Reaction of the Metal-Substituted Vinylidene Complex $Cp'(CO)_2Mn[{=}C{=}(H){-}Fp^*]$ with Excess BuLi, Giving Acylated Dinuclear Bridging Alkenyl Complexes, $Cp'MnCp^*Fe[\mu\text{-}CH{=}C(E){-}C({=}O){-}Bu](\mu\text{-}CO)(CO)_2$ (E = H, Me): Confirmation of the Intramolecular 1,2-H Shift Mechanism Proposed for the Fluxional Process of the Cationic Diiron μ-Ethynyl Complexes $[\{(\eta^5\text{-}C_5R_5)Fe(CO)_2\}_2(\mu\text{-}C{\equiv}C{-}H)]BF_4$[1]

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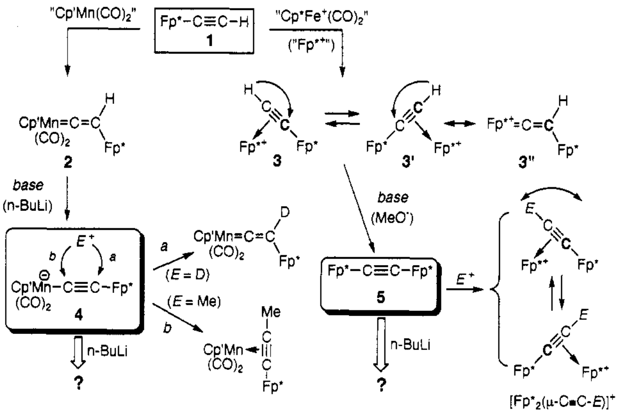
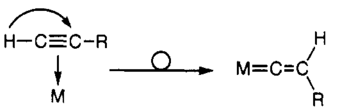
Summary: Reaction of the heterobimetallic bridging vinylidene complex $Cp'Mn(CO)_2[{=}C{=}C(H)Fp^*]$ (2) with an excess amount of n-BuLi followed by quenching with electrophiles produces the dinuclear bridging μ-η^1-(Fe):η^2(Mn)-3-oxo-hept-1-en-1-yl complexes $Cp'MnCp^*Fe[\mu\text{-}CH{=}C(E){-}C({=}O){-}Bu](\mu\text{-}CO)(CO)_2$ [E = H (6a), Me (6b)] via nucleophilic addition to the anionic ethynediyl intermediate $[Cp'(CO)_2Mn{-}C{=}C{-}Fe(CO)2Cp^*]^-$ (7) resulting from deprotonation of 2. It has been proved that the previously reported reaction of the cationic diiron μ-ethynyl complex $[Fp^*_2(\mu\text{-}C{\equiv}C{-}H)]BF_4$ (3) (isoelectronic with 2) follows a similar reaction pathway. Crystal data for 6b: monoclinic, space group C2/c, a = 33.862(5) Å, b = 9.140(4) Å, c = 16.815(5) Å, β = 98.72(2)°, V = 5144(5) Å³, Z = 8.

Introduction

In previous papers we reported the synthesis and characterization of the dinuclear complexes 2[2] and 3[3] containing a C_2H bridge (Scheme 1). Treatment of $Fp^*{-}C{\equiv}C{-}H$ (1) with 16e species, "$Cp'Mn(CO)_2$" and "$Cp^*Fe^+(CO)_2$", produced 2 and 3 (BF_4 salt), respectively. Although they were isoelectronic complexes, the dominant resonance contributors of 2 and 3 proved to be the vinylidene structure and the η^2-alkyne complex-type structure, respectively, depending on the electron-donating abilities of the metal components, as revealed by the crystallographic and MO analyses.[2] In addition, variable temperature ^{13}C-NMR analysis revealed that 3 was fluxional via the reversible intramolecular 1,2-H shift, which contrasted with the windshield wiper like oscillation mechanism observed for dinuclear μ-acetylide complexes with a substituent at the β-carbon atom, $M_2(\mu\text{-}C{\equiv}C{-}R)$ (R ≠ H) (see, for example, the behavior of $[Fp^*_2(\mu\text{-}C{\equiv}C{-}E)]^+$ shown in Scheme 1).[3] Because a contribution of the vinylidene structure 3″ to 3 was indicated by the X-ray and NMR analyses, the fluxional property [3→(3′↔)3″] provided the first experimental evidence for the 1,2-H shift mechanism of the 1-alkyne-to-vinylidene ligand transformation within a transition metal coordination sphere (eq 1).[4] This widely accepted mechanism had been

Scheme 1




(1)

supported so far only by an EHMO calculation.[5] On the other hand, whereas the $Mn{=}C{=}C(H)Fe$ linkage in 2 proved to be rigid, 2 itself should arise from the 1,2-H shift reaction of the η^2-intermediate $Cp'Mn(CO)_2(\eta^2\text{-}Fp^*{-}C{\equiv}C{-}H)$ analogous to 3.

The 1,2-H shift of 3 suggesting an acidic property of the C_2H bridge prompted us to examine deprotonation reactions of 2 and 3 (Scheme 1). As expected, both 2 and 3 were readily deprotonated by the action of bases to generate the ethynediyl species 4 and 5, respectively, and subsequent treatment with electrophiles afforded dinuclear adducts.[2,3,6]

Herein we wish to report the results of further reaction of 4 and 5 with a nucleophile (n-BuLi)[7] and confirmation

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[1] Abbreviations used in this paper: Cp′ = η^5-C_5H_4Me; Cp* = η^5-C_5Me_5; Cp$^\#$ = η^5-C_5Me_4Et, Fp* = Cp*Fe(CO)$_2$; Fp$^\#$ = Cp$^\#$Fe(CO)$_2$.

[2] Akita, M.; Ishii, N.; Takabuchi, A.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1994**, *13,* 258-268.

[3] Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. *Organometallics* **1990**, *9,* 816-825.

[4] (a) Bruce, M. I. *Chem. Rev.* **1991**, *91,* 197-257. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22,* 60-128.

[5] Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68,* 1461-1506.

[6] Akita, M.; Terada, M.; Oyama, S.; Sugimoto, S.; Moro-oka, Y. *Organometallics* **1991**, *10,* 1561-1568.

[7] The reaction of 3 with BuLi was reported previously. Akita, M.; Terada, M.; Moro-oka, Y. *Organometallics* **1991**, *10,* 2962-2965.

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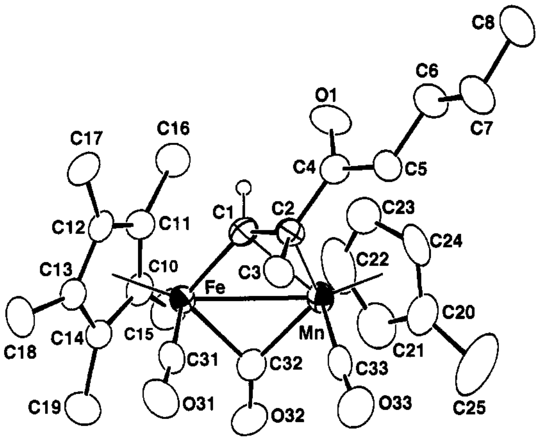


Figure 1. Molecular structure of **6b** drawn at the 30% probability level.

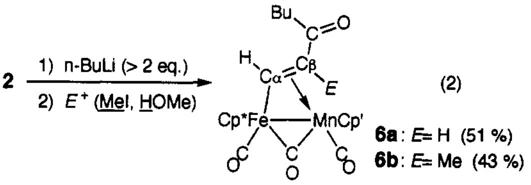
Table 1. Crystallographic Data for 6b

formula	$C_{27}H_{35}O_4FeMn$	d_{calcd}/g·cm^{-3}	1.380
fw	534.4	μ/cm^{-1}	10.63
space group	*C*2/*c*	temp/°C	25
a/Å	33.862(5)	2θ/deg	5–50
b/Å	9.140(4)	no. of data collcd	4925
c/Å	16.815(5)	no. of data with $F^2 > 3\sigma(F^2)$	2380
β/deg	98.72(2)	no. of variables	298
V/Å^3	5144(5)	*R*	0.0574
Z	8	R_w	0.0679

of the intramolecular 1,2-H shift mechanism proposed for the fluxional process of **3**.

Results and Discussion

Reaction of the Heterobimetallic μ-Vinylidene Complex 2 with an Excess Amount of *n*-BuLi. Treatment of **2** with 1.3 equiv of *n*-BuLi gave the monoanionic intermediate **4**, which produced two types of adducts after quenching with electrophiles, as described above (Scheme 1). However, addition of an excess amount (>2 equiv) of *n*-BuLi generated another anionic species **7**, which, upon treatment with electrophiles [H$^+$ (MeOH), Me$^+$ (MeI)], afforded heterobimetallic complexes **6** with a Bu group (eq 2). The structure of **6b** determined crystallographically (Figure 1 and Tables 1–3) contains the pentanoyl-substituted vinyl group which is coordinated to the Fe and Mn centers in η^1- and η^2-modes, respectively. In accord with this structure, the ^{1}H- and ^{13}C-NMR signals for the C$_\alpha$H and C$_\beta$(H) moieties of the bridging vinyl parts of **6a,b** were observed in lower [C$_\alpha$H$_\alpha$: δ_C(C$_\alpha$) 191.8 (**6a**), 198.6 (**6b**); δ_H(H$_\alpha$) 11.37 (**6a**), 11.71 (**6b**)] and higher field [C$_\beta$(H$_\beta$): δ_C(C$_\beta$) 69.9 (**6a**), 86.8 (**6b**); δ_H(C$_\beta$H) 3.36 (**6a**)], respectively, as reported for the isoelectronic cationic dinuclear μ-alkenyl complexes of Fe and Ru, [Cp$_2$M$_2$(μ-η^1:η^2-alkenyl)(μ-CO)(CO)$_2$]$^+$.[8] The Fe–Mn separation in **6b** is comparable to those of related complexes.[9] As is evident from the structure, the externally added electrophile is bonded to C$_\beta$ and, irrespective of the electrophiles, a hydrogen atom is attached to the bridging carbon atom (C$_\alpha$).

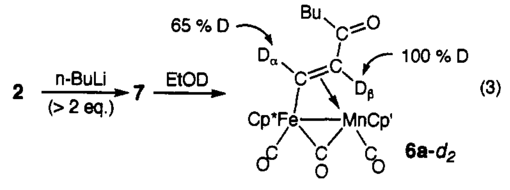


(2)

Table 2. Positional Parameters and B_{eq} (Å^2) for 6b

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}
Fe	0.38594(3)	0.2145(1)	0.11495(6)	3.33(5)
Mn	0.40829(4)	0.2710(1)	–0.02665(7)	3.83(6)
O1	0.3147(2)	0.1454(8)	–0.1419(4)	7.1(4)
O31	0.3814(2)	0.5110(7)	0.1715(4)	6.5(4)
O32	0.4690(2)	0.2967(8)	0.1194(4)	6.4(4)
O33	0.4211(2)	0.5879(8)	–0.0211(4)	7.2(4)
C1	0.3545(2)	0.214(1)	0.0103(5)	3.8(4)
C2	0.3419(2)	0.3246(8)	–0.0457(5)	3.7(4)
C3	0.3308(3)	0.479(1)	–0.0242(5)	4.4(4)
C4	0.3207(3)	0.274(1)	–0.1262(5)	4.4(4)
C5	0.3065(3)	0.386(1)	–0.1906(5)	4.4(4)
C6	0.2873(3)	0.322(1)	–0.2699(6)	5.2(5)
C7	0.2699(3)	0.433(1)	–0.3293(6)	6.3(5)
C8	0.2481(3)	0.367(1)	–0.4060(6)	7.5(6)
C10	0.4136(3)	0.0146(9)	0.1700(5)	3.8(4)
C11	0.3753(3)	–0.0165(9)	0.1299(5)	3.9(4)
C12	0.3469(3)	0.067(1)	0.1613(5)	3.8(4)
C13	0.3677(3)	0.153(1)	0.2247(5)	3.9(4)
C14	0.4095(2)	0.1240(9)	0.2289(5)	3.6(4)
C15	0.4521(3)	–0.058(1)	0.1612(7)	6.3(6)
C16	0.3656(3)	–0.135(1)	0.0667(6)	5.6(5)
C17	0.3025(3)	0.064(1)	0.1403(6)	5.4(5)
C18	0.3490(3)	0.244(1)	0.2821(5)	5.8(5)
C19	0.4426(3)	0.187(1)	0.2869(6)	5.8(5)
C20	0.4472(4)	0.272(1)	–0.1163(8)	6.2(6)
C21	0.4635(4)	0.182(2)	–0.0548(9)	7.7(8)
C22	0.4368(6)	0.071(2)	–0.0459(8)	8.6(9)
C23	0.4048(4)	0.084(1)	–0.1050(8)	6.8(7)
C24	0.4103(4)	0.212(1)	–0.1499(5)	6.4(6)
C25	0.4685(5)	0.394(2)	–0.149(1)	14(1)
C31	0.3820(3)	0.396(1)	0.1451(5)	4.1(4)
C32	0.4367(3)	0.274(1)	0.0841(5)	4.3(4)
C33	0.4146(3)	0.463(1)	–0.0224(5)	4.6(5)

In order to determine the electronic state of the anionic intermediate **7**, it was quenched by EtOD. As a result, the α- and β-hydrogen atoms of the bridging vinyl part in **6a** were 65% and 100% deuterated, respectively (eq 3), and therefore **7** proved to be a *dianonic* species.[10,11]



(3)

On the basis of the structure of **6**, the dianionic intermediate **7** was assigned to a μ-vinylidene species, and its plausible formation mechanism is summarized in Scheme 2. **2** is deprotonated by the first equivalent of *n*-BuLi to give **4**. Then the second equivalent of *n*-BuLi attacks a CO ligand of the neutral Fp* part in **4** to form the dianionic acyl intermediate **8**. Similar nucleophilic addition to CO was assumed in the reaction of an iron

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(8) (a) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417–1426. (b) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1983**, 1427–1431. (c) Casey, C. P.; Fagan, P. J.; Miles, W.; Marder, S. R. *J. Mol. Catal.* **1983**, *21*, 173–188. (d) Casey, C. P.; Marder, S.; Adams, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 7700–7705. (e) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043–4053. (f) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053–4059.

(9) Fong, R. H.; Lin, C.-H.; Idomoumaz, H.; Hersh, W. H. *Organometallics* **1993**, *12*, 503–516.

(10) The D atoms were not incorporated after quenching, because treatment of **6a** with LiOEt in EtOD–THF did not induce H–D exchange of **6a**. We are grateful to the reviewer suggesting this experiment.

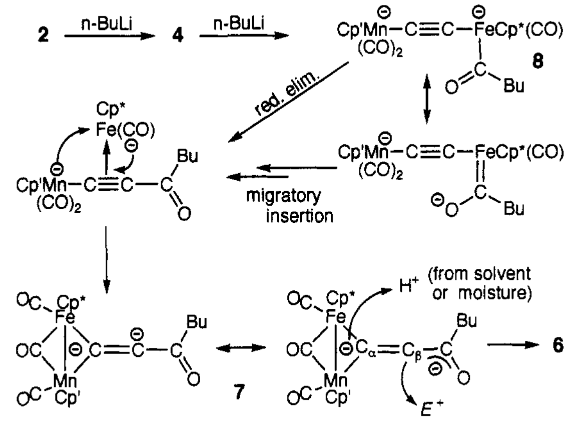
(11) Attempted isolation of **7** as PPN$^+$ and NR$_4^+$ salts has been unsuccessful. IR and ^{1}H-NMR monitoring of a reaction mixture before quenching by electrophiles indicated the presence of a couple of species which could not be characterized by the spectroscopic methods alone.

Table 3. Selected Structural Parameters for 6b[a]

	Bond Lengths		
Fe–Mn	2.656(2)	C2–C3	1.52(1)
Fe–C1	1.914(8)	C2–C4	1.50(1)
Fe–C10~14	2.142	C4–O1	1.22(1)
Fe–C31	1.74(1)	C31–O31	1.145(9)
Fe–C32	1.948(9)	C32–O32	1.18(1)
Mn–C1	2.078(8)	C33–O33	1.16(1)
Mn–C2	2.277(8)	C–C(Bu)	1.51
Mn–C20~25	2.14	C–C(Cp*)	1.41
Mn–C32	1.962(9)	C–Me(Cp*)	1.50
Mn–C33	1.77(1)	C–C(Cp′)	1.39
C1–C2	1.40(1)	C20–C25	1.48(2)
	Bond Angles		
Mn-Fe-C1	51.0(2)	C1-C2-C4	116.0(7)
Mn-Fe-C31	96.9(3)	Mn-C2-C3	116.1(6)
Mn-Fe-C32	47.4(3)	Mn-C2-C4	112.7(6)
Fe-Mn-C1	45.7(2)	C3-C2-C4	113.6(7)
Fe-Mn-C2	76.0(2)	C2-C4-O1	122.3(8)
Fe-Mn-C32	47.0(3)	C2-C4-C5	119.5(8)
Fe-Mn-C33	101.9(3)	C5-C4-O1	118.2(8)
C1-Mn-C2	37.2(3)	Fe-C31-O31	173.6(8)
Fe-C1-C2	133.4(6)	Fe-C32-O32	134.6(7)
Fe-C1-Mn	83.3(3)	Fe-C32-Mn	85.6(4)
C2-C1-Mn	79.1(5)	Mn-C32-O32	139.8(7)
C1-C2-Mn	63.7(5)	Mn-C33-O33	175.6(9)
C1-C2-C3	124.8(7)		

[a] Bond lengths in angstroms and bond angles in degrees. Values without standard deviations are averaged ones.

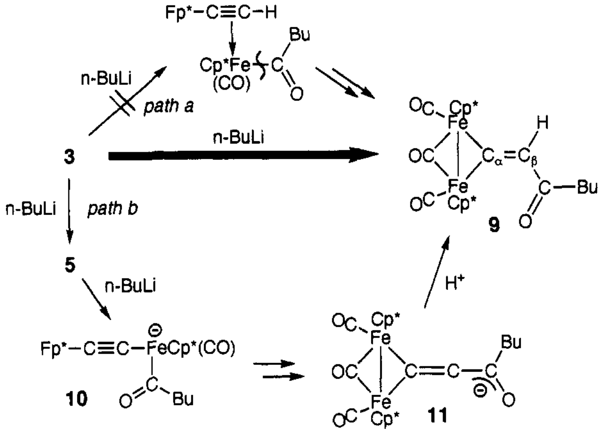
Scheme 2



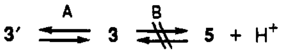
acetylide complex Fp—C≡C—Me with n-BuLi giving an acylated product.[12] Reductive elimination or migratory insertion toward the oxycarbene ligand would give the η^2-intermediate. Subsequent intramolecular electron transfer finally leads to the dianionic species **7** where the dinegative charges delocalize over the dimetallic skeleton and the enolate part. The externally added electrophile reacts with the enolate functional group and the bridging carbon atom (C_α) picks up H^+ probably from the solvent or moisture to give the final product **6**. Although the order of the two addition reactions is not clear, the EtOD experiment (eq 3) where $C_\alpha H$ is not completely deuterated suggests that the protonation (reaction at C_α) precedes the reaction at the enolate moiety.

Reconsideration of the Mechanism of the Reaction of 3 with *n*-BuLi and Confirmation of the Intramolecular 1,2-H Shift Mechanism Proposed for the Fluxional Process of 3. We already reported the reaction of **3** similar to eq 2 giving the acyl-substituted vinylidene complex **9** (Scheme 3).[7] At that time, on the basis of the retention of the C—H bond in the product **9**, we proposed a mechanism by way of insertion of Fp*—C≡C—H into the Fe—C(=O)Bu moiety resulting from nucleophilic addition to an Fe—CO ligand (path a in Scheme 3). Moreover, this mechanism was adopted as evidence to discern between the *intramolecular* 1,2-H shift mechanism of the fluxional process of **3** (equilibrium A in Scheme 4; see also Scheme 1) and the reversible H^+-dissociation mechanism (equilibrium B in Scheme 4). Although the coalescence of the Cp*, CO, and C_2H signals (^{13}C-NMR at room temperature) could be explained in terms of either of the mechanisms, the apparent retention of the C—H bond in **9** favored the intramolecular mechanism (path a).[3,7]

Scheme 3



Scheme 4



However, Scheme 2 led us to another mechanism which involved the ethynediyl complex **5** (isoelectronic with **4**) as a key intermediate (path b in Scheme 3). Namely, the first equivalent of n-BuLi may deprotonate **3** to give **5** and subsequent nucleophilic addition of the second equivalent of BuLi to a CO ligand generates the anionic acyl intermediate **10**. Successive reaction similar to Scheme 2 finally leads to the monoanionic intermediate **11** analogous to **7**, which would pick up a proton to give the final product **9**.

The reaction with BuLi actually proceeded via path b, as revealed by the following two experiments: (1) Quenching of a reaction mixture of **3** and BuLi with EtOD afforded **9**-d where the $C_\beta H$ was deuterated completely (eq 4).[13] (2)

$$3 + n\text{-BuLi} \xrightarrow[\text{(2) EtOD}]{\text{(1) -78 °C} \rightarrow \text{room temp/THF}} 9\text{-}d \qquad (4)$$

$$5 + n\text{-BuLi} \xrightarrow[\text{(2) MeOH}]{\text{(1) -78 °C} \rightarrow \text{room temp/THF}} 9 \qquad (5)$$

Treatment of the plausible intermediate **5** with BuLi also produced **9** (eq 5).[13] Therefore our previous mechanism (path a) must be corrected. Thus it turned out that the reactions of the isoelectronic complexes **2** and **3** with BuLi were quite similar.

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[12] Wong, A.; Pawlick, R. V.; Thomas, C. G.; Leon, D. R.; Liu, L.-K. *Organometallics* **1991**, *10*, 530–532.

[13] The reactions were carried out in essentially the same manner as described in ref 7 by using EtOD (eq 4) and **5** (eq 5) as the quenching agent and the starting material, respectively.

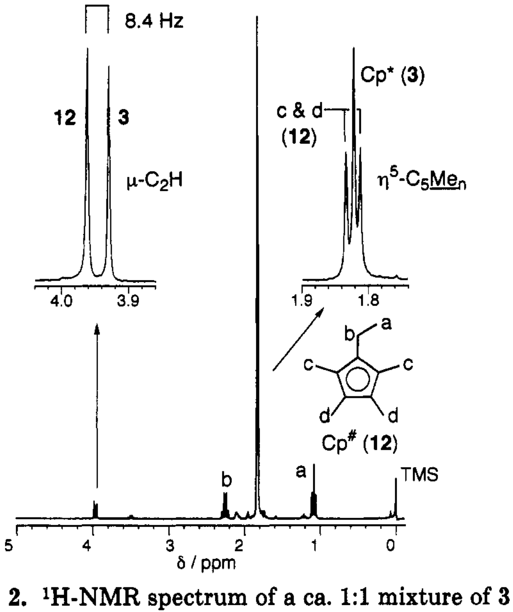
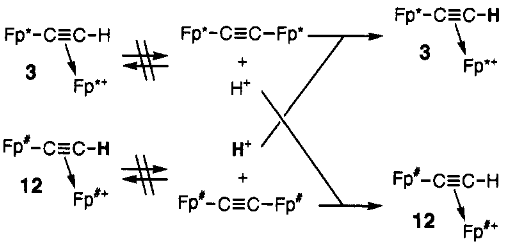


Figure 2. ^{1}H-NMR spectrum of a ca. 1:1 mixture of **3** and **12** (observed at 27 °C at 270 MHz in $CDCl_3$).

Scheme 5



Now we must reconsider the fluxional mechanism of **3**, because it has become evident that the C_2–H bond is not retained during the reaction of **3** with BuLi in contrast to our previous assumption. So the problem was further examined by a ^{1}H-NMR technique; i.e. a mixed sample of **3** and its η^5-C_5Me_4Et analogue **12** (BF_4 salt) was subjected to ^{1}H-NMR analysis. If the fluxional process follows the H^+-dissociation mechanism (equilibrium B in Scheme 4), a released proton would be incorporated into either **3** or **12** and, as a result, the $C_2\mathit{H}$ signals of **3** and **12** should coalesce at a higher temperature (Scheme 5). In the ^{1}H-NMR spectrum of a ca. 1:1 mixture of **3** and **12** observed with a 270-MHz spectrometer at room temperature (Figure 2: the Cp* and Cp# signals appeared as single sets of signals at room temperature), the $C_2\mathit{H}$ signals of **3** (δ 3.93) and **12** (δ 3.96) (separated by 8.4 Hz) were observed distinctly.[14] Thus the *intramolecular* 1,2-H shift mechanism proposed for the fluxional process of **3** (equilibrium A in Scheme 4)[3] has been confirmed by the absence of the *intermolecular* H^+-dissociation process as well as the negative $\Delta S^{\ddagger}$ value (−8.6 eu)[3] observed for the fluxional process. Therefore, in the deprotonation of **2** and **3**, bases do not react with a free, dissociated H^+ but attack the $C_2\mathit{H}$ atom in the substrates.

Experimental Section

General Considerations. All manipulations were carried out under an argon atmosphere by using standard Schlenk tube techniques. Ether, THF, and hexanes were dried over Na–K alloy, distilled, and stored under Ar. **2**, **3**, and **5** were prepared according to our previous papers.[2,3,6] *n*-BuLi (Aldrich) was purchased and used as received.

^{1}H- and ^{13}C-NMR spectra were recorded on JEOL EX-90 (^{1}H, 90 MHz) and JEOL GX-270 spectrometers (^{1}H, 270 MHz; ^{13}C, 67.9 MHz). Solvents for NMR measurements containing 1% TMS were dried over molecular sieves and distilled under reduced pressure. IR spectra were recorded on a JASCO FT/IR 5300 spectrometer.

Preparation of 6a. To a THF solution (9 mL) of **2** (139 mg, 0.301 mmol) cooled at −78 °C was added *n*-BuLi (1.6 M, 0.38 mL, 0.6 mmol). After the mixture was stirred for 1 h at the same temperature, MeOH (1 mL) was added dropwise. The resulting mixture was warmed gradually to ambient temperature. Removal of the volatiles under reduced pressure, extraction with ether, and filtration through an alumina pad [activity II–IV: Merck Art. 1097] followed by crystallization from ether–hexanes gave **6a** (80.0 mg, 0.153 mmol, 51% yield) as a green black solid. **6a**: ^{1}H-NMR (C_6D_6) δ 0.86 (3H, t, J = 6.4 Hz, Me in Bu), 1.27 (2H, m, CH_2), 1.51 (15H, s, Cp*), 1.7 (2H, m, CH_2), 2.08 (3H, brs, $C_5H_4\mathit{Me}$), 2.43 (2H, t, J = 6.5 Hz, $COCH_2$), 3.36 (1H, d, J = 10 Hz, Fe—CH=C*H*), 3.74, 3.91, 3.99, 4.10 (1H × 4, m, $C_5\mathit{H}_4Me$), 11.37 (1H, d, J = 10 Hz, Fe—CH=); ^{13}C-NMR (C_6D_6) δ 9.5 (q, J_{CH} = 126 Hz, $C_5\mathit{Me}_5$), 13.1, 14.2 (q × 2, J_{CH} = 127 Hz, $C_5H_4\mathit{Me}$ and Me in Bu), 23.0, 27.1 (t × 2, J_{CH} = 128 Hz, CH_2CH_2), 42.5 (t, J = 129 Hz, $\mathit{C}H_2CO$), 69.9 (d, J = 157 Hz, C_β), 84.7, 85.9, 87.8, 88.4 (d × 4, J not analyzed, CH in Cp′), 97.8 (s, C_5Me_5), 99.4 (s, ipso-C in Cp′), 191.8 (d, J = 148 Hz, C_α), 205.0 (s, C=O), 214.2 (s, Fe—CO), 236 (br s, Mn—CO), 273.0 (s, μ-CO); IR (KBr) ν(C≡O) 1955, 1917, 1754, ν(C=O) 1671 cm^{-1}. Anal. Calcd for $C_{26}H_{33}O_4FeMn$: C, 59.88; H, 6.52. Found: C, 60.02; H, 6.39.

Preparation of 6b. The reaction was carried out in essentially the same manner as described for **6a** by using **2** (139 mg, 0.301 mmol), *n*-BuLi (1.6 M, 0.41 mL, 0.66 mmol), and MeI (0.2 mL, 3.2 mmol) in place of MeOH. **6b** was obtained as green black crystals (69.6 mg, 0.130 mmol, 43% yield). **6b**: ^{1}H-NMR (C_6D_6) δ 0.91 (3H, t, J = 7.1 Hz, Me in Bu), 1.35 (2H, m, CH_2), 1.57 (15H, s, Cp*), 1.7 (2H, m, CH_2), 1.88 (3H, s, C=CMe), 2.08 (3H, s, $C_5H_4\mathit{Me}$), 2.64 (2H, t, J = 6.8 Hz, $COCH_2$), 3.64, 3.98, 4.03 (2H × 1 and 1H × 2, m, $C_5\mathit{H}_4Me$), 11.71 (1H, s, Fe—CH=); ^{13}C-NMR (C_6D_6) δ 9.5 (q, J_{CH} = 126 Hz, $C_5\mathit{Me}_5$), 13.3, 14.3 (q × 2, J_{CH} = 127 Hz, $C_5H_4\mathit{Me}$ and Me in Bu), 23.1, 24.5, 27.0 (CH=C*Me* and CH_2CH_2, not analyzed), 40.4 (t, J = 129 Hz, $\mathit{C}H_2CO$), 86.8 (s, C_β), 85.6, 86.7, 87.5, 88.1 (d × 4, CH in Cp′, J_{CH}'s were not analyzed), 98.3 (s, C_5Me_5), 100.3 (s, ipso-C in Cp′), 198.6 (d, J = 140 Hz, C_α), 204.0 (s, C=O), 217.2 (s, Fe—CO), 236 (br s, Mn—CO), 273.9 (s, μ-CO); IR (KBr) ν(C≡O) 1926, 1888, 1770, ν(C=O) 1660 cm^{-1}. Anal. Calcd for $C_{27}H_{35}O_4FeMn$: C, 60.69; H, 6.60. Found: C, 60.81; H, 6.75.

Preparation of 12 (BF_4 Salt). **12** was prepared in a manner similar to that for **3**[3] starting from $Fp^{\#}_2$, which was obtained by the reaction of *c*-C_5Me_4EtH[15] with $Fe(CO)_5$ in refluxing xylenes[16] ($Fp^{\#}_2 \rightarrow Fp^{\#}$—I $\rightarrow Fp^{\#}$—C≡C—H and $[Fp^{\#}(THF)]BF_4 \rightarrow$ **12**).[17] Data for **12**: ^{1}H-NMR ($CDCl_3$) δ 1.08 (6H, t, J = 7.6 Hz, $C\mathit{H}_3CH_2$), 1.81 (6H, s, Me), 1.83 (6H, s, Me), 2.25 (4H, q, J = 7.6 Hz, $CH_3C\mathit{H}_2$), 3.98 (1H, s, C_2H); IR (KBr) ν(≡C—H) 3157, ν(C≡O) 2045, 2016, 1981, 1956, ν(C≡C) 1811 cm^{-1}. Anal. Calcd for $C_{28}H_{35}O_4Fe_2BF_4$: C, 53.06; H, 5.52. Found: C, 52.53; H, 5.43.

X-ray Crystallography of 6b. **6b** was recrystallized from an ether–hexanes mixed solvent system, and a suitable crystal was mounted on a glass fiber. The diffraction measurement was made on a Rigaku AFC-5R automated four-circle diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.710 59 Å). The unit cell was determined and refined by a least-squares method using 24 independent reflections. Data were collected with the ω scan technique. If $\sigma(I)/I$ was more than 0.1, a scan was repeated up to three times and the results were added to the first scan. Three standard reflections were monitored at every 150 measurements. All data processing was performed on a Micro

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[14] The $C_2\mathit{H}$ signals were observed distinctly even by a 60-MHz spectrometer.

[15] Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1–5.

[16] Cathline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094.

[17] Details will be reported elsewhere.

Vax II computer by using the TEXSAN structure solving program system obtained from the Rigaku Corp., Tokyo, Japan. Neutral scattering factors were obtained from the standard source.[18] In the reduction of data, Lorentz, polarization, and empirical absorption corrections (Ψ scan) were made.

The structure was solved by a combination of the direct method and Fourier synthesis (MITHRIL and DIRDIF). All the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms located at the calculated positions (C–H = 0.95 Å) were not refined.

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Supplementary Material Available: Tables of anisotropic thermal parameters and bond lengths and angles for **6b** (5 pages). Ordering information is given on any current masthead page.

OM940117U

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[18] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1975; Vol. 4.