Vinylidene and Carbyne Complexes Derived from the Reactions of $OsCl(PPh_3)(PCP)$ (PCP = 2,6-$(PPh_2CH_2)_2C_6H_3$) with Terminal Acetylenes

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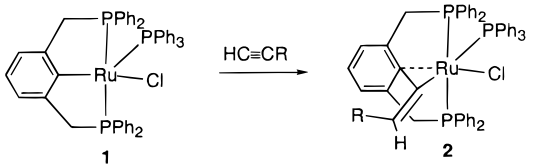
Received February 15, 2000

Treatment of $OsCl_2(PPh_3)_3$ with 1,3-$(PPh_2CH_2)_2C_6H_4$ led to the formation of the coordinatively unsaturated complex $OsCl(PPh_3)(PCP)$ (PCP = 2,6-$(PPh_2CH_2)_2C_6H_3$). Reactions of $OsCl(PPh_3)(PCP)$ with RC≡CH (R = Ph, *t*-Bu, $C(OH)Ph_2$) gave $OsCl(=C=CHR)(PPh_3)(PCP)$. Treatment of $OsCl(=C=CHPh)(PPh_3)(PCP)$ and $OsCl(=C=CHC(OH)Ph_2)(PPh_3)(PCP)$ with HCl produced the carbyne complexes $OsCl_2(\equiv CCH_2Ph)(PCP)$ and $OsCl_2(\equiv CCH=CPh_2)(PCP)$, respectively. The solid-state structures of $OsCl(PPh_3)(PCP)$ and $OsCl(=C=CHPh)(PPh_3)$-(PCP) have been determined by X-ray diffraction.

Introduction

Reactions of terminal acetylenes HC≡CR with coordinatively unsaturated compounds could often lead to vinylidene complexes.[1] It has also been established that vinylidene complexes $L_nMR'(=C=CHR)$ can undergo C−R′ bond formation reactions via migratory insertion reactions of R′ to the α-carbon of the vinylidene ligand.[2] This implies that reactions of HC≡CR with transition metal complexes L_nM-R' may go though vinylidene intermediates $L_nM-R'(=C=CHR)$ to give vinyl complexes $L_nM-R'C=CHR$. In fact, coupling reactions between acetylide and vinylidene ligands have been reported for many reactions of HC≡CR with certain complexes to give η^3-R_3CHR complexes and catalytic dimerization or oligomerization reactions of terminal acetylenes.[3−5] Although interesting, examples of coupling between vinylidene and other ligands such as hydride,[6] alkyl, vinyl,[7−9] and aryl ligands in the reactions of terminal acetylenes with transition metal complexes are still rather limited.

We have recently shown that reactions of $RuCl(PPh_3)(PCP)$ (PCP = 2,6-$(PPh_2CH_2)_2C_6H_3$) with terminal acetylenes RC≡CH lead to the formations of the unusual coupling products $RuCl(PPh_3)(\eta^4$-RCH=C-2,6-$(PPh_2CH_2)_2C_6H_3)$ (eq 1).[10a,b] Although not observed, the



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vinylidene complexes $RuCl(=C=CHR)(PPh_3)(PCP)$ were

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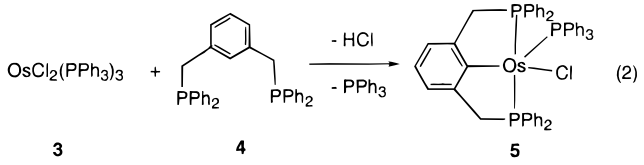
10.1021/om000150i CCC: $19.00
Publication on Web 08/17/2000

proposed to be the intermediates for the coupling reactions. These reactions represent rare examples of coupling between aryl and vinylidene ligands in the reactions of L_nM-Ar with terminal acetylenes. To see if similar coupling reactions would also occur and if the vinylidene intermediates could be observed with related osmium system, we have prepared the analogous osmium complex $OsCl(PPh_3)(PCP)$ and investigated its reactivity toward HC≡CR (R = Ph, *t*-Bu, $C(OH)Ph_2$). We have been able to isolate the vinylidene complexes $OsCl(=C=CHR)(PPh_3)(PCP)$ from the reactions. The vinylidene complexes, however, do not undergo similar coupling reactions, but can be used to prepare osmium carbyne complexes.

Results and Discussion

Preparation and Spectroscopic Characterization of $OsCl(PPh_3)(PCP)$. The coordinatively unsaturated complex $OsCl(PPh_3)(PCP)$ (**5**) was prepared by the reaction of $OsCl_2(PPh_3)_3$ (**3**) with ligand **4** in 2-propanol (eq 2). Formally one molecule of HCl was elimi-



nated from the reaction. The reaction is quite similar to the preparation of the analogous complex $RuCl(PPh_3)(PCP)$[10a,11] and $RuCl(PPh_3)((2,6\text{-}P(i\text{-}Pr)_2CH_2)_2C_6H_3)$.[12] In addition to ruthenium,[10–12] a large number of complexes with PCP or related phosphine ligands have been previously reported for Rh, Pt, Pd, Ir, and Ni.[13]

The spectroscopic data of the green compound **5** is consistent with a square-pyramidal complex with PPh_3 occupying the apical position. In particular the $^{31}P\{^1H\}$ NMR spectrum of the green compound **5** in C_6D_6 showed a doublet at 27.9 ppm for the PPh_2 groups and a triplet at 7.9 ppm ($J(PP)$ = 11.3 Hz) for the PPh_3 ligand. Virtual doublet of triplet signals at 3.57 and 2.46 ppm were observed in the ^1H NMR spectrum (in C_6D_6) for the methylene protons, indicating that the two PPh_2 groups are trans to each other.[14]

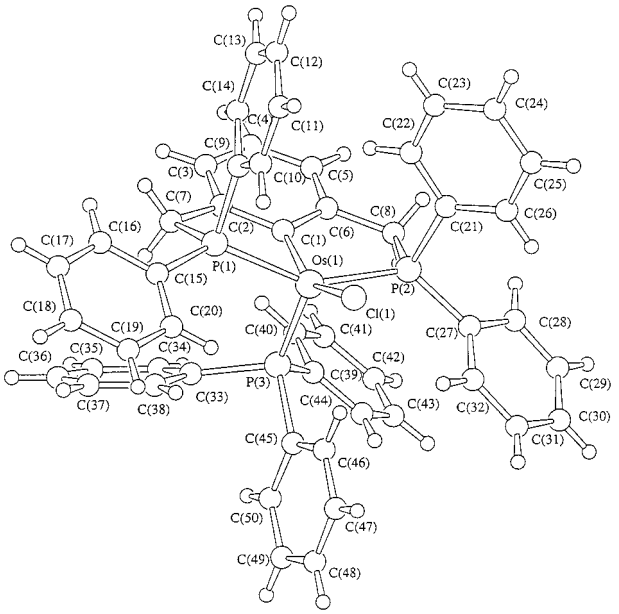


Figure 1. Molecular structure for OsCl(PPh3)(PCP). The thermal ellipsoids are shown at the 50% probability level.

Table 1. Crystal Data and Refinement Details for $OsCl(PPh_3)(PCP)$ (5) and $OsCl(=C=CHPh)(PPh_3)(PCP)\cdot H_2O$ ($6\cdot H_2O$)

	5	**6**·H_2O
formula	$C_{50}H_{42}ClP_3Os$	$C_{58}H_{48}ClP_3Os\cdot H_2O$
fw	961.46	1081.54
cryst sys	monoclinic	monoclinic
space group	$P2_1/a$ (#14)	$P2_1/n$
a, Å	14.042(1)	13.6143(11)
b, Å	17.496(2)	16.4298(13)
c, Å	17.082(2)	22.1628(17)
β, deg	95.74(2)	96.276(2)
V, Å^3	4175.6(7)	4927.7(7)
Z	4	4
d_{calc}, g cm^{-3}	1.529	1.458
radiation, Mo Kα, Å	0.07107	0.071073
2*θ* max, deg	47.9	55.08
scan type	*ω*	*ω*
no. of reflns collected	7058	32 732
no. of ind reflns	6754 (R_{int} = 4.4%)	11 316 (R_{int} = 10.49%)
no. of obsd reflns	4439 ($F > 3\sigma(F)$)	7351 ($F > 4\sigma(F)$)
no. of params refined	496	578
final *R* indices (obsd data)	R = 5.4%, R_w = 7.0%	R = 4.83%, R_w = 10.70%
goodness of fit	2.51	0.937
largest diff peak, e Å^{-3}	2.99	1.480
largest diff hole, e Å^{-3}	−2.80	−1.105

Table 2. Selected Bond Distances and Angles for $OsCl(PPh_3)(PCP)$

Bond Distances (Å)			
Os(1)−Cl(1)	2.427(4)	Os(1)−P(1)	2.312(4)
Os(1)−P(2)	2.313(4)	Os(1)−P(3)	2.231(4)
Os(1)−C(1)	2.04(1)		
Bond Angles (deg)			
Cl(1)−Os(1)−P(1)	94.8(1)	Cl(1)−Os(1)−P(2)	91.9(1)
Cl(1)−Os(1)−P(3)	122.6(1)	Cl(1)−Os(1)−C(1)	152.7(4)
P(1)−Os(1)−P(2)	149.9(1)	P(1)−Os(1)−P(3)	102.6(1)
P(1)−Os(1)−C(1)	78.6(4)	P(2)−Os(1)−P(3)	98.4(1)
P(2)−Os(1)−C(1)	82.1(4)	P(3)−Os(1)−C(1)	84.7(4)

The structure of **5** has been confirmed by an X-ray diffraction study. The molecular geometry of **5** is depicted in Figure 1. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively. Overall, the structure is very similar to that of $RuCl(PPh_3)(PCP)$.[10c] The structure of **5** can be viewed as a distorted square pyramid with the

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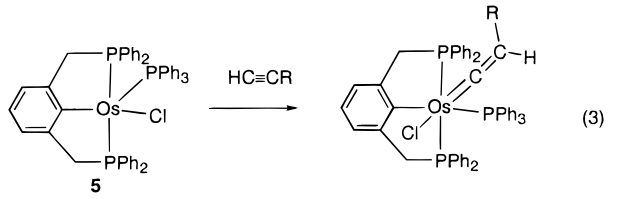
PPh_3 ligand located at the apex. The four atoms Cl(1), P(1), C(1), and P(2) form the base and the osmium center is above the square base toward the apical position. The distortion from square pyramid is clearly indicated by the difference in the P(3)−Os−C(1) (84.7(4)°) and P(3)−Os−Cl(1) (122.6(1)°) angles. The P(1)−Os−P(2) angle (149.9(1)°) is significantly smaller than those expected for complexes with trans-deposited phosphines. The small angle may be caused by the small bite angle of the PCP ligand. The small bite angle of the PCP ligand may also cause P(1)−Os−C(1) (78.6(4)°) and P(2)−Os−C(1) (82.1(4)°) angles to be significantly smaller than P(1)−Os−Cl(1) (94.8(1)°) and P(2)−Os−Cl(1) (91.9(1)°) angles. The Os−C(1) bond length of 2.04(1) Å is close to those observed for Os−C(aryl) bonds in complexes such as $OsH(C_6H_4\text{-}2\text{-}(E\text{-}CH{=}CHPh))(CO)(P(i\text{-}Pr)_3)_2$ (2.136(7) Å),[15] $Os(C_2Ph)(NH{=}CPhC_6H_4)(CO)(P(i\text{-}Pr)_3)_2$ (2.089(7) Å),[16] and Os(PyPh-4-Br)Cl(CO)$(PPh_3)_2$ (2.050(9) Å).[17]

Reactions of Complex 5 with PhC≡CH and *t*-BuC≡CH. Reaction of PhC≡CH with complex **5** in CH_2Cl_2 produced the vinylidene complex OsCl(=C=CHPh)(PPh_3)(PCP) (**6**) (eq 3). The structure of complex



6 is supported by the NMR data as well as elemental analysis. The meridional geometry of the PCP ligand is supported by the virtual triplet ^1H and ^{13}C signals of the CH_2 groups.[14] The PPh_3 is trans to the central aromatic ring of the PCP ligand, as indicated by the large $^2J(C_{ipso}-PPh_3)$ coupling constant (61.8 Hz). The presence of the vinylidene ligand is supported by the $^{13}C\{^1H\}$ NMR spectrum (in $CDCl_3$), which exhibited an Os=*C* signal at 303.7 ppm and an Os=C=*C*H signal at 109.7 ppm. For comparison, the α- and *β*-carbon signals of the vinylidene ligand in OsHCl(=C=CHCy)(CO)(P(*i*-$Pr)_3)_2$ were observed at 326.9 and 121.9 ppm, respectively.[6b] The vinylidene proton signal in complex **6** was observed at 0.91 ppm in the ^1H NMR spectrum (in $CDCl_3$).

The structure of **6** has been confirmed by an X-ray diffraction study. The molecular geometry of **6** is depicted in Figure 2. The crystallographic details and selected bond distances and angles are given in Tables 1 and 3, respectively. The structure of **6** can be viewed as a distorted octahedron with a meridional PCP ligand and a vinylidene ligand trans to a chloride. The distortion could be mainly attributed to the small bite angle of the PCP ligand as reflected by the P(1)−Os(1)−P(2) angle (157.13(5)°). The angle is larger than that in complex **5**, but is still significantly smaller than that expected for trans-deposited phosphines. The Os−C(aryl) bond distance (2.133(5) Å) is slightly longer than

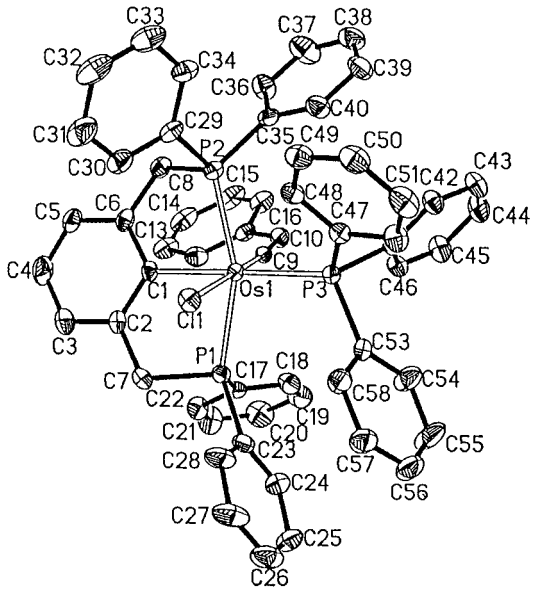


Figure 2. Molecular structure for OsCl(=C=CHPh)-(PPh3)(PCP). The thermal ellipsoids are shown at the 40% probability level.

Table 3. Selected Bond Distances and Angles for $OsCl(=C=CHPh)(PPh_3)(PCP)\cdot H_2O$

Bond Distances (Å)			
Os(1)−Cl(1)	2.5128(15)	Os(1)−P(1)	2.3889(14)
Os(1)−P(2)	2.3547(15))	Os(1)−P(3)	2.4536(14)
Os(1)−C(1)	2.133(5)	Os(1)−C(9)	1.819(6)
C(9)−C(10)	1.337(8)	C(10)−C(11)	1.453(9)

Bond Angles (deg)			
C(9)−Os(1)−C(1)	91.3(2)	C(9)−Os(1)−P(1)	95.53(17)
C(9)−Os(1)−P(2)	82.63(17)	C(9)−Os(1)−P(3)	97.01(17)
C(9)−Os(1)−Cl(1)	178.58(16)	C(1)−Os(1)−P(1)	78.45(15)
C(1)−Os(1)−P(2)	78.80(15)	C(1)−Os(1)−P(3)	171.58(16)
C(1)−Os(1)−Cl(1)	87.10(16)	P(1)−Os(1)−P(2)	157.13(5)
P(1)−Os(1)−P(3)	101.76(5)	P(1)−Os(1)−Cl(1)	83.30(5)
P(2)−Os(1)−P(3)	101.10(5)	P(2)−Os(1)−Cl(1)	97.92(5)
P(3)−Os(1)−Cl(1)	84.58(5)	Os(1)−C(9)−C(10)	173.6(5)
C(9)−C(10)−C(11)	126.1(6)		

that in **5**. The Os(1)−C(9) and C(9)−C(10) bond distances and Os−C(9)−C(10) angle are normal compared to those reported for osmium vinylidene complexes such as $Os(=C=CHSiMe_3)(CH=CHSiMe_3)Cl(P(i\text{-}Pr)_3)_2$,[7] $OsCl_2$-$(=C=CHPh)(P(i\text{-}Pr)_3)(P(i\text{-}Pr)_2CH_2CH_2NMe_2)]$,[18]

$[Cp^*Os(=C=CHCMe_3)(CO)(PPh_3)]BF_4$,[19] and $Os(=C=CC_6H_8)(CO)_2(PPh_3)_2$.[20] It is also interesting to note that the phenyl group of the vinylidene ligand is oriented toward the central aromatic ring of the PCP ligand, probably to minimize the steric interaction with the PPh_3 ligand. Such an orientation is in agreement with the geometry of the vinyl group in compounds **2** assuming that compounds **2** were formed from RuCl(=C=CHR)(PPh_3)(PCP) with a similar conformation.[10a,b]

Treatment of complex **5** in CH_2Cl_2 with *t*-BuC≡CH produced the analogous vinylidene complex OsCl(=C=CH(*t*-Bu))(PPh_3)(PCP) (**7**). The complex has very similar ^{31}P NMR data to **6**, implying that the two complexes have very similar structure. The presence of the vi-

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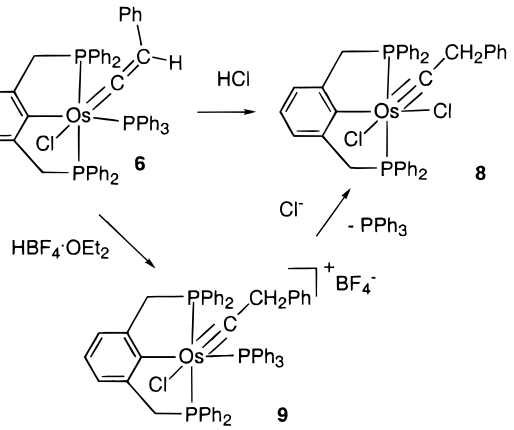
nylidene ligand is supported by the $^{13}C\{^1H\}$ NMR spectrum (in CD_2Cl_2), which exhibited Os=*C* signal at 299.3 ppm and Os=C=*C*H signal at 117.2 ppm, and the ^1H NMR spectrum (in C_6D_6), which showed the vinylidene proton signal at −0.51 ppm. Complexes of the formula OsCl(=C=CHR)(PPh_3)(PCP) are interesting as examples of well-characterized complexes with both vinylidene and alkyl ligands, which are still very limited.[1]

Several mechanisms have been proposed for the formation of mononuclear vinylidene complexes from the reactions of coordinatively unsaturated complexes with terminal acetylenes.[21−26] Vinylidene complexes may be formed intramolecularly from a π-acetylene complex $L_nM(\eta^2$-HC≡CR) by direct 1,2-hydrogen shift, or from a hydrido−alkynyl complex L_nMH(C≡CR) by 1,3-hydrogen shift of the hydride to the β-carbon of the alkynyl ligand.[21,22,26] Vinylidene complexes may also be formed though hydrido−alkynyl complexes L_nMH(C≡CR) intermolecularly by a bimolecular hydrogen shift process[23] or by dissociation of a proton from the metal center followed by addition of the proton to the β-carbon of the alkynyl ligand.[24,25] In our case, we have not been able to detect the expected π-acetylene complexes or the hydrido−alkynyl complexes. Thus the detailed mechanism is not very clear. However, intermolecular hydrogen shift processes are unlikely considering the results of some deuterium-labeling experiments. Treatment of OsCl(PPh_3)(PCP) with a mixture of PhC≡CD and *t*-BuC≡CH produced OsCl(=C=CDPh)(PPh_3)(PCP) and OsCl(=C=CH(*t*-Bu))(PPh_3)(PCP). Reaction of OsCl(PPh_3)(PCP) with PhC≡CH in the presence of D_2O produced only OsCl(=C=CHPh)(PPh_3)(PCP). These results are inconsistent with intermolecular hydrogen shift processes, but are consistent with intramolecular hydrogen shift processes. It is likely that our vinylidene complexes are formed via OsCl(HC≡CR)(PPh_3)(PCP) by a 1,2-hydrogen shift process, as calculations have shown that the 1,2-hydrogen shift process is usually more favorable than the 1,3-hydrogen shift process.[21,22]

Formation of Carbyne Complexes from Complex 6. As mentioned previously, the complex RuCl(PPh_3)(PCP) reacted with PhC≡CH to give the coupling product RuCl(PPh_3)(η^4-PhCH=C-2,6-(PPh_2CH_2)$_2C_6H_3$). In this reaction, the vinylidene complex RuCl(=C=CHPh)(PPh_3)(PCP) was proposed as the key intermediate, which appears to be too reactive to be observed.[10b] We have tried to induce similar intramolecular coupling reaction of complex **6** by standing at room temperature or heating solutions of complex **6** in solvents such as THF, benzene, or chloroform. However, the expected coupling product was not observed in the experiments.

As indicated by $^{31}P\{^1H\}$ NMR, no appreciable reaction occurred when solutions of complex **6** in THF-d_8 and C_6D_6 were allowed to stand at room temperature for 2 days. When a red-brown C_6D_6 solution of **6** was stood at room temperature for a week or heated for a day, partial decomposition of complex **6** occurred to give a purple solution, which showed only ^{31}P NMR signals of complex **6** (major) and Ph_3PO (minor). Decomposition of **6** in commercially available $CDCl_3$ also occurred. Thus when a $CDCl_3$ solution of **6** was stored at room temperature for a day, a small amount of NMR active species which shows a singlet $^{31}P\{^1H\}$ signal at 14.5 ppm was produced along with PPh_3. As indicated by in situ $^{31}P\{^1H\}$ NMR, decomposition of **6** is not completed even after the solution was stored for 3 days. Long storage of the solution (8 days) led to complete decomposition of **6** to give a purplish-blue solution, which showed no ^{31}P signals except that of Ph_3PO. The initial decomposition product having the $^{31}P\{^1H\}$ signal at 14.5 ppm was identified to be the carbyne complex $OsCl_2$(≡CCH_2Ph)(PCP) (**8**), which can be readily prepared by treating **6** with aqueous hydrochloric acid (Scheme 1).

Scheme 1



Complex **8** was characterized by elemental analysis and NMR, IR, and MS spectroscopy. The meridional geometry of the PCP ligand is supported by the virtual triplet CH_2 signals of the PCP ligand in the ^1H and ^{13}C NMR spectra.[14] The presence of the Os≡CCH_2Ph group is indicated by ^1H and ^{13}C NMR. In particular, the ^1H NMR spectrum (in $CDCl_3$) showed the CH_2 signal at 1.35 ppm, and the ^{13}C NMR spectrum (in $CDCl_3$) showed the ≡C and CH_2 signals at 284.2 and 55.0 ppm, respectively. For comparison, the CH_2 proton signal was observed at 2.04 ppm and the ^{13}C signals for ≡C and CH_2 were observed at 264.68 and 56.95 ppm for $OsHCl_2$(≡CCH_2Ph)(P(*i*-Pr)$_3$)$_2$.[27a] Reported osmium carbyne complexes closely related to **8** include $OsHCl_2$(≡CR)(PR′$_3$)$_2$ (PR′$_3$ = P(*i*-Pr)$_3$,[27,28] PCy_3[29]), $OsCl_2$(≡C−CH=CRPh)(P(*i*-Pr)$_2CH_2CO_2$Me)(P(*i*-Pr)$_2CH_2CO_2$) (R = Ph, Me),[18] and $OsCl_2$(SCN)(≡CC_6H_4−NMe_2)(PPh_3)$_2$.[30]

In the protonation of **6** with hydrochloric acid, the carbyne complex **8** was likely formed by protonation of the vinylidene ligand to give [OsCl(PPh_3)(≡CCH_2Ph)-

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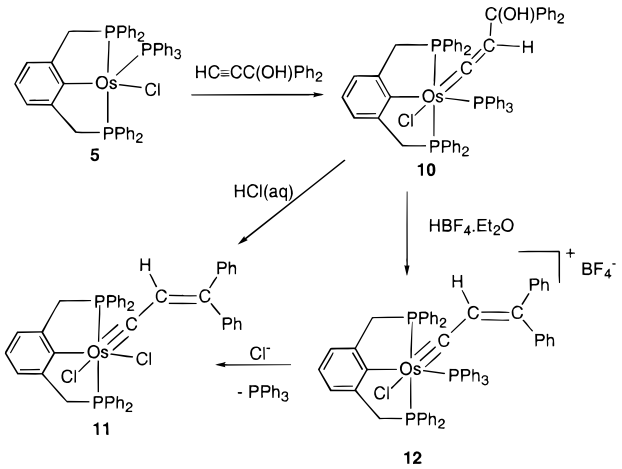
(PCP)]$^+$, followed by substitution of the PPh_3 with Cl^-. Formation of **8** from $CDCl_3$ solution of **6** is also likely initiated by protonation of the vinylidene ligand with water or a trace amount of acid present in the solvent. Protonation of vinylidene ligands to give carbyne complexes is one of the typical reactions of vinylidene complexes.[1] To determine if [OsCl(≡CCH$_2$Ph)(PPh$_3$)(PCP)]$^+$ was the intermediate in the formation of complex **8**, we have prepared complex [OsCl(≡CCH$_2$Ph)(PPh$_3$)(PCP)]BF$_4$ (**9**) by reacting complex **5** with HBF$_4$·Et$_2$O and investigated the reactivity of **9** toward Cl^-. Indeed, **8** was produced rapidly and cleanly on treatment of **9** with NEt$_3$CH$_2$PhCl. This observation supports that [OsCl(≡CCH$_2$Ph)(PPh$_3$)(PCP)]$^+$ is the intermediate in the formation of complex **8**. Several monocationic osmium carbyne complexes related to complex **9** have been reported, for example, [OsCl$_2$(≡CCH$_2$Ph)(H$_2$O)(P(*i*-Pr$_3$)$_2$]BF$_4$,[27b] [OsCl$_2$(≡C-tolyl)(H$_2$O)(PPh$_3$)$_2$]$^+$,[30,31] [CpOsCl(≡CR)(P(*i*-Pr)$_3$)]$^+$,[32] and [OsH(OAc)(≡CR)(P(*i*-Pr)$_3$)$_2$]$^+$.[33]

During the course of investigating the chemical properties of complex **9**, it was found that complex **9** reacted with excess water to give complex **6**. Thus one of the CH_2 protons of Os≡CCH$_2$Ph was deprotonated by water. The deprotonation reaction can be related to the acidic nature of the protons α to the carbyne carbon. Deprotonation reactions of protons α to the carbyne carbons by bases are known reactions. For example, OsHCl$_2$(≡CCH$_2$Ph)(P(*i*-Pr$_3$)$_2$ can be deprotonated by NaOMe to give OsHCl(=C=CHPh)(P(*i*-Pr$_3$)$_2$,[27b] [Cp((CO)$_2$Re≡CCH$_3$)]$^+$ can be deprotonated by THF to give Cp(CO)$_2$Re=C=CH$_2$,[34] and [Cp(CO)$_2$Mn≡C−CH=CPh$_2$)]$^+$ can be deprotonated by water or THF to give Cp(CO)$_2$Mn=C=C=CPh$_2$.[35]

Reaction of Complex 5 with Ph$_2$(OH)CC≡CH. Ph$_2$(OH)CC≡CH has often been used as the reagent to prepare hydroxyvinylidene or allenylidene complexes. For example, a hydroxyvinylidene complex has been obtained from its reaction with RuCl$_2$(P(*i*-Pr)$_2$CH$_2$CO$_2$Me)$_2$;[36] allenylidene complexes have been prepared from its reactions with complexes such as [CpRu(PMe$_3$)$_2$]$^+$,[37] [RuCl(dppm)$_2$]$^+$,[38] [RuCl(dppe)$_2$]$^+$,[39] [CpOs(CO)(P(*i*-Pr)$_3$)]$^+$,[40] [(η^5-C$_9$H$_7$)M(PPh$_3$)$_2$]$^+$ (M = Ru, Os),[41] [Os(C(CO$_2$Me)=CH$_2$)(O=CMe$_2$)(CO)(P(*i*-Pr)$_3$)$_2$]$^+$,[42] and CpOsCl(P(*i*-Pr)$_3$).[43] To see if hydroxyvinylidene or allenylidene complexes or coupling product via these intermediates could be obtained, reaction of Ph$_2$(OH)CC≡CH with complex **5** was investigated. Treatment of Ph$_2$(OH)CC≡CH with complex **5** in CH_2Cl_2 produced the hydoxyvinylidene complex OsCl(=C=CHC(OH)Ph$_2$)(PPh$_3$)(PCP) (**10**) (see Scheme 2). The presence of the vinylidene ligand in complex **10** is indicated by the ^{1}H NMR spectrum (in CD_2Cl_2), which showed the vinylidene proton signal at 0.84 ppm and the OH signal at 0.32 ppm. The similarity in the coordination spheres of complex **6** and **10** is reflected in their ^{31}P NMR data.

Scheme 2



Complex **10** is stable in the solid state in an inert atmosphere. However, it slowly decomposes in solvents such as $CHCl_3$, THF, and benzene. For example, after solutions of **10** in C_6D_6 or $CDCl_3$ were allowed to stand at room temperature for 2 days, the intensity of the ^{31}P{^{1}H} signals due to **10** decreased, and a new singlet ^{31}P{^{1}H} signal at 14.6 (in C_6D_6) or 14.8 ppm (in $CDCl_3$) appeared along with that of Ph_3PO. The new compound having the ^{31}P chemical shift of 14.8 ppm (in $CDCl_3$) was identified to be the vinylcarbyne complex OsCl$_2$(≡CCH=CPh$_2$)(PCP) (**11**), which can be obtained easily by reacting complex **10** with aqueous HCl. The presence of the Os≡CCH=CPh$_2$ group in complex **11** is indicated by ^{1}H and ^{13}C NMR. In particular, the ^{1}H NMR spectrum (in CD_2Cl_2) showed a CH= signal at 4.74 ppm, and the ^{13}C{^{1}H} NMR spectrum (in CD_2Cl_2) showed = C, CH=, and =CPh$_2$ signals at 275.0, 131.8, and 154.0 ppm. In the protonation reaction of complex **10** with aqueous HCl, complex **11** is presumably formed by electrophilic abstraction of the OH group of **10** by H^+ to give [OsCl(≡C−CH=CPh$_2$)(PPh$_3$)(PCP)]$^+$, followed by substitution reaction of PPh_3 with Cl^-. In fact, [OsCl(≡C−CH=CPh$_2$)(PPh$_3$)(PCP)]BF$_4$ (**12**) could be prepared by reaction of complex **10** with HBF_4 and reacted with PhCH$_2$NEt$_3$Cl to give complex **11**.

Comments on the Reactivity of HC≡CR toward MCl(PPh$_3$)(PCP) (M = Ru, Os). It is interesting to note that reactions of RuCl(PPh$_3$)(PCP) with HC≡CR gave the coupling products RuCl(PPh$_3$)(η^4-RCH=C-2,6-(PPh$_2$CH$_2$)$_2$C$_6$H$_3$), while the analogous reactions with OsCl(PPh$_3$)(PCP) produced the vinylidene complexes OsCl(=C=CHR)(PPh$_3$)(PCP). In the case of ruthenium, the coupling products are likely produced from the

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vinylidene intermediates $RuCl(=C=CHR)(PPh_3)(PCP)$, although they could not be observed. In the case of osmium, the vinylidene complexes can be isolated, but they cannot be converted to the corresponding coupling products. The difference could be related to the stronger Os−C and Os=C bonds.[44] Ruthenium and osmium complexes with similar composition may adopt different isomeric forms that have been noted previously.[2a,7] For example, $OsHCl_2(\equiv CCH_2Ph)(PR'_3)_2$ ($PR'_3 = PCy_3$,[29] $P(i\text{-}Pr)_3$[27,28]) are carbyne complexes, while $RuCl_2(=CHCH_2Ph)(PR'_3)_2$ ($PR'_3 = PCy_3$,[45] $P(i\text{-}Pr)_3$[46]) are carbene complexes. Similarly, $Os(=C=CHSiMe_3)(CH=CHSiMe_3)Cl(P(i\text{-}Pr)_3)_2$ can be isolated from the reaction of $HC\equiv CSiMe_3$ with $OsH_3Cl(P(i\text{-}Pr)_3)_2$, but the coupling product $[Ru(\eta^3\text{-}Me_3SiCH=C-CH=CHSiMe_3)(CO)(P(t\text{-}Bu)_2Me)_2]^+$ was obtained from the reaction of $HC\equiv CSiMe_3$ with $RuH(OTf)(CO)(P(t\text{-}Bu)_2Me)_2$.[7] Concerning the pattern of the stability of isomeric forms, Caulton et al. have recently noted that ruthenium favors structures with a maximum number of C−C and C−H bonds within the ligands, while osmium favors structures with a maximum number of metal−ligands bonds.[2a] Our results fit the pattern well.

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 materials $OsCl_2(PPh_3)_3$,[47] 1,3-$(PPh_2CH_2)_2C_6H_4$,[48] and $HC\equiv CC(OH)Ph_2$[49] were prepared according to literature methods. All other reagents were used as purchased from Aldrich Chemical Co.

Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were collected on a JEOL EX-400 spectrometer (400 MHz) or a Bruker ARX-300 spectrometer (300 MHz). ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts relative to 85% H_3PO_4. MS spectra were recorded on a Finnigan TSQ7000 spectrometer.

$OsCl(PPh_3)(PCP)$ (5). A mixture of 1,3-$(PPh_2CH_2)_2C_6H_4$ (1.01 g, 2.13 mmol) and $OsCl_2(PPh_3)_3$ (1.86 g, 1.77 mmol) in 50 mL of degassed 2-propanol was refluxed for 8 h. The solid was collected by filtration, washed with 2-propanol (2 × 50 mL), and dried under vacuum overnight. Yield: 1.1 g, 65%. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 27.9 (d, $J(PP) = 11.3$ Hz), 7.9 (t, $J(PP) = 11.3$ Hz). ^1H NMR (300.13 MHz, C_6D_6): δ 8.04−6.52 (m, 38 H, PPh_3, PPh_2, C_6H_3), 3.57 (dt, $J(HH) = 15.9$ Hz, $J(PH) = 6.1$ Hz, 2 H, CH_2), 2.46 (dt, $J(HH) = 15.9$ Hz, $J(PH) = 6.1$ Hz, 2 H, CH_2). Anal. Calcd for $C_{50}H_{42}ClP_3Os$: C, 62.33; H, 4.60. Found: C, 62.50; H, 4.62.

$OsCl(=C=CHPh)(PPh_3)(PCP)$ (6). To a CH_2Cl_2 (60 mL) solution containing $OsCl(PPh_3)(PCP)$ (0.30 g, 0.31 mmol) was added phenylacetylene (0.3 mL, 3.0 mmol). The reaction mixture was stirred for 30 min to give a brownish-red solution. The solvent was evaporated to dryness under vacuum. A pink solid was obtained when ether (50 mL) was added. The solid was collected by filtration, washed with ether (50 mL) and hexane (50 mL), and dried under vacuum overnight. Yield: 0.20 g, 61%. A crystalline sample of **6** could be obtained by slow evaporation of solvent of a saturated solution of $OsCl(=C=CHPh)(PPh_3)(PCP)$ in wet CH_2Cl_2. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 6.4 (d, $J(PP) = 11.9$ Hz), −8.5 (t, $J(PP) = 11.9$ Hz). ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.91 (br, 1 H, Os=C=CH), 4.10 (dt, $J(HH) = 15.3$ Hz, $J(PH) = 4.4$ Hz, 2 H, CH_2), 4.48 (dt, $J(HH) = 15.3$ Hz, $J(PH) = 4.0$ Hz, 2 H, CH_2), 7.60−5.50 (m, 43 H, PPh_3, PPh_2, C_6H_3, C_6H_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 303.7 (q, $J(PC) = 8.7$ Hz, Os=C), 158.0 (d, $J(PC) = 61.8$ Hz, C(aryl)), 146.4−121.4 (m, other aromatic carbons), 109.7 (s, Os=C=CH), 48.3 (td, $J(PC) = 19.3$, 5.3 Hz, PCP−CH_2). Anal. Calcd for $C_{58}H_{48}ClP_3Os\cdot H_2O$: C, 64.41; H, 4.66. Found: C, 64.43; H, 4.77. The presence of water in the sample has been confirmed by an X-ray diffraction study (see below).

$OsCl(=C=CH(t\text{-}Bu))(PPh_3)(PCP)$ (7). To a CH_2Cl_2 (60 mL) solution containing $OsCl(PPh_3)(PCP)$ (0.50 g, 0.52 mmol) was added *tert*-butylacetylene (0.19 mL, 1.56 mmol). The reaction mixture was stirred for 15 min to give a brownish-red solution. The solvent was evaporated to dryness under vacuum. A pink solid was obtained when ether (50 mL) was added. The solid was collected by filtration, washed with ether (3 × 30 mL), and dried under vacuum overnight to give 0.36 g of crude product (67%). The solid was redissolved in 2 mL of CH_2Cl_2. Slowly addition of hexane (30 mL) to the dichloromethane solution produced a pink solid, which was collected by filtration, washed with ether and hexane, and dried under vacuum. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 7.5(d, $J(PP) = 12.8$ Hz), −10.9 (t, $J(PP) = 12.8$ Hz). ^1H NMR (300.13 MHz, C_6D_6): δ −0.51 (q, $J(PH) = 3.0$ Hz, 1 H, Os=C=CH), 0.37 (s, 9 H, CMe_3), 4.30 (dt, $J(HH) = 15.5$ Hz, $J(PH) = 4.7$ Hz, 2 H, CH_2), 4.89 (dt, $J(HH) = 15.5$ Hz, $J(PH) = 4.4$ Hz, 2 H, CH_2), 7.96−6.96 (m, 38 H, PPh_3, PPh_2, C_6H_3). $^{13}C\{^1H\}$ NMR (100.40, MHz, CD_2Cl_2): δ 299.3 (dt, $J(PC) = 6.9$, 11.0 Hz, Os=C), 160.6 (d, $J(PC) = 73.4$ Hz, C(aryl)), 147.2−121.7 (m, other aromatic carbons), 117.2 (s, Os=C=CH), 49.4 (td, $J(PC) = 19.1$, 5.1 Hz, PCP−CH_2). Anal. Calcd for $C_{56}H_{52}ClP_3Os$: C, 64.45; H, 5.02. Found: C, 64.60; H, 5.12**.** FAB-MS (NBA, *m/e*): 1009 ($[M - Cl]^+$), 782 ($[M - PPh_3]^+$).

$OsCl_2(\equiv CCH_2Ph)(PCP)$ (8). A 37% hydrochloric acid solution (0.04 mL, 0.56 mmol) was added to a CH_2Cl_2 (50 mL) solution of $OsCl(=C=CHPh)(PPh_3)(PCP)$ (0.15 g, 0.14 mmol). The resulting mixture was stirred at room temperature for 1 h to give a yellowish-green solution. The solvent was evaporated to dryness under vacuum. A light green solid was obtained when ether (30 mL) was added. The solid was collected by filtration, washed with ether (2 × 30 mL), and dried under vacuum overnight. Yield: 0.096 g, 82%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 14.5 (s). ^1H NMR (300.13 MHz, $CDCl_3$): δ 1.35 (s, 2 H, $Os\equiv CCH_2$), 3.44 (dt, $J(HH) = 17.7$ Hz, $J(PH) = 4.5$ Hz, 2 H, CH_2), 4.44 (dt, $J(HH) = 17.7$ Hz, $J(PH) = 5.4$ Hz, 2 H, CH_2), 8.00−5.92 (m, 28 H, PPh_2, C_6H_3, C_6H_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 284.2 (t, $J(PC) = 11.4$ Hz, Os≡C), 150.4 (s, C(aryl)), 147.3−122.7 (m, other aromatic carbons), 55.0 (s, $Os\equiv CCH_2$), 45.0 (t, $J(PC) = 18.5$ Hz, PCP−CH_2). Anal. Calcd for $C_{40}H_{34}Cl_2P_2Os$: C, 57. 35; H, 4.09, Cl, 8.46. Found: C, 57.26; H, 4.14; Cl, 8.16.

$[OsCl(\equiv CCH_2Ph)(PPh_3)(PCP)]BF_4$ (9). HBF_4 (60 μL, 0.44 mmol, 54% solution in ether) was added to a brownish-red CH_2Cl_2 solution (40 mL) of $OsCl(=C=CHPh)(PPh_3)(PCP)$ (0.30 g, 0.28 mmol). The reaction mixture was stirred at room temperature for 30 min to give a dark brown solution. The volume of the reaction mixture was reduced to ca. 5 mL, and ether (20 mL) was added slowly with stirring to give a pale brown solid. The crude product was collected by filtration, washed with ether (2 × 30 mL), and dried under vacuum overnight (0.21 g, 65.6%). The crude product was redissolved in 20 mL of THF. After filtration, the filtrate was concentrated in vacuo to 5 mL. Addition of ether (20 mL) to the residue produced a

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pale brown solid, which was collected by filtration, washed with ether (3 × 30 mL), and dried under vacuum overnight to give 0.15 g (yield, 46.9%) of product. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 11.3 (d, J(PP) = 13.4 Hz), −12.1 (t, J(PP) = 13.4 Hz). ^1H NMR (300.13 MHz, $CDCl_3$): δ 1.27 (s, 2 H, Os≡CCH_2), 3.30 (dt, J(HH) = 16.4 Hz, J(PH) = 4.8 Hz, 2 H, CH_2), 4.36 (dt, J(HH) = 16.4 Hz, J(PH) = 5.3 Hz, 2 H, CH_2), 7.45−5.55 (m, 43 H, PPh_3, PPh_2, C_6H_3, C_6H_5). Anal. Calcd for $C_{58}H_{49}BClF_4P_3Os$·THF: C, 60.86; H, 4.70. Found: C, 61.30; H, 4.60. The presence of THF in the sample is clearly indicated by the ^1H NMR signals of THF at 1.59 and 3.41 ppm (in CD_2Cl_2).

OsCl(=C=CHC(OH)Ph$_2$)(PPh$_3$)(PCP) (10). A mixture of OsCl(PPh_3)(PCP) (0.30 g, 0.31 mmol) and 1,1-diphenylpropyn-1-ol (0.13 g, 0.65 mmol) in 50 mL of CH_2Cl_2 was stirred at room temperature for 30 min to give a brownish-red solution. The solvent was evaporated to dryness under vacuum. A pale pink solid was obtained when ether (50 mL) was added. The solid was collected by filtration, washed with ether (50 mL) and hexane (50 mL), and dried under vacuum overnight. Yield: 0.20 g, 56%. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 6.4 (d, J(PP) = 12.6 Hz), −10.3 (t, J(PP) = 12.6 Hz). ^1H NMR (300.13 MHz, CD_2Cl_2): δ 0.32 (s, 1 H, C(OH)), 0.84 (q, J(PH) = 3.3 Hz, 1 H, Os=C=CH), 3.95 (dt, J(HH) =15.4 Hz, J(PH) = 4.5 Hz, 2 H, CH_2), 4.36 (dt, J(HH) = 15.4 Hz, J(PH) = 4.4 Hz, 2 H, CH_2), 7.8−6.7 (m, 48 H, PPh_3, PPh_2, C_6H_3, C_6H_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 293.9 (q, J(PC) = 8.5 Hz, Os=C), 156.5 (d, J(PC) = 62.1 Hz, C(aryl)), 146.3−112.6 (m, other aromatic and olefinic carbons), 65.7 (s, C(OH)), 48.2 (td, J(PC) = 19.5, 5.1 Hz, PCP−CH_2). Anal. Calcd for $C_{65}H_{54}ClOP_3Os$: C, 66.74; H, 4.65. Found: C, 66.90; H, 4.86.

OsCl$_2$(≡CCH=CPh$_2$)(PCP) (11). A 37% hydrochloric acid solution (0.04 mL, 0.56 mmol) was added to a CH_2Cl_2 (50 mL) solution of OsCl(=C=CHC(OH)Ph_2)(PPh_3)(PCP) (0.30 g, 0.26 mmol). The resulting mixture was stirred at room temperature for 1 h to give a yellowish-green solution. The solvent was evaporated to dryness under vacuum. A light green solid was obtained when ether (30 mL) was added. The solid was collected by filtration, washed with ether (2 × 30 mL), and dried under vacuum overnight. Yield: 0.16 g, 75%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 14.8 (s). ^1H NMR (300.13 MHz, CD_2Cl_2): δ 3.53 (dt, J(HH) = 16.4 Hz, J(PH) = 5.0 Hz, 2 H, CH_2), 4.52 (dt, J(HH) = 16.4 Hz, J(PH) = 5.1 Hz, 2 H, CH_2), 4.74 (t, J(PH) = 1.8 Hz, 1H, CH=), 6.48−8.00 (m, 48 H, PPh_3, PPh_2, C_6H_3, C_6H_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 275.0 (t, J(PC) = 11.5 Hz, Os≡C), 160.4 (s, C(aryl)), 154.0 (s, Os≡C−CH=*C*), 131.8 (s, Os≡C−*C*H), 147.3−102.2 (m, other aromatic carbons), 44.5 (t, J(PC) = 19.4 Hz, PCP−CH_2). Anal. Calcd for $C_{47}H_{38}Cl_2P_2Os$: C, 60.97; H, 4.14; Cl, 7.68. Found: C, 60.65; H, 4.55; Cl, 8.29.

[OsCl(≡CCH=CPh$_2$)(PPh$_3$)(PCP)]BF$_4$ (12). HBF_4 (60 μL, 0.44 mmol, 54% solution in ether) was added to a brownish-red CH_2Cl_2 solution (40 mL) of OsCl(=C=CHC(OH)Ph_2)(PPh_3)(PCP) (0.30 g, 0.26 mmol). The reaction mixture was stirred at room temperature for 30 min to give a brownish-orange solution. The volume of the reaction mixture was reduced to ca. 5 mL, and ether (30 mL) was added slowly with stirring to give a brownish-orange solid. The crude product was collected by filtration, washed with ether (2 × 30 mL), and dried under vacuum overnight (0.23 g, 71.9%). The crude product was redissolved in 20 mL of dichloromethane. After filtration, the filtrate was concentrated in vacuo to 5 mL. Addition of ether (20 mL) to the residue produced a brownish-orange solid, which was collected by filtration, washed with ether (3 × 30 mL), and dried under vacuum overnight to give 0.18 g (yield, 56.2%) of product. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 10.5 (d, J(PP) = 12.6 Hz), −19.3 (t, J(PP) = 12.6 Hz). ^1H NMR (300.13 MHz, $CDCl_3$): δ 3.1 (s, 1 H, Os≡CCH), 3.30 (dt, J(HH) = 15.8 Hz, J(PH) = 4.3 Hz, 2 H, CH_2), 4.43 (dt, J(HH) = 15.8 Hz, J(PH) = 4.8 Hz, 2 H, CH_2), 7.6−5.8 (m, 48 H, PPh_3, PPh_2, C_6H_3, C_6H_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 277.5 (q, J(PC) = 9.3 Hz, Os≡C), 166.2 (s, Os≡C−CH=*C*), 158.1 (s, C(aryl)), 123.7 (s, Os≡C−*C*H), 145.3−128.2 (m, other aromatic carbons), 47.0 (td, J(PC) = 20.6, 6.0 Hz, PCP−CH_2). Anal. Calcd for $C_{65}H_{53}BClF_4P_3Os$: C, 63.00; H, 4.31. Found: C, 62.81; H, 4.50.

Crystallographic Analysis for OsCl(PPh$_3$)(PCP). Suitable crystals for X-ray diffraction study were grown by slow diffusion of ether to a saturated solution of OsCl(PPh_3)(PCP) in CH_2Cl_2. A red prism crystal of OsCl(PPh_3)(PCP) having approximate dimensions of 0.22 × 0.20 × 0.15 mm was mounted in a glass capillary and used for X-ray structure determination. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) with ω−2θ scan ($2\theta_{max}$ = 48°). The data were corrected for Lorentz and polarization effects. Absorption corrections by ψ-scan method[50] (transmission factors (0.591−1.000) were also applied. The structure was solved by direct methods (SIR88)[51] and refined by full-matrix least-squares analysis on F (all non-hydrogen atoms anisotropically) to give R = 0.054, R_w = 0.070 for 4439 independent observed reflections [$F > 3\sigma(F)$]. All calculations were performed using TeXsan crystallographic software package[52] on a Silicon-Graphics Computer.

Crystallographic Analysis for OsCl(=C=CHPh)(PPh$_3$)(PCP)·H$_2$O. Crystals of **6** suitable for X-ray diffraction study were grown by slow evaporation of solvent of a saturated solution of OsCl(=C=CHPh)(PPh_3)(PCP) in wet CH_2Cl_2. A water molecule is cocrystallized with **6**. A pink plate crystal of OsCl(=C=CHPh)(PPh_3)(PCP)·H_2O having approximate dimensions of 0.14 × 0.10 × 0.10 mm was mounted in 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)[53] (from 0.732 to 1 on I). The structure was solved by direct methods and refined by full-matrix least-squares analysis on F^2 using the SHELXTL (version 5.10)[54] program package. All non-hydrogen atoms were refined anisotropically. The H atoms of the solvent water molecules were located from a difference Fourier map but not refined. The remaining H atoms were placed in ideal positions and refined via a riding model with assigned isotropic thermal parameters.

Acknowledgment. The authors 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 displace coefficients, and anisotropic displacement coefficients for OsCl(PPh_3)(PCP) and OsCl(=C=CHPh)(PPh_3)(PCP)·H_2O. The material is available free of charge via the Internet at http://pubs.acs.org.

OM000150I

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