ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

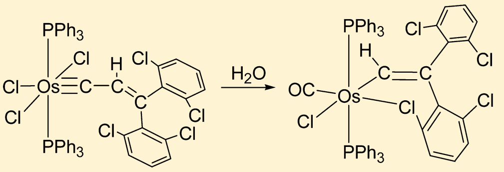
Hydrolysis of Osmium and Ruthenium Carbyne Complexes

Jiangxi Chen, Herman Ho-Yung Sung, Ian Duncan Williams, and Guochen Jia*

Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Supporting Information

ABSTRACT: Hydrolysis reactions of $MCl_3(\equiv CCH{=}C(ArCl)_2)(PPh_3)_2$ (M = Ru, Os) were investigated. Treatment of $OsCl_3(\equiv CCH{=}C(o,o'\text{-}C_6H_3Cl_2)_2)(PPh_3)_2$ with water produced the six-membered metallacycle $OsCl(\kappa C,\kappa Cl\text{-}CH{=}C(o,o'\text{-}C_6H_3Cl_2)_2)(CO)(PPh_3)_2$. Reactions of $MCl_3(\equiv CCH{=}C(o\text{-}C_6H_4Cl)_2)(PPh_3)_2$ (M = Ru, Os) produced the related six-membered metallacycles $MCl(\kappa C,\kappa Cl\text{-}CH{=}C(o\text{-}C_6H_4Cl)_2)(CO)(PPh_3)_2$.



INTRODUCTION

There has been much interest in the chemistry of carbyne complexes of group 8 metals, especially those of ruthenium and osmium,[1] because of their relevance to catalysis and/or synthesis of organometallic and organic compounds. Ruthenium and osmium alkenylcarbyne complexes represent a particularly interesting class of carbyne complexes of group 8 metals. In the past, a number of alkenylcarbyne complexes of ruthenium[2,3] and osmium[4,5] have been reported. Interesting reactions of such complexes have also been revealed. For example, complexes such as $[(p\text{-cymene})Ru{\equiv}CCH{=}CAr_2)(PR_3)]^{2+}$,[6] $RuCl_3(\equiv CCH{=}CPh_2)(PPh_3)_2$,[7] and $[CpOs(\equiv CCH{=}CPh_2)(P^iPr_3)(CO)](PF_6)_2$[8] can rearrange to indenylidene complexes. The osmium complex $[Os(CH{=}CHPh)(\equiv CCH{=}CPh_2)(CH_3CN)_2(P^iPr_3)_2][BF_4]_2$ reacts with carbon monoxide to give a dienylcarbene derivative.[9] Osmium complexes of the type $[OsL_n(R')(\equiv CCH{=}CR_2)]^{n+}$ (R′ = H, vinyl) react with neutral ligands L′ such as CH_3CN to give the carbene complexes $[OsL_nL'({=}CR'CH{=}CR_2)]^{n+}$.[10] Ruthenium complexes of the type $[Cp^*Ru(\equiv CCH{=}CRR')(dippe)][BF_4]_2$ (dippe = 1,2-bis(diisopropylphosphino)ethane) react with a variety of reagents such as ketones, 1,3-dicarbonyl compounds, and aromatic compounds at the γ-carbon to give a series of alkylated vinylidene complexes.[11] Osmium complexes such as $OsCl_3(\equiv CCH{=}CRCH{=}CR'Cl)(PPh_3)_2$ and $OsCl_3(\equiv CCH{=}C(o\text{-}C_6H_4Cl)_2)(PPh_3)_2$ can be used to prepare osmabenzyne complexes through their zinc reduction reactions.[12] In this work, we report hydrolysis reactions of $MCl_3(\equiv CCH{=}C(o\text{-}ArCl)_2)(PPh_3)_2$ (M = Ru, Os), which lead to the isolation of six-membered metallacycles involving a bridging chloride of the aryl ring.

RESULTS AND DISCUSSION

Hydrolysis Reaction of *mer*-$OsCl_3(\equiv CCH{=}C(o,o'\text{-}C_6H_3Cl_2)_2)(PPh_3)_2$. We have recently shown that the osmium complex $OsCl_3(\equiv CCH{=}C(o\text{-}C_6H_4Cl)_2)(PPh_3)_2$ can react with zinc to give an osmanaphthalyne complex.[12a] In an effort to extend the chemistry, we have prepared the related carbyne complex $OsCl_3(\equiv CCH{=}C(o,o'\text{-}C_6H_3Cl_2)_2)(PPh_3)_2$ (**3**). During the process, we found that **3** can react with H_2O to give an interesting six-membered metallacycle involving a bridging chloride of the aryl ring.

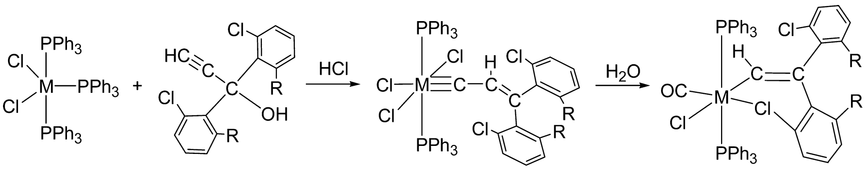
Complex **3** was prepared from the one-pot reaction of $OsCl_2(PPh_3)_3$ (**1**) with alkynol **2** and $HPPh_3BF_4$ in the presence of NaCl in CH_2Cl_2 (Scheme 1). Its structure has been confirmed by X-ray diffraction. The molecular structure of **3** is shown in Figure 1, and selected bond distances and angles are given in Table 1. The solid-state structure is supported by solution NMR data.

Complex **3** can be stored as a solid under an inert atmosphere for months without appreciable decomposition. As monitored by NMR, complex **3** was slowly converted to a new species in a wet THF solution. Further investigation shows that the new species is the interesting six-membered metallacycle $OsCl(\kappa C,\kappa Cl\text{-}CH{=}C(o,o'\text{-}C_6H_3Cl_2)_2)(CO)(PPh_3)_2$ (**4**) (Scheme 1). The conversion was almost complete after a mixture of **3** and excess (ca. 49 equiv of) H_2O suspended in THF was stirred at room temperature for 12 h or heated at 50 °C for 8 h (Scheme 1).

Complex **4** was isolated as a yellow solid and has been characterized by NMR and elemental analysis as well as X-ray diffraction. The molecular structure of **4** is shown in Figure 2, and selected bond distances and angles are given in Table 2. As shown in Figure 2, the complex can be described as a distorted octahedron containing two trans PPh_3 ligands and two cis chloride ligands. The most interesting feature of the structure is that it contains a nonplanar six-membered metallacycle with one of the chlorides of the aryl rings bound to osmium. The Os−C1 bond distance of 2.045(2) Å is within the range of Os−C(vinyl) bonds (1.897−2.195 Å).[13,14] The Os−Cl2(bridged) bond (2.5385(6) Å) is longer than the Os−Cl1(terminal) bond (2.4811(6) Å) and is close to that (2.574(1) Å) in the related complex $OsH(\kappa O,\kappa Cl\text{-}OC_6Cl_5)(CO)(P^iPr_3)_2$.[15] The C(4)−Cl(2)−Os(1) angle (106.77(8)°) is significantly larger than that in $OsH(\kappa O,\kappa Cl\text{-}OC_6Cl_5)(CO)(P^iPr_3)_2$ (98.4(2)°).[15]

Received: July 26, 2011
Published: November 3, 2011

Scheme 1



1 (M = Os) **2** (R = Cl) **3** (M = Os, R = Cl) **4** (M = Os, R = Cl)
5 (M = Os, R = H) **6** (M = Os, R = H)
7 (M = Ru) **8** (R = H) **9** (M = Ru, R = H) **10** (M =Ru; R = H)

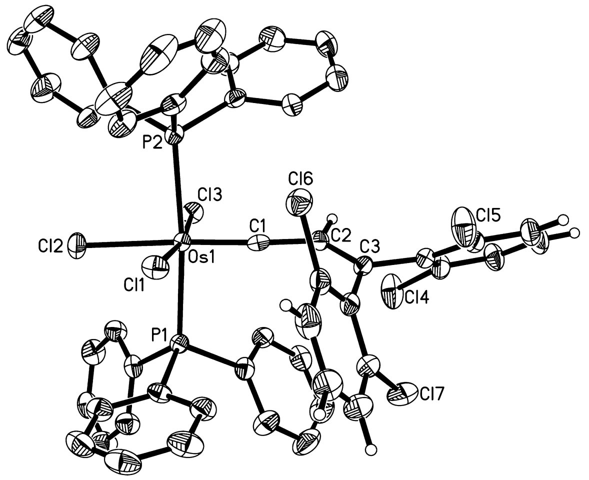


Figure 1. ORTEP drawing of **3** with ellipsoids at the 35% probability level. The hydrogen atoms on the PPh_3 ligands are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Osmium Carbyne Complexes $OsCl_3(\equiv CCH{=}C(o,o'\text{-}C_6H_3Cl_2)_2)(PPh_3)_2$ (3) and $OsCl_3(\equiv CCH{=}C(o\text{-}C_6H_4Cl)_2)(PPh_3)_2$ (5)

	3	5
Os(1)−P(1)	2.4427(14)	2.431(2)
Os(1)−P(2)	2.4797(14)	2.4416(19)
Os(1)−Cl(1)	2.3687(12)	2.3756(16)
Os(1)−Cl(2)	2.4516(13)	2.4607(16)
Os(1)−Cl(3)	2.4062(12)	2.4252(16)
Os(1)−C(1)	1.755(5)	1.744(6)
C(1)−C(2)	1.408(7)	1.416(8)
C(2)−C(3)	1.347(7)	1.347(8)
C(2)−C(1)−Os(1)	170.1(4)	166.4(5)
C(1)−Os(1)−P(1)	92.72(16)	94.6(2)
C(1)−Os(1)−P(2)	93.23(16)	91.9(2)
C(1)−Os(1)−Cl(1)	96.58(16)	96.7(2)
C(1)−Os(1)−Cl(2)	176.77(15)	175.6(2)
C(1)−Os(1)−Cl(3)	91.31(16)	87.3(2)

Consistent with the solid-state structure, the $^{13}C\{^1H\}$ NMR spectrum of **4** shows the Os−CH signal as a triplet at 158.1 ppm with a J_{PC} coupling constant of 5.5 Hz, the Os−CH=*C* signal as a singlet at 141.6 ppm, and the CO signal at 180.0 ppm as a triplet with a J_{PC} coupling constant of 11.7 Hz. As indicated by the solid-state structure shown in Figure 2, the six-membered metallacycle of **4** is not planar and therefore the two PPh_3 ligands are magnetically inequivalent. At room temperature, the $^{31}P\{^1H\}$ NMR spectrum of **4** shows a sharp singlet at 7.5 ppm, indicating that the conformation of the six-membered metallacycle changes rapidly in solution at this temperature.

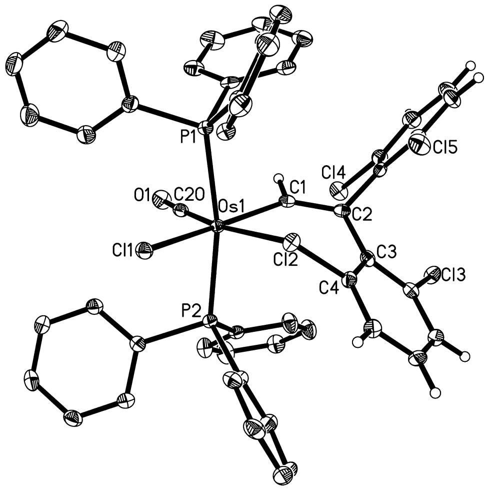


Figure 2. ORTEP drawing of **4** with ellipsoids at the 50% probability level. The solvent and the hydrogen atoms on the PPh_3 ligands are omitted for clarity.

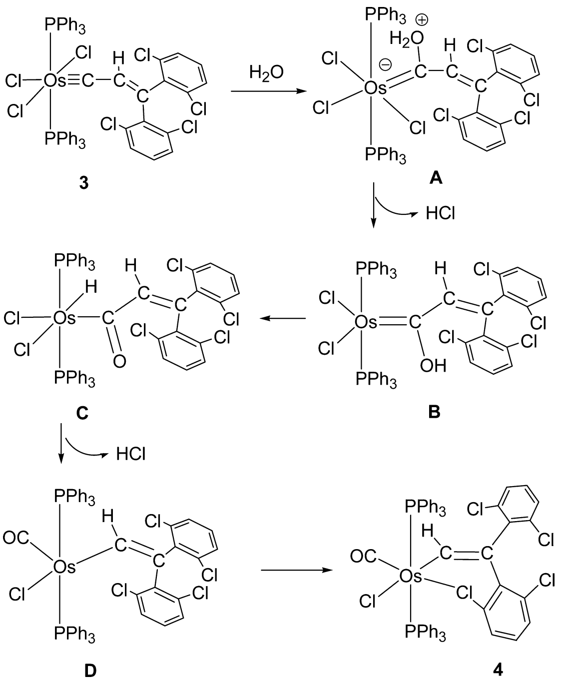
Table 2. Selected Bond Distances (Å) and Angles (deg) for Metallacycles $OsCl(\kappa C,\kappa Cl\text{-}CH{=}C(o,o'\text{-}C_6H_3Cl_2)_2)(CO)(PPh_3)_2$ (4) and $RuCl(\kappa C,\kappa Cl\text{-}CH{=}C(o\text{-}C_6H_4Cl)_2)(CO)(PPh_3)_2$ (10)

	4 (M = Os)	**10** (M = Ru)
M(1)−C(1)	2.045(2)	2.057(5)
C(1)−C(2)	1.355(3)	1.369(9)
C(2)−C(3)	1.483(3)	1.485(9)
C(3)−C(4)	1.405(3)	1.383(9)
C(4)−Cl(2)	1.754(2)	1.755(6)
M(1)−Cl(2)	2.5385(6)	2.5150(16)
M(1)−Cl(1)	2.4811(6)	2.4853(15)
M(1)−C(20)	1.813(2)	1.824(7)
M(1)−P(1)	2.3905(6)	2.4137(15)
M(1)−P(2)	2.3842(6)	2.3774(15)
M(1)−C(1)−C(2)	133.77(18)	133.0(5)
C(1)−C(2)−C(3)	124.4(2)	126.1(6)
C(2)−C(3)−C(4)	123.9(2)	126.1(6)
C(3)−C(4)−Cl(2)	118.48(18)	121.0(5)
C(4)−Cl(2)−M(1)	106.77(8)	109.6(2)
Cl(2)−M(1)−C(1)	81.58(7)	84.28(18)
Cl(2)−M(1)−Cl(1)	83.116(19)	85.91(5)
Cl(2)−M(1)−C(20)	168.52(7)	172.53(19)
C(1)−M(1)−C(20)	86.95(10)	88.4(3)
C(1)−M(1)−Cl(1)	163.26(6)	169.46(17)
C(1)−M(1)−P(1)	86.86(6)	88.72(16)
C(1)−M(1)−P(2)	102.48(6)	94.07(16)

The fluxional process is slowed down at low temperature. Thus, two doublet $^{31}P\{^1H\}$ signals were observed when the temperature was below −41 °C. For example, the $^{31}P\{^{1}H\}$ NMR spectrum at −78 °C shows two doublets at 9.64 and 5.89 ppm with a large J_{PP} coupling constant of 275.8 Hz, as expected for two trans-disposed PPh_3 ligands.

Scheme 2 shows a plausible mechanism for the formation of **4** from the reaction of **3** with H_2O. Water could serve as a nucleophile to attack the carbyne carbon of **3** to give intermediate **A**, which can eliminate a molecule of HCl to give **B**. A *β*-H elimination of **B** would give **C**, which undergoes CO deinsertion and elimination of another molecule of HCl to give **D**. The final product **4** could then be formed by coordinating one of the chlorides of the aryl groups to the osmium center.

Scheme 2



Reactions of Fischer carbynes with nucleophiles at the carbyne carbon to give carbene complexes are well-known reactions.[16] For osmium carbyne complexes, nucleophilic addition reactions of methanol have been reported: for example, the reactions of CpOs(CPh)(L) (L = $P^{i}Pr_3$, $P^{i}Pr_2CH{=}CH_2$) with MeOH to give CpOsH(=C(OMe)Ph)(L)[17] and the reaction of $[Os(CPh)(NH_3)_5]^{3+}$ with MeOH to give $[Os(=C(OMe)Ph)(NH_3)_5]^{2+}$.[18]

Complex **4** is interesting because it represents a rare example of six-membered haloarene complexes of osmium. A search of the CCDC database shows that $[OsCl(\kappa O,\kappa Cl\text{-}OC_6Cl_5)(CO)(P^{i}Pr_3)_2]$[15] is the only reported structurally characterized haloarene complex of osmium, although a number of haloraene complexes of other transition metals are known.[19] Furthermore, most of the reported chelating chloroarene complexes are either five-membered-ring[20] or four-membered-ring[21] metallacycles. Complex **4** appeared to be the first structurally characterized six-membered chelating chloroarene transition-metal complex.

Hydrolysis Reaction of *mer*-$OsCl_3(\equiv CCH{=}C(o\text{-}C_6H_4Cl)_2)(PPh_3)_2$. In order to see whether a similar reaction can also occur for other osmium carbyne complexes, we have studied the reaction of *mer*-$OsCl_3(\equiv CCH{=}C(o\text{-}C_6H_4Cl)_2)(PPh_3)_2$ (**5**) with H_2O under similar reaction conditions.

It was found that *mer*-$OsCl_3(\equiv CCH{=}C(o\text{-}C_6H_4Cl)_2)(PPh_3)_2$ (**5**) is less reactive toward H_2O than complex **3**. When a mixture of **5** and excess (ca. 270 equiv of) H_2O suspended in THF was stirred at 50 °C for 22 h, complex **5** was partially converted to the expected product **6**, which was isolated in about 26% yield (Scheme 1).

The identity of the complex **6** is inferred from its ^{31}P and ^{13}C NMR data. The $^{31}P\{^{1}H\}$ NMR spectrum shows two doublets at 9.37 and 4.41 ppm with a large J_{PP} coupling constant of 286.2 Hz, as expected for two trans-disposed PPh_3 ligands. In the $^{13}C\{^{1}H\}$ NMR spectrum, the CO signal was observed at 179.9 ppm as a triplet with a J_{PC} coupling constant of 11.6 Hz. The signal of Os−CH was located at 150.5 ppm as a triplet with a J_{PC} coupling constant of 6.2 Hz, and that of Os−CH=C was located at 145.7 ppm as a singlet.

We also studied the reaction of *mer*-$OsCl_3(\equiv CCH{=}CPh_2)(PPh_3)_2$ with H_2O. No appreciable reaction was observed after a suspension of *mer*-$OsCl_3(\equiv CCH{=}CPh_2)(PPh_3)_2$ and excess H_2O in THF was stirred at room temperature for 1 week or heated at 50 °C for 1 day.

Hydrolysis Reactions of *mer*-$RuCl_3(\equiv CCH{=}C(o\text{-}C_6H_4Cl)_2)(PPh_3)_2$ (9). We next studied the reaction of the related ruthenium carbyne complex *mer*-$RuCl_3(\equiv CCH{=}C(o\text{-}C_6H_4Cl)_2)(PPh_3)_2$ (**9**) with H_2O. Complex **9** can be prepared from the one-pot reaction of $RuCl_2(PPh_3)_3$ (**7**) with alkynol **8** and HCl in CH_2Cl_2 (Scheme 1). Its structure is inferred by its solution NMR data. In particular, the $^{31}P\{^{1}H\}$ NMR spectrum of **9** shows a singlet at 13.7 ppm and the ^{1}H NMR spectrum shows the Ru≡CC*H* signal at 5.29 ppm as a triplet with a J_{PH} coupling constant of 2.2 Hz. The NMR data are similar to those of the analogous complex *mer*-$RuCl_3(\equiv CCH{=}CPh_2)(PPh_3)_2$.[7]

It was found that complex **9** is more reactive toward H_2O than complex **5**. When a mixture of **9** and excess (ca. 73 equiv of) H_2O was stirred at room temperature for 40 min, it was completely transformed to complex **10** (Scheme 1).

Complex **10** has been characterized by NMR and elemental analysis as well as X-ray diffraction. The molecular structure of **10** is shown in Figure 3, and selected bond distances and angles are given in Table 2. Overall, the structure is similar to that of **4**.

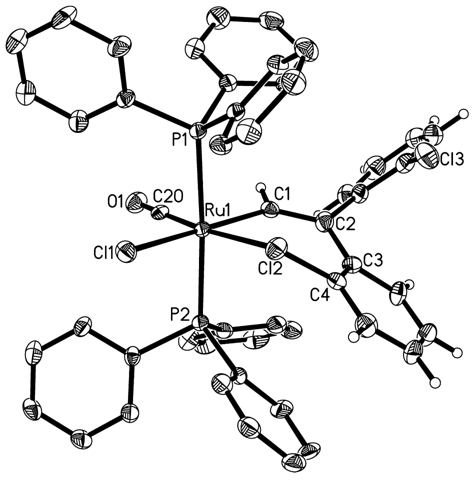


Figure 3. ORTEP drawing of **10** with ellipsoids at the 35% probability level. The solvent and the hydrogen atoms on PPh_3 ligands are omitted for clarity.

The Ru−C1 bond distance of 2.057(5) Å is within the range of Ru−C(vinyl) bonds (1.973−2.161 Å).[13,22] As expected, the Ru−Cl2(bridged) bond (2.5150(16) Å) is longer than the Ru−Cl1(terminal) bond (2.4853(15) Å). The Ru−Cl2(bridged) bond (2.5150(16) Å) is close to those (2.5240(13), 2.4978(13) Å) in $\mathrm{Ru(PPh_2CH_2CH_2P^iPr_2)(\kappa O,\kappa Cl\text{-}OC_6Cl_5)_2}$[23] and shorter than those (2.547(2), 2.604(2) Å) in $\mathrm{Ru_3(CO)_8(\kappa O,\kappa Cl\text{-}OC_6H_4Cl)_2}$.[24] The C(4)−Cl(1)−Ru(1) angle (109.6(2)°) is close to that (106.77(8)°) of complex **4**.

Consistent with the solid-state structure, the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum of **10** shows the Ru−CH signal as a triplet at 166.3 ppm with a J_{PC} coupling constant of 8.7 Hz and that of Ru−CH═C as a singlet at 145.1 ppm. The CO signal was located at 204.1 ppm as a triplet with a J_{PC} coupling constant of 16.9 Hz. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum shows two doublets at 32.58 and 29.07 ppm with a large coupling constant of 305.8 Hz.

Reported structurally characterized ruthenium haloarene complexes include $\mathrm{[Ru(PPh_2CH_2CH_2P^iPr_2)(\kappa O,\kappa Cl\text{-}OC_6Cl_5)_2]}$,[23] $\mathrm{Ru_3(CO)_8(\kappa O,\kappa Cl\text{-}OC_6H_4Cl)_2}$,[24] $\mathrm{[CpRu(CO)(PPh_3)(}p\mathrm{\text{-}IC_6H_4CH_3)]PF_6}$,[25] $\mathrm{Ru(PPh_3)_2(\kappa O,\kappa Br\text{-}OC_6H_2Br_3)_2}$,[26] $\mathrm{Ru(PMe_2Ph)_2(SC_6F_5)_2(\kappa S,\kappa F\text{-}C_6F_5)}$[27] and $\mathrm{[RuCl_2(PPh_3)(\kappa P,\kappa N,\kappa F\text{-}PPh_2CH_2C(^tBu){=}NN{=}CHC_6H_3F_2)}$.[28] We also noted that the reaction of the ruthenium carbyne complex $\mathrm{[Ru(CPh)ICl(CO)(PPh_3)_2)]^+}$ with $\mathrm{H_2O}$ was reported to give $\mathrm{RuPhCl(CO)_2(PPh_3)_2}$.[1a]

In summary, we have investigated the hydrolysis reactions of $\mathrm{MCl_3({\equiv}CCH{=}C(}o\mathrm{\text{-}ArCl)_2)(PPh_3)_2}$ (M = Ru, Os), which produced the interesting six-membered metallacycles $\mathrm{MCl(\kappa C,\kappa Cl\text{-}CH{=}C(}o\mathrm{\text{-}ArCl)_2)(CO)(PPh_3)_2}$.

■ EXPERIMENTAL SECTION

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, ether, THF) or calcium hydride ($\mathrm{CH_2Cl_2}$). The propargyl alcohols were prepared from the reactions of ethynylmagnesium bromide or $\mathrm{LiC{\equiv}CSiMe_3}$ with related ketones, following a procedure similar to that for the preparation of $\mathrm{HC{\equiv}CC(OH)Ph_2}$.[29] $\mathrm{OsCl_2(PPh_3)_3}$[30] and $\mathrm{RuCl_2(PPh_3)_3}$[31] 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). $^1\mathrm{H}$, $^{13}\mathrm{C}\{^1\mathrm{H}\}$, and $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra were collected on a Bruker ARX-400 spectrometer (400 MHz). $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR shifts are relative to TMS, and $^{31}\mathrm{P}$ chemical shifts are relative to 85% $\mathrm{H_3PO_4}$.

***mer*-$\mathrm{OsCl_3(\equiv CCH{=}C(}o,o'\mathrm{\text{-}C_6H_3Cl_2)_2)(PPh_3)_2}$ (3).** A mixture of $\mathrm{OsCl_2(PPh_3)_3}$ (2.007 g, 1.91 mmol), $\mathrm{HC{\equiv}CC(OH)(}o,o'\mathrm{\text{-}C_6H_3Cl_2)_2}$ (**2**; 0.797 g, 2.30 mmol), $\mathrm{HPPh_3BF_4}$ (1.348 g, 3.85 mmol), and NaCl (1.376 g, 23.5 mmol) in $\mathrm{CH_2Cl_2}$ (40 mL) was stirred for 48 h to give a brownish green suspension. The solvent was removed completely under vacuum, and the residue was extracted with benzene (30 mL × 3) and then filtered. The solvent of the extract was removed under vacuum. The residue was dissolved in $\mathrm{CH_2Cl_2}$ (8 mL) and the solution carefully layered with diethyl ether (60 mL). The mixture stood at room temperature for 3 days to give green crystals with a brown solution, which was separated by filtration. The solid was washed with diethyl ether (20 mL × 2) and hexane (20 mL) and dried under vacuum to give **3** as a green solid. Yield: 0.577 g, 26.2%. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (161.98 MHz, $\mathrm{CD_2Cl_2}$): δ −12.1 (s). $^1\mathrm{H}$ NMR (400.13 MHz, $\mathrm{CD_2Cl_2}$): δ 4.81 (t, *J*(PH) = 2.1 Hz, 1H, Os≡CC*H*), 7.07−7.23 (m, 3H, *Ph*$\mathrm{Cl_2}$), 7.23−7.41 (m, 21H, 18H for P*Ph* and 3H for *Ph*$\mathrm{Cl_2}$), 7.73−7.83 (m, 12H, P*Ph*). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.62 MHz, $\mathrm{CD_2Cl_2}$): δ 259.6 (t, *J*(PC) = 10.8 Hz, Os≡C), 147.2 (s, Os≡C-CH═C), 139.2 (s, *Ph*$\mathrm{Cl_2}$), 136.5 (s, Os≡CCH═C), 134.7 (t, *J*(PC) = 4.9 Hz, P*Ph*), 134.5 (s, *Ph*$\mathrm{Cl_2}$), 134.3 (s, *Ph*$\mathrm{Cl_2}$), 130.0 (s, *Ph*$\mathrm{Cl_2}$), 129.7 (s, P*Ph*), 129.6 (s, *Ph*$\mathrm{Cl_2}$), 129.5 (t, *J*(PC) = 26.8 Hz, P*Ph*), 128.6 (s, *Ph*$\mathrm{Cl_2}$), 128.4 (s, *Ph*$\mathrm{Cl_2}$), 126.8 (t, *J*(PC) = 5.0 Hz, P*Ph*). Anal. Calcd for $\mathrm{C_{51}H_{37}Cl_7OsP_2}$: C, 53.26; H, 3.24. Found: C, 53.34; H, 3.40.

$\mathrm{OsCl(\kappa C,\kappa Cl\text{-}CH{=}C(}o,o'\mathrm{\text{-}C_6H_3Cl_2)_2)(CO)(PPh_3)_2}$ (4). To a suspension of **3** (260 mg, 0.226 mmol) in THF (20 mL) was added $\mathrm{H_2O}$ (0.2 mL, 11.1 mmol). The mixture was stirred at 50 °C for 8 h to give a clear yellow solution. The solvent was removed completely under vacuum, and the residue was loaded on a silica gel column that was flashed with dichloromethane/hexane (v/v 1/4) and then eluted with dichloromethane/hexane (v/v 10/1). The yellow band was collected. The solvents were removed under vacuum to give **4** as a yellow solid. Yield: 174 mg, 70.4%. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (161.98 MHz, $\mathrm{CD_2Cl_2}$, 25 °C): δ 7.5 (s). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (161.98 MHz, $\mathrm{CD_2Cl_2}$, −78 °C): δ 9.64 (d, *J*(PP) = 275.8 Hz), 5.89 (d, *J*(PP) = 275.8 Hz). $^1\mathrm{H}$ NMR (400.13 MHz, $\mathrm{CD_2Cl_2}$): δ 6.27 (dd, *J*(HH) = 8.0, 1.2 Hz, 1H, *Ph*$\mathrm{Cl_2}$), 6.40 (t, 1H, *J*(HH) = 8.0 Hz, *Ph*$\mathrm{Cl_2}$), 6.93 (dd, *J*(HH) = 8.0 Hz, 1H, 1.2 Hz, *Ph*$\mathrm{Cl_2}$), 7.00 (t, *J*(HH) = 7.9 Hz, 1H, *Ph*$\mathrm{Cl_2}$), 7.21 (d, *J*(HH) = 7.9 Hz, 2H, *Ph*$\mathrm{Cl_2}$), 7.24−7.38 (m, 18H, P*Ph*), 7.50−7.65 (m, 12H, P*Ph*), 8.44 (t, *J*(PH) = 5.1 Hz, 1H, Os−C*H*). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.62 MHz, $\mathrm{CD_2Cl_2}$): δ 180.0 (t, *J*(PC) = 11.7 Hz, Os(CO)), 158.1 (t, *J*(PC) = 5.5 Hz, Os−CH), 141.6 (s, Os−CH═C), 138.4 (s, *Ph*$\mathrm{Cl_2}$), 133.8 (t, *J*(PC) = 5.1 Hz, P*Ph*), 132.0 (s, *Ph*$\mathrm{Cl_2}$), 131.2 (t, *J*(PC) = 25.4 Hz, P*Ph*), 129.3 (s, P*Ph*), 127.7 (s, *Ph*$\mathrm{Cl_2}$), 127.3 (t, *J*(PC) = 5.0 Hz, P*Ph*), 125.8 (s, *Ph*$\mathrm{Cl_2}$), 125.7 (s, *Ph*$\mathrm{Cl_2}$), 125.5 (s, *Ph*$\mathrm{Cl_2}$). Anal. Calcd for $\mathrm{C_{51}H_{37}Cl_5OOsP_2}$: C, 55.93; H, 3.40. Found: C, 55.77; H, 3.48.

***mer*-$\mathrm{OsCl_3(\equiv CCH{=}C(}o\mathrm{\text{-}C_6H_4Cl)_2)(PPh_3)_2}$ (5).** This known complex **5**[12a] was prepared by the following modified procedure. A mixture of $\mathrm{OsCl_2(PPh_3)_3}$ (1.360 g, 1.30 mmol), $\mathrm{HC{\equiv}CC(OH)(}o\mathrm{\text{-}C_6H_4Cl)_2}$ (**8**; 0.426 g, 1.54 mmol), $\mathrm{HPPh_3BF_4}$ (1.001 g, 2.86 mmol), and NaCl (1.236 g, 21.1 mmol) in $\mathrm{CH_2Cl_2}$ (40 mL) was stirred for 48 h to give a brownish green suspension. The solvent was removed completely under vacuum, and the residue was extracted with benzene (30 mL × 3) and the extract then filtered. The solvent of the extract was removed under vacuum. The residue was dissolved in $\mathrm{CH_2Cl_2}$ (8 mL). Addition of diethyl ether (20 mL) gave a green precipitate and a brown solution, which was separated by filtration. The solid was washed with diethyl ether (20 mL × 2) and hexane (20 mL) and then dried under vacuum to give **5** as a green solid. Yield: 0.711 g, 50.6%. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (161.98 MHz, $\mathrm{CD_2Cl_2}$): δ −14.2 (s). $^1\mathrm{H}$ NMR (400.13 MHz, $\mathrm{CD_2Cl_2}$): δ 4.56 (t, *J*(PH) = 1.8 Hz, 1H, Os≡CC*H*), 6.74 (dd, *J*(HH) = 7.9, 1.0 Hz, 1H, *Ph*Cl), 7.03 (dd, *J*(HH) = 7.9, 1.0 Hz, 1H, *Ph*Cl), 7.15−7.28 (m, 4 H, *Ph*Cl), 7.28−7.38 (m, 19H, 18H for P*Ph* and 1H for *Ph*Cl), 7.41 (t, *J*(HH) = 7.6 Hz, 1H, *Ph*Cl), 7.73−7.82 (m, 12H, P*Ph*). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.62 MHz, $\mathrm{CD_2Cl_2}$): δ 262.4 (t, *J*(PC) = 11.2 Hz, Os≡C), 156.1 (s, CH═C(*o*-ClPh)$_2$), 139.0 (s, CH═C-(*o*-ClPh)$_2$), 137.8 (s, *Ph*Cl), 135.7 (s, *Ph*Cl), 134.4 (t, *J*(PC) = 5.0 Hz, P*Ph*), 132.8 (s, *Ph*Cl), 131.0 (s, *Ph*Cl), 130.9 (s, *Ph*Cl), 130.5 (s, *Ph*Cl), 130.1 (s, *Ph*Cl), 130.0 (s, *Ph*Cl), 129.9 (t, *J*(PC) = 26.2 Hz, P*Ph*), 129.8 (s, *Ph*Cl), 129.7 (s, P*Ph*), 129.0 (s, *Ph*Cl), 127.4 (s, *Ph*Cl), 126.9 (t, *J*(PC) = 5.0 Hz, P*Ph*), 126.3 (s, *Ph*Cl). Anal. Calcd for $\mathrm{C_{51}H_{39}Cl_5OsP_2}$: C, 56.65; H, 3.64. Found: C, 56.62; H, 3.75. Its structure has been confirmed by X-ray diffraction. The molecular structure is shown in Figure 4, and selected bond distances and angles are given in Table 1.

$\mathrm{OsCl(\kappa C,\kappa Cl\text{-}CH{=}C(}o\mathrm{\text{-}C_6H_4Cl)_2)(CO)(PPh_3)_2}$ (6). To a suspension of **5** (44 mg, 0.041 mmol) in THF (20 mL) was added $\mathrm{H_2O}$ (0.2 mL, 11.1 mmol). The mixture was stirred at 50 °C for 22 h to give a greenish-yellow solution. The solvent was removed completely under vacuum, and the residue was loaded on a silica gel column that was flashed with dichloromethane/hexane (v/v 1/5) and then eluted with dichloromethane/hexane (v/v 5/1). The yellow band was collected. The solvents were removed under vacuum to give **6** as a yellow solid. Yield: 11 mg, 26.2%. Further eluting with diethyl ether gave a green solid (26 mg) containing mainly the starting materials. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (161.98 MHz, $\mathrm{CD_2Cl_2}$): δ 9.37 (d, *J*(PP) = 286.2 Hz), 4.41 (d, *J*(PP) = 286.7 Hz). $^1\mathrm{H}$ NMR (400.13 MHz, $\mathrm{CD_2Cl_2}$): δ 6.44 (d, *J*(HH) = 8.0 Hz, 1H, *Ph*Cl), 6.50 (d, *J*(HH) = 7.8 Hz, 1H, *Ph*Cl), 6.54−6.61 (m, 2H, *Ph*Cl), 6.86 (t, *J*(HH) = 7.6 Hz, 1H, *Ph*Cl), 7.06−7.15 (m, 2H, *Ph*Cl), 7.20−7.41 (m, 19H, *Ph*Cl and P*Ph*), 7.45−7.56 (m, 7H, P*Ph* and Os−C*H*), 7.65−7.78 (m, 6H, P*Ph*). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.62 MHz, $\mathrm{CD_2Cl_2}$): δ 179.9 (t, *J*(PC) = 11.6 Hz, Os(CO)), 150.5

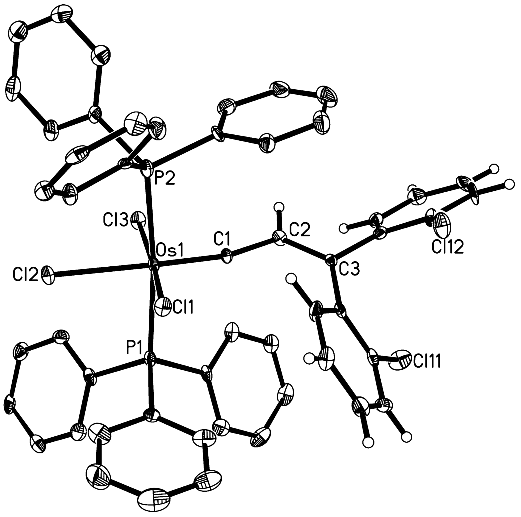


Figure 4. ORTEP drawing of **5** with ellipsoids at the 35% probability level. The hydrogen atoms on the PPh_3 ligands are omitted for clarity.

(t, J(PC) = 6.2 Hz, Os−C*H*), 145.7 (s, Os−CH═*C*), 139.7 (s, *Ph*Cl), 133.9 (d, J(PC) = 9.0 Hz, P*Ph*), 133.5 (d, J(PC) = 9.1 Hz, P*Ph*), 132.3 (d(br), J(PC) = 48.3 Hz, P*Ph*), 132.0 (s, *Ph*Cl), 130.4 (s, *Ph*Cl), 130.2 (d(br), J(PC) = 47.2 Hz, P*Ph*), 129.3 (s, P*Ph*), 129.1 (s, P*Ph*), 128.9 (s, *Ph*Cl), 128.1 (s, *Ph*Cl), 127.1 (d, J(PC) = 9.6 Hz, P*Ph*), 126.9 (s, *Ph*Cl), 126.8 (s, *Ph*Cl), 126.2 (s, *Ph*Cl), 126.1 (s, *Ph*Cl), 124.8 (s, *Ph*Cl). Anal. Calcd for $C_{51}H_{39}Cl_3OOsP_2$: C, 59.68; H, 3.83. Found: C, 59.52; H, 4.14.

***mer*-RuCl$_3$(≡CCH═C(*o*,*o*′-C$_6$H$_4$Cl)$_2$)(PPh$_3$)$_2$ (9).** To a mixture of $RuCl_2(PPh_3)_3$ (1.210 g, 1.26 mmol) and HC≡CC(OH)(*o*-$C_6H_4Cl)_2$ (**8**; 0.440 g, 1.59 mmol) in CH_2Cl_2 (50 mL) was slowly added hydrogen chloride (1.0 M in diethyl ether, 2.8 mL, 2.8 mmol). The reaction mixture was stirred at room temperature for 2 h to give a reddish yellow solution. Then it was filtered via a filter paper to remove a small amount of purple precipitate. The volume of the filtrate was reduced to ca. 5 mL under vacuum, and then diethyl ether (50 mL) was slowly added with stirring to produce a yellow precipitate. After the mixture was stirred for a further 20 min, it was filtered. The yellow solid was washed with diethyl ether (30 mL × 2) again and dried under vacuum to give **9** as a yellow solid. Yield: 0.862 g, 68.8%. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2): δ 13.7 (s). ^1H NMR (400.13 MHz, CD_2Cl_2): δ 5.29 (t, J(PH) = 2.2 Hz, 1H, Ru≡CC*H*), 6.74 (dd, J(HH) = 7.8, 1.2 Hz, 1H, *Ph*Cl), 7.03 (dd, J(HH) = 7.9, 1.0 Hz, 1H, *Ph*Cl), 6.95−7.40 (m, 25 H, 18 H for P*Ph* and 7 H for *Ph*Cl), 7.80−7.90 (m, 12 H, P*Ph*). Anal. Calcd for $C_{51}H_{39}Cl_5RuP_2$: C, 61.74; H, 3.96. Found: C, 62.00; H, 4.18.

RuCl(*κC*,*κCl*-CH═C(*o*-C$_6$H$_4$Cl)$_2$)(CO)(PPh$_3$)$_2$ (10). To a suspension of **9** (150 mg, 0.151 mmol) in THF (20 mL) was added H_2O (0.2 mL, 11.1 mmol). The mixture was stirred at room temperature for 40 min to give a yellow solution. The solvent was removed completely under vacuum, and the residue was loaded on a silica gel column that was flashed with dichloromethane/hexane (v/v 1/5) and then eluted with dichloromethane/hexane (v/v 5/1). The yellow band was collected. The solvents were removed under vacuum to give **10** as a yellow solid. Yield: 98 mg, 69.0%. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2): δ 32.58 (d, J(PP) = 305.8 Hz), 29.07 (d, J(PP) = 306.1 Hz). ^1H NMR (400.13 MHz, CD_2Cl_2): δ 6.39 (d, J(HH) = 8.0 Hz, 1H, *Ph*Cl), 6.59−6.68 (m, 4H, *Ph*Cl and Ru−C*H*), 6.80−6.90 (m, 1H, *Ph*Cl), 7.07−7.18 (m, 2H, *Ph*Cl), 7.20−7.43 (m, 20H, *Ph*Cl and P*Ph*), 7.50−7.88 (m, 6H, P*Ph*). $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2): δ 204.1 (t, J(PC) = 16.9 Hz, Ru(*C*O)), 166.3 (t, J(PC) = 8.7 Hz, Ru−*C*H), 145.1 (s, Ru−CH═*C*), 139.2 (s, *Ph*Cl), 135.4 (s, *Ph*Cl), 133.7 (d(br), J(PC) ≈ 31.2 Hz, P*Ph*), 132.4 (d(br), J(PC) ≈ 40.0 Hz, P*Ph*), 131.7 (s, *Ph*Cl), 130.7 (d(br), J(PC) ≈ 39.4 Hz, P*Ph*), 130.2 (s, *Ph*Cl), 129.2 (s, *Ph*Cl), 129.1 (s, P*Ph*), 128.2 (s, *Ph*Cl), 127.2 (br, P*Ph*), 127.1 (s, *Ph*Cl), 126.6 (s, *Ph*Cl), 126.3 (s, *Ph*Cl), 126.1 (s, *Ph*Cl), 125.3 (s, *Ph*Cl). Anal. Calcd for $C_{51}H_{39}Cl_3ORuP_2$: C, 65.36; H, 4.19. Found: C, 65.22; H, 4.32.

Crystal Structure Analyses. Crystals were grown by slowly evaporating the solvent from their saturated solutions. The crystals of **4** and **10** were from toluene and benzene, respectively, whereas those of **3** and **5** were from dichloromethane/hexane. The diffraction intensity data of **4** were collected with a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Lattice determination and data collection were carried out using SMART v.5.625 software. Data reduction and absorption correction by empirical methods were performed using SAINT v 6.26 and SADABS v 2.03, respectively. The diffraction intensity data of **3**, **5**, and **10** were collected with an Oxford Diffraction Gemini S Ultra

Table 3. Crystallographic Details for Complexes 3−5 and 10

	3	4·$C_6H_5CH_3$	5	10·$^3/_2C_6H_6$
empirical formula	$C_{51}H_{37}Cl_7OsP_2$	$C_{58}H_{45}Cl_5OOsP_2$	$C_{51}H_{39}Cl_5OsP_2$	$C_{60}H_{48}Cl_3ORuP_2$
formula wt	1150.10	1187.33	1081.21	1054.34
temp, K	298(2)	100(2)	173(2)	173(2)
wavelength, Å	1.541 78	0.710 73	0.710 73	1.541 78
cryst syst	orthorhombic	triclinic	monoclinic	triclinic
space group	$P2_12_12_1$	$P\bar{1}$	$I2/a$	$P\bar{1}$
a, Å	10.3624(3)	10.2620(8)	25.295(2)	11.4372(6)
b, Å	14.9316(7)	11.6363(10)	12.8976(7)	12.3519(6)
c, Å	29.4464(13)	23.4763(19)	29.254(3)	18.4620(9)
α, deg	90	76.4000(10)	90	108.436(5)
β, deg	90	79.0880(10)	112.843(10)	91.266(4)
γ, deg	90	66.4540(10)	90	101.520(47)
V, Å^3	4556.2(3)	2483.5(4)	8795.3(13)	2414.2(2)
Z	4	2	8	2
d(calcd), Mg/m^3	1.677	1.588	1.633	1.450
θ range for data collecn, deg	5.39−67.49	1.80−27.00	2.56−26.00	4.90−66.60
no. of rflns collected	23 919	27 519	33 708	11 926
no. of indep rflns	8139 (R(int) = 0.0559)	10 625 (R(int) = 0.0260)	8578 (R(int) = 0.1069)	7658 (R(int) = 0.0505)
no. of data/restraints/params	8139/0/551	10 625/0/605	8578/0/532	7658/66/604
goodness of fit on F^2	1.005	1.043	1.008	1.033
final R indices ($I > 2\sigma(I)$)	R1 = 0.0274, wR2 = 0.0515	R1 = 0.0232, wR2 = 0.0545	R1 = 0.0565, wR2 = 0.0737	R1 = 0.0627, wR2 = 0.1506
largest diff peak and hole, e Å^{-3}	0.838 and −0.463	1.316 and −0.621	2.235 and −1.942	1.815 and −0.809

X-ray diffractometer. Monochromated Cu Kα radiation (λ = 1.541 78 Å) was used for **3** and **10**, and monochromated Mo Kα radiation (λ = 1.541 78 Å) was used for **5**. Lattice determination, data collection, and reduction were carried out using CrysAlisPro 171.33.46. Absorption correction was performed using SADABS built into the CrysAlisPro program suite. Structure solution and refinement for all compounds were performed using the Olex2 software package[32] (with embedded SHELXTL[33]). All the structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least squares on F^2. Compound **3** crystallizes in chiral space group $P2_12_12_1$, but crystals showed considerable racemic twinning (the minor component was refined to 45.3%). All non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms, except as noted separately. Further details on crystal data, data collection, and refinement are summarized in Table 3.

ASSOCIATED CONTENT

Supporting Information

CIF files giving X-ray crystallographic data for **3** (CCDC 835113), **4** (CCDC 835114), **5** (CCDC 835115), and **10** (CCDC 835116). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: chjiag@ust.hk.

ACKNOWLEDGMENTS

This work was supported by the Hong Kong Research Grant Council (Project No. HKUST 601007, 601408, HKUST18/CRF/08).

REFERENCES

(1) For reviews, see for example: (a) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121−198. (b) Roper, W. R. In *Transition Metal Carbyne Complexes*; Kreissl, F. R., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1993; pp 155−168. (c) Jia, G. *Coord. Chem. Rev.* **2007**, *251*, 2167−2187.

(2) See for example: (a) Pavlik, S.; Mereiter, K.; Puchberger, K.; Kirchner, K. *J. Organomet. Chem.* **2005**, *690*, 5497−5507. (b) Caskey, S. R.; Stewart, M. H.; Ahn, Y. J.; Johnson, M. J. A.; Rowsell, J. L. C.; Kampf, J. W. *Organometallics* **2007**, *26*, 1912−1923. (c) Rigaut, S.; Touchard, D.; Dixneuf, P. H. *Organometallics* **2003**, *22*, 3980−3984. (d) Bustelo, E.; Jimenez-Tenorio, M.; Mereiter, K.; Puerta, M. C.; Valerga, P. *Organometallics* **2002**, *21*, 1903−1911. (e) Amoroso, D.; Snelgrove, J. L.; Conrad, J. C.; Drouin, S. D.; Yap, G. P. A.; Fogg, D. E. *Adv. Synth. Catal.* **2002**, *344*, 757−763. (f) Jung, S.; Brandt, C. D.; Werner, H. *New J. Chem.* **2001**, *25*, 1101−1103.

(3) For recent examples of other ruthenium carbyne complexes, see: (a) Boone, M. P.; Brown, C. C.; Ancelet, T. A.; Stephan, D. W. *Organometallics* **2010**, *29*, 4369−4374. (b) Ledoux, N.; Drozdzak, R.; Allaert, B.; Linden, A.; Voorta, P. V. D.; Verpoorta, F. *Dalton Trans.* **2007**, 5201−5210. (c) Beach, N. J.; Walker, J. M.; Jenkins, H. A.; Spivak, G. J. *J. Organomet. Chem.* **2006**, *691*, 4147−4152. (d) Beach, N. J.; Williamson, A. E.; Spivak, G. J. *J. Organomet. Chem.* **2005**, *690*, 4640−4647. (e) Caskey, S. R.; Stewart, M. H.; Ahn, Y. J.; Johnson, M. J. A.; Kampf, J. W. *Organometallics* **2005**, *24*, 6074−6076. (f) Jung, S.; Ilg, K.; Brandt, C. D.; Wolf, J.; Werner, H. *Eur. J. Inorg. Chem.* **2004**, 469−480. (g) Beach, N. J.; Jenkins, H. A.; Spivak, G. J. *Organometallics* **2003**, *22*, 5179−5181. (h) Conrad, J. C.; Amoroso, D.; Czechura, P.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2003**, *22*, 3634−3636. (i) Jung, S.; Ilg, K.; Brandt, C. D.; Wolf, J.; Werner, H. *Dalton Trans.* **2002**, 318−327. (j) Gonzalez-Herrero, P.; Weberndorfer, B.; Ilg, K.; Wolf, J.; Werner, H. *Organometallics* **2001**, *20*, 3672−3685. (k) Coalter, J. N.; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2000**, *24*, 925−927. (l) Gonzalez-Herrero, P.; Weberndorfer, B.; Ilg, K.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3266−3269. (m) Stuer, W.; Wolf, J.; Werner, H.; Schwab, P.; Schulz, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3421−3423.

(4) See for example: (a) Collado, A.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2011**, *30*, 1930−1941. (b) Collado, A.; Esteruelas, M. A.; López, F.; Mascareñas, J. L.; Oñate, E.; Trillo, B. *Organometallics* **2010**, *29*, 4966−4974. (c) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; Mozo, S.; Oñate, E. *Organometallics* **2010**, *29*, 4071−4079. (d) Buil, M. L.; Esteruelas, M. A.; Garcés, K.; Oñate, E. *Organometallics* **2009**, *28*, 5691−5696. (e) Richter, B.; Werner, H. *Organometallics* **2009**, *28*, 5137−5141. (f) Bolaño, T.; Alba Collado, A.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2009**, *28*, 2107−2111. (g) Buil, M. L.; Esteruelas, M. A.; Garcés, K.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 4680−4690. (h) Castarlenas, R.; Esteruelas, M. A.; Lalrempuia, R.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 795−798. (i) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 3965−3973. (j) Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Organometallics* **2004**, *23*, 3021−3030. (k) Wen, T. B.; Hung, W. Y.; Zhou, Z. Y.; Lo, M. F.; Williams, I. D.; Jia, G. *Eur. J. Inorg. Chem.* **2004**, 2837−2846. (l) Wen, T. B.; Zhou, Z. Y.; Lo, M. F.; Williams, I. D.; Jia, G. *Organometallics* **2003**, *22*, 5217−5225. (m) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 3283−3292. (n) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. *Organometallics* **2000**, *19*, 2585−2596. (o) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2184−2193. (p) Wen, T. B.; Cheung, Y. K.; Yao, J.; Wong, W. T.; Zhou, Z. Y.; Jia, G. *Organometallics* **2000**, *19*, 3803−3809. (q) Crochet, P.; Esteruelas, M. A.; López, A. M.; Martínez, M. P.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 4500−4509. (r) Crochet, P.; Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1998**, *17*, 3479−3486. (s) Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657−4667. (t) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683−4689.

(5) For recent examples of other osmium carbyne complexes, see: (a) Liu, B.; Xie, H.; Wang, H.; Wu, L.; Zhao, Q.; Chen, J.; Wen, T. B.; Cao, Z.; Xia, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 5461−5464. (b) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2008**, *27*, 3547−3555. (c) Lee, J. H.; Pink, M.; Smurnyy, Y. D.; Caulton, K. G. *J. Organomet. Chem.* **2008**, *693*, 1426−1438. (d) Stewart, M. H.; Johnson, M. J.; Kampf, J. W. *Organometallics* **2007**, *26*, 5102−5110. (e) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 2129−2132. (f) Lee, J. H.; Pink, M.; Caulton, K. G. *Organometallics* **2006**, *25*, 802−804. (g) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2004**, *23*, 4858−4870. (h) Barrio, P.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2004**, *126*, 1946−1947. (i) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2003**, *22*, 2472−2485. (j) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 414−425. (k) Weberndörfer, B.; Henig, G.; Hockless, D. C. R.; Bennett, M. A.; Werner, H. *Organometallics* **2003**, *22*, 744−758.

(6) (a) Castarlenas, R.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4524−4527. (b) Bassetti, M.; Centola, F.; Sémeril, D.; Bruneau, C.; Dixneuf, P. H. *Organometallics* **2003**, *22*, 4459−4466. (c) Castarlenas, R.; Vovard, C.; Fischmeister, C.; Dixneuf, P. H. *J. Am. Chem. Soc.* **2006**, *128*, 4079−4089. (d) Antonucci, A.; Bassetti, M.; Bruneau, C.; Dixneuf, P. H.; Pasquini, C. *Organometallics* **2010**, *29*, 4524−4531.

(7) Shaffer, E. A.; Chen, C. L.; Beatty, A. M.; Valente, E. J.; Schanz, H. J. *J. Organomet. Chem.* **2007**, *692*, 5221−5233.

(8) Asensio, A.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 5787−5798.

(9) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2009**, *131*, 2064−2065.

(10) (a) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2008**, *27*, 6367−6370. (b) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2007**, *129*, 8850−8859. (c) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 2037−2041. (d) Bolaño, T.; Castarlenas, R.;

Esteruelas, M. A.; Modrego, F. J.; Oñate, E. *J. Am. Chem. Soc.* **2005**, *127*, 11184−11195.

(11) (a) Bustelo, E.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **2006**, *25*, 4019−4025. (b) Pino-Chamorro, J. A.; Bustelo, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2009**, *28*, 1546−1557.

(12) (a) He, G.; Zhu, J.; Hung, W. Y.; Wen, T. B.; Sung, H. H. Y.; Williams, I. D.; Lin, Z.; Jia, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 9065−9068. (b) Chen, J.; Shi, C.; Sung, H. H. Y.; Williams, I. D.; Lin, Z.; Jia, G. *Angew. Chem., Int. Ed.* **2011**, *50*, 7295−7299.

(13) Based on a search of the Cambridge Structural Database, CSD version 5.32 (May 2011).

(14) For examples, see the following. (a) $[Os(OTf)(NC_5H_4CH{=}CH)(NC_5H_4CH{=}CH_2)(P^iPr_3)]OTf$ (1.995(2) Å): Esteruelas, M. A.; Fernandez-Alvarez, F. J.; Oliván, M.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 4596−4597. (b) $CpOs(CH{=}CHCOMe)(P^iPr_3)$ (1.989(4) Å): Esteruelas, M. A.; Hernandez, Y. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 5989−6000. (c) $Os(SnPh_2Cl)(NC_5H_4CH{=}CH)(H_2)(P^iPr_3)_2$ (2.068(4) Å): Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 1428−1438. (d) $OsCl(CH{=}CH(p\text{-tolyl})(CO)(PPh_3)_3$ (2.105(7) Å): Xia, H.; Wen, T. B.; Hu, Q. Y.; Wang, X.; Chen, X.; Shek, L. Y.; Williams, I. D.; Wong, K. S.; Wong, G. K. L.; Jia, G. *Organometallics* **2005**, *24*, 562−569. (e) $OsCl(CH{=}CHPh)(O)_2(PiPr_3)_2$ (1.979(30) Å): Bourgault, M.; Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *Organometallics* **1997**, *16*, 636−645. (f) $[Os(CH{=}CHPh)({=}C{=}C{=}CPh_2)(CH_3CN)_2(PiPr_3)_2]BF_4$ (2.053(3) Å): Bolano, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 3965−3973. (g) $Os(CH{=}CHCH_2NH_2)Cl(CO)(nPrNH_2)(PiPr_3)$ (2.040(3) Å): Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2010**, *29*, 6298−6307.

(15) Tena, M. A.; Niirnberg, O.; Werner, H. *Chem. Ber.* **1993**, *126*, 1597−1602.

(16) Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281−2309.

(17) (a) Esteruelas, M. A.; Gonzalez, A. I.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 414−425. (b) Esteruelas, M. A.; Gonzalez, A. I.; López, A. M.; Oñate, E. *Organometallics* **2004**, *23*, 4858−4870.

(18) Hodges, L. M.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1993**, *32*, 371−372.

(19) (a) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89−115. (b) Plenio, H. *Chem. Rev.* **1997**, *97*, 3363−3384.

(20) See for example: (a) Kreickmann, T.; Arndt, S.; Schrock, R. R.; Muller, P. *Organometallics* **2007**, *26*, 5702−5711. (b) Budzelaar, P. H. M.; Moonen, N. N. P.; Gelder, R.; Smits, J. M. M.; Gal, A. W. *Eur. J. Inorg. Chem.* **2000**, 753−769. (c) Whitcomb, D. R.; Rajeswaran, M. *Polyhedron* **2006**, *25*, 2033−2038. (d) Tonzetich, Z. J.; Jiang, A. J.; Schrock, R. R.; Muller, P. *Organometallics* **2006**, *25*, 4725−4727. (e) Schrock, R. R.; Adamchuk, J.; Ruhland, K.; Lopez, L. P. H. *Organometallics* **2003**, *22*, 5079−5091.

(21) (a) Alonso, P. J.; Fornies, J.; Garcia-Monforte, M. A.; Martin, A.; Menjon, B.; Rillo, C. *J. Organomet. Chem.* **2007**, *692*, 3236−3247. (b) Ben-Ari, E.; Gandelman, M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 4714−4715. (c) Wu, F.; Dash, A. K.; Jordan, R. F. *J. Am. Chem. Soc.* **2004**, *126*, 15360−15361.

(22) For recent examples, see: (a) Liu, F.; Wu, X. H.; Xia, J. L.; Jin, S.; Yu, G. A.; Liu, S. H. *J. Organomet. Chem.* **2010**, *695*, 809−815. (b) Naeem, S.; Thompson, A. L.; Delaude, L.; Wilton-Ely, J. D. E. T. *Chem. Eur. J.* **2010**, *16*, 10971−10974. (c) Naeem, S.; White, A. J. P.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Organometallics* **2010**, *29*, 2547−2556. (d) Hill, A. F.; Niess, B.; Schultz, M.; White, A. J. P.; Williams, D. J. *Organometallics* **2010**, *29*, 6488−6492. (e) Davies, D. L.; Al-Duaij, O.; Fawcett, J.; Singh, K. *Organometallics* **2010**, *29*, 1413−1420. (f) Wolf, R.; Plois, M. *Eur. J. Inorg. Chem.* **2010**, 4419−4442. (g) Chung, C. P.; Chen, C. C.; Lin, Y. C.; Liu, Y. H.; Wang, Y. *J. Am. Chem. Soc.* **2009**, *131*, 18366−18375. (h) Macgregor, M. J.; Hogarth, G.; Thompson, A. L.; Wilton-Ely, J. D. E. T. *Organometallics* **2009**, *28*, 197−208. (i) Pichlmaier, M.; Winter, R. F.; Zabel, M.; Zalis, S. *J. Am. Chem. Soc.* **2009**, *131*, 4892−4903. (j) Wu, X. H.; Jin, S.; Liang, J. H.; Li, Z. Y.; Yu, G. A.; Liu, S. H. *Organometallics* **2009**, *28*, 2450−2459. (k) Esteruelas, M. A.; Fernandez, I.; Fuertes, S.; López, A. M.; Oñate, E.; Sierra, M. A. *Organometallics* **2009**, *28*, 4876−4879. (l) Kowalski, K.; Linseis, M.; Winter, R. F.; Zabel, M.; Zalis, S.; Kelm, H.; Kruger, H. J.; Sarkar, B.; Kaim, W. *Organometallics* **2009**, *28*, 4196−4209.

(23) Fries, G.; Wolf, J.; Pfeiffer, M.; Stalke, D.; Werner, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 564−566.

(24) Darensbourg, D. J.; Fonta, J. B.; Chojnacki, S. S.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1994**, *33*, 3526−3532.

(25) Kulawiec, R. J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **1990**, *9*, 745−755.

(26) Sinha, P. K.; Falvello, L. R.; Peng, S. M.; Bhattacharya, S. *Polyhedron* **2000**, *19*, 1673−1680.

(27) (a) Catala, R. M.; Cruz-Garritz, D.; Hills, A.; Hughes, D. L.; Richards, R. L.; Sosa, P.; Torrens, H. *Chem. Commun.* **1987**, 261−262. (b) Catala, R. M.; Cruz-Garritz, D.; Sosa, P.; Terreros, P.; Torrens, H.; Hills, A.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1989**, *359*, 219−232.

(28) Perera, S. D.; Shaw, B. L.; Thornton-Pett, M. *Inorg. Chim. Acta* **2001**, *325*, 151−154.

(29) Gabbutt, C. D.; Heron, B. M.; Instone, A. C.; Thomas, D. A.; Partington, S. M.; Hursthouse, M. B.; Gelbrich, T. *Eur. J. Org. Chem.* **2003**, 1220−1230.

(30) Hoffmann, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221−4228.

(31) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237−240.

(32) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339−341.

(33) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.