ORGANOMETALLICS

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Preparation of Half-Sandwich Alkoxycarbene Complexes of Osmium(II)

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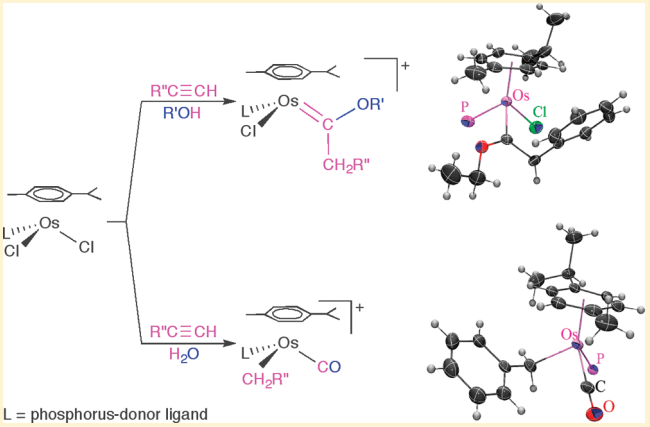
Supporting Information

ABSTRACT: Alkoxy-alkylcarbene complexes [OsCl{=C(OR′)CH$_2$R″}(η^6-*p*-cymene)L]BPh$_4$ (**1**−**4**) [R′ = Me, Et; R″ = Ph, *p*-tolyl, Bu^t; L = P(OMe)$_3$, P(OEt)$_3$, PPh(OEt)$_2$, PPh$_2$OEt] were prepared by allowing dichloro compounds OsCl$_2$(η^6-*p*-cymene)L to react with terminal alkyne R″C≡CH in alcohol. Ethoxy-methylcarbene [OsCl{=C(OEt)CH$_3$}(η^6-*p*-cymene)L]BPh$_4$ (**5**) was also prepared from reaction with trimethylsilyl acetylene. A reaction path for the formation of compounds **1**−**5**, involving the nucleophilic attack of alcohol on intermediate vinylidene complexes, is discussed. Acetylide derivatives OsCl(C≡CAr)(η^6-*p*-cymene)L (**6**, **7**) [Ar = Ph, *p*-tolyl; L = P(OMe)$_3$, P(OEt)$_3$, PPh(OEt)$_2$] were prepared by reacting dichloro compounds OsCl$_2$(η^6-*p*-cymene)L with lithium acetylide (Li$^+$[ArC≡C]$^-$) in thf. Protonation reaction with Brønsted acids of **6** and **7** led to vinylidene cations [OsCl{=C=C(H)Ar}(η^6-*p*-cymene)L]$^+$. Complexes OsCl$_2$(η^6-*p*-cymene)L also reacted with both PhC≡CH and (CH$_3$)$_3$SiC≡CH in the presence of H$_2$O to give alkyl-carbonyl derivatives [Os(η^1-CH$_2$Ph)(CO)(η^6-*p*-cymene)L]BPh$_4$ (**8**) and [Os(η^1-CH$_3$)(CO)(η^6-*p*-cymene)L]BPh$_4$ (**9**). The complexes were characterized spectroscopically (IR and ^{1}H, ^{13}C, ^{31}P NMR) and by X-ray crystal structure determinations of [OsCl{=C(OEt)CH$_2$Ph}(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh$_4$ (**1c**), [OsCl{=C(OEt)CH$_2$Ph}(η^6-*p*-cymene)(PPh$_2$OEt)]BPh$_4$ (**1d**), and [Os(η^1-CH$_2$Ph)(CO)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh$_4$ (**8c**).



INTRODUCTION

Transition metal carbene complexes[1] are an important class of compounds that continue to be extensively studied, both for their chemical reactivity and for catalytic applications in several processes, including olefin metathesis and carbon−carbon and carbon−heteroatom coupling reactions.[2]

A large number of carbene complexes were thus prepared for several metals,[1] although third-row transition metals have traditionally been considered of no practical use in catalysis, because they form bonds stronger than their 3d and 4d homologues with the ligands typically involved in catalytic transformations.[3] In the iron triad, for example, osmium has been used to prepare stable models of reactive intermediates, proposed in catalytic transformations with ruthenium.[4] Nevertheless, the carbene chemistry of osmium has been extensively developed in recent years, and a large number of osmium(0) and osmium(II) complexes containing either Os=CR$_2$ or Os=C(H)R units have been prepared.[5] Instead, less attention has been paid to Fisher-type carbene complexes containing heteroatoms, and the alkoxycarbene Os=C(OR′)R″ are quite rare.[6]

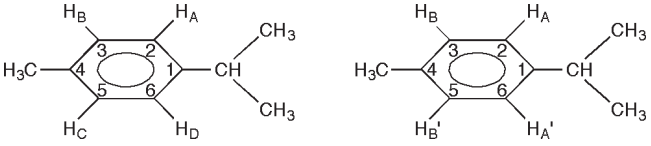
In the course of our investigations on half-sandwich arene complexes of the iron triad,[7] we have now found that the dichloro compounds OsCl$_2$(*p*-cymene)L (L = phosphite, phosphonite, or phosphinite) react with terminal alkynes RC≡CH in alcohol to give novel alkoxycarbene derivatives. The results of these studies, which include the synthesis and characterization of new alkoxy-alkylcarbene, acetylide, and η^1-alkyl derivatives of osmium(II), are reported here.

EXPERIMENTAL SECTION

General Comments. All synthetic work was carried out under argon using standard Schlenk techniques or an inert atmosphere drybox. Once isolated, the complexes were found to be relatively stable in air, but were stored at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. OsO$_4$ was a Pressure Chemical Co. (USA) product, used as received. Phosphonite PPh(OEt)$_2$ and phosphinite PPh$_2$OEt were prepared by the method of Rabinowitz and Pellon,[8] while P(OEt)$_3$ and P(OMe)$_3$ were Aldrich products, purified by distillation under nitrogen. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a

Received: November 25, 2010
Published: February 22, 2011

Chart 1



Perkin-Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra (^{1}H, ^{13}C, ^{31}P) were obtained on an AVANCE 300 Bruker spectrometer at temperatures between −90 and +30 °C, unless otherwise noted. ^{1}H and ^{13}C spectra are referred to internal tetramethylsilane; assignments are referred to Chart 1. ^{31}P{^{1}H} chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. COSY, HMQC, and HMBC NMR experiments were performed with standard programs. The SwaN-MR and iNMR software packages[9] were used to treat NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C was measured on a CDM 83 radiometer. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova (Italy).

Synthesis of Complexes. Compounds [OsCl(μ-Cl)(η^6-*p*-cymene)]$_2$ and $OsCl_2(\eta^6$-*p*-cymene)L [L = P(OMe)$_3$, P(OEt)$_3$, PPh(OEt)$_2$, PPh_2OEt] were prepared following the reported methods.[7b,c,10]

[OsCl{=C(OEt)CH$_2$Ar}(η^6-*p*-cymene)L]BPh$_4$ (1, 2) [Ar = Ph (1), *p*-tolyl (2); L = P(OMe)$_3$ (a), P(OEt)$_3$ (b), PPh(OEt)$_2$ (c), PPh$_2$OEt (d)]. In a 25 mL three-necked round-bottomed flask were placed 0.2 mmol of the appropriate chloro complex $OsCl_2(\eta^6$-*p*-cymene)L, 137 mg (0.4 mmol) of $NaBPh_4$, and 3.5 mL of ethanol. An excess of the appropriate alkyne ArC≡CH (0.6 mmol) was added to the resulting mixture, which was stirred for 3 h. A yellow solid slowly separated out, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield ≥75%.

1a: ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.41−6.86 (m, 25H, Ph), 5.39 (d, HA *p*-cym, J_{AB} = 6.1, J_{AC} = 1.0, J_{AD} = 0.6 Hz), 5.32 (d, HB *p*-cym, J_{BC} = 0.6, J_{BD} = 1.0 Hz), 5.24 (d, HC *p*-cym, J_{CD} = 6.0 Hz), 5.15 (d, HD *p*-cym), 5.09, 4.29 [d, 2H, =C(*CH*$_2$Ph), J_{HH} = 13.4 Hz], 4.73 [q, 2H, =C(O*CH*$_2$CH$_3$), J_{HH} = 7.1 Hz], 3.69 (d, 9H, CH$_3$ phos, J_{PH} = 11.5 Hz), 2.61 (m, 1H, CH), 2.00 (s, 3H, *p*-CH$_3$ *p*-cym), 1.51 [t, 3H, =C(OCH$_2$*CH*$_3$), J_{HH} = 7.1 Hz], 1.22, 1.18 (d, 6H, CH$_3$ ^{i}Pr, J_{HH} = 7.1 Hz) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 76.5 (br) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 290.3 (d, Os=C, J_{CP} = 18 Hz), 165−122 (m, Ph), 117.85 (s, C1 *p*-cym), 103.20 (s, C4 *p*-cym), 89.21 (s, C5 *p*-cym), 88.39 (s, C3 *p*-cym), 85.88 (s, C6 *p*-cym), 85.77 (s, C2 *p*-cym), 78.5 [s, =C(O*CH*$_2$CH$_3$)], 55.15 (d, CH$_3$ phos, J_{CP} = 7.8 Hz), 54.6 [br, =C(*CH*$_2$Ph)], 31.14 (s, CH), 22.42, 21.91 (s, CH$_3$ ^{i}Pr), 18.38 (s, *p*-CH$_3$ *p*-cym), 14.74 [s, =C(OCH$_2$*CH*$_3$)] ppm. Anal. Calcd for $C_{47}H_{55}BClO_4OsP$: C, 59.33; H, 5.83; Cl, 3.73. Found: C, 59.54; H, 5.91; Cl, 3.58.

1b: ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.37−6.86 (m, 25H, Ph), 5.37 (d, HA *p*-cym, J_{AB} = 5.7, J_{AC} = 0.4, J_{AD} = 1.1 Hz), 5.35 (d, HB *p*-cym, J_{BC} = 1.1, J_{BD} = 0.4 Hz), 5.16 (d, HC *p*-cym, J_{CD} = 5.7 Hz), 5.11 (d, HD *p*-cym), 5.04, 4.33 [d, 2H, =C(*CH*$_2$Ph), J_{HH} = 13.3 Hz], 4.34 [m, 2H, =C(O*CH*$_2$CH$_3$)], 3.99, 3.84 (m, 6H, CH$_2$ phos), 2.58 (m, 1H, CH), 2.00 (s, 3H, *p*-CH$_3$ *p*-cym), 1.50 [t, 3H, =C(OCH$_2$*CH*$_3$), J_{HH} = 7.0 Hz], 1.27 (t, 9H, CH$_3$ phos, J_{HH} = 7.0 Hz), 1.13, 1.10 (d, 6H, CH$_3$ ^{i}Pr, J_{HH} = 7.1 Hz) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, −60 °C) δ: 75.2 (s) ppm. Anal. Calcd for $C_{50}H_{61}BClO_4OsP$: C, 60.45; H, 6.19; Cl, 3.57. Found: C, 60.64; H, 6.09; Cl, 3.49%.

1c: ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.56−6.87 (m, 30H, Ph), 5.48 (d, HA *p*-cym, J_{AB} = 6.7, J_{AC} = 0.4, J_{AD} = 0.8 Hz), 5.43 (d, HB *p*-cym, J_{BC} = 0.8, J_{BD} = 0.4 Hz), 5.40 (d, HC *p*-cym, J_{CD} = 6.7 Hz), 5.32 (d, HD *p*-cym), 5.37, 2.97 [d, 2H, =C(*CH*$_2$Ph), J_{HH} = 13.2 Hz], 4.43, 4.31 [m, 2H, =C(O*CH*$_2$CH$_3$)], 4.11, 3.98 (m, 4H, CH$_2$ phos), 2.59 (m, 1H, CH), 1.98 (s, 3H, *p*-CH$_3$ *p*-cym), 1.47, 1.42 (t, 6H, CH$_3$ phos, J_{HH} = 7.0 Hz), 1.38 [t, 3H, =C(OCH$_2$*CH*$_3$), J_{HH} = 7.0 Hz], 1.16, 1.14 (d, 6H, CH$_3$ ^{i}Pr, J_{HH} = 7.1 Hz) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 95.7 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 286.5 (d, Os=C, J_{CP} = 15.9 Hz), 165−122 (m, Ph), 119.24 (d, br, C1 *p*-cym, J_{CP} = 1.4 Hz), 105.21 (br, C4 *p*-cym), 93.01 (d, C3 *p*-cym, J_{CP} = 3.4 Hz), 88.31 (d, C6 *p*-cym, J_{CP} = 3.1 Hz), 86.91 (d, C2 *p*-cym, J_{CP} = 5.9 Hz), 86.38 (s, br, C5 *p*-cym), 76.58 [s, =C(O*CH*$_2$CH$_3$)], 65.1, 64.5 (d, CH$_2$ phos, J_{CP} = 9.9, J_{CP} = 7.3 Hz), 54.3 [br, =C(*CH*$_2$Ph)], 31.1 (s, CH), 22.25, 21.96 (s, CH$_3$ ^{i}Pr), 17.97 (s, *p*-CH$_3$ *p*-cym), 16.29, 16.28 (d, CH$_3$ phos, J_{CP} = 7.3 Hz), 14.59 [s, =C(OCH$_2$*CH*$_3$)] ppm. Anal. Calcd for $C_{54}H_{61}BClO_3OsP$: C, 63.24; H, 6.00; Cl, 3.46. Found: C, 63.39; H, 6.07; Cl, 3.52.

1d: ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 6.86−5.76 (m, 35H, Ph), 5.28 (d, HA *p*-cym, J_{AB} = 6.2, J_{AC} = 0.4, J_{AD} = 0.8 Hz), 5.00 (d, HB *p*-cym, J_{BC} = 0.8, J_{BD} = 0.4 Hz), 5.16 (d, HC *p*-cym, J_{CD} = 6.2 Hz), 5.14 (d, HD *p*-cym), 5.21, 3.63 [d, 2H, =C(*CH*$_2$Ph), J_{HH} = 12.8 Hz], 4.63 [m, 2H, =C(O*CH*$_2$CH$_3$)], 3.74, 3.58 (m, 2H, CH$_2$ phos), 2.57 (m, 1H, CH), 1.96 (s, 3H, *p*-CH$_3$ *p*-cym), 1.42 [t, 3H, =C(OCH$_2$*CH*$_3$), J_{HH} = 7.0 Hz], 1.25, 1.24 (t, 3H, CH$_3$ phos, J_{HH} = 7.0 Hz), 1.14, 1.12 (d, 6H, CH$_3$ ^{i}Pr, J_{HH} = 7.1 Hz) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 81.3 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 291.8 (d, Os=C, J_{CP} = 15.0 Hz), 165−122 (m, Ph), 116.17 (s, br, C1 *p*-cym), 99.95 (s, br, C4 *p*-cym), 93.00 (s, br, C5 *p*-cym), 87.82 (s, br, C3 *p*-cym), 86.65 (s, br, C2 *p*-cym), 85.14 (d, C6 *p*-cym, J_{CP} = 6.4 Hz), 76.71 [s, =C(O*CH*$_2$CH$_3$)], 66.07 (d, CH$_2$ phos, J_{CP} = 12.3 Hz), 54.8 [br, =C(*CH*$_2$Ph)], 30.89 (s, CH), 22.43, 21.63 (s, CH$_3$ ^{i}Pr), 17.60 (s, *p*-CH$_3$ *p*-cym), 16.17 (d, CH$_3$ phos, J_{CP} = 7.5 Hz), 14.43 [s, =C(OCH$_2$*CH*$_3$)] ppm. Anal. Calcd for $C_{58}H_{61}BClO_2OsP$: C, 65.87; H, 5.81; Cl, 3.35. Found: C, 66.00; H, 5.95; Cl, 3.48.

2c: ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.56−6.86 (m, 29H, Ph), 5.47 (d, HA *p*-cym, J_{AB} = 6.4, J_{AC} = 0.4, J_{AD} = 0.8 Hz), 5.40 (d, HB *p*-cym, J_{BC} = 0.8, J_{BD} = 0.4 Hz), 5.39 (d, HC *p*-cym, J_{CD} = 6.4 Hz), 5.30 (d, HD *p*-cym), 5.30, 2.91 [d, 2H, =C(*CH*$_2$Ar), J_{HH} = 12.9 Hz], 4.42, 4.27 [m, 2H, =C(O*CH*$_2$CH$_3$)], 4.09, 3.97 (m, 4H, CH$_2$ phos), 2.59 (m, 1H, CH), 2.33 (s, 3H, CH$_3$ *p*-tolyl), 1.96 (s, 3H, *p*-CH$_3$ *p*-cym), 1.43 [t, 3H, =C(OCH$_2$*CH*$_3$), J_{HH} = 7.0 Hz], 1.40, 1.37 (t, 6H, CH$_3$ phos, J_{HH} = 7.0 Hz), 1.15, 1.14 (d, 6H, CH$_3$ ^{i}Pr, J_{HH} = 7.1 Hz) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 95.9 (s) ppm. Anal. Calcd for $C_{55}H_{63}BClO_3OsP$: C, 63.55; H, 6.11; Cl, 3.41. Found: C, 63.71; H, 6.02; Cl, 3.63.

[OsCl{=C(OMe)CH$_2$Ph}(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh$_4$ (3c). This complex was prepared exactly like the related ethoxy derivatives **1** and **2** using methanol instead of ethanol as a solvent; yield 72%. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.55−6.86 (m, 30H, Ph), 5.47 (d, HA *p*-cym, J_{AB} = 6.4, J_{AC} = 0.4, J_{AD} = 0.8 Hz), 5.41 (d, HB *p*-cym, J_{BC} = 0.8, J_{BD} = 0.4 Hz), 5.41 (d, HC *p*-cym, J_{CD} = 6.4 Hz), 5.31 (d, HD *p*-cym), 5.27, 2.95 [d, 2H, =C(*CH*$_2$Ph), J_{HH} = 13.2 Hz], 4.08, 3.95 (m, 4H, CH$_2$ phos), 4.01 [s, 3H, =C(OCH$_3$)], 2.56 (m, 1H, CH), 1.98 (s, 3H, *p*-CH$_3$ *p*-cym), 1.43, 1.37 (t, 6H, CH$_3$ phos, J_{HH} = 7.0 Hz), 1.14, 1.12 (d, 6H, CH$_3$ ^{i}Pr, J_{HH} = 7.1 Hz) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 95.8 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 288.1 (d, Os=C, J_{CP} = 16 Hz), 165−122 (m, Ph), 118.69 (s, C1 *p*-cym), 105.93 (s, br, C4 *p*-cym), 92.07 (d, C5 *p*-cym, J_{CP} = 2.8 Hz), 88.24 (d, C6 *p*-cym, J_{CP} = 2.9 Hz), 87.35 (d, C2 *p*-cym, J_{CP} = 5.2 Hz), 86.77 (s, br, C3 *p*-cym), 66.70 [s, =C(O*CH*$_3$)], 65.60, 64.55 (d, CH$_2$ phos, J_{CP} = 9.9, J_{CP} = 7.1 Hz), 53.40 [s, =C(*CH*$_2$Ph)], 31.15 (s, CH), 22.29, 21.92 (s, CH$_3$ ^{i}Pr), 18.21 (s, *p*-CH$_3$ *p*-cym), 16.26, 16.16 (d, CH$_3$ phos, J_{CP} = 4.3, J_{CP} = 5.7 Hz) ppm. Anal. Calcd for $C_{53}H_{59}BClO_3OsP$: C, 62.93; H, 5.88; Cl, 3.50. Found: C, 63.01; H, 5.99; Cl, 3.65.

[OsCl{=C(OEt)CH$_2$Bu^t}(η^6-*p*-cymene){P(OMe)$_3$}]BPh$_4$ (4a). In a 25 mL three-necked round-bottomed flask were placed 100 mg (0.19 mmol) of $OsCl_2(\eta^6$-*p*-cymene){P(OMe)$_3$}, 130 mg (0.38 mmol) of $NaBPh_4$, and 2 mL of ethanol. An excess of *tert*-butyl acetylene,

HC≡CBu^t, (68 μL, 0.54 mmol) was added to the resulting mixture, which was stirred for 5 h. A yellow solid slowly separated out, which, after cooling of the reaction mixture to complete the precipitation, was filtered and crystallized from CH_2Cl_2 and ethanol; yield 65%. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.32−6.89 (m, 20H, Ph), 5.49 (d, HA *p*-cym, J_{AB} = 6.2, J_{AC} = 0.6, J_{AD} = 0.8, J_{HP} = 1.9 Hz), 5.61 (d, HB *p*-cym, J_{BC} = 0.8, J_{BD} = 0.8, J_{HP} = 1.8 Hz), 5.42 (d, HC *p*-cym, J_{CD} = 6.2, J_{HP} = 1.3 Hz), 5.11 (d, HD *p*-cym, J_{HP} = 0.5 Hz), 4.87 [m, 2H, =C(OCH_2CH$_3$)], 3.62, 2.97 [d, 2H, =C(CH_2Bu^t), J_{HH} = 19.0 Hz], 3.69 (d, 9H, CH_3 phos, J_{HP} = 11.4 Hz), 2.74 (m, 1H, CH), 2.11 (s, 3H, *p*-CH_3 *p*-cym), 1.61 [t, 3H, =C(OCH$_2$CH_3), J_{HH} = 7.0 Hz], 1.32, 1.24 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 7.1 Hz), 1.04 (s, 9H, CH_3 Bu^t) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 73.2 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 295.07 (br, Os=C), 165−122 (m, Ph), 121.7 (br, C1 *p*-cym), 100.3 (br, C4 *p*-cym), 88.74 (s, C3 *p*-cym), 85.76 (s, C2 *p*-cym), 85.44 (s, C5 *p*-cym), 85.33 (s, C6 *p*-cym), 80.68 [s, =C(OCH_2CH$_3$)], 73.7 [s, br, =C(CH_2Bu^t)], 55.36 (d, CH_3 phos, J_{CP} = 8.0 Hz), 33.84 (s, C Bu^t), 31.29 (s, CH), 30.22 (s, CH_3 Bu^t), 23.18, 21.10 (s, CH_3 ^{i}Pr), 18.50 (s, *p*-CH_3 *p*-cym), 14.97 [s, =C(OCH$_2$CH_3)] ppm. Anal. Calcd for $C_{45}H_{59}BClO_4OsP$: C, 58.03; H, 6.38; Cl, 3.81. Found: C, 58.16; H, 6.49; Cl, 3.97.

[OsCl{=C(OEt)CH$_3$}(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh$_4$ (5c). In a 25 mL three-necked round-bottomed flask were placed 100 mg (0.17 mmol) of OsCl$_2$(η^6-*p*-cymene){PPh(OEt)$_2$}, 116 mg (0.34 mmol) of $NaBPh_4$, and 3 mL of ethanol. An excess of trimethylsilyl acetylene, HC≡CSi(CH$_3$)$_3$, (73.6 μL, 0.51 mmol) was added to the resulting mixture, which was stirred for 5 h. By cooling the resulting solution to −25 °C, a yellow solid slowly separated out, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield 55%. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.80−6.88 (m, 25H, Ph), 5.50 (d, HA *p*-cym, J_{AB} = 6.4, J_{AC} = 0.6, J_{AD} = 0.6 Hz), 5.46 (d, HB *p*-cym, J_{BC} = 0.6, J_{BD} = 0.6 Hz), 5.50 (d, HC *p*-cym, J_{CD} = 6.4 Hz), 5.42 (d, HD *p*-cym), 4.22, 4.04 [m, 2H, =C(OCH_2CH$_3$)], 4.06, 3.96, 3.88 (m, 4H, CH_2 phos), 2.59 (m, 1H, CH), 2.23 [s, 3H, =C(CH$_3$)], 2.07 (s, 3H, *p*-CH_3 *p*-cym), 1.50 [t, 3H, =C(OCH$_2$CH_3), J_{HH} = 7.0 Hz], 1.37, 1.34 (t, 6H, CH_3 phos, J_{HH} = 7.0 Hz), 1.20, 1.14 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 7.1 Hz) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 96.53 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 285.1 (d, Os=C, J_{CP} = 15.8 Hz), 164−122 (m, Ph), 119.54 (s, C1 *p*-cym), 106.42 (s, C4 *p*-cym), 92.03 (d, C3 *p*-cym, J_{CP} = 2.6 Hz), 89.44 (s, C5 *p*-cym), 88.48 (s, C6 *p*-cym), 85.88 (d, C2 *p*-cym, J_{CP} = 4.4 Hz), 75.27 [s, =C(OCH_2CH$_3$)], 64.98, 64.37 (d, CH_2 phos, J_{CP} = 9.6, J_{CP} = 6.8 Hz), 39.11 [br, =C(CH_3)], 31.12 (s, CH), 22.49, 21.95 (s, CH_3 ^{i}Pr), 18.18 (s, *p*-CH_3 *p*-cym), 16.0 (t, CH_3 phos, $J_{CP\ apparent}$ = 16.4 Hz), 14.45 [s, =C(OCH$_2$CH_3)] ppm. Anal. Calcd for $C_{48}H_{57}BClO_3OsP$: C, 60.72; H, 6.05; Cl, 3.73. Found: C, 60.59; H, 5.94; Cl, 3.81.

OsCl(C≡CAr)(η^6-*p*-cymene)L (6, 7) [Ar = Ph (6), *p*-tolyl (7); L = P(OMe)$_3$ (a), P(OEt)$_3$ (b), PPh(OEt)$_2$ (c)]. An excess of lithium acetylide Li$^+$[ArC≡C]$^-$ (0.68 mmol, 0.38 mL of a 1.8 M solution in thf) was added to a solution of the appropriate complex OsCl$_2$(η^6-*p*-cymene)L (0.17 mmol) in 10 mL of thf cooled to −196 °C. The reaction mixture was allowed to reach room temperature and stirred for 3 h. The solvent was removed under reduced pressure to give an oil, which was triturated with *n*-hexane (5 mL). A red-brown solid slowly separated out and was filtered and crystallized from toluene and *n*-hexane; yield ≥75%.

6a: IR (KBr) cm^{-1}: $\nu_{C\equiv C}$ 2095 (m). ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.34−7.12 (m, 5H, PhC≡C), 5.63 (d, 2H, HA, HA′ *p*-cym, J_{HH} = 5.6 Hz), 5.50 (d, 2H, HB, HB′ *p*-cym, J_{HH} = 5.6 Hz), 3.73 (d, 9H, CH_3 phos, J_{HP} = 9.8 Hz), 2.79 (m, 1H, CH), 2.21 (s, 3H, *p*-CH_3 *p*-cym), 1.23 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 7.1 Hz) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 74.9 (s) ppm. Anal. Calcd for $C_{21}H_{28}ClO_3OsP$: C, 43.11; H, 4.82; Cl, 6.06. Found: C, 42.92; H, 4.99; Cl, 6.25.

6b: IR (KBr) cm^{-1}: $\nu_{C\equiv C}$ 2085 (m). ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.36−7.10 (m, 5H, PhC≡C), 5.61 (d, 2H, HA, HA′ *p*-cym, J_{HH} = 5.6 Hz), 5.47 (d, 2H, HB, HB′ *p*-cym, J_{HH} = 5.6 Hz), 4.08 (qnt, 6H, CH_2 phos), 2.80 (m, 1H, CH), 2.20 (s, 3H, *p*-CH_3 *p*-cym), 1.31 (t, 9H, CH_3 phos, J_{HH} = 7.0 Hz), 1.24 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 7.1 Hz) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 70.4 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 132−125 (m, Ph), 128.7 (d, br, Cα), 100.79 (d, C1 *p*-cym, J_{CP} = 2.7 Hz), 95.31 (d, C4 *p*-cym, J_{CP} = 2.8 Hz), 81.64 (d, C2/C6 *p*-cym, J_{CP} = 5.3 Hz), 80.85 (d, C3/C5 *p*-cym, J_{CP} = 6.2 Hz), 62.75 (d, CH_2 phos, J_{CP} = 6.0 Hz), 30.60 (s, CH), 22.38 (s, CH_3 ^{i}Pr), 18.04 (s, *p*-CH_3 *p*-cym), 16.30 (d, CH_3 phos, J_{CP} = 2.3 Hz) ppm. Anal. Calcd for $C_{24}H_{34}ClO_3OsP$: C, 45.96; H, 5.46; Cl, 5.65. Found: C, 46.12; H, 5.39; Cl, 6.80.

6c: IR (KBr) cm^{-1}: $\nu_{C\equiv C}$ 2086 (m). ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.66, 7.44 (m, 10H, Ph), 5.52 (d, 2H, HA, HA′ *p*-cym, J_{HH} = 5.6 Hz), 5.39 (d, 2H, HB, HB′ *p*-cym, J_{HH} = 5.6 Hz), 4.12, 3.97 (m, 4H, CH_2 phos), 2.64 (m, 1H, CH), 2.06 (s, 3H, *p*-CH_3 *p*-cym), 1.32 (t, 6H, CH_3 phos, J_{HH} = 7.0 Hz), 1.16 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 7.1 Hz) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 93.2 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 136.87 (s, Cβ), 131−127 (m, Ph), 128.5 (d, Cα, J_{CP} = 5.6 Hz), 100.81 (d, C1 *p*-cym, J_{CP} = 7.1 Hz), 93.50 (d, C4 *p*-cym, J_{CP} = 1.9 Hz), 81.81 (d, C3/C5 *p*-cym, J_{CP} = 5.5 Hz), 81.25 (d, C2/C6 *p*-cym, J_{CP} = 5.2 Hz), 63.66 (d, CH_2 phos, J_{CP} = 7.7 Hz), 30.4 (s, CH), 22.30 (s, CH_3 ^{i}Pr), 17.7 (s, *p*-CH_3 *p*-cym), 16.28 (d, CH_3 phos, J_{CP} = 6.9 Hz) ppm. Anal. Calcd for $C_{28}H_{34}ClO_2OsP$: C, 51.01; H, 5.20; Cl, 5.38. Found: C, 50.88; H, 5.13; Cl, 5.52.

7b: IR (KBr) cm^{-1}: $\nu_{C\equiv C}$ 2090 (m). ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.37−7.05 (m, 4H, Ph *p*-tolyl), 5.61 (d, 2H, HA, HA′ *p*-cym, J_{HH} = 5.6 Hz), 5.47 (d, 2H, HB, HB′ *p*-cym, J_{HH} = 5.6 Hz), 4.10 (qnt, 6H, CH_2 phos), 2.80 (m, 1H, CH), 2.35 (s, 3H, CH_3 *p*-tolyl), 2.20 (s, 3H, *p*-CH_3 *p*-cym), 1.27 (t, 9H, CH_3 phos, J_{HH} = 7.0 Hz), 1.23 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 7.1 Hz) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 70.4 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 132−125 (m, Ph), 127.8 (d, Cα, J_{CP} = 4.8 Hz), 100.80 (d, C1 *p*-cym, J_{CP} = 2.7 Hz), 95.32 (d, C4 *p*-cym, J_{CP} = 2.8 Hz), 81.69 (d, C2/C6 *p*-cym, J_{CP} = 5.2 Hz), 80.85 (d, C3/C5 *p*-cym, J_{CP} = 6.2 Hz), 62.74 (d, CH_2 phos, J_{CP} = 6.0 Hz), 30.61 (s, CH), 22.38 (s, CH_3 ^{i}Pr), 21.22 (s, CH_3 *p*-tolyl), 18.05 (s, *p*-CH_3 *p*-cym), 16.30 (d, CH_3 phos, J_{CP} = 6.4 Hz) ppm. Anal. Calcd for $C_{25}H_{36}ClO_3OsP$: C, 46.83; H, 5.66; Cl, 5.53. Found: C, 47.01; H, 5.78; Cl, 5.70.

[Os(η^1-CH$_2$Ph)(CO)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh$_4$ (8c). In a 25 mL three-necked round-bottomed flask were placed 100 mg (0.17 mmol) of OsCl$_2$(η^6-*p*-cymene)[PPh(OEt)$_2$], 116 mg (0.34 mmol) of $NaBPh_4$, 4.5 mL of acetone, and 1 mL of H_2O. An excess of phenylacetylene, PhC≡CH (60 μL, 0.54 mmol), was added to the resulting mixture, which was stirred for 3 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL). A yellow solid slowly separated out and was filtered and crystallized from CH_2Cl_2 and ethanol; yield 65%. IR (KBr) cm^{-1}: ν_{CO} 1970 (s). ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.62−6.84 (m, 30H, Ph), 5.53 (d, HA *p*-cym, J_{AB} = 6.4, J_{AC} = 0.4, J_{AD} = 0.5, J_{HP} = 1.6 Hz), 5.15 (d, HB *p*-cym, J_{BC} = 0.5, J_{BD} = 0.4, J_{HP} = 1.6 Hz), 5.46 (d, HC *p*-cym, J_{CD} = 6.4, J_{HP} = 1.6 Hz), 5.34 (d, HD *p*-cym, J_{HP} = 1.6 Hz), 3.91 (m, 4H, CH_2 phos), ABX spin system (A, B = ^{1}H, X = ^{31}P), δ_A 3.34, δ_B 3.11, J_{AB} = 10.3, J_{AX} = 6.8, J_{BX} = 3.5 Hz (2H, CH_2Ph), 2.35 (m, 1H, CH), 1.85 (s, 3H, *p*-CH_3 *p*-cym), 1.43, 1.39 (t, 6H, CH_3 phos, J_{HH} = 7.0 Hz), 1.04, 0.97 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 7.1 Hz) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 99.4 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 177.7 (d, C=O, J_{CP} = 20.4 Hz), 165−122 (m, Ph), 121.82 (d, C1 *p*-cym, J_{CP} = 4.5 Hz), 113.62 (s, C4 *p*-cym), 100.78 (d, C5 *p*-cym, J_{CP} = 2.4 Hz), 97.16 (d, C6 *p*-cym, J_{CP} = 6.6 Hz), 96.30 (d, C3 *p*-cym, J_{CP} = 2.7 Hz), 92.84 (s, br, C2 *p*-cym), 64.76 (m, CH_2 phos), 32.04 (s, CH), 23.00, 22.84 (s, CH_3), 18.10 (s, *p*-CH_3 *p*-cym), 16.03 (m, CH_3 phos), −5.20 (d, CH_2-Os, J_{CP} = 8.2 Hz) ppm. Anal. Calcd for $C_{52}H_{56}BO_3OsP$: C, 64.99; H, 5.87. Found: C, 65.15; H, 6.03.

[Os(η^1-CH$_3$)(CO)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh$_4$ (9c). This complex was prepared exactly like the related benzyl derivative **8c** using trimethylsilyl acetylene, HC≡CSi(CH$_3$)$_3$, as a reagent; yield

Table 1. Crystal Data and Structure Refinement

	1c	1d	8c
empirical formula	$C_{54}H_{61}BClO_3OsP$	$C_{58}H_{61}BClO_2OsP$	$C_{52}H_{56}BO_3OsP$
fw	1025.46	1057.50	960.95
temperature	293(2) K	293(2) K	293(2) K
wavelength	0.71073 Å	0.71073 Å	0.71073 Å
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
unit cell dimens	a = 12.3115(10) Å	a = 18.222(3) Å	a = 13.5866(10) Å
	b = 14.1504(12) Å	b = 14.828(2) Å	b = 13.5816(11) Å
	c = 14.4752(12) Å	c = 18.678(3) Å	c = 24.7454(18) Å
	α = 75.418(2)°		
	β = 77.243(2)°	β = 101.077(3)°	β = 94.385(2)°
	γ = 87.722(2)°		
volume	2380.0(3) Å^3	4952.6(14) Å^3	4552.8(6) Å^3
Z	2	4	4
density (calcd)	1.431 Mg/m^3	1.418 Mg/m^3	1.402 Mg/m^3
absorp coeff	2.811 mm^{-1}	2.703 mm^{-1}	2.877 mm^{-1}
F(000)	1044	2152	1952
cryst size	0.40 × 0.21 × 0.15 mm	0.47 × 0.19 × 0.10 mm	0.26 × 0.18 × 0.10 mm
θ range for data collection	1.49 to 25.03°	1.43 to 25.01°	1.65 to 25.03°
index ranges	$-14 \le h \le 14$	$-21 \le h \le 21$	$-15 \le h \le 16$
	$-16 \le k \le 16$	$-17 \le k \le 13$	$-16 \le k \le 13$
	$-17 \le l \le 17$	$-22 \le l \le 22$	$-24 \le l \le 29$
reflns collected	17 984	25 716	23 320
indep reflns	8343 [R(int) = 0.0498]	8689 [R(int) = 0.0762]	7957 [R(int) = 0.0499]
reflns obsd (>2σ)	6509	5114	5091
data completeness	0.990 fc	0.996	0.989
absorp corr	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents
max. and min transmn	1.000 and 0.739	1.000 and 0.602	1.000 and 0.810
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	8343/0/556	8689/0/582	7957/0/528
goodness-of-fit on F^2	1.044	0.975	1.008
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0381	R_1 = 0.0412	R_1 = 0.0375
	wR_2 = 0.0729	wR_2 = 0.0825	wR_2 = 0.0817
R indices (all data)	R_1 = 0.0607	R_1 = 0.0954	R_1 = 0.0818
	wR_2 = 0.0823	wR_2 = 0.1125	wR_2 = 0.1074
largest diff peak and hole	1.420 and −0.897 e Å^{-3}	1.260 and −1.515 e Å^{-3}	0.714 and −0.622 e Å^{-3}

≥60%. IR (KBr) cm^{-1}: ν_{CO} 1977 (s). ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.57−6.87 (m, 25H, Ph), 5.62 (d, HA *p*-cym, J_{AB} = 6.6, J_{AC} = 0.4, J_{AD} = 0.5, J_{HP} = 1.0 Hz), 5.22 (d, HB *p*-cym, J_{BC} = 0.5, J_{BD} = 0.4, J_{HP} = 1.0 Hz), 5.36 (d, HC *p*-cym, J_{CD} = 6.6, J_{HP} = 1.4 Hz), 5.66 (d, HD *p*-cym, J_{HP} = 1.2 Hz), 3.85 (m, 4H, CH_2 phos), 2.44 (m, 1H, CH), 1.89 (s, 3H, *p*-CH_3 *p*-cym), 1.38, 1.33 (t, 6H, CH_3 phos, J_{HH} = 7.0 Hz), 1.17, 1.13 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 7.1 Hz), 0.66 (d, CH_3-Os, J_{HP} = 6 Hz) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 100.9 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 177.1 (d, C═O, J_{CP} = 18.9 Hz), 165−122 (m, Ph), 120.92 (d, C1 *p*-cym, J_{CP} = 2.6 Hz), 115.82 (s, C4 *p*-cym), 94.74 (d, C5 *p*-cym, J_{CP} = 5.6 Hz), 94.29 (d, C6 *p*-cym, J_{CP} = 5.2 Hz), 94.16 (s, C2 *p*-cym), 93.81 (s, C3 *p*-cym), 64.32, 64.15 (d, CH_2 phos, J_{CP} = 8.9, J_{CP} = 7.8 Hz), 31.85 (s, CH), 23.75, 22.71 (s, CH_3 ^{i}Pr), 18.34 (s, *p*-CH_3 *p*-cym), 16.00, 15.90 (d, CH_3 phos, J_{CP} = 4.8, J_{CP} = 5.2 Hz), −33.51 (d, CH_3-Os, J_{CP} = 9.1 Hz) ppm. Anal. Calcd for $C_{46}H_{52}BO_3OsP$: C, 62.43; H, 5.92. Found: C, 62.35; H, 5.84.

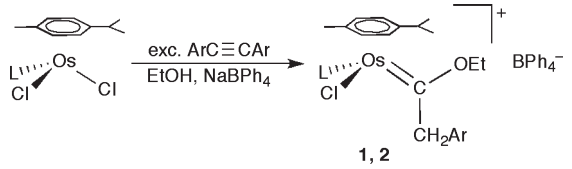
[OsCl{═C═C(H)Ph}(η^6-*p*-cymene){PPh(OEt)$_2$}]$^+$Y$^-$ [A] (Y = BPh$_4$, BF$_4$, CF$_3$SO$_3$). *Method 1:* In a 25 mL three-necked round-bottomed flask were placed 60 mg (0.10 mmol) of $OsCl_2$(η^6-*p*-cymene)[PPh(OEt)$_2$], 34 mg (0.10 mmol) of $NaBPh_4$, and 10 mL of acetone. An excess of phenylacetylene (34 μL, 0.30 mmol) was added to the resulting solution, which was stirred for 4 h. The solvent was removed under reduced pressure, leaving an oil, which was characterized as such.

Method 2: In a 25 mL three-necked round-bottomed flask were placed 100 mg (0.17 mmol) of $OsCl_2$(η^6-*p*-cymene)[PPh(OEt)$_2$], 44 mg (0.17 mmol) of silver triflate $AgCF_3SO_3$ (AgOTf), and 7 mL of dichloromethane. The reaction mixture was stirred for 24 h in the dark and filtered to remove the solid AgCl, and then an excess of phenylacetylene (57 μL, 0.51 mmol) was added. The resulting solution was stirred for 8 h, and then the solvent removed under reduced pressure to give an oil, which was characterized as such.

Method 3: A solution of the complex OsCl(C≡CPh)(η^6-*p*-cymene)-[PPh(OEt)$_2$] (**6c**) (20 mg, 0.03 mmol) in 0.6 mL of CH_2Cl_2 was placed in a 5 mm NMR tube, cooled to −80 °C, and treated with a slight excess of either HBF_4 (0.035 mmol, 5.0 μL of a 54% solution in Et_2O) or HOTf (0.035 mmol, 3.1 μL). The tube was inserted into the probe (precooled to −80 °C) of the NMR instrument, and the spectra were recorded from −80 to +20 °C.

dx.doi.org/10.1021/om101105s |*Organometallics* 2011, 30, 1558–1568

Scheme 1[a]



[a] Ar = Ph (**1**), *p*-tolyl (**2**); L = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**), $PPh(OEt)_2$ (**c**), PPh_2OEt (**d**).

^1H NMR (CD_2Cl_2, 25 °C) δ: 4.38 ppm (s, 1H, =CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 95.8 ppm (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 278.0 ppm (d, C=Os, J_{CP} = 10.5 Hz).

Crystal Structure Determination of [OsCl(η^6-*p*-cymene){=C(OEt)CH_2Ph}{$PPh(OEt)_2$}]BPh_4 (1c), [OsCl(η^6-*p*-cymene){=C(OEt)CH_2Ph}(PPh_2OEt)]BPh_4 (1d), and [Os(η^1-CH_2Ph)(CO)(η^6-*p*-cymene){$PPh(OEt)_2$}]BPh_4 (8c). Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and were corrected for Lorentz and polarization effects. The software SMART[11] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[12] for integration of intensity of reflections and scaling, and SADABS[13] for empirical absorption correction. The crystallographic treatment of the compound was performed with the Oscail program[14] The structures were solved by Patterson methods for **1d** and by direct methods for **1c** and **8c** and refined by a full-matrix least-squares based on F^2.[15] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. Details of crystal data and structural refinement are given in Table 1. The three compounds possess a chiral center in the osmium atom, although both enantiomers are present in the unit cell.

RESULTS AND DISCUSSION

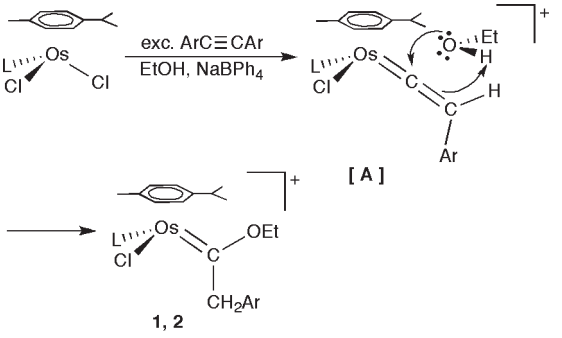
Preparation of Carbene Complexes. Half-sandwich dichloro complexes $OsCl_2(\eta^6$-*p*-cymene)L react with terminal alkynes ArC≡CH (Ar = Ph, *p*-tolyl) in ethanol to give the ethoxycarbene derivatives [OsCl{=C(OEt)CH_2Ar}(η^6-*p*-cymene)L]BPh_4 (**1**, **2**), which were isolated as BPh_4 salts (Scheme 1) and characterized.

Crucial for successful synthesis is the presence of the salt $NaBPh_4$, which probably favors the substitution of the chloride ligand in the starting complex, allowing final derivatives **1** and **2** to be obtained in good yields.

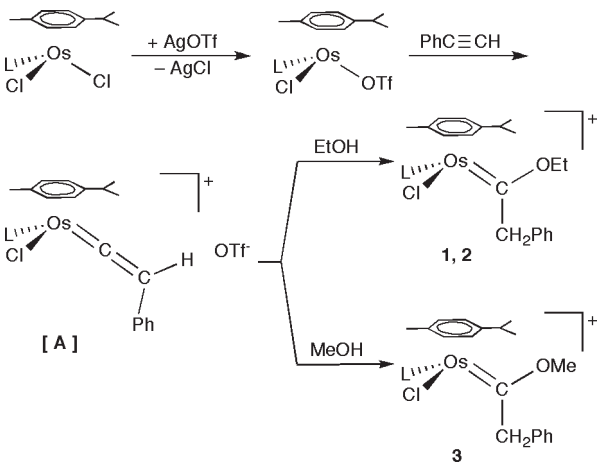
The formation of an ethoxycarbene from the reaction of terminal alkynes with dichloro complexes $OsCl_2(\eta^6$-*p*-cymene)L is somewhat surprising, but may be explained according to the reaction path shown in Scheme 2, which involves the initial formation of a vinylidene intermediate [**A**]. Nucleophilic attack by the oxygen atom of ethanol on the Cα of the vinylidene followed by proton transfer gives the final ethoxy-benzyl carbene complexes **1** and **2**.

In order to support the proposed reaction path, we attempted either to isolate the intermediate vinylidene complex [**A**] or, at least, to identify its presence in the reaction mixture. At first, we treated the dichloro complex $OsCl_2(\eta^6$-*p*-cymene)L, in the presence of $NaBPh_4$, with phenylacetylene in CH_2Cl_2, but no reaction was observed, perhaps owing to the insolubility of $NaBPh_4$ in this solvent. We therefore changed to acetone and did observe a reaction, resulting in a purplish-red solution.

Scheme 2



Scheme 3



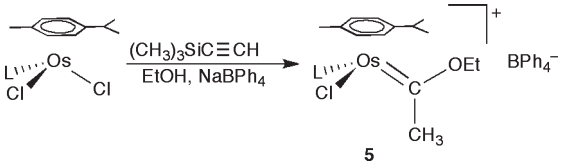
Unfortunately, the isolated product was a mixture containing only traces of the hypothesized vinylidene species [**A**]. The major compound present in the mixture was [Os(η^1-CH_2Ph)(CO)(η^6-*p*-cymene)L]BPh_4 (**8**), formed by hydrolysis of the alkyne (see below) with the traces of H_2O always present in "anhydrous" acetone. We therefore used a different strategy to prepare the vinylidene intermediate [**A**], involving the reaction of the dichloro precursor first with silver triflate, to form the triflate intermediate OsCl(κ^1-OTf)(η^6-*p*-cymene)L, and then with an excess of phenylacetylene in dichloromethane as solvent (Scheme 3).

The triflate intermediate quickly reacts with phenylacetylene to give the purple solution, from which we were not able to isolate a solid, but only an oily product. However, its NMR spectra strongly suggest the presence of the vinylidene complex [**A**], showing a doublet at 278.0 ppm (J_{CP} = 10.5 Hz) in the ^{13}C spectrum, which is attributed to the Cα carbon atom of a vinylidene species. In an HMQC experiment, this ^{13}C signal was correlated with the singlet observed at 4.38 ppm in the ^1H NMR spectrum and attributed to the =CH(Ph) proton of the vinylidene ligand, fitting the proposed formulation.

The triflate ligand is labile in the complex OsCl(κ^1-OTf)(η^6-*p*-cymene)L and may be substituted by the alkyne, which then tautomerizes[2h,16] on the metal center to give the vinylidene intermediate. The fact that this vinylidene complex is really the

dx.doi.org/10.1021/om101105s |*Organometallics* 2011, 30, 1558–1568

Scheme 4



proposed intermediate [**A**] of the reaction path (Scheme 2) is confirmed by treatment with ethanol, which gives the ethoxycarbene final product **1** (Scheme 3). Furthermore, as expected, the addition of methanol to a solution of [**A**] gives the methoxycarbene complex $[OsCl\{=C(OMe)CH_2Ph\}(\eta^6\text{-}p\text{-cymene})L]BPh_4$ (**3**), which can be isolated as a BPh_4 salt and characterized. The same methoxycarbene derivative **3** was also prepared directly by treating the dichloro complex $OsCl_2(\eta^6\text{-}p\text{-cymene})L$ with terminal alkyne ArC≡CH, with methanol as a solvent (see Scheme 1).

Nucleophilic attack of alcohol on the Cα carbon atom of the allenylidene[17] ligand [Os]=C=C=CR′R″ has previously been reported in osmium complexes,[6a,e] affording alkoxy-alkenyl carbene derivatives $[Os\{=C(OR)CH=CR'R''\}(CH_3CN)_4(IPr)(OTf)_2]$ [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene] and $[OsCl(\eta^6\text{-mes})(PMe_3)\{=C(OR)CH=CPh_2\}]PF_6$ (mes = 1,3,5-trimethylbenzene). The reaction of our *p*-cymene osmium(II) fragment containing phosphite, phosphonite, or phosphinite ligands highlights the fact that the vinylidene intermediate can also undergo nucleophilic attack on the Cα atom, yielding alkoxy-alkylcarbene derivatives $[Os]\{=C(OR)CH_2R\}$ (**1**−**3**).

The reaction of dichloro precursors was also extended to other terminal alkynes, such as *tert*-butyl and trimethylsilyl acetylene. The results showed that, while with $Bu^tC{\equiv}CH$ the expected ethoxyneopentylcarbene complex $[OsCl\{=C(OEt)CH_2Bu^t\}(\eta^6\text{-}p\text{-cymene})L]BPh_4$ (**4**) could be isolated, the reaction with trimethylsilyl acetylene gives the ethoxymethylcarbene derivative $[OsCl\{=C(OEt)CH_3\}(\eta^6\text{-}p\text{-cymene})L]BPh_4$ (**5**), which was isolated in good yields and characterized (Scheme 4).

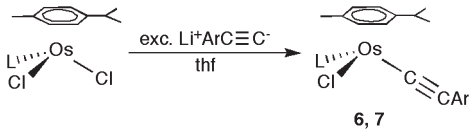
The formation of complex **5**, involving cleavage of the C−$Si(CH_3)_3$ bond, is somewhat surprising, because the Si−C bond is known to be quite inert to cleavage in many organometallic complexes.[18] However, a few examples of cleavage of the trimethylsilyl group have been reported,[19] one of which[20] involves a trimethylsilyl vinylidene complex of Ru, very similar to our probable vinylidene intermediate [**A**].

The behavior of half-sandwich complexes $OsCl_2(\eta^6\text{-}p\text{-cymene})L$ toward terminal alkynes prompted us to extend the study to acetylide. Results show that the reaction with an excess of lithium acetylide proceeds in thf with the substitution of one chloride and the formation of acetylide complexes $OsCl(C{\equiv}CAr)(\eta^6\text{-}p\text{-cymene})L$, which were isolated in good yields and characterized (Scheme 5).

Substitution of both the chloride ligands in the $OsCl_2(\eta^6\text{-}p\text{-cymene})L$ precursors to yield bis(acetylide) complexes was not observed, either in the presence of a large excess of $Li^+[ArC{\equiv}C]^-$ or when long reaction times were applied, and monoacetylides **6** and **7** were the only isolated products. Refluxing conditions yielded only decomposition products.

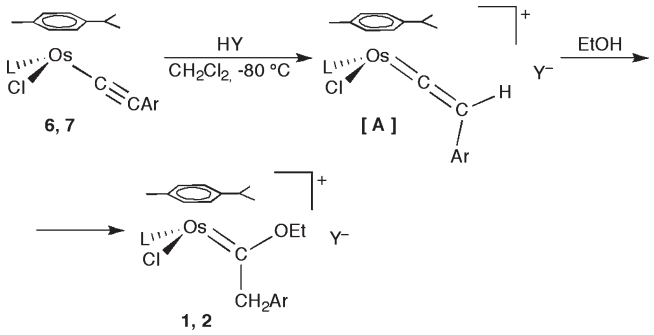
The acetylide complexes $OsCl(C{\equiv}CAr)(\eta^6\text{-}p\text{-cymene})L$ (**6**, **7**) react with Brønsted acids [HBF_4 or CF_3SO_3H (HOTf)] at −80 °C to give the vinylidene derivative $[OsCl\{=C=C(H)Ar\}(\eta^6\text{-}p\text{-cymene})L]^+$ [**A**], as shown in Scheme 6.

Scheme 5[a]



[a] Ar = Ph (**6**), *p*-tolyl (**7**).

Scheme 6[a]



[a] HY = HOTf, HBF_4.

Unfortunately, we were not able to obtain the vinylidene complex as a solid, but only as a rather unstable oil. However, NMR data of the protonated solution of complex $OsCl(C{\equiv}CPh)(\eta^6\text{-}p\text{-cymene})[PPh(OEt)_2]$ (**6c**) with HOTf clearly support the formation of the vinylidene complex [**A**]: the ^{13}C NMR spectrum shows the characteristic signal of the Cα carbenic carbon atom of the vinylidene ligand at 278 ppm, and the proton spectra of a singlet at 4.38 ppm, attributed to the =CH(Ph) vinylidene proton (see above), matching the proposed formulation.

Protonated solutions of acetylide complexes **6** and **7** reacted with ethanol to yield the ethoxycarbene derivatives **1** and **2**, as further support to the proposed reactivity of half-sandwich complexes $OsCl_2(\eta^6\text{-}p\text{-cymene})L$ with terminal alkynes.

Good analytical data were obtained for complexes **1**−**7**, which were isolated as yellow or reddish-brown solids, stable in air and in solution of common organic solvents, where they behave as either 1:1 (**1**−**5**) or nonelectrolytes[21] (**6**, **7**). IR and NMR (^1H, ^{13}C, ^{31}P) data confirmed the proposed formulations, which were further supported by X-ray crystal structure determination of complexes $[OsCl(\eta^6\text{-}p\text{-cymene})\{=C(OEt)CH_2Ph\}\{PPh(OEt)_2\}]BPh_4$ (**1c**) and $[OsCl(\eta^6\text{-}p\text{-cymene})\{=C(OEt)CH_2Ph\}(PPh_2OEt)]BPh_4$ (**1d**), ORTEP representations of which are given in Figure 1, at a probability level of 30%.

The structure of complexes **1c** and **1d** consists of a tetraphenyl borate anion (not shown in the figures) and a cation formed by an osmium atom η^6-coordinated to a *p*-cymene molecule and to three donor atoms, leading to the formation of a "three-legged piano stool" structure. These ligands are a chloride ligand, a Fisher-type carbene group, and a phosphorus-donor ligand. The geometry of the complexes can be considered to be octahedral and is marked by values for the angles C(11)−Os−P, Cl−Os−P, and C(11)−Os−Cl, in any case not more than 2.3° from 90°.

The average Os−C bond distance for the *p*-cymene ligand is 2.272(7) Å in both compounds (Table 2). These bond lengths are close to those of other related complexes[7b,22,23] and also show the different *trans* influence of the other ligands, since Os−C(1) and Os−C(6), *trans* to the Fisher carbene ligand in each

dx.doi.org/10.1021/om101105s |*Organometallics* 2011, 30, 1558–1568

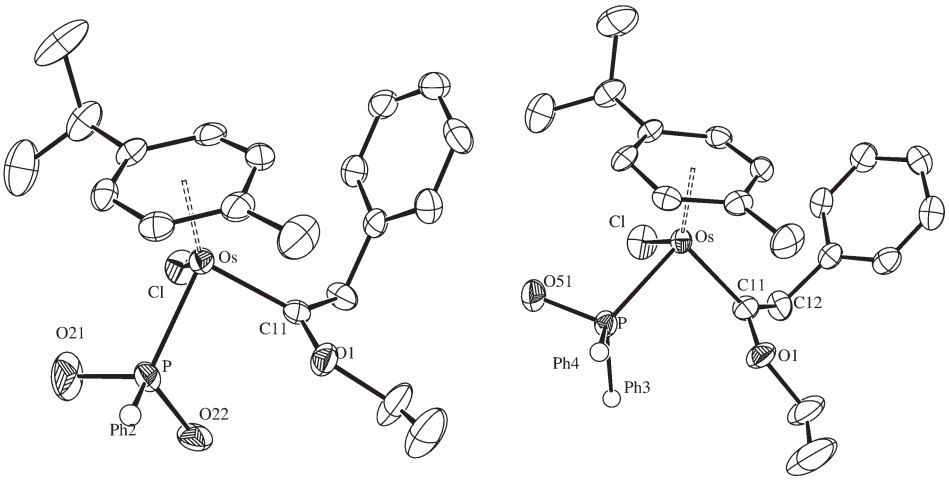


Figure 1. Left: The cation of **1c**. Right: The cation of **1d**. In the phosphorus-donor ligands, ethoxy groups are represented only by the oxygen atoms, and phenyl rings by simple spheres. The hydrogen atoms are omitted.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Compounds 1c and 1d

	1c	1d
Os−CT01	1.7841(1)	1.7804(4)
Os−C(11)	1.981(5)	1.982(7)
Os−Cl	2.4149(14)	2.405(2)
Os−P	2.2869(15)	2.314(2)
Os−C(1)	2.324(5)	2.340(7)
Os−C(2)	2.289(5)	2.277(7)
Os−C(3)	2.294(5)	2.272(7)
Os−C(4)	2.234(5)	2.230(7)
Os−C(5)	2.201(5)	2.189(7)
Os−C(6)	2.303(5)	2.324(7)
O(1)−C(11)	1.311(6)	1.295(9)
CT01−Os−C(11)	127.92(13)	128.2(2)
CT01−Os−Cl	123.78(4)	122.46(6)
CT01−Os−P	127.38(4)	126.08(5)
C(11)−Os−Cl	88.72(15)	90.7(2)
C(11)−Os−P	87.70(14)	89.5(2)
P−Os−Cl	88.87(6)	88.18(8)
O(1)−C(11)−C(12)	117.3(4)	117.4(7)
O(1)−C(11)−Os	118.7(4)	119.6(5)
C(12)−C(11)−Os	123.7(4)	123.0(6)

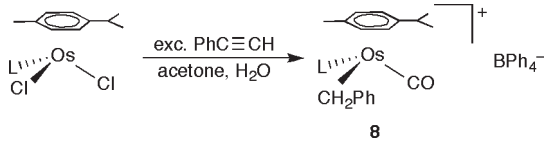
complex, are longer. The atom labeled as C(6) also corresponds to the isopropyl-substituted carbon atom, and we found that this is usually the longer metal−C bond in *p*-cymene complexes.[7b,22] The distance Os−C(3), *trans* to the phosphorus donor ligand, is also slightly longer than the other ones, in both compounds, and causes a slight lack of planarity in the *p*-cymene ligand, showing small differences between the compounds. The distances from the osmium atom to the centroid of the benzene ring of the cymene ligand are 1.780(4) and 1.784(1) Å, respectively. The rms values for this plane are 0.0264 and 0.0276, respectively, with maximum deviation for C(6) and C(3), for both compounds. The Os−P bond length is slightly longer in the case of the phosphonite $PPh(OEt)_2$ ligand, 2.314(2) Å, than that of the phosphinite $PPh_2(OEt)$, 2.287(2) Å.[24] The Os−Cl bond length is 2.410(2) Å on average for both compounds, matching literature values well.[7b,22−25]

The Os−C(carbene) bond lengths are 1.982(7) and 1.983(5) Å for both compounds, slightly longer than those found for other Os-non-Fischer-carbene complexes[6a,26] but similar to other Fischer-carbene complexes,[6f,27] in accordance with the usual features for this kind of heteroatom-stabilized carbene complexes.[28] The sum of angles around the carbene C(11) atom is 359.9°, showing the planarity of this atom (which is consistent with sp^2 hybridization). In addition, the distance from the carbene carbon to the ethoxy oxygen, on average 1.303(1) Å, is intermediate between that expected for carbon−oxygen single and double bonds, reflecting intermediate bond order. This is a value typically found in Fischer-type carbene complexes.[27] In each of compounds **1d** and **1c**, the $=C(OEt)CH_2Ph$ ligand is oriented so that the phenyl groups are directed toward the *p*-cymene ligand, as previously observed for Fe and Ru half-sandwich complexes with similar ligands.[29]

As well as the signals of *p*-cymene, phosphorus-donor ligand, and BPh_4^-, the ^{1}H NMR spectra of carbene complexes $[OsCl\{=C(OR')CH_2R''\}(\eta^6\text{-}p\text{-cymene})L]BPh_4$ (**1**−**4**) (R′ = Me, Et; R″ = Ph, *p*-tolyl, Bu^t) show the characteristic resonances of the R′ and R″ substituents of the carbene. In particular, the methyl or ethyl substituents of the alkoxy OR′ are singlets (**3c**) or triplets and quartets (**4c**), respectively, whereas benzyl and neopentyl protons CH_2R'' appear as two doublets at 5.37−3.62 and 4.33−2.91 ppm. The multiplicity of this signal is due to the presence of a chiral center, which makes the two CH_2R'' protons diastereotopic, with different values of chemical shift and J_{HH} values of 19.0−12.8 Hz. In addition, coupling between benzyl and neopentyl protons and the P nucleus of the phosphorus-donor ligand was not observed, probably owing to the small value of J_{HP}. However, diagnostic for the presence of the carbene ligand are the ^{13}C NMR spectra, which show a doublet at 295.07−286.50 ppm (J_{CP} = 15.0−18.0 Hz), characteristic of carbene carbon resonance. The signals of substituents OR′ and CH_2R'', as well as those of the supporting ligands *p*-cymene and phosphite, phosphonite, or phosphinite, are also present in the spectra, and their attributions were confirmed by HMQC and HMBC experiments.

The ^{1}H NMR spectra of the complex $[OsCl\{=C(OEt)CH_3\}(\eta^6\text{-}p\text{-cymene})\{PPh(OEt)_2\}]BPh_4$ (**5c**), obtained by reaction with

Scheme 7[a]



[a] L = PPh(OEt)$_2$ (**c**).

$(CH_3)_3SiC{\equiv}CH$, do not show the signal of the trimethylsilyl substituent but a singlet at 2.23 ppm, correlated in a HMBC experiment with the ^{13}C carbene carbon resonance at 285.1 ppm (J_{CP} = 15.8 Hz) and attributed to the methyl substituent of the carbene ligand. Instead, the signal of the ethoxy substituent appears as two multiplets, at 4.22 and 4.04 ppm for the CH_2 protons, and one triplet at 1.50 ppm (J_{HH} = 7.0 Hz) for the CH_3 ones. The ^{13}C NMR spectra also support the presence of the carbene ligand $=C(OEt)CH_3$, showing a doublet at 285.1 ppm (J_{CP} = 15.8 Hz) of the carbene carbon atom, a singlet at 39.11 ppm of the methyl substituent, and two singlets at 75.27 (CH_2) and 14.45 ppm (CH_3) of the ethoxy group, fitting the proposed formulation for complex **5c**.

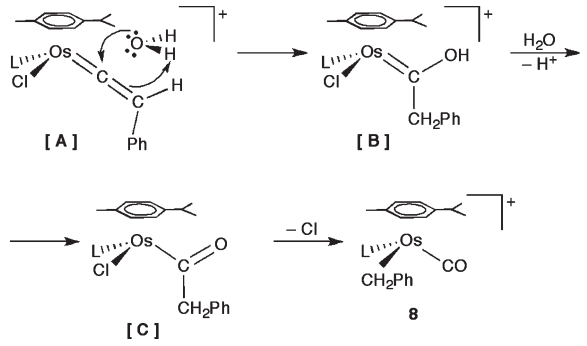
The IR spectra of the acetylide complexes $OsCl(C{\equiv}CAr)(\eta^6$-*p*-cymene)L (**6**, **7**) show a medium-intensity band at 2085−2095 cm^{-1} due to the $\nu_{C\equiv C}$ of the acetylide ligand. However, support for the presence of this ligand comes from the ^{13}C NMR spectra, which, besides the signals of the *p*-cymene and phosphite or phosphonite carbons, also show one doublet at 128.7−127.8 ppm (J_{CP} = 5.6−4.8 Hz), attributed to the Cα carbon resonance, and one singlet at 136.8 ppm, due to the Cβ of the acetylide ligand. The ^1H NMR spectrum of complex $OsCl(C{\equiv}C$-*p*-tolyl)$(\eta^6$-*p*-cymene)[P(OEt)$_3$] (**7b**) also shows a singlet at 2.35 ppm of the methyl substituent of the *p*-tolyl, which, in an HMQC experiment, was correlated with a singlet at 21.22 ppm in the ^{13}C spectrum, matching the proposed formulation for acetylide complexes **6** and **7**.

Hydrolysis of Alkyne. The facile reaction of the half-sandwich vinylidene complex $[OsCl\{{=}C{=}C(H)Ar\}(\eta^6$-*p*-cymene)L$]^+$ [**A**] with alcohols, leading to alkoxycarbene derivatives **1**−**5**, prompted us to study the reaction with other nucleophiles, such as water, to test whether related carbenes could be obtained. Results show that dichloro complexes $OsCl_2(\eta^6$-*p*-cymene)L do react with phenylacetylene in the presence of H_2O, but give alkyl-carbonyl derivatives $[Os(\eta^1\text{-}CH_2Ph)(CO)(\eta^6$-*p*-cymene)L$]BPh_4$ (**8**), which were isolated in good yields and characterized (Scheme 7).

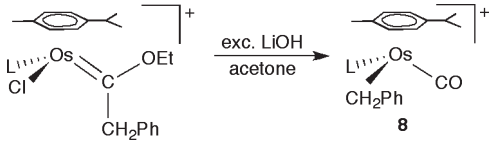
The formation of benzyl-carbonyl complex **8**, instead of the expected hydroxycarbene $[OsCl\{{=}C(OH)(CH_2Ph)\}(\eta^6$-*p*-cymene)L$]BPh_4$, was somewhat surprising, but may be explained as due to the instability of hydroxycarbene [**B**] (Scheme 8) formed by nucleophilic attack of H_2O on the vinylidene species [**A**]. Deprotonation of the same oxycarbene [**B**] with an excess of H_2O gave acyl complex [**C**], which, by CO deinsertion of the acyl ligand and concurrent loss of the Cl^- ligand, afforded the final carbonyl complex **8**.

Therefore, the reaction entails hydrolysis of the terminal alkyne, with C≡C bond cleavage and formation of an alkyl-carbonyl derivative. Metal-assisted hydrolysis of alkyne with H_2O has previously been reported for some metals,[30−32] and a pathway similar to that of Scheme 8 has been proposed for ruthenium complexes.[31a] In our case, the isolation of alkoxycarbene complexes like **1**−**5** strongly supports the formation of the key intermediate [**B**], which makes the reaction path of the type of Scheme 8 for C≡C bond cleavage of the terminal alkyne a very plausible proposition. It is worth noting

Scheme 8

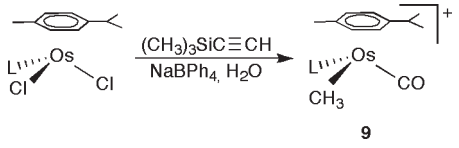


Scheme 9[a]



[a] L = PPh(OEt)$_2$ (**c**).

Scheme 10[a]



[a] L = PPh(OEt)$_2$ (**c**).

that the alkyl-carbonyl complex $[Os(\eta^1\text{-}CH_2Ph)(CO)(\eta^6$-*p*-cymene)L$]BPh_4$ (**8**) was also obtained by treating ethoxycarbene complexes $[OsCl\{{=}C(OEt)CH_2Ph\}(\eta^6$-*p*-cymene)L$]BPh_4$ (**1**) with an excess of LiOH in acetone (Scheme 9).

Substitution of the OEt group of the carbene by OH^- should take place, affording hydroxycarbene [**B**], which, in the presence of an excess of LiOH, yields the final carbonyl compound **8**.

Trimethylsilyl acetylene was also reacted with $OsCl_2(\eta^6$-*p*-cymene)L in the presence of H_2O, but the resulting compound was the methyl-carbonyl derivative $[Os(\eta^1\text{-}CH_3)(CO)(\eta^6$-*p*-cymene)L$]BPh_4$ (**9**) (Scheme 10).

The formation of the desilylated product **9** suggests that, besides hydrolysis, also C−Si bond cleavage takes place with the alkyne $HC{\equiv}CSi(CH_3)_3$, as previously observed in the case of carbene complex **5**.

Good analytical data were obtained for carbonyl complexes $[Os(\eta^1\text{-}CH_2Ph)(CO)(\eta^6$-*p*-cymene)$\{PPh(OEt)_2\}]BPh_4$ (**8c**) and $[Os(\eta^1\text{-}CH_3)(CO)(\eta^6$-*p*-cymene)$\{PPh(OEt)_2\}]BPh_4$ (**9c**), which were isolated as yellow solids stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes.[21] IR and NMR (^1H, ^{31}P, ^{13}C) data support the proposed formulation, which was further confirmed by X-ray crystal structure determination of complex **8c**, an ORTEP representation of which is shown in Figure 2. The structure of this complex also consists of a tetraphenyl borate anion (not shown in the figure) and a cation formed by an osmium atom η^6 coordinated to a *p*-cymene

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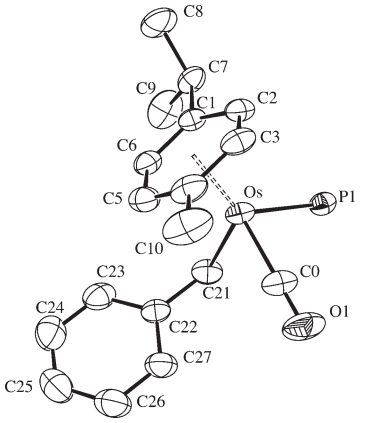

Figure 2. ORTEP representation of the cation of **8c**. The substituents of the phosphonite ligand are not shown. The hydrogen atoms are omitted.

molecule and to three ligands, which are now a carbonyl group, a η^1-benzyl group, and a phosphonite $PPh(OEt)_2$ ligand. Again, the half-sandwich structure is of the typical "three-legged piano stool" type. As is well known for this kind of half-sandwich complex, the overall geometry should be considered as octahedral and is marked by near-90° values for angles C(0)−Os−C(21), 87.4(3)°, C(0)−Os−P(1), 86.4(3)°, and C(21)−Os−P(1), 86.3(2)°. The average Os−C bond distance for the *p*-cymene ligand is 2.312 (7) Å, slightly longer than those found for the previous complexes, e.g., the distance from the osmium atom to the centroid of the benzene ring, 1.8298(3) Å. Between these Os−C bond lengths, the longer match with the atom labeled C(1), *trans* to the carbonyl group, also corresponds to the isopropyl-substituted carbon atom, and we found that this is usually the longer metal−C bond in *p*-cymene complexes.[7b,22]

At this point, it is interesting to note that, in complexes **1d** and **1c**, the disposition of the *p*-cymene ligand is staggered, in such a way that a carbon−carbon bond is *trans* to each monodentated ligand. However, in alkyl complex **8c**, the disposition of the η^6-ligand is almost perfectly eclipsed with the other ligands, so that the C(1) [C(1)−CT−Os−C(0) torsion angle of 171.9(4)°] is *trans* to the carbonyl ligand, the C(3) [C(3)−CT−Os−C(21) torsion angle of 168.4(4)°] is *trans* to the alkyl ligand, and the C(5) [C(5)−CT−Os−P(1) torsion angle of 165.6(4)°] is *trans* to the phosphonite ligand.

Os−P and Os−C (carbonyl) bond lengths are 2.282(2) and 1.863(8) Å, respectively, but, as they are normal values, they are not commented on further here. The Os−C(benzyl) bond length is 2.169(7) Å, clearly longer than that found for carbene-osmium complexes [(η^6-*p*-cymene)OsCl(=CHPh)(L)], 1.919(4) Å.[33] To our knowledge, there is no benzyl complex with Os deposited in the CCDC,[34] but some η^1-alkyl complexes—for example, neopentyl complexes—can be found in the literature with similar distances.[35] The parameters of the ligand are similar to those found for other benzyl complexes, with a C(22)−C(21)−Os angle of 115.6(5)°, slightly more acute than those found in iridium complexes [IrCp*Cl(η^1-CH_2Ph)(CO)], 117.7(4)°,[36] or 117.8(4)° in the tungsten complex [WCp*(NO)(η^1-CH_2Ph)(η^3-CH_2CHCHMe)].[37]

The IR spectra of complexes **8** and **9** show strong bands at 1970 (**8c**) or 1977 (**9c**) cm^{-1} attributed to the ν_{CO} of the carbonyl ligand. As well as the signals characteristic of *p*-cymene and $PPh(OEt)_2$, the ^{1}H NMR spectrum of **8c** shows two doublets of doublets at 3.34 and 3.11 ppm [ABX spin system (A, B = ^{1}H, X = ^{31}P) J_{AB} = 10.3, J_{AX} = 6.8, J_{BX} = 3.5 Hz)] attributed to the benzyl protons of the η^1-CH_2Ph ligand. Owing to the chirality of the complexes, the two CH_2R protons are prochiral and are coupled with each other and with the phosphorus nucleus of the phosphonite, giving the observed dd pattern. In the ^{13}C NMR spectra, the carbon resonance falls at −5.20 ppm, whereas the CO carbon signal appears as a doublet at 177.7 ppm (J_{CP} = 20.4 Hz), fitting the formulation found in the solid state by X-ray analysis. In the proton NMR spectrum of compound [Os(η^1-CH_3)(CO)(η^6-*p*-cymene){$PPh(OEt)_2$}]BPh_4 (**9c**), the methyl resonance of the η^1-CH_3 ligand appears as a doublet at 0.66 ppm (J_{HP} = 6 Hz), whereas the ^{13}C spectrum, besides the signals of *p*-cymene and phosphonite, also has a doublet at 177.1 ppm (J_{CP} = 18.9 Hz), attributed to a carbonyl carbon resonance, matching the formulation proposed for the complex.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for 8c

Os−C(0)	1.863(8)
Os−CT1	1.8298(3)
Os−C(1)	2.358(6)
Os−C(3)	2.321(7)
Os−C(5)	2.292(8)
C(0)−O(1)	1.135(8
Os−C(21)	2.169(7)
Os−P(1)	2.282(2)
Os−C(2)	2.277(6)
Os−C(4)	2.318(7)
Os−C(6)	2.306(7)
C(21)−C(22)	1.497(10)
C(0)−Os−C(21)	87.4(3)
C(21)−Os−P(1)	86.3(2)
CT1−Os−C(21)	123.0(2)
O(1)−C(0)−Os	177.8(8)
C(0)−Os−P(1)	86.4(3)
CT1−Os−C(0)	129.1(2)
CT1−Os−P(1)	130.42(4)
C(22)−C(21)−Os	115.6(5)

CONCLUSIONS

Half-sandwich *p*-cymene fragments containing phosphorus donors as supporting ligands are reported to be able to stabilize alkoxy-alkylcarbene complexes of the type [OsCl{=C(OR′)CH_2R″}(η^6-*p*-cymene)L]BPh_4. The synthesis of the carbene derivatives involves a highly reactive vinylidene intermediate, [OsCl{=C=C(H)R″}(η^6-*p*-cymene)L]$^+$, which can react either with alcohol R′OH to yield alkoxycarbene or with H_2O to afford alkyl-carbonyl derivatives [Os(η^1-CH_2R)(CO)(η^6-*p*-cymene)L]BPh_4. The preparation of half-sandwich acetylide derivatives OsCl(C≡CAr)(η^6-*p*-cymene)L is also reported.

ASSOCIATED CONTENT

Supporting Information. Crystallographic data for compounds **1c**, **1d**, and **8c** (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

The financial support of MIUR (Rome)-PRIN 2007 is gratefully acknowledged. We thank Mrs. Daniela Baldan, from the Università Ca' Foscari Venezia (Italy), for her technical assistance.

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