

Coupling Reaction of Phenylacetylene with $\text{OsH}_n(\text{PPh}_3)(2,6\text{-}(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$ ($n = 1, 3$)

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Received August 29, 2003

Treatment of $\text{OsCl}(\text{=C=CHPh})(\text{PPh}_3)(\text{PCP})$ with thallium acetate produces the vinylidene complex $\text{Os}(\text{O}_2\text{CCH}_3)(\text{=C=CHPh})(\text{PCP})$. Treatment of $\text{OsCl}(\text{PPh}_3)(\text{PCP})$ with NaH in wet THF produces a mixture of the monohydride $\text{OsH}(\text{PPh}_3)(\text{PCP})$ and the trihydride $\text{OsH}_3(\text{PPh}_3)(\text{PCP})$. The latter complexes react with phenylacetylene to give $\text{Os}(\text{C}\equiv\text{CPh})(\text{=C=CHPh})(\text{PPh}_3)(1\text{-}(\text{CHPh}=\text{C})\text{-}2,6\text{-}(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$.

Introduction

It has been established that vinylidene complexes $\text{L}_n\text{MR}'(\text{=C=CHR})$ can undergo migratory insertion reactions of R' to the α -carbon of the vinylidene ligands to give $\text{L}_n\text{M}(\text{CR}'=\text{CHR})$.^{1,2} As reactions of terminal acetylenes $\text{HC}\equiv\text{CR}$ with coordinatively unsaturated compounds could often lead to vinylidene complexes, one might expect that reactions of terminal acetylenes $\text{HC}\equiv\text{CR}$ with transition metal complexes $\text{L}_n\text{M}-\text{R}'$ may go through vinylidene intermediates $\text{L}_n\text{M}-\text{R}'(\text{=C=CHR})$ to give coupling complexes $\text{L}_n\text{M}-\text{R}'\text{C}=\text{CHR}$. Indeed, there are many examples of coupling reactions between acetylide and vinylidene ligands, especially in the reactions of $\text{HC}\equiv\text{CR}$ with certain complexes to give RC_3HR complexes and in catalytic dimerization or oligomerization of terminal acetylenes.^{3–5} In contrast, only a few coupling reactions between vinylidene and other ligands such as hydride,⁶ vinyl,^{7–10} and aryl^{11a,b}

ligands in the reactions of terminal acetylenes with transition metal complexes are known.

In our efforts to investigate the coupling reactions between vinylidene and aryl ligands, we have studied the reactions of terminal acetylenes with $\text{MCl}(\text{PPh}_3)(\text{PCP})$ ($\text{M} = \text{Ru, Os}$; $\text{PCP} = 2,6\text{-}(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3$).^{11a,b} It is found that reactions of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ with $\text{HC}\equiv\text{CR}$ lead to the formation of the coupling products $\text{RuCl}(\text{PPh}_3)(1\text{-}(\text{RCH}=\text{C})\text{-}2,6\text{-}(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$ ^{11a,b} through the vinylidene intermediates $\text{RuCl}(\text{=C=CHR})(\text{PPh}_3)(\text{PCP})$. In contrast, the analogous osmium complex $\text{OsCl}(\text{PPh}_3)(\text{PCP})$ reacts with $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{Ph, Bu}^t, \text{C}(\text{OH})\text{-Ph}_2$) to give the vinylidene complexes $\text{OsCl}(\text{=C=CHR})(\text{PPh}_3)(\text{PCP})$, which do not undergo coupling reactions similar to those of their ruthenium analogues.¹² In a related study, Gusev et al. have shown that the reaction of $\text{HC}\equiv\text{CBu}^t$ with $\text{RuHCl}(1,3\text{-}(\text{PBu}_2^t\text{-CH}_2)_2\text{C}_6\text{H}_4)$ gives the coupling product $\text{RuCl}(\text{=C=CHBu}^t)(1\text{-}(\text{CHBu}^t=\text{C})\text{-}2,6\text{-}(\text{PBu}_2^t\text{CH}_2)_2\text{C}_6\text{H}_3)$, while the reaction of $\text{HC}\equiv\text{CBu}^t$ with $\text{OsH}_2\text{Cl}(2,6\text{-}(\text{PBu}_2^t\text{CH}_2)_2\text{C}_6\text{H}_3)$ gives the vinylidene complex $\text{OsCl}(\text{=C=CHBu}^t)(2,6\text{-}(\text{PBu}_2^t\text{CH}_2)_2\text{C}_6\text{H}_3)$.¹³ These results suggest that metals

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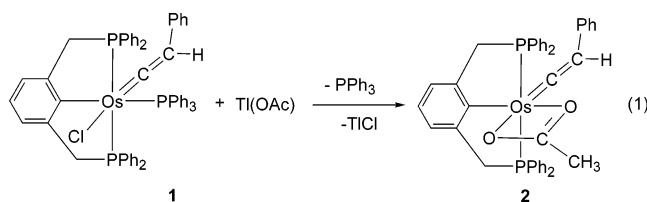
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can have drastic effects on the coupling reactions between vinylidene and hydrocarbyl ligands. One might also expect that the ligand environment may also influence the course of coupling reactions of vinylidene ligands. To this end, we have investigated the reaction of $\text{OsCl}(\text{C}=\text{CHPh})(\text{PPh}_3)(\text{PCP})$ with thallium acetate and the reactions of the hydride complexes $\text{OsH}_n(\text{PPh}_3)(\text{PCP})$ ($n = 1, 3$) with $\text{HC}\equiv\text{CPh}$. It should be noted that PCP and related ligands are receiving increasing attention in organometallic chemistry and catalysis.¹⁴ Several other reports have appeared in the literature on the chemistry and catalytic properties of ruthenium^{15–17} and osmium¹⁸ complexes with PCP or related ligands.

Results and Discussion

Synthesis and Characterization of $\text{Os}(\text{O}_2\text{CCH}_3)(\text{C}=\text{CHPh})(\text{PCP})$. In an attempt to induce aryl–vinylidene coupling, we have treated the vinylidene complex $\text{OsCl}(\text{C}=\text{CHPh})(\text{PPh}_3)(\text{PCP})$ (**1**)¹² with thallium acetate, hoping that the acetate ligand will replace the chloride and function as a bidentate ligand to push the aryl group to migrate to the α -carbon of the vinylidene ligand. In reality, reaction of **1** with thallium acetate produces the vinylidene complex $\text{Os}(\text{O}_2\text{CCH}_3)(\text{C}=\text{CHPh})(\text{PCP})$ (**2**) and the PPh_3 ligand is liberated (eq 1).



The structure of **2** can be readily assigned on the basis of elemental analysis and NMR and MS spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in C_6D_6 displayed only a singlet at 27.3 ppm. The ^1H NMR spectrum (in C_6D_6) displayed two sets of virtual doublets of triplet ^1H signals at 4.37 and 4.23 ppm for the methylene protons of the PCP ligand, indicating that the two PPh_2 groups are *trans* to each other and that the PCP ligand is coordinated in a meridional fashion.¹⁹ Consistent with

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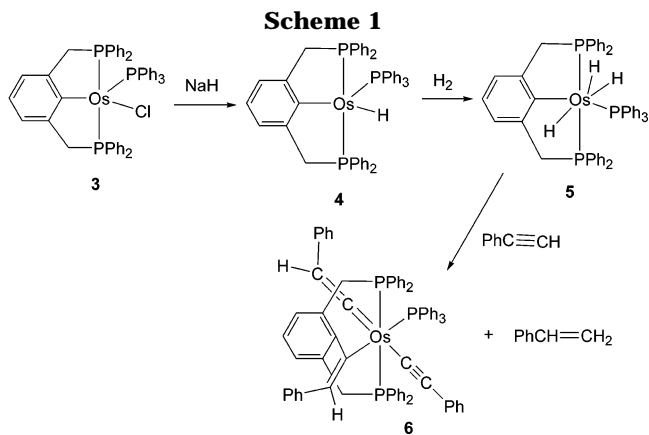
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the geometry, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (in CD_2Cl_2) showed a virtual triplet ^{13}C signal for the methylene carbons at 44.5 ppm. The presence of the vinylidene ligand is supported by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (in CD_2Cl_2), which exhibited the $\text{Os}=\text{C}$ signal at 300.4 ppm and the $\text{Os}=\text{C}=\text{CH}$ signal at 109.2 ppm, and the ^1H NMR spectrum (in C_6D_6), which showed the vinylidene proton signal at 2.60 ppm. The presence of the acetate ligand is indicated by the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data. In particular, the ^1H NMR spectrum (in C_6D_6) showed the CH_3 signal at 1.44 ppm, and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (in CD_2Cl_2) showed the carbonyl and CH_3 signals at 185.1 and 25.6 ppm, respectively.

Synthesis and Characterization of $\text{OsH}(\text{PPh}_3)(\text{PCP})$ and $\text{OsH}_3(\text{PPh}_3)(\text{PCP})$. Treatment of $\text{OsCl}(\text{PPh}_3)(\text{PCP})$ (**3**) with NaH in THF under an argon atmosphere produced a mixture of the monohydride $\text{OsH}(\text{PPh}_3)(\text{PCP})$ (**4**) and the trihydride $\text{OsH}_3(\text{PPh}_3)(\text{PCP})$ (**5**) (Scheme 1). The H_2 needed for the formation of **5** in the reaction is presumably generated in situ from the reaction of NaH with trace water present in the solution. When the reaction was performed under a H_2 atmosphere, the trihydride complex **5** was obtained quantitatively. However, both **4** and **5** cannot be isolated in pure form because of their air-sensitivity, and therefore they were characterized in situ and used immediately once generated.

The structure of **4** can be assigned on the basis of its NMR spectroscopic data. In particular, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in $\text{THF}-d_8$ showed a doublet at 25.2 ppm for the PPh_2 groups and a triplet at 11.7 ppm for the PPh_3 ligand with a $J(\text{PP})$ of 9.9 Hz. The ^{31}P NMR data are very similar to those of the chloride complex $\text{OsCl}(\text{PPh}_3)(\text{PCP})$ (**3**),¹² implying that the two compounds have similar structures, i.e., square pyramid with the bulky PPh_3 ligand occupying the apical site. Consistent with the structure, the ^1H NMR spectrum in $\text{THF}-d_8$ displayed a hydride signal at -11.84 ppm (dt, $J(\text{PH}) = 18.0, 19.5$ Hz).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** in $\text{THF}-d_8$ showed a doublet at 25.1 ppm for the PPh_2 groups and a triplet at 19.8 ppm for the PPh_3 ligand with a $J(\text{PP})$ of 12.6 Hz. The room-temperature ^1H NMR spectrum in $\text{THF}-d_8$ showed two hydride signals at -4.79 ppm (dt, $J(\text{PH}) = 24.9, 14.1$ Hz) and -6.98 ppm (br s) with relative intensities of 1:2. The magnitude of the $J(\text{PH})$ constants for the OsH resonance suggests that the hydride is *cis* to all three phosphorus atoms. The ^1H NMR in $\text{THF}-d_8$ did not change appreciably when the temperature is lowered to -70 °C. The structure of **5** could be assigned

as either a trihydride complex $\text{OsH}_3(\text{PPh}_3)(\text{PCP})$ with two of the hydrides exchanging rapidly or a hydrido-dihydrogen complex $\text{OsH}(\text{H}_2)(\text{PPh}_3)(\text{PCP})$. To distinguish the two possibilities, we have measured the T_1 values of the OsH_2 resonance at -6.98 ppm. The minimum T_1 value for the hydride signal was found to be 89.6 ms at 270 K (300 MHz). The long $T_{1(\text{min})}$ value indicates that the $\text{H}\cdots\text{H}$ interaction is very weak if it exists at all.²⁰ We also failed to detect $J(\text{HD})$ coupling for the partially deuterated samples of $\text{OsH}_x\text{D}_{3-x}(\text{PPh}_3)(\text{PCP})$. On the basis of the spectroscopic data, we tentatively assign the complex as a seven-coordinated pentagonal bipyramidal trihydride complex. Consistent with this structure, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in THF-d_8 showed the $\text{Os}-\text{C}_{\text{ipso}}$ signal at 154.8 ppm as a doublet with a $^2J(\text{PC})$ coupling of 36.2 Hz. The magnitude of the $^2J(\text{PC})$ coupling constant is much smaller than those observed for other osmium-PCP complexes, in which the PPh_3 is *trans* to the orthometalated carbon. For example, the $^2J(\text{PC})$ is 60.4 Hz for the structurally characterized complex $\text{OsCl}(\text{H}_2)(\text{PPh}_3)(\text{PCP})$.^{18e} Many seven-coordinated osmium trihydride complexes have been reported.^{18a,21}

Reaction of $\text{OsH}(\text{PPh}_3)(\text{PCP})$ and $\text{OsH}_3(\text{PPh}_3)(\text{PCP})$ with $\text{PhC}\equiv\text{CH}$. Treatment of a freshly prepared benzene solution of **5** with excess $\text{PhC}\equiv\text{CH}$ produced the coupling product $\text{Os}(\text{C}\equiv\text{CPh})(=\text{C}=\text{CHPh})(\text{PPh}_3)(1-(\text{CHPh}=\text{C})-2,6-(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$ (**6**). As indicated by in situ NMR experiments, the reaction also produced ca. 1.7 equiv of styrene and some oligomers of phenylacetylene (Scheme 1). **6** is also produced when a mixture of **4** and **5** was treated with phenylacetylene. Although **6** is the only metal-containing product, the presence of oligomeric phenylacetylene makes its purification difficult and limits the isolated yield. An analytically pure sample of **6** was obtained in 56% yield by column chromatography on neutral alumina.

The structure of **6** could not be assigned confidently on the basis of the spectroscopic data. Thus a single-crystal X-ray diffraction study was carried out. The molecular structure of **6** is depicted in Figure 1. The crystallographic details and selected bond distance and angles are given in Tables 1 and 2, respectively.

The crystal structure reveals that three molecules of phenylacetylene have been incorporated into the osmium center: one in the form of vinylidene, one in the form of acetylide, and the other one linked to the central aromatic ring of PCP and osmium as a vinyl substituent $\text{C}=\text{CHPh}$. The coordination geometry around osmium can be described as a distorted octahedron with the PPh_3 *trans* to the vinyl ligand. The bite angle $\text{P}(1)-\text{Os}(1)-\text{P}(2)$ ($147.97(6)^\circ$) is close to that of $\text{OsCl}(\text{PPh}_3)(\text{PCP})$ ($149.9(1)^\circ$)¹² and significantly smaller than those in

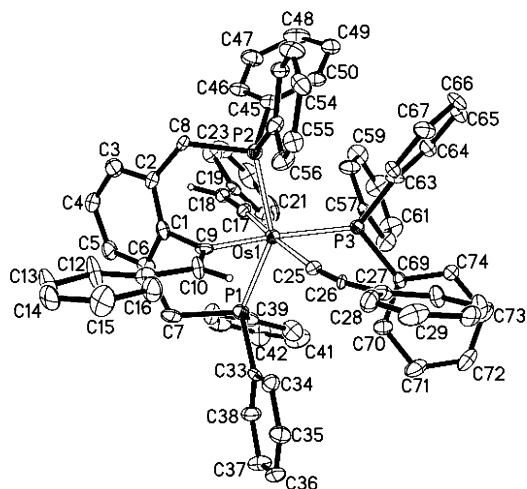


Figure 1. Molecular structure of $\text{Os}(\text{C}\equiv\text{CPh})(=\text{C}=\text{CHPh})(\text{PPh}_3)(1-(\text{CHPh}=\text{C})-2,6-(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$ (**6**).

Table 1. Crystal Data and Structure Refinement for $\text{Os}(\text{C}\equiv\text{CPh})(=\text{C}=\text{CHPh})(\text{PPh}_3)(1-(\text{CHPh}=\text{C})-2,6-(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)\cdot 3\text{C}_6\text{H}_6$

empirical formula	$\text{C}_{74}\text{H}_{59}\text{OsP}_3\cdot 3\text{C}_6\text{H}_6$
fw	1465.65
temperature	294(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell dimens	$a = 11.897(3)$ Å, $\alpha = 93.799(6)^\circ$ $b = 12.121(3)$ Å, $\beta = 101.487(7)^\circ$ $c = 26.035(6)$ Å, $\gamma = 97.342(6)^\circ$
volume	3632.9(14) Å ³
Z	2
density(calcd)	1.340 g/cm ³
abs coeff	1.868 mm ⁻¹
θ range for data collection	1.70–23.31°
no. of refls collected	16 931
no. of indep refls	10440 ($R_{\text{int}} = 0.0837$)
no. of obsd refls [$I > 2\sigma(I)$]	5144
max. and min. transmn	1.0000 and 0.8352
no. of data/restraints/params	10 440/27/865
goodness-of-fit on F^2	0.821
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0697$, $wR_2 = 0.1297$
largest diff peak and hole	1.287 and -1.458 e ⁻ Å ⁻³

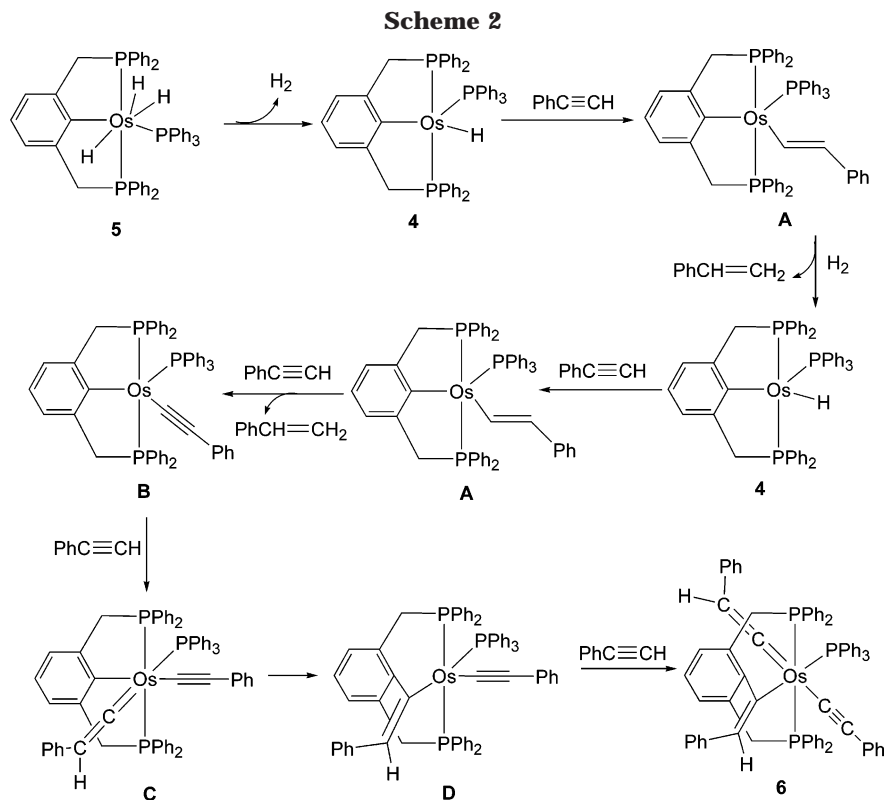
Table 2. Selected Bond Lengths and Angles for $\text{Os}(\text{C}\equiv\text{CPh})(=\text{C}=\text{CHPh})(\text{PPh}_3)(1-(\text{CHPh}=\text{C})-2,6-(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)\cdot 3\text{C}_6\text{H}_6$ (6**· $3\text{C}_6\text{H}_6$)**

Bond Distances (Å)			
$\text{Os}(1)-\text{P}(1)$	2.3883(15)	$\text{Os}(1)-\text{P}(2)$	2.4075(14)
$\text{Os}(1)-\text{P}(3)$	2.4108(17)	$\text{Os}(1)-\text{C}(9)$	2.155(6)
$\text{Os}(1)-\text{C}(17)$	1.869(6)	$\text{Os}(1)-\text{C}(25)$	2.109(6)
$\text{C}(1)-\text{C}(9)$	1.483(8)	$\text{C}(9)-\text{C}(10)$	1.316(8)
$\text{C}(17)-\text{C}(18)$	1.273(8)	$\text{C}(25)-\text{C}(26)$	1.169(8)
Bond Angles (deg)			
$\text{P}(1)-\text{Os}(1)-\text{P}(2)$	147.97(6)	$\text{P}(2)-\text{Os}(1)-\text{P}(3)$	100.76(5)
$\text{P}(1)-\text{Os}(1)-\text{P}(3)$	108.67(5)	$\text{C}(9)-\text{Os}(1)-\text{P}(3)$	163.03(17)
$\text{C}(17)-\text{Os}(1)-\text{C}(25)$	174.9(2)	$\text{C}(9)-\text{Os}(1)-\text{P}(1)$	77.52(14)
$\text{P}(1)-\text{Os}(1)-\text{P}(1)$	83.21(16)	$\text{C}(25)-\text{Os}(1)-\text{P}(1)$	97.74(14)
$\text{C}(17)-\text{Os}(1)-\text{C}(9)$	99.9(2)	$\text{C}(25)-\text{Os}(1)-\text{C}(9)$	85.2(2)
$\text{C}(17)-\text{Os}(1)-\text{P}(2)$	81.12(15)	$\text{C}(25)-\text{Os}(1)-\text{P}(2)$	100.34(14)
$\text{C}(9)-\text{Os}(1)-\text{P}(2)$	77.90(13)	$\text{C}(17)-\text{Os}(1)-\text{P}(3)$	96.57(19)
$\text{C}(25)-\text{Os}(1)-\text{P}(3)$	78.38(17)	$\text{C}(1)-\text{C}(9)-\text{Os}(1)$	104.8(4)
$\text{C}(10)-\text{C}(9)-\text{Os}(1)$	129.8(5)	$\text{C}(10)-\text{C}(9)-\text{C}(1)$	125.3(5)
$\text{C}(9)-\text{C}(10)-\text{C}(11)$	127.8(6)	$\text{C}(18)-\text{C}(17)-\text{Os}(1)$	175.5(5)
$\text{C}(17)-\text{C}(18)-\text{C}(19)$	138.3(6)	$\text{C}(26)-\text{C}(25)-\text{Os}(1)$	172.5(5)

$\text{OsCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)(\text{PCP})$ ($157.13(5)^\circ$),¹² $\text{RuCl}(\text{PPh}_3)(1-(\text{PhCH}=\text{C})-2,6-(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$ ($159.17(6)^\circ$),^{11a,b} and $\text{RuCl}(\text{C}\equiv\text{C}(\text{CH}_2\text{Bu})_2)(1-(\text{Bu}'\text{CH}=\text{C})-2,6-(\text{CH}_2\text{PBu}'_2)_2\text{C}_6\text{H}_3)$ ($163.53(3)^\circ$).¹³ The $\text{Os}-\text{C}(\text{vinyl})$ ($2.155(6)$ Å),

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Os–C (alkynyl) (2.109(6) Å), and Os=C (vinylidene) (1.869(6) Å) as well as the corresponding Os–C–C bond angles are normal compared to those reported for osmium alkenyl,^{2c,22} alkynyl,²³ or vinylidene^{8,24} complexes.

Consistent with the solid-state structure, the ³¹P{¹H} NMR spectrum in CD₂Cl₂ showed a doublet at 5.8 ppm for the PPh₂ groups and a triplet at –4.2 ppm for the PPh₃ ligand (*J*(PP) = 4.5 Hz). The presence of the vinylidene ligand is supported by the ¹³C{¹H} NMR spectrum (in CD₂Cl₂), which exhibited the Os=C signal at 306.6 ppm and the Os=C=CH signal at 110.1 ppm, and the ¹H NMR spectrum (in CD₂Cl₂), which showed the vinylidene proton signal at –0.37 ppm. The vinyl proton signal appeared as a quartet at 7.95 ppm (*J*(PH) = 3.5 Hz) in the ¹H NMR spectrum or a singlet in the ¹H{³¹P} NMR spectrum. In the ¹³C{¹H} NMR spectrum, the signal of the α-carbon of the vinyl group appeared at 144.7 ppm (dt, *J*(PC) = 41.7, 17.8 Hz). The magnitude of the coupling constants agrees well with the *trans*

deposition of the vinyl and PPh₃ ligands. The β-carbon signal of the vinyl group was observed at 132.8 ppm (t, *J*(PC) = 6.2 Hz). The presence of the acetylide ligand is also supported by the infrared spectrum, which showed the characteristic absorption of C≡C stretching at 2080.9 cm⁻¹. Complex **6** is interesting because it represents a rare example of mononuclear complexes with acetylide, vinyl, and vinylidene ligands.

Scheme 2 shows a plausible mechanism for the formation of **6**. Complex **5** may lose an H₂ molecule first to give the 16e monohydride **4**, which then undergoes an insertion reaction with PhC≡CH to give the vinyl intermediate **A**. The vinyl complex **A** can then react with the H₂ to liberate styrene and regenerate the monohydride **4**. Similar reactions are well documented for hydrogenation of alkynes by metal hydride complexes. Complex **4** can again react with an additional molecule of PhC≡CH to give the vinyl intermediate **A**, which now can react with another molecule of PhC≡CH to give styrene and acetylide intermediate **B**. Reactions of vinyl complexes with terminal alkynes to give acetylide complexes and olefins are well-established reactions.²⁵ Reaction of **B** with PhC≡CH could then give vinylidene complex **C**, which can then undergo coupling reactions to give the coordinatively unsaturated intermediate **D**. Reaction of intermediate **D** with PhC≡CH would give complex **6**. To gain information on the reaction mechanism, the reaction of **5** with excess phenylacetylene has been monitored by NMR. Unfortunately, no intermediates can be identified.

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It is noted that reaction of $\text{OsCl}(\text{PPh}_3)(\text{PCP})$ with $\text{RC}\equiv\text{CH}$ produces the vinylidene complexes $\text{OsCl}(\text{C}=\text{CHR})(\text{PPh}_3)(\text{PCP})$, which do not undergo coupling reactions. In contrast, reactions of $\text{OsH}_n(\text{PPh}_3)(\text{PCP})$ ($n = 1, 3$) with $\text{PhC}\equiv\text{CH}$ produce the unusual coupling product $\text{Os}(\text{C}\equiv\text{CPh})(\text{C}=\text{CHPh})(\text{PPh}_3)(1-(\text{CHPh}=\text{C})-2,6-(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$. Probably, the presence of strong σ -donor ligand (e.g., the acetylide ligand in the intermediate **C**) weakens the $\text{Os}=\text{C}$ and $\text{Os}-\text{C}$ bonds, therefore facilitating the coupling reaction.

Experimental Section

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium-benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane, CHCl_3). The starting materials $\text{OsCl}(\text{PPh}_3)(\text{PCP})$ and $\text{OsCl}(\text{C}=\text{CHPh})(\text{PPh}_3)(\text{PCP})$ were prepared according to literature methods.¹² Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were collected on a Bruker ARX-300 spectrometer (300 MHz). ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 .

$\text{Os}(\text{O}_2\text{CCH}_3)(\text{C}=\text{CHPh})(\text{PCP})$ (2). A mixture of $\text{OsCl}(\text{C}=\text{CHPh})(\text{PPh}_3)(\text{PCP})$ (0.60 g, 0.56 mmol) and TIOAc (0.22 g, 0.85 mmol) in THF (60 mL) was stirred at room temperature for 24 h to give a brownish-red solution along with a pale precipitate. The solvent was removed under vacuum to give a pale brown solid, which was extracted with benzene (30 mL). The insoluble TiCl_4 was removed by filtration. After the filtrate was concentrated to ca. 5 mL, hexane (30 mL) was added slowly to give a pink solid. The solid was collected by filtration, washed with hexane (2×30 mL), and dried under vacuum overnight. Yield: 0.29 g, 63%. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6): δ 27.3 (s). ^1H NMR (300.13 MHz, C_6D_6): δ 1.44 (s, 3 H, O_2CCH_3), 2.60 (t, $J(\text{PH}) = 3.1$ Hz, 1 H, $\text{Os}=\text{C}=\text{CH}$), 4.23 (dt, $J(\text{HH}) = 15.7$ Hz, $J(\text{PH}) = 4.7$ Hz, 2 H, CH_2), 4.37 (dt, $J(\text{HH}) = 15.7$ Hz, $J(\text{PH}) = 4.4$ Hz, 2 H, CH_2), 7.88–6.87 (m, 28 H, PPh_2 , C_6H_5 , C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CD_2Cl_2): δ 300.4 (t, $J(\text{PC}) = 11.0$ Hz, $\text{Os}=\text{C}$), 185.1 (s, O_2CCH_3), 151.8 (s, $\text{Os}-\text{C}(\text{aryl})$), 149.7–122.6 (m, other aromatic carbons), 109.2 (t, $J(\text{PC}) = 3.7$ Hz, $\text{Os}=\text{C}=\text{CH}$), 44.50 (t, $J(\text{PC}) = 17.9$ Hz, CH_2), 25.6 (s, O_2CCH_3). Anal. Calcd for $\text{C}_{42}\text{H}_{36}\text{O}_2\text{P}_2\text{Os}$: C, 61.16; H, 4.40. Found: C, 61.19; H, 4.60. FAB-MS (NBA, m/z): 825 (M^+).

$\text{OsH}(\text{PPh}_3)(\text{PCP})$ (4). Due to its low stability, this compound was not isolated but was prepared and characterized in situ. To an NMR tube charged with $\text{OsCl}(\text{PPh}_3)(\text{PCP})$ (30 mg) and excess NaH was added degassed THF- d_8 (0.5 mL) under an argon atmosphere. After the mixture was shaken for 2 min, the NMR tube was put in an ultrasonic bath for 5 min. to give a brown solution. The NMR spectrum of the brown solution indicates that it is a mixture of **4** and **5** in ca. 1:2 ratio. Characterization data for **4**: $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, THF- d_8): δ 25.2 (d, $J(\text{PP}) = 9.9$ Hz), 11.7 (t, $J(\text{PP}) = 9.9$ Hz). ^1H NMR (300.13 MHz, THF- d_8): δ -11.84 (dt, $J(\text{PH}) = 18.0$, 19.5 Hz, 1 H, OsH), 3.73 (dt (br), $J(\text{HH}) = 15.2$ Hz, $J(\text{PH}) = 4.4$ Hz, 2 H, CH_2), 4.46 (dt (br), $J(\text{HH}) = 15.2$ Hz, $J(\text{PH}) = 3.5$ Hz, 2 H, CH_2), 6.76–7.68 (m, PPh_3 , PPh_2 , C_6H_5).

$\text{OsH}_3(\text{PPh}_3)(\text{PCP})$ (5). Due to its low stability, this compound was not isolated but was prepared and characterized in situ. The NMR sample containing a mixture of **4** and **5** prepared above was refilled with dihydrogen gas to give a pink solution. The NMR spectra of the resulting solution were collected. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, THF- d_8): δ 25.1 (d, $J(\text{PP}) = 12.6$ Hz), 19.8 (t, $J(\text{PP}) = 12.6$ Hz). ^1H NMR (300.13 MHz, THF- d_8): δ -6.98 (br s, $W_{1/2} = 23.1$ Hz, 2 H, OsH_2), -4.79 (dt, $J(\text{PH}) = 24.9$, 14.1 Hz, 1 H, OsH), 3.89 (br d, $J(\text{HH}) = 16.0$ Hz, 2 H, CH_2), 4.12 (br d, $J(\text{HH}) = 16.0$ Hz, 2 H, CH_2), 7.97–

6.70 (m, 38 H, PPh_3 , PPh_2 , C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, THF- d_8): δ 154.8 (d, $J(\text{PC}) = 36.2$ Hz, $\text{Os}-\text{C}(\text{aryl})$), 149.0–121.8 (m, other aromatic carbons), 50.4 (td, $J(\text{PC}) = 19.4$, 3.0 Hz, CH_2). T_1 [ms, OsH_2 , 300.13 MHz, THF- d_8]: 121.2 (298 K), 89.8 (273 K), 89.6 (270 K), 89.8 (265 K), 98.6 (253 K), 117.9 (235 K).

$\text{Os}(\text{C}\equiv\text{CPh})(\text{C}=\text{CHPh})(\text{PPh}_3)(1-(\text{CHPh}=\text{C})-2,6-(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$ (6). A mixture of $\text{OsCl}(\text{PPh}_3)(\text{PCP})$ (0.50 g, 0.52 mmol) and NaH (0.12 g, 5.0 mmol) in THF (15 mL) was stirred under a H_2 atmosphere at RT for 1 h to give a light brown solution. The solvent was removed under vacuum. The residue was extracted with benzene (30 mL) under a H_2 atmosphere and then filtered under an argon atmosphere to give a pink solution. Phenylacetylene (0.58 mL, 5.2 mmol) was added to the pink solution. The mixture was stirred under an argon atmosphere for 1 h to give a brown solution. The volume of the reaction mixture was reduced to ca. 1 mL under vacuum. Then hexane (40 mL) was added slowly with stirring to give a pale brown solid, which was collected by filtration, washed with hexane (2×30 mL), and dried under vacuum. The crude product was redissolved in 2 mL of CH_2Cl_2 and passed through a neutral alumina column using benzene as the eluting solvent. The pink band was collected, and the solvent was removed completely to give a pink solid. Yield: 0.36 g, 56%. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2): δ 5.8 (d, $J(\text{PP}) = 4.5$ Hz), -4.2 (t, $J(\text{PP}) = 4.5$ Hz). ^1H NMR (300.13 MHz, CD_2Cl_2): δ -0.37 (t, $J(\text{PH}) = 4.1$ Hz, 1 H, $\text{Os}=\text{C}=\text{CH}$), 3.45 (dt, $J(\text{HH}) = 14.2$ Hz, $J(\text{PH}) = 4.5$ Hz, 2 H, CH_2), 4.08 (dt, $J(\text{HH}) = 14.2$ Hz, $J(\text{PH}) = 4.1$ Hz, 2 H, CH_2), 7.95 (q, $J(\text{PH}) = 3.5$ Hz, 1 H, $\text{PCP}-\text{C}=\text{CHPh}$), 4.81–8.31 (m, 53 H, PPh_3 , PPh_2 , C_6H_5 , C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.4 MHz, CD_2Cl_2): δ 306.6 (td, $J(\text{PC}) = 16.7$, 9.0 Hz, $\text{Os}=\text{C}$), 167.6 (td, $J(\text{PC}) = 8.9$, 3.0 Hz, *ipso-C* of PCP aryl), 144.7 (dt, $J(\text{PH}) = 41.7$, 17.8 Hz, $\text{PCP}-\text{C}=\text{CHPh}$), 132.8 (t, $J(\text{PC}) = 6.7$ Hz, $\text{PCP}-\text{C}=\text{CHPh}$), 140.4–121.4 (m, other aromatic carbons), 119.0 (dt, $J(\text{PH}) = 25.3$, 9.7 Hz, $\text{Os}-\text{C}(\text{CPh})$), 126.1 (br s, $\equiv\text{CPh}$), 110.1 (t, $J(\text{PH}) = 8.9$ Hz, $\text{Os}=\text{C}=\text{CH}$), 43.3 (t, $J(\text{PC}) = 19.4$ Hz, CH_2 of PCP). The ^{13}C assignments were supported by DEPT, $^1\text{H}-^{13}\text{C}$ COSY, and $^1\text{H}-^{13}\text{C}$ COLOC spectra. IR (KBr): 2080.9 cm^{-1} [$\nu(\text{C}\equiv\text{C})$]. Anal. Calcd for $\text{C}_{74}\text{H}_{59}\text{P}_3\text{Os}$: C, 72.18; H, 4.83. Found: C, 72.25; H, 5.02. FAB-MS (NBA, m/z): 1232 (M^+), 970 ($[\text{M} - \text{PPh}_3]^+$).

Crystallographic Analysis. Crystals suitable for X-ray diffraction were grown from a saturated solution of **6** in benzene. Intensity data were collected on a Bruker SMART CCD area detector and corrected for SADABS (Siemens Area Detector Absorption).²⁶ The structure was 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)²⁷ program package. All non-hydrogen atoms were refined anisotropically. Three benzene solvent molecules were cocrystallized in the packing. The benzene solvent molecules and the phenyl ring of the vinylidene ligand were refined with fixed C–C bond distances restraints. Hydrogen atoms were placed in the ideal positions and refined as riding atoms. Further details on crystal data and data collection 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 displacement coefficients, and anisotropic displacement coefficients for $\text{Os}(\text{C}\equiv\text{CPh})(\text{C}=\text{CHPh})(\text{PPh}_3)(1-(\text{CHPh}=\text{C})-2,6-(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_3)$ (**6**). This material is available free of charge via the Internet at <http://pubs.acs.org>. OM034141W

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