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.

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 $(CO)_5$ -WCH(OCH₃)C₆H₅⁻ 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 $(\overline{CO})_5W = C(CH_3)_2$ appeared impractical since reaction of $(CO)_5W=C(OCH_3)CH_3$ with n-BuLi gave predominantly deprotonation rather than addition⁶ 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 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 (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 $(C_5H_5)(CO)_2Fe=$ CHCH₃⁺, although spectroscopically undetectable, was generated from $(C_5H_5)(CO)_2$ FeCH $(OCH_3)CH_3$,³ from (C_5H_5) - $(CO)_2$ FeCH $[S(CH_3)(C_6H_5)]CH_3$ ^{+,2} or from (C_5H_5) -(CO)₂FeCH=CH₂^{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-

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carbene complexes; for example, $(C_5H_5)[(C_6H_5)_2PCH_2CH_2P (C_6H_5)_2$]Fe=CH₂⁺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 (C₅H₅)(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.

Two approaches to dimethylcarbene complex 1 (Scheme I) were investigated: the electrophilic demethoxylation of $(C_5H_5)(C_5H_5)$ $O_2FeC(OCH_3)(CH_3)_2$ (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 $[(C_5H_5)(CO)_2FeC_5]$ $(OCH_3)CH_3]^+BF_4^-$ (5)¹⁴ would provide a simple route to 3, but side reactions involving deprotonation^{6,15} to give $(C_5H_5)(CO)_2$ - $FeC(OCH_3) = CH_2$ (6) or demethylation to give $(C_5H_5)(CO)_2$ - $FeCOCH_3$ (7) also were anticipated. We have observed all three types of reaction with various organometallic reagents. Reaction of 5 with MeLi in CH₂Cl₂ at -78 °C gave a 1:1 mixture of addition product 3^{16} and deprotonation product 6^{17} reaction of 5 with CH₃MgI gave predominately demethylation product 7; reaction of 5 with LiCu(CH₃)₂ in CH₂Cl₂-Et₂O 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 (C₅H₅)(CO)₂FeCOC(CH₃)=CH₂ (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

(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: ¹H NMR $(CD_2Cl_2) \delta$ 5.36 (s, 5 H), 4.60 (s, 3 H), 3.15 (s, 3 H); ¹³C NMR (acetone- d_6 , 0.02 M Cr(acac)₃) δ 336.0 (Fe=C), 209.7 (CO), 89.2 (C₅H₅), 87.1 (OCH₃), 68.7 (CH₃); IR (CH₂Cl₂) 2060, 2014 cm⁻¹. The related PF₆⁻¹² and CF₃SO₃⁻³ salts have been prepared previously.

(15) Davison, A.; Reger, D. L. J. Am. Chem. Soc. 1972, 94, 9237. (16) 3: 1 H NMR (C₆D₆) δ 4.18 (s, 5 H), 3.10 (s, 3 H), 1.64 (s, 6 H); 13 C NMR (C₆D₆) δ 219.0 (s), 89.2 (s), 87.2 (d), 52.1 (q), 39.1 (q); IR (CHCl₃) 2000, 1944 cm⁻¹

(17) 6 was not isolated but was observed by ¹H NMR ((CDCl₃) δ 4.80 (s,

(1) **b** was not isolated bit was observed by 11 HAR ((CDCl₃) 0.50 (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 (CDCl₃) δ 5.53 (br s, 1 H), 4.89 (s, 1 H), 4.73 (s, 5 H), 2.09 (s, 3 H); ¹³C[¹H] NMR (C₆D₆) δ 216.8, 152.3, 125.4, 85.5, 39.2; IR (CHCl₃) 2005, 1961, 1581 cm⁻¹; mp 28–31 °C; m/e calcd for C₁₀H₁₀FeO₂ 218.0029, obsd 218.0029. The conversion of 3 to 4 is apparently not an acid-catalyzed process since addition of small amounts of KHSO4 did not

(19) 8: ¹H NMR (CDCl₃) δ 5.37 (s, 1 H), 5.28 (s, 1 H), 4.83 (s, 5 H), 1.75 (s, 3 H); ¹³C[¹H] NMR (C₆C₆) δ 251.7, 215.0, 157.8, 119.1, 86.4, 18.9; IR (CHCl₃) 2007, 1967, 1624, 1597 cm⁻¹; mp 24–28 °C; *m/e* calcd for C₁₁H₁₀FeO₃ 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 HBF₄ (~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 CD₂Cl₂ 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 HBF₄ 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 HBF₄ 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 carbone carbon atom of metal-carbone 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 ironpropene 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 (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 HBF₄ addition to 4 (0.90 g, 4.1 mmol) was stirred with isobutylene (1.3 g, 24 mmol) in 10 mL of CH₂Cl₂ 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-28OX, 60 °C) and identified by spectral and chromatographic comparison with an authentic sample.²⁴ Similarly, 1 prepared by HBF₄ 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

(20) 9: ¹H NMR (acetone- d_{5}) 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, lowtemperature ¹H NMR indicated that decomposition to a 1:1 mixture of 1/9 had occurred

had occurred. (22) 10: ¹H NMR (CD₂Cl₂) 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); ¹³Cl¹H} NMR (CD₂Cl₂) δ 214.9, 86.3, 58.7 ($J_{C-P} = 10$ Hz), 30.0, 21.8 ($J_{C-P} = 100$ Hz); IR (CH₂Cl₂) 2023, 1984 cm⁻¹. (23) Kreissi, F. R.; Fischer, E. O.; Kreiter, C. G.; Fischer, H. Chem. Ber.

1973, 106, 1262.

(24) An authentic sample of 1,1,2,2-tetramethylcyclopropane was prepared by addition of ICH₂ZnI to (CH₃)₂C=C(CH₃)₂: Rawson, R. J.; Harrison, I. T. J. Org. Chem. 1970, 35, 2057. Simmons, H. E.; Smith, R. D. J. Am. Chem. Soc. 1959, 81, 4256.

(25) 1,1-Dimethyl-2-phenylcyclopropane was isolated by preparative gas chromatography (20% SE-30, 135 °C) and identified by spectral and chromatographic comparison with an authentic sample⁴ prepared by reaction of 1-phenyl-3-methylbut-2-en-1-one with hydrazine and NaOH.

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 (C₅H₅)(CO)[(C₆-H₅)₃P]FeC(CH₃)=CH₂ (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(CH₃)₂+BF₄⁻ (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 δ 3.13 for the equivalent methyl groups of the dimethylcarbene ligand, a singlet at δ 5.13 for the C₅H₅ unit, and a multiplet at δ 7.5 for the protons of the P(C₆H₅)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⁺[(C₅H₅)Fe(CO)₂]⁻, 12152-20-4.

poses with a half-life of 15 min at 40 °C.

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

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