

# Preparation of half-sandwich diazoalkane complexes of osmium



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## ARTICLE INFO

### Article history:

Received 1 October 2015

Accepted 15 November 2015

Available online 2 December 2015

### Keywords:

Osmium  
Half-sandwich  
Diazoalkane  
Synthesis  
Phenyldiethoxyphosphine

## ABSTRACT

Diazoalkane complexes  $[\text{OsCl}(\eta^6\text{-}p\text{-cymene})(\text{N}_2\text{CAr1Ar2})\{\text{PPh}(\text{OEt})_2\}] \text{BPh}_4$  (**1**, **2**) [ $\text{Ar1} = \text{Ar2} = \text{Ph}$ ;  $\text{Ar1} = \text{Ph}$ ,  $\text{Ar2} = p\text{-tolyl}$ ;  $\text{Ar1} = \text{H}$ ,  $\text{Ar2} = \text{COOEt}$ ] were prepared by allowing compounds  $\text{OsCl}_2(\eta^6\text{-}p\text{-cymene})\{\text{PPh}(\text{OEt})_2\}$  to react with diazoalkane in ethanol. Diazo-pyridine derivatives  $[\text{OsCl}(\eta^6\text{-}p\text{-cymene})\{\kappa^1\text{-}(4\text{-C}_5\text{H}_4\text{N})(\text{Ph})\text{CN}_2\}\text{L}] \text{BPh}_4$  (**3**, **4**) [ $\text{L} = \text{PPh}(\text{OEt})_2$ ,  $\text{P}(\text{OEt})_3$ ] were also prepared by reacting chloro-compounds  $\text{OsCl}_2(\eta^6\text{-}p\text{-cymene})\text{L}$  with 4-[diazo(phenyl)methyl]pyridine,  $(4\text{-C}_5\text{H}_4\text{N})\text{PhCN}_2$ , in ethanol. Treatment of diazoalkane complexes **1** and **2** with  $\text{CH}_2=\text{CH}_2$  (1 atm) and  $\text{PhC}\equiv\text{CH}$  in ethanol led to ethylene  $[\text{OsCl}(\eta^2\text{-CH}_2=\text{CH}_2)(\eta^6\text{-}p\text{-cymene})\{\text{PPh}(\text{OEt})_2\}] \text{BPh}_4$  (**5**) and carbene  $[\text{OsCl}(\text{C}(\text{CH}_2\text{Ph})(\text{OEt}))(\eta^6\text{-}p\text{-cymene})\{\text{PPh}(\text{OEt})_2\}] \text{BPh}_4$  (**6**) derivatives.

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## 1. Introduction

Diazoalkanes  $\text{Ar1Ar2CN}_2$  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  $\text{M} = \text{CAr1Ar2}$  was observed in  $\eta^2\text{-CN}$  coordinated species [3f,9,10], whereas  $\eta^1$ -bonded diazoalkane gave dinitrogen  $[\text{M}]\text{-N}_2$  complexes [3f], transfer of carbene to imine [9f], or cleavage of the  $\text{N-N}$  bond of the  $\text{Ar1Ar2CN}_2$  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  $[\text{M}]\text{-N}_2\text{CAr1Ar2}$  yielding  $\eta^2$ -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  $[\text{OsH}(\text{N}_2\text{CAr1Ar2})\text{L}_4] \text{BPh}_4$ , 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 ( $\text{Ar}$ ,  $\text{N}_2$ ) 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.  $\text{OsO}_4$  was a Pressure Chemical Co. (USA) product, used as received. Phosphites  $\text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OEt})_3$  and triisopropylphosphine  $\text{P}(\text{Pr})_3$  were Aldrich products, purified by distillation, whereas phenyldiethoxyphosphine  $\text{PPh}(\text{OEt})_2$  and diphenylethoxyphosphine  $\text{PPh}_2\text{OEt}$  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 ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) were obtained on AVANCE 300 Bruker spectrometer at temperatures between  $-80$  and  $+30$  °C, unless otherwise noted.  $^1\text{H}$  and  $^{13}\text{C}$  spectra are referenced to internal tetramethylsilane;  $^{31}\text{P}\{^1\text{H}\}$  chemical shifts are reported with respect to 85%  $\text{H}_3\text{PO}_4$ , 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  $10^{-3} \text{ mol dm}^{-3}$  solutions of the complexes in  $\text{CH}_3\text{NO}_2$  at 25 °C were measured with a Radiometer CDM 83.

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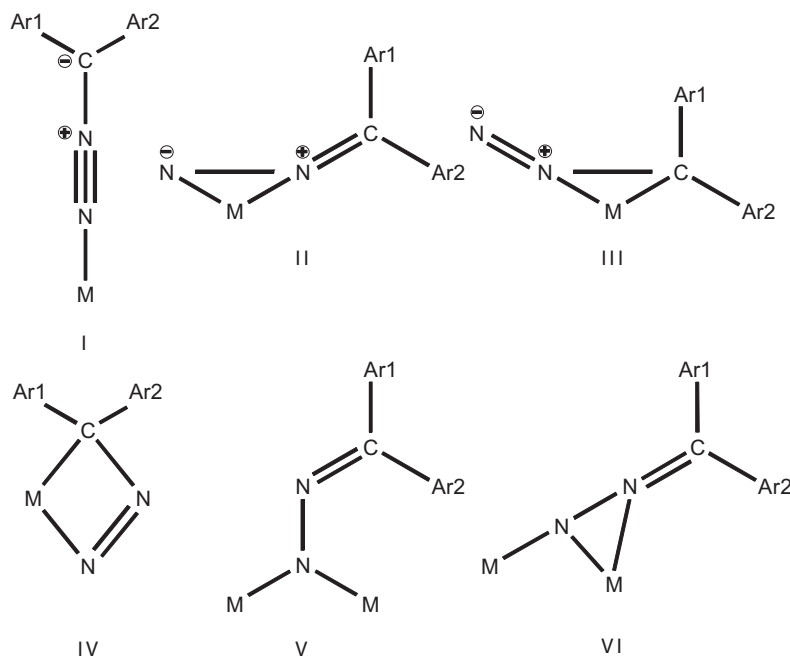


Chart 1. Diazoalkane coordination modes.

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

### 2.3. $[\text{OsCl}(\eta^6\text{-}p\text{-cymene})(\text{N}_2\text{C}(\text{H})\text{Ar}_1\text{Ar}_2)\{\text{PPh}(\text{OEt})_2\}] \text{BPh}_4$ (**1**) [ $\text{Ar}_1 = \text{Ar}_2 = \text{Ph}$ (**a**); $\text{Ar}_1 = \text{Ph}$ , $\text{Ar}_2 = p\text{-tolyl}$ (**b**)]

In a 25-mL three-necked round-bottomed flask were placed 100 mg (0.17 mmol) of solid  $[\text{OsCl}_2(\eta^6\text{-}p\text{-cymene})\{\text{PPh}(\text{OEt})_2\}]$ , an excess of the appropriate diazoalkane  $\text{Ar}_1\text{Ar}_2\text{CN}_2$  (0.5 mmol), an excess of  $\text{NaBPh}_4$  (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  $\text{CH}_2\text{Cl}_2$  and EtOH. Yield: 138 mg (76%) for **1a**, 144 mg (78%) for **1b**.

**1a**: IR (KBr pellet):  $\nu_{\text{N}_2}$  1897 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 7.75–6.85 (m, 35H, Ph), 5.68, 5.65, 5.58, 5.48 (d, 4H, Ph *p*-cym), 3.82 (m, 4H,  $\text{CH}_2$ ), 2.45 (m, 1H, CH  $\text{Pr}^i$ ), 2.05 (s, 3H,  $\text{CH}_3$  *p*-cym), 1.22 (d, 6H,  $\text{CH}_3$   $\text{Pr}^i$ ), 1.14 (t, 6H,  $\text{CH}_3$  phos).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 92.9 ppm.  $\Lambda_{\text{M}} = 52.6 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ .  $\text{C}_{57}\text{H}_{59}\text{BClN}_2\text{O}_2\text{OsP}$  (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):  $\nu_{\text{N}_2}$  1925 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 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,  $\text{CH}_2$ ), 2.45 (m, 1H, CH  $\text{Pr}^i$ ), 2.39 (s, 3H,  $\text{CH}_3$  *p*-tol), 2.04 (s, 3H,  $\text{CH}_3$  *p*-cym), 1.16, 1.13 (t, 6H,  $\text{CH}_3$  phos), 1.11, 1.10 (d, 6H,  $\text{CH}_3$   $\text{Pr}^i$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 94.1.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 160–119 (m, Ph), 110.6 (d, C4 *p*-cym), 82.9 (br,  $\text{CN}_2$ ), 93.2, 82.1 (d), 80.7 (br), 79.5 (d) (Ph *p*-cym), 63.85 (d,  $J_{\text{CP}} = 7.1$  Hz,  $\text{CH}_2$ ), 31.12 (s, CH  $\text{Pr}^i$ ), 23.0, 22.6 (s,  $\text{CH}_3$   $\text{Pr}^i$ ), 21.3 (s,  $J_{\text{CP}} = 6.5$ ,  $\text{CH}_3$  *p*-tol), 18.5 (s,  $\text{CH}_3$  *p*-cym), 16.5 (d,  $\text{CH}_3$  phos) ppm.  $\Lambda_{\text{M}} = 51.9 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ .  $\text{C}_{58}\text{H}_{61}\text{BClN}_2\text{O}_2\text{OsP}$  (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. $[\text{OsCl}(\eta^6\text{-}p\text{-cymene})\{\text{N}_2\text{C}(\text{H})\text{COOEt}\}\{\text{PPh}(\text{OEt})_2\}] \text{BPh}_4$ (**2**)

In a 25-mL three-necked round-bottomed flask were placed 100 mg (0.17 mmol) of solid  $[\text{OsCl}_2(\eta^6\text{-}p\text{-cymene})\{\text{PPh}(\text{OEt})_2\}]$ , an excess of  $\text{NaBPh}_4$  (0.34 mmol, 116 mg), an excess of ethyldiazoacetate  $\text{N}_2\text{C}(\text{H})\text{COOEt}$  (0.68 mmol, 71  $\mu\text{L}$ ) 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):  $\nu_{\text{N}_2}$  1960 (m),  $\nu_{\text{CO}}$  1727 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 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,  $\text{CH}_2$  phos), 3.62 (q, 2H,  $\text{CH}_2$  COOEt), 2.47 (m, 1H, CH  $\text{Pr}^i$ ), 1.92 (s, 3H,  $\text{CH}_3$  *p*-cym), 1.38 (m, 3H,  $\text{CH}_3$  COOEt + 6H,  $\text{CH}_3$  phos), 1.19, 1.17 (d, 6H,  $\text{CH}_3$   $\text{Pr}^i$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 91.3 (s) ppm.  $\Lambda_{\text{M}} = 52.2 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ .  $\text{C}_{48}\text{H}_{55}\text{BClN}_2\text{O}_4\text{OsP}$  (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. $[\text{OsCl}(\eta^6\text{-}p\text{-cymene})\{\kappa^1\text{-(4-C}_5\text{H}_4\text{N})(\text{Ph})\text{CN}_2\}\text{L}] \text{BPh}_4$ (**3**, **4**) [ $\text{L} = \text{PPh}(\text{OEt})_2$ (**3**), $\text{P}(\text{OEt})_3$ (**4**)]

In a 25-mL three-necked round-bottomed flask were placed 0.17 mmol of solid  $[\text{OsCl}_2(\eta^6\text{-}p\text{-cymene})\text{L}]$ , an excess of diazoalkane  $(4\text{-C}_5\text{H}_4\text{N})(\text{Ph})\text{CN}_2$  (0.51 mmol, 100 mg), an excess of  $\text{NaBPh}_4$  (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  $\text{CH}_2\text{Cl}_2$  and EtOH. Yield: 160 mg (88%) for **3**, 163 mg (92%) for **4**.

**3**: IR (KBr pellet):  $\nu_{\text{N}_2}$  2044 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 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,  $\text{CH}_2$ ), 2.54 (m, 1H, CH  $\text{Pr}^i$ ), 2.12 (s, 3H,  $\text{CH}_3$  *p*-cym), 1.39, 1.32 (t, 6H,  $\text{CH}_3$  phos), 1.16, 1.14 (d, 6H,  $\text{CH}_3$   $\text{Pr}^i$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 98.9 ppm.

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