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Articles

Synthesis and Characterization of Bimetallic Ruthenium Complexes Bridged with Linear C_4H_4 and $C_6H_4O_2$ Ligands

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Reaction of $Me_3SiC\equiv CC\equiv CSiMe_3$ with $RuHCl(CO)(PPh_3)_3$ in CH_2Cl_2 produced $RuCl(\eta^1\text{-}C(C\equiv CSiMe_3)=CHSiMe_3)(CO)(PPh_3)_2$, which on treatment with dppe gave $RuCl(\eta^1\text{-}C(C\equiv CSiMe_3)=CHSiMe_3)(CO)(PPh_3)(dppe)$. Reaction of $RuHCl(CO)(PPh_3)_3$ with $HC\equiv CC\equiv CH$ generated in situ from the reaction of $Me_3SiC\equiv CC\equiv CSiMe_3$ with $n\text{-}Bu_4NF/NH_4F/H_2O$ produced $[RuCl(CO)(NH_3)(PPh_3)_2]_2(\mu\text{-}CH=CHCH=CH)$, whereas the same reaction without the NH_4F afforded $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH=CHCH=CH)$. Complex $[RuCl(CO)(NH_3)(PPh_3)_2]_2(\mu\text{-}CH=CHCH=CH)$ reacted with excess PEt_3 and *t*-BuNC to give $[RuCl(CO)(PEt_3)_3]_2(\mu\text{-}CH=CHCH=CH)$ and $\{[Ru(t\text{-}BuNC)_3(PPh_3)_2]_2(\mu\text{-}COCH=CHCH=CHCO)\}Cl_2$, respectively. The structure of $[RuCl(CO)(PEt_3)_3]_2(\mu\text{-}CH=CHCH=CH)$ has been confirmed by X-ray diffraction.

Introduction

The synthesis and characterization of bimetallic and polymeric organometallic compounds with π-conjugated bridges are attracting considerable interest.[1,2] During the past decades, a large number of conjugated organometallic bimetallic complexes with hydrocarbon chains serving as σ,σ-, σ,π-, or π,π-bound bridging ligands have been reported. Most of the conjugated organometallic bimetallic complexes with σ,σ-bridging hydrocarbon chains are those with metal−C(sp) linkages, for example, C_x-bridged,[3,4] bis(acetylide),[5] bis(carbyne),[6] bis(vinylidene),[7] and bis(allenylidene) complexes.[8]

Bimetallic complexes with carbon chains containing only sp^2-hybridized carbons are interesting because many conjugated organic materials (for example, polyacetylenes, push/pull stilbenes, and polyenes) have only sp^2 carbons in their backbones.[9] Only a few complexes with linear C_nH_n ($n = 2$,[10,11] 4,[12,13] 5,[14] 6[15]) bridges have

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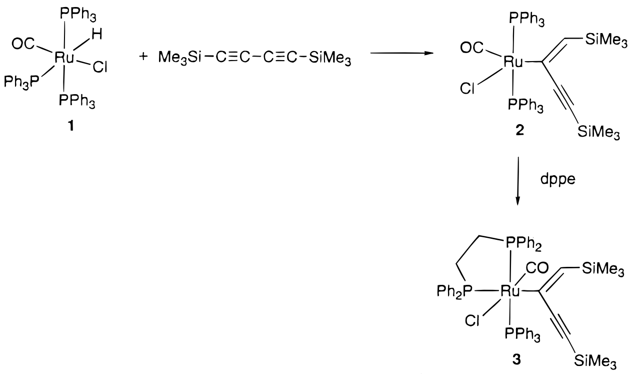
been reported. Other reported bimetallics with metal−C(sp^2) linkages include complexes with C_2R_2 bridges,[16,17] a μ-1,4-PhC═CH−CH═CPh bridge,[18] CH═CHArCH═CH bridges,[19] aryl bridges,[20] and 1,3-bimetalated cyclobutenylidene (C_4R_3) bridges.[21] Very recently, the C_5H_5N-bridged complex (t-$Bu_3SiO)_3$Nb═CH−CH═CH−CH═CH−N═Nb(OSi-t-Bu$)_3$ was reported.[22]

In principle, insertion reactions of diacetylenes with metal hydride complexes could provide an entry to bimetallic complexes with metal vinyl linkages. However, such reactions have only been sparsely explored for such purposes.[14,19] In this report, we present the synthesis and characterization of conjugated bimetallic complexes derived from the insertion reactions of RuHCl(CO)$(PPh_3)_3$ with HC≡CC≡CH.

Results and Discussion

Reaction of $Me_3SiC≡CC≡CSiMe_3$ with RuHCl(CO)$(PPh_3)_3$, Preparation of RuCl(η^1-C(C≡CSiMe$_3$)═CHSiMe$_3$)(CO)(PPh$_3$)$_2$. Insertion reactions of RC≡CR′ with RuHCl(CO)$(PPh_3)_3$ at room temperature to give the five-coordinated vinyl complexes RuCl(CR═CHR′)(CO)$(PPh_3)_2$ have been reported by several groups.[23−25] In principle, the hydride complex RuHCl(CO)$(PPh_3)_3$ (**1**) may react with 0.5 equiv of commercially available $Me_3SiC≡CC≡CSiMe_3$ to give bis-insertion products [RuCl(CO)$(PPh_3)_2]_2$(μ-$C_4H_2(SiMe_3)_2$), which could then be desilylated to give [RuCl(CO)$(PPh_3)_2]_2$(μ-C_4H_4). Thus, the reaction of $Me_3SiC≡CC≡CSiMe_3$ with RuHCl(CO)$(PPh_3)_3$ was investigated.

Scheme 1



Addition of excess of $Me_3SiC≡CC≡CSiMe_3$ to a suspension of RuHCl(CO)$(PPh_3)_3$ in CH_2Cl_2 produced an orange-brown solution from which the mono-insertion complex **2** was easily isolated as an orange-yellow solid (Scheme 1). The presence of the C(C≡CSiMe$_3$)═CHSiMe$_3$ group in complex **2** is indicated by the ^{1}H and ^{13}C NMR spectra. In particular, the ^{1}H NMR spectrum (in $CDCl_3$) showed the vinyl signal at 5.23 ppm and the $SiMe_3$ signals at 0.15 and 0.22 ppm; the ^{13}C NMR spectrum (in $CDCl_3$) showed the $SiMe_3$ signals at −1.1 and 0.8 ppm and the C_3CH signals at 98.8 (s, ≡CSiMe$_3$), 114.5 (s, ≡C), 143.1 (s, ═CH), and 152.6 ppm (t, J(PC) = 8.4 Hz, Ru−C═). Reported complexes related to complex **2** are RuCl(η^1-C(C≡CR)═CHR)(CO)$(PPh_3)_2$ (R = t-Bu, n-Bu, CMe$_2$OH, Ph, Cy, p-MeC$_6$H$_4$).[25a,26−28] In these complexes, C(C≡CR)═CHR has been proposed to be an η^1 ligand, and this bonding mode in RuCl(η^1-C(C≡C-t-Bu)═CH-t-Bu)(CO)$(PPh_3)_2$ has been confirmed by X-ray diffraction.[28] Complex **2** has a color and ^{31}P NMR

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data similar to those of the reported five-coordinated complexes $RuCl(\eta^1\text{-}C(C{\equiv}CR){=}CHR)(CO)(PPh_3)_2$[25a,26,27] and thus most likely has $C(C{\equiv}CSiMe_3){=}CHSiMe_3$ in an η^1 manner. The possibility of η^3 bonding for $C(C{\equiv}CSiMe_3){=}CHSiMe_3$ in **2** cannot be excluded completely in view of the fact that a number of complexes with $\eta^3\text{-}C(C{\equiv}CR){=}CHR$ or $\eta^3\text{-}C(C{\equiv}CR){=}CHR'$ ligands have been reported.[29] In addition, reaction of $Me_3SiC{\equiv}CCH{=}CHSiMe_3$ with $RuHCl(CO)(PPh_3)_3$ is reported to give $RuCl(CO)(C(CH{=}CHSiMe_3){=}CHSiMe_3)(PPh_3)_2$, in which one of the olefin double bonds interacts with the Ru center very weakly, as indicated by X-ray diffraction study.[24]

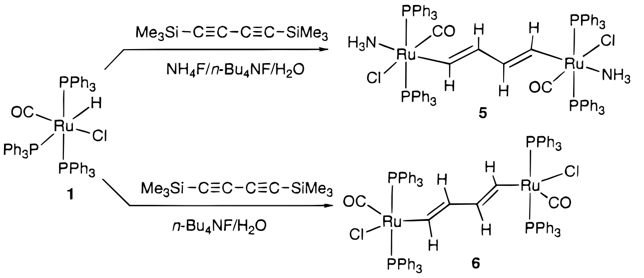
To clarify the structure, we have converted complex **2** into the air-stable complex $RuCl(\eta^1\text{-}C(C{\equiv}CSiMe_3){=}CHSiMe_3)(CO)(PPh_3)(dppe)$ (**3**) by treatment with dppe (Scheme 1). The geometry of complex **3** can be readily assigned based on ^{31}P NMR and ^{13}C NMR spectroscopic data. The PPh_3 is trans to one of the PPh_2 groups of dppe, as indicated by the large $J(PPh_3{-}PPh_2)$ coupling constant (307.7 Hz). The vinyl group is trans to the other PPh_2 group of the dppe ligand, as indicated by the large $^2J(PPh_2{-}C)$ coupling constant (60.9 Hz). The geometry around ruthenium in complex **3** is similar to those of recently reported mononuclear complexes $RuCl(CH{=}CHR)(CO)(PPh_3)(PP)$ (PP = dppm, dppe, and dppp).[19a] The ^{13}C signals of the $C{\equiv}C$ triple bond in **3** is very similar to those found with **2**, suggesting at most a weak interaction with the ruthenium center in **2**.

It is probably not surprising that complex **2** is produced instead of $RuCl(Me_3SiC{=}CHC{\equiv}CSiMe_3)(CO)(PPh_3)_2$. Reactions of $HC{\equiv}CR$ and $PhC{\equiv}CC{\equiv}CPh$ with $RuHCl(CO)(PPh_3)_3$ have been reported previously to give $RuCl(CH{=}CHR)(CO)(PPh_3)_2$ and $RuCl(C(C{\equiv}CPh){=}CHPh)(CO)(PPh_3)_2$, respectively.[23−25] It is likely that the regiochemistry for the insertion reaction of $RuHCl(CO)(PPh_3)_3$ with $RC{\equiv}CR'$ is determined by steric effects in that the larger group in the products tends to be as far away as possible from the ruthenium center.

Complex **2** does not undergo further insertion reaction with $RuHCl(CO)(PPh_3)_3$, as demonstrated by the reaction of $RuHCl(CO)(PPh_3)_3$ with less than 1 equiv of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ or the reaction of isolated **2** with $RuHCl(CO)(PPh_3)_3$. Similarly complex **3** also failed to undergo an insertion reaction with $RuHCl(CO)(PPh_3)_3$. Steric effects are the likely reason for the low reactivity of the $C{\equiv}C$ functional group in **2** and **3** toward insertion reactions with $RuHCl(CO)(PPh_3)_3$. It was thought that removal of the bulky $SiMe_3$ group from **2** and **3** may increase the reactivity of the $C{\equiv}C$ functional group toward insertion reactions. Unfortunately, **2** and **3** did not react with the desilylating agents NH_4F or $n\text{-}Bu_4NF$ at room temperature and decomposed to an undefined mixture in refluxing THF in the presence of NH_4F or $n\text{-}Bu_4NF$.

Preparation of $[RuCl(CO)(NH_3)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH{=}CH)$ and $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH{=}CH)$. Since reactions of $HC{\equiv}CR$ with $RuHCl(CO)(PPh_3)_3$ usually give $RuCl(CH{=}CHR)(CO)(PPh_3)_2$, it was anticipated that reaction of $RuHCl(CO)(PPh_3)_3$ with $HC{\equiv}CC{\equiv}CH$ might lead to the linear C_4H_4-bridged bimetallic complex $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CH{-}CH{=}CH)$. Since terminal acetylenes $RC{\equiv}CH$ can be generated from the reactions of $RC{\equiv}CSiMe_3$ with base/ROH or F^- agents,[30] we attempted to generate $HC{\equiv}CC{\equiv}CH$ from commercially available $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$. Initially one-pot reactions of $RuHCl(CO)(PPh_3)_3$ with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ in CH_2Cl_2 in the presence of desilylating reagents such as K_2CO_3/MeOH, KOH/MeOH, NH_4F, and $n\text{-}Bu_4NF$ were attempted, with a hope that $HC{\equiv}CC{\equiv}CH$ would be generated in situ and then react to give the insertion product. Reactions of $RuHCl(CO)(PPh_3)_3$ with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ in CH_2Cl_2 in the presence of NH_4F led to the formation of $RuHCl(CO)(NH_3)(PPh_3)_2$ (**4**) as the predominant product. The same compound can be obtained from the reactions of $RuHCl(CO)(PPh_3)_3$ with NH_4F or aqueous NH_3. Reaction of $RuHCl(CO)(PPh_3)_3$ with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ in CH_2Cl_2 in the presence of other desilylating reagents led to uncharacterized mixtures.

Scheme 2



It was found that the six-coordinated C_4H_4-bridged bimetallic complex **5** could be prepared by bubbling the vapor (presumably a mixture of $HC{\equiv}CC{\equiv}CH$, NH_3, THF) from a mixture of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, NH_4F, $n\text{-}Bu_4NF$ on silica gel, and H_2O in THF, with gentle heating, through a suspension of $RuHCl(CO)(PPh_3)_3$ in CH_2Cl_2 (Scheme 2). In this reaction, the C_4H_4-bridged complex **5** was produced along with some uncharacterized species. The amount of complex **5** formed appears to be dependent on the reaction time and the rate of bubbling. Pure samples of **5** could be obtained by washing the crude product with a small amount of CH_2Cl_2. Complex **5** is likely produced from the reaction of the complex $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}C_4H_4)$ (**6**) with NH_3. Several closely related mononuclear complexes $Ru(CH{=}CHR)Cl(L)(CO)(PPh_3)_2$ have been reported recently from the reactions of $HC{\equiv}CR$ with $RuHCl(L)(CO)(PPh_3)_2$ (L is a 2e nitrogen donor ligand).[31] In the latter reactions, five-coordinate intermediate $Ru(CH{=}CHR)Cl(CO)(PPh_3)_2$ has been proposed. Both NH_4F and Bu_4NF appear to be important for the formation of complex **5**. If only NH_4F was used, the hydride complex **4** along with some uncharacterized species were produced. A black material and a small amount of complex $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}C_4H_4)$ (**6**) were formed if only $n\text{-}Bu_4NF$ was used. Apparently, $n\text{-}Bu_4NF$ helps to generate $HC{\equiv}CC{\equiv}CH$.

The yield for complex **6** could be improved if $HC{\equiv}CC{\equiv}CH$ was generated slowly by dropping a THF

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(29) See for example: (a) Yang, S. M.; Chan, M. C. W.; Cheung, K. K.; Che, C. M.; Peng, S. M. *Organometallics* **1997**, *16*, 2819, and references therein. (b) Bianchini, C.; Innocenti, P.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1996**, *15*, 272, and references therein.

(30) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988; Chaper 7, p 45.

(31) Santos, A.; López, J.; Galán, A.; González, J. J.; Tinoco, P.; Echavarren, A. M. *Organometallics* **1997**, *16*, 3482.

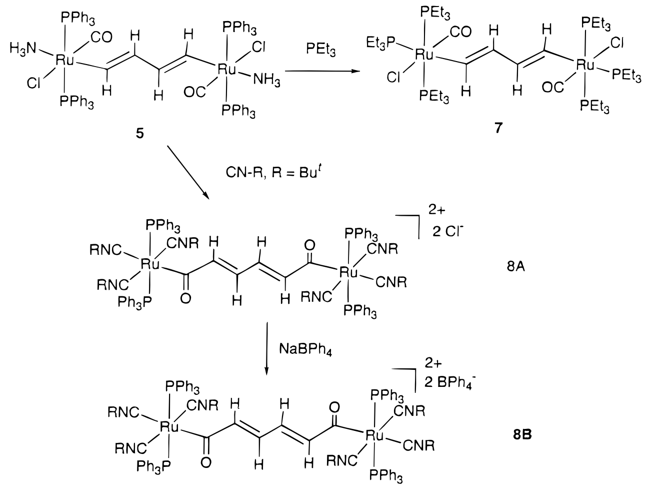
solution of *n*-Bu_4NF into a prewarmed THF solution of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$. In this way, complex **6** was obtained along with uncharacterized species as a red-dish-brown suspension in CH_2Cl_2. A slow dropping rate of *n*-Bu_4NF results in a better yield of complex **6**. As the solubility of complex **6** in organic solvents is poor, pure samples of **6** could be obtained by washing the crude product with acetone, chloroform, or CH_2Cl_2.

Compound **5** was characterized by ^{31}P and ^1H NMR, IR spectroscopy, and elemental analysis. The presence of NH_3 in **5** is indicated by the observation of the ^1H signal at 0.86 ppm assignable to NH_3 (in $CDCl_3$) and an IR band at 3374 cm^{-1} assignable to ν(N−H). The ^1H chemical shift for NH_3 in **5** is within the range reported for other NH_3 complexes, for example, 0.09 ppm with $[Ru(C{\equiv}CPh)(NH_3)(dppe)_2]PF_6$[32] and 2.28 ppm with $[Ru(C{\equiv}CPh)(NH_3)(PMe_3)_4]PF_6$.[33] The presence of the C_4H_4 bridge is indicated by the ^1H NMR spectrum which showed AA′BB′XX′ (X = PPh_3) vinyl signals at 4.63 and 5.89 ppm (Ru−CH). The C_4H_4 unit is assigned a trans geometry because the ^3J(H−H) coupling constants are very similar to those reported for (1*E*,3*E*)-$Me_3SnCH{=}CH{-}CH{=}CHSnMe_3$.[34] The geometry around ruthenium in complex **5** is assigned by analogy to those of mononuclear complexes $RuHCl(CH{=}CHR)(L)(CO)(PPh_3)_2$, where L is a two-electron nitrogen donor ligand.[31] Unfortunately, **5** is not soluble enough in common organic solvents to get a good ^{13}C NMR spectrum. Compound **6** has also been characterized by ^{31}P and ^1H NMR, IR spectroscopy, and elemental analysis. Again poor solubility in common organic solvents precluded a good ^{13}C NMR spectrum.

Previously reported C_4H_4-bridged bimetallic complexes are limited to $[CpFe(LL')]_2(\mu\text{-}CH{=}CHCH{=}CH)$ (LL′ = $(CO)_2$, dppm, $(CO)(PPh_3)$, $(CO)(PMe_3)$).[12,13] The complex $[CpFe(CO)_2]_2(\mu\text{-}CH{=}CHCH{=}CH)$ was prepared from the reaction of $[CpFe(CO)_2]^-$ with *cis*-dichlorocyclobutene,[12] and $[CpFe(LL')]_2(\mu\text{-}CH{=}CHCH{=}CH)$ (LL′ = dppm, $(CO)(PPh_3)$, $(CO)(PMe_3)$) were prepared from the photochemical reactions of $[CpFe(CO)_2]_2(\mu\text{-}CH{=}CHCH{=}CH)$ with dppm, PPh_3, and PMe_3, respectively.[13] The route reported here provides an alternative and probably more versatile route to C_4H_4-bridged bimetallic complexes.[35]

Reactions of $[RuCl(CO)(NH_3)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH{=}CH)$ and $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH{=}CH)$ with PEt_3 and *t*-BuNC. To obtain more soluble C_4H_4-bridged bimetallic complexes, we have tried to replace the PPh_3 and NH_3 ligands in complexes **5** and **6** with PEt_3 or *t*-BuNC (Scheme 3). As expected, both **5** and **6** reacted with PEt_3 to give $[RuCl(CO)(PEt_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CH)$ (**7**). The PEt_3 ligands in complex **7** are meridional, as indicated by the AM_2 pattern ^{31}P NMR spectrum. The presence of the C_4H_4 bridge is indicated by the ^1H NMR spectrum (in CD_2Cl_2), which showed the vinyl proton signals at 6.22 ppm (Ru−CH=C*H*) and 6.64 ppm (Ru−C*H*=CH), and the ^{13}C NMR spectrum (in CD_2Cl_2), which showed the vinyl signals at 144.7 ppm for β-CH and 151.6 ppm for α-CH. The vinyl group is trans to the unique PEt_3 ligand, as indicated by the large $^2J(C{-}PEt_3)$ coupling constant (74.4 Hz). The structure has been confirmed by an X-ray diffraction study (see below).

Scheme 3



Complex **5** reacted with *t*-BuNC to give the diacyl-bridged complex $\{[Ru(t\text{-}BuNC)_3(PPh_3)_2]_2(\mu\text{-}COCH{=}CHCH{=}CHCO)\}Cl_2$ (**8A**). Similar mononuclear ruthenium complexes such as $[Ru(COR)(t\text{-}BuNC)_3(PPh_3)_2]^+$ and $[Ru(COR)(t\text{-}BuNC)_2(CO)(PMe_2Ph)_2]^+$ are known.[36,37] Interestingly, although $RuCl(CH{=}CHR)(CO)(R'NC)(PPh_3)_2$ can be prepared from the reaction of $RuCl(CH{=}CHR)(CO)(PPh_3)_2$ with R′NC,[36] our attempts to prepare the neutral isocyanide adduct $[RuCl(CO)(t\text{-}BuNC)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH{=}CH)$ were unsuccessful. The presence of the linear $C_6H_4O_2$ group in complex **8A** is supported by the ^{13}C NMR spectrum (in CD_2Cl_2), which showed an Ru−acyl signal at 256.6 ppm, a CO*C*H signal at 147.3 ppm, and the other CH signal at 124.3 ppm. For comparison, the ^{13}C signals for the acyl carbon signal was observed at 260.5 ppm[37] for $[Ru(COPh)(t\text{-}BuNC)_2(CO)(PMe_2Ph)_2]^+$ and at 258.1 ppm[36] for $[Ru(COCH{=}CHCMe_3)(t\text{-}BuNC)_3(PPh_3)_2]^+$. Complex **8A** is air stable, and the counteranion Cl^- can be readily replaced with BPh_4^- to give complex **8B**. Complex **8** is a rare example of a conjugated diacyl bimetallic complex. $[CpFe(CO)_2]_2(\mu\text{-}OCArCO)$ is an example of a reported diacyl-bridged complex, prepared by the reaction of $[CpFe(CO)_2]^-$ with ClOCArCOCl.[38]

Description of the Structure of $[RuCl(CO)(PEt_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CH)$ (7). The molecular structure of complex **7** is shown in Figure 1. The crystallo-

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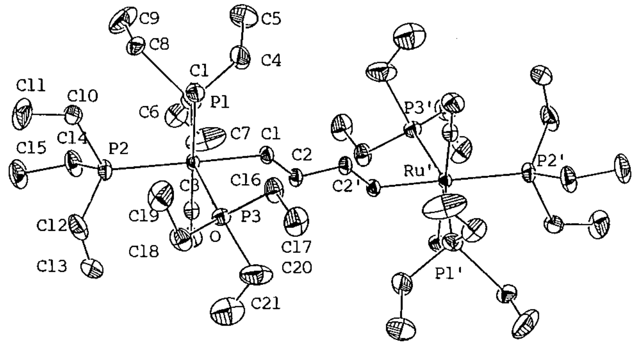

Figure 1. Molecular structure for $[RuCl(CO)(PEt_3)_3]_2(\mu$-$CH{=}CHCH{=}CH)$. Hydrogen atoms are omitted for clarity.

Table 1. Crystal Data and Refinement Details for $[RuCl(CO)(PEt_3)_3]_2(\mu$-$CH{=}CHCH{=}CH)$

formula	$C_{49}H_{94}Cl_2O_2P_6Ru_2$
fw	1096.09
color and habit	yellow rectangle
crys syst	monoclinic
space group	$P2_1/a$
a, Å	14.293(6)
b, Å	12.576(3)
c, Å	15.257(3)
α, deg	90.00(2)
β, deg	99.19(3)
γ, deg	90.00(3)
V, Å^3	2707.3(1)
Z	2
d_{calc}, g cm^{-3}	1.337
abs coeff, mm^{-1}	17.001
F(000)	2152
radiation (Mo Kα), Å	$\lambda = 0.071\,073$
2θ range, deg	2.7−50.0
scan type	$\omega - 2\theta$
index range	$0 \leq h \leq 17$
	$0 \leq k \leq 14$
	$-18 \leq l \leq 18$
reflns collected	5189
ind reflns	4996 ($R_{int} = 0.017$)
obsd reflns	2823 ($F \geq 3\sigma(F)$)
abs correction	semiempirical
max. and min. transmission	0.9989 and 0.9046
quantity minimized	3529 ($F \geq 4\sigma(F)$)
final R indices (obs data)	$R = 5.3\%$
	$R_w = 6.4\%$
R indices (all data)	$R = 6.1\%$
	$R_w = 6.7\%$
goodness of fit	1.201
data-to-parameter ratio	15.668:1
largest diff peak, e Å^{-3}	0.573
largest diff hole, e Å^{-3}	−0.071

graphic details and selected bond distances and angles are given in Tables 1 and 2, respectively. The geometry around ruthenium can be described as a distorted octahedron with three meridionally bound PEt_3 ligands and the vinyl group trans to the unique PEt_3 ligands, as indicated by the solution NMR spectroscopic data. The distortion could be attributed to the steric interaction of the PEt_3 ligands as reflected in the P(2)−Ru−P(1) (99.96(9)°) and P(2)−Ru−P(3) (97.9(1)°) angles. The unique Ru−P bond (2.440(3) Å) is slightly longer than those of the mutually trans Ru−P bonds (2.400(2) and 2.397(3) Å), probably due to the strong trans influence of the vinyl ligand in complex **7**. For comparison, the mutually trans Ru−P bonds are also shorter than the Ru−P bond trans to a hydride in $[RuH(PMe_2Ph)_5]^+$ [39] and shorter than the Ru−P bond trans to a vinyl ligand in $RuH(CH{=}CMeCO_2Bu)(CO)(PPh_3)_3$.[40] It is noted that many meridional tris(phosphines)ruthenium complexes (for example, $RuH(OAc)(PPh_3)_3$,[41a] $RuCl_2(PPh_3)_3$[41b]) have mutually trans Ru−P bonds longer than the unique Ru−P bond.

The two ruthenium centers are bridged symmetrically by a C_4H_4 ligand. The C_4H_4 ligand showed a single (1.44(1) Å)/double (1.34(2) Å) carbon−carbon bond alternation. The vinyl ligand has a trans configuration. The Ru−C(vinyl) bond distance of 2.088(8) Å is within the range reported for ruthenium vinyl complexes, for example, $RuCl(CH{=}CH{-}R)(CO)(Me_2Hpz)(PPh_3)_2$ (R = C_3H_7, (2.05(1) Å;[42] R = CMe_3, 2.063(7) Å;[43] Me_2Hpz = 3,5-dimethylpyrazole), $[Ru(Me_2OCC{=}CHCO_2Me)(CO)(CH_3CN)_2(PPh_3)_2]^+$ (2.12(5) Å),[44] $TpRu(C(C{\equiv}CPh){=}CHPh)(CO)(PPh_3)$ (2.090(12) Å),[45] and $RuCl(PhC{=}CH{-}Ph)(CO)(PPh_3)_2$ (2.03 (1) Å).[23a] The C−C bond distances of the C_4H_4 unit are very similar to that of $[CpFe(CO)_2]_2(\mu$-$CH{=}CHCH{=}CH)$.[12b]

In summary, reaction of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ with $RuHCl(CO)(PPh_3)_3$ gives the mononuclear complex $RuCl(\eta^1$-$C(C{\equiv}CSiMe_3){=}CHSiMe_3)(CO)(PPh_3)_2$. In contrast, reaction of $HC{\equiv}CC{\equiv}CH$ with $RuHCl(CO)(PPh_3)_3$ afforded a bimetallic complex with a linear C_4H_4 bridge that can be converted into a diacyl bridge (COC_4H_4CO) by CO insertion.

Experimental Section

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

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 compound $RuHCl(CO)(PPh_3)_3$[46] was prepared according to a literature method. All other reagents were used as purchased from Aldrich or Strem, USA.

$RuCl(\eta^1$-$C(C{\equiv}CSiMe_3){=}CHSiMe_3)(CO)(PPh_3)_2$ (2). To a suspension of $RuHCl(CO)(PPh_3)_3$ (0.50 g, 0.53 mmol) in 50 mL of CH_2Cl_2 was added $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ (1.02 g, 5.25 mmol). The reaction mixture was stirred overnight to give an orange-brown solution. The volume of the reaction mixture was then reduced to ca. 5 mL under vacuum. Addition of hexane (100 mL) to the reaction mixture produced a yellow solid, which was collected by filtration, washed with hexane (30 mL), and then dried under vacuum. Yield: 0.41 g, 88%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 33.3 (s). ^1H NMR ($CDCl_3$, 300.13 MHz): δ 0.15 (s, 9 H, $SiMe_3$), 0.22 (s, 9 H, $SiMe_3$), 5.23 (s, 1 H, =CH), 7.39−7.73 (m, 30 H, 2 PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ −1.1 (s, $SiMe_3$), 0.8 (s, $SiMe_3$), 98.8 (s, ≡CSiMe$_3$), 114.5 (s, ≡C), 127.8 (t, J(PC) = 4.9 Hz, m-Ph), 129.8 (s, p-Ph), 131.9 (t, J(PC) = 22.2 Hz, $ipso$-Ph), 134.6 (t, J(PH) = 5.7 Hz, o-Ph), 143.1 (s, =CH), 152.6 (t, J(PC) = 8.4 Hz, Ru−C=), 207.6

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[RuCl(CO)(PEt_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CH)$

Bond Lengths (Å)

Ru−Cl	2.484(2)	Ru−P(1)	2.400(2)	Ru−P(2)	2.440(3)
Ru−P(3)	2.397(3)	Ru−C(1)	2.088(8)	Ru−C(3)	1.834(9)
C(3)−O	1.13(1)	C(1)−C(2)	1.34(2)	C(2)−C′(2)	1.44(1)

Bond Angles (deg)

Cl−Ru−P(1)	87.52(9)	Cl−Ru−P(2)	91.74(8)	Cl−Ru−P(3)	86.4(1)
Cl−Ru−C(1)	88.8(2)	Cl−Ru−C(3)	178.9(2)	P(1)−Ru−P(2)	99.96(9)
P(1)−Ru−P(3)	161.26(9)	P(1)−Ru−C(1)	81.0(2)	P(1)−Ru−C(3)	93.1(3)
P(2)−Ru−P(3)	97.9(1)	P(2)−Ru−C(1)	178.9(2)	P(2)−Ru−C(3)	89.6(2)
P(3)−Ru−C(1)	81.2(2)	P(3)−Ru−C(3)	92.6(2)	C(1)−Ru−C(3)	89.9(3)
Ru−C(1)−C(2)	132.0(6)	C(1)−C(2)−C′(2)	126(1)		

(t, *J*(PC) = 16.0 Hz, Ru−CO). IR (KBr, cm^{-1}): ν(C≡C) 2094 (w), ν(CO) 1924 (s). Anal. Calcd for $C_{47}H_{49}ClOP_2Si_2Ru$: C, 63.82; H, 5.58. Found: C, 63.52; H, 5.57.

RuCl(η^1-C(C≡CSiMe$_3$)=CHSiMe$_3$)(CO)(PPh$_3$)(dppe) (3). To a solution of complex **2** (0.20 g, 0.23 mmol) in 10 mL of dichloromethane was added dppe (0.090 g, 0.23 mmol). The reaction mixture was stirred at room temperature for 20 min to give a pale green solution. The volume of the reaction mixture was then reduced to ca. 2 mL under vacuum. Addition of hexane (30 mL) to the reaction mixture produced a white solid. The solid was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.21 g, 91%. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 45.5 (d, *J*(PP) = 307.7 Hz, PPh$_2$), 32.4 (d, *J*(PP) = 16.5 Hz, PPh$_2$), 30.2 (dd, *J*(PP) = 307.7, 16.5 Hz, PPh$_3$). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 0.22 (s, 9 H, SiMe$_3$), 0.89 (s, 9 H, SiMe$_3$), 2.0−3.0 (m, 4 H, CH$_2$), 6.10 (d, *J*(PH) = 1.1 Hz, 1 H, =CH), 7.0−8.0 (m, 35 H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ −1.0 (s, SiMe$_3$), −0.2 (s, SiMe$_3$), 26.8 (dd, *J*(PC) = 28.1, 15.3 Hz, PCH$_2$), 30.8 (m, PCH$_2$), 99.5 (s, ≡*C*SiMe$_3$), 118.2 (s, C≡), 126.7−136.3 (m, Ph), 152.7 (dm, *J*(PC) = 60.9 Hz, Ru−*C*=C), 153.0 (s, =*C*HSiMe$_3$), 202.3 (td, *J*(PC) = 12.7, 9.1 Hz, Ru−CO). IR (KBr, cm^{-1}): ν(C≡C) 2111 (m), ν(CO) 1930 (s). Anal. Calcd for $C_{55}H_{58}ClOP_3Si_2Ru$: C, 64.72; H, 5.73. Found: C, 64.46; H, 5.85.

RuHCl(CO)(NH$_3$)(PPh$_3$)$_2$ (4). To a suspension of RuHCl(CO)(PPh$_3$)$_3$ (0.20 g, 0.21 mmol) in 30 mL of THF was added NH_4F (0.10 g, 2.70 mmol). The reaction mixture was stirred overnight at room temperature to give a pale green solution. The volume of the reaction mixture was then reduced to ca. 2 mL under vacuum. Addition of ether (30 mL) to the reaction mixture produced a white solid, which was collected by filtration, washed with methanol (10 mL), hexane (10 mL), and ether (10 mL), and then dried under vacuum. Yield: 0.12 g, 81%. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 46.6 (s). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ −14.50 (t, *J*(PH) = 18.0 Hz, 1 H, Ru−H), 0.78 (s, 3 H, NH$_3$), 7.41−7.82 (m, 30 H, 2 PPh$_3$). Anal. Calcd for $C_{37}H_{34}ClNOP_2Ru\cdot 2H_2O\cdot 0.5NH_3$: C, 59.12; H, 5.30; N, 2.80. Found: C, 59.20; H, 5.20; N, 2.70.

[RuCl(CO)(NH$_3$)(PPh$_3$)$_2$]$_2$(μ-CH=CHCH=CH) (5). A Schlenk flask containing RuHCl(CO)(PPh$_3$)$_3$ (3.00 g, 3.15 mmol) suspended in 50 mL of CH_2Cl_2 was connected to another Schlenk flask containing Me$_3$SiC≡CC≡CSiMe$_3$ (1.0 g, 5.1 mmol), NH_4F (1.0 g, 27 mmol), *n*-Bu$_4$NF on silica gel (1.0 g, 1.1 mmol F$^-$), H_2O (0.5 mL), and THF (10 mL). The volatile contents (presumably, HC≡CC≡CH, THF, NH$_3$) in the second flask were then introduced, in the form of vapor generated by heating (at ca. 70 °C), to the flask containing RuHCl(CO)(PPh$_3$)$_3$. The suspension of RuHCl(CO)(PPh$_3$)$_3$ in CH_2Cl_2 changed into a clear yellow solution when most of the THF was evaporated (ca. 2 h). The volume of the yellow solution was then reduced to ca. 10 mL under vacuum, and 200 mL of ether was added to give a yellow solid. The solid was collected by filtration, washed with ether (30 mL) and small amount of CH_2Cl_2, and then dried under vacuum. Yield: 1.2 g, 52%. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 37.8 (s). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 0.86 (s, 6 H, 2 NH$_3$), 7.21−7.73 (m, 60 H, 4 PPh$_3$). The C_4H_4 unit showed an AA′BB′XX′ (X = PPh$_3$) pattern with δA = 4.63 (Ru−CH=C*H*), δB = 5.89 ppm (Ru−CH) and *J*(AB) = 15.3, *J*(AA′) = 10.0, and *J*((BX) = 2 Hz. IR (KBr, cm^{-1}): ν(N−H) 3374 (m), ν(CO) 1914 (s). Anal. Calcd for $C_{78}H_{70}Cl_2N_2O_2P_4Ru_2$: C, 63.98; H, 4.82; N, 1.91. Found: C, 63.71; H, 4.98; N, 1.88.

[RuCl(CO)(PPh$_3$)$_2$]$_2$(μ-CH=CHCH=CH) (6). A Schlenk flask containing RuHCl(CO)(PPh$_3$)$_3$ (2.00 g, 2.10 mmol) suspended in 20 mL of CH_2Cl_2 was connected to another Schlenk flask containing Me$_3$SiC≡CC≡CSiMe$_3$ (1.0 g, 5.1 mmol), H_2O (0.5 mL), and THF (10 mL). The latter flask was heated to ca. 70 °C, followed by slow addition of *n*-Bu$_4$NF solution (1.0 mmol in 20 mL of THF) from a dropping funnel with a dropping rate of ca. 1 mL/min. The volatile contents (presumably, HC≡CC≡CH, THF) in the second flask were introduced, in the form of vapor generated by heating, to the flask containing RuHCl(CO)(PPh$_3$)$_3$. The suspension of RuHCl(CO)(PPh$_3$)$_3$ in CH_2Cl_2 changed to a reddish-brown suspension when most of the THF was evaporated. The volume of the yellow solution was then reduced to ca. 10 mL under vacuum. The solid was collected by filtration, washed with ether (20 mL) and acetone (30 mL), and then dried under vacuum. Yield: 1.1 g, 71%. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 28.3 (s). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 5.20 (d, *J*(HH) = 11.0 Hz, 2 H, β-CH), 6.94−7.73 (m, 62 H, 2 Ru−CH, 4 PPh$_3$). IR (KBr, cm^{-1}): ν(CO) 1926 (s). Anal. Calcd for $C_{78}H_{64}Cl_2O_2P_4Ru_2$: C, 65.50; H, 4.51. Found: C, 65.06; H, 4.79.

[RuCl(CO)(PEt$_3$)$_3$]$_2$(μ-CH=CHCH=CH) (7). To a suspension of complex **4** (0.300 g, 0.205 mmol) in 5 mL of CH_2Cl_2 was added 2.5 mL of a THF solution of PEt$_3$ (1.0 M, 2.5 mmol). The reaction mixture was stirred for 30 min to give a colorless solution. Addition of 50 mL of Et_2O to the reaction mixture produced a white solid. The solid was collected by filtration, washed with ether, and dried under vacuum. Yield: 0.18 g, 81%. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz, −20 °C): δ 0.6 (t, *J*(PP) = 19.3 Hz), 5.8 (d, *J*(PP) = 19.3 Hz). ^{1}H NMR (CD_2Cl_2, 300.13 MHz, −20 °C): δ 1.00−1.15 (m, 54 H, CH$_3$), 1.79−1.88 (m, 36 H, CH$_2$), 6.22 (m, 2 H, Ru−CH=C*H*), 6.64 (m, 2 H, Ru−C*H*=CH). The ^{31}P and ^{1}H NMR spectra were recorded at −20 °C because the ^{31}P and ^{1}H signals are somewhat broad at room temperature. ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): 7.6 (s, CH$_3$), 8.23 (d, *J*(PC) = 2.7 Hz, CH$_3$), 17.1 (t, *J*(PC) = 12.7 Hz, CH$_2$), 19.2 (d, *J*(PC) = 15.1 Hz, CH$_2$), 144.7 (s, Ru−CH=*C*H), 151.6 (brd, *J*(PC) = 74.4 Hz, Ru−CH), 204.1 (q, *J*(PC) = 13.4 Hz, CO). IR (KBr, cm^{-1}): ν(CO) 1904 (s). Anal. Calcd for $C_{42}H_{94}Cl_2O_2P_6Ru_2$: C, 46.28; H, 8.69; Cl, 6.50. Found, 45.99; H, 8.43; Cl, 6.66.

{[Ru(*t*-BuNC)$_3$(PPh$_3$)$_2$]$_2$(μ-COCH=CHCH=CHCO)}Cl$_2$ (8A). To a suspension of complex **4** (0.200 g, 0.137 mmol) in 20 mL of dichloromethane was added *t*-BuNC (0.20 mL, 1.8 mmol). The reaction mixture was stirred at room temperature overnight to give an orange-red solution. The volume of the reaction mixture was then reduced to ca. 2 mL under vacuum. Addition of 30 mL of hexane to the reaction mixture produced a red solid. The solid was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.22 g, 83%. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 36.1 (s). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 1.02 (s, 4 *t*-BuNC), 1.06 (s, 2 *t*-BuNC), 7.36−7.51 (m, Ph). The C_4H_4 unit showed an AA′BB′ pattern with δA = 4.93, δB = 6.04 (CO−C*H*) ppm and *J*(AB) = 13.8, *J*(AA′)

= 12.0 Hz. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ 29.2 (s, C*Me*$_3$), 29.3 (s, C*Me*$_3$), 57.6 (s, *C*Me$_3$), 57.7 (s, *C*Me$_3$), 124.3 (s, COCH=*C*H), 128.1 (t, *J*(PC) = 4.7 Hz, *m*-Ph), 130.2 (s, *p*-Ph), 133.6 (t, *J*(PC) = 5.3 Hz, *o*-Ph), 134.0 (t, *J*(PC) = 22.3 Hz, *ipso*-Ph), 146.4 (br, Ru−CN), 147.3 (s, CO−*CH*=CH), 148.3 (brt, *J*(PC) = 13.2 Hz, Ru−CN), 256.6 (t, *J*(PC) = 9.4 Hz, Ru−CO). IR (KBr, cm^{-1}): ν(C≡N) 2140 (s), ν(C=O) 1630 (br, m). Anal. Calcd for $C_{108}H_{118}Cl_2O_2N_6P_4Ru_2{\cdot}5H_2O$: C, 64.24; H, 6.39. Found, C, 64.39; H, 6.27.

{[Ru(*t*-BuNC)$_3$(PPh$_3$)$_2$]$_2$(*μ*-COCH=CHCH=CHCO)}(BPh$_4$)$_2$. (8B). To a solution of complex **8A** (0.20 g, 0.10 mmol) in 20 mL of CH_2Cl_2 was added $NaBPh_4$ (0.40 g, 1.2 mmol). The reaction mixture was stirred at room temperature for 20 min to give an orange solution. The volume of the reaction mixture was reduced to ca. 2 mL under vacuum. Addition of hexane (30 mL) produced an orange solid, which was collected by filtration, washed with methanol (10 mL) and hexane (10 mL), and then dried under vacuum. Yield: 0.25 g, 95%. The NMR data are essentially the same as those of complex **8A**, except the additional ^{1}H and ^{13}C signals of BPh_4^-. Anal. Calcd for $C_{156}H_{158}B_2O_2N_6P_4Ru_2$: C, 75.05; H, 6.38. Found: C, 74.86; H, 6.38.

Crystallographic Analysis for [RuCl(CO)(PEt$_3$)$_3$]$_2$(*μ*-CH=CHCH=CH) (7). Suitable crystals for X-ray diffraction study were obtained by slow diffusion of ether to a CH_2Cl_2 solution saturated with complex **7**. A specimen of dimension 0.22 × 0.25 × 0.44 mm^3 was mounted on a glass fiber and used for X-ray structure determination. The diffraction data were collected on a Enraf/Nonius CAD4-VAX/2100 X-ray diffractometer at 293 K. The crystal system was monoclinic with space group $P2_1/a$. A total of 5189 intensity measurements were made using the $2\theta-\theta$ scan technique in the range $2.7° \leq 2\theta \leq 50°$ (Mo Kα radiation). Of these, 4996 were unique (R_{int} = 1.7%) and 3529 observed with $F = 4\sigma(F)$, which were used for structure solution and refinement using the Nonius MolEN program package.[47] Solution by direct methods yielded the positions of all non-hydrogen atoms. Refinement by full-matrix least-squares resulted in final discrepancy indices R = 5.3%, R_w = 6.4% with GOF = 1.201. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens were revealed in difference Fourier maps, but then placed geometrically determined positions with d_{C-H} = 0.96 Å and refined isotropically with riding constraints and group thermal parameters. The data:parameter ratio was 15.668: 1, and residual electron density/hole +0.573/-0.071 e Å^{-3}. Further crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively.

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Supporting Information Available: Tables of crystallographic details, bond distances and angles, atomic coordinates and equivalent isotropic displace coefficients, anisotropic displacement coefficients, and positional and thermal parameter for hydrogen for [RuCl(CO)(PEt$_3$)$_3$]$_2$(*μ*-CH=CHCH=CH) (6 pages). Ordering information is given on any current masthead page.

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