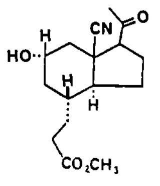
surprisingly—to provide the proper C/D trans stereochemistry.[13]

The possibility of using a sequence starting with the conjugate addition of a cyano group was difficult to evaluate, since the only reported case with the parent acetylhydrindene corresponding to **10** involves potassium cyanide[14] and results in a predominance of the *cis*-indan derivative.[15] Our initial results, using the *tert*-butyldimethylsilyl ether of **10** and diethylaluminum cyanide in benzene,[16] gave a disappointing 4:1 ratio of trans to cis products. The stereochemical difficulty was resolved, however, when it was found that the same reaction (excess Et_2AlCN, dry benzene, room temperature, 5 min) on the *free* hydroxy compound[17] gave the single adduct **11** in 81% yield. The corresponding dioxolane **12** (mp 131-132 °C) had its structure unambiguously confirmed by X-ray analysis.[18]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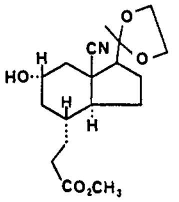
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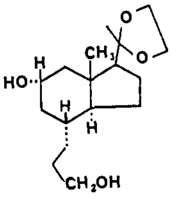
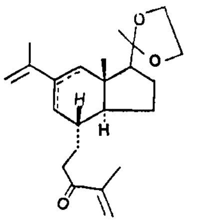
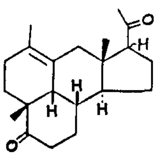
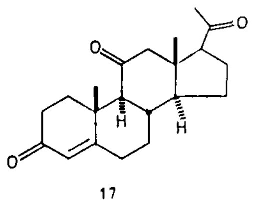

13

All centers of the target **14** had now been correctly introduced, and it remained only to perform some simple group transformations. Reduction of the cyano group to the imine (lithium aluminum hydride, refluxing tetrahydrofuran, 2.5 days, 90% yield) and Wolff-Kishner reduction (84% yield) of either the imine[19] or the corresponding aldehyde (excess 15% acetic acid) gave the diol **13** (mp 104-105 °C),[10] which was finally oxidized to the required **14** (pyridinium dichromate,[20] 88% yield) (mp 133-135 °C);[10] NMR δ 0.7 (s, 3 H), 1.24 (s, 3 H).

The efficiency of the construction of the indan derivative **14** prompted us to attempt the correction of two minor drawbacks of the previously reported sequence[1] by which we had converted **2** to **1**. The first problem in that conversion came from the production of a small amount of isomeric diene in the dehydration of the lithium isopropenyl reaction product from **14**: this problem disappeared when we found that the undesired diene contaminant was converted to the correct cycloadduct **16** in the presence of a catalytic amount of rhodium chloride.[21] The diene *mixture* **15** (40% from **14**) thus gave **16** in 93% yield when refluxed in ethanol in the presence of a trace of rhodium chloride trihydrate.[22] The second problem, formation of a small amount of undesired exo adduct in the Diels-Alder reaction, simply did not arise in the present series, which starts with **14** rather than with **2**: only the desired endo adduct **16** could be detected. It was transformed, as in the previous series, into (±)-11-keto progesterone **17** (mp 159-161 °C), which gave NMR, IR, and mass spectral data identical with those of a sample of authentic "natural" material. The overall yield from the indanonepropionic acid **14** was 60%.


15


16


17

This sequence represents a rather concise synthesis of 11-keto progesterone, in which the 21 carbons (originating from 1 mol each of *o*-cresol, cyclopentanone, acetic acid, hydrogen cyanide, and 2 mol of 2-bromopropene) all appear in the 21 carbons of 11-keto progesterone.[23]

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their support of this work.

Registry No. (±)-**3**, 81768-79-8; **4**, 81768-80-1; (±)-**5**, 70682-37-0; **6**, 69697-74-1; (±)-**7**, 81768-81-2; (±)-**8**, 81768-82-3; (±)-**8** alcohol, 81768-83-4; (±)-**9**, 81768-84-5; (±)-**10**, 81768-85-6; (±)-**11**, 81768-86-7; (±)-**12**, 81768-87-8; (±)-**12** imine, 81768-88-9; (±)-**13**, 81768-89-0; (±)-**14**, 81768-90-3; (±)-**15**, isomer 1, 81768-91-4; (±)-**15**, isomer 2, 81768-92-5; (±)-**16**, 81768-93-6; (±)-**17**, 81800-93-3; cyclopentanone, 120-92-3; isopropenyl acetate, 108-22-5.

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(13) Including attempts to direct conjugate addition to the β-face by treatment of the (axial) hydroxy epimer of **10** (obtained together with **10** (1:1) by L-Selectride reduction of **8** with trimethylaluminum and nickel acetylacetonate) (cf.: Bagnell, L.; Meisters, A.; Mole, T.; *Aust. J. Chem.* **1975**, *28*, 817.)

(14) Meyer, W. L.; Wolfe, J. F. *J. Org. Chem.* **1964**, *29*, 170.

(15) Nagata, W.; Yioshioka, M. "Organic Reactions"; Wiley: New York, 1977; Vol. 25, Chapter 3.

(16) Predominant, or exclusive, formation of *trans*-hydrindans, but in cases when the acetylhydrindene was part of a rigid tetracyclic system, has been observed previously: Nagata, W.; Terasawa, T. *Tetrahedron Lett.* **1963**, 865, and other instances in ref 15.

(17) It may be that the free hydroxyl group stops the addition at the kinetic product. It may also be the result of directional influence by the hydroxyl; see: Barlett, P. A.; Green, F. R., III *J. Am. Chem. Soc.* **1978**, *100*, 4858.

(18) We thank Dr. Peter Corfield for this determination.

(19) Cf.: Nagata, W.; Itazaki, H. *Chem. Ind. (London)* **1964**, 1194.

(20) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.

(21) Cf.: Grieco, P.; Nishizawa, M.; Marinovic, N.; Ehmann, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 7102. Cramer, R. *Ibid.* **1966**, *88*, 2272.

(22) The dioxolane protecting group is hydrolyzed under these conditions. Alternatively, the diene mixture **15** can be refluxed for 1 h with Merck 40-63 silica gel 60 in methylene chloride. Under these conditions, although it was necessary to chromatograph the reaction product to remove the small amount of undesired diene in **15**, the adduct (cf. **16**) was then obtained, still protected as its 20-dioxolane (90% yield).

(23) Of course, any practical application of this route would require solving the problem of chirality induction in the formation of **3**.

On the Mechanism of Hydrogenolysis of Linear Hydrocarbons and Its Relationship to the Fischer-Tropsch Reaction

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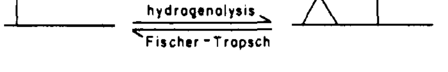
Received January 20, 1982

The hydrogenolysis of linear hydrocarbons over heterogeneous transition-metal catalysts converts the initial alkane, in the presence of H_2, to lower chain hydrocarbons (eventually methane).

Sinfelt[1] has proposed that the hydrogenolysis of ethane to methane proceeds via a dehydrogenated 1,2-adsorbed intermediate, which next undergoes C-C bond cleavage to produce C_1 fragments that are rapidly hydrogenated to methane. In contrast, the hydrogenolysis of higher alkanes was suggested to proceed via a dehydrogenated 1,3-adsorbed intermediate.

As opposed to the earlier mechanisms, we consider that the C-C bond cleavage involves the rearrangement of a metal alkyl linkage (i.e., deinsertion) to form a surface-bound methylene and the next lower homologous metal alkyl. This mechanism for C-C bond cleavage is the reverse of our recently proposed mechanism for C-C bond formation in the Fischer-Tropsch reaction (eq 1).[2,3]



(1)

We have constructed two theoretical models for the hydrogenolysis of linear hydrocarbons. In the first case we assume a metal *n*-alkyl species is formed by the selective cleavage of a

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† Deceased, December 10, 1981.

(1) Sinfelt, J. H. *Adv. Catal.* **1973**, *23*, 91.

(2) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181.

(3) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1981**, *103*, 1287.

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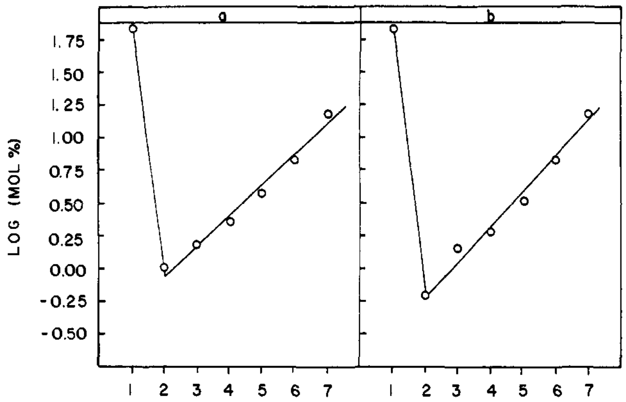

Figure 1. (a) Plot of log (mol %) vs. carbon number for the distribution of linear hydrocarbons produced from the hydrogenolysis of 1-octene over a Ni catalyst. (b) Plot of log (mol %) vs. carbon number for the distribution of linear hydrocarbons produced from the hydrogenolysis of *n*-octane over a Ni catalyst. The lines from C_2 to C_7 represent the least-squares fit for the data.

terminal C–H bond, which then undergoes deinsertion to form a surface methylene and the next lower homologous metal alkyl. The alkyl fragments can continue the deinsertion process, can be hydrogenated to the alkane, or can undergo β-hydride elimination to the 1-alkene. The surface methylenes are reduced to methane. Equations for calculating a product distribution for the hydrogenolysis of any linear C_n alkane are given in eq 2 (C_x = alkane

$$\text{mol fraction of } C_x = (1-\rho)\rho^{n-x}$$
$$\text{mol fraction of } CH_4 = 2\rho^{n-1} + \sum_{i=1}^{n-2}\rho^i \qquad (2)$$

of carbon number x (x varies from 2 to n)), where ρ represents the probability of methylene deinsertion. When the calculated distribution is plotted as log (mol %) vs. carbon number, the coordinates for C_2–C_n form a straight line of positive slope. Also, the mol % of CH_4 closely correlates to ρ.

In our second model we assume a statistical distribution of *n*-alkyl and branched alkyl species is formed via random C–H bond cleavage. The branched fragments undergo C–C bond cleavage with equal probability on either side of the surface-bound carbon, yielding linear alkyl and alkylidene fragments. The alkylidenes are reduced to *n*-alkyls. All *n*-alkyl fragments undergo stepwise degradation as described in our first model. If the probability of C–C cleavage is represented by ρ, a theoretical product distribution can be calculated. This model predicts that the hydrogenolysis of any linear C_n alkane will produce, for $\rho = 0.5$, equimolar quantities of C_2–C_{n-1} products. In contrast to our first model, essentially equimolar amounts of C_2–C_{n-1} products are still predicted as ρ is varied.

We have examined the products from the reactions of *n*-octane and 1-octene with H_2 at low conversion over silica-supported Ni, Ru, and Co catalysts. In contrast to all previous studies, the α-olefin was included with the assumption that it would selectively afford an *n*-alkyl species.[4]

The hydrogenolysis of 1-octene or *n*-octane over Ni at 230 °C produced *n*-alkanes exclusively. When the data are plotted as log (mol %) vs. carbon number (Figure 1), the coordinates form a straight line of positive slope from C_2 to C_7[5] which according to our first model indicates the stepwise degradation of an *n*-alkyl ligand. Furthermore, if a ρ value is calculated that produces a theoretical distribution with a slope equal to the experimental slope, the experimental mol % of CH_4 does indeed closely correlate to the calculated ρ value (1-octene: mol % of CH_4 = 56.4, $\rho = 0.58$; *n*-octane: mol% of CH_4 = 56.6, $\rho = 0.54$).[6] It is significant that *n*-octyl ligands are selectively formed from 1-octene as well as from *n*-octane. Other workers have reported results consistent with this type of selective, stepwise degradation of *n*-alkanes over Ni.[7]

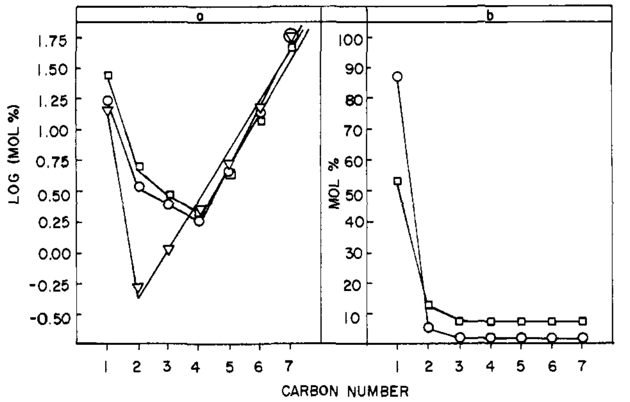

Figure 2. (a) Plots of log (mol %) vs. carbon number for the distribution of linear hydrocarbons produced from the hydrogenolysis of 1-octene over Co (○) and Ru (□) catalysts at 200 °C and over a Co (△) catalyst at 125 °C. The lines from C_4 to C_7 for Co and Ru at 200 °C and from C_2 to C_7 for Co at 125 °C represent the least-squares fit for the data. (b) Plots of mol % vs. carbon number for the distribution of linear hydrocarbons produced from the hydrogenolysis of *n*-octane over Co (○) or Ru (□) catalysts.

The hydrogenolysis of 1-octene over Ru or Co at 200 °C produced entirely linear hydrocarbons (α- and β-olefins and alkanes). The coordinates (Figure 2a) from C_4 to C_7 form a straight line of positive slope,[8] indicative of selective, stepwise *n*-alkyl degradation. However, the coordinates from C_2 to C_4 approximate a line negative slope, indicative of stepwise chain growth via the "polymerization" of CH_2 ligands.[3] The reaction also produced higher linear hydrocarbons from C_9 to C_{11}.[9] These observations and the law of microscopic reversibility lead us to consider that the products are the result of a combination of stepwise chain propagation and degradation, consistent with the scheme in eq 1.

The divergent behavior between Ni and Co or Ru may be attributed to the lower activity of Ni toward chain propagation as seen in the Fischer–Tropsch reaction.[2] However, when 1-octene is passed over Co at 125 °C, a plot similar to the Ni reaction is obtained (Figure 2a)[10] indicating that C_2–C_7 alkanes are generated solely by stepwise degradation (only linear products observed). Higher linear C_9–C_{11} products are also produced at the lower temperature.

The hydrogenolysis of *n*-octane over Ru at 125 °C or Co at 230 °C resulted in products (all *n*-alkanes) that produce the plots shown in Figure 2b. In both cases equimolar quantities of C_3–C_7 products were formed, which suggests that the initial C–H bond cleavage is random and that the reaction proceeds in a manner consistent with our second model. No homologation of the *n*-octane was observed although homologation of alkanes is thermodynamically favorable when accompanied by degradation.[11]

The key step in our two models of linear alkane hydrogenolysis is the methylene deinsertion reaction, which represents a new mechanism for the catalytic cleavage of C–C bonds. We conclude that our two mechanisms readily account for and are consistent with the experimentally observed distributions and suggest that

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[4] (a) Hiroto, K.; Hironaka, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2638. (b) Eischens, R. P.; Pliskin, W. A. *Adv. Catal.* **1959**, *11*, 1.

[5] 1-Octene: slope = 0.23, $r = 0.990$; *n*-octane: slope = 0.27, $r = 0.995$.

[6] Due to the condition of low conversion, the experimental mol % of CH_4 was obtained from the renormalized product distribution including the least-squares value for C_8.

[7] (a) Matsumoto, H.; Saito, Y.; Yoneda, Y. *J. Catal.* **1970**, *19*, 101. (b) Kikuchi, E.; Morita, Y. *Ibid.* **1969**, *15*, 217. (c) Kochloefl, K.; Bazant, V. *Ibid.* **1968**, *10*, 140.

[8] Ru: slope = 0.44, $r = 0.991$; Co: slope = 0.49, $r = 0.995$.

[9] Under similar conditions, the reaction of ethylene over Ru or Co also led to stepwise chain propagation, producing up to C_{10} hydrocarbons.

[10] Slope = 0.41, $r = 0.992$.

[11] O'Donohoe, C.; Clarke, J. K. A.; Rooney, J. J. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 345.

the two schemes are plausible alternatives to currently accepted mechanisms.

Acknowledgment. We thank the Robert A. Welch Foundation, the National Science Foundation, the Department of Energy, and the Exxon Education Foundation for financial assistance.

Registry No. Octane, 111-65-9; 1-octene, 111-66-0; Co, 7440-48-4; Ru, 7440-18-8; Ni, 7440-02-0.

Synthesis of Electrophilic (Dimethylcarbene)iron Complexes

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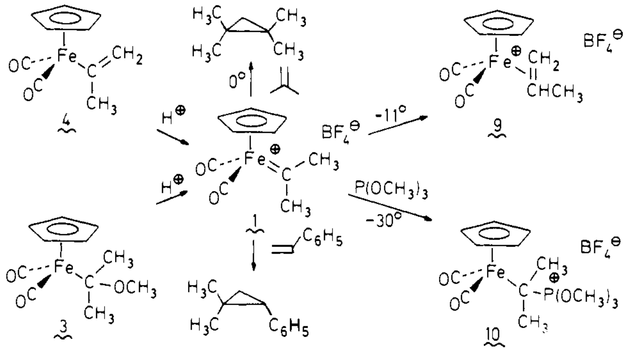
Received March 5, 1982

Transition-metal carbene complexes are promising reagents for electrophilic cyclopropanations.[1-3] Earlier we had shown that $(CO)_5W{=}CHC_6H_5$ could be generated at −78 °C from $(CO)_5WCH(OCH_3)C_6H_5^-$ and was a reagent for the selective formation of cis cyclopropanes.[4] We were interested in developing a reagent for transfer of the dimethylcarbene group as a route to *gem*-dimethylcyclopropanes.[5] The use of $(CO)_5W{=}C(CH_3)_2$ appeared impractical since reaction of $(CO)_5W{=}C(OCH_3)CH_3$ with *n*-BuLi gave predominantly deprotonation rather than addition[6] and since generation of $(CO)_5W{=}C(CH_3)C_6H_5$ led to rapid hydrogen migration to give $(CO)_5W$(styrene) and other products.[7] Stable dimethylcarbene complexes ($(C_5H_5)(CO)_2M{=}C(CH_3)_2$ (M = Mn, Re)) have been prepared by Fischer[8] but there has been no report of their reaction with alkenes. On the basis of work by Pettit,[9] Brookhart,[3,10] Helquist,[2,11] and Cutler,[12] $(C_5H_5)(CO)_2Fe{=}C(CH_3)_2^+$ (**1**) appeared to offer greater promise as an electrophilic cyclopropanating agent than organotungsten reagents. $(C_5H_5)(CO)_2Fe{=}CHC_6H_5^+$,[10] $(C_5H_5)(CO)_2Fe{=}CH_2^+$,[9,11] and $(C_5H_5)(CO)_2Fe{=}CHCH_3^+$ [2,3] were shown to be high-yield cyclopropanating reagents. More importantly $(C_5H_5)(CO)_2Fe{=}CHCH_3^+$, although spectroscopically undetectable, was generated from $(C_5H_5)(CO)_2FeCH(OCH_3)CH_3$,[3] from $(C_5H_5)(CO)_2FeCH[S(CH_3)(C_6H_5)]CH_3^+$,[2] or from $(C_5H_5)(CO)_2FeCH{=}CH_2$[2,12] and reacted with alkenes to give methylcyclopropanes faster than it rearranged to $(C_5H_5)(CO)_2Fe(CH_2{=}CH_2)^+$. Phosphines have been shown to stabilize iron-carbene complexes; for example, $(C_5H_5)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe{=}CH_2^+$[13] and $(C_5H_5)(CO)[(C_6H_5)_3P]Fe{=}CHCH_3^+$ [3,12] are both stable enough to be observed directly by NMR at room temperature. Here we report the synthesis of the unstable dimethylcarbene complex $(C_5H_5)(CO)_2Fe{=}C(CH_3)_2^+BF_4^-$ (**1**), its reaction with isobutylene and styrene to give *gem*-dimethylcyclopropanes, and its in situ rearrangement to a propene complex. In addition, the synthesis and isolation of a stable phosphine-substituted dimethylcarbene complex $(C_5H_5)(CO)[(C_6H_5)_3P]Fe{=}C(CH_3)_2^+BF_4^-$ (**2**) is described.

Scheme I



Two approaches to dimethylcarbene complex **1** (Scheme I) were investigated: the electrophilic demethoxylation of $(C_5H_5)(CO)_2FeC(OCH_3)(CH_3)_2$ (**3**) and the protonation of the vinyl compound $(C_5H_5)(CO)_2FeC(CH_3){=}CH_2$ (**4**). In principle, addition of a methyl organometallic reagent to $[(C_5H_5)(CO)_2FeC(OCH_3)CH_3]^+BF_4^-$ (**5**)[14] would provide a simple route to **3**, but side reactions involving deprotonation[6,15] to give $(C_5H_5)(CO)_2FeC(OCH_3){=}CH_2$ (**6**) or demethylation to give $(C_5H_5)(CO)_2FeCOCH_3$ (**7**) also were anticipated. We have observed all three types of reaction with various organometallic reagents. Reaction of **5** with MeLi in CH_2Cl_2 at −78 °C gave a 1:1 mixture of addition product **3**[16] and deprotonation product **6**;[17] reaction of **5** with CH_3MgI gave predominately demethylation product **7**; reaction of **5** with $LiCu(CH_3)_2$ in CH_2Cl_2–Et_2O at −78 °C gave addition product **3** in 45–50% isolated yield and small, variable amounts of **6**.

The 2-methoxy-2-propyl addition product **3** is thermally unstable; upon heating to 60 °C in benzene for 8 h, **3** loses methanol and is converted to isopropenyliron compound **4**[18] in 80% isolated yield. Isopropenyliron compound **4** is more conveniently prepared in two steps by reaction of methacryloyl chloride (102 mmol) with $Na^+[(C_5H_5)Fe(CO)_2]^-$ (100 mmol) in THF at 0 °C, which gives $(C_5H_5)(CO)_2FeCOC(CH_3){=}CH_2$ (**8**) (15.9 g, 64%)[19] followed by photolysis of **8** (14.8 g, 60 mmol) in hexane–toluene with a 450-W medium-pressure mercury lamp for 2 h, which gives

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(1) For recent reviews see: Casey, C. P. In "Reactive Intermediates"; Jones, M., Moss, R. A., Eds; Wiley: New York, 1981; Vol. II, Chapter 4. Casey, C. P. *CHEMTECH* **1979**, 378.

(2) Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 1862 and references therein.

(3) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979 and references therein.

(4) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.

(5) For other methods for preparing 1,1-dimethylcyclopropanes from alkenes see: Corey, E. J.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 3911. Corey, E. J.; Jautelat, M. *Ibid.* **1967**, *89*, 3912. Zurqiyah, A.; Castro, C. E. *J. Org. Chem.* **1969**, *34*, 1504.

(6) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1976**, *118*, 309. Reaction of CH_3Li with $(CO)_5W{=}C(OCH_3)CH_3$ gives a binuclear bridging alkylidene complex: Levisalles, J.; Rudler, H.; Dahan, F.; Jeannin, Y. *Ibid.* **1980**, *188*, 193.

(7) Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2533.

(8) Fischer, E. O.; Clough, R. L.; Besl, G.; Kreissl, F. R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 543. Fischer, E. O.; Clough, R. L.; Stuckler, P. *J. Organomet. Chem.* **1976**, *120*, C6.

(9) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044.

(10) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. *Ibid.* **1980**, *102*, 7802.

(11) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473.

(12) Bodnar, T.; LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 3292. Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31.

(13) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203.

(14) **5** was prepared by treatment of $(C_5H_5)(CO)_2FeCOCH_3$ (**7**) with $(CH_3)_3O^+BF_4^-$ in CH_2Cl_2. **5**: ^1H NMR (CD_2Cl_2) δ 5.36 (s, 5 H), 4.60 (s, 3 H), 3.15 (s, 3 H); ^{13}C NMR (acetone-d_6, 0.02 M Cr(acac)$_3$) δ 336.0 (Fe=C), 209.7 (CO), 89.2 (C_5H_5), 87.1 (OCH_3), 68.7 (CH_3); IR (CH_2Cl_2) 2060, 2014 cm^{-1}. The related PF_6^- [12] and $CF_3SO_3^-$ [3] salts have been prepared previously.

(15) Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237.

(16) **3**: ^1H NMR (C_6D_6) δ 4.18 (s, 5 H), 3.10 (s, 3 H), 1.64 (s, 6 H); ^{13}C NMR (C_6D_6) δ 219.0 (s), 89.2 (s), 87.2 (d), 52.1 (q), 39.1 (q); IR ($CHCl_3$) 2000, 1944 cm^{-1}.

(17) **6** was not isolated but was observed by ^1H NMR (($CDCl_3$) δ 4.80 (s, 5 H), 4.59 (d, J = 1.5 Hz), 4.02 (d, J = 1.5 Hz), 3.52 (s, 3 H)): Casey, C. P.; Tukada, H.; Miles, W. H. *Organometallics*, in press.

(18) **4**: ^1H NMR ($CDCl_3$) δ 5.53 (br s, 1 H), 4.89 (s, 1 H), 4.73 (s, 5 H), 2.09 (s, 3 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 216.8, 152.3, 125.4, 85.5, 39.2; IR ($CHCl_3$) 2005, 1961, 1581 cm^{-1}; mp 28–31 °C; *m/e* calcd for $C_{10}H_{10}FeO_2$ 218.0029, obsd 218.0029. The conversion of **3** to **4** is apparently not an acid-catalyzed process since addition of small amounts of $KHSO_4$ did not accelerate loss of methanol.

(19) **8**: ^1H NMR ($CDCl_3$) δ 5.37 (s, 1 H), 5.28 (s, 1 H), 4.83 (s, 5 H), 1.75 (s, 3 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 251.7, 215.0, 157.8, 119.1, 86.4, 18.9; IR ($CHCl_3$) 2007, 1967, 1624, 1597 cm^{-1}; mp 24–28 °C; *m/e* calcd for $C_{11}H_{10}FeO_3$ 245.9979, obsd 245.9979.

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