of CH_2Cl_2 under high vacuum. Diethyl ether (15 mL) was added, and the resulting precipitate was filtered, washed with diethyl ether (2 × 5 mL), and dried under vacuum to give a 4:3:2 ratio of **19**, **20**-*E* and **20**-*Z* (215 mg, 82%) as a dark reddish brown solid. ^1H NMR (acetone-d_6): **19**, δ 7.65–7.3 (m, C_6H_5), 5.78 (s, C_5H_5), 5.6 (m, μ-CCH), 3.9 (d, J = 13 Hz, C*H*H), 3.2 (d, J = 13 Hz, CH*H*), 1.68 (d, J = 6.7 Hz, CH_3); **20**-*E*, δ 12.27 (s, μ-CH), 7.65–7.3 (m, C_6H_5), 5.81 (s, C_5H_5), 3.91 (s, CH_2), 1.27 (s, CH_3); **20**-*Z*, δ 12.01 (s, μ-CH), 7.65–7.3 (m, C_6H_5), 5.75 (s, C_5H_5), 2.83 (s, CH_2), 2.26 (s, CH_3). IR (CH_2Cl_2): 2037 (s), 2016 (s), 2005 (w), 1851 (m) cm^{-1}.

Similarly, reaction of *trans*-1-propenylbenzene (0.46 mmol) with 1-*d* (0.24 mmol) gave a 4:3:2 mixture of **19**-*d*:**20**-*E*-*d*:**20**-*Z*-*d* (110 mg, 77%) as a red-brown solid. $^2H\{^1H\}$ NMR (acetone): δ 3.9, 3.3, 2.8.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CH_2C_6H_5)$ (21). A saturated aqueous solution of $NaHCO_3$ (2 mL) was added to a stirred solution of **19**, **20**-*E*, and **20**-*Z* (210 mg, 0.35 mmol) in acetone (40 mL). After 20 min, solvent was evaporated and the resulting solid was purified by column chromatography (alumina, 3:1 hexane/CH_2Cl_2) to give **21** (126 mg, 80%) as red crystals. ^1H NMR (acetone-d_6): δ 7.5–7.2 (m, C_6H_5), 5.04, 4.97 (C_5H_5), 4.30 (d, J = 15.1 Hz, C*H*H), 4.12 (d, J = 15.1 Hz, CH*H*), 2.33 (s, CH_3). ^{13}C NMR (CD_3NO_2): δ 274.2, 262.7 (μ-CO, μ-C), 214.1, 213.9 (CO), 143.8, 141.8 (ipso, μ-C=*C*), 129.8, 129.6 (d, J = 160 Hz, C_6H_5), 126.9 (d, J = 163 Hz, C_6H_5), 88.8 (d, J = 178 Hz, C_5H_5), 49.5 (t, J = 123 Hz, CH_2), 25.6 (q, J = 129 Hz, CH_3). IR (CH_2Cl_2): 1990 (s), 1952 (w), 1784 (m) cm^{-1}. HRMS for $C_{23}H_{20}Fe_2O_3$: calcd, 456.0105; found, 456.0110.

Similarly, deprotonation of a mixture of **19**-*d*, **20**-*E*-*d* and **20**-*Z*-*d* (0.12 mmol) gave $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CHDC_6H_5)$ (**21**-*d*) (40 mg, 75%). $^2H\{^1H\}$ NMR (acetone): δ 4.26, 4.10.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_2CH_3)_2)$ (22) and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CH_2CH_2CH_3)$ (23). A solution of *trans*-2-pentene (0.13 atm, 235 mL, 1.28 mmol) and **1** (170 mg, 0.35 mmol) in CH_2Cl_2 (25 mL) was warmed from −78 °C to ambient temperature. Recrystallization from acetone–ether gave a brown-red solid (110 mg, 57%). This solid was dissolved in acetone (25 mL) and stirred with aqueous bicarbonate. Column chromatography (alumina, 3:1 hexane/CH_2Cl_2) gave a 1.5:1 mixture of **22** and **23** (60 mg, 42% from **1**). ^1H NMR (acetone-d_6): **22**, δ 4.95 (C_5H_5), 2.87 (m, CH_2), 1.22 (t, J = 7.5 Hz, CH_3); **23**, δ 4.96, 4.94 (C_5H_5), 2.8 (m, CH_2), 2.43 (s, =CCH_3), 1.7 (m, CH_2Me), 1.05 (t, J = 7.5 Hz, CH_2CH_3).

Low-Temperature Reaction of 1 with *trans*-2-Butene. *trans*-2-Butene (0.033 atm, 9.0 mL, 12.4 μmol) was condensed into an NMR tube containing **1** (3 mg, 6.2 μmol) and CD_2Cl_2 (0.34 mL) at −196 °C. The tube was sealed under vacuum and agitated with a Vortex Genie at −78 °C to dissolve **1**. The tube was maintained at −60 °C for 3 h and then centrifuged at −78 °C. The initial ^1H NMR spectrum at −22 °C indicated the presence of ~50% unreacted **1** (δ 22.8, CH) and ~50% alkylidyne complex **2** [δ 2.35 (m, CH_2), 1.80 (d, J = 6.2 Hz, $CHCH_3$), 1.23 (t, J = 7.1 Hz, CH_2CH_3)]; no resonance (≤1%) due to **3**-*E* (δ 11.68 (FeCH)) or **3**-*Z* (δ 11.61 (FeCH)) was observed. When the solution was warmed to −13 °C for ~30 min, resonances assigned to **3**-*E* and **3**-*Z* began to grow in and resonances due to **1** disappeared. After the solution was warmed to room temperature, a 2.3:1.0:1.5 equilibrium mixture of **2**:**3**-*E*:**3**-*Z* was seen by NMR.

Low-Temperature Reaction of 1 with *cis*-2-Butene. *cis*-2-Butene (0.024 atm, 9.0 mL, 8.9 μmol) was condensed into an NMR tube containing **1** (3 mg, 6.2 μmol). After 28 h at −50 °C, the sample was promptly analyzed by ^1H NMR at −30 °C. Analysis of the spectra indicated that less than 5% of **1** remained and that an 85:6:9 mixture of **2**:**3**-*E*:**3**-*Z* was formed. Upon warming to ambient temperature an equilibrium mixture of **2**:**3**-*E*:**3**-*Z* was seen. The small amounts of **3**-*E* and **3**-*Z* are probably due to rearrangement of **2** either during the extended period of time at −60 °C needed to obtain high conversion of **1** or upon unavoidable sample warming in transferring the tube to the NMR spectrometer.

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Steric and Electronic Factors Influencing the Amounts of μ-Alkylidyne and μ-Alkenyl Products Obtained from Reaction of Diiron Methylidyne Complexes with Alkenes

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The reaction of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**1**) with vinylcyclopropane followed by deprotonation with NMe_3 gave $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH{=}CHCHCH_2CH_2)$ (**13**) in 78% yield. Through deprotonation–reprotonation studies and deuterium labeling using 1-*d*, it was determined that 2-methyl-1-butene, 2-methyl-2-butene, and 1-methylcyclopentene gave both μ-alkylidyne and μ-alkenyl complexes as kinetic products in their reaction with **1**. The reaction of **1** with 9,9-dimethyl-10-methylene-9,10-dihydroanthracene, **19**, gave the μ-alkylidyne complex **20** as the major isomer in 71% yield. The reaction of $[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**32**) with 1-pentene produced $[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}CCH_2CH_2CH_2CH_2CH_3)^+PF_6^-$ (**33**) in 65% yield. However, the reaction of **32** with isobutylene gave the μ-alkenyl complex $[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHCH(CH_3)_2)^+PF_6^-$ (**35**) in 82% yield.

The cationic diiron μ-methylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**1**) reacts with alkenes to form new carbon–carbon bonds and produces either μ-alkylidyne or μ-alkenyl complexes.[1-5] The formation of

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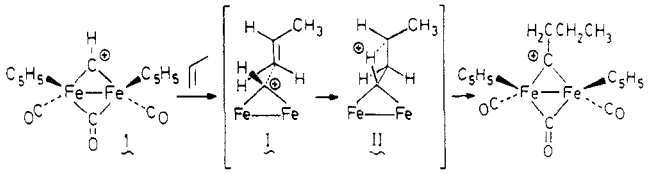
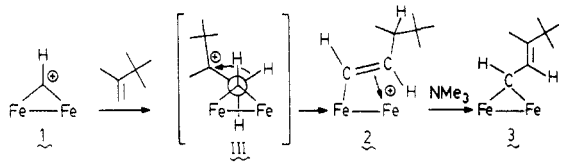
μ-alkylidyne products from terminal alkenes such as propene is proposed to occur via the rate-determining transition state I which involves only carbon–carbon bond formation.[4] This is followed by a 1,3-hydride shift which requires the geometry shown in II.

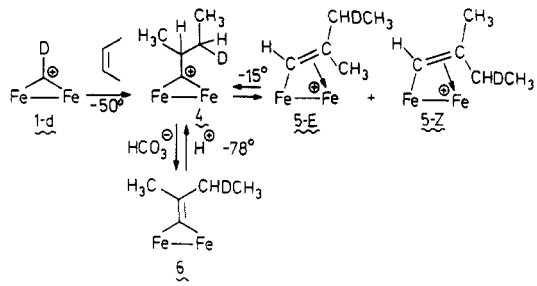


The direct formation of μ-alkenyl complexes occurred with some alkenes such as 2,3,3-trimethyl-1-butene.[2,5] The reaction was proposed to proceed by initial formation of a carbocation intermediate, followed by a 1,2-hydrogen shift via transition state III.



The transition states for the rate-determining step of μ-alkylidyne and μ-alkenyl formation are very similar and involve only carbon–carbon bond formation. The partitioning of the cationic intermediate between μ-alkylidyne and μ-alkenyl complexes is determined largely by steric and electronic effects which affect the relative energies of the product determining transition states II and III.[4] For purposes of discussion, we define the α alkene carbon as the carbon which forms a new carbon–carbon bond to 1 and the β alkene carbon as the remote carbon. Large substituents on either the α- or β-carbon of the reacting alkene destabilize transition state II for μ-alkylidyne formation more than transition state III for μ-alkenyl formation. Electron-donating substituents on the β-carbon of the reacting alkene stabilize transition state III for μ-alkenyl formation more than transition state II for μ-alkylidyne formation. Apparently, the β-carbon of the reacting alkene bears more positive charge in III than in II. In part, this can explain why μ-alkenyl products are most commonly seen for alkenes capable of reacting with 1 to form relatively stable carbocation intermediates.

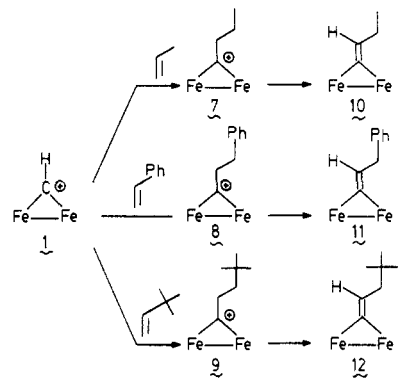
The reaction of 1,2-disubstituted alkenes such as 2-butene or cyclohexene with methylidyne complex 1 produces an equilibrating mixture of μ-alkylidyne complexes and μ-alkenyl complexes.[6] These equilibrating mixtures react with $NaHCO_3$ to produce μ-alkenylidene complexes which arise from deprotonation of the μ-alkylidyne complex. Reaction of 1-*d* with *cis*-2-butene gave μ-alkylidyne complex **4** and two isomeric μ-alkenyl complexes **5**-*E* and **5**-*Z* with the deuterium label located exclusively on the methylene group of the ethyl group.[6] This labeling result establishes that 1 reacts with *cis*-2-butene to produce a kinetically formed μ-alkylidyne complex which then equilibrates with μ-alkenyl complexes.



Throughout our examination of the reaction of alkenes with methylidyne complex 1, we sought to elucidate the factors which control μ-alkylidyne or μ-alkenyl formation. In this paper, we report subtle changes in the substituents on the alkene and on the diiron complex that control the nature of the product formed by altering the relative energies of the product-determining transition states II and III.

Results and Discussion

Reaction of 1 with Cyclopropylethylene. Reaction of 1 with mono-substituted alkenes such as propene, styrene, or 3,3-dimethyl-1-butene gave μ-alkylidyne products $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_2CH_3)^+PF_6^-$ (**7**), $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_2C_6H_5)^+PF_6^-$ (**8**), or $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_2C(CH_3)_3)^+PF_6^-$ (**9**) in 78, 81, and 85% yields, respectively. The alkylidyne complexes **7**, **8**, and **9** produced in these hydrocarbation reactions were further characterized by reaction with trimethylamine which produced the deprotonated μ-alkenylidene complexes $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2CH_3)$ (**10**), $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2C_6H_5)$ (**11**), and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2C(CH_3)_3)$ (**12**).

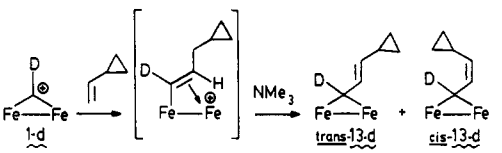


In contrast, reaction of vinylcyclopropane with 1 directly produced a μ-alkenyl complex which was deprotonated to give a vinyl carbene complex. When a red suspension of 1 and vinylcyclopropane in CH_2Cl_2 was warmed from −78 to 0 °C and the resulting brown solution was treated with trimethylamine, the vinyl carbene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH{=}\overline{CHCHCH_2CH_2})$ (**13**) was isolated in 78% yield after column chromatography. Previously we have shown that vinyl carbene complexes are readily formed by deprotonation of cationic μ-alkenyl complexes (**2** → **3**; 81% yield).[5]

Two isomers having different carbon–carbon double-bond configurations, *trans*-**13** and *cis*-**13**, were observed in a 4:1 ratio. In the ^1H NMR spectrum of *trans*-**13**, the proton on the bridging carbene carbon appears as a doublet at δ 11.6 (J = 12.3 Hz) and the two vinyl hydrogens appear as two doublet of doublets at δ 6.9 and 5.5 and have J_{trans}

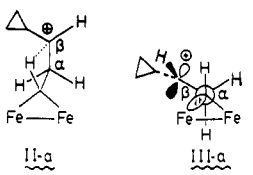
(1) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134–1136.
(2) Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950–4951.
(3) Casey, C. P.; Fagan, P. J.; Miles, W. H.; Marder, S. R. *J. Mol. Catal.* **1983**, *21*, 173–188.
(4) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043–4053.
(5) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053–4059.
(6) (a) Casey, C. P.; Meszaros, M. W.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 3680–3681. (b) Casey, C. P.; Meszaros, M. W.; Marder, S. R.; Bly, R. K.; Fagan, P. J. *Organometallics*, preceding paper in this issue.

= 14.1 Hz. For *cis*-**13**, the proton on the carbene carbon appears as a doublet at δ 12.2 (J = 12.7 Hz) and the two vinyl hydrogens appear as a doublet of doublets at δ 6.7 and 5.7 with J_{cis} = 11 Hz.

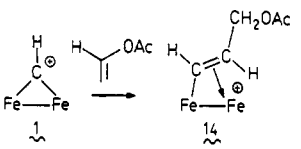


To determine whether the reaction of vinylcyclopropane with **1** produced a μ-alkenyl complex directly or via rearrangement of an initially formed μ-alkylidyne complex, the reaction of deuterated methylidyne complex **1**-*d* with vinylcyclopropane was studied and the resulting μ-alkenyl complex was directly deprotonated with trimethylamine. In the resulting vinyl carbene complex **13**-*d*, the deuterium label was located exclusively at the μ-carbene center. The site of the label in **13**-*d* was established by the absence of the δ 12.2 and 11.6 resonances in the ^{1}H NMR and the appearance of resonances at δ 12.3 and 11.8 in the ^{2}H NMR. This clearly establishes that vinylcyclopropane reacts with the bridging methylidyne complex to form a carbocation intermediate that subsequently undergoes a 1,2-hydrogen migration to produce the μ-alkenyl complex.

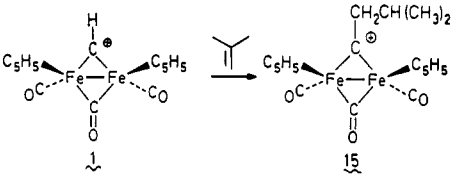
Vinylcyclopropane is the only nonheteroatom monosubstituted alkene that reacts with **1** to form a μ-alkenyl complex directly.[7] Both more sterically crowded alkenes such as 3,3-dimethyl-1-butene and styrene and less crowded alkenes such as propene react with **1** to give μ-alkylidyne complexes. The cyclopropyl substituent, which is a substantially better electron donor than phenyl,[8,10] stabilizes intermediate IIIa more than IIa. The β-carbon in transition state IIIa is apparently more electropositive than in IIa and can be selectively stabilized by strong electron donor substituents.



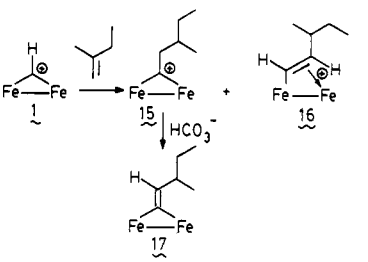
In related chemistry, we have observed that vinyl acetate reacts with **1** to give μ-alkenyl complex **14**.[7] In this case, the strongly electron-donating acetoxy group selectively stabilizes transition state III for μ-alkenyl formation.



Reaction of 1 with 1,1-Dialkyl-Substituted Alkenes. Bulky substituents on the β-carbon of a reacting alkene destabilize transition state II for μ-alkylidyne formation more than transition state III for μ-alkenyl formation. Thus, the reaction of **1** with isobutylene produced μ-alkylidyne complex **15**,[4] but the reaction of **1** with 2,3,3-trimethyl-1-butene gave the μ-alkenyl complex **2**.[5]



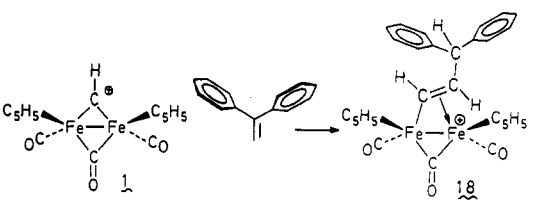
To better define the crossover point between μ-alkylidyne and μ-alkenyl formation, the reaction of **1** with 2-methyl-1-butene was studied. A 9:1 mixture of μ-alkylidyne complex $[(C_5H_5)(Co)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH(CH_3)CH_2CH_3)^+PF_6^-$ (**15**) and μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH(CH_3)CH_2CH_3)^+PF_6^-$ (**16**) was obtained in 89% yield. The presence of the two isomers was established by ^{1}H NMR.



When this 9:1 mixture was treated with aqueous $NaHCO_3$, the μ-alkylidyne complex **15** was rapidly deprotonated to give a 3:2 mixture of two diastereomers of the μ-alkenylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH(CH_3)CH_2CH_3)$ (**17**) which was isolated as a bright red ether-soluble solid in 79% yield. The μ-alkenyl complex **16** did not react with aqueous bicarbonate and was isolated as a dark brown ether-insoluble solid in 7% yield. In previous work,[11] we had found that μ-alkylidyne complexes are more rapidly deprotonated than μ-alkenyl complexes.

Bulky substituents on the β-carbon of an alkene destabilize both transition state II for μ-alkylidyne formation and transition state III for μ-alkenyl formation. When a solution of 1,1-di-*tert*-butylethylene and **1** was monitored by ^{1}H NMR at ambient temperature, no new diiron complexes were observed. Only slow decomposition of **1** was seen. The presence of two *tert*-butyl groups completely inhibited reaction with **1**.

Reaction of 1 with 1,1-Diaryl-Substituted Alkenes. The reaction of **1** with 1,1-diphenylethylene produces the μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH(C_6H_5)_2)^+PF_6^-$ (**18**).[5]



To help determine whether this preference for μ-alkenyl formation is the result of selective steric destabilization of transition state IIb by the propellar-like phenyl groups, or of selective electronic stabilization of the more positive carbon of IIIb, we examined the reaction of **1** with 9,9-dimethyl-10-methylene-9,10-dihydroanthracene, **19**, a flat 1,1-diaryl-substituted alkene. If steric effects are responsible for μ-alkenyl formation from 1,1-diphenylethylene,

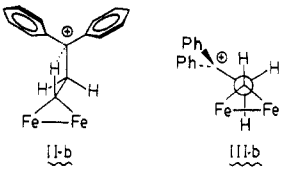
(7) Casey, C. P.; Gohdes, M. A.; Meszaros, M. W. *Organometallics* **1986**, *5*, 196–199.

(8) From ^{1}H NMR ketone basicity studies methylcyclopropyl ketone (pK = –5.9) is far more basic than methyl isopropyl ketone (pK = –7.4) and significantly more basic than acetophenone (pK = –6.4).[9]

(9) Levy, G. C.; Cargioli, J. D.; Racela, W. *J. Am. Chem. Soc.* **1970**, *92*, 6238–6246.

(10) For a review of cyclopropylmethyl cations see: Richey, H. G. In *Carbonium Ions*; Olah, G. A., Schlerer, P. von R., Eds.; Wiley-Interscience: New York, 1972; Vol III, Chapter 25.

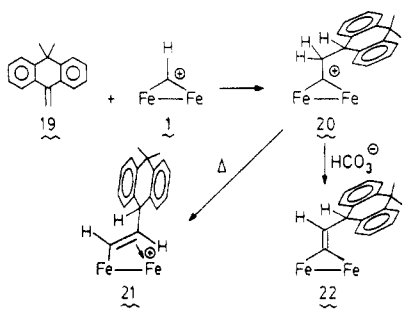
(11) (a) Casey, C. P.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 7197–7198. (b) Casey, C. P.; Marder, S. R.; Adams, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 7700–7705.



II-b III-b

then the less crowded geometry of **19** might lead to a switch to μ-alkylidyne formation. If electronic effects are responsible for μ-alkenyl formation, the flat π-system of **19** should be able to act as a better electron donor and μ-alkenyl complex formation should be even more favorable than in the case of 1,1-diphenylethylene.

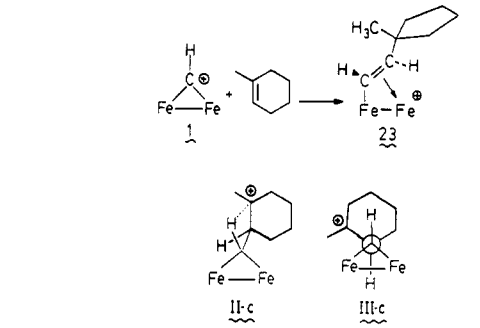
The reaction of methylidyne complex **1** with **19** in CH_2Cl_2 at ambient temperature produced the μ-alkylidyne complex **20** in 71% yield. Analysis by ^1H NMR indicated small amounts (<10%) of the μ-alkenyl complex **21**. When solid **20** was heated at 80 °C for 18 h, the μ-alkenyl complex **21** was formed in 86% yield.



The small amount of μ-alkenyl complex **21** observed in the reaction of **19** with **1** could be a kinetically formed product or the result of partial thermal rearrangement of μ-alkylidyne complex **20**.[11] In either case, we conclude that locking the aryl rings of a 1,1-diarylethylene into the plane of the alkene changes the nature of the kinetically formed product from a μ-alkenyl complex as seen for 1,1-diphenylethylene to a μ-alkylidyne complex as seen for **19**. The major effect responsible for production of a μ-alkenyl complex from 1,1-diphenylethylene is that the large propellar like phenyl rings at the β-carbon destabilize transition state IIb for μ-alkylidyne formation.

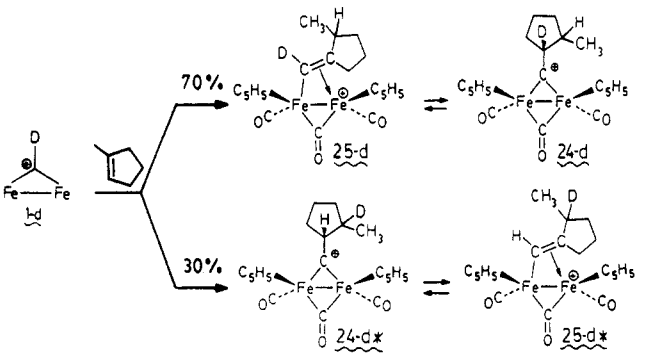
Reaction of 1 with 2-Methyl-2-butene and with 1-Methylcyclopentene. Alkyl substituents on either the α- or β-carbon of the alkene undergoing reaction with **1** push the reaction toward a preference for μ-alkenyl complex formation. Thus, while the two β-alkyl substituents of isobutylene or the one α-alkyl and one β-alkyl substituent of cyclohexene are insufficient to overcome the normal preference for μ-alkylidyne formation, the presence of two β-alkyl substituents and one α-alkyl substituent in 1-methylcyclohexene bring about formation of a μ-alkenyl product. In going from IIc to IIIc, the α-alkyl substituent of 1-methylcyclohexene is rotated away from the diiron center to a sterically less congested site. Transition state III can accommodate a single α-alkyl substituent quite well, but a second α-alkyl group cannot be accommodated because it would be directed toward the crowded diiron portion of the molecule. In IIIc, the ring carbon is in an anti-periplanar arrangement with respect to a carbon–iron σ-bond and is ideally situated for a carbon migration to give the ring contracted product **23**.

We examined the reaction of 1-methylcyclopentene with **1** to see what would occur if carbon migration were blocked by the inability to form a strained cyclobutane ring. The reaction of methylidyne complex **1** with 1-methylcyclopentene gave a 2:1 equilibrating mixture of μ-alkylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCHCH(CH_3)CH_2CH_2\dot{C}H_2)^+PF_6^-$ (**24**) and μ-alkenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}\overline{CCH(CH_3)CH_2CH_2\dot{C}H_2})^+PF_6^-$ (**25**) in 78% yield. The reaction of this equilibrating mixture with trimethylamine produced the μ-alkenylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}\overline{CCH(CH_3)CH_2CH_2CH_2})$ (**26**) in 90% yield. The rapid equilibration of μ-alkenyl complexes and μ-alkylidyne complexes with two β-alkyl substituents has been seen previously.[11] The μ-alkenyl complex **25** is in rapid equilibrium with μ-alkylidyne complex **24** which is deprotonated to give the μ-alkenylidene complex **26**.



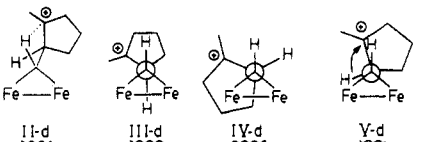
1 23

II-c III-c



To determine the kinetic product of the reaction, 1-methylcyclopentene was reacted with **1**-*d*. Integration of the ^2H NMR spectrum of the reaction mixture established that 70% of the reaction occurred via kinetic formation of μ-alkenyl complex **25**-*d* (δ 12.0) which then equilibrated with μ-alkylidyne complex **24**-*d* (δ 5.6) and that 30% of the reaction occurred by kinetic formation of μ-alkylidyne complex **24**-*d** (δ 3.0) which then equilibrated with μ-alkenyl complex **25**-*d** (δ 2.9).

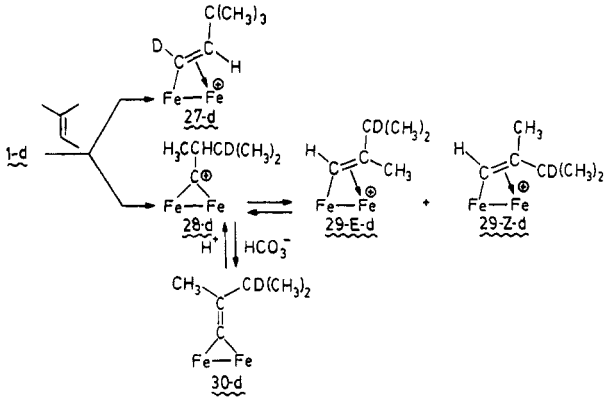
Transition state IIId which would lead to four-member-ring formation is greatly destabilized, and no product is seen from this pathway. This allows μ-alkylidyne formation via IId to be seen to the extent of 30%. 1-Methylcyclopentene is the only alkene for which hydrogen migration is preferred over alkyl migration in μ-alkenyl formation. Hydrogen migration via IVd in which the migrating hydrogen is anti-periplanar with respect to a carbon–iron σ-bond would seem highly unlikely since the α-ring carbon atom would be directed towards the sterically congested diiron center. Instead, we suggest that unassisted hydrogen migration occurs via Vd to the extent of 70%.



II-d III-d IV-d V-d

A mixture of kinetically formed μ-alkylidyne and μ-alkenyl complexes was also observed in the reaction of 2-methyl-2-butene with **1** at 0 °C. The cationic products

were shown by ^{1}H NMR to be a 1.0:2.0:1.4:1.0 mixture of the μ-alkenyl complex formed by methyl migration $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHC(CH_3)_3]^+PF_6^-$ (**27**) and an equilibrating mixture of μ-alkylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH(CH_3)CH(CH_3)_2)^+PF_6^-$ (**28**) and two isomeric μ-alkenyl complexes $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C(CH_3)CH(CH_3)_2)^+PF_6^-$ (**29-*E*** and **29-*Z***). Three resonances for protons on the α-carbon of μ-alkenyl complexes were observed. Singlets at δ 12.04 and 11.76 were assigned to **29-*E*** and **29-*Z***, and a doublet (J = 13 Hz) at 11.88 was assigned to **27**. A characteristic resonance at δ 5.05 (dq, J = 6.5, 2.7 Hz) was assigned to the protons on the α-carbon of μ-alkylidyne complex **28**.



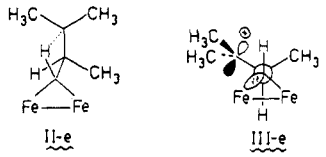
When a CH_2Cl_2 solution of this mixture of products was treated with an aqueous solution of $NaHCO_3$, a bright red solution was obtained. Addition of diethyl ether to the CH_2Cl_2 solution resulted in precipitation of the dark brown cationic μ-alkenyl complex **27** (16% yield). The neutral μ-alkenylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CH_3)CH(CH_3)_2]$ (**30**) was isolated from the remaining solution in 60% yield after column chromatography. In the ^{1}H NMR cationic μ-alkenyl complex **27**, resonances assigned to the vinyl hydrogens appear as doublets (J_{trans} = 13 Hz) at δ 11.88 and 3.57 and the *tert*-butyl resonance appears as a singlet at δ 1.29. In the ^{1}H NMR of μ-alkenylidene complex **30**, resonances assigned to the diastereotopic methyl groups of the isopropyl unit appear as doublets (J = 7 Hz) at δ 1.39 and 1.13 and resonances assigned to the methyl group attached to the vinylidene carbon appears as a singlet at δ 2.35.

Protonation of μ-alkenylidene complex **30** with $HBF_4{\cdot}OEt_2$ in ether gave an immediate red precipitate which was shown by ^{1}H NMR to be a 2.0:1.4:1.0 equilibrating mixture of μ-alkylidyne complex **28** and the isomeric μ-alkenyl complexes **29-*E*** and **29-*Z***.

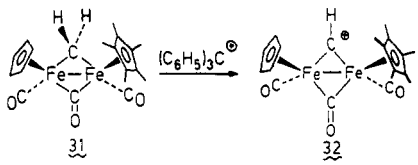
To determine the nature of the kinetically formed products, the reaction of **1-*d*** with 2-methyl-2-butene was studied and a similar 1.0:2.0:1.4:1.0 mixture of **27-*d*:28-*d*:29-*E*-*d*:29-*Z*-*d*** was observed. In the ^{2}H NMR, resonances were observed at δ 11.9 for deuterium on the α-carbon of the methyl migration product **27-*d*** and at δ 3.2, 2.8, and 1.1 for the $-CDMe_2$ unit of **28-*d***, **29-*E*-*d***, and **29-*Z*-*d***; no resonance was observed near δ 5 for deuterium on the β-carbon of μ-alkylidyne complex **28**. The presence of deuterium in the $-CDMe_2$ unit was further established by collapse of ^{1}H NMR doublets at δ 1.36, 1.30, and 0.84 to singlets upon deuteration.

The mixture of deuterated complexes was treated with aqueous bicarbonate, and the deuterated μ-alkenylidene complex **30-*d*** was isolated. In the ^{2}H NMR, a singlet at δ 3.5 established the presence of a $-CDMe_2$ group.

These results establish that there are two kinetically formed products: μ-alkenyl complex **27** formed by methyl migration via transition state IIIe and μ-alkylidyne complex **28** formed by C–H addition across the alkene via transition state IIe. As in the case of the other μ-alkylidyne complexes with two β-alkyl substituents, μ-alkylidyne complex **28** and the two isomeric μ-alkenyl complexes **29-*E*** and **29-*Z*** are in rapid equilibrium.[6,11] In the present case, this equilibrium was demonstrated by deprotonation–reprotonation reactions.

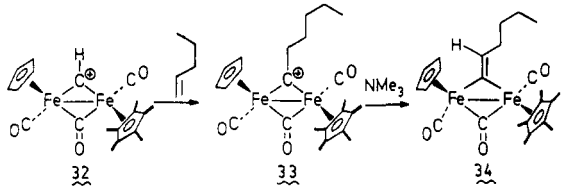


Reaction of *trans*-$[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (32) with Alkenes. To further elucidate the factors that control the mode of reaction of methylidyne complexes with alkenes, we have modified the ligand environment about the iron centers by introducing one or two pentamethylcyclopentadienyl ligands. Treatment of a 4:1 *cis*:*trans* mixture of μ-methylene complex $[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}CH_2)$ (**31**) with $(C_6H_5)_3C^+PF_6^-$ gave a 3:2 mixture of μ-methylidyne complex $[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**32**). We are not certain whether the C_5Me_5 and C_5H_5 ligands are cis or trans to one another in the major isomer.



Bridging methylidyne complex **32** is more robust than methylidyne complex **1**. Whereas **1** decomposes in CD_2Cl_2 at ambient temperature with a half-life of 2 h, methylidyne complex **32** has a half-life of 2 days in CD_2Cl_2. The ratio of isomers of **32** does not change as decomposition occurs, indicating that either both *cis*- and *trans*-**32** decompose at comparable rates or (more likely) that they are in equilibrium at ambient temperature.

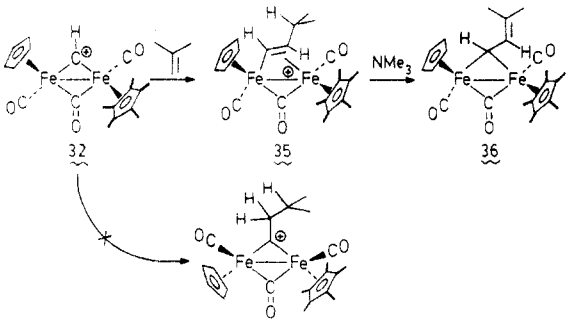
The reaction of **32** with 1-pentene produced the μ-hexylidyne complex $[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}CCH_2CH_2CH_2CH_2CH_3)^+PF_6^-$ (**33**) in 65% yield. Deprotonation of **33** with trimethylamine produced the μ-hexenylidene complex $[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2CH_2CH_2CH_3)$ (**34**) in 61% yield.



The IR spectrum of hexylidyne complex **33** and hexenylidene complex **34** exhibit the characteristic cis-substituted carbonyl stretches with the stronger band at higher energy (**33**, 2030 (s), 2001 (w) cm^{-1}; **34**, 1983 (s), 1940 (w) cm^{-1}). This suggests that only *cis*-**32** is reacting with the alkene and that *cis*- and *trans*-**32** are in equilibrium. Alternatively, the cis and trans isomers of μ-hexylidyne complex **33** might be in equilibrium and the cis isomer might be thermodynamically favored. Examination of models show that cis C_5Me_5 and C_5H_5 ligands would not be in close contact.

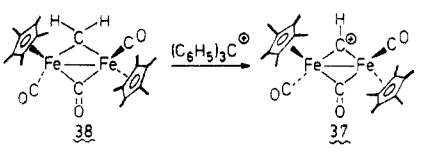
While 1-pentene reacts with either **1** or **32** to produce μ-alkylidyne complexes, the reaction of isobutylene with **32** produces a μ-alkenyl complex in contrast to the reaction with **1** which gave a μ-alkylidyne complex. The reaction

of isobutylene with methylidyne complex **32** produced the 3-methyl-1-butenyl complex $[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHCH(CH_3)_2)^+PF_6^-$ (**35**) in 82% yield. Deprotonation with trimethylamine produced the vinyl carbene complex $[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}CHCH{=}C(CH_3)_2)$ (**36**) as violet crystals in 76% yield.



There are two possible pathways for formation of μ-alkenyl complex **35**. First, hydrocarbation of isobutylene by **32** could produce μ-alkylidyne complex A which subsequently rearranges to μ-alkenyl complex **35**. Second, electrophilic addition of **32** to isobutylene could produce a carbocation that rearranges directly to the μ-alkenyl complex **35**. Our studies[11] of the rate of rearrangement of bis-C_5H_5-substituted μ-alkylidyne to μ-alkenyl complexes suggest that the rearrangement of the putative C_5Me_5-substituted μ-alkylidyne complex A with one alkyl substituent on the β-carbon would be slow at ambient temperature. The stability of the related C_5Me_5-substituted μ-hexylidyne complex **33** supports this view. We suggest that mono-C_5Me_5-substituted methylidyne complex **32** presents an asymmetric environment to an incoming isobutylene molecule that leads to a preference for the twisted transition state leading to μ-alkenyl complex formation.

To test the effect of an even more crowded ligand environment at iron, we synthesized the bis-C_5Me_5-substituted methylidyne complex *trans*-$[(C_5Me_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**37**) by reaction of the corresponding methylene complex **38**[12] with $(C_6H_5)_3C^+PF_6^-$. Because of the very bulky nature of the two C_5Me_5 ligands, only the trans isomer of **37** was observed. When a solution of **37** and isobutylene in CD_2Cl_2 was monitored by ^1H NMR at ambient temperature over a 3-day period, no new resonances attributable to alkene addition products were observed. Only slow disappearance of **37** was noted. Evidently, isobutylene is sterically shielded from the μ-methylidyne group by a C_5Me_5 and CO ligand on each face of the complex.



Experimental Section

General Data. See earlier paper in this series.[4]

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH{=}\overline{CHCHCH_2CH_2})$ (13). Vinylcyclopropane (0.025 mL, 18 mg, 0.264 mmol) was injected into a stirred suspension of **1** (103 mg, 0.212 mmol) in CH_2Cl_2 (25 mL) at −78 °C, and the reaction mixture was warmed to 0 °C. After 20 min, NMe_3 (6.27 mmol) was condensed into the reaction mixture at −78 °C. Solvent was evaporated under high vacuum at ambient temperature, and the resulting solid was purified by column chromatography (alumina, 1:3 CH_2Cl_2/hexane) to give bright red crystalline **13** (66 mg, 78%), which was shown to be a 4:1 mixture of trans and cis double bond isomers. ^1H NMR (acetone-d_6): *trans*-**13**, δ 11.63 (d, J = 12.3 Hz, μ-CH), 6.89 (dd, J = 12.5, 14.1 Hz, μ-CHC*H*=), 5.49 (dd, J = 14.1, 9.2 Hz, =CH), 4.69 (10 H, C_5H_5), 1.4 (m, 1 H, CH), 0.82 (m, 2 H, C*H*H), 0.49 (m, 2 H, CH*H*); *cis*-**13**, δ 12.2 (d, J = 12.7 Hz, μ-CH), 6.7 (dd, J = 12.7, 11.1 Hz, μ-CHC*H*=), 5.49 (=CH), 4.76 (10 H, C_5H_5), 1.4, 0.97, 0.55 (m, cyclopropyl). $^{13}C\{^1H\}$ NMR (CD_3NO_2): *trans*-**13**, δ 275.8 (μ-CO), 214.9 (CO), 166.7 (μ-CH), 157.2 (μ-CHCH=), 127.2 (μ-CHCH=*C*H), 89.3 (C_5H_5) 14.2 (CH), 8.1 (CH_2); *cis*-**13**, δ 266.8, 213.8, 166.7, 156.5, 124.4, 88.9, 11.5, 4.7. IR (CH_2Cl_2): 1975 (s), 1940 (w), 1783 (m) cm^{-1}. HRMS for $C_{19}H_{18}Fe_2O_3$: calcd, 405.9949; found, 405.9953.

Similarly, the products of the reaction of vinylcyclopropane (0.10 mmol) and 1-*d* (0.087 mmol) in CH_2Cl_2 (15 mL) at 0 °C were treated directly with NMe_3 (6.4 mmol) to give **13**-*d* (74%). $^2H\{^1H\}$ (acetone): δ 12.34, 11.76.

Reaction of 2-Methyl-1-butene with 1. 2-Methyl-1-butene (100 μl, 0.90 mmol) was added to a stirred solution of **1** (135 mg, 0.28 mmol) in CH_2Cl_2 (40 mL) at ambient temperature. Solvent was evaporated. The resulting solids were recrystallized from acetone–ether to give a 9:1 mixture of **15**:**16** (137 mg, 89%). ^1H NMR (acetone-d_6): **15**, δ 5.67, and 5.66 (C_5H_5), 5.50 (d, J = 7 Hz, μ-CC*H*H), 5.48 (d, J = 5.7 Hz, μ-CCH*H*), 2.8 (m, CH), 1.55 (m, CH_2), 1.09 (d, J = 6.2 Hz, CH_3), 1.06 (t, J = 7 Hz, CH_3); **16**, δ 12.10 (d, J = 13 Hz, μ-CH), 5.73 and 5.63 (C_5H_5), 3.40 (dd, J = 13, 7 Hz, =CH), 2.15 (m, =CHC*H*), 1.75 (m, CH_2), 1.21 (d, J = 6.5 Hz, CH_3), 1.13 (t, J = 7.4 Hz, CH_3).

A saturated aqueous solution of $NaHCO_3$ (2 mL) was added to a solution of **15** and **16** (137 mg, 0.25 mmol) in acetone (40 mL). Solvent was evaporated, and the resulting solid was recrystallized from acetone–ether to give a red solution and a dark brown solid, **16** (10 mg, 7%), which was isolated by filtration. The red solution was evaporated to dryness, and the resulting solid was purified by column chromatography (alumina, 3:1 hexane/CH_2Cl_2) to give **17** (80 mg, 79%) as a red solid, which was shown to be a 3:2 mixture of diastereomers by ^1H NMR. ^1H NMR (acetone-d_6): **17** (major diastereomer), δ 6.85 (d, J = 9.3 Hz, =CH), 4.96 and 4.89 (C_5H_5), 2.7 (m, CH), 1.6 (m, CH_2), 1.34 (d, J = 6.7 Hz, CH_3), 0.92 (t, J = 7.4 Hz, CH_3); **17** (minor diastereomer), δ 6.88 (d, J = 9.2 Hz, =CH), 4.95 and 4.90 (C_5H_5), 2.7 (m, CH), 1.5 (m, CH_2), 1.19 (t, J = 7.4 Hz, CH_3), 1.10 (d, J = 6.7 Hz, CH_3). ^{13}C NMR (CD_3NO_2): **17** (major diastereomer), 274.5 and 264.8 (μ-C and μ-CO), 214.0 (CO), 148.6 (d, J = 150 Hz, =CH), 88.7 (d, J = 179 Hz, C_5H_5), 45.6 (d, J = 121 Hz, CH), 32.8 (t, J = 120 Hz, CH_2), 23.6 (q, J = 124 Hz, CH_3), 13.1 (q, J = 121 Hz, CH_2CH_3); **17** (minor diastereomer), 264.5, 148.8, 88.5, 45.1, 22.8. IR (CH_2Cl_2): 1994 (s), 1953 (w), 1782 (m) cm^{-1}. HRMS for $C_{19}H_{20}Fe_2O_3$: calcd, 408.0105; found, 408.0095.

Reaction of 1-Methylcyclopentene with 1. A solution of 1-methylcyclopentene (0.68 mmol) and **1** (130 mg, 0.27 mmol) in CH_2Cl_2 (25 mL) was warmed from −78 to 0 °C. Solvent was evaporated, and the resulting solid was recrystallized from acetone–ether to give a 2:1 mixture of **24**:**25** (120 mg, 78%). ^1H NMR (acetone-d_6): **24**, δ 5.72, 5.70 (C_5H_5), 5.6 (m, CH), 2.95 (m, μ-CHC*H*Me, μ-CHC*H*H), 2.5 (m, μ-CHCH*H*), 2.3–1.5 (m, CH_2CH_2), 1.30 (d, J = 7.1 Hz, CH_3); **25**, δ 12.02 (b s, μ-CH), 5.84, 5.83, 5.51, 5.50 (C_5H_5), 2.7 (m, CHMe), 2.3–1.5 (m, CH_2CH_2), 1.65 (m, =CCH_2), 1.5 (d, J = 7.1 Hz, CH_3). IR (KBr): 2035 (s), 1983 (s), 1940 (w), 1848 (m) cm^{-1}.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}\overline{CCH(CH_3)CH_2CH_2CH_2})$ (26). NMe_3 (6.4 mmol) was condensed into a stirred solution of **25** and **26** (120 mg, 0.21 mmol) in CH_2Cl_2 (20 mL) at −78 °C. Solvent was evaporated, and the resulting solid was purified by column chromatography (alumina, Et_2O) to give two diastereomers of **26** (80 mg, 90%) as a red solid. ^1H NMR (acetone-d_6): δ 4.95, 4.92, 4.90, 4.86 (C_5H_5), 3.4–2.7 (=CCH), 2.2–1.5 (m, CH_2), 1.43 (d, J = 7.1 Hz, CH_3), 1.42 (d, J = 6.9 Hz, CH_3). ^{13}C NMR (CD_3NO_2): δ 275.2, 255.1, 254.0 (μ-C and μ-CO); 213.9 (CO); 156.5, 155.9 (=CR_2); 88.7 (d, J = 179 Hz, C_5H_5); 46.9 (d, J = 132 Hz, CHMe); 43.0 (d, J = 128 Hz, CHMe); 40.6 (t, J = 128 Hz, CH_2); 38.1 (t, J = 128 Hz, CH_2); 37.0 (t, J = 135 Hz, CH_2); 36.2 (t, J = 132 Hz, CH_2); 26.6 (t, J = 130 Hz, CH_2); 25.3 (t, J = 130 Hz,

(12) Wright, M. E.; Nelson, G. O. *J. Organomet. Chem.* **1984**, *263*, 371–373.

CH_2); 22.9 (q, J = 124 Hz, CH_3); 21.8 (q, J = 128 Hz, CH_3). IR (CH_2Cl_2): 1993 (s), 1951 (w), 1778 (m) cm^{-1}. HRMS calcd for $C_{20}H_{20}Fe_2O_3$ 420.0105, found 420.0107.

Similarly, reaction of 1-methylcyclopentene (0.80 mmol) with **1-*d*** (140 mg, 0.29 mmol) in CH_2Cl_2 (45 mL) gave **24-*d*, 25-*d*, 24-*d**** and **25-*d**** (140 mg, 85%). ^2H $\{^1H\}$ NMR (acetone) δ 12.0 (0.19 D, μ-CD, **25-*d***); 5.6 (0.51 D, μ-CCD, **24-*d***); 3.0, 2.9 (0.30 D, CDMe, **24-*d**** and **25-*d****).

Reaction of 2-Methyl-2-butene with 1. 2-Methyl-2-butene (0.11 mL, 1.0 mmol) was added to **1** (100 mg, 0.21 mmol) in CH_2Cl_2 (15 mL) at −78 °C and warmed to 0 °C. Solvent was evaporated and the resulting solid was recrystallized from acetone/ether to give a 1.0:2.0:1.4:1.0 mixture of **27**:**28**:**29-*E***:**29-*Z*** (61 mg, 52%).

A solution of 2-methyl-2-butene (200 μL, 1.86 mmol) and **1** (610 mg, 1.26 mmol) in CH_2Cl_2 (60 mL) was stirred at ambient temperature. A saturated aqueous solution of $NaHCO_3$ (2 mL) was added and the solution turned bright red. Solvent was evaporated and the resulting solid was recrystallized from CH_2Cl_2/ether to give a dark brown precipitate and a red solution. **27** (110 mg, 16%) was isolated as a red brown solid by filtration. The solution was evaporated and the residue was purified by column chromatography (alumina, 1:3 CH_2Cl_2/hexane) to give **30** (310 mg, 60%) as red crystals.

For **30**: ^1H NMR (acetone-d_6) δ 4.97, 4.96 (10 H, C_5H_5), 3.46 (septet, J = 7 Hz, CH), 2.35 (s, CH_3), 1.39, 1.13 (d, J = 7 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 270.3, 258.1 (μ-C, μ-CO), 212.1, 211.8 (CO), 148.3 (=CR_2), 86.9 (C_5H_5), 41.1 (CH), 22.9, 21.7, 19.5 (CH_3); IR (CH_2Cl_2) 1998 (s), 1954 (w), 1785 (m) cm^{-1}; HRMS for $C_{19}H_{20}Fe_2O_3$, calcd 408.0105, found 408.0109.

For **27**: ^1H NMR (acetone-d_6) δ 11.88 (d, J = 13 Hz, μ-CH), 5.70 (s, C_5H_5), 3.57 (d, J = 13 Hz, =CH), 1.29 (s, 9 H, CH_3); $^{13}C\{^1H\}$ (CD_3NO_2) δ 239.2 (μ-CO), 213.1 (CO), 165.1 (μ-CH), 118.0 (=CHR), 90.7 (C_5H_5), 40.0 (CMe_3), 30.1 (CH_3); IR (CH_2Cl_2) 2061 (s), 2003 (w), 1857 (m) cm^{-1}.

Anal. Calcd for $C_{19}H_{21}F_6Fe_2O_3P$: C, 41.19; H, 3.82. Found: C, 41.16; H, 3.63.

Similarly, reaction of 2-methyl-2-butene (0.64 mmol) with **1-*d*** (130 mg, 0.27 mmol) in CH_2Cl_2 (30 mL) gave **27-*d*, 28-*d*, 29-*E*-*d***, and **29-*Z*-*d*** (90 mg, 60%). $^2H\{^1H\}$ NMR (acetone): δ 11.9 (μ-CD, **27**-D), 3.2 ($CDMe_2$, **28-*d***), 2.8 ($CDMe_2$, **29-*E*-*d***), 1.1 ($CDMe_2$, **29-*Z*-*d***).

The reaction of aqueous $NaHCO_3$ and a mixture of **27-*d*, 28-*d*, 29-*E*-*d***, and **29-*Z*-*d*** (90 mg, 0.16 mmol) gave **30-*d*** (49 mg, 75%). $^2H\{^1H\}$ NMR (acetone): δ 3.5.

Protonation of 30. A solution of $HBF_4 \cdot OEt_2$ (50 μL, 0.74 mmol) and **30** (85 mg, 0.21 mmol) in ether (15 mL) was warmed from −50 °C to ambient temperature. The resulting precipitate was filtered, washed with ether (3 × 3 mL), and dried under high vacuum to give a 2.0:1.4:1.0 ratio of **28**, **29-*E***, and **29-*Z*** (85 mg, 74%). ^1H NMR (acetone-d_6): **28**, δ 5.72 and 5.71 (s, 10 H, C_5H_5), 5.05 (dq, J = 6.5, 2.7 Hz, μ-CCH), 3.2 (m, $CHMe_2$), 1.94 (d, J = 6.5 Hz, $CHCH_3$), 1.30 (d, J = 6.7 Hz, $CH(CH_3)Me$), 1.23 (d, J = 6.5 Hz, $CH(Me)CH_3$); **29-*E***, δ 12.04 (s, μ-CH), 5.70 (s, C_5H_5), 2.74 (septet, J = 6.7 Hz, $CHMe_2$), 1.36 (d, J = 6.7 Hz, 6 H, CH_3), 1.26 (s, CH_3); **29-*Z***: δ 11.76 (s, μ-CH), 5.68 (s, C_5H_5), 2.3 (s, CH_3), 1.3 (m, $CHMe_2$), 0.84 (d, J = 6.9 Hz, 6 H, CH_3).

Reaction of 9,9-Dimethyl-10-methylene-9,10-dihydroanthracene (19) with 1. A solution of **19** (100 mg, 0.45 mmol) and **1** (200 mg, 0.41 mmol) in CH_2Cl_2 (10 mL) was warmed from −78 °C to ambient temperature. Solvent was evaporated under high vacuum, and the resulting solid was recrystallized from acetone–ether to give μ-alkylidyne complex **20** (206 mg, 71%) as a dark brown solid. ^1H NMR showed the presence of about 10% μ-alkenyl complex **21**. ^1H NMR (acetone-d_6): δ 7.9–7.1 (m, 8 H), 5.665 (s, C_5H_5), 5.662 (s, C_5H_5), 5.54 (d, J = 6 Hz, μ-CCH_2), 1.86 (s, CH_3), 1.76 (s, CH_3), μ-CCH_2CH not observed. IR (CH_2Cl_2): 2042 (s), 2010 (w), 1859 (m) cm^{-1}.

Thermal Rearrangement of 20. Solid **20** (5 mg, 7.1 μmol) was heated at 80 °C for 18 h. The solid was dissolved in acetone-d_6 and analyzed by ^1H NMR. The solid consisted of 86% μ-alkenyl complex **21**, 12% starting material **20**, and 2% $(C_5H_5)Fe(CO)_3^+PF_6^-$.

For **21**: ^1H NMR (acetone-d_6) δ 12.39 (d, J = 12.1 Hz, μ-CH), 7.8–7.3 (m, 8 H), 5.75 (s, 10 H, C_5H_5), 4.87 (d, J = 8.6 Hz, =$CHCH$), 3.24 (dd, J = 8.6, 12.2 Hz, =CH), 1.78 (s, CH_3), 1.47 (s, CH_3); IR (CH_2Cl_2) 2026 (s), 1992 (w), 1863 (m) cm^{-1}.

Deprotonation of 20. An acetone solution of μ-alkylidyne complex **20** (89 mg, 0.126 mmol) was stirred with aqueous $NaHCO_3$ for 1 h at ambient temperature. Solvent was evaporated, and the residue was purified by column chromatography (alumina, 3:1 hexane/CH_2Cl_2) to give μ-alkenylidene complex **22** (38 mg, 54%). ^1H NMR (acetone-d_6): δ 8.4, 7.7, 7.6, 7.37, 7.33, 7.25, 7.2, 7.1 (multiplets, 8 H), 7.85 (d, J = 10 Hz, =CH), 5.34 (d, J = 10 Hz, =$CHCH$), 5.15, 5.00 (s, C_5H_5), 1.94, 1.46 (s, CH_3). IR (CH_2Cl_2): 1998 (s), 1962 (w), 1791 (m) cm^{-1}. HRMS (m − 2CO) for $C_{29}H_{26}Fe_2O$: calcd, 502.0681; found, 502.0679.

$[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)_2$ (38). $(C_5Me_5)Fe(CO)_2Br$ (525 mg, 1.61 mmol) and $(C_5H_5)Fe(CO)_2K$ (347 mg, 1.61 mmol) were stirred in 20 mL of THF at −78 °C for 1 h and then warmed to ambient temperature. ^1H NMR of the product mixture indicated 90% mixed ring iron dimer **38**, with 5% $[(C_5H_5)Fe(CO)(\mu\text{-}CO)]_2$ and 5% $[(C_5Me_5)Fe(CO)(\mu\text{-}CO)]_2$ present as minor impurities. Evaporation of solvent and chromatography (alumina, 9:1 hexane/toluene) led to the isolation of red-brown crystalline **38** (430 mg, 63%) as the middle band. ^1H NMR (C_6D_6): δ 4.40 (s, C_5H_5), 1.53 (s, C_5Me_5). IR (THF): 1987 (m), 1942 (s), 1772 (s) cm^{-1}.

Anal. Calcd for $C_{19}H_{20}Fe_2O_4$: C, 53.91; H, 4.76. Found: C, 53.95; H, 4.78.

Interestingly, the reaction of $(C_5H_5)Fe(CO)_2I$ with $(C_5Me_5)Fe(CO)_2^-K^+$ gave a 1:1 mixture of $[(C_5H_5)Fe(CO)(\mu\text{-}CO)]_2$ and $[(C_5Me_5)Fe(CO)(\mu\text{-}CO)]_2$, with no evidence for mixed-dimer formation.

***cis*- and *trans*-$[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}CH_2)$ (*cis*- and *trans*-31).** A THF solution of $(C_6H_5)_3P{=}CH_2$ (7.2 mmol, prepared from $(C_6H_5)_3PCH_3Br$ and n-BuLi) was added to a solution of **38** (prepared in situ from 2.4 mmol of $(C_5Me_5)Fe(CO)_2Br$ and 2.4 mmol of $(C_5H_5)Fe(CO)_2K$). The reaction mixture was refluxed for 4 days, the solvent was removed under vacuum, and the oily residue was chromatographed (alumina, 95:5 hexane/toluene) to give *trans*- and *cis*-**31** (419 mg, 42%, 4:1 trans:cis) containing about 10% of **38**. This mixture was used without further purification in the synthesis of **32**. Recrystallization from hexane at −78 °C gave an analytically pure 2:1 mixture of *trans*- and *cis*-**31**. ^1H NMR (C_6D_6): *cis*-**31**, δ 9.10 (s, μ-CHH), 9.05 (s, μ-CHH), 4.35 (s, C_5H_5), 1.44 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *cis*-**31**, δ 147.7 (μ-CH_2), 96.9 (C_5Me_5), 82.9 (C_5H_5), 9.6 ($C_5(CH_3)_5$); the carbonyl resonances are overlapping with those of *trans*-**31**; *trans*-**31**: δ 277.1 (μ-CO), 215.3 (CO), 214.9 (CO), 150.3 (μ-CH_2), 97.8 (C_5Me_5), 85.6 (C_5H_5), 9.1 ($C_5(CH_3)_5$). IR (CH_2Cl_2): 1970 (m), 1925 (s), 1771 (m) cm^{-1}.

Anal. Calcd for $C_{19}H_{22}Fe_2O_3$: C, 55.65; H, 5.41; Fe, 27.24. Found: C, 55.50; H, 5.50; Fe, 27.39.

The major isomer was assigned the trans configuration on the basis of the IR spectrum. For *cis*-$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$, the high-energy symmetric band (1986 cm^{-1}) is more intense than the low energy asymmetric band (1942 cm^{-1}); for *trans*-$[(C_5Me_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ a single band is seen at 1909 cm^{-1}. The highest energy band at 1970 cm^{-1} is assigned to the symmetric stretch of *cis*-**31**; the weaker asymmetric stretch of *cis*-**31** is buried under the intense band at 1925 cm^{-1} due to *trans*-**31**.

***cis*- and *trans*-$[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (*cis*- and *trans*-32).** $(C_6H_5)_3C^+PF_6^-$ (0.173 g, 0.45 mmol) in CH_2Cl_2 (3 mL) was added to bridging methylene complex **31** (0.205 g, 0.50 mmol) in CH_2Cl_2 (3 mL) at 0 °C. The reaction mixture was stirred at ambient temperature for 10 min. Dropwise addition of hexane (15 mL) at 0 °C led to precipitation of a red microcrystalline solid which was washed with hexane (2 × 15 mL) and dried under vacuum to give pure *cis*- and *trans*-**32** (217 mg, 87%), mp 130 °C (dec). ^1H NMR (CD_2Cl_2) indicated a 3:2 mixture of two isomers of **32**. Major isomer: δ 22.25 (s, μ-CH), 5.30 (s, C_5H_5), 1.86 (s, $C_5(CH_3)_5$). Minor isomer: δ 22.24 (s, μ-CH), 5.26 (s, C_5H_5), 1.82 (s, $C_5(CH_3)_5$). IR (CH_2Cl_2): 2045 (s), 2010 (s), 1851 (m) cm^{-1}.

***cis*-$[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](\mu\text{-}CO)(\mu\text{-}C(CH_2)_4CH_3)^+PF_6^-$ (33).** A solution of **32** (204 mg, 0.368 mmol) and 1-pentene (3.2 mmol) in 10 mL of CH_2Cl_2 was warmed from −78 °C to ambient temperature. Solvent was evaporated, and the residue was recrystallized from CH_2Cl_2–ether to give **33** (150 mg, 65%). ^1H NMR ($CDCl_3$): δ 5.29 (s, C_5H_5), 5.10 (m, μ-CCH_2), 1.84 (s, $C_5(CH_3)_5$), 1.4–2.1 (m, 6 H), 0.93 (t, J = 7.1 Hz, CH_3). $^{13}C\{^1H\}$ NMR (acetone-d_6, 0 °C): δ 497.6 (μ-C), 256.9 (μ-CO), 208.8

(CO), 104.4 (C_5Me_5), 91.2 (C_5H_5), 72.1 (μ-CCH_2), 31.8, 22.2, 13.5 ($(CH_2)_3CH_3$); 8.8 ($C_5(CH_3)_5$). IR (CH_2Cl_2): 2030 (s), 2001 (w), 1842 (m) cm^{-1}.

***cis*-[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](μ-CO)(μ-C=CH-$(CH_2)_3CH_3$) (34).** NMe_3 (2.1 mmol) was added to a solution of **33** (86 mg, 0.14 mmol) in 3 mL of CH_2Cl_2 at -78 °C. Solvent was evaporated at ambient temperature, and the oily residue was crystallized from 2 mL of hexane at -78 °C to give **34** (40 mg, 51%). ^1H NMR (C_6D_6): δ 7.00 (t, J = 6.9 Hz, μ-C=CH), 4.51 (s, C_5H_5), 2.95 (m, =CHCH_2), 1.2-1.9 (m, 4 H), 1.46 (s, C_5Me_5), 1.08 (t, J = 7.0 Hz, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 0 °C): δ 274.5, 272.1 (μ-CO, μ-C), 213.1, 212.1 (CO), 134.9 (C=CH-), 96.5 (C_5Me_5), 85.5 (C_5H_5), 37.1, 34.5, 23.1, 14.7 ($CH_2CH_2CH_2CH_3$), 9.3 ($C_5(CH_3)_5$). IR (CH_2Cl_2): 1983 (s), 1940 (w), 1769 (m) cm^{-1}. HRMS for $C_{24}H_{30}Fe_2O_3$: calcd, 478.0885; found, 478.0891.

***cis*-[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](μ-CO)(μ-η^1,η^2-*trans*-CH=CHCH$(CH_3)_2$)$^+PF_6^-$ (35).** A solution of **32** (190 mg, 0.32 mmol) and isobutylene (0.72 mmol) in 10 mL of CH_2Cl_2 was warmed from -78 °C to ambient temperature. Solvent was evaporated, and the residue was recrystallized from CH_2Cl_2-ether to give **35** (172 mg, 82%). ^1H NMR ($CDCl_3$): δ 10.85 (d, J = 11.5 Hz, μ-CH=C), 5.03 (s, C_5H_5), 3.52 (dd, J = 9.3, 11.5 Hz, μ-CH=CH), 2.40 (m, C$H$$Me_2$), 1.90 (s, C_5Me_5), 1.46 (d, J = 6.5 Hz, CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN, 0 °C): δ 215.0 (CO), 180.6 (μ-CH=CH-), 106.6 (μ-CH=CH-), 103.7 (C_5Me_5), 87.7 (C_5H_5), 39.9 ($CHMe_2$), 26.1 (CH_3), 21.8 (CH_3), 9.6 ($C_5(CH_3)_5$). IR (CH_2Cl_2): 2015 (s), 1995 (m), 1859 (m) cm^{-1}.

Anal. Calcd for $C_{23}H_{29}F_6Fe_2O_3P$: C, 45.28; H, 4.79. Found: C, 44.91; H, 4.87.

[(C_5Me_5)(CO)Fe][(C_5H_5)(CO)Fe](μ-CO)(μ-CHCH=C-$(CH_3)_2$) (36). NMe_3 (2.1 mmol) was added to a solution of **35** (86 mg, 0.14 mmol) in 3 mL of CH_2Cl_2 at -78 °C. Solvent was evaporated at ambient temperature, and the residue was dissolved in toluene. The toluene solution was filtered and evaporated to dryness. The resulting violet crystalline solid was washed with hexane to give **36** (50 mg, 76%). ^1H NMR (CD_2Cl_2): δ 10.77 (d, J = 12.8 Hz, μ-CH), 6.73 (d, J = 12.8 Hz, μ-CH-CH=), 4.70 (s, C_5H_5), 2.10 (s, CH_3), 1.83 (s, CH_3), 1.66 (s, C_5Me_5). ^{13}C NMR (C_6D_6, 0 °C): δ 275.4 (s, μ-CO), 214.4, 213.4 (s, CO), 165.8 (d, J = 132 Hz, μ-CH), 154.0 (d, J = 150 Hz, μ-CHCH=), 120.3 (s, CH=CMe_2), 96.6 (s, C_5Me_5), 85.6 (d, J = 180 Hz, C_5H_5), 26.3 (q, J = 128 Hz, =C(CH_3)CH_3), 19.0 (q, J = 128 Hz, =C(CH_3)CH_3), 9.1 (q, J = 128 Hz, $C_5(CH_3)_5$). IR (CH_2Cl_2): 1980 (s), 1916 (m), 1779 (m) cm^{-1}. HRMS: for $C_{23}H_{28}Fe_2O_3$: calcd, 464.0729; found, 464.0737.

[(C_5Me_5)(CO)Fe]$_2$(μ-CO)(μ-CH)$^+PF_6^-$ (37) and Isobutylene. The initial ^1H NMR spectrum obtained from a solution of [(C_5Me_5)(CO)Fe]$_2$(μ-CO)(μ-CH_2)[12] (**38**) (7.0 mg, 15 μmol) and $(C_6H_5)_3C^+PF_6^-$ (7.0 mg, 18 μmol) in 0.3 mL of CD_2Cl_2 had a broad ($\omega_{1/2}$ = 223 Hz) band centered at δ 13 in addition to other resonances. After 20 min, the broad resonance disappeared and peaks at δ 21.63 (μ-CH) and δ 1.84 (C_5Me_5) assigned to **37** appeared.

An impure sample of **37** was obtained from the reaction of **38** (128 mg, 0.26 mmol) and $(C_6H_5)_3C^+PF_6^-$ (95 mg, 0.25 mmol) in 4 mL of CH_2Cl_2 at ambient temperature. The solution was cooled to -78 °C, and hexane was added to precipitate a purple-black solid (120 mg) which was washed with hexane. ^1H NMR indicated a 1:0.5 ratio of **37**:$(C_6H_5)_3CX$. When a solution of **37** (5 mg, 7 μmol) and isobutylene (30 μmol) in 0.3 mL of CD_2Cl_2 at ambient temperature was monitored by ^1H NMR, no new resonances were seen initially. After 24 h, the resonance at δ 21.6 due to **37** was still visible, but many resonances due to decomposition products were observed.

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Chemistry Derived from Ruthenium Atoms. 2.[1] Synthesis and Reactivity of the Monocarbonyl Complexes Formed from Ruthenium–Cyclohexadiene Cocondensates

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Ruthenium atoms generated from an electron beam furnace have been cocondensed with either 1,3- or 1,4-cyclohexadiene, and CO subsequently has been added at -196 °C. The initial product of the syntheses has been characterized as Ru(CO)(η^5-C_6H_7)(η^3-C_6H_9) (1). In solution at room temperature 1 underwent a thermal rearrangement to Ru(CO)(η^4-C_6H_8)$_2$ (2) ($t_{1/2}$ = 96 min at 31 °C). Prolonged reflux of 2 in the presence of free 1,3-cyclohexadiene and under CO (1 atm) yielded the bis(allyl) complex Ru(CO)$_2$(η^3:η^3-$C_{12}H_{16}$) (5) via C-C coupling of the diene ligands. Hydride abstraction from 1 and 2 using $[Ph_3C]BF_4$ gave [Ru(CO)(η^6-C_6H_6)(η^3-C_6H_9)]BF_4 (3) and [Ru(CO)(η^5-C_6H_7)(η^4-C_6H_8)]BF_4 (4), respectively. The reverse reactions 3 → 1 and 4 → 2 occurred on treatment with $NaBH_4$, and the hydride additions were assigned exo to the ruthenium atom (deuterium labeling). The transformation 4 → 2 is not consistent with a charge-controlled nucleophilic addition.

Introduction

A large and diverse range of mononuclear ruthenium complexes bearing two C_6–C_8 cyclic hydrocarbon ligands are now known.[2-12] Convenient syntheses from chloro-ruthenium complexes have been developed, chiefly by Bennett[6] and by Vitulli,[7] and in general the resulting or-

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