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Notes

Reaction of 19-Valence-Electron Sandwich Complexes with Alkyl Halides. A Radical-Clock Investigation

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Summary: The organometallic radicals $CoCp_2$ (1) and $CpFe(HMB)$ ($HMB = C_6Me_6$; 2) react with the radical-clock reagent 5-hexenyl iodide to give unrearranged addition products, while with cyclopropylmethyl halides both unrearranged cyclopropylmethyl and rearranged 3-butenyl addition products are formed. The rate constant for radical addition was estimated from the product ratios. For 1 a lower bound of $k_2 \geq 5.8 \times 10^8\ s^{-1}$ at 67 °C was obtained, while for 2 a value of $k_2 = (1.2 \pm 0.2) \times 10^9\ s^{-1}$ at 25 °C was determined. Thus, both 1 and 2 are extremely efficient radical scavengers.

Sandwich complexes with 19 valence electrons such as cobaltocene ($CoCp_2$, 1) and (cyclopentadienyl)(hexamethylbenzene)iron ($CpFe(HMB)$, 2) are strongly reducing organometallic radicals.[1] A very characteristic reaction of cobaltocene is the oxidative addition of alkyl halides RX (as e.g. MeI, CCl_4, $PhCH_2Br$) (eq 1).[2] This reaction

$$2CoCp_2 + RX \rightarrow [CoCp_2]X + CpCo(5\text{-}exo\text{-}RC_5H_5) \qquad (1)$$

is thought to proceed by a radical mechanism,[2e] consisting of a slow electron-transfer step (eq 2) with concomitant or, given some stability of the radical anion $[RX]^{\bullet-}$, fast subsequent formation of the free radical $R^\bullet$ (eq 3) and of a subsequent addition of $R^\bullet$ to a second molecule of 1 (eq 4). The radical addition step (4) could be verified

$$CoCp_2 + RX \rightarrow [CoCp_2]^+ + [RX]^{\bullet-} \qquad (2)$$

$$[CoCp_2]^+ + [RX]^{\bullet-} \rightarrow [CoCp_2]X + R^\bullet \qquad (3)$$

$$CoCp_2 + R^\bullet \rightarrow CpCo(5\text{-}exo\text{-}RC_5H_5) \qquad (4)$$

independently; the radical $^\bullet C(CN)Me_2$, formed by thermal decomposition of azoisobutyronitrile, is scavenged by cobaltocene with high efficiency.[3] However, a direct proof for the intermediacy of free radicals apparently is not known.

Analogous oxidative-addition reactions have also been observed for $CpFe(C_6H_6)$,[4a] 2,[4b] $CpNi(C_4Ph_4)$,[5] and $(1,3,5\text{-}C_6H_3Me_3)Co(C_4Ph_4)$.[5] It should be noted here that 2 can form two regioisomeric addition products (eq 5), obtained from addition to the Cp and the HMB ligands, respectively.[4b]

$$\begin{aligned} 2CpFe(HMB) + RX \rightarrow{} & [CpFe(HMB)]X + \\ & (1 - x)Fe(5\text{-}exo\text{-}RC_5H_5)(HMB) + \\ & xCpFe(6\text{-}exo\text{-}RC_6Me_6) \qquad (5) \end{aligned}$$

$$0 \leq x \leq 1$$

A powerful chemical technique to prove the intermediacy of free radicals is the use of radical-clock reactions.[6] In these reactions a radical-clock reagent is used to generate a primary radical which can either form products directly or alternatively rearrange followed by product formation. The appearance of rearrangement products gives evidence for the intermediacy of the radical. A number of radical-clock systems with a wide range of rearrangement rates is known.[6] We have now investigated the oxidative addition reactions of 1 and 2 with the radical-clock reagents 5-hexenyl iodide (**3**) and cyclopropylmethyl halides (**4a**, X = I; **4b**, X = Br). The rearrangement of the cyclopropylmethyl radical is about 400–500 times faster than that of the 5-hexenyl system.[6b,c]

Results

$CoCp_2$ (**1**) reacts with 5-hexenyl iodide (**3**) (in hexane, reflux, 3 days) to give the 5-hexenyl addition product **5** and the salt 1I. The more reactive CpFe(HMB) (**2**) (in THF, room temperature, 4 h) gives the two regioisomeric products **6** and **7** in the ratio 2.8:1 and 2I. In both experiments rearrangement products with a cyclopentylmethyl substituent could not be detected.

In contrast to these observations cyclopropylmethyl iodide (**4a**) reacts with **1** in boiling THF (3 days) to give the two isomers **8a,b** in a ratio of 1:12. The rearrangement product **8b** with a 3-butenyl group predominates. In a control experiment it was found that the iodide **4a** undergoes some isomerization (ca. 20%, after 3 days at

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(1) For a general review see: Astruc, D. *Chem. Rev.* **1988,** *88,* 1189.

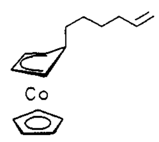
(2) (a) Kemmitt, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 5, p 244. (b) Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1959,** 3753. (c) Herberich, G. E.; Bauer, E. *J. Organomet. Chem.* **1969,** *16,* 301. (d) Herberich, G. E.; Bauer, E.; Schwarzer, J. *J. Organomet. Chem.* **1969,** *17,* 445. (e) Herberich, G. E.; Schwarzer, J. *J. Organomet. Chem.* **1972,** *34,* C43.

(3) Herberich, G. E.; Schwarzer, J. *Angew. Chem.* **1970,** *82,* 883; *Angew. Chem., Int. Ed. Engl.* **1970,** *9,* 897.

(4) (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Petrakova, V. A.; *J. Organomet. Chem.* **1977,** *136,* 363. (b) Herberich, G. E.; Klein, W. *Chem. Ber.* **1989,** *122,* 2125.

(5) Herberich, G. E.; Klein, W.; Koelle, U.; Spiliotis, D. *Chem. Ber.* **1992,** *125,* 1589.

(6) (a) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988,** *21,* 206. (b) Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989,** *111,* 275. (c) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991,** *113,* 5687.



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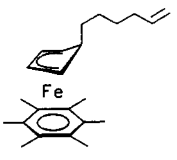

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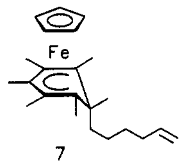

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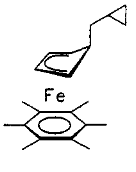
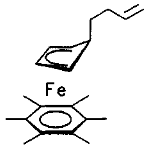
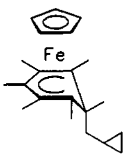
reflux temperature) when catalytic amounts of **1** were added, but not in THF alone. The reaction of the bromide **4b** with **2** in THF at ambient temperature gives four products. Addition of the primary cyclopropylmethyl radical produces the two regioisomers **9a** and **10a** in a ratio of 1.7:1, while rearrangement to the 3-butenyl radical and subsequent addition produces the rearrangement products **9b** and **10b** in a ratio of 3.0:1; the overall ratio of unrearranged versus rearranged products is 1:3.5. No 3-butenyl bromide was found when unconsumed **4b** was recovered. All products were obtained in yields between 78 and 95% and were characterized as mixtures.



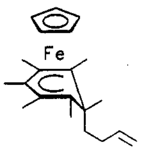
9a



9b



10a



10b

Having proved the radical nature of the mechanism, we may detail the kinetic model pertaining to eqs 2–4 in Scheme I, choosing the reaction of **1** with the iodide **4a** as an example. The rate-determining step is the electron transfer (eq 2) which results in formation of the primary cyclopropylmethyl radical ($R^{\bullet}$) (eq 3). This can then undergo two competing reactions: the formation of **8a** and the rearrangement to the 3-butenyl radical ($R'^{\bullet}$), which subsequently forms the rearrangement product **8b**.

By using the usual steady-state assumptions for $R^{\bullet}$ and $R'^{\bullet}$ and taking into account the stoichiometry of the reaction, one can show that the final concentration C_{8a}^{∞} of the product **8a** is given by eq 6, where C_1^0 denotes the initial concentration of **1** and k_2 and k_3 are the rate constants as defined in Scheme I. As the product distribution is fully determined by k_2 and k_3, no information can be obtained for the rate constant k_4. However,

$$C_{8a}^{\infty} = \frac{C_1^0}{2} + \frac{k_3}{2k_2}\ln\left(\frac{k_3}{k_2C_1^0 + k_3}\right) \qquad (6)$$

it seems safe to assume that k_4 is of the same magnitude as k_2.

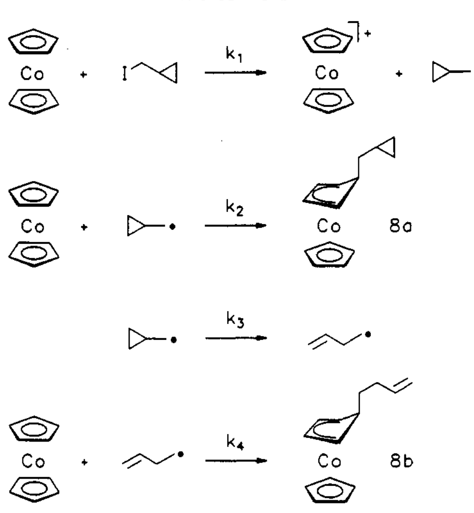
The temperature dependence of k_3 is known to be

$$\log(k_3\ (\mathrm{s})) = 13.15 - \frac{7.05 \times 4184}{2.3RT} \qquad (7)$$

(RT is given in SI units) and $k_3 = 4.1 \times 10^8\ \mathrm{s}^{-1}$ at 67 °C. With the given concentrations C_1^0 (0.120 mol/L) and C_{8a}^{∞} (4.6×10^{-3} mol/L) the rate constant k_2 is calculated to be $(5.8 \pm 1.0) \times 10^8\ \mathrm{s}^{-1}$ at 67 °C; because of the parallel catalytic isomerization of the iodide **4a** this value is a lower bound to the true rate constant.

The reaction of **2** with the bromide **4b** is described by the same type of equation as far as the overall concentration of the regioisomers **9a** and **10a** is concerned. These isomers are formed by competing reactions with rate constants $k_{2\text{-Cp}}$ and $k_{2\text{-HMB}}$; hence

Scheme I



$$k_2 = k_{2\text{-Cp}} + k_{2\text{-HMB}}$$

$$\frac{k_{2\text{-Cp}}}{k_{2\text{-HMB}}} = \frac{C_{9a}}{C_{10a}}$$

With these relations, the rate constant $k_3 = 9.4 \times 10^7\ \mathrm{s}^{-1}$ at 25 °C, and the given concentrations (C_1^0 = 0.047 mol/L, $C_{9a+10a}^{\infty} = 5.2 \times 10^{-3}$ mol/L) the rate constants $k_2 = (1.2 \pm 0.2) \times 10^9\ \mathrm{s}^{-1}$, $k_{2\text{-Cp}} = (7.8 \pm 1.2) \times 10^8\ \mathrm{s}^{-1}$, and $k_{2\text{-HMB}} = (4.6 \pm 0.7) \times 10^8\ \mathrm{s}^{-1}$ at 25 °C were obtained.

Discussion

The rate-determining electron-transfer step (eq 2) usually is a slow reaction. Once the primary radical is formed, the subsequent radical addition step is extremely fast, and only the very fastest radical-clock systems find sufficient time to show rearrangement. Indeed, the slow 5-hexenyl radical is scavenged by **1** and **2** without noticeable rearrangement, while the cyclopropylmethyl radical, which is known to rearrange at rates 2–3 orders of magnitude higher than 5-hexenyl,[6b,c] does rearrange to a certain extent prior to product formation. Thus, our observations show that both **1** and **2** are extremely efficient radical scavengers.

In agreement with our earlier work,[5] the iron complex **2** shows a marked preference for radical addition at the cyclopentadienyl ligand. This regioselectivity reflects the higher spin density at the Cp ligand as compared to the HMB ligand.[7]

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Pentane and hexane were distilled from Na/K alloy; toluene was distilled from sodium, and ethereal solvents were distilled from sodium benzophenone ketyl. Alumina for chromatography (Woelm) was heated under a high vacuum at 300 °C and deactivated (7% H_2O, deoxygenated) after cooling.

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[7] Astruc, D.; Hamon, J.-R.; Althoff, G.; Román, E.; Batail, P.; Michaud, P.; Mariot, J.-P.; Varret, F.; Cozak, D. *J. Am. Chem. Soc.* **1979**, *101*, 5445.

NMR spectra were recorded on a Varian VXR 500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125.70 MHz), a Bruker WH 270 PFT spectrometer (^{1}H, 270 MHz; ^{13}C, 67.88 MHz), and a Bruker WP 80 PFT spectrometer (^{1}H, 80 MHz). The digital resolution was <0.5 Hz/point for ^{1}H and <1.0 Hz/point for ^{13}C spectra.

Materials. CoCp$_2$ (**1**)[8] and CpFe(HMB) (**2**)[7,9] were prepared as described previously. 5-Hexenyl iodide (**3**) and the cyclopropylmethyl halides (**4a,b**) were made from the corresponding alcohols by mesylation followed by a Finkelstein reaction and were purified by distillation. Other chemicals were used as received.

Preparation of 5. A solution of CoCp$_2$ (**1**; 1.08 g, 5.7 mmol) and 5-hexenyl iodide (**3**; 0.97 g, 4.6 mmol) in hexane (50 mL) was refluxed. After 4 days the color of the solution had changed from black to red. The red solution was filtered through a layer (5 cm) of alumina, and this layer was eluted with hexane (2 × 20 mL). Removal of the volatiles in vacuo gave **5** (0.72 g, 92%) as a red oil. MS (m/z (I_{rel})): 272 (70, M$^+$), 189 (100, CoCp$_2^+$). ^{1}H NMR (C$_6$D$_6$; δ): 4.60 (s, Cp); 5-hexenyl (primed numbers in parentheses refer to atoms of the group R), 5.75 (m, 5′-H), 4.85–5.1 (m, 2H, 6′-H), 1.91 ("q", 2H, 4′-H), 0.9–1.3 (m, 4H, 2′-/3′-H), 0.56 ("t", 2H, 1′-H); η^4-C$_5$H$_5$R, 5.05 ("t", $^3J + {}^4J$ = 4.0 Hz, 2-/3-H), 2.65 ("q", 1-/4-H), 2.59 (m, 5-*endo*-H). ^{13}C NMR (C$_6$D$_6$/C$_6$H$_6$; δ): 79.2 (dtt, ^1J = 174, ^3J = 8, ^2J = 5 Hz, Cp); 5-hexenyl, 138.9 (d, ^1J = 150 Hz, C-5′), 114.6 (tt, ^1J = 155, ^3J = 6 Hz, C-6′), 41.5 (t, ^1J = 125 Hz, C-4′), for C-1′/2′/3′, 34.0 (t, ^1J = 125 Hz), 29.2 (t, ^1J = 124 Hz), and 25.3 (t, ^1J = 124 Hz); η^4-C$_5$H$_5$R, 74.7 (dt, ^1J = 175, ^3J = 5.5 Hz, C-2/3), 52.4 (d, ^1J = 138 Hz, C-5), 44.4 (d, ^1J = 168 Hz, C-1/4).

Reaction of CpFe(HMB) (2) with 5-Hexenyl Iodide (3). To a stirred solution of **2** (1.05 g, 3.7 mmol) in 50 mL of THF was added **3** (0.47 g, 2.2 mmol) at −78 °C. The reaction became noticeable at −40 °C. The temperature was increased to room temperature over a period of 4 h, and the solution turned orange-red. The solvent was removed under vacuum and the residue extracted with hexane. The red filtrate was evaporated in vacuo to dryness, yielding a mixture of **6** and **7** (ratio 2.8:1; 0.62 g, 91%) as a red, air-sensitive oil. MS (m/z (I_{rel})): 366 (50, M$^+$), 283 (99, CpFe(HMB)$^+$), 218 (37, Fe(HMB)$^+$). Anal. Calcd for C$_{23}$H$_{34}$Fe: C, 75.40; H, 9.35. Found: C, 75.07; H, 9.01.

Compound 6. ^{1}H NMR (C$_6$D$_6$, δ): 2.00 (s, HMB); 5-hexenyl, 5.75 (ddt, $^3J_{\text{trans}}$ = 16.3, $^3J_{\text{cis}}$ = 9.9, $^3J_{4,5}$ = 6.2 Hz, 5′-H), 4.98 (m, 2H, 6′-H), 1.44–0.40 (m, 8H, 1′-/2′-/3′-/4′-H); η^4-C$_5$H$_5$R, 4.10 ("t", $^3J + {}^4J$ = 4.0 Hz, 2-/3-H), 1.55 ("q", 1-/4-H), 2.18 (m, 5-*endo*-H). ^{13}C NMR (C$_6$D$_6$; δ): 91.1 (s, HMB), 17.1 (q, ^1J = 126 Hz, HMB); 5-hexenyl, 139.5 (d, ^1J = 149 Hz, C-5′), 114.3 (t, ^1J = 153 Hz, C-6′), 41.8 (t, ^1J = 125 Hz, C-4′), for C-1′/-2′/3′ 34.3 (t, ^1J = 122 Hz), 29.7 (t, ^1J = 125 Hz), 25.6 (t, ^1J = 126 Hz); η^4-C$_5$H$_5$R, 73.4 (dquin, ^1J = 171, $^3J + {}^2J$ = 6 Hz, C-2/3), 53.1 (d, ^1J = 131 Hz, C-5), 44.9 (d, ^1J = 167 Hz, C-1/4).

Compound 7. ^{1}H NMR (C$_6$D$_6$; δ): 3.68 (s, Cp); 5-hexenyl, 5.66 (m, 5′-H), 4.91 (m, 2H, 6′-H), 1.25–0.96 (m, 8H, 1′-/2′-/3′-/4′-H); η^5-C$_6$Me$_6$R, 2.36 (s, 3-Me), 1.81 (s, 2-/4-Me), 1.43 (s, 1-/5-Me), 1.33 (s, 6-*endo*-Me).

Reaction of CoCp$_2$ (1) with Cyclopropylmethyl Iodide (4a). A solution of **1** (1.16 g, 6.1 mmol) and **4a** (1.2 g, 6.6 mmol) in THF (50 mL) was refluxed for 3 days. Workup as for **5** gave a mixture of **8a,b** (ratio 1:12; 0.65 g, 86%) as a red oil. MS (m/z (I_{rel})): 244 (16, M$^+$), 189 (100, CoCp$_2^+$), 124 (65, CoCp$^+$).

Compound 8a. ^{1}H NMR (C$_6$D$_6$; δ): 4.595 (s, Cp); cyclopropylmethyl, 0.840 (m, 2H, 1′-H), 0.420 (m, 2 H, 3′-H$_a$), 0.270 (m, 2H, 3′-H$_b$), −0.147 (m, 2′-H); η^4-C$_5$H$_5$R, 5.034 (m, 2-/3-H), 2.740 (m, 5-*endo*-H), 2.672 (m, 1-/4-H). ^{13}C NMR (C$_6$D$_6$/C$_6$H$_6$; δ): 79.1 (dtt, ^1J = 174, ^3J = 8, ^2J = 5 Hz, Cp); cyclopropylmethyl, 30.3 (t, ^1J = 124 Hz, C-1′), 8.3 (d, ^1J = 166 Hz, C-2′), 4.7 (t, ^1J = 150 Hz, C-3′); η^4-C$_5$H$_5$R, 74.7 (dt, ^1J = 175, ^3J = 6 Hz, C-2/3), 53.3 (d, ^1J = 140 Hz, C-5), 44.6 (d, ^1J = 170 Hz, C-1/4).

Compound 8b. ^{1}H NMR (C$_6$D$_6$; δ): 4.570 (s, Cp); 3-butenyl, 5.652 (ddtm, $^3J_{\text{trans}}$ = 17.1, $^3J_{\text{cis}}$ = 10.4, $^3J_{3',2'}$ = 6.8 Hz, 3′-H), 4.936 (dm, $^3J_{\text{trans}}$ = 17.1 hz, 4′-H$_{\text{trans}}$), 4.895 (dm, $^3J_{\text{cis}}$ = 10.4 Hz, 4′-H$_{\text{cis}}$), 1.714 (tdm, $^3J_{2',1'}$ = 7.0, $^3J_{2',3'}$ = 6.8 Hz, 2H, 2′-H), 0.610 (tdm, $^3J_{1',2'}$ = 7.0, $^3J_{1',1}$ = 6.7 Hz, 2H, 1′-H); η^4-C$_5$H$_5$R, 5.008 (m, 2-/3-H), 2.615 (m, 1-/4-H), 2.555 (tm, $^3J_{5\text{endo},1'}$ = 6.7 Hz, 5-*endo*-H). ^{13}C NMR (C$_6$D$_6$/C$_6$H$_6$; δ): 79.1 (dtt, ^1J = 174, ^3J = 8, ^2J = 5 Hz, Cp); 3-butenyl, 139.3 (d, ^1J = 147 Hz, C-3′), 114.1 (t, ^1J = 155 Hz, C-4′), 40.8 (t, ^1J = 125 Hz, C-2′), 30.3 (t, ^1J = 124 Hz, C-1′); η^4-C$_5$H$_5$R, 74.7 (dt, ^1J = 175, ^3J = 6 hz, C-2/3), 52.5 (d, ^1J = 142 Hz, C-5), 44.2 (d, ^1J = 171 Hz, C-1/4).

Reaction of CpFe(HMB) (2) with Cyclopropylmethyl Bromide (4b). **4b** (0.19 g, 1.4 mmol) was added to **2** (0.66 g, 2.3 mmol) in THF (50 mL) at room temperature. Workup as for **8a,b** yielded a mixture of the four isomers **9a,b** and **10a,b** (ratio 1.7:7.1:1:2.4; 0.31 g, 78%) as a red, air-sensitive oil. MS (m/z (I_{rel})): 338 (27, M$^+$), 283 (100, CpFe(HMB)$^+$), 218 (36, Fe(HMB)$^+$), 121 (60, FeCp$^+$). The collected volatiles were concentrated at ambient pressure to ca. 40%. A ^{1}H NMR spectrum showed only signals of **4b** in THF; no impurities and specifically no signals for 3-butenyl bromide were found.

Compound 9a. ^{1}H NMR (C$_6$D$_6$; δ): 1.99 (s, HMB); cyclopropylmethyl, 0.64 (m, 2H, 1′-H), 0.56 (m, 2′-H), 0.21 (m, 2H, 3′-H$_a$), −0.02 (m, 2H, 3′-H$_b$); η^4-C$_5$H$_5$R, 4.09 ("t", $^3J + {}^4J$ = 3.7 Hz, 2-/3-H), 1.59 ("q", 1-/4-H), 2.44 (tt, $^3J_{5\text{endo},1'}$ = 6.3, $^3J_{5\text{endo},1/4}$ = 2.2 Hz, 5-*endo*-H). ^{13}C{^{1}H} NMR (C$_6$D$_6$; δ): 90.94 (HMB), 17.01 (HMB); cyclopropylmethyl, 28.65 (C-1′), 8.19 (C-2′), 4.52 (C-3′); η^4-C$_5$H$_5$R, 73.28 (C-2/3), 44.89 (C-1/4), 53.26 (C-5).

Compound 9b. ^{1}H NMR (C$_6$D$_6$; δ): 1.98 (s, HMB); 3-butenyl, 5.78 (ddt, $^3J_{\text{trans}}$ = 17.1, $^3J_{\text{cis}}$ = 10.1, $^3J_{3',2'}$ = 6.8 Hz, 3′-H), 5.01 (dq, $^3J_{\text{trans}}$ = 17.1, $^4J_{4',2'} + {}^2J_{4',4''}$ = 1.7 Hz, 4′-H$_{\text{trans}}$), 4.93 (dm, $^3J_{\text{cis}}$ = 10.1 Hz, 4′-H$_{\text{cis}}$), 1.90 (tdm, $^3J_{2',1'}$ = 7.8, $^3J_{2',3'}$ = 6.8 Hz, 2H, 2′-H), 0.79 (m, 2H, 1′-H); η^4-C$_5$H$_5$R, 4.07 ("t", $^3J + {}^4J$ = 3.7 Hz, 2-/3-H), 1.50 ("q", 1-/4-H), 2.27 (tt, $^3J_{5\text{endo},1'}$ = 6.4, $^3J_{5\text{endo},1/4}$ = 2.4 Hz, 5-*endo*-H). ^{13}C{^{1}H} NMR (C$_6$D$_6$; δ): 90.98 (HMB), 17.09 (HMB); 3-butenyl, 140.04 (C-3′), 114.62 (C-4′), 40.61 (C-2′), 30.49 (C-1′); η^4-C$_5$H$_5$R, 73.28 (C-2/3), 44.34 (C-1/4), 52.27 (C-5).

Compound 10a. ^{1}H NMR (C$_6$D$_6$; δ): 3.69 (s, Cp); cyclopropylmethyl, 0.12 (m, 2H, 1′-H), 0.18 (m, 2′-H), 3′-H$_a$ hidden, −0.27 (m, 2H, 3′-H$_b$); η^5-C$_6$Me$_6$R, 2.32 (s, 3-Me), 1.78 (s, 2-/4-Me), 1.45 (s, 1-/5-Me), 1.44 (s, 6-*endo*-Me). ^{13}C{^{1}H} NMR (C$_6$D$_6$; δ): 76.54 (Cp); cyclopropylmethyl, 28.65 (C-1′), 6.47 (C-2′), 4.98 (C-3′); η^5-C$_6$Me$_6$R, 88.98 (C-3), 86.95 (C-2/4), 43.26 (C-1/5), 41.36 (C-6), 23.81 (6-*endo*-Me), 18.16, 17.12, and 17.05 (Me-1/2/3/4/5).

Compound 10b. ^{1}H NMR (C$_6$D$_6$; δ): 3.67 (s, Cp); 3-butenyl, 5.57 (ddt, $^3J_{\text{trans}}$ = 17.1, $^3J_{\text{cis}}$ = 10.1, $^3J_{3',2'}$ = 6.7 Hz, 3′-H), 4.89 (dq, $^3J_{\text{trans}}$ = 17.1, $^4J_{4',2'} + {}^2J_{4',4''}$ = 1.7 Hz, 4′-H$_{\text{trans}}$), 4.83 (dm, $^3J_{\text{cis}}$ = 10.1 Hz, 4′-H$_{\text{cis}}$), 1.62 (m, 2H, 2′-H), 0.34 (m, 2H, 1′-H); η^5-C$_6$Me$_6$R, 2.30 (s, 3-Me), 1.77 (s, 2-/4-Me), 1.39 (s, 1-/5-Me), 1.30 (s, 6-*endo*-Me). ^{13}C{^{1}H} NMR (C$_6$D$_6$; δ): 76.56 (Cp); 3-butenyl, 140.15 (C-3′), 113.44 (C-4′), 41.00 (C-2′), 28.65 (C-1′); η^5-C$_6$Me$_6$R, 89.20 (C-3), 86.95 (C-2/4), 43.23 (C-1/5), 41.41 (C-6), 23.20 (6-*endo*-Me), 18.19, 17.12, and 17.05 (Me-1/2/3/4/5).

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Supplementary Material Available: Text giving details of the kinetic calculations in this work (3 pages). Ordering information is given on any current masthead page.

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(8) Cordes, J. F. *Chem. Ber.* **1962**, *95*, 3084.

(9) Astruc, D.; Hamon, J.-R.; Lacoste, M.; Desbois, M.-H.; Madonik, A.; Román, E. In *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: Amsterdam, 1988; Vol. IV, p 172.