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Addition of Carbon Nucleophiles to (μ-Alkenyl)diiron Complexes

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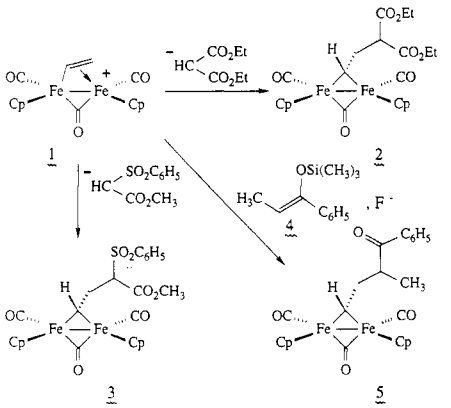
The reaction of μ-vinyl complex $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)\}^+PF_6^-$ (1) with the sodium salt of diethyl malonate gave the μ-alkylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH_2CH(CO_2CH_2CH_3)_2]$ (2) in 86% yield. 1 also reacted with the sodium salt of methyl (phenylsulfonyl)acetate to produce μ-alkylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH_2CH(CO_2CH_3)(SO_2C_6H_5)]$ (3) in 88% yield. The reaction of μ-alkenyl complex $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH_2CH_2CH_3]\}^+CF_3SO_3^-$ (6) with the sodium salt of diethyl malonate gave alkylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)\{\mu\text{-}CHCH[CH(CO_2CH_2CH_3)_2]CH_2CH_2CH_3\}$ (7) in 64% yield. Addition of $Li(CH_3CuCN)$ to 1 produced alkyl-substituted alkylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2CH_3)$ (10) in 100% yield.

The ability of the $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)$ system to stabilize both neutral and cationic bridging hydrocarbyl groups makes these diiron complexes very useful in the construction of new carbon–carbon bonds. Cationic diiron complexes possessing the μ-alkenyl ligand such as 1 were prepared by Pettit by hydride abstraction from the neutral μ-ethylidene complex.[1] More substituted μ-alkenyl complexes are readily prepared by thermal rearrangement of μ-alkylidyne complexes[2] or by acidification of the complexes $(C_5H_5)_2Fe_2(CO)(\mu\text{-}CO)[\mu\text{-}C(O)C_2R_2]$.[3] Preliminary investigations indicated that μ-alkenyl complexes are readily attacked by simple nucleophiles such as H^-,[3] CH_3Li, *n*-BuLi, CH_3OH,[1] and LiC_6H_4-*p*-CH_3[4] to generate neutral diiron alkylidene complexes. Here we report that μ-alkenyl complexes react with a broad range of functionalized carbon nucleophiles to produce new neutral diiron alkylidene complexes.

When a suspension of $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)\}^+PF_6^-$ (1) (100 mg, 0.201 mmol) was stirred with the sodium salt of diethyl malonate (1 equiv) in THF at room temperature for 4.5 h, the addition of malonate to the β-vinyl carbon produced the μ-alkylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH_2CH(CO_2CH_2CH_3)_2]$ (2). Evaporation of THF under vacuum, extraction of the residue with CH_2Cl_2, filtration, and precipitation with hexane produced 2 in 86% yield as orange-red microcrystals. The key ^1H NMR spectral feature of 2 is the low-field chemical shift of the μ-CH proton at δ 11.45. Only a single isomer was observed. The cis arrangement of the Cp and terminal CO ligands of 2 is assigned on the basis of the observation of a single C_5H_5 resonance in both the ^1H and ^{13}C NMR spectra. This assignment was confirmed by the observation of a single terminal CO resonance at δ 213.9 in the ^{13}C NMR and by the appearance of infrared bands at 1989 (s) and 1945 (w) cm^{-1} consistent with cis terminal CO ligands. The stereochemistry of the alkyl group on the bridging carbon relative to the Cp groups is not known. The less crowded isomer with the alkyl group trans to the Cp groups is shown in Scheme I.

Similar reactions of μ-vinyl complex 1 with other carbon nucleophiles were observed. Reaction of 1 equiv of the sodium salt of methyl(phenylsulfonyl)acetate with a suspension of 1 in THF occurred over 1 h at room temperature to give μ-alkylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH_2CH(CO_2CH_3)(SO_2C_6H_5)]$ (3) as a single diastereomer in 88% yield. No reaction between 1 and the enol silyl ether (*Z*)-trimethyl[(1-phenyl-1-propenyl)oxy]-silane (4) was observed even at 70 °C in THF. However, reaction of enol silyl ether 4 with 1 in the presence of 2 equiv of tetrabutylammonium fluoride led to formation of the μ-alkylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH_2CH(CH_3)COC_6H_5]$ (5) as a single diastereomer in 42% yield after chromatography. The reactivity of these (μ-alkenyl)diiron complexes toward nucleophiles is apparently substantially less than that of cobalt-stabilized carbocations generated by Lewis acid addition to cobalt-complexed propargylic ethers.[5] These cobalt systems react stereoselectively with enol silyl ethers in the absence of added fluoride.

Scheme I



Alkyl-substituted μ-alkenyl ligands also reacted with carbon nucleophiles. Addition of the sodium salt of diethyl malonate to the μ-pent-1-enyl complex $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH_2CH_2CH_3]\}^+CF_3SO_3^-$ (6) led to formation of neutral μ-alkylidene $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)\{\mu\text{-}CHCH[CH(CO_2CH_2CH_3)_2]CH_2CH_2CH_3\}$ (7) in 64% yield. Likewise, addition of the sodium salt of methyl (phenylsulfonyl)acetate to 6 gave $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)\{\mu\text{-}CHCH[CH(CO_2CH_3)(SO_2C_6H_5)]CH_2CH_2CH_3\}$ (8) in 60% yield as a 1:1 mixture of diastereomers. Addition of basic nucleophiles to complex 6 occurs in preference to deprotonation of a γ-proton which would have produced the neutral μ-pent-2-enylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH{=}CHCH_2CH_3)$ (9). Deprotonation of 6 occurs with $N(CH_3)_3$ to produce 9.[6]

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(2) Casey, C. P.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 7197.
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(4) Casey, C. P.; Marder, S. R.; Adams, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 7700.
(5) Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128.
(6) Similar transformations involving conversion of μ-alkenyl complexes to μ-vinyl carbene complexes have been reported: (a) Casey, C. P.; Woo, L. K.; Fagan, P. J.; Palermo, R. E.; Adams, B. R. *Organometallics* **1987**, *6*, 447. (b) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053. (c) Casey, C. P.; Meszaros, M. W.; Marder, S. R.; Bly, R. K.; Fagan, P. J. *Organometallics* **1986**, *5*, 1873.

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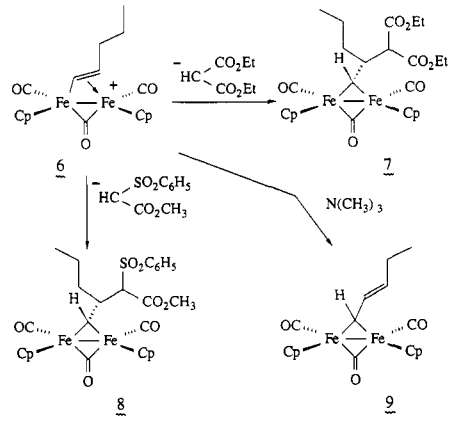
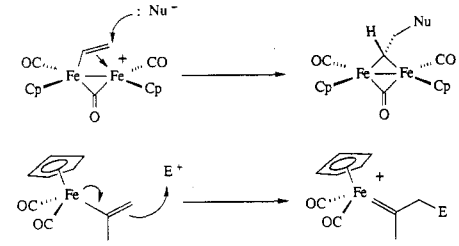


Pettit reported that reactions of complex **1** with organolithium reagents (RLi) produces the corresponding $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2R)$ complexes (**10**, R = CH_3, 82%; **11**, R = *n*-Bu, 80%).[1] We have found that the cuprate formed from 1 equiv each of CuCN and CH_3Li is the method best suited to transfer CH_3^- to μ-alkenyl complexes. Addition of $Li(CH_3CuCN)$ to **1** and **6** produced alkyl-substituted alkylidene complexes **10** in 100% isolated yield and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH(CH_3)\text{-}CH_2CH_2CH_3]$ (**12**) in 98% isolated yield.

There is an interesting reactivity difference between neutral monoiron and cationic diiron μ-alkenyl complexes. Neutral monoiron alkenyl complexes react with *electrophiles* at the β-vinyl carbon to produce cationic monoiron alkylidene complexes.[7,8] In contrast, cationic diiron μ-alkenyl complexes react wiith *nucleophiles* to produce neutral diiron μ-alkylidene complexes.



Taking advantage of this new class of efficient, versatile carbon–carbon bond-forming reaction in organic syntheses awaits the development of efficient procedures for cleavage of the μ-alkylidene ligand from the diiron complexes. Cleavage reactions are under active investigation.

Experimental Section

^1H NMR spectra were normally obtained on a Bruker WP200, WP270, or AM500 spectrometer. ^{13}C NMR spectra from samples containing 0.07 M $Cr(acac)_3$ as a shiftless relaxation agent were obtained on a Bruker AM 500 spectrometer (126 MHz). Infrared spectra were measured on a Beckman 4230 or Mattson Polaris (FT) spectrometer. Mass spectra were determined on a Kratos MS-80. Elemental analyses[9] were performed by Galbraith Laboratories, Inc. (Knoxville, TN) or by Schwarzkopf Laboratories (Woodside, NY).

Diethyl ether, THF, and hexane were distilled immediately prior to use from purple solutions of sodium and benzophenone. CH_2Cl_2 and CD_2Cl_2 were dried over CaH_2. $(CD_3)_2CO$ was dried over B_2O_3. Air-sensitive materials were manipulated in an inert-atmosphere glovebox or by standard Schlenk techniques.

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH_2CH(CO_2CH_2CH_3)_2]$ (2). A mixture of **1** (100 mg, 0.20 mmol) and the sodium salt of diethyl malonate (36 mg, 0.20 mmol) in 30 mL of THF was stirred at room temperature for 4.5 h. Solvent was evaporated under vacuum, and the residue was dissolved in 10 mL of CH_2Cl_2 and filtered. Addition of hexane precipitated **2**, which was filtered, washed with 2 × 5 mL of hexane, and isolated as orange-red microcrystals (89 mg, 86%): ^1H NMR (270 MHz, acetone-d_6) δ 11.45 (t, J = 8.3 Hz, μ-CHR), 4.89 (s, 10 H, C_5H_5), 4.26 (apparent qd with peak separations of 7.2 and 1.2 Hz, AB portion of ABX_3, CH_2CH_3), 3.88 (t, J = 7.6 Hz, μ-$CHCH_2CH$), 3.58 (t, J = 8.0, μ-$CHCH_2$), 1.29. (t, J = 7.1 Hz, 6 H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6, 0.07 M $Cr(acac)_3$) δ 271.6 (μ-CO), 213.9 (CO), 169.8 ($CO_2CH_2CH_3$), 169.4 (μ-CHR), 88.4 (C_5H_5), 61.6 ($COCH_2CH_3$), 58.2 (μ-$CHCH_2CH$), 54.5 (μ-$CHCH_2$), 14.5 (CH_3); IR (CH_2Cl_2) 1989 (s), 1945 (w), 1785 (m), 1730 (w), 1610 (w) cm^{-1}; HRMS calcd for M − CO $C_{21}H_{24}Fe_2O_6$ 484.0271, found 484.0262.

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH_2CH(CO_2CH_3)(SO_2C_6H_5)]$ (3). A mixture of **1** (200 mg, 0.40 mmol) and the sodium salt of methyl (phenylsulfonyl)acetate (94 mg, 0.40 mmol) in 30 mL of THF was stirred at room temperature for 1 h. The solution was filtered, and THF was evaporated under vacuum. The residue was dissolved in 10 mL of CH_2Cl_2, and addition of hexane precipitated **3** which was filtered and isolated as a red powder (200 mg, 88%): ^1H NMR (500 MHz, acetone-d_6) δ 11.11 (dd, J = 10.8, 5.7 Hz, μ-CHR), 7.93 (d, J = 7.3 Hz, *o*-C_6H_5), 7.75 (t, J = 7.4 Hz, *p*-C_6H_5), 7.65 (t, J = 7.9 Hz, *m*-C_6H_5), 4.87 (s, C_5H_5), 4.84 (s, C_5H_5), 4.54 (dd, J = 11.3, 3.2 Hz, μ-$CHCH_2CH$), 3.82 (s, CO_2CH_3), 3.81 (ddd, J = 13.9, 11.4, 5.7 Hz, μ-$CHCHH$), 3.35 (ddd, J = 13.9, 10.8, 3.2 Hz, μ-$CHCHH$); $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6, 0.07 M $Cr(acac)_3$) δ 270.7 (μ-CO), 213.6, 213.2 (CO), 167.3 (CO_2CH_3), 164.2 (μ-CHR), 139.1 (ipso-C_6H_5), 135.0 (*p*-C_6H_5), 130.0, 129.8 (*o*-, *m*-C_6H_5), 88.5, 88.4 (C_5H_5), 76.0 (μ-$CHCH_2CH$), 53.2 (CO_2CH_3), 51.9 (μ-$CHCH_2$); IR (CH_2Cl_2) 1980 (s), 1943 (w), 1786 (m) cm^{-1}; HRMS calcd for M − CO $C_{23}H_{22}Fe_2O_6S$ 537.9835, found 537.9835.

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH_2CH(CH_3)COC_6H_5]$ (5). A solution of $(C_4H_9)_4N^+F^-$ (200 mg, 0.76 mmol) and enol silyl ether **4** (173 mg, 0.84 mmol) in THF (5 mL) was cooled to −78 °C and added to a suspension of **1** (200 mg, 0.40 mmol) in THF (30 mL) at −78 °C. The suspension was stirred for 0.5 h at room temperature. THF was evaporated under vacuum, and the residue was extracted into CH_2Cl_2 (2 mL) and purified by column chromatography (alumina, diethyl ether) to give **5** as a red solid (81 mg, 42%): ^1H NMR (270 MHz, acetone-d_6) δ 11.81 (dd, J = 8.6, 7.7 Hz, μ-CHR), 8.20 (d, J = 7.8 Hz, *o*-C_6H_5), 7.67–7.53 (m, *m*-, *p*-C_6H_5), 4.87 (s, C_5H_5), 4.74 (s, C_5H_5), 4.13 (sextet, J = 6.6 Hz, $CHCH_3$), 3.71 (dt, J = 14.2, 6.9 Hz, μ-$CHCHH$), 3.15 (ddd, J = 14.3, 8.6, 6.1 Hz, μ-$CHCHH$), 1.46 (d, J = 6.9 Hz, CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 0.07 M $Cr(acac)_3$) δ 272.8 (μ-CO), 212.9, 212.8 (CO), 204.1 (COC_6H_5), 173.5 (μ-CHR), 137.2 (ipso-C_6H_5), 132.9 (*p*-C_6H_5), 128.8, 128.2 (*o*-, *m*-C_6H_5), 87.3, 87.2 (C_5H_5), 59.7 (μ-$CHCH_2$), 46.7 (μ-$CHCH_2CH$), 18.2 (CH_3); IR (CH_2Cl_2) 1974 (s), 1933 (w), 1776 (m) cm^{-1}; HRMS calcd for M − CO $C_{23}H_{22}Fe_2O_3$ 458.0267, found 458.0270.

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)\{\mu\text{-}CHCH[CH(CO_2CH_2CH_3)_2]\text{-}CH_2CH_2CH_3\}$ (7). A mixture of **6** (100 mg, 0.18 mmol) and the sodium salt of diethyl malonate (33 mg, 0.18 mmol) in 30 mL of THF was stirred at room temperature for 1 h. Solvent was evaporated under vacuum, and the residue was dissolved in 10 mL of CH_2Cl_2 and was filtered. Addition of hexane precipitated **7** which was filtered, washed with 2 × 5 mL of hexane, and isolated as an orange-red solid (64 mg, 64%): ^1H NMR (270 MHz, CD_2Cl_2) δ 11.57 (d, J = 12.1 Hz, μ-CHR), 4.79 (s, C_5H_5), 4.75 (s, C_5H_5), 4.38 (dq, J = 11.0, 7.2 Hz, CO_2CHHCH_3), 4.33 (d, J = 2.1 Hz, $CH(CO_2CH_2CH_3)_2$), 4.32 (dq, J = 11.0, 7.2 Hz, CO_2CHHCH_3), 4.16 (dq, J = 10.8, 7.2 Hz, CO_2CHHCH_3), 4.12 (dq, J = 10.8, 7.1 Hz, CO_2CHHCH_3), 3.14 (m, μ-$CHCH$), 2.29 (m, μ-$CHCHCHH$), 2.07 (m, μ-$CHCHCHH$), 1.50 (m, $CH_2CH_2CH_3$), 1.39 (t, J = 7.1 Hz, CH_3), 1.21 (t, J = 7.1 Hz, CH_3), 0.94 (t, J = 7.3 Hz, CH_3); $^{13}C\{^1H\}$ (126 MHz, acetone-d_6, 0.07 M $Cr(acac)_3$) δ 271.6 (μ-CO), 214.1, 213.6 (CO), 180.2 (μ-CHR), 169.9, 169.5 ($CO_2CH_2CH_3$), 62.4, 61.3,

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(8) Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119.

(9) Carbon analysis of our hydrocarbyl-bridged diiron complexes have been variable but consistently low by 1.5–3.5%. Lukehart[10] has had similar difficulties with hydrocarbyl-bridged iron–platinum compounds. Consequently, we have relied on HRMS for establishing elemental composition and on ^1H and ^{13}C NMR for demonstration of homogeneity of our samples.

(10) Afzal, D.; Lukehart, C. M. *Organometallics* **1987**, *6*, 546.

61.2, 61.0 (CO_2CH_2, μ-CHCHR, μ-CHCHRCH), 41.7 (CH_2CH_2C-H_3), 22.4 ($CH_2CH_2CH_3$), 15.1, 14.6, 14.2 (CH_3); IR (CH_2Cl_2) 1985 (s), 1945 (w), 1785 (m), 1750 (w), 1725 (w), 1610 (w) cm^{-1}; HRMS calcd for M - CO $C_{24}H_{30}Fe_2O_6$ 526.0740, found 526.0746. Anal. Calcd for $C_{25}H_{30}Fe_2O_7$: C, 54.18; H, 5.46. Found: C, 54.15; H, 5.69.

$[C_5H_5(CO)Fe]_2(\mu$-CO)$\{\mu$-CHCH[CH(CO_2CH_3)($SO_2C_6H_5$)]-$CH_2CH_2CH_3\}$ (8). A mixture of **6** (200 mg, 0.37 mmol) and the sodium salt of methyl (phenylsulfonyl)acetate (87 mg, 0.37 mmol) in 30 mL of THF was stirred at room temperature for 0.5 h. The solution was filtered, and the THF was evaporated under vacuum. The residue was dissolved in 10 mL of CH_2Cl_2 and addition of hexane precipitated **8**, which was filtered, washed with 5 mL of hexane, and isolated as a red solid (133 mg, 60%). ^1H NMR (200 MHz, CD_2Cl_2): major isomer, δ 12.11 (d, J = 12.1 Hz, μ-CHR), 8.06-7.56 (m, C_6H_5), 4.92 (s, C_5H_5), 4.77 (s, C_5H_5), 3.47 (s, CO_2CH_3), 3.4-1.5 (complex multiplets, μ-CHC*H*($CH_2CH_2CH_3$)C*H*RR'), 0.95 (t, J = 7.3 Hz, CH_3); minor isomer, δ 11.23 (d, J = 11.8 Hz, μ-CHR), 8.06-7.56 (m, C_6H_5), 4.82 (s, C_5H_5), 4.67 (s, C_5H_5), 3.81 (s, CO_2CH_3), 3.4-1.5 (complex multiplets, μ-CHC*H*-($CH_2CH_2CH_3$)C*H*RR'), 1.01 (t, J = 7.3 Hz, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 0.07 M Cr(acac)$_3$): major isomer, δ 271.2 (μ-CO), 212.5, 211.8 (CO), 180.1 (μ-CHR), 166.7 (CO_2CH_3), 141.1 (ipso-C_6H_5), 133.7 (*p*-C_6H_5), 128.9, 128.3 (*o*-, *m*-C_6H_5), 87.9, 87.6 (C_5H_5), 77.2 (μ-CHCHCH), 64.3 (μ-CHCH), 52.1 (CO_2CH_3), 40.3 ($CH_2CH_2CH_3$), 21.6 ($CH_2CH_2CH_3$), 14.2 (CH_3); minor isomer, δ 270.5 (μ-CO), 212.1, 211.7 (CO), 175.2 (μ-CHR), 166.0 (CO_2CH_3), 140.3 (ipso-C_6H_5), 133.7 (*p*-C_6H_5), 129.0, 128.6 (*o*-, *m*-C_6H_5), 87.8, 87.5 (C_5H_5), 78.3 (μ-CHCHCH), 59.4 (μ-CHCH), 52.3 (CO_2CH_3), 39.2 ($CH_2CH_2CH_3$), 22.3 ($CH_2CH_2CH_3$), 14.6 (CH_3). IR (CH_2Cl_2): 1978 (s), 1939 (w), 1782 (m), 1745 (w) cm^{-1}. HRMS: calcd for M - CO $C_{26}H_{28}Fe_2O_6S$ 580.0305, found 580.0268.

$[C_5H_5(CO)Fe]_2(\mu$-CO)$(\mu$-CHCH$_2$CH$_3$) (10)[1]. A clear solution of Li(CH_3CuCN) prepared by stirring CH_3Li (0.17 mmol) and CuCN (16 mg, 0.18 mmol) in THF at -20 °C was cooled to -78 °C and added to a stirred suspension of **1** (75 mg, 0.15 mmol) in THF (20 mL) at -78 °C. The mixture was stirred for 1 h at room temperature, and the THF was evaporated under vacuum. The residue was extracted into CH_2Cl_2 (2 mL) and purified by column chromatography (alumina, diethyl ether) to give **10** as a red solid (56 mg, 100%): ^1H NMR (270 MHz, acetone-d_6) δ 11.86 (t, J = 8.3 Hz, μ-CHR), 4.85 (s, 10 H, C_5H_5), 3.10 (dq, J = 8.1, 7.2 Hz, μ-CHCH_2), 1.47 (t, J = 7.2 Hz, CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6, 0.07 M Cr(acac)$_3$) δ 273.1 (μ-CO), 214.4 (CO), 182.1 (μ-CHR), 88.2 (C_5H_5), 50.3 (μ-CHCH$_2$), 20.8 (CH_3).

$[C_5H_5(CO)Fe]_2(\mu$-CO)$[\mu$-CHCH(CH_3)$CH_2CH_2CH_3$] (12). A solution of Li(CH_3CuCN) prepared from CH_3Li (0.40 mmol) and CuCN (40 mg, 0.44 mmol) in THF at -20 °C was added by syringe to a stirred suspension of **6** (200 mg, 0.37 mmol) in THF (20 mL) at -78 °C. THF was evaporated under vacuum, and the residue was extracted into CH_2Cl_2 (2 mL) and purified by column chromatography (alumina, diethyl ether) to give **12** as a red solid (149 mg, 98%): ^1H NMR (270 MHz, CD_2Cl_2) δ 11.64 (d, J = 11.4 Hz, μ-CHR), 4.73 (s, 10 H, C_5H_5), 2.5-1.4 (multiplets, μ-CHC*H*-(CH_3)CH_2CH_2CH_3), 1.47 (d, J = 6.3 Hz, μ-CHCHCH_3), 0.97 (t, J = 7.2 Hz, $CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6, 0.07 M Cr(acac)$_3$) δ 273.1 (μ-CO), 214.4 (CO), 188.2 (μ-CHR), 88.3 (C_5H_5), 58.0 (μ-CHCH), 45.5 ($CH_2CH_2CH_3$), 25.6 (CH_3), 21.4 ($CH_2CH_2CH_3$), 14.6 (CH_3); IR (CH_2Cl_2) 1974 (s), 1933 (w), 1772 (m) cm^{-1}; HRMS calcd for $C_{19}H_{22}Fe_2O_3$ 410.0267, found 410.0253.

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Registry No. 1, 87858-04-6; 2, 112840-90-1; 3, 112840-91-2; 4, 66323-99-7; 5, 112840-92-3; 6, 112924-67-1; 7, 112840-93-4; 8 (isomer 1), 112840-97-8; 8 (isomer 2), 112924-68-2; 9, 112840-94-5; 10, 112840-95-6; 12, 112840-96-7; $(C_4H_9)_4N^+F^-$, 429-41-4; Li(CH_3CuCN), 41753-78-0; sodium diethyl malonate, 51923-79-6; sodium methyl(phenylsulfonyl)acetate, 60729-65-9.

Homogeneous Catalysis. Conversion of 4-Pentenals to Cyclopentanones by Efficient Rhodium-Catalyzed Hydroacylation

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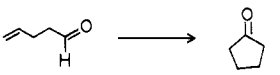
A variety of complexes of the type [Rh(diphosphine)]$^+$ have been investigated as catalysts for hydroacylation, the intramolecular cyclization of 4-pentenals to cyclopentanones. All of the complexes studied effect this conversion in weakly or noncoordinating solvents at 20 °C, but the most effective catalyst was found to be the rhodium(I) species containing diphos ($(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$). This complex converts 4-pentenal at a remarkably fast rate of one turnover every 6 s at 20 °C in CH_3NO_2 and CH_2Cl_2 solutions. These catalysts are effective for 4-pentenals bearing mono substituents at the 2-, 3-, 4-, and 5-positions and disubstitution at the 3-position. Disubstitution at the 2-position slows the rate and effectiveness of catalysis considerably, and substrates having disubstitution at the terminal 5-position are not turned over by these catalysts. For the diphos catalyst, between 100 and 800 rapid turnovers are observed at 1 molar percent catalyst depending on the substrate. After this, the catalysis becomes sluggish because of substrate decarbonylation leading to the catalytically inactive [Rh(diphos)(CO)$_2$]$^+$ species. Even when the dicarbonylated species is present, catalysis continues because of substrate-induced dissociation of the carbonyl ligands. Unlike the case of hydroacylation with the [Rh(PPh_3)$_3$Cl] complex no cyclopropanes are produced with these catalysts. Double-bond migration is a competing reaction, the extent of which depends on the substrate and the diphosphine catalyst, but in general it is a minor side reaction and it is not rate-limiting.

Hydroacylation, a process having no direct organic analogy, can be induced by certain rhodium(I) complexes. The most extensively investigated form of this reaction involves the intramolecular addition of the hydrogen atom and the acyl group derived from an aldehyde moiety to the carbon atoms of an olefin (eq 1). Because hydroacylation



(1)

involves the activation of carbon-hydrogen bonds and their

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