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Reaction of the cationic diiron .mu.-(.eta.1:.eta.2)acetylide complexes [(FP)2(C.tplbond.CR)]BF4 (R = H, Ph) with NaOMe

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Reaction of the Cationic Diiron μ-η^1:η^2-Acetylide Complexes $[(FP)_2(C{\equiv}CR)]BF_4$ (R = H, Ph) with NaOMe

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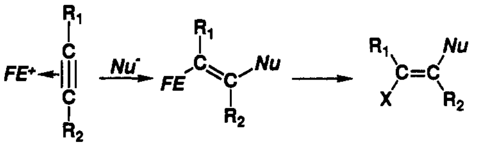
The reaction of $[(Fp^*)_2(C{\equiv}CH)]BF_4$ (**1a**; $Fp^* = (\eta^5\text{-}C_5Me_5)Fe(CO)_2$) with NaOMe in THF results in deprotonation to afford $Fp^*C{\equiv}CFp^*$ (**2**) in 41% yield. On the other hand, the reaction of $[(Fp)_2(C{\equiv}CPh)]BF_4$ (**1c**) ($Fp = (\eta^5\text{-}C_5H_5)Fe(CO)_2$) with NaOMe produces the metallacyclic adduct $Cp(OC)Fe[C(Ph){=}C(Fp)C({=}O)OMe]$ (**3**), whose structure has been confirmed by derivatization to (Z)-3-$Fp(Ph){=}C(H)COOMe$ (**4**) by acid hydrolysis as well as comparison with **5** (a reaction product of **1b**). The reaction of $[(Fp^*)_2(C{\equiv}CPh)]BF_4$ (**1b**) with NaOMe gives a complicated mixture containing the mononuclear metallacyclic complex $Cp^*(OC)Fe[C(Ph){=}C(H)C({=}O)OMe]$ (**5**) and the dinuclear μ-vinylidene complex $(Cp^*)_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(Ph)COOMe]$ (**6**). **5** may be formed via Fe–C bond cleavage of the dinuclear complex **9** (the Fp* analogue of **3**). The regiochemistry observed for the present systems is completely different from that observed for nucleophilic addition to $[CpFe^+(CO)(PR_3)(\eta^2\text{-alkyne})]$ complexes, where the η^2-alkyne ligand is attacked by nucleophiles to give alkenyl complexes. Formation of **3**, **6**, and **9** (**5**) may be interpreted as follows. Nucleophilic attack of ^-OMe at a coordinated CO ligand will lead to the formation of an acyl intermediate. Subsequent migratory insertion of the η^2-C≡C functional group into the resulting Fe–acyl bond may form two types of acyl-substituted alkenyl ligands depending on the orientation of the η^2-FP-C≡CR ligand. When the two iron groups are attached to the two different olefinic carbon atoms, intramolecular coordination of the acyl oxygen atom to the coordinatively unsaturated metal center results in the formation of the five-membered metallacyclic products **3** and **9** (**5**). In contrast, when the two iron groups are bonded to the same olefinic carbon atom, the vinylidene complex **6** may be formed via dative Fe–Fe bond interaction. In addition, it turns out that nucleophilic attack at a CO ligand rather than a η^2-alkyne ligand is not peculiar to dinuclear complexes. Thus, the reaction of $[Fp^+(PhC{\equiv}CPh)]BF_4$ with NaOMe affords the metallacyclic adduct $Cp(OC)Fe[-C(Ph){=}C(Ph)C({=}O)OMe]$ (**11**). The structures of **4** and **5** have been determined by single-crystal X-ray diffraction studies. Crystal data: **4**, $C_{17}H_{14}O_4Fe$, space group $P\bar{1}$, $a = 11.104$ (4) Å, $b = 12.958$ (4) Å, $c = 7.502$ (2) Å, $\alpha = 91.14$ (3)°, $\beta = 102.28$ (3)°, $\gamma = 131.34$ (2)°, $V = 772.7$ (5) Å^3, $Z = 2$, $R = 0.0406$; **5**, $C_{21}H_{24}O_3Fe$, space group $P\bar{1}$, $a = 9.846$ (3) Å, $b = 13.591$ (2) Å, $c = 8.532$ (3) Å, $\alpha = 91.84$ (2)°, $\beta = 119.32$ (2)°, $\gamma = 98.92$ (2)°, $V = 975.5$ (5) Å^3, $Z = 2$, $R = 0.0398$.

Introduction

In a previous paper we reported the preparation and divergent fluxional behavior of cationic diiron μ-η^1:η^2-acetylide complexes, $[(FP)_2(C{\equiv}CR)]BF_4$ (**1a**, FP = Fp*, R = H; **1b**, FP = Fp*, R = Ph, **1c**, FP = Fp, R = Ph; $Fp^* = (\eta^5\text{-}C_5Me_5)Fe(CO)_2$, $Fp = (\eta^5\text{-}C_5H_5)Fe(CO)_2$).[1] The spectroscopic and crystallographic characterization has revealed the contribution of a vinylidene complex resonance structure ($FP^+{=}C{=}C(R)FP$) in addition to the dominant contribution of a π-complex resonance structure ($FP^+(\eta^2\text{-}FPC{\equiv}CR)$) (Scheme I). The divergent fluxional behavior observed by means of variable-temperature ^{13}C NMR spectroscopy has been interpreted by wiperlike oscillation of the PhC≡C ligand in **1b**,**c** and by fast proton movement between the two acetylide carbon atoms in **1a**.

It has been well-known that a η^2-alkyne ligand coordinated to a cationic metal center is susceptible to nucleophilic attack to give an alkenyl complex.[2] Subsequent transformation of the metal part in the resulting alkenyl complex affords a substituted alkene. Thus, detailed studies by Reger et al. using $[CpFe^+(CO)(PR_3)(\eta^2\text{-alkyne})]$ complexes have revealed that the reaction sequence shown in eq 1 serves as a promising method for stereospecific synthesis of highly functionalized alkenes.[3]



(1)

FE = CpFe(CO)(PR$_3$)

In the case of nucleophilic addition to **1** several reaction sites are available, as shown in Scheme I. An alkenyl complex will be formed by addition of a nucleophile to the C≡C part, as observed for Reger's system (path a,b). Owing to the contribution of the vinylidene complex form, the α-carbon atom (path a) may be more susceptible to nucleophilic attack than the β-carbon atom (path b). On the other hand, nucleophilic attack at a coordinated CO ligand will lead to the formation of an acyl intermediate, which may be subsequently transformed to a final product via migration or insertion (path c,c′). A nucleophile may attack the CP (η^5-C_5R_5) ligand from the exo side of the ring to give a η^4-C_5R_5–Nu ligand (path d,d′). A hydride addition reaction to a $[CpFe^+(CO)(PR_3)(\eta^2\text{-alkyne})]$ complex is interpreted in terms of such an intermediate.[4] Finally, when R = H, deprotonation may become a viable route (path e).

We have been studying the reactivity of **1** toward various nucleophiles, and herein the full details of the reaction of **1** with NaOMe are disclosed.

Results and Discussion

Reaction of $[(Fp^*)_2(C{\equiv}C{-}H)]BF_4$ (1a) with NaOMe. When **1a** was treated with NaOMe in THF, the

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

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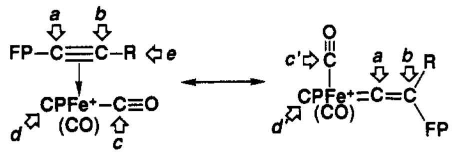
Scheme I



diiron μ-η^1:η^1-ethynediyl complex **2** was obtained in 41% yield after purification by column chromatography (eq 2).

$$\underset{\mathbf{1a}}{[(\mathrm{Fp}^*)_2(\mathrm{C{\equiv}CH})]\mathrm{BF}_4} \xrightarrow[\mathrm{THF}]{\mathrm{NaOMe}} \underset{\mathbf{2}\ (41\%)}{\mathrm{Fp}^*\mathrm{C{\equiv}CFp}^*} \quad (2)$$

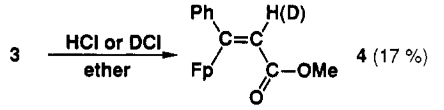
The symmetric structure of **2** was indicated by its ^{1}H and ^{13}C NMR data, and the molecular ion peak (m/e = 522) was detected by FDMS. The chemical shift of the acetylenic carbon atoms in **2** (δ 98.1) is comparable to that in a rhenium analogue, $(\mathrm{OC})_5\mathrm{ReC{\equiv}CRe(CO)}_5$ (δ 94.4).[5a,b] The rhenium analogue and several heterobimetallic μ-η^1:η^1-ethynediyl complexes[5c] have been prepared in a manner similar to eq 2.

Reaction of [Fp$_2$(C≡C—Ph)]BF$_4$ (1c) and [Fp*$_2$(C≡C—Ph)]BF$_4$ (1b) with NaOMe. The reaction of **1c** with NaOMe in THF gave deep green oil **3** in 62% yield (eq 3). The ^{13}C NMR spectrum of **3** contained two Cp's,

$$\underset{\mathbf{1c}}{[\mathrm{Fp}_2(\mathrm{C{\equiv}CPh})]\mathrm{BF}_4} \xrightarrow[\mathrm{THF}]{\mathrm{NaOMe}} \underset{62\%}{\text{deep green oil } \mathbf{3}} \quad (3)$$

Ph, OMe, and five quarternary carbon signals in addition to a low-field absorption at δ 240.6 characteristic of a carbene carbon. Although **3** proved to be a dinuclear complex, the structure of **3** could not be assigned on the basis of its spectral data.

In order to get information on the structure, **3** was degraded to a mononuclear complex by acid hydrolysis. Treatment of **3** with 1 M HCl aqueous solution in ether gave the yellow mononuclear complex **4** (eq 4). Although

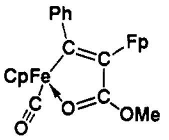


(4)

the ^{1}H and ^{13}C NMR and IR data indicated that **4** was a trisubstituted olefin with Fp, Ph, and C(O)OMe substituents, the stereochemistry of the olefinic part could not be determined by spectroscopic analyses alone. The structure of **4** was then determined to be (Z)-Fp(Ph)C=C(H)COOMe by a single-crystal X-ray diffraction study (vide infra).

Treatment of **3** with DCl gave **4**-d (eq 4). The disappearance of the olefinic proton signal in the ^{1}H NMR spectrum as well as the change of the coupling pattern of the methyne carbon signal (δ 132.3, triplet with $J_{\mathrm{C-D}}$ = 23.9 Hz) revealed that the olefinic proton was specifically deuterated. This result suggested that in the starting complex **3** an iron group was attached to the methyne carbon. Although the ν(C=O) absorption of the ester group in **4** was observed at 1704 cm^{-1}, that of **3** could not be found in the range 1800–1600 cm^{-1}. In addition, **3** contained only three terminal CO stretching vibrations. These IR data indicated the coordination of the ester C=O group to one of the two metal centers. Then, a metallacyclic structure (Chart I), which was also supported by the mass spectral data (m/e = 486), was assumed as a possible structure for the deep green oil **3**. This assignment was finally confirmed by comparison of the spectral features with those of **5** (a reaction product of **1b**), whose structure was unequivocally determined by single-crystal X-ray crystallography (vide infra).

Chart I

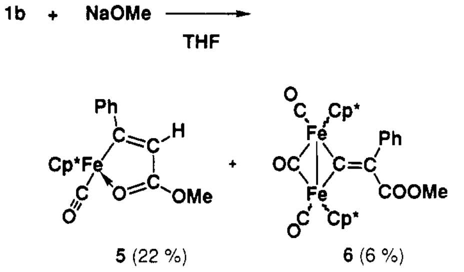


3

Table I. Crystallographic Data for 4 and 5

	4	5
formula	$C_{17}H_{14}O_4Fe$	$C_{21}H_{24}O_3Fe$
fw	338.13	380.25
space group	$P\bar{1}$	$P\bar{1}$
a/Å	11.104 (4)	9.846 (3)
b/Å	12.958 (4)	13.591 (2)
c/Å	7.502 (2)	8.532 (3)
α/deg	91.14 (3)	91.84 (2)
β/deg	102.28 (3)	119.32 (2)
γ/deg	131.34 (2)	98.92 (2)
Z	2	2
V/Å^3	772.7 (5)	975.5 (5)
d_{cald}	1.45	1.29
cryst size	0.25 × 0.30 × 0.55	0.40 × 0.25 × 0.55
μ/cm^{-1}	9.269	7.342
2θ/deg	2–60	2–55
no. of data collected	3828	4789
no. of unique data with $F > 3\sigma$	2922	3742
no. of variables	298	369
data/variables	9.8	10.1
p	0.02	0.005
R	0.0406	0.0398
R_{w}	0.0442	0.0369

The reaction of **1b** with NaOMe afforded a complicated reaction mixture, from which deep green crystals of **5** and blue-violet crystals of **6** were isolated in 22 and 6% yield, respectively, after chromatographic separation followed by repeated recrystallization (eq 5). Except for the fact that **5** was a mononuclear complex, the spectroscopic features of **5** were very close to those of **3**, as exemplified by the ^{13}C NMR spectrum containing a low-field carbenic carbon resonance (δ 247.0). As determined by a single-crystal X-ray diffraction study (vide indra), **5** contained a metallacyclic structure in which the oxygen atom of the ester C=O group was coordinated to the Fe atom. The blue-violet product **6** was assigned to the vinylidene complex $(\mathrm{Cp}^*)_2\mathrm{Fe}_2(\mathrm{CO})_2(\mu\text{-CO})[\mu\text{-C{=}C(Ph)COOMe}]$ on the basis of a ^{13}C NMR signal appearing at very low field (δ 335.7)[6] as well as the bridging carbonyl ligand (δ 275.5; ν(C=O) 1767 cm^{-1}). Only one isomer, presumably the trans isomer,



(5)

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Table II. Positional Parameters for the Non-Hydrogen Atoms of 4

atom	*x*	*y*	*z*	*B*(eq), Å^2
CP[a]	0.49074	0.24554	0.25455	
Fe	0.59338 (3)	0.27851 (3)	0.48624 (5)	4.22 (1)
C1	0.6308 (3)	0.4113 (2)	0.6824 (3)	3.60 (8)
C2	0.5267 (3)	0.3907 (3)	0.7729 (4)	3.96 (9)
C3	0.3509 (3)	0.2604 (3)	0.7502 (4)	4.6 (1)
C4	0.1144 (5)	0.1675 (3)	0.8491 (7)	8.4 (2)
C5	0.8019 (3)	0.5566 (3)	0.7367 (3)	3.86 (9)
C6	0.9254 (4)	0.5958 (3)	0.8937 (4)	5.2 (1)
C7	1.0846 (4)	0.7311 (3)	0.9434 (5)	6.1 (1)
C8	1.1208 (4)	0.8283 (3)	0.8390 (5)	5.7 (1)
C9	1.0000 (5)	0.7919 (3)	0.6852 (5)	6.5 (1)
C10	0.8402 (4)	0.6565 (3)	0.6323 (4)	5.3 (1)
C11	0.3672 (5)	0.1903 (3)	0.2883 (6)	8.0 (2)
C12	0.4192 (9)	0.1272 (3)	0.2396 (7)	11.6 (3)
C13	0.572 (1)	0.226 (1)	0.2111 (6)	19.2 (7)
C14	0.6141 (6)	0.3573 (7)	0.2448 (6)	10.2 (3)
C15	0.4818 (5)	0.3270 (4)	0.2890 (5)	8.1 (2)
C16	0.8004 (4)	0.3477 (3)	0.5717 (4)	5.3 (1)
C17	0.5236 (4)	0.1567 (3)	0.6305 (5)	5.4 (1)
O1	0.2700 (3)	0.1460 (2)	0.6551 (4)	6.8 (1)
O2	0.2858 (3)	0.2874 (2)	0.8543 (3)	6.31 (9)
O3	0.9309 (3)	0.3859 (3)	0.6229 (4)	8.2 (1)
O4	0.4876 (4)	0.0794 (3)	0.7265 (4)	9.5 (2)

[a] CP is the centroid of the Cp ring (C11–C15).

Table III. Positional Parameters for the Non-Hydrogen Atoms of 5

atom	*x*	*y*	*z*	*B*(eq), Å^2
CP[a]	0.72341	0.18333	0.79002	
Fe	0.67828 (3)	0.25106 (2)	0.92666 (5)	4.04 (1)
C1	0.8225 (3)	0.3236 (2)	1.1688 (3)	4.35 (8)
C2	0.8175 (3)	0.4230 (2)	1.1776 (4)	5.4 (1)
C3	0.7070 (3)	0.4509 (2)	1.0094 (4)	5.5 (1)
C4	0.5791 (5)	0.5724 (3)	0.8305 (6)	8.9 (2)
C5	0.9275 (3)	0.2815 (2)	1.3336 (3)	4.77 (8)
C6	0.8732 (4)	0.1908 (2)	1.3756 (4)	5.7 (1)
C7	0.9709 (4)	0.1511 (3)	1.5308 (4)	7.4 (1)
C8	1.1240 (5)	0.1986 (3)	1.6443 (5)	8.0 (2)
C9	1.1823 (4)	0.2884 (3)	1.6062 (5)	7.4 (1)
C10	1.0846 (4)	0.3304 (2)	1.4531 (4)	6.2 (1)
C11	0.8636 (3)	0.2056 (2)	0.8990 (4)	5.6 (1)
C12	0.7777 (3)	0.2598 (2)	0.7569 (4)	6.0 (1)
C13	0.6151 (3)	0.2079 (2)	0.6577 (3)	5.6 (1)
C14	0.6044 (3)	0.1219 (2)	0.7423 (4)	5.5 (1)
C15	0.7563 (3)	0.1214 (2)	0.8941 (4)	5.3 (1)
C16	1.0396 (4)	0.2297 (3)	1.0287 (6)	8.3 (2)
C17	0.8464 (6)	0.3562 (3)	0.7154 (7)	10.9 (2)
C18	0.4847 (5)	0.2376 (3)	0.4910 (5)	8.9 (2)
C19	0.4560 (5)	0.0413 (3)	0.6817 (5)	8.1 (2)
C20	0.8014 (5)	0.0370 (3)	1.0097 (5)	8.6 (2)
C21	0.5426 (3)	0.2073 (2)	0.9969 (3)	3.99 (7)
O1	0.6250 (2)	0.3873 (1)	0.8729 (2)	5.02 (6)
O2	0.6904 (3)	0.5466 (1)	1.0023 (3)	7.51 (9)
O3	0.4584 (2)	0.1760 (1)	1.0450 (2)	6.17 (7)

[a] CP is the centroid of the Cp* ring (C10–C14).

was selectively formed because of the steric repulsion between two Cp* groups. Similar compounds have been obtained by the reaction of 1 with other nucleophiles and have been structurally characterized.[7]

Molecular Structure and Spectral Assignment of 4 and 5. The crystallographic data, positional parameters, and selected interatomic distances and bond angles for 4 and 5 are summarized in Tables I–V, and the ORTEP drawings are reproduced in Figures 1 (4) and 2 (5).

The overall structure of 4 can be described as methyl (*Z*)-3-Fp-cinnamate. The structure of the Fp part is a typical three-legged piano-stool structure, and the structural parameters of the organic residue fall in the typical range of those of organic functional groups.[8]

Table IV. Selected Interatomic Distances (Å) and Bond Angles (deg) for 4

Interatomic Distances			
Fe–C1	1.999 (3)	C2–H2	0.94 (6)
Fe–O1	3.346 (3)	C3–O1	1.200 (4)
Fe–CP[a]	1.729	C3–O2	1.347 (5)
Fe–C16	1.768 (4)	O2–C4	1.448 (4)
Fe–C17	1.752 (3)	C–C(Ph)	1.357–1.386
C1–C2	1.341 (5)	C–C(Cp)	1.333–1.433
C1–C5	1.495 (2)	C16–O3	1.140 (5)
C2–C3	1.478 (3)	C17–O4	1.142 (5)
Bond Angles			
CP–Fe–C1	120.86	C2–C3–O1	128.6 (4)
CP–Fe–C16	125.00	C3–C2–H2	112 (3)
CP–Fe–C17	126.45	O1–C3–O2	122.1 (3)
C1–Fe–C16	93.9 (2)	C3–O2–O4	115.3 (3)
C1–Fe–C17	89.6 (2)	C1–C5–C6	120.8 (3)
C16–Fe–C17	91.3 (2)	C1–C5–C10	121.1 (2)
Fe–C1–C2	130.2 (1)	C–C–C(Ph)	119.4–121.1
Fe–C1–C5	114.8 (2)	C–C–C(Cp)	105.7–109.6
C1–C2–H2	120 (3)	Fe–C16–O3	176.6 (4)
C1–C2–C3	128.0 (3)	Fe–C16–O4	175.6 (4)

[a] CP is the centroid of the Cp ring (C11–C15).

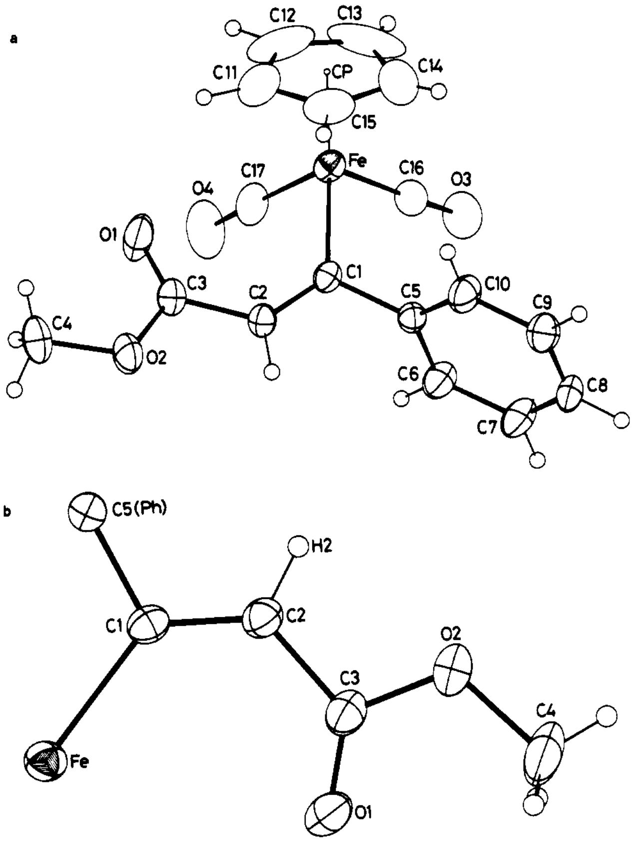

Figure 1. Molecular structure of 4 drawn at the 30% probability level: (a) perspective view; (b) view of the olefinic part.

On the other hand, 5 contains a metallacyclic structure with an O-coordinated ester group, as clearly indicated by the short Fe–O1 distance (2.009 Å; cf. 3, 3.364 Å). A similar metallacyclic structure has been found in the group 6 complexes CP(OC)$_2$M[C(R^1)=C(R^2)C(R^3)C(=O)R^4] (CP = Cp, Cp*; M = Cr, Mo, W) studied by Alt et al.[9] When the structural parameters associated with the metallacyclic part are compared with those of 4 and the tungsten com-

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Table V. Selected Interatomic Distances (Å) and Bond Angles (deg) for 5

	Interatomic Distances		
Fe–C1	1.954 (2)	C2–C3	1.421 (4)
Fe–O1	2.009 (2)	C3–O1	1.246 (3)
Fe–C21	1.748 (3)	C3–O2	1.336 (3)
Fe–C(Cp*)	2.009–2.128	O2–C4	1.432 (4)
Fe–CP[a]	1.723	C–C(Ph)	1.362–1.403
C1–C2	1.361 (4)	C–C(Cp*)	1.405–1.436
C1–C5	1.478 (3)	C–Me(Cp*)	1.498–1.527
C2–H2	0.95 (3)	C21–O3	1.128 (4)
	Bond Angles		
CP–Fe–C1	128.39	C2–C3–O1	120.9 (2)
CP–Fe–O1	120.37	C2–C3–O2	118.3 (2)
CP–Fe–C21	126.48	O1–C3–O2	120.7 (2)
C1–Fe–O1	81.99 (8)	Fe–O1–C3	111.2 (2)
C1–Fe–C21	89.3 (1)	C3–O2–C4	116.9 (2)
O1–Fe–C21	98.7 (1)	C1–C5–C6	120.8 (2)
Fe–C1–C2	112.9 (2)	C1–C5–C10	121.8 (3)
Fe–C1–C5	127.2 (2)	C–C–C(Ph)	119.65–121.76
C2–C1–C5	119.9 (2)	C–C–C(Cp*)	106.88–108.73
C1–C2–H2	125 (2)	C–C–Me(Cp*)	124.97–126.29
C1–C2–C3	113.0 (2)	Fe–C21–O3	177.2 (2)
H2–C2–C3	122 (2)		

[a] CP is the centroid of the Cp* ring (C10–C14).

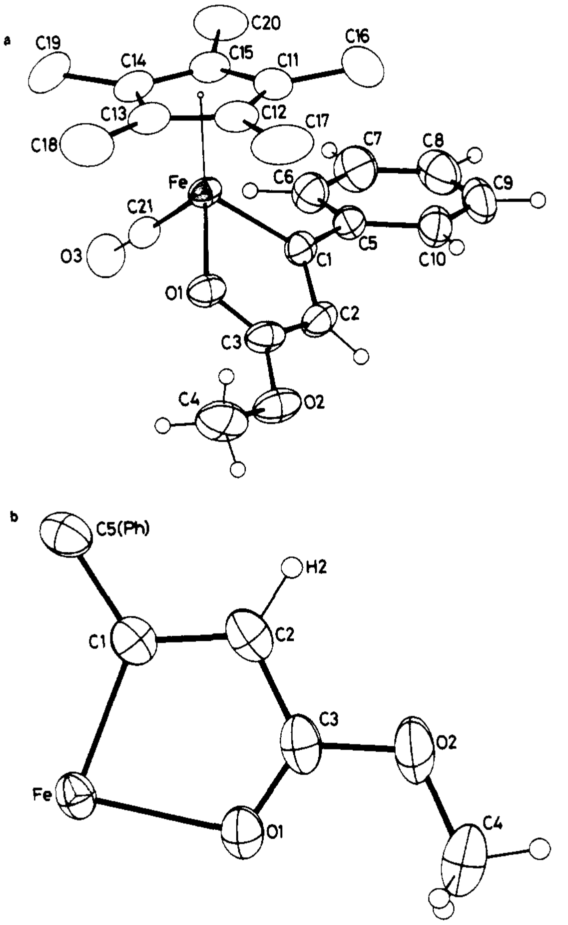
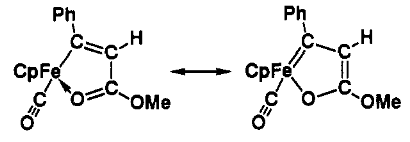


Figure 2. Molecular structure of **5** drawn at the 30% probability level: (a) perspective view; (b) view of the metallacyclic part.

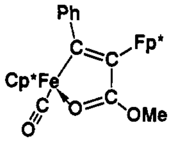
plex $Cp^*(OC)_2W[C(Me){=}C(Me)C(Me)C(O)Me]$ (**7**),[9] **5** shows very close similarities to **7** (Table VI). Elongation of d_2 (0.020 Å) and d_4 (0.046 Å) and shortening of d_1 (0.045 Å) and d_3 (0.057 Å) compared with those in **4** suggests contribution of the carbene structure **8** (Scheme II). Slight differences in d_3, d_4, and d_5 between **5** and **7** should be attributed to additional resonance structures brought about by the OMe group, and differences in d_1 and d_5 should be due to the dissimilar atomic radii of Fe and W.

Scheme II



8

Chart II



9

On the basis of this formulation the ^{13}C NMR signal of **5** observed at δ 247.0 is assigned to C1, which assumes carbene character.[10] In accord with this assignment, the tungsten complex **7** contains a signal in the same region (δ 253.5), and the C1 atom in **4**, for which contribution of a carbene structure such as **8** is not available, resonates in the usual olefinic carbon region (δ 168.7). The $\nu(C{\equiv}O)$ absorption of **5** shifts to lower energies (1895 cm^{-1}), and $\delta(C{\equiv}O)$ slightly shifts to lower field (δ 218.0) when compared to those of Fp* complexes ($\nu(C{\equiv}O)$ 2020–1950 cm^{-1}, $\delta(C{\equiv}O)$ 214–215). These changes may be brought about by the increased back-donation from Fe to C≡O caused by replacement of one of two CO ligands in an Fp* complex by a less electron withdrawing ester sp^2 oxygen atom. The deep green oil **3** also contains the ^{13}C NMR signal at low field (δ 240.7) as well as $\nu(C{\equiv}O)$ absorptions at lower energies (1916 cm^{-1}). The remaining two $\nu(C{\equiv}O)$ absorptions at higher energies are observed in the typical region for those of Fp complexes, and the two CO ligands in the Fp group are separately observed by ^{13}C NMR spectroscopy because of a chiral metal center in the metallacycle. These spectroscopic features are consistently interpreted in terms of the metallacyclic structure shown in Chart I.

Mechanism of the Reaction of 1b,c with NaOMe. The reaction of **1c** with NaOMe produced the dinuclear metallacycle **3**. Hydrolysis of **3** resulted in cleavage of the Fe–C bond with retention of stereochemistry, and at the same time, the coordinated ester sp^2 oxygen atom was replaced by a CO ligand.

The reaction of **1b** with NaOMe afforded the mononuclear complex **5** along with the dinuclear vinylidene complex **6**. **5** was supposed to be formed by the Fe–C bond cleavage of the transient dinuclear complex $[Cp^*(OC)FeC(Ph){=}C(Fp^*)(C{=}O)OMe]$ (**9**; the Fp* analog of **3**) (Chart II). We could actually isolate orange solids containing a few products (see Experimental Section). The ^1H NMR spectra of the mixture in $CDCl_3$ showed that the intensities of the signals due to **5** and Fp*Cl[11] increased with the consumption of a set of three singlet signals at δ 1.57, 1.68 (Cp* region), and 3.53 (OMe region), which might be attributed to **9**, and that the methyne carbon was not deuterated during decomposition in $CDCl_3$. In addition, when the reaction mixture was treated with alumina that was pretreated with D_2O, no deuterium was incorporated, as confirmed by ^1H NMR as well as ^2H NMR spectroscopy. It could be therefore presumed that the Fe–C bond cleavage of **9** took place prior to workup be-

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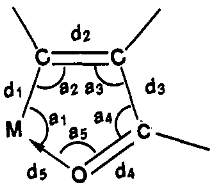
(10) Mann, B. F.; Taylor, B. F. *^{13}C-NMR Data for Organometallic Compounds*; Academic: New York, 1981.

(11) Clegg, W.; Compton, N. A.; Errington, R. J.; Norman, N. C. *J. Chem. Soc., Dalton Trans.* **1988**, 1671.

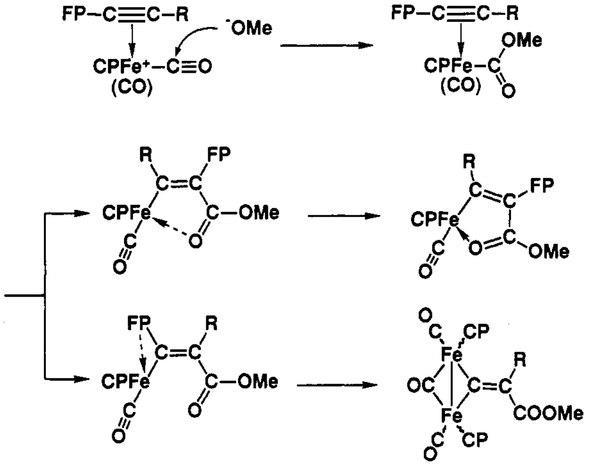
Table VI. Structural Parameters for the Metallacyclic Part of 4, 5, and 7[a]



complex	d_1	d_2	d_3	d_4	d_5	a_1	a_2	a_3	a_4	a_5
4	1.999	1.341	1.478	1.200	3.364		130.2	128.0	128.6	
5	1.954	1.361	1.421	1.246	2.009	81.99	112.9	113.0	120.9	111.2
7	2.145	1.360	1.389	1.294	2.104	73.9	115.6	114.5	117.6	117.9

[a] *d* values are in Å in *a* values in deg.

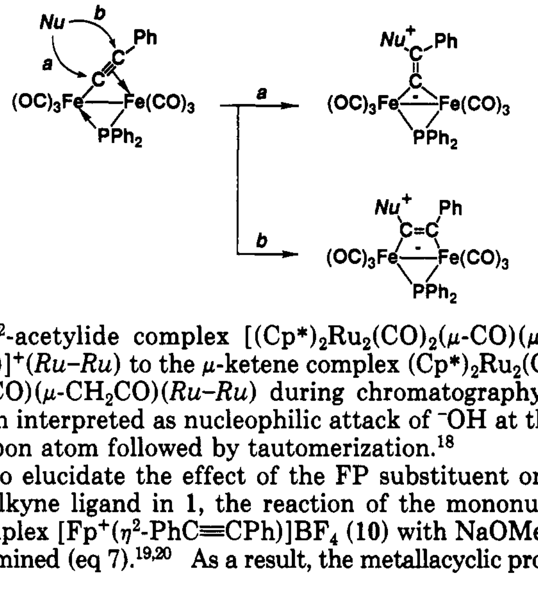
Scheme III



cause of the steric effect of the Fp* group.

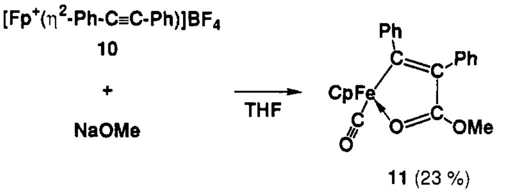
A plausible mechanism for the formation of 3, 6, and 9 is shown in Scheme III.[12] Nucleophilic attack of ⁻OMe at the CO ligand forms an acyl intermediate. Subsequent insertion of the C≡C bond into the resulting Fe—acyl bond forms an acyl-substituted alkenyl ligand. In this step two modes of insertion are possible, depending on the orientation of the η^2-alkyne ligand. At the last stage of the reaction, in the absence of an exogeneous ligand coordination of the sp^2 oxygen atom of the ester group or dative Fe–Fe bond formation will lead to the formation of the coordinatively saturated final products 3, 6, and 9.

In contrast to the well-documented nucleophilic addition to a coordinated CO[13] or η^2-alkyne ligand,[2,3] the reaction of transition-metal complexes containing both ligands has been less extensively studied. According to Reger's works[3] nucleophiles including ⁻OMe (with the exception of H^-[4] and R_2N^- and R^-,[14] which add to a Cp ring) attack the η^2-alkyne ligand in [CpFe$^+$(CO)(PR$_3$)(η^2-alkyne)] complexes to give η^1-alkenyl complexes. Although the reactivity of [Fp$^+$(η^2-alkyne)] complexes toward nucleophiles has been less extensively studied, it has been reported that hydride[15] and very mild carbon nucleophiles such as π-electrons of alkenes and alkynes[16] attack the η^2-alkyne ligand. A similar reaction pattern has been observed in the reaction of a polynuclear μ-η^1:η^2-acetylide complex with nucleophiles. For example, the reaction of a diiron phosphide-bridged μ-η^1:η^2-acetylide complex with group 15 nucleophiles afforded two types of products, as shown in eq 6.[17] The transformation of the diruthenium μ-η^1:η^2-acetylide complex [(Cp*)$_2$Ru$_2$(CO)$_2$(μ-CO)(μ-C≡CH)]$^+$(*Ru–Ru*) to the μ-ketene complex (Cp*)$_2$Ru$_2$(CO)$_2$(μ-CO)(μ-CH$_2$CO)(*Ru–Ru*) during chromatography has been interpreted as nucleophilic attack of ⁻OH at the α-carbon atom followed by tautomerization.[18]



(6)

To elucidate the effect of the FP substituent on the η^2-alkyne ligand in 1, the reaction of the mononuclear complex [Fp$^+$(η^2-PhC≡CPh)]BF$_4$ (10) with NaOMe was examined (eq 7).[19,20] As a result, the metallacyclic product



(7)

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[12] Concomitant formation of a small amount of (FP)$_2$ was evident in every reaction of 1 with NaOMe. (FP)$_2$ may arise from β-elimination of (FP)OMe, which may be formed by either dissociation of the η^2-alkyne ligand from the CpFe(CO)(η^2-alkyne)(COOMe) intermediate followed by migration of the MeO group to the metal center or dissociation of the η^2-alkyne ligand in 1 followed by addition of ⁻OMe. Since 1 is stable in the presence of THF, we suppose that (FP)$_2$ is formed by way of the former reaction route; i.e., the formation of (FP)$_2$ is also initiated by the nucleophilic addition of ⁻OMe to a CO ligand.

[13] Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139.

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

[15] Reger, D. L.; Coleman, C. J.; McElligot, P. J. *J. Organomet. Chem.* **1979**, *171*, 73.

[16] Rosenblum, M. *J. Organomet. Chem.* **1986**, *300*, 191.

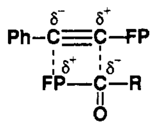
[17] Carty, A. *Pure Appl. Chem.* **1982**, *54*, 113.

[18] Doherty, N. M.; Fildes, M. J.; Forrow, N. J.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1355.

[19] Rosenblum et al. reported that methanolysis of [Fp$^+$(η^2-EtC≡CEt)]BF$_4$ afforded [Fp$^+$(η^2-Et(H)C═C(OMe)Et)]BF$_4$. This reaction has been interpreted as the initial nucleophilic attack of MeOH at the η^2-alkyne ligand to form the η^1-alkenyl complex FpC(Et)═C(OMe)Et followed by protonolysis of the Fe–C σ bond, although no intermediate was observed (Bates, D. J.; Rosenblum, M.; Samuels, S. B. *J. Organomet. Chem.* **1981**, *209*, C55).

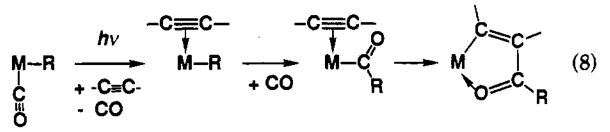
[20] Stirring 1a in MeOH afforded Fp*C(O)CH$_3$ in low yield. The acetyl complex may be formed by the initial attack of MeOH at the α-carbon, giving Fp*C(OMe)═C(H)Fp*, protonolysis of the Fe-CH═ bond, and hydrolysis of the resulting vinyl ether complex Fp*C(OMe)═CH$_2$. The Fp analogue FpC(OMe)═CH$_2$ was reported to be readily hydrolyzed to give the corresponding acetyl complex (Casey, C. P.; Tukada, H.; Miles, W. H. *Organometallics* **1982**, *1*, 1083). This is the only indication that a nucleophile might attack the α-carbon in 1.

Chart III



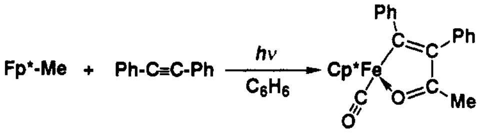
11 was isolated in 23% yield along with Fp_2 (31% yield). No indication of the formation of the η^1-alkenyl complex FpC(Ph)=C(OMe)Ph was observed. The structure of **11** was determined on the basis of the diagnostic δ_{CO} absorption at low field (237.8 ppm) and ν_{CO} bands at lower energies (1934 cm^{-1}). Consequently, the nucleophilic attack of the $^-$OMe anion at a terminal CO ligand rather than a η^2-alkyne ligand in a [CpFe$^+$(CO)(L)(η^2-RC≡CR)] complex seems to be a general reaction route irrespective of substituents (R) when L = CO. Our results contrast strikingly with the results when L = PR_3.[21] The different regiochemistry may be explained in terms of a steric effect. When a nucleophile attacks a η^2-alkyne ligand, the nucleophile may approach from an opposite side of the metal center. However, in the case of attack at a CO ligand a nucleophile should approach the CO ligand from its lateral side in order to interact with its π^* orbital. Under such circumstances the nucleophile should suffer steric repulsion with other ancillary ligands. When L is a bulky ligand such as PPh_3 and $P(OPh)_3$, the attack at a CO ligand will be greatly hindered, as revealed by the structure determination of [CpFe(CO)(P(OPh)$_3$(RC≡CR)]SbF$_6$ complexes.[22,23]

There are several precedents for the second step, i.e. insertion of a C≡C functional group into a metal–acyl bond.[24] Generally, irradiation of an alkylmetal carbonyl complex in the presence of alkyne results in the formation of an acyl-substituted alkenyl ligand (eq 8). In most cases the product is stabilized by the formation of a metallacyclic structure, i.e. intramolecular coordination of the acyl oxygen atom to the metal center. Actually, irradiation of Fp*CH$_3$ in benzene in the presence of PhC≡CPh gave the metallacyclic product **12** (eq 9).



(8)

As to the orientation of the alkyne ligand in the insertion step, it has been frequently observed that an electron-accepting substituent such as Ph, C(O)OR, and CF$_3$ tends to occupy the α-position in the metallacycle, while only 1-alkynes have been examined as asymmetrically substituted alkynes.[24] The orientation found in the major products **3** and **9** may be explained by electrostatic interaction as shown in Chart III. On the other hand, **6** should be formed via coupling with the oppositely directed alkyne. In this case, a dative M→M interaction should promote the migratory insertion of the C≡C group, and the insertion step may become irreversible by construction of a very stable vinylidene structure with a metal–metal bond and two bridging ligands.



(9)

12

Conclusion

The reaction of cationic diiron μ-η^1:η^2-phenylethynyl complexes [(FP)$_2$(C≡CPh)]BF$_4$ (**1b,c**) with NaOMe takes place at the terminal carbonyl ligand in the cationic FP part. The C≡C functional group inserts into the resulting Fe—acyl bond to give the metallacyclic product or the vinylidene complex. It should be noted that such regiochemistry on addition of $^-$OMe is not peculiar to dinuclear complexes, and a metallacyclic adduct is formed by the reaction of [Fp$^+$(η^2-PhC≡CPh)]BF$_4$ (**10**). The present study also reveals that an initial nucleophilic attack of a nucleophile at a coordinated CO ligand instead of a η^2-alkyne ligand leads to successful three-component C—C bond formation among an exogeneous Nu and endogeneous CO and C≡C groups in a one-pot reaction to form an enone structure (α,β-unsaturated carbonyl compounds). In contrast, in the case of the ethynyl complex [(Fp)*$_2$(C≡CH)]BF$_4$ (**1a**) Fp*C≡CFp* is formed by deprotonation.

Experimental Section

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

THF and CH$_2$Cl$_2$ were dried over Na–K/benzophenone and P$_2$O$_5$, respectively, distilled, and stored under argon. Solvents for NMR measurements containing 0.5% TMS as an internal standard were dried over molecular sieves, distilled under reduced pressure, and stored under argon. **1a–c** were prepared according to the method in our previous paper.[1] Fp*Me was prepared by treatment of NaFp*[25] with MeI. **10** was prepared according to the published method.[26] NaOMe was prepared by dissolving Na in dry MeOH followed by removal of the solvent under reduced pressure. Alumina (activity II–III: Merck Art. 1097) was used for chromatographic separation. ^{1}H and ^{13}C NMR spectra were recorded on JEOL FX-100 (100 MHz) and a 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 the Tokyo Institute of Technology.

Reaction of [(Fp*)$_2$(C≡CH)]BF$_4$ (1a) with NaOMe. 1a (1.98 g, 3.26 mmol) and NaOMe (0.63 g, 11.8 mmol) were stirred overnight in THF (45 mL). After evaporation of the volatiles the products were extracted with ether. Salts were removed by filtration through a short alumina column, and the products were

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[21] No product resulting from attack at CO in [CpFe$^+$(CO)(PR$_3$)(η^2-alkyne] complexes has been observed: Reger, D. L. Personal communication.

[22] Reger, D. L.; Klaeren, S. A.; Lebioda, L. *Organometallics* **1988**, *7*, 189.

[23] A preliminary EHMO calculation on [CpFe$^+$(CO)$_2$(η^2-HC≡CH)] (A) and [CpFe$^+$(CO)(PH$_3$)(η^2-HC≡CH)] (B) has revealed that in both complexes the CO carbon atoms are slightly positively charged and the HC≡CH carbon atoms are slightly negatively charged and that substitution of one of the two CO ligands in A with PH$_3$ does not result in an increase of negative charge on the CO carbon or increase of positive charge on the HC≡CH carbon in the ground state. (No significant difference in charge on the CO and HC≡CH carbon atoms has been observed between A and B.) Slippage of the η^2-HC≡CH ligand, which promotes nucleophilic addition (Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *104*, 4308), may be facilitated in the case of B with an unsymmetrical electronic structure.

[24] (a) Booth, B. L.; Hargreaves, R. G. *J. Chem. Soc. A* **1970**, 308. (b) Watson, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055. (c) Murray, T. F.; Norton, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4107. (d) Bottrill, M.; Green, M.; O'Brien, E. O.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 292. (e) Davidson, J. L.; Shiralian, M.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1984**, 2167. (f) Carmona, E.; Gutierrez-Puebla, E.; Monge, A.; Marin, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1984**, *3*, 1438. (g) Burkhardt, E. B.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022.

[25] Guerchais, V.; Astruc, D.; Nunn, C. M.; Cowley, A. H. *Organometallics* **1990**, *9*, 1036.

[26] Reger, D. L.; Coleman, C. J.; McElligot, P. J. *J. Organomet. Chem.* **1979**, *171*, 73.

separated by column chromatography. Elution with CH_2Cl_2/hexane (1/3) gave a purple band (Fp*)$_2$). Subsequent elution with CH_2Cl_2 gave an orange band, from which **2** (0.69 g, 1.33 mmol, 41% yield) was isolated as brick red crystals by recrystallization from ether/hexanes: ^{1}H NMR (C_6D_6(δ 1.78 (s, C_5Me_5); ^{13}C NMR (C_6D_6) δ 9.9 (q, J = 127.8 Hz, $C_5\mathit{Me}_5$), 96.2 (s, C_5Me_5), 98.1 (s, $C{\equiv}C$), 217.5 (s, $C{\equiv}O$); IR (KBr) 1995, 1953 cm^{-1}. Anal. Calcd for $C_{28}H_{30}O_4Fe$: C, 60.29; H, 5.79. Found: C, 60.33; H, 5.66.

Reaction of [(Fp)$_2$(C≡CPh)]BF$_4$ (1c) with NaOMe. **1c** (4.20 g, 7.80 mmol) and NaOMe (1.26 g, 23.3 mmol) were stirred in THF (40 mL) for 1 h at room temperature. After evaporation of the volatiles the products were extracted with ether and the inorganic salts were separated by centrifugation. The organometallic products were adsorbed on alumina (4 g), and the solvent was removed under reduced pressure. The residue was put on the top of an alumina column (2 cm × 25 cm) made up in hexane. Collection of the green band eluted with CH_2Cl_2/hexane (1/3) followed by evaporation gave a deep green oil, which was dissolved in CH_2Cl_2 and was filtered through a short alumina column (2 cm × 2 cm) under argon. Removal of the solvent under reduced pressure gave spectroscopically pure **3** (2.37 g, 4.83 mmol, 62% yield) as a deep green oil. We could not get an analytically pure sample. **3**: ^{1}H NMR (acetone-d_6) δ 3.69 (s, 3 H, OMe), 4.23 (s, 5 H, Cp), 4.83 (s, 5 H, Cp), 7.01–7.38 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 53.4 (q, J = 147.5 Hz, OMe), 82.2 (d, J = 177.0 Hz, Cp), 85.4 (d, J = 180.8 Hz, Cp), 111.2 (s, $=C$—Fe), 123.6 (d, J = 157.7 Hz, *p* Ph), 123.7 (d, J = 157.7 Hz, *m* Ph), 127.3 (dd, J = 159.0, 6.4 Hz, *o* Ph), 157.9 (s, ipso Ph), 183.9 (s, $C{=}O$), 215.9, 216.0, 219.2 (s × 3, $C{\equiv}O$), 240.7 (s, $=C$—Ph); IR (CH_2Cl_2) 2008, 1958, 1916 cm^{-1}.

Hydrolysis of 3. A 1 M aqueous HCl solution (3 mL) was added to **3** (514.5 mg, 1.05 mmol) dissolved in ether (10 mL), and the mixture was stirred for 2 h at room temperature. The aqueous layer was removed by a pipet, and the remaining organic layer was dried over $MgSO_4$. After separation of $MgSO_4$ the organometallic products were adsorbed on alumina and the product was isolated by column chromatography. Collection of the yellow band followed by recrystallization from CH_2Cl_2/hexane gave **4** (61.2 mg, 0.18 mmol, 17% yield) as orange-yellow crystals: ^{1}H NMR (benzene-d_6) δ 3.52 (s, 3 H, OMe), 4.15 (s, 1 H, $=CH$), 4.33 (s, 5 H, Cp), 6.77–7.59 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 50.7 (q, J = 146.2 Hz, OMe), 86.3 (d, J = 181.2, Cp), 124.2 (dt, J = 155.7, 6.8 Hz, *m* Ph), 125.1 (dt, J = 162.1, 7.2 Hz, *p* Ph), 127.8 (dd, J = 157.4, 8.0 Hz, *o* Ph), 132.3 (d, J = 157.3 Hz, $=CH$), 159.2 (t, J = 6.4 Hz, ipso Ph), 168.7 (s, $=C$Fp), 187.8 (s, $C{=}O$), 214.0 (s, $C{\equiv}O$); IR (Ch_2Cl_2) 2024, 1974, 1703 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_4Fe$: C, 60.38; H, 4.17. Found: C, 60.52; H, 4.21.

Reaction of [(Fp*)$_2$(C≡CPh)]BF$_4$ (1b) with NaOMe. **1b** (1.57 g, 2.31 mmol) and NaOMe (0.16 g, 2.96 mmol) were stirred overnight in THF (40 mL). After extraction with ether and removal of salts as described above, the products were separated by column chromatography. (Fp*)$_2$ was eluted at first. A deep green band containing **5** and (Fp*)$_2$ was eluted with CH_2Cl_2/hexane (1/(8–15)). **5** (0.18 g, 0.51 mmol, 22% yield) was isolated as green crystals after removal of (Fp*)$_2$ by repeating recrystallization from ether/hexane three times. Elution with CH_2Cl_2 gave a blue-violet band, from which **6** (55 mg, 0.145 mmol, 6% yield) was isolated as violet crystals. Orange solids (21 mg) were obtained by further elution with CH_2Cl_2. **5**: ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 15 H, C_5Me_5), 3.69 (s, 3 H, OMe), 6.18 (s, 1 H, $=CH$), 7.0–7.3 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 9.1 (q, J = 126.9 Hz, $C_5\mathit{Me}_5$), 52.8 (q, J = 147.4 Hz, OMe), 90.5 (s, C_5Me_5), 117.6 (d, J = 164.6 Hz, $=CH$), 125.9 (dt, J = 159.5, 6.9 Hz, *m* Ph), 127.4 (dt, J = 159.5, 6.9 Hz, *p* Ph), 127.6 (dd, J = 159.4, 6.9 Hz, *o* Ph), 150.4 (m, ipso Ph), 179.9 (q, J = 3.4 Hz, $C{=}O$), 218.0 (s, CO), 247.0 (dt, J = 3.2, 5.2 Hz, *C*Ph); IR (KBr) 1895, 1574, 1565, 1472, 1449, 1352 cm^{-1}. Anal. Calcd for $C_{19}H_{24}O_3Fe$: C, 66.36; H, 6.31. Found: C, 65.70; H, 6.34. **6**: ^{1}H NMR ($CDCl_3$; 270 MHz) δ 1.32 (s, 15 H, C_5Me_5), 1.67 (s, 15 H, C_5Me_5), 3.81 (s, 3 H, OMe), 7.18 (t 1 H, J = 6.9 Hz, *p* Ph), 7.32 (t, 2 H, J = 7.3 Hz, *m* Ph), 7.58 (d 2 H, J = 7.2 Hz, *o* Ph); ^{13}C NMR ($CDCl_3$) δ 8.6 (q, J = 126.9 Hz, $C_5\mathit{Me}_5$), 9.1 (q, J = 128.6 Hz, $C_5\mathit{Me}_5$), 50.9 (q, J = 145.7 Hz, OMe), 100.0 (s, C_5Me_5), 100.1 (s, C_5Me_5), 125.3 (dt, J = 159.5, 7.8 Hz, *p* Ph), 127.5 (dd, J = 159.4, 7.8 Hz, *o* Ph), 131.1 (dt, J = 159.5, 7.7 Hz, *m* Ph), 142.8 (t, J = 7.7 Hz, ipso Ph), 145.0 (s, $=C$Ph), 168.1 (s, *C*OOMe), 215.3 (s, CO), 216.7 (s, CO), 275.5 (s, μ-CO), 335.7 (s, μ-*C*=CPh); IR (KBr) 1951, 1924, 1776, 1677 cm^{-1}. Anal. Calcd for $C_{33}H_{38}O_5Fe_2$: C, 63.31; H, 6.07. Found: C, 63.39; H, 5.83.

Reaction of [(Fp*)$_2$(C≡CPh)]BF$_4$ (1b) with NaOMe Followed by Treatment with D$_2$O-Pretreated Alumina. The reaction of **1b** (0.88 g, 1.29 mmol) with NaOMe (0.30 g, 5.53 mmol) was carried out in THF (12 mL) as shown above. After the volatiles were evaporated, the products were extracted with ether and salts were removed by filtration through a Celite pad. To the resulting solution was added D_2O-treated alumina, which was prepared by stirring alumina (1.2 g) with D_2O (1 mL) overnight followed by evaporation. After 2 h the mixture was worked up as described above, and **6** (0.10 g, 0.26 mmol, 20% yield) was obtained. The methyne proton was not deuterated as revealed by ^{1}H NMR spectroscopy, and no signal was observed by ^{2}H NMR measurement.

Reaction of [Fp$^+$(PhC≡CPh)]BF$_4$ (10) with NaOMe. To a stirred suspension of **10** (1.92 g, 4.36 mmol) in THF (80 mL) cooled at −78 °C was added NaOMe (898 mg, 16.6 mmol) in small portions. The mixture was gradually warmed to room temperature with stirring, and during that time the mixture darkened. After separation of salts by filtration through an alumina pad the products were separated by column chromatography, which gave brown and purple bands (eluted with CH_2Cl_2/hexane 1/4). **11** (396.1 mg, 0.986 mmol, 23% yield) was isolated from the brown band as black crystals after recrystallization from ether/hexane. (Fp)$_2$ (240.2 mg, 0.68 mmol, 31% yield) was obtained by evaporation of the purple band. Two other unknown fractions in low yields (brownish yellow, 16 mg; dark brown, 19 mg) were also obtained. **11**: ^{1}H NMR ($CDCl_3$) δ 3.71 (s, 3 H, OMe), 4.38 (s, 5 H, Cp), 6.9–7.4 (m, 10 H, Ph × 2); ^{13}C NMR ($CDCl_3$) δ 53.4 (q, J = 147.5 Hz, OMe), 82.3 (d, J = 177.0 Hz, Cp), 125.2 (dt, J = 160.2, 6.1 Hz, *m* Ph), 125.4 (dt, J = 161.8, 6.9 Hz, *p* Ph), 125.7 (dd, J = 158.7, 7.7 Hz, *o* Ph), 127.5 (dd, J = 161.7, 7.6 Hz, *o* Ph), 130.4 (dt, J = 160.2, 6.9 Hz, *m* Ph), 131.3 (s, FeC=*C*), 136.4, (t, J = 7.6 Hz, ipso Ph), 152.7 (t, J = 6.1 Hz, ipso Ph), 179.5 (s, *C*OOMe), 218.4 (s, CO), 237.8 (s, FeCPh); IR (CH_2Cl_2) 1934 cm^{-1}; IR (KBr) 1947, 1921 cm^{-1}. Anal. Calcd for $C_{22}H_{18}O_3Fe$: C, 68.41; H, 4.70. Found: C, 68.71; H, 4.98.

Photolysis of Fp*Me in the Presence of PhC≡CPh. A benzene solution (30 mL) of Fp*Me (1.023 g, 3.90 mmol) and PhC≡CPh (943 mg, 5.30 mmol) was irradiated for 32 h by a high-pressure mercury lamp. Separation by column chromatography gave Fp*Me (425 mg, 1.62 mmol, 42% recovery), (Fp*)$_2$ (179 mg, 0.362 mmol, 18% yield), and the red-violet oil **12** (352 mg, 0.800 mmol, 21% yield). An analytically pure sample of **12** could not be obtained. **12**: ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 15 H, C_5Me_5), 2.03 (s, 3 H, CH_3), 7.0–7.6 (m, 10 H, Ph × 2); ^{13}C NMR ($CDCl_3$) δ 8.9 (q, J = 126.9 Hz, $C_5\mathit{Me}_5$), 25.8 (q, J = 128.0 Hz, $\mathit{C}H_3CO$), 92.2 (s, C_5Me_5), 125.3 (dt, J = 161.1, 6.9 Hz, *p* Ph), 125.5 (dt, J = 159.4, 8.6 Hz, *p* Ph), 126.0 (dt, J = 159.5, 6.0 Hz, *m* Ph), 126.6 (dd, J = 159.4, 6.8 Hz, *o* Ph), 127.7 (dd, J = 159.4, 8.6 Hz, *o* Ph), 130.9 (dt, J = 159.4, 6.0 Hz, *m* Ph), 139.7 (t, J = 6.9 Hz, ipso Ph), 146.2 (s, FeC=*C*), 150.9 (t, J = 6.0, ipso Ph), 206.6 (q, J = 5.7 Hz, $C{=}O$), 217.1 (s, CO), 262.7 (s, FeCPh); IR (KBr) 1916 cm^{-1}.

Single-Crystal X-ray Diffraction Studies. Suitable crystals were mounted on glass fibers. Diffraction measurements were made on the Rigaku AFC-5 automated four-circle diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.71058 Å). Unit cells were determined and refined by a least-squares method for 25 independent reflections with 25° < 2θ < 30°. Data were collected with the ω–2θ scan technique, and the scan speed was 6°/min. If $\sigma(F)/F$ 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 after every 100 measurements. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a FACOM A-70 computer by using the R-CRYSTAN structure solving system obtained from the Rigaku Corp., Tokyo, Japan. Neutral scattering factors were obtained from the standard sources.[27] In the reduction of data, Lorentz and polarization corrections were made and no absorption correction

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

was made. Full-matrix least-squares refinement minimized the function $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/[\sum(F_o)^2 + (pF_o)^2]$.

4 and 5 were crystallized in a triclinic system. The positions of Fe atoms were located by the direct method (4) and the Patterson method (5). Subsequent difference Fourier maps revealed the positions of all atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters and all hydrogen atoms with isotropic thermal parameters.

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Note Added in Proof: After submission of this paper two reports on the (μ-η^1:η^1-ethynediyl)dimetal complex (μ-C_2)[CpM(CO)$_n$]$_2$ (M = W, n = 3;[28a] M = Ru, n = 2[28b]) appeared.

Supplementary Material Available: Tables of positional parameters of the hydrogen atoms, anisotropic thermal parameters, and all bond distances and angles for 4 and 5 (17 pages); tables of observed and calculated structure factors for 4 and 5 (36 pages). Ordering information is given on any current masthead page.

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Analytical Study of a Series of Substituted (2,2′-Bipyridyl)(pentamethylcyclopentadienyl)rhodium and -iridium Complexes with Regard to Their Effectiveness as Redox Catalysts for the Indirect Electrochemical and Chemical Reduction of NAD(P)$^+$

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The influence of the substituents in the 2,2′-bipyridine ligands of $[(C_5Me_5)Rh(bpy)(H_2O)]Cl_2$ complexes on their electrochemical behavior and their effectiveness as redox catalysts toward the chemical (using formate as donor) or indirect electrochemical reduction of NAD(P)$^+$ to NAD(P)H have been studied in detail. The electrochemically or chemically reduced complexes have been shown to act as hydride atom transfer agents. The intermediate rhodium hydride complex was identified by ^{1}H NMR spectroscopy by using 6,6′-dimethyl-2,2′-bipyridine as the ligand. The catalytic efficiency is decreased by electron-withdrawing substituents in the 2,2′-bipyridine ligand, while it is increased by electron-donating substituents. Because of steric effects, substituents in the 6-position of the ligand slow down the catalytic reaction. The formation of the rhodium hydride complexes by formate shows a Michaelis type kinetic behavior, if the formate concentration is varied while the hydride transfer to NAD$^+$ is zero order in NAD$^+$. A number of effective catalysts for the NAD(P)$^+$ reduction have thus been obtained.

Introduction

To a great extent, the reduced forms of nicotinamide adenine dinucleotide (NADH) or nicotinamide adenine dinucleotide phosphate (NADPH) are the hydride donors in enzymatic reductions. The application of enzymes as extraordinarily effective biocatalysts in organic synthesis is increasing. Reactions catalyzed by dehydrogenases are of special value for organic synthesis, because they possess high chemo-, regio-, and stereospecifity. Therefore an effective and broadly applicable regeneration method for NADH and NADPH is indispensable.

The most frequently used procedure is enzyme-catalyzed regeneration of NADH or NADPH.[1] A system for continuous production of amino acids with regeneration of NADH with formate catalyzed by formate dehydrogenase is technically already highly developed.[2] But these enzyme-coupled cofactor regeneration systems are rather complicated, because they include two enzymes, two products, and two substrates. Indirect electrochemical regeneration of NAD(P)H from NAD(P)$^+$ using methylviologen as mediator is shown to be possible under cocatalysis of special redox enzymes or microorganisms.[3] These enzymes are able to accept electrons from the me-

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