Scheme II. In summary, this study has provided another striking example of the unique capabilities of chiral transition-metal centers in stoichiometric asymmetric synthesis and foreshadows a much broader range of reactions that will be possible with $(\eta\text{-}C_5H_5)$-$Re(NO)(PPh_3)$ systems.

Supplementary Material Available: Characterization of **1a–c** and **2a–c** (5 pages).[10] Ordering information is given on any current masthead page.

# Hydrocarbation: Addition of the C–H Bond of a Cationic Bridging Iron–Methylidyne Complex to Alkenes

Charles P. Casey* and Paul J. Fagan†

Department of Chemistry, University of Wisconsin Madison, Wisconsin 53706

Received March 25, 1982

The addition of element-to-hydrogen bonds to alkenes is a fundamental step in many catalytic and stoichiometric transformations.[1] The synthetic utility of this general reaction type is exemplified by the hydroboration[2] and hydrozirconation[3] reactions. Here we report that the bridging iron–methylidyne complex $[cis\text{-}Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)]^+PF_6^-$ (**1**)[4] (Cp = η-C_5H_5) reacts with a variety of alkenes to add the methylidyne *carbon–hydrogen* bond across the carbon–carbon double bond. This "hydrocarbation" reaction provides an unprecedented method for carbon–carbon bond formation. Metal-bound methylidyne ligands have been proposed as intermediates in the catalytic reduction of CO,[5] and addition of a methylidyne C–H bond to an alkene is a potential homologation step in these processes.

The cationic iron–methylidyne complex **1** can be viewed as a relatively stable secondary carbonium ion stabilized by electron donation from the two iron centers.[6] Complex **1** is synthesized
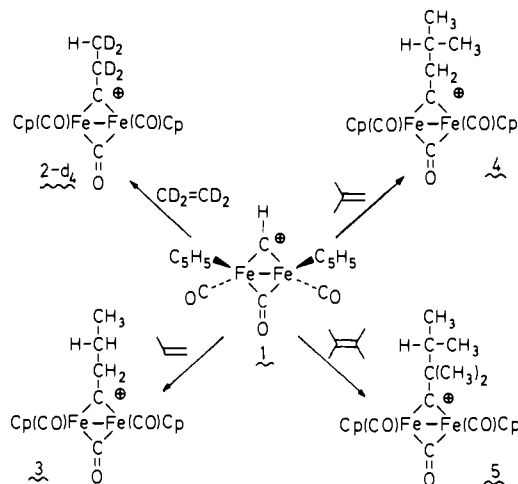
from the bridging methylene complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$[4,7] by hydride abstraction with $(C_6H_5)_3C^+PF_6^-$ and is consequently a more stable cation than the triphenylmethyl cation. In spite of its relative thermodynamic stability, the methylidyne complex **1** is a very reactive electrophile and forms stable adducts with $N(CH_3)_3$, $(CH_3)_3CO^-$, and CO by addition of the nucleophile to the methylidyne carbon[7b,8] as well as reacting with alkenes as described here.

When a slurry of the red iron–methylidyne complex **1** in CH_2Cl_2 was stirred under an ethylene atmosphere and warmed from –78 °C to room temperature, a maroon crystalline product was formed. Evaporation of solvent in vacuo followed by recrystallization of the product from acetone–ether gave the propylidyne complex $[cis\text{-}Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_3)]^+PF_6^-$ (**2**) in 65% yield.[9,10] The spectroscopic properties of **2** are comparable to those of related cationic iron carbyne complexes which were first prepared by Nitay et al.[6a]

The reaction of **1** with excess ethylene in CD_2Cl_2 at –20 °C was monitored by ^1H NMR spectroscopy. The time for 50% conversion of **1** to **2** was approximately 15 min at –20 °C, and no detectable intermediates or side reactions were noted. Furthermore, we have never observed further reaction of alkenes with the alkylidyne hydrocarbation products (vide infra).[11] Thus, the methylidyne C–H bond of **1** has unique reactivity not possessed by the C–CH_2CH_3 bond of **2**; similar observations have been made in the cases of hydroboration and hydrozirconation.[2,3]

The reaction of **1** with CD_2=CD_2 (>95% deuterated) in CD_2Cl_2 gives **2-d_4** in which >90% of the proton originally bonded to the methylidyne carbon of **1** has been delivered to the methyl group of **2-d_4** as determined by ^1H NMR spectroscopy.[12] This establishes that **2** is formed by 1,2-addition of carbon and hydrogen to ethylene and rules out the possibility that **2** arises by electrophilic addition of **1** to ethylene followed by two sequential 1,2 hydrogen shifts in an intermediate such as **I**.

† National Science Foundation Postdoctoral Fellow.

(1) See for example: (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980; Chapters 2–4. (b) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 291–294, 537–544. (c) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079–2090 and references therein.

(2) (a) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Synthesis via Boranes"; Wiley-Interscience: New York, 1975. (b) Pelter, A.; Smith, K. "Comprehensive Organic Chemistry"; Jones, D. N., Ed.; Pergamon Press: Oxford, 1979; Vol. III, pp 695–790.

(3) (a) Schwarz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333–340. (b) Carr, D. B.; Yoshifuji, M.; Shoer, L. I.; Gall, D. S.; Schwarz, J. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 127.

(4) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134–1136.

(5) (a) Shriver, D. F. *ACS Symp. Ser.* **1981**, *152*, 1–18. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–490. (c) Ponec, V. *Catal. Rev.—Sci. Eng.* **1978**, *18*, 151–171. (d) Biloen, P.; Helle, J. N.; Sachtler, W. M. H. *J. Catal.* **1979**, *58*, 95–107. (e) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103.

(6) (a) Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620–3622. (b) Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plaas, D.; Taylor, G. E. *J. Organomet. Chem.* **1980**, *198*, C43–C49.

(7) (a) Korswagen, R.; Alt, R.; Speth, D.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1049–1051. (b) Kao, S. C.; Lu, P. P. Y.; Pettit, R., submitted for publication and private communication.

(8) Fagan, P. J.; Casey, C. P., unpublished results.

(9) **2**: ^1H NMR (acetone-d_6) δ 5.66 (10 H, s, Cp), 5.46 (2 H, q, $J = 6.6$ Hz, CH_2), 1.81 (3 H, t, $J = 6.6$ Hz, CH_3); $^{13}C\{^1H\}$NMR (acetone-d_6) δ 504.7 (μ-C^+), 252.4 (μ-CO), 208.9 (CO), 93.1 (Cp), 70.6 (CH_2), 16.2 (CH_3); IR (Nujol) 2040 (s), 2005 (m), 1855 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{15}O_3PF_6Fe_2$: C, 37.54; H, 2.95; P, 6.05. Found: C, 37.88; H, 3.22; P, 5.99.

(10) The complex $[cis\text{-}Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)]^+BF_4^-$, which has been characterized by X-ray crystallography and contains cis-carbonyl ligands, has an IR spectrum similar to that of **2**.[6b]

(11) A similar lack of reactivity has been noted for the complex [cis-$Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)]^+BF_4^-$, which will only react with propene photochemically: Dyke, A. F.; Guerchais, J. E.; Knox, S. A. R.; Roue, J.; Short, R. L.; Taylor, G. E.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 537–538.

(12) **2-d_4**: ^1H NMR (acetone-d_6) δ 5.66 (10 H, s, Cp), 1.75 (1 H, br s, CD_2H). Integration of the resonance due to the CD_2H group relative to the area under the expected region for a CDH resonance sets a lower limit of 90% for incorporation of the proton into the CD_2H group.

Communications to the Editor

J. Am. Chem. Soc., Vol. 104, No. 18, 1982 4951
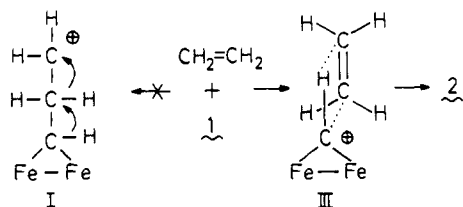
Complex **1** reacts with propene and isobutylene regiospecifically to add the electron-deficient carbon of **1** to the least substituted carbon of the alkene and the hydrogen to the most substituted alkene carbon. Thus, the regiochemistry of C–H addition to alkenes in hydrocarbation is the same as that observed for B–H addition in hydroboration reactions.[2] Reaction of **1** with propene and isobutylene gave [cis-Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CCH$_2$CH$_2$CH$_3$)]$^+$PF$_6^-$ (**3**) and {cis-Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-CCH$_2$CH(CH$_3$)$_2$]}$^+$PF$_6^-$ (**4**) in 72% and 70% isolated yields, respectively.[13a,b]

The reaction of **1** with 2,3-dimethyl-2-butene gives {cis-Cp$_2$Fe$_2$(CO)$_2$(μ-CO)[μ-CC(CH$_3$)$_2$C(CH$_3$)$_2$H]}$^+$PF$_6^-$ (**5**) in 74% yield.[13c] The ^{13}C chemical shift of the bridging carbyne carbon of **5** is δ 526.4 and is the lowest field ^{13}C chemical shift reported for a diamagnetic complex. The formation of **5** again demonstrates that hydrocarbation involves a 1,2-addition of a C–H bond across an alkene and shows that hydrocarbation of sterically crowded alkenes is possible.

In an attempt to determine the stereochemistry of hydrocarbation, we examined the reaction of the methylidyne complex **1** with 1-methylcyclohexene. However, we were surprised to find that none of the expected hydrocarbation product **6** was obtained. Instead, a complex rearrangement occurs to give the cationic μ-vinyliron complex [cis-Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(trans-μ-CH=CH—C(CH$_3$)CH$_2$CH$_2$CH$_2$CH$_2$)]$^+$PF$_6^-$ (**7**).[14] Variable-temperature ^{1}H and ^{13}C NMR studies establish a fluxional process in which the μ-vinyl group migrates from one iron center to the other.[15]
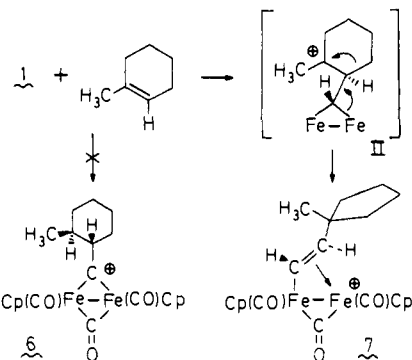
The ring contraction to give **7** is reminiscent of carbonium ion skeletal rearrangements[16] and might proceed via the intermediate carbocation II. Thus carbon–carbon bond migration in II would lead directly to the π-bonded μ-vinyl cation **7**. It seems unlikely that a similar cation (I) could be involved in the hydrocarbation of ethylene, since this would involve formation of a primary carbonium ion center. Moreover, if the addition of **1** to 2,3-dimethyl-2-butene to give **5** proceeded through a cation, then products arising from methyl group migration might have been expected but were not observed.

One possible mechanism for hydrocarbation is concerted 1,2-addition of the methylidyne C–H bond to the alkene proceeding via a four-center transition state in which the C–H bond is aligned along the C=C bond of the alkene as in III.[17] For alkenes such as ethylene, propene, 3,3-dimethyl-1-butene, styrene, isobutylene, and 2,3-dimethyl-2-butene where the least substituted carbon of the alkene is symmetrically substituted, we have seen clean hydrocarbation. However, for 1-methylcyclohexene and other alkenes,[19] which are unsymmetrically substituted at the least substituted carbon of the alkene, a carbocation-like rearrangement to give μ-vinyl products was observed. Possibly, unsymmetrical substitution sterically interferes with the alignment of the C–H bond along the C=C bond, which is required for hydrocarbation, and reaction occurs via a conformation in which the C–H and C=C bonds are not aligned. This could lead to the formation of a cation such as II and the observed rearrangement product **7**.

We are continuing to examine the mechanistic features of this hydrocarbation reaction and the competing rearrangement processes. Whatever the mechanistic details, the feasibility of formally inserting an alkene into a C–H bond has been demonstrated, and many significant parallels to hydroboration chemistry have been established.

(13) (a) **3**: ^{1}H NMR (acetone-d_6) δ 5.68 (10 H, s, Cp), 5.54 (2 H, t, J = 7 Hz, CCH$_2$), 2.32 (2 H, sextet, J = 7 Hz, CH$_2$CH$_3$), 1.23 (3 H, t, J = 7 Hz, CH$_3$). ^{13}C{^{1}H} NMR (acetone-d_6) δ 503.5 (μ-C$^+$), 252.4 (μ-CO), 207.8 (CO), 93.4 (Cp), 79.6 (C$^+$CH$_2$), 26.3 (CH$_2$CH$_3$), 14.3 (CH$_3$). IR (Nujol) 2038 (s), 2003 (m), 1855 (s) cm^{-1}. Anal. Calcd for C$_{17}$H$_{17}$O$_3$PF$_6$Fe$_2$: C, 38.82; H, 3.26; P, 5.89. Found: C, 38.78; H, 3.47; P, 5.51. (b) **4**: ^{1}H NMR (acetone-d_6) δ 5.66 (10 H, s, Cp), 5.46 (2 H, d, J = 7 Hz, CH$_2$), 3.01 (1 H, nonet, J = 7 Hz, CH), 1.13 (6 H, d, J = 7 Hz, CH$_3$); ^{13}C{^{1}H} NMR (acetone-d_6) δ 504.6 (μ-C$^+$), 252.7 (μ-CO), 208.4 (CO), 93.6 (Cp), 86.9 (CH$_2$), 35.9 (CH), 23.5 (CH$_3$); IR (Nujol) 2040 (s), 2008 (m), 1850 (s) cm^{-1}. Anal. Calcd for C$_{18}$H$_{19}$O$_3$PF$_6$Fe$_2$: C, 40.04; H, 3.55; P, 5.74. Found: C, 39.97; H, 3.65; P, 5.78. (c) **5**: ^{1}H NMR (acetone-d_6) δ 5.79 (10 H, s, Cp), 3.19 (1 H, septet, J = 7 Hz, CH), 1.81 (6 H, s, J = 7 Hz, CC(CH$_3$)$_2$), 1.00 (6 H, d, J = 7 Hz, CH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (acetone-d_6) δ 526.4 (μ-C$^+$), 252.4 (μ-CO), 209.3 (CO), 93.8 (Cp), 80.7 (C(CH$_3$)$_2$), 42.9 (CH(CH$_3$)$_2$), 27.1 (CH$_3$), 20.2 (CH$_3$); IR (Nujol) 2032 (s), 2002 (m), 1857 (s) cm^{-1}. Anal. Calcd for C$_{20}$H$_{23}$O$_3$PF$_6$Fe$_2$: C, 42.29; H, 4.08; P 5.45. Found: C, 42.49; H, 4.30; P, 5.23.

(14) **7**: ^{1}H NMR (CD$_2$Cl$_2$, 30 °C) δ 11.59 (1 H, d, J = 12.5 Hz, FeCH=CH), 5.33 (10 H, s, Cp), 3.68 (1 H, d, J = 12.5 Hz, FeCH=CH), 1.88 (6 H, br m, cyclopentyl), 1.62 (2 H, br m, cyclopentyl), 1.24 (3 H, s, CH$_3$); ^{1}H NMR (CD$_2$Cl$_2$, –70 °C) δ 11.51 (1 H, d, J = 12.5 Hz, FeCH=CH), 5.44 (5 H, s, Cp), 5.16 (5 H, s, Cp), 3.55 (1 H, d, J = 12.5 Hz, FeCH=CH), 1.88 (3 H, br m, cyclopentyl), 1.73 (3 H, br m, cyclopentyl), 1.58 (1 H, br m, cyclopentyl), 1.46 (1 H, br m, cyclopentyl), 1.12 (3 H, s, CH$_3$); ^{13}C{^{1}H} NMR (acetone-d_6, 0 °C) δ 242.0 (μ-CO), 212.3 (CO), 166.3 (FeCH=CH, J_{CH} = 154 Hz from gated decoupled spectrum), 114.3 (FeCH=CH, J_{CH} = 147 Hz from gated decoupled spectrum), 90.8 (Cp), 51.0 (CCH$_3$), 41.0 (CH$_2$), 27.2 (CH$_3$), 25.8 (CH$_2$); ^{13}C{^{1}H} NMR (acetone-d_6, –82 °C) δ 243.5 (μ-CO), 215.8 (CO), 209.0 (CO), 167.4 (FeCH=CH), 112.1 (FeCH=CH), 93.0 (Cp), 89.1 (Cp), 50.8 (CCH$_3$), 44.0 (CH$_2$), 36.0 (CH$_2$), 27.5 (CH$_3$), 26.2 (CH$_2$), 25.4 (CH$_2$); IR (CH$_2$Cl$_2$) 2027 (s), 2002 (m), 1868 (m) cm^{-1}. Anal. Calcd for C$_{21}$H$_{23}$O$_3$PF$_6$Fe$_2$: C, 43.48; H, 4.00; P, 5.34. Found: C, 43.35; H, 3.84; P, 5.22. Coalescence of the Cp proton resonances of **7** occurs at –42 °C. τ_c = 5.99 × 10^{-3} s; $\Delta G^\ddagger$ (–42 °C) = 11.0 kcal mol^{-1}.

(15) Fluxional μ-vinyliron complexes have previously been reported:[7b] Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1980**, 441–442. Nesmeyanov, A. N.; Rybinskaya, M. I.; Rybin, L. V.; Kaganovich, V. S.; Petrovskii, P. V. *J. Organomet. Chem.* **1971**, *31*, 257–267.

(16) (a) Saunders, M.; Chandrasekhar, J.; Von Ragué Schleyer, P. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 1–53 and references therein. (b) Olah, G. A. "Carbocations and Electrophilic Reactions"; Wiley: New York, 1974; pp 42–43, 116–122.

(17) It should be noted that III is similar to an edge-protonated cyclopropane.[16a,18] Other possible intermediates in the hydrocarbation reaction include corner-protonated cyclopropanes[16a,18] arising from bonding of both alkene carbons to the methylidyne carbon and metallacyclic compounds arising from addition of the alkene to the methylidyne carbon and to iron.

(18) Saunders, M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *Acc. Chem. Res.* **1973**, *6*, 53–59.

(19) The reaction of **1** with cis-2-butene, trans-2-butene, cyclohexene, cyclopentene, and 1-methylcyclopentene yields the expected hydrocarbation products as well as μ-vinyl cationic products resulting from migration of a *hydrogen* atom: Fagan, P. J.; Casey, C. P., unpublished results.