Organometallics **2000,** *19,* 3757−3761

Articles

Unexpected Formation of Osmium Carbyne and Vinylidene Complexes from the Reaction of $OsCl_2(PPh_3)_3$ with $HC\equiv CCMe_3$

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Received April 11, 2000

Treatment of $OsCl_2(PPh_3)_3$ with $HC\equiv CCMe_3$ produced a mixture of $OsCl_3(\equiv CCH_2CMe_3)(PPh_3)_2$ and $OsCl(=C=CHCMe_3)(C(C\equiv CCMe_3)=CHCMe_3)(PPh_3)_2$. The structures of the new complexes have been confirmed by X-ray diffraction studies.

Introduction

Ruthenium vinylidene complexes of the type $RuCl_2(=C=CHR)(PR'_3)_2$ have been reported as early as 1991. The first example of these complexes was $RuCl_2(=C=CHCMe_3)(PPh_3)_2$, which was prepared from the reaction of $HC\equiv CCMe_3$ with $RuCl_2(PPh_3)_3$.[1] Since then, several new $RuCl_2(=C=CHR)(PR'_3)_2$ complexes have been prepared from either the reactions of $HC\equiv CR$ with dichloro ruthenium complexes such as $RuCl_2H_2(PR'_3)_2$ ($R' =$ Cy, *i*-Pr),[2] $[RuCl_2(P(i\text{-}Pr)_3)_2]_n$,[3] $RuCl_2(MeCN)_2(P(i\text{-}Pr)_3)_2$,[3] and $[RuCl_2(p\text{-cumene})]_2/PR'_3$[3] or the reaction of $RuCl_2(=CHPh)(PCy_3)_2$ with 1,2-propadiene.[4] These vinylidene complexes are interesting because they are catalytically active for olefin metathesis reactions.[4,5] In contrast to ruthenium, related osmium vinylidene complexes of the type $OsCl_2(=C=CHR)(PR'_3)_2$ have not been reported, despite the fact that a large number of other osmium vinylidene complexes have been prepared.[6−11] With the hope of obtaining $OsCl_2(=C=CHR)(PPh_3)_2$, we have studied the reactions of $OsCl_2(PPh_3)_3$ with $HC\equiv CR$. To our knowledge, reactions of $OsCl_2(PPh_3)_3$ with $HC\equiv CR$ have not been well studied, except for the reaction of $OsCl_2(PPh_3)_3$ with $HC\equiv CC(OH)Ph_2$ to give $OsCl_2(=C=C=CPh_2)(PPh_3)_2$.[12] In this report, we wish to describe the reaction of $OsCl_2(PPh_3)_3$ with $HC\equiv CCMe_3$.

Results and Discussion

Treatment of $OsCl_2(PPh_3)_3$ (**1**)[13] with $HC\equiv CCMe_3$ in benzene produced a yellow precipitate and a reddish brown solution. The precipitate was identified to be the carbyne complex $OsCl_3(\equiv CCH_2CMe_3)(PPh_3)_2$ (**2**), which was isolated in 41% yield. From the brown solution, the novel complex $OsCl(=C=CHCMe_3)(C(C\equiv CCMe)=CHCMe_3)(PPh_3)_2$ (**3**) could be isolated in 39% yield (Scheme 1). The expected vinylidene complex $OsCl_2(=C=CHCMe_3)(PPh_3)_2$ could not be isolated from the reaction,

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10.1021/om000306e CCC: $19.00
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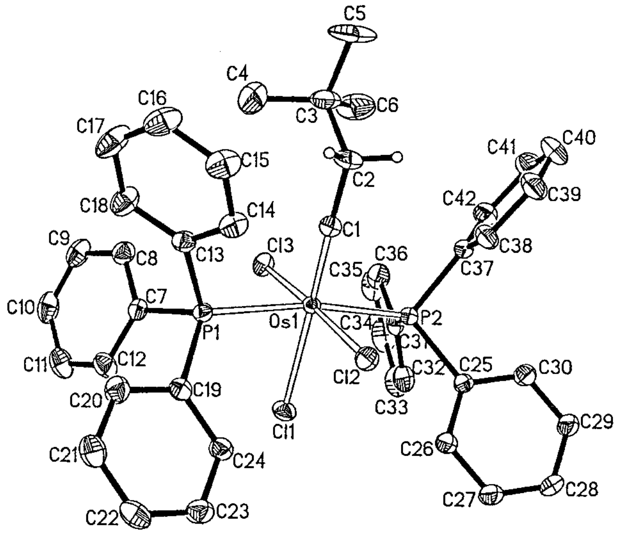
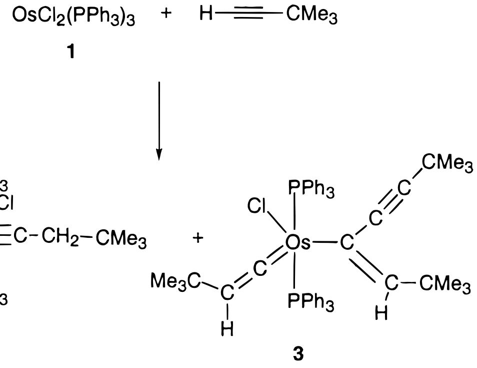


Figure 1. Molecular structure for $OsCl_3(\equiv CCH_2CMe_3)(PPh_3)_2$.

Scheme 1



however. Formation of complexes **2** and **3** from the reaction is somewhat unexpected, since the reaction of $HC{\equiv}CCMe_3$ with $RuCl_2(PPh_3)_3$ has been reported to give $RuCl_2({=}C{=}CHCMe_3)(PPh_3)_2$[1] and the reaction of $HC{\equiv}CC(OH)Ph_2$ with $OsCl_2(PPh_3)_3$ has been reported to give $OsCl_2({=}C{=}C{=}CPh_2)(PPh_3)_2$.[12]

Complex **2** has been characterized by NMR spectroscopy as well as an X-ray diffraction study. A view of the molecular geometry of **2** is shown in Figure 1. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively. The geometry around osmium in **2** can be viewed as a distorted octahedron with two PPh_3 ligands at the apical positions and the three chloride and $\equiv CCH_2CMe_3$ ligands on the equatorial plane. The Os−C(carbyne) bond distance is at 1.728(3) Å, which is fully consistent with those reported previously.[6,10a−c,14,15] Consistent with the solid-state structure, the ^1H NMR spectrum displayed the $\equiv CCH_2$ proton signal at 0.88 ppm, the ^{13}C NMR spectrum exhibited the carbyne signal at 290.1 ppm, and the $^{31}P\{^1H\}$ NMR spectrum displayed only a singlet at −12.3 ppm. Reported compounds closely related to **2** include $OsHCl_2(\equiv CR)(PR'_3)_2$ (PR'_3 = P(*i*-Pr)$_3$,[15,16] PCy_3[6]), $OsCl_2(\equiv CCH{=}CRPh)(P(i\text{-}Pr)_2CH_2CO_2Me)(P(i\text{-}Pr)_2CH_2CO_2)$ (R = Ph, Me),[14] and $OsCl_2(SCN)(\equiv CC_6H_4NMe_2)(PPh_3)_2$.[17]

Table 1. Crystal Data and Refinement Details for $2\cdot{}^1/_2CH_2Cl_2$ and 3

	$2\cdot{}^1/_2CH_2Cl_2$	3
formula	$C_{42}H_{41}Cl_3P_2Os\cdot{}^1/_2CH_2Cl_2$	$C_{54}H_{49}ClP_2Os$
fw	946.70	995.60
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	12.9208(13)	12.3785(13)
b, Å	20.381(2)	13.8032(14)
c, Å	16.6709(16)	17.2639(17)
α, deg	90	78.280(2)
β, deg	104.406(2)	70.488(2)
γ, deg	90	65.374(2)
V, Å^3	4252.0(7)	2520.4(4)
Z	4	2
d_{calcd}, g cm^{-3}	1.479	1.312
radiation (Mo Kα), Å	0.710 73	0.710 73
θ range, deg	1.91−27.54	1.25−27.56
no. of rflns collected	27 942	16 949
no. of obsd rflns ($I > 2\sigma(I)$)	7146	8616
no. of indep rflns	9696 (R_{int} = 4.79%)	11 421 (R_{int} = 3.77%)
no. of params refined	496	531
final *R* indices ($I > 2\sigma(I)$)	R1 = 3.58%, wR2 = 8.48%	R_1 = 4.66%, wR2 = 10.49%
goodness of fit	0.960	0.959
largest diff peak, e Å^{-3}	1.347	2.528
largest diff hole, e Å^{-3}	−0.749	−2.146

Table 2. Selected Bond Distances (Å) and Angles (deg) for $2\cdot{}^1/_2CH_2Cl_2$ and 3

Compound $2\cdot{}^1/_2CH_2Cl_2$			
Os(1)−P(1)	2.4476(8)	Os(1)−P(2)	2.4407(8)
Os(1)−Cl(1)	2.4767(8)	Os(1)−Cl(2)	2.4164(8)
Os(1)−Cl(3)	2.3852(8)	Os(1)−C(1)	1.728(3)
C(1)−C(2)	1.448(4)	C(2)−C(3)	1.557(5)
C(1)−Os(1)−Cl(1)	177.79(9)	Cl(2)−Os(1)−Cl(3)	175.99(3)
P(2)−Os(1)−P(1)	169.77(3)	C(2)−C(1)−Os(1)	176.8(2)
C(1)−Os(1)−Cl(2)	90.99(9)	C(1)−Os(1)−Cl(3)	92.86(9)
Cl(1)−Os(1)−Cl(2)	91.19(3)	Cl(1)−Os(1)−Cl(3)	84.96(3)
C(1)−Os(1)−P(1)	95.56(10)	C(1)−Os(1)−P(2)	94.67(10)
Cl(2)−Os(1)−P(1)	90.64(3)	Cl(2)−Os(1)−P(2)	89.70(3)
Cl(3)−Os(1)−P(1)	90.10(3)	Cl(3)−Os(1)−P(2)	88.87(3)
P(1)−Os(1)−Cl(1)	84.83(3)	P(2)−Os(1)−Cl(1)	84.94(3)
C(1)−C(2)−C(3)	117.0(3)		
Compound 3			
Os(1)−P(1)	2.3848(8)	Os(1)−P(2)	2.3719(7)
Os(1)−C(1)	1.802(2)	Os(1)−C(7)	2.047(2)
Os(1)−Cl(1)	2.3986(8)	C(1)−C(2)	1.332(3)
C(7)−C(8)	1.343(4)	C(7)−C(13)	1.420(3)
C(13)−C(14)	1.194(4)		
C(1)−Os(1)−C(7)	96.84(10)	C(1)−Os(1)−Cl(1)	125.27(8)
C(7)−Os(1)−Cl(1)	137.88(7)	P(1)−Os(1)−P(2)	176.08(2)
C(1)−Os(1)−P(2)	87.29(8)	C(7)−Os(1)−P(2)	90.97(8)
C(1)−Os(1)−P(1)	88.92(8)	C(7)−Os(1)−P(1)	90.48(8)
P(1)−Os(1)−Cl(1)	89.84(3)	P(2)−Os(1)−Cl(1)	91.53(3)
C(2)−C(1)−Os(1)	179.0(2)	C(1)−C(2)−C(3)	130.6(3)
C(8)−C(7)−Os(1)	135.96(17)	C(13)−C(7)−Os(1)	100.13(17)
C(8)−C(7)−C(13)	123.9(2)	C(7)−C(8)−C(9)	129.3(2)
C(7)−C(13)−C(14)	176.2(3)	C(13)−C(14)−C(15)	172.3(3)

The solid-state structure of complex **3** has also been determined by an X-ray diffraction study. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively. A view of the molecular geometry of **3** is shown in Figure 2. It reveals

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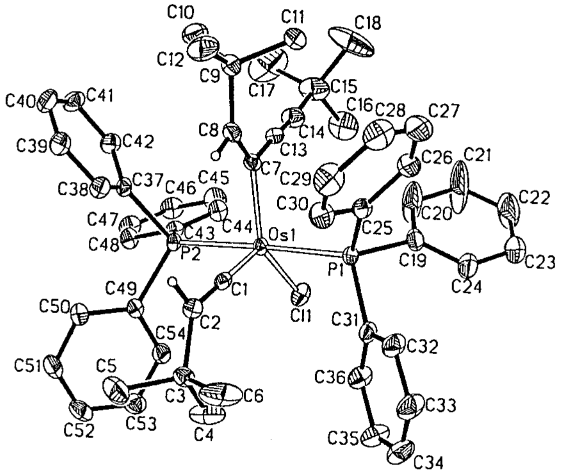

Figure 2. Molecular structure for $OsCl(=C=CHCMe_3)(C(C\equiv CMe_3)=CHCMe_3)(PPh_3)_2$.

that three molecules of $HC\equiv CCMe_3$ have been incorporated into the osmium center, one in the form of the vinylidene ligand $=C=CHCMe_3$ and the other two in the form of the vinyl ligand $C(C\equiv CCMe_3)=CHCMe_3$. The ligand $C(C\equiv CCMe_3)=CHCMe_3$ is likely formed from the intramolecular coupling of the $C\equiv CCMe_3$ and $=C=CHCMe_3$ units (see discussion below). The overall geometry around osmium in complex **3** can be described as a distorted trigonal bipyramid with the two PPh_3 ligands at the apical positions. The equatorial positions are occupied by Cl, $=C=CHCMe_3$, and $C(C\equiv CCMe_3)=CHCMe_3$ ligands. A number of complexes with η^3-$C(C\equiv CR)=CHR$ or η^3-$C(C\equiv CR)=CHR'$ ligands have been reported in which the $C\equiv C$ triple bond is coordinated to metals.[18] In complex **3**, the interaction between the $C\equiv C$ triple bond and the Os center must be weak, if it exists at all, as the Os−C(13) and Os−C(14) distances are quite long (over 2.6 Å). Another interesting feature of structure **3** is that the carbon atoms of the vinylidene unit (C(1), C(2), C(3)) and the $C(C\equiv CCMe_3)=CHCMe_3$ unit (C(7), C(8), C(9), C(13), C(14), C(15)) are essentially coplanar with Os and Cl. Such a feature is very similar to that observed for the related compound $OsCl(=C=CHSiMe_3)(CH=CHSiMe_3)(P(i\text{-}Pr)_3)_2$.[8]

Complexes with both vinyl and vinylidene ligands are interesting, as such complexes have been proposed as intermediates in the coupling of terminal acetylenes with vinyl ligands.[8,19−21] Until now, very few complexes with both vinyl and vinylidene ligands have been isolated,[22] and only $OsCl(=C=CHSiMe_3)(CH=CHSiMe_3)(P(i\text{-}Pr)_3)_2$ has previously been structurally characterized.[8]

In solution, complex **3** is fluxional. At room temperature, complex **3** exhibited two broad $^{31}P\{^1H\}$ signals at 5.6 and 7.8 ppm. The two broad signals merged to a singlet at 6.3 ppm when the temperature was raised to 42 °C. Two sharp $^{31}P\{^1H\}$ signals in about a 2:1 ratio at 5.8 and 8.6 ppm were observed when the temperature was lowered to −38 °C. The ^1H NMR spectrum showed similar features. At room temperature, only one set of ^1H signals was observed for the vinylidene and vinyl groups. At low temperature, two sets of ^1H signals were observed for the vinylidene and vinyl groups. The two sets of NMR data for complex **3** at low temperature could be attributed to the two rotational isomers due to the different orientations of the CMe_3 group of the vinylidene ligand. The two isomers of **3** observed in solution at low temperature could also, in principle, arise from the rotation about the Os−vinyl bond. Quantum-mechanical calculations[23] on the model complex $OsCl(=C=CH_2)(C(C\equiv CH)=CH_2)(PH_3)_2$ suggest that the isomers of **3** observed in solution at low temperature are derived from the rotation of the vinylidene ligand about the Os−vinylidene bond rather than the rotation of the vinyl group. The barrier of vinylidene rotation is calculated to be ca. 12.0 kcal/mol at the B3LYP level of theory, large enough to freeze the rotation at low temperature. The rotational barrier of the vinyl group is found to be much lower (ca. 6.0 kcal/mol), which is too small to be responsible for the observation of the two isomers. In the solid-state structure of **3**, the CMe_3 group of the vinylidene unit is on the same side of Cl. The CMe_3 group could also be on the same side of the vinyl group, although this rotational isomer is expected to be less stable, owing to the larger steric interaction between the CMe_3 group and the $C(C\equiv CCMe_3)=CHCMe_3$ unit. At high temperature, the two isomers interconvert very rapidly due to the fast rotation of the vinylidene ligand; thus, only one set of NMR signals was observed. At low temperature, rotation of the vinylidene ligand is frozen out; thus, two isomers could be detected by NMR spectroscopy. Rotation about metal−vinylidene bonds on the NMR time scale has been observed previously[10e,24] for complexes such as $OsHCl(=C=CHPh)(P(i\text{-}Pr)_3)_2$,[10e] $[(C_7H_7)Mo(=C=CHR)(dppe)]^+$,[24a] and $[CpRu(=C=CHR)(Ph_2PCH_2CHMePPh_2)]^+$.[24b]

Scheme 2 shows a plausible mechanism for the formation of **2** and **3**. Reaction of **1** with $HC\equiv CCMe_3$ can lead to the formation of the hydrido−acetylide intermediate **A**. Intermediate **A** can then undergo reductive elimination of HCl to give the acetylide complex **C** or isomerization to give the vinylidene complex **B**. Related osmium vinylidene complexes $OsHCl(=C=CHR)(PR_3)_2$ have been reported previously.[6,7] Protonation of the vinylidene complex **B** with HCl would give the carbyne complex **2**. It is also possible that the carbyne complex **2** is formed by direct protonation of **B** with **A** (without prior release of HCl from **A**). The

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[18] 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.

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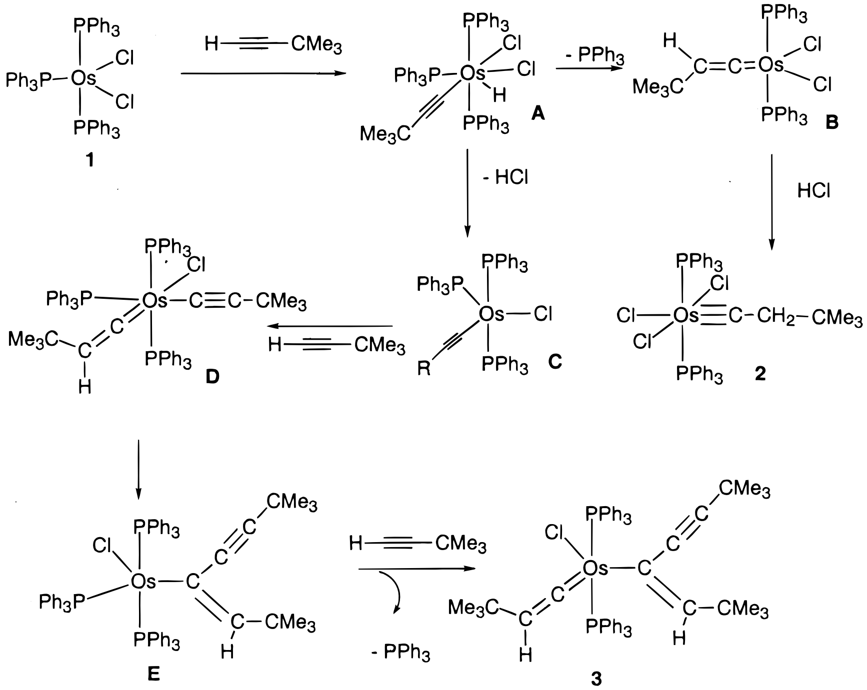
[23] Density functional calculations at the B3LYP level were performed on the model complex $OsCl(=C=CH_2)(C(C\equiv CH)=CH_2)(PH_3)_2$. The basis set used for C and H atoms was 6-31G**. For Os, Cl, and P atoms, an effective core potential with the LanL2DZ basis set was employed.

[24] (a) Beddoes, R. L.; Biton, C.; Grime, R. W.; Ricalton, A.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1995**, 2973. (b) Consiglio, G.; Morandini, F. *Inorg. Chim. Acta* **1987**, *127*, 79. (c) Gamasa, M. P.; Gimeno, J.; Lastra, E.; Martin, B. M. P. *Organometallics* **1992**, *11*, 1373. (d) Senn, D. W.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096. (e) Consiglio, G.; Bangerter, F.; Darpin, C. *Organometallics* **1984**, *3*, 1446. (f) Boland-Lussler, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628.

Scheme 2



acetylide complex **C** could react with another molecule of $HC{\equiv}CCMe_3$ to give intermediate **D**, which could undergo a coupling reaction to give **E**. Reaction of **E** with $HC{\equiv}CCMe_3$ would produce complex **3**. As implied in Scheme 2, elimination of HCl from **A** is the key step for the formation of **3**, and the eliminated HCl is also responsible for the formation of the carbyne complex **2**. Consistent with the proposed mechanism, it was shown that reaction of **1** with $HC{\equiv}CCMe_3$ in the presence of NEt_3 leads to the formation of complex **3** only, while reaction of **1** with $HC{\equiv}CCMe_3$ in the presence of added $HPPh_3Cl$ only leads to the formation of complex **2**.

In summary, the reaction of $OsCl_2(PPh_3)_3$ with $HC{\equiv}CCMe_3$ did not lead to isolation of the expected vinylidene complex $OsCl_2({=}C{=}CHCMe_3)(PPh_3)_2$ but, rather, a mixture of the novel complexes $OsCl({=}C{=}CHCMe_3)(C(C{\equiv}CCMe_3){=}CHCMe_3)(PPh_3)_2$ and $OsCl_3({\equiv}CCH_2CMe_3)$.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium−benzophenone (hexane, ether, THF), sodium (benzene), or calcium hydride (CH_2Cl_2). The starting material $OsCl_2(PPh_3)_3$ was prepared according to the literature method.[13] All other reagents were used as purchased from Aldrich Chemical Co.

Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were collected on a Bruker ARX-300 spectrometer (300 MHz). ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4.

Preparation of $OsCl_3({\equiv}CCH_2CMe_3)(PPh_3)_2$ (2) and $OsCl({=}C{=}CHCMe_3)(C(C{\equiv}CCMe_3){=}CHCMe_3)(PPh_3)_2$ (3). A mixture of $OsCl_2(PPh_3)_3$ (0.60 g, 0.57 mmol) and $HC{\equiv}CCMe_3$ (0.42 mL, 3.42 mmol) in 15 mL of benzene was stirred at room temperature for 3 days to give a yellow microcrystalline solid and a reddish brown solution. The volume of the reaction mixture was reduced to 5 mL. The yellow solid was then collected by filtration, washed with benzene and hexane, and dried under vacuum overnight. Yield: 0.21 g, 41%. The yellow solid was identified to be **2**. Selected characterization data for **2**: $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ −12.3 (s). ^1H NMR (300.13 MHz, CD_2Cl_2): δ 0.49 (s, 9 H, $C(CH_3)_3$), 0.88 (s, 2 H, $Os{\equiv}CCH_2$), 7.43−7.34 (m, 18 H, PPh_3), 7.94−7.87 (m, 12 H, PPh_3). $^{13}C\{^1H\}$ NMR (100.40 MHz, CD_2Cl_2): δ 290.1 (t, $J(PC) = 9.24$ Hz, $Os{\equiv}C$), 136.3−128.3 (m, PPh_3), 65.20 (s, $OsC\mathit{C}H_2$), 33.54 (s, $\mathit{C}(CH_3)_3$), 30.63 (s, $C(\mathit{C}H_3)_3$). Anal. Calcd for $C_{42}H_{41}Cl_3P_2Os$: C, 55.78; H, 4.57. Found: C, 55.69; H, 4.60. The solvents of the filtrate obtained above were removed in vacuo to dryness, and the brown residue was extracted with 2 mL of CH_2Cl_2. After addition of 30 mL of hexane, the reddish brown solution was allowed to stand at −8 °C for several days to give **3** as a brown microcrystalline solid, which was collected on a filter frit, washed with hexane, and dried under vacuum overnight. Yield: 0.22 g, 39%. Selected characterization data for **3**: $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 298 K) δ 5.6 (br), 7.8 (br); ^1H NMR (300.13 MHz, CD_2Cl_2, 298 K) δ 0.15 (br, 1 H, $Os{=}C{=}CH$), 0.36 (br, 9 H, $C(CH_3)_3$), 0.59 (br, 9 H, $C(CH_3)_3$), 1.04 (br, 9 H, $C(CH_3)_3$), 4.14 (br, 1 H, $OsC{=}C\mathit{H}C(CH_3)_3$), 7.64−7.30 (m, 30 H, PPh_3); $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 298 K) δ 274.5 (br, $Os{=}C$), 149.5 (s, $OsC{=}\mathit{C}HCMe_3$), 136.43−128.29 (m, other aromatic C and $-C{\equiv}C-$), 121.26 (br, $Os{=}C{=}\mathit{C}H$), 36.20 (s, $\mathit{C}(CH_3)_3$), 33.01 (s, $C(\mathit{C}H_3)_3$), 30.7 (s, $\mathit{C}(CH_3)_3$), 30.5 (s, $C(\mathit{C}H_3)_3$), 29.48 (br, $C(\mathit{C}H_3)_3$), 26.94 (br, $\mathit{C}(CH_3)_3$). Anal. Calcd for $C_{54}H_{59}ClP_2Os$: C, 65.14; H, 5.97. Found: C, 65.12; H, 6.01.

Crystallographic Analysis for $2{\cdot}{}^1/_2CH_2Cl_2$. Suitable crystals of **2** for X-ray diffraction study were grown by layering hexane over a CH_2Cl_2 solution of **2**. CH_2Cl_2 is cocrystallized with **2**. A yellow plate crystal having approximate dimensions of 0.20 × 0.18 × 0.09 mm^3 was mounted on a glass fiber and used for X-ray structure determination. Intensity data were collected on a Bruker SMART CCD area detector. The intensity data were corrected for SADABS (Siemens area detector absorption) (from 0.718 to 1 on I). Of 27 942 reflections collected, 9696 were unique and 7146 were observed with $I > 2\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the Bruker SHELXTL (version 5.10) program package. All non-hydrogen atoms were refined anisotropically. The H atoms, except those for the disordered CH_2Cl_2, were placed in ideal positions and refined via a riding model with assigned isotropic thermal parameters. The asymmetric unit contains a half-molecule of CH_2Cl_2, in which one of the Cl atoms is disordered over two sites (Cl(5), Cl(6)), which were refined with occupancy factors of 0.25. Application of fixed C−Cl distance restraints led to final convergence with $R_F = 0.0358$ and $R_{wF^2} = 0.0848$.

Crystallographic Analysis for 3. Suitable crystals of **3** for X-ray diffraction study were grown by layering hexane over a CH_2Cl_2 solution of **3**. A pink plate crystal of **3** having approximate dimensions of 0.23 × 0.20 × 0.05 mm^3 was mounted on a glass fiber and used for X-ray structure determination. Intensity data were collected on a Bruker SMART CCD area detector. The intensity data were corrected for SADABS (Siemens area detector absorption) (from 0.623 to 0.922 on I). Of 16 949 reflections collected, 11 421 were unique and 8616 were observed with $I > 2\sigma(I)$. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The two vinyl protons (H2A and H8A) were located from the difference Fourier map and refined isotropically. The remaining H atoms were placed in ideal positions and refined via a riding model with assigned isotropic thermal parameters. At convergence $R_F = 0.0466$, $R_{wF^2} = 0.1049$, and the maximum peak in the difference map is 2.528 e $Å^{-3}$ in the vicinity of the Os atom, due to the strong absorption of osmium.

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

Supporting Information Available: Tables of crystallographic details, bond distances and angles, atomic coordinates and equivalent isotropic displacement coefficients, and anisotropic displacement coefficients for $OsCl_3(\equiv CCH_2CMe_3)(PPh_3)_2 \cdot {}^1/_2CH_2Cl_2$ and $OsCl(=C=CHCMe_3)(C(C\equiv CCMe_3)=CHCMe_3)(PPh_3)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000306E