Organometallics **2005,** *24,* 769−772

Synthesis and Characterization of $C_{10}H_{10}$-Bridged Bimetallic Ruthenium Complexes

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Received August 16, 2004

Summary: Treatment of $RuHCl(CO)(PPh_3)_3$ *with* $(3E,5E,7E)\text{-}HC{\equiv}CCH{=}CHCH{=}CHCH{=}CHC{\equiv}CH$ *produces* $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CHCH{=}CH)$*. The latter complex reacts with* PMe_3 *to give* $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CHCH{=}CH)$*, the structure of which has been confirmed by X-ray diffraction. The electrochemical properties of the latter* $C_{10}H_{10}$*-bridged complex have been investigated.*

Introduction

There has been much interest in the synthesis and properties of bimetallic complexes with conjugated hydrocarbon ligands bridging metal centers.[1,2] C_x and $(CH)_x$ are probably the simplest hydrocarbon bridging ligands. The synthesis and properties of bimetallic complexes with C_x bridges have been intensively investigated, and a number 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 been synthesized in recent years.[2] In contrast to bimetallic complexes with C_x bridges, the number of bimetallic complexes with $(CH)_x$ bridges are still rather limited. Previously reported examples of $(CH)_x$-bridged bimetallic complexes are limited to a few with $(CH)_2$,[3] $(CH)_4$,[4−6] $(CH)_5$,[7] $(CH)_6$,[8,9] and $(CH)_8$[10] bridges. Related bimetallic complexes of the types $L_nM{=}C(OR)CH{=}CHC(OR){=}ML_n$ or $L_nM{=}CRRCR{=}ML_n$[11] and $L_nMCH{=}CHArCH{=}CHML_n$[12] are also known. In this work, we wish to report the synthesis, characterization, and electrochemical properties of the first $(CH)_{10}$-bridged bimetallic complexes.

Results and Discussion

Reactions of $RuHCl(CO)(PPh_3)_3$ with $HC{\equiv}CR$ are known to give $RuCl(CH{=}CHR)(CO)(PPh_3)_2$.[13,14] The reaction has been used to prepare bimetallic complexes such as $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CHArCH{=}CH)$[12] and $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}(CH{=}CH)_x)$ (x = 2,[6] 3,[9] 4[10]). Thus, it was reasoned that bimetallic complexes with a $C_{10}H_{10}$ bridge might be obtained by starting from the reaction

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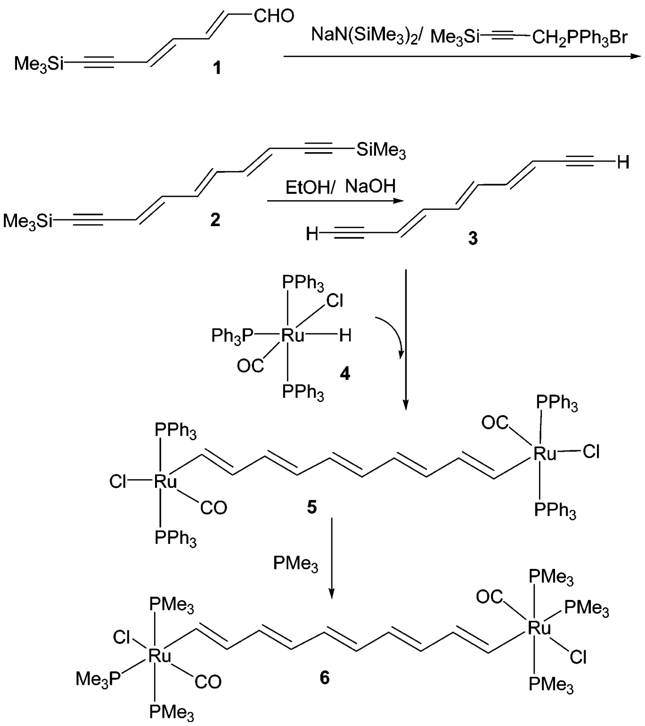
10.1021/om0493659 CCC: \$30.25

Scheme 1



of $RuHCl(CO)(PPh_3)_3$ with the dialkyne (3*E*,5*E*,7*E*)-$HC{\equiv}CCH{=}CHCH{=}CHCH{=}CHC{\equiv}CH$.

The previously unknown dialkyne (3*E*,5*E*,7*E*)-$HC{\equiv}CCH{=}CHCH{=}CHCH{=}CHC{\equiv}CH$ (**3**) was prepared by the route shown in Scheme 1. The Wittig reaction of (2*E*,4*E*)-$Me_3SiC{\equiv}CCH{=}CHCH{=}CHCHO$ (**1**)[15] with $Me_3SiC{\equiv}CCH_2PPh_3Br$ in the presence of $NaN(SiMe_3)_2$ produced the precursor compound **2**. Treatment of **2** with NaOH produced **3**, which was isolated as a yellow solid. Compound **3** is thermally unstable and polymerized readily when stored at room temperature. Thus, it was used immediately after it was produced. The identity of compound **3** can be easily identified by NMR spectroscopy. In particular, the ^1H NMR spectrum (in C_6D_6) showed one ≡CH signal at 2.88 ppm and three =CH signals at 5.30, 5.70, and 6.47 ppm; the $^{13}C\{^1H\}$ NMR spectrum (in C_6D_6) showed the acetylenic carbon signals at 81.5 and 82.8 ppm and the vinyl signals at 111.8, 133.6, and 142.3 ppm.

Treatment of **3** with the ruthenium hydride complex $RuHCl(CO)(PPh_3)_3$ (**4**) in dichloromethane produced the insertion product $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CHCH{=}CH)$ (**5**), which can be isolated as a purple solid in 87% yield (Scheme 1). The complex has been characterized by NMR and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum (in CD_2Cl_2) showed a singlet at 29.3 ppm, the chemical shift of which is typical for $RuCl(CH{=}CHR)(CO)(PPh_3)_2$.[10] In the ^1H NMR spectrum (in CD_2Cl_2), the Ru−CH signal was observed at 8.11 ppm. Treatment of **5** with PMe_3 produced the six-coordinated complex $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CHCH{=}CH)$ (**6**). The PMe_3 ligands in **6** must be meridionally coordinated to ruthenium, as indicated by the AM_2 pattern $^{31}P\{^1H\}$ NMR spectrum. The presence of the $(CH)_{10}$ chain is confirmed by the ^1H NMR spectrum (in CD_2Cl_2), which showed the vinyl proton signals at 8.05 (Ru−CH), 6.89 (β-CH), 6.54 (γ,δ-CH), and 6.30 (ε-CH) ppm.

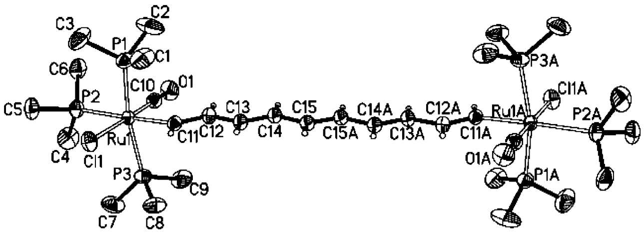


Figure 1. Molecular structure of $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CHCH{=}CH)$ (**6**).

Table 1. Crystal Data and Structure Refinement Details for 6

formula	$C_{30}H_{64}Cl_2O_2P_6Ru_2$
formula wt	915.67
wavelength, Å	0.71073
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	8.9468(11)
b, Å	8.5865(5)
c, Å	16.3021(10)
β, deg	113.1590(10)
V, Å^3	2438.4(3)
Z	2
d_{calcd}, g cm^{-3}	1.247
abs coeff, mm^{-1}	0.947
$F(000)$	944
θ range, deg	2.34−27.52
index ranges	$-24 \le h \le 24$, $-11 \le k \le 11$, $-21 \le l \le 21$
no. of rflns	26 628
no. of indep rflns	5545 (R(int) = 0.0348)
no. of data/restraints/params	5545/0/190
goodness of fit on F^2	0.999
final R indices ($I > 2\sigma(I)$)	R1 = 0.0319, wR2 = 0.0693
largest diff peak and hole, e Å^{-3}	0.493 and −0.172

Table 2. Selected Bond Distances (Å) and Angles (deg) for 6[a]

Ru(1)−C(10)	1.815(3)	Ru(1)−C(11)	2.084(2)
Ru(1)−P(3)	2.3565(7)	Ru(1)−P(1)	2.3599(7)
Ru(1)−P(2)	2.4048(7)	Ru(1)−Cl(1)	2.4798(6)
O(1)−C(10)	1.141(3)	C(11)−C(12)	1.336(3)
C(12)−C(13)	1.441(3)	C(13)−C(14)	1.344(3)
C(14)−C(15)	1.430(3)	C(15)−C(15)#1	1.334(5)

C(10)−Ru(1)−C(11)	91.15(11)	C(10)−Ru(1)−P(3)	91.98(8)
C(11)−Ru(1)−P(3)	80.99(6)	C(10)−Ru(1)−P(1)	93.37(8)
C(11)−Ru(1)−P(1)	82.75(6)	P(3)−Ru(1)−P(1)	162.97(3)
C(10)−Ru(1)−P(2)	88.61(8)	C(11)−Ru(1)−P(2)	178.04(6)
P(3)−Ru(1)−P(2)	100.97(3)	P(1)−Ru(1)−P(2)	95.31(3)
C(10)−Ru(1)−Cl(1)	179.22(8)	C(11)−Ru(1)−Cl(1)	89.30(7)
P(3)−Ru(1)−Cl(1)	88.72(3)	P(1)−Ru(1)−Cl(1)	86.04(3)
P(2)−Ru(1)−Cl(1)	90.93(2)	O(1)−C(10)−Ru(1)	179.2(3)
C(12)−C(11)−Ru(1)	130.83(19)	C(11)−C(12)−C(13)	125.4(2)
C(14)−C(13)−C(12)	124.7(3)	C(13)−C(14)−C(15)	125.2(3)
C(15)#1−C(15)−C(14)	125.2(4)		

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

The structure of **6** has been confirmed by an X-ray diffraction study. The molecular structure of complex **6** 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 symmetrically by a linear $(CH)_{10}$ bridge with an inversion center at the midpoint of the C15−C15A bond. The geometry around ruthenium can be described as a distorted octahedron with three meridionally bound

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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 P(1)−Ru−P(2) (95.31(3)°), P(3)−Ru−P(2) (100.97(3)°), C(11)−Ru−P(1) (82.75(6)°), and C(11)−Ru−P(3) (80.99(6)°) angles, probably due to the steric interaction between the PMe_3 ligands. As in the complexes $RuH(CH{=}CMeCO_2Bu)(CO)(PPh_3)_3$[16] and $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$,[10] the unique Ru−P(2) bond (2.4048(7) Å) of **6** is slightly longer than those of the mutually trans Ru−P bonds (2.3599(7) and 2.3565(7) Å), due to the strong trans influence of the vinyl ligand. The Ru−C and C(α)−C(β) bond distances of complex **6** are within the range of those reported for ruthenium vinyl complexes.[17]

The $(CH)_{10}$ ligand shows a single/double carbon−carbon bond alternation. All the olefinic double bonds are in a trans geometry. The formal double bonds have an average bond distance of 1.338 Å, and the formal single bonds have an average bond distance of 1.436 Å. The difference in the average single- and double-bond distances is 0.098 Å, which is similar to those in $PhCH{=}CH(CH{=}CH)_2CH{=}CHPh$ (0.092 Å)[18] and $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$ (0.099 Å).[10] Like the complex $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CH)$,[10] the vinyl group is also essentially coplanar with Cl−Ru−CO. The atoms Cl(1), Ru(1), C(10), O(1), C(11), and C(12) are in a plane with a maximum deviation from the least-squares plane of 0.096 Å for Ru(1). The carbon atoms of the $(CH)_{10}$ chain and the ruthenium atoms are also essentially coplanar, with a maximum deviation from the least-squares plane of 0.050 Å for C(15). The coplanarity of the vinyl group and CO is expected, because stabilization due to the π interaction of CO and vinyl with metal centers is maximized in such a conformation.[19]

Electrochemical Study. The cyclic voltammogram of complex **6** has been collected in dichloromethane containing 0.10 M $n\text{-}Bu_4NClO_4$ as the supporting electrolyte. As shown in Figure 2a, the cyclic voltammogram of **6** has two partially resolved oxidation waves at −0.004 and 0.089 V vs Ag/AgCl (or −0.225 and −0.132 V vs Fc/Fc^+). These oxidation waves can be easily visualized when the primary voltammogram was convolved by the semiderivative method (Figure 2b). These two oxidation waves can be attributed to the formation of $[(PMe_3)_3(CO)ClRu(CH{=}CH)_5RuCl(CO)(PMe_3)_3]^+$ and $[(PMe_3)_3(CO)ClRu{=}CH(CH{=}CH)_4CH{=}RuCl(CO)(PMe_3)_3]^{2+}$, respectively. The peak separation of the two oxidation waves for complex **6** is at 0.09 V. Observation of two oxidation waves for complex **6** may imply that the two metal centers can interact with each other.

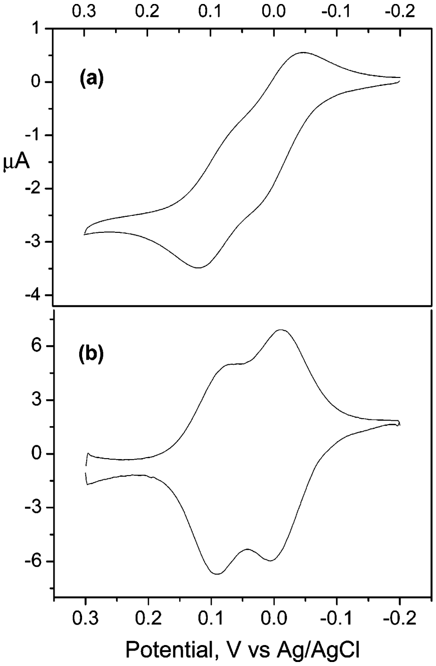

Figure 2. (a) Cyclic voltammogram of **6** in 0.10 M $n\text{-}Bu_4NPF_6/CH_2Cl_2$ (Pt electrode, V vs Ag/AgCl, scan rate 10 mV/s, 25 °C). (b) Corresponding semidifferential data of the primary voltammogram.

As one might expect, the peak separation of the oxidation waves of complex **6** is smaller than those reported for the $(CH)_4$-bridged complex $Cp(dppm)Fe(CH{=}CH)_2Fe(dppm)Cp$ (0.44 V),[4b] the $(CH)_6$-bridged complex $(PMe_3)_3(CO)ClRu(CH{=}CH)_3RuCl(CO)(PMe_3)_3$ (0.38 V),[9] and the $(CH)_8$-bridged complex $(PMe_3)_3(CO)ClRu(CH{=}CH)_4RuCl(CO)(PMe_3)_3$ (0.24 V).[10] We noted that there is a sharp dropoff in the wave separation between $(CH)_8$ and $(CH)_{10}$ complexes relative to that between $(CH)_6$ and $(CH)_8$ complexes, although we are not clear about the reason. The smaller wave separation of complex **6** may suggest that the interaction of the metal centers is weak. However, it should be noted that the potential difference of a symmetrical bimetallic complex, which may exhibit parallel variations with electronic coupling parameters (V_{ab}), is a thermodynamic quantity relating to the thermodynamic stability of mixed-valence species. It depends on a through-bridge electronic interaction as well as other factors.[20]

Summary. We have prepared bimetallic complexes with metal centers bridged by $(CH)_{10}$. The structure of $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CHCH{=}CHCH{=}CH)$ (**6**) has been confirmed by X-ray diffraction. An electrochemical study shows that the metal centers in the bimetallic complex **6** 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 $RuHCl(CO)(PPh_3)_3$[21] and (2*E*,4*E*)-

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[20] Roué, S.; Lapinte, C.; Bataille, T. *Organometallics* **2004**, *22*, 2558 and references therein.

[21] Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F.; Wonchoba, E. R.; Parshall, G. W. *Inorg. Synth.* **1974**, *15*, 45.

(TMS)C≡CCH=CHCH=CHCHO[15] 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_3PO_4. The assignments of ^{1}H and ^{13}C NMR data for the alkenyl groups are based on 2D NMR experiments.

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 at a scan rate of 10 mV/s in CH_2Cl_2 containing 0.10 M *n*-Bu_4NPF_6 as the supporting electrolyte. The primary voltammogram of **6** was convolved by the semiderivative method to provide clear visual resolution of the redox waves. The peak potentials reported were referenced to Ag/AgCl. The ferrocene/ferrocenium redox couple was located at 0.221 V under our experimental conditions.

(3*E*,5*E*,7*E*)-(TMS)C≡CCH=CHCH=CHCH=CHC≡CTMS (2). To a slurry of (3-(trimethylsilyl)-2-propynyl)-triphenylphosphonium bromide (0.82 g, 1.8 mmol) in THF (25 mL) was added $NaN(TMS)_2$ (0.72 mL, 1.8 mmol, 2.5 M in THF). This mixture was stirred at room temperature for 30 min, after which a solution of (2*E*,4*E*)-(TMS)C≡CCH=CHCH=CHCHO (0.29 g, 1.63 mmol) in THF (20 mL) was added via syringe, and the resulting solution was stirred for 1 h. Water (50 mL) was added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and then concentrated. The residue was purified by column chromatography (silica gel, hexane) to give a bright yellow solid. Yield: 0.32 g, 72%. Anal. Calcd for $C_{16}H_{24}Si_2$: C, 70.51; H, 8.88. Found: C, 70.67, H, 9.02. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 0.20 (s, 18 H, $SiMe_3$), 5.68 (d, *J*(HH) = 15.3 Hz, 2 H, =CH), 6.35 (m, 2 H, =CH), 6.64 (m, 2 H, =CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ −0.37 (s, $SiMe_3$), 99.2 (s, C≡C), 104.2 (s, C≡C), 112.6 (s, =CH), 133.9 (s, =CH), 141.8 (s, =CH).

(3*E*,5*E*,7*E*)-HC≡CCH=CHCH=CHCH=CHC≡CH (3). A solution of (3*E*,5*E*,7*E*)-(TMS)C≡CCH=CHCH=CHCH=CHC≡CTMS (1.60 g, 5.87 mmol) in EtOH (20 mL) was added to a mixture of a sodium hydroxide aqueous solution (50%, 10 mL) and EtOH (80 mL). The resulting solution was stirred for 4 h. A 70 mL portion of the saturated aqueous solution of sodium chloride was added. The solution was extracted with 4 × 60 mL of ether. The solvent was removed to give a brown-yellow solid. Yield: 0.48 g, 65%. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 2.88 (s, 2 H, HC≡C), 5.30 (d, *J*(HH) = 15.4 Hz, 2 H, =CH), 5.70 (m, 2 H, =CH), 6.47 (m, 2 H, =CH). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 81.5 (s, H*C*≡C), 82.8 (s, *C*≡CH), 111.8 (s, =CH), 133.6 (s, =CH), 142.3 (s, =CH).

$[RuCl(CO)(PPh_3)_2]_2$(*μ*-CH=CHCH=CHCH=CHCH=CHCH=CH) (5). To a suspension of $RuHCl(CO)(PPh_3)_3$ (3.50 g, 3.67 mmol) in CH_2Cl_2 (50 mL) was added dropwise a solution of (3*E*,5*E*,7*E*)-HC≡CCH=CHCH=CHCH=CHC≡CH (0.300 g, 2.38 mmol) in CH_2Cl_2 (30 mL). The reaction mixture was stirred for 30 min to give a red solution. The 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: 2.4 g, 87%. Anal. Calcd for $C_{84}H_{70}Cl_2O_2P_4Ru_2$: C, 66.89; H, 4.68. Found: C, 66.69; H, 4.80. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 29.3 (s). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 5.63 (m, 4 H, δ,ϵ-CH), 6.08 (m, 4 H, β,γ-CH), 7.44−7.76 (m, 60 H, PPh_3), 8.11 (br d, *J*(HH) = 12.7 Hz, 2 H, Ru−CH).

$[RuCl(CO)(PMe_3)_3]_2$(*μ*-CH=CHCH=CHCH=CHCH=CHCH=CH) (6). To a solution of $[RuCl(CO)(PPh_3)_2]_2$(*μ*-CH=CHCH=CHCH=CHCH=CHCH=CH) (0.50 g, 0.33 mmol) in CH_2Cl_2 (20 mL) was added a 5 mL THF solution of PMe_3 (1.0 M, 5.00 mmol). The reaction mixture was stirred for 15 h. The volatile materials were removed under vacuum. The solid was redissolved in benzene (3 mL). Addition of hexane (40 mL) to the residue produced a pale yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.20 g, 66%. Anal. Calcd for $C_{30}H_{64}Cl_2O_2P_6Ru_2$: C, 39.35; H, 7.05. Found: C, 38.82; H, 6.55. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ −20.8 (t, *J*(PP) = 22.8 Hz), −8.95 (d, *J*(PP) = 22.8 Hz). ^{1}H NMR (300.13 MHz, C_6D_6): δ 1.16 (d, *J*(PH) = 6.7 Hz, 18 H, PMe_3), 1.21 (t, *J*(PH) = 3.4 Hz, 36 H, PMe_3), 6.30 (m, 2 H, ϵ-CH), 6.54 (m, 4 H, γ,δ-CH), 6.89 (m, 2 H, β-CH), 8.05 (m, 2 H, Ru−CH).

Crystallographic Analysis for $[RuCl(CO)(PMe_3)_3]_2$(*μ*-CH=CHCH=CHCH=CHCH=CHCH=CH) (6). Crystals suitable for X-ray diffraction were grown from a CH_2Cl_2 solution layered with diethyl ether. A yellow single crystal with approximate dimensions of 0.20 × 0.20 × 0.10 mm^3 was mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Bruker Apex CCD area detector at 100 K and were corrected by semiempirical methods from equivalents. 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) program package. The molecule is centrosymmetric with the inversion center at the midpoint of C15 and C15A; thus, the crystallographic asymmetric unit contains half of one molecule. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced at their geometric positions and refined as riding atoms. Further crystallographic details are summarized in Table 1.

Acknowledgment. We acknowledge financial support from the Hong Kong Research Grants Council and the National Natural Science Foundation of China (No. 20242010).

Supporting Information Available: Tables of bond distances and angles, atomic coordinates and equivalent isotropic displacement coefficients, and anisotropic displacement coefficients for $[RuCl(CO)(PMe_3)_3]_2$(*μ*-CH=CHCH=CHCH=CHCH=CHCH=CH) (**6**); these data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0493659