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Preparation of half-sandwich ethylene complexes of Osmium(II)

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ABSTRACT

Ethylene complexes [OsCl(η^6-*p*-cymene)(η^2-$CH_2{=}CH_2$)*L*]BPh_4 (**1, 2**) [*L* = $P(OMe)_3$, $P(OEt)_3$, $PPh(OEt)_2$, ^{t}BuNC) were prepared by allowing the dichloro compounds $OsCl_2$(η^6-*p*-cymene)*L* to react with $CH_2{=}CH_2$ in mild conditions (1 atm). Treatment of **1** with amine or hydrazine yielded [OsCl(*p*-tolyl-NH_2)(η^6-*p*-cymene){$PPh(OEt)_2$}]BPh_4 (**3**) or [OsCl(η^6-*p*-cymene)(CH_3NHNH_2){$PPh(OEt)_2$}]BPh_4 (**4**) derivatives. The vinylidene cation [OsCl{=C=C(H)Ph}(η^6-*p*-cymene){$PPh(OEt)_2$}]$^+$ (**5**$^+$) was also prepared from **1** and PhC≡CH. The complexes were characterized spectroscopically and by X-ray crystal structure determination of [OsCl(η^6-*p*-cymene)(η^2-$CH_2{=}CH_2$){$P(OMe)_3$}]BPh_4 (**1a**). The nature of the Os–ethylene bond was investigated from a computational point of view.

1. Introduction

The coordination of an alkene to a transition metal fragment occupies an important place in organometallic chemistry [1,2], not only due to the significant changes in structure and chemical reactivity that the alkene coordination to a central metal may induce [3,4], but also due to the influence that the metal fragment may have in its catalytic transformations [5]. A number of alkene complexes have been prepared [1,3,4,6] for different central metals with various types of ligands, in order to probe the most important factors which influence the stability of the coordinated alkene and its reactivity in stoichiometric and catalytic organic reactions.

However, the number of reported alkene complexes for the metals of the iron triad is still limited, compared with other metal triads [7] such as those of cobalt and nickel, and the known ethylene complexes for osmium are still few [8].

We have a long-standing interest in the chemistry of arene complexes [9] of the iron triad and, during our studies on the reactivity of *p*-cymene complexes of osmium, we found that ethylene may coordinate to the metal fragment [OsCl(η^6-*p*-cymene)*L*]$^+$ (*L* = phosphite) in very mild conditions.

We report here the results of these studies, including the synthesis and characterization of ethylene complexes of osmium stabilized by the *p*-cymene ligand.

2. Experimental section

2.1. General comments

All synthetic work was carried out in an appropriate atmosphere (Ar, N_2) using standard Schlenk techniques or an inert atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, allowing their characterization; nonetheless they were stored under nitrogen 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. Phosphines $PPh(OEt)_2$ and PPh_2OEt were prepared by the method of Rabinowitz and Pellon [10], and $P(OMe)_3$ and $P(OEt)_3$ were Aldrich products, purified by distillation under nitrogen. Isocyanides RNC (*R* = *p*-tolyl, *p*-methoxy) were obtained by the method of Ziehn [11], and ^{t}BuNC was an Aldrich product used as received. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin–Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra (^1H, ^{13}C, ^{31}P) were obtained on AVANCE 300 Bruker spectrometer at temperatures between −90 and +30 °C, unless otherwise stated. ^1H and ^{13}C spectra are referred to internal tetramethylsilane and ^{31}P {^1H} ones to 85% H_3PO_4 with downfield shifts considered positive. COSY, NOESY, HMQC and HMBC NMR experiments were performed with standard programs. The iNMR software package [12] was 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 Radiometer

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CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova (Italy).

2.2. Synthesis of complexes

Complexes [OsCl(μ-Cl)(η^6-*p*-cymene)]$_2$, OsCl$_2$(η^6-*p*-cymene)*L* [*L* = P(OMe)$_3$, P(OEt)$_3$, PPh(OEt)$_2$] and OsCl$_2$(η^6-*p*-cymene)(CNR) (*R* = ^{t}Bu, *p*-tolyl) were prepared following the methods previously reported [9d,13].

*2.3. [OsCl(η^6-p-cymene)(η^2-CH$_2$=CH$_2$)L]BPh$_4$ (1) [P = P(OMe)$_3$ (**a**), P(OEt)$_3$ (**b**), PPh(OEt)$_2$ (**c**)]*

In a 25-mL three-necked round-bottomed flask were placed a solid sample of the appropriate complex OsCl$_2$(η^6-*p*-cymene)*L* (0.38 mmol), an excess of NaBPh$_4$ (0.77 mmol, 0.26 g), and 4 mL of ethanol. The resulting mixture was stirred under an ethylene atmosphere (1 atm) at room temperature for 24 h. The yellow solid which separated out was filtered and crystallized under ethylene from CH$_2$Cl$_2$ and ethanol; yield ≥90%.

1a: ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ (see Chart 1): 7.40–6.87 (m, 20 H, BPh$_4$), ABCDX spin syst (X = ^{31}P), δ_A 5.77, δ_B 5.21, δ_C 5.87, δ_D 5.73, $J_{AB} = 6.2$, $J_{AC} = 0.8$, $J_{AD} = 1.2$, $J_{Ax} = 0.1$, $J_{BC} = 1.2$, $J_{BD} = 0.8$, $J_{Bx} = 1.0$, $J_{CD} = 6.2$, $J_{Cx} = 1.6$, $J_{Dx} = 1.2$ (4 H, Ph *p*-cym), EFGHX spin syst (X = ^{31}P), $\delta_E = \delta_G$ 4.15, $\delta_F = \delta_H$ 3.15, $J_{EG} = J_{FH} = 9.7$, $J_{EH} = J_{FG} = 9.0$, $J_{EF} = J_{GH} = 0.6$, $J_{Ex} = J_{Gx} = 4.4$, $J_{Fx} = J_{Hx} = 1.9$ Hz (4 H, CH$_2$ ethylene), 3.87 (d, 9 H, $J_{HP} = 11.0$, CH$_3$ phos), 2.43 (m, 1 H, $J_{HH} = 6.9$, CH ^{i}Pr), 1.20 (d, 3 H, $J_{HH} = 7.0$, CH$_3$ *p*-cym), 1.15 (d, 6 H, $J_{HH} = 6.9$, CH$_3$ ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: 60.4 (s). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: 165–122 (m, BPh$_4$), 116.96 (d, $J_{CP} = 2.8$, C1 *p*-cym), 106.24 (d, $J_{CP} = 1.0$, C4), 91.30 (d, $J_{CP} = 4.2$, C5), 90.01 (d, $J_{CP} = 2.1$, C3), 88.61 (d, $J_{CP} = 1.3$, C6), 88.11 (d, $J_{CP} = 3.0$, C2), 56.77 (d, $J_{CP} = 9.5$, CH$_3$ phos), 50.02 (d, $J_{CP} = 3.6$, CH$_2$ ethylene), 31.07 (s, CH ^{i}Pr), 22.02, 21.67 (s, CH$_3$ ^{i}Pr), 17.98 (s, CH$_3$ *p*-cym). $\Lambda_M = 56.2\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. C$_{39}H_{47}$BClO$_3$OsP (831.26): C 56.35, H, 5.70, Cl 4.26; found C 56.11, H 5.81, Cl 4.08%.

1b: ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ: 7.35–6.90 (m, 20 H, BPh$_4$), ABCDX, δ_A 5.77, δ_B 5.18, δ_C 5.87, δ_D 5.69, $J_{AB} = 6.0$, $J_{AC} = 0.5$, $J_{AD} = 1.3$, $J_{Ax} = 0.7$, $J_{BC} = 1.3$, $J_{BD} = 0.5$, $J_{Bx} = 0.4$, $J_{CD} = 6.0$, $J_{Cx} = 0.8$, $J_{Dx} = 0.3$ (4 H, Ph *p*-cym), EFGHX spin syst (X = ^{31}P), $\delta_E = \delta_G$ 4.15, $\delta_F = \delta_H$ 3.14, $J_{EG} = J_{FH} = 11.2$, $J_{EH} = J_{FG} = 9.1$, $J_{EF} = J_{GH} = 0.6$, $J_{Ex} = J_{Gx} = 4.4$, $J_{Fx} = J_{Hx} = 1.9$ (m, 4 H, CH$_2$ ethylene), 4.06 (m, 6 H, CH$_2$ phos), 2.46 (m, 1 H, $J_{HH} = 7.0$, CH ^{i}Pr), 1.90 (s, 3 H, CH$_3$ *p*-cym), 1.33 (td, 9 H, $J_{HH} = 7.0$, $J_{HH} = 0.46$, CH$_3$ phos), 1.20 ($J_{HH} = 6.9$), 1.17 ($J_{HH} = 6.9$) (d, 6 H, CH$_3$ ^{i}Pr). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: 55.49 (s). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: 165-122 (m, BPh$_4$), 117.13 (d, $J_{CP} = 2.8$, C1 *p*-cym), 105.32 (s, C4), 91.46 (d, $J_{CP} = 4.2$, C5), 90.48 (d, $J_{CP} = 2.2$, C3), 88.55 (d, $J_{CP} = 1.3$, C6), 88.06 (d, $J_{CP} = 6.7$, C2), 66.14 (d, $J_{CP} = 9.9$, CH$_2$ phos), 49.77 (d, $J_{CP} = 3.4$, CH$_2$ ethylene), 30.98 (s, CH ^{i}Pr), 21.96, 21.69 (s, CH$_3$ ^{i}Pr), 17.82 (s, CH$_3$ *p*-cym), 16.29 (d, $J_{CP} = 6.4$, CH$_3$ phos). $\Lambda_M = 52.8\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. C$_{42}H_{53}$BClO$_3$OsP (873.34): C 57.76, H 6.12, Cl 4.06; found C 57.55, H 6.02, Cl 4.29%.

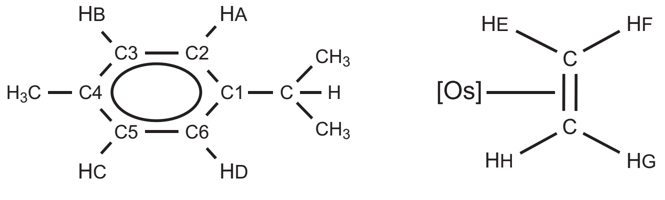


Chart 1. Labeling scheme of the *p*-cymene and ethylene ligands used for the NMR study.

1c: ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ: 7.85–6.86 (m, 25 H, Ph), ABCDX, δ_A 5.52, δ_B 5.62, δ_C 5.07, δ_D 5.66, $J_{AB} = 5.9$, $J_{AC} = 0.6$, $J_{AD} = 1.0$, $J_{Ax} = 0.6$, $J_{BC} = 1.0$, $J_{BD} = 0.6$, $J_{Bx} = 1.7$, $J_{CD} = 5.9$, $J_{Cx} = 1.6$, $J_{Dx} = 1.5$ (4 H, Ph *p*-cym), EFGHX spin syst (X = ^{31}P), $\delta_E = \delta_G$ 4.24, $\delta_F = \delta_H$ 3.11, $J_{EG} = J_{FH} = 9.5$, $J_{EH} = J_{FG} = 9.2$, $J_{EF} = J_{GH} = 0.6$, $J_{Ex} = J_{Gx} = 3.8$, $J_{Fx} = J_{Hx} = 2.1$ (4 H, CH$_2$ ethylene), 4.04 (m, 4 H, CH$_2$ phos), 2.28 (m, 1 H, CH ^{i}Pr), 1.68 (s, 3 H, CH$_3$ *p*-cym), 1.39 ($J_{HH} = 7.0$), 1.33 ($J_{HH} = 7.0$) (t, 6 H, CH$_3$ phos), 1.09 ($J_{HH} = 6.7$), 1.07 ($J_{HH} = 6.6$) (d, 6 H, CH$_3$ ^{i}Pr). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: 84.2 (s). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: 165–122 (m, Ph), 116.24 (d, $J_{CP} = 1.8$, C1 *p*-cym), 104.06 (s, C4), 91.65 (d, $J_{CP} = 2.3$, C5), 90.37 (d, $J_{CP} = 3.7$, C3), 86.57 (d, $J_{CP} = 5.8$, C6), 81.22 (d, $J_{CP} = 5.2$, C2), 66.96, 66.93, 66.26 (d, $J_{CP} = 11.0$, CH$_2$ phos), 51.00 (d, $J_{CP} = 1.5$, CH$_2$ ethylene), 30.74 (s, CH ^{i}Pr), 21.95, 21.50 (s, CH$_3$ ^{i}Pr), 17.31 (s, CH$_3$ *p*-cym), 16.31 ($J_{CP} = 6.7$), 16.22 ($J_{CP} = 6.6$) (d, CH$_3$ phos). $\Lambda_M = 53.5\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. C$_{46}H_{53}$BClO$_2$OsP (905.38): C 61.02, H 5.90, Cl, 3.92; found C 59.84, H 6.02, Cl 3.70%.

*2.4. [OsCl(η^6-p-cymene)(η^2-CH$_2$=CH$_2$)(CN^{t}Bu)]BPh$_4$ (**2**)*

In a 25-mL three-necked round-bottomed flask were placed 0.20 g (0.41 mmol) of OsCl$_2$(η^6-*p*-cymene)(CN^{t}Bu), an excess of NaBPh$_4$ (0.82 mmol, 0.28 g) and 4 mL of ethanol. The resulting mixture was stirred under an ethylene atmosphere (1 atm) at room temperature for 30 h. A yellow solid separated out which was filtered and crystallized under ethylene from CH$_2$Cl$_2$ and ethanol; yield ≥80%. IR (KBr) ν_{CN}: 2191 (s) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, −30 °C)δ: 7.85–6.86 (m, 20 H, BPh$_4$), ABCD, δ_A 5.05, δ_B 5.15, δ_C 5.49, δ_D 5.09, $J_{AB} = 6.0$, $J_{AC} = 0.7$, $J_{AD} = 1.2$, $J_{BC} = 1.2$, $J_{BD} = 0.7$, $J_{CD} = 6.0$ (4 H, Ph *p*-cym), EFGH spin syst (X = ^{31}P), $\delta_E = \delta_G$ 4.04, $\delta_F = \delta_H$ 3.47, $J_{EG} = J_{FH} = 17.6$, $J_{EH} = J_{FG} = 9.6$, $J_{EF} = J_{GH} = 0.6$ (4 H, CH$_2$ ethylene), 2.41 (m, 1 H, CH ^{i}Pr), 1.54 (s, 9 H, CH$_3$ ^{t}Bu), 1.31 (s, 3 H, CH$_3$ *p*-cym), 1.15 ($J_{HH} = 6.9$), 1.14 ($J_{HH} = 6.8$) (d, 6 H, CH$_3$ ^{i}Pr). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: 165–122 (m, BPh$_4$), 111.24 (s, C1 *p*-cym), 105.73 (s, C4), 89.39 (s, C5), 88.47 (s, C3), 88.24 (s, C6), 86.32 (s, C2), 60.17 (s, C≡N), 57.91 (s, CH$_2$ ethylene), 31.56 (s, CH ^{i}Pr), 31.23 (s, CMe$_3$ ^{t}Bu), 30.29 (s, CH$_3$ ^{t}Bu), 22.00, 21.91 (s, CH$_3$ ^{i}Pr), 18.08 (s, CH$_3$ *p*-cym). $\Lambda_M = 55.1\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. C$_{41}H_{47}$BClNOs (790.31): C 62.31, H 5.99, N 1.77, Cl 4.49; found C 62.13, H 6.10, N 1.68, Cl 4.71%.

*2.5. [OsCl(p-tolyl-NH$_2$)(η^6-p-cymene){PPh(OEt)$_2$}]BPh$_4$ (**3**) and [OsCl(η^6-p-cymene)(CH$_3$NHNH$_2$){PPh(OEt)$_2$}]BPh$_4$ (**4**)*

To a solution of [OsCl(η^6-*p*-cymene)(η^2-CH$_2$=CH$_2$){PPh(OEt)$_2$}]BPh$_4$ (100 mg, 0.11 mmol) in CH$_2$Cl$_2$ (10 mL) was added an excess of *p*-toluidine (0.33 mmol, 35 mg), in one case, or an excess of methylhydrazine (0.33 mmol, 18 μL) in the other. The reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to give an oil, which was treated with ethanol (3 mL) containing an excess of NaBPh$_4$ (0.22 mmol, 75 mg). A yellow solid slowly separated out, which was filtered and crystallised from CH$_2$Cl$_2$ and ethanol; yield ≥80%.

3: $\Lambda_M = 52.8\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. C$_{51}H_{58}$BClNO$_2$OsP (984.48): C 62.22, H 5.94, N 1.42, Cl 3.60; found C 62.08, H 6.08, N 1.55, Cl 3.42%.

4: $\Lambda_M = 54.1\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. C$_{45}H_{55}$BClN$_2O_2$OsP (923.40): C 58.53, H 6.00, N 3.03, Cl 3.84; found C 58.71, H 5.87, N 3.15, Cl 3.64%.

IR and NMR data were exactly the same of the related complexes previously prepared [9d,30].

*2.6. [OsCl{=C=C(H)Ph}(η^6-p-cymene){PPh(OEt)$_2$}]$^+$CF$_3$SO$_3^-$ (**5**)*

An excess of phenylacetylene (0.33 mmol, 37 μL) was added to a solution of [OsCl(η^6-*p*-cymene)(η^2-CH$_2$=CH$_2$){PPh(OEt)$_2$}]BPh$_4$ (100 mg, 0.11 mmol) in CH$_2$Cl$_2$ (7 mL) and the reaction mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure to give an oil, which was characterised as such. ^1H and ^{13}C NMR data were exactly the same of the related complex previously prepared [9b].

2.7. *X-ray structure determination*

Air stable, yellow crystals of **1a**, suitable for X-ray diffraction, were obtained by crystallization from CH_2Cl_2 and ethanol. A crystal of **1a** was mounted on a Bruker APEXII CCD diffractometer equipped with a CCD detector and cooled, using a cold nitrogen stream, to 120(2) K for the data collection. The space group was determined from the systematic absences and confirmed by the successful refinement, while the cell constants were refined, at the end of the data collection with the data reduction software SAINT [14]. The experimental conditions for the data collections, crystallographic and other relevant data are listed in Table 1 and in the Supporting Information. Collected intensities were corrected for Lorentz and polarization factors [14] and empirically for absorption using the SADABS program [15].

The structure was solved by direct and Fourier methods and refined by full matrix least squares [16], minimizing the function $[\Sigma w(F_o^2 - (1/k)F_c^2)^2]$ and using anisotropic displacement parameters for all atoms, except the hydrogens.

The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model ($B(H) = aB(C_{bonded})(Å^2)$, $a = 1.5$ for the the methyl groups and $a = 1.2$ for the others); the H atoms of the ethylene moiety were refined with their B's treated as above. Refining Flack's parameter tested the handedness of the structure [17].

No extinction correction was deemed necessary. Upon convergence the final Fourier difference map showed no significant peaks.

All calculations and plotting were carried out with the PC version of SHELX-97 [16], WINGX [18], ORTEP [18] and Mercury programs [19].

2.8. *Theoretical calculations*

The computational geometry optimization of the complexes was carried out by the hybrid DFT EDF2 method [20] without symmetry constraints, in combination with the LACVP** basis set (BS1), which is a combination of the 6–31G(d,p) basis set with the LANL2DZ effective core basis set. The atoms between hydrogen and argon are described with the 6–31G(d,p) basis set, and the heavier atoms are modeled with the LANL2DZ basis set [21]. Further refining was carried out with the hybrid DFT B3PW91 functional [22] in combination with a polarized triple-ζ quality basis set (BS2) composed by the 6–311G(d,p) basis set on the light atoms and the LANL2TZ(f) basis set on the metal center [23]. "Restricted" formalism was applied in all calculations and the stationary points were characterized as true minima by IR simulation. Atomic charges were derived from Mulliken population analysis. Energy differences (ΔE) between the complexes and the corresponding metal fragments and free ligands were calculated on the basis of equation: $\Delta E = E(\text{complex}) - E(\text{metal fragment}) - E(\text{olefin})$. Results were corrected for zero-point vibrational energy and the basis set superposition error [24]. [Os]–olefin dissociation energy was also studied for each complex by a series of restricted single-point energy calculations at fixed [Os]–olefin lengths longer than those of equilibrium, up to 9 Å. Dissociation energy (E_D) was calculated on the basis of equation: $E_D = E_\infty - E_{eq}$, where E_{eq} is equilibrium energy and E_∞ was obtained by fitting the computed energy values (E) and the M–olefin distances (r) according to the following equation: $E = E_\infty - Ae^{-Br}$, where E_∞, A and B are the parameters to be optimized.

DFT EDF2 calculations were carried out with Spartan 08 [25] on a x86-64 workstation based on an Intel Core I7 940 processor. Gaussian 09 was used for the calculations based on the B3PW91 functional [26]. DFT B3PW91 calculations were performed at CINECA (Centro Italiano di Supercalcolo, Bologna, Italy) on an IBM P6-575 workstation equipped with 64-bit IBM Power6 processors.

3. Results and discussion

Ethylene reacts in mild conditions (1 atm, room temperature) with dichloro complexes $OsCl_2(\eta^6\text{-}p\text{-cymene})L$ in the presence of $NaBPh_4$ to give η^2-ethylene derivatives $[OsCl(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-}CH_2{=}CH_2)L]BPh_4$ (**1**), which were isolated as yellow solids and characterized (Scheme 1).

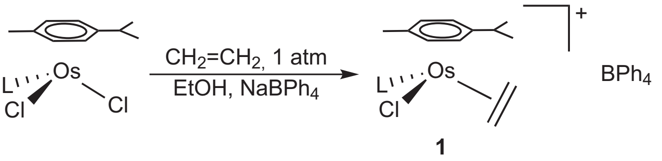
Important for successful synthesis was the presence of the salt $NaBPh_4$, which probably favors substitution of the chloride ligand in the starting complexes, thus allowing derivatives **1** to be obtained in good yields.

Studies of the reaction of dichloro complexes $OsCl_2(\eta^6\text{-}p\text{-cymene})L$ with $CH_2{=}CH_2$ showed that only phosphines with small cone angles, such as $P(OMe)_3$, $P(OEt)_3$ and $PPh(OEt)_2$, allow the ethylene to be coordinated to the metal center of the fragment $[OsCl(\eta^6\text{-}p\text{-cymene})L]^+$. Instead, with bulkier phosphines such as PPh_2OEt, PPh_3 or P^iPr_3 no formation of alkene complex **1** was observed. The important role of steric factors in determining the coordination of alkene to the *p*-cymene fragment was further confirmed by reacting propylene $CH_3CH{=}CH_2$ with $OsCl_2(\eta^6\text{-}p\text{-cymene})L$ which, at 1 atm, did not yield any η^2-alkene derivative. Even with the less bulky phosphite $P(OMe)_3$, coordination of the propylene was not observed in any studied conditions; this negative result suggests that only ethylene, in mild conditions, can bind to the metal center

Table 1
Experimental data for the X-ray diffraction study of compound **1a**.

Formula	$C_{39}H_{47}BClO_3OsP$
Fw	831.20
Data coll. *T*, K	120(2)
Cryst syst.	Orthorhombic
Space group (no.)	*Pna2₁* (33)
a, Å	27.002(2)
b, Å	12.6690(7)
c, Å	10.2909(6)
V, $Å^3$	3520.4(3)
Z	4
$\rho_{(calcd)}$, g cm^{-3}	1.568
μ, cm^{-1}	37.80
Radiation	MoKα (graphite monochrom., $\lambda = 0.71073$ Å)
θ range, deg	$1.78 \le \theta \le 29.46$
No. independent data	9179
No. obs. Refctl. (n_o) $[|F_o|^2 > 2.0\sigma(|F|^2)]$	8565
No. of param. refined (n_v)	427
R (obsd reflns)[a]	0.0207
R_w^2 (obsd reflns)[b]	0.0458
GOF[c]	1.023

[a] $R = \sum(|F_o - (1/k)F_e|)/\sum|F_o|$.
[b] $R_w^2 = \{\sum[w(F_o^2 - (1/k)F_c^2)^2]/\sum w|F_0^2|^2]\}^{1/2}$.
[c] $GOF = [\sum_w(F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$.



Scheme 1. $L = P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**), $PPh(OEt)_2$ (**c**).

of a *p*-cymene fragment [OsCl(η^6-*p*-cymene)*L*]$^+$, containing small cone-angle phosphines.

As isocyanides, RNC, are also ligands with little steric hindrance and π-acceptor ability quite comparable with those of phosphites, we reacted isocyanide complex OsCl$_2$(η^6-*p*-cymene)(RNC) with ethylene in the presence of NaBPh$_4$ and did observed the formation of ethylene derivative [OsCl(η^6-*p*-cymene)(η^2-CH$_2$=CH$_2$)(RNC)] BPh$_4$ (**2**), as shown in Scheme 2.

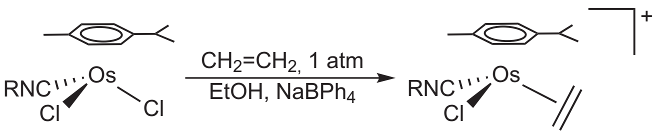
However, a pure solid sample could only be obtained with *tert*-butyl isocyanide, and only an oil was separated with *p*-tolylNC. In this case too, propylene CH$_3$CH=CH$_2$ did not react even with isocyanide precursors OsCl$_2$(η^6-*p*-cymene)(RNC) and no alkene complex was obtained.

We have also reacted with CH$_2$=CH$_2$ the *p*-cymene complexes OsCl$_2$(η^6-*p*-cymene)*L* containing carbonyl or pyrazole as supporting ligands, but did not observe any formation of η^2-ethylene complexes. Therefore, it seems that only with phosphite having small cone angle or with *tert*-butyl isocyanide can the *p*-cymene fragment "OsCl(η^6-*p*-cymene)*L*" bind only the smallest of alkenes, under mild conditions.

Ethylene complexes **1** and **2** were isolated as yellow solids stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes [27]. Elemental analyses and spectroscopic data (IR and ^{1}H, ^{31}P, ^{13}C NMR) support this formulation, which was confirmed by the X-ray crystal structure determination of complex [OsCl(η^6-*p*-cymene)(η^2-CH$_2$=CH$_2$){P(OMe)$_3$}]BPh$_4$ (**1a**) (Fig. 1).

The immediate coordination sphere of the Os atom consists of the η^6-*p*-cymene ring, the P and Cl atoms and the η^2-C$_2$H$_4$ ligand, resulting in a three-legged piano-stool coordination. The ethylene ligand is asymmetrically bonded to the Os center (Os–C 2.231(3) Å and 2.265(3) Å respectively); these distances are quite long and fall in the upper range of those reported for other Os complexes containing a coordinated double bond (in the range 2.16–2.25 Å) [8c,i,j,28] and are comparable with those found in the octahedral [OsH(C$_2$H$_4$)$_2$(PMe$_2$Ph)$_3$]$^+$ [8c] complex where the C$_2$H$_4$ moiety is *trans* to a hydride ligand (2.235(6) and 2.247(6) Å respectively). We note, however, that in those three-legged piano-stool structures where only one "η^2–C$_2$H$_4$" moiety is coordinated to the metal center [8j,28c] the Os–C separations are usually shorter (in the range 2.08–2.21 Å).

The C=C separation at 1.373(5) Å falls in the range reported in the literature (1.36–1.44 Å) [8c,i,j,28,29] and is shorter than the average value of 1.392 Å expected for a coordinated unsubstituted ethylene fragment [29]. We note that these distances are consistent with a weakly bonded ligand in keeping with the reactivity of this complex and the results of the DFT calculations reported below. The C$_2$H$_4$ ligand makes an angle of 58.1(2)° with the mean-plane defined by atoms P, Cl and the mid-point of the C=C bond. The *p*-cymene ligand is distorted upon coordination to the Os atom, as shown by the significantly different metal-carbon separations (in the range 2.22–2.32 Å) and by small, but significant, deviations from planarity of the aromatic ring (max. deviation from the least-squares plane defined by atom C1–C6, +0.04 Å, with atoms C3 and C6 closer to the Os). The C–C bonds in the *p*-cymene ring are also different (see caption to Fig. 1) and the shortest C–C (1.398(4) Å) involves the atom (C1) with the longest separation from the metal center. Os–P and Os–Cl distances are unexceptional.



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Scheme 2. *R* = ^{t}Bu.

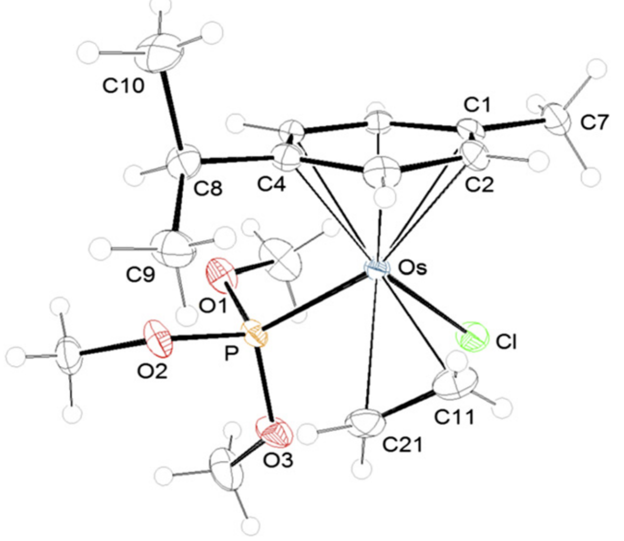


Fig. 1. Molecular structure of [OsCl(η^6-*p*-cymene)(η^2-CH$_2$=CH$_2$){P(OMe)$_3$}]$^+$ (**1a**$^+$). Thermal ellipsoids are drawn at 50% probability. Relevant bond lengths (Å) and angles (deg): Os–Cl 2.3962(7), Os–P 2.2864(7), Os–C11 2.231(3), Os–C21 2.265(3), C11–C21 1.373(5), Os–C1 2.318(3), Os–C2 2.289(2), Os–C3 2.220(3), Os–C4 2.278(3), Os–C5 2.226(3), Os–C6 2.222(3), C1–C2 1.398(4), C2–C3 1.441(4), C3–C4 1.413(4), C4–C5 1.428(4), C5–C6 1.406(5), P–Os–Cl 85.89(3), P-Os-C$_b$ 93.9(2), Cl-Os-C$_b$ 84.2(2) (C$_b$ is the midpoint of the C=C bond).

The position of BPh$_4^-$ anions with respect to cations is informative and this is shown in Fig. 2. There are short contacts between the BPh$_4^-$ anion and the cationic osmium complex in the range 2.3–2.8 Å, the other packing distances being longer than 3.0 Å. We note that the anion is placed away from the ethylene ligand and close to the phosphite methoxy groups. NOESY NMR experiments (showing a correlation between the methoxy hydrogen atoms of P(OMe)$_3$ and the phenyl protons of BPh$_4^-$) indicate that similar arrangements of the anions also occur in solution. There are no short intermolecular contacts involving the ethylene ligands.

At room temperature, beside the signals of *p*-cymene and phosphite ligands and the BPh$_4^-$ anion, the ^{1}H NMR spectra of phosphine complexes [OsCl(η^6-*p*-cymene)(η^2-CH$_2$=CH$_2$)L]BPh$_4$

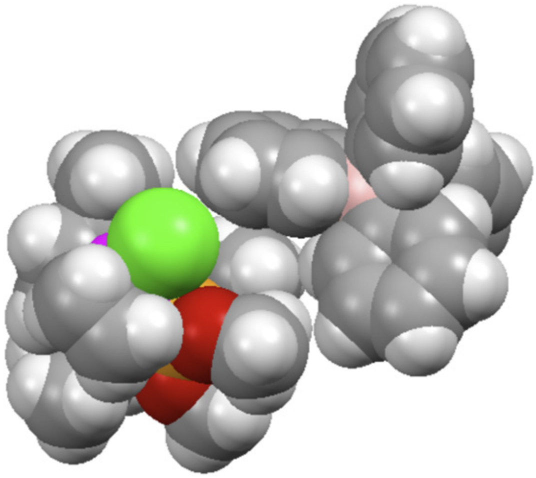


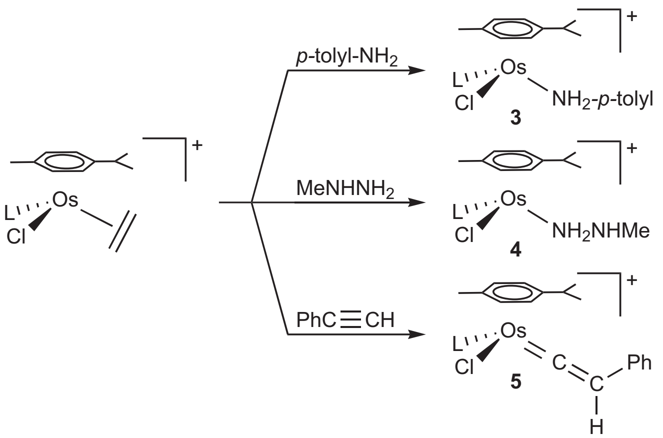
Fig. 2. Space filling model of [OsCl(η^6-*p*-cymene)(η^2-CH$_2$=CH$_2$)*L*]BPh$_4$.

(**1**) show two multiplets at 4.24–4.14 and 3.15–3.11 ppm, attributed to the protons of the coordinate ethylene. Lowering the sample temperature caused a variation in the spectra but, even at −90 °C, ethylene peaks were still broadened, suggesting that rotation of $CH_2{=}CH_2$ is still present at this temperature. The multiplicity of signals is due to the presence of a chiral center in the molecule, which makes the protons of ethylene two-by-two diastereotopic, thus appearing at different values of chemical shift and coupled with the phosphorus of the phosphine. The pattern may be simulated by an ABCDX model ($X = {}^{31}P$) with the parameters reported in Experimental section and the good fit between experimental and calculated spectra strongly support the proposed attributions. The ^{31}P NMR spectra of **1** appear as sharp singlets, whereas the ^{13}C spectra, show the characteristic signals of supporting ligands and display a singlet at 51.00–49.77 ppm, which was correlated, in a HMQC experiment, with the two ethylene proton multiplets at 4.24–3.10 ppm and attributed to η^2-$CH_2{=}CH_2$ carbon resonances, matching the proposed formulation.

The IR spectrum of isocyanide complex [OsCl(η^6-*p*-cymene)(η^2-$CH_2{=}CH_2$)(CN^tBu)]BPh_4 (**2**) shows a strong band at 2191 cm^{-1} due to ν_{CN} of the isocyanide ligand. The ^1H NMR spectrum confirms the presence of the ^tBuNC group, showing a singlet at 1.54 ppm of the protons of the ^tBu substituents. The spectrum also contains two multiplets of the ethylene hydrogen atoms (at 4.04 and 3.47 ppm respectively). The ^{13}C NMR spectrum confirms the presence of the η^2-$CH_2{=}CH_2$ ligand, showing a singlet at 57.91 ppm, which was correlated, in a HMQC experiment, with the proton multiplets at 4.04 and 3.47 ppm and attributed to ethylene carbon resonances. The spectrum also shows the characteristic signals of *p*-cymene and the two singlets at 60.17 and 31.23 ppm of the ^tBu substituent of the isocyanide ligand, matching the proposed formulation.

Reactivity studies on ethylene complexes **1** and **2** with nucleophilic reagents were also carried out, to test whether reactions on coordinate alkene would occur. Unfortunately, results only showed substitution of the η^2-$CH_2{=}CH_2$ ligand by amine or hydrazine, affording related *p*-cymene derivatives **3** and **4** (Scheme 3).

The relative lability of the coordinate ethylene was also confirmed by the reaction with PhC≡CH, which afforded vinylidene cations [OsCl{=C=C(H)Ph}(η^6-*p*-cymene)*L*]$^+$ (**5**) through an initial substitution of η^2-$CH_2{=}CH_2$ with alkyne, which tautomerizes on the metal center, yielding the final vinylidene species **5**. Although complexes **3**–**5** are known [9b,d,30], the use of ethylene complexes **1** and **2** as precursors is an easy new method for their preparation.



Scheme 3. $L = P(OMe)_3$, $P(OEt)_3$, $PPh(OEt)_2$, ^tBuNC.

3.1. DFT calculations

Theoretical studies were carried out on ethylene and propylene complexes [OsCl(η^6-*p*-cymene)(η^2-$CH_2{=}CH_2$){$P(OMe)_3$}]$^+$ (**OsP-ethylene**), [OsCl(η^6-*p*-cymene)(η^2-$CH_2{=}CHCH_3$){$P(OMe)_3$}]$^+$ (**OsP-propylene**), [OsCl(η^6-*p*-cymene)(η^2-$CH_2{=}CH_2$)(CN^tBu)]$^+$ (**OsC-ethylene**) and [OsCl(η^6-*p*-cymene)(η^2-$CH_2{=}CHCH_3$)(CN^tBu)]$^+$ (**OsC-propylene**). Tables S2 and S3 list a selection of computed bond lengths and, in the case of **OsP-ethylene**, a comparison with data from the X-ray structure determination of **1a** is made. Both computational approaches used (EDF2/BS1 and B3PW91/BS2) gave comparable bond lengths. Fig. 3 shows the ground-state optimized geometry of **OsP-ethylene**. The overall match between X-ray and calculated geometry is good, the main differences being the relative orientation of the *p*-cymene ligand and a few dihedral angles in $P(OMe)_3$, which are probably due to interactions between complex and counterion (see above). The calculated values for some bond lengths, such as the olefin C=C (C11–C21), Os–Cl and Os–P, are slightly overestimated. In particular, both EDF2/BS1 and B3PW91/BS2 calculations predict the length of the olefin C=C bond about 2% higher than the experimental value.

The Os–C(ethylene) and the C=C (ethylene) bond lengths are almost unaffected by substitution of the ancillary ligand $P(OMe)_3$ with CN^tBu. The olefin C=C double bond is only slightly weakened (~5%) by coordination to the metal fragments, matching reactivity and structural results. In addition, the Os–C(olefin) and C=C (olefin) bond lengths are similar in the ethylene and propylene complexes for both metal fragments. Replacement of the ancillary ligand and the olefin do not greatly influence the Os–olefin interaction, as shown by the energy values for dissociation of the alkene molecule from Os complexes (E_D) and energy differences between the complexes and the corresponding metal fragments and free olefins (ΔE) (see Table S4). All examined complexes have similar E_D

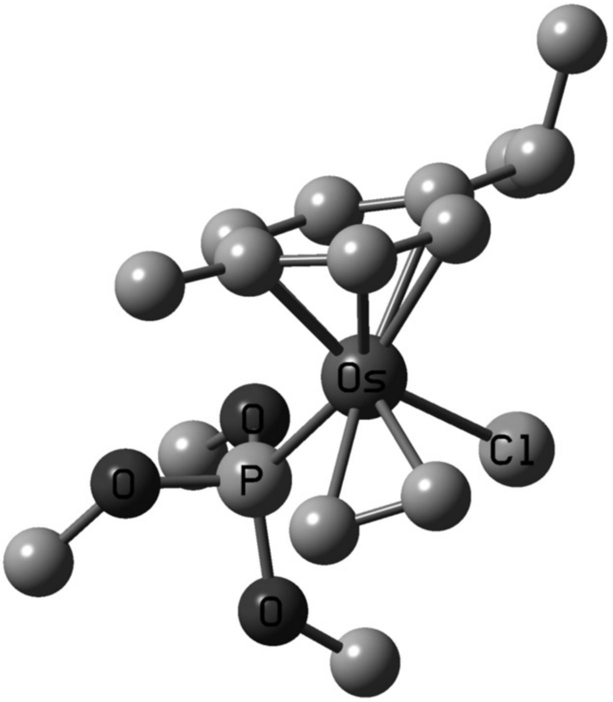


Fig. 3. Equilibrium geometry of OsP–ethylene (B3PW91/BS2). Hydrogen atoms omitted for clarity. Selected bond lengths (Å): C=C (olefin) 1.402; Os–C(olefin) 2.235, 2.214; Os–C(cymene) 2.288, 2.221, 2.193, 2.247, 2.243, 2.348; Os–P 2.314; Os–Cl 2.403.

values, in the range 56–61 kcal/mol. The ΔE values show weak variations when the ancillary or alkene ligands are changed and are in the range $-24 - -27$ kcal/mol according to the EDF2/BS1 method and between -22 and -25 kcal/mol with the B3PW91/BS2 DFT approach. All these results support the idea that the lack of coordination of propylene to *p*-cymene fragments under mild conditions is due to kinetic factors, related to the bulkiness of the ligands rather than to thermodynamic factors.

Preliminary experimental studies on the reactivity of ethylene complexes **1** and **2** toward nucleophilic reagents indicated that no significant activation of the ethylene molecule occurs in these novel osmium complexes. This hypothesis is confirmed by the very weak variation of the Mulliken charge of the carbon atoms in the ethylene molecules upon coordination to $[\mathrm{OsCl}(\eta^6\text{-}p\text{-cymene})\{\mathrm{P(OMe)_3}\}]^+$ and $[\mathrm{OsCl}(\eta^6\text{-}p\text{-cymene})(\mathrm{CN}^t\mathrm{Bu})]^+$. The Mulliken charge value for the free ethylene molecule is -0.246 a.u., computed at the B3PW91/BS2 level, but is -0.241 a.u. (average) in **OsP-ethylene** and -0.222 a.u. (average) in **OsC-ethylene**. Comparable results were obtained at the EDF2/BS1 level of theory (see Table S5). This small variation in the Mulliken charge may indicate similar contributions to the Os–ethylene bond of the olefin → metal donation and metal → olefin π-back-donation.

4. Conclusions

In this paper we report the preparation of ethylene complexes of osmium stabilised by the *p*-cymene ligand. The facile substitution of the η^2-$\mathrm{CH_2{=}CH_2}$ ligand allowed new half-sandwich derivatives to be obtained. The structural parameters and the nature of the Os–ethylene bond in the ethylene complexes are also discussed.

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Appendix A. Supporting material

CCDC 851830 contains the supplementary crystallographic data for this paper as a cif file. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.12.032.

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