Organometallics **2003,** *22,* 5217−5225 5217

Vinylidene, Allenylidene, and Carbyne Complexes from the Reactions of $[OsCl_2(PPh_3)_3]$ with $HC{\equiv}CC(OH)Ph_2$

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Received August 2, 2003

Treatment of $[OsCl_2(PPh_3)_3]$ with $HC{\equiv}CC(OH)Ph_2$ in benzene at room temperature produces $[(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os({=}C{=}CHC(OH)Ph_2)(PPh_3)_2]$, *fac*-$[OsCl_3({\equiv}C{-}CH{=}CPh_2)(PPh_3)_2]$, *mer*-$[OsCl_3({\equiv}C{-}CH{=}CPh_2)(PPh_3)_2]$, and $[OsCl_2({=}C{=}C{=}CPh_2)(CO)(PPh_3)_2]$. The latter two complexes are the major products when the reaction is carried out in refluxing toluene. Treatment of $[OsCl_2(PPh_3)_3]$ with $HC{\equiv}CC(OH)Ph_2$ in the presence of HCl produces *fac*-$[OsCl_3({\equiv}C{-}CH{=}CPh_2)(PPh_3)_2]$ and *mer*-$[OsCl_3({\equiv}C{-}CH{=}CPh_2)(PPh_3)_2]$. Treatment of $[OsCl_2(PPh_3)_3]$ with $HC{\equiv}CC(OH)Ph_2$ in the presence of $HPPh_3BF_4$ produces $[OsCl_2({\equiv}C{-}CH{=}CPh_2)(H_2O)(PPh_3)_2]BF_4$. The structures of all the new complexes have been confirmed by X-ray diffraction.

Introduction

Reactions of $[RuCl_2(PPh_3)_3]$ and related compounds with $HC{\equiv}CR$ or $HC{\equiv}CC(OH)RR'$ have been studied by several groups.[1−5] These reactions usually lead to the formation of vinylidene or allenylidene complexes. For example, treatment of $[RuCl_2(PPh_3)_3]$ with $HC{\equiv}CCMe_3$ produces $[RuCl_2({=}C{=}CHCMe_3)(PPh_3)_2]$;[1] reaction of $[RuCl_2(PPh_3)_3]$ with $HC{\equiv}CC(OH)Ph_2$ in the presence of $NaPF_6$ in dichloromethane gives the bimetallic complex $[Ru_2(\mu\text{-}Cl)_3({=}C{=}C{=}CPh_2)_2(PPh_3)_4]PF_6$.[2] In refluxing THF, $[RuCl_2(PPh_3)_3]$ reacts with $HC{\equiv}CC(OH)Ph_2$ to give the 3-phenyl-1-indenylidene complex $[RuCl_2(C_9H_5Ph)(PPh_3)_2]$ via the allenylidene intermediate $[RuCl_2({=}C{=}C{=}CPh_2)(PPh_3)_2]$.[3,4] Reaction of $[RuCl_2(PPh_3)_3]$ with $HC{\equiv}CC(OH)Ph_2$ in the presence of PCy_3 in refluxing THF gives the allenylidene complex $[RuCl_2({=}C{=}C{=}CPh_2)(PCy_3)_2]$.[4] These vinylidene or allenylidene complexes are interesting because they are catalytically active for olefin metathesis.[6]

We have studied the reactions of $[OsCl_2(PPh_3)_3]$ with terminal acetylenes, to see if related osmium vinylidene or allenylidene complexes can be similarly obtained. We have previously reported the reactions of $[OsCl_2(PPh_3)_3]$ with $HC{\equiv}CR$ (R = *t*-Bu, $SiMe_3$).[7,8] It was shown that the expected osmium vinylidene complexes could not be isolated from the reactions. Instead, we have isolated carbyne complexes $[OsCl_3({\equiv}CCH_2R)(PPh_3)_2]$, osmabenzyne complexes, and vinyl-vinylidene complexes $[OsX(C(C{\equiv}CR){=}CHR)({=}C{=}CHR)(PPh_3)_2]$ (X = Cl, $C{\equiv}CR$) from the reactions. The purpose of this paper is to report the reaction of $[OsCl_2(PPh_3)_3]$ with $HC{\equiv}CC(OH)Ph_2$. During the course of the study, it was briefly reported that the allenylidene complex $[OsCl_2({=}C{=}C{=}CPh_2)(PPh_3)_2]$ can be isolated in 98% yield from the reaction of $[OsCl_2(PPh_3)_3]$ with $HC{\equiv}CC(OH)Ph_2$.[3] In our study, however, the allenylidene complex could not be obtained. Rather, we have isolated several new osmium complexes including the dinuclear complex $[(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os({=}C{=}CHC(OH)Ph_2)(PPh_3)_2]$, trichlorovinylcarbyne complexes *fac*-$[OsCl_3({\equiv}C{-}CH{=}CPh_2)(PPh_3)_2]$ and *mer*-$[OsCl_3({\equiv}C{-}CH{=}CPh_2)(PPh_3)_2]$, and the carbonyl allenylidene complex $[OsCl_2({=}C{=}C{=}CPh_2)(CO)(PPh_3)_2]$. It is noted that well-characterized osmium allenylidene complexes are still rare. Reported osmium allenylidene complexes include $[(\eta^5\text{-}C_9H_7)Os({=}C{=}C{=}CR_2)(PPh_3)_2]PF_6$ ($R_2 = Ph_2$, $C_{12}H_8$),[9] $[CpOsCl({=}C{=}C{=}CPh_2)(P(i\text{-}Pr)_3)]$,[10] $[CpOs({=}C{=}C{=}CR_2)(P(i\text{-}Pr)_3)_2]PF_6$,[11]

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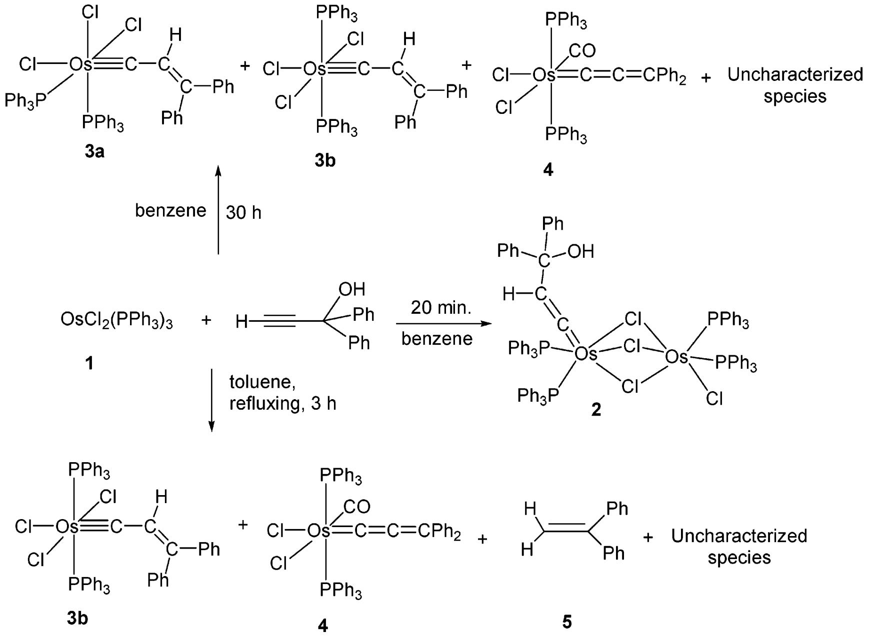
10.1021/om034082m CCC: $25.00 © 2003 American Chemical Society
Publication on Web 11/06/2003

Scheme 1



$[(\eta^5\text{-arene})OsX(=C=C=CR_2)(L)]PF_6$,[12] $[(PPh_3)_2CpOs=C=C=CHC\equiv C-OsCpPPh_3)_2]^+$,[13] and $[Os(C(CO_2Me)=CH_2)(=C=C=CPh_2)(CO)(P(i\text{-}Pr)_3)_2]BF_4$.[14]

Results and Discussion

Reaction of $[OsCl_2(PPh_3)_3]$ with $HC\equiv CC(OH)Ph_2$. The reaction of $[OsCl_2(PPh_3)_3]$ (**1**) with $HC\equiv CC(OH)Ph_2$ (1:2) in C_6D_6 at room temperature has been monitored by NMR spectroscopy. After $[OsCl_2(PPh_3)_3]$ (**1**) was mixed with $HC\equiv CC(OH)Ph_2$ for 20 min, the $^{31}P\{^1H\}$ NMR spectrum showed the signals of the starting material **1** (~50%), the liberated PPh_3, and the dinuclear monovinylidene complex $[(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os(=C=CHC(OH)Ph_2)(PPh_3)_2]$ (**2**). Two small doublet ^{31}P signals of an unknown species at 3.1 and −15.0 ppm ($J(PP) = 11.5$ Hz) also appeared at this moment. The signals of **2** grew up first in further reaction and then decreased with gradual consumption of the starting materials, while those due to the later unknown complex grew up gradually along with the signals of the carbyne complex *mer*-$[OsCl_3(\equiv CCH=CPh_2)(PPh_3)_2]$ (**3b**) and the carbonyl allenylidene complex $[OsCl_2(=C=C=CPh_2)(CO)(PPh_3)_2]$ (**4**). After 24 h, the ^{31}P NMR spectrum became very complicated, showing the major signals of **3b**, **4**, the above-mentioned unknown complex, and another unknown signal at −40.2 ppm in a ratio of ca. 2:1:4:1. A small amount of *fac*-$[OsCl_3(\equiv CCH=CPh_2)(PPh_3)_2]$ (**3a**) was precipitated out in the NMR tube. While complexes **2**, **3**, and **4** can be isolated from preparative scale reactions, the products with ^{31}P signals at 3.1, −15.0, and −40.2 ppm cannot be isolated in pure form and characterized.

To isolate the vinylidene complex $[(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os(=C=CHC(OH)Ph_2)(PPh_3)_2]$ (**2**), $[OsCl_2(PPh_3)_3]$ (**1**) was allowed to react with $HC\equiv CC(OH)Ph_2$ (1:1.2) in benzene at room temperature for 20 min. The unreacted **1** was removed by precipitation with ether. The ether extractant was then stood at RT overnight to give **2** as brownish yellow microcrystals (Scheme 1). Isolated **2** is sparingly soluble in benzene and slightly soluble in CH_2Cl_2.

To isolate the other products mentioned above, $[OsCl_2(PPh_3)_3]$ (**1**) was allowed to react with $HC\equiv CC(OH)Ph_2$ (1:4) in benzene at room temperature for 30 h. The reaction produced a small amount of a brown microcrystalline solid and a brown solution. The brown solid was identified to be the facial isomer of the trichlorovinylcarbyne complex *fac*-$[OsCl_3(\equiv C-CH=CPh_2)(PPh_3)_2]$ (**3a**). From the brown solution, the greenish meridonal trichlorovinylcarbyne complex *mer*-$[OsCl_3(\equiv C-CH=CPh_2)(PPh_3)_2]$ (**3b**) can be isolated by recrystallization. As indicated by the $^{31}P\{^1H\}$ NMR spectrum, the reaction also produced several other products, including a small amount of the carbonyl-containing allenylidene complex $[OsCl_2(=C=C=CPh_2)(CO)(PPh_3)_2]$ (**4**). Unfortunately, we have not been able to isolate them in pure form from the reaction mixture.

Complex **2** has been characterized by elemental analyses, NMR spectroscopy, and X-ray diffraction. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively. A view of the molecular geometry of **2** is shown in Figure 1. The coordination geometry around each osmium center can be described as a distorted octahedron. The Os(1)−C(1)−C(2) unit is nearly linear with an angle of 171.2(11)°. The Os(1)−C(1) and C(1)−C(2) bond distances are at 1.844(14) and 1.303(16) Å, respectively, which are well comparable with those reported for other osmium vinylidene complexes.[15−22] The hydroxyl proton

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Table 1. Crystallrograsphic Details for Complexes 2, 3a, 3b, 4, and 6

	2·$1.5CH_2Cl_2$	**3a**·$1/2CH_2Cl_2$	**3b**·$3CH_2Cl_2$	**4**	**6**·CH_2Cl_2
empirical formula	$C_{87}H_{72}Cl_4OOs_2P_4$·$1.5CH_2Cl_2$	$C_{51}H_{41}Cl_3OsP_2$·$1/2CH_2Cl_2$	$C_{51}H_{41}Cl_3OsP_2$·$3CH_2Cl_2$	$C_{52}H_{40}Cl_2OOsP_2$	$C_{51}H_{43}BCl_2F_4OOsP_2$·$CH_2Cl_2$
fw	1906.92	1054.79	1267.11	1003.88	1166.63
temperature, K	293(2)	294(2)	100(2)	293(2)	200(2)
radiation (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$C2/c$
a, Å	19.385(7)	10.2014(19)	12.0745(5)	10.252(2)	36.139(8)
b, Å	24.464(8)	11.842(2)	24.2282(11)	28.712(6)	11.437(2)
c, Å	19.910(6)	19.869(4)	18.1144(8)	14.822(3)	24.023(5)
α, deg	90	80.411(4)	90	90	90
β, deg	90.000(7)	88.742(4)	102.3690(10)	94.057(4)	102.914(6)
γ, deg	90	68.163(4)	90	90	90
V, $Å^3$	9442(5)	2194.8(7)	5176.2(4)	4352.0(15)	9678(4)
Z	4	2	4	4	8
d_{calcd}, g cm^{-3}	1.341	1.596	1.626	1.532	1.601
abs coeff, mm^{-1}	2.994	3.258	3.027	3.165	2.976
F(000)	3780	1050	2520	2000	4640
cryst size, mm^3	0.30 × 0.25 × 0.10	0.28 × 0.20 × 0.18	0.46 × 0.10 × 0.05	0.32 × 0.10 × 0.08	0.38 × 0.08 × 0.05
θ range, deg	1.95 to 27.61	1.99 to27.53	1.43 to28.28	1.98 to 27.56	1.74 to 26.51
no. of reflns collected	63 261	14 771	44 935	29 234	26964
no. of indep reflns	21 734 (R_{int} = 0.1468)	9944 (R_{int} = 0.0255)	12 356 (R_{int} = 0.0369)	10 031 (R_{int} = 0.0465)	10050 (R_{int} = 0.0669)
no. of obsd reflns ($I > 2\sigma(I)$)	7661	8035	10909	6794	7444
abs corr	SADABS	SADABS	SADABS	SADABS	SADABS
no. of data/restraints/params	21 734/11/931	9944/2/530	12 356/0/613	10 031/0/523	10 050/0/586
goodness-of-fit on F^2	0.942	0.931	1.035	0.889	1.148
final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0661$, $wR_2 = 0.1666$	$R_1 = 0.0356$, $wR_2 = 0.0708$	$R_1 = 0.0287$, $wR_2 = 0.0634$	$R_1 = 0.0366$, $wR_2 = 0.0703$	$R_1 = 0.0625$, $wR_2 = 0.1033$
largest peak and hole, e $Å^{-3}$	1.531 and −1.619	1.472 and −0.890	1.223 and −0.720	1.515 and −1.263	1.934 and −1.958

Table 2. Selected Bond Lengths and Angles for [$(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os(=C=CHC(OH)Ph_2)(PPh_3)_2$]·$1.5CH_2Cl_2$ (2·$1.5CH_2Cl_2$)

Bond Distances (Å)			
Os(1)−C(1)	1.844(14)	Os(2)−Cl(4)	2.397(4)
Os(1)−P(1)	2.352(4)	Os(2)−P(3)	2.281(4)
Os(1)−P(2)	2.349(4)	Os(2)−P(4)	2.272(4)
Os(1)−Cl(1)	2.528(3)	Os(2)−Cl(1)	2.541(3)
Os(1)−Cl(2)	2.441(4)	Os(2)−Cl(2)	2.410(3)
Os(1)−Cl(3)	2.471(3)	Os(2)−Cl(3)	2.533(3)
C(1)−C(2)	1.303(16)	C(2)−C(3)	1.450(17)
C(3)−O(1)	1.426(14)		
Bond Angles (deg)			
C(2)−C(1)−Os(1)	171.2(11)	C(1)−C(2)−C(3)	124.6(13)
P(2)−Os(1)−P(1)	101.71(14)	P(4)−Os(2)−P(3)	97.36(14)
P(1)−Os(1)−Cl(1)	93.49(13)	P(3)−Os(2)−Cl(1)	169.41(12)
P(2)−Os(1)−Cl(1)	102.18(12)	P(4)−Os(2)−Cl(1)	89.86(13)
P(1)−Os(1)−Cl(2)	166.26(12)	P(3)−Os(2)−Cl(2)	94.34(13)
P(2)−Os(1)−Cl(2)	89.99(13)	P(4)−Os(2)−Cl(2)	95.79(12)
P(1)−Os(1)−Cl(3)	89.92(12)	P(3)−Os(2)−Cl(3)	93.60(12)
P(2)−Os(1)−Cl(3)	167.95(14)	P(4)−Os(2)−Cl(3)	167.93(12)
C(1)−Os(1)−P(1)	91.0(4)	P(4)−Os(2)−Cl(4)	95.58(13)
C(1)−Os(1)−P(2)	87.7(4)	P(3)−Os(2)−Cl(4)	98.02(14)
C(1)−Os(1)−Cl(1)	168.0(4)	Cl(4)−Os(2)−Cl(1)	88.93(12)
C(1)−Os(1)−Cl(2)	96.7(4)	Cl(4)−Os(2)−Cl(2)	161.98(13)
C(1)−Os(1)−Cl(3)	88.9(4)	Cl(4)−Os(2)−Cl(3)	87.87(12)
Cl(2)−Os(1)−Cl(3)	78.90(11)	Cl(2)−Os(2)−Cl(3)	78.28(11)
Cl(2)−Os(1)−Cl(1)	76.84(12)	Cl(2)−Os(2)−Cl(1)	77.16(11)
Cl(3)−Os(1)−Cl(1)	80.01(11)	Cl(3)−Os(2)−Cl(1)	78.62(11)
Os(1)−Cl(1)−Os(2)	84.34(10)	Os(2)−Cl(2)−Os(1)	89.10(12)
Os(1)−Cl(3)−Os(2)	85.69(10)		

is weakly hydrogen bonded to one of the bridging Cl (O(1)···Cl(3) = 3.317(11) Å, O(1)−H(1)···Cl(3) = 164.4°). There are many reported examples of hydrogen-bonding interaction involving coordinated halides, either terminal[17−19] or bridging in nature.[23]

Consistent with the solid state structure, the ^{31}P NMR spectrum (in CD_2Cl_2) of **2** displayed four sets of doublet resonances with equal intensity at −4.2 (d, *J*(PP) = 8.6 Hz), −11.4 (d, *J*(PP) = 8.6 Hz), −19.7 (d, *J*(PP) = 16.7 Hz), and −21.1 (d, *J*(PP) = 16.7 Hz) ppm, indicating the presence of four inequivalent phosphorus nuclei of a dinuclear structure devoid of symmetry. The presence of the hydroxyvinylidene ligand is supported by the appearance of a broad singlet at 2.37 ppm assignable to the hydroxy proton and a broad singlet at 0.71 ppm assignable to the vinylidene proton in the ^1H NMR spectrum (in CD_2Cl_2). The $^{13}C\{^1H\}$ NMR spectrum was not collected due to the poor solubility.

Complex **2** is presumably formed from the reaction of the intermediate [$OsCl_2(=C=CHC(OH)Ph_2)(PPh_3)_2$] with unreacted [$OsCl_2(PPh_3)_3$]. The five-coordinated vinylidene complex [$OsCl_2(=C=CHPh)(P(i\text{-}Pr)_3)_2$], which is closely related to the intermediate, has recently been reported by Esteruelas et al.[17] Although many osmium vinylidene complexes have been reported,[15−22,24] complex **2** represents a rare example of chloro-bridged dinuclear osmium vinylidene complexes. Related ruthe-

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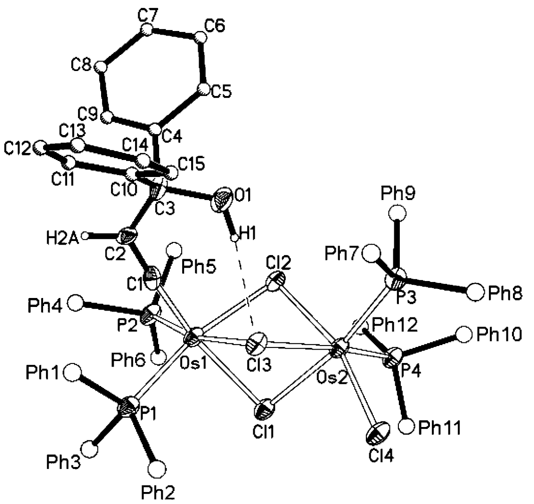

Figure 1. Molecular structure of $[(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os({=}C{=}CHC(OH)Ph_2)(PPh_3)_2]$ (**2**). The phenyl rings of the PPh_3 ligands are represented by the sphere 'O' for clarity.

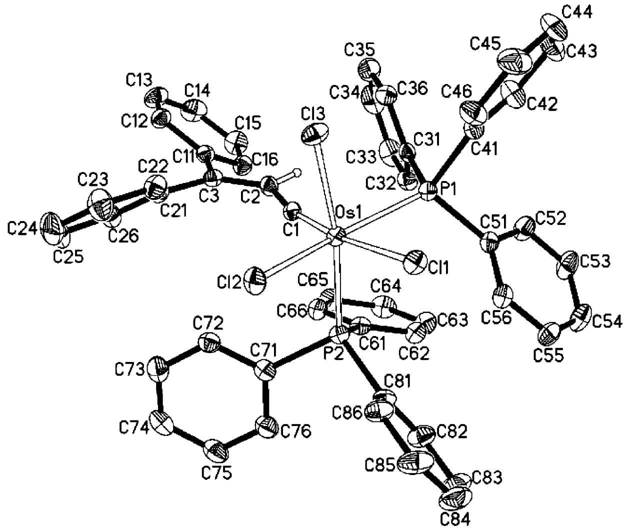

Figure 2. Molecular structure of *fac*-$[OsCl_3({\equiv}C{-}CH{=}CPh_2)(PPh_3)_2]$ (**3a**).

nium dinuclear allenylidene complexes $[Ru_2(\mu\text{-}Cl)_3({=}C{=}C{=}CAr_2)_2(PPh_3)_4]PF_6$ and $[Ru_2(\mu\text{-}Cl)_2Cl_2({=}C{=}C{=}CPh_2)_2(TPPMS)_4]^{4-}$ have recently been reported by Dixneuf et al.[2] and Peruzzini et al.,[5e] respectively.

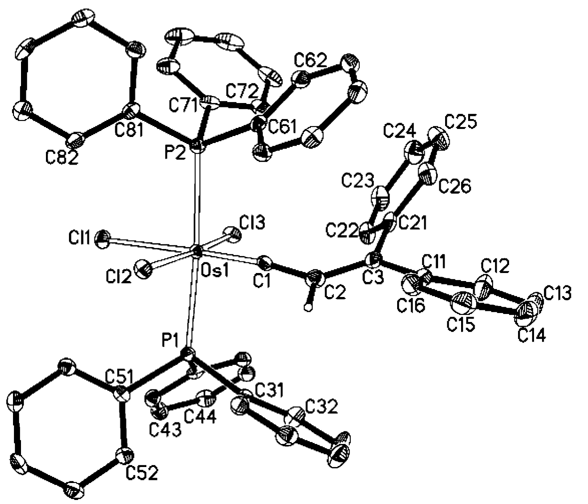

Figure 3. Molecular structure of *mer*-$[OsCl_3({\equiv}C{-}CH{=}CPh_2)(PPh_3)_2]$ (**3b**).

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for *fac*-$[OsCl_3({\equiv}C{-}CH{=}CPh_2)(PPh_3)_2]\cdot 1/2(CH_2Cl_2)$ ($\mathbf{3a}\cdot 1/2CH_2Cl_2$) and *mer*-$[OsCl_3({\equiv}C{-}CH{=}CPh_2)(PPh_3)_2]\cdot 3CH_2Cl_2$ ($\mathbf{3b}\cdot 3CH_2Cl_2$)

$\mathbf{3a}\cdot 1/2CH_2Cl_2$		$\mathbf{3b}\cdot 3CH_2Cl_2$	
Os(1)−C(1)	1.750(4)	Os(1)−C(1)	1.750(3)
C(1)−C(2)	1.405(6)	C(1)−C(2)	1.395(4)
C(2)−C(3)	1.361(6)	C(2)−C(3)	1.364(4)
Os(1)−P(1)	2.4224(11)	Os(1)−P(1)	2.4334(7)
Os(1)−P(2)	2.4100(11)	Os(1)−P(2)	2.4409(7)
Os(1)−Cl(1)	2.4723(10)	Os(1)−Cl(1)	2.4955(6)
Os(1)−Cl(2)	2.4024(11)	Os(1)−Cl(2)	2.4162(6)
Os(1)−Cl(3)	2.4374(11)	Os(1)−Cl(3)	2.3697(6)
C(2)−C(1)−Os(1)	168.6(3)	C(2)−C(1)−Os(1)	168.4(2)
C(3)−C(2)−C(1)	130.0(4)	C(3)−C(2)−C(1)	127.6(3)
C(2)−C(3)−C(11)	117.8(4)	C(2)−C(3)−C(11)	119.2(3)
C(2)−C(3)−C(21)	123.6(4)	C(2)−C(3)−C(21)	122.4(3)
C(21)−C(3)−C(11)	118.6(3)	C(21)−C(3)−C(11)	118.4(2)
P(1)−Os(1)−P(2)	99.64(4)	P(1)−Os(1)−P(2)	175.87(2)
Cl(1)−Os(1)−Cl(2)	84.04(4)	Cl(1)−Os(1)−Cl(2)	89.87(2)
Cl(2)−Os(1)−Cl(3)	84.61(4)	Cl(3)−Os(1)−Cl(2)	172.78(2)
Cl(1)−Os(1)−Cl(3)	86.76(4)	Cl(2)−Os(1)−P(2)	89.43(2)
P(1)−Os(1)−Cl(1)	81.49(4)	P(1)−Os(1)−Cl(1)	87.62(2)
P(1)−Os(1)−Cl(2)	164.45(4)	Cl(3)−Os(1)−P(1)	91.94(2)
P(1)−Os(1)−Cl(3)	88.91(4)	Cl(2)−Os(1)−P(1)	87.69(2)
P(2)−Os(1)−Cl(1)	97.04(4)	P(2)−Os(1)−Cl(1)	89.42(2)
P(2)−Os(1)−Cl(2)	87.73(4)	Cl(3)−Os(1)−Cl(1)	82.91(2)
P(2)−Os(1)−Cl(3)	171.06(4)	Cl(3)−Os(1)−P(2)	90.55(2)
C(1)−Os(1)−P(1)	91.38(13)	C(1)−Os(1)−P(1)	90.21(9)
C(1)−Os(1)−P(2)	87.51(13)	C(1)−Os(1)−P(2)	92.74(9)
C(1)−Os(1)−Cl(1)	172.08(13)	C(1)−Os(1)−Cl(1)	177.81(9)
C(1)−Os(1)−Cl(2)	102.67(13)	C(1)−Os(1)−Cl(2)	89.81(9)
C(1)−Os(1)−Cl(3)	89.67(13)	C(1)−Os(1)−Cl(3)	97.40(9)

The molecular structures of complexes **3a** and **3b** have also been confirmed by X-ray diffraction studies. The crystallographic details and selected bond distances and angles are given in Tables 1 and 3, respectively. The molecular geometries of **3a** and **3b** are shown in Figures 2 and 3, respectively. The osmium center in each complex has a distorted octahedral geometry. In complex **3a**, the two PPh_3 ligands are in a *cis*-arrangement (P(1)−Os−P(2), 99.64(4)°) and the three chloride ligands are also mutually *cis*-disposed with one of them being *trans* to the carbyne ligand. In complex **3b**, the two PPh_3 ligands are *trans* to each other, occupying the axial positions, and the three chlorides and the vinylcarbyne ligand lie in the equatorial plane. The Os−C(carbyne) bond distances and the Os−C(1)−C(2) bond angles in both complexes (1.750(4) Å and 168.6(3)° in **3a**, 1.750(3) Å and 168.4(2)° in **3b**) are almost identical, which are comparable to those reported previously for other osmium-carbyne complexes.[19,20,25−29] The C(1)−C(2) and C(2)−C(3) bond distances in both complexes (1.405(6) and 1.361(6) Å in **3a**, 1.395(4) and 1.364(4) Å

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(24) For additional examples of recent work on Os vinylidene complexes, see for example: (a) Baya, M.; Esteruelas, M. A. *Organometallics* **2002**, *21*, 2332. (b) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 3283. (c) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 4875. (d) Ferrando, G.; Gérard, H.; Spivak, G. J.; Coalter, J. N., III; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **2001**, *40*, 6610. (e) Marchenko, A. V.; Gérard, H.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2001**, *25*, 1244.

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in **3b**) as well as the bond angles around C(2) and C(3) atoms (117.8(4) and 130.0(4)° in **3a**, 118.4(2)° and 127.6(3)° in **3b**) are consistent with the vinylcarbyne formulation. The P(1)−Os−P(2) angle of **3a** (99.64(4)°) is significantly deviated from the ideal value of 90°, due to the steric interaction of the phenyl groups of the PPh_3 ligands.

The solid state structures of **3a** and **3b** are fully supported by their solution NMR spectroscopic data. In the $^{31}P\{^1H\}$ NMR spectra, complex **3a** displayed a singlet at −14.6 ppm (in CD_2Cl_2), while complex **3b** displayed a singlet at −16.0 ppm (in CD_2Cl_2). The most characteristic spectroscopic features in the ^1H NMR spectra of **3a** and **3b** are the signals of the vinyl protons of $C\mathit{H}{=}CPh_2$, which appeared as triplets at 3.10 ppm ($J(PH) = 3.5$ Hz, in CD_2Cl_2) for **3a** and 4.25 ppm ($J(PH) = 2.1$ Hz, in CD_2Cl_2) for **3b**. The $^{13}C\{^1H\}$ spectrum (in CD_2Cl_2) of **3a** exhibited a triplet at 267.4 ppm for $Os\equiv \mathit{C}$ ($J(PC) = 15.7$ Hz) and two singlets at 167.3 and 131.7 ppm for the vinyl carbons $CH{=}\mathit{C}Ph_2$ and $\mathit{C}H{=}CPh_2$, respectively. The $^{13}C\{^1H\}$ spectrum (in CD_2Cl_2) of **3b** showed a triplet at 266.3 ppm for $Os\equiv \mathit{C}$ ($J(PC) = 11.4$ Hz) and two singlets at 163.1 and 131.8 ppm for the vinyl carbons $CH{=}\mathit{C}Ph_2$ and $\mathit{C}H{=}CPh_2$, respectively.

Reported compounds closely related to **3a** and **3b** include [$OsCl_3(\equiv CR)(PPh_3)_2$] (R = Me, CH_2CMe_3),[7,8] [$OsHCl_2(\equiv CR')(PR_3)_2$] (R = Cy, *i*-Pr),[27,29,30] [$OsCl_2(\equiv C{-}CH{=}CRPh)(P(i\text{-}Pr)_2CH_2CO_2Me)(P(i\text{-}Pr)_2CH_2CO_2)$] (R = Ph, Me),[20] and [$OsCl_2(SCN)(\equiv CC_6H_4NMe_2)(PPh_3)_2$].[31] In all the previously reported complexes, the two PR_3 ligands are *trans* to each other. Complex **3a** appears to be the first [$OsX_3(\equiv CR)(PR'_3)_2$] complex with two *cis* PR_3 ligands.

During the course of collecting the ^{13}C and $^1H-^{13}C$ COSY NMR spectra of **3a**, it was found that **3a** slowly isomerizes to **3b** at room temperature. As indicated by the ^{31}P and ^1H NMR spectra, ca. 8% of **3a** is converted to **3b** after an initially pure sample of **3a** in CD_2Cl_2 was allowed to stand at RT for 20 h. The isomerization was completed if a solution of **3a** in $CHCl_3$ was refluxed for 1 h. The isomerization is probably not surprising, as it is anticipated that the *cis*-arrangement of the two PPh_3 ligands in **3a** is thermodynamically less favorable due to the steric repulsion between the two bulky PPh_3 ligands.

As mentioned previously, the carbonyl allenylidene complex **4** was produced in the reaction of [$OsCl_2(PPh_3)_3$] with $HC\equiv CC(OH)Ph_2$. At room temperature, the compound was formed slowly as a minor product, and it is difficult to isolate the compound. To encourage the formation of **4**, the reaction has been carried out in refluxing toluene. The reaction also produced a mixture of products. The three major phosphorus-containing products showed singlet ^{31}P signals at −15.8, −12.4, and −1.9 ppm in a ratio of ca. 4:2:1 (in C_6D_6). The signals at −15.8, −12.4 ppm are due to **3b** and **4**, respectively. These complexes can be isolated in 27% and 16% yield, respectively, by fractional crystallization followed by column chromatography. The third product with a ^{31}P signal at −1.9 ppm could not be isolated in pure form and identified. In addition, we also isolated the organic compound 1,1-diphenylethylene (**5**) from the reaction mixture, which could be formed from the hydrolysis of an allenylidene ligand in the reaction (see below). **5** has been characterized by MS and ^1H NMR. In particular, the FAB-MS displayed the expected molecular ion peak at $m/z = 180.1$, and the ^1H NMR spectrum (in $CDCl_3$) is identical to the reported one,[32] showing a singlet at 5.59 ppm with an integration ratio of 1:5 relative to those of the aromatic proton signals. This reaction also produced another organic compound, which shows a characteristic singlet ^1H NMR signal at 6.11 ppm (in C_6D_6) and a molecular ion peak at $m/z = 398$ in the FAB-MS spectrum. On the basis of the ^1H NMR and MS data, we tentatively assign it as $CPh_2{=}C{=}CHC\equiv CC(OH)Ph_2$.

Table 4. Selected Bond Lengths and Bond Angles for [$OsCl_2({=}C{=}C{=}CPh_2)(CO)(PPh_3)_2$] (4)

Bond Distances (Å)			
Os(1)−C(1)	1.898(4)	Os(1)−C(4)	1.866(5)
C(1)−C(2)	1.235(6)	C(2)−C(3)	1.356(6)
Os(1)−P(1)	2.4346(11)	Os(1)−P(2)	2.4296(12)
Os(1)−Cl(1)	2.4494(12)	Os(1)−Cl(2)	2.4505(12)
C(4)−O(1)	1.116(5)		
Bond Angles (deg)			
P(1)−Os(1)−P(2)	177.58(4)	Cl(1)−Os(1)−Cl(2)	89.99(5)
P(1)−Os(1)−Cl(1)	86.35(4)	P(2)−Os(1)−Cl(1)	93.91(4)
P(1)−Os(1)−Cl(2)	86.29(4)	P(2)−Os(1)−Cl(2)	91.30(4)
C(1)−Os(1)−P(1)	94.11(12)	C(4)−Os(1)−P(1)	94.32(13)
C(1)−Os(1)−P(2)	85.80(12)	C(4)−Os(1)−P(2)	88.10(13)
C(2)−C(1)−Os(1)	173.4(4)	C(1)−C(2)−C(3)	172.0(5)
O(1)−C(4)−Os(1)	178.9(4)	C(1)−Os(1)−C(4)	88.69(19)
C(2)−C(3)−C(11)	122.7(4)	C(2)−C(3)−C(21)	116.8(4)
C(1)−Os(1)−Cl(1)	176.12(12)	C(4)−Os(1)−Cl(1)	87.43(15)
C(1)−Os(1)−Cl(2)	93.89(12)	C(4)−Os(1)−Cl(2)	177.30(15)

The solid state structure of complex **4** 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 4, respectively. A view of the molecular geometry of **4** is shown in Figure 4, which reveals that **4** contains an allenylidene and a carbonyl ligand. The overall geometry around osmium in **4** can be described as a distorted octahedron with the two PPh_3 ligands at the axial positions. The equatorial positions are occupied by the two *cis*-disposed Cl atoms, CO, and allenylidene ligands. The diphenylallenylidene ligand is bound to the metal in a nearly linear fashion with Os−C(1)−C(2) and C(1)−C(2)−C(3) angles of 173.4(4)° and 172.0(5)°, respectively. The Os−C(1) bond distance of 1.898(4) Å is about 0.05 Å shorter than that found in the complex [$Os(C(CO_2Me){=}CH_2)({=}C{=}C{=}CPh_2)(CO)(P(i\text{-}Pr_3)_2$]$BF_4$ (1.947(6) Å),[14] but is statistically identical to the values found in osmium-allenylidene complexes [$CpOsCl({=}C{=}C{=}CPh_2)(P(i\text{-}Pr)_3)$] (1.875(6) Å),[10] [$(\eta^5\text{-}C_9H_7)Os({=}C{=}C{=}CPh_2)(PPh_3)_2$]$PF_6$ (1.895(4) Å),[9] and [$(\eta^6\text{-mes})OsCl({=}C{=}C{=}CPh_2)(PMe_3)$]$PF_6$ (1.90(1) Å).[12] The C(1)−C(2) bond length of 1.235(6) Å compares well with those reported for the four previously structurally characterized osmium alle-

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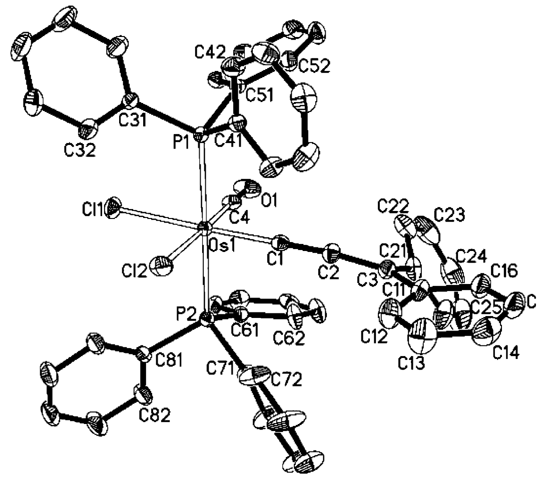


Figure 4. Molecular structure of $[\mathrm{OsCl_2(=C=C=CPh_2)(CO)(PPh_3)_2}]$ (**4**).

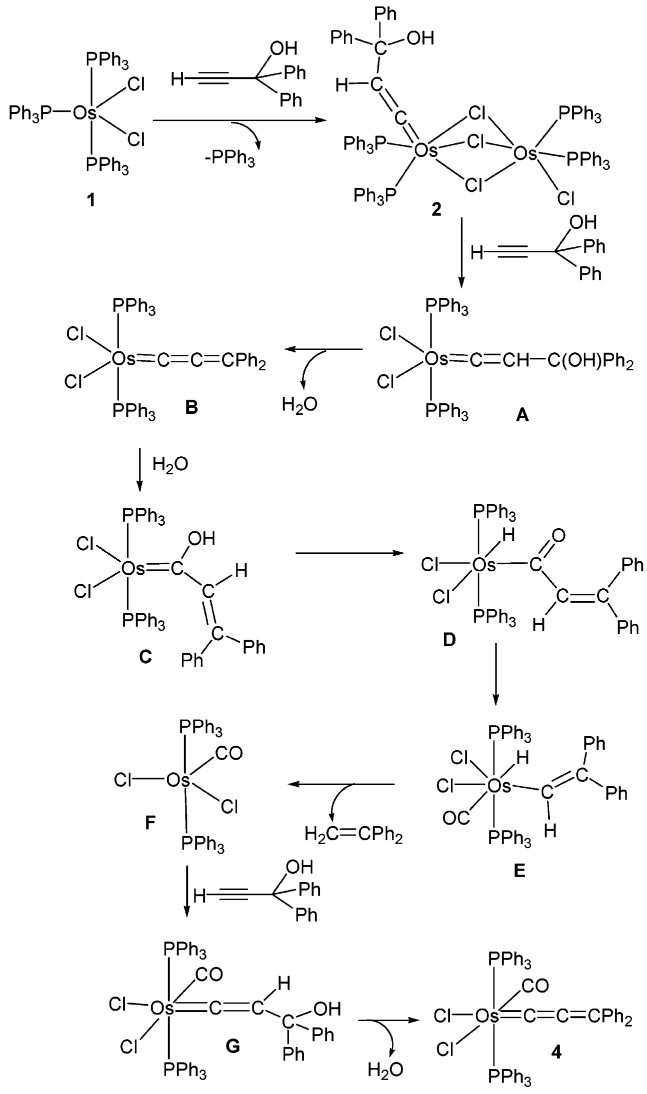
nylidene complexes (1.250(8),[14] 1.222(9),[10]1.265(6),[9] and 1.27(1)[12] Å, respectively). However, it is significantly shorter than the bond length expected for a C=C double bond (1.30 Å), indicating a substantial contribution of the canonical form $[\mathrm{Os}]^-\mathrm{-C{\equiv}C-C^+Ph_2}$ to the structure of **4**. A similar conclusion has been reached in the structural analysis of other allenylidene complexes.[9,10,12,14]

Consistent with the solid state structure, the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum of **4** displayed a triplet at 278.0 ppm with a J(PC) of 8.9 Hz assignable to the α-carbon of the allenylidene ligand and two singlets at 208.1 and 156.3 ppm assignable to the corresponding β- and γ-carbons, respectively. The presence of the CO ligand is supported by the triplet $^{13}\mathrm{C}\{^1\mathrm{H}\}$ resonance at 173.4 ppm with a J(PC) of 8.2 Hz. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum (in $\mathrm{C_6D_6}$) displayed a singlet at −12.4 ppm.

Comments on the Formation of 3 and 4 in the Reaction of $[\mathrm{OsCl_2(PPh_3)_3}]$ with $\mathrm{HC{\equiv}CC(OH)Ph_2}$. Reaction of $[\mathrm{OsCl_2(PPh_3)_3}]$ with $\mathrm{HC{\equiv}CC(OH)Ph_2}$ in refluxing toluene was previously reported to give the allenylidene complex $[\mathrm{OsCl_2(=C=C=CPh_2)(PPh_3)_2}]$ in 98% isolated yield. However, the allenylidene complex could be not obtained, in our hand, from the reaction carried out either in refluxing toluene or in benzene at room temperature. Instead, we have isolated the dinuclear complex $[\mathrm{(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os(=C=CHC(OH)Ph_2)(PPh_3)_2}]$, the carbyne complexes *fac*-$[\mathrm{OsCl_3({\equiv}C-CH=CPh_2)(PPh_3)_2}]$ (**3a**) and *mer*-$[\mathrm{OsCl_3({\equiv}C-CH=CPh_2)(PPh_3)_2}]$ (**3b**), and the carbonyl-containing allenylidene $[\mathrm{OsCl_2(=C=C=CPh_2)(CO)(PPh_3)_2}]$ (**4**). The allenylidene complex $[\mathrm{OsCl_2(=C=C=CPh_2)(PPh_3)_2}]$, however, could serve as the intermediate for the formation of **3** and **4**.

A plausible mechanism for the formation of **4** is shown in Scheme 2. Reaction of **1** with $\mathrm{HC{\equiv}CC(OH)Ph_2}$ initially produces the dinuclear hydroxyvinylidene complex **2**, which has been isolated. **2** can react with additional $\mathrm{HC{\equiv}CC(OH)Ph_2}$ to generate $[\mathrm{OsCl_2(=C=CH\text{-}(C(OH)Ph_2)(PPh_3)_2}]$ (**A**). The hydroxyvinylidene **A** then can undergo dehydration to give the allenylidene complex $[\mathrm{OsCl_2(=C=C=CPh_2)(PPh_3)_2}]$ (**B**). Reactions of 1-alkynols with late transition metal complexes via hydroxyvinylidene intermediates have proven to be one of the most convenient routes to allenylidene derivatives.[33,34] For example, reaction of $[\mathrm{RuCl_2(PPh_3)_3}]$ with

Scheme 2



$\mathrm{HC{\equiv}CC(OH)Ph_2}$ in the presence of $\mathrm{NaPF_6}$ in dichloromethane produces the bimetallic complex $[\mathrm{Ru_2(\mu\text{-}Cl)_3\text{-}(=C=C=CPh_2)_2(PPh_3)_4]PF_6}$,[2] reaction of $[\mathrm{RuCl_2(PPh_3)_3}]$ with $\mathrm{HC{\equiv}CC(OH)Ph_2}$ in refluxing THF produces the 3-phenyl-1-indenylidene complex $[\mathrm{RuCl_2(C_{10}H_5Ph)\text{-}(PPh_3)_2}]$, which is presumably formed by intramolecular rearrangement of an allenylidene intermediate,[3,4] and reaction of $\mathrm{HC{\equiv}CC(OH)Ph_2}$ with $[\mathrm{RuCl_2(PPh_3)_3}]$ in the presence of $\mathrm{PCy_3}$ in refluxing THF produces the allenylidene complex $[\mathrm{RuCl_2(=C=C=CPh_2)(PCy_3)_2}]$.[4] Nucleophilic addition of water (generated from dehydration) to the $\mathrm{C_\alpha{-}C_\beta}$ double bond of the allenylidene **B** could produce the hydroxycarbene complex **C**. Addition of water to $\mathrm{C_\alpha{-}C_\beta}$ of allenylidene ligands to give hydroxycarbene complexes has been reported for the reactions of water with $[\mathrm{CpRu(=C=C=CPh_2)(CO)(P\text{-}(\mathit{i}\text{-}Pr)_3)]BF_4}$[35] and $[\mathrm{Re(=C=C=CHPh)(CO)(MeC(CH_2\text{-}PPh_2)_3)]OTf}$.[36] The hydroxycarbene intermediate **C** may

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rearrange to the hydrido-acyl intermediate **D**, which could undergo deinsertion of CO to give hydrido-vinyl complex **E**. Subsequent reductive elimination of $CH_2{=}CPh_2$ would give $OsCl_2(CO)(PPh_3)_2$ (**F**). The organic compound $CH_2{=}CPh_2$ has been isolated and characterized by MS and ^1H NMR in our study. Reaction of **F** with $HC{\equiv}CC(OH)Ph_2$ can then lead to the allenylidene complex **4** via the hydroxyvinylidene intermediate **G**. Reactions of allenylidene complexes with water to give carbonyl complexes have been recently reported by Bianchini et al.[37] They have shown that the ruthenium allenylidene complex *fac,cis*-[$RuCl_2({=}C{=}C{=}CPh_2)(PNP)$] (PNP = $MeCH_2CH_2N(CH_2CH_2PPh_2)_2$) reacts with water to produce the carbonyl derivative [$RuCl_2(CO)(PNP)$] and free $CH_2{=}CPh_2$ via regioselective cleavage of the $C_\alpha{-}C_\beta$ bond. In this system, use of D_2O gives the corresponding deuterated $D_2C{=}CPh_2$, indicating that both terminal hydrogens come from water.

Formation of the trichlorovinylcarbyne complexes **3a** and **3b** from the reaction could be related to the protonation of vinylidene or allenylidene intermediates (**A** or **B**) by HCl. The HCl could be generated by dehydrochlorination of the osmium starting material. We have previously shown that reaction of [$OsCl_2(PPh_3)_3$] with $HC{\equiv}CCMe_3$ leads to the formation of the dehydrochlorinated complex [$OsClC(C{\equiv}CCMe_3){=}CHCMe_3)({=}C{=}CHCMe_3)(PPh_3)_2$] and the trichlorocarbyne complex [$OsCl_3({\equiv}CCH_2CMe_3)(PPh_3)_2$].[7] The dehydrochlorinated complexes [$Os(C{\equiv}CSiMe_3)(C(C{\equiv}CSiMe_3){=}CHSiMe_3)({=}C{=}CHSiMe_3)(PPh_3)_2$] and [$OsCl(C(C{\equiv}CSiMe_3){=}CHSiMe_3)({=}C{=}CHSiMe_3)(PPh_3)_2$] were also produced in the reaction of [$OsCl_2(PPh_3)_3$] with $HC{\equiv}CSiMe_3$.[8] Thus it is reasonable to speculate that dehydrochlorination might also occur in the reaction of [$OsCl_2(PPh_3)_3$] with $HC{\equiv}CC(OH)Ph_2$, although we could not isolate the dehydrochlorinated products from the reaction. The low yields of complexes **3** and **4** can be related to the formation of dehydrochlorinated species. As mentioned previously, the reaction of [$OsCl_2(PPh_3)_3$] with $HC{\equiv}CC(OH)Ph_2$ also led to the formation of an organic compound, which is tentatively formulated as $CPh_2{=}C{=}CHC{\equiv}CC(OH)Ph_2$. This compound could be generated by acetylide-allenylidene coupling through the intermediate [$OsCl(C{\equiv}CC(OH)Ph_2)({=}C{=}C{=}CPh_2)(PPh_3)_2$].

Reaction of [$OsCl_2(PPh_3)_3$] with $HC{\equiv}CC(OH)Ph_2$ in the Presence of Acids. To prove that formation of the trichlorovinylcarbyne complexes **3a** and **3b** is related to the presence of acid, we have carried out the reaction of [$OsCl_2(PPh_3)_3$] with $HC{\equiv}CC(OH)Ph_2$ in the presence of HCl. Indeed, treatment of [$OsCl_2(PPh_3)_3$] with $HC{\equiv}CC(OH)Ph_2$ in the presence of HCl resulted in the formation of a mixture of *fac*- and *mer*-trichlorovinylcarbyne isomers **3a** and **3b** as the only products (Scheme 3). Interestingly, reaction of [$OsCl_2(PPh_3)_3$] with $HC{\equiv}CCMe_3$ in the presence of HCl produces only *mer*-[$OsCl_3({\equiv}CCH_2CMe_3)(PPh_3)_2$].[7]

When the reaction was carried out with DCl (99% D, 20 wt % in D_2O solution), the isolated carbyne complexes have ca. 30% deuterium incorporated at the vinyl group of **3a** and **3b**, as indicated by the ^1H and ^2H NMR spectra. The results suggest that formation of the vinylcarbyne complexes **3a** and **3b** may involve both electrophilic abstraction of the OH group of the hydroxyvinylidene intermediate [$OsCl_2({=}C{=}CHC(OH)Ph_2)(PPh_3)_2$] (**A**) and protonation of the allenylidene intermediate [$OsCl_2({=}C{=}C{=}CPh_2)(PPh_3)_2$] (**B**), with the former being favored.

Scheme 3

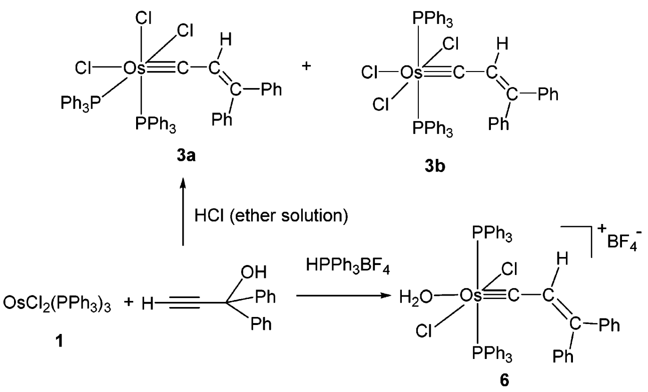

Table 5. Selected Bond Lengths and Bond Angles for [$OsCl_2({\equiv}C{-}CH{=}CPh_2)(H_2O)(PPh_3)_2]BF_4{\cdot}CH_2Cl_2$ ($6{\cdot}CH_2Cl_2$)

Bond Distances (Å)			
Os(1)−P(1)	2.4387(18)	Os(1)−P(2)	2.4447(18)
Os(1)−Cl(1)	2.3626(19)	Os(1)−Cl(2)	2.3516(17)
Os(1)−C(1)	1.735(6)	Os(1)−O(1)	2.209(5)
C(1)−C(2)	1.420(9)	C(2)−C(3)	1.348(10)
C(3)−C(11)	1.482(9)	C(3)−C(21)	1.474(9)
Bond Angles (deg)			
P(1)−Os(1)−P(2)	174.32(6)	Cl(2)−Os(1)−Cl(1)	158.51(7)
C(1)−Os(1)−O(1)	178.9(3)	C(2)−C(1)−Os(1)	172.4(6)
C(1)−Os(1)−P(1)	92.8(2)	C(1)−Os(1)−P(2)	91.8(2)
C(1)−Os(1)−Cl(1)	100.1(2)	C(1)−Os(1)−Cl(2)	101.3(2)
O(1)−Os(1)−P(1)	86.59(13)	O(1)−Os(1)−P(2)	88.79(13)
O(1)−Os(1)−Cl(1)	78.97(15)	O(1)−Os(1)−Cl(2)	79.62(15)
Cl(1)−Os(1)−P(1)	88.60(6)	Cl(1)−Os(1)−P(2)	87.26(7)
Cl(2)−Os(1)−P(1)	91.98(6)	Cl(2)−Os(1)−P(2)	90.45(6)
C(3)−C(2)−C(1)	126.8(7)	C(2)−C(3)−C(11)	118.3(6)
C(2)−C(3)−C(21)	123.1(7)	C(21)−C(3)−C(11)	118.6(6)

Even the weak acid $HPPh_3BF_4$ promotes the formation of carbyne complexes. Thus treatment of [$OsCl_2(PPh_3)_3$] with $HC{\equiv}CC(OH)Ph_2$ in the presence of $HPPh_3BF_4$ produced the aqua carbyne complex [$OsCl_2({\equiv}CCH{=}CPh_2)(H_2O)(PPh_3)_2]BF_4$ (**6**).

Complex **6** has been characterized by elemental analyses and NMR spectroscopy as well as X-ray diffraction study. The crystallographic details and selected bond distances and angles are given in Tables 1 and 5, respectively. A view of the molecular geometry of **6** is shown in Figure 5. The osmium center in **6** has a distorted octahedral geometry with two *trans* PPh_3 ligands. The vinylcarbyne ligand is *tran*s to the coordinated water molecule (C(1)−Os−O(1) = 178.9(3)°), while the two Cl atoms are also mutually *trans*-disposed, bending toward the water molecule (Cl(1)−Os−Cl(2) = 158.51(7)°). The short Os−C(1) bond distance (1.735(6) Å) and the Os−C(1)−C(2) bond angle (172.4(6)°) in **5** are fully consistent with carbyne character,[19,20,25−29] which are comparable to those in complexes **3a** and **3b** (1.750(4) Å and 168.6(3)° in **3a**, 1.750(3) Å and 168.4(2)° in **3b**). The C(1)−C(2) and C(2)−C(3) bond distances (1.420(9) and 1.348(10) Å, respectively) are in the expected range for vinylcarbyne formulation. One of the hydrogen atoms of the coordinated water molecule is

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[37] Bianchini, C.; Peruzzini, M.; Zanobini, F.; Lopez, C.; de los Rios, I.; Romerosa, A. *Chem. Commun.* **1999**, 443.

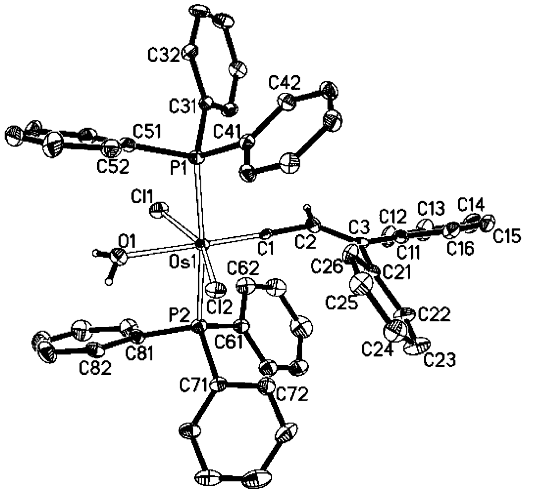

Figure 5. Molecular structure of the cation of [$OsCl_2$-($\equiv$C$-$CH$=$$CPh_2$)($H_2O$)($(PPh_3)_2$]$BF_4$ (**5**).

hydrogen bonded to one of the F atoms of the BF_4^- counteranion (O(1)$\cdots$F(1) = 2.677(8) Å, O(1)$-$H(1A)$\cdots$F(1) = 164.4°). Hydrogen bonding between coordinated water and uncomplexed BF_4^- anion has been reported previously for other complexes.[38]

The solution NMR spectroscopic data are consistent with the coordination sphere of **6** as determined by the X-ray diffraction study. In particular, the ^{1}H NMR spectrum (in CD_2Cl_2) displayed a triplet at 5.07 ppm (J(PH) = 1.5 Hz) assignable to the vinyl proton C*H*$=$$CPh_2$. The $^{13}C\{^1H\}$ NMR spectrum (in CD_2Cl_2) showed a triplet at 281.0 ppm for Os$\equiv$*C* (J(PC) = 10.4 Hz) and two singlets at 168.6 and 131.8 ppm for the vinyl carbons CH$=$*C*Ph_2 and *C*H$=$$CPh_2$, respectively. The $^{31}P\{^1H\}$ NMR spectrum displayed only a singlet at 0.2 ppm. The hydrogen bonding is apparently broken in solution, as the ^{19}F NMR spectrum of **6** in CD_2Cl_2 showed only a singlet at $-$153.0 ppm for the BF_4^- counteranion. The closely related osmium aqua-carbyne complex [$OsCl_2$($\equiv$$CC_6H_4NMe_2$)($H_2O$)$(PPh_3)_2$]$^+$ was reported by Roper in 1983.[31]

The allenylidene complex [$OsCl_2$($=$C$=$C$=$$CPh_2$)$(PPh_3)_2$] was previously reported to be isolated in 98% yield from the reaction of [$OsCl_2(PPh_3)_3$] with HC$\equiv$CC(OH)Ph_2. In our study, however, the allenylidene complex could not be obtained. Instead, we have isolated several new osmium complexes including the dinuclear complex [$(PPh_3)_2$ClOs(μ-Cl)$_3$Os($=$C$=$CHC(OH)Ph_2)$(PPh_3)_2$], trichlorovinylcarbyne complexes *fac*-[$OsCl_3$($\equiv$C$-$CH$=$$CPh_2$)$(PPh_3)_2$] and *mer*-[$OsCl_3$($\equiv$C$-CH=$$CPh_2$)$(PPh_3)_2$], and the carbonyl-containing allenylidene complex [$OsCl_2$($=$C$=$C$=$$CPh_2$)(CO)$(PPh_3)_2$].

Experimental Section

All manipulations were carried out under a nitrogen atmosphere using standard Schlenck techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, ether, THF), sodium (benzene), or calcium hydride (CH_2Cl_2). The starting materials [$OsCl_2(PPh_3)_3$][39] and HC$\equiv$CC(OH)Ph_2[40] were prepared according to the literature methods. All other reagents were used as purchased from Aldrich Chemical Co.

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

[$(PPh_3)_2$ClOs(μ-Cl)$_3$Os($=$C$=$CHC(OH)Ph_2)$(PPh_3)_2$] (2). A mixture of [$OsCl_2(PPh_3)_3$] (0.50 g, 0.48 mmol) and HC$\equiv$CC(OH)Ph_2 (0.12 g, 0.58 mmol) in benzene (10 mL) was stirred at room temperature for 20 min. The volume of the reaction mixture was reduced to ca. 1 mL. Addition of ether (30 mL) to the residue gave a green precipitate and a brown solution, which were separated by filtration. The green precipitate was identified to be the starting material [$OsCl_2(PPh_3)_3$], which was washed with ether (2 × 10 mL) and dried under vacuum (0.36 g). The ether washing solution and the brown filtrate were collected together, and the volume was reduced to half. The solution was stored at RT overnight to give a brownish-yellow microcrystalline solid, which was collected by filtration, washed with ether (2 × 5 mL), and dried under vacuum. Yield: 46 mg, 11%. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ $-$4.2 (d, J(PP) = 8.6 Hz), $-$11.4 (d, J(PP) = 8.6 Hz), $-$19.7 (d, J(PP) = 16.7 Hz), $-$21.1 (d, J(PP) = 16.7 Hz). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 0.71 (br, 1 H, Os$=$C$=$C*H*), 2.37 (br, 1 H, disappeared when treated with D_2O, C(O*H*)Ph_2), 6.70$-$7.66 (m, 70 H, C_6H_5, PPh_3). Anal. Calcd for $C_{87}H_{72}Cl_4P_4OOs_2$: C, 58.72; H, 4.08. Found: C, 58.90; H, 4.14.

***fac*-[$OsCl_3$($\equiv$C$-$CH$=$$CPh_2$)$(PPh_3)_2$] (3a) and *mer*-[$OsCl_3$($\equiv$C$-CH=$$CPh_2$)$(PPh_3)_2$] (3b) from the Reaction of [$OsCl_2(PPh_3)_3$] with 1,1-Diphenylpropyn-1-ol at RT.** A solution of [$OsCl_2(PPh_3)_3$] (0.50 g, 0.48 mmol) and 1,1-diphenylpropyn-1-ol (0.40 g, 1.9 mmol) in benzene (10 mL) was stirred for 30 min and then allowed to stand at room temperature for 30 h to give a brownish solution and a small amount of brown precipitate, which were separated by filtration. The brown microcrystalline solid was washed with ether (2 × 3 mL), dried under vacuum, and identified to be **3a**. Yield: 10 mg, 2%. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ $-$14.6 (s). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 3.10 (t, J(PH) = 3.5 Hz, 1 H, C*H*$=$$CPh_2$), 6.71$-$8.03 (m, 40 H, C_6H_5, PPh_3). $^{13}C\{^1H\}$ NMR (100.4 MHz, CD_2Cl_2): δ 267.4 (t, J(PC) = 15.7 Hz, Os$\equiv$*C*), 167.3 (s, CH$=$*C*Ph_2), 131.7 (s, *C*H$=$$CPh_2$), 139.3$-$127.8 (m, PPh_3, C_6H_5). Anal. Calcd for $C_{51}H_{41}Cl_3P_2Os$: C, 60.51; H, 4.08. Found: C, 60.90; H, 4.54. FAB-MS (NBA, *m/z*): 977.1 ([M $-$ Cl]$^+$). The filtrate obtained above was concentrated to ca. 1 mL, and hexane (30 mL) was added slowly with stirring to give a brown precipitate, which was filtered, washed with ether (2 × 10 mL) and hexane (2 × 15 mL), and subsequently dried under vacuum. Recrystallization of the crude product in 1 mL of benzene provided green crystals of **3b**, which were collected by filtration, washed with ether (5 mL), and dried under vacuum overnight. Yield: 43 mg, 9%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ $-$16.1 (s). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 4.25 (t, J(PH) = 2.2 Hz, 1 H, C*H*$=$$CPh_2$), 7.08$-$7.88 (m, 40 H, C_6H_5, PPh_3). $^{13}C\{^1H\}$ NMR (100.4 MHz, CD_2Cl_2): δ 266.3 (t, J(PC) = 11.4 Hz, Os$\equiv$*C*), 163.1 (s, CH$=$*C*Ph_2), 131.8 (s, *C*H$=$$CPh_2$), 139.4$-$127.4 (m, PPh_3, C_6H_5). Anal. Calcd for $C_{51}H_{41}Cl_3P_2Os$: C, 60.51; H, 4.08. Found: C, 60.35; H, 4.18. FAB-MS (NBA, *m/z*): 977.1 ([M $-$ Cl]$^+$).

***mer*-[$OsCl_3$($\equiv$C$-$CH$=$$CPh_2$)$(PPh_3)_2$] (3b) and [$OsCl_2$(CO)($=C=C=$$CPh_2$)$(PPh_3)_2$] (4) from the Reaction of [$OsCl_2(PPh_3)_3$] with 1,1-Diphenylpropyn-1-ol in Reflux-**

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[38] See for example: (a) Funaioli, T.; Cavazza, C.; Marchetti, F.; Fachinetti, G. *Inorg. Chem.* **1999**, *38*, 3361. (b) Leung, W. H.; Chan, E. Y. Y.; Wong, W. T. *Inorg. Chem.* **1999**, *38*, 136. (c) Sanford, M. S.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 5384. (d) Mui, H. D.; Brumaghim, J. L.; Gross, C. L.; Girolami, G. S. *Organometallics* **1999**, *18*, 3264.

[39] Hoffmann, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221.

[40] Jones, E. R. H.; Lee, H. H.; Whiting, M. C. *J. Chem. Soc.* **1960**, 3483.

ing Toluene. A mixture of [OsCl$_2$(PPh$_3$)$_3$] (0.60 g, 0.57 mmol) and 1,1-diphenylpropyn-1-ol (0.27 g, 1.3 mmol) in toluene (60 mL) was refluxed for 3 h to give a brownish-red solution. The solvent was removed under vacuum, and the resulting oil was dissolved in CH$_2$Cl$_2$ (2 mL). Addition of hexane (50 mL) to the residue gave a brown precipitate, which was collected by filtration, washed with hexane (2 × 20 mL), and dried under vacuum (0.51 g). The brown filtrate and the washing solution were also collected and evaporated to dryness under vacuum to give a brownish oil, which was extracted with 20 mL of hexane and filtered. The hexane extractant was reduced to ca. 2 mL and then passed through a silica gel column using hexane as the eluting solvent. The light yellow first eluant was collected. Removal of the solvent gave a drop of light yellow oil, which was identified to be CH$_2$=CPh$_2$ (**5**). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 5.59 (s, 2 H, CH$_2$), 7.43−7.49 (m, 10 H, Ph). FAB-MS (NBA, *m*/*z*): 180.1 (M$^+$). The brown solid obtained above was transferred to a Schlenk tube and treated with 2 mL of benzene. The solution was allowed to stand at room temperature for 1 day to give **3b** as a green microcrystalline solid, which was separated from the mother liquid, washed with ether (2 mL), and dried under vacuum overnight. Yield: 0.13 g, 23%. The mother liquid and the ether washing solution were collected together and dried under vacuum. The residue was extracted with 2 mL of benzene and passed through a silica gel column (1.5 × 20 cm). Elution with benzene gave a mixture of CH$_2$=CPh$_2$ (**5**) and CPh$_2$=C=CH−C≡C−C(OH)Ph$_2$. Spectroscopic data for CPh$_2$=C=CH−C≡C−C(OH)-Ph$_2$ are as follows. ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ 6.11 (s, 1 H, =CH), 7.04−7.66 (m, 20 H, Ph). FAB-MS (NBA, *m*/*z*): 398 (M$^+$). After the column was further flushed with benzene to wash away the yellow polymers and oligomers, CH$_2$Cl$_2$ was used to elute **4** as a brick-red solution. The solvent was removed completely to give a brownish-red solid. Yield: 0.089 g, 16%. An analytically pure sample of **4** can be obtained by recrystllization from CH$_2$Cl$_2$/hexane. ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ −12.4(s). ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ 6.96−7.12 (m, 22 H, *m*-C$_6$H$_5$, PPh$_3$), 7.48 (t, *J*(HH) = 7.4 Hz, 2 H, *p*-C$_6$H$_5$), 7.76 (d, *J*(HH) = 7.7 Hz, 2 H, *o*-C$_6$H$_5$), 8.35 (m, 12 H, PPh$_3$). ^{13}C{^{1}H} NMR (100.4 MHz, CD$_2$Cl$_2$): δ 278.0 (t, *J*(PC) = 8.9 Hz, Os=*C*), 208.1 (s, Os=C=*C*), 173.4 (t, *J*(PC) = 8.2 Hz, Os−*C*O), 156.3 (s, Os=C=C=*C*), 146.8−128.0 (m, PPh$_3$, C$_6$H$_5$). Anal. Calcd for C$_{52}$H$_{40}$Cl$_2$OP$_2$Os: C, 62.21; H, 4.02. Found: C, 62.26; H, 4.17. After the brick-red complex **4** was eluted, the column was washed with CH$_2$Cl$_2$/ether to give a brownish-green solution, followed by removal of solvent and recrystallization from benzene to give additional green complex **3b** (23 mg, total yield 27%).

Reaction of [OsCl$_2$(PPh$_3$)$_3$] with 1,1-Diphenylpropyn-1-ol in the Presence of HCl. To a solution of [OsCl$_2$(PPh$_3$)$_3$] (0.50 g, 0.48 mmol) and 1,1-diphenylpropyn-1-ol (0.30 g, 1.4 mmol) in CH$_2$Cl$_2$ (15 mL) was added HCl·OEt$_2$ (1.50 mL, 1.5 mmol, 1.0 M in ether solution). The reaction mixture was stirred at room temperature for 8 h to give a brownish-green solution. The volume of the solution was reduced to ca. 1 mL, and benzene (20 mL) was added slowly with stirring to give a yellowish-green microcrystalline solid. The mixture was stirred for 20 min, and the solid was collected by filtration, washed with ether (2 × 20 mL), and dried under vacuum overnight; it was identified to be **3a**. Yield: 78 mg, 16%. The filtrate was concentrated to ∼3 mL, and ether (30 mL) was added slowly with stirring to give a green precipitate, which was collected by filtration, washed with ether (2 × 20 mL), and dried under vacuum overnight. The solid was identified to be **3b**. Yield: 0.22 g, 45%.

[OsCl$_2$(≡C−CH=CPh$_2$)(H$_2$O)(PPh$_3$)$_2$]BF$_4$ (6). A mixture of [OsCl$_2$(PPh$_3$)$_3$] (0.50 g, 0.48 mmol), 1,1-diphenylpropyn-1-ol (0.21 g, 0.96 mmol), and HPPh$_3$BF$_4$ (0.44 g, 1.26 mmol) in CH$_2$Cl$_2$ (15 mL) and benzene (10 mL) was stirred for 8 h to give a green precipitate. The volume of the solution was reduced to one-half. The green solid was collected by filtration, washed with ether (3 × 30 mL), and dried under vacuum overnight. Yield: 0.31 g, 59%. ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$): δ 0.2 (s). ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$): δ 5.07 (t, *J*(PH) = 1.5 Hz, 1 H, C*H*=CPh$_2$), 6.80−7.69 (m, 40 H, C$_6$H$_5$, PPh$_3$). ^{13}C{^{1}H} NMR (100.4 MHz, CD$_2$Cl$_2$): δ 281.0 (t, *J*(PC) = 10.4 Hz, Os≡*C*), 168.6 (s, CH=*C*Ph$_2$), 131.8 (s, *C*H=CPh$_2$), 138.6−127.6 (m, PPh$_3$, C$_6$H$_5$). ^{19}F NMR (282.4 MHz CD$_2$Cl$_2$): δ −153.0 (s). IR (KBr, cm^{-1}): ν(OH) 3500 (m), ν(BF) 1086 (s). Anal. Calcd for C$_{51}$H$_{43}$BCl$_2$F$_4$OP$_2$Os: C, 56.63; H, 4.01. Found: C, 56.74; H, 4.40.

Crystal Structure Analyses. Crystals suitable for X-ray diffraction were grown from CH$_2$Cl$_2$ solutions of **2**, **3a**, **3b**, **4**, and **6** layered with hexane. Data collections were performed on a Bruker SMART CCD area detector for **2**, **3a**, and **4** and on a Bruker Apex CCD area detector for **3b** and **6**, by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Empirical absorption corrections (SADABS)[41] were applied. All structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full matrix least-squares on F^2 using the Bruker SHELXTL (Version 5.10)[42] program package. All non-hydrogen atoms were refined anisotropically. The solvating CH$_2$Cl$_2$ molecules in **2** and one of the CH$_2$Cl$_2$ solvent molecules in **3b** are disordered and were refined with suitable restraints. The H atom of the OH group in **2** and those of the coordinated water molecule in **6** were located from the difference Fourier maps and constrained to ride on the respective O atom. The remaining hydrogen atoms were introduced at their geometric positions and refined as riding atoms. Further details on crystal data, data collection, and refinements are summarized in Table 1.

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

Supporting Information Available: Tables of bond distances and angles, atomic coordinates and equivalent isotropic displace coefficients, and anisotropic displacement coefficients for [(PPh$_3$)$_2$ClOs(μ-Cl)$_3$Os(=C=CHC(OH)Ph$_2$)-(PPh$_3$)$_2$] (**2**), *fac*-[OsCl$_3$(≡C−CH=CPh$_2$)(PPh$_3$)$_2$] (**3a**), *mer*-[OsCl$_3$(≡C−CH=CPh$_2$)(PPh$_3$)$_2$] (**3b**), [OsCl$_2$(=C=C=CPh$_2$)-(CO)(PPh$_3$)$_2$] (**4**), and [OsCl$_2$(≡C−CH=CPh$_2$)(H$_2$O)(PPh$_3$)$_2$]BF$_4$ (**6**). This material is available free of charge via the Internet at http://pubs.acs.org.

OM034082M

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(41) Sheldrick G. M. *SADABS*, Empirical Absorption Correction Program; University of Göttingen: Germany, 1996.

(42) Bruker. *SHELXTL Reference Manual* (Version 5.1); Bruker Analytical X-Ray Systems Inc.: Madison, WI, 1997.