Synthesis and Characterization of Linear $(CH)_8$-Bridged Bimetallic Ruthenium Complexes

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Received June 3, 2002

Reactions of $HC\equiv CCH_2CH(OR)CH(OR)CH_2C\equiv CH$ ($R = H$, $MeSO_2$) with $RuHCl(CO)(PPh_3)_3$ produced $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH_2CH(OR)CH(OR)CH_2CH{=}CH)$, which on treatment with PMe_3 gave $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH_2CH(OR)CH(OR)CH_2CH{=}CH)$. Treatment of $RuHCl(CO)(PPh_3)_3$ with (3*E*,5*E*)-$HC\equiv CCH{=}CHCH{=}CHC\equiv CH$ produced $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$. The later complex reacted with PMe_3, 4-phenylpyridine (PhPy), and 2,6-$(Ph_2PCH_2)_2C_5H_3N$ (PMP) to give $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$, $[RuCl(CO)(PhPy)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$, and $[RuCl(CO)(PMP)]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$, respectively. The structures of $RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH_2CH(OH)CH(OH)CH_2CH{=}CH)$ and $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$ 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] Linear C_x and $(CH)_x$ are probably the simplest hydrocarbon bridging ligands. In the past decade, the synthesis and properties of bimetallic complexes with C_x bridges have been intensively investigated. A variety of complexes of the type $L_nM(\mu\text{-}C_x)M'L'_n$ with x up to 20 and with M or M′ = Re, Fe, Ru, Pt, Pd, Mn, W, and Rh have now been synthesized.[3−11] These complexes can behave like molecular wires and have luminescent properties. In contrast to bimetallic complexes with C_x bridges, very few studies have been carried out with bimetallic complexes with linear $(CH)_x$ bridges, despite the fact that many conjugated organic materials (e.g., polyacetylenes, push/pull stilbenes) have only sp^2 hybridized carbons in their backbones.[12] Previously reported examples of $(CH)_x$-bridged bimetallic complexes are limited to a few of those with linear $(CH)_2$,[13] $(CH)_4$,[14−16] $(CH)_5$,[17] and $(CH)_6$[18] bridges. Related to $(CH)_x$-bridged bimetallic complexes, several bimetallic complexes of

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10.1021/om020442e CCC: \$22.00
Publication on Web 10/19/2002

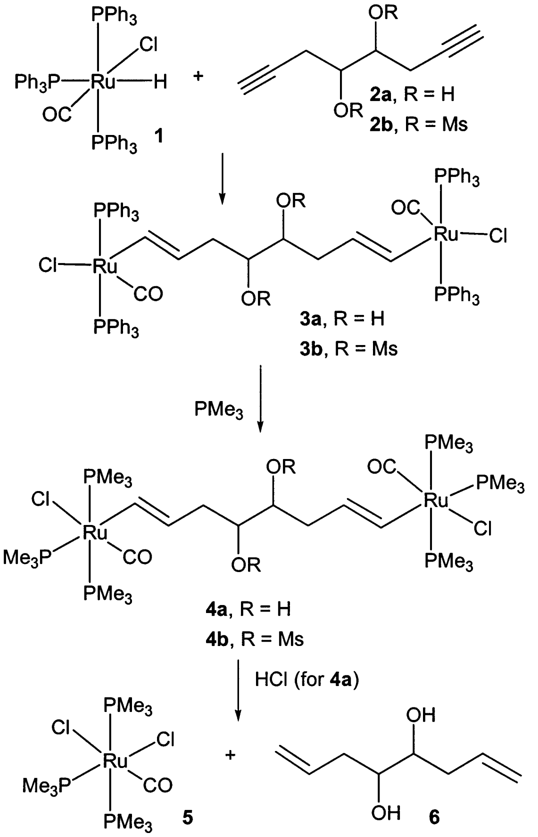
type $L_nM{=}C(OR){-}CH{=}CH{-}C(OR){=}ML_n$ and $L_nM{=}CR{-}R{-}CR{=}ML_n$ have been synthesized.[19] In this report, the synthesis, characterization, and electrochemical properties of (CH)$_8$-bridged bimetallic complexes will be described.

Results and Discussion

Reactions of $HC{\equiv}CCH_2CH(OR)CH(OR)CH_2C{\equiv}CH$ (2a, R = H, 2b, R = Ms) with $RuHCl(CO)(PPh_3)_3$ (1). Reactions of $RuHCl(CO)(PPh_3)_3$ (**1**) with $HC{\equiv}CR$ are known to give $RuCl(CH{=}CHR)(CO)(PPh_3)_2$.[20,21] The reaction has been used to prepare bimetallic complexes such as $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CH{-}Ar{-}CH{=}CH)$[22] and $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CH{-}CH{=}CH)$.[16] Thus it is expected that reactions of **1** with **2** will produce $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH_2CH(OR)CH(OR)CH_2CH{=}CH)$ (**3**). Compounds **3** were synthesized because they are potentially useful precursors to linear (CH)$_8$-bridged bimetallic complexes and they could be used to compare the properties with those of bimetallic complexes containing a linear (CH)$_8$ bridge.

The compound $HC{\equiv}CCH_2CH(OH)CH(OH)CH_2C{\equiv}CH$ (**2a**) was obtained from the reaction of $LiC{\equiv}CH$ with racemic 1,3-butadiene diepoxide.[23] Treatment of **1** with **2a** in dichloromethane produced the expected insertion product **3a** (Scheme 1), which can be readily characterized by the NMR and analytical data. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 showed AB pattern ^{31}P signals at 30.5 and 29.8 ppm with a $^2J(PP)$ coupling of 322.4 Hz. The magnitude of the coupling constant indicates that the two PPh_3 ligands are trans to each other. Monomeric complexes $RuCl(RC{=}CHR')(CO)(PPh_3)_2$ are known to adopt a distorted trigonal bipyramidal geometry with the two PPh_3 ligands in the apical positions.[20] Thus it is reasonable to assume that complex **3a** has a similar geometry around ruthenium. Observation of two ^{31}P signals for **3a** with such a structure is expected, because the two ruthenium centers are equivalent by symmetry, but the two PPh_3 ligands on each ruthenium is chemically nonequivalent due to the presence of the asymmetric carbon center (CH(OH)). In the ^1H NMR spectrum (in CD_2Cl_2), the vinylic proton signals were observed at 7.18 and 4.68 ppm with a $^3J(HH)$ coupling constant of 13.4 Hz. The magnitude of the coupling constant indicates that the two vinylic protons are in trans geometry and that the acetylene is cis inserted into the Ru−H bond.

Scheme 1



The 16e complex **3a** can be converted to the six-coordinated 18e complex $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH_2CH(OH)CH(OH)CH_2CH{=}CH)$ (**4a**) by treatment with PMe_3. Complex **4a** has been characterized by elemental analysis and multinuclear (^1H, ^{31}P, and ^{13}C) NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 showed a doublet at −8.2 ppm for the mutually trans PMe_3 and a triplet at −20.0 ppm for the unique PMe_3, indicating that the PMe_3 ligands are meridionally coordinated to ruthenium. Apparently, the mutually trans PMe_3 ligands, which are nonequivalent, coincidently have the same chemical shift. The $^{13}C\{^1H\}$ NMR spectrum (in $CDCl_3$) showed the signals of the bridging ligand at 160.8 (Ru-*C*H), 129.9 (Ru−CH=*C*H), 53.2 (CH(OH)), and 43.7 (CH_2) ppm. The vinyl group is trans to the unique PMe_3, as indicated by the large $^2J(PC)$ coupling constant (76.4 Hz). The structure of **4a** has been confirmed by X-ray diffraction (see below).

The compound $HC{\equiv}CCH_2CH(OMs)CH(OMs)CH_2C{\equiv}CH$ (**2b**) was prepared by treating **2a** with $MsCl/NEt_3$. Reaction of **1** with **2b** produced $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH_2CH(OMs)CH(OMs)CH_2CH{=}CH)$ (**3b**), which can be isolated as a red solid in high yield (Scheme 1). Complex **3b** could also be converted to the six-coordinated complex $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH_2CH(OMs)CH(OMs)CH_2CH{=}CH)$ (**4b**) by treatment with excess PMe_3. Compounds **3b** and **4b** have been characterized by elemental analysis and multinuclear (^1H, ^{31}P, and ^{13}C) NMR spectroscopy. Except for the additional NMR signals of OMs, the NMR data of complexes **3b**

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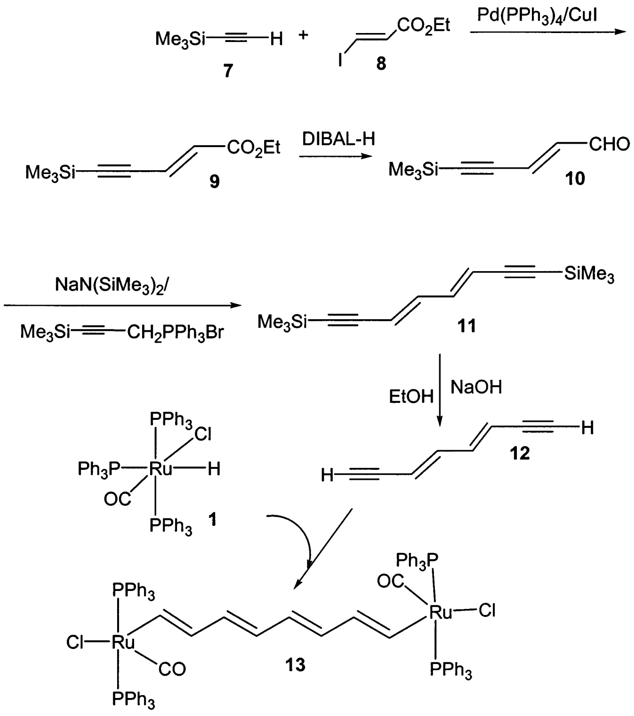
and **4b** are very similar to those of **3a** and **4a**, respectively, suggesting that they have similar coordination spheres.

Alcohols $RCH_2CH(OH)R'$ could be converted to olefins $RCH{=}CHR'$ on treatment with acids.[24] Dehydration of hydroxyhydrocarbon ligands promoted by Lewis acids is also known. For example, Werner et al. have observed that the rhodium complexes $RhCl(P(i\text{-}Pr)_3)_2({=}C{=}CHC(OH)RR')$ reacted with alumina to give either vinylvinylidene complexes or allenylidene complexes;[25] we have shown that $RuCl(CH{=}CHCH(OH)CHRR')(CO)(PPh_3)_2$ reacted with alumina to give dienyl complexes $RuCl(CH{=}CHCH{=}CRR')(CO)(PPh_3)_2$.[21f] Dehydration reactions of $RuCl(CH{=}CH\text{-}cyclo\text{-}C_6H_{10}(OH))(CO)(P(i\text{-}Pr)_3)_2$[26] and $RuCl(CH{=}CHCH(OH)'CHRR')(CO)(BSD)(PPh_3)_2$ (BSD = benzo-2,1,3-selenadiazole) have also been described.[27] In this work, we have reacted complexes **3a** and **4a** with various acids, to see if complexes with a linear $(CH)_8$ bridge could be prepared. No reaction was observed when **3a** was treated with alumina at room temperature. Complex **3a** decomposed to a complicated mixture when it was treated with $HBF_4{\cdot}Et_2O$ or P_2O_5. Attempts to obtain $(CH)_8$-bridged bimetallic complexes by treating **4a** with various acids also failed. No reaction was observed when **4a** was treated with acidic alumina at room temperature. A mixture of species were obtained when complex **4a** was treated with P_2O_5. One the decomposed products was identified to be *trans-mer*-$RuCl_2(CO)(PMe_3)_3$ (**5**).[28] Complex **4a** reacted rapidly with aqueous HCl to give **5** and $CH_2{=}CHCH_2CH(OH)CH(OH)CH_2CH{=}CH_2$ (**6**).[29]

It is known that mesylates $RCH_2CH(OMs)R'$ could be converted to olefins $RCH{=}CHR'$ by base-induced elimination of HOMs.[30] Thus the reactions of **4b** with various bases were attempted with a hope to prepare $(CH)_8$-bridged bimetallic complexes by elimination of HOMs. However, no reactions were observed when **4b** was treated with K_2CO_3 or proton sponge. When **4b** was treated with the strong base $NaN(SiMe_3)_2$, a mixture of complexes was obtained. The ^1H NMR spectrum of the crude product did not show the characteristic CH(OMs) signals of **4b**, but showed many new peaks in the region 5−8 ppm, suggesting that elimination of HOMs from **4b** occurred. However, the $^{31}P\{^1H\}$ NMR spectrum showed multipletes around −20 and −8 ppm, the chemical shifts of which are very close to those of the starting material **4b**, implying that a mixture of species was generated. It was impossible to get pure compounds from the reactions.

Scheme 2



Preparation of (3*E*,5*E*)-HC≡CCH=CHCH=CHC≡CH (12). The results discussed above indicate that well-defined conjugated bimetallic complexes with a linear $(CH)_8$ bridge could not be prepared from complexes **3** and **4**. Thus it is necessary to find alternative routes to prepare bimetallic complexes with a linear $(CH)_8$ bridge. To this end, we have prepared the dialkyne (3*E*,5*E*)-$HC{\equiv}CCH{=}CHCH{=}CHC{\equiv}CH$ (**12**) and investigated its reaction with $RuHCl(CO)(PPh_3)_3$. Compound **12** has previously been briefly mentioned in a communication.[31] In that work, **12** was generated by desilylation of (3*E*,5*E*)-$Me_3SiC{\equiv}CCH{=}CHCH{=}CHC{\equiv}CSiMe_3$ (**11**), which was obtained in very low yield together with cis−cis, and cis−trans isomers by multistep synthesis from *trans*-$HC{\equiv}CCH_2CH{=}CHCH_2C{\equiv}CH$. However the detailed procedure to the compounds as well as the NMR spectroscocopic data of **12** were not given. It appears that the reported synthetic route is very laborious, and it is difficult to obtain pure **12** in substantial quantity. Thus we have developed a simpler synthetic route to **12**.

Our synthetic route to **12** is outline in Scheme 2. Reactions of (*E*)-$ICH{=}CHCO_2Et$ (**8**)[32] with $HC{\equiv}CSiMe_3$ (**7**) in the presence of $PdCl_2(PPh_3)_2$/CuI produced (*E*)-$Me_3SiC{\equiv}CCH{=}CHCO_2Et$ (**9**). Compound **9** could also be made by reacting $Me_3SiC{\equiv}CCHO$ with $(EtO)_2P(O)CH_2CO_2Et$ in the presence of NaH.[33] Reduction of **9** with DIBALH in THF produced the aldehyde **10**. The aldehyde **10** underwent a Wittig reaction with $Me_3SiC{\equiv}CCH_2PPh_3Br$ (using $NaN(SiMe_3)_2$ as the base) to produce compound **11**. Treatment of **11** with NaOH produced **12**, which was isolated as a pale yellow solid. Compound **12** is unstable and polymerized readily when stored at room temperature. Thus it should be used immediately after it was produced. Compound **12** can be readily characterized by NMR spectroscopy. In

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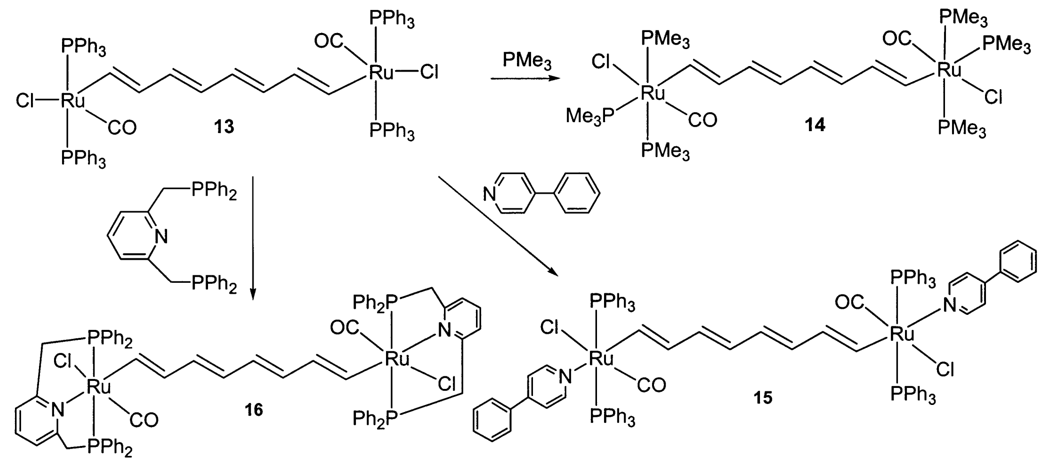
Scheme 3



particular, the ^{1}H NMR spectrum (in C_6D_6) showed one $\equiv$CH signal at 2.79 ppm and two =CH signals at 5.26 and 6.30 ppm; the $^{13}C\{^1H\}$ NMR spectrum (in C_6D_6) showed the acetylenic carbon signals at 82.0 and 82.7 ppm and the vinyl signals at 113.3 and 141.9 ppm.

Preparation of Bimetallic Complexes from 12. Reaction of **12** with **1** in dichloromethane produced the insertion product $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$ (**13**), which can be isolated as a purple solid in 92% yield (Scheme 2). In the ^{1}H NMR spectrum in CD_2Cl_2, the Ru−CH signal was observed at 7.96 ppm; the γ-CH and δ-CH were observed at 6.00 and 5.54 ppm, respectively; the β-CH is buried in the signals of PPh_3. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 showed a singlet at 29.4 ppm, which is typical for $RuCl(CH{=}CHR)(CO)(PPh_3)_2$.

Several related $(CH)_8$-bridged bimetallic complexes were prepared from complex **13**. Treatment of **13** with PMe_3 produced the six-coordinated complex $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$ (**14**). The PMe_3 ligands in **14** are meridionally coordinated to ruthenium, as indicated by the AM_2 pattern $^{31}P\{^1H\}$ NMR spectrum. The presence of the $(CH)_8$ chain is indicated by the ^{1}H NMR spectrum (in CD_2Cl_2), which showed the vinyl proton signals at 7.51 (Ru−CH), 6.45 (β-CH), 6.22 (γ-CH), and 5.93 (δ-CH) ppm. In the $^{13}C\{^1H\}$ NMR spectrum (in CD_2Cl_2), the CH signals were observed at 172.7 (Ru−CH), 139.3 (β-CH), 137.2 (γ-CH), and 125.0 (δ-CH) ppm. The vinyl group is trans to the unique PMe_3, as indicated by the large $^2J(PC)$ coupling constant (78.0 Hz). The structure of **14** has been confirmed by X-ray diffraction study (see below).

Reactions of **13** with 4-phenylpyridine and $2,6\text{-}(Ph_2PCH_2)_2C_5H_3N$ (PMP) give the corresponding six-coordinated complexes $[RuCl(PhPy)(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$ (**15**) and $[RuCl(CO)(PMP)]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$ (**16**), respectively. These complexes have been characterized by NMR spectroscopy and elemental analysis. Closely related mononuclear complexes $RuCl(CH{=}CHR)(L)(CO)(PPh_3)_2$ (L = 2e nitrogen donor ligands) have been prepared from the reaction of HC$\equiv$CR with $RuHCl(L)(CO)(PPh_3)_2$.[34] A few ruthenium PMP complexes have been reported recently, for example, $RuCl_2(PPh_3)(PMP)$ and $RuHX(PPh_3)(PMP)$ (X = Cl, OAc).[35]

Many C_8-bridged bimetallic complexes have been reported, for example, $Cp^*(NO)(PR_3)Re{-}(C{\equiv}C)_4{-}Re(NO)(PR_3)Cp^*$,[7] $Cp^*(dppe)Fe{-}(C{\equiv}C)_4{-}Fe(dppe)Cp^*$,[8] $((tolyl)_3P)_2(tolyl)Pt{-}(C{\equiv}C)_4{-}Pt(tolyl)(P(tolyl)_3)_2$,[9a] $(tolyl)_3P)_2(C_6F_5)Pt{-}(C{\equiv}C)_4{-}Pt(C_6F_5)(P(tolyl)_3)_2$,[9b] $Cp^*(CO)_2Fe{-}(C{\equiv}C)_4{-}Fe(CO)_2Cp^*$,[10] $Cp(CO)_3M{-}(C{\equiv}C)_4{-}M(CO)_3Cp$ (M = Mo, W),[11a] and $Cp(PPh_3)_2Ru{-}(C{\equiv}C)_4{-}Ru(PPh_3)_2Cp$.[11b] To our knowledge, complexes **13**−**16** are the first examples of $(CH)_8$-bridged bimetallic complexes. In fact, only a few bimetallic complexes with linear $(CH)_x$ bridges are known. Reported $(CH)_x$-bridged bimetallic complexes include $(TMP)Ru{=}CH{-}CH{=}Ru(TMP)$ (TMP = tetramesitylporphyrin),[13a] $Cp(Me_3P)_2Ru{-}CH{=}CH{-}ZrClCp_2$,[13b,c] $CpL_2Fe{-}(CH{=}CH)_2{-}FeCp(L_2)$ (L_2 = dppm, $(CO)_2$, $(PPh_3)(CO)$),[14] $Cl_2(PCy_3)_2Ru{=}CH{-}CH{=}CH{-}CH{=}RuCl_2(PCy_3)_2$,[15] $(PMe_3)_3(CO)ClRu{-}(CH{=}CH)_2{-}RuCl(CO)(PMe_3)_3$,[16] $[(dppe)(PPh_3)(CO)ClRu{=}CH{-}CH{=}CH\text{-}CH{=}CH{-}RuCl(CO)(PPh_3)(dppe)]BF_4$,[17b] and $(dme)(RO)_2(ArN)Mo{=}CH{-}(CH{=}CH)_2{-}CH{=}MoNAr)(OR)_2(dme)$ (dme = $MeOCH_2CH_2OMe$).[18]

Description of the Structures of 4a and 14. The molecular structure of $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH_2CH(OH)CH(OH)CH_2CH{=}CH)$ (**4a**) 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 ruthenium centers linked by a $CH{=}CHCH_2CH(OH)CH(OH)CH_2CH{=}CH$ bridge. The two ruthenium centers are related by a C_2 rotation axis. The geometry around ruthenium can be described as a distorted octahedron with three meridionally bound PMe_3 ligands. The vinyl group is trans to the unique PMe_3 ligand, and the chloride is trans to the CO, as suggested by the solution NMR data. The mutually trans PMe_3 ligands are bent away from the unique PMe_3 but toward the vinyl ligand, as reflected by the P(1)−Ru−P(2) (96.32(3)°), P(1)−Ru−P(3) (94.80(3)°), C(11)−Ru−P(2) (84.49(6)°), and C(11)−Ru−(P3) (84.46(6)°) angles. Such a structural feature could be related to the steric interaction between the PMe_3 ligands. As one might expect, the unique Ru−P(1) bond (2.4010(7) Å)

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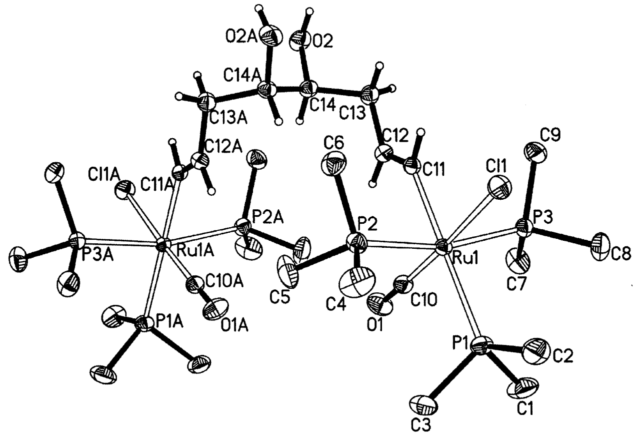

Figure 1. Molecular structure of $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH_2CH(OH)CH(OH)CH_2CH{=}CH)$ (**4a**). The hydrogen atoms of PMe_3 are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Crystal Data and Structure Refinements for $[RuCl(CO)(PMe_3)_3]_2$-(μ-$Ch{=}CHCH_2CH(OH)CH(OH)CH_2CH{=}CHCH{=}CH$) (4a) and $[RuCl(CO)(PMe_3)_3]_2$-(μ-$CH{=}CHCH{=}CHCH{=}CHCH{=}CH$) (14)

	4a	14
formula	$C_{28}H_{62}Cl_2O_2P_6Ru_2$	$C_{28}H_{66}Cl_2O_4P_6Ru_2$
fw	889.64	925.67
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a, Å	8.5217(12)	27.0706(17)
b, Å	9.0370(12)	8.5615(6)
c, Å	15.631(12)	18.7152(12)
α, deg	84.307(3)	
β, deg	80.258(3)	93.4720(10)
γ, deg	64.880(2)	
V, Å^3	1073.7(3)	4329(5)
Z	1	4
d_{calc}, g cm^{-3}	1.376	1.420
θ range, deg	2.00 to 27.53	1.51 to 26.37
no. of reflns collected	7409	11 734
no. of ind reflns	4881 ($R_{int} = 2.07\%$)	4413 ($R_{int} = 2.44\%$)
no. of obsd reflns	3912 ($I > 2\sigma(I)$)	
no. of params refined	197	190
final R indices ($I > 2\sigma(I)$)	$R = 3.48\%$, $wR_2 = 7.83\%$	$R = 3.06\%$, $wR_2 = 6.55\%$
goodness of fit	0.952	1.049
largest diff peak, e Å^{-3}	0.731	0.493
largest diff hole, e Å^{-3}	−0.583	−0.307

is slightly longer than those of the mutually trans Ru−P bonds (2.3559(7) and 2.3592(7) Å), due to the strong trans influence of the vinyl ligand. It is noted that mutually trans Ru−P bonds are also shorter than the Ru−P bond trans to a vinyl ligand in $RuH(CH{=}CMeCO_2Bu)(CO)(PPh_3)_3$[36] and $[RuCl(CO)(PEt_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CH)$.[16] Complexes such as $RuH(OAc)(PPh_3)_3$[37] and $RuCl_2(PPh_3)_3$,[38] where the unique phosphorus is not trans to a strong trans influence ligand, have mutually trans Ru−P bonds longer than the unique Ru−P bond. The Ru−C and C(α)−C(β) bond distances of complex **4a** are within the range of those reported for ruthenium vinyl complexes.[39] It is very interesting to note that the vinyl groups are essentially coplanar with Cl−Ru−CO. Thus the atoms Cl(1), Ru(1), C(10), O(1), C(11), and C(12) form a plane with maximum deviation from the least-squares plane of 0.049 Å for C(11). The coplanarity of the vinyl group and CO is expected because stabilization due to π interaction of CO and vinyl with metal centers is maximized in such a conformation.[40]

Molecules of **4a** are assembled in an interesting chain structure in the solid state through weak intermolecular hydrogen bonding between the two OH groups and the two CO ligands (see Figure 2). The O···OC distance is 3.189(3) Å, which is at the upper end of those of reported examples.[41] Hydrogen bonding involving carbonyl ligands is currently receiving considerable attention in the field of solid state intermolecular interactions.[41]

The molecular structure of complex $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$ (**14**) is depicted in Figure 3. The crystallographic details and selected bond distances and angles are given in Tables 1 and 3, respectively. As shown in Figure 3, the compound contains two ruthenium centers linked symmetrically by a linear $(CH)_8$ bridge. There is an inversion center at the midpoint of the C4−C4A bond. Overall, the geometry around ruthenium is very similar to that of **4a**.

The $(CH)_8$ ligand shows a single/double carbon−carbon bond alternation. All the olefinic double bonds are in trans geometry. Like complex **4a**, the vinyl groups are also essentially coplanar with Cl−Ru−CO. The atoms Cl(1), Ru(1), C(01), O(1), C(1), and C(2) are in a plane with maximum deviation from the least-squares plane of 0.025 Å for C(1). The carbon atoms of the $(CH)_8$ chain and the ruthenium atoms are also essentially coplanar, with maximum deviation from the least-squares plane of 0.033 Å for C(1). The formal double bonds have an average bond distance of 1.344 Å, and the formal single bonds have an average bond distance of 1.443 Å. The difference in the average single and double bond distances is 0.099 Å. The structural parameters of the $(CH)_8$ chain are similar to those of $PhCH{=}CH(CH{=}CH)_2CH{=}CHPh$[42] and $[MoTp^*Cl(NO)]_2(\mu\text{-}4,4'\text{-}NC_5H_4(CH{=}CH)_4C_5H_4N)$.[43] In these complexes, the difference in the average single and double bond distances is 0.092 and 0.11 Å, respectively.

Electrochemical Study. Electrochemistry has often be used to probe metal−metal interactions in bimetallic complexes with σ,σ-bridging hydrocarbon chains.[1g] Electrochemical properties of bimetallic complexes with C_x-bridges have been extensively studied by cyclic volta-

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $[\mathrm{RuCl(CO)(PMe_3)_3}]_2$($\mu$-CH═CHCH$_2$CH(OH)CH(OH)CH$_2$CH═CHCH═CH) (4a)

Bond Distances (Å)

Ru(1)−P(1)	2.4010(7)	Ru(1)−P(2)	2.3559(7)	Ru(1)−P(3)	2.3592(7)
Ru(1)−Cl(1)	2.4688(7)	Ru(1)−C(10)	2.096(3)	Ru(1)−C(11)	1.832(3)
C(11)−C(12)	1.316(3)	C(12)−C(13)	1.498(4)	C(13)−C(14)	1.521(3)
C(14)−C(14A)[a]	1.525(5)	O(1)−C(10)	1.122(3)		

Bond Angles (deg)

P(1)−Ru(1)−P(2)	96.32(3)	P(1)−Ru(1)−P(3)	94.80(3)
P(1)−Ru(1)−Cl(1)	93.25(3)	P(1)−Ru(1)−C(10)	89.75(9)
P(1)−Ru(1)−C(11)	179.05(7)	P(2)−Ru(1)−P(3)	166.90(3)
P(2)−Ru(1)−Cl(1)	85.48(3)	P(2)−Ru(1)−C(10)	93.85(8)
P(2)−Ru(1)−C(11)	84.49(6)	P(3)−Ru(1)−C1(1)	87.01(3)
P(3)−Ru(1)−C(10)	93.09(8)	P(3)−Ru(1)−C(11)	84.46(6)
Cl(1)−Ru(1)−C(10)	176.98(9)	Cl(1)−Ru(1)−C(11)	87.29(7)
C(10)−Ru(1)−C(11)	89.71(11)	Ru(1)−C(10)−O(1)	177.9(3)
Ru(1)−C(11)−C(12)	132.8(2)		

[a] Symmetry transformations used to generate equivalent atoms: $-x+1$, y, $-z+1/2$.

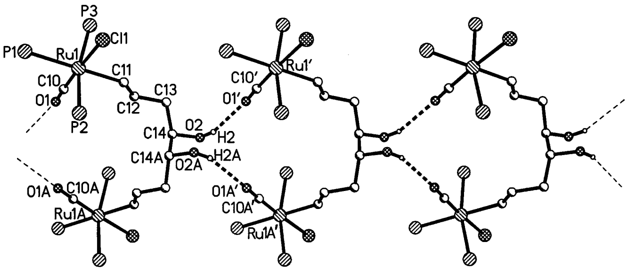

Figure 2. Hydrogen-bonding interactions in $[\mathrm{RuCl(CO)(PMe_3)_3}]_2$($\mu$-CH═CHCH$_2$CH(OH)CH(OH)CH$_2$CH═CH) (**4a**). The methyl groups of PMe$_3$ and the hydrogen atoms (except the OH) are omitted for clarity.

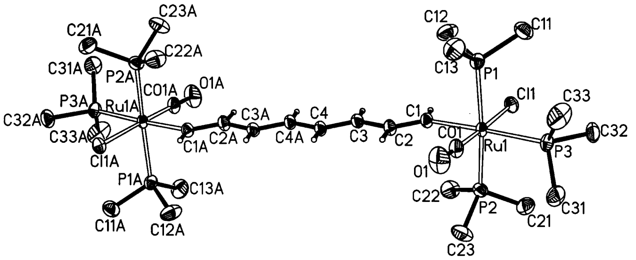

Figure 3. Molecular structure of $[\mathrm{RuCl(CO)(PMe_3)_3}]_2$($\mu$-CH═CH−CH═CH−CH═CH−CH═CH) (**14**). The hydrogen atoms of PMe$_3$ are omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[\mathrm{RuCl(CO)(PMe_3)_3}]_2$-($\mu$-CH═CHCH═CHCH═CHCH═CH) (14)

Bond Distances (Å)

Ru(1)−P(1)	2.3604(8)	Ru(1)−P(2)	2.3662(9)	Ru(1)−P(3)	2.4056(8)
Ru(1)−Cl(1)	2.4771(8)	Ru(1)−C(1)	2.095(3)	Ru(1)−C(01)	1.817(3)
C(1)−C(2)	1.333(4)	C(2)−C(3)	1.450(4)	C(3)−C(4)	1.345(4))
C(4)−C(4A)[a]	1.435(5)	O(1)−C(01)	1.145(4)		

Bond Angles (deg)

P(1)−Ru(1)−P(2)	167.48(3)	P(1)−Ru(1)−P(3)	95.60(3)
P(1)−Ru(1)−Cl(1)	86.06(3)	P(1)−Ru(1)−C(1)	85.59(8)
P(1)−Ru(1)−C(01)	93.42(11)	P(2)−Ru(1)−P(3)	94.10(3)
P(2)−Ru(1)−Cl(1)	85.38(3)	P(2)−Ru(1)−C(1)	85.01(9)
P(2)−Ru(1)−C(01)	94.80(11)	P(3)−Ru(1)−C1(1)	94.04(3)
P(3)−Ru(1)−C(1)	177.59(9)	P(3)−Ru(1)−C(01)	88.07(10)
Cl(1)−Ru(1)−C(1)	88.12(9)	Cl(1)−Ru(1)−C(01)	177.86(10)
C(1)−Ru(1)−C(01)	88.77(13)	Ru(1)−C(01)−O(1)	178.8(4)
Ru(1)−C(1)−C(2)	132.7(2)	C(1)−C(2)−C(3)	125.4(3)
C(2)−C(3)−C(4)	126.1(3)	C(3)−C(4)−C(4A)[a]	125.8(4)

[a] Symmetry transformations used to generate equivalent atoms: $-x+2$, $-y$, $-z+1$.

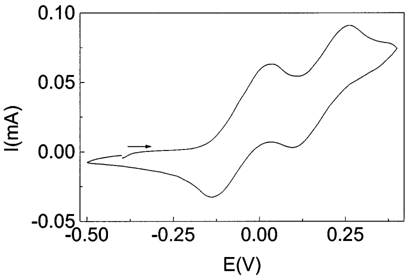

Figure 4. Cyclic voltammogram of $[\mathrm{RuCl(CO)(PMe_3)_3}]_2$($\mu$-CH═CH−CH═CH−CH═CH−CH═CH) (**14**).

mmetry. In contrast, electrochemical properties of bimetallic complexes with (CH)$_x$ bridges have rarely been exploited. In this work, we have collected cyclic voltammograms of complexes **14**−**16** in dichloromethane containing 0.10 M n-Bu$_4$NClO$_4$ as the supporting electrolyte. For comparison, the cyclic voltammogram of complex **4b** has also been collected.

The cyclic voltammograms of complexes **14**−**16** have very similar features. The cyclic voltammogram of complex **14** is shown in Figure 4. As shown in Figure 4, complex **14** exhibited two partially reversible oxidation waves at −0.06 and 0.18 V vs Ag/AgCl. These two waves can be attributed to the formation of $[\mathrm{(PMe_3)_3(CO)ClRu{-}(CH{=}CH)_4{-}RuCl(CO)(PMe_3)_3}]^+$ and $[\mathrm{(PMe_3)_3(CO)ClRu{=}CH{-}(CH{=}CH)_3{-}CH{=}RuCl(CO)(PMe_3)_3}]^{2+}$, respectively. The pyridine-containing complexes **15** and **16** can be oxidized more easily compared to the PMe$_3$-containing complex **14**. Complex **15** showed two partially reversible oxidation waves at −0.19 and −0.02 V vs Ag/AgCl. The two oxidation waves of complex **16** were observed at −0.22 and −0.08 V vs Ag/AgCl. These two waves can be attributed to the formation of $[\mathrm{L_5Ru{-}(CH{=}CH)_4{-}RuL_5}]^+$ and $[\mathrm{L_5Ru{=}CH{-}(CH{=}CH)_3{-}CH{=}RuL_5}]^{2+}$, respectively.

The peak separations of the two oxidation waves for complexes **14**, **15**, and **16** are dependent on ligands and are at 0.24, 0.17, and 0.14 V, respectively. The peak separations are smaller than that reported for the (CH)$_4$-bridged complex Cp(dppm)Fe−(CH═CH)$_2$−Fe(dppm)Cp (0.44 V).[14b] Observation of two oxidation waves for complexes **14**−**17** may imply that the two metal centers can interact with each other. For comparison, it is noted that the cyclic voltammogram of complex **4a**, in which the metal centers are connected by the nonconjugated bridge CH═CH−CH$_2$CH(OMs)-

CH(OMs)CH$_2$CH=CH, showed only one irreversible oxidation peak at 1.09 V vs Ag/AgCl.

The electrochemical properties of C$_8$-bridged bimetallic complexes Cp*(dppe)Fe−(C≡C)$_4$−Fe(dppe)Cp*[8] and Cp*(NO)(PR$_3$)Re−(C≡C)$_4$−Re(NO)(PR$_3$)Cp*[7] have been reported. The complex Cp*(dppe)Fe−(C≡C)$_4$−Fe(dppe)Cp* exhibits two oxidation waves at −0.23 and 0.20 V vs SCE with a peak separation of 0.43 V; the complex Cp*(NO)(PPh$_3$)Re−(C≡C)$_4$−Re(NO)(PPh$_3$)Cp* exhibits two oxidation waves at 0.24 and 0.52 V vs SCE with a peak separation of 0.28 V; the complex Cp*(NO)(PCy$_3$)Re−(C≡C)$_4$−Re(NO)(PCy$_3$)Cp* exhibited two oxidation waves at 0.11 and 0.43 V vs SCE with a peak separation of 0.22 V.

Summary. We have successfully prepared bimetallic complexes with metal centers bridged by CH=CHCH$_2$CH(OH)CH(OH)CH$_2$CH=CH or CH=CHCH=CHCH=CHCH=CH. The structures of [RuCl(CO)(PMe$_3$)$_3$]$_2$(μ-CH=CHCH$_2$CH(OH)CH(OH)CH$_2$CH=CH) (**4a**) and [RuCl(CO)(PMe$_3$)$_3$]$_2$(μ-CH=CHCH=CHCH=CHCH=CH) (**14**) have been confirmed by X-ray diffraction. Electrochemical study shows that the metal centers in bimetallic complexes containing the CH=CHCH=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$_3$)$_3$,[44] HC≡CCH$_2$CH(OH)CH(OH)CH$_2$C≡CH,[23] ethyl (*E*)-3-iodo-2-propenate,[32] and 2,6-(Ph$_2$PCH$_2$)$_2$C$_5$H$_3$N (PMP)[45] were prepared according to literature methods. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were collected on a Bruker ARX-300 spectrometer (300 MHz). ^{1}H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H$_3$PO$_4$.

The electrochemical measurements were performed with a PAR model 273 potentiostat. 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$_2$Cl$_2$ containing 0.10 M *n*-Bu$_4$NClO$_4$ as the supporting electrolyte. The peak potentials reported were referenced to Ag/AgCl. The ferrocene/ferrocenium redox couple was located at 0.26 V under our experimental conditions.

[RuCl(CO)(PPh$_3$)$_2$]$_2$(μ-CH=CHCH$_2$CH(OH)CH(OH)CH$_2$CH=CH) (3a). A solution of 1,7-octadiyne-4,5-diol (**2a**) (155 mg, 1.12 mmol) in CH$_2$Cl$_2$ (5 mL) was slowly added to a suspension of RuHCl(CO)(PPh$_3$)$_3$ (2.15 g, 2.26 mmol) in CH$_2$Cl$_2$ (30 mL). The reaction mixture was stirred at room temperature for 5 min, and then the volume of the blood red reaction mixture was reduced to ca. 5 mL under vacuum. Diethyl ether (60 mL) was added to the reaction mixture to give an orange solid. The solid was collection by filtration, washed with diethyl ether (3 × 30 mL), and dried under vacuum. Yield: 1.32 g, 77.7%. Anal. Calcd for C$_{82}$H$_{72}$Cl$_2$O$_4$P$_4$Ru$_2$: C, 64.80; H, 4.78. Found: C, 64.71; H, 4.82. ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$): δ 30.5 (d, *J*(PP) = 322.4 Hz), 29.8 (d, *J*(PP) = 322.4 Hz). ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$): δ 1.9 (br, 4 H, CH$_2$), 2.8 (br, 2 H, C*H* (OH)), 4.68 (m, 2 H, Ru−CH=C*H*), 7.18 (d, J(HH) = 13.4 Hz, 2 H, Ru−CH), 7.4−7.7 (m, 60 H, PPh$_3$). ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ 42.0 (s, CH$_2$), 53.5 (s, CH(OH)), 128.2−135.1 (m, PPh$_3$), 132.5 (s, Ru−CH=*C*H), 142.3 (t, *J*(PC) = 9.8 Hz, Ru−CH), 203.1 (t, *J*(PC) = 15.6 Hz, Ru−CO).

[RuCl(CO)(PMe$_3$)$_3$]$_2$(μ-CH=CHCH$_2$CH(OH)CH(OH)CH$_2$CH=CH) (4a). A 1 M THF solution of PMe$_3$ (10 mL, 10 mmol) was added to a solution of complex **3a** (0.40 g, 0.26 mmol) in THF (30 mL). The reaction mixture was stirred at room temperature for 3 days to give a light pink solution. The volume of the reaction mixture was reduced to ca. 5 mL under vacuum. Addition of diethyl ether (40 mL) to the residue generated a white solid, which was collected by filtration, washed with diethyl ether (2 × 30 mL), and dried under vacuum. Yield: 0.18 g, 71%. Anal. Calcd for C$_{28}$H$_{66}$Cl$_2$O$_4$P$_6$Ru$_2$: C, 36.28; 7.18. Found: C, 36.75; H, 6.95. ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$): δ −20.0 (t, *J*(PP) = 22.5 Hz), −8.2 (d, *J*(PP) = 22.5 Hz). ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$): δ 1.47 (t, *J*(PH) = 3.2 Hz, 18 H, PMe$_3$), 1.48 (t, *J*(PH) = 3.2 Hz, 18 H, PMe$_3$), 1.56 (d, *J*(PH) = 6.5 Hz, 18 H, PMe$_3$), 2.38 (br, 4 H, CH$_2$), 3.61 (m, 2 H, C*H*(OH)), 5.53 (m, 2 H, Ru−CH=C*H*), 6.94 (m, 2 H, Ru−CH). ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ 16.4 (t, *J*(PC) = 7.8 Hz, PMe$_3$), 19.9 (d, *J*(PC) = 20.7 Hz, PMe$_3$), 43.7 (d, *J*(PC) = 8.2 Hz, CH$_2$), 53.2 (t, *J*(PC) = 27.2 Hz, CH(OH)), 129.9 (s, Ru−CH=*C*H), 160.8 (dt, *J*(PC) = 76.4, 16.2 Hz, Ru−CH), 202.4 (q, *J*(PC) = 13.9 Hz, Ru−CO).

4,5-Bis(methanesulfonyl)-1,7-octadiyne (2b). To a vigorously stirred solution of **2a** (0.25 g, 1.80 mmol) in CH$_2$Cl$_2$ (20 mL) pre-cooled at 0 °C was slowly added methanesulfonyl chloride (0.40 mL, 5.2 mmol) and then triethylamine (0.80 mL, 5.7 mmol), while the temperature was maintained at 0 °C. After the addition was completed, the mixture was allowed to warm to room temperature and stirred for an additional 30 min, and the reaction was quenched with 1 N HCl aqueous solution. The organic layer was separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (10 mL). The combined organic extracts were washed with saturated (NH$_4$)$_2$SO$_4$ and NaCl solutions, dried over MgSO$_4$, filtered, and concentrated to give an oil. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 1:1) to give **2b** as a yellow oil. Yield: 0.36 g, 68%. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 2.28 (s, 2 H, HC≡C), 2.93 (m, 4 H, CH$_2$), 3.27 (s, 6 H, CH$_3$), 5.12 (m, 2 H, *H*COSO$_2$Me). ^{13}C{^{1}H} NMR (75.47 MHz, CDCl$_3$): δ 21.7 (s, CH$_2$), 38.8 (s, CH$_3$), 72.8 (s, H*C*≡C), 76.9 (s, C≡CH), 77.1 (s, H*C*OSO$_2$Me).

[RuCl(CO)(PPh$_3$)$_2$]$_2$(μ-CH=CHCH$_2$CH(OMs)CH(OMs)CH$_2$CH=CH) (3b). To a suspension of RuHCl(CO)(PPh$_3$)$_3$ (3.20 g, 3.36 mmol) in CH$_2$Cl$_2$ (50 mL) was slowly added a solution of **2b** (0.57 g, 1.9 mmol) in CH$_2$Cl$_2$ (20 mL). The reaction mixture was stirred for 30 min to give a red solution, which was filtered through a column of Celite. The solvent of the filtrate was removed under vacuum. The residue was washed with diethyl ether and dried under vacuum to give a deep red solid. Yield: 2.4 g, 86%. Anal. Calcd for C$_{84}$H$_{76}$Cl$_2$O$_8$P$_4$S$_2$Ru$_2$: C, 60.25; H, 4.58. Found: C, 60.31; H, 4.60. ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$): δ 30.0 (d, *J*(PP) = 320.2 Hz), 29.0 (d, *J*(PP) = 320.2 Hz). ^{1}H NMR (CD$_2$Cl$_2$, 300.13 MHz): δ 1.93 (m, 2 H, C*H*H), 2.25 (m, 2 H, CH*H*), 2.74 (s, 6 H, Me), 4.42 (s, 2 H, *H*COSO$_2$Me), 4.61 (m, 2 H, RuCH=C*H*), 7.24−7.67 (m, 62 H, PPh$_3$, Ru−CH).

[RuCl(CO)(PMe$_3$)$_3$]$_2$(μ-CH=CHCH$_2$CH(OMs)CH(OMs)CH$_2$CH=CH) (4b). To a solution of complex **3b** (1.60 g, 1.28 mmol) in THF (50 mL) was added a 1 M THF solution of PMe$_3$ (13.0 mL, 13.0 mmol). The reaction mixture was stirred for 15 h. The solvents were removed completely. Diethyl ether (40 mL) was added, and the mixture was stirred for 30 min to give a white solid, which was collected by filtration, washed with diethyl ether, and dried under vacuum to give a white solid. Yield: 1.2 g, 87%. Anal. Calcd for C$_{30}$H$_{70}$Cl$_2$O$_8$P$_6$S$_2$Ru$_2$·0.5C$_2$H$_5$OC$_2$H$_5$: C, 34.35; H, 6.77. Found: C, 34.33; H, 6.48. ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ −20.0 (t, *J*(PP) =

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23.6 Hz), −8.0 (d, *J*(PP) = 23.1 Hz). ^{1}H NMR (300.13 MHz, C_6D_6): *δ* 1.22 (d, *J*(PH) = 6.6 Hz, 18 H, PMe_3), 1.44 (t, *J*(PH) = 3.6 Hz, 18 H, PMe_3), 1.48 (t, *J*(PH) = 3.3 Hz, 18 H, PMe_3), 2.79 (s, 6 H, $MeSO_3$), 3.10 (br, 4 H, CH_2), 5.44 (s, 2 H, *H*COSO$_2$-Me), 6.00 (m, 2 H, RuCH=C*H*), 7.63 (m, 2 H, Ru−CH).

Reaction of Hydrochloric Acid with [RuCl(CO)(PMe$_3$)$_3$]$_2$(*μ*-CH=CHCH$_2$CH(OH)CH(OH)CH$_2$CH=CH). A mixture of **4a** (60 mg, 0.065 mmol), $CDCl_3$ (0.5 mL), and hydrochloric acid (37% aqueous solution, 0.05 mL) was allowed to stand for 30 min. The solution was subjected to column chromatography (silica gel, eluent: MeOH) to give $RuCl_2(CO)(PMe_3)_3$ (**5**)[28] and $CH_2{=}CHCH_2CH(OH)CH(OH)CH_2CH{=}CH_2$ (**6**),[29] which have been reported previously. Characterization data for **5**: $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3OD): *δ* −8.8 (d, *J*(PP) = 29.6 Hz), 10.4 (t, *J*(PP) = 29.6 Hz). ^{1}H NMR (300.13 MHz, CD_3OD): *δ* 1.55 (d, *J*(PH) = 9.5 Hz, 9 H, PMe_3), 1.59 (t, *J*(PH) = 3.8 Hz, 18 H, PMe_3). Characterization data for **6**: ^{1}H NMR (300.13 MHz, CD_3OD): *δ* 2.34 (m, 4 H, CH_2), 3.39 (br, 2 H, OH), 3.58 (m, 2 H, OCH), 5.14 (m, 4 H, =CH_2), 5.90 (m, 2 H, =CH).

(*E*)-Me$_3$SiC≡CCH=CHCOOEt (9). To a mixture of ethyl (*E*)-3-iodo-2-propenate (6.47 g, 28.6 mmol), $PdCl_2(PPh_3)_2$ (0.30 g, 0.43 mmol), and CuI (0.050 g, 0.26 mmol) in Et_3N (100 mL) was added trimethylsilylacetylene (3.34 g, 34.0 mmol). The reaction mixture was stirred at 50 °C for 15 h. After the mixture was cooled to room temperature, diethyl ether (100 mL) and water (100 mL) were added, and the aqueous layer was extracted with 2 × 70 mL of diethyl ether. The combined organic layers were dried over $MgSO_4$. The solvents were removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, eluent: ethyl acetate/hexane, 2:98) to give a yellow oil. Yield: 4.3 g, 77%. The compound has been synthesized previously by an alternative route.[33] ^{1}H NMR (300.13 MHz, $CDCl_3$): *δ* 0.23 (s, 9 H, $SiMe_3$), 1.29 (t, *J*(HH) = 7.0 Hz, 3 H, CH_3), 4.22 (q, *J*(HH) = 7.0 Hz, 2 H, OCH_2), 6.25 (d, *J*(HH) = 16.0 Hz, 1 H, HC=), 6.72 (d, *J*(HH) = 16.0 Hz, 1 H, =C*H*COOEt). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): *δ* −0.7 (s, $SiMe_3$), 13.9 (s, CH_3), 60.5 (s, OCH_2), 101.0 (s, C≡*C*SiMe$_3$), 104.5 (s, *C*≡CSiMe$_3$), 124.5 (s, HC=), 130.9 (s, =*C*HCOOEt), 165.5 (s, CO).

(*E*)-Me$_3$SiC≡CCH=CHCHO (10). A solution of **9** (2.62 g, 13.4 mmol) in CH_2Cl_2 (30 mL) was cooled to −78 °C. A 1 M CH_2Cl_2 solution of diisobutylalumium hydride (13.0 mL, 13.0 mmol) was slowly added to the solution at such a rate that the temperature did not exceed −75 °C. The reaction mixture was stirred at −75 to −70 °C for an additional 1 h. Then MeOH (10 mL) was slowly added while the temperature of the mixture was maintained at −75 °C. Immediately after the addition, a 20% aqueous potassium tartrate solution (30 mL) was added to the cold reaction mixture. The cooling bath was removed, the mixture was stirred for 15 min, and then diethyl ether (20 mL) was added. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 15 mL). The combined organic layers were dried over $MgSO_4$. The solvents were then removed by rotary evaporation. The residue was purified by column chromatograph (silica gel, eluent: ethyl acetate in hexane = 5%, 10% in turn) to give a yellow oil. Yield: 1.4 g, 69%. Anal. Calcd for $C_8H_{12}OSi$: C, 63.11; H, 7.94. Found: C, 62.57; H, 7.71. MS(CI): *m*/*z* 153 [M + 1]. ^{1}H NMR (300.13 MHz, $CDCl_3$): *δ* 0.26 (s, 9 H, $SiMe_3$), 6.47 (dd, *J*(HH) = 15.9, 7.4 Hz, 1 H, =C*H*CHO), 6.59 (d, *J*(HH) = 15.9 Hz, 1 H, =C*H*), 9.56 (d, *J*(HH) = 7.4 Hz, 1 H, CHO). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): *δ* −0.9 (s, $SiMe_3$), 100.2 (s, C≡*C*SiMe$_3$), 110.9 (s, *C*≡CSiMe$_3$), 131.7 (s, HC=), 139.7 (s, =*C*HCHO), 192.7 (s, CHO).

(*3E,5E*)-Me$_3$SiC≡CCH=CHCH=CHC≡CSiMe$_3$ (11). To a slurry of (3-trimethylsilyl-2-propynyl)triphenylphosphonium bromide (3.58 g, 7.89 mmol) in THF (40 mL) was added a 1 M THF solution of $NaN(SiMe_3)_2$ (7.5 mL, 7.5 mmol). The mixture was stirred at room temperature for 30 min, and then a solution of **10** (1.20 g, 7.89 mmol) in THF (20 mL) was added slowly. The resulting solution was stirred for 30 min, and then water (80 mL) was added. The layers were separated, and the aqueous layer was further extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with a saturated aqueous solution of sodium chloride (2 × 50 mL) and dried over $MgSO_4$, filtered, and then concentrated under rotary evaporation. The crude product was purified by column chromatography (silica gel, eluent: hexane) to give a yellow solid. Yield: 1.1 g, 59%. ^{1}H NMR (300.13 MHz, $CDCl_3$): *δ* 0.21 (s, 18 H, $SiMe_3$), 5.70 (m, 2 H, HC=), 6.63 (m, 2 H, =CH). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): *δ* −0.3 (s, $SiMe_3$), 99.5 (s, C≡C), 103.9 (s, C≡C), 113.5 (s, CH=CH), 141.2 (s, CH=CH).

(*3E,5E*)-HC≡CCH=CHCH=CHC≡CH (12). To a mixture of sodium hydroxide aqueous solution (50%, 10 mL) and EtOH (80 mL) was slowly added **11** (1.4 g, 5.9 mmol) in EtOH (20 mL). The resulting solution was stirred for 4 h, and then a saturated aqueous solution of sodium chloride (70 mL) was added to the mixture. The solution was extracted with hexane (4 × 60 mL). The solvents of the extraction were removed to give a brown-yellow solid. Yield: 0.41 g, 68%. ^{1}H NMR (300.13 MHz, C_6D_6): *δ* 2.79 (d, *J*(HH) = 2.2 Hz, 2 H, HC≡C), 5.26 (m, 2 H, HC=C), 6.30 (m, 2 H, =C*H*-C≡C). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6): *δ* 82.0 (s, H*C*≡C), 82.7 (s, *C*≡CH), 113.3 (s, HC=), 141.9 (s, =CH).

[RuCl(CO)(PPh$_3$)$_2$]$_2$(*μ*-CH=CHCH=CHCH=CHCH=CH) (13). To a suspension of $RuHCl(CO)(PPh_3)_3$ (3.5 g, 3.67 mmol) in CH_2Cl_2 (50 mL) was slowly added a solution of **12** (0.300 g, 2.94 mmol) in CH_2Cl_2 (30 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. 10 mL under vacuum. Addition of hexane (80 mL) to the residue produced a purple solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 2.5 g, 92%. Anal. Calcd for $C_{82}H_{68}Cl_2O_2P_4Ru_2$: C, 66.44; H, 4.62. Found: C, 66.38; H, 4.88. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): *δ* 29.4 (s). ^{1}H NMR (300.13 MHz, CD_2Cl_2): *δ* 5.54 (m, 2 H, *δ*-CH), 6.00 (m, 2 H, *γ*-CH), 7.41−7.73 (m, 62 H, *β*-CH, PPh_3), 7.96 (br d, *J*(HH) = 12.7 Hz, 2 H, Ru−CH).

[RuCl(CO)(PMe$_3$)$_3$]$_2$(*μ*-CH=CHCH=CHCH=CHCH=CH) (14). To a solution of complex **13** (0.5 g, 0.34 mmol) in CH_2Cl_2 (50 mL) was added a 1 M THF solution of PMe_3 (5.0 mL, 5.0 mmol). The reaction mixture was stirred for 10 h. The volume of the reaction mixture was reduced to ca. 2 mL, and then hexane (20 mL) was added. The pale yellow solid was collected by filtration, washed with hexane, and dried over vacuum. Yield: 0.26 g, 86%. Anal. Calcd for $C_{28}H_{62}Cl_2O_2P_6Ru_2{\cdot}CH_2Cl_2$: C, 35.74; H, 6.62. Found: C, 36.00; H, 6.16. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): *δ* −20.5 (t, *J*(PP) = 22.6 Hz), −8.45 (d, *J*(PP) = 22.6 Hz). ^{1}H NMR (300.13 MHz, CD_2Cl_2): *δ* 1.45 (t, *J*(PH) = 3.4 Hz, 36 H, PMe_3), 1.52 (d, *J*(PH) = 6.8 Hz, 18 H, PMe_3), 5.93 (m, 2 H, *δ*-CH), 6.22 (m, 2 H, *γ*-CH), 6.45 (m, 2 H, *β*-CH), 7.51 (ddt, *J*(HH) = 17.0 Hz, *J*(PH) = 8.8, 4.0 Hz, 2 H, Ru−CH). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): *δ* 17.8 (t, *J*(PC) = 15.3 Hz, PMe_3), 21.1 (d, *J*(PC) = 20.8 Hz, PMe_3), 125.0 (s, *δ*-CH), 137.2 (s, *γ*-CH), 139.3 (s, *β*-CH), 172.7 (dt, *J*(PC) = 78.0, 18.5 Hz, Ru−CH), 203.8 (q, *J*(PC) = 11.5 Hz, CO).

[RuCl(PhPy)(CO)(PPh$_3$)$_2$]$_2$(*μ*-CH=CHCH=CHCH=CHCH=CH) (15). A mixture of complex **13** (0.50 g, 0.34 mmol) and 4-phenylpyridine (0.21 g, 1.36 mmol) in CH_2Cl_2 (30 mL) was stirred for 30 min. The solution was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 5 mL under vacuum. Addition of hexane (30 mL) to the residue produced a yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.51 g, 84%. Anal. Calcd for $C_{104}H_{86}Cl_2N_2O_2P_4Ru_2{\cdot}CH_2Cl_2$: C, 67.17; H, 4.72; N, 1.49. Found: C, 67.46; H, 5.14; N, 1.55. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): *δ* 25.2 (s). ^{1}H NMR (300.13 MHz, CD_2Cl_2): *δ* 5.74 (m, 2 H, *δ*-CH), 6.00 (m, 2 H, *γ*-CH), 6.88 (br, 4 H, $C_5H_2H_2N$), 7.27−7.65 (m, 72 H, Ph, *β*-CH), 8.20 (br d, *J*(HH) = 16.1 Hz, 2 H, Ru−CH), 8.57 (br, 4 H, $C_5H_2H_2N$).

[RuCl(CO)(PMP)]₂(*μ*-CH=CHCH=CHCH=CHCH=CH) (16). A mixture of complex **13** (0.50 g, 0.34 mmol) and PMP (0.32 g, 0.70 mmol) in CH_2Cl_2 (30 mL) was stirred for 15 h. The solution was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 5 mL under vacuum. Addition of hexane (30 mL) to the residue produced a pale yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.38 g, 89%. Anal. Calcd for $C_{72}H_{62}Cl_2N_2O_2P_4Ru_2$: C, 62.47; H, 4.52; N, 2.02. Found: C, 62.19; H, 4.76; N, 2.02. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 48.8 (s). ^1H NMR (300.13 MHz, CD_2Cl_2): δ 4.26 (m, 4 H, $CH\mathit{H}(C_5H_3N)CH\mathit{H}$), 4.66 (m, 4 H, $C\mathit{H}H(C_5H_3N)C\mathit{H}H$), 5.34 (m, 2 H, δ-CH), 5.71 (m, 2H, γ-CH), 7.15−7.78 (m, 42 H, PPh_2, β-CH), 7.95 (m, 2 H, Ru−CH).

Crystallographic Analysis for $[RuCl(CO)(PMe_3)_3]_2(\mu$-$CH{=}CHCH_2CH(OH)CH(OH)CH_2CH{=}CH)$ (4a). Crystals suitable for X-ray diffraction were grown from a CH_2Cl_2 solution layered with hexane. A crystal was mounted on a glass fiber, and the diffraction intensity data were collected on a Bruker CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 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 6.26 and SADABS version 2.03. Structure solution and refinement were performed using the SHELXTL version 6.10 software package. The molecule has a crystallographic 2-fold axis; thus the asymmetric unit contains half of one molecule. All non-hydrogen atoms were refined anisotropically. The hydroxy proton was seen in the Fourier difference map, and all hydrogens were included in their idealized positions and refined using a riding model. Further crystallographic details are summarized in Table 1, and selected bond distances and angles are given in Table 2.

Crystallographic Analysis for $[RuCl(CO)(PMe_3)_3]_2(\mu$-$CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$ (14). Crystals suitable for X-ray diffraction were grown from a CH_2Cl_2 solution layered with hexane. A colorless single crystal with approximate dimensions of 0.20 × 0.20 × 0.15 mm was mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Bruker SMART CCD area detector and corrected for SADABS (Siemens Area Detector Absorption)[46] (from 0.7975 to 1.0000 on I). The structure was solved by Patterson methods, expanded by difference Fourier syntheses, and refined by full matrix least-squares on F^2 using the Bruker SHELXTL (version 5.10)[47] program package. The molecule is centrosymmetric, with the inversion center at the midpoint of C4 and C4A; thus the crystallographic asymmetric unit contains half of one molecule. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms (H1, H2, H3, H4) of the C_8H_8 backbone were located from the difference Fourier maps and refined with isotropic thermal parameters. The remaining hydrogen atoms were introduced at their geometric positions and refined as riding atoms. Further crystallographic details are summarized in Table 1, and selected bond distances and angles are given in Table 3.

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

Supporting Information Available: Tables of bond distances and angles, atomic coordinates and equivalent isotropic displacement coefficients, and anisotropic displacement coefficients for $[RuCl(CO)(PMe_3)_3]_2(\mu$-$CH{=}CHCH_2CH(OH)CH(OH)CH_2CH{=}CH)$ (**4a**) and $[RuCl(CO)(PMe_3)_3]_2(\mu$-$CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$ (**14**). The materials are available free of charge via the Internet at http://pubs.acs.org.

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