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the two schemes are plausible alternatives to currently accepted mechanisms.

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Synthesis of Electrophilic (Dimethylcarbene)iron Complexes

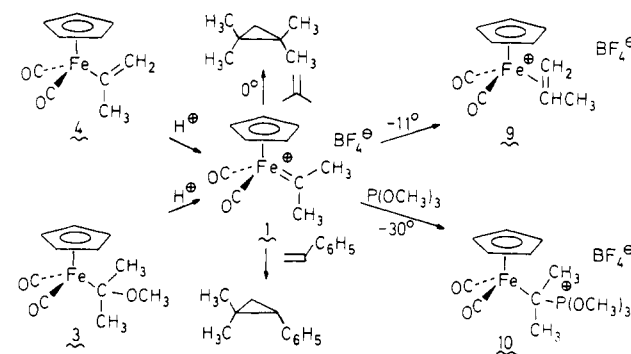
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Transition-metal carbene complexes are promising reagents for electrophilic cyclopropanations.¹⁻³ Earlier we had shown that $(\text{CO})_5\text{W}=\text{CHC}_6\text{H}_5$ could be generated at -78°C from $(\text{CO})_5\text{WCH}(\text{OCH}_3)\text{C}_6\text{H}_5^-$ 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 $(\text{CO})_5\text{W}=\text{C}(\text{CH}_3)_2$ appeared impractical since reaction of $(\text{CO})_5\text{W}=\text{C}(\text{OCH}_3)\text{CH}_3$ with *n*-BuLi gave predominantly deprotonation rather than addition⁶ and since generation of $(\text{CO})_5\text{W}=\text{C}(\text{CH}_3)\text{C}_6\text{H}_5$ led to rapid hydrogen migration to give $(\text{CO})_5\text{W}(\text{styrene})$ and other products.⁷ Stable dimethylcarbene complexes $(\text{C}_5\text{H}_5)(\text{CO})_2\text{M}=\text{C}(\text{CH}_3)_2$ ($\text{M} = \text{Mn}, \text{Re}$) have been prepared by Fischer⁸ 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 $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{C}(\text{CH}_3)_2^+$ (**1**) appeared to offer greater promise as an electrophilic cyclopropanating agent than organotungsten reagents. $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{CHC}_6\text{H}_5^+$,¹⁰ $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{CH}_2^+$,^{9,11} and $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{CHCH}_3^+$ ^{2,3} were shown to be high-yield cyclopropanating reagents. More importantly $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{CHCH}_3^+$, although spectroscopically undetectable, was generated from $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCH}(\text{OCH}_3)\text{CH}_3$,³ from $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCH}[\text{S}(\text{CH}_3)(\text{C}_6\text{H}_5)]\text{CH}_3^+$,² or from $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCH}=\text{CH}_2$,^{2,12} and reacted with alkenes to give methylcyclopropanes faster than it rearranged to $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2=\text{CH}_2)^+$. Phosphines have been shown to stabilize iron-

Scheme I



carbene complexes; for example, $(\text{C}_5\text{H}_5)[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]\text{Fe}=\text{CH}_2^+$ ¹³ and $(\text{C}_5\text{H}_5)(\text{CO})[(\text{C}_6\text{H}_5)_3\text{P}]\text{Fe}=\text{CHCH}_3^+$ ^{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 $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{C}(\text{CH}_3)_2^+\text{BF}_4^-$ (**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 $(\text{C}_5\text{H}_5)(\text{CO})[(\text{C}_6\text{H}_5)_3\text{P}]\text{Fe}=\text{C}(\text{CH}_3)_2^+\text{BF}_4^-$ (**2**) is described.

Two approaches to dimethylcarbene complex **1** (Scheme I) were investigated: the electrophilic demethoxylation of $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeC}(\text{OCH}_3)(\text{CH}_3)_2$ (**3**) and the protonation of the vinyl compound $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeC}(\text{CH}_3)=\text{CH}_2$ (**4**). In principle, addition of a methyl organometallic reagent to $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeC}(\text{OCH}_3)\text{CH}_3]^+\text{BF}_4^-$ (**5**)¹⁴ would provide a simple route to **3**, but side reactions involving deprotonation^{6,15} to give $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeC}(\text{OCH}_3)=\text{CH}_2$ (**6**) or demethylation to give $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCOCH}_3$ (**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 $\text{LiCu}(\text{CH}_3)_2$ in $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ 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 $\text{Na}^+[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ (100 mmol) in THF at 0°C , which gives $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCOC}(\text{CH}_3)=\text{CH}_2$ (**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 $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCOCH}_3$ (**7**) with $(\text{CH}_3)_3\text{O}^+\text{BF}_4^-$ in CH_2Cl_2 . **5**: ^1H NMR (CD_2Cl_2) δ 5.36 (s, 5 H), 4.60 (s, 3 H), 3.15 (s, 3 H); ^{13}C NMR (acetone- d_6 , 0.02 M $\text{Cr}(\text{acac})_3$) δ 336.0 ($\text{Fe}=\text{C}$), 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^- salts have been prepared previously.

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(16) **3**: ^1H NMR (C_6D_6) δ 4.18 (s, 5 H), 3.10 (s, 3 H), 1.64 (s, 6 H); ^{13}C NMR (C_6D_6) δ 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 ^1H NMR (CDCl_3) δ 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**: ^1H NMR (CDCl_3) δ 5.53 (br s, 1 H), 4.89 (s, 1 H), 4.73 (s, 5 H), 2.09 (s, 3 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 216.8, 152.3, 125.4, 85.5, 39.2; IR (CHCl_3) 2005, 1961, 1581 cm^{-1} ; mp 28–31 $^\circ\text{C}$; m/e calcd for $\text{C}_{10}\text{H}_{10}\text{FeO}_2$ 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**: ^1H NMR (CDCl_3) δ 5.37 (s, 1 H), 5.28 (s, 1 H), 4.83 (s, 5 H), 1.75 (s, 3 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 251.7, 215.0, 157.8, 119.1, 86.4, 18.9; IR (CHCl_3) 2007, 1967, 1624, 1597 cm^{-1} ; mp 24–28 $^\circ\text{C}$; m/e calcd for $\text{C}_{11}\text{H}_{10}\text{FeO}_3$ 245.9979, obsd 245.9979.

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 $-23^\circ C$ to a stirred solution of HBf_4 (~ 0.08 mmol) in 2 mL of ether at $-23^\circ C$ 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 $-23^\circ C$ and pumped dry at $-23^\circ C$. The dry precipitate was dissolved in CD_2Cl_2 at $-23^\circ C$, and the 1H NMR of the solution was taken at $-40^\circ C$. The 1H NMR consisted of singlets at δ 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 $-23^\circ C$ also gave dimethylcarbene complex 1 as a yellow precipitate identified by low-temperature NMR.

Solutions of dimethylcarbene complex 1 decompose at $-11^\circ C$ 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 ($101 \pm 5\%$ 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 $-23^\circ C$ 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 $-78^\circ C$. 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 $0^\circ C$ to produce 1,1,2,2-tetramethylcyclopropane (δ 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 $2^\circ C$ over 50 min. 1,1,2,2-Tetramethylcyclopropane (20% yield) was isolated by preparative gas chromatography (UCON-5/HB-28OX, $60^\circ C$) 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 $20^\circ C$ 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 cyclopropanation 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 $0^\circ C$ 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 $88^\circ C$.²⁸ The 1H NMR (270 MHz) of 2 consists of a singlet at δ 3.13 for the equivalent methyl groups of the dimethylcarbene ligand, a singlet at δ 5.13 for the C_5H_5 unit, and a multiplet at δ 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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ESR Study of 2-Adamantyl and 2-(Trimethylsiloxy)-2-adamantyl Radicals¹

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In spite of a number of ESR studies on 2-adamantyl radicals in adamantane matrix² as well as in solution,³ the hfs parameters have not been determined accurately to date; γ 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 γ hydrogen hyperfine splitting constants (hfsc), while the 2-unsubstituted

(20) 9: 1H NMR (acetone- d_6) δ 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) δ 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) δ 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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