Preparation of Homo- and Heterobimetallic μ-η^2-(C,C)-Ketene Complexes, $FpCH_2COML_n$, and Transformation of the Bridging Ketene Ligand into Various C2 Functional Groups

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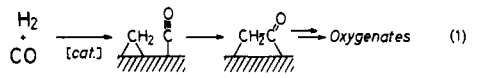
Eight examples of homo- and heterobimetallic μ-ketene complexes, $FpCH_2COML_n$ [3-7: Fp = $(\eta^5$-$C_5H_5)Fe(CO)_2$; M = Fe, Mo, Ni, Mn, Co; L = Cp, CO, PR_3], are prepared by acylation of an iron-substituted acetyl chloride with various transition-metal anions. IR studies reveal the significant contribution of a π-complex $Fp^+[CH_2{=}C(O^-)Fp]$ (10) in addition to an oxycarbene structure $FpCH_2C(O^-){=}Fp^+$ (11) which is well-established for mononuclear acyl complexes. As a typical example, $FpCH_2COFp$ (**3a**) is subjected to chemical transformations relevant to catalytic CO hydrogenation. While **3a** is not susceptible to carbonylation to lead to a μ-malonyl complex, decarbonylation results in quantitative liberation of ketene molecule or ligand substitution instead of formation of a μ-methylene complex. Reduction of **3a** by $LiAlH_4$ affords C3 products as major components. Reaction of **3a** with electrophiles takes place at the acyl oxygen atom to give cationic binuclear oxycarbene complexes $FpCH_2C(OR){=}Fp^+TfO^-$ (TfO = CF_3SO_3) (18-20) which exhibit bimodal reactivities toward both nucleophiles and electrophiles. Hard nucleophiles attack the most electrophilic carbene center, soft nucleophiles attack the alkyl side Fp group, and electrophilic reaction takes place at the methylene terminus.

Introduction

Catalytic transformation of syngas may be regarded as reductive polymerization of carbon monoxide.[1] Carbon monoxide adsorbed on a catalyst surface is hydrogenated to give C1 fragments such as CH_xO or CH_x species with retention or disruption of the C-O bond. Successive C-C coupling and functionalization on the catalyst surface lead to the formation of a variety of hydrocarbons and oxygenates. Among possible C2 surface species, ketene arising from coupling between CH_2 and CO has been postulated as the origin of oxygenated products[2] (eq 1).

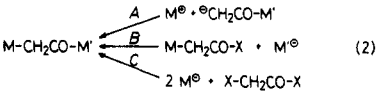


(1)

While μ-methylene complexes[3] have been prepared as a model for surface methylene species, to date only two systems, a diruthenium μ-methylene complex without a metal-metal bond[4] and trinuclear osmium μ-methylene clusters,[5] have been reported to be carbonylated to μ-ketene complexes. In these complexes no interaction between metal centers bridged by the ketene ligand is observed. Other μ-methylene complexes are inert toward CO insertion[3] presumably because of the thermodynamic stability of the three-membered dimetallacyclopropane skeleton, although a μ-ketene complex with a metal-metal bond has been recently prepared by hydration of a μ-acetylide complex.[6,4b]

Methylenation of a metal carbonyl complex is also available. Shapley et al.[7a] reported the first example of a μ_3-η^3-(C,C,O)-ketene complex[7] prepared by the reaction of $Ru_3(CO)_{10}$(dppm) with diazomethane (dppm = bis(diphenylphosphino)methane).

To elucidate general reactivities of the μ-ketene ligand,[8] indirect preparative methods for μ-ketene complexes leading to heterobimetallic systems[9] are sought. Three strategies are possible for construction of a μ-ketene skeleton (eq 2). Trapping a metallaenolate by metal cation



(2)

(route A) and metalation of haloacetyl halide (route C)[4a] were unsuccessful when M or M' = $CpFe(CO)_2$.[10] However, employment of a more stable phosphine-substituted ferraenolate following route A led to successful preparation of heterobimetallic μ-η^2-(C,O)- and μ-η^2-(C,C)-ketene complexes as recently reported by Floriani et al.[11] In this article we describe preparation of various heterobimetallic

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μ-η^2-(C,C)-ketene complexes by route B and successive functionalization of the μ-ketene ligand.[12,13]

Results and Discussion

Preparation and Spectral Characterization of Heterobimetallic μ-Ketene Complexes. Heterobimetallic μ-ketene complexes **3–7** were prepared by the reactions of various metal anions with an iron-substituted acetyl chloride **2**, which was obtained by chlorination of the corresponding carboxylic acid **1**[14] with oxalyl dichloride

$$(\eta^5\text{-}C_5H_4R)Fe(CO)_2CH_2COOH \xrightarrow[CH_2Cl_2]{(COCl)_2}$$

1a, R = H
1b, R = Me

$$(\eta^5\text{-}C_5H_4R)Fe(CO)_2CH_2COCl \xrightarrow[ML_n^-]{THF}$$

2a, R = H
2b, R = Me

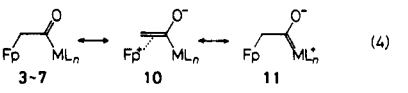
$$(\eta^5\text{-}C_5H_4R)Fe(CO)_2CH_2COML_n \quad (3)$$

3a, R = H; ML_n = $CpFe(CO)_2$; 27%
3b, R = H; ML_n = $Cp'Fe(CO)_2$; 13%
3c, R = Me; ML_n = $CpFe(CO)_2$; 21%
3d, R = Me; ML_n = $Cp'Fe(CO)_2$; 11%
4, R = H; ML_n = $CpMo(CO)_2(PPh_3)$; 35%
5, R = H; ML_n = $CpNi(CO)$; 37%
6, R = H; ML_n = $Mn(CO)_5$; 74%
7, R = H; ML_n = $Co(CO)_3(PMe_2Ph)$; 66%

Cp = η^5-C_5H_5, Cp′ = η^5-C_5H_4Me

(eq 3). After separation of dimetallic complexes, $FpML_n$, by column chromatography, **3–6** were isolated as yellow to orange crystals and **7** as yellow oil in moderate yields. Spectral data for very moisture sensitive **2a** [^{1}H NMR ($CDCl_3$) δ 1.91 (CH_2), 4.95 (Cp); IR (CH_2Cl_2) ν(C≡O) 2029, 1973 cm^{-1}, ν(C=O) 1755 cm^{-1}] supported the acyl chloride structure and were in good agreement with those of $FpCH_2COI$ [ν(C≡O) 2022, 1977, ν(C=O) 1754 cm^{-1}], which was prepared by addition of iodide anion to a cationic mononuclear η^2-(C,C)-ketene complex.[15] The presence of the acyl chloride function was also confirmed by methanolysis, affording a methyl ester, $FpCH_2COOMe$. The same procedure for preparation of a tungsten-substituted acetyl chloride has been recently reported by Bergman.[16]

Spectral features of **3–7** are approximately characterized as superposition of $FpCH_3$ and CH_3COML_n, which possess the alkyl-side and the acyl-side partial structures of the μ-ketene complexes, respectively (Tables I, II, and III). For example, **3a** contains two nonequivalent Fp groups and a μ-ketene bridge consistent with the formal structure, $Fp_ACH_2COFp_B$. The Cp signals (^{1}H and ^{13}C NMR) in higher fields and the terminal CO signal (^{13}C) in lower field are assigned to those of Fp_A and the remainder to those of Fp_B when compared with $FpCH_3$ **8** and CH_3COFp **9a**.[17,18] (Table I) The assignments are further confirmed by comparison with labeled compounds **3b–d**.[19] In particular, the triplet acyl carbon signal (δ 253.28, $^2J_{C-H}$ = 3.0 Hz) appearing in the same region as that of **9a** clearly demonstrates that the methylene carbon is directly attached to the acyl carbon. In other words, the two Fp groups are bridged by the μ-ketene ligand. The IR spectrum of **3a** contains five absorptions in the range of 1500–2100 cm^{-1} (Table II). Among four ν(C≡O) absorptions, those of the highest and the third highest frequencies are attributed to Fp_A and the remaining two absorptions to those of Fp_B, since they are in good agreement with those of **8** and **9a**,[20] respectively. Furthermore no evidence for bridging carbonyl ligands characteristic of diiron carbonyl cyclopentadienyl complexes with a metal–metal bond such as $[CpFe(\mu\text{-}CO)(CO)]_2$ and $Cp_2Fe_2(\mu\text{-}CR_2)(\mu\text{-}CO)(CO)_2$ has been obtained by IR and ^{13}C NMR.[21] On the other hand, the ν(C=O) absorption of the μ-ketene bridge appears at lower frequencies by 35 cm^{-1} when compared with that of **9a**. The shift should be caused by the contribution of a π-complex **10** in addition to an oxycarbene structure **11**,[22] which is well-established for mononuclear acyl metal complexes (eq 4). **10** arises from back donation of d



(4)

electrons of Fp_A to the C=O group at β-position (so-called the "β-effect"[14]) and its contribution is manifested by the positive value of a term $\Delta\nu$(C=O) [= ν(C=O; acetyl complex) − ν(C=O; μ-ketene complex)].[23] The red shift ($\Delta\nu > 0$) is generally observed for μ-ketene complexes hitherto reported except for $CpRu(CO)_2CH_2CORuCp(CO)_2$. (Tables II and IV) In accord with this consideration $FpCH_2CH_2COFp$ (**12**), which lacks suitable π-resonance forms for back donation to the acyl group at γ-position, shows very small change in $\Delta\nu$(C=O).

Similar results observed for **4–7** (Tables I–III)[24] verify that the structures of **3–7** are characterized as 1,4-dimetalla-2-butanones without mutual interaction between Fe and M, and that the significant contribution of **10** is generally observed. The stereochemical configurations around the metal centers (M) deduced as follows are usual: **4** (the piano-stool structure with two CO ligands in trans orientation);[25] **6** (the octahedral coordination);[26] **7** (the trigonal-bipyramidal configuration with three CO ligands in equatorial positions).[27]

Reactivity of the Diiron μ-Ketene Complex 3a Relevant to Catalytic CO Hydrogenation. As a typical example, the diiron μ-ketene complex **3a** was subjected to

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(23) The methylene protons of **3a** remained as a singlet signal even at −80 °C, while up-field shift for Cp and CH_2 resonances similar to **8** and **9a** was observed in toluene-d_8.

(24) $^2J_{C-H}$'s for **4**, **6**, and **7** can not be observed owing to coupling with the ^{31}P nucleus (**4**) and quadrapole of the ^{55}Mn and ^{59}Co nuclei (**6** and **7**).

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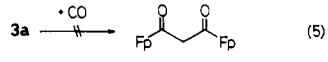
Table I. ^1H and ^{13}C NMR Spectral Data for 3-7 (η^5-C_5H_4R)Fe(CO)$_2$$CH_2$COML$_n$[j]

complex	R	nucleus	C_5H_4R	CO	CH_2	C=O	CO	C_5H_4R	M
3a	H	^1H	4.17		2.57			4.37	Fe
		^{13}C	85.34 (d, 180.1)	217.19	30.01 (t, 136.5)	253.28 (t, 2.9)[a]	216.95	86.97 (d, 178.9)	
3b	H	^1H	4.18		2.62			1.66 4.25 (t, 2.2)[b] 4.35 (t, 2.2)[b]	Fe
		^{13}C	85.33 (d, 180.7)	217.35	29.92 (t, 136.1)	255.07 (t, 3.1)[a]	217.23	13.00 (q, 128.2) 85.57 (d, 178.2) 87.94 (d, 177.0) 103.16	
3c	Me	^1H	1.44 4.04 (t, 2.0)[b] 4.17 (t, 2.2)[b]		2.59			4.39	Fe
		^{13}C	12.43 (q, 128.6) 84.69 (d, 179.5) 85.18 (d, 176.4) 102.16	217.61	31.93 (t, 135.5)	253.03 (t, 3.1)[a]	217.07	87.69 (d, 179.4)	
3d	Me	^1H	1.45 4.05 (t, 1.9)[b] 4.18 (t, 2.2)[b]		2.63			1.64 4.25 (t, 2.2)[b] 4.36 (t, 2.2)[b]	Fe
		^{13}C	12.45 (q, 128.2) 84.66 (d, 181.0) 85.16 (d, 178.2) 102.09	217.66	31.91 (t, 135.5)	254.67 (t, 3.0)[a]	217.45	13.03 (q, 127.8) 85.60 (d, 179.5) 88.03 (d, 179.5) 103.13	
4[d]	H	^1H	4.19		3.25			4.97 (d, 1.2)[c]	Mo
		^{13}C	85.07 (d, 178.2)	217.81	32.23 (t, 134.9)	262.82 (d, 10.7)[e]	239.88 (d, 23.2)[e]	96.64 (d, 177.0)	
5	H	^1H	4.11		2.39			5.23	Ni
		^{13}C	85.43 (d, 180.7)	216.39	26.28 (t, 138.0)	234.68 (t, 3.7)[a]	189.98	92.72 (d, 174.5)	
6	H	^1H	4.06		2.47				Mn
		^{13}C	85.67 (d, 181.3)	216.29	30.78 (t, 136.6)	260.12	208.93[g] 210.89[h]		
7[f]	H	^1H	4.19		2.85 (d, 2.2)[c]				Co
		^{13}C	85.67 (d, 179.0)	216.29	29.09 (dt, 27.5,[e] 136.6)	243.91 (d, 27.6)[e]	200.35 (d, 18.3)[e]		
8	H	^1H	4.03		0.30				
		^{13}C[i]	85.3	218.4	−23.5				
9a		^1H			2.41			4.16	Fe
		^{13}C[i]			52.0	254.4	215.7	86.9	
12	H	^1H	4.03		1.70–1.90(m) 3.02–3.20(m)			4.24	Fe
		^{13}C	85.41 (d, 179.0)	217.81	−2.12 (t, 136.5) 74.80 (t, 129.7)	251.88	215.75	86.38 (d, 180.1)	

[a] $^2J_{C-H}$. [b] A_2B_2 pattern apparently observed as triplet signals. [c] J_{P-H}. [d] PPh_3: ^1H NMR δ 6.97–7.15, 7.37–7.72 (m, Ph); ^{13}C NMR δ 130.13 (dd, 2.5,[e] 163.6), 133.50 (dd, 11.0,[e] 161.1), 136.97 (d, 43.9)[e]. One of Ph signals overlaps with the C_6D_6 triplet. A solvating CH_2Cl_2 molecule was observed at δ 4.28 (^1H) and δ 53.30 (t, J = 178.2 Hz; ^{13}C). [e] J_{C-P}. [f] PMe_2Ph: ^1H NMR δ 1.16 (d, 8.8,[c] Me), 6.98–7.07, 7.28–7.49 (m, Ph); ^{13}C NMR δ 18.47 (dq, 24.1,[e] 129.3), 128.70 (dd, 6.9,[e] 158.4), 129.81 (dd, 9.1,[e] 148.0), 130.21 (d, 196.2), 135.85 (d, 40.2)[e]. [g] trans. [h] cis. [i] Reference 17a. [j] ^1H (100 MHz) and ^{13}C (125 MHz) NMR spectra were recorded in C_6D_6 at 27 °C except **6** and **7** (^{13}C NMR in $CDCl_3$ at −20 °C) and **8** and **9a** (^{13}C NMR in $CHCl_3$). Values in parentheses are multiplicity and coupling constant. Coupling constants unless otherwise stated are $^1J_{C-H}$.

reactions relevant to catalytic CO hydrogenation.

Carbonylation[28] to lead to a μ-malonyl complex, $FpCOCH_2COFp$ (eq 5), was attempted under following



(5)

conditions: (i) CO (50 atm), 120 °C, 12 h, in toluene;[29] (ii) $AlCl_3$ + CO;[30] (iii) catalyst $[Cp_2Fe]PF_6$/CO;[31] (iv) PR_3 (R = Ph and Me)/CH_3CN.[32] Except for under condition (iv) (R = Me), where spontaneous formation of Fp_2 was observed, **3a** was recovered and no evidence for CO insertion was obtained, because the adjacent electron-withdrawing

Table II. IR Spectral Data (cm^{-1}) for 3-7[a]

complex	ν(C=O)	ν(C≡O; Fe)	ν(C≡O; M)	$\Delta\nu$(C=O)[b]	M
3a	1612	1999, 1950	2016, 1959	35	Fe
3b	1611	1997, 1943	2017, 1960	36	Fe
3c	1618	1996, 1948	2017, 1956	29	Fe
3d	1612	1996, 1943	2013, 1953	35	Fe
4	1585	2006, 1957	1930, 1843	20	Mo
5	1649	2009, 1967	2009[c]	55	Ni
6	1581	2088,[c] 2042 (sh), 2031 (sh), 1988, 1982 (sh)		77	Mn
7	1620	2010, 1966	2036, 1966[c]	71[d]	Co
8		2003, 1948			
9a	1647		2015, 1960		Fe
12	1645	1999, 1953	2010, 1953	2	Fe

[a] Spectra were recorded as CH_2Cl_2 solutions. [b] $\Delta\nu$(C=O) = ν(C=O; acetyl complex) − ν(C=O; μ-ketene complex). [c] Overlapping with each other. [d] Compared with a $PMePh_2$ analogue.

>C=O group reduced electron density at the migration center (methylene group) and suppressed its nucleophilic

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Table III. Selected Spectral Data for Acetyl Complexes, CH_3COML_n

	^{1}H NMR, δ		^{13}C NMR, δ			IR, cm^{-1}	
ML_n	CH_3	L_n	CH_3	CO	L_n	ν(C≡O)	ν(C=O)
$CpMo(CO)_2(PPh_3)$ (trans)	2.62 (d, 2)	5.03 (Cp)[a,b]	50.51	263.2 (d, 10.6)	96.19 (Cp)[c,d] 263.2 (d, 23.6, CO)	1945, 1853	1605[a,e]
CpNi(CO)	2.60	5.38 (Cp)[a,f]				2025	1704[f,g]
$Mn(CO)_5$	2.24[h,i]		52.6	255.0	210.0[a,j] (209.1, 210.0)[k]	*l*	1658[g,m]
$Co(CO)_3(PMePh_2)$	2.63[h,n]		51.5	*o*	201.4 (br, CO)[n]	2049 (w), 1984 (s), 1962 (s)	1691[n,p]

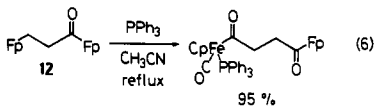
[a] In chloroform-d_0 or -d_1. [b] Reference 25b. [c] In dichloromethane-d_0 or -d_2. [d] Reference 25c. [e] Reference 25a. [f] Reference 55. [g] In carbon tetrachloride. [h] In benzene-d_0 or -d_6. [i] Kraihanzel, C. S.; Maples, P. K. *Inorg. Chem.* **1968**, *7*, 1806. [j] Darst, K. P.; Lukehart, C. M. *J. Organomet. Chem.* **1978**, *161*, 1. [k] In THF–acetone-d_6 at −115 °C, ref 26. [l] Complex absorptions. [m] Beck, W.; Hieber, W.; Tengler, H. *Chem. Ber.* **1961**, *94*, 862. [n] Reference 27. [o] Not observed. [p] In cyclohexane.

Table IV. Comparison of ν(C=O) Absorptions of μ-Ketene Complexes with Acetyl complexes

μ-Ketene Complex	ν(C=O)	[Δν][a]	solvent	ref	acetyl complex	ν(C=O)	solvent	ref
$CpRu(CO)_2CH_2CORuCp(CO)L$					$CpRu(CO)L\text{-}COCH_3$		*b*	40b
L = CO	1622	[−2]	hexane	4a	L = CO	1620		
L = PMe_3	1568	[30]	hexane	4a	L = PPh_3	1593		
$Cp_2Ru_2(CO)_2(\mu\text{-}CH_2CO)(\mu\text{-}CO)[Ru\text{-}Ru]$	1634		C_2Cl_4	4b	L = PCy_3	1610		
$Cp^*Ru(CO)_2CH_2CORuCp^*(CO)_2$[c]	1591	[34]	CH_2Cl_2	6	$Cp^*Ru(CO)_2COCH_3$[c]	1625	CH_2Cl_2	*d*
$Cp^*Ru_2(CO)_2(\mu\text{-}CH_2CO)(\mu\text{-}CO)[Ru\text{-}Ru]$[c]	1568		CH_2Cl_2	6				
$Os_3(CO)_{12}(\mu\text{-}CH_2CO)$	1573	[47]	KBr	5a,b	$Os_3(CO)_{11}(\mu\text{-I})COCH_3$	1620	CH_2Cl_2	*e*
$[Os_3(CO)_{10}(\mu\text{-X})(\mu\text{-}CH_2CO)]^-$				5c,d				
X = Cl	1556		CH_2Cl_2					
X = Br	1554		CH_2Cl_2					
X = I	1551		CH_2Cl_2					
X = NCO	1561		CH_2Cl_2					
$(Ph_3P)AuCH_2COFeCp(CO)(PPh_3)$	1555	[45]	KBr	11	$CpFe(CO)(PPh_3)COCH_3$	1600	KBr	11
$CpFe(CO)_2CH_2COFeCp(CO)(PPh_3)$	1553	[47]	KBr	*f*				

[a] Δν = ν(C=O; acetyl complex) − ν(C=O; μ-ketene complex). [b] Not specified. [c] Cp* = η^5-C_5Me_5. [d] Suzuki, H.; Omori, H.; Moro-oka, Y., private communication. [e] Morrison, E. D.; Bassner, S. L.; Geoffroy, G. L. *Organometallics* **1986**, *5*, 408. [f] This work.

attack to the terminal CO ligand.[33] A (μ-oxopropanediyl)diiron complex **12** bearing the >C=O group at more remote position (β to the migrating center) was quantitatively converted to a μ-succinyl complex by the reaction with PPh_3 in refluxing CH_3CN (eq 6). Migrating



(6)

abilities of the alkyl-side moieties in these homologues **3a** and **12** were evaluated by oxidative methanolysis (eq 7 and 8).[34] In accord with the above discussion **3a** afforded only

$$\mathbf{3a} \xrightarrow[\text{(ii) MeOH}]{\text{(i) CO/Br}_2\text{/CH}_2\text{Cl}_2} \underset{5\%}{\text{MeOCOCH}_2\text{COOMe}} + \underset{87\%}{\text{BrCH}_2\text{COOMe}} \quad (7)$$

$$\mathbf{12} \xrightarrow[\text{(ii) MeOH}]{\text{(i) CO/Br}_2\text{/CH}_2\text{Cl}_2} \underset{14\%}{\text{MeOCOCH}_2\text{CH}_2\text{COOMe}} + \underset{44\%}{\text{BrCH}_2\text{CH}_2\text{COOMe}} \quad (8)$$

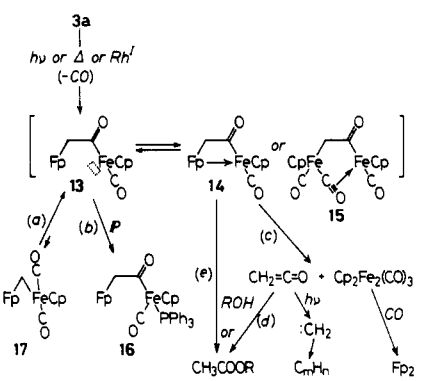
a trace amount of the CO-inserted diester.

Decarbonylation to lead to a μ-methylene complex as reported for diruthenium[4] and triosmium μ-ketene complexes[5] was also attempted. Photolysis[35] of **3a** in benzene produced Fp_2 in an almost quantitative yield accompanied by trace amounts of C1–C3 hydrocarbons (6%) (eq 9).

$$\mathbf{3a} \xrightarrow[C_6H_6]{h\nu} Fp_2 + C_mH_n + CH_3COOEt \quad (9)$$

additive:				
none	95%	6% (m = 1-3)		
EtOH, 3 equiv	93%	<0.01%		94%

Scheme I



Addition of ethanol (2–3 equiv) resulted in the formation of ethyl acetate in 94% yield instead of hydrocarbons. Therefore we concluded that hydrocarbons arose from oligomerization of methylene (:CH_2) generated by irradiation of the liberated ketene.[36] Thermolysis in the presence of methanol in toluene at 150 °C similarly gave Fp_2 and methyl acetate (eq 10). $RhCl(PPh_3)_3$, an effective

$$\mathbf{3a} \xrightarrow[\text{20 equiv of MeOH, toluene}]{150\ ^\circ\text{C}} \underset{91\%}{Fp_2} + \underset{85\%}{CH_3COOMe} \quad (10)$$

decarbonylating reagent,[37] could also remove CO ligand

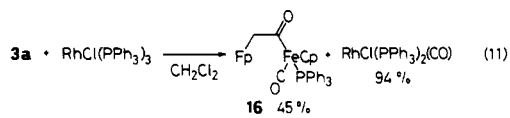
(33) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.
(34) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814.
(35) Alexander, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 1729.
(36) Russell, R. L.; Rowland, F. S. *J. Phys. Chem.* **1979**, *83*, 2073. Since we can not detect methylated benzenes, which should be formed by the reaction between benzene and :CH_2, the methylene species may not exist as a discrete molecule as proposed by one of the reviewers.
(37) (a) Alexander, J. J.; Wojcicki, A. *Inorg. Chem.* **1973**, *12*, 74. (b) Kuhlmann, E. J.; Alexander, J. J. *J. Organomet. Chem.* **1979**, *174*, 81. The action of $[Rh(\mu\text{-Cl})(PPh_3)_2]_2$ afforded a complex mixture of intractable products, and $Cp_2Fe_2(CH_2)(CO)_3$ could not be detected by TLC.

Table V. Spectral Data for 18a–20 $FpCH_2C(OR)=Fp^+$ TfO^-[a]

complex	nucleus	CH_2	=C<	R	Cp	CO	ν(C≡O)
18a	^1H	3.17		4.03	5.19, 5.24		2053, 2025,
	^{13}C	30.14	299.07	64.50	87.98 (d, 183.1)	212.01, 214.58	1998, 1981
		(t, 148.1)		(q, 151.1)	89.02 (d, 181.6)		
19	^1H	3.03		13.6 (br)	5.03, 5.14		2051, 2021,
	^{13}C	32.24	302.74		86.62 (d, 181.6)	211.90, 214.77	1995, 1979
		(t, 145.0)			87.95 (d, 183.1)		
20	^1H	3.27		0.44	5.16, 5.17		2051, 2024,
	^{13}C	36.50	305.25	0.52	86.95 (d, 183.4)	212.06, 214.89	1994, 1978
		(t, 147.0)		(q, 120.0)	88.68 (d, 183.4)		
21	^1H	3.19		4.62	5.39		2066, 2016
	^{13}C	46.81	334.30	68.45	89.33	209.13	
		(q, 129.7)		(q, 152.6)	(q, 184.6)		
22	^1H	2.76–3.00		4.00	5.46		2065, 2021
	^{13}C	26.44	147.10	62.71	87.71	208.00, 211.72	
		(t, 161.2)	(d, 184.9)	(q, 148.3)	(d, 187.0)		

[a] ^1H(100 MHz) and ^{13}C(68 MHz) NMR spectra were obtained in CD_2Cl_2 at 27 °C and IR spectra in CH_2Cl_2. Values in parentheses are multiplicity and $^1J_{C-H}$. The ^{13}C NMR signals due to TfO were observed at δ 121.3 (q, J_{C-F} = 320 Hz) for all complexes.

from **3a**, but orange phosphine-substituted diiron μ-ketene complex **16** was obtained (eq 11). These results are ra-



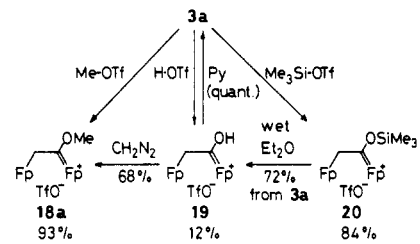
(11)

tionalized by Scheme I. On the initial decarbonylation a coordinatively unsaturated species **13** should be generated. In order to produce μ-methylene complex **17**, migration of the $FpCH_2$ group (path a) should subsequently take place. However, this pathway may be energetically disadvantageous because of electronic repulsion between the highly nucleophilic migrating group and the electron-rich metal center.[33] **13** has some lifetime, possibly owing to equilibrium with a dative metal–metal bonded form **14**[4a] or a π-bonded form **15**, and is actually trapped by PPh_3 in the case of the reaction with the Wilkinson complex (path b). Although we could obtain no evidence for **13–15**, the metal–metal bond formation led to the formation of Fp_2 and ketene (path c), and acetate ester should be formed by alcoholysis of the liberated ketene molecule (path d) or **14** (path e).

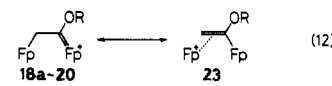
Finally, **3a** was treated with various reducing agents. While H_2 and BH_3·THF[38] were inert, $LiAlH_4$ converted **3a** to a complex mixture of organic products after acidic hydrolysis. GLC analyses of the gas phase and the liquid phase showed that propane and *n*-propyl alcohol were the main products, respectively. The inserted carbon atom should originate from the coordinated CO as studied for **8** and **9a** by Atwood et al.[39] **3a** was also reduced by $NaBH_4$ in THF during 24 h, but unfortunately, any organic products other than Fp_2 (>90 % by ^1H NMR) could not be detected by GLC analyses before or after acidolysis or by an NMR experiment in THF-d_8.

Conversion of the Diiron μ-Ketene Complex 3a into Binuclear Oxycarbene Complexes.[12b] To activate the μ-ketene moiety toward reducing agents (nucleophiles) **3a** was converted into cationic oxycarbene complexes **18a–20** by the treatment with electrophiles (ROTf: R = Me, H and $SiMe_3$; TfO = CF_3SO_3).[40,41] (Scheme II) Cationic

Scheme II



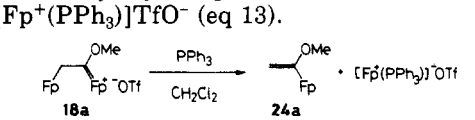
character of the products is demonstrated by ν(C≡O)'s of higher energy, the down-field shift of Cp resonances (^1H and ^{13}C NMR) and the upfield shift of CO carbon signals when compared with those of the parent complex **3a**. (Table V) Above all the quaternary carbon signals resonating in very low field (δ ca. 300) are characteristic of electrophilic carbene carbon.[40d] When their chemical-shift values are compared with those of an α-methoxyethylidene complex **21**, $[Fp^+{=}CMe(OMe)]TfO^-$,[40d] and a methyl vinyl ether complex **22**, $[Fp^+(CH_2{=}CHOMe)]TfO^-$,[42] which are mononuclear counterparts corresponding to cationic parts of two possible resonance forms **18a** and **23** (eq 12), the



(12)

carbene carbons of **18a–20** fall between them and in the vicinity of **21** as well. Upfield shift of **18a–20** from **21** by δ 30 is caused by partial neutralization of the positive charge owing to the "β-effect". The charge delocalization is also suggested by ν(C≡O) absorptions appearing between those of neutral and cationic mononuclear Fp complexes.

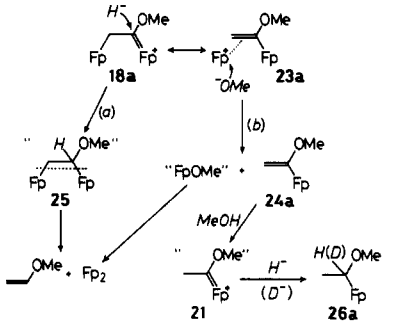
Thus, cationic binuclear oxycarbene complexes should be regarded as hydrids of two resonance forms, **18a–20** and **23**, with substantial contribution of the latter in contrast to the parent complex **3a** for which **10** is detected only by the positive value of Δν. Such contribution is also demonstrated by a chemical reaction. Treatment of **18a** with an equimolar amount of PPh_3[43] quantitatively liberated an α-methoxyvinyl complex **24** with concomitant formation of $[Fp^+(PPh_3)]TfO^-$ (eq 13).



(13)

(38) van Doorn, A.; Masters, C.; Volger, H. C. *J. Organomet. Chem.* **1976**, *105*, 245.
(39) Wong, A.; Atwood, J. D. *J. Organomet. Chem.* **1981**, *210*, 395.
(40) (a) Green, M. L. H.; Hurley, C. R. *J. Organomet. Chem.* **1967**, *10*, 188. (b) Green, M. L. H.; Mitchard, L. C.; Swanwick, M. G. *J. Chem. Soc. A* **1971**, 794. (c) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (d) Casey, C. P.; Miles, W. H.; Tukada, H. *Ibid.* **1985**, *107*, 2924. (e) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.
(41) Very similar transformations of an anionic μ-ketene complex were reported by Geoffroy et al. See ref 5f.
(42) Cutler, A.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1974**, *77*, 381.
(43) Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93.

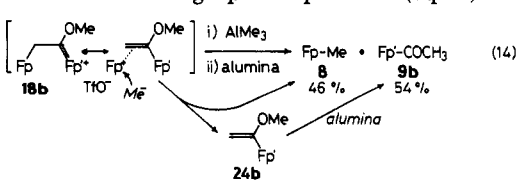
Scheme III



Though the three oxycarbene complexes obtained were thermally stable, **20** was so sensitive to moisture that desilylation in wet ether readily took place to give **19**. The hydroxycarbene complex **19** showed enough acidity to be neutralized by pyridine, regenarating **3a** in a quantitative yield, and to be converted to the methoxy analogue **18a** by the treatment with diazomethane.[40b] Hence, interconversion among **3a**, **18a**, **19**, and **20** was realized as shown in Scheme II. The binuclear oxycarbene complexes, cationically activated forms of **3a**, were next subjected to reduction.

When **18a** was treated with various borohydride reagents (HBR_3^-) in THF, Fp_2 and methyl vinyl ether (an enol ether of acetaldehyde) were produced in quantitative yields (Scheme III). Their formation was interpreted by the initial hydride attack at the most electrophilic carbene carbon followed by the metal–metal bond formation (path a), although no evidence for transient μ-methoxyethylene complex **25** was obtained. Since labeled methoxycarbene complex **18b**, $[FpCH_2C(OMe)=Fp'^+]TfO^-$ [Fp′ = $(\eta^5$-$C_5H_4Me)Fe(CO)_2$], afforded a 1:2:1 mixture of iron dimers, Fp_2, FpFp′, and Fp'_2, the last step involved a very rapid radical process. On the other hand, when **18a** was treated with $NaBH_4$ in basic media (NaOMe/MeOH) following Brookhart's procedures,[40c] α-methoxyethyl complex **26a** was obtained in 27% yield in addition to Fp_2 and methyl vinyl ether. Under this basic condition the reaction partly set off by the initial nucleophilic attack of MeO^- to the cationic center in **23a**. The reaction path illustrated in Scheme III (path b) was confirmed by the following experiments. (i) The reaction of **18b** labeled at the carbene-side iron center afforded labeled product **26b**, $CH_3CH(OMe)Fp'$. (ii) Addition of NaOMe to **18a** released **24a** in a similar manner to PPh_3. (iii) Reduction of isolated **24a**[44] gave **26a** in 22% yield, and neither Fp_2 nor vinyl ether was formed. (iv) The action of $NaBD_4$ in CH_3OH resulted in deuteration at the α-position of **26a-*d*₁**. (v) The reaction of $[Fp^+(THF)]BF_4^-$ with NaOMe gave Fp_2 presumably via β-elimination of a transient "Fp–OMe" species followed by dimerization during workup.

When **18b** was allowed to react with trimethylaluminum (a carbon nucleophile), FpMe, **8**, and $Fp'COCH_3$, **9b**, were isolated after chromatographic separation (eq 14). $AlMe_3$



(14)

alkylated the alkyl-side Fp group with liberation of **24b**, which was readily hydrolyzed to give **9b** during workup.

(44) Casey, C. P.; Tukada, H.; Miles, W. H. *Organometallics* **1982**, *1*, 1083.

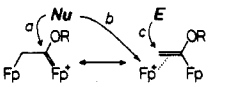
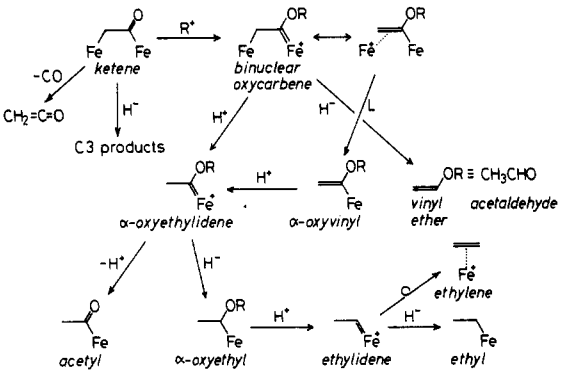
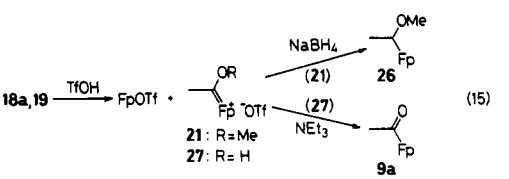


Figure 1. Reactivities of cationic binuclear oxycarbene complexes.

Scheme IV



Since the π-complex resonance form **23** can be also regarded as an enol ether complex, subsequent reaction with electrophiles is possible. Protonation of **18a** and **19** with an excess amount of TfOH proceeded during 12 h to give FpOTf and cationic mononuclear α-oxycarbene complexes **21** and **27** (eq 15). For example, when 1equiv of TfOH



(15)

was added to a CD_2Cl_2 solution of **3a**, **3a** [^1H NMR (CD_2Cl_2) δ 2.54 (CH_2), 4.83, 4.85 (2Cp)] disappeared upon mixing and new signals assignable to **19** [δ 3.03 (CH_2), 5.03, 5.14 (2Cp), 13.6 (OH)] emerged in slightly lower field, respectively. Successive addition of 2 equiv of TfOH brought about gradual conversion to **27** [δ 3.12 (CH_3), 5.29 (Cp), 14.4 (OH)] and FpOTf [δ 5.21 (Cp)],[45] which were assigned by comparison with authentic samples. Because it was difficult to isolate **21** and **27** in pure forms from the reaction mixture, their structures were ascertained by derivation to tractable forms **26** and **9a**, respectively.

The diverse reactivities observed for **18–20** are attributed to two possible resonance forms. (Figure 1) The reaction with hard nucleophiles such as hydride takes place at the most electrophilic carbene center (route A), with soft nucleophiles such as phosphine, alkoxide, and alkylaluminum at the alkyl-side Fp (route B) and with electrophiles at the nucleophilic methylene terminus (route C).

Consequently, starting from a diiron μ-ketene species we now postulate a network of C2 organic fragments and compounds[46] as depicted in Scheme IV.

Experimental Section

General Data. All manipulations were performed under argon atmosphere by using Schlenk tube technique.

Solvents were dried over appropriate drying agents, distilled, and stored under argon (THF (tetrahydrofuran), ether, benzene, toluene, hexane: Na–K/benzophenone; CH_2Cl_2: P_2O_5). $[Cp_2Fe]PF_6$,[47] $RhCl(PPh_3)_3$,[48] MeOTf,[49] and Me_3SiOTf[50] were

(45) Manganiello, F. J.; Oon, S. M.; Radcliffe, M. D.; Jones, W. M. *Organometallics* **1985**, *4*, 1069.

(46) (a) Crawford, E. J.; Lambert, C.; Menard, K. P.; Cutler, A. R. *J. Am. Chem. Soc.* **1985**, *107*, 3130. (b) Crawford, E. J.; Bodner, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6202.

(47) Hendrickson, D. N.; Sohn, Y. S.; Gray, H. B. *Inorg. Chem.* **1971**, *10*, 1559.

prepared according to the reported methods. Other organic reagents were used as purchased. Metal carbonyl complexes were prepared according to the published methods: Fp_2,[51] $FpCH_2COOH$,[14] $CpMo(CO)_2(PPh_3)I$,[52] $[CpNi(CO)]_2$,[51] $[Co(CO)_3(PMe_2Ph)]_2$,[53] $FpCH_2CHO$,[42] and $CH_2{=}C(OMe)Fp$.[44]

^1H NMR spectra were recorded on the JEOL FX-100 (100 MHz), and ^{13}C NMR spectra were observed on the JEOL GX-500 (125 MHz) and the JEOL GX-270 (68 MHz). All the solvents for NMR measurements containing 1% tetramethylsilane (TMS) as an internal standard were dried over molecular sieves, degassed and distilled in vacuo. IR spectra were obtained on the Hitachi 260-50 spectrometer in a fixed cell (0.2 mm) unless otherwise stated. Mass spectra were obtained on the Hitachi gas chromatography–mass spectrometer M-80 by using columns packed with Porapak Q (gas) and Silicon SE-30 (others). The GLC analyses of the reaction products were made on a Hitachi 163 gas chromatograph using the same columns as were used for the GC–MS analyses. The HPLC analyses were carried out on the Hitachi 633A liquid chromatograph with the Hitachi 635M UV detector using a Lichrosphere 100 RP-18 (5 μm) column (Merck) eluted with H_2O–acetonitrile (1:4). Column chromatography was performed on alumina (activity II–III; Merck Art. 1097) unless otherwise stated and the eluting solvents were used without purification. Melting points were measured with the Büchi melting points determinator 510 in a capillary sealed in vacuo and were uncorrected. Elemental analyses were performed by using the analytical facilities in the Research Laboratory of Resources Utilization at the Tokyo Institute of Technology.

Reaction of $FpCH_2COOH$ (1a) with $(COCl)_2$. To an orange-yellow suspension of **1a** (1.121 g, 4.75 mmol) in 10 mL CH_2Cl_2 was added oxalyl dichloride (0.42 ml, 4.81 mmol) via syringe at room temperature. After vigorous gas evolution had seased, a homogeneous deep orange-red solution was obtained. Evaporation of the solvent under reduced pressure left reddish orange crystals of **2a** (1.184 g, 4.66 mmol, 98% yield), mp 56 °C. Anal. Calcd for $C_9H_7ClO_3Fe$: C, 42.48; H, 2.77; Cl, 13.93. Found: C, 43.18; H, 3.09; Cl, 13.08.

Since **2a,b** were very sensitive to moisture, we used the crude product without further purification, and the structure and the purity were confirmed by ^1H NMR and IR spectra (see text) and methanolysis.

After addition of a mixture of MeOH (1 mL) and Et_3N (1 mL) to a THF solution of **2a** [prepared from 210 mg (0.852 mmol) of **1a** and 0.10 mL of oxalyl dichloride] the mixture was further stirred for 1 h. Evaporation of the volatiles, extraction with CH_2Cl_2, and purification by column chromatography gave $FpCH_2COOMe$[14] in 76% yield (162 mg, 0.648 mmol).

Preparation of $FpCH_2COFp$ (3a). To a cooled solution (−78 °C) of **2a** [prepared from 741 mg of **1a** and 0.28 mL of oxalyl dichloride] in 10 mL of THF was dropped NaFp generated by reduction of Fp_2 (557 mg, 1.57 mmol) with 1% sodium amalgam (Na 0.1 g) in THF (10 mL). After 1 h of stirring at −78 °C, the reaction mixture was gradually warmed to room temperature. Then, the solvent was removed under reduced pressure and the residue was chromatographed on alumina (2 cm × 20 cm). The first yellow band, ferrocene (68 mg, 0.34 mmol), and the second deep purple-red band, Fp_2 (421 mg, 1.57 mmol, 31%), were eluted with CH_2Cl_2–hexane (1:4). Elution of the third yellow band with CH_2Cl_2–hexane (1:1) followed by recrystallization from Et_2O–hexane afforded **3a** (325 mg, 0.83 mmol, 27%) as orange-yellow needles, mp 77 °C. Anal. Calcd for $C_{16}H_{12}O_5Fe_2$: C, 48.53; H, 3.06. Found: C, 48.48; H, 3.08.

Preparation of 3b–d. **3b–d** were prepared in the essentially same method as described for **3a**. **3b** (13%) mp 90 °C. Anal. Calcd for $C_{17}H_{14}O_5Fe_2$: C, 49.80; 3.44. Found: C, 50.09; H, 3.31. **3c** (21%) mp 90 °C. Anal. Calcd for $C_{17}H_{14}O_5Fe_2$: C, 49.80; H, 3.44. Found: C, 49.58; H, 3.73. **3d** (11%) mp 90 °C. Anal. Calcd for $C_{18}H_{16}O_5Fe_2$: C, 50.96; H, 3.77. Found: C, 50.62; H, 3.71.

Preparation of $FpCH_2COMoCp(CO)_2(PPh_3)$ (4). Na[$CpMo(CO)_2(PPh_3)$][54] [generated by reduction of $CpMo(CO)_2(PPh_3)I$ (2.80 g, 4.67 mmol) with 1% sodium amalgam (Na, 0.1 g) in 20 mL THF at room temperature] was added dropwise to a THF solution (20 mL) of **2a** [prepared from **1a** (1.09 g, 4.62 mmol) and $(COCl)_2$ (0.41 mL, 4.70 mmol)] cooled at −78 °C. The stirring was continued for another hour. After gradual warming to room temperature, the solvent was evaporated under reduced pressure. The products were separated into three fractions by column chromatography (2 cm × 20 cm). The first fraction eluted with CH_2Cl_2– hexane (1:4) contained Fp_2 (118 mg, 0.33 mmol, 7%). Elution with CH_2Cl_2–hexane (1:3) gave an unidentified yellow-green solid (350 mg) followed by yellow zone, from which **4** was isolated as yellow crystals (1.11 g, 1.62 mmol, 35%). **4** was solvated by one molecule of CH_2Cl_2, mp 157 °C. Anal. Calcd for $C_{34}H_{27}O_5PFeMo{\cdot}CH_2Cl_2$: C, 53.66; H, 3.73; Cl, 9.05. Found: C, 53.27; H, 3.77; Cl, 8.96.

Preparation of $FpCH_2CONiCp(CO)$ (5). Na[$CpNi(CO)$] solution[55] was prepared by reduction of $[CpNi(CO)]_2$ (1.107 g, 3.65 mmol) with sodium naphthalene (1.0 M THF solution, 7.5 mL) in 35 mL THF at −20 °C. To the resulting solution cooled at −78 °C was added a THF solution of **2a** prepared from 1.72 g (7.29 mmol) of **1a** and $(COCl)_2$ (0.41 mL, 4.70 mmol). Stirring was continued at the same temperature for 1 h. After the solution warmed to room temperature, the solvent was removed under reduced pressure. Chromatographic separation (2 cm × 20 cm) gave three products. $[CpNi(CO)]_2$ (310 mg, 1.02 mmol, 28%) was eluted at first [CH_2Cl_2–hexane (1:20)] followed by brown band of $FpNiCp(CO)$[56] [115 mg, 0.37 mmol, 5%; CH_2Cl_2–hexane (1:10)]. Finally, an orange band was eluted with CH_2Cl_2–hexane (1:5). Recrystallization gave **5** as orange crystals (1.00 g, 2.70 mmol, 37%), mp 91 °C. Anal. Calcd for $C_{15}H_{12}O_4FeNi$: C, 48.59; H, 3.26. Found: C, 48.47; H, 3.24.

Preparation of $FpCH_2COMn(CO)_5$ (6). To a cooled THF solution (20 mL) of **2a** prepared from 1.777 g (7.53 mmol) of **1a** and 0.66 mL of $(COCl)_2$ was added Na[$Mn(CO)_5$], generated by 1% sodium amalgam reduction (Na, 0.22 g) of $[Mn(CO)_5]_2$ (1.467 g, 3.77 mmol) in 30 mL of THF, and the mixture was stirred at −78 °C for 1 h. As soon as the reaction temperature reached room temperature, the solvent was removed under reduced pressure. Extraction with benzene (40 mL) and filtration through alumina (3 cm × 1 cm) followed by evaporation resulted in an orange solid. Recrystallization from CH_2Cl_2–hexane afforded **6** as orange crystals (2.31 g, 5.57 mmol, 74%), mp 74 °C. Anal. Calcd for $C_{14}H_7O_8FeMn$: C, 40.62; H, 1.70. Found C, 40.22; H, 1.63.

Preparation of $FpCH_2COCo(CO)_3(PMe_2Ph)$ (7). Na[$Co(CO)_3(PMe_2Ph)$][57] was prepared by reduction of $[Co(CO)_3(PMe_2Ph)]_2$ (2.38 g, 4.41 mmol) by 1% sodium amalgam (Na, 0.3 g) in THF (30 mL). The resulting solution was added dropwise to a cooled THF solution (15 mL) of **2a** prepared from 2.08 g (8.83 mmol) of **1a** and 0.78 mL (8.94 mmol) of $(COCl)_2$. The mixture was stirred at −78 °C for 1 h and the volatiles were removed in vacuo. Extraction with benzene (40 mL) followed by chromatography on alumina (2 cm × 15 cm) gave yellow oil **7** (2.918 g, 2.91 mmol, 66%). Anal. Calcd for $C_{20}H_{18}O_6PFeCo$: C, 48.03; H, 3.63. Found: C, 47.68; H, 3.52.

Preparation of $FpCH_2CH_2COFp$ (12). NaFp (20.0 mmol) in 30 mL of THF was added to $BrCH_2CH_2COOSiMe_3$ (5.6 g, 25 mmol; prepared from β-bromopropionic acid and chlorotrimethylsilane in ether by using triethylamine as a base, 88% yield, bp 78–83 °C/15 mmHg) dissolved in 20 mL THF at −78 °C. The mixture was gradually warmed to room temperature while being stirred. Evaporation of the volatiles and extraction with ether followed by column chromatography on silica gel gave purple Fp_2 [eluted with CH_2Cl_2–hexane (1:1)] and yellow $FpCH_2CH_2COOH$ (3.25 g, 13 mmol, 65%; eluted with acetone). ^1H NMR ($CDCl_3$) δ 1.30–1.87 (m, CH_2), 2.27–2.83 (m, CH_2), 4.70 (s, Cp), 11.3 (br, OH).

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12 was prepared in a similar manner to **3a**, starting from 1.60 g of $FpCH_2CH_2COOH$ (6.3 mmol), oxalyl dichloride (0.87 mL, 10 mmol) and 6.4 mmol of NaFp, and was isolated as yellow crystals (1.68 g, 4.1 mmol, 65%), mp 110 °C. Anal. Calcd for $C_{17}H_{14}O_5Fe$: C, 49.80; H, 3.44. Found C, 50.01; H, 3.50.

Attempted Carbonylation of 3a. (i) CO. A toluene solution (10 mL) of **3a** (175 mg, 0.44 mmol) in an autoclave was pressurized to 50 atm and was heated in an oil bath at 120 °C for 12 h. The residue contained the recovered **3a** (74%) and a decomposed product, Fp_2 (20%), as determined by NMR.

(ii) $AlCl_3$/CO and (iii) CO/$[Cp_2Fe]PF_6$. The reactions were carried out following Shriver's[30] and Magnuson's procedures,[31] respectively.

(iv) PPh_3. A CD_3CN solution (0.6 mL) of **3a** (48 mg, 0.12 mmol) and PPh_3 (64 mg, 0.29 mmol) were sealed in a NMR tube under argon and were heated at 70 °C. After 24 h, **3a** was observed as a sole component.

(v) PMe_3. Upon addition of PMe_3 (1.06 M toluene solution, 0.51 mL, 0.54 mmol) to **3a** (71 mg, 0.18 mmol) dissolved in 5 mL of THF at −78 °C, the orange solution turned deep purple. Evaporation of the solvent gave Fp_2 in 97% yield (62 mg).

Carbonylation of 12 Induced by PPh_3. An acetonitrile solution (10 mL) of **12** (202 mg, 0.492 mmol) and PPh_3 (194 mg, 0.73 mmol) was refluxed for 12 h. After consumption of **12** was checked by thin-layer chromatography (TLC), the μ-succinyl complex (313 mg, 0.465 mmol, 95% yield) was isolated as yellow-orange crystals by column chromatography, mp 76 °C. ^1H NMR (C_6D_6) δ 2.33–3.87 (4 H, m, CH_2CH_2), 4.28 (5 H, s, Cp), 4.38 (5 H, d, J_{P-H} = 1.2 Hz, Cp), 6.93–7.13, 7.39–7.81 (15 H, m, Ph). IR (CH_2Cl_2): 2011, 1954, 1914, 1641, 1603 cm^{-1}. Anal. Calcd for $C_{35}H_{29}O_5PFe_2$: C, 62.53; H, 4.35. Found: C, 62.39; H, 4.40.

Oxidative Methanolysis of 3a and 12. To a CH_2Cl_2 solution of **3a** or **12** saturated with CO was added 3 equiv of Br_2 diluted with CH_2Cl_2 at −20 °C. After 20 min, excess MeOH was added, and the products were analyzed by GLC and GC-MS.

Photolysis of 3a. **3a** (50.0 mg, 0.13 mmol) was weighed in a 50 mL Schlenk tube capped with a rubber septum. After evacuation, the cock was closed and benzene (5 mL) was added via syringe through the septum. The mixture was irradiated by a high-pressure Hg lamp for 1 h, and gradually changed to purple color. The organic products in the gas phase and the liquid phase were separately sampled through the septum by a microsyringe, and were analyzed by GLC. The gas-phase contained CH_4 (0.5%), $CH_2{=}CH_2$ (2%) and $CH_2{=}CHCH_3$ (4%). The organometallic product was determined to be Fp_2 (95%) by ^1H NMR after evaporation of the solvent.

Photolysis of **3a** (58.2 mg, 0.15 mmol) in the presence of ethanol (26 μL, 0.44 mmol) was similarly carried out and gave ethyl acetate (94%) and Fp_2 (93%).

Thermolysis of 3a. A sealed tube containing a toluene solution (5 mL) of **3a** (51.0 mg, 0.13 mmol) and methanol (0.1 mL, 2.58 mmol) was heated in an oil bath at 150 °C for 2 h. Methyl acetate (85%) and Fp_2 (91%) were formed as determined by GLC and HPLC analyses.

Reaction of 3a with the Wilkinson Complex. **3a** (233 mg, 0.56 mmol) and $RhCl(PPh_3)_3$ (523 mg, 0.56 mmol) were dissolved in CH_2Cl_2 (8 mL) and stirred at room temperature for 6 h. A pale colored solid, precipitating during the reaction, $RhCl(PPh_3)_2(CO)$ (450 mg, 0.53 mmol, 94%), was collected by filtration. Chromatographic separation of the filtrate afforded **16** as orange powder (182 mg, 0.25 mmol, 45%), mp 156 °C. ^1H NMR (C_6D_6) δ 2.81 (1 H, dd, J_{H-H} = 11.1 Hz, J_{P-H} = 0.9 Hz, one of diastereotopic methylene protons), 2.96 (1 H, d, J_{H-H} = 11.1 Hz, another methylene proton), 4.14 (5 H, s, Cp), 4.44 (5 H, d, J_{P-H} = 1.3 Hz, $CpFe(CO)(PPh_3)$), 6.92–7.12 (9 H, m, Ph), 7.61–7.89 (6 H, m, Ph). IR (KBr): 1995, 1943, 1903, 1553 cm^{-1}. Anal. Calcd for $C_{33}H_{27}O_4PFe_2$: C, 62.89; H, 4.32. Found: C, 63.01; H, 4.50.

Reduction of 3a with $LiAlH_4$. **3a** (58 mg, 0.15 mmol) and $LiAlH_4$ (108 mg, 2.6 mmol) were placed in a Schlenk tube capped with a rubber septum. After evacuation, the cock was closed and THF (5 mL) was added via syringe. The reaction mixture was stirred for 5 h and changed to green. GLC analysis of the gas phase revealed the formation of CH_4 (1%), C_2H_4 (1%), C_2H_6 (1%), and C_3H_8 (5%). Then, after argon was introduced, aqueous 6 M HCl (5 mL) was slowly added to the reaction mixture at 0 °C. The formation of *n*-propyl alcohol (48%) was confirmed by GLC and GC–MS analyses. Many other components in very low yields were not determined.

Preparation of $[FpCH_2C(OMe){=}Fp^+]TfO^-$ (18a). **3a** (1.10 g, 2.78 mmol) and MeOTf (1.1 mL, 9.7 mmol) were stirred in CH_2Cl_2 (5 mL) at ambient temperature for 2 h. After disappearance of the ν(C=O) absorption was checked, the solvent was removed under reduced pressure. The residue was washed with ether (5 mL × 2) and recrystallized from CH_2Cl_2–ether to give **18a** (1.45 g, 2.59 mmol, 93% yield) as orange microcrystals, mp 111 °C. Anal Calcd for $C_{18}H_{15}F_3O_8SFe_2$: C, 38.10; H, 2.70. Found C, 38.55; H, 2.63.

Starting from **3b** (580 mg, 1.41 mmol) and MeOTf (0.32 mL, 2.80 mmol) **18b** was similarly obtained as orange powders (396 mg, 0.69 mmol, 49%), mp 75 °C. ^1H NMR ($CDCl_3$) δ 1.99 (3 H, s, C_5H_4Me), 3.19 (2 H, s, CH_2), 4.03 (3 H, s, OMe), 4.85–5.03, 5.03–5.14 (4 H, m, C_5H_4Me), 5.23 (5 H, s, Cp). IR (CH_2Cl_2): 2045, 2014, 1996, 1958 cm^{-1}. Anal. Calcd for $C_{19}H_{17}F_3O_8SFe_2$: C, 39.75; H, 2.99. Found C, 39.80; H, 3.10.

Protonation of 3a. Upon addition of TfOH (22 μL, 0.25 mmol) to a benzene solution (5 mL) of **3a** (126 mg, 0.319 mmol) a deep red oil settled. The supernatant was removed by a syringe. After being washed with ether (10 mL × 3), the oil was dissolved in CH_2Cl_2 (0.4 mL) and was cooled at −20 °C. **19** (16.4 mg, 0.03 mmol, 12% yield) was isolated as reddish orange crystals, mp 218 °C. Anal. Calcd for $C_{17}H_{13}F_3O_8SFe_2$: C, 37.39; H, 2.40. Found: 37.01; H, 2.15.

Silylation of 3a. After addition of Me_3SiOTf (0.40 mL, 2.1 mmol) to **3a** (565 mg, 1.43 mmol) dissolved in CH_2Cl_2 (5 mL), the solvent was removed under reduced pressure. The resulting residue was recrystallized from CH_2Cl_2–ether to give **20** as orange crystals (743 mg, 1.20 mmol, 84%). Because **20** could not be isolated in an analytically pure form, owing to its sensitivity to moisture, the structure was determined by spectral analyses.

Hydrolysis of 20. To a CH_2Cl_2 solution (5 mL) of **20** [prepared from **3a** (783 mg, 1.98 mmol) and Me_3SiOTf (0.58 mL, 3.0 mmol)] was added 30 mL of ether (not dehydrated but purged with argon for 5 min). Orange powdered **19** (795 mg, 1.42 mmol, 72%), precipitating during stirring at room temperature was collected by filtration and was washed with dry ether (5 mL × 3), mp 220 °C. Anal. Calcd for $C_{17}H_{13}F_3O_8SFe_2$: C, 37.39; H, 2.40. Found C, 37.50; H, 2.45.

Preparation of $[Fp^+{=}C(OMe)CH_3]TfO^-$ (21). A CH_2Cl_2 solution (5 ml) of **9a** (380 mg, 1.70 mmol) and MeOTf (0.38 mL, 3.4 mmol) was stirred at ambient temperature for 4 h. After the completion of the reaction was checked by disappearance of the ν(C=O) absorption at 1648 cm^{-1}, the solvent was evaporated. Washing with ether (5 mL × 4) gave off-white solid **21**, which was dried in vacuo. Since **21** decomposed upon exposure to air, the structure was determined by NMR and IR spectra and by comparison with the BF_4^- analogue.[40d] **21**: mp 60–64 °C.

Preparation of $[Fp^+(CH_2{=}CHOMe)]TfO^-$ (22). $FpCH_2CHO$ (2.50 g, 11.4 mmol) and MeOTf (1.3 mL, 20.0 mmol) were stirred in 10 mL of CH_2Cl_2 at ambient temperature for 2 h. Removal of the solvent, two washings with ether followed by recrystallization from CH_2Cl_2–ether gave **22** (3.63 g, 9.46 mmol, 83%) as yellow crystals, mp 87–89 °C. Anal. Calcd for $C_{11}H_{11}F_3O_6SFe$: C, 34.40; H, 2.89. Found: C, 34.30; H, 2.86.

Reaction of 19 with Pyridine. **19** (50.0 mg, 0.092 mmol), pyridine (15 mL, 0.183 mmol) and $CDCl_3$ (0.5 mL) were sealed in an NMR tube. Dissolution by ultrasonification resulted in precipitation of a white solid, presumably PyH^+TfO^-. ^1H NMR and IR analyses of the mixture after centrifugation revealed the quantitative formation of **3a**.

Reaction of 19 with Diazomethane. An ethereal solution (ca. 10 mL) of diazomethane[58] generated from 1.6 g of *N*-methyl-*N*-nitrosotosylamide was added to **19** (84.5 mg, 0.155 mmol) dissolved in 5 mL CH_2Cl_2. Immediate gas evolution was observed. After 3 h the volatiles were evaporated. Washing with ether (5 mL × 2) and recrystallization from CH_2Cl_2–ether gave **18a** (59 mg, 0.11 mmol) in 68% yield. The ether layer contained **3a** (<10%).

Reaction of 18a with PPh_3. Upon dissolution of **3a** (101 mg, 0.18 mL) and PPh_3 (47 mg, 0.18 mmol) in CH_2Cl_2 (5 mL) a yellow

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homogeneous solution was obtained. Quantitative formation of **24** and $[Fp^+(PPh_3)]TfO^-$ was revealed by ^1H NMR analysis of the evaporated residue. (**24**) ^1H NMR (CD_2Cl_2): δ 3.51 (3 H, s, Me), 3.95 (1 H, d, J = 2.0 Hz, $=CH_2$), 4.57 (1 H, d, J = 2.0 Hz, $=CH_2$), 4.87 (5H, s, Cp).

Addition of ether (20 mL) to the residue dissolved in a minimum amount of acetone resulted in precipitation of pale yellow $[Fp^+(PPh_3)]TfO^-$ (95 mg, 0.17 mmol, 95%),[59] mp 218 °C. ^1H NMR (CD_2Cl_2): δ 5.30 (5 H, d, J_{P-H} = 1.5 Hz, Cp), 7.27–7.68 (15 H, m, Ph). IR (CH_2Cl_2): 2067, 2011 cm^{-1}. Anal. Calcd for $C_{26}H_{20}F_3O_5PFe$: C, 56.14; H, 3.62. Found: C, 56.10; H, 3.64.

The ether layer was passed through alumina to give **9a** (31 mg, 0.14 mmol, 78%), actually a hydrolyzed product of **24**.

Reaction of 18a with Various Borohydride Reagents. The reaction was carried out in an evacuated Schlenk tube capped with a rubber septum with THF as a solvent. GLC analysis of the gas phase using propylene as an internal standard indicated the formation of methyl vinyl ether (>90%), which was determined by comparison of the GLC retention time with an authentic sample and by GC–MS. Fp_2 (>95%) was detected as a sole organometallic product by ^1H NMR of the residue.

Similar results were obtained when $NaBH_4$, KBH_4, $NaBH_3CN$, $LiBHEt_3$, and $LiAlH_4$ were used as reducing agents.

Reaction of 18a under Basic Conditions. The reaction was carried out by following Brookhart's procedures.[40c]

Na (290 mg, 12.7 mmol) and $NaBH_4$ (241 mg, 6.36 mmol) were successively dissolved in MeOH (15 mL). To the resulting mixture cooled at 0 °C was added dropwise a CH_2Cl_2 solution (5 mL) of **18a** (440 mg, 0.785 mmol). After 5 min of stirring, the yield of methyl vinyl ether was determined to be 54% by GLC analysis of the liquid phase by using isobutyl vinyl ether as an internal standard. Then, 180 mL of water was added and the organometallic products were extracted with CH_2Cl_2 (10 mL × 3) and dried over $MgSO_4$. Separation by column chromatography gave **26a** (50 mg, 0.212 mmol, 27%) and Fp_2 (114 mg, 0.321 mmol, 41%).

Reduction using $NaBD_4$ instead of $NaBH_4$ gave **26a-d_1**. ^1H NMR (C_6D_6); δ 1.75 (3 H, s, $CDCH_3$), 3.12 (3 H, s, OMe), 4.19 (5 H, s, Cp). IR (KBr) ν(C–D) 2120, ν(C≡O) 1987, 1928, 1909 cm^{-1}.

Reduction of 18b. Reduction of **18b** gave **26b** as an yellow oil in 13% yield. The structure was determined by comparison of spectral data with an authentic sample prepared by reduction of **9b** according to Brookhart's method[40c] (77% isolated). **9b** was obtained in 51% yield by the reaction of NaFp′ with acetyl chloride.

26b: mp 5 °C. ^1H NMR (C_6D_6): δ 1.53 (3 H, s, C_5H_4Me), 1.79 (3 H, d, j = 6.1 Hz, $CHCH$), 3.20 (3 H, s, Me), 4.09–4.18 (4 H, m, C_5H_4), 4.88 (1 H, q, J = 6.1 Hz, $CHCH_3$). IR (liquid film): 1993, 1933 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O_3Fe$: C, 52.83; H, 5.64. Found: C, 52.48; H, 5.71.

9b: mp 22 °C. ^1H NMR (C_6D_6): δ 1.97 (3 H, s, C_5H_4Me), 2.57 (3 H, s, $COCH_3$), 4.63–4.77 (4 H, m, C_5H_4Me). IR (liquid film): 2021, 1957, 1648 cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_3Fe$: C, 51.32; H, 4.31. Found: C, 51.41; H, 4.39.

Reaction of 18a with NaOMe. NaOMe (0.65 mmol) in 1.5 mL of MeOH was added to a CH_2Cl_2 solution (3 mL) of **18a** (282 mg, 0.504 mmol) at −78 °C. After removal of the solvent at room temperature, the products were extracted with hexane. **24a** (85%)[44] and Fp_2 (93%) were detected as major products by ^1H NMR analysis.

Reduction of 24a. A CH_2Cl_2 solution (2 mL) of **24a** (87 mg, 0.37 mL) was dropped into a MeOH solution (7 mL) containing 3.7 mmol of NaOMe and 67 mg (1.8 mmol) of $NaBH_4$ at 0 °C. Workup as described above[40c] gave **26a** (26 mg, 0.077 mmol, 21% yield).

Reaction of 18b with $AlMe_3$. To **18b** (164 mg, 0.286 mmol) suspended in toluene (10 mL) was added $AlMe_3$ (0.35 M toluene solution, 1 mL) at −78 °C. A homogeneous solution was obtained near 0 °C, which darkened at room temperature. Separation by column chromatography afforded **8** (25.0 mg, 0.130 mmol, 46%) and **9b** (36.0 mg, 0.15 mmol, 54%).

Protonation of 18a. A mixture of **18a** (259 mg, 0.463 mmol) and TfOH (0.12 mL, 1.39 mmol) dissolved in 5 mL of CH_2Cl_2 was stirred at room temperature for 12 h. Quantitative formation of **21** and FpOTf was confirmed by ^1H NMR and IR spectra. (A singlet ^1H NMR signal at δ 5.21 observed for protonation of both **18a** and **19** was tentatively assigned to FpOTf. Treatment of FpI with AgOTf afforded a product having a singlet absorption at the same δ value.) The resulting mixture was treated with a $NaBH_4$ (78 mg, 2.0 mmol)–NaOMe (4 mmol)–MeOH (18 mL) system.[40c] Chromatographic separation gave **26a** (62.3 mg, 0.264 mmol, 57%) as yellow crystals.

Protonation of 19. A CH_2Cl_2 solution (5 mL) of **3a** (170 mg, 0.429 mmol) was treated with TfOH (0.11 mL, 1.29 mmol) at room temperature for 12 h. The formation of **27** and FpOTf was revealed by ^1H NMR and IR. Then, 4 mmol (0.56 mL) of triethylamine was added dropwise. **9a** (72 mg, 0.326 mmol, 76%) was isolated from the reaction mixture by column chromatography.

An authentic sample of **27** was prepared by mixing **9a** with a slight excess amount of TfOH in CD_2Cl_2. ^1H NMR (CD_2Cl_2): δ 3.12 (3 H, s, CH_3), 5.29 (5 H, s, Cp), 14.4 (1 H, br, OH). IR (CH_2Cl_2): 2064, 2012 cm^{-1}.

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Registry No. **1a**, 12300-79-7; **2a**, 107040-54-0; **2b**, 111615-22-6; **3a**, 107040-55-1; **3b**, 107040-56-2; **3c**, 111615-23-7; **3d**, 111582-06-0; **4**, 107040-57-3; **5**, 107040-58-4; **6**, 107040-59-5; **7**, 107040-60-8; **8**, 12080-06-7; **9a**, 12108-22-4; **9b**, 111582-19-5; **12**, 111582-08-2; **16**, 107040-61-9; **18a**, 111582-10-6; **18b**, 111582-12-8; **19**, 111582-14-0; **20**, 111582-16-2; **21**, 76624-84-5; **22**, 111582-17-3; **24a**, 82246-54-6; **26a**, 74171-11-2; **26a-d_1**, 111615-25-9; **26b**, 111582-18-4; **27**, 111582-20-8; $FpCH_2CO_2Me$, 12214-69-6; NaFp, 12152-20-4; $Na[Cp'Fe(CO)_2]$, 97279-76-0; $Na[CpMo(CO)_2(PPh_3)]$, 33503-71-8; Na[CpNi(CO)], 65836-26-2; $Na[Mn(CO)_5]$, 13859-41-1; $Na[Co(CO)_3(PMe_2Ph)]$, 69302-83-6; $FpCH_2CH_2COOH$, 111582-07-1; Fp_2, 38117-54-3; $(PPh_3)(CO)CpFeCOCH_2CH_2COFp$, 111615-24-8; $FpCH_2CHO$, 55337-26-3; $[Fp^+(PPh_3)]TFO^-$, 90858-61-0; FpOTF, 95865-48-8; $RhCl(PPh_3)_3$, 14694-95-2; $RhCl(PPh_3)_2(CO)$, 13938-94-8; $BrCH_2CH_2COSiMe_3$, 18187-28-5; $MeO_2CCH_2CO_2Me$, 108-59-8; $BrCH_2CO_2Me$, 96-32-2; $MeO_2CCH_2CH_2CO_2Me$, 106-65-0; $BrCH_2CH_2CO_2Me$, 3395-91-3; $CH_2=CHCH_3$, 115-07-1; $CH_2=CH_2$, 74-85-1; CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; β-bromopropionic acid, 590-92-1; ethyl acetate, 141-78-6; methyl acetate, 79-20-9; *n*-propyl alcohol, 71-23-8; methyl vinyl ether, 107-25-5.

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