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Preparation of half-sandwich diazoalkane complexes of osmium

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ABSTRACT

Diazoalkane complexes [OsCl(η^6-*p*-cymene)(N_2CAr1Ar2){PPh$(OEt)_2$}]BPh_4 (**1**, **2**) [Ar1 = Ar2 = Ph; Ar1 = Ph, Ar2 = *p*-tolyl; Ar1 = H, Ar2 = COOEt] were prepared by allowing compounds $OsCl_2(\eta^6$-*p*-cymene)[PPh$(OEt)_2$] to react with diazoalkane in ethanol. Diazo-pyridine derivatives [OsCl(η^6-*p*-cymene){κ^1-(4-C_5H_4N)(Ph)CN_2}L]BPh_4 (**3**, **4**) [L = PPh$(OEt)_2$, P$(OEt)_3$] were also prepared by reacting chloro-compounds $OsCl_2(\eta^6$-*p*-cymene)L with 4-[diazo(phenyl)methyl]pyridine, (4-C_5H_4N)$PhCN_2$, in ethanol. Treatment of diazoalkane complexes **1** and **2** with CH_2=CH_2 (1 atm) and PhC≡CH in ethanol led to ethylene [OsCl(η^2-CH_2=CH_2)(η^6-*p*-cymene){PPh$(OEt)_2$}]BPh_4 (**5**) and carbene [OsCl{=C(CH_2Ph)(OEt)}(η^6-*p*-cymene){PPh$(OEt)_2$}]BPh_4 (**6**) derivatives.

1. Introduction

Diazoalkanes Ar1Ar2CN_2 can coordinate to transition metals, giving stable and isolable complexes [1–6]. The properties of these complexes are of current interest, not only thanks to the close relationship with dinitrogen fixation [7,8] but also for their rich and various reactivity [1–6]. Thus, extrusion of dinitrogen with formation of carbene M = CAr1Ar2 was observed in η^2-CN coordinated species [3f,9,10], whereas η^1-bonded diazoalkane gave dinitrogen [M]–N_2 complexes [3f], transfer of carbene to imine [9f], or cleavage of the N—N bond of the Ar1Ar2CN_2 group [3g]. Dipolar (3 + 2) cycloaddition of coordinate diazoalkane with alkene and alkyne affording 3H-pyrazole derivatives has recently been reported [5], as well as hydrolysis of [M]–N_2CAr1Ar2 yielding η^2-diazene derivatives [6].

A number of diazoalkane complexes have been reported [1–6] for several metal centres, displaying a variety of coordination modes (Chart 1) and reactivities. However, in contrast with Fe and Ru, diazoalkane complexes of osmium are very rare and, apart from [OsH(N_2CAr1Ar2)L_4]BPh_4, described 15 years ago [11], no other example of this metal has been reported.

We are interested in the chemistry of diazoalkane complexes and have recently reported the synthesis and reactivity of half-sandwich ruthenium derivatives with *p*-cymene [4], cyclopentadienyl [5a,b] and indenyl [5c] as supporting ligands. The interesting properties shown by these compounds prompted us to extend our study to osmium, to test whether diazoalkane complexes could be prepared and how their properties change. The results are given here.

2. Experimental

2.1. General comments

All synthetic work was carried out in an appropriate atmosphere (Ar, N2) using standard Schlenk techniques or a vacuum atmosphere dry-box. 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. Phosphites P$(OMe)_3$, P$(OEt)_3$ and triisopropylphosphine P(^{i}Pr)$_3$ were Aldrich products, purified by distillation, whereas phenyldiethoxyphosphine PPh$(OEt)_2$ and diphenylethoxyphosphine PPh_2OEt were prepared by the method of Rabinowitz and Pellon [12]. Diazoalkanes were prepared following the known methods [13]. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on Perkin-Elmer Spectrum One FT-IR spectrophotometer. NMR spectra (^{1}H, ^{13}C, ^{31}P) were obtained on AVANCE 300 Bruker spectrometer at temperatures between −80 and +30 °C, unless otherwise noted. ^{1}H and ^{13}C spectra are referenced to internal tetramethylsilane; ^{31}P{^{1}H} chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The COSY, HMQC and HMBC NMR experiments were performed using their standard programs. The iNMR software package [14] 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 were measured with a Radiometer CDM 83.

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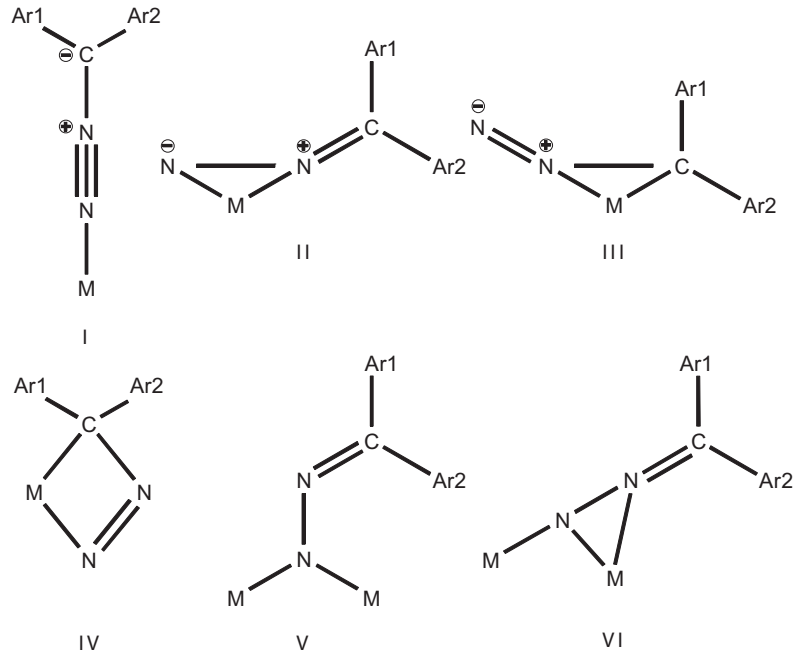


Chart 1. Diazoalkane coordination modes.

Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze del Farmaco of the University of Padua, Italy.

2.2. Synthesis of complexes

Compounds $[OsCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ and $[OsCl_2(\eta^6\text{-}p\text{-cymene})L]$ [L = $P(OMe)_3$, $P(OEt)_3$, $PPh(OEt)_2$, PPh_2OEt, $P(^iPr)_3$] were prepared following the reported methods [15,16].

2.3. [OsCl(η^6-p-cymene)($N_2CAr1Ar2$){PPh(OEt)$_2$}]BPh_4 (**1**) [Ar1 = Ar2 = Ph (**a**); Ar1 = Ph, Ar2 = p-tolyl (**b**)].

In a 25-mL three-necked round-bottomed flask were placed 100 mg (0.17 mmol) of solid $[OsCl_2(\eta^6\text{-}p\text{-cymene})\{PPh(OEt)_2\}]$, an excess of the appropriate diazoalkane $Ar1Ar2CN_2$ (0.5 mmol), an excess of $NaBPh_4$ (0.34 mmol, 116 mg) and 4 mL of ethanol. The reaction mixture was stirred at room temperature for 4 h and then the solid that formed was filtered and crystallised from CH_2Cl_2 and EtOH. Yield: 138 mg (76%) for **1a**, 144 mg (78%) for **1b**.

1a: IR (KBr pellet): ν_{N_2} 1897 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.75–6.85 (m, 35H, Ph), 5.68, 5.65, 5.58, 5.48 (d, 4H, Ph *p*-cym), 3.82 (m, 4H, CH_2), 2.45 (m, 1H, CH Pr^i), 2.05 (s, 3H, CH_3 *p*-cym), 1.22 (d, 6H, CH_3 Pr^i), 1.14 (t, 6H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 92.9 ppm. Λ_M = 52.6 Ω^{-1} mol^{-1} cm^2. $C_{57}H_{59}BClN_2O_2OsP$ (1071.56): *Anal.* calc.: C, 63.89; H, 5.55; Cl, 3.31; N, 2.61. Found: C, 63.68; H, 5.47; Cl, 3.43; N, 2.67%.

1b: IR (KBr pellet): ν_{N_2} 1925 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.60–6.87 (m, 34H, Ph), 5.66, 5.64, 5.56, 5.47 (d, 4H, Ph *p*-cym), 3.81, 3.64 (m, 4H, CH_2), 2.45 (m, 1H, CH Pr^i), 2.39 (s, 3H, CH_3 *p*-tol), 2.04 (s, 3H, CH_3 *p*-cym), 1.16, 1.13 (t, 6H, CH_3 phos), 1.11, 1.10 (d, 6H, CH_3 Pr^i). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 94.1. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 160–119 (m, Ph), 110. 6 (d, C4 *p*-cym), 82.9 (br, CN_2), 93.2, 82.1 (d), 80.7 (br), 79.5 (d) (Ph *p*-cym), 63.85 (d, J_{CP} = 7.1 Hz, CH_2), 31.12 (s, CH Pr^i), 23.0, 22.6 (s, CH_3 Pr^i), 21.3 (s, J_{CP} = 6.5, CH_3 *p*-tol), 18.5 (s, CH_3 *p*-cym), 16.5 (d, CH_3 phos) ppm. Λ_M = 51.9 Ω^{-1} mol^{-1} cm^2. $C_{58}H_{61}BClN_2O_2OsP$ (1085.58): *Anal.* calc.: C, 64.17; H, 5.66; Cl, 3.27; N, 2.58. Found: C, 64.02; H, 5.78; Cl, 3.13; N, 2.65%.

2.4. [OsCl(η^6-p-cymene){$N_2C(H)COOEt$}{PPh(OEt)$_2$}]BPh_4 (**2**)

In a 25-mL three-necked round-bottomed flask were placed 100 mg (0.17 mmol) of solid $[OsCl_2(\eta^6\text{-}p\text{-cymene})\{PPh(OEt)_2\}]$, an excess of $NaBPh_4$ (0.34 mmol, 116 mg), an excess of ethyldiazoacetate $N_2C(H)COOEt$ (0.68 mmol, 71 μL) and 10 mL of ethanol. The reaction mixture was stirred at room temperature for 6 h and then concentrated to about 2 mL by removing the solvent under reduced pressure. The resulting solution was cooled to −25 °C and the yellow solid which slowly separated out was filtered and crystallised from ethanol. Yield: 76 mg (45%). IR (KBr pellet): ν_{N_2} 1960 (m), ν_{CO} 1727 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.95–6.87 (m, 25H, Ph), 5.58, 5.37, 5.30, 5.08 (d, 4H, Ph *p*-cym), 4.26, 3.98 (m, 4H, CH_2 phos), 3.62 (q, 2H, CH_2 COOEt), 2.47 (m, 1H, CH Pr^i), 1.92 (s, 3H, CH_3 *p*-cym), 1.38 (m, 3H, CH_3 COOEt + 6H, CH_3 phos), 1.19, 1.17 (d, 6H, CH_3 Pr^i). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 91.3 (s) ppm. Λ_M = 52.2 Ω^{-1} mol^{-1} cm^2. $C_{48}H_{55}BClN_2O_4OsP$ (991.43): *Anal.* calc.; C, 58.15; H, 5.59; Cl, 3.58; N, 2.83. Found: C, 57.97; H, 5.63; Cl, 3.45; N, 2.71%.

2.5. [OsCl(η^6-p-cymene){κ^1-(4-C_5H_4N)(Ph)CN_2}L]BPh_4 (**3**, **4**) [L = PPh(OEt)$_2$ (**3**), P(OEt)$_3$ (**4**)]

In a 25-mL three-necked round-bottomed flask were placed 0.17 mmol of solid $[OsCl_2(\eta^6\text{-}p\text{-cymene})L]$, an excess of diazoalkane (4-C_5H_4N)(Ph)CN_2 (0.51 mmol, 100 mg), an excess of $NaBPh_4$ (0.34 mmol, 116 mg) and 4 mL of ethanol. The reaction mixture was stirred for 24 h and then the solid that formed was filtered and crystallised from CH_2Cl_2 and EtOH. Yield: 160 mg (88%) for **3**, 163 mg (92%) for **4**.

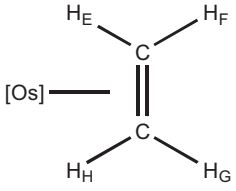
3: IR (KBr pellet): ν_{N_2} 2044 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 8.32–6.72 (m, 34H, Ph + Py), 5.58, 5.56, 5.31, 5.22 (d, 4H, Ph *p*-cym), 4.11, 4.03, 3.90, 3.82 (m, 4H, CH_2), 2.54 (m, 1H, CH Pr^i), 2.12 (s, 3H, CH_3 *p*-cym), 1.39, 1.32 (t, 6H, CH_3 phos), 1.16, 1.14 (d, 6H, CH_3 Pr^i). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 98.9 ppm.

Λ_M = 52.6 Ω^{-1} mol^{-1} cm^2. $C_{56}H_{58}BClN_3O_2OsP$ (1072.55): *Anal.* calc.: C, 62.71; H, 5.45; Cl, 3.31; N, 3.92. Found: C, 62.54; H, 5.52; Cl, 3.19; N, 3.80%.

4: IR (KBr pellet): ν_{N_2} 2050 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 8.44 (d, 2H, J_{HH} = 7.2 Hz, H2, H6 Py), 7.60–6.85 (m, 27H, Ph + H3, H5 Py), 5.58, 5.57, 5.42, 5.24 (d, 4H, Ph *p*-cym), 3.90 (m, 4H, CH_2), 2.63 (m, 1H, CH Pr^i), 2.14 (s, 3H, CH_3 *p*-cym), 1.22 (t, 6H, CH_3 phos), 1.18 (d, 6H, CH_3 Pr^i). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 70.5. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 165–118 (m, Ph + C3 Py), 155.19 (d, J_{CP} = 2.6, C2, C6 Py), 111.06 (d, J_{CP} = 5.0, C4 *p*-cym), 97.91 (d, J_{CP} = 2.2, C1 *p*-cym), 82.87 (d, J_{CP} = 2.6), 81.69 (d, J_{CP} = 2.0), 81.62 (d, J_{CP} = 2.7), 78.09 (d, J_{CP} = 2.6) (C2, C3, C5, C6 *p*-cym), 63.66 (d, J_{CP} = 7.1, CH_2), 30.85 (s, CH Pr^i), 22.61, 21.81 (s, CH_3 Pr^i), 18.18 (s, CH_3 *p*-cym), 16.18 (d, J_{CP} = 6.5, CH_3 phos) ppm. Λ_M = 53.5 Ω^{-1} mol^{-1} cm^2. $C_{52}H_{58}BClN_3O_3OsP$ (1040.50): *Anal.* calc.: C, 60.02; H, 5.62; Cl, 3.41; N, 4.04. Found: C, 59.84; H, 5.70; Cl, 3.29; N, 4.13%.

2.6. [OsCl(η^2-CH_2=CH_2)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh$_4$ (**5**)

A solution of [OsCl(η^6-*p*-cymene){N_2C(Ph)(*p*-tolyl)}{PPh(OEt)$_2$}]BPh$_4$ (**1b**) (100 mg, 0.09 mmol) in CH_2Cl_2 (7 mL) was stirred under an ethylene atmosphere (1 atm) for 3 h. The solvent was removed under reduced pressure to leave an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.18 mmol, 62 mg). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol. Yield: 56 mg (67%). ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.85–6.87 (m, 25H, Ph), ABCDX, δ_A 5.53, δ_B 5.61, δ_C 5.0 7, δ_D 5.67, 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 Hz (4H, Ph *p*-cym), EFGHX spin syst (X = ^{31}P), δ_E = δ_G 4.24, δ_F = δ_H 3.12, 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 (4H, CH_2 ethylene), 4.02 (m, 4H, CH_2 phos), 2.28 (m, 1H, CH ^{i}Pr), 1.68 (s, 3H, CH_3 *p*-cym), 1.39 (J_{HH} = 7.0), 1.32 (J_{HH} = 7.0) (t, 6H, CH_3 phos), 1.09 (J_{HH} = 6.7), 1.07 (J_{HH} = 6.6) (d, 6H, CH_3 ^{i}Pr). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 84.2 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 165–122 (m, Ph), 116.25 (d, J_{CP} = 1.8, C1 *p*-cym), 104.04 (s, C4), 91.65 (d, J_{CP} = 2.3, C5), 90.39 (d, J_{CP} = 3.7, C3), 86.55 (d, J_{CP} = 5.8, C6), 81.22 (d, J_{CP} = 5.2, C2), 66.98, 66.92, 66.26 (d, J_{CP} = 11.0, CH_2 phos), 51.00 (d, J_{CP} = 1.5, CH_2 ethylene), 30.76 (s, CH ^{i}Pr), 21.95, 21.53 (s, CH_3 ^{i}Pr), 17.30 (s, CH_3 *p*-cym), 16.30 (J_{CP} = 6.7), 16.20 (J_{CP} = 6.6 Hz) (d, CH_3 phos) ppm. Λ_M = 52.3 Ω^{-1} mol^{-1} cm^2. $C_{46}H_{53}BClO_2OsP$ (905.38): C, 61.02; H, 5.90; Cl, 3.92. Found: C, 59.79; H, 5.83; Cl, 3.73%.



2.7. [OsCl{=C(CH_2Ph)(OEt)}(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh$_4$ (**6**)

An excess of phenylacetylene PhC≡CH (0.27 mmol, 30 μL) was added to a solution of [OsCl(η^6-*p*-cymene){N_2C(Ph)(*p*-tolyl)}{PPh(OEt)$_2$}]BPh$_4$ (**1b**) (100 mg, 0.09 mmol) in CH_2Cl_2 (5 mL) and the reaction mixture was stirred for 3 h. The solvent was removed under reduced pressure to leave an oil, which was triturated with ethanol (3 mL) containing an excess of $NaBPh_4$ (0.18 mmol, 62 mg). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol. Yield: 71 mg (75%). ^{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), 5.42 (d, HB *p*-cym, J_{BC} = 0.8, J_{BD} = 0.4), 5.40 (d, HC *p*-cym, J_{CD} = 6.7), 5.33 (d, HD *p*-cym), 5.37, 2.98 [d, 2H, J_{HH} = 13.2, =C(CH_2Ph)], 4.41, 4.32 [m, 2H, =C(OCH_2CH$_3$)], 4.11, 3.98 (m, 4H, CH_2 phos), 2.60 (m, 1H, CH), 1.98 (s, 3H, CH_3 *p*-cym), 1.48, 1.42 (t, 6H, J_{HH} = 7.0, CH_3 phos), 1.38 [t, 3H, J_{HH} = 7.0, =C(OCH$_2$$CH_3$)], 1.16, 1.14 (d, 6H, J_{HH} = 7.1, CH_3 Pr^i). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 95.8 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 286.5 (d, J_{CP} = 15.9, Os = C), 165–122 (m, Ph), 119.26 (d, br, J_{CP} = 1.4, C1 *p*-cym), 105.20 (br, C4 *p*-cym), 93.02 (d, J_{CP} = 3.4, C3 *p*-cym), 88.30 (d, J_{CP} = 3.1, C6 *p*-cym), 86.90 (d, J_{CP} = 5.9, C2 *p*-cym), 86.38 (s, br, C5 *p*-cym), 76.56 [s, =C(OCH_2CH$_3$)], 65.1, 64.5 (d, J_{CP} = 9.9, J_{CP} = 7.3, CH_2 phos), 54.3 [br, =C(CH_2Ph)], 31.1 (s, CH), 22.25, 21.95 (s, CH_3 ^{i}Pr), 17.98 (s, *p*-CH_3 *p*-cym), 16.30, 16.28 (d, J_{CP} = 7.3, CH_3 phos), 14.59 [s, =C(OCH$_2$$CH_3$)] ppm. Λ_M = 53.6 Ω^{-1} mol^{-1} cm^2. $C_{54}H_{61}BClO_3OsP$ (1025.53): C, 63.24; H, 6.00; Cl, 3.46. Found: C, 63.07; H, 6.09; Cl, 3.35%.

3. Results and discussion

3.1. Preparation of diazoalkane complexes

Diazoalkane complexes [OsCl(η^6-*p*-cymene)(N_2CAr1Ar2){PPh(OEt)$_2$}]BPh$_4$ (**1**) were prepared by reacting the chlorocompound [OsCl$_2$(η^6-*p*-cymene){PPh(OEt)$_2$}] with an excess of diazoalkane in ethanol, as shown in Scheme 1.

The reaction proceeds with the substitution of one chloride by Ar1Ar2CN_2 and the formation of cationic complexes **1** and **2**. Crucial for successful synthesis is the presence of $NaBPh_4$ salt which, labilising the Cl$^-$ ligand, favours the formation of diazoalkane complexes, separated as BPh_4^- salts and characterised.

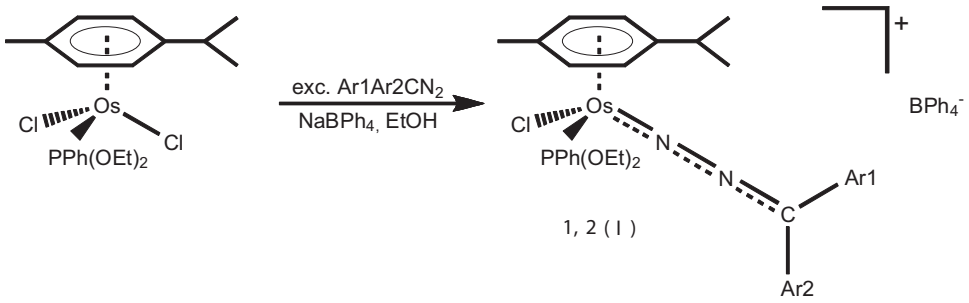
The reaction with diazoalkane was extended to analogous *p*-cymene complexes containing ligands different from PPh(OEt)$_2$, such as phosphites P(OR)$_3$ (R = Me, Et), phosphinite PPh_2OEt, or phosphines PPh_3 and P(^{i}Pr)$_3$, but in no case were stable diazoalkane complexes separated. The reaction did proceed with a colour change of the solution, but no stable compounds were isolated, suggesting that only the fragment [OsCl(η^6-*p*-cymene)L]$^+$ containing phenyldiethoxyphosphine PPh(OEt)$_2$ can stabilise diazoalkane derivatives. Probably, only with this phosphine the electronic and steric factors of the ligand allow the separation of stable complexes **1** and **2**.

Diaryldiazoalkanes with Ph and *p*-tolyl substituents give stable complexes **1a** and **1b**, whereas with diazofluorene they turned out to be unstable and were not isolated in pure form. Instead, ethyldiazoacetate N_2C(H)COOEt gave a stable isolable derivative (**2**).

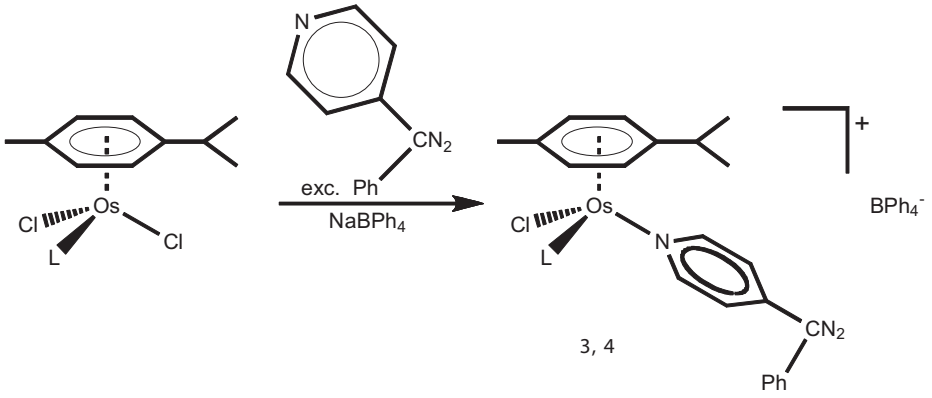
Comparison of our results with those of related fragments [RuCl(η^6-*p*-cymene)L]$^+$ [L = P(OR)$_3$, PPh(OEt)$_2$] [4] indicates that stable diazoalkane complexes can be prepared with both metals, but not with the diazofluorene ligand, which gives unstable species in both cases. Instead, different behaviour by the two metals was observed in the reaction of the triisopropylphosphine precursor [RuCl$_2$(η^6-*p*-cymene){P(^{i}Pr)$_3$}] (M = Ru, Os) with diazofluorene, which afforded the new sandwich complex [Ru(η^5-alkoxyfluorene)(η^6-*p*-cymene)]$^+$ [4], in the case of ruthenium. Neither sandwich complexes nor diazoalkane derivatives, but only decomposition products, were obtained with osmium.

Chlorocomplexes [OsCl$_2$(η^6-*p*-cymene)L] (L = PPh(OEt)$_2$, P(OR)$_3$] were also treated with 4-[diazo(phenyl)methyl]pyridine (4-C_5H_4N)(Ph)CN_2 in the presence of $NaBPh_4$, and the reaction was seen to proceed with the substitution of one Cl$^-$ ligand and the formation of κ^1-pyridine complexes [OsCl(η^6-*p*-cymene){κ^1-(4-C_5H_4N)(Ph)CN_2}L]BPh$_4$ (**3**, **4**), which were isolated and characterised (Scheme 2).

In this case, the pyridinic nitrogen atom does bind to osmium instead of the diazo group: it affords a new pyridine complex with



Scheme 1. Ar1 = Ar2 = Ph (**1a**); Ar1 = Ph, Ar2 = *p*-tolyl (**1b**); Ar1 = H, Ar2 = COOEt (**2**).



Scheme 2. L = $PPh(OEt)_2$ (**3**), $P(OEt)_3$ (**4**).

a free diazo group which, however, is not favoured in competition with the pyridine for the metal centre.

The new diazoalkane complexes $[OsCl(\eta^6\text{-}p\text{-cymene})(N_2CAr1Ar2)\{PPh(OEt)_2\}]BPh_4$ (**1**, **2**) were isolated as yellow-orange solids stable in air and in solution of polar organic solvents, in which they behave as 1:1 electrolytes [17]. Analytical and spectroscopic (IR, NMR) data support the proposed formulations.

The IR spectra of complexes **1** and **2** show a medium-intensity band at 1960–1897 cm^{-1}, attributed to the $\nu_{N=N=C}$ of the diazoalkane ligand. Comparison of these values with those of diazoalkane complexes of known structure [1,5] suggested singly-bent geometry **I** (Scheme 1) for the $Ar1Ar2CN_2$ group. In addition, the spectrum of the ethyldiazoacetate complex $[OsCl(\eta^6\text{-}p\text{-cymene})\{N_2C(H)COOEt\}\{PPh(OEt)_2\}]BPh_4$ (**2**) shows a strong band at 1727 cm^{-1}, due to the ν_{CO} of the COOEt substituent.

Besides the signals of the ancillary ligands *p*-cymene and PPh $(OEt)_2$ and the anion BPh_4^-, the proton NMR spectra show the characteristic resonances of substituents of the diazo group. In particular, the methyl group of the *p*-tolyl of **1b** is a singlet at 2.39 ppm, whereas the spectrum of **2** shows a quartet at 3.62 and a triplet at 1.38 ppm of the ethyl group of the COOEt substituent. The CH proton is masked by the multiplets of the methylene protons of $PPh(OEt)_2$. In the ^{13}C NMR spectra of **1b**, the broad signal at 82.9 ppm was attributed to the CN_2 carbon resonance of the diazoalkane, whereas the singlet at 21.3 ppm was due to the methyl group of the *p*-tolyl substituent. The signals of the *p*-cymene and $PPh(OEt)_2$ ligands were also present. In the temperature range +20 to −80 °C, the ^{31}P NMR spectra of **1** and **2** are singlets at 94.1–91.3 ppm, fitting the proposed formulations for the complexes.

The IR spectra of the pyridine-diazo complexes $[OsCl(\eta^6\text{-}p\text{-cymene})\{\kappa^1\text{-}(4\text{-}C_5H_4N)(Ph)CN_2\}L]BPh_4$ (**3**, **4**) show a strong band at 2050–2044 cm^{-1}, attributed to the ν_{N_2} of the diazoalkane. This value is only slightly shifted with respect to free diazoalkane, matching the N_{Py} coordination of the $(4\text{-}C_5H_4N)(Ph)CN_2$ group. The presence of this ligand was confirmed by both ^1H and ^{13}C NMR spectra, which showed the characteristic signals of the pyridine substituent and of the ancillary ligands *p*-cymene and PPh $(OEt)_2$. In the temperature range between +20 and −80 °C, the ^{31}P NMR spectra show a singlet at 98.9 (**3**) and 70.5 (**4**) ppm, fitting the proposed formulations for the complexes.

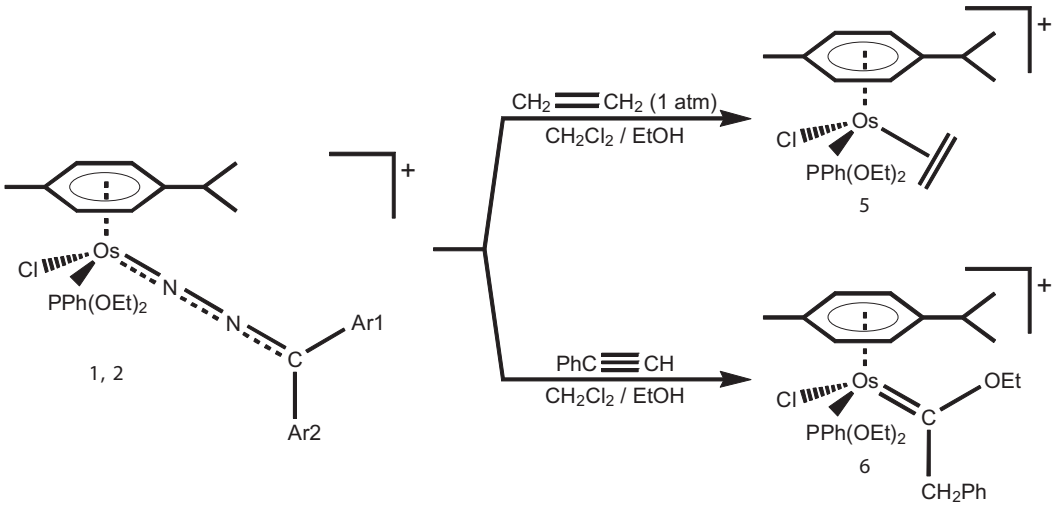
3.2. Reactions with alkenes and alkynes

Diazoalkane complexes $[OsCl(\eta^6\text{-}p\text{-cymene})(N_2CAr1Ar2)\{PPh(OEt)_2\}]BPh_4$ (**1**, **2**) were treated with ethylene and phenylacetylene under mild conditions. The results are shown in Scheme 3.

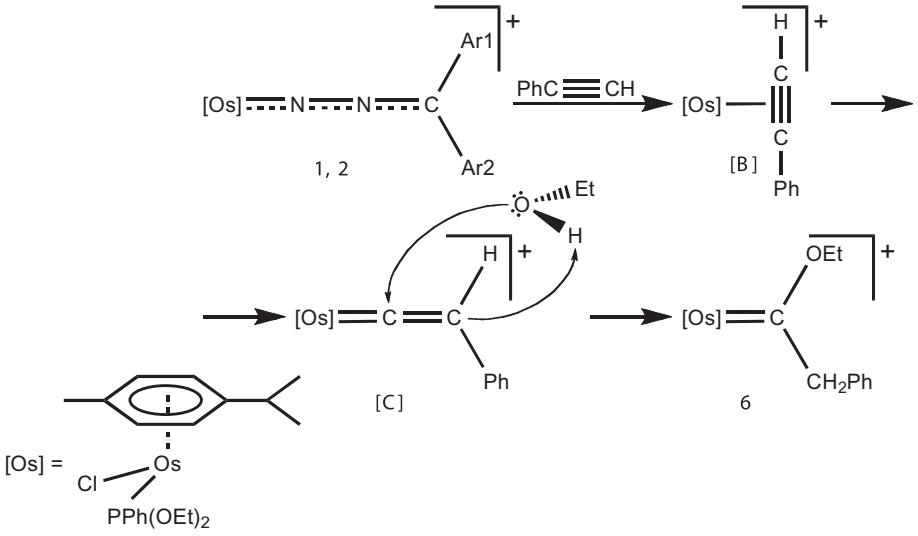
In mild conditions (1 atm, RT), $CH_2{=}CH_2$ reacts with complexes **1**, **2** to give the ethylene complex [18] $[OsCl(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-}CH_2{=}CH_2)\{PPh(OEt)_2\}]BPh_4$ (**5**), which was isolated and characterised. The reaction proceeds with the substitution of diazoalkane and the formation of the $\eta^2\text{-}CH_2{=}CH_2$ derivative **5**. This result was somewhat surprising, since diazoalkanes coordinated to the half-sandwich fragment $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)L]^+$ (L = phosphite) often undergo (3 + 2) cycloaddition to ethylene, affording 3H-pyrazole derivatives [5a,b]. Instead, our Os *p*-cymene fragment did not appear to be able to activate the coordinated $N_2CAr1Ar2$ to cyclisation, and substitution was the only observed reaction.

Phenylacetylene also reacts with **1**, **2** to give the alkoxycarbene complex $[OsCl\{{=}C(OEt)(CH_2Ph)\}(\eta^6\text{-}p\text{-cymene})\{PPh(OEt)_2\}]BPh_4$ (**6**), the formation of which probably involves substitution of N_2-CAr1Ar2 with phenylacetylene to afford an η^2-alkyne intermediate ([**B**], Scheme 4).

Tautomerisation [19] of π-alkyne on the metal centre gives vinylidene intermediate [**C**], which undergoes nucleophilic attack [20] by ethanol, yielding final carbene derivatives **6**. Therefore, phenylacetylene also substitutes the diazoalkane bonded to the



Scheme 3.



Scheme 4. Reaction path.

osmium fragment, affording the known alkoxycarbene derivative [20] as final product.

These results show that diazoalkane is labile in half-sandwich osmium complexes **1** and **2** and allows the preparation of ethylene and carbene derivatives. Both ethylene **5** and carbene **6** compounds were isolated as yellow stable solids and characterised by analytical and spectroscopic data. Significant appears the proton spectrum of the CH_2=CH_2 complex **5**, which shows two multiplets at 4.24 and 3.12 ppm, attributed to the protons of the coordinated ethylene. The multiplicity of signals is due to the presence of a chiral centre in the molecule which makes the protons of ethylene two-by-two diastereoisotopic, thus appearing at different chemical shift values and coupled with the phosphorus of the phosphine. The multiplet may be simulated by an EFGHX model (X = ^{31}P) with the parameters reported in the Experimental section and the good fit between the experimental and calculated spectra strongly supports the proposed attributions.

Besides the signals of ancillary ligands, the ^{1}H NMR spectra of the alkoxycarbene complex **6** show the characteristic resonance of the OC_2H_5 and CH_2Ph substituents of the carbene, which appear as a quartet and a triplet the former, and as two doublets at 5.37 and 2.98 ppm the latter. However, diagnostic for the presence of the carbene ligand is the ^{13}C NMR spectrum, which shows a doublet at 286.5 ppm (J_{CP} = 15.9 Hz), characteristic of the carbene carbon resonance. In addition, the signals of the substituents OC_2H_5 and CH_2Ph as well as those of the supporting ligands *p*-cymene and $PPh(OEt)_2$ are also present, in agreement with the proposed formulation.

4. Conclusions

This paper reports that the half-sandwich fragment [OsCl(η^6-*p*-cymene)L]$^+$ with $PPh(OEt)_2$ as a supporting ligand can stabilise diazoalkane complexes. κ^1-Pyridine-diazoalkane derivatives [OsCl(η^6-*p*-cymene){κ^1-(4-C_5H_4N)(Ph)CN_2}L]BPh_4 were also prepared. Reaction of [OsCl(η^6-*p*-cymene)(N_2CAr1Ar2){$PPh(OEt)_2$}]BPh_4 with ethylene and phenylacetylene proceeds with substitution of the Ar1Ar2CN_2 group, yielding new derivatives.

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