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Synthesis and Characterization of Bimetallic Ruthenium Complexes Bridged with C_5H and Related Ligands

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Treatment of $[(\eta^5\text{-C}_5\text{R}_5)\text{Ru(L)}_2]\text{BF}_4$ (R = Me, $(\text{L})_2$ = dppe; R = H, $(\text{L})_2 = (\text{PPh}_3)_2$) with 0.45 equiv of $\text{HC}{\equiv}\text{CCH(OH)C}{\equiv}\text{CH}$ led to the formation of the C_5H_2-bridged compounds $[(\eta^5\text{-C}_5\text{R}_5)(\text{L})_2\text{Ru}{=}\text{C}{=}\text{C}{=}\text{CHCH}{=}\text{C}{=}\text{Ru(L)}_2(\eta^5\text{-C}_5\text{R}_5)](\text{BF}_4)_2$. The C_5H_2-bridged compounds reacted with alumina to give the C_5H-bridged compounds $[(\eta^5\text{-C}_5\text{R}_5)(\text{L})_2\text{Ru}{=}\text{C}{=}\text{C}{=}\text{CHC}{\equiv}\text{CRu(L)}_2(\eta^5\text{-C}_5\text{R}_5)]\text{BF}_4$. The structure of the C_5H-bridged complex $[\text{Cp(PPh}_3)_2\text{Ru}{=}\text{C}{=}\text{C}{=}\text{CHC}{\equiv}\text{CRu(PPh}_3)_2\text{Cp}]\text{BPh}_4$ has been confirmed by X-ray diffraction and shows the bridging C_5H ligand to be symmetric with a delocalized π-system. Reaction of $[(\eta^5\text{-C}_5\text{R}_5)(\text{L})_2\text{Ru}{=}\text{C}{=}\text{C}{=}\text{CHC}{\equiv}\text{CRu(L)}_2(\eta^5\text{-C}_5\text{R}_5)]\text{BF}_4$ with acetone in the presence of KOH or KOBu^t produced $(\eta^5\text{-C}_5\text{R}_5)(\text{L})_2\text{RuC}{\equiv}\text{CCH(CH}_2\text{COMe)C}{\equiv}\text{CRu(L)}_2(\eta^5\text{-C}_5\text{R}_5)$.

Introduction

Bimetallic organometallic compounds with π-conjugated bridges have recently attracted considerable attention, because of their unusual intrinsic chemical, physical, and material properties.[1,2] A large number of interesting conjugated organometallic bimetallic complexes without metal−metal bonding have been reported, including those with C_x-bridged complexes $\text{L}_n\text{MC}_x\text{M}'\text{L}_n'$,[3,4] $(\text{CH})_x$-bridged complexes,[5] C_4R_2-bridged complexes with M≡C linkages such as $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Mo}{\equiv}\text{CCH}{=}\text{CHC}{\equiv}\text{Mo}[\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3]$[6] or complexes with M=C linkages such as $[(\text{C}_5\text{H}_4\text{SiMe}_3)_2(\text{CO})\text{Nb}{=}\text{C}{=}\text{CMe-CMe}{=}\text{C}{=}\text{Nb(CO)}(\text{C}_5\text{H}_4\text{SiMe}_3)_2](\text{BPh}_4)_2$,[7] and 1,3-bimetalated cyclobutenylidene (C_4R_3) complexes.[8]

Despite the fact that a large number of conjugated bimetallic organometallic complexes have been reported, there are still very limited bimetallic complexes with conjugated hydrocarbon chains of odd numbers of carbon atoms linking two metal centers. To this end, we have investigated the reactions of $\text{HC}{\equiv}\text{CCH(OH)C}{\equiv}\text{CH}$ with $[\text{CpRu(PPh}_3)_2]^+$ and $[\text{Cp*Ru(dppe)}]^+$. Reactions of 1-alkynols with $[(\text{C}_5\text{R}_5)\text{Ru(L)}_2]^+$ and other coordinatively unsaturated ruthenium(II) complexes have been intensively studied.[9] These reactions can lead to the formation of hydroxyvinylidenes,[10] allenylidenes,[11−14] vinylvinylidenes,[15] and other unusual coupling products,[16]

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depending on the auxiliary ligands and alkynols. Thus, bimetallic complexes bridged with hydrocarbon chains of five carbon atoms may be produced from the reactions of $HC\equiv CC(OH)C\equiv CH$ with $[CpRu(PPh_3)_2]^+$ and $[Cp^*Ru(dppe)]^+$. Here we wish to report the synthesis, characterization, and properties of interesting bimetallic complexes derived from these reactions, including C_5H_2- and C_5H-bridged complexes. A preliminary account of this work has been published.[17]

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, benzene) or calcium hydride (CH_2Cl_2). The starting materials Cp*RuCl(dppe),[18] $CpRuCl(PPh_3)_2$,[19] and $HC\equiv CC(OH)C\equiv CH$[20] 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 are 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.

[Cp*(dppe)Ru=C=C=CHCH=C=Ru(dppe)Cp*](BF_4)$_2$ (3). $AgBF_4$ (0.292 g, 1.49 mmol) was added to a solution of Cp*RuCl(dppe) (1.00 g, 1.50 mmol) in THF (50 mL). The reaction mixture was stirred for 1 h to give an orange solution. Addition of $HC\equiv CCH(OH)C\equiv CH$ (54 mg, 0.67 mmol) to the orange solution produced a purple solution. The solution was stirred for a further 1 h at room temperature, and then the solvent was removed under vacuum to give a purple solid. The solid was extracted with CH_2Cl_2 (5 mL). Addition of 30 mL of ether to the CH_2Cl_2 solution yielded a purple precipitate. The purple solid was collected by filtration, washed with ether, and then dried under vacuum. Yield: 0.83 g, 74%. Anal. Calcd for $C_{77}H_{80}B_2F_8P_4Ru_2$: C, 61.45; H, 5.36. Found: C, 61.39; H, 5.50. IR (KBr, cm^{-1}): 3055 (w), 2909 (w), 1953 (s), 1881 (m), 1627 (w), 1529 (s), 1438 (s), 1168 (m), 1061 (s). UV−vis (CH_2Cl_2): $\lambda_{max}(\epsilon)$ 528 (4.2×10^4 M^{-1} cm^{-1}), 230 nm (7.8×10^4 M^{-1} cm^{-1}). ^1H NMR ($CDCl_3$): δ 7.03−7.80 (m, 40 H, 8 Ph), 6.01 (d, ^3J(HH) = 11.7 Hz, 1 H, Ru=C=C=CH), 3.90 (d, ^3J(HH) = 11.7 Hz, 1 H, Ru=C=CH), 2.40−2.70 (m, 8 H, 4 CH_2), 1.63 (s, 15 H, 5 CH_3), 1.49 (s, 15 H, 5 CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 76.9 (s), 67.5 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 353.7 (t, *J*(PC) = 15.6 Hz, Ru=*C*=CH), 281.1 (t, *J*(PC) = 19.6 Hz, Ru=*C*=C=CH), 188.9 (s, Ru=C=*C*=CH), 132.8 (s, Ru=C=C=*C*H), 128.1 (s, Ru=C=*C*H), 135.3−128.9 (m, Ph), 106.0 (s, *C*$_5$Me$_5$), 101.7 (s, *C*$_5$Me$_5$), 30.2−28.7 (m, CH_2), 10.7 (s, C$_5$*Me*$_5$), 10.5 (s, C$_5$*Me*$_5$).

[Cp(PPh_3)$_2$Ru=C=C=CHCH=C=Ru(PPh_3)$_2$Cp](BF_4)$_2$ (4). To a blue solution of **6** (0.20 g, 0.13 mmol) in 5 mL of CH_2Cl_2 was added 1 equiv of $HBF_4\cdot Et_2O$ to give a purple solution. The volume of the reaction mixture was reduced until a purple solid began to form, and ether (20 mL) was then added to complete the precipitation. The deep purple solid was collected by filtration, washed with hexane (10 mL) and ether (10 mL), and then dried under vacuum. Yield: 0.16 g, 76%. Anal. Calcd for $C_{87}H_{72}B_2F_8P_4Ru_2$: C, 64.62; H, 4.49. Found: C, 64.39; H, 4.57. ^1H NMR (CD_2Cl_2): δ 8.30 (d, ^3J(HH) = 11.7 Hz, 1 H, Ru=C=C=CH), 7.53−6.88 (m, 60 H, 12 Ph), 5.98 (d, ^3J(HH) = 11.7 Hz, 1 H, Ru=C=CH), 5.43 (s, 5 H, Cp), 4.97 (s, 5 H, Cp). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 46.7 (s), 37.6 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 359.1 (t, *J*(PC) = 15.1 Hz, Ru=*C*=CH), 282.4 (t, *J*(PC) = 19.2 Hz, Ru=*C*=C=CH), 191.1 (s, Ru=C=*C*=CH), 138.0 (s, Ru=C=C=*C*H), 134.3 (s, Ru=C=*C*H), 121.6−135.8 (m, Ph), 97.3 (s, Cp), 92.3 (s, Cp).

[Cp*(dppe)Ru=C=C=CHC≡CRu(dppe)Cp*]BF_4 (5). Method A. A 5 g amount of neutral alumina was added to a purple solution of **3** (1.0 g, 0.66 mmol) in 25 mL of CH_2Cl_2. The reaction mixture turned blue immediately. The alumina was removed by filtration and washed with CH_2Cl_2 to give a deep blue solution. The solvent was then removed completely under vacuum to give a blue solid. Yield: 0.81 g, 86%. Anal. Calcd for $C_{77}H_{79}BF_4P_4Ru_2$: C, 65.25; H, 5.62. Found: C, 65.16; H, 5.60. IR (KBr, cm^{-1}): 3056 (w), 2903 (w), 1881 (s), 1575 (w), 1437 (m), 1096 (m), 1029 (m), 698 (m), 533 (m). UV−vis (CH_2Cl_2): λ_{max} (ϵ) 630 (5.8×10^4 M^{-1} cm^{-1}), 230 nm (8.0×10^4 M^{-1} cm^{-1}). ^1H NMR ($CDCl_3$): δ 7.05−7.48 (m, 41 H, 8 Ph, C_5H), 2.30−2.74 (m, 8 H, 4 CH_2), 1.51 (s, 30 H, 10 CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 78.4 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 225.6 (t, *J*(PC) = 20.9 Hz, C(α)), 163.1 (s, C(β)), 128.5 (s, C(γ)), 135.8−127.6 (m, Ph), 97.5 (s, *C*$_5$Me$_5$), 29.8−29.2 (m, CH_2), 9.7 (s, C$_5$*Me*$_5$).

Method B. A purple CH_2Cl_2 solution (5 mL) of crude **3** (ca. 3.00 mmol) prepared from the reactions of [Cp*Ru(dppe)]BF_4 and $HC\equiv CCH(OH)C\equiv CH$ was loaded onto a column of neutral alumina (20 cm). The column was eluted with CH_2Cl_2/acetone (5:1) to give a blue solution. The solvents of the blue solution were removed under vacuum to give a blue solid. The solid was collected by filtration, washed with ether (20 mL) and hexane (20 mL), and dried under vacuum to give 1.2 g (58%) of pure **5** as indicated by NMR.

After the blue compound **5** was eluted, the column was further washed with acetone to give a brown solution. The solvent of the brown solution was removed under vacuum to give a yellowish brown solid, which was identified as [Cp*Ru(CO)(dppe)]BF_4 (**7**; 95 mg, 4.2% yield). Anal. Calcd for $C_{37}H_{39}BF_4OP_2Ru$: C 59.29; H, 5.25. Found: C, 59.09; H, 5.46. IR (KBr, cm^{-1}): 1975 (s) [ν(C≡O)]. ^1H NMR ($CDCl_3$): δ 7.08−7.58 (m, 20 H, 4 Ph), 2.60−2.80 (m, 4 H, CH_2), 1.62 (m, 15 H, 5 CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 70.4 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 202.7 (t, *J*(PC) = 16.0 Hz, C≡O), 132.3−128.7 (m, Ph), 99.4 (s, *C*$_5$Me$_5$), 29.6−30.2 (m, CH_2), 9.6 (s, C$_5$*Me*$_5$).

[Cp(PPh_3)$_2$Ru=C=C=CHC≡CRu(PPh_3)$_2$Cp]BF_4 (6). To a solution of $CpRuCl(PPh_3)_2$ (1.10 g, 1.53 mmol) in THF (10 mL)/CH_2Cl_2 (10 mL) was added $AgBF_4$ (301 mg, 1.51 mmol). The reaction mixture was stirred for a further 15 min to give a brown solution. Addition of $HC\equiv CCH(OH)C\equiv CH$ (55 mg, 0.69 mmol) to the reaction mixture produced a purple solution immediately. The solution was stirred for an additional 15 min at room temperature. The solvent of the reaction mixture was removed under vacuum, and the purple residue was extracted with CH_2Cl_2 to give a purple solution. The purple solution was passed through a column of neutral alumina (10 cm) using CH_2Cl_2/acetone (8:1) as the eluent to give a blue solution. The volume of the blue solution was reduced under vacuum until a blue solid formed, and ether (20 mL) was added to complete the precipitation. The blue solid was collected by filtration, washed with ether (20 mL), and hexane (20 mL) and then dried under vacuum. Yield: 0.70 g, 61%. Anal. Calcd for $C_{87}H_{71}BF_4P_4Ru_2$: C, 68.33; H, 4.68. Found: C, 68.19; H, 5.06. IR (KBr, cm^{-1}): 3052 (w), 1881 (s), 1572 (w), 1481 (m), 1435 (m), 1091 (m). UV−vis (CH_2Cl_2): λ_{max} (ϵ) 600 (7.2×10^4 M^{-1} cm^{-1}), 230 nm (6.8×10^4 M^{-1} cm^{-1}). ^1H NMR (CD_2Cl_2): δ 7.88 (quintet, ^5J(PH) = 1.1 Hz, 1 H, −CH=), 7.33−7.13 (m, 60 H, 12 Ph), 4.72 (s, 10 H, 2 Cp). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ

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46.8 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 228.5 (t, $^2J(PC) = 21.7$ Hz, C(α)), 168.5 (s, C(β)), 133.1 (s, C(γ)), 136.9−127.8 (m, Ph), 89.3 (s, Cp).

Air Oxidation of $[Cp^*(dppe)Ru{=}C{=}C{=}CHC{\equiv}CRu(dppe)Cp^*]BF_4$. An appropriate amount of complex **5** was dissolved in $CDCl_3$ in an NMR tube. After ^{31}P and ^1H NMR spectra of the solution were collected, the solution in the NMR tube was exposed to air. ^{31}P and ^1H NMR spectra of the sample were collected again after the solution was exposed to air for 1 day, 2 days, 3 days, 5 days, 1 week, and 2 weeks. The experiment showed that the intensities of the signals due to complex **5** gradually decreased and those due to $[Cp^*Ru(CO)(dppe)]BF_4$ (**7**) gradually increased. Complex **7** appeared to be the predominant diamagnetic phosphorus-containing decomposition product. At the end of 2 weeks, the solution contained both complexes **5** and **7** in an ratio of *ca.* 3:2. Pure samples of complex $[Cp^*Ru(CO)(dppe)]BF_4$ could be obtained by chromatography.

Air Oxidation of $[Cp(PPh_3)_2Ru{=}C{=}C{=}CHC{\equiv}CRu(PPh_3)_2Cp]BF_4$. An appropriate amount of complex **6** was dissolved in $CDCl_3$ in an NMR tube. After ^{31}P and ^1H NMR spectra of the solution were collected, the solution in the NMR tube was then exposed to air. ^{31}P and ^1H NMR spectra of the sample were collected again after the solution was exposed to air for 1 day, 2 days, 3 days, 5 days, 1 week, and 2 weeks. The experiment showed that the intensities of the signals due to complex **6** gradually decreased and those due to complex $[CpRu(CO)(PPh_3)_2]BF_4$ (**8**) and $PPh_3{=}O$ gradually increased. Signals due to other uncharacterized species were also observed. At the end of 2 weeks, the signals due to complex **6** almost completely disappeared and those of complex **8** and $PPh_3{=}O$ became predominant. Pure samples of $[CpRu(CO)(PPh_3)_2]BF_4$ could be obtained by chromatography.

$Cp^*(dppe)RuC{\equiv}CCH(CH_2COMe)C{\equiv}CRu(dppe)Cp^*$ (9). To a solution of **5** (0.179 g, 0.126 mmol) in acetone (10 mL) was added $KOBu^t$ (28 mg, 0.25 mmol). The reaction mixture turned yellow in 10 min and was stirred for a further 1 h at room temperature. The solvent of the reaction mixture was removed under vacuum, and the residue was extracted with hexane (100 mL) to give a yellow solution. The hexane was removed completely under vacuum to give a yellow solid. Yield: 152 mg, 87%. Anal. Calcd for $C_{80}H_{84}OP_4Ru_2$: C, 69.24, H, 6.10. Found: C, 69.65; H, 5.95. IR (KBr, cm^{-1}): 2080 (m) [ν(C≡C)], 1704 (m) [ν(C=O)]. ^1H NMR ($CDCl_3$): δ 6.88−7.74 (m, 40 H, 8 Ph), 3.80 (t, 1 H, $^3J(HH) = 7.2$ Hz, C≡CCHC≡C), 2.44−2.72 (m, 4 H, 2 CH_2), 2.08 (d, $^3J(HH) = 7.2$ Hz, 2 H, $CH_2C{=}O$), 1.80−2.04 (m, 4 H, 2 CH_2), 1.53 (s, 3 H, $COCH_3$), 1.49 (s, 30 H, 10 CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 81.6 (d, $J(PP) = 11.6$ Hz), 80.4 (d, $J(PP) = 11.6$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 209.9 (s, C=O), 140.2−137.2 (m, *ipso*-Ph), 134.2−126.9 (m, *o,m,p*-Ph). 106.6 (s, RuC≡*C*), 102.1 (t, $^2J(PC) = 25.4$ Hz, Ru*C*≡C), 91.8 (s, C_5Me_5), 53.9 (s, $CH_2C{=}O$), 29.4 (s, $CH_3C{=}O$), 28.7−29.1 (m, PCH_2), 22.5 (s, RuC≡C*C*H), 10.0 (s, C_5Me_5).

$Cp(PPh_3)_2RuC{\equiv}CCH(CH_2COMe)C{\equiv}CRu(PPh_3)_2Cp$ (10). To a solution of **6** (0.193 g, 0.126 mmol) in acetone (10 mL) was added $KOBu^t$ (28 mg, 0.25 mmol). The reaction mixture turned yellow and was stirred for 15 min at room temperature. The solvent was removed under vacuum to give a brown solid, and the residue was extracted with 10 mL of hexane/benzene (2/1 v/v) to give a yellow solution. The solvents were removed completely under vacuum to give a yellow solid. Yield: 158 mg, 84%. Anal. Calcd for $C_{90}H_{76}OP_4Ru_2$: C, 72.08; H, 5.11. Found: C, 72.46; H, 5.03. IR (KBr, cm^{-1}): 2087 (m) [ν(C≡C)], 1703 (m) [ν(C=O)]. ^1H NMR (CD_2Cl_2): δ 7.80−7.09 (m, 60 H, 12 Ph), 4.31 (s br, 11 H, 2 C_5H_5, C≡CCHC≡C, the latter proton is buried in the Cp signal, as confirmed by a C−H COSY experiment), 2.37 (d, $J(HH) = 6.8$ Hz, 2 H, CH_2), 1.71 (s, 3 H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 48.9 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 208.1 (s, C=O), 139.7−139.0 (m, *ipso*-Ph), 133.8−126.7 (m, *o,m,p*-Ph), 112.5 (s, RuC≡*C*), 89.5 (t, $^2J(PC) = 24.7$ Hz, Ru*C*≡C), 53.4 (s, $CH_2C{=}O$), 29.9 (s, $CH_3C{=}O$), 26.3 (s, RuC≡C*C*H).

Crystallographic Analysis of $[Cp(PPh_3)_2Ru{=}C{=}C{=}CHC{\equiv}CRu(PPh_3)_2Cp]BPh_4{\cdot}CH_2Cl_2{\cdot}Et_2O$. Suitable crystals for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of $[Cp(PPh_3)_2Ru{=}C{=}C{=}CHC{\equiv}CRu(PPh_3)_2Cp]BF_4$ containing $NaBPh_4$ at room temperature. A specimen of dimensions 0.3 × 0.3 × 0.6 mm was mounted on a glass fiber and used for X-ray structure determination. The diffraction data were collected on a Siemens P4-RA diffractometer at 228 K. The crystal system was triclinic, and the space group **is** $P\bar{1}$. A total of 16 347 intensity measurements were made using the 2θ-θ scan technique in the range 3.0−50° (Mo Kα radiation). Of these, 15 668 were unique ($R_{int} = 2.37\%$) and 7491 observed ($F \geq 4\sigma(F)$), which were used for structure solution and refinement employing the SHELXTL PLUS program package. Solution by direct methods yielded the positions of all non-hydrogen atoms. Refinement by full-matrix least squares resulted in final discrepancy indices of $R = 6.25\%$ and $R_w = 5.21\%$ with GOF = 1.16. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens, including that on the central bridging carbon atom C(3), were revealed in difference Fourier maps but then placed in geometrically determined positions with $d_{C-H} = 0.96$ Å and refined isotropically with riding constraints and group thermal parameters. The data to parameter ratio was 6.7:1 and the residual electron density 0.74 e Å^{-3}. Further crystallographic details are given in Table 1, and selected bond distances and angles are listed in Table 2.

Table 1. Crystal Data and Refinement Details for $[Cp(PPh_3)_2Ru{=}C{=}C{=}CHC{\equiv}CRu(PPh_3)_2Cp]BPh_4{\cdot}CH_2Cl_2{\cdot}Et_2O$

formula	$C_{116}H_{103}BCl_2OP_4Ru$
fw	1920.7
color and habit	dark green rod
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	15.431(5)
b, Å	17.466(3)
c, Å	19.143(3)
α, deg	80.33(2)
β, deg	81.03(2)
γ, deg	69.02(2)
V, Å^3	4723(2)
Z	2
d_{calcd}, g cm^{-3}	1.396
abs coeff, mm^{-1}	0.496
F(000)	1988
radiation	Mo Kα (λ = 0.071 073 Å)
2θ range, deg	3.0−50
scan type	2θ−θ
scan speed, deg/min	variable; 5.00−60.00° in ω
scan range (ω), deg	1.02 plus Kα separation
std rflns	3 measd every 150 rflns
index range	$0 \leq h \leq 15$, $-19 \leq k \leq 20$, $-22 \leq l \leq 22$
no. of rflns collected	16 347
no. of indep rflns	15 688 ($R_{int} = 2.37\%$)
no. of obsd rflns	7491 ($F > 4.0\sigma(F)$)
abs corr	semiempirical
weight scheme	unit weight
no. of params refined	1111
final *R* indices (obsd data), %	$R = 6.25$, $R_w = 5.21$
goodness of fit	1.16
largest diff peak, largest diff hole, e Å^{-3}	0.74, −1.03

Results and Discussion

Synthesis of C_5H_2- and C_5H-Bridged Bimetallic Complexes. As shown in Scheme 1, C_5H_2- and C_5H-bridged complexes can be readily prepared from the reactions of HC≡CCH(OH)C≡CH with appropriate ruthenium precursors.

Treatment of $[Cp^*Ru(dppe)]BF_4$ or $[Cp^*Ru(THF)(dppe)]BF_4$ (generated in situ from the reaction of $Cp^*RuCl(dppe)$ (**1**) with $AgBF_4$ in THF) with 0.45 equiv of HC≡CCH(OH)C≡CH caused an immediate color

Table 2. Selected Bond Distances and Angles for $[Cp(PPh_3)_2Ru{=}C{=}C{=}CHC{\equiv}CRu(PPh_3)_2Cp]BPh_4{\cdot}CH_2Cl_2{\cdot}Et_2O$

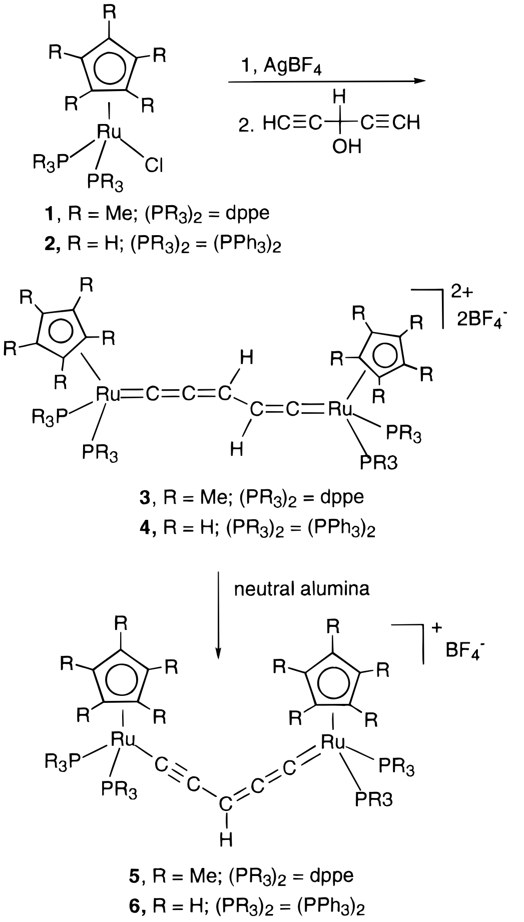
Bond Distances (Å)

Ru(1)−P(1)	2.305(3)	Ru(1)−P(2)	2.307(3)
Ru(2)−P(3)	2.304(3)	Ru(2)−P(4)	2.335(3)
Ru(1)−C(11)	2.253(12)	Ru(1)−C(12)	2.259(10)
Ru(1)−C(13)	2.259(9)	Ru(1)−C(14)	2.263(8)
Ru(1)−C(15)	2.224(10)	Ru(2)−C(21)	2.248(13)
Ru(2)−C(22)	2.232(11)	Ru(2)−C(23)	2.249(11)
Ru(2)−C(24)	2.267(13)	Ru(2)−C(25)	2.260(12)
Ru(1)−C(1)	1.933(8)	Ru(2)−C(5)	1.913(10)
C(1)−C(2)	1.241(12)	C(2)−C(3)	1.364(11)
C(3)−C(4)	1.387(16)	C(4)−C(5)	1.256(15)

Bond Angles (deg)

P(1)−Ru(1)−P(2)	102.7(1)	P(1)−Ru(1)−C(1)	85.3(3)
P(2)−Ru(1)−C(1)	90.0(3)	P(3)−Ru(2)−P(4)	101.4(1)
P(3)−Ru(2)−C(5)	89.8(1)	P(4)−Ru(2)−C(5)	89.8(1)
Ru(1)−C(1)−C(2)	176.6(8)	C(1)−C(2)−C(3)	166.5(12)
C(2)−C(3)−C(4)	130.3(11)	C(3)−C(4)−C(5)	167.4(10)
C(4)−C(5)−Ru(2)	176.6(8)		

Scheme 1



1, R = Me; $(PR_3)_2$ = dppe
2, R = H; $(PR_3)_2$ = $(PPh_3)_2$

3, R = Me; $(PR_3)_2$ = dppe
4, R = H; $(PR_3)_2$ = $(PPh_3)_2$

5, R = Me; $(PR_3)_2$ = dppe
6, R = H; $(PR_3)_2$ = $(PPh_3)_2$

change from orange to purple. The purple C_5H_2-bridged compound $[Cp^*(dppe)Ru{=}C{=}C{=}CHCH{=}C{=}Ru(dppe)Cp^*](BF_4)_2$ (**3**) could be isolated in good yield from the reaction mixture using ether as the precipitating solvent. Compound **3** can be easily deprotonated by alumina or silica gel to give the C_5H-bridged complex $[Cp^*(dppe)Ru{=}C{=}C{=}CHC{\equiv}CRu(dppe)Cp^*]BF_4$ (**5**). Deprotonation of vinylidene complexes with alumina to give corresponding σ-acetylide complexes has been reported previously.[16b,21]

The above reactions can be applied to synthesize C_5H_2- and C_5H-bridged bimetallic complexes containing the $CpRu(PPh_3)_2$ moiety. Treatment of $[CpRu(PPh_3)_2]BF_4$ or $[CpRu(THF)(PPh_3)_2]BF_4$ (generated in situ from the reaction of $CpRuCl(PPh_3)_2$ (**2**) with $AgBF_4$ in THF/CH_2Cl_2) with 0.45 equiv of $HC{\equiv}CCH(OH)C{\equiv}CH$ led to the formation of the analogous C_5H_2-bridged complex $[Cp(PPh_3)_2Ru{=}C{=}C{=}CHCH{=}C{=}Ru(PPh_3)_2Cp](BF_4)_2$ (**4**) as the predominant product. Difficulty was encountered in the attempt to obtain analytically pure compound **4** from the reaction mixture using column chromatography, as complex **4** was readily deprotonated by alumina or silica gel to form the C_5H-bridged compound $[Cp(PPh_3)_2Ru{=}C{=}C{=}CHC{\equiv}CRu(PPh_3)_2Cp]BF_4$ (**6**). In fact, an analytically pure sample of **6** can be readily obtained by passing the reaction mixture through a column of neutral alumina or silica gel. Analytically pure samples of **4** can be obtained conversely by the quantitative reaction of $HBF_4{\cdot}Et_2O$ with pure samples of complex **6**.

The C_5H_2-bridged compounds **3** and **4** are probably formed *via* the dehydration of the hydroxyvinylidene intermediates $[(C_5R_5)(PR_3)_2Ru{=}C{=}CHCH(OH)CH{=}C{=}Ru(PR_3)_2(C_5R_5)](BF_4)_2$. Although we were unable to isolate these intermediates, it has been established that reactions of coordinatively unsaturated complexes with simple 1-alkynols can lead to allenylidene or vinylvinylidene complexes *via* hydroxyvinylidene intermediates.[10−16,22] For example, spontaneous dehydration of hydroxyvinylidene intermediates to give allenylidene complexes occurred in the reactions of 1-alkynol with electrophilic ruthenium centers such as $[CpRu(PR_3)_2]^+$,[11] $[(\eta^5\text{-}C_9H_7)Ru(PR_3)_2]^+$,[13] $[RuCl(dppm)_2]^+$,[12a−c] and $[RuCl(N(CH_2CH_2PPh_2)_3)]^+$.[12e] Stable ruthenium hydroxyvinylidene complexes can only be isolated with more electron rich metal centers such as $[Cp^*Ru(PMe_2Ph)_2]^+$,[10] and $RuCl_2((i\text{-}Pr)_2PCH_2CO_2Me)_2$.[22b]

Complexes **3**−**6** are moderately air-sensitive compounds. Although they can be handled briefly in air in the solid state, decomposition was observed when their solutions were exposed to air. When solutions of complexes **3** and **5** were exposed to air for several days or longer, the carbonyl complex $[Cp^*Ru(CO)(dppe)]BF_4$ (**7**) was produced as the major decomposition product, which was readily characterized by spectroscopic methods and by elemental analysis. In particular, the IR spectrum showed a strong absorption at 1975 cm^{-1} assignable to $\nu(C{\equiv}O)$ and the ^{13}C NMR showed a C≡O resonance at 202.7 ppm (t, $J(PC) = 16.0$ Hz). Exposure of complexes **4** and **6** to air for several days or longer led to the isolation of the known complex $[CpRu(CO)(PPh_3)_2]^+$ (**8**).[23] It was also noted that small amounts of the carbonyl complexes **7** and **8** could be obtained in the purification of the C_5H-bridged complexes **5** and **6** using column chromatography. Reactions of ruthenium vinylidene complexes with oxygen or water to give

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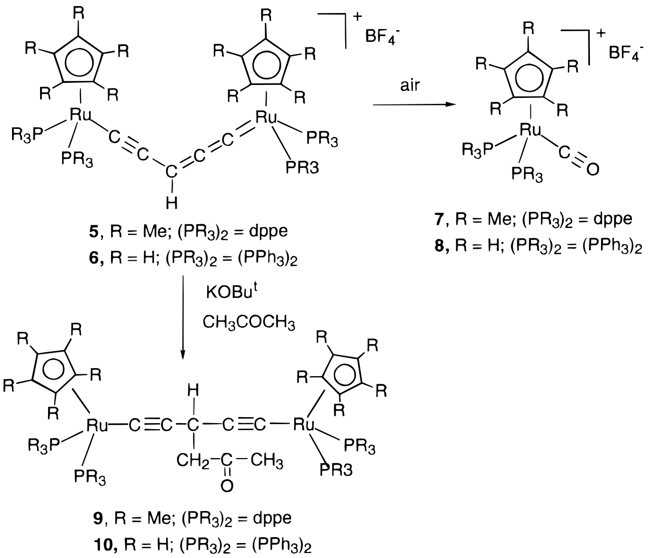
Scheme 2



5, R = Me; (PR$_3$)$_2$ = dppe
6, R = H; (PR$_3$)$_2$ = (PPh$_3$)$_2$

7, R = Me; (PR$_3$)$_2$ = dppe
8, R = H; (PR$_3$)$_2$ = (PPh$_3$)$_2$

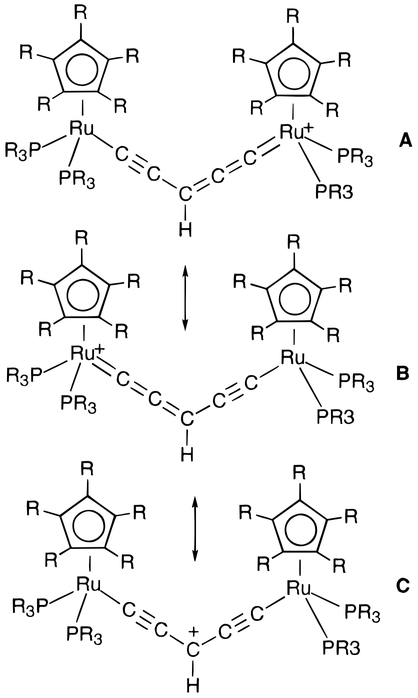
9, R = Me; (PR$_3$)$_2$ = dppe
10, R = H; (PR$_3$)$_2$ = (PPh$_3$)$_2$

corresponding CO-containing complexes have been reported for several cases.[10,24 25]

Spectroscopic Characterization of C_5H_2- and C_5H-Bridged Bimetallic Complexes. The C_5H_2-bridged complexes **3** and **4** have been characterized by IR and multinuclear NMR spectroscopy and elemental analysis. In the ^{1}H NMR spectrum of complex **3** (in CDCl$_3$), the signals for Ru=C=CH and Ru=C=C=CH were observed at 3.90 (d, J(HH) = 11.7 Hz) and 6.01 ppm (d, J(HH) = 11.7 Hz), respectively. The Ru$_2$(μ-C$_5$H$_2$) assembly of complex **3** is indicated by ^{13}C NMR (in CDCl$_3$), which showed resonances at 353.7 (t, J(PC) = 15.6 Hz), 281.1 (t, J(PC) = 19.6 Hz), 188.9 (s), 132.8 (s), and 128.1 (s) ppm for the five carbons in Ru=C=C=CHCH=C=Ru. The signals at 281.1, 188.9, and 132.8 ppm can be assigned to the Ru=C=C=CH group,[9] and those at 353.7 and 128.1 ppm can be assigned to the Ru=C=CH group.[9] The ^{1}H and ^{13}C NMR assignments have been confirmed by the ^{1}H$-$^{13}C COSY spectrum. Consistent with the structure, the ^{31}P NMR spectrum of **3** in CDCl$_3$ gave two singlets for the dppe ligand at 76.9 and 67.5 ppm. IR bands assignable to ν(C=C=CHCH=C) at *ca.* 1953 (s) and 1881 (m) cm^{-1} were also observed for **3**.

The presence of the Ru$_2$(μ-C$_5$H$_2$) assembly in complex **4** is indicated by ^{1}H and ^{13}C NMR. In the ^{1}H NMR spectrum of complex **4** in CD$_2$Cl$_2$, the signals for Ru=C=CH and Ru=C=C=CH were observed at 8.30 (d, J(HH) = 11.7 Hz) and 5.98 ppm (d, J(HH) = 11.7 Hz), respectively. In the ^{13}C NMR spectrum of complex **4** in CD$_2$Cl$_2$, the resonances for the five carbons of Ru=C=C=CHCH=C=Ru were observed at 282.4 (t, J(PC) = 19.2 Hz, Ru=*C*=C=CH), 191.1 (s, Ru=C=*C*=CH), 138.0 (s, Ru=C=C=*C*H), 134.3 (s, *C*H=C=Ru), and 359.1 ppm (t, J(PC) = 15.1 Hz, CH=*C*=Ru). Consistent with the structure, the ^{31}P NMR spectrum in CD$_2$Cl$_2$ gave two singlets for the PPh$_3$ ligands at 46.7 and 37.6 ppm.

The presence of the Ru$_2$(μ-C$_5$H) unit in complexes **5** and **6** is supported by their IR and multinuclear NMR spectroscopic data. In the IR spectra, a strong IR band assignable to ν(C=C=C) was observed at *ca.* 1881 cm^{-1} for both **5** and **6**. The ^{13}C NMR of complex **5** (in CDCl$_3$) displayed the signals for the five carbons of Ru=C=C=CHC≡CRu at 225.6 (t, ^2J(PC) = 20.9 Hz, C(α)), 163.1 (s, C(β)), and 128.4 ppm (s, C(γ)) ppm. The ^{13}C signals for the five carbons of Ru=C=C=CHC≡CRu of complex **6** (in CD$_2$Cl$_2$) were observed at 228.5 (t, ^2J(PC) = 21.7 Hz, C(α)), 168.5 (s, C(β)), and 133.1 ppm (s, C(γ)). In the ^{1}H NMR spectrum of complex **6** (in CD$_2$Cl$_2$), the C$_5$H signal was observed as a quintet at 7.88 ppm with ^5J(PH) = 1.1 Hz. For complex **5**, the C$_5$H signal was not readily seen in the normal ^{1}H NMR spectrum, presumably buried in the signals (7.05−7.48 ppm) of the phenyl groups. This was confirmed by a ^{1}H-^{13}C COSY spectrum, which indicated that the signal for the C$_5$H proton should appear at 7.38 ppm. The ^{13}C data associated with Ru$_2$(μ-C$_5$H) groups indicated that the C$_5$H-bridged complexes have a symmetric delocalized structure with two identical ruthenium centers. Structures **A**−**C** are three of the possible resonance structures for the C$_5$H-bridged complexes of the type [(C$_5$R$_5$)(PR$_3$)$_2$Ru=C=C=CHC≡CRu(PR$_3$)$_2$(C$_5$R$_5$)]$^+$. Consistent with the delocalized structure, the ^{1}H NMR spectra gave only one Cp* signal for **5** and one Cp signal for **6** and the ^{31}P NMR spectra gave only one singlet at 78.4 ppm for the dppe ligand for **5** and only one singlet at 46.8 ppm for the PPh$_3$ ligand for **6**.



Solid-State Structure of [Cp(PPh$_3$)$_2$Ru=C=C=CHC≡CRu(PPh$_3$)$_2$Cp]BPh$_4$. To confirm the structures of complexes **5** and **6**, we have attempted to grow their crystals for X-ray diffraction study. Unfortunately, crystals of good quality could not be obtained for **5** and **6**. However, by substituting the BF$_4^-$ counteranion in complex **6** with BPh$_4^-$, we have successfully obtained good-quality crystals of [Cp(PPh$_3$)$_2$Ru=C=C=CHC≡CRu(PPh$_3$)$_2$Cp]BPh$_4$,which cocrystallized with ether and CH$_2$Cl$_2$. A view of the molecular structure of the cation [Cp(PPh$_3$)$_2$Ru=C=C=CHC≡CRu(PPh$_3$)$_2$Cp]$^+$ is shown

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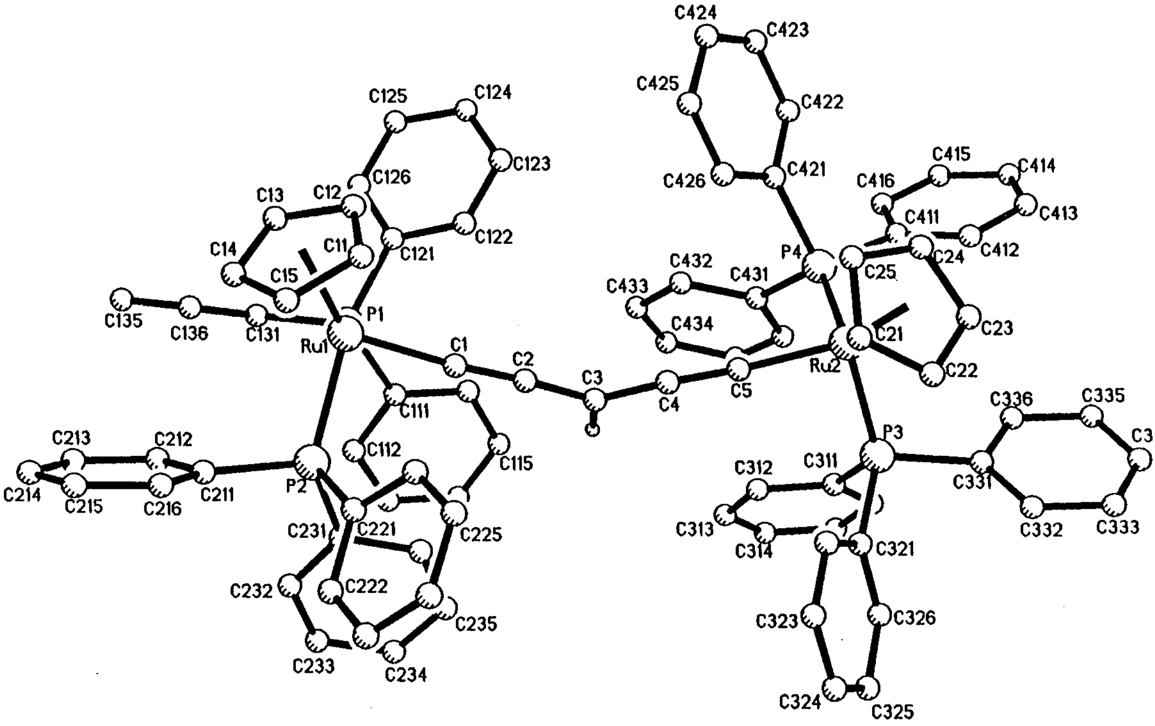

Figure 1. Molecular structure for the cation $[CpRu(PPh_3)_2C{=}C{=}CHC{\equiv}CRu(PPh_3)_2Cp]^+$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Ruthenium Allenylidene and Acetylide Complexes

complex	Ru−C(α)	C(α)−C(*β*)	C(*β*)−C(*γ*)	Ru−C(α)−C(*β*)	C(α)−C(*β*)−C(*γ*)	ref
$[CpRu(PPh_3)_2C{=}C{=}CHC{\equiv}CRu(PPh_3)_2Cp]^+$	1.933(8)	1.241(12)	1.364(11)	176.6(8)	166.5(12)	this work
	1.913(8)	1.256(15)	1.387(16)	176.6(8)	167.4(11)	
$[Cp(PMe_3)_2Ru{=}C{=}C{=}CPh_2]^+$	1.884(5)	1.256(8)	1.329(9)	175.9(5)	175.1(7)	11
$[(C_9H_7)(PPh_3)_2Ru{=}C{=}C{=}CPh_2]^+$	1.878(5)	1.260(7)	1.353(7)	168.5(5)	168.2(7)	13a
$[(C_9H_7)(PPh_3)_2Ru{=}C{=}C{=}C(C_{13}H_{20})]^+$	1.889(5)	1.256(1)	1.339(7)	173.6(4)	173.2(5)	16b
$[(dppm)_2ClRu{=}C{=}C{=}C(C_{14}H_{10})]^+$	1.85(2)	1.29(3)	1.39(3)	179.0(2)	177.0(2)	12b
$(PO)_2Cl_2Ru{=}C{=}C{=}CPh_2$	1.84(1)	1.27(2)	1.34(2)	178(1)	175(1)	22b
$[(NP_3)ClRu{=}C{=}C{=}C(OMe)CH{=}CPh_2]^+$	1.921(5)	1.254(7)	1.369(7)	174.1(3)	170.2(6)	12e
$[Cp^*{}_2Cl_2Ru_2(\mu\text{-}S\text{-}i\text{-}Pr)_2{=}C{=}C{=}CPh_2]^+$	1.94(2)	1.24(2)	1.36(2)	174(1)	165(2)	14
$[Cp(PPh_3)_2Ru]_2(\mu\text{-}C_4)$	2.001(3)	1.217(4)	1.370(6)	178.9(2)	177.2(3)	4d
$Cp(PPh_3)_2RuC{\equiv}CCOCH_3$	1.996(3)	1.212(5)	1.427(5)	176.1(3)	169.8(3)	4d
$Cp(PPh_3)_2RuC{\equiv}CPh$	2.017(5)	1.214(7)	1.462(8)	177.7(4)	170.6(5)	26
$Cp(dppe)RuC{\equiv}CPh$	2.009(3)	1.204(5)	1.444(5)	178.1(3)	176.3(4)	26
$Cp(PPh_3)_2RuC{\equiv}CC_6H_4\text{-}4\text{-}NO_2$	1.989(7)	1.224(10)	1.430(9)	177.7(6)	174.5(7)	27
$Cp(PMe_3)_2RuC{\equiv}CPh$	1.994(5)	1.202(8)	1.432(7)	175.9(4)	175.0(9)	27
$Cp(PMe_3)_2RuC{\equiv}CC_6H_4\text{-}4\text{-}NO_2$	1.99(2)	1.23(2)	1.43(3)	178(2)	177(3)	27
$Cp(Ph_2PCH_2CHMePPh_2)RuC{\equiv}CPh$	2.038(7)	1.172(9)		179.4(7)	172(1)	28
$Cp(PPh_3)_2RuC{\equiv}CC(O_2CCF_3){=}CMe_2$	2.02(1)	1.20(1)	1.42(2)	175.1(11)	175.2(14)	29
$[Cp(PPh_3)_2RuC{\equiv}CFc]PF_6$	1.99(2)	1.19(2)	1.38(3)	173(2)	178(3)	30
$[Cp(CO)_2Ru]_2(\mu\text{-}C{\equiv}C)$	2.05(1)	1.19(1)		178.1(9)		4g
$Cp(PMe_3)_2RuC{\equiv}CZrClCp_2$	1.989(13)	1.251(2)		169.9(3)		5d

in Figure 1, and selected bond distances and angles are given in Table 2. For comparison, selected structural data for several ruthenium acetylide and allenylidene complexes are also collected in Table 3.

The structure can be described as two three-legged piano stools symmetrically bridged with a C_5H unit. The four PPh_3 ligands are bonded to ruthenium almost symmetrically with Ru−P bond distances in the range 2.304(3)−2.335(3) Å. The Ru−P bond distances are within the range of those reported for related ruthenium complexes such as $CpRu(PPh_3)_2C{\equiv}CPh$[26] and $[CpRu(PPh_3)_2{=}C{=}CPhMe]I$.[26] The Ru−C(Cp) bond distances are in the range 2.224(10)−2.267(13) Å. These values are also similar to those reported for related Cp ruthenium complexes, such as $CpRu(PPh_3)_2C{\equiv}CPh$[26] and $[CpRu(PPh_3)_2{=}C{=}CPhMe]I$.[26]

The most interesting feature of the structure is in the C_5H moiety. The C_5H unit bridges the two ruthenium centers in a V-shape (C(2)−C(3)−C(4) = 130.3(11)°) in a nearly symmetric manner. The C(2)−C(3)−C(4) angle is slightly larger than those typically observed for carbons in a sp^2 environment, probably due to the repulsion between the π-bonding electron pairs of C(α)−C(*β*). For comparison, the C−C−C angles for C=CHC fragments were observed in the range 123.6−128.5° for several ruthenium vinylidene complexes $L_nRu{=}C{=}CHR$ (e.g. $[CpRu(PMe_3)_2{=}C{=}CHMe]PF_6$, $Cp^*RuCl(P(i\text{-}Pr)_2\text{-}CH_2CO_2Me){=}C{=}CHCO_2Me$, and $[Cp^*Ru(PMe_2Ph)_2{=}C{=}CHPh]^+$).[10,15,16a,31−33] The RuC_3H chain is not strictly

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linear with angles of Ru(1)−C(1)−C(2) = 176.6(8)°, C(1)−C(2)−C(3) = 166.5(12)°, C(3)−C(4)−C(5) = 167.4(10)°, and C(4)−C(5)−Ru(2) = 176.6(8)°. These angles are within the range of those reported for $RuC\equiv CR$ or $Ru{=}C{=}C{=}CRR'$ complexes, as shown in Table 3.

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 Ru−C(α) ((1.933(8), 1.913((10) Å), C(α)−C(β) (1.241(12), 1.256(15) Å), and C(β)−C(γ) (1.364(11), 1.387(16) Å) bond distances. The average Ru−C(α) distance of 1.923 Å is at the upper end of those observed for ruthenium allenylidene complexes (1.84(1)−1.94(2) Å) and is longer than those observed for ruthenium vinylidene complexes of the type $[(C_5R_5)Ru(PR_3)_2{=}C{=}CHR]^+$ and $[(C_9H_7)Ru(PR_3)_2{=}C{=}CHR]^+$ (in the range of 1.76−1.87 Å for 17 such complexes in the Cambridge Crystallographic Structure Database, October 1996 Release)[10,15,16a,26,29,31−39] but is considerably shorter than those observed for ruthenium acetylide complexes of the type $CpRuL_2C\equiv CR'$ (1.989−2.05 Å; see Table 3). The average C(α)−C(β) bond distance of 1.249 Å corresponds to a bond order between 2 and 3. It is comparable to those found for ruthenium allenylidene complexes (in the range 1.24−1.27 Å) and is at the lower end for those observed for the vinylidene complexes of the type $[(C_5R_5)Ru(PR_3)_2{=}C{=}CHR]^+$ and $[(C_9H_7)Ru(PR_3)_2{=}C{=}CHR]^+$ (in the range 1.25−1.36 Å),[10,15,16a,29,31−39] and at the upper end for those typically observed for ruthenium acetylide complexes of the type $CpRuL_2C\equiv CR$ (1.19−1.25 Å; see Table 3). The average C(β)−C(γ) bond distance (1.376 Å) corresponds to a bond order between 1 and 2. It is at the upper end of the bond distances observed for allenylidene complexes and is significantly shorter than that expected for $C(sp^2)-C(sp)$ single bonds. For example, $C(sp)-C(sp^2)$ bond distances were observed at 1.427(5) Å for $CpRu(PPh_3)_2C\equiv CCOCH_3$[4d] and at 1.462(4) Å for $CpRu(PPh_3)_2C\equiv CPh$.[26] Thus, the solid-state structural data support the idea that complex **6** has a delocalized structure with contributions from the resonance structures **A**−**C**.

The orientation of the C_5H unit is similar to those observed for $[CpRu(PMe_3)_2{=}C{=}C{=}CPh_2]PF_6$[11] and $[(C_9H_7)Ru(PPh_3)_2{=}C{=}C{=}CR_2]^+$ ($R_2 = Ph_2, C_{13}H_{20}$).[13a,16b] Such an orientation is expected on the basis of theoretical calculations of allenylidene complexes so that maximum π-stabilization between the metal and the C(α) atom can be achieved.[40]

Reactions of C_5H-Bridged Complexes. Bimetallic complexes with C_x bridges are of considerable current interest.[2] It is relatively more difficult to prepare complexes with C_x bridges where x is odd, and examples of complexes bridged with C_3 or C_5 have only been synthesized recently by Gladysz *et. al.* through multistep synthesis.[3a,e] We have attempted to convert the easily accessible C_5H-bridged complexes to C_5-bridged complexes by removing the hydrogen from the C_5H unit.

In principle, C_5H-bridged complexes $[(C_5R_5)(PR_3)_2Ru{=}C{=}C{=}CHC\equiv CRu(PR_3)_2(C_5R_5)]^+$ could be converted to C_5-bridged complexes $[(C_5R_5)(PR_3)_2Ru{=}C{=}C{=}C{=}C{=}Ru(PR_3)_2(C_5R_5)]^{2+}$ by removing a H^- from the C_5H unit. As Ph_3CBF_4 has been successfully used previously to abstract H^- in organometallic synthesis,[41] we have treated the C_5H-bridged complexes **5** and **6** with Ph_3CBF_4. Unfortunately, reactions of the C_5H-bridged complexes **5** and **6** with Ph_3CBF_4 in our hands led to complicated mixtures from which the carbonyl complexes **7** and **8** can be isolated in low yields.

In an alternative way of converting the C_5H-bridged complexes to C_5-bridged complexes, the C_5H-bridged complexes **5** and **6** were treated with bases in the presence or absence of oxidizing agents, in the hope that the C_5H unit could be deprotonated. Reactions of **5** with KOH or $KOBu^t$ in THF or CH_2Cl_2 led to unidentified products. No reactions were observed when solutions of **5** in THF or CH_2Cl_2 were treated with KOH. When the blue complex **5** was treated with KOH or $KOBu^t$ in acetone, the color changed immediately to yellow and the bimetallic complex $Cp^*(dppe)RuC\equiv C\text{-}CH(CH_2COMe)C\equiv CRu(dppe)Cp^*$ (**9**) was isolated in good yield (see Scheme 2). Complex **9** is air-sensitive in solution and the carbonyl complex $[Cp^*Ru(CO)(dppe)]BF_4$ was produced when its solution was exposed to air for 1 week.

Complex **9** may be produced by the attack on complex **5** of $[CH_2COCH_3]^-$ generated from the reaction of CH_3COCH_3 with KOH or $KOBu^t$. It is known that nucleophiles can attack C(α) or C(γ) carbons of allenylidene groups to form carbene[22g] or acetylide complexes.[13a,42]

Complex **9** was characterized by elemental analysis and IR and ^1H, ^{31}P, and ^{13}C NMR spectroscopy. The presence of $C\equiv C$ and $C{=}O$ functional groups is indicated by its IR spectrum, which showed IR bands at 2080 cm^{-1} assignable to $\nu(C\equiv C)$ and at 1704 cm^{-1} assignable to $\nu(C{=}O)$. The structural assignment was confirmed by ^{13}C NMR, which displayed resonances for the bridging ligand at 209.9 (s, C=O), 106.6 (s, $RuC\equiv C$), 102.1 (t, $^2J(PC) = 25.4$ Hz, $RuC\equiv C$), 53.9 (s, $CH_2C{=}O$), 29.4 (s, $CH_3C{=}O$), and 22.5 ppm (s, $RuC\equiv CCH$), in addition to the signals of dppe and Cp* ligands. In support of the structure, the ^1H NMR spectrum in CD_2Cl_2 showed signals at 3.80 ppm (t, 1 H, $J(HH) = 7.2$ Hz) assignable to $C\equiv CCH$, 2.08 ppm (d, $J(HH) = 7.2$ Hz) assignable to $CH_2C{=}O$, and 1.53 ppm assignable to $CH_3C{=}O$. These ^1H and ^{13}C NMR assignments have been deduced from ^{13}C DEPT and 2D NMR experiments ($^1H-^1H$, $^1H-^{13}C$ COSY, COLOC). Consistent with this structure, the ^{31}P NMR spectrum in $CDCl_3$ displayed two doublets at 81.6 and 80.4 ppm with $J(PP) = 11.6$

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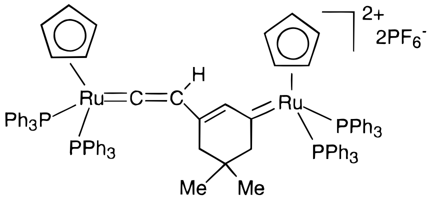
Hz. The ^{31}P NMR data indicate that the two ruthenium centers are equivalent and that the two PPh_2 groups of the dppe ligand are magnetically inequivalent. The inequivalence of the two PPh_2 groups in complex **9** is expected because of the presence of H, CH_2COCH_3, and Cp*Ru(dppe)C≡C groups at the γ-carbon atom.

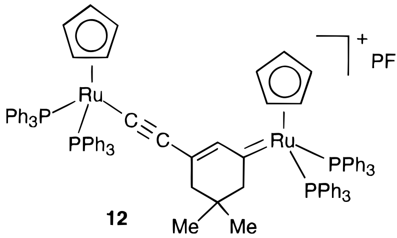
Like complex **5**, the C_5H-bridged complex **6** also reacted with acetone in the presence of $KOBu^t$ or KOH to form the bimetallic complex $Cp(PPh_3)_2RuC{\equiv}CCH(CH_2COMe)C{\equiv}CRu(PPh_3)_2Cp$ (**10**). The spectroscopic data for μ-$C{\equiv}CCH(CH_2COCH_3)C{\equiv}C$ in complex **10** are very similar to those observed for the analogous complex **9**.

It is probably not surprising to observe that the C_5H-bridged complexes $[(C_5R_5)(PR_3)_2Ru{=}C{=}C{=}CHC{\equiv}CRu(PR_3)_2(C_5R_5)]^+$ were not deprotonated by KOH or $KOBu^t$, as the 19-electron complexes $(C_5R_5)(PR_3)_2Ru{=}C{=}C{=}C{=}C{=}C{=}Ru(PR_3)_2(C_5R_5)$ would be generated when the C_5H unit is deprotonated. To overcome this problem, deprotonation reactions were carried out in the presence of oxidizing agents such as Cp_2FeBF_4, Ph_3CBF_4, and $AgBF_4$.[43] Unfortunately we have not been able to obtain C_5-bridged complexes from these reactions yet. When the blue C_5H-bridged complex **5** was treated with Cp_2FeBF_4, Ph_3CBF_4, or $AgBF_4$ in the presence of $KOBu^t$ or KOH, a mixture of products was obtained, from which $[Cp^*Ru(CO)(dppe)]BF_4$ could be isolated. As indicated by in situ ^{31}P NMR, a major phosphorus-containing greenish species (possibly a C_5-bridged complex) was produced when **5** was treated with $AgBF_4$ in the presence of basic alumina. However, the greenish product appears to be very unstable and decomposed during attempts at purification or collection of ^{13}C NMR spectra even at −20 °C. It is noted 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 extremely light-sensitive and decomposed in hours even in the dark.[3a]

Electronic Spectra of the Bimetallic Complexes. The C_5H_2- and C_5H-bridged complexes are intensely colored complexes. The C_5H_2-bridged complex **3** has an intense purple color with strong absorption bands at 230 ($\epsilon = 7.8 \times 10^4$ M^{-1} cm^{-1}) and 528 nm ($\epsilon = 4.2 \times 10^4$ M^{-1} cm^{-1}). The C_5H-bridged complex **5** has an intense blue color with strong absorption bands at 230 ($\epsilon = 8.0 \times 10^4$ M^{-1} cm^{-1}) and 630 nm ($\epsilon = 5.8 \times 10^4$ M^{-1} cm^{-1}). Complex **9**, which is not conjugated, only shows a strong absorption band near 230 nm. Since complexes **3**, **5**, and **9** all have a strong absorption near 230 nm, this absorption must be associated with the electronic transitions involving Cp*Ru(dppe). The band around 528 nm for **3** could be assigned to the electronic transition involving the $Ru{=}C{=}C{=}CHCH{=}C{=}Ru$ unit, and the band around 630 nm for **5** could be assigned to the electronic transition involving $Ru{=}C{=}C{=}CHC{\equiv}CRu$. Like complex **5**, the C_5H-bridged complex **6** also has an intense blue color with strong absorption bands at 230 ($\epsilon = 6.8 \times 10^4$ M^{-1} cm^{-1}) and 600 nm ($\epsilon = 7.2 \times 10^4$ M^{-1} cm^{-1}).



11



12

Reported bimetallic complexes closely related to the C_5H_2- and C_5H-bridged complexes are complexes **11** and **12**.[16a] Complex **11** is related to the C_5H_2-bridged complexes in that they all contain one Ru=C and one Ru=C=C linkage. Complex **12** is related to the C_5H-bridged complexes in that they all contain a RuC≡C and a Ru=C linkage in some of the resonance structures. Interestingly, complex **11** also has a deep red-purple color with a strong absorption band at 498 nm ($\epsilon = 1.2 \times 10^4$ M^{-1} cm^{-1}), which is similar to that of the C_5H_2-bridged complex **3** (528 nm ($\epsilon = 4.2 \times 10^4$ M^{-1} cm^{-1})). Complex **12** has a strong absorption band at 575 nm ($\epsilon = 1.9 \times 10^4$ M^{-1} cm^{-1}), which is similar to those of complexes **5** (630 nm ($\epsilon = 5.8 \times 10^4$ M^{-1} cm^{-1})) and **6** (600 nm ($\epsilon = 7.2 \times 10^4$ M^{-1} cm^{-1})). The deep purple or blue colors observed for complexes **3**−**6**, **11**, and **12** are undoubtedly related to the extended electron delocalization in these complexes. It should be mentioned that strong absorption bands in the visible region were also observed for the C_3-bridged complex $[Cp^*Re(NO)(PPh_3)(\mu\text{-}C_3)Mn(CO)_2Cp)]^+$ (ϵ_{max}(392 nm) = 56 000 M^{-1} cm^{-1}) and the C_5-bridged complex $[Cp^*Re(NO)(PPh_3)(\mu\text{-}C_5)Mn(CO)_2(C_5Cl_5)]^+$ (ϵ_{max}(480 nm) = 60 000 M^{-1} cm^{-1}).[3a,e]

In conclusion, this study shows that conjugated C_5H_2- and C_5H-bridged bimetallic complexes could be easily prepared from reactions of HC≡CCH(OH)C≡CH with coordinated unsaturated d^6 complexes $[(\eta^5\text{-}C_5R_5)Ru(PR_3)_2]^+$. The C_5H-bridged complexes have fully conjugated structures, as indicated by the solution NMR and solid-state X-ray diffraction data.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, all bond lengths, all bond angles, anisotropic displacement coefficients, and H-atom coordinates and isotropic displacement coefficients for $[Cp(PPh_3)_2Ru{=}C{=}C{=}CHC{\equiv}CRu(PPh_3)_2Cp]BPh_4{\cdot}CH_2Cl_2{\cdot}Et_2O$ (13 pages). Ordering information is given on any current masthead page.

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