Organometallics **1997,** *16,* 3557−3560

Notes

Synthesis of Symmetrical C_5H_5-Bridged Dimeric Ruthenium Complexes

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Received February 25, 1997[⊗]

Summary: Reaction of $HC{\equiv}CCH(OH)C{\equiv}CH$ *and dppe with* $RuHCl(CO)(PPh_3)_3$ *produced* $[RuCl(CO)(PPh_3)(dppe)]_2(\mu\text{-}CH{=}CH{-}CH(OH){-}CH{=}CH)$, *which was converted to the* C_5H_5*-bridged complex* $[(dppe)(PPh_3)(CO)ClRu{-}CH{=}CH{-}CH{=}CH{-}CH{=}RuCl(CO)(PPh_3)(dppe)]BF_4$ *on treatment with* $HBF_4{\cdot}Et_2O$.

There has been considerable interest in the synthesis and characterization of dimeric and polymeric organometallic compounds with π-conjugated bridges because of their structural, chemical, and material properties.[1,2] A large number of conjugated organometallic dimeric complexes with hydrocarbon chains serving as σ,σ, σ,π, or π,π bound bridging ligands have been reported. Examples of interesting dimeric complexes reported recently include C_x-bridged complexes $L_nMC_xM'L'_n$,[3,4] C_5H-bridged complexes,[5] bis(carbyne) complexes (e.g., $[(Me_3SiNCH_2CH_2)_3N]Mo{\equiv}C{-}CH{=}CH{-}C{\equiv}Mo[N(CH_2CH_2NSiMe_3)_3]$,[6] bis(vinylidene) complexes (e.g., $(P\text{-}i\text{-}Pr_3)_2ClRh{=}C{=}CH{-}CH{=}C{=}RhCl(P\text{-}i\text{-}Pr_3)_2$),[7] bis(allenylidene) complexes (e.g., $[Cl(dppe)_2Ru{=}C{=}C{=}CH{-}C_6H_4{-}CH{=}C{=}C{=}RuCl(dppe)_2](PF_6)_2$),[8] and 1,3-bimetalated cyclobutenylidene (C_4R_3) complexes.[9]

Dimeric complexes with linear C_nH_n bridges are interesting, especially in view of the fact that many conjugated organic materials (for example, polyacetylenes, push/pull stilbenes, and polyenes) have only sp^2 carbons in their backbones.[10] However, very limited examples of such complexes are known. Previously reported complexes with linear C_nH_n bridges are limited to several complexes with a C_2H_2 bridge (e.g., $Cp_2ClZr{-}CH{=}CH{-}Ru(PPh_3)_2Cp$),[11,12] C_4H_4 bridge (e.g., $Cp(dppm)Fe{-}CH{=}CH{-}CH{=}CH{-}Fe(dppm)Cp$),[13] and C_6H_6 bridge (e.g., $(DME)((CF_3)_2MeCO)_2(ArN)Mo{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}Mo(NAr)(OCMe(CF_3)_2)(DME)$.[14] Complexes with C_5H_5 bridging two different metal centers have been reported recently in a communica-

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

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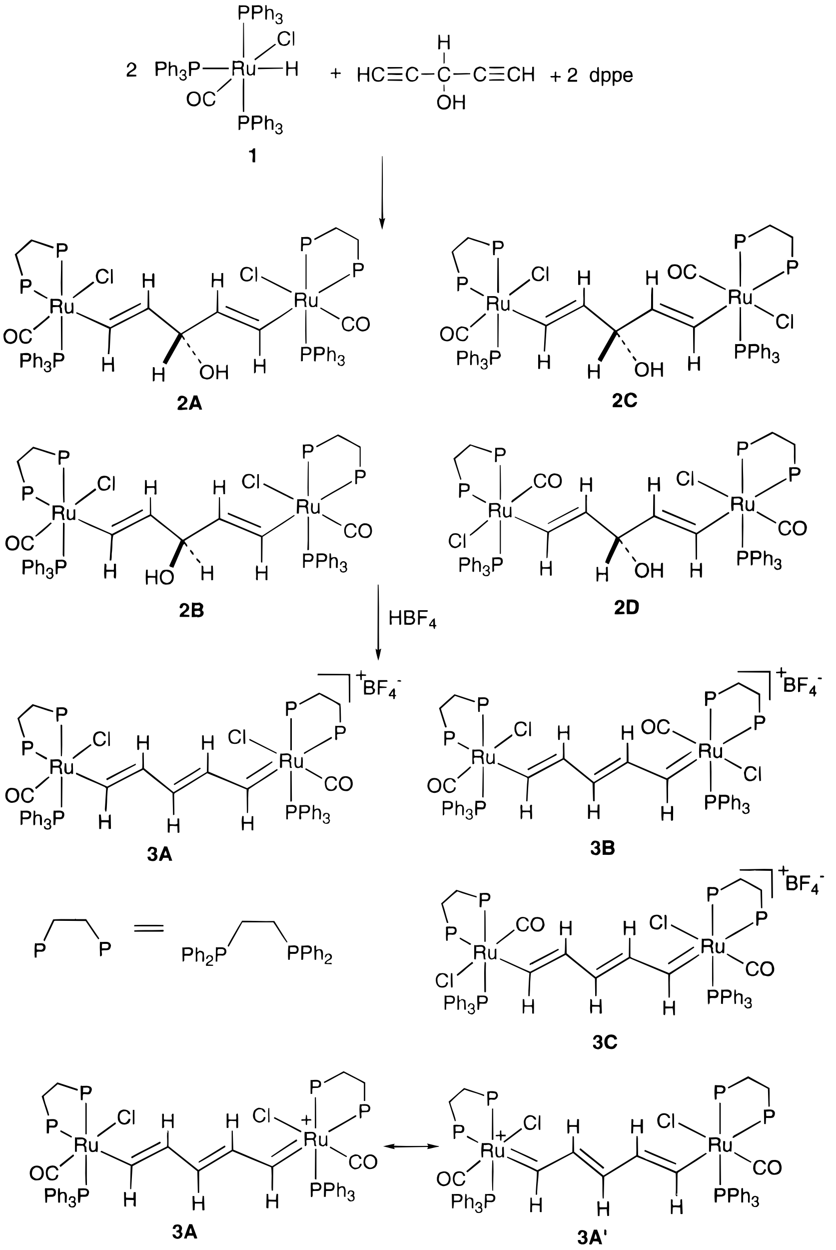
S0276-7333(97)00140-4 CCC: $14.00

Scheme 1



tion.[15] To our knowledge, symmetrical dimeric complexes bridged with $(CH)_x$ where x is odd are still unknown. To this end, we wish to report a simple method to prepare symmetrical C_5H_5-bridged dimeric ruthenium complexes. Reported complexes closely related to the C_5H_5-bridged complexes are the tetrairon complexes bridged with C_7H_5 and C_5H_3[16] and (t-$Bu_3SiO)_3Nb{=}CH{-}CH{=}CH{-}CH{=}CH{-}N{=}Nb(OSi$-$t$-$Bu_3)_3$.[17]

Results and Discussion

Sequential additions of HC≡CCH(OH)C≡CH[18] and dppe to a suspension of $RuHCl(CO)(PPh_3)_3$[19] (**1**) in CH_2Cl_2 produced a light purple solution from which [RuCl(CO)(PPh_3)(dppe)]$_2$(μ-CH=CH−CH(OH)−CH=CH) (**2**) can be isolated (Scheme 1). Complex **2** is likely formed by the reaction of dppe with the intermediate $[RuCl(CO)(PPh_3)_2]_2$(μ-CH=CH−CH(OH)−CH=CH). Reactions of $RuHCl(CO)(PPh_3)_3$ with terminal acetylenes HC≡CR are known to give RuCl(CH=CHR)(CO)$(PPh_3)_2$.[20] Related mononuclear complexes RuCl(CH=CHR)(CO)(PPh_3)(dppe) (R = t-Bu, p-tolyl) have been prepared similarly from the one-pot reaction of dppe, HC≡CR, and $RuHCl(CO)(PPh_3)_3$ *via* the intermediate RuCl(CH=CHR)(CO)$(PPh_3)_2$.[21] We have previously reported that reaction of $RuHCl(CO)(PPh_3)_3$ with HC≡CCH(OH)C≡CH lead to the isolation of $(PPh_3)_2$(CO)ClRu−CH=CH−CH=CH−CH=RuCl(OH)(CO)$(PPh_3)_2$, via the intermediate $[RuCl(CO)(PPh_3)_2]_2$(μ-

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$CH{=}CH{-}CH(OH){-}CH{=}CH$). The stability of complex **2** with respect to OH migration (in comparison to $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CH{-}CH(OH){-}CH{=}CH)$) can be attributed to the fact complex **2** is coordinatively saturated.

Complex **2** was characterized by elemental analysis and NMR and IR spectroscopy. The presence of the μ-$CH{=}CH{-}CH(OH){-}CH{=}CH$ group in complex **2** is indicated by the ^1H NMR and IR data. The vinylic protons in complex **2** are *trans* disposed, as indicated by the $^3J(HH)$ coupling constants ($J(HH) = 16{-}17$ Hz).[22] The geometry around ruthenium of complex **2**, which is consistent with the ^1H and ^{31}P NMR data, is proposed by analogy to that of $RuCl(CH{=}CHR)(CO)(PPh_3)(dppe)$.[21] Because of the presence of two chiral ruthenium centers and the presence of H and OH groups in the central carbon atom, four isomers of complex **2** are expected (Scheme 1). The presence of these isomers is indicated by the observation of four sets of ABM-pattern ^{31}P NMR signals and three sets of ^1H signals for μ-$CH{=}CH{-}CH(OH){-}CH{=}CH$. These isomers can be separated into two portions based on their solubility difference in benzene. In benzene, the *meso* isomers **2A** and **2B** are slightly soluble but the *dl* isomers **2C** and **2D** are essentially insoluble. Structures **2A** and **2B** are assigned to the benzene-soluble isomers because the isolated solid exhibited two sets of ABM-pattern ^{31}P NMR signals and two sets of ^1H signals for μ-$CH{=}CH{-}CH(OH){-}CH{=}CH$. Structures **2C** and **2D** are assigned to the isomers insoluble in benzene because the isolated solid exhibited two sets of ABM-pattern ^{31}P NMR signals but only one set of ^1H signals for CH(OH). As isomers **2C** and **2D** are enantiomers, they cannot be differentiated by ^1H and ^{31}P NMR. However, all the phosphorus atoms in isomer **2C** or **2D** are chemically inequivalent due to the lack of symmetry. Thus, two sets of ABM-pattern ^{31}P signals and one set of ^1H signals for CH(OH) are expected for **2C** and **2D**. *Meso* and *dl* diastereomers were also observed for complexes such as $[RuCl(CO)(PPh_3)(dppf)]_2(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)$ and $[RuCl(CO)(PPh_3)(dppf)]_2(\mu\text{-}CH{=}CHC_6H_4CH{=}CH)$.[21]

Treatment of complex **2** with $HBF_4{\cdot}Et_2O$ produced the deep purple C_5H_5-bridged compound $[(dppe)(PPh_3)(CO)ClRu{-}CH{=}CH{-}CH{=}CH{-}CH{=}RuCl(CO)(PPh_3)(dppe)]BF_4$ (**3**). Abstraction of an OH group from hydroxyvinyl groups to give vinylcarbene complexes has been reported previously, for example, in the preparation of $[Ru({=}CH{-}CH{=}CRR')Cl(CO)(P\text{-}i\text{-}Pr_3)_2]BF_4$[23] and $[CpFe(CO)_2{=}CH{-}CH{=}CMe_2]BF_4$.[24] Complex **3** exists as *meso* (**3A**) and *dl* (**3B**, **3C**) diastereomers, and these diastereomers can be prepared in pure form by protonation of preseparated isomers of **2** with $HBF_4{\cdot}Et_2O$. As NMR cannot differentiate the enantiomers **3B** and **3C**, two sets of ^1H, ^{31}P, and ^{13}C NMR data were observed for **3** as expected: one set for isomer **3A** and the other set for **3B** and **3C**. The meridional arrangement of the three phosphorus atoms in complex **3** is readily assigned by the ^{31}P NMR data. The presence of the $Ru_2(\mu\text{-}C_5H_5)$ assembly in complex **3** is confirmed by the ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectra, the ^1H signals for α-CH, β-CH, and γ-CH of the $Ru_2(\mu\text{-}C_5H_5)$ unit were observed near 13.0, 6.5, and 6.3 ppm, respectively. The $^3J(HH)$ coupling constants between the vinylic protons are in the range of 12−15 Hz, implying that the olefinic protons are *trans* disposed.[22] In the ^{13}C NMR spectra, the ^{13}C signals for α-CH, β-CH, and γ-CH of the $Ru_2(\mu\text{-}C_5H_5)$ unit were observed near 276, 144, and 153 ppm, respectively. The ^{13}C signals for α-CH appeared as a doublet of triplets with typical $J(PC)_{trans}$ (73 Hz) and $J(PC)_{cis}$ (10 Hz) coupling constants, implying that the C_5H_5 ligand is *trans* to a phosphorus atom.

The downfield ^1H and ^{13}C chemical shifts for the α-CH group clearly indicate the presence of an Ru=CH linkage.[25] For comparison, the ^1H signal for Ru=CH was observed at 19.06 ppm for $RuCl_2(PCy_3)_2({=}CH{-}CH{=}CH_2)$[26] and that for Ru−CH was observed at 7.70 ppm for $RuCl(CH{=}CH{-}CH(OH)Ph)(CO)(P\text{-}i\text{-}Pr_3)_2$;[23] the ^{13}C signal for Ru=CH was observed at 296.00 ppm for $RuCl_2(PCy_3)_2({=}CH{-}CH{=}CH_2)$[26] and that for Ru−CH was observed at 143.53 ppm for $RuCl(CH{=}CH\text{-}cyclo\text{-}C_6H_9)(CO)(P\text{-}i\text{-}Pr_3)_2$.[23] The observation of only one ^1H and ^{13}C signal for α-CH and β-CH of the μ-C_5H_5 bridge in each of the diastereomers implies that the dimeric compound has a delocalized structure with two identical ruthenium centers. For example, the resonance structures **3A** and **3A′** can be drawn for the *meso* isomer **3A**. Consistent with the delocalized structure, only one ABM-pattern ^{31}P NMR signal was observed for each of the diastereomers.

Further support for the delocalized structure is from the cyclic voltammetry measurements. Complex **3A** showed two irreversible oxidation peaks at 1.15 and 1.63 V and a reversible reduction peak at −1.21 V *vs* ferrocene. The separation of 0.48 V for the oxidation peaks supports the idea the complex **3A** has a delocalized structure. For comparison, the peak separation is in the range of 0.41−0.45 V for the oxidation of the C_4H_4-bridged complexes $Cp(LL)Fe{-}CH{=}CH{-}CH{=}CH{-}Fe(LL)Cp$ (LL = dppm, $(CO)(PPh_3)$, $(CO)(PMe_3)$, $(CO)_2$),[13] and 0.36 V for the oxidation of $[RuCl(dppe)_2]_2(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)$.[27]

Complex **3** has an intensive purple color. In the UV−vis spectra of complex **3**, intensive absorptions at 229 and 532 nm were observed. It may be noted that the related C_5-bridged complex $[Cp^*Re(NO)(PPh_3)(\mu\text{-}C_5)Mn(CO)_2(C_5Cl_5)]^+$ [3a] and the C_4H_4-bridged complex $[Cp(dppm)Fe{=}CH{-}CH{=}CH{-}CH{=}Fe(dppm)Cp]^{2+}$ [13b] show strong absorptions in similar regions as well. Interestingly, 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 extremely light sensitive and decomposed in hours, even

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in the dark.[3a] In contrast, the C_5H_5-bridged complex appears stable in solution and in the solid state in an inert atmosphere.

In summary, we have developed a simple method to prepare the first symmetrical C_5H_5-bridged complexes which have a delocalized structure.

Experimental Section

All manipulations were carried out at room temperature under 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 compounds $HC{\equiv}CC(OH)C{\equiv}CH$[18] and $RuHCl(CO)(PPh_3)_3$[19] were prepared according to literature methods. All other reagents were used as purchased from Aldrich or Strem.

Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^1H, ^{13}C, and ^{31}P 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 are relative to 85% H_3PO_4.

Preparation of Complex 2. To a suspension of $RuHCl(CO)(PPh_3)_3$ (1.10 g, 1.15 mmol) in 30 mL of CH_2Cl_2 was added $HC{\equiv}CCH(OH)C{\equiv}CH$ (46 mg, 0.58 mmol). The reaction mixture was stirred for *ca*. 1 min to give a red solution. Then dppe (0.90 g, 2.3 mmol) was added to the reaction mixture, and the resulting mixture was stirred for 45 min to give a light purple solution. The volume of the reaction mixture was reduced to *ca*. 10 mL under vacuum. Addition of ether (250 mL) produced a pale purple solid, which was collected by filtration, washed with hexane and ether, and dried under vacuum. Yield: 0.91 g, 91%. NMR spectra of the solid indicated that it was an isomeric mixture. To separate the isomers, the solid was extracted with 2 × 125 mL of benzene. The benzene-insoluble white solid was collected by filtration, washed with hexane and ether, and dried under vacuum. NMR data showed that the benzene-insoluble solid is a mixture of isomers **2C** and **2D** (sometimes contaminated with very small amounts of **2A** and **2B**). The volume of the benzene-soluble fraction was reduced to *ca*. 2 mL under vacuum, and ether (25 mL) and hexane (25 mL) were added to give a white solid, which was collected by filtration, washed with ether and hexane, and dried under vacuum. NMR data showed that the benzene-soluble solid is a mixture of isomers **2A** and **2B**. Selected characterization data for isomers **2A** and **2B**: $^{31}P\{^1H\}$ NMR ($CDCl_3$) showed two ABM systems $\delta A = 22.07$, $\delta B = 24.32$, $\delta M = 40.08$ ppm, $J(AB) = 17.9$, $J(AM) = 315.2$, $J(BM) = 0$ Hz; $\delta A' = 24.66$, $\delta B' = 27.89$, $\delta M' = 40.88$ ppm, $J(A'B') = 17.0$, $J(A'M') = 314.6$, $J(B'M') = 0$ Hz. ^1H NMR ($CDCl_3$): δ 8.46−6.95 (m, Ph, Ru−CH), 6.13 (dm, $J(HH) = 16.7$ Hz, Ru−CH=CH), 5.99 (dm, $J(HH) = 16.0$ Hz, Ru−CH=CH'), 5.11 (br, CH(OH)), 4.78 (br, CH'(OH)), 2.7−2.2 (m, CH_2), 1.13 (d, $J(HH) = 5.0$ Hz, OH′), 0.12 (d, $J(HH) = 3.2$ Hz, OH). IR (KBr, cm^{-1}): 3456 (br, ν(OH)), 1942 (s, ν(CO)). Anal. Calcd for $C_{95}H_{84}Cl_2O_3P_6Ru_2$: C, 65.88; H, 4.86. Found: C, 65.72; H, 4.80. Selected characterization data for isomers **2C** and **2D**: $^{31}P\{^1H\}$ NMR ($CDCl_3$) showed two ABM systems $\delta A = 22.24$, $\delta B = 24.51$, $\delta M = 39.69$ ppm, $J(AB) = 18.2$, $J(AM) = 313.8$, $J(BM) = 0$ Hz; $\delta A' = 24.64$, $\delta B' = 26.02$, $\delta M' = 39.20$ ppm, $J(A'B') = 17.7$, $J(A'M') = 314.7$, $J(B'M') = 0$ Hz. ^1H NMR ($CDCl_3$): δ 7.49−6.90 (m, Ph, Ru−CH), 5.41 (dm, $J(HH) = 16.6$ Hz, Ru−CH=CH), 5.17 (dm, $J(HH) = 17.0$ Hz, Ru−CH=CH'), 4.19 (br, CH(OH)), 2.8−2.2 (m, CH_2), 0.43 (d, $J(HH) = 3.7$ Hz, OH). IR (KBr, cm^{-1}): 3446 (br, ν(OH)), 1944 (s, ν(CO)). Anal. Calcd for $C_{95}H_{84}Cl_2O_3P_6Ru_2$: C, 65.88; H, 4.86. Found: C, 65.68; H, 5.00.

Preparation of 3. Isomer **3A** was prepared from a mixture of isomers **2A** and **2B**. $HBF_4{\cdot}Et_2O$ (54%, 20 μL, *ca* 0.15 mmol) was added to a CH_2Cl_2 (20 mL) solution of **2A** and **2B** (0.21 g, 0.12 mmol) to give a deep purple solution immediately. The volume of the reaction mixture was reduced to *ca*. 2 mL under vacuum, and ether (30 mL) was then added to give a purple solid which was collected by filtration, washed with ether and hexane, and dried under vacuum. Yield: 0.16 g, 74%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 45.24 (dd, $J(PP) = 269.1$, 6.5 Hz), 26.07 (dd, $J(PP) = 23.6$, 6.5 Hz), 23.62 (dd, $J(PP) = 269.1$, 23.6 Hz). ^1H NMR ($CDCl_3$): δ 13.04 (dd, $J(HH) = 15.3$ Hz, $J(PH) = 8.1$ Hz, 2 H, α-CH), 7.76−7.00 (m, PPh_2, PPh_3), 6.54 (m, 2 H, β-CH), 6.33 (t, $J(HH) = 12.0$ Hz, 1 H, γ-CH), 2.92−2.62 (m, 8 H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 275.8 (dt, $J(PC) = 72.1$, 11.2 Hz, α-CH), 199.1 (td, $J(PC) = 12.5$, 7.4 Hz, Ru−CO), 152.7 (t, $^4J(PC) = 6.7$ Hz, γ-CH), 143.6 (s, β-CH), 133.8−127.6 (m, Ph), 30.1 (dd, $J(PC) = 34.3$, 8.8 Hz, CH_2), 25.2 (dd, $J(PC) = 24.8$, 14.6 Hz, CH_2). IR (KBr, cm^{-1}): 1950 (s, ν(CO)). UV−vis (CH_2Cl_2): λ_{max} (ϵ) 229 (8×10^4 M^{-1} cm^{-1}), 532 nm (5×10^4 M^{-1} cm^{-1}). Anal. Calcd for $C_{95}H_{83}BCl_2F_4O_2P_6Ru_2$: C, 63.31; H, 4.64. Found: C, 63.41; H, 5.29. Isomers **3B** and **3C** were prepared similarly from a mixture of isomers **2C** and **2D**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 45.9 (dd, $J(PP) = 269.5$, 7.9 Hz), 27.1 (dd, $J(PP) = 23.8$, 7.9 Hz), 22.8 (dd, $J(PP) = 269.5$, 7.9 Hz). ^1H NMR ($CDCl_3$): δ 13.10 (dd, $J(HH) = 15.0$, $J(PH) = 8.4$ Hz, 2 H, α-CH), 6.47 (m, 2 H, β-CH), 6.31 (t, $J(HH) = 11.8$ Hz, 1 H, γ-CH), 7.63−6.96 (m, Ph), 2.41−2.90 (m, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 276.7 (dt, $J(PC) = 72.7$, 9.9 Hz, α-CH), 200.5 (td, $J(PC) = 12.3$, 7.6 Hz, Ru−CO), 153.5 (brt, $^4J(PC) = 6.4$ Hz, γ-CH), 144.2 (s, β-CH), 134.7−128.3 (m, Ph), 29.9 (dd, $J(PC) = 26.8$, 9.8 Hz, CH_2), 25.4 (dd, $J(PC) = 28.4$, 15.0 Hz, CH_2). IR (KBr, cm^{-1}): 1958 (s, ν(CO)). UV−vis (CH_2Cl_2): λ_{max} (ϵ) 229 (8×10^4 M^{-1} cm^{-1}), 532 nm (4×10^4 M^{-1} cm^{-1}). Anal. Calcd for $C_{95}H_{83}BCl_2F_4O_2P_6Ru_2$: C, 63.31; H, 4.64. Found: 62.44; H, 5.28.

Electrochemical Measurements. Cyclic voltammograms of complex **3A** were recorded in CH_2Cl_2 containing *ca*. 5 mM complex **3A** and 0.10 M Bu_4NClO_4 as the supporting electrolyte. An EG & G Princeton Applied Research Model 270/250 potentiostat was employed. Cells were fitted with glassy carbon as the working electrode, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. The potentials were reported relative to ferrocene.

Acknowledgment. The authors acknowledge financial support from the Hong Kong Research Grants Council. The authors also acknowledge the help of Dr. Xiaoyuan Li and Mr. Jian Shan Ye with the electrochemical experiments.

OM970140Q