Synthesis and Electrochemical Properties of C_5H−Bridged Bimetallic Iron, Ruthenium, and Osmium Complexes

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Treatment of $[CpOs(PPh_3)_2]BF_4$ in THF with 0.5 equiv of $HC{\equiv}CCH(OH)C{\equiv}CH$ followed by Al_2O_3 gave the C_5H-bridged compound $[Cp(PPh_3)_2Os{=}C{=}C{=}CHC{\equiv}COs(PPh_3)_2Cp]BF_4$. The analogous iron complex $[Cp(dppe)Fe{=}C{=}C{=}CHC{\equiv}CFe(dppe)Cp]BPh_4$ has been prepared similarly. The structure of $[Cp(PPh_3)_2Os{=}C{=}C{=}CHC{\equiv}COs(PPh_3)_2Cp]BF_4$ has been confirmed by X-ray diffraction. The electrochemical properties of $[Cp(dppe)Fe{=}C{=}C{=}CHC{\equiv}CFe(dppe)Cp]BPh_4$, $[Cp(PPh_3)_2Ru{=}C{=}C{=}CHC{\equiv}CRu(PPh_3)_2Cp]BF_4$, and $[Cp(PPh_3)_2Os{=}C{=}C{=}CHC{\equiv}COs(PPh_3)_2Cp]BF_4$ have been studied by cyclic voltammetry.

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Introduction

Bi- and polymetallic organometallic compounds with π-conjugated bridges have attracted considerable interest, due to their structural and material properties.[1,2] During the past few decades, a large number of such organometallic systems have been constructed with hydrocarbon chains serving as σ,σ-, σ,π-, or π,π-bound bridging ligands. Linear C_x, $(CH)_x$, and C_xH_y (where y is smaller than x) groups are among the simplest σ,σ-bridging hydrocarbon chains that can be used to build conjugated bi- or polymetallic organometallic complexes. In fact, numerous complexes with linear C_x[3] and $(CH)_x$[4] bridges have been synthesized and characterized. In contrast, fewer complexes with linear C_xH_y (where y is smaller than x) bridges have been reported. C_4H_2-bridged complexes $L_nM{=}C{=}CHCH{=}C{=}ML_n$ and $L_nM{\equiv}CCH{=}CHC{\equiv}ML_n$ are examples of such complexes.[5]

We have recently reported a simple method to synthesize the C_5H-bridged ruthenium complexes $[(C_5R_5)(L)_2Ru{=}C{=}C{=}CHC{\equiv}CRu(L)_2(C_5R_5)]BF_4$ ($R = H$, $(L)_2 = (PPh_3)_2$; $R = Me$, $(L)_2 =$ dppe).[6] It is interesting to note that the C_5-bridged complex $[Cp^*Re(NO)(PPh_3)(\mu\text{-}C_5)Mn(CO)_2(C_5Cl_5)]BF_4$ was reported to be light-sensitive and decomposed in hours even in the dark, but the C_5H-bridged complexes are stable species which can be stored under an inert atmosphere for months. Continuing our interest in the synthesis and properties of conjugated organometallic systems, we have now synthesized C_5H-bridged iron and osmium complexes and investigated the electrochemical properties of $[Cp(dppe)Fe{=}C{=}C{=}CHC{\equiv}CFe(dppe)Cp]BPh_4$, $[Cp(PPh_3)_2Ru{=}C{=}C{=}CHC{\equiv}CRu(PPh_3)_2Cp]BF_4$, and $[Cp(PPh_3)_2Os{=}C{=}C{=}CHC{\equiv}COs(PPh_3)_2Cp]BF_4$. A few complexes closely

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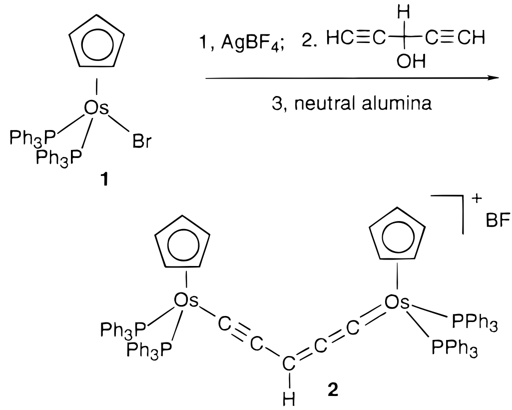
related to the C_5H-bridged complexes have been reported, including bimetallic complexes with linear C_5,[7] C_5H_5,[4g,h] and C_4CR[7,8] bridges and mononuclear complexes of the type $L_nM{=}C{=}C{=}C{=}C{=}CR_2$.[9] However, the electrochemical properties of these compounds have scarcely been exploited.

Results and Discussion

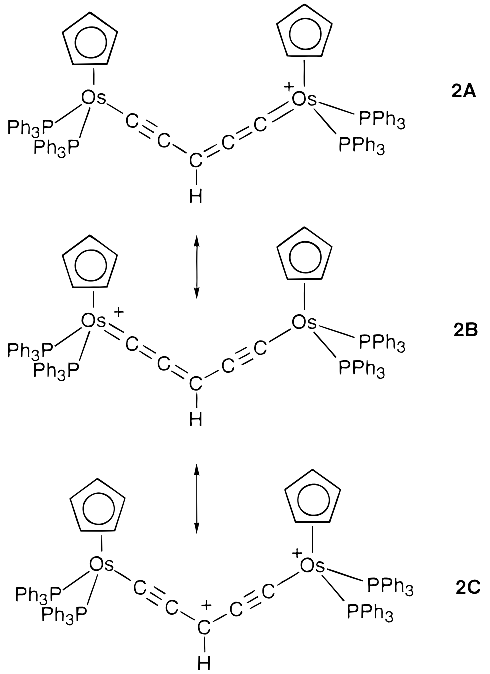
Synthesis and Spectroscopic Characterization of C_5H-Bridged Osmium and Iron Bimetallic Complexes. Reactions of coordinatively unsaturated complexes $[(C_5R_5)M(L)_2]^+$ (M = Fe, Ru, Os) with 1-alkynols are known to give vinylidene or allenylidene complexes.[10] On the basis of the reactivity, we have recently reported the preparation of the purple C_5H_2-bridged compounds $[(C_5R_5)(L)_2Ru{=}C{=}C{=}CHCH{=}C{=}Ru(L)_2(C_5R_5)](BF_4)_2$ (R = H, $(L)_2 = (PPh_3)_2$; R = Me, $(L)_2$ = dppe) from the reactions of $[(C_5R_5)Ru(L)_2]BF_4$ with $HC{\equiv}CCH(OH)C{\equiv}CH$.[6] It was shown that the C_5H_2-bridged complexes are highly acidic and could be readily deprotonated by Al_2O_3 to give the blue C_5H-bridged compounds $[(C_5R_5)(L)_2Ru{=}C{=}C{=}CHC{\equiv}CRu(L)_2(C_5R_5)]BF_4$. In this work, we have tried to use a similar strategy to prepare analogous osmium and iron C_5H-bridged complexes, in order to study the effect of metals on the properties of C_5H-bridged complexes.

The C_5H-bridged osmium complex $[Cp(PPh_3)_2Os{=}C{=}C{=}CHC{\equiv}COs(PPh_3)_2Cp]BF_4$ (**2**) could be obtained by starting from $CpOsBr(PPh_3)$ (**1**)[11] and $HC{\equiv}CCH(OH)C{\equiv}CH$.[12] Treatment of $[CpOs(PPh_3)_2]BF_4$ (generated in situ from the reaction of $CpOsBr(PPh_3)_2$ in THF with $AgBF_4$) with 0.5 equiv of $HC{\equiv}CCH(OH)C{\equiv}CH$ produced immediately an intense red solution. The red solution showed NMR signals assignable to the C_5H_2-bridged complex$[Cp(PPh_3)_2Os{=}C{=}C{=}CHCH{=}C{=}Os(PPh_3)_2Cp](BF_4)_2$, which proved to be difficult to obtain in pure form. Fortunately, pure samples of the blue C_5H-bridged osmium complex **2** could be obtained from the red mixture after column chromatography on alumina (Al_2O_3) (Scheme 1). Thus, deprotonation of the vinylidene intermediate by alumina occurred during the chromatographic process. Deprotonation of vinylidene complexes with alumina to give the corresponding σ-acetylide complexes has been noted previously.[13] Reactions of $HC{\equiv}CC(OH)Ph_2$ with appropriate unsaturated osmium complexes have been previously employed to prepare osmium allenylidene complexes such as $[(\eta^5\text{-}C_9H_7)Os(C{=}C{=}CPh_2)(PPh_3)_2]PF_6$,[14] $[Os(C(CO_2Me){=}CH_2)(C{=}C{=}CPh_2)(CO)(P(i\text{-}Pr)_3)_2]BF_4$,[15] and $CpOsCl({=}C{=}C{=}CPh_2)(P(i\text{-}Pr)_3)$.[16]

Scheme 1



Complex **2** was characterized by elemental analysis, NMR, and UV spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 displayed a singlet at −0.7 ppm for the PPh_3 ligands, and the ^1H NMR spectrum in CD_2Cl_2 exhibited a singlet at 4.88 ppm for the two Cp rings. In the $^{13}C\{^1H\}$ NMR spectrum in CD_2Cl_2, the C(α), C(β), and C(γ) resonances were observed at 196.2 (t, $^2J(PC)$ = 14.8 Hz), 171.4 (s), and 130.6 (s) ppm, respectively. The NMR spectroscopic data indicate that complex **2** has a delocalized structure with two identical osmium centers. The structures **2A−C** are the possible resonance structures for complex **2**. The structure of **2** has been confirmed by an X-ray diffraction study (see below).



It is interesting to note that the signal for the C_5H proton in the ^1H NMR spectrum of **2** was observed at 10.55 ppm, which is significantly downfield from that (8.30 ppm) observed for the ruthenium analogue [Cp-

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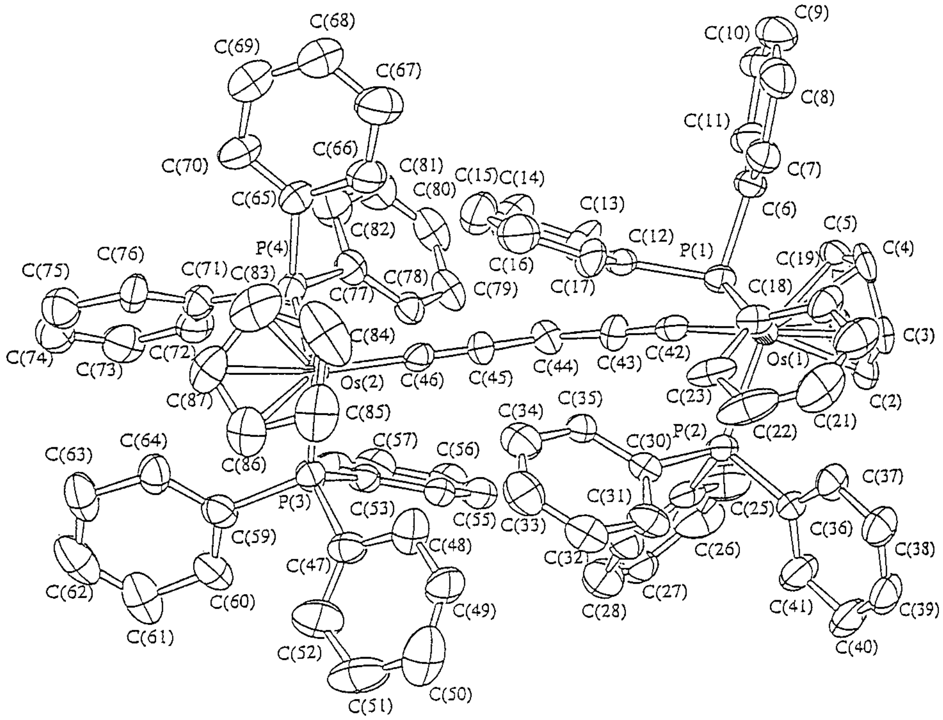
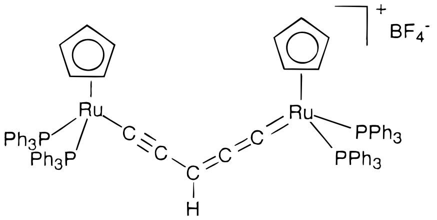


Figure 1. Molecular structure for the cation [CpOs(PPh$_3$)$_2$C=C=CHC≡COs(PPh$_3$)$_2$Cp]$^+$.

(PPh$_3$)$_2$Ru=C=C=CHC≡CRu(PPh$_3$)$_2$Cp]BF$_4$ (**3**). The observation may imply that the central carbon of the C$_5$H unit in the osmium complex has more carbon cation character.



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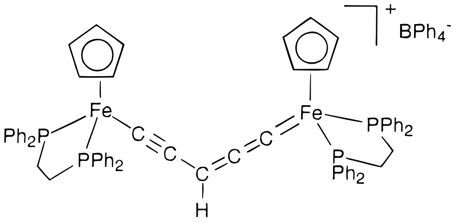

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The analogous iron compound [Cp(dppe)Fe=C=C=CHC≡CFe(dppe)Cp]BF$_4$ was also produced by treating [CpFe(dppe)]BF$_4$ with HC≡CCH(OH)C≡CH, followed by passing the crude reaction mixture through a column of neutral alumina. However, the reaction is not as clean as in the cases of ruthenium and osmium. As indicated by NMR, other uncharacterized phosphorus-containing complexes were also present in the product even after column chromatography. To further purify the product, the cationic C$_5$H-bridged complex was precipitated out from methanol with NaBPh$_4$ as [Cp(dppe)Fe=C=C=CHC≡CFe(dppe)Cp]BPh$_4$ (**4**). Attempt to obtain an analytically pure sample failed. Its identity, however, is clearly indicated by its MS and NMR spectra. In particular, MS (FAB, NBA matrix) showed a cluster of peaks around *m/e* 1099, which corresponds to [Cp(dppe)-Fe=C=C=CHC≡CFe(dppe)Cp]$^+$. The ^{1}H NMR spectrum (in CD$_2$Cl$_2$) displayed a CH signal at 6.50 ppm. As reflected by the ^{31}P and ^{13}C NMR data, complex **4** also has a delocalized structure. ^{31}P{^{1}H} NMR in CD$_2$Cl$_2$ showed a singlet at 102.3 ppm for the dppe ligand. The ^{13}C{^{1}H} NMR spectrum (in CD$_2$Cl$_2$) showed the C(α), C(β), and C(γ) resonances at 223.3 (t, ^2J(PC) = 38.9 Hz), 176.0 (s), and 122.9 (s) ppm.

All the C$_5$H-bridged complexes have an intense blue color. The osmium complex **2** has a strong absorption at 583 nm, the ruthenium complex **3** has a strong absorption at 600 nm, and the iron complex **4** has a strong absorption at 722 nm. The absorption can be attributed to an electronic transition involving the M$_2$-(μ-C$_5$H) units. Bimetallic complexes with metal centers bridged with linear C$_5$,[7] C$_5$H$_5$,[4g,h] and C$_4$CR[7,8] chains also have intense colors. Like the ruthenium analogues, the C$_5$H-bridged complexes **2** and **4** are also stable species that can be stored under an inert atmosphere for months without decomposition.

Solid-State Structure of [Cp(PPh$_3$)$_2$Os=C=C=CH−C≡COs(PPh$_3$)$_2$Cp]BF$_4$. The structure of complex **2** has been confirmed by X-ray diffraction. A view of the molecular structure of the cation [Cp(PPh$_3$)$_2$Os=C=C=CHC≡COs(PPh$_3$)$_2$Cp]$^+$ is shown in Figure 1. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively. Overall the structure is similar to that of the analogous ruthenium complex [Cp(PPh$_3$)$_2$Ru=C=C=CHC≡CRu(PPh$_3$)$_2$-Cp]$^+$.[6]

The structure can be described as two three-legged piano stools bridged with a C$_5$H unit. The four PPh$_3$ ligands are bonded to osmium with almost equal Os−P bond distances (in the range 2.316(2)−2.325(5) Å). The Os−P bond distances are close to those reported for related osmium complexes such as CpOs(PPh$_3$)$_2$X (X = Cl,[17] Br,[18] OTf[11a]) and [(η^5-C$_9$H$_7$)Os(=C=C=CPh$_2$)-(PPh$_3$)$_2$]$^+$.[14]

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Table 1. Crystal Data and Refinement Details for $[Cp(PPh_3)_2Os{=}C{=}C{=}CHC{\equiv}COs(PPh_3)_2Cp]BF_4 \cdot CH_2Cl_2 \cdot 2H_2O$

formula	$C_{88}H_{77}BCl_2F_4O_2P_4Ru$
fw	1828.58
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	16.445(1)
b, Å	21.222(2)
c, Å	22.436(2)
β, deg	95.56(2)
V, Å^3	7793(1)
Z	4
d_{calcd}, g cm^{-3}	1.56
radiation	Mo Kα ($\lambda = 0.710\,69$ Å)
$2\theta_{max}$, deg	51.2
scan type	ω
no. of rflns collected	38 571
no. of indep rflns	14712 ($R_{int} = 4.7\%$)
no. of obsd rflns	9903 ($F > 3.0\sigma(F)$)
no. of params refined	904
final R indices (obsd data), %	$R = 3.8$, $R_w = 4.5$
goodness of fit	2.72
largest diff peak, e Å^{-3}	1.52
largest difference hole, e Å^{-3}	−1.36

Table 2. Selected Bond Distances and Angles for $[Cp(PPh_3)_2Os{=}C{=}C{=}CHC{\equiv}COs(PPh_3)_2Cp]BPh_4 \cdot CH_2Cl_2 \cdot 2H_2O$

Bond Distances (Å)			
Os(1)−P(1)	2.322(2)	Os(1)−P(2)	2.316(2)
Os(2)−P(3)	2.320(2)	Os(2)−P(4)	2.325(2)
Os(1)−C(1)	2.242(8)	Os(1)−C(2)	2.239(8)
Os(1)−C(3)	2.274(8)	Os(1)−C(4)	2.256(7)
Os(1)−C(5)	2.270(8)	Os(2)−C(83)	2.252(10)
Os(2)−C(84)	2.228(9)	Os(2)−C(85)	2.266(9)
Os(2)−C(86)	2.281(9)	Os(2)−C(87)	2.306(9)
Os(1)−C(42)	1.943(8)	Os(2)−C(46)	1.974(9)
C(42)−C(43)	1.24(1)	C(43)−C(44)	1.39(1)
C(44)−C(45)	1.32(1)	C(45)−C(46)	1.19(1)

Bond Angles (deg)			
P(1)−Os(1)−P(2)	97.66(7)	P(1)−Os(1)−C(42)	94.5(2)
P(2)−Os(1)−C(42)	83.0(2)	P(3)−Os(2)−P(4)	100.18(8)
P(3)−Os(2)−C(46)	88.9(2)	P(4)−Os(2)−C(46)	88.5(1)
Os(1)−C(42)−C(43)	174.2(4)	C(42)−C(43)−C(44)	175.3(9)
C(43)−C(44)−C(45)	128.2(8)	C(44)−C(45)−C(46)	163.4(9)
C(45)−C(46)−Os(2)	176.1(7)		

The C_5H unit bridges the two osmium centers in a "V" shape (C(43)−C(44)−C(45) = 128.2(8)°) in a nearly symmetrical manner. The orientation of the C_5H unit is similar to that observed for the osmium allenylidene complex $[(\eta^5\text{-}C_9H_7)Os({=}C{=}C{=}CPh_2)(PPh_3)_2]^+$.[14] Such an orientation is expected on the basis of theoretical calculations of allenylidene complexes so that maximum π-stabilization between metal and the C(α) atom can be achieved.[19] The OsC_3H chain is not strictly linear, having the angles Os(1)−C(42)−C(43) = 174.2(4)°, C(42)−C(43)−C(44) = 175.3(9)°, C(44)−C(45)−C(46) = 163.4(9)°, and C(45)−C(46)−Os(2) = 176.1(7)°. These angles are similar to those reported for $OsC{\equiv}CR$[20] and $Os{=}C{=}C{=}CPh_2$[14−16] complexes. The symmetric nature of the C_5H unit indicated by the solution NMR data is also reflected by the solid-state structure, which showed comparable Os−C(α) (1.943(8), 1.974(9) Å), C(α)−C(β) (1.24(1), 1.19(1) Å), and C(β)−C(γ) (1.39(1), 1.32(1) Å) bond distances. The average Os−C(α) distance of 1.958 Å is near the upper end of those in osmium allenylidene complexes (for example, $CpOsCl(C{=}C{=}CPh_2)(P(i\text{-}Pr)_3)$, 1.875(6) Å;[16] $[Os(C(CO_2Me){=}CH_2)(C{=}C{=}CPh_2)(CO)(P(i\text{-}Pr)_3)_2]BF_4$, 1.947(6) Å;[15] $[(\eta^5\text{-}C_9H_7)Os(C{=}C{=}CPh_2)(PPh_3)_2]^+$, 1.895(4) Å),[14] is shorter than those in osmium acetylide complexes,[20] and is longer than those in the vinylidene complexes $OsCl_2({=}C{=}CHPh)(P(i\text{-}Pr)_3)((i\text{-}Pr)_2PCH_2CH_2NMe_2)$[21] and $OsCl({=}C{=}CHSiMe_3)(CH{=}CHSiMe_3)(P(i\text{-}Pr)_3)_2$.[22] The average C(α)−C(β) bond distance of 1.22 Å is near the lower end of those found for the osmium allenylidene complexes mentioned above[14−16] and is similar to those observed for osmium acetylide complexes.[20] The average C(β)−C(γ) bond distance (1.36 Å) corresponds to a bond order between 1 and 2. It is within the range of the bond distances observed for osmium allenylidene complexes and is shorter than that expected for C(sp^2)−C(sp) single bonds. For example, the C(sp)−C(sp^2) single-bond distances were observed at 1.420 (11) Å for $Os(C{\equiv}CPh)(NH{=}CPhC_6H_4)(P(i\text{-}Pr)_3)_2$[20b] and at 1.426 (12) Å for $OsCl(dppm)_2C{\equiv}CC_5H_4FeCp$.[20e] Thus, the solid-state structural data support the idea that complex **2** has a delocalized structure with contributions from the resonance structures **2A**−**C**.

Table 3. Cyclic Voltammetry Data (V) for Complexes 2−4

complex	$E_{ox}(1)$	$E_{ox}(2)$	$E_{ox}(3)$
$\{[CpFe(dppe)]_2(\mu\text{-}C_5H)\}BPh_4$	−1.15	0.12[a]	0.47[a]
$\{[CpRu(PPh_3)_2]_2(\mu\text{-}C_5H)\}BF_4$	−1.30[a]	0.68[b]	1.04[b]
$\{[CpOs(PPh_3)_2]_2(\mu\text{-}C_5H)\}BF_4$	−1.10[a]	0.74[b]	1.10[b]

[a] Partially reversible peak, taken as the midpoint between anodic and cathodic peaks. [b] Irreversible peak.

Electrochemical Study. Electrochemistry has often been used to probe metal−metal interactions in bimetallic complexes with σ,σ-bridging hydrocarbon chains.[1b,d,23] To this end we have collected the cyclic voltammograms of the C_5H-bridged complexes **2**−**4** in dichloromethane containing 0.10 M $n\text{-}Bu_4NClO_4$ as the supporting electrolyte. The results of the electrochemical experiments are presented in Table 3, in which the peak potentials are referenced to Ag/AgCl.

The cyclic voltammograms of complexes **2**−**4** showed very similar features. As illustrated in Figure 2, the cyclic voltammogram of iron complex **4** exhibits a reversible reduction wave at −1.15 V and two partially reversible oxidation waves at 0.12 and 0.47 V, respectively. The cyclic voltammogram of ruthenium complex **3** exhibits a reversible reduction wave at −1.30 V and two irreversible oxidation waves at 0.68 and 1.04 V, respectively. The cyclic voltammogram of osmium complex **2** is very similar to that of complex **3**.

To better understand the electrochemical behavior of the C_5H-bridged complexes, we have carried out a

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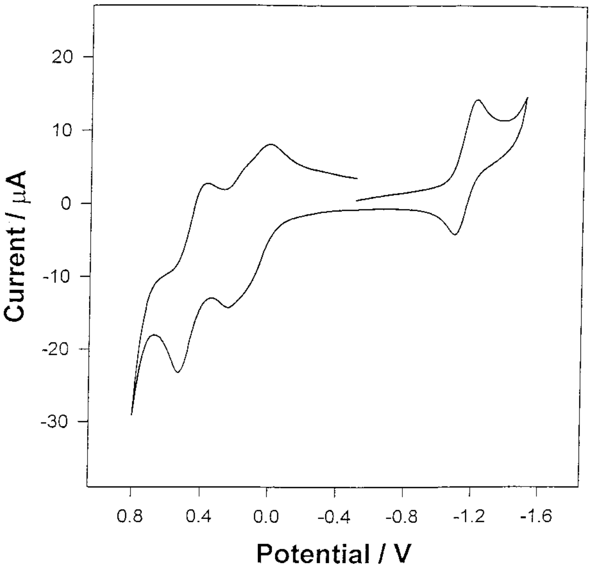


Figure 2. Cyclic voltammogram for [CpFe(dppe)C=C=CHC≡CFe(dppe)Cp]$^+$ in CH_2Cl_2 (scan rate 100 mV/s, vs Ag/AgCl).

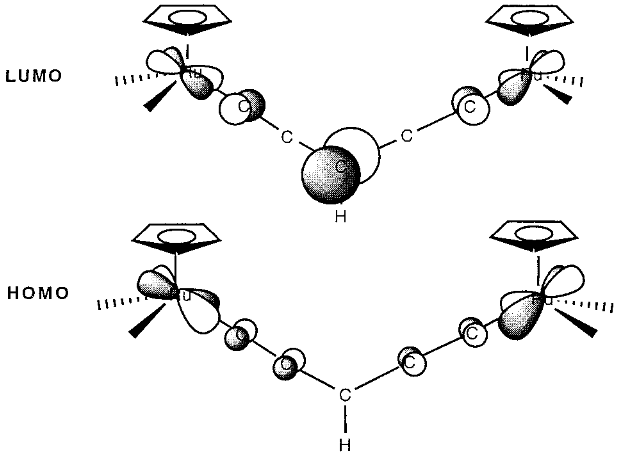
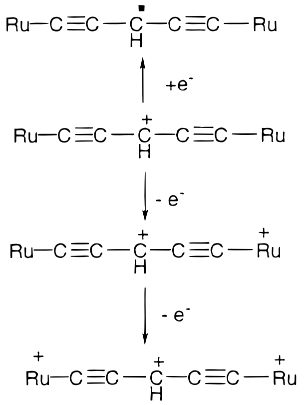


Figure 3. Sketches of the HOMO and LUMO of [CpRu(PH$_3$)$_2$C=C=CHC≡CRu(PH$_3$)$_2$Cp]$^+$.

preliminary computational study on the electronic structure of the model complex [Cp(PH$_3$)$_2$Ru=C=C=CHC≡CRu(PH$_3$)$_2$Cp]$^+$.[24] The computational results show that both the HOMO and LUMO of the model complex are composed of the antibonding combinations of primarily ruthenium d orbitals and carbon p orbitals of the main π system of the C_5H unit. As illustrated in Figure 3, the HOMO has more metal d orbital character and the LUMO has more carbon p orbital character.

On the basis of the computational results and electrochemical properties of related complexes, the electrochemical process corresponding to the waves is tentatively suggested in Scheme 2, using ruthenium complex **3** as the example. The reduction wave at −1.30 V could be attributed to the reduction of the C_5H ligand. In support of this proposition, CpRuCl(PPh$_3$)$_2$ does not show a similar wave in the same region. It is noted that the ruthenium allenylidene complexes [RuX(=C=C=CR$_2$)(dppe)$_2$]$^+$ show reduction waves near −1.0 V vs ferrocenium/ferrocene.[25] The oxidation waves at 0.68 and 1.04 V could be attributed to the oxidation of the two ruthenium centers. As expected, the first oxidation potential for the ruthenium complex is higher than that of the analogous ruthenium acetylide complexes of the type CpRu(C≡CR)(PPh$_3$)$_2$.[26] It should be noted that there are several possible resonance structures for each of the species, but only one of the resonance forms for each of the species is shown in Scheme 2.

Scheme 2[a]



[a] Ru = CpRu(PPh$_3$)$_2$.

The peak separation of the two oxidation waves at 0.68 and 1.04 V for ruthenium complex **3** is 0.36 V. The peak separations for the corresponding two oxidation waves of iron complex **4** and osmium complex **2** are also at about 0.36 V. For comparison, peak separations were observed at 0.20 V for the reduction of {[RuCl(dppe)$_2$]$_2$(μ-*p*-C=C=CHC$_6$H$_4$CH=C=C)}(PF$_6$)$_2$,[27] 0.36 V for the oxidation of [RuCl(dppe)$_2$]$_2$(μ-*p*-C≡CC$_6$H$_4$C≡C),[28] 0.37 V for the oxidation of [RuCl(dppm)$_2$]$_2$(μ-*p*-C≡CC$_6$H$_4$C≡C),[2d] 0.53 V for the oxidation of [Cp*Re(NO)(PPh$_3$)]$_2$(μ-C$_4$),[3a] 0.72 V for the oxidation of [Cp*Fe(dppe)]$_2$(μ-C$_4$),[5e] and 0.44 V for the oxidation of [CpFe(dppm)]$_2$(μ-CH=CHCH=CH).[4e] The peak separations of 0.36 V for the C_5H-bridged complexes may imply that the two metal centers have a substantial interaction. The strength of the metal−metal interaction in the C_5H-bridged complexes, however, could not be assessed definitely only on the basis of the electrochemistry data because of the irreversible nature of the oxidation waves and the fact that wave separations of bimetallic systems are related to many other factors.[23]

In summary, we have prepared new C_5H-bridged osmium and iron complexes from the reactions of HC≡CCH(OH)C≡CH with coordinatively unsaturated d^6 complexes [(η^5-C$_5$R$_5$)M(PR$_3$)$_2$]$^+$. The C_5H-bridged iron, ruthenium, and osmium complexes showed similar structural and electrochemical properties.

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(24) Density functional calculations at the B3LYP level were performed on the model complex [Cp(PH$_3$)$_2$Ru(μ-C$_5$H)Ru(PH$_3$)$_2$Cp]$^+$ on the basis of the experimentally determined geometry. The basis set used for C and H atoms was 6-31G. For Ru and P atoms, an effective core potential with a LanL2DZ basis set was employed.

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Experimental Section

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium−benzophenone (hexane, ether, THF), sodium (benzene), or calcium hydride (CH_2Cl_2). The starting materials CpFeCl(dppe),[29] $CpOsBr(PPh_3)_2$,[11] $CpRuCl(PPh_3)_2$,[30] $HC{\equiv}CC(OH)C{\equiv}CH$,[12] and complex **3**[6] were prepared according to literature methods. All other reagents were used as purchased from Aldrich Chemical Co.

Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were collected on a JEOL EX-400 spectrometer (400 MHz) or a Bruker ARX-300 spectrometer (300 MHz). ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts relative to 85% H_3PO_4. IR spectra were collected on a Perkin-Elmer 1600 spectrometer. UV−vis spectra were recorded on a Milton Roy Spectronic 3000 spectrometer.

The electrochemical measurements were performed with a PAR Model 273 potentiostiat. 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 of 100 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 0.50 V under our experimental conditions.

$[Cp(PPh_3)_2Os{=}C{=}C{=}CHC{\equiv}COs(PPh_3)_2Cp]BF_4$ (2). To a solution of $CpOsBr(PPh_3)_2$ (1.0 g, 1.16 mmol) in THF (30 mL) was added $AgBF_4$ (0.23 g, 1.16 mmol). The reaction mixture was stirred for 30 min to give a brown solution. Addition of $HC{\equiv}CCH(OH)C{\equiv}CH$ (45.5 mg, 0.58 mmol) to the reaction mixture produced a red solution immediately. The solution was stirred for an additional 15 min at room temperature. The solvent of the reaction mixture was removed under vacuum to give a red residue. The NMR of the residue showed signals assignable to $[Cp(PPh_3)_2Os{=}C{=}C{=}CHCH{=}C{=}Os(PPh_3)_2Cp](BF_4)_2$. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −5.4(s), −0.3 (s). ^1H NMR (CD_2Cl_2): δ 5.12 (s, 5 H, Cp), 5.67 (s, 5 H, Cp), 4.00 (d, J(HH) = 11.7 Hz, 1 H, =CH), 10.34 (d, J(HH) = 11.7 Hz, 1 H, =CH). The red residue was redissolved in 5 mL of THF, and the solution was passed through a column of neutral alumina (11 × 2.5 cm) using THF/acetone (1:1) as the eluent to give a blue solution. The volume of the blue solution was reduced under vacuum, and hexane was added to complete the precipitation. The blue solid was collected by filtration, washed with hexane, and then dried under vacuum. Yield: 0.55 g, 55%. UV/vis (CH_2Cl_2): λ_{max} (ϵ) 583 nm (8.2×10^4 M^{-1} cm^{-1}), 232 nm (5.0×10^4 M^{-1} cm^{-1}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −0.7 (s). ^1H NMR (CD_2Cl_2): δ 4.88 (s, 10 H, Cp), 7.15−7.46 (m, 60 H, Ph), 10.55 (qnt, ^5J(PH) = 0.9 Hz, 1 H, −CH=). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 86.1 (s, Cp), 130.6 (s, CH), 127.3−137.2 (m, Ph), 171.4 (s, C_β), 196.2 (t, ^2J(PC) = 14.8 Hz, C_α). Anal. Calcd for $C_{87}H_{71}BF_4P_4Os_2$: C, 61.19; H, 4.19. Found: C, 61.21; H, 4.22.

$[Cp(dppe)Fe{=}C{=}C{=}CHC{\equiv}CFe(dppe)Cp]BPh_4$ (4). To a solution of $CpFeCl(dppe){\cdot}CHCl_3$ (1.0 g, 1.48 mmol) in THF (30 mL) was added $AgBF_4$ (0.29 g, 1.46 mmol). The reaction mixture was stirred for 30 min to give a dark brown solution. Addition of $HC{\equiv}CCH(OH)C{\equiv}CH$ (57.5 mg, 0.73 mmol) to the reaction mixture produced a violet solution immediately. The solution was stirred for an additional 15 min at room temperature. The solvent of the reaction mixture was removed under vacuum, the violet residue was redissolved in 5 mL of CH_2Cl_2, and the violet solution was passed through a column of neutral alumina (11 × 2.5 cm) using acetone as the eluent to give a greenish blue solution. The volume of the greenish blue solution was reduced under vacuum to give a greenish blue residue. The residue was redissolved in a minimum amount of methanol, and a saturated methanol solution of $NaBPh_4$ was added to afford a greenish blue solid. The solid was collected by filtration, washed with ether and hexane, and then dried under vacuum. Yield: 0.50 g, 48%. The compound can be further purified with a silica gel column using CH_2Cl_2 as the eluent. However, the sample was still contaminated with a small amount of an unknown species having a singlet ^{31}P signal at 92.2 ppm, and therefore satisfactory analytical data could not be obtained. Selected characterization data for **4**. UV/vis (CH_2Cl_2): λ_{max} 722, 231 nm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 102.3 (s). ^1H NMR (CD_2Cl_2): δ 2.3−2.7 (m, CH_2), 4.66 (s, Cp), 6.50 (qnt, ^5J(PH) = 2.0 Hz, −CH=), 6.9−7.6 (m, Ph). ^{13}C NMR (CD_2Cl_2): δ 26.7 (m, CH_2), 85.4 (s, Cp), 122.9 (s, C_γ), 128.0−139.0 (m, Ph), 176.0 (s, C_β), 223.3 (t, ^2J(PC) = 38.9 Hz, C_α). MS (FAB, NBA matrix): 1099 (M^+).

Crystallographic Analysis for $[Cp(PPh_3)_2Os{=}C{=}C{=}CHC{\equiv}COs(PPh_3)_2Cp]BF_4$ (2). Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of ether into a CH_2Cl_2 solution saturated with complex **2** at room temperature. One molecule of CH_2Cl_2 and two molecules of H_2O were cocrystallized with the complex. A crystal of dimensions 0.21 × 0.23 × 0.34 mm^3 was mounted on a glass fiber by means of epoxy resin on an Enraf-Nonius diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 76 Å) for unit-cell determination and data collection. A summary of crystallographic data and structure, solution, and refinement details is given in Table 1. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR88)[31] and subsequently refined by difference Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. All calculations were performed using the TEXSAN crystallographic software package.[32] Selected bond distances and angles are given in Table 2.

Acknowledgment. We acknowledge financial support from the Hong Kong Research Grants Council.

Supporting Information Available: Tables of crystallographic details, bond distances and angles, atomic coordinates and equivalent isotropic displacement coefficients, and anisotropic displacement coefficients for $[Cp(PPh_3)_2Os{=}C{=}C{=}CHC{\equiv}COs(PPh_3)_2Cp]BF_4{\cdot}CH_2Cl_2{\cdot}2H_2O$ and ^1H and $^{31}P\{^1H\}$ NMR spectra of $[Cp(dppe)Fe{=}C{=}C{=}CHC{\equiv}CFe(dppe)Cp]BPh_4$ in CD_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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