ethyl acetate (ca. twice the volume of methylene chloride used) and the solution refrigerated overnight. Filtration afforded 1.55 g (58%) of **4a** as bright yellow crystals, mp 200–204 °C dec. ^1H NMR ($CDCl_3$, Me_4Si): δ -0.02 (t, 3 H), 0.09 (t, 3 H), 0.74 (q, 2 H), 2.16 (q, 2 H), 7.3–7.5 (m, 18 H), 7.6–7.8 (m, 12 H).

Preparation of 6a. A stirred suspension of chlorotris(triphenylphosphine)rhodium(I) (2.00 g, 2.16 mmol) in dry toluene (15 mL) under a nitrogen atmosphere was treated at 25 °C with propionyl chloride (0.30 g, 3.24 mmol). The mixture was heated to 70 °C, stirred for 1 h, and then cooled to room temperature, and to it was added hexane (15 mL). The precipitated solids were collected by filtration, washed with hexane, and then dried in vacuo to yield the crude product as an orange-red solid. The product was dissolved in methylene chloride containing a small amount of ethyl acetate, and then this solution was filtered to remove any insolubles. The filtrate was treated with additional ethyl acetate (ca. twice the volume of methylene chloride used) and the solution refrigerated overnight. Filtration afforded 1.31 g (80%) of **6a** as orange-red crystals, mp 200–204 °C dec. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.78 (t, 3 H), 2.94 (q, 2 H), 7.3–7.5 (m, 18 H), 7.6–7.8 (m, 12 H).

Preparation of 5b. To a stirred suspension of chlorobis(ethylene)rhodium(I) dimer (1.00 g, 2.62 mmol) in dry toluene under a nitrogen atmosphere was added at 25 °C dimethylphenylphosphine (1.45 g, 10.5 mmol). The resultant dark solution was stirred at room temperature for 30 min and then was treated with propionic anhydride (1.02 g, 7.86 mmol). The reaction mixture was stirred at room temperature for 18 h, and then to it was added hexane (15 mL). The precipitated solids were collected by filtration, washed with hexane, and then dried in vacuo to yield 2.34 g of the crude product as an off-white solid. The product was dissolved in methylene chloride containing a small amount of ethyl acetate and then filtered to remove any insolubles. The filtrate was treated with additional ethyl acetate (ca. twice the volume of methylene chloride used) and the solution refrigerated overnight. Filtration afforded 1.18 g (41%) of **5b** as white crystals, mp 144–145 °C dec. ^1H NMR ($CDCl_3$, Me_4Si): δ 1.09 (t, 3 H), 1.16 (t, 3 H), 1.35 (broad d, 6 H), 1.73 (broad m, 6 H), 2.32 (q, 2 H), 3.44 (m, 2 H), 7.1–7.27 (m, 4 H), 7.28–7.5 (m, 6 H).

Preparation of 7b. To a stirred suspension of chlorobis(ethylene)rhodium(I) dimer (1.00 g, 2.62 mmol) in dry toluene (15 mL) under a nitrogen atmosphere was added at 25 °C dimethylphenylphosphine (1.45 g, 10.5 mmol). The resultant dark solution was stirred at room temperature for 30 min and then was treated with propionyl chloride (0.61 g, 6.55 mmol). The reaction mixture was stirred at room temperature for 1 h, and then to it was added hexane (15 mL). The precipitated solids were collected by filtration, washed with hexane, and then dried in vacuo to yield 2.50 g of the crude product as a yellow powder. The product was dissolved in methylene chloride containing a small amount of ethyl acetate, and then this solution was filtered to remove any insolubles. The filtrate was treated with additional ethyl acetate (ca. twice the volume of methylene chloride used) and the solution refrigerated overnight. Filtration afforded 1.55 g (58%) of **7b** as bright yellow crystals, mp 145–148 °C dec. ^1H NMR ($CDCl_3$, Me_4Si): δ 1.14 (t, 3 H), 1.33 (d, 6 H), 1.81 (d, 6 H), 3.86 (t, 2 H), 7.2–7.6 (m, 10 H).

Preparation of 9a. To a stirred suspension of chlorobis(ethylene)rhodium(I) dimer (0.75 g, 1.96 mmol) in dry toluene (15 mL) under a nitrogen atmosphere was added at 25 °C dimethylphenylphosphine (1.89 g, 13.8 mmol). The resultant dark solution was stirred at room temperature for 30 min and then was treated with propionyl chloride (0.73 g, 7.86 mmol). The reaction mixture was stirred at room temperature for 1 h, and then to it was added hexane (15 mL). The supernatant liquid was decanted from the solid, which was then washed with hexane and dried in vacuo. The product was dissolved in methylene chloride containing a small amount of ethyl acetate and then filtered to remove any insolubles. The filtrate was treated with additional ethyl acetate (ca. twice the volume of methylene chloride used) and the solution refrigerated overnight. Filtration afforded 1.45 g (57%) of **9a** as yellow crystals, mp 150–154 °C dec. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.67 (t, 3 H), 1.27 (d, 6 H), 1.86 (m, 12 H), 2.79 (q, 2 H), 7.2–7.5 (m, 15 H).

Acknowledgment. We gratefully acknowledge Dr. J. Lee, Dr. B. Tobias, and Mr. S. Mullins for obtaining the NMR spectra and Mr. J. Mahlberg and Mr. J. Burtard for performing the IR analyses.

Reaction of Cationic Diiron μ-η^1:η^2-Acetylide Complexes $[(FP)_2(C{\equiv}CR)]BF_4$ (R = H, Ph) with Carbon Nucleophiles and Hydride. Formation of μ-Vinylidene Complexes

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Summary: The reaction of a cationic diiron μ-η^1:η^2-acetylide complex $[(FP)_2(C{\equiv}CH)]BF_4$ (**1**) with RLi (R = *n*-Bu, *t*-Bu) affords an acyl-substituted vinylidene complex $Cp^*{}_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}CH(COR)]$ (**3a**, R = *n*-Bu; **3b**, R = *t*-Bu). The structure of **3b** has been determined by single-crystal X-ray diffraction study. [Crystal data for **3b**: space group $P2_1/c$, a = 17.460 (2) Å, b = 9.495 (2) Å, c = 17.446 (2) Å, β = 100.480 (9)°, V = 2843.8 (7) Å^3, Z = 4, R = 0.0822.] **3** may be formed by an initial nucleophilic attack of R^- to a CO ligand in the cationic Fp* part, followed by insertion of the C≡C part into the Fe–C(O)R bond and metal–metal bond formation. The reaction of **1** with $LiHBEt_3$ affords a parent μ-vinylidene complex $Cp^*{}_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ (**4**). A plausible reaction pathway involves nucleophilic addition of H^- to a CO ligand and successive intramolecular hydride transfer from the formyl ligand to the β position of the C≡CH ligand.

The reactivity of $CpFe^+(CO)(L)(\eta^2\text{-alkyne})$ complexes [L = PR_3, $P(OR)_3$] toward nucleophiles has been extensively studied by Reger et al.[1] Most nucleophiles attack the coordinated η^2-alkyne ligand from the exo side to give trans-η^1-alkenyl ligands, which have been successively derivatized to functionalized alkenes (Scheme I). Exceptions are H^-,[2] R_2N^-,[3] and RLi,[3] which add to the Cp ring, and subsequent intramolecular hydride transfer from the transient η^4-C_5H_5–Nu ligand to the η^2-alkyne ligand results in the formation of cis-η^1-alkenyl ligands.

We have been studying the reactivity of cationic diiron μ-η^1:η^2-acetylide complexes $[(FP)_2(C{\equiv}CR)]BF_4$ [**1**, FP = Fp*, R = H; **2a**, FP = Fp*, R = Ph; **2b**, FP = Fp, R = Ph; FP = $(CP)Fe(CO)_2$, CP = η^5-$C_5R'_5$; Cp, Fp (R′ = H); Cp*,

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[1] Reger, D. L. *Acc. Chem. Res.* **1988**, *21*, 229.

[2] Reger, D. L.; Belmore, K. A.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 5710.

[3] Reger, D. L.; Klaeren, S. A.; Lebioda, L. *Organometallics* **1986**, *5*, 1072.

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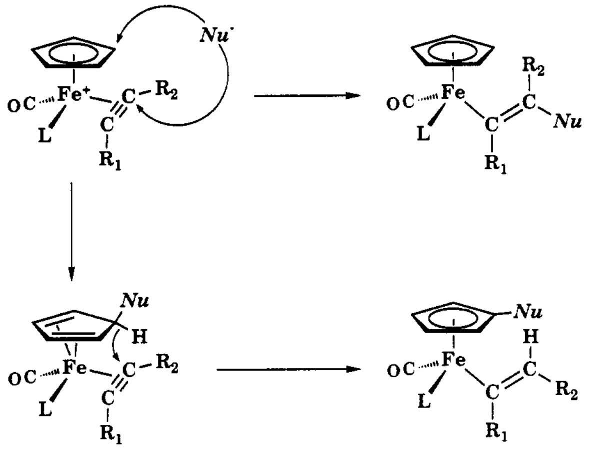
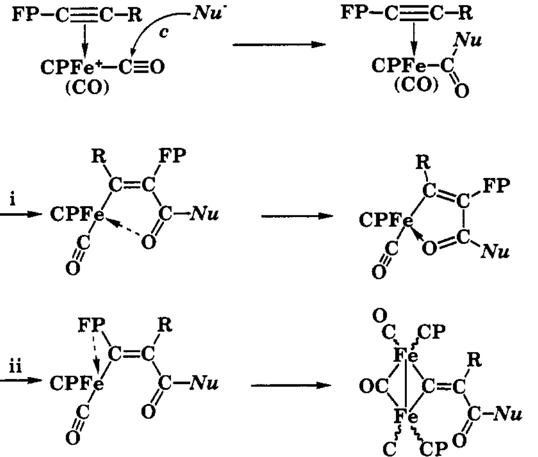
Scheme I

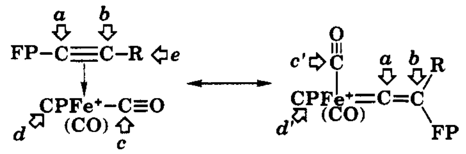


Scheme II



FP = CPFe(CO)$_2$; CP = η^5-C$_5$R′$_5$.
Fp, Cp : R′ = H. Fp*, Cp* : R′ = Me.

Chart I



FP = CPFe(CO)$_2$; CP = η^5-C$_5$R′$_5$.
Fp, Cp : R′ = H. Fp*, Cp* : R′ = Me.

Table I. Crystallographic Data for 3b

formula	C$_{30}$H$_{40}$O$_4$Fe$_2$
fw	576.34
space group	$P2_1/c$
a/Å	17.460 (2)
b/Å	9.495 (2)
c/Å	17.446 (2)
β/deg	100.480 (9)
Z	4
V/Å^3	2843.8 (7)
d_{calcd}/g cm^{-3}	1.35
μ/cm^{-1}	9.91
2θ/deg	2–50
no. of unique data with $F > 3\sigma$	2956
no. of variables	374
data/variables	7.9
R	0.0822
R_w	0.1053

Table II. Positional Parameters and B_{eq} Values for Non-Hydrogen Atoms of 3b

atom	x	y	z	B_{eq}, Å^2
CP1[a]	0.29387	0.65268	0.68465	
CP2	0.30103	0.34349	0.96942	
Fe1	0.28233 (7)	0.52297 (15)	0.75551 (7)	2.06 (4)
Fe2	0.30366 (7)	0.48492 (15)	0.90261 (7)	2.06 (4)
O1	0.2256 (6)	0.2459 (9)	0.7052 (5)	5.7 (3)
O2	0.3480 (5)	0.7692 (9)	0.9530 (5)	4.5 (3)
O3	0.4376 (5)	0.4331 (8)	0.8283 (4)	3.8 (2)
O4	0.1573 (5)	0.7320 (9)	0.9461 (5)	4.1 (3)
C1	0.2482 (7)	0.3547 (12)	0.7291 (6)	2.9 (4)
C2	0.3303 (6)	0.6565 (12)	0.9311 (7)	2.6 (3)
C3	0.3726 (7)	0.4637 (11)	0.8291 (6)	2.6 (3)
C10	0.2239 (7)	0.6588 (11)	0.6650 (6)	2.7 (3)
C11	0.2740 (7)	0.5650 (11)	0.6345 (6)	2.6 (3)
C12	0.3516 (7)	0.5927 (13)	0.6731 (7)	3.4 (4)
C13	0.3490 (7)	0.7040 (13)	0.7277 (7)	3.5 (4)
C14	0.2707 (7)	0.7428 (11)	0.7230 (6)	2.5 (3)
C15	0.1370 (7)	0.6748 (16)	0.6332 (7)	4.6 (4)
C16	0.2487 (10)	0.4693 (15)	0.5656 (7)	5.9 (5)
C17	0.4268 (10)	0.5255 (19)	0.6551 (9)	7.7 (6)
C18	0.4186 (8)	0.7755 (15)	0.7774 (8)	5.4 (5)
C19	0.2389 (10)	0.8657 (12)	0.7650 (8)	5.2 (5)
C20	0.3232 (8)	0.4235 (11)	1.0220 (6)	3.1 (3)
C21	0.3720 (7)	0.3408 (11)	0.9829 (6)	2.6 (3)
C22	0.3215 (7)	0.2617 (11)	0.9242 (6)	2.7 (3)
C23	0.2433 (8)	0.2952 (13)	0.9282 (7)	3.7 (4)
C24	0.2445 (7)	0.3965 (13)	0.9896 (7)	3.8 (4)
C25	0.3489 (9)	0.5145 (14)	1.0931 (7)	5.3 (5)
C26	0.4586 (7)	0.3234 (15)	1.0057 (8)	4.5 (4)
C27	0.3520 (9)	0.1479 (12)	0.8757 (8)	5.0 (5)
C28	0.1719 (9)	0.2236 (15)	0.8803 (8)	5.9 (5)
C29	0.1725 (9)	0.4456 (17)	1.0195 (9)	6.6 (5)
C31	0.2166 (6)	0.5542 (10)	0.8311 (5)	2.0 (3)
C32	0.1448 (7)	0.6046 (13)	0.8285 (6)	2.6 (3)
C33	0.1153 (6)	0.6843 (11)	0.8882 (6)	2.6 (3)
C34	0.0263 (7)	0.7190 (14)	0.8724 (7)	3.4 (3)
C35	0.0086 (11)	0.8211 (26)	0.8039 (10)	8.0 (7)
C36	−0.0197 (11)	0.5844 (26)	0.8559 (14)	7.7 (7)
C37	0.0044 (9)	0.7890 (19)	0.9437 (10)	6.0 (5)

[a] CP1 and CP2 are the centroids of C10–C14 and C20–24, respectively.

Fp* (R′ = Me)][4] [(FP)$^+$(η^2-alkyne) complexes where alkyne = (FP)C≡CR] toward nucleophiles. When the two dominant resonance contributors of 1 and 2, which have been revealed by spectroscopic analyses as well as X-ray diffraction study,[4a] are taken into account, several reaction sites are available, as shown in Chart I. We recently reported that the reaction of the phenylethynyl complex 2 with NaOMe took place at a CO ligand and subsequent insertion of the C≡C part into the resulting Fe–C(O)OMe bond afforded metallacyclic adducts (CP)(OC)Fe[C(Ph)=C(FP)C(O)OMe] (Scheme II: path c-i).[4b] On the other hand, treatment of the ethynyl complex 1 with NaOMe resulted in deprotonation to give a μ-(η^1:η^1-ethynediyl complex Fp*C≡CFp*. Herein we disclose the results of the reactions of 1 and 2 with carbon nucleophiles and hydride.

Results and Discussion

Reaction of 1 with RLi. When 1 was treated with RLi (R = n-Bu, t-Bu) in THF at −78 °C, purple crystals of 3 (**a**, R = n-Bu; **b**, R = t-Bu) were obtained in 37% and 47% yield, respectively, after chromatographic separation followed by recrystallization from ether–hexanes (eq 1). The presence of a bridging carbonyl group (IR, ^{13}C NMR) in-

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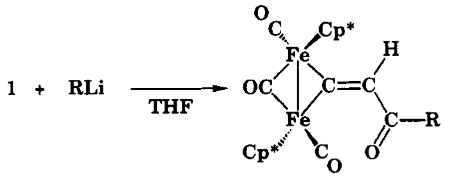
(4) (a) Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. *Organometallics* **1990**, *9*, 816. (b) Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. *Organometallics* **1991**, *10*, 1561.



(1)

3a (R = *n*-Bu) : 37 %
3b (R = *t*-Bu) : 47 %

dicates that **3** is a dinuclear complex with a metal–metal bond. **3** also contains an acyl group as well as a quarternary carbon signal at very low field ($\delta \sim 330$ ppm), which is characteristic of the α carbon of a bridging vinylidene ligand.[5] The molecular structure of **3b** has been determined unequivocally by X-ray crystallography to be a μ-vinylidene complex with an acyl group at the vinylidene terminus, which is consistent with the spectral data. An ORTEP drawing is reproduced in Figure 1, and crystallographic data, positional parameters, and important interatomic distances and bond angles are summarized in Tables I–III. The structural parameters associated with the vinylidene part are comparable to previously reported diiron μ-vinylidene complexes.[5,6]

A plausible mechanism for formation of **3** may be partly similar to that for the reaction of **2** with NaOMe,[4b] as shown in Scheme II (path c-ii). Nucleophilic attack of R^- to a CO ligand may give an acyl functional group. In the next insertion step two reaction pathways, which depend on the orientation of the $Fp^*C\equiv CH$ group, are possible. Actually the reaction with RLi follows path ii and the acyl-substituted μ-vinylidene complex **3** is formed, and no trace of products resulting from path i is detected. In contrast to the present reaction, the reaction of **2** with NaOMe affords a metallacyclic product via coupling with the oppositely oriented $C\equiv C$ group (path i).[4b] (Particularly, the metallacycle is obtained as a sole adduct by the reaction of **2b** with NaOMe.) Because both electrostatic interaction and steric repulsion shown in Chart II may favor path i over path ii, some other reaction mechanism should operate in the present system, for example, migratory insertion of the $Fp^*C\equiv CR$ ligand promoted by an attractve metal–metal interaction.

In addition, it should be noted that RLi does not deprotonate **1a** (e in Chart I) but attacks a CO ligand, while **1a** is readily deprotonated by NaOMe to give $Fp^*C\equiv CFp^*$.[4b] The factor that determines the reaction pathway is not clear at the present time. However, the fact that **1a** cannot be deprotonated by stronger bases such as RLi and hydride (vide infra) has clarified that the fluxional process of **1a** is an intramolecular one, as discussed in our previous paper.[4a]

The reaction of **1a** with other carbon nucleophiles such as MeLi·LiBr, $LiCuMe_2$, and $NaCH(COOMe)_2$ resulted in deprotonation to give $Fp^*C\equiv CFp^*$ or decomposition induced by nucleophilic attack of X^- to give $Fp^*C\equiv CH$ and Fp^*X (X originates from MeBr or CuI). In addition, the reaction of the phenyl analogue **2a** with carbon nucleophiles did not afford a μ-vinylidene complex like **3** but a complicated mixture of products in low yields consisting of $Fp^*C\equiv CPh$, Fp^*_2, $Fp^*C(H){=}C(Ph)C\equiv CPh$,[7] and so on.

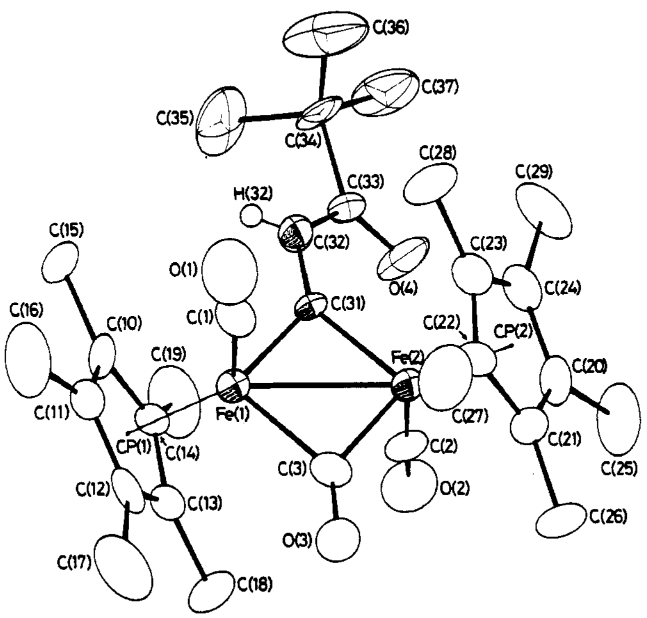
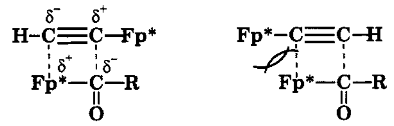
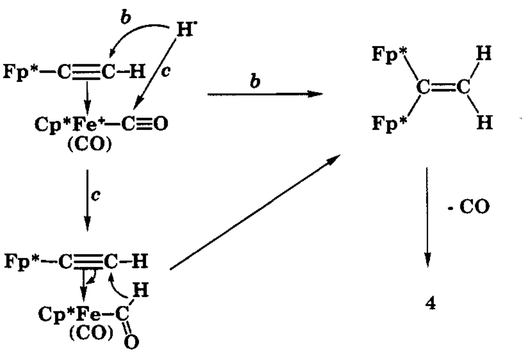


Figure 1. ORTEP drawing of **3b** drawn at the 30% probability level.

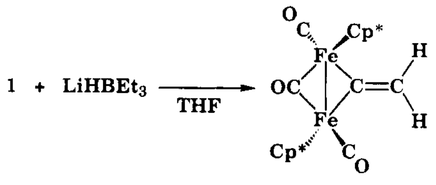
Chart II



Scheme III



Reaction of 1 with Super-Hydride. Treatment of **1** with $LiHBEt_3$ in THF gave purple powders **4** in 31% yield (eq 2). On the basis of the symmetrical structure indicated



(2)

4 (31 %)

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(7) Analytical data for $Fp^*CH{=}C(Ph)C\equiv CPh$ are as follows. ^1H NMR ($CDCl_3$): δ 1.83 (15 H, s, C_5Me_5), 7.13 (1 H, t, $J = 6.9$ Hz, *p*-Ph), 7.20–7.42 (5 H, br, Ph), 7.52 (2 H, d, $J = 6.3$ Hz, Ph), 7.61 (2 H, d, $J = 7.4$ Hz, Ph), 8.09 (1 H, s, CH=). ^{13}C NMR ($CDCl_3$): δ 9.7 (q $J = 127.7$ Hz, C_5Me_5), 88.7 (s, $C\equiv C$), 94.8 (s, $C\equiv C$), 96.4 (s, C_5Me_5), 125.05 (t, $J = 7.6$ Hz, *ipso*-Ph), 125.13 (dt, $J = 157.2$, 6.9 Hz, *m*-Ph), 125.4 (dt, $J = 163.2$, 7.6 Hz, *p*-Ph), 127.1 (dt, $J = 161.8$, 7.7 Hz, *p*-Ph), 128.0 (dd, $J = 160.2$, 7.6 Hz, *o*-Ph), 128.1 (dd, $J = 160.3$, 7.6 Hz, *o*-Ph), 131.2 (dt, $J = 160.2$, 6.9 Hz, *m*-Ph), 134.3 (s, *C*=CH), 142.3 (t, $J = 6.9$ Hz, *ipso*-Ph), 167.5 (d, $J = 137.3$ Hz, =CH), 216.3 (s, CO). IR (KBr): 2188 ($\nu_{C\equiv C}$), 1993, 1942 cm^{-1} ($\nu_{C\equiv O}$). FD-MS: *m/e* 450 (M^+).

Table III. Important Bond Lengths (Å) and Angles (deg) for 3b

Bond Lengths			
Fe1–Fe2	2.551 (2)	C–C(Cp*1)	1.40–1.42 (2)
Fe1–C1	1.74 (1)	C–Me(CP*1)	1.51–1.53 (2)
Fe1–C3	1.93 (1)	C–C(Cp*2)	1.41–1.44 (2)
Fe1–C31	1.92 (1)	C–Me(Cp*2)	1.50–1.53 (2)
Fe1–C(Cp*)	2.13–2.18 (1)	C31–C32	1.34 (2)
Fe2–C2	1.74 (1)	C32–C33	1.45 (2)
Fe2–C3	1.93 (1)	C33–C34	1.56 (2)
Fe2–C31	1.900 (9)	C33–O4	1.22 (1)
Fe2–C(Cp*)	2.13–2.17 (1)	C34–C35	1.52 (2)
O1–C1	1.16 (1)	C34–C36	1.51 (3)
O2–C2	1.16 (1)	C34–C37	1.52 (2)
O3–C3	1.18 (2)		
Bond Angles			
C1–Fe1–CP1	121.9	C3–Fe2–Fe1	48.6 (3)
C1–Fe1–C31	96.0 (5)	C–C–C(Cp*1)	107.7–108.7
C1–Fe1–C3	96.2 (5)	C–C–Me(Cp*1)	123.7–127.4
CP1–Fe1–C31	121.8	C–C–C(Cp*2)	106.8–109.4
CP1–Fe1–C3	118.8	C–C–Me(Cp*2)	122.4–128.5
C31–Fe1–C3	96.1 (5)	C32–C31–Fe2	141.3 (8)
C1–Fe1–Fe2	96.7 (4)	C32–C31–Fe1	134.9 (8)
CP1–Fe1–Fe2	141.4	Fe1–C31–Fe2	83.7 (4)
C31–Fe1–Fe2	47.8 (3)	C31–C32–C33	127.9 (10)
C3–Fe1–Fe2	48.4 (4)	C32–C33–O4	123.2 (10)
C2–Fe2–CP2	123.7	C34–C33–O4	119.8 (10)
C2–Fe2–C31	90.2 (5)	C32–C33–C34	116.9 (9)
C2–Fe2–C3	97.0 (5)	C36–C34–C37	108.8 (14)
CP2–Fe2–C31	125.2	C36–C34–C35	111.4 (13)
CP2–Fe2–C3	116.8	C36–C34–C33	109.4 (12)
C31–Fe2–C3	97.0 (5)	C37–C34–C35	108.5 (13)
C2–Fe2–Fe1	97.9 (4)	C37–C34–C33	109.8 (9)
C31–Fe2–Fe1	48.5 (3)	C35–C34–C33	109.0 (11)

by the IR and NMR data and a quarternary carbon signal characteristic of a μ-vinylidene group, the structure of 4 is assigned to $Cp^*{}_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$. 4 contains only one stereoisomer (presumably trans), although the stereochemistry cannot be determined on the basis of spectral data alone. The Cp analogue of 4 prepared by a different method consists of an equilibrated mixture of the cis and trans isomers.[8]

4 appears to be formed by direct nucleophilic attack of H^- to the β-carbon of the μ-ethynyl ligand (path b of Scheme III) followed by metal–metal bond formation via decarbonylation. However, the observations that the α-carbon of the ethynyl ligand may be more electrophilic than the β-carbon owing to the vinylidene complex type resonance structure (Chart I) and that both ^-OMe and R^- attack a CO ligand indicate that a mechanism other than the direct attack on the β-carbon may operate in this reaction. A possible mechanism involves nucleophilic attack to a CO ligand followed by hydride transfer from the resulting formyl group to the β-carbon of the $Fp^*C{\equiv}CH$ ligand. (path c of Scheme III). Similar intramolecular hydride transfer from a η^4-C_5H_5Nu ligand to a coordinated $C{\equiv}C$ moiety has been already established, as described in the introduction.[2,3] In the present case the hydride transfer to lead to 4 appears to be energetically favorable compared to the insertion of the $C{\equiv}C$ part into the resulting Fe–CHO bond to lead to $Cp^*{}_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}CH(CHO)]$.

The reaction of the phenyl analogue **2a** afforded a complicated mixture containing $Fp^*C(H){=}C(Ph)C{\equiv}CPh$,[7] $Fp^*C{\equiv}CPh$, and so on.

Experimental Section

All manipulations were carried out by using standard Schlenk tube techniques.

THF was dried over Na–K/benzophenone, distilled, and stored under argon. 1 and 2 were prepared according to our previous paper.[4a] RLi's were purchased from Aldrich and used as received. Alumina (activity II–III: Merck Art. 1097) was used for column chromatography. ^1H and ^{13}C NMR spectra were recorded on JEOL FX-100 (100 MHz) and JEOL GX-270 (68 MHz) spectrometers, respectively, at 27 °C. IR spectra were obtained on a Hitachi 260-50 spectrometer. Mass spectra were obtained on a Hitachi M-80 spectrometer. Elemental analyses were performed by using the facilities in the Research Laboratory of Resources Utilization at Tokyo Institute of Technology.

Reaction of 1 with *n*-BuLi. To a suspension of 1 (296 mg, 0.49 mmol) in THF (30 mL) cooled at −78 °C was added *n*-BuLi (1.62 M hexane solution, ~40 mL, 0.65 mmol). After 5 min the mixture was warmed to room temperature, and stirring was continued overnight. After evaporation of the volatiles the products were extracted with ether, filtered through an alumina plug, and separated by column chromatography. After eluton of $Fp^*{}_2$ with CH_2Cl_2–hexanes (1:3) a purple band was eluted with CH_2Cl_2–hexanes (1:1 → 2:1). **3a** (103 mg, 0.18 mmol, 37% yield) was obtained as purple crystals after recrystallization from ether–hexanes. Analytical data for **3a** are as follows. ^1H NMR (C_6D_6): δ 1.03 (3 H, t, J = 7.1 Hz, CH_3), ~1.3 (2 H, m, CH_2CH_3), 1.49 (15 H, s, C_5Me_5), 1.64 (15 H, s, C_5Me_5), 1.9–2.2 (2 H, m, $CH_2CH_2CH_3$), 2.80 (2 H, t, J = 7.2 Hz, CH_2–C(O)), 8.32 (1 H, s, =CH). ^{13}C NMR (C_6D_6): δ 8.8 (q, J = 127.6 Hz, C_5Me_5), 9.5 (q, J = 127.6 Hz, C_5Me_5), 14.4 (q, J = 123.8 Hz, CH_3), 23.4 (t, J = 124.6 Hz, CH_2CH_3), 28.2 (t, J = 125.4 Hz, $CH_2CH_2CH_3$), 43.2 (q, J = 124.6 Hz, CH_2CO), 99.0 (s, C_5Me_5), 99.9 (s, C_5Me_5), 137.2 (d, J = 153.4 Hz, =CH), 190.7 (s, C=O), 214.4 (s, CO), 215.3 (s, CO), 276.2 (s, μ-CO), 334.9 (s, >C=CH). IR (KBr): 1958, 1927, 1773, 1649 cm^{-1}. Anal. Calcd for $C_{30}H_{40}O_4Fe_2$: C, 62.55; H, 6.94. Found: C, 62.07; H, 7.24.

Reaction of 1 with *t*-BuLi. The reaction was carried out in a manner similar to the reaction with *n*-BuLi by using 1.07 g (1.76 mmol) of 1 and 2.6 mmol of *t*-BuLi (1.7 M hexane solution). **3b** (470 mg, 0.83 mmol, 47%) was obtained as purple crystals by recrystallization from ether–hexanes. Analytical data for **3b** are as follows. ^1H NMR (C_6D_6): δ 1.51 (15 H, s, C_5Me_5), 1.55 (9 H, s, CMe_3), 1.63 (15 H, s, C_5Me_5), 8.56 (1 H, s, =CH). ^{13}C NMR (C_6D_6): δ 8.9 (q, J = 126.8 Hz, C_5Me_5), 9.5 (q, J = 126.9 Hz, C_5Me_5), 28.3 (q, J = 125.0 Hz, CMe_3), 42.7 (s, CMe_3), 99.1 (s, C_5Me_5), 99.8 (s, C_5Me_5), 132.5 (d, J = 150.8 Hz, =CH), 195.5 (s, C=O), 214.4 (s, CO), 215.4 (s, CO), 276.4 (s, μ-CO), 337.2 (s, >C=CH). IR (KBr): 1955, 1920, 1772, 1642 cm^{-1}. Anal. Calcd for $C_{30}H_{40}O_4Fe_2$: C, 62.55: H, 6.94. Found: C, 62.55; H, 7.34.

Reaction of 1 with $LiHBEt_3$. To a suspension of 1 (550 mg, 0.91 mmol) in THF (10 mL) cooled at −78 °C was added $LiHBEt_3$ (1.0 M THF solution, 1 mL, 1.0 mmol). After 2 h the volatiles were removed under reduced pressure and the products were extracted with ether and separated by column chromatography. Elution with CH_2Cl_2–hexanes (1:15 → 1:12) gave a purple band from which 4 (135 mg, 0.28 mmol, 31% yield) was isolated as a purple powder after recrystallization from ether–hexanes. Analytical data for 4 are as follows. ^1H NMR (C_6D_6): δ 1.65 (30 H, s, $C_5Me_5 \times 2$), 6.63 (2 H, s, $=CH_2$). ^{13}C NMR (C_6D_6): δ 8.9 (q, J = 127.4 Hz, C_5Me_5), 97.7 (s, C_5Me_5), 113.4 (t, J = 156.1 Hz, $=CH_2$), 214.2 (s, CO), 279.1 (s, μ-CO), 295.5 (s, $>C{=}CH_2$). IR (KBr) 1923, 1770 cm^{-1}. Anal. Calcd for $C_{25}H_{32}O_3Fe_2$: C, 61.00; H, 6.55. Found: C, 60.56; H, 6.57.

Single-Crystal X-ray Diffraction Study. Diffraction measurements were made on a Rigaku AFC-5 automated four-circle diffractometer in the range of $2 < 2\theta < 50°$ by using the graphite-monochromated Mo Kα radiation (λ = 0.71068 Å). Crystal data were collected in Table I. Data were corrected for Lorentz and polarization effects. An empirical absorption correction was also made. Structure solution and refinement (the direct method) were carried out by using the R-CRYSTAN structure-solving program system (obtained from the Rigaku Corp., Tokyo, Japan). All the non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms bonded to the *t*-Bu group and the vinylidene group were refined with iso-

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[8] (a) Kau, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911. (b) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499.

tropic thermal parameters.

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Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters, and additional bond lengths and angles (11 pages); a table of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

(Benzyne)chromium Tricarbonyl. Preparation and Structure of $Ru_3(CO)_9\{\mu_3\text{-}P[C_6H_5Cr(CO)_3]\}[\mu_3\text{-}C_6H_4Cr(CO)_3]$ and $Ru_3(CO)_7(\mu_3\text{-}C_6H_4)\{\mu\text{-}PPh[C_6H_5Cr(CO)_3]\}_2$

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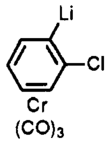
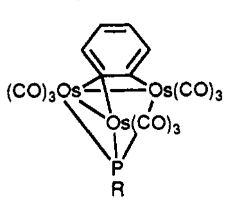
Summary: $Ru_3(CO)_9\{\mu_3\text{-}P[C_6H_5Cr(CO)_3]\}[\mu_3\text{-}C_6H_4Cr(CO)_3]$ (2) is prepared by reacting $Ru_3(CO)_{12}$ with $PhP[C_6H_5Cr(CO)_3]_2$. The crystal structure shows the aryne moiety, $C_6H_4Cr(CO)_3$, η^2 bound to three Ru atoms that are part of a Ru_3P butterfly arrangement. A Cr→Ru bond is proposed. The P atom is bound to the $C_6H_5Cr(CO)_3$ moiety and three Ru atoms. In contrast, the product of the thermal decomposition of $Ru_3(CO)_{11}PPh_2[C_6H_5Cr(CO)_3]$ is the $\mu_3\text{-}\eta^2$-benzyne complex $Ru_3(CO)_7(\mu_3\text{-}\eta^2\text{-}C_6H_4)\{\mu\text{-}PPh[C_6H_5Cr(CO)_3]\}_2$ (3). Crystals of 2 are monoclinic, with a = 16.918 (2) Å, b = 10.612 (3) Å, c = 19.241 (2) Å, β = 113.64 (2)°, Z = 4, and space group $P2_1/n$, and those of $3 \cdot CH_2Cl_2$ are monoclinic, with a = 22.411 (2) Å, b = 17.314 (4) Å, c = 26.191 (4) Å, β = 111.68 (1)°, Z = 8 (two molecules per asymmetric unit), and space group $P2_1/n$. The structures were solved by heavy-atom methods and were refined by full-matrix least-squares procedures to R = 0.043 and 0.037 for 6096 and 10 119 reflections with $I \geq 3\sigma(I)$, respectively.

The possible existence of (benzyne)chromium tricarbonyl has been investigated by Semmelhack and Ullenius,[1] who claimed that the thermal decomposition of the reasonably stable lithio derivative 1 proceeded at 0 °C, with elimination of lithium chloride to provide the novel aryne. However, the evidence is not very convincing. We now report that (benzyne)chromium tricarbonyl can be trapped as part of a ruthenium–carbonyl cluster.



1



4

The complex $Ru_3(CO)_9\{\mu_3\text{-}P[C_6H_5Cr(CO)_3]\}[\mu_3\text{-}C_6H_4Cr(CO)_3]$ (2; Figure 1) is easily prepared in greater than 50% yield by heating $Ru_3(CO)_{12}$ with the tertiary phosphine $PhP[C_6H_5Cr(CO)_3]_2$ (L) in refluxing heptane for 5 h.[2,3] The other major product is the monosubstituted derivative $Ru_3(CO)_{11}L$. The reaction proceeds slower in refluxing cyclohexane, and TLC monitoring reveals that 2 is formed from $Ru_3(CO)_{11}L$. This thermolysis to produce (benzyne)chromium tricarbonyl is so far unique to ruthenium complexes of $PPh[C_6H_5Cr(CO)_3]_2$.

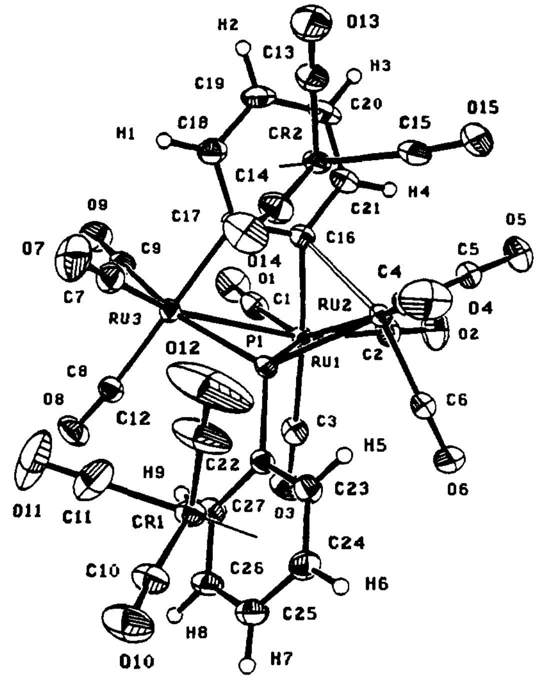


Figure 1. Perspective view of 2 (50% probability thermal ellipsoids are shown for the non-hydrogen atoms).

In contrast, $Ru_3(CO)_{10}\{PPh_2[C_6H_5Cr(CO)_3]\}$ decomposes at 88 °C in heptane to afford $Ru_3(CO)_7(\mu_3\text{-}C_6H_4)\{\mu\text{-}PPh[C_6H_5Cr(CO)_3]\}_2$ (3; Figure 2), a new member of the now well-established class of benzyne derivatives in which the aryne moiety is μ_3,η^2 bound to a M_3 fragment (M = Ru, Os).[3]

The aryne moiety in 2 contains an unsymmetrically bound $Cr(CO)_3$ group; the Cr(2)–C bond lengths range from 2.297 (5) Å for Cr(2)–C(16) to 2.208 (6) Å for Cr-

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[1] Semmelhack, M. F.; Ullenius, C. *J. Organomet. Chem.* **1982**, *235*, C10.

[2] The thermal decomposition of arylphosphine derivatives of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ is known to lead to clusters containing aryne fragments;[3] however, attempts to prepare ferrocyne-containing clusters by this method have not been successful to date.[3a,b]

[3] E.g.: (a) Cullen, W. R.; Chacon, S. T.; Bruce, M. I.; Einstein, F. W. B.; Jones, R. H. *Organometallics* **1988**, *7*, 2273. (b) Bruce, M. I.; Shawkataly, O. B.; Snow, M. R.; Tiekink, E. R. T.; Cullen, W. R. *Organometallics* **1990**, *9*, 2910. (c) Bruce, M. I.; Guss, J. M.; Mason, R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1983**, *251*, 261. (d) Deeming, A. J.; Kabir, S. E.; Powell, N. I.; Bates, P. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 1529.

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