met.-Org. Chem.* **1991**, *2*, 143.

(2) (a) Seitz, W. J.; Saha, A. K.; Casper, D.; Hossain, M. M. *Tetrahedron Lett.* **1992**, *33*, 7755. (b) Seitz, W. J.; Saha, A. K.; Hossain, M. M. *Organometallics* **1993**, *12*, 2604. (c) Seitz, W. J.; Hossain, M. M. *Tetrahedron Lett.* **1994**, *35*, 7561.

(3) A preliminary communication has appeared, see: Vargas, R. M.; Theys, R. D. Hossain, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 777.

S0276-7333(97)00698-5 CCC: $15.00
Publication on Web 03/06/1998

Scheme 1



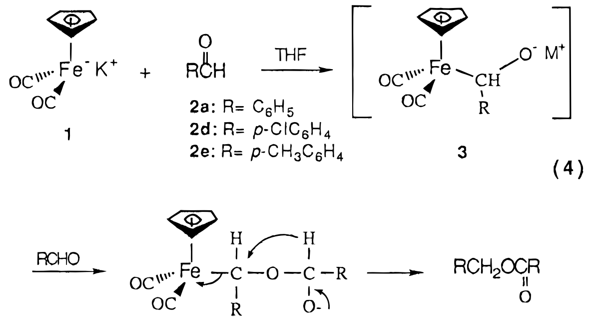
reaction to other aldehydes with the Fp anion and to reaction of aldehydes with the indenyldicarbonyliron anion (η^5-C_9H_7)(CO)$_2$Fe$^-$.

Results and Discussion

The Fp anion **1** reacts with aldehydes **2** in THF to form the alkoxides **3**. The presumed alkoxides were captured by chlorotrimethylsilane to provide the siloxyiron complexes **4** (Scheme 1).

Yields for the complexes **4** ranged from 42% to 79%. Most of the complexes were formed by use of an excess of aldehyde (3 equiv) and a limited amount of Fp anion (1 equiv). Later, it was discovered that an excess of Fp anion (2 equiv) actually could give a considerably higher yield, as exemplified by **4d**. With the aldehyde in excess, a 40% yield was obtained, whereas with the Fp anion in excess, a 79% yield was realized. In every case, byproducts from this general reaction included the silyl complex Fp−SiMe$_3$ and the Fp dimer in varying amounts.

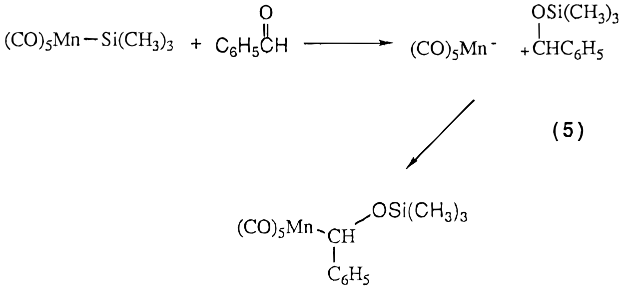
Apparently, the reaction depicted in Scheme 1 represents the first successful nucleophilic addition of a transition metal anion complex to an aldehyde. No reaction was observed at room temperature between the manganese pentacarbonyl anion and benzaldehyde.[4] The greater nucleophilicity of the Fp anion may be one reason for its successful addition to benzaldehyde.[5] The trapping agent is also critical. Treatment of the alkoxide intermediate with methyl iodide or trimethyloxonium tetrafluoroborate only generated the methyl complex (η^5-C_5H_5)(CO)$_2$Fe−CH$_3$ and Fp dimer, [(η^5-C_5H_5)(CO)$_2$Fe]$_2$. No Fp−CH(OCH$_3$)R was formed, indicating that neither CH$_3$I nor (CH$_3$)$_3$O$^+$BF$_4^-$ was an effective trapping reagent for the alkoxide **3** intermediate. The temperature of the reaction was later found to be very critical. Recently, Yamashita[6] reported that at room temperature the Fp anion catalyzes the dimerization of aromatic aldehydes to form esters via the alkoxides **3** (eq 4). This latest observation solidifies our findings of nucleophilic addition of the Fp anion to the aldehydes.



(4)

Precendence exists for a proposed alkoxide intermediate with other transition metal moieties. Gladysz proposed the existence of a related manganese alkoxide anion (CO)$_5$Mn(C$_6$H$_5$CHO$^-$Li$^+$) as a fleeting intermediate in the reduction of the manganese pentacarbonyl acyl complex by trialkylborohydrides.[7] Hegedus provided indirect evidence for the intermediacy of the chromium pentacarbonyl dianion (CO)$_5$Cr$^-$(NR$_2$′CRO$^-$) after nucleophilic addition of Cr(CO)$_5^{2-}$ to tertiary amides.[8]

The possibility that either an insertion mechanism or a substitution mechanism was involved in forming the precursor was also dispelled. The (α-siloxybenzyl)manganese pentacarbonyl complex has been synthesized via a proposed insertion mechanism between the manganese silyl complex (CO)$_5$Mn−SiMe$_3$ and benzaldehyde (eq 5).[9] No analogous reaction was observed between the silyl complex (η^5-C_5H_5)(CO)$_2$Fe−SiMe$_3$[10] and the aldehyde under the reaction conditions. We also considered the possibility that chlorotrimethylsilane and the aldehyde were reacting in situ to form α-chloroalkyl silyl ethers. Jung[11] reported that iodotrimethylsilane reacts exothermally at room temperature with aldehydes to form α-iodoalkyl silyl ethers. This



(5)

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[4] Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6766.

[5] King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417.

[6] Ohishi, T.; Shiotani, Y.; Yamashita, M. *Organometallics* **1994**, *13*, 4641.

[7] Selover, J. C.; Marsi, M.; Parker, D. W.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, *206*, 317.

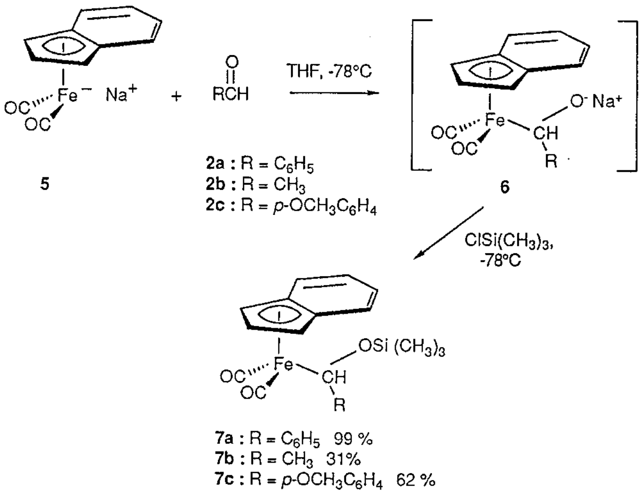
[8] Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702.

[9] (a) Johnson, D. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6433. (b) Johnson, D. L.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 2508.

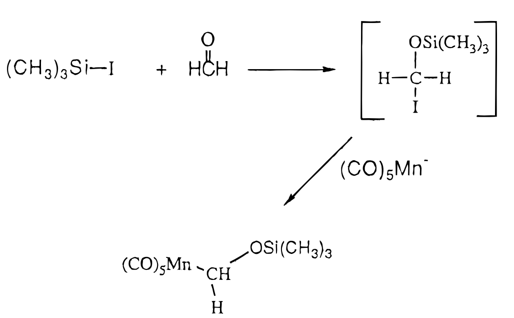
[10] Piper, T. S.; Lemal, D.; Wilkinson G. *Naturwissenschaften* **1956**, *43*, 129.

[11] Jung, M. E.; Mossman, A. B.; Lyster, M. A. *J. Org. Chem.* **1978**, *43*, 3698.

Scheme 2



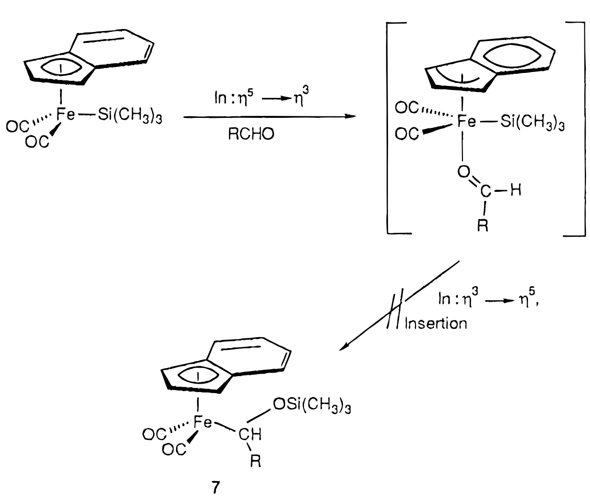
method was used by Gladysz to make $(CO)_5MnCH_2(OSi(CH_3)_3)$ via a proposed S_N2 mechanism (eq 6).[12] In our case, we observed no reaction between $ClSiMe_3$ and benzaldehyde at room temperature or low temperature, discounting a similar S_N2 mechanism. Therefore, the mechanistic pathways illustrated in eqs 5 and 6 do not appear to be involved in forming **4**.



(6)

To expand the scope of our new reaction to related organometallic nucleophiles, we evaluated the reactivity of the (η^5-indenyl)iron metalate **5**[13] and several aldehydes **2** under similar reaction conditions to the Fp analogues. Treatment with chlorotrimethylsilane captured the presumed alkoxide intermediate to produce the indenyl-ligated (α-siloxyalkyl)iron complexes **7** (Scheme 2).

As mentioned previously, we saw no reaction between the silyl complex containing the η^5-C_5H_5 (Cp) ligand and aldehydes. However, with the indenyl (In) complexes, it is well-known that this ligand can undergo η^5- to η^3-ring slippage to bind incoming nucleophiles. For this reason, an alternative mechanism is possible involving η^5- to η^3-ring slippage with ligation of the aldehyde followed by insertion (eq 7). To discount this mechanism, $In(CO)_2Fe{-}SiMe_3$[14] and the aldehydes **2** were stirred in THF under similar conditions to those used for formation of the precursors **7**. After workup of the reaction mixtures, no (α-siloxyalkyl)iron complexes were detected, only starting materials were isolated. This clearly demonstrated that the mechanism shown in eq 7 is not the one in effect for formation of complexes **7**.



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The isolated yields are slightly higher for the indenyl-ligated anion than with the Fp anion when using benzaldehyde and *p*-anisaldehyde. By using a larger excess of *p*-anisaldehyde, the yield of **7c** was improved from 52% to 62%. A major byproduct in the synthesis of **7c** was the dimer $[In(CO)_2Fe]_2$.[13,15] Minor byproducts included the silyl complex $In(CO)_2Fe{-}SiMe_3$ and the pinacol silyl ether $[(p\text{-}OCH_3Ph)CH{-}(OSiMe_3)]_2$,[9b] the latter is thought to be formed by decomposition of the product **7c**.[16]

The isolated yield of the acetaldehyde-generated precursor **7b** (31%) from the indenyl-ligated anion was much lower than that from the Fp anion (70%). The reason for this lower yield is not yet understood. The major byproducts of the synthesis of **7b** were the dimer $[In(CO)_2Fe]_2$, the silyl complex $In(CO)_2Fe{-}SiMe_3$, and, interestingly, the hydride complex $In(CO)_2Fe{-}H$.[17]

To order to determine the potential synthetic utility of the (α-siloxyalkyl)iron complexes **4** as precursors in the generation of electrophilic iron carbene complexes for cyclopropanation, each was separately treated with 1.1−1.7 equiv of trimethylsilyl triflate at −78 °C in the presence of 2−4 equiv of an olefin (Scheme 3).

The yields and stereochemistry for the products of these cyclopropanation reactions are summarized in Table 1. It is readily apparent from these unoptimized results that the new precursors **4a,b,e,g** are efficient. They also exhibit high cis selectivity when reacted with acyclic alkenes. In addition, precursor **4a** shows very high endo selectivity with cyclopentene. Reaction of styrene with precursor **4c** provided the cis isomer as the major product, exhibiting higher selectivity (4:1) than the related α-methoxy complex $Cp(CO)_2Fe{-}CH(OCH_3)(p\text{-}OCH_3C_6H_5)$ with propene (2:1).[18] Precursor **4d** also provided the only cis isomer with styrene. Precursor **4h** preferred the trans isomer when reacted with styrene. This is consistent with the related α-methoxy complex $Cp(CO)_2Fe{-}CH(OCH_3)(CH{=}C(CH_3)_2)$, reported previously.[1g]

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[12] Brinkman, K. C.; Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1056.

[13] Forschner, T. C.; Cutler A. R. *Inorg. Chim. Acta* **1985**, *102*, 113.

[14] Pannell, K. H.; Lin, S.-H.; Kapoor, R. N.; Cervantes-Lee, F.; Pinon, M.; Parkanyi, L. *Organometallics* **1990**, *9*, 2454.

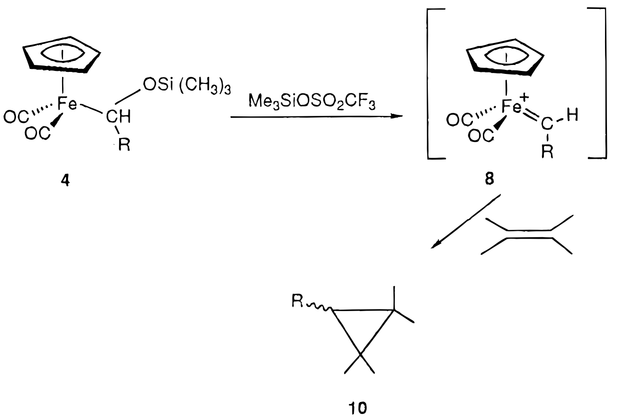
[15] Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1958**, 646.

[16] The cyclopentadienyl analogue **4c** decomposes to the same silyl pinacol ether, see: Vargas, R.; Hossain, M. M. *Tetrahedron Lett.* **1993**, *34*, 2727.

[17] Ahmed, H.; Brown, D. A.; Fitzpatrick, N. J.; Glass, W. K. *Inorg. Chim. Acta* **1989**, *164*, 5.

[18] Broom, M. B. H. Ph.D. Dissertation, University of North Carolina, 1982.

Scheme 3



Scheme 4

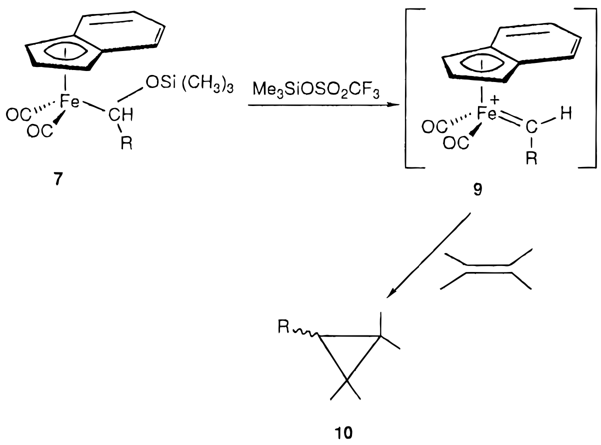


Table 1. Cyclopropanes from Precursors 4

precursor	olefin	yield (%)	
4a (R = Ph)	styrene	68	(all cis)[a,b]
	cyclopentene	62	(all endo)[a,b]
	2-methyl-2-butene	88	(all cis)[a,b]
4b (R = CH_3)	styrene	72	(all cis)[b,d]
4c (R = *p*−OCH_3Ph)	styrene	38	(4:1)*a*−*c*
4d (R = *p*-ClPh)	styrene	30	(all cis)[a,b]
4e (R = *p*−CH_3Ph)	styrene	81	(all cis)[a,b]
4g (R = *o*-OCH_3Ph)	styrene	87	(12:1)[a,b]
	1,1-diphenylethene	61[a]	
4h (R = $CHCMe_2$)	styrene	44	(1:2)[a,b,c]

[a] Isolated, unoptimized yield. [b] Ratios were determined by GC and/or ^1H NMR spectroscopy. [c] Cis:trans ratio. [d] Determined by GC with results calibrated against an internal standard.

To order to verify that these complexes could indeed generate the carbene in situ, low-temperature ^1H and ^{13}C NMR studies were undertaken using the (α-siloxybenzyl)iron complex **4a** as a representative example. Treatment of complex **4a**, at −40 °C in CD_2Cl_2 with trimethylsilyl triflate, generated a distinctive peak in the proton NMR at 16.79 ppm, characteristic of the carbene $Cp(CO)_2Fe^+{=}CHPh$ (**8a**). By monitoring this reaction using ^{13}C NMR under the same conditions, a peak at 342.4 ppm was detected as an absorption, which is also characteristic of **8a**. The location of these peaks in the ^1H and ^{13}C NMR are in agreement with data observed for formation of **8a** from the (α-methoxybenzyl)iron complex $Cp(CO)_2Fe{-}CH(OCH_3)Ph$.[1b]

The indenyl-ligated precursors **7** also provided cyclopropanes in an efficient and selective manner (Scheme 4 and Table 2). The reaction conditions for **7** were similar to those conditions outlined for precursors **4**, with the exception that the reaction times were extended for **7b,c**. In comparison to the Cp-ligated precursor **4a**, the phenyl-substituted precursor **7a** gave a slightly lower cyclopropane yield with styrene. On the other hand, the yields were excellent with both cyclopentene and 2-methyl-2-butene, which are higher, in the bicyclic case significantly higher, than for precursor **4a**. This may be partly due to the extended reaction times for precursor **7a**. It was discovered later that longer reaction times gave higher yields for precursors **7**. No extended reaction times were evaluated for precursors **4**. For the methyl-substituted precursor **7b**, a lower yield was obtained with styrene than for precursor **4b**. For the *p*-methoxyphenyl precursor **7c**, a significantly higher yield was obtained with styrene than when precursor **4c** was used. This yield may again be related, in part, to the longer reaction times used for **7c**.

Table 2. Cyclopropanes from Precursors 7

precursor	olefin	yield (%)	
7a (R = Ph)	styrene	61	(all cis)[a,b]
	cyclopentene	95	(all endo)[a,b]
	2-methyl-2-butene	95	(all cis)[a,b]
7b (R = CH_3)	styrene	64	(all cis)[b,d]
7c (R = *p*-OCH_3Ph)	styrene	89	(4:1)[a−c]

[a] Isolated, unoptimized yield. [b] Ratios were determined by GC and/or ^1H NMR spectroscopy. [c] cis:trans ratio. [d] Determined by GC with results calibrated against an internal standard.

The selectivities for precursors **4a**−**c** and **7a**−**c** were identical when comparing their counterpart. This was a little surprising since we anticipated some variation in the selectivities owing to the greater steric bulk of the indenyl ligand. Since the indenyldicarbonyliron dimer is not commercially available, use of the readily available cyclopentadienyldicarbonyliron dimer would be more advantageous for preparation of the (α-siloxyalkyl)iron precursors and, in turn, for cyclopropanation. However, unlike the Cp-ligated complexes, the indenyl-ligated complexes **7a,c** have been shown to undergo direct carbonylation under mild reaction conditions to form their acyl analogues.[19]

Conclusion

A simple route to the synthesis of secondary electrophilic iron carbene precursors from readily available aldehydes and iron metalates has been devised. This route works well with both saturated and unsaturated aldehydes. The cyclopentadienyl-ligated anion $Cp(CO)_2Fe^-$ and the indenyl-ligated anion $In(CO)_2Fe^-$ were nucleophilically added to aldehydes in an efficient manner. The (α-siloxyalkyl)iron complexes produced, upon treatment with chlorotrimethylsilane, were found to be effective starting materials for in situ generation of carbene complexes, which generally produced cyclopropanes in a stereoselective fashion in high yields.

Future work on this project will focus on extension of this method to other metalates. In addition, application of these reactions to asymmetric synthesis of cyclopropanes is in progress.[20]

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(19) Theys, R. D.; Hossain, M. M. *Organometallics* **1994**, *13*, 866.
(20) Theys, R. D.; Hossain, M. M. *Tetrahedron Lett.* **1995**, *36*, 5113.

Experimental Section

General Information. All reactions and manipulations of transition metal complexes were performed under a dry nitrogen atmosphere using standard Schlenk line and/or drybox techniques. All glassware required for the above was either flamed under vacuum or dried in an oven prior to use.

Tetrahydrofuran (Baker, reagent grade) and diethyl ether (EM Science, reagent grade) were freshly distilled under a nitrogen atmosphere from sodium benzophenone ketyl. Dichloromethane (Baker, HPLC grade) was distilled under nitrogen from phosphorus pentoxide. Pentane (technical grade) was purified by sequential stirring overnight with concentrated sulfuric acid, washing with water, drying over Na_2SO_4 (anhydrous), distilling, and redistilling prior to use from sodium under nitrogen.

The aromatic aldehydes (benzaldehyde, *p*-anisaldehyde, *p*-chlorobenzaldehyde, *p*-tolualdehyde, and trifluoro-*p*-tolualdehyde) were sequentially extracted with saturated sodium bicarbonate, washed with water, stored over $MgSO_4$ (anhydrous), and freshly distilled under vacuum. Acetaldehyde was stirred twice over $NaHCO_3$, dried with $CaSO_4$ (anhydrous), and then distilled at atmospheric pressure. 3-Methyl-2-butenal was dried over anhydrous $CaSO_4$ and distilled twice under vacuum with the receiver flask cooled to −78 °C. *o*-Anisaldehyde (Lancaster) was used without purification. Chlorotrimethylsilane was distilled at atmospheric pressure and then stored in a desiccator. Indenyliron dicarbonyl dimer was synthesized according to the literature procedure.[13] Cyclopentadienyliron dicarbonyl dimer, styrene, cyclopentene, and 2-methyl-2-butene were obtained from Aldrich Chemical Co. and used without further purification unless stated otherwise. Trimethylsilyl triflate ($CF_3SO_3SiMe_3$) was obtained from Lancaster and used without treatment. Chlorotrimethylsilane and all of the aldehydes were obtained from Aldrich Chemical Co. Deuterated chloroform (Isotec) was refluxed over phosphorus pentoxide, degassed several times with liquid nitrogen, distilled under vacuum from P_2O_5 using a Schlenk flask and stored under nitrogen.

^1H and ^{13}C spectra were obtained in $CDCl_3$ on a Bruker 250 and 62.9 MHz NMR spectrometer, respectively. Chemical shifts for the ^1H NMR spectra were determined by utilizing residual $CHCl_3$ (δ 7.24) as an internal reference. ^{13}C NMR resonances were measured from $CDCl_3$ (77.0 ppm). Infrared spectra were recorded using a Nicolet MX-1 FTIR spectrometer. Mass spectra were determined on a Hewlett-Packard 5985B (H/P) GC/MS system, operated in DIP (direct insertion probe) EI-70 eV, and HR-MS were determined on a GC/MS VG-AUTOSPEC-3000. For the CH microanalyses, a Perkin-Elmer 240c elemental analyzer was employed. A Varian Aerograph GC Series 1700 with a 3% SE-30 column (6 ft × 1/4 in.) or a Varian Aerograph GC Series 1200 with a 5% SE-52, 80/100 A/W column (8 ft × 1/8 in.) was used to analyze the isomeric purity of the cyclopropanes generated from the Cp-ligated complexes **4**. A Hewlett-Packard 5880A GC with a cross-linked 5% PhMe silicone high-performance capillary column was used to analyze for the isomeric purity of the cyclopropanes generated from the indenyl-ligated complexes **7**.

$Cp(CO)_2Fe{-}CH(OSiMe_3)R$, 4a,b (R = Ph, CH_3). General Procedure. A 0.6−1.5 mmol sample of iron dimer $[Cp(CO)_2Fe]_2$ was dissolved in 20−50 mL of degassed THF and added to 6−12 mmol of sodium metal in a 1% Na−Hg amalgam at 0 °C.[21] After addition, the mixture was warmed to room temperature and stirred for 1 h. The Fp anion which formed was transferred to another flask using a filter stick. The Fp anion solution was cooled to −78 °C, and 1.2−12 mmol of the aldehyde was added dropwise. This mixture was stirred for 1 h at −78 °C, after which 1.2−3 mmol of chlorotrimethylsilane was added and stirred for an additional 1 h at −78 °C. The solvent was removed under reduced pressure, and the residue was dissolved in a small amount of THF for transfer to a water-jacketed chromatography column containing silica gel (40−140 mesh) in pentane. **4b** was eluted with pentane in 70% yield as a reddish-brown oil containing 10% of the iron silyl complex $Fp{-}SiMe_3$.[10] For **4a**, initial elution with pentane gave 5% $Fp{-}SiMe_3$ and subsequent elution with a 5% THF/pentane mixture gave **4a** in 78% yield as a yellow-brown oil. The following spectral characteristics were obtained. **4a:** ^1H NMR ($CDCl_3$, 250 MHz) δ 7.19 (m, 5H, Ph), 6.56 (s, 1H, FeCH), 4.50 (s, 5H, C_5H_5), 0.00 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 217.4 (CO), 155.9 (C_{ipso}), 127.6, 123.8, 123.2 (Ph), 87.0 (C_5H_5), 86.0 (FeCH), 0.0 ($Si(CH_3)_3$); IR (CH_2Cl_2) ν_{CO} 1948, 2004 cm^{-1}; MS(EI) 357 $(M)^+$ (not observed), 240, 212, 179, 149, 121. Anal. Calcd for $FeC_{17}H_{20}O_3Si$: C, 57.17; H, 5.60. Found: C, 57.48; H, 5.49. **4b:** ^1H NMR ($CDCl_3$, 250 MHz) δ 5.66 (q, 1H, J = 6 Hz, FeCH), 4.71 (s, 5H, C_5H_5), 1.66 (d, 3H, J = 6 Hz, CH_3), 0.07 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 217.8, 216.9 (CO), 86.2 (C_5H_5), 81.7 (FeCH), 35.9 (CH_3), 0.2 ($Si(CH_3)_3$); IR (CH_2Cl_2) ν_{CO} 1944, 2000 cm^{-1}. CH analysis was attempted, but the precursor was too air-sensitive to analyze in this fashion.

$Cp(CO)_2Fe{-}CH(OSiMe_3)R$, 4c−g (R = *p*-$OCH_3Ph$, *p*-ClPh, *p*-$CH_3Ph$, *p*-$CF_3Ph$, *o*-$OCH_3Ph$). General Procedure. A 1.0−1.6 mmol sample of FpK[22] was dissolved in 25−50 mL of THF and cooled to −78 °C, and 0.5 (R = *p*-ClPh, *p*-CH_3Ph) to 4.8 mmol of aldehyde was added dropwise. After the reaction mixture was stirred for 1−3 h at −78 °C, 0.5−1.6 mmol of chlorotrimethylsilane was added. Stirring was continued for 1 h, and the temperature was maintained at −78 °C. The solvent was removed under reduced pressure, and separation with a water-jacketed column was achieved on silica gel (40−140 mesh) using a 2−5% THF/pentane mixture (**4d**) or a 2% ether/pentane mixture (**4e**). **4d** (79%) was isolated as yellow crystals and **4e** (68%) as a cream-colored solid. For complexes **4c**, **4f**, and **4g** separation was achieved on neutral Al_2O_3 (activity 2) using a 2% THF/pentane mixture. Isolation of **4c** (57%) as a cream-colored solid, **4f** (42%) as yellow crystals, and **4g** (79%) as an orange viscose oil resulted. The following spectral characteristics were obtained. **4c:** ^1H NMR ($CDCl_3$, 250 MHz) δ 7.14 (d, 2H, J = 9 Hz, Ph), 6.73 (d, 2H, J = 9 Hz, Ph), 6.58 (s, 1H, FeCH), 4.50 (s, 5H, C_5H_5), 3.77 (s, 3H, OCH_3), −0.01 (s, 9H, $Si(CH_3)_3$); IR (CH_2Cl_2) ν_{CO} 1945, 2002 cm^{-1}; MS(EI) 386 $(M)^+$ (not observed), 209, 177, 149, 121. Anal. Calcd for $FeC_{18}H_{22}O_4Si$: C, 55.96; H, 5.74. Found: C, 55.74; H, 5.45. **4d:** ^1H NMR ($CDCl_3$, 250 MHz) δ 7.13 (s, 4H, Ph), 6.50 (s, 1H, FeCH), 4.51 (s, 5H, C_5H_5), 0.00 (s, 9H, $Si(CH_3)_3$); IR (CH_2Cl_2) ν_{CO} 1948, 2006 cm^{-1}. Anal. Calcd for $FeC_{17}H_{19}O_3SiCl$: C, 52.26; H, 4.90. Found: C, 52.57; H, 4.84. **4e:** ^1H NMR ($CDCl_3$, 250 MHz) δ 7.01 (m, 4H, Ph), 6.57 (s, 1H, FeCH), 4.50 (s, 5H, C_5H_5), 2.25 (s, 3H, CH_3), 0.00 (s, 9H, $Si(CH_3)_3$); IR (CH_2Cl_2) ν_{CO} 1946, 2003 cm^{-1}. Anal. Calcd for $FeC_{18}H_{22}O_3Si$: C, 58.38; H, 5.99. Found: C, 58.77; H, 6.08. **4f:** ^1H NMR ($CDCl_3$, 250 MHz) δ 7.44 (d, 2H, J = 8 Hz, Ph), 7.30 (d, 2H, J = 8 Hz, Ph), 6.54 (s, 1H, FeCH), 4.54 (s, 5H, C_5H_5), 0.03 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 216.6 (CO), 160.1 (C_{ipso}), 123.0, 124.7, 127.7 (Ph), 102.7 (CF_3), 87.0 (C_5H_5), 69.0 (FeCH), 0.0 ($Si(CH_3)_3$); IR (CH_2Cl_2) ν_{CO} 1951, 2007 cm^{-1}. **4g:** ^1H NMR ($CDCl_3$, 250 MHz) δ 7.52 (d, 1H, J = 7 Hz, Ph), 7.01 (t, 1H, J = 7 Hz, Ph), 6.89 (t, 1H, J = 7 Hz, Ph), 6.76 (s, 1H, FeCH), 6.69 (d, 1H, J = 7 Hz, Ph), 4.60 (s, 5H, C_5H_5), 3.80 (s, 3H, OCH_3), 0.00 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 216.7, 215.5 (CO), 150.7 (C_{ipso}), 144.5, 125.7, 124.5, 120.4, 109.1 (Ph), 86.4 (Cp), 62.9 (FeCH), 54.5 (OCH_3), 0.0 ($Si(CH_3)_3$); IR (CH_2Cl_2) ν_{CO} 1943, 1999 cm^{-1}. We are unable to obtain analytically pure samples of **4f** and **4g** for acceptable CH analysis.

$Cp(CO)_2Fe{-}CH(OSiMe_3)(CH{=}C(CH_3)_2)$, 4h. Specific Procedure. To a solution of 1.4 mmol of FpK in 20 mL of

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[21] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.
[22] Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 284.

THF at −78 °C, 4.1 mmol of 3-methyl-2-butenal in 10 mL of THF was added dropwise. After 1 h of stirring at −78 °C, 1.4 mmol of chlorotrimethylsilane was added. Stirring was continued for an additional 1 h at −78 °C. Due to the thermal instability of this complex, it was not purified by column chromatography. Instead, the solvent was removed under reduced pressure and quickly cooled to −78 °C. Complex **4h** was isolated in 63% yield as a reddish-brown oil after extraction of the crude reaction mixture with pentane at −78 °C and subsequent removal of the solvent under reduced pressure. The isolated complex **4h** contained small impurities of Fp dimer and starting aldehyde. **4h:** ^{1}H NMR ($CDCl_3$, 250 MHz, −40 °C) δ 6.35 (d, 1H, J = 10 Hz, FeCH), 5.69 (d, 1H, J = 10 Hz, CCH=C), 4.68 (s, 5H, C_5H_5), 1.60 (s, 3H, CH_3), 1.55 (s, 3H, CH_3) 0.01 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz, −40 °C) δ 216.8 (CO), 118.2, 139.1 (CH=C), 86.1 (C_5H_5), 66.9 (FeCH), 25.6 (CH_3), 18.2 (CH_3), 0.1 ($Si(CH_3)_3$); IR (CH_2Cl_2) ν_{CO} 1945, 2012 cm^{-1}.

In(CO)$_2$Fe−CH(OSiMe$_3$)R, 7a−c, (R=Ph, CH$_3$, *p*-O-CH$_3$Ph. General Procedure. A 0.25−0.45 mmol sample of iron dimer $[In(CO)_2Fe]_2$[13] was dissolved in 20−45 mL of THF. This solution was degassed and added to 2.0−6.0 mmol of sodium metal in a 1% Na−Hg amalgam at room temperature. This mixture was stirred for 2−3 h, cooled to −78 °C, transferred via cannula to another sidearm flask, and cooled to −78 °C, and 0.50−2.0 mmol (for R = Ph, *p*-OCH_3Ph, 1 equiv, for R = CH_3, all 4 equiv added at one time) of aldehyde was added. The reaction mixture was allowed to stir for 1 h (2 h for R = CH_3) at −78 °C, then an additional 1.5−3.0 mmol of aldehyde was added and stirring was continued for 2 h more at −78 °C. A 0.60−1.0 mmol amount of chlorotrimethylsilane was added dropwise over 5 min and allowed to stir for an additional 1 h. The solvent was removed under reduced pressure, and the product was separated with a water-jacketed chromatography column on neutral Al_2O_3 (activity 3) using a 1−2% CH_2Cl_2/pentane mixture for **7a,c** or pentane for **7b**. Isolation of **7a** (99%), **7b** (31%), and **7c** (52%) as orange oils was achieved. The following spectral characteristic were obtained. **7a**: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.04−7.26 (m, 9H, In and Ph), 6.30 (s, 1H, Fe−CH), 5.25 (br s, 1H, In, H_1 or H_3), 4.90 (br s, 1H, In, H_3 or H_1), 4.84 (t, 1H, J = 3 Hz, In, H_2), 0.02 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 216.5, 216.8 (CO), 154.8 (C_{ipso}), 123.2, 124.0, 124.1, 124.4, 126.0, 126.3, 127.6 (In, benzo C's and Ph), 105.9 (In, C_2), 104.0, 105.4 (In, $C_{3a,7a}$), 73.7, 74.0 (In, $C_{1,3}$), 70.2 (Fe−CH), 0.0 ($Si(CH_3)_3$); IR (CH_2Cl_2) ν_{CO} 1999, 1942 cm^{-1}. **7b:** ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.39 (m, 2H, In, benzo), 7.08 (m, 2H, In, benzo), 5.40 (br s, 1H, In, H_1 or H_3), 5.31 (br s, 1H, In, H_3 or H_1), 5.14 (q, 1H, J = 6 Hz, Fe−CH), 4.90 (t, 1H, J = 3 Hz, In, H_2), 1.59 (d, 3H, J = 6 Hz, Fe−C−CH_3), 0.06 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 216.3, 217.4 (CO), 123.9, 124.4, 125.9, 126.2 (In, benzo C's), 105.1, 106.3 (In, $C_{3a,7a}$), 101.9 (In, C_2), 72.8, 73.2 (In, $C_{1,3}$), 70.6 (Fe−CH), 35.3 (Fe−C−CH_3), 0.2 ($Si(CH_3)_3$); IR (CH_2Cl_2): ν_{CO} 1999, 1938 cm^{-1}. **7c:** ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.32 (m, 2H, In, benzo), 7.16 (d, J = 9 Hz, 2H, Ph), 7.04 (m, 2H, In, benzo), 6.76 (d, J = 9 Hz, 2H, Ph), 6.32 (s, 1H, FeCH), 5.25 (br s, 1H, In, H_1 or H_3), 4.97 (br s, 1H, In, H_3 or H_1), 4.80 (t, J = 3 Hz, 1H, In, H_2), 3.79 (s, 3H, OCH_3), 0.01 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 216.6, 216.9 (CO), 156.0 (C_{ipso}), 147.2 (C_{para}), 112.7, 123.9, 124.3, 125.9, 126.1 (In, benzo C's and Ph), 106.1 (In, C_2), 105.5, 104.3 (In, $C_{3a,7a}$), 73.6, 73.9 (In, $C_{1,3}$), 70.2 (Fe−CH), 55.1 (OCH_3), 0.0 ($Si(CH_3)_3$); IR (CH_2Cl_2) ν_{CO} 1998, 1940 cm^{-1}.

Cyclopropanations from Complexes 4a−e and 7a,c. General Procedure. A 0.15−1.5 mmol (1 equiv) sample of the precursor was dissolved in 4−10 mL of CH_2Cl_2 and 0.3−3.0 mmol (2 equiv) of the alkene added. The solution was cooled to −78 °C, and 0.21−1.6 mmol (1.1 equiv) of trimethylsilyl triflate was introduced. In general, the color of the reaction mixture changed from yellow-orange to purple. The solution was then stirred for varied amounts of time depending on the perceived stability of the generated carbene. The solution was stirred for 10 min with complexes **4a,c,7a** and for 1 h with complexes **4d,e**, all at −78 °C. The solution was stirred for 1 h at −78 °C and then warmed to room temperature over 0.5 h for complex **7c**. Sixty−seventy milliliters of pentane was added to precipitate all of the iron salts. Neutralization of the decanted liquid by a saturated $NaHCO_3$ solution, separation, and passing of the neutralized organic layer through a short column of neutral alumina (activity 1 or 3) gave a colorless liquid. The eluant was dried over $MgSO_4$ (anhydrous) or used as is for distillation. The solvent was removed by simple distillation under atmospheric pressure or by rotary evaporation (**7c**) under reduced pressure. In most cases, this mixture was directly analyzed by ^{1}H NMR to determine the isomeric (cis/trans or endo/exo) ratios or by gas chromatography. *cis*-1,2-Diphenylcyclopropane,[23] *endo*-6-phenylbicyclo[3.1.0]hexane,[23] and *cis*-1,3,-trimethyl-2-phenylcyclopropane[23] generated from **4a** or **7a** and the corresponding alkenes were isolated by Kugelrohr distillation or by column chromatography on silica or alumina (activity III). *cis*- and *trans*-1-(*p*-methoxyphenyl)-2-phenylcyclopropanes[24] generated from **4c** or from **7c** and styrene were isolated by Kugelrohr distillation or by column chromatography on alumina (activity III). *cis*-1-(*p*-Methylphenyl)-2-phenylcyclopropane[25] and *cis*-1-(*p*-chlorophenyl)-2-phenylcyclopropane[25] generated from styrene and **4d** and **4e**, respectively, were isolated by Kugelrohr distillation. The yields and isomeric ratios are listed in Tables 1 and 2.

Cyclopropanations from Complexes 4b and 7b. General Procedure. Due to the air sensitivity of these precursors, the cyclopropanation reactions were carried out immediately after purification. A 0.15−0.27 mmol (1 equiv) sample of the precursor was dissolved in 4−8 mL of CH_2Cl_2, and 0.34−0.54 mmol (ca. 2 equiv) of styrene was added. The solution was cooled to −78 °C, and 0.16−0.33 mmol (ca. 1.1 equiv) of trimethylsilyl triflate was introduced. The color of the solution immediately changed from yellow-orange to purple. With complex **4b**, this mixture was stirred for 10 min at −78 °C and an internal standard (dodecane) added. With complex **7b**, the reaction mixture was stirred for 0.5 h at −78 °C and *n*-decane added as an internal standard. Subsequently, 50−60 mL of pentane was added, the decanted solution neutralized with saturated $NaHCO_3$ in water solution and the organic layer passed through a short column of neutral alumina (activity 1). Gas chromatographic analysis and comparison with an authentic sample indicated that only *cis*-1-methyl-2-phenylcyclopropane[23] was produced in 72% and 68% yields from **4b** and **7b**, respectively.

Cyclopropanation from Complex 4g. The cyclopropantion reaction was carried out in the similar manner as previously described for complex **4c**. An 87% yield of a 12:1 cis:trans ratio of 1-(*o*-methoxyphenyl)-2-phenylcyclopropane was prepared from complex **4c** and styrene. These cyclopropanes were characterized by spectroscopic methods. *cis*-1-(*o*-Methoxyphenyl)-2-phenylcyclopropane: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.02−6.86 (m, Ph), 6.71 (t, 1H, J = 7.8 Hz, Ph), 6.62 (d, 1H, J = 8.1 Hz, Ph), 3.61 (s, 3H, OCH_3), 2.48 (t, 2H, J = 7.4 Hz, CH), 1.39 (t, 2H, J = 7.4 Hz, CH_2); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 159.0, 139.1, 129.4, 128.2, 127.2, 127.0, 126.8, 125.2, 119.8, 110.0, (Ph), 55.3 (OCH_3), 23.4, 20.4 (CH), 10.1 (CH_2). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 86.00; H, 7.11. *trans*-1-(*o*-Methoxyphenyl)-2-phenylcyclopropane: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.33−7.14 (m, 7H, Ph), 7.05 (t, 1H, J = 7.8 Hz, Ph), 6.62 (d, 1H, J = 8.1 Hz, Ph), 3.61 (s, 3H, OCH_3), 2.14 (m, 2H, CH), 1.34−1.47 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 158.3, 143.0, 128.2, 127.4, 126.6, 126.2, 125.6,

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

(24) Hixson, S. S.; Garrett, D. W. *J. Am. Chem. Soc.* **1974**, *96*, 4872.

(25) Hoffmann, J. M.; Graham, K. J.; Rowell, Ch. F. *J. Org. Chem.* **1975**, *40*, 3005.

125.2, 120.5, 110.5 (Ph), 55.5 (OCH_3), 26.5, 21.6 (CH), 16.9 (CH_2). HR-MS calcd for $C_{16}H_{16}O$ 224.120115, found 224.124643. A white solid sample of 1-(*o*-methoxyphenyl)-2,2-diphenylcyclopropane in 61% yield was also prepared from complex **4g** and 1,1-diphenylethene and characterized by the following spectroscopic methods: ^1H NMR ($CDCl_3$, 250 MHz) δ 7.55−6.64 (m, 14H, Ph), 3.91 (s, 3H, OCH_3), 3.06 (m, 1H, CH), 2.03 (m, 1H, CH_2), 1.58 (m, 1H, CH_2); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 158.9, 147.5, 141.4, 129.9, 128.7, 128.2, 127.7, 127.3, 127.2, 126.9, 125.9, 125.7, 119.9, 109.7 (Ph), 55.30 (OCH_3), 38.3 (CPh_2), 26.3 (CH), 17.8 (CH_2). Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.92; H, 6.62.

Cyclopropanation from Complex 4h. Specific Procedure. Due to the instability of precursor **4h**, the cyclopropanation reaction was carried out immediately after purification. A 1.25 mmol (1 equiv) sample of **4h** was dissolved in 5 mL of CH_2Cl_2, cooled to −60 °C, and treated with 6.0 mmol (ca. 5 equiv) of styrene. To this solution, 2.2 mmol (ca. 1.5 equiv) of trimethylsilyl triflate was added. An immediate change in color from reddish-yellow to reddish-orange occurred. The reaction was stirred for 30 min at −60 °C, and the solvent was removed under reduced pressure. The resulting reddish oil was cooled to −60 °C, and a solution of 2.0 mmol of NaI in 5 mL of acetone was transferred to the oil. Stirring was continued for 20 min at room temperature, and the acetone was removed by rotary evaporation. Pentane was then added to the residue and transferred to a saturated $NaHCO_3$ solution. The neutralized mixture was dried over anhydrous Na_2SO_4 and filtered through a small plug of sea sand. The solvent was removed by rotary evaporation, and the crude product was eluted from a silica gel column with a 1−5% mixture of ethyl acetate in pentane.

1-Phenyl-2-(2-methyl-1-propenyl)cyclopropane[1i,26] was obtained in an isolated yield of 44%. This mixture was analyzed by both ^1H NMR and gas chromatography (column temperature 140 °C; R_t (cis) 4.35 min, R_t (trans) 5.15 min). A 1:2 cis:trans ratio of isomers was indicated.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank Frank Laib and Keith Krumnow for their technical assistance.

OM970698Y

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(26) Kuo, G. H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806.