Synthesis and Characterization of $[OsCl_2(=C=CHR)(PPh_3)_2]$ and Related Complexes

Ting Bin Wen,[a] Wai Yiu Hung,[a] Zhong Yuan Zhou,[b] Man Fung Lo,[a] Ian D. Williams,[a] and Guochen Jia*[a]

Keywords: Carbyne ligands / Osmium / Vinylidene ligands

Treatment of $[OsCl_2(PPh_3)_3]$ with $HC{\equiv}CR$ (R = Ph, *p*-tolyl, CMe_3) in the presence of HCl gives the corresponding trichloro(carbyne) complexes $[OsCl_3({\equiv}CCH_2R)(PPh_3)_2]$ in good yields. The vinylidene complexes $[OsCl_2(=C=CHR)(PPh_3)_2]$ (R = Ph, *p*-tolyl, CMe_3) are, in turn, prepared from the reactions of the carbyne complexes $[OsCl_3({\equiv}CCH_2R)(PPh_3)_2]$ with NEt_3. These new vinylidene complexes are hygroscopic and react with H_2O to give (aqua)(vinylidene) complexes $[OsCl_2(H_2O)(=C=CHR)(PPh_3)_2]$. The structures of several of these new complexes have been determined by X-ray diffraction studies.

Introduction

(Vinylidene)ruthenium complexes[1] of the type $[RuCl_2(=C=CHR)(PR'_3)_2]$ have attracted attention because they are catalytically active for olefin metathesis,[2a−2c] dimerization and carboxylation of terminal alkynes,[2d] and they can be used as precursors to other vinylidene complexes.[2d,2e] A number of such complexes have been prepared from the reactions of $HC{\equiv}CR$ with dichlororuthenium complexes such as $[RuCl_2(PPh_3)_3]$,[3,4] $[RuCl_2H_2(PR'_3)_2]$ (R′ = Cy, *i*Pr),[5] $[RuCl_2(PiPr_3)_2]_n$,[6] $[RuCl_2(MeCN)_2(PiPr_3)_2]$,[6] $[RuCl_2(p\text{-cymene})]_2/PR'_3$[6] and $[\{RuCl_2(TPPMS)_2\}Na_2]_2{\cdot}4H_2O$ [TPPMS = $Ph_2P(2\text{-}OSO_2C_6H_4)Na$][7] or from the reaction of $[RuCl_2(=CHPh)(PCy_3)_2]$ with 1,2-propadiene.[2a]

In contrast to ruthenium, the chemistry of related (vinylidene)osmium complexes of the type $[OsCl_2(=C=CHR)(PR'_3)_2]$ is still underdeveloped, despite the fact that a large number of other (vinylidene)osmium complexes have been prepared.[8−21] To the best our knowledge, only $[OsCl_2(=C=CHPh)(PiPr_3)_2]$, which was produced by elimination of the imine ligands from the (imine)(vinylidene) complexes $[OsCl_2(=C=CHPh)(NH=CR_2)(PiPr_3)_2]$ [CR_2 = CMe_2, $C(CH_2)_5$] in refluxing toluene, has been reported by Esteruelas and co-workers.[13]

Prompted by the facile preparation of the (vinylidene)ruthenium complex $[RuCl_2(=C=CHCMe_3)(PPh_3)_2]$ from the reaction of $HC{\equiv}CCMe_3$ with $[RuCl_2(PPh_3)_3]$, we have attempted to prepare analogous (vinylidene)osmium complexes $[OsCl_2(=C=CHR)(PPh_3)_2]$ from the reactions of $[OsCl_2(PPh_3)_3]$ with $HC{\equiv}CR$. However, it was found that the expected vinylidene complexes $[OsCl_2(=C=CHR)(PPh_3)_2]$ could not be isolated from the reactions of $[OsCl_2(PPh_3)_3]$ with $HC{\equiv}CR$ (R = CMe_3,[22] $SiMe_3$ [23]). Instead, the reactions afford a series of complexes including 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, $C{\equiv}CR$).[22,23] It was suggested that these complexes are formed via vinylidene intermediates $[OsCl_2(=C=CHR)(PPh_3)_2]$, although attempts to isolate them from the reactions failed. In this report, we will show that the vinylidene complexes $[OsCl_2(=C=CHR)(PPh_3)_2]$ can be obtained from the deprotonation reactions of (carbyne)osmium complexes $[OsCl_3({\equiv}CCH_2R)(PPh_3)_2]$.

Results and Discussion

Preparation of Carbyne Complexes $[OsCl_3({\equiv}CCH_2R)(PPh_3)_2]$

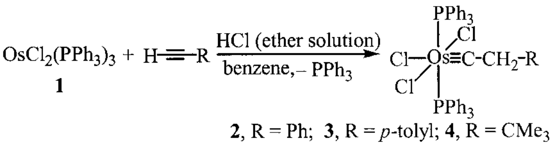
We have previously shown that the carbyne complexes $[OsCl_3({\equiv}CCH_2CMe_3)(PPh_3)_2]$ (**4**) and $[OsCl_3({\equiv}CCH_3)(PPh_3)_2]$ (**5**) are formed as one of the products from the reaction of $[OsCl_2(PPh_3)_3]$ (**1**) with $HC{\equiv}CCMe_3$ and $HC{\equiv}CSiMe_3$, respectively.[22,23] It was suspected that the carbyne complexes were produced by protonation of the vinylidene intermediates $[OsCl_2(=C=CHR)(PPh_3)_2]$ with HCl generated in situ. Thus, it was expected that carbyne

---

[a] Department of Chemistry and Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong, P. R. China
[b] Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University,
Kowloon, Hong Kong, P. R. China

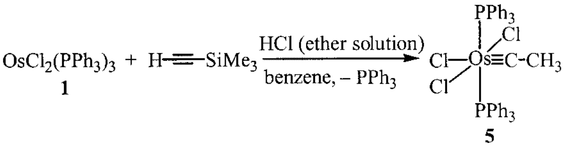
DOI: 10.1002/ejic.200400003

complexes $[OsCl_3(\equiv CCH_2R)(PPh_3)_2]$ might be readily prepared from the reaction of $[OsCl_2(PPh_3)_3]$ (**1**) with $HC\equiv CR$ in the presence of HCl. Indeed, treatment of $[OsCl_2(PPh_3)_3]$ (**1**) with $HC\equiv CR$ (R = Ph, *p*-tolyl, CMe_3) and HCl gave exclusively the corresponding (carbyne)trichloro complexes $[OsCl_3(\equiv CCH_2R)(PPh_3)_2]$ (**2−4**) in good yields [Equation (1)].



(1)

The analogous reaction of **1** with $HC\equiv CSiMe_3$ in the presence of HCl led to the known desilylated (carbyne)trichloro complex $[OsCl_3(\equiv CCH_3)(PPh_3)_2]$ (**5**), which was isolated as a yellow solid in 71% yield [Equation (2)]. It is assumed that reaction of **1** with $HC\equiv CSiMe_3$ initially generates the vinylidene intermediate $[OsCl_2(=C=CHSiMe_3)(PPh_3)_2]$, which reacts with HCl to give the (carbyne)trichloro complex $[OsCl_3(\equiv CCH_2SiMe_3)(PPh_3)_2]$. Desilylation of the later carbyne complex by electrophilic reagents (e.g. HCl or H_2O) produces the carbyne complex **5**. There are many reports on the cleavage of Si−C bonds by H_2O or acids to give C−H bonds.[24−27]



(2)

The new complexes **2** and **3** were characterized by multinuclear NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra (in $CDCl_3$) of complexes **2** and **3** display singlet ^{31}P signals at $\delta = -12.9$ and -12.1 ppm, respectively. The ^1H NMR spectra (in $CDCl_3$) display the $\equiv CCH_2$ proton signals at $\delta = 1.77$ (for **2**) and 1.72 ppm (for **3**). The $^{13}C\{^1H\}$ NMR spectra (in CD_2Cl_2) exhibit the resonances of the C-α atoms of the carbyne ligands as a triplet at $\delta = 278.2$ (**2**) and 280.1 ppm (**3**) and the signals of the CH_2 carbon atoms as a singlet at $\delta = 57.3$ (**2**) and 57.1 ppm (**3**). The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopic data suggest that the two PPh_3 ligands in **2** and **3** are *trans* to each other and that the carbyne ligand is *trans* to a chloro ligand.

The structure of **2** was confirmed by an X-ray diffraction study. A view of the molecular geometry of **2** is shown in Figure 1. Selected bond lengths and angles are given in Table 1. Similarly to **4**,[22] the geometry around the osmium atom in **2** can be viewed as a distorted octahedron with two PPh_3 ligands at the axial positions and the three chlorides and the carbyne ligand in the equatorial plane. The Os−C(1)−C(2) unit in **2** is almost linear with a bond angle of 174.8(3)°. The Os−C(carbyne) bond length in **2** [1.734(3) Å] is nearly identical to that in **4** [1.728(3) Å],[22] and is within the range of those reported previously for other (carbyne)osmium complexes.[10,16,18,22,24,25,27−34] As expected, the Os−Cl(1) bond [2.4621(8) Å] is significantly longer than the mutually *trans* bonds Os−Cl(2) [2.4105(7) Å] and

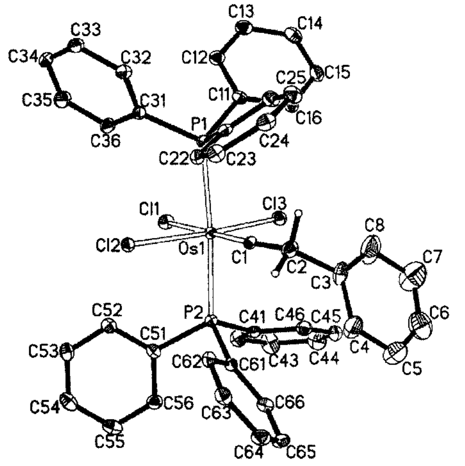


Figure 1. Molecular structure for $[OsCl_3(\equiv CCH_2Ph)(PPh_3)_2]$ (**2**)

Table 1. Selected bond lengths [Å] and bond angles [°] for $[OsCl_3(\equiv CCH_2Ph)(PPh_3)_2]\cdot 1.5C_6H_6$ ($\mathbf{2}\cdot 1.5C_6H_6$) and $[OsCl_3(\equiv CCH_3)(PPh_3)_2]\cdot CH_2Cl_2$ ($\mathbf{5}\cdot CH_2Cl_2$)

	2	5		2	5
Os(1)−C(1)	1.734(3)	1.724(5)	C(1)−C(2)	1.457(5)	1.434(7)
Os(1)−P(1)	2.4501(8)	2.4476(14)	Os(1)−P(2)	2.4339(8)	2.4426(14)
Os(1)−Cl(1)	2.4621(8)	2.4827(13)	Os(1)−Cl(2)	2.4105(7)	2.3845(13)
Os(1)−Cl(3)	2.3874(8)	2.4227(14)	C(2)−C(3)	1.515(5)	
P(2)−Os(1)−P(1)	175.83(3)	176.16(4)	Cl(3)−Os(1)−Cl(2)	170.77(3)	178.56(5)
C(1)−Os(1)−Cl(1)	173.84(10)	175.40(17)	C(2)−C(1)−Os(1)	174.8(3)	174.0(5)
P(1)−Os(1)−Cl(1)	92.46(3)	89.57(5)	P(2)−Os(1)−Cl(1)	84.71(3)	87.86(5)
Cl(2)−Os(1)−P(1)	86.72(3)	87.41(5)	Cl(2)−Os(1)−P(2)	90.16(3)	89.74(5)
Cl(3)−Os(1)−P(1)	92.21(3)	91.84(5)	Cl(3)−Os(1)−P(2)	90.43(3)	90.96(5)
Cl(2)−Os(1)−Cl(1)	88.81(3)	88.65(5)	Cl(3)−Os(1)−Cl(1)	82.07(3)	90.12(5)
C(1)−Os(1)−P(1)	89.87(10)	91.32(17)	C(1)−Os(1)−P(2)	93.26(10)	91.47(17)
C(1)−Os(1)−Cl(2)	97.02(10)	94.44(18)	C(1)−Os(1)−Cl(3)	92.14(10)	86.81(18)
C(1)−C(2)−C(3)	111.1(3)				

Os−Cl(3) [2.3874(8) Å], due to the strong *trans* influence of the carbyne ligand.

The structure of **5** has been previously assigned on the basis of NMR spectroscopic data.[23] Its structure was now also confirmed by an X-ray diffraction study. A view of the molecular geometry of **5** is shown in Figure 2. Selected bond lengths and angles are given in Table 1. Overall, the structural features of **5** are similar to those of **2** and **4**.

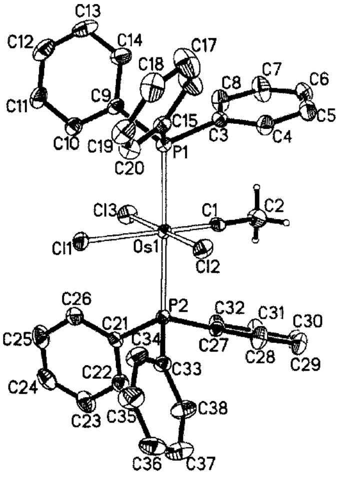
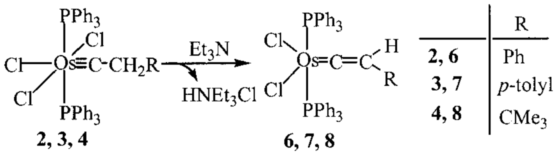


Figure 2. Molecular structure for [$OsCl_3(\equiv CCH_3)(PPh_3)_2$] (**5**)

The chemistry of (carbyne)osmium complexes has received considerable attention, especially in recent years.[8,10,13,15−19,20a,20c,20d,20e,21−25,28−38] Reported compounds closely related to **2−5** include [$OsCl_3(\equiv CPh)(PPh_3)_2$],[35] [$OsCl_2(SCN)(\equiv CC_6H_4NMe_2)(PPh_3)_2$],[35] [$OsHCl_2(\equiv CR')(PR_3)_2$] (R = Cy, *i*Pr),[19,24,25,36] [$OsHCl(OPh)(\equiv CMe)(P\textit{i}Pr_3)_2$],[19] and [$OsCl_2(\equiv C-CH=CRPh)[P(\textit{i}Pr)_2CH_2CO_2Me][P(\textit{i}Pr)_2CH_2CO_2)]$] (R = Ph, Me).[34] The analogous carbyne complex [$OsCl_3(\equiv CPh)(PPh_3)_2$] was previously obtained from the reaction of HCl with [$OsCl(\equiv CPh)(O_2CO)(PPh_3)_2$], which was in turn prepared from the reaction of [$OsCl(\equiv CPh)(CO)(PPh_3)_2$] with O_2.[35b] Thus, the reactions reported here represent a much simpler route to (carbyne)osmium complexes of the type [$OsX_3(\equiv CR')(PR_3)_2$] (X = halide).

Preparation of Vinylidene Complexes [$OsCl_2(=C=CHR)(PPh_3)_2$]

Deprotonation of (carbyne)metal complexes is one of the common routes to prepare vinylidene complexes. For example, deprotonation of [$CpOsH(\equiv CCH_2Ph)[P(\textit{i}Pr_3)]BF_4$, [$OsH(OAc)(\equiv CCH_3)(P\textit{i}Pr_3)_2]BF_4$, [$OsHCl_2(\equiv CCH_2Ph)(P\textit{i}Pr_3)_2$], and [$CpMn(\equiv CCH_3)(CO)_2]BCl_4$ produces the vinylidene complexes [$CpOsH(=C=CHPh)(P\textit{i}Pr_3)$],[17] [$OsH(OAc)(=C=CH_2)(P\textit{i}Pr_3)_2$],[21] [$OsHCl(=C=CHPh)(P\textit{i}Pr_3)_2$][37] and [$CpMn(=C=CH_2)(CO)_2$],[39] respectively. Thus, it was reasoned that the vinylidene complexes [$OsCl_2(=C=CHR)(PPh_3)_2$] might be obtained by treatment of the easily accessible (carbyne)trichloro complexes [$OsCl_3(=CCH_2R)(PPh_3)_2$] with bases. Indeed, the (carbyne)trichloro complexes **2−4** were readily deprotonated by NEt_3 to give the corresponding moisture-sensitive dichloro(vinylidene) complexes **6−8**, which can be isolated in good to excellent yields [Equation (3)].



(3)

Our attempt to isolate the vinylidene complex [$OsCl_2(=C=CH_2)(PPh_3)_2$] from the deprotonation reaction of the (carbyne)trichloro complex [$OsCl_3(\equiv CCH_3)(PPh_3)_2$] (**5**) failed, however. The in situ $^{31}P\{^1H\}$ NMR spectrum for the reaction of **5** with NEt_3 in CD_2Cl_2 also showed a new broad peak at $\delta \approx 3.7$ ppm, which is similar to those observed for the in situ reactions of [$OsCl_3(\equiv CCH_2R)(PPh_3)_2$] (R = Ph or *p*-tolyl, CMe_3) with NEt_3, indicative of the formation of the vinylidene complex [$OsCl_2(=C=CH_2)(PPh_3)_2$]. However, after workup with a procedure similar to that used for the isolation of **6−8**, the isolated solid showed the $^{31}P\{^1H\}$ NMR signal of **5** and several unidentified broad peaks. Apparently, the initially formed vinylidene complex decomposes during workup.

The solid-state structure of the vinylidene complex **8** was determined by an X-ray diffraction study. A view of the molecular geometry of **8** is shown in Figure 3. Selected bond lengths and angles are given in Table 2. The geometry around the osmium atom in **8** may be described as a distorted trigonal bipyramid with two PPh_3 ligands at the axial positions and the other three ligands in the equatorial plane. The deviation is reflected by the P(1)−Os−P(2) angle [168.13(2)°] (which is bent away from the vinylidene ligand) and the Cl(1)−Os−Cl(2) angle [149.31(2)°]. The Cl−Os−Cl angle is close to that calculated for the model complex [$OsCl_2(=C=CH_2)(PH_3)_2$] (146.9°)[40] and the X−M−X angles observed in the analogous compounds

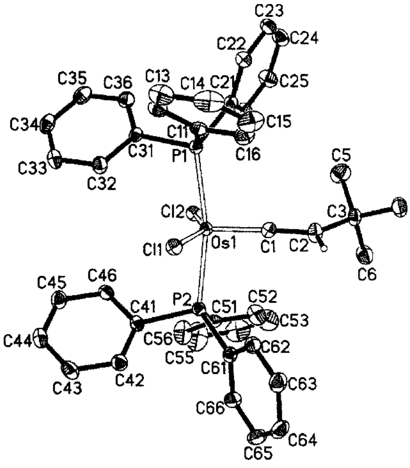


Figure 3. Molecular structure for [$OsCl_2(=C=CHCMe_3)(PPh_3)_2$] (**8**)

$[RuBr_2(=C=CHCMe_3)(PPh_3)_2]$ [144.81(7)°][3b] and $[RuCl_2(=C=C[Se(iPr)Ph](PPh_3)_2]$ [148.89(6)°].[41] The Cl−Ru−Cl angles in the vinylidene complexes $[RuCl_2(=C=CHPh)(PR_3)_2]$ [PR_3: PCy_3 = 158.31(7)°[5b]/156.93(2)°;[6] $PiPr_3$ = 158.63(4)°[6]] are significantly larger, however. The Os−C(1)−C(2) unit is nearly linear, with an Os−C(1)−C(2) angle of 175.5(2)° and Os−C(1) and C(1)−C(2) bond lengths of 1.796(3) and 1.320(4) Å, respectively, which compare well with those reported for other (vinylidene)osmium complexes.[8−16]

Table 2. Selected bond lengths [Å] and bond angles [°] for $[OsCl_2(=C=CHCMe_3)(PPh_3)_2]$ (**8**)

Os(1)−Cl(1)	2.3399(7)	Os(1)−Cl(2)	2.3457(6)
Os(1)−P(1)	2.3698(7)	Os(1)−P(2)	2.3690(7)
Os(1)−C(1)	1.796(3)	C(1)−C(2)	1.320(4)
C(2)−C(3)	1.521(4)		
P(1)−Os(1)−P(2)	168.13(2)	Cl(1)−Os(1)−Cl(2)	149.31(2)
C(1)−Os(1)−Cl(1)	103.28(8)	C(1)−Os(1)−Cl(2)	107.39(8)
Cl(1)−Os(1)−P(1)	88.22(2)	Cl(2)−Os(1)−P(1)	89.69(2)
Cl(1)−Os(1)−P(2)	87.27(2)	Cl(2)−Os(1)−P(2)	88.61(2)
C(1)−Os(1)−P(1)	96.15(9)	C(1)−Os(1)−P(2)	95.57(9)
C(2)−C(1)−Os(1)	175.5(2)	C(1)−C(2)−C(3)	129.1(3)

As mentioned previously, (vinylidene)osmium complexes with the general composition $[OsCl_2(=C=CHR)(PR_3)_2]$ are still very rare. Esteruelas et al. recently reported the vinylidene complex $[OsCl_2(=C=CHPh)(PiPr_3)_2]$, which was prepared by elimination of the imine ligands from the (imine)(vinylidene) complexes $[OsCl_2(=C=CHPh)(NH=CR_2)(PiPr_3)_2]$ [CR_2 = CMe_2, $C(CH_2)_5$] in a refluxing toluene solution.[13] As far as we know, complex **8** is the first structurally characterized osmium complex of this kind. Other reported five-coordinate (vinylidene)osmium complexes include $[OsHCl(=C=CHR)(PR'_3)_2]$ (PR'_3 = PCy_3, $PiPr_3$],[19,24,37,42] $[OsCl(=N=CR_2)(=C=CHPh)(PiPr_3)_2]$,[13] $[OsCl(=C=CHR)(2,6\text{-}[P(tBu)_2CH_2]_2C_6H_3)]$,[11] $[Os[C(C{\equiv}CR)=CHR)Cl(=C=CHR)(PPh_3)_2]$[22,23] and $[Os(CH=CHSiMe_3)Cl(=C=CHPh)(PiPr_3)_2]$.[43] These compounds adopt a Y-shaped geometry around the osmium atom.

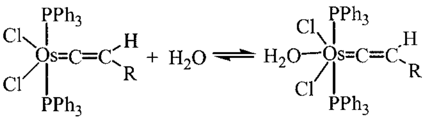
Consistent with the solid-state structure, a freshly prepared and vacuum-dried sample of **8** in freshly distilled dry CD_2Cl_2 at room temperature shows a singlet $^{31}P\{^1H\}$ signal at δ = 3.4 ppm. The ^1H NMR spectrum in CD_2Cl_2 exhibits a triplet at δ = 1.20 ppm with a P-H coupling constant of 3.6 Hz for the vinylidene =CH proton and the $^{13}C\{^1H\}$ NMR spectrum displays two triplets at δ = 274.1 ($J_{P,C}$ = 12.5 Hz) and 120.5 ppm ($J_{P,C}$ = 5.5 Hz), which are due to C-α and -β of the vinylidene ligand, respectively.

Complexes **6** and **7** presumably have similar structures, as indicated by their NMR spectroscopic data. Freshly prepared and vacuum-dried samples of **6** and **7** in freshly distilled CD_2Cl_2 at room temperature show the $^{31}P\{^1H\}$ signals at δ = 9.6 and 9.2 ppm, respectively. The ^1H NMR spectra exhibits triplets at δ = 2.56 and 2.46 ppm for the vinylidene =C*H* protons of **6** and **7**, respectively. The $^{13}C\{^1H\}$ NMR spectra displays C-α signals of the vinylidene ligands at δ = 280.8 and 281.0 ppm for **6** and **7**, respectively.

Preparation of (Aqua)(vinylidene) Complexes $[OsCl_2(H_2O)(=C=CHR)(PPh_3)_2]$

During the process of recording the $^{31}P\{^1H\}$ NMR spectra of the vinylidene complexes **6** and **7** with commercially available CD_2Cl_2, it was found that the chemical shifts of the signals of the vinylidene complexes changed with different batches of solvent and with time when a non-sealed NMR tube was used. It was suspected that this change might be caused by coordination of water present in solution to give the (aqua)(vinylidene) complexes $[OsCl_2(H_2O)(=C=CHR)(PPh_3)_2]$, which equilibrate with $[OsCl_2(=C=CHR)(PPh_3)_2]$. As a result of fast dissociation and association of water, only one ^{31}P signal with an average ^{31}P shift is observed at room temperature. Different amounts of water present in the solution will therefore affect the relative amounts of the five-coordinate vinylidene complexes and the corresponding six-coordinate (aqua)(vinylidene) complexes, therefore resulting in different ^{31}P chemical shifts in the NMR spectra. This speculation was confirmed by experiments. At low temperature, the $^{31}P\{^1H\}$ NMR spectra in commercial CD_2Cl_2 show two singlets. The chemical shift of one of the ^{31}P signals is close to that of $[OsCl_2(=C=CHAr)(PPh_3)_2]$ in freshly dried CD_2Cl_2. The other signal can therefore be attributed to $[OsCl_2(H_2O)(=C=CHR)(PPh_3)_2]$. Treatment of a blue solution of **6** or **7** in CD_2Cl_2 in an NMR tube with a drop of water gave an orange solution immediately, the $^{31}P\{^1H\}$ NMR spectra of which shows sharp singlets at δ ≈ −3.6 or −3.8 ppm, respectively. The chemical shifts are very close to those of the ^{31}P signals suspected for the (aqua)(vinylidene) complexes observed at low temperature. The possibility of isomerism arising from the rotation of the vinylidene group at low temperature can be excluded because such a rotation does not generate two different electronically favourable conformers.

The (aqua)(vinylidene) complexes $[OsCl_2(H_2O)(=C=CHPh)(PPh_3)_2]$ (**9**) and $[OsCl_2(H_2O)(=C=CH\text{-}p\text{-}tolyl)(PPh_3)_2]$ (**10**) were isolated as orange solids on a preparative scale by treatment of **6** and **7** with excess water [Equation (4)]. Orange solids of **9** and **10** were also obtained when blue solids of **6** and **7** were exposed to air for 18 h.



6, 7, 8 **9, 10, 11**

	R
6, 9	Ph
7, 10	*p*-tolyl
8, 11	CMe_3

(4)

The solid-state structure of **9** (Figure 4) was confirmed by an X-ray diffraction study. Selected bond lengths and angles are given in Table 3. The geometry around the osmium atom in **9** can be viewed as a distorted octahedron with two PPh_3 ligands *trans* to each other lying in the axial positions. The equatorial plane is formed by two chloro, the vinylidene and water ligands with the coordinated water molecule *trans* to the vinylidene ligand [O(1W)−Os−C(1) = 175.8(2)°]. The two mutually *trans*-disposed chloro ligands severely bend away from the vinylidene ligand and toward the water molecule with a Cl(1)−Os−Cl(2) angle of 158.56(5)° and Cl(1)−Os−O and Cl(2)−Os−O angles of 81.13(11)° and 77.53(11)°, respectively. These angles deviate greatly from the ideal value of 180° for a *trans* angle and 90° for a *cis* angle. The vinylidene ligand is bound to the metal atom in a nearly linear fashion with an Os−C(1)−C(2) angle of 174.7(6)°. The Os−C(1) [1.812(7) Å] and C(1)−C(2) [1.298(8) Å] bond lengths are similar to those of **8**, and compare well with those observed in other (vinylidene)osmium complexes.[8−16] The Os−O bond length is 2.289(4) Å, which is close to those in [$OsCl(=C=CHPh)(NH=CMe_2)(H_2O)(PiPr_3)_2$]OTf [2.281(6) Å],[14] [$OsCl(=CHPh)(H_2O)(CO)(PiPr_3)_2$]$BF_4$ [2.182(5) Å],[44a] [$OsMe(H_2O)(CO)_2(PMe_3)_2$]OTf [2.155(6) Å],[44b] [$Cp^*Os(\eta^3\text{-}C_4H_7)Me(H_2O)$]$BF_4$ [44c] [2.158(5) Å] and [$OsCl_2(H_2O)(\equiv CCH=CPh_2)(PPh_3)_2$]$BF_4$ [2.209(5) Å].[45]

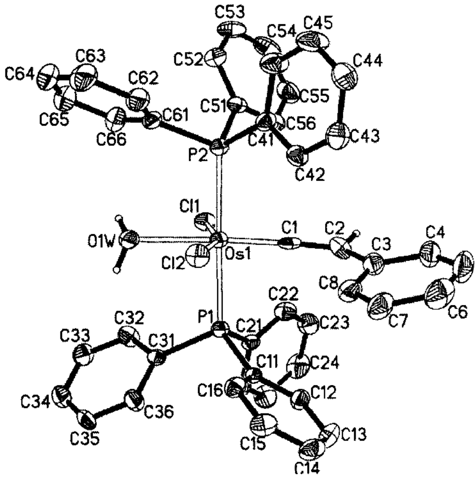


Figure 4. Molecular structure for [$OsCl_2(H_2O)(=C=CHPh)(PPh_3)_2$] (**9**)

Table 3. Selected bond lengths [Å] and angles [°] for [$OsCl_2(H_2O)(=C=CHPh)(PPh_3)_2$]·$C_6H_6$ (**9**·C_6H_6)

Os(1)−P(1)	2.3848(15)	Os(1)−P(2)	2.3959(15)
Os(1)−Cl(1)	2.3699(15)	Os(1)−Cl(2)	2.3886(14)
Os(1)−C(1)	1.812(7)	Os(1)−O(1 W)	2.289(4)
C(1)−C(2)	1.298(8)	C(2)−C(3)	1.479(9)
P(1)−Os(1)−P(2)	178.88(5)	Cl(1)−Os(1)−Cl(2)	158.56(5)
C(1)−Os(1)−O(1W)	175.8(2)	C(2)−C(1)−Os(1)	174.7(6)
C(1)−C(2)−C(3)	127.2(7)	O(1W)−Os(1)−P(1)	91.07(9)
O(1W)−Os(1)−Cl(1)	81.13(11)	O(1W)−Os(1)−Cl(2)	77.58(11)
C(1)−Os(1)−Cl(1)	102.54(18)	C(1)−Os(1)−Cl(2)	98.83(19)
C(1)−Os(1)−P(1)	87.08(16)	C(1)−Os(1)−P(2)	91.96(16)
Cl(1)−Os(1)−P(1)	88.84(5)	P(1)−Os(1)−Cl(2)	94.06(6)
Cl(1)−Os(1)−P(2)	90.83(6)	Cl(2)−Os(1)−P(2)	86.64(6)
O(1W)−Os(1)−P(2)	89.93(10)		

The water in **9** and **10** is only weakly bound to the metal center. Thus, when the orange solids of **9** or **10** are placed under vacuum for 3 h, the color changed to blue, indicating the reformation of **6** or **7**. Similarly, if the isolated orange solids of **9** or **10** are redissolved in CD_2Cl_2, the $^{31}P\{^1H\}$ NMR spectra at room temperature show a broad signal with a chemical shift significantly downfield from those observed in the presence of added water, indicating that water is partially dissociated and the equilibrium shown in Equation (4) occurs in solution. Thus, the NMR spectroscopic data of **9** and **10** have to be collected in the presence of added water. The $^{13}C\{^1H\}$ NMR spectrum of **9** in a CD_2Cl_2 solution saturated with H_2O shows the Os=C $^{13}C\{^1H\}$ signal as a triplet at δ = 289.1 ppm ($J_{P,C}$ = 11.4 Hz). The ^1H NMR signal of $=C=CH_2$ of **9** is observed at δ = 2.48 ppm at room temp. and at δ = 2.61 ppm at 211 K. The ^1H NMR signal of H_2O is observed at δ = 1.95 ppm at 211 K. The NMR spectroscopic data of **9** are consistent with the solid-state structure. Complex **10** presumably has a structure similar to that of **9**, as judged by its spectroscopic data.

As indicated by NMR experiments, complex **8** also reacts with water to give the (aqua)(vinylidene) complex [$OsCl_2(H_2O)(=C=CHCMe_3)(PPh_3)_2$] (**11**). Thus, the $^{31}P\{^1H\}$ NMR spectrum of a sample of **8** in commercially available CD_2Cl_2 at room temperature shows a singlet at δ = 2.8 ppm which is slightly upfield from that obtained with dry CD_2Cl_2. At 188 K, this singlet splits into two peaks at δ = 3.6 and −10.2 ppm, which can be attributed to [$OsCl_2(=C=CHCMe_3)(PPh_3)_2$] (**8**) and [$OsCl_2(H_2O)(=C=CHCMe_3)(PPh_3)_2$] (**11**), respectively. Similarly, the ^1H NMR spectrum in CD_2Cl_2 at room temperature shows one C=CH signal at δ = 1.17 ppm and at 188 K two C=CH signals at δ = 1.50 and 0.91 ppm, which can be assigned to **8** and **11**, respectively. The water proton signal appears as a broad peak at δ = 2.12 ppm at room temperature, which sharpens at low temperature with a similar chemical shift and gives a relative integration of 2:1 with the less-intense vinylidene signal of **11**. As further evidence for the formation of **11**, addition of a drop of water to a solution of **8** in commercial CD_2Cl_2 in an NMR tube causes the ^{31}P signal to shift from δ = 2.8 ppm to −5.8 ppm, and the ^1H signal of =CCH to shift from δ = 1.17 ppm to 0.91 ppm. The upfield shift of the ^{31}P signal is expected because the relative amount of **11** is increased when the concentration of water in the solution is increased. However, the ^{31}P shift cannot, even in the presence of excess water, reach the value of δ = −10.2 ppm observed for **11** at low temperature, suggesting that the equilibrium constant is small (see below).

During the process of the NMR study, it was found that these vinylidene species (**8** and **11**) are unstable in solution, especially in the presence of added water. The major decomposition product is the carbyne complex **4**. Other detectable decomposition species include a small amount of PPh_3 and others showing unidentified doublet and triplet signals. The decomposition is likely initiated by the protonation of the vinylidene ligand of **11** with water present in the solution. Owing to the instability and incomplete conversion of **8** to **11**, even in the presence of excess water, complex **11** could not be isolated.

NMR Study of the Equilibria

We carried out variable-temperature $^{31}P\{^1H\}$ and ^1H NMR experiments to study the dynamic process between $[OsCl_2(=C=CHR)(PPh_3)_2]$ and $[OsCl_2(H_2O)(=C=CHR)(PPh_3)_2]$. As an illustration, the $^{31}P\{^1H\}$ NMR spectra of a sample of **6** in wet CD_2Cl_2 (the Os/H_2O molar ratio in solution is 1:0.2) at different temperatures are shown in Figure 5. At room temperature (298 K), the ^{31}P signal is a singlet at δ = 9.1 ppm, which broadens and shifts upfield upon decreasing the temperature to 239 K. The upfield shift of the ^{31}P signal on lowering the temperature indicates that the equilibrium is shifted toward the formation of the (aqua)(vinylidene) complex **9** at lower temperature. The singlet separates into two peaks with unequal intensities when the temperature is lowered below 217 K. At 198 K, two sharp singlets in about a 5:1 ratio at δ = 11.6 and −3.4 ppm are observed, due to the ^{31}P signals of **6** and **9**, respectively. Similarly, in the ^1H NMR spectrum in CD_2Cl_2 at room temperature, the Os=C=CH vinylidene proton displays only one triplet at δ = 2.54 ppm with a P-H coupling constant of 3.3 Hz. This signal is somewhat broader when the temperature is lowered and at 190 K gives rise to two broad singlets (the broadening is probably due to unresolved coupling with the ^{31}P nuclei) at δ = 2.71 and 2.65 ppm in an approximate ratio of 5:1. The water proton signal at 190 K appears as a singlet at δ = 1.88 ppm with a relative integration of 2:1 with the less-intense vinylidene signal at δ = 2.65 ppm. The water content in the solution affects the appearance of the variable-temperature spectra. Thus, when a solution with an Os/H_2O molar ratio of 1:1.6 was used in the variable-temperature experiments, the NMR spectra show a singlet ^{31}P signal with a chemical shift between those of **6** and **9** at room temperature, as one might expect, but only show the signal of the (aqua)(vinylidene) complex **9**, while the signal of **6** cannot be detected, when the temperature is lowered below 255 K, due to the higher affinity of the metal center for H_2O at low temperature. The variable-temperature spectra of **7**/**10** and **8**/**11** show spectroscopic features similar to those of **6** and **8**.

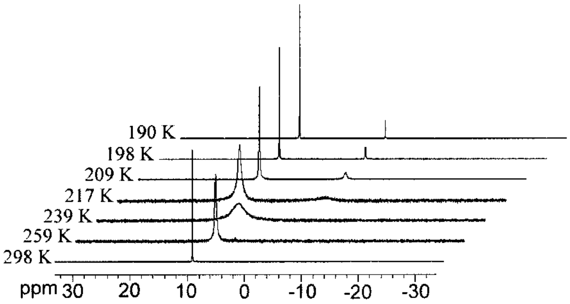


Figure 5. The variable-temperature $^{31}P\{^1H\}$ NMR spectra of $[OsCl_2(=C=CHPh)(PPh_3)_2]$ (**6**) and $[OsCl_2(H_2O)(=C=CHPh)(PPh_3)_2]$ (**9**) in wet CD_2Cl_2 (Os/H_2O molar ratio in solution = 1:0.2) at 121.5 MHz

The equilibrium constants at several temperatures (between 298 and 270 K) were estimated on the basis of variable-temperature $^{31}P\{^1H\}$ and ^1H NMR measurements of samples of **9**, **10** and **11** in CD_2Cl_2. The relative amounts of the five-coordinate vinylidene complexes and their corresponding (aqua)(vinylidene) complexes were calculated from the average ^{31}P chemical shifts assuming that the chemical shifts of five-coordinate vinylidene complexes and their corresponding (aqua)(vinylidene) complexes do not change with temperature.[46] The relative concentrations of coordinated and free water in the solution can be obtained from the integrals of the H_2O signals in the ^1H NMR spectra and the concentrations of the aqua complexes. The equilibrium constants at different temperatures calculated based

Table 4. Parameters for the equilibria between $[OsCl_2(=C=CHR)(PPh_3)_2]$ and $[OsCl_2(H_2O)(=C=CHR)(PPh_3)_2]$

$[OsCl_2(=C=CHPh)(PPh_3)_2] + H_2O \rightleftarrows [OsCl_2(H_2O)(=C=CHPh)(PPh_3)_2]$ (**9**)

T [K]	298	292	282	270
K[a]	202.7	312.6	788.9	3085
ln$K$	5.312	5.745	6.671	8.034
ΔG^0 [kcal·mol^{-1}]	−3.15	−3.33	−3.73	−4.30

$[OsCl_2\{=C=CH(p\text{-tolyl})\}(PPh_3)_2] + H_2O \rightleftarrows [OsCl_2(H_2O)\{=C=CH(p\text{-tolyl})\}(PPh_3)_2]$ (**10**)

T [K]	298	287	280	270
K[b]	172.1	506.9	1197	4684
ln$K$	5.148	6.228	7.087	8.452
ΔG^0 [kcal·mol^{-1}]	−3.05	−3.55	−3.94	−4.53

$[OsCl_2(=C=CHCMe_3)(PPh_3)_2] + H_2O \rightleftarrows [OsCl_2(H_2O)(=C=CHMe_3)(PPh_3)_2]$ (**11**)

T (K)	298	290	285	279	275
K[c]	15.51	35.22	69.37	172.8	416.4
ln$K$	2.741	3.562	4.239	5.152	6.032
ΔG^0 [kcal·mol^{-1}]	−1.62	−2.05	− 2.40	−2.86	−3.30

[a] The values were obtained with a CD_2Cl_2 solution having an Os/H_2O molar ratio of 1:1.6. [b] The values were obtained with a CD_2Cl_2 solution having an Os/H_2O molar ratio of 1:1. [c] The values were obtained with a CD_2Cl_2 solution having an Os/H_2O molar ratio of 1:0.4.

on these data are summarized in Table 4. A plot of ln$K$ against reciprocal absolute temperature gave a straight line. According to the equation ln$K = -(\Delta H^0/R)(1/T) + \Delta S^0/R$, the standard enthalpy and the standard entropy change of the reaction can be calculated from the slope of the straight line and the intercept, respectively. Approximate values of $\Delta H^0 = -22.7$ kcal·mol^{-1} and $\Delta S^0 = -70.96$ cal·mol^{-1}·K^{-1} were calculated for the equilibrium between **8** and **11** in CD_2Cl_2, and the value of ΔG^0 at 298 K was −1.62 kcal·mol^{-1}. For the equilibrium between **6** and **9** in CD_2Cl_2, the relevant values were calculated to be $\Delta H^0 = -15.7$ kcal·mol^{-1}, $\Delta S^0 = -42.3$ cal·mol^{-1}·K^{-1} and $\Delta G^0_{(298)} = -3.15$ kcal·mol^{-1}. These results indicate that formation of the (aqua)(vinylidene) is exothermic and that the equilibria are shifted to the (aqua)(vinylidene) complexes when the temperature is lowered, as mentioned previously.

As can be seen from Table 4, the equilibrium constant at room temperature for **6/9** is similar to that of **7/11** and is about 13 times as large as that of **8/11**, indicating that [$OsCl_2(=C=CHAr)(PPh_3)_2$] (**6** and **7**) have a higher affinity for H_2O than [$OsCl_2(=C=CHCMe_3)(PPh_3)_2$] (**8**). This difference may be related to that fact that CMe_3 is more electron-donating than Ar, thus the Lewis acidities of **6** and **7** are higher than that of **8**.

Conclusions

Reaction of [$OsCl_2(PPh_3)_3$] with terminal acetylenes HC≡CR (R = Ph, *p*-tolyl, CMe_3) in the presence of HCl readily produced the carbyne complexes [$OsCl_3(\equiv CCH_2R)(PPh_3)_2$]. Due to the acidic nature of the protons α to the carbyne carbon atom, the vinylidene complexes [$OsCl_2(=C=CHR)(PPh_3)_2$] (R = CMe_3, Ph, *p*-tolyl) can be easily prepared from these carbyne complexes by treatment with NEt_3. Interestingly, these vinylidene complexes are hygroscopic and react with water to give [$OsCl_2(H_2O)(=C=CHR)(PPh_3)_2$] reversibly. Dynamic NMR studies show that the vinylidene complexes [$OsCl_2(=C=CHR)(PPh_3)_2$] (R = Ph, *p*-tolyl) have a higher tendency to form the aqua complexes than does [$OsCl_2(=C=CHCMe_3)(PPh_3)_2$]. Thus, the (aqua)(vinylidene) complexes [$OsCl_2(=C=CHR)(H_2O)(PPh_3)_2$] (R = Ph, *p*-tolyl) could be isolated by treatment of the anhydrous vinylidene complexes with water.

Experimental Section

General: All manipulations were carried out at room temperature under nitrogen using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium/benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane, $CHCl_3$). The starting material [$OsCl_2(PPh_3)_3$][47] was prepared according to literature methods. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were collected with a Bruker ARX-300 spectrometer (300 MHz) or a JOEL EX-400 spectrometer (400 MHz). ^{1}H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4.

[$OsCl_3(\equiv C-CH_2Ph)(PPh_3)_2$] (2): HCl·$OEt_2$ (1.00 mL,1.0 M in diethyl ether solution, 1.0 mmol) and HC≡CPh (0.32 mL, 2.9 mmol) were added to a solution of [$OsCl_2(PPh_3)_3$] (0.50 g, 0.48 mmol) in benzene (15 mL). The reaction mixture was stirred at room temperature for 6 h to give a yellow microcrystalline solid, which was collected by filtration, washed with diethyl ether (2 × 20 mL) and dried under vacuum (0.33 g). The filtrate was concentrated to ca. 5 mL, and addition of diethyl ether (20 mL) to the residue produced additional yellow solid, which was collected by filtration, washed with diethyl ether (2 × 20 mL), and dried under vacuum overnight (0.05 g). Total yield: 0.38 g (86%). ^{1}H NMR (399.65 MHz, $CDCl_3$): δ = 1.77 (s, 2 H, Os≡CCH_2), 6.46 (d, $J_{H,H}$ = 7.1 Hz, 2 H, *o*-C_6H_5), 7.08 (t, $J_{H,H}$ = 7.6 Hz, 2 H, *m*-C_6H_5), 7.19 (t, $J_{H,H}$ = 7.6 Hz, 1 H, *p*-C_6H_5), 7.29−7.38 (m, 18 H, P*Ph*$_3$), 7.81−7.86 (m, 12 H, P*Ph*$_3$) ppm. ^{13}C{^{1}H} NMR (100.4 MHz, CD_2Cl_2): δ = 278.2 (t, $J_{P,C}$ = 11.1 Hz, Os≡*C*), 134.9−125.0 (m, C_6H_5, PPh_3), 57.3 (s, Os≡C*C*H_2) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = −12.9 (s) ppm. $C_{44}H_{37}Cl_3OsP_2$ (924.3): calcd. C 57.18, H 4.04; found C 57.35, H 4.19.

[$OsCl_3\{\equiv C-CH_2(p\text{-tolyl})\}(PPh_3)_2$] (3): HCl·$OEt_2$ (1.00 mL, 1.0 M in diethyl ether solution, 1.0 mmol) and 4-ethynyltoluene (0.24 mL, 1.9 mmol) were added to a solution of [$OsCl_2(PPh_3)_3$] (0.50 g, 0.48 mmol) in benzene (15 mL). The reaction mixture was stirred at room temperature for 6 h to give a yellow microcrystalline solid, which was collected by filtration, washed with diethyl ether (2 × 20 mL) and dried under vacuum (0.32 g). The filtrate was concentrated to about 5 mL, and addition of diethyl ether (20 mL) to the residue produced additional yellow solid, which was collected by filtration, washed with diethyl ether (2 × 15 mL), and dried under vacuum overnight (31 mg). Total yield: 0.35 g (78%). ^{1}H NMR (399.65 MHz, $CDCl_3$): δ = 1.72 (s, 2 H, Os≡C*C*H_2), 2.22 (s, 3 H, $C_6H_4CH_3$), 6.21 (d, $J_{H,H}$ = 8.0 Hz, 2 H, C_6H_4) 6.79 (d, $J_{H,H}$ = 8.0 Hz, 2 H, C_6H_4), 7.30 (m, 18 H, PPh_3), 7.80 (m, 12 H, PPh_3) ppm. ^{13}C{^{1}H} NMR (100.4 MHz, CD_2Cl_2): δ = 280.1 (t, $J_{P,C}$ = 12.0 Hz, Os≡*C*), 138.0−122.1 (m, C_6H_5, PPh_3), 57.1 (s, Os≡C*C*H_2), 21.2 (s, C_6H_4-CH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = −12.1 (s) ppm. $C_{45}H_{39}Cl_3OsP_2$ (938.3): calcd. C 57.60, H 4.19; found C 57.40, H 4.34.

[$OsCl_3(\equiv CCH_2CMe_3)(PPh_3)_2$] (4): HC≡C$CMe_3$ (0.28 mL, 2.3 mmol) and HCl·OEt_2 (0.80 mL, 0.80 mmol, 1.0 M in diethyl ether solution) were added to a solution of [$OsCl_2(PPh_3)_3$] (0.40 g, 0.38 mmol) in benzene (15 mL). The reaction mixture was stirred at room temperature for 6 h to give a yellow microcrystalline solid, which was collected by filtration, washed with diethyl ether (2 × 20 mL) and dried under vacuum (0.20 g). The filtrate was concentrated to ca. 3 mL, and addition of diethyl ether (20 mL) to the residue produced additional yellow solid, which was collected by filtration, washed with diethyl ether (2 × 20 mL), and dried under vacuum overnight (0.08 g). Total yield: 0.28 g (82%). The spectroscopic data have been reported previously.[22]

[$OsCl_3(\equiv CCH_3)(PPh_3)_2$] (5): HC≡C$SiMe_3$ (0.27 mL, 1.9 mmol) and HCl·OEt_2 (1.20 mL, 1.0 M in diethyl ether solution, 1.2 mmol) were added to a solution of [$OsCl_2(PPh_3)_3$] (0.50 g, 0.48 mmol) in benzene (15 mL). The reaction mixture was stirred at room temperature for 8 h to give a yellow microcrystalline solid, which was collected by filtration, washed with diethyl ether (2 × 20 mL) and dried under vacuum (0.25 g). The filtrate was concentrated to ca. 3 mL, and addition of diethyl ether (20 mL) to the residue produced additional yellow solid, which was collected by filtration, washed with diethyl ether (2 × 15 mL), and dried under vacuum overnight (0.04 g). Total yield: 0.29 g (71%). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 0.04 (t, $J_{P,H}$ = 2.5 Hz, 3 H, CH_3), 7.36−7.43 (m, 18 H, PPh_3), 7.89−7.96 (m, 12 H, PPh_3) ppm. $^{13}C\{^1H\}$ NMR (100.40 MHz, CD_2Cl_2): δ = 283.7 (t, $J_{P,C}$ = 12.3 Hz, $Os{\equiv}C$), 135.1−127.9 (m, PPh_3), 36.9 (s, $Os{\equiv}C\text{-}CH_3$) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = −13.5 (s) ppm. $C_{38}H_{33}Cl_3OsP_2$ (848.2): calcd. C 53.81, H 3.92; found C 53.60, H 4.18.

$[OsCl_2(=C=CHPh)(PPh_3)_2]$ (6): NEt_3 (0.43 mL, 3.1 mmol) was added to a CH_2Cl_2 (40 mL) solution of $[OsCl_3(\equiv CCH_2Ph)(PPh_3)_2]$ (0.57 g, 0.62 mmol). The reaction mixture rapidly changed color from yellow to blue. After stirring for 1 h, the solvent was removed completely under vacuum and the resulting blue solid was extracted with benzene (30 mL). The extract was filtered through Celite to remove the insoluble $Et_3N{\cdot}HCl$. The filtrate was concentrated to ca. 1 mL and diethyl ether was slowly added to give a blue solid, which was collected by filtration, washed with diethyl ether (2 × 10 mL) and dried under vacuum overnight. Yield: 0.47 g (85%). ^{1}H NMR (300.13 MHz, freshly distilled CD_2Cl_2): δ = 2.56 (t, $J_{P,H}$ = 3.3 Hz, 1 H, $Os{=}C{=}CH$), 6.48 (d, $J_{H,H}$ = 7.4 Hz, 2 H, $o\text{-}C_6H_5$), 6.71 (t, $J_{H,H}$ = 7.4 Hz, 1 H, $p\text{-}C_6H_5$), 7.02 (t, $J_{H,H}$ = 7.4 Hz, 2 H, $m\text{-}C_6H_5$), 7.25−7.41 (m, 18 H, PPh_3), 7.57−7.64 (m, 12 H, PPh_3) ppm. $^{13}C\{^1H\}$ NMR (100.4 MHz, freshly distilled CD_2Cl_2): δ = 280.8 (br., $Os{=}C$), 135.0−124.3 (m, C_6H_5, PPh_3), 112.1 (t, $J_{P,C}$ = 4.8 Hz, $Os{=}C{=}CH$) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, freshly distilled CD_2Cl_2): δ = 9.6 (s) ppm. $C_{44}H_{36}Cl_2OsP_2$ (887.8): calcd. C 59.53, H 4.09; found C 59.54, H 4.01.

$[OsCl_2\{=C=CH(p\text{-tolyl})\}(PPh_3)_2]$ (7): NEt_3 (0.44 mL, 3.2 mmol) was added to a CH_2Cl_2 (40 mL) solution of $[OsCl_3\{\equiv CCH_2(p\text{-tolyl})\}(PPh_3)_2]$ (0.50 g, 0.53 mmol). The reaction mixture rapidly changed color from yellow to blue. After stirring for 1 h, the solvent was removed completely under vacuum and the resulting blue solid was extracted with benzene (30 mL). The extract was filtered through Celite to remove the insoluble $Et_3N{\cdot}HCl$. The filtrate was concentrated to ca. 1 mL and diethyl ether was slowly added to give a blue solid, which was collected by filtration, washed with diethyl ether (2 × 10 mL) and dried under vacuum overnight. Yield: 0.42 g (88%). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 2.39 (s, 3 H, $C_6H_4CH_3$), 2.46 (t, $J_{P,H}$ = 3.4 Hz, 1 H, $Os{=}C{=}CH$), 6.40 (d, $J_{H,H}$ = 8.0 Hz, 2 H, C_6H_4), 6.87 (d, $J_{H,H}$ = 8.0 Hz, 2 H, C_6H_4), 7.33−7.41 (m, 18 H, PPh_3), 7.59−7.62 (m, 12 H, PPh_3) ppm. $^{13}C\{^1H\}$ NMR (100.4 MHz, freshly distilled CD_2Cl_2): δ = 281.0 (br., $Os{=}C$), 135.0−124.9 (m, C_6H_4, PPh_3), 112.0 (t, $J_{P,C}$ = 4.5 Hz, $Os{=}C{=}CH$), 20.9 (s, $C_6H_4\text{-}CH_3$) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, freshly distilled CD_2Cl_2): δ = 9.2 (s) ppm. $C_{45}H_{38}Cl_2OsP_2$ (901.8): calcd. C 59.93, H 4.25; found C 59.76, H 4.26.

$[OsCl_2(=C=CHCMe_3)(PPh_3)_2]$ (8): NEt_3 (0.31 mL, 1.7 mmol) was added with stirring to a solution of $[OsCl_3(\equiv CCH_2CMe_3)(PPh_3)_2]$ (0.50 g, 0.55 mmol) in CH_2Cl_2 (50 mL). The reaction solution changed color from orange to brown immediately. The reaction mixture was stirred at room temperature for 1 h and the solvent was removed completely under vacuum. The brown solid was extracted with benzene (15 mL) and the extract filtered through Celite to remove the insoluble $Et_3N{\cdot}HCl$. The volume of the brown filtrate was reduced to ca. 1 mL. Addition of diethyl ether (20 mL) to the residue produced a purple solid, which was collected by filtration, washed with diethyl ether (2 × 10 mL) and hexane (20 mL) and dried under vacuum overnight. Yield: 0.29 g (61%). ^{1}H NMR (300.13 MHz, freshly distilled CD_2Cl_2): δ = 0.54 [s, 9 H, $C(CH_3)_3$], 1.20 (t, $J_{P,H}$ = 3.6 Hz, 1 H, $Os{=}C{=}CH$), 7.42−7.51 (m, 18 H, PPh_3), 7.66−7.71 (m, 12 H, PPh_3) ppm. The signal of H_2O appears at room temp. at δ = 1.73 ppm and at 211 K at δ = 1.86 ppm with an integral of 2:1 relative to that of the vinylidene signal. $^{13}C\{^1H\}$ NMR (100.40 MHz, freshly distilled CD_2Cl_2): δ = 274.1 (t, $J_{P,C}$ = 12.5 Hz, $Os{=}C$), 134.9−128.4 (m, PPh_3), 120.5 (t, $J_{P,C}$ = 5.5 Hz, $Os{=}C{=}CH$), 32.60 [s, $C(CH_3)_3$], 27.47 [s, $C(CH_3)_3$] ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, freshly distilled CD_2Cl_2): δ = 3.4 (s) ppm. FAB-MS (NBA): m/z = 868 [M^+]. $C_{42}H_{40}Cl_2OsP_2$ (867.8): calcd. C 58.13, H 4.65; found C 58.49, H 4.53.

$[OsCl_2(H_2O)(=C=CHPh)(PPh_3)_2]$ (9): Water (0.2 mL) was added to a blue solution of $[OsCl_2(=C=CHPh)(PPh_3)_2]$ (0.15 g, 0.17 mmol) in CH_2Cl_2 (10 mL). The solution turned orange immediately. After stirring for 20 min, the solvent was pumped off to give an orange paste. Diethyl ether (10 mL) was added to the residue to give an orange solid, which was collected by filtration, washed with diethyl ether (2 × 5 mL) and dried under vacuum for 30 min. Yield: 0.14 g (91%). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 2.48 (t, $J_{P,H}$ = 3.3 Hz, 1 H, $Os{=}C{=}CH$), 6.70 (d, $J_{H,H}$ = 7.2 Hz, 2 H, $o\text{-}C_6H_5$), 6.76 (t, $J_{H,H}$ = 7.4 Hz, 1 H, $p\text{-}C_6H_5$), 7.08 (t, $J_{H,H}$ = 7.4 Hz, 2 H, $m\text{-}C_6H_5$), 7.28−7.40 (m, 18 H, PPh_3), 7.70−7.76 (m, 12 H, PPh_3) ppm. The signal of H_2O appears at room temp. at δ = 1.77 ppm and at 211 K at δ = 1.95 ppm with an integral of 2:1 relative to that of the vinylidene =CH signal. $^{13}C\{^1H\}$ NMR (100.4 MHz, CD_2Cl_2): δ = 289.1 (t, $J_{P,C}$ = 11.4 Hz, $Os{=}C$), 134.7−123.8 (m, C_6H_5, PPh_3), 112.3 (t, $J_{P,C}$ = 4.4 Hz, $Os{=}C{=}CH$) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2 in the presence of a drop of water): δ = −3.6 (s) ppm. $C_{44}H_{38}Cl_2OOsP_2$ (905.8): calcd. C 58.34, H 4.23; found C 58.54, H 4.42.

$[OsCl_2(H_2O)\{=C=CH(p\text{-tolyl})\}(PPh_3)_2]$ (10): Water (0.2 mL) was added to a blue solution of $[OsCl_2\{=C=CH(p\text{-tolyl})\}(PPh_3)_2]$ (0.15 g, 0.17 mmol) in CH_2Cl_2 (10 mL). The solution turned orange immediately. After stirring for 20 min, the solvent was pumped off to give an orange paste. Diethyl ether (10 mL) was added to the residue to give an orange solid, which was collected by filtration, washed with diethyl ether (2 × 5 mL) and dried under vacuum for 30 min. Yield: 0.14 g (89%). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 2.38 (s, 3 H, $C_6H_4CH_3$), 2.42 (t, $J_{P,H}$ = 3.5 Hz, 1 H, $Os{=}C{=}CH$), 6.62 (d, $J_{H,H}$ = 8.0 Hz, 2 H, C_6H_4), 6.92 (d, $J_{H,H}$ = 8.0 Hz, 2 H, C_6H_4), 7.30−7.37 (m, 18 H, PPh_3), 7.70−7.73 (m, 12 H, PPh_3) ppm. The signal of H_2O appears at room temp. at δ = 1.73 ppm and at 190 K at δ = 1.86 ppm with an integral of 2:1 relative to that of the vinylidene =CH signal. $^{13}C\{^1H\}$ NMR (100.4 MHz, CD_2Cl_2): δ = 293.7 (t, $J_{P,C}$ = 14.1 Hz, $Os{=}C$), 135.1−125.4 (m, C_6H_4, PPh_3), 112.5 (t, $J_{P,C}$ = 4.5 Hz, $Os{=}C{=}CH$), 20.8 (s, $C_6H_4\text{-}CH_3$) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = −3.8 (s) ppm. $C_{45}H_{40}Cl_2P_2OOs$ (919.9): calcd. C 58.76, H 4.38; found C 58.63, H 4.12.

Observation of 11: Owing to the instability and incomplete conversion of **8** to **11**, **11** could not be isolated but could be detected when a solution of **8** in commercially available CD_2Cl_2 was monitored by variable-temperature $^{31}P\{^1H\}$ and ^{1}H NMR experiments. Characterization data of **11**: ^{1}H NMR (300.13 MHz, CD_2Cl_2, 188 K): δ = 0.91 (br. s, 1 H, $Os{=}C{=}CH$), 2.38 (br., 2 H, H_2O) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 188 K): δ = −10.2 (br. s) ppm.

Crystal-Structure Analyses: Crystals suitable for X-ray diffraction were grown by layering hexane on CH_2Cl_2 solutions of **2**, **5** and **8**, or cooling a warm solution of **9** in benzene. Data collection was performed with a Bruker Apex CCD Area Detector for **2** and **8** and with a Bruker SMART CCD Area Detector for **5** and **9**, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) in all

Table 5. Crystallographic details for [$OsCl_3(\equiv CCH_2Ph)(PPh_3)_2$]·$1.5C_6H_6$ (**2**·$1.5C_6H_6$), [$OsCl_3(\equiv CCH_3)(PPh_3)_2$]·$CH_2Cl_2$ (**5**·CH_2Cl_2), [$OsCl_2(=C=CHCMe_3)(PPh_3)_2$] (**8**) and [$OsCl_2(H_2O)(=C=CHPh)(PPh_3)_2$]·$C_6H_6$ (**9**·C_6H_6)

Compound	**2**·$1.5C_6H_6$	**5**·CH_2Cl_2	**8**	**9**·C_6H_6
Empirical formula	$C_{44}H_{37}Cl_3OsP_2\cdot 1.5C_6H_6$	$C_{38}H_{33}Cl_3OsP_2\cdot CH_2Cl_2$	$C_{42}H_{40}Cl_2OsP_2$	$C_{44}H_{38}Cl_2OOs\ P_2\cdot C_6H_6$
Formula mass	1041.39	933.06	867.78	983.89
Temperature [K]	100(2)	293(2)	180(2)	293(2)
Radiation (Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$	$P2_1/n$
a [Å]	9.9952(7)	10.6256(9)	22.2749(10)	16.106(2)
b [Å]	13.9065(10)	12.9185(12)	9.5252(4)	12.3804(14)
c [Å]	17.7242(12)	14.0763(12)	18.7580(8)	21.477(3)
α [°]	110.6600(10)	78.341(2)	90	90
β [°]	97.6520(10)	89.708(2)	113.2070(10)	96.382(3)
γ [°]	98.292(2)	81.302(2)	90°	90
V [Å^3]	2235.6(3)	1869.9(3)	3657.9(3)	4255.9(9)
Z	2	2	4	4
$d_{calcd.}$ [g·cm^{-3}]	1.547	1.657	1.576	1.536
Abs. coeff. [mm^{-1}]	3.139	3.880	3.749	3.234
F(000)	1042	920	1728	1968
Crystal size [mm]	0.36 × 0.10 × 0.08	0.36 × 0.32 × 0.25	0.32 × 0.25 × 0.25	0.32 × 0.32 × 0.10
θ range [°]	1.60 to 27.88	1.94 to 27.53	2.36 to 28.31°	1.90 to 27.57
No. of reflns. collected	19208	12564	21881	27413
No. of indep. reflns.	10057 (R_{int} = 0.0318)	8431 (R_{int} = 0.0353)	8561 (R_{int} = 0.0260)	9785 (R_{int} = 0.0849)
No. of obsd. reflns. [$I > 2\sigma(I)$]	8921	7060	7617	4759
Absorption correction	SADABS	SADABS	SADABS	SADABS
Data/restraints/params	10057/0/532	8431/3/434	8561/0/428	9785/0/506
Goodness-of-fit on F^2	0.992	0.989	1.037	0.764
Final R_{int} [$I > 2\sigma(I)$]	R_1 = 0.0303, wR_2 = 0.0696	R_1 = 0.0428, wR_2 = 0.1021	R_1 = 0.0261, wR_2 = 0.0583	R_1 = 0.0425, wR_2 = 0.0637
Largest peak/hole (e·Å^{-3})	1.798/−0.974	2.236/−0.950	1.639/−0.519	1.312/−0.799

cases. Empirical absorption corrections (SADABS)[48] 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)[49] program package. All non-hydrogen atoms were refined anisotropically. 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 5. CCDC-227451 (**2**·$1.5C_6H_6$), -227452 (**5**·CH_2Cl_2), -227453 (**8**) and -227454 (**9**·C_6H_6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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

---

[1] For reviews on vinylidene complexes, see for example: [1a] M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197−257. [1b] M. I. Bruce, A. G. Swincer, *Adv. Organomet. Chem.* **1983**, *22*, 59−128. [1c] C. Bruneau, P. H. Dixneuf, *Acc. Chem. Res.* **1999**, *32*, 311−323. [1d] M. C. Puerta, P. Valerga, *Coord. Chem. Rev.* **1999**, 193−195, 977−1025.

[2] [2a] P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100−110. [2b] H. Katayama, F. Ozawa, *Chem. Lett.* **1998**, 67−68. [2c] H. Katayama, H. Urushima, F. Ozawa, *J. Organomet. Chem.* **2000**, *606*, 16−25. [2d] T. Opstal, F. Verpoort, *Synlett* **2003**, 314−320. [2e] J. Louie, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2001**, *40*, 247−249.

[3] [3a] Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh, J. Y. Satoh, *J. Am. Chem. Soc.* **1991**, *113*, 9604−9610. [3b] Y. Wakatsuki, N. Koga, H. Yamazaki, K. Morokuma, *J. Am. Chem. Soc.* **1994**, *116*, 8105−8111.

[4] Reactions of [$RuCl_2(PPh_3)_3$] with $HC\equiv CC(OH)Ar_2$ can also lead to related allenylidene complexes: [4a] D. Touchard, S. Guesmi, M. Bouchaib, P. Haquette, A. Daridor, P. H. Dixneuf, *Organometallics* **1996**, *15*, 2579−2581. [4b] K. J. Harlow, A. F. Hill, J. D. E. T. Wilton-Ely, *J. Chem. Soc., Dalton Trans.* **1999**, 285−291. [4c] H. J. Schanz, L. Jafarpour, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 5187−5190. [4d] A. Fürstner, O. Guth, A. Düffels, G. Seidel, M. Liebl, B. Gabor, R. Mynott, *Chem. Eur. J.* **2001**, *7*, 4811−4820.

[5] [5a] C. Grünwald, O. Gevert, J. Wolf, P. González-Herrero, H. Werner, *Organometallics* **1996**, *15*, 1960−1962. [5b] J. Wolf, W. Stüer, C. Grünwald, O. Gevert, M. Laubender, H. Werner, *Eur. J. Inorg. Chem.* **1998**, 1827−1834. [5c] J. Wolf, W. Stüer, C. Grünwald, H. Werner, P. Schwab, M. Schulz, *Angew. Chem. Int. Ed.* **1998**, *37*, 1124−1126.

[6] H. Katayama, F. Ozawa, *Organometallics* **1998**, *17*, 5190−5196.

[7] M. Saoud, A. Romerosa, M. Peruzzini, *Organometallics* **2000**, *19*, 4005−4007.

[8] P. Barrio, M. A. Esteruelas, E. Oñate, *Organometallics* **2003**, *22*, 2472−2485.

[9] J. Gimeno, M. Gonzalez-Cueva, E. Lastra, E. Perez-Carreño, S. García-Granda, *Inorg. Chim. Acta* **2003**, *347*, 99−106.

[10] P. Barrio, M. A. Esteruelas, E. Oñate, *Organometallics* **2002**, *21*, 2491−2503.

[11] D. G. Gusev, T. Maxwell, F. M. Dolgushin, M. Lyssenko, A. J. Lough, *Organometallics* **2002**, *21*, 1095−1100.

[12] M. Baya, P. Crochet, M. A. Esteruelas, A. M. López, J. Modrego, E. Oñate, *Organometallics* **2001**, *20*, 4291−4294.

[13] R. Castarlenas, M. A. Esteruelas, E. Gutiérrez-Puebla, E. Oñate, *Organometallics* **2001**, *20*, 1545−1554.

[14] R. Castarlenas, M. A. Esteruelas, E. Oñate, *Organometallics* **2000**, *19*, 5454−5463.

[15] T. B. Wen, Y. Y. Cheung, J. Z. Yao, W. T. Wong, Z. Y. Zhou, G. Jia, *Organometallics* **2000**, *19*, 3803−3809.

[16] M. A. Esteruelas, M. Oliván, E. Oñate, N. Ruiz, M. A. Tajada, *Organometallics* **1999**, *18*, 2953−2960.

[17] M. Baya, M. A. Esteruelas, *Organometallics* **2002**, *21*, 2332−2335.

[18] R. Castarlenas, M. A. Esteruelas, E. Oñate, *Organometallics* **2001**, *20*, 3283−3295.

[19] G. Ferrando, H. Gérard, G. J. Spivak, J. N. Coalter III, J. C. Huffman, O. Eisenstein, K. G. Caulton, *Inorg. Chem.* **2001**, *40*, 6610−6621.

[20] For additional examples of recent work on (vinylidene)Os complexes, see for example: [20a] M. Baya, M. A. Esteruelas, E. Oñate, *Organometallics* **2001**, *20*, 4875−4886. [20b] A. V. Marchenko, H. Gérard, O. Eisenstein, K. G. Caulton, *New. J. Chem.* **2001**, *25*, 1244−1255. [20c] M. L. Buil, M. A. Esteruelas, C. García-Yebra, E. Gutiérrez-Puebla, M. Oliván, *Organometallics* **2000**, *19*, 2184−2193. [20d] M. A. Esteruelas, C. García-Yebra, M. Oliván, E. Oñate, M. A. Tajada, *Organometallics* **2000**, *19*, 5098−5106. [20e] M. Baya, P. Crochet, M. A. Esteruelas, E. Gutiérrez-Puebla, A. M. López, J. Modrego, E. Oñate, N. Vela, *Organometallics* **2000**, *19*, 2585−2596. [20f] M. L. Buil, M. A. Esteruelas, *Organometallics* **1999**, *18*, 1798−1800. [20g] C. Bohanna, M. L. Buil, M. A. Esteruelas, E. Oñate, C. Valero, *Organometallics* **1999**, *18*, 5176−5179.

[21] M. L. Buil, O. Eisenstein, M. A. Esteruelas, C. García-Yebra, E. Gutiérrez-Puebla, M. Oliván, E. Oñate, N. Ruiz, M. A. Tajada, *Organometallics* **1999**, *18*, 4949−4959.

[22] T. B. Wen, S. Y. Yang, Z. Y. Zhou, Z. Lin, C. P. Lau, G. Jia, *Organometallics* **2000**, *19*, 3757−3761.

[23] T. B. Wen, Z. Y. Zhou, G. Jia, *Angew. Chem. Int. Ed.* **2001**, *40*, 1951−1954.

[24] H. Werner, S. Jung, B. Weberndörfer, J. Wolf, *Eur. J. Inorg. Chem.* **1999**, 951−957.

[25] J. Espuelas, M. A. Esteruelas, F. J. Lahoz, L. A. Oro, N. Ruiz, *J. Am. Chem. Soc.* **1993**, *115*, 4683−4869.

[26] See for example: [26a] C. Bianchini, A. Marchi, L. Marvelli, M. Peruzzini, A. Romerosa, R. Rossi, *Organometallics* **1996**, *15*, 3804−3816. [26b] Y. Kawata, M. Sato, *Organometallics* **1997**, *16*, 1093−1096.

[27] H. Werner, R. W. Lass, L. O. Gevert, J. Wolf, *Organometallics* **1997**, *16*, 4077−4088.

[28] M. A. Esteruelas, A. I. González, A. M. López, E. Oñate, *Organometallics* **2003**, *22*, 414−425.

[29] P. Crochet, M. A. Esteruelas, A. M. López, M. P. Martínez, M. Oliván, E. Oñate, N. Ruiz, *Organometallics* **1998**, *17*, 4500−4509.

[30] L. J. Baker, G. R. Clark, C. E. F. Rickard, W. R. Roper, S. D. Woodgate, L. J. Wright, *J. Organomet. Chem.* **1998**, *551*, 247−259.

[31] M. A. Esteruelas, A. M. López, N. Ruiz, J. I. Tolosa, *Organometallics* **1997**, *16*, 4657−4667.

[32] A. M. LaPointe, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1995**, *117*, 4802−4813.

[33] L. M. Hodges, M. Sabat, W. D. Harmon, *Inorg. Chem.* **1993**, *32*, 371−372.

[34] B. Weber, P. Steinert, B. Windmüller, J. Wolf, H. Werner, *J. Chem. Soc., Chem. Commun.* **1994**, 2595−2596.

[35] [35a] G. R. Clark, N. R. Edmonds, R. A. Pauptit, W. R. Roper, J. M. Waters, A. H. Wright, *J. Organomet. Chem.* **1983**, *244*, C57−C60. [35b] M. A. Gallop, W. R. Roper, *Adv. Organomet. Chem.* **1986**, *25*, 121−198.

[36] G. J. Spivak, J. N. Coalter, M. Oliván, O. Eisenstein, K. G. Caulton, *Organometallics* **1998**, *17*, 999−1001.

[37] M. Bourgault, A. Castillo, M. A. Esteruelas, E. Oñate, N. A. Ruiz, *Organometallics* **1998**, *17*, 636−645.

[38] For additional examples of recent work on (carbyne)Os complexes, see: [38a] M. Baya, M. A. Esteruelas, E. Oñate, *Organometallics* **2002**, *21*, 5681−5684. [38b] H. Chen, R. Liu, W. H. Myers, W. D. Harman, *J. Am. Chem. Soc.* **1998**, *120*, 509−520. [38c] G. J. Spivak, K. G. Caulton, *Organometallics* **1998**, *17*, 5260−5266. [38d] M. L. Spera, H. Chen, M. W. Moody, M. M. Hill, W. D. Harman, *J. Am. Chem. Soc.* **1997**, *119*, 12772−12778.

[39] C. Kelly, L. A. Mercando, M. R. Terry, N. Lugan, G. L. Geoffroy, Z. Xu, A. L. Rheingold, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1053−1054.

[40] S. Y. Yang, T. B. Wen, G. Jia, Z. Lin, *Organometallics* **2000**, *19*, 5477−5483.

[41] A. F. Hill, A. G. Hulkes, A. J. P. White, D. J. Williams, *Organometallics* **2000**, *17*, 371−373.

[42] [42a] M. Oliván, E. Clot, O. Eisenstein, K. G. Caulton, *Organometallics* **1998**, *17*, 3091−3100. [42b] M. Oliván, E. Clot, O. Eisenstein, K. G. Caulton, *Organometallics* **1998**, *17*, 897−901. [42c] M. Oliván, O. Eisenstein, K. G. Caulton, *Organometallics* **1997**, *16*, 2227−2229.

[43] D. Huang, M. Oliván, J. C. Huffman, O. Eisenstein, K. G. Caulton, *Organometallics* **1998**, *17*, 4700−4706.

[44] [44a] H. Werner, W. Stüer, J. Wolf, M. Laubender, B. Weberndörfer, R. Herbst-Irmer, C. Lehmann, *Eur. J. Inorg. Chem.* **1999**, 1889−1897. [44b] G. Bellachioma, G. Cardaci, A. Macchioni, F. Valentini, C. Zuccaccia, E. Foresti, P. Sabatino, *Organometallics* **2000**, *19*, 4320−4326. [44c] H. D. Mui, J. L. Brumaghim, C. J. Cross, G. S. Girolami, *Organometallics* **1999**, *18*, 3264−3272.

[45] T. B. Wen, Z. Y. Zhou, M. F. Lo, I. D. Williams, G. Jia, *Organometallics* **2003**, *22*, 5217−5225.

[46] P. J. Hore, *Nuclear Magnetic Resonance*, Oxford University Press Inc., New York, **1995**, pp. 44−55.

[47] P. R. Hoffmann, K. G. Caulton, *J. Am. Chem. Soc.* **1975**, *97*, 4221−4228.

[48] G. M. Sheldrick, *SADABS, Empirical Absorption Correction Program*, University of Göttingen, Germany, **1996**.

[49] Bruker, *SHELXTL™ Reference Manual* (Version 5.1), Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA, **1997**.

Received January 2, 2004
Early View Article