Synthesis and Characterization of $(CH{=}CH)_3$-Bridged Heterobimetallic Ferrocene−Ruthenium Complexes

Ping Yuan,[†] Sheng Hua Liu,*,[†] Weicheng Xiong,[†] Jun Yin,[†] Guang-ao Yu,[†] Ho Yung Sung,[‡] Ian D. Williams,[‡] and Guochen Jia[‡]

Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China, and Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Received November 30, 2004

The complex $Fc(CH{=}CH)_2C{\equiv}C$-TMS (Fc = ferrocenyl) was obtained from Wittig olefination of $FcCH_2PPh_3Br$ with TMS-$C{\equiv}CCH{=}CHCHO$ in THF. The conjugated monometallic diene can be desilylated to give $Fc(CH{=}CH)_2C{\equiv}CH$, which reacted with $RuHCl(CO)(PPh_3)_3$ to produce $Fc(CH{=}CH)_3RuCl(CO)(PPh_3)_2$. Treatment of the latter complex with PMe_3, 4-phenylpyridine (PhPy), 2,6-$(Ph_2PCH_2)_2C_5H_3N$ (PMP), and KTp (Tp = hydridotris(pyrazolyl)-borate) gave $Fc(CH{=}CH)_3RuCl(CO)(PMe_3)_3$, $Fc(CH{=}CH)_3RuCl(CO)(PhPy)(PPh_3)_2$, $Fc(CH{=}CH)_3RuCl(CO)(PMP)$, and $Fc(CH{=}CH)_3RuTp(CO)(PPh_3)$, respectively. The structures of $Fc(CH{=}CH)_2C{\equiv}CH$ and $Fc(CH{=}CH)_3RuCl(CO)(PMe_3)_3$ have been confirmed by X-ray diffraction.

Introduction

Bimetallic and polymetallic complexes with conjugated hydrocarbon ligands bridging metal centers are attracting considerable current interest.[1,2] Bimetallic complexes with polyynediyl bridges, $M-(C{\equiv}C)_n-M'$, constitute the most fundamental class of carbon-based molecular wires, and they have been proposed for construction of nanoscale electronic devices.[3] To date, C_1, C_2, C_3, C_4, C_5, C_6, C_8, C_{10}, C_{12}, C_{16}, and C_{20} adducts have been isolated.[4−13] In contrast, very few studies have been carried out with bimetallic complexes with polyenediyl bridges, despite the fact that many conjugated organic materials (e.g. polyacetylenes, push/pull stilbenes) have only sp^2-hybridized carbon in their backbones and polyacetylenes have high electrical conductivity (up to 10^5 S cm^{-1}) upon doping.[14] Nonbranched monodisperse π-conjugated oligoenes $R(CR'{=}CR'')_nR$ (R′, R″ = H, Me, R = Ar, CHO, n = 3, 5, ..., 11) have been synthesized, and they have promising electronic and

† Central China Normal University.

‡ The Hong Kong University of Science and Technology.

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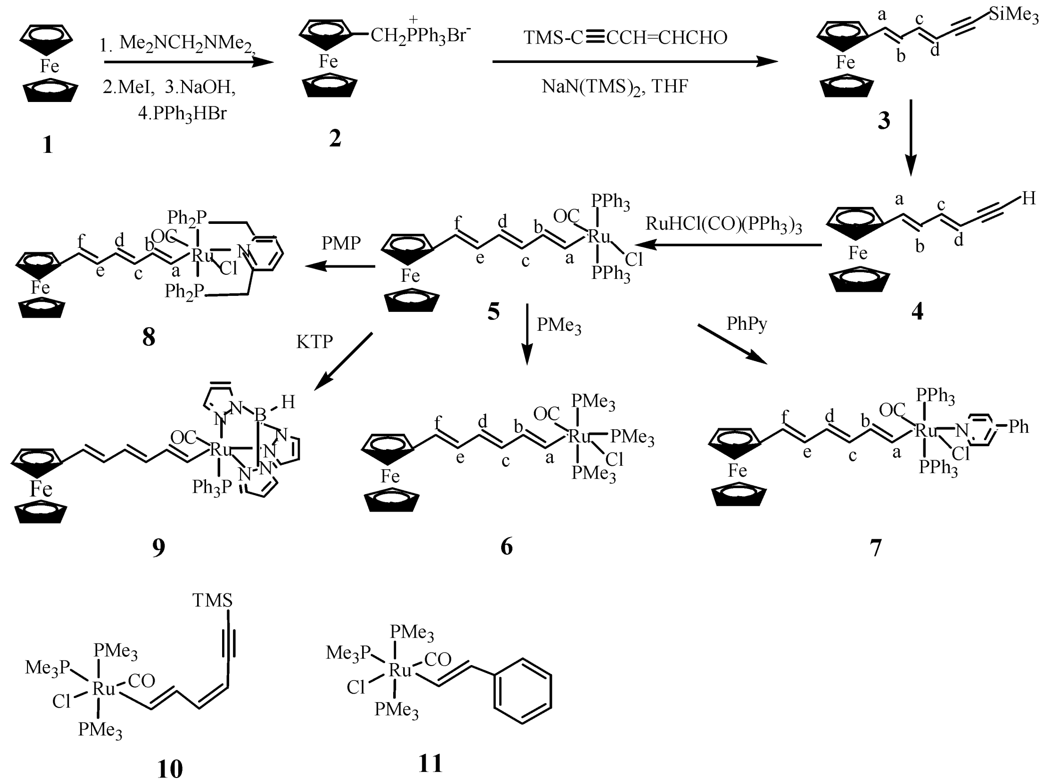
Publication on Web 02/25/2005

Scheme 1



optical properties.[15] Previously reported examples of $(CH)_x$-bridged bimetallic complexes are limited to a few of those with nonbranched $(CH)_2$,[16] $(CH)_4$,[17,19c] $(CH)_5$,[18] $(CH)_6$,[19] and $(CH)_8$[20] bridges, and most of them have the same end groups. Heterobimetallic complexes may have second-order NLO properties.[21] In fact, heterobimetallic complexes related to $(CH)_x$-bridged bimetallic complexes such as $(CO)_3M{=}C(OCH_3){-}(CH{=}CH)_n{-}(C_5H_4)Fe(C_5H_5)$ ($M = W$, Cr, $n = 1{-}4$) have been synthesized, and they have high β values.[22] In this report, the synthesis, characterization, and electrochemical properties of $(CH{=}CH)_3$-bridged heterobimetallic ferrocene−ruthenium complexes will be described.

Results and Discussion

Synthesis of the Complex $Fc(CH{=}CH)_2C{\equiv}CH$ (4). The general synthetic route for the preparation of heterobimetallic polyenes is outlined in Scheme 1. The ferrocene-containing phosphonium bromide **2** was prepared in four steps: aminomethylation of ferrocene forms the tertiary amine $FcCH_2NMe_2$, methylation of the tertiary amine forms the quarternary ammonium $FcCH_2NMe_3^+$, which reacts with sodium hydroxide to form the alcohol $FcCH_2OH$,[23] and reaction of the alcohol with triphenylphosphonium hydrobromide produces the complex $FcCH_2P^+Ph_3Br^-$ (**2**). Complex **2** has been characterized by NMR and elemental analysis. The ^{31}P NMR spectrum in $CDCl_3$ showed a singlet at 19.79 ppm. The ^1H NMR spectrum in $CDCl_3$ is much like that of the compound ((1′,2,2′,3,3′,4,4′,5-octamethylferrocenyl)-methyl)triphenylphosphonium bromide.[24]

The ferrocenyl-derived triphenylphosphonium bromide **2** underwent a Wittig reaction with the aldehyde TMS-C≡CCH=CHCHO (using $NaN(TMS)_2$ as the base) to produce the complex $FcCH{=}CHCH{=}CHC{\equiv}CSiMe_3$ (**3**). This complex was obtained as a mixture of 3*E*,5*E* and 3*E*,5*Z* isomers, which can be separated by chromatography on silica gel. It was characterized by ^1H NMR, and its structure has been further confirmed by its reaction with Bu_4NF to give the complex $FcCH{=}CHCH{=}CHC{\equiv}CH$ (**4**), which was confirmed by an X-ray

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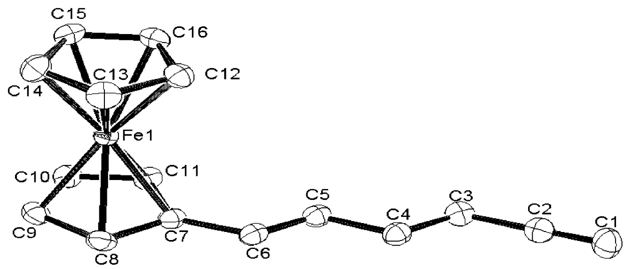

Figure 1. Molecular structure of Fc-CH═CHCH═CHC≡CH (**4**).

diffraction study (Figure 1). Treatment of **3** with n-Bu_4NF in THF produced complex **4**, which was isolated as a red crystalline solid.

Synthesis of Heterobimetallic Complexes. The complex FcCH═CHCH═CHC≡CH (**4**) reacted with $RuHCl(CO)(PPh_3)_3$ to give the insertion product Fc−$(CH{=}CH)_3$−$RuCl(CO)(PPh_3)_2$ (**5**), which can be isolated as a red solid in 80% yield. This compound has been characterized by NMR and elemental analysis. The ^{31}P NMR spectrum in CD_2Cl_2 showed a singlet at 30.35 ppm, which is typical for RuCl((*E*)-CH═CHR)(CO)$(PPh_3)_2$.[25a] The ^1H NMR spectrum in CD_2Cl_2 displayed the Ru−CH signal at 7.94 ppm, the chemical shift of which is similar to those of the complexes $[RuCl(CO)(PPh_3)_2]_2$-(μ-$(CH{=}CH)_n$) and $[RuCl(CO)(PPh_3)_2]_2$ (μ-CH═CH−Ar−CH═CH), and there were three singlet signals of Cp ($C_5H_5FeC_5H_4$) at 4.01, 4.11, and 4.21 ppm. The five-coordinated complex **5** is air-sensitive, especially in solution.

Several related $(CH{=}CH)_3$-bridged heterobimetallic six-coordinated complexes were prepared from complex **5**. Treatment of **5** with PMe_3 produced the six-coordinated complex $Fc(CH{=}CH)_3RuCl(CO)(PMe_3)_3$ (**6**). The complex is stable in solution and can be purified by chromatography on silica gel. The PMe_3 ligands in **6** are meridionally coordinated to ruthenium, as indicated by the AM_2 pattern ^{31}P NMR spectrum. The ^1H NMR (^{31}P-decoupled) spectrum in CD_2Cl_2 displayed the Ru−CH signal at 7.94 ppm with a ^3J(HH) coupling constant of 16.7 Hz. The magnitude of the coupling constant indicates that the two vinylic protons (Ru−CH═CH) are in a trans geometry and that the acetylene is cis-inserted into the Ru−H bond. The structure of **6** has been confirmed by an X-ray diffraction study (Figure 2).

Reaction of **5** with 4-phenylpyridine (PhPy), 2,6-$(Ph_2PCH_2)_2C_5H_3N$ (PMP), and KTp (Tp = hydridotris-(pyrazolyl)borate) give the corresponding six-coordinated complexes $Fc(CH{=}CH)_3RuCl(CO)(PhPy)(PPh_3)_2$ (**7**), $Fc(CH{=}CH)_3RuCl(CO)(PMP)$ (**8**), and $Fc(CH{=}CH)_3RuTp(CO)(PPh_3)$ (**9**), respectively. These complexes have been characterized by NMR spectroscopy and elemental analysis. The closely related mononuclear complexes RuCl(CH═CHR)(L)(CO)$(PPh_3)_2$ (L = 2e nitrogen donor ligands) have been previously prepared from the reaction of HC≡CR with RuHCl(L)(CO)-$(PPh_3)_2$.[25] A few ruthenium PMP complexes, for example $RuCl_2(PPh_3)(PMP)$ and $RuHX(PPh_3)(PMP)$ (X = Cl, OAc),[26] have also been reported. The homonuclear bimetallic complexes $[RuCl(PhPy)(CO)(PPh_3)_2]_2$($\mu$-$(CH{=}CH)_n$) ($n$ = 3, 4), $[RuCl(CO)(PMP)]_2$(μ-$(CH{=}CH)_n$) (n = 3, 4),[19b,20b] and $[RuTp(CO)(PPh_3)]_2$(μ-$(CH{=}CH)_2$−C_6H_4−$(CH{=}CH)_2$)[27] were also reported recently.

Crystal Structures of Complexes 4 and 6. The molecular structure of Fc-CH═CHCH═CHC≡CH (**4**) is depicted in Figure 1. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively. As shown in Figure 1, the compound contains two trans carbon−carbon double bonds. The structure displayed an extended conformation where the C(5)−C(6) double bond and the Cp remained nearly coplanar, with a maximum deviation from the least-squares plane of 0.0177 Å for C(6). The molecular structure of FcCH═CHCH═CHCH═CHRuCl-(CO)$(PMe_3)_3$ (**6**) is depicted in Figure 2. The crystallographic details and selected bond distances and angles are given in Tables 3 and 4, respectively. The complex contains a ferrocenyl moiety with a cyclopentadienyl ring substituted with a CH═CHCH═CHCH═CH group linked to a ruthenium center. The ruthenium center is a distorted octahedron with three meridionally bound PMe_3 ligands. The vinyl group is trans to a PMe_3 ligand, and the CO group is trans to the chloride group, as suggested by NMR data. The overall geometry around the ruthenium center is closely related to the bimetallic ruthenium complex $[RuCl(CO)(PMe_3)_3]_2$(μ-CH═CHCH═CHCH═CHCH═CH).[20] It is worth noting that the vinyl groups are essentially coplanar with Cl−Ru−CO. Thus, Ru(1), Cl(1), C(51) O(1), C(45), and C(46) form a plane with a maximum deviation from the least-squares plane of 0.0149 Å for C(45). Such a coplanar phenomenon of the vinyl group and CO is expected, due to the strong π-interaction between CO and vinyl with metal centers in such a conformation.[20,31] The $(CH)_6$ unit shows a single/double alternation pattern of carbon−carbon bonds. All of the olefinic double bonds are in a trans geometry. The formal double bonds have an average bond distance of 1.342 Å, and the formal single bonds have an average bond distance of 1.455 Å. The difference between the average single- and double-bond distances is 0.113 Å. The structural parameters of the $(CH)_6$ chain are similar to those of $[RuCl(CO)(PMe_3)_3]_2$(μ-CH═CHCH═CHCH═CHCH═CH),[20] $[MoTp^*Cl(NO)]_2$(μ-4,4′-$NC_5H_4(CH{=}CH)_4C_5H_4N$),[32] and PhCH═CH$(CH{=}CH)_2$-CH═CHPh.[33] In these compounds, the differences in the average single- and double-bond distances are 0.099, 0.11, and 0.092 Å, respectively.

Electrochemical Study. The cyclic voltammogram of complex **6** is shown in Figure 3. As shown in Figure 3, complex **6** exhibited two partially reversible oxidation waves at 0.37 and 0.51 V vs Ag/AgCl with a scan

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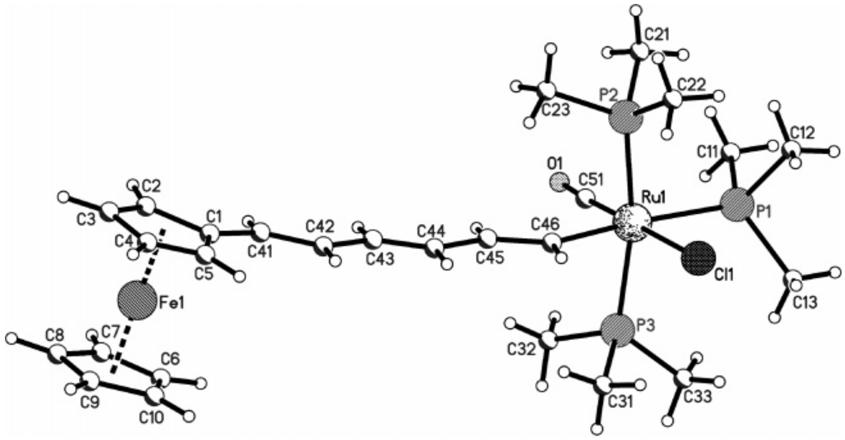

Figure 2. Molecular structure of $C_5H_5FeC_5H_4CH{=}CHCH{=}CHCH{=}CHRuCl(CO)(PMe_3)_3$ (**6**).

Table 1. Crystallographic Data and Structure Refinement Details for Complex 4

formula	$C_{16}H_{14}Fe$
formula wt	262.12
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	14.1566(17)
b, Å	7.6311(9)
c, Å	11.8956(14)
α, deg	90
β, deg	103.094(2)
γ, deg	90
V, Å^3	1251.7(3)
Z	4
d_{calcd}, g cm^{-3}	1.391
θ range, deg	2.95–28.27
no. of rflns collected	7539
no. of indep rflns	3012 (R(int) = 2.26%)
final R indices ($I > 2\sigma(I)$)	R1 = 0.0353, wR2 = 0.0874
goodness of fit	1.04
largest diff peak, e Å^{-3}	0.286
largest diff hole, e Å^{-3}	−0.187

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of Complex 4

Bond Lengths			
C(1)–C(2)	1.171(3)	C(5)–C(6)	1.322(3)
C(2)–C(3)	1.417(3)	C(7)–C(6)	1.457(3)
C(3)–C(4)	1.334(3)	Fe(1)–C(7)	2.045(2)
C(4)–C(5)	1.436(3)		
Bond Angles			
C(1)–C(2)–C(3)	177.8(2)	C(8)–C(7)–C(6)	125.76(19)
C(4)–C(3)–C(2)	123.2(2)	C(11)–C(7)-C(6)	127.20(19)
C(3)–C(4)–C(5)	126.1(2)	C(8)–C(7)–C(11)	107.02(18)
C(6)–C(5)–C(4)	124.0(2)	C(9)–C(8)–C(7)	108.8(2)
C(5)–C(6)–C(7)	127.2(2)		

Table 3. Crystal Data and Structure Refinement Details for Compound 6

formula	$C_{26}H_{43}ClFeOP_3Ru$
formula wt	656.88
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	13.467(3)
b, Å	14.134(3)
c, Å	16.930(3)
β, deg	112.050(3)
V, Å^3	2986.5(10)
Z	4
d_{calcd}, g/cm^3	1.461
θ range, deg	2.18–25.00
no. of rflns collected	14 775
no. of indep rflns	5127 (R(int) = 0.0394)
no. of data/restraints/params	5127/6/298
goodness of fit on F^2	1.053
final R indices ($I > 2\sigma(I)$)	R1 = 0.0511, wR2 = 0.1277
R indices (all data)	R1 = 0.0710, wR2 = 0.1354
largest diff peak and hole, e Å^{-3}	0.984 and −0.783

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) of Complex 6

Bond Lengths (Å)			
Ru(1)–P(1)	2.3772(19)	C(1)–C(41)	1.497(10)
Ru(1)–P(2)	2.3702(14)	C(41)–C(42)	1.360(10)
Ru(1)–P(3)	2.3642(15)	C(42)–C(43)	1.444(10)
Ru(1)–Cl(1)	2.496(3)	C(43)–C(44)	1.293(10)
Ru(1)–C(51)	1.792(10)	C(44)–C(45)	1.424(10)
Ru(1)–C(46)	2.067(8)	C(45)–C(46)	1.374(12)
Bond Angles (deg)			
C(51)–Ru(1)–P(1)	100.2(3)	P(2)–Ru(1)–Cl(1)	90.59(7)
C(51)–Ru(1)–P(2)	90.5(3)	P(3)–Ru(1)–Cl(1)	90.90(7)
C(51)–Ru(1)–P(3)	88.1(3)	P(3)–Ru(1)–P(1)	99.80(7)
C(51)–Ru(1)–Cl(1)	178.9(3)	P(3)–Ru(1)–P(2)	168.12(5)
C(51)–Ru(1)–C(46)	93.1(4)	C(42)–C(41)–C(1)	121.4(7)
C(46)–Ru(1)–P(1)	166.5(2)	C(41)–C(42)–C(43)	121.0(6)
C(46)–Ru(1)–P(2)	86.1(2)	C(44)–C(43)–C(42)	128.2(7)
C(46)–Ru(1)–P(3)	82.3(2)	C(43)–C(44)–C(45)	133.0(7)
C(46)–Ru(1)–Cl(1)	86.9(2)	C(46)–C(45)–C(44)	126.9(9)
P(1)–Ru(1)–Cl(1)	79.80(9)	C(45)–C(46)–Ru(1)	131.0(7)
P(2)–Ru(1)–P(1)	92.06(7)	O(1)–C(51)–Ru(1)	176.6(9)

ranging from 0 to 1.0 V, showing that, at the electrode surface, the neutral bimetallic complex underwent two successive one-electron oxidations to yield the mono- and dication, respectively. Cyclic voltammograms of related monometallic iron (**4**) and ruthenium complexes ($RuCl(CO)(PMe_3)_3$((*E,Z*)-$CH{=}CHCH{=}CHCC{\equiv}CH$) (**10**) and $RuCl(CO)(PMe_3)_3$((*E*)-$CH{=}CHPh$) (**11**)) were measured under identical conditions. The cyclic voltammogram of iron complex **4** showed only one reversible oxidation at 0.51 V. The cyclic voltammograms of both monometallic ruthenium complexes **10** (0.94 V) and **11** (0.97 V) showed one irreversible oxidation peak at a potential similar to that of the nonconjugated bimetallic complex $[RuCl(CO)(PMe_3)_3]_2(\mu$-$CH{=}CHCH_2CH(OMs)$-$CH(OMs)CH_2CH{=}CH)$, which showed one irreversible oxidation peak at 1.09 V vs Ag/AgCl. (The ferrocene/ferrocenium redox couple was located at 0.26 V under the experimental condition of ref 20.)

The first oxidation wave at 0.37 V in the cyclic voltammogram of complex **6** is tentatively ascribed to the ferrocene–ferrocenium couple. Substitution of the end hydrogen in the iron complex **4** by the ruthenium end group renders oxidation 0.14 V more favorable. The second oxidation, which should have more ruthenium character, is about 0.4 V more favorable than that of the monometallic ruthenium complexes. This can be

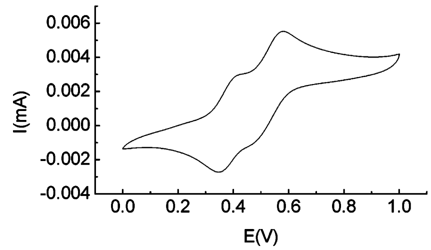

Figure 3. Cyclic voltammogram of complex **6**.

attributed to the strong electronic communications between the iron end group and the ruthenium end group.

Complex **7** showed two partially reverisible oxidation waves at 0.41 and 0.32 V. Complexes **8** and **9** have only one oxidation wave at 0.47 and 0.44 V, respectively, with a scan ranging from 0 to 1.0 V; both of them are reversible with $\Delta E_P = 0.07$ V. These results show that changes of the ligands of Ru have a large effect on the oxidation potentials of the ferrocene moiety. The dependence of the redox potentials of the ferrocene moiety on the Ru moiety suggests that significant electronic communication between the ferrocene moiety and the Ru center occurs via the polyene linker.

Summary. We have successfully prepared bimetallic complexes bridged by CH=CHCH=CHCH=CH with different end groups. The structures of FcCH=CHCH=CHC≡CH and FcCH=CHCH=CHCH=CHRuCl(CO)(PMe_3)$_3$ have been confirmed by X-ray diffraction. Electrochemical studies have shown that the metals linked through the CH=CHCH=CHCH=CH bridge interact with each other.

Experimental Section

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium−benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane, $CHCl_3$). The starting materials RuHCl(CO)(PPh_3)$_3$,[28] TMS-C≡CCH=CHCHO,[20b] 1-(hydroxymethyl)ferrocene,[23] 2,6-(Ph_2PCH_2)$_2$$C_5H_3N$ (PMP),[29] and KTp[30] were prepared according to literature methods, and complexes **10**[19b] and **11** were also prepared according to literature methods. Elemental analyses (C, H, N) were performed by the Microanalytical Services, College of Chemistry, CCNU. ^{1}H, ^{13}C, and ^{31}P NMR spectra were collected on a Varian MERCURY Plus 400 spectrometer (400 MHz). ^{1}H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4.

The electrochemical measurements were performed on an Autolab PGSTAT 30 instrument. A three-component electrochemical cell was used with a glassy-carbon electrode as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl electrode as the reference electrode. The cyclic voltammograms were collected with a scan rate ranging from 50 to 200 mV/s in CH_2Cl_2 containing 0.10 M n-Bu_4NClO_4 as the supporting electrolyte. The peak potentials reported were referenced to Ag/AgCl. The ferrocene/ferrocenium redox couple was located at 0.49 V under our experimental conditions.

$FcCH_2P^+Ph_3Br^-$ (2). A mixture of 1-(hydroxymethyl)ferrocene (0.85 g, 3.96 mmol) and triphenylphosphonium hydrobromide (1.36 g, 3.96 mmol) in 120 mL of toluene was refluxed for 2 h until separation from the eutectic condensate was completed in a Dean−Stark trap. After cooling, a yellow solid precipitated, which was filtered off, washed with 20 mL of ether, and dried. Yield: 2.02 g, 94%. Anal. Calcd for $C_{29}H_{26}$BrPFe: C, 64.36; H, 4.84. Found: C, 63.98; H, 4.70. ^{31}P NMR (160 MHz, $CDCl_3$): δ 19.79 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.98 (s, 2H, CH_2), 3.97 (s, 2H, $C_5H_2H_2CH_2$), 4.06 (s, 2H, $C_5H_2H_2$ CH_2), 4.36 (s, 5H, C_5H_5), 7.71 (m, 15H, PPh_3).

FcCH=CHCH=CHC≡CSiMe$_3$ (3). To a slurry of (ferrocenylmethyl)triphenylphosphonium bromide (**2**; 1.95 g, 3.6 mmol) in THF (40 mL) was added a 2 M THF solution of NaN($SiMe_3$)$_2$ (1.8 mL, 3.6 mmol). The mixture was stirred for 30 min, and then a solution of the aldehyde Me_3SiC≡CCH=CHCHO (0.5 g, 3.29 mmol) in THF (20 mL) was added slowly. The resulting solution was stirred for another 30 min, and then water (50 mL) was added. The layers were separated, and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with a saturated aqueous solution of sodium chloride (2 × 20 mL), dried over $MgSO_4$, filtered, and then concentrated under rotary evaporation. The crude product was purified by column chromatography (silica gel, eluted with petroleum ether) to give a red solid. Yield: 0.38 g, 34%. Anal. Calcd for $C_{19}H_{22}$SiFe: C, 68.26; H, 6.63. Found: C, 67.88; H, 6.75. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.20 (s, 9H, $SiMe_3$), 4.10 (s, 5H, C_5H_5Fe), 4.29 (s, 2H, $C_5H_2H_2$C≡), 4.38 (s, 2H, $C_5H_2H_2$C≡), 5.58 (d, 1H, J(HH) = 15.2 Hz, d-CH), 6.42 (m, 2H, a,b-CH), 6.69 (q, 1H, J(HH) = 8.4, 15.2 Hz, c-CH).

FcCH=CHCH=CHC≡CH (4). To a solution of complex **3** (0.16 g, 0.5 mmol) in THF (10 mL) was slowly added a 1 M THF solution of n-$Bu_4N^+F^-$ (0.5 mL, 1 M in THF) with stirring. After 2 h, the solvent was removed to give a red oil. The crude product was purified by column chromatography to give red crystals. Yield: 0.12 g, 96%. Anal. Calcd for $C_{16}H_{14}$Fe: C, 73.31; H, 5.38. Found: C, 73.10; H, 5.52. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.01 (d, J(HH) = 2.0 Hz, 1H, ≡CH), 4.04 (s, 5H, C_5H_5Fe), 4.23 (s, 2H, Fe$C_5H_2H_2$C=), 4.32 (s, 2H, Fe$C_5H_2H_2$C=), 5.48 (q, J(HH) = 2.0, 15.6 Hz, 1H, d-CH), 6.35 (m, 2H, a,b-CH), 6.65 (q, J(HH) = 8.8, 15.6 Hz, 1H, c-CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 67.15, 69.34, 69.56, 79.21 (s, C_5H_5, C_5H_4), 81.82, 83.72 (s, C≡C), 106.84, 125.18, 134.80, 144.06 (s, a,b,c,d-CH).

FcCH=CHCH=CHCH=CHRuCl(CO)(PPh$_3$)$_2$ (5). To a suspension of RuHCl(CO)(PPh_3)$_3$ (0.80 g, 0.84 mmol) in CH_2Cl_2 (20 mL) was slowly added a solution of **4** (0.26 g, 0.99 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred for 30 min to give a red solution. The reaction mixture was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 5 mL under vacuum. Addition of hexane (50 mL) to the residue produced a red solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.64 g, 80%. Anal. Calcd for $C_{53}H_{45}ClOP_2$FeRu: C, 66.85; H, 4.76. Found: C, 67.10; H, 4.57. ^{31}P NMR (160 MHz, CD_2Cl_2): δ 30.35 (s). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.01 (s, 5H, C_5H_5), 4.11 (s, 2H, $C_5H_2H_2$C=), 4.21 (s, 2H, $C_5H_2H_2$C=), 5.45 (m, 1H, d-CH), 5.91 (q, J(HH) = 10.8, 14.2 Hz, 1H, c-CH), 6.02 (d, J(HH) = 15.6 Hz, 1H, f-CH), 6.18 (q, J(HH) = 10.8, 15.4 Hz, 1H, e-CH), 7.35 (m, 31H, b-CH, PPh_3), 7.92 (d, J(HH) = 12.4 Hz, 1H, Ru−H).

FcCH=CHCH=CHCH=CHRuCl(CO)(PMe$_3$)$_3$ (6). To a solution of complex **5** (0.18 g, 0.19 mmol) in CH_2Cl_2 (30 mL) was added a 1 M THF solution of PMe_3 (2.0 mL, 2.0 mmol). The reaction mixture was stirred overnight. The solvent of the reaction mixture was removed under vacuum. The residue was purified by column chromatography (silica gel, eluted with 20/80 acetone/petroleum ether) to give a red solid. Yield: 0.93 g, 79%. Anal. Calcd for $C_{26}H_{42}ClOP_3$FeRu: C, 47.61; H, 6.45. Found: C, 47.65; H, 6.51. ^{31}P NMR (160 MHz, CD_2Cl_2): δ −19.42 (t, J(PP) = 24.2 Hz), −7.89 (d, J(PP) = 24.2 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.28 (t, J(PH) = 3.4 Hz, 18H, PMe_3), 1.35 (d, J(PH) = 6.8 Hz, 9H, PMe_3), 4.04 (s, 5H, C_5H_5), 4.11 (s, 2H, $C_5H_2H_2$C=), 4.25 (s, 2H, $C_5H_2H_2$C=), 5.79 (q, J(HH) = 10.8, 14.4 Hz, 1H, d-CH), 6.04 (d, J(HH) = 15.6 Hz, 1H, f-CH), 6.14 (q, J(HH) = 10.4, 14.4 Hz, 1H, c-CH), 6.30 (m, 2H, b,e-CH), 7.94 (m, 1H, a-CH). ^{13}C NMR (100 MHz, $CDCl_3$):

δ 16.79 (t, J(PC) = 15.3 Hz, PMe_3), 20.03 (d, J(PC) = 21.0 Hz, PMe_3), 66.57, 68.83, 69.46, 85.29 (s, C_5H_5, C_5H_4), 122.78, 126.33, 129.31, 137.93 (s, b,c,d,e,f-CH), 176.24 (Ru–CH), 202.81 (CO).

FcCH=CHCH=CHCH=CHRuCl(CO)(PhPy)(PPh_3)$_2$ (7). A mixture of complex **5** (0.18 g, 0.19 mmol) and 4-phenylpyridine (0.06 g, 0.38 mmol) in CH_2Cl_2 (20 mL) was stirred for 30 min. The solution was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 2 mL under vacuum. Addition of hexane (15 mL) to the residue produced a red solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.18 g, 85%. Anal. Calcd for $C_{64}H_{54}ClNOP_2FeRu$: C, 69.41; H, 4.92. Found: C, 69.81; H, 4.75. ^{31}P NMR (160 MHz, CD_2Cl_2): δ 26.14 (s). ^1H NMR (400 MHz, CD_2Cl_2): δ 4.06 (s, 5H, C_5H_5), 4.19 (s, 2H, $C_5H_2H_2C$=), 4.30 (s, 2H, $C_5H_2H_2C$=), 5.50 (q, J(HH) = 11.0, 14.6 Hz, 1H, d-CH), 5.68 (q, J(HH) = 10.0, 16.0 Hz, 1H, c-CH), 6.07 (m, 1H, f-CH), 6.31 (q, J(HH) = 11.0, 15.2 Hz, 1H, e-CH), 6.77 (br, 2H, $C_5H_2H_2N$), 7.40 (m, 36H, Ph, b-CH), 8.43 (br d, J(HH) = 15.6 Hz, 3H, Ru–CH, $C_5H_2H_2N$).

FcCH=CHCH=CHCH=CHRuCl(CO)(PMP) (8). A mixture of complex **5** (0.18 g, 0.19 mmol) and PMP (0.09 g, 0.19 mmol) in CH_2Cl_2 (20 mL) was stirred for 15 h. The solution was filtered through a column of Celite. The volumn of the filtrate was reduced to ca. 2 mL under vacuum. Addition of hexane (20 mL) to the residue produced a yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.14 g, 86%. Anal. Calcd for $C_{48}H_{42}ClNOP_2FeRu$: C, 63.83; H, 4.69. Found: C, 64.16; H, 4.43. ^{31}P NMR (160 MHz, CD_2Cl_2): δ 49.83 (s). ^1H NMR (400 MHz, CD_2Cl_2): δ 3.95 (s, 5H, C_5H_5), 4.06 (s, 2H, $C_5H_2H_2C$=), 4.13 (m, 4H, $C_5H_2H_2C$=, CHH(C_5H_3N)CHH), 4.49 (m, 2H, CHH(C_5H_3N)CHH), 5.05 (m, 1H, d-CH), 5.28 (m, 1H, c-CH), 5.85 (m, 1H, f-CH,), 6.16 (m, 1H, e-CH), 7.27–8.78 (m, 25H, Ph, C_5H_3N, Ru–CH, b-CH).

FcCH=CHCH=CHCH=CHRuTp(CO)(PPh_3) (9). A mixture of complex **5** (0.18 g, 0.19 mmol) and KTp (0.18 g, 0.21 mmol) in CH_2Cl_2 (20 mL) was stirred for 2 h. The solution was filtered through a column of Celite to remove the KCl. The volume of the filtrate was reduced to ca. 2 mL under vacuum. Addition of hexane (20 mL) to the residue produced a red solid, which was collected by filtration, washed with hexane, and dried over vacuum. Yield: 0.14 g, 85%. Anal. Calcd for $C_{44}H_{40}BN_6OPFeRu$: C, 60.92; H, 4.65. Found: C, 61.26; H, 4.88. ^{31}P NMR (160 MHz, CD_2Cl_2): δ 49.23 (s). ^1H NMR (400 MHz, CD_2Cl_2): δ 4.01 (s, 5H, C_5H_5), 4.11 (s, 2H, $C_5H_2H_2C$=), 5.23 (s, 2H, $C_5H_2H_2C$=), 5.67 (m, 1H, d-CH), 5.88–7.73 (m, 30H, PPh_3, Ru–CH, b,c,e,f-CH, Tp).

Crystallographic Analysis for Fc(CH=CH)$_2$C≡CH (4). Crystals suitable for X-ray diffraction were grown from a hexane solution cooled to −20 °C. A crystal was mounted on a glass fiber, and the diffraction intensity data were collected on a Bruker CCD 4K diffractometer with graphite-monochromated M*o* Kα radiation (λ = 0.710 73 Å). Lattice determination and data collection were carried out using SMART version 5.625 software. Data reduction and absorption corrections were performed using SAINT version 6.45 and SADABS version 2.03. Structure solution and refinement were performed using the SHELXTL version 6.14 software package. All non-hydrogen atoms were refined anisotropically. All hydrogens were included in their idealized positions and refined using a riding model. Further crystallographic details were summarized in Table 1, and selected bond distances and angles are given in Table 2.

Crystallographic Analysis for Fc(CH=CH)$_3$RuCl(CO)(PMe_3)$_3$ (6). Crystals suitable for X-ray diffraction were grown from a benzene solution layered with hexane. A red bar-shaped crystal of $C_5H_5FeC_5H_4$CH=CHCH=CHCH=CHRuCl(CO)(PMe_3)$_3$ (**6**), with dimensions 0.30 × 0.15 × 0.10 mm^3, was mounted on a glass fiber, and diffraction intensity data were collected by a Bruker Apex CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 100(2) K. Lattice determination and data collection were carried out using SMART version 5.625 software. Data reduction and absorption correction were performed using SAINT version 6.26 and SADABS version 2.03. Structure solution and refinement were performed using SHELXTL version 6.10 software package. All non-hydrogen atoms (except for those disordered atoms) were refined anisotropically. Further crystallographic details are given in Table 3, and selected bond distances and angles are given in Table 4.

Acknowledgment. We acknowledge financial support from the National Natural Science Foundation of China (Nos. 20242010 and 20472023), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, and the National Key Project for Basic Research of China (No. 2004CCA00100).

Supporting Information Available: CIF files giving crystallographic data for $C_5H_5FeC_5H_4$CH=CHCH=CHC≡CH (**4**) and $C_5H_5FeC_5H_4$CH=CHCH=CHCH=CHRuCl(CO)(PMe_3)$_3$ (**6**). This material is available free of charge via the Internet at http://pubs.acs.org.

OM0490637