Robert H. Crabtree thanks the Camille and Henry Dreyfus Foundation for a Fellowship, and Johnson Matthey for the loan of iridium.

Supplementary Material Available: A figure showing the complete molecular structure and tables of structure factors, positional parameters, anisotropic thermal parameters, and selected bond lengths and angles (18 pages). Ordering information is given on any current masthead page.

Fragmentation and Carbonylation of Dithioformate via Addition of Electrophilic Alkynes to Fe(η^2-HCS$_2$Me) Complexes. X-ray Crystal Structure of FeCH(SMe)COC(CO$_2$Me)=C(CO$_2$Me)S(CO)(PMe$_3$)$_2$

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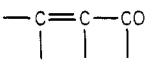
Summary: The complex Fe(η^2-HCS$_2$Me)(CO)$_2$(PMe$_3$)$_2$ has been obtained from a Fe(η^2-CS$_2$) precursor. It reacts with electrophilic alkynes with cleavage of the coordinated C=S bond, and insertion of both the C≡C bond and carbon monoxide takes place to afford six-membered metallacycle derivatives. Fe(η^2-CH(SMe)COC(CO$_2$Me)=C(CO$_2$Me)S(CO)(PMe$_3$)$_2$ crystallizes in the triclinic space group $P\bar{1}$ (No. 2), with a = 8.957 (2) Å, b = 10.440 (2) Å, c = 14.005 (2) Å, α = 70.60 (1)°, β = 83.40 (2)°, γ = 67.96 (2)°, and Z = 2.

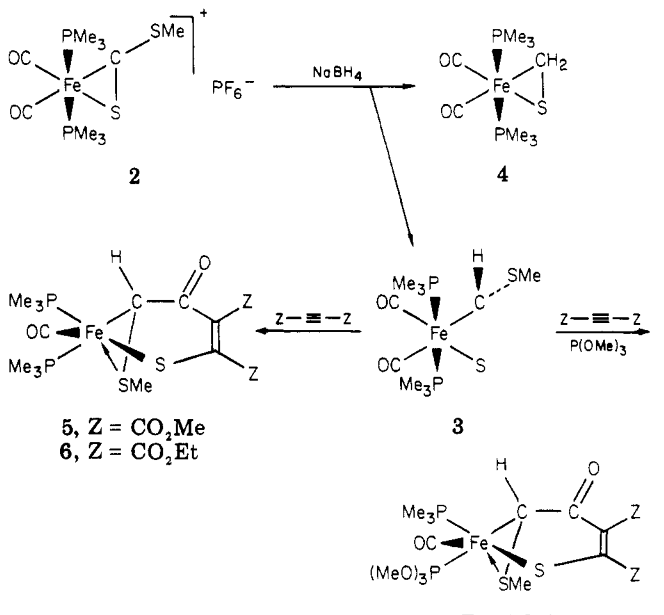
Fragmentation of sulfur–carbon bonds by transition-metal centers has attracted interest recently in the search for processes allowing the desulfurization of substrates such as thiocarbonates to afford dioxolanylidene–iron complexes[1] and thioketones to offer new applications to organic synthesis[2] or of dithioesters,[3] dithiocarbonates,[3] and thiolates[4] to produce new polymetallic species from metal carbonyls. We report here a novel reaction which involves the cleavage, via electrophilic addition, of a coordinated carbon–sulfur double bond, with concomitant insertion of an alkyne and of carbon monoxide, and which affords a new six-membered ring corresponding to the formal insertion of a



$$-\underset{|}{C}=\underset{|}{C}-\underset{|}{CO}$$

fragment into the C=S bond of a coordinated dithioformate.

Scheme I



The addition of sodium borohydride to a THF solution of the cationic complex **2**, obtained directly from Fe(η^2-CS$_2$)(CO)$_2$(PMe$_3$)$_2$ (**1**),[5] led to the formation of two yellow derivatives, **3** and **4** (Scheme I). The main product, **3**,[6] was isolated in 51% yield by crystallization in pentane whereas complex **4** was obtained in 5% yield by thick-layer chromatography of the crystallization solution.[7] Complex **3** has been identified as an η^2-dithioformateiron complex rather than the expected iron hydride derivative analogous to Os(H)(η^1-CS$_2$Me)(CO)$_2$(PPh$_3$)$_2$ obtained under similar conditions[8] (^{13}C NMR δ (*C*HSMe) = 60.9 (dt, $^1J_{CH}$ = 56 Hz, $^2J_{PC}$ = 9.9 Hz)[9]).

In order to study the activation by the iron center of the coordinated η^2-HCS$_2$Me group the reaction of **3** with alkynes has been examined. Although no reaction was observed with diphenylacetylene or 3-hexyne, complex **3** reacted in benzene with 1 equiv of dimethyl acetylenedicarboxylate to afford after 1 h at room temperature, a red complex isolated in 70% yield with thick-layer chromatography and identified as the metallacycle **5**[10] (Scheme

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[1] Daub, J.; Endress, G.; Erhardt, U.; Jogun, K. H.; Kappler, J.; Laumer, A.; Pfiz, R.; Stezowski, J. J. *Chem. Ber.* **1982**, *115*, 1787.

[2] Alper, H.; Root, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 4251. Laycock, D. E.; Alper, H. *J. Org. Chem.* **1981**, *46*, 289.

[3] Patin, H.; Mignani, G.; Van Hulle, M. T. *Tetrahedron Lett.* **1979**, 2441. Patin, H.; Mignani, G.; Benoit, A.; Le Marouille, J. Y.; Grandjean, D. *Inorg. Chem.* **1981**, *20*, 4351.

[4] Adams, R. D.; Yang, L. W. *J. Am. Chem. Soc.* **1982**, *104*, 4115. Adams, R. D.; Katahira, D. A.; Yang, L. W. *Organometallics*, **1982**, *1*, 235. Adams, R. D. *Acc. Chem. Res.* **1983**, *16*, 67.

[5] (a) Le Bozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Inorg. Chem.* **1978**, *17*, 2568. (b) Touchard, D.; Le Bozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Ibid.* **1981**, *20*, 1811.

[6] **3**: mp 101–102 °C; IR (Nujol) 1962, 1892 cm^{-1}; mass spectrum, *m/e* 355.990 (calcd for M$^+$ (C$_{10}$H$_{22}$O$_2$P$_2$S$_2$Fe), 355.989). Anal. Found: C, 34.14; H, 6.19; P, 17.33; S, 17.63. Calcd for C$_{10}$H$_{22}$O$_2$P$_2$S$_2$Fe: C, 33.72; H, 6.22; P, 17.39; S, 18.00.

[7] **4**: mp 81–82 °C; IR (Nujol) 1955, 1887 cm^{-1}; mass spectrum, *m/e* 310.002 (calcd for M$^+$, 310.001). Anal. Found: C, 34.93; H, 6.64; S, 10.18. Calcd for C$_9$H$_{20}$O$_2$P$_2$SFe: C, 34.85; H, 6.50; S, 10.33. ^{1}H NMR (60 MHz) δ (C$_6$D$_6$) 2.82 (t, CH$_2$S, J_{PH} = 5.2 Hz).

[8] Collins, T. J.; Roper, W. R.; Town, K. G. *J. Organomet. Chem.* **1976**, *121*, C41.

[9] Additional NMR data for **3**: ^{1}H NMR (60 MHz) 4.67 (d, CH, $^3J_{PH}$ = 7.0 Hz), 2.47 (s, SMe), 1.24 (d), and 0.90 (d, PMe$_3$, $^2J_{PH}$ = 8.2 Hz); ^{13}C NMR (20.115 MHz) δ (C$_6$D$_6$) 218.4 (t, CO, $^2J_{PC}$ = 28.0 Hz), 215.9 (t, CO, $^2J_{PC}$ = 28.7 Hz), 24.5 (s, SMe); ^{31}P NMR (32.38 MHz) δ (C$_6$D$_6$) 20.98 and 8.18 ($^2J_{PP}$ = 185.5 Hz).

[10] **5**: mp 172–174 °C. Anal. Found: C, 38.51; H, 5.64; S, 13.09. Calcd for C$_{16}$H$_{28}$O$_6$P$_2$S$_2$Fe: C, 38.57; H, 5.66; S, 12.87. Mass spectrum, *m/e* 478 (M$^+$), 450.018 (calcd for (M − CO)$^+$, 450.020).

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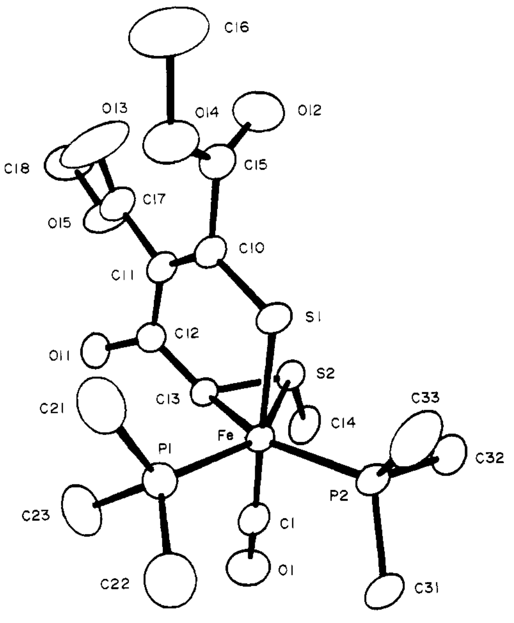
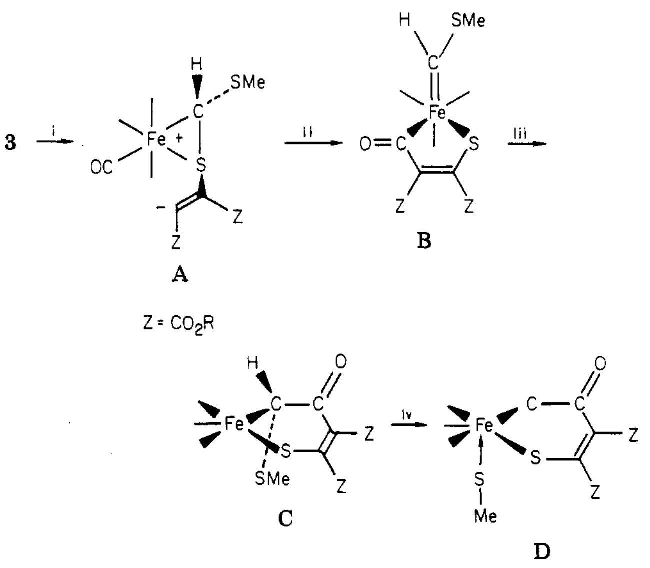


Figure 1. ORTEP view of **5**. Selected bond distances (Å) and angles (deg) Fe–S(1) 2.305 (1), Fe–S(2), 2.272 (1), Fe–P(1) 2.224 (1), Fe–P(2) 2.252 (1), Fe–C(1) 1.742 (2), Fe–C(13) 2.067 (2), C(13)–S(2) 1.783 (2), C(14)–S(2) 1.820 (2), S(1)–C(10) 1.718 (3); P(1)–Fe–P(2) 103.67 (2), S(1)–Fe–C(1) 176.50 (6), S(2)–Fe–C(13) 48.24 (4), Fe–C(13)–S(2) 71.90 (6), Fe–C(13)–C(12) 121.3 (1), S(2)–C(13)–C(12) 123.6 (1).

I). Complex **5** (IR (Nujol) 1895, 1715, 1685 cm^{-1}) shows in the NMR[11] spectra two nonequivalent CO$_2$Me and PMe$_3$ groups and only one terminal carbonyl. Similarly, complex **3** was reacted with diethyl acetylenedicarboxylate to afford in 65% yield the corresponding metallacyclic derivative **6**.[12]

The structure of **5** has been established by X-ray diffraction.[13,14] Figure 1 shows a view of the molecule with the atom numbering scheme used along with some pertinent bond distances and angles. The equatorial sites of the distorted triangular-bipyramidal molecule are occupied by the PMe$_3$ groups and the carbon–sulfur C(13)–S(2) single bond which is roughly in the same plane as the Fe, P(1), and P(2) atoms. The axial positions are occupied by the remaining carbonyl and the sulfido atom S(1) (C(1)–Fe–S(1) = 176.50 (6)°) of the novel chelating ligand which behaves as a four-electron ligand. Indeed the CHSMe group brings three electrons to the metal as suggested by the Fe–C(13) single bond (2.067 (2) Å) almost trans to the P(2) atom and a shorter Fe–S(2) bond distance (2.272 (1) Å) than the Fe–S(1) bond length (2.305 (1) Å). The coordinated C(13)–S(2) bond distance (1.738 (2) Å) has been significantly lengthened as compared to those of the precursors of type Fe(η^2-CS$_2$) and Fe(η^2-CS$_2$CH$_2$Ph)[15] for which a double bond character had been attributed. We suggest that the formation of complexes **5** and **6** from **3** can be rationalized according to Scheme II involving successive processes i–iv: (i) electrophilic addition of the alkyne to the coordinated nucleophilic sulfur atom; (ii) addition of the nucleophilic carbon of the alkyne fragment in A to the cis carbonyl, with subsequent cleavage of the C–S bond to afford the carbene–iron moiety B; (iii) insertion of the carbene ligand into the iron–acyl bond of the metallacycle to afford the 16-electron species C; (iv) coordination of the sulfur atom of the SMe group to yield the final products **5–6**. In support of step i we have shown that (a) the coordinated sulfur atom in **3** is quite nucleophilic—it readily reacted with methyl iodide at room temperature to afford both isomers of [Fe(η^2-MeSCHSMe)(CO)$_2$(PMe$_3$)$_2$]PF$_6$ (**8**)[16]— and (b) complex **3** is inert toward nonelectrophilic alkynes (Z = Ph or Et) at 80 °C. Step ii is consistent with Roper's proposal that an [Os(η^2-CH$_2$SMe]$^+$ moiety behaves like the isomeric [Os(=CH$_2$)SMe]$^+$;[17] addition of dimethyl acetylenedicarboxylate to complex **3** (25 °C) in the presence of 1 equiv of P(OMe)$_3$ results in formation of complex **5** (47%) together with derivatives **7** (12%)[18]. Complexes **7** were not

Scheme II



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(11) ^{1}H NMR (100 MHz) δ (CDCl$_3$, 32 °C) 3.99 (s), and 3.71 (s) (CO$_2$*Me*), 2.00 and 1.98 (S*Me*), 1.60 and 1.37 (d, PMe$_3$, $^2J_{PH}$ = 9.7 Hz); ^{31}P NMR (32.38 MHz) δ (CDCl$_3$, 36 °C) 25.7 and 16.6 ($^2J_{PP}$ = 15.1 Hz); ^{13}C NMR (20.115 MHz) δ (CDCl$_3$, −30 °C) 215.0 (dd, CO, $^2J_{PC}$ = 26.4 and 33.0 Hz), 199.5 (s, CO), 168.4 and 165.7 (s, CO$_2$Me), 167.1 (d, S—C=, $^2J_{PC}$ = 16.5 Hz), 121.0 (s, C=), 53.1 and 52.2 (s, CO$_2$Me), 23.6 (s, SMe). The CH signals are masked in the ^{1}H and ^{13}C NMR by the CO$_2$Me signals.

(12) **6**: mp 158–160 °C; mass spectrum, *m/e* 526 (M$^+$), 498.051 (calcd for (M − CO)$^+$, 498.051). Anal. Found: C, 40.79; H, 5.85. Calcd for C$_{18}$H$_{32}$O$_6$P$_2$S$_2$Fe: C, 41.07; H, 6.12. ^{1}H NMR (100 MHz) δ (CDCl$_3$, 32 °C) 4.23 and 4.17 (q, CO$_2$*CH*$_2$CH$_3$, $^3J_{HH}$ = 7 Hz), 3.68 (dd, CHS, $^3J_{PH}$ = 2.9 and 1.2 Hz), 2.00 and 1.97 (SMe), 1.60 and 1.38 (d, PMe$_3$, $^2J_{PH}$ = 9.5 Hz), 1.01 and 0.98 (t, CO$_2$CH$_2$*CH*$_3$); ^{31}P NMR (32.38 MHz) δ (CD$_2$Cl$_2$, 36 °C) 25.5 and 15.7 ($^2J_{PP}$ = 15.1 Hz). ^{13}C{^{1}H} NMR (20.115 MHz) δ (CDCl$_3$, 36 °C) 216.1 (dd, CO, $^2J_{PC}$ = 26.8 and 33.0 Hz), 199.5 (s, C=O), 167.7 and 165.5 (s, *C*O$_2$Me), 164.5 (d, S—C=, $^2J_{PC}$ = 17.9 Hz), 125.6 (s, C=), 61.5 and 60.6 (s, OCH$_2$), 52.8 (dd, CH, $^2J_{PC}$ = 4.9 and 6.1 Hz), 23.7 (s, SCH$_3$), 14.2 and 14.0 (s, CH$_2$CH$_3$). ^{13}C NMR (no decoupling, CDCl$_3$, 36 °C) δ 52.8 (dq, CH, $^1J_{CH}$ = 164.8 Hz, $^2J_{PC}$ = 4.9 and 6.1 Hz).

(13) Crystal data for FeSC(CO$_2$Me)=C(CO$_2$Me)COCHSMe(CO)(PMe$_3$)$_2$ (**5**): space group $P\bar{1}$ (No. 2), a = 8.957 (2) Å, b = 10.440 (2) Å, c = 14.005 (2) Å, α = 70.60 (1)°, β = 83.40 (2)°, γ = 67.96 (2)°, Z = 2, M_r = 498.32, d_{calcd} = 1.45 g cm^{-3}. The structure was solved by a combination of Patterson and difference Fourier techniques;[14] least-squares refinement on 3295 reflections ($F^2 > 3.0\sigma(F)^2$ produced the final residual R_F = 0.033 and R_{wF} = 0.041.

(14) Diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer. All calculations were done on a Digital Equipment Corp. PDP 11/45 computer using the Enraf-Nonius SDP program library.

(15) The coordinated C–S bond length is 1.676 (7) Å in Fe(η^2-CS$_2$)(CO)$_2$(PPh$_3$)(PMe$_3$)^{5a} and 1.634 (3) Å in [Fe(η^2-CS$_2$CH$_2$Ph)(CO)$_2$(PMe$_3$)$_2$]PF$_6$.^{5b}

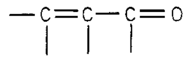
(16) The isomeric mixture of **8** was isolated after treatment with NaPF$_6$. Anal. Found: C, 25.70; H, 4.88; S, 12.52. Calcd for C$_{11}$H$_{25}$F$_6$O$_2$P$_3$S$_2$Fe: C, 25.60; H, 4.88; S, 12.42. ^{1}H NMR δ (CD$_2$Cl$_2$) 4.15 and 3.96 (m, CH), 2.55, 2.39, 2.21, and 2.19 (SMe), 1.78 and 1.65 (m, PMe$_3$); IR (Nujol) 2030, 2020 (sh) cm^{-1}.

(17) Headford, C. E. L. and Roper, W. R. *J. Organomet. Chem.* **1983**, *244*, C53.

(18) **7**: mp 150–152 °C; mass spectrum, *m/e* 546 (M$^+$), 518.006 (Calcd. for (M − CO)$^+$ (C$_{15}$H$_{28}$O$_8$P$_2$S$_2$Fe, 518.005), 442 [M − (CO, PMe$_3$)]$^+$, 394 [M − (CO, P(OMe)$_3$)]$^+$; ^{1}H NMR δ (CD$_2$Cl$_2$) 3.87 and 3.72 (CO$_2$Me), 3.68 and 3.63 (d, P(OMe)$_3$, $^3J_{PH}$ = 8.5 Hz), 2.10, 2.07, 2.06, and 2.00 (SMe), 1.60 and 1.39 (d, PMe$_3$, $^2J_{PH}$ = 9.3 and 10.0 Hz). The CH groups are masked. ^{31}P NMR δ (CD$_2$Cl$_2$, 36 °C) 174.4 and 171.4 (P(OMe)$_3$), 23.8 and 16.4 (PMe$_3$, $^2J_{PP}$ = 41.2 Hz); IR (Nujol) 1940 cm^{-1} (s, br).

formed when 5 was refluxed for 1 h in benzene with an excess of $P(OMe)_3$; only 5 was recovered, and no exchange of PMe_3 by $P(OMe)_3$ was observed by treatment of 3 with an excess of $P(OMe)_3$. This suggests that during the reaction a vacant site must be created on the iron atom to allow the incorporation of the $P(OMe)_3$ group leading to 7 and this supports step iv.

This unique incoorporation of a



$-C=C-C=O$

fragment into a carbon–sulfur double bond is unprecedented. The use of this reaction in organic synthesis is under investigation.

Acknowledgment. Authors are grateful to Prof. M. S. Brookhart and M. F. Lappert for helpful discussions.

Registry No. 2, 71004-25-6; 3, 88968-59-6; 4, 88968-60-9; 5, 88968-61-0; 6, 88968-62-1; 7, 88968-63-2; 8 (isomer 1), 89016-43-3; 8 (isomer 2), 88968-65-4; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; $EtO_2CC{\equiv}CCO_2Et$, 762-21-0.

Supplementary Material Available: Tables of crystallographic data, interatomic distances and angles, final positional and thermal parameters, and structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

Competitive Redox-Catalyzed Migratory Carbonyl Insertion and β-Elimination in Iron Alkyl Complexes[1]

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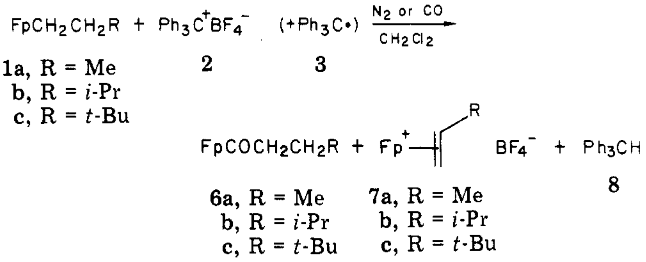
Summary: At reduced temperatures in the presence of carbon monoxide, migratory carbonyl insertion can compete with triphenylcarbenium-induced β-elimination in $(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2CH_2R$ (R = Me, *i*-Pr, *t*-Bu) complexes. The insertion is a catalytic, radical-chain process initiated by a one-electron transfer from Fe(II)–alkyl complex to cation. Added triphenylmethyl radical retards the rate of insertion but leaves the rate of elimination virtually unchanged.

Migratory carbonyl insertion accompanies β-elimination in the triphenylcarbenium-induced reactions of Fp norbornyls.[2] To examine the generality and mechanism of such competitive insertion and elimination we have studied the reaction of some conformationally mobile Fp alkyls (1)[3] with triphenylmethyl tetrafluoroborate (2).

Typically[4] (run 2, Table I), precooled, equiequivalent solutions of 1a[5] and 2[6] in carbon monoxide blanketed dichloromethane were mixed, and the mixture was stirred at −78 °C for 1 h and then at −20 °C overnight. Sequential concentration under vacuum, addition of diethyl ether at 0 °C, filtration, and washing with ether gave pale yellow crystals of $(\eta^5$-cyclopentadienyl$)(\eta^2$-propene)dicarbonyliron tetrafluoroborate (**7a**, 69%).[7] Chromatography of the concentrated, combined filtrate and washings at −10 °C on activity III alumina with 2% diethyl ether in pentane gave triphenylmethane (**8**, 71%) and $(\eta^5$-cyclopentadienyl$)(\eta^1$-butanoyl)dicarbonyliron (**6a**, 13%).[8c] In runs 8, 9, and 17 1 equiv of triphenylmethyl radical (**3**)[9] was mixed with **1** prior to the addition of **2**.



Our results reveal that migratory carbonyl insertion *can* compete with β-elimination even in simple, conformationally mobile Fp alkyls. Under carbon monoxide both **1a** and **1b** react with **2** to produce mixtures of the acyl and the π-complex, **6** and **7**, respectively (runs 2, 3, 13, 14); **1b** does so under nitrogen as well (run 10). When the β-hydrogen is hindered and/or cannot attain an antiperiplanar conformation relative to iron,[10] insertion may be the ex-

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[1] Bly, R. S.; Bly, R. K.; Silverman, G. S. "Abstracts of Papers", 186th National Meeting of the American Chemical Society, Aug 28–Sept 2, 1983, Washington, DC; ORGN 33.

[2] Bly, R. S.; Silverman, G. S.; Bly, R. K. "Abstracts of Papers", 34th Southeast Regional Meeting of the American Chemical Society, Nov 3–5, 1982, Birmingham, AL; Abstr. No. 324.

[3] Fp = $(\eta^5\text{-}C_5H_5)(CO)_2Fe$; Fp′ = $(\eta^5\text{-}C_5H_5)(Ph_3P)(CO)Fe$.

[4] Dry, oxygen-free solvents and standard Schlenk techniques were employed throughout.

[5] Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 68–69.

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[7] (a) Green, M. L. H.; Nagy, P. L. I. *J. Chem. Soc.* **1963**, 189–197. (b) Laycock, D. E.; Baird, M. C. *Inorg. Chim. Acta* **1980**, *42*, 263–266. (c) Cutler, A.; Ehntholt, D.; Giering, W. P., Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495–3507.

[8] (a) **1b**: IR (CH_2Cl_2) 2001, 1945 cm^{-1}; ^1H NMR $(CDCl_3)$ δ 4.74 (s, 5 H, Cp), 1.45 (m, 5 H, $-CH_2CH_2CH<$), 0.98 (d, J = 5.4 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR $(CDCl_3)$ δ 217.67 ($-C{\equiv}O$), 85.30 (Cp), 47.68 ($>CH$), 32.55 ($>CH_2$), 22.45 (CH_3), 1.15 ($FpCH_2-$). (b) **1c**: mp 33–34 °C; IR $(CDCl_3)$ 2000, 1945 cm^{-1}; ^1H NMR $(CDCl_3)$ δ 4.65 (s, 5 H, Cp), 1.05–1.55 (m, 4 H, $FpCH_2CH_2-$), 0.85 (s, 9 H, CH_3); $^{13}C\{^1H\}$ NMR $(CDCl_3)$ δ 217.63 ($-C{\equiv}O$), 85.32 (Cp), 52.40 ($>C<$), 32.98 ($>CH_2$), 29.17 (CH_3), −2.41 ($FpCH_2-$). Although **1c** has been prepared previously (Whitesides, G. M.; Boschetto, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 1529–1531. Jacobson, S. E.; Wojcicki, A. *Ibid.* **1973**, *95*, 6962–6970. Dizikes, L. J.; Wojcicki, A *Ibid.* **1977**, *99*, 5295–5303. Rogers, W. N.; Page, J. A.; Baird, M. C. *Inorg. Chem.* **1981**, *20*, 3521–3528), its spectral characteristics have not been elaborated. (c) **6a**: IR (CH_2Cl_2) 2012, 1957, 1639 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 4.85 (s, 5 H, Cp), 2.87 (t, J_{ab} = 7.2 Hz, 2 H, $FpCOCH_2{}^a$), 1.34 (~sextet, $J_{ba} \cong J_{bc} \sim 7.2$ Hz, 2 H, $>CH_2{}^b$), 0.77 (t, J_{cb} = 7.1 Hz, 3 H, $CH_3{}^c$); $^{13}C\{^1H\}$ NMR $(CDCl_3)$ δ 259.52 ($>C{=}O$), 214.5 ($-C{\equiv}O$), 86.38 (Cp), 68.63 (FpCOC), 18.67 ($>CH_2$), 13.59 (CH_3); MS *m/e* 248$[M]^{+\cdot}$, 220$[M - CO]^{+\cdot}$, 192 $[M - 2CO]^{+\cdot}$, 205 $[M - C_3H_7]^{+\cdot}$, 177 $[M - COC_3H_7]^{+\cdot}$. Anal. Calcd for $C_{11}H_{12}FeO_3$: C, 53.26; H, 4.88. Found: C, 53.67; H, 4.98. (d) **6b**: IR (CH_2Cl_2) 2022, 1960, 1641 cm^{-1}, ^1H NMR $(CDCl_3)$ δ 4.90 (s, 5 H, Cp), 2.86 (t, J = 7.2 Hz, 2 H, $FpCOCH_2-$), 1.40 (m, 3 H, $-CH_2CH<$), 0.90 (d, J = 5.4 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR $(CDCl_3)$ δ 256.38 ($>C{=}O$), 214.44 ($-C{\equiv}O$), 86.31 (Cp), 64.66 (FpCOC), 33.87 ($>CH$?), 27.5 ($>CH_2$?), 22.32 (CH_3); MS, *m/e* 276 $[M]^{+\cdot}$, 248 $[M - CO]^{+\cdot}$, 220 $[M - 2CO]^{+\cdot}$, 205 $[M - C_5H_{11}]^{+\cdot}$, 177 $[M - COC_5H_{11}]^{+\cdot}$, 121 $[M - (COC_5H_{11} + 2CO)]^{+\cdot}$. (e) **6c**: mp 47–49 °C; IR (CH_2Cl_2) 2022, 1960, 1647 cm^{-1}; ^1H NMR $(CDCl_3)$ δ 4.94 (s, 5 H, Cp), 2.84 (t, J = 7.5 Hz, 2 H, $FpCOCH_2-$), 1.40 (t, J = 7.5 Hz, 2 H, $>CH_2$), 0.90 (s, 9 H, CH_3); $^{13}C\{^1H\}$ NMR $(CDCl_3)$ δ 256.78 ($>C{=}O$), 214.40 ($-C{\equiv}O$), 86.30 (Cp), 62.39 (FpCOC), 38.32 ($>C<$?), 29.92 ($>CH_2$?), 29.14 (CH_3); MS *m/e* 290 $[M]^{+\cdot}$, 262 $[M - CO]^{+\cdot}$, 234 $[M - 2CO]^{+\cdot}$, 205 $[M - C_6H_{13}]^{+\cdot}$, 177 $[M - COC_6H_{13}]^{+\cdot}$, 121 $[M - (COC_6H_{13} + 2CO)]^{+\cdot}$. (f) **7b**: IR (CH_2Cl_2) 2081, 2041 cm^{-1}; ^1H NMR $[(CD_3)_2CO]$ δ 5.9 (s, 5 H, Cp), 5.1–5.6 (m, 1 H, $=CH-$), 3.9 (d, J = 9 Hz, 1 H, *cis*-$=CH_2$), 3.5 (d, J = 15 Hz, *trans*-$=CH_2$), 1.4 (d, J = 5.4 Hz, 3 H, CH_3), 1.04 (d, J = 5.4 Hz, 3 H, CH_3); $^{13}C\{^1H\}$ NMR $[(CD_3)_2CO$, 0 °C$]$ δ 211.77 ($-C{\equiv}O$), 209.07 ($-C{\equiv}O$), 96.67 ($=CH-$), 90.18 (Cp), 51.06 ($=CH_2$), 34.8 ($>CH$), 24.98 (CH_3), 24.12 (CH_3).

[9] As an equilibrium mixture with the dimer prepared by treating triphenylchloromethane with excess zinc at room temperature (Isaacs, N. S. "Experiments in Physical Organic Chemistry"; Macmillan: New York, 1969, pp 216–217) and decanting the resultant clear supernatant solution.

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