the two schemes are plausible alternatives to currently accepted mechanisms.

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**Registry No.** Octane, 111-65-9; 1-octene, 111-66-0; Co, 7440-48-4; Ru, 7440-18-8; Ni, 7440-02-0.

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## Synthesis of Electrophilic (Dimethylcarbene)iron Complexes

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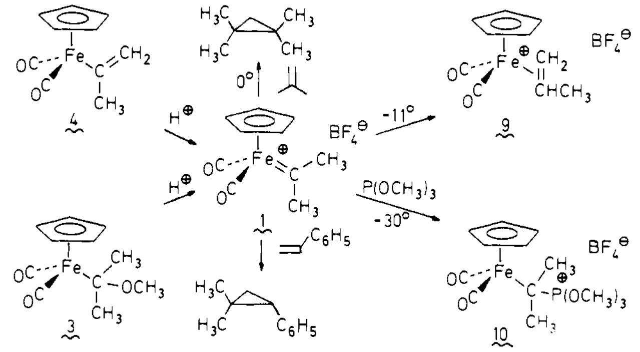
Transition-metal carbene complexes are promising reagents for electrophilic cyclopropanations.[1-3] Earlier we had shown that $(CO)_5W{=}CHC_6H_5$ could be generated at −78 °C from $(CO)_5WCH(OCH_3)C_6H_5^-$ and was a reagent for the selective formation of cis cyclopropanes.[4] We were interested in developing a reagent for transfer of the dimethylcarbene group as a route to *gem*-dimethylcyclopropanes.[5] The use of $(CO)_5W{=}C(CH_3)_2$ appeared impractical since reaction of $(CO)_5W{=}C(OCH_3)CH_3$ with *n*-BuLi gave predominantly deprotonation rather than addition[6] and since generation of $(CO)_5W{=}C(CH_3)C_6H_5$ led to rapid hydrogen migration to give $(CO)_5W$(styrene) and other products.[7] Stable dimethylcarbene complexes ($(C_5H_5)(CO)_2M{=}C(CH_3)_2$ (M = Mn, Re)) have been prepared by Fischer[8] but there has been no report of their reaction with alkenes. On the basis of work by Pettit,[9] Brookhart,[3,10] Helquist,[2,11] and Cutler,[12] $(C_5H_5)(CO)_2Fe{=}C(CH_3)_2^+$ (**1**) appeared to offer greater promise as an electrophilic cyclopropanating agent than organotungsten reagents. $(C_5H_5)(CO)_2Fe{=}CHC_6H_5^+$,[10] $(C_5H_5)(CO)_2Fe{=}CH_2^+$,[9,11] and $(C_5H_5)(CO)_2Fe{=}CHCH_3^+$ [2,3] were shown to be high-yield cyclopropanating reagents. More importantly $(C_5H_5)(CO)_2Fe{=}CHCH_3^+$, although spectroscopically undetectable, was generated from $(C_5H_5)(CO)_2FeCH(OCH_3)CH_3$,[3] from $(C_5H_5)(CO)_2FeCH[S(CH_3)(C_6H_5)]CH_3^+$,[2] or from $(C_5H_5)(CO)_2FeCH{=}CH_2$[2,12] and reacted with alkenes to give methylcyclopropanes faster than it rearranged to $(C_5H_5)(CO)_2Fe(CH_2{=}CH_2)^+$. Phosphines have been shown to stabilize iron–carbene complexes; for example, $(C_5H_5)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe{=}CH_2^+$[13] and $(C_5H_5)(CO)[(C_6H_5)_3P]Fe{=}CHCH_3^+$[3,12] are both stable enough to be observed directly by NMR at room temperature. Here we report the synthesis of the unstable dimethylcarbene complex $(C_5H_5)(CO)_2Fe{=}C(CH_3)_2^+BF_4^-$ (**1**), its reaction with isobutylene and styrene to give *gem*-dimethylcyclopropanes, and its in situ rearrangement to a propene complex. In addition, the synthesis and isolation of a stable phosphine-substituted dimethylcarbene complex $(C_5H_5)(CO)[(C_6H_5)_3P]Fe{=}C(CH_3)_2^+BF_4^-$ (**2**) is described.

Scheme I



Two approaches to dimethylcarbene complex **1** (Scheme I) were investigated: the electrophilic demethoxylation of $(C_5H_5)(CO)_2FeC(OCH_3)(CH_3)_2$ (**3**) and the protonation of the vinyl compound $(C_5H_5)(CO)_2FeC(CH_3){=}CH_2$ (**4**). In principle, addition of a methyl organometallic reagent to $[(C_5H_5)(CO)_2FeC(OCH_3)CH_3]^+BF_4^-$ (**5**)[14] would provide a simple route to **3**, but side reactions involving deprotonation[6,15] to give $(C_5H_5)(CO)_2FeC(OCH_3){=}CH_2$ (**6**) or demethylation to give $(C_5H_5)(CO)_2FeCOCH_3$ (**7**) also were anticipated. We have observed all three types of reaction with various organometallic reagents. Reaction of **5** with MeLi in $CH_2Cl_2$ at −78 °C gave a 1:1 mixture of addition product **3**[16] and deprotonation product **6**;[17] reaction of **5** with $CH_3MgI$ gave predominately demethylation product **7**; reaction of **5** with $LiCu(CH_3)_2$ in $CH_2Cl_2$–$Et_2O$ at −78 °C gave addition product **3** in 45–50% isolated yield and small, variable amounts of **6**.

The 2-methoxy-2-propyl addition product **3** is thermally unstable; upon heating to 60 °C in benzene for 8 h, **3** loses methanol and is converted to isopropenyliron compound **4**[18] in 80% isolated yield. Isopropenyliron compound **4** is more conveniently prepared in two steps by reaction of methacryloyl chloride (102 mmol) with $Na^+[(C_5H_5)Fe(CO)_2]^-$ (100 mmol) in THF at 0 °C, which gives $(C_5H_5)(CO)_2FeCOC(CH_3){=}CH_2$ (**8**) (15.9 g, 64%)[19] followed by photolysis of **8** (14.8 g, 60 mmol) in hexane–toluene with a 450-W medium-pressure mercury lamp for 2 h, which gives

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(14) **5** was prepared by treatment of $(C_5H_5)(CO)_2FeCOCH_3$ (**7**) with $(CH_3)_3O^+BF_4^-$ in $CH_2Cl_2$. **5**: $^1$H NMR ($CD_2Cl_2$) $\delta$ 5.36 (s, 5 H), 4.60 (s, 3 H), 3.15 (s, 3 H); $^{13}$C NMR (acetone-$d_6$, 0.02 M Cr(acac)$_3$) $\delta$ 336.0 (Fe=C), 209.7 (CO), 89.2 ($C_5H_5$), 87.1 ($OCH_3$), 68.7 ($CH_3$); IR ($CH_2Cl_2$) 2060, 2014 cm$^{-1}$. The related $PF_6^-$[12] and $CF_3SO_3^-$[3] salts have been prepared previously.

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(16) **3**: $^1$H NMR ($C_6D_6$) $\delta$ 4.18 (s, 5 H), 3.10 (s, 3 H), 1.64 (s, 6 H); $^{13}$C NMR ($C_6D_6$) $\delta$ 219.0 (s), 89.2 (s), 87.2 (d), 52.1 (q), 39.1 (q); IR ($CHCl_3$) 2000, 1944 cm$^{-1}$.

(17) **6** was not isolated but was observed by $^1$H NMR (($CDCl_3$) $\delta$ 4.80 (s, 5 H), 4.59 (d, $J$ = 1.5 Hz), 4.02 (d, $J$ = 1.5 Hz), 3.52 (s, 3 H)): Casey, C. P.; Tukada, H.; Miles, W. H. *Organometallics*, in press.

(18) **4**: $^1$H NMR ($CDCl_3$) $\delta$ 5.53 (br s, 1 H), 4.89 (s, 1 H), 4.73 (s, 5 H), 2.09 (s, 3 H); $^{13}$C{$^1$H} NMR ($C_6D_6$) $\delta$ 216.8, 152.3, 125.4, 85.5, 39.2; IR ($CHCl_3$) 2005, 1961, 1581 cm$^{-1}$; mp 28–31 °C; *m/e* calcd for $C_{10}H_{10}FeO_2$ 218.0029, obsd 218.0029. The conversion of **3** to **4** is apparently not an acid-catalyzed process since addition of small amounts of $KHSO_4$ did not accelerate loss of methanol.

(19) **8**: $^1$H NMR ($CDCl_3$) $\delta$ 5.37 (s, 1 H), 5.28 (s, 1 H), 4.83 (s, 5 H), 1.75 (s, 3 H); $^{13}$C{$^1$H} NMR ($C_6D_6$) $\delta$ 251.7, 215.0, 157.8, 119.1, 86.4, 18.9; IR ($CHCl_3$) 2007, 1967, 1624, 1597 cm$^{-1}$; mp 24–28 °C; *m/e* calcd for $C_{11}H_{10}FeO_3$ 245.9979, obsd 245.9979.

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**4** (9.04 g, 69%) and some $[(C_5H_5)Fe(CO)_2]_2$.

Addition of isopropenyliron compound **4** (10 mg, 0.046 mmol) in 2 mL of ether at −23 °C to a stirred solution of $HBF_4$ (~0.08 mmol) in 2 mL of ether at −23 °C led to the immediate formation of a yellow precipitate identified spectroscopically as dimethylcarbene complex **1**. Solvent was decanted, and the yellow precipitate was washed twice with ether at −23 °C and pumped dry at −23 °C. The dry precipitate was dissolved in $CD_2Cl_2$ at −23 °C, and the $^1H$ NMR of the solution was taken at −40 °C. The $^1H$ NMR consisted of singlets at $\delta$ 5.66 (5 H) and 3.73 (6 H), assigned to the cyclopentadienyl and the methyl hydrogens of dimethylcarbene complex **1**. In addition, small resonances due to ether and to propene complex **9** were also seen. Reaction of $(C_5H_5)(CO)_2FeC(OCH_3)(CH_3)_2$ (**3**) with $HBF_4$ in ether at −23 °C also gave dimethylcarbene complex **1** as a yellow precipitate identified by low-temperature NMR.

Solutions of dimethylcarbene complex **1** decompose at −11 °C in $CD_2Cl_2$ with a half-life of ~70 min to give $(C_5H_5)(CO)_2Fe(CH_2{=}CHCH_3)^+BF_4^-$ (**9**) nearly quantitatively (101 ± 5% as indicated by NMR).[20,21] In a preparative reaction, **1** prepared by $HBF_4$ addition to **4** (127 mg, 0.628 mmol) was warmed to room temperature in 0.5 mL of $CH_2Cl_2$ to give **9** (150 mg, 78%) as a yellow powder.[20]

Further evidence for **1** in solution comes from trapping **1** with $P(OCH_3)_3$. Addition of several equivalents of $P(OCH_3)_3$ to a $CD_2Cl_2$ solution of **1** at −23 °C led to the immediate disappearance of the $^1H$ NMR signals assigned to **1** and to the appearance of the new resonances assigned to $(C_5H_5)(CO)_2FeC[P(OCH_3)_3](CH_3)_2^+BF_4^-$ (**10**).[22] In a larger scale reaction, $P(OMe)_3$ (0.17 mL, 1.4 mmol) was added to a suspension of **1** (420 mg, 1.37 mmol) in 5 mL of $CH_2Cl_2$ at −78 °C. Addition of ether (25 mL) gave yellow, crystalline **10** (470 mg, 70%).[22] The addition of nucleophiles to the carbene carbon atom of metal–carbene complexes is a characteristic reaction of electrophilic carbene complexes.[12,23]

The reaction of dimethylcarbene complex **1** with isobutylene gives a mixture of 1,1,2,2-tetramethylcyclopropane and iron–propene complex **9**. When isobutylene (~0.2 M, 1.5 equiv) was added to a 1.4:1 mixture of dimethylcarbene complex **1**/propene complex **9** in $CD_2Cl_2$, a reaction occurred at 0 °C to produce 1,1,2,2-tetramethylcyclopropane ($\delta$ 0.05 (2 H), 1.02 (12 H); 33% based on **1**). In addition, signals due to propene complex **9** increased, showing that there was a competition between cyclopropanation of isobutylene and thermal decomposition of **1**. In a preparative experiment, **1** prepared by $HBF_4$ addition to **4** (0.90 g, 4.1 mmol) was stirred with isobutylene (1.3 g, 24 mmol) in 10 mL of $CH_2Cl_2$ while the solution was warmed from −40 to 2 °C over 50 min. 1,1,2,2-Tetramethylcyclopropane (20% yield) was isolated by preparative gas chromatography (UCON-5/HB-280X, 60 °C) and identified by spectral and chromatographic comparison with an authentic sample.[24] Similarly, **1** prepared by $HBF_4$ addition to **4** (140 mg, 0.64 mmol) reacted with styrene (8 mmol) in 1.5 mL of $CH_2Cl_2$ upon warming from −65 to 20 °C to give 1,1-dimethyl-2-phenylcyclopropane (45% GC yield).[25] It should be noted that isobutylene and styrene were among the most reactive alkenes in cyclopropanation by $(CO)_5W{=}CHC_6H_5$[4] and that **1** gives only modest yields of cyclopropanes even with concentrated solutions of these reactive alkenes. In the case of the less reactive 1-octene, no cylcopropanation was observed upon treatment with **1**.

We next set out to prepare $(C_5H_5)(CO)[(C_6H_5)_3P]Fe{=}C(CH_3)_2^+BF_4^-$ (**2**) with the expectation that the electron-donating triphenylphosphine ligand would increase the stability of the dimethylcarbene complex and allow its isolation at room temperature. Photolysis of **8** (1.5 g, 6.1 mmol) and $P(C_6H_5)_3$ (1.6 g, 6.1 mmol) in hexane–benzene produced $(C_5H_5)(CO)[(C_6H_5)_3P]FeC(CH_3){=}CH_2$ (**11**) (1.39 g, 51% yield).[26] Protonation of **11** (0.55 g, 1.2 mmol) with $HBF_4$ (4.0 mmol) in diethyl ether at 0 °C led to the precipitation and isolation of $(C_5H_5)(CO)[(C_6H_5)_3P]Fe{=}C(CH_3)_2^+BF_4^-$ (**2**) (0.61 g, 93%) as a yellow crystalline solid.[27] **2** is stable as a solid at room temperature and decomposes upon heating in $CD_2Cl_2$ with a half-life of ~30 min at 88 °C.[28] The $^1H$ NMR (270 MHz) of **2** consists of a singlet at $\delta$ 3.13 for the equivalent methyl groups of the dimethylcarbene ligand, a singlet at $\delta$ 5.13 for the $C_5H_5$ unit, and a multiplet at $\delta$ 7.5 for the protons of the $P(C_6H_5)_3$ ligand. The single CO ligand of **2** gives rise to an intense band at 1993 $cm^{-1}$ in the IR spectrum ($CH_2Cl_2$).

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**Registry No. 1**, 81939-62-0; **2**, 81939-64-2; **3**, 81939-65-3; **4**, 38960-10-0; **5**, 81939-66-4; **6**, 81939-67-5; **7**, 12108-22-4; **8**, 81939-68-6; **9**, 37668-14-7; **10**, 81939-70-0; **11**, 70569-00-5; 1,1,2,2-tetramethylcyclopropane, 4127-47-3; 1,1-dimethyl-2-phenylcyclopropane, 36825-29-3; isobutylene, 115-11-7; styrene, 100-42-5; $Na^+[(C_5H_5)Fe(CO)_2]^-$, 12152-20-4.

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(20) **9**: $^1H$ NMR (acetone-$d_6$) $\delta$ 5.75 (s, 5 H), 5.3 (m, 1 H), 4.01 (d, $J$ = 8 Hz, 1 H), 3.59 (d, $J$ = 14 Hz, 1 H), 1,85 (d, $J$ = 6 Hz, 3 H). **9** has previously been reported: Faller, J. W.; Johnson, B. V. *J. Organomet. Chem.* **1975**, *88*, 101.

(21) When solid **1** was warmed to room temperature for 15 min, low-temperature $^1H$ NMR indicated that decomposition to a 1:1 mixture of **1**/**9** had occurred.

(22) **10**: $^1H$ NMR ($CD_2Cl_2$) $\delta$ 4.98 (s, 5 H), 3.15 (d, $J_{P-H}$ = 10 Hz, 9 H), 1.45 (d, $J_{P-H}$ = 22 Hz, 6 H); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 214.9, 86.3, 58.7 ($J_{C-P}$ = 10 Hz), 30.0, 21.8 ($J_{C-P}$ = 100 Hz); IR ($CH_2Cl_2$) 2023, 1984 $cm^{-1}$.

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(26) **11** can also be obtained by photolysis of 4 and $P(C_6H_5)_3$. **11** has been prepared previously by hydride addition to a cationic iron–allene complex: Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73.

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(28) The $CF_3SO_3^-$ salt related to **2** is substantially less stable and decomposes with a half-life of 15 min at 40 °C.

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# ESR Study of 2-Adamantyl and 2-(Trimethylsiloxy)-2-adamantyl Radicals[1]

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In spite of a number of ESR studies on 2-adamantyl radicals in adamantane matrix[2] as well as in solution,[3] the hfs parameters have not been determined accurately to date; $\gamma$ irradiation of adamantane studied by different groups has produced conflicting results.[2,4] We now report the first detailed analysis of the ESR spectra of 2-adamantyl and 2-(trimethylsiloxy)-2-adamantyl radicals in solution. The present results offer definitive evidence that the 2-(trimethylsiloxy)-2-adamantyl radical is nonplanar and inverts at rates comparable to the difference in its $\gamma$ hydrogen hyperfine splitting constants (hfsc), while the 2-unsubstituted

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