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Preparation and reactivity of half-sandwich hydrazine complexes of ruthenium and osmium

Gabriele Albertin [a,*], Stefano Antoniutti [a], Jesús Castro [b]

[a] Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Dorsoduro 2137, 30123 Venezia, Italy
[b] Departamento de Química Inorgánica, Universidade de Vigo, Facultade de Química, Edificio de Ciencias Experimentais, 36310 Vigo (Galicia), Spain

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ABSTRACT

Hydrazine complexes [MCl(η^6-*p*-cymene)(RNHNH$_2$)L]BPh$_4$ (**1**–**6**) [M = Ru, Os; R = H, Me, Ph; L = P(OEt)$_3$, PPh(OEt)$_2$, PPh$_2$OEt] were prepared by allowing dichloro complexes MCl$_2$(η^6-*p*-cymene)L to react with hydrazines RNHNH$_2$ in the presence of NaBPh$_4$. Treatment of ruthenium complexes [RuCl(η^6-*p*-cymene)(RNHNH$_2$)L]BPh$_4$ with Pb(OAc)$_4$ led to acetate complex [Ru(κ^2–O$_2$CCH$_3$)(η^6-*p*-cymene)L]BPh$_4$ (**7**). Instead, the reaction of osmium derivatives [OsCl(η^6-*p*-cymene)(CH$_3$NHNH$_2$)L]BPh$_4$ with Pb(OAc)$_4$ afforded the methyldiazenido complex [Os(CH$_3$N$_2$)(η^6-*p*-cymene)L}]BPh$_4$ (**8**). Treatment with HCl of this diazenido complex **8** led to the methyldiazene cation [OsCl(CH$_3$N=NH)(η^6-*p*-cymene)L}]$^+$ (**9**$^+$). The complexes were characterised spectroscopically and by X-ray crystal structure determination of [OsCl(η^6-*p*-cymene)(PhNHNH$_2$){PPh(OEt)$_2$}]BPh$_4$ (**6b**) and [Ru(κ^2–O$_2$CCH$_3$)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh$_4$ (**7b**).

1. Introduction

The chemistry of transition metal complexes containing hydrazine NH$_2$NH$_2$ or substituted hydrazine RNHNH$_2$ as ligands continues to be studied, not only due to interest in the differing coordination modes and interesting reactivity shown by these ligands [1–4], but also due to the relationship of hydrazine with the nitrogen fixation process [5–7].

Hydrazine is reported to coordinate both η^1- and η^2- to a metal centre, and may also behave as a bridging μ–η^2 ligand [1–4]. Coordinated NH$_2$NH$_2$ can either give stable 1,2-diazene complexes [M]–NH=NH, by both oxidation [5] and deprotonation with a strong base [4], or undergo reduction to ammonia [5b,6,7a,8]. Hydrazine has also been shown to be a substrate of nitrogenase and has been trapped as an intermediate during enzyme turnover [9].

A number of hydrazine RNHNH$_2$ complexes of several transition metals have been reported in the past 30 years, mainly with π-acceptors such as carbonyl, phosphine and cyclopentadienyl as ancillary ligands [1–4]. Less attention has been devoted to arene ligands and, for the iron triad, only a few examples of hydrazine complexes containing arene as supporting ligand have been reported [10].

We are interested in the chemistry of diazo complexes and have reported the synthesis and reactivity of hydrazine complexes of the iron triad stabilised by phosphite, carbonyl or tris(pyrazolyl)borate ligands, of the type [MH(RNHNH$_2$)L$_4$]$^+$, [M(RNHNH$_2$)$_2$L$_4$]$^{2+}$, [M(CO)(RNHNH$_2$)L$_4$]$^{2+}$, [M(Tp)(RNHNH$_2$)L(PPh$_3$)]$^+$ [M = Fe, Ru, Os; Tp = tris(pyrazolyl)borate; L = P(OEt)$_3$, PPh(OEt)$_2$] [11].

We have now extended these studies with the aim of introducing the arene ligands into the diazo chemistry of the iron triad. In this paper, we report the synthesis and reactivity of new hydrazine complexes of ruthenium and osmium stabilised 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 a vacuum atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored in an inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. RuCl$_3$·3H$_2$O and OsO$_4$ were Pressure Chemical Co. (USA) products, used as received. Phosphites PPh(OEt)$_2$ and PPh$_2$OEt were prepared by the method of Rabinowitz and Pellon [12]. Instead, P(OEt)$_3$ (Aldrich) was used as received. Hydrazine NH$_2$NH$_2$ was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method [13]. High-grade (99.99%) lead(IV) acetate was purchased from Aldrich. Other reagents were

* Corresponding author. Fax: +39 0 41 234 8917.
E-mail address: albertin@unive.it (G. Albertin).

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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, ^{31}P, ^{13}C) were obtained on AC200 or AVANCE 300 Bruker spectrometers 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. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche of the University of Padua, Italy.

2.2. Synthesis of complexes

Compounds $RuCl_2(\eta^6$-*p*-cymene)L and $OsCl_2(\eta^6$-*p*-cymene)L [L = $P(OEt)_3$, $PPh(OEt)_2$, PPh_2OEt] were prepared following the methods previously reported [15,16].

2.2.1. [RuCl(η^6-p-cymene)(RNHNH$_2$)L]BPh$_4$ (**1**–**3**) [R = H (1), Me (2), Ph (3); L = P(OEt)$_3$ (a), PPh(OEt)$_2$ (b), PPh$_2$OEt (c)]

In a 25-mL three-necked round-bottomed flask were placed 0.30 mmol of the appropriate $RuCl_2(\eta^6$-*p*-cymene)L complex, an excess of $NaBPh_4$ (0.60 mmol, 0.20 g), 3 mL of ethanol and 5 mL of dichloromethane. A slight excess of the appropriate hydrazine $RNHNH_2$ (0.31 mmol) was added to the resulting solution cooled to −196 °C. The reaction mixture was left to reach room temperature, stirred for 5 h and then the solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 mL). By cooling to −25 °C of the resulting solution, a yellow solid slowly separated out, which was filtered and crystallised from ethanol. Yield: 154 mg (65%) for **1a**, 187 mg (76%) for **1b**, 202 mg (79%) for **1c**, 166 mg (69%) for **2a**, 193 mg (77%) for **2b**, 216 mg (83%) for **2c**, 181 mg (70%) for **3a**, 228 mg (85%) for **3b**.

1a: IR (KBr pellet): ν_{NH} = 3336, 3300, 3255 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) see Chart 1: δ = 7.48–6.86 (m, 20H, BPh_4), 5.52 (d, 1H, HA *p*-cym, J_{AB} = 6.3 Hz), 5.49 (d, 1H, HC *p*-cym, J_{CD} = 6.2), 5.35 (d, 1H, HD *p*-cym), 5.18 (d, 1H, HB *p*-cym), 4.11 (m, 6H, CH_2), 3.82, 3.75 (br, 2H, M–NH_2), 2.73 (br, 2H, N–NH_2), 2.69 (m, 1H, CH ^{i}Pr), 2.06 (s, 3H, CH_3 *p*-cym), 1.33 (t, 9H, CH_3 phos, J_{HH} = 7.0), 1.21 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 6.9) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 115.1 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 164–122 (m, BPh_4), 114.35 (d, C1 *p*-cym, J_{CP} = 3.3), 104.45 (d, C4 *p*-cym, J_{CP} = 2.1), 92.39 (d, C5 *p*-cym, J_{CP} = 7.2), 89.62 (d, C2 *p*-cym, J_{CP} = 7.0), 87.95 (d, br, C3 *p*-cym), 87.81 (d, br, C6 *p*-cym), 64.78 (d, CH_2, J_{CP} = 3.4), 31.04 (s, CH ^{i}Pr), 22.53, 21.97 (s, CH_3 ^{i}Pr), 18.59 (s, CH_3 *p*-cym), 16.36 (d, CH_3 phos, J_{CP} = 6.1) ppm. Λ_M = 53.4 Ω^{-1} mol^{-1} cm^2. $C_{40}H_{53}BClN_2O_3PRu$ (788.17): C 60.96, H 6.78, N 3.55, Cl 4.50; found C 61.16, H 6.66, N 3.37, Cl 4.38%.

1b: IR (KBr pellet): ν_{NH} = 3323, 3283, 3239 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.56–6.89 (m, 25H, Ph), 5.49 (d, 1H, HC *p*-cym, J_{CD} = 6.2 Hz), 5.45 (d, 1H, HD *p*-cym), 5.30 (d, 1H, HA *p*-cym, J_{AB} = 6.3), 5.28 (d, 1H, HB *p*-cym), 4.02, 3.90 (m, 4H, CH_2), 3.60, 3.51 (m, br, 2H, M–NH_2), 2.63 (m, br, 2H, N–NH_2), 2.57 (m, 1H, CH ^{i}Pr), 1.90 (s, 3H, CH_3 *p*-cym), 1.36 (t, 6H, CH_3 phos), 1.15, 1.13 (d, 6H, CH_3 ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 144.0 (s) ppm. Λ_M = 55.1 Ω^{-1} mol^{-1} cm^2. $C_{44}H_{53}BClN_2O_2PRu$ (820.21): C 64.43, H 6.51, N 3.42, Cl 4.32; found C 64.20, H 6.39, N 3.28, Cl 4.56%.

1c: IR (KBr pellet): ν_{NH} = 3334, 3289, 3255 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.82–6.85 (m, 30H, Ph), 5.46 (d, 1H, HC *p*-cym, J_{CD} = 6.1 Hz), 5.43 (d, 1H, HD *p*-cym), 5.37 (d, 1H, HA *p*-cym, J_{AB} = 6.1), 5.31 (d, 1H, HB *p*-cym), 3.82–3.50 (m, 2H, CH_2), 3.58, 3.51 (m, br, 2H, M–NH_2), 2.67 (br, 2H, N–NH_2), 2.63 (m, 1H, CH ^{i}Pr), 2.00 (s, 3H, CH_3 *p*-cym), 1.20 (t, 3H, CH_3 phos, J_{HH} = 7.0), 1.17, 1.10 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 6.9) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 128.1 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, Ph), 112.86 (d, br, C1 *p*-cym), 102.01 (d, br, C4 *p*-cym), 93.73 (d, C6 *p*-cym, J_{CP} = 5.8), 89.10 (d, C2 *p*-cym, J_{CP} = 5.5), 88.42 (d, br, C3 *p*-cym), 88.15 (d, br, C5 *p*-cym), 66.04 (d, CH_2, J_{CP} = 13.9), 30.96 (s, CH ^{i}Pr), 22.76, 21.75 (s, CH_3 ^{i}Pr), 18.16 (s, CH_3 *p*-cym), 16.24 (d, CH_3 phos, J_{CP} = 6.7) ppm. Λ_M = 49.6 Ω^{-1} mol^{-1} cm^2. $C_{48}H_{53}BClN_2OPRu$ (852.25): C 67.65, H 6.27, N 3.29, Cl 4.16; found C 67.42, H 6.15, N 3.17, Cl 4.33%.

2a: IR (KBr pellet): ν_{NH} = 3295, 3261 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.34–6.87 (m, 20H, BPh_4), 5.60 (d, 1H, HA *p*-cym, J_{AB} = 6.3 Hz), 5.58 (d, 1H, HB *p*-cym), 5.51 (d, 1H, HC *p*-cym, J_{CD} = 6.1), 5.27 (d, 1H, HD *p*-cym), 4.55 (dm, br, 2H, NH_2), 4.29 (m, 1H, NH), 4.15 (m, 6H, CH_2), 2.71 (m, 1H, CH ^{i}Pr), 2.52 (d, 3H, N–CH_3, J_{HH} = 6.2), 2.07 (s, 3H, CH_3 *p*-cym), 1.35 (t, 9H, CH_3 phos), 1.23, 1.21 (d, 6H, CH_3 ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 114.9 (s) ppm. Λ_M = 51.8 Ω^{-1} mol^{-1} cm^2. $C_{41}H_{55}BClN_2O_3PRu$ (802.19): C 61.39, H 6.91, N 3.49, Cl 4.42; found C 61.18, H 7.03, N 3.36, Cl 4.22%.

2b: IR (KBr pellet): ν_{NH} = 3389, 3261 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.59–6.86 (m, 25H, Ph), 5.53 (d, 1H, HC *p*-cym, J_{CD} = 6.1 Hz), 5.41 (d, 1H, HA *p*-cym), 5.33 (d, 1H, HB *p*-cym, J_{AB} = 6.4), 5.30 (d, 1H, HD *p*-cym), 4.18–3.95 (m, 4H, CH_2), 4.15, 3.71 (d, br, 2H, NH_2), 3.59 (m, 1H, NH), 2.61 (m, 1H, CH ^{i}Pr), 2.33 (d, 3H, N–CH_3, J_{HH} = 6.0 Hz), 1.94 (s, 3H, CH_3 *p*-cym), 1.41, 1.39 (t, 6H, CH_3 phos), 1.18, 1.16 (d, 6H, CH_3 ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 144.8 (s) ppm. Λ_M = 54.4 Ω^{-1} mol^{-1} cm^2. $C_{45}H_{55}BClN_2O_2PRu$ (834.24): C 64.79, H 6.65, N 3.36, Cl 4.25; found C 64.61, H 6.49, N 3.18, Cl 4.42%.

2c: IR (KBr pellet): ν_{NH} = 3285, 3261 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.69–6.85 (m, 30H, Ph), 5.61 (d, 2H, HC, HD *p*-cym, J_{CD} = 5.8 Hz), 5.48 (d, 1H, HA *p*-cym, J_{AB} = 5.8), 5.39 (d, 1H, HB *p*-cym), 4.02 (dm, 2H, NH_2), 3.84, 3.61 (m, 2H, CH_2), 3.47 (m, br, 1H, NH), 2.68 (m, 1H, CH ^{i}Pr), 2.20 (d, 3H, N–CH_3, J_{HH} = 6.3), 2.06 (s, 3H, CH_3 *p*-cym), 1.24 (t, 3H, CH_3 phos, J_{HH} = 7.0), 1.22, 1.14 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 7.0) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 129.4 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, Ph), 112.45 (d, C1 *p*-cym, J_{CP} = 4.6), 103.08 (d, br, C4 *p*-cym), 93.60 (d, C6 *p*-cym, J_{CP} = 6.1), 88.76 (d, C2 *p*-cym, J_{CP} = 4.3), 88.41 (d, br, C5 *p*-cym), 87.54 (d, br, C3 *p*-cym), 66.22 (d, CH_2, J_{CP} = 14.0), 43.46 (s, N–CH_3), 31.11 (s, CH ^{i}Pr), 22.76, 21.92 (s, CH_3 ^{i}Pr), 18.36 (s, CH_3 *p*-cym), 16.23 (d, CH_3 phos, J_{CP} = 6.9) ppm. Λ_M = 53.7 Ω^{-1} mol^{-1} cm^2. $C_{49}H_{55}BClN_2O_2PRu$ (866.28): C 67.94, H 6.40, N 3.23, Cl 4.09; found C 67.73, H 6.28, N 3.13, Cl 4.27%.

3a: IR (KBr pellet): ν_{NH} = 3355, 3254 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.36–6.78 (m, 25H, Ph), 5.71, 5.08 (d, br, 2H, NH_2), 5.62 (d, 1H, HA *p*-cym, J_{AB} = 6.1 Hz), 5.57 (d, 1H, HC *p*-cym, J_{CD} = 5.8), 5.48 (d, 1H, HB *p*-cym), 5.23 (d, 1H, HD *p*-cym), 5.38 (t, br, 1H, NH), 4.13 (m, 6H, CH_2), 2.75 (m, 1H, CH ^{i}Pr), 2.07 (s, 3H, CH_3 *p*-cym), 1.27 (t, 9H, CH_3 phos), 1.27, 1.26 (d, 6H, CH_3 ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 114.0 (s) ppm. Λ_M = 54.0 Ω^{-1} mol^{-1} cm^2. $C_{46}H_{57}BClN_2O_3PRu$ (864.26): C 63.93, H 6.65, N 3.24, Cl 4.10; found C 63.71, H 6.56, N 3.12, Cl 4.29%.

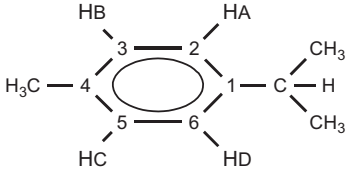


Chart 1. Labelling scheme of the *p*-cymene ligand used for the NMR study.

3b: IR (KBr pellet): ν_{NH} = 3283 (m, br) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.84–6.56 (m, 30H, Ph), 5.77 (d, br, 1H, NH), 5.61 (d, 1H, HA *p*-cym, J_{AB} = 6.1 Hz), 5.45 (d, 1H, HD *p*-cym, J_{CD} = 6.1), 5.43 (d, 1H, HC *p*-cym), 5.35 (d, 1H, HB *p*-cym), 5.37, 4.31 (d, br, 2H, NH_2, J_{HH} = 8.2), 4.20–3.90 (m, 4H, CH_2), 2.67 (m, 1H, CH ^{i}Pr, J_{HH} = 6.8), 1.96 (s, 3H, CH_3 *p*-cym), 1.38, 1.36 (t, 6H, CH_3 phos, J_{HH} = 7.2), 1.21, 1.20 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 6.9) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 144.6 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, Ph), 115.6 (s, br, C1 *p*-cym), 103.25 (s, br, C4 *p*-cym), 90.62 (d, C2 *p*-cym, J_{CP} = 4.2), 82.29 (d, C5 *p*-cym, J_{CP} = 3.6), 88.20 (br, C3 *p*-cym), 87.71 (br, C6 *p*-cym), 64.77, 64.19 (d, CH_2, J_{CP} = 9.0, J_{CP} = 8.1), 31.26 (s, CH ^{i}Pr), 22.39, 21.94 (s, CH_3 ^{i}Pr), 18.24 (s, CH_3 *p*-cym), 16.47, 16.24 (d, CH_3 phos, J_{CP} = 6.5, J_{CP} = 7.6) ppm. Λ_M = 53.6 Ω^{-1} mol^{-1} cm^2. $C_{50}H_{57}BClN_2O_2PRu$ (896.31): C 67.00, H 6.41, N 3.13, Cl 3.96; found C 66.79, H 6.30, N 3.01, Cl 4.12%.

2.2.2. [OsCl(η^6-*p*-cymene)(RNHNH$_2$)L]BPh$_4$ (4–6) [R = H (4), Me (5), Ph (6); L = P(OEt)$_3$ (a), PPh(OEt)$_2$ (b), PPh$_2$OEt (c)]

In a 25-mL three-necked round-bottomed flask were placed 0.13 mmol of the appropriate $OsCl_2(\eta^6$-*p*-cymene)L complex, an excess of $NaBPh_4$ (0.26 mmol, 89 mg), 3 mL of ethanol and 5 mL of dichloromethane. The resulting solution was cooled to −196 °C and a slight excess of the appropriate hydrazine $RNHNH_2$ (0.14 mmol) was added. The reaction mixture was allowed to reach room temperature and then stirred for 24. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL). By cooling to −25 °C of the resulting solution, yellow crystals separated out, which were collected and recrystallised from ethanol. Yield: 89 mg (75%) for**4b**, 75 mg (65%) for **5a**, 85 mg (71%) for **5b**, 98 mg (79%) for **5c**, 87 mg (70%) for **6a**, 100 mg (78%) for **6b**.

4b: IR (KBr pellet): ν_{NH} = 3323, 3255, 3244 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.68–6.88 (m, 25H, Ph), 5.52 (d, 1H, HC *p*-cym, J_{CD} = 5.7 Hz), 5.46 (d, 1H, HD *p*-cym), 5.44 (d, 1H, HB *p*-cym, J_{AB} = 5.7), 5.35 (d, 1H, HA *p*-cym), 4.40, 4.27 (br, 2H, M–NH_2), 4.09–3.75 (m, 4H, CH_2), 2.65 (br, 2H, N–NH_2), 2.53 (m, 1H, CH ^{i}Pr), 2.02 (s, 3H, CH_3 *p*-cym), 1.35, 1.34 (t, 6H, CH_3 phos, J_{HH} = 7.0), 1.17, 1.15 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 7.0) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 97.6 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–122 (m, Ph), 108.4 (d, C1 *p*-cym, J_{CP} = 3.0), 96.93 (d, C4 *p*-cym, J_{CP} = 1.9), 83.78 (d, C2 *p*-cym, J_{CP} = 4.6), 83.20 (d, C5 *p*-cym, J_{CP} = 6.7), 80.67 (d, C6 *p*-cym, J_{CP} = 2.6), 77.53 (s, br, C3 *p*-cym), 65.03, 64.14 (d, CH_2, J_{CP} = 9.3, J_{CP} = 7.0), 30.81 (s, CH ^{i}Pr), 22.46, 22.21 (s, CH_3 ^{i}Pr), 18.13 (s, CH_3 *p*-cym), 16.31, 16.15 (d, CH_3 phos, J_{CP} = 6.5, J_{CP} = 7.6) ppm. Λ_M = 51.1 Ω^{-1} mol^{-1} cm^2. $C_{44}H_{53}BClN_2O_2OsP$ (909.37): C 58.11, H 5.87, N 3.08, Cl 3.90; found C 58.27, H 5.74, N 3.19, Cl 3.76%.

5a: IR (KBr pellet): ν_{NH} = 3310, 3277 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.33–6.87 (m, 20H, BPh_4), 5.69 (d, 1H, HC *p*-cym, J_{CD} = 5.9 Hz), 5.62 (d, 1H, HA *p*-cym, J_{AB} = 5.9), 5.57 (d, 1H, HD *p*-cym), 5.45 (d, 1H, HB *p*-cym), 5.41, 5.24 (d, br, 2H, NH_2), 4.13 (m, 6H, CH_2), 3.53 (m, br, 1H, NH), 2.68 (m, 1H, CH ^{i}Pr), 2.51 (d, 3H, N–CH_3, J_{HH} = 6.4), 2.16 (s, 3H, CH_3 *p*-cym), 1.34 (t, 9H, CH_3 phos, J_{HH} = 7.0), 1.24, 1.22 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 6.8) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 69.8 (s) ppm. Λ_M = 53.5 Ω^{-1} mol^{-1} cm^2. $C_{41}H_{55}BClN_2O_3OsP$ (891.35): C 55.25, H 6.22, N 3.14, Cl 3.98; found C 55.07, H 6.35, N 3.02, Cl 4.21%.

5b: IR (KBr pellet): ν_{NH} = 3289, 3255 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.61–6.86 (m, 25H, Ph), 5.60 (d, 2H, HA, HC *p*-cym, J_{AB} = 5.9, J_{CD} = 6.0 Hz), 5.48 (d, 1H, HD *p*-cym), 5.52 (d, 1H, HB *p*-cym), 4.85 (t, br), 4.60 (d, br) (2H, NH_2, J_{HH} = 8.8, J_{HH} = 8.3), 4.16–3.84 (m, 4H, CH_2), 3.47 (m, 1H, NH), 2.58 (m, 1H, CH ^{i}Pr), 2.28 (d, 3H, N–CH_3, J_{HH} = 6.2), 2.08 (s, 3H, CH_3 *p*-cym), 1.38 (t, 6H, CH_3 phos, J_{HH} = 7.0), 1.20, 1.19 (d, 6H, CH_3 ^{i}Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 99.0 (s) ppm. Λ_M = 52.9 Ω^{-1} mol^{-1} cm^2. $C_{45}H_{55}BClN_2O_2OsP$ (923.40): C 58.53, H 6.00, N 3.03, Cl 3.84; found C 58.30, H 5.89, N 2.92, Cl 3.98%.

5c: IR (KBr pellet): ν_{NH} = 3317, 3272, 3244 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.78–6.82 (m, 30H, Ph), 5.80 (d, 1H, HA *p*-cym, J_{AB} = 6.0 Hz), 5.64 (d, 1H, HD *p*-cym, J_{CD} = 6.0), 5.63 (d, 2H, HB, HC *p*-cym), 4.65 (t, br), 4.52 (m, br) (2H, NH_2), 3.90–3.78, 3.59–3.47 (m, 2H, CH_2), 3.31 (m, br, 1H, NH), 2.65 (m, 1H, CH ^{i}Pr), 2.16 (s, 3H, CH_3 *p*-cym), 2.14 (d, 3H, N–CH_3, J_{HH} = 6.4), 1.25, 1.18 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 7.0), 1.22 (t, 3H, CH_3 phos, J_{HH} = 7.1) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 87.3 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165.4–122.1 (m, Ph), 105.22 (d, br, C1 *p*-cym), 97.60 (d, br, C4 *p*-cym), 80.59 (d, C6 *p*-cym, J_{CP} = 4.3), 84.99 (d, C5 *p*-cym, J_{CP} = 6.2), 79.80 (d, C2 *p*-cym, J_{CP} = 2.5), 78.33 (d, br, C3 *p*-cym), 65.82 (d, CH_2, J_{CP} = 12.9), 43.43 (s, N–CH_3), 31.01 (s, CH ^{i}Pr), 22.79, 22.44 (s, CH_3 ^{i}Pr), 18.23 (s, CH_3 *p*-cym), 16.11 (d, CH_3 phos, J_{CP} = 7.2) ppm. Λ_M = 48.8 Ω^{-1} mol^{-1} cm^2. $C_{49}H_{55}BClN_2O_2OsP$ (955.44): C 61.60, H 5.80, N 2.93, Cl 3.71; found C 61.38, H 5.69, N 2.80, Cl 3.84%.

6a: IR (KBr pellet): ν_{NH} = 3287, 3248 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.63–6.62 (m, 25H, Ph), 6.15 (t, br, 1H, NH), 5.67 (d, 2H, HA, HD *p*-cym, J_{AB} = J_{CD} = 5.6 Hz), 5.60 (d, 1H, HC *p*-cym), 5.45 (d, 1H, HB *p*-cym), 5.60, 3.97 (d, br, 2H, NH_2, J_{HH} = 9.5), 4.21–4.01 (m, 6H, CH_2), 2.72 (m, 1H, CH ^{i}Pr), 2.18 (s, 3H, CH_3 *p*-cym), 1.28 (t, 9H, CH_3 phos, J_{HH} = 7.0), 1.27, 1.26 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 6.9) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 89.2 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–115 (m, Ph), 108.01 (d, C1 *p*-cym, J_{CP} = 4.0), 99.94 (s, br, C4 *p*-cym), 86.17 (d, C2 *p*-cym, J_{CP} = 3.2), 83.89 (d, C5 *p*-cym, J_{CP} = 6.3), 81.80 (d, C6 *p*-cym, J_{CP} = 6.5), 78.4 (s, br, C3 *p*-cym), 65.01 (d, CH_2, J_{CP} = 10.5), 30.84 (s, CH ^{i}Pr), 22.66, 22.37 (s, CH_3 ^{i}Pr), 18.51 (s, CH_3 *p*-cym), 16.25 (d, CH_3 phos, J_{CP} = 6.7) ppm. Λ_M = 50.7 Ω^{-1} mol^{-1} cm^2. $C_{46}H_{57}BClN_2O_3OsP$ (953.42): C 57.95, H 6.03, N 2.94, Cl 3.72; found C 57.71, H 5.93, N 2.82, Cl 3.88%.

6b: IR (KBr pellet): ν_{NH} = 3273 (m), 3245 (m, br) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.65–6.52 (m, 30H, Ph), 6.01 (t, br, 1H, NH, J_{HH} = 8.8 Hz), 5.77, 5.44 (d, 2H, NH_2, J_{HH} = J_{HH} = 8.8), 5.72 (d, 2H, HC, HD, *p*-cym, J_{CD} = 5.8), 5.64 (d, 1H, HA *p*-cym, J_{AB} = 5.8), 5.58 (d, 1H, HB *p*-cym), 4.17–3.79 (m, 4H, CH_2), 2.62 (m, 1H, CH ^{i}Pr), 2.05 (s, 3H, CH_3 *p*-cym), 1.32, 1.31 (t, 6H, CH_3 phos), 1.23, 1.21 (d, 6H, CH_3 ^{i}Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 98.9 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 165–115 (m, Ph), 109.61 (s, br, C1 *p*-cym), 97.57 (s, br, C4 *p*-cym), 83.59 (s, br, C3 *p*-cym), 82.73 (s, br, C5 *p*-cym), 80.17 (s, br, C6 *p*-cym), 76.90 (br, C2 *p*-cym), 65.32, 63.55 (d, CH_2, J_{CP} = 9.3, J_{CP} = 7.8), 31.05 (s, CH ^{i}Pr), 22.50, 22.32 (s, CH_3 ^{i}Pr), 18.13 (s, CH_3 *p*-cym), 16.32, 16.11 (d, CH_3 phos, J_{CP} = 7.4, J_{CP} = 8.0) ppm. Λ_M = 51.4 Ω^{-1} mol^{-1} cm^2. $C_{50}H_{57}BClN_2O_2OsP$ (985.47): C 60.94, H 5.83, N 2.84, Cl 3.60; found C 60.76, H 5.91, N 2.95, Cl 3.43%.

2.2.3. [Ru(κ^2–O_2CCH_3)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh$_4$ (**7b**)

A solid sample of hydrazine complex [RuCl(η^6-*p*-cymene)($RNHNH_2$)L]BPh_4 (**1**–**3**) (0.17 mmol) was placed in a 25-mL three-necked round-bottomed flask fitted with a solid-addition side arm containing a slight excess of $Pb(OAc)_4$ (0.18 mmol, 80 mg). Dichloromethane (10 mL) was added, the solution cooled to −30 °C and $Pb(OAc)_4$ portionwise added over 20–30 min to the cold stirring solution. The solution was brought to 0 °C, stirred for 5 min, and then the solvent was removed at 0 °C under reduced pressure. The oil obtained was triturated with ethanol (2 mL) containing $NaBPh_4$ (58 mg, 0.17 mmol) and the resulting solution stirred at 0 °C until a brown solid separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol. Yield: 62 mg (45%). ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.56–6.86 (m, 25H, Ph), 5.59 (d, 2H, HC, HD *p*-cym), 5.42 (d, 2H, HA, HB *p*-cym, J_{AB} = 6.0 Hz), 3.92 (m, 4H, CH_2), 3.13 (d, 3H, CH_3COO, J_{HH} = 2.2), 2.36 (m, 1H, CH ^{i}Pr), 1.84 (s, 3H, CH_3 *p*-cym), 1.34 (t, 6H, CH_3 phos, J_{HH} = 7.8), 1.19 (d, 6H, CH_3 ^{i}Pr) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 144.2 (s) ppm. $^{13}C\{^1H\}$

NMR (CD_2Cl_2, 25 °C): δ = 185.5 (d, br, COO), 165–121 (m, Ph), 113.6 (s, br, C1 *p*-cym), 99.0 (s, br, C4 *p*-cym), 89.2 (d, C2, C6 *p*-cym, J_{CP} = 4.1), 86.7 (d, br, C3, C5 *p*-cym), 64.8 (d, CH_2, J_{CP} = 9.0), 30.9 (s, CH ^{i}Pr), 25.1 (s, br, CH_3COO), 22.7, 22.1 (s, CH_3 ^{i}Pr), 18.45 (s, CH_3 *p*-cym), 16.43 (d, CH_3 phos, J_{CP} = 7.5) ppm. Λ_M = 56.3 Ω^{-1} mol^{-1} cm^2. $C_{46}H_{52}BO_4PRu$ (811.76): C 68.06, H 6.46; found C 67.82, H 6.33%.

2.2.4. [Os(CH_3N_2)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh_4 (**8b**)

This complex was prepared by treating the methylhydrazine complex [Os(η^6-*p*-cymene)(CH_3NHNH_2){PPh(OEt)$_2$}]BPh_4 (**5b**) (0.15 mmol, 139 mg) with $Pb(OAc)_4$ at −30 °C in CH_2Cl_2 following the method used for the synthesis of **7b**. Yield: 84 mg (63%). IR (KBr pellet): ν_{NN} = 1698 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.58–6.87 (m, 25H, Ph), 5.60 (d, 2H, HA, HB *p*-cym, J_{AB} = 6.3 Hz), 5.50 (d, 1H *p*-cym), 5.38 (d, 2H, HC, HD *p*-cym, J_{CD} = 6.3), 4.08–3.74 (m, 4H, CH_2), 3.49 (d, 3H, CH_3N, J_{HH} = 2.5), 2.70 (m, 1H, CH ^{i}Pr), 2.41 (s, 3H, CH_3 *p*-cym), 1.35, 1.33 (t, 6H, CH_3 phos, J_{HH} = 7.0), 1.24 (d, 6H, CH_3 ^{i}Pr, J_{HH} = 7.0) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 110.7 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 164–122 (m, Ph), 113.00 (d, C1 *p*-cym, J_{CP} = 3.6), 98.75 (s, br, C4 *p*-cym), 86.40 (d, C5 *p*-cym, J_{CP} = 2.5), 86.00 (d, C3 *p*-cym, J_{CP} = 1.8), 81.83 (d, C2 *p*-cym, J_{CP} = 4.3), 81.67 (d, C6 *p*-cym, J_{CP} = 3.5), 64.61, 64.50 (d, CH_2, J_{CP} = 7.0), 37.05 (d, CH_3N_2, J_{CP} = 5.7), 32.65 (s, CH ^{i}Pr), 24.45, 24.40 (s, CH_3 ^{i}Pr), 20.02 (s, CH_3 *p*-cym), 16.35, 16.26 (d, CH_3 phos, J_{CP} = 7.3) ppm. Λ_M = 52.9 Ω^{-1} mol^{-1} cm^2. $C_{45}H_{52}BN_2O_2OsP$ (884.92): C 61.08, H 5.92, N 3.17; found C 59.94, H 5.81, N 3.28%.

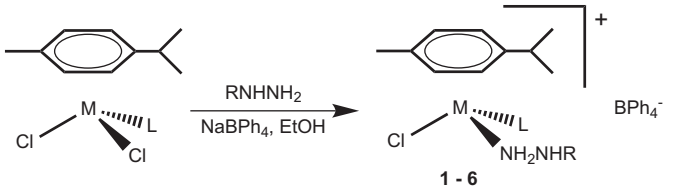
2.2.5. OsCl($CH_3N{=}NH$)(η^6-*p*-cymene){PPh(OEt)$_2$}]$^+BPh_4^-$ (**9b**)

This complex was prepared only in solution by reacting [Os(CH_3N_2)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh_4 (**8b**) (100 mg, 0.11 mmol) in 4 mL of CD_2Cl_2 with a slight excess of HCl (0.12 mmol, 40 μL of a 3 *M* solution in diethylether) at −80 °C. The solution was allowed to reach 0 °C and then NMR spectra were recorded.^{1}H NMR (CD_2Cl_2, 25 °C): δ = 13.6 (s, br, 1H, =NH), 7.70–6.98 (m, 25H, Ph), 5.58, 5.53, 5.40, 5.31 (d, 4H, Ph *p*-cym), 4.13, 3.98 (m, 4H, CH_2), 3.20 (t, 3H, CH_3N=), 2.66 (m, 1H, CH ^{i}Pr), 2.03 (s, 3H, CH_3 *p*-cym), 1.33 (t, 6H, CH_3 phos), 1.21, 1.18 (d, 6H, CH_3 ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 101.02 (s) ppm.

2.3. X-ray crystallography

Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) with graphite monochromated Mo–Kα radiation (λ = 0.71073 Å), and were corrected for Lorentz and polarisation effects. The software SMART [17] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT [18] for integration of intensity of reflections and scaling, and SADABS [19] for empirical absorption correction.

The structures were solved and refined with the Oscail program [20] by Patterson (**6b**) or direct (**7b**) methods and refined by a full-matrix least-squares based on F^2 [21]. For the compound **6b**, the Squeeze program was used to correct the reflection data for the diffuse scattering due to disordered EtOH solvent [22]. Compound **7b** crystallises in the monoclinic $P2_1/n$ space group with two unit formula in the asymmetric unit, and any attempt to look for any other symmetry was unsuccessful. Careful study of the structures showed us true differences between both units (see discussion). Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters, except that on the NH group (in **6b**), which was found in the electronic density map and refined with isotropic displacement parameters. Details of crystal data and structural refinement are given in Table 3.



Scheme 1. M = Ru (**1**–**3**), Os (**4**–**6**); R = H (**1**, **4**), Me (**2**, **5**), Ph (**3**, **6**); L = P(OEt)$_3$ (**a**), PPh(OEt)$_2$ (**b**), PPh_2OEt (**c**).

3. Results and discussion

Half-sandwich dichloro complexes [15] of ruthenium and osmium MCl_2(η^6-*p*-cymene)L react with hydrazine NH_2NH_2 or monosubstituted hydrazines $RNHNH_2$ in the presence of $NaBPh_4$ to give hydrazine derivatives [MCl(η^6-*p*-cymene)($RNHNH_2$)L]BPh_4 (**1**–**6**), which were isolated in good yields and characterised (Scheme 1).

Crucial for the separation of compounds **1**–**6** as solids was the use of equimolar amounts of reagents and starting the reaction at a low temperature. The addition of an excess of hydrazine to the dichloro precursors MCl_2(η^6-*p*-cymene)L caused some decomposition, which led to oily products difficult to purify.

It is worth noting that only one chloride ligand in the MCl_2(η^6-*p*-cymene)L precursors may be substituted by $RNHNH_2$ yielding monohydrazine derivatives **1**–**6**. The use of an excess of hydrazine never yielded bis(hydrazine) complexes [M(η^6-*p*-cymene)($RNHNH_2$)$_2$L]$^{2+}$, but only led to decomposition products.

The hydrazine complexes of Ru and Os [MCl(η^6-*p*-cymene)($RNHNH_2$)L]BPh_4 (**1**–**6**) were obtained as yellow or orange solids, stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes [23]. Analytical and spectroscopic (IR and ^{1}H, ^{31}P, ^{13}C NMR) data support the proposed formulation, which was further confirmed by X-ray crystal structure determination of complex [OsCl(η^6-*p*-cymene)($PhNHNH_2$){PPh(OEt)$_2$}]BPh_4 (**6b**), the ORTEP [24] of which is shown in Fig. 1.

The structure consists of a tetraphenylborate anion (not shown) and a cation formed of an osmium atom η^6-coordinated to a *p*-cymene molecule and to three donor atoms – chloride, phosphonite PPh(OEt)$_2$ and phenylhydrazine-κ-N ligands – leading to the formation of a "three-legged piano stool" structure. Selected bond lengths and angles for the metal environment of the cation are listed in Table 1. The overall geometry of the complex should be considered as octahedral, although the angles P–Os–Cl, N(1)–

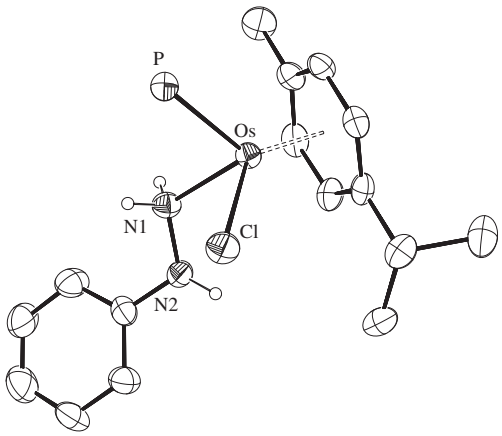


Fig. 1. ORTEP [24] view of the cation of **6b**, drawn at 30% probability level. Tetraphenylborate anion and most hydrogen atoms have been omitted for clarity. Atom labelled as P represents a PPh(OEt)$_2$ group.

Table 1
Selected bond lengths [Å] and angles [°] for **6b**.

Os-CT1	1.7217(2)	Os–P	2.2948(13)
Os–N(1)	2.154(4)	Os–Cl	2.4060(12)
Os–C(21)	2.287(4)	Os–C(24)	2.235(5)
Os–C(22)	2.193(5)	Os–C(25)	2.168(5)
Os–C(23)	2.197(5)	Os–C(26)	2.264(4)
N(1)–N(2)	1.437(5)	N(2)–C(1)	1.415(6)
CT1–Os–N(1)	126.78(11)	N(1)–Os–P	88.39(11)
CT1–Os–P	129.45(3)	N(1)–Os–Cl	81.46(11)
CT1–Os–Cl	129.31(3)	P–Os–Cl	85.78(5)
N(2)–N(1)–Os	114.7(3)	C(1)–N(2)–N(1)	115.9(4)

CT represents the centroid of the benzene ring of the *p*-cymene ligand.

Os–P and N(1)–Os–Cl are more acute than expected, with an average of 85.2(2)°. The lower value, 81.4(2)°, corresponds to the N–Os–Cl angle, and it is noteworthy that a similar effect was found in a recently published benzylideneamine ruthenium complex [25]. Any weak hydrogen bond interaction (not found) or simply steric hindrance of the phosphane ligand could explain this value.

The average Os–C bond distance for the *p*-cymene ligand is 2.224(5) Å, and the distance from the osmium atom to the centroid of the benzene ring of the cymene ligand is 1.7217(2) Å. These values are slightly shorter than those found in other related complexes [26] and show more regularity than other *p*-cymene osmium derivatives. As usual for this kind of complex, the longer value corresponds to the atom labelled as C(21), the isopropyl substituted carbon atom. The Os–P bond length, 2.295(2) Å, is similar to other related complexes [26] and does not need further comment. The Os–N bond distance, 2.154(4) Å, is shorter than those found in other hydrazine osmium complexes [5b,11c,27]. To the best of our knowledge [CSD database, CSD version 5.32 (February 2011 updated)], except for a cluster compound containing a bridging pentafluorophenylhydrazine ligand [28], no other phenylhydrazine osmium complex has been described. The hydrazine ligand adopts a *trans* conformation in the Os–N–N–C group, but the Os–N–N–C torsion angle, 160.6(4)°, is slightly different from the quasi-planar value found in other phenylhydrazine complexes [29]. The N(1)–N(2) bond distance, 1.437(5) Å, is consistent with a N–N single bond, and the N(2)–C(ring) bond distance is slightly shorter, 1.415(6) Å, but still consistent with a sp^3 character for the nitrogen atom. The angles around both nitrogen atoms are very similar, 114.7(3) and 115.9(4)°. These values usually differ more greatly from each other, as found both in a phenylhydrazine molybdenum complex [29], with values of 112.8(4) and 117.4(5)°, or in the cationic osmium complex $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4]^{2+}$ [11c], where the angles around the donor nitrogen atoms are 120° (sp^2 hybridization). Values close to 120° are also found for dinuclear molybdenum complexes with both phenyldiazenido and phenylhydrazine [30].

The IR spectra of hydrazine complexes $[MCl(\eta^6\text{-}p\text{-cymene})(NH_2NH_2)L]BPh_4$ (**1**, **4**) show three medium-intensity bands at 3336–3239 cm^{-1}, attributed to the ν_{NH} of the hydrazine ligand. However, its presence is confirmed by the ^1H NMR spectra, which show two slightly broad multiplets between 4.40 and 3.51 ppm, attributed to the metal-N-bonded NH_2 group. The multiplicity of signals is due to the presence of a chiral centre in the molecule, which makes the two NH_2 protons diastereotopic, with different chemical shifts and J_{HH} values of about 9 Hz. A slightly broad multiplet at 2.73–2.63 ppm is also present in the ^1H NMR spectra which, in a COSY experiment, was correlated with two multiplets at 4.40–3.51 ppm and attributed to the end-on NH_2 group of hydrazine.

The IR spectra of methylhydrazine complexes $[MCl(\eta^6\text{-}p\text{-cymene})(CH_3NHNH_2)L]BPh_4$ (**2**, **5**) show two medium-intensity absorptions at 3317–3261 cm^{-1}, attributed to the ν_{NH} of the methylhydrazine. The ^1H NMR spectra confirm the presence of CH_3NHNH_2, showing two slightly broad multiplets between 5.18 and 3.70 ppm for the NH_2 protons, only one multiplet at 4.29–3.31 ppm of the NH proton, and a sharp doublet at 2.52–2.14 ppm of the methyl substituent of the CH_3NHNH_2 ligand.

The proton signals of the phenylhydrazine ligand in complexes $[MCl(\eta^6\text{-}p\text{-cymene})(PhNHNH_2)L]BPh_4$ (**3**, **6**) fall at a higher frequency than the related hydrazines. In particular, a broad triplet appears at 6.15–5.38 ppm, and was attributed to the NH protons, whereas two slightly broad multiplets, due to the diastereotopic NH_2 protons, appear between 5.77 and 4.38 ppm, fitting the presence of the phenylhydrazine ligand.

The ^1H NMR spectra of all hydrazine complexes **1**–**6** also show the characteristic signals of both *p*-cymene and phosphite ligands, with splitting of some signals due to the presence of a chiral centre in the molecule. The ^{13}C spectra support the presence of the *p*-cymene and phosphite ligands and, in the case of methylhydrazine complexes, also show a singlet at 43.46–43.43 ppm for the methyl substituent. In the temperature range between +20 and −80 °C, the ^{31}P NMR spectra are sharp singlets, matching the proposed formulation for the complexes.

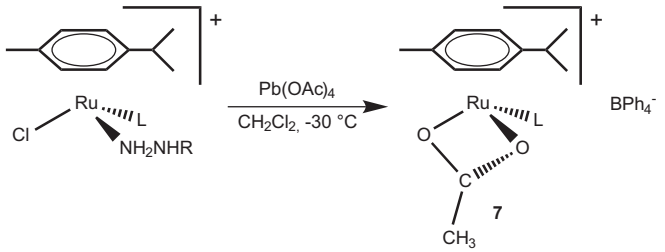
Hydrazine complexes of ruthenium have been reported with several supporting ligands such as phosphine, phosphite, isocyanide, diene, arene and tris(pyrazolyl)borate [1–4,11a,31]. Instead, hydrazine complexes of osmium are rare [8a,11c,27,32] and no example with arene ligands has been reported. The use of $OsCl_2(\eta^6\text{-}p\text{-cymene})L$ as a precursor allowed the first arene osmium hydrazine complexes to be prepared.

Reactivity studies of our hydrazine complexes **1**–**6** towards oxidation with $Pb(OAc)_4$ were undertaken, and the results are shown in Scheme 2 for Ru compounds and Scheme 3 for Os ones.

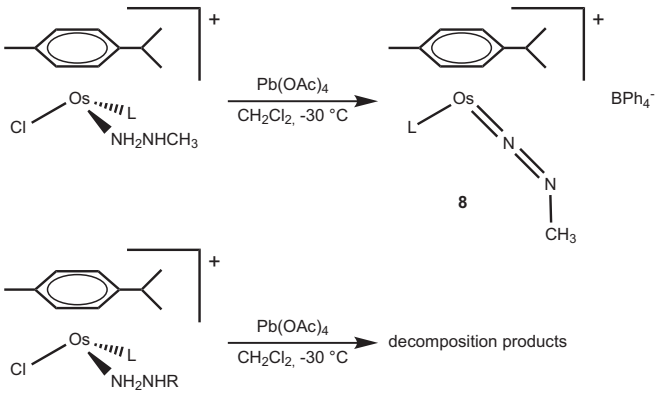
Hydrazine complexes of ruthenium $[RuCl(\eta^6\text{-}p\text{-cymene})(RNHNH_2)L]BPh_4$ (**1**–**3**) react with an equimolar amount of $Pb(OAc)_4$ at −30 °C in CH_2Cl_2 to give a purple solution, from which a reddish solid, characterised as the acetate complex $[Ru(\kappa^2\text{–}O_2CCH_3)(\eta^6\text{-}p\text{-cymene})L]BPh_4$ (**7**), was obtained. The formation of the chelate complex **7** is somewhat surprising, because the coordinated hydrazines are known to undergo oxidation with $Pb(OAc)_4$ to give diazene RN=NH derivatives. However, taking into account the fact that hydrazine complexes **1**–**3** do not react with the acetate ion, the formation of complex **7** may be explained on the basis of the path shown in Scheme 4.

$Pb(OAc)_4$ oxidises the coordinate hydrazine to diazene [**A**], which is probably unstable and can be substituted by the acetate ion. The κ^2-coordination of the CH_3COO^- group gives also rise to substitution of the Cl^- ligand, affording the final $[Ru(\kappa^2\text{–}O_2CCH_3)(\eta^6\text{-}p\text{-cymene})L]BPh_4$ (**7**) derivative.

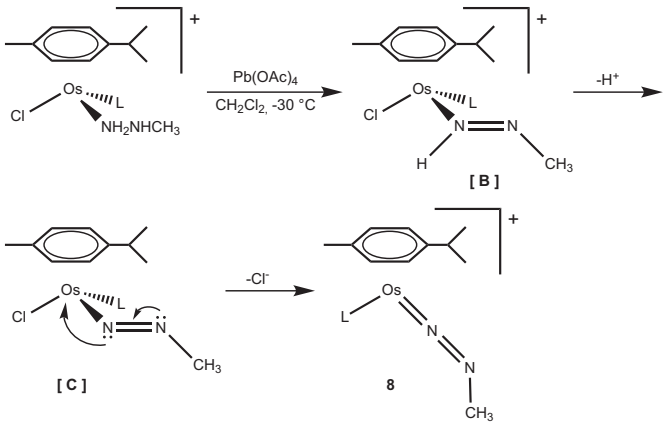
Different behaviour is shown by osmium complexes **4**–**6**, which react with $Pb(OAc)_4$ at −30 °C to give, in the case of the methylhydrazine complex $[OsCl(\eta^6\text{-}p\text{-cymene})(CH_3NHNH_2)L]BPh_4$, an orange solid characterised as the methyldiazenido derivative $[Os(CH_3N_2)(\eta^6\text{-}p\text{-cymene})L]BPh_4$ (**8**) (Scheme 3). Instead, reaction



Scheme 2. R = H, Me, Ph; L = $PPh(OEt)_2$ (**b**).



Scheme 3. R = H, Ph; L = $PPh(OEt)_2$ (**b**).



Scheme 5. L = $PPh(OEt)_2$ (**b**).

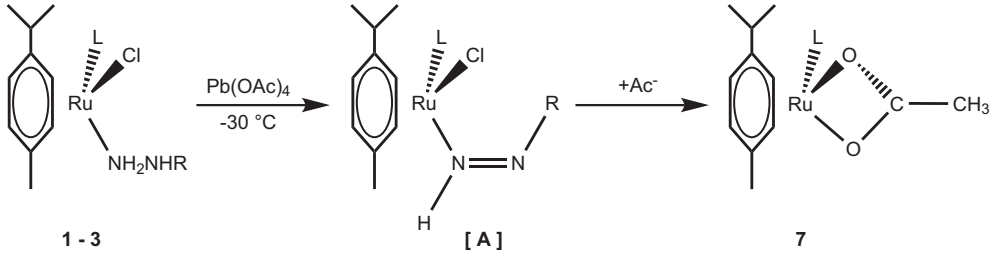
of the hydrazine and phenylhydrazine complexes with $Pb(OAc)_4$ led to an orange solution, from which only intractable oils containing decomposition products were isolated. The formation of methyldiazenido complex **8** from reaction of the methylhydrazine complex with $Pb(OAc)_4$ is not surprising, and may be explained on the basis of oxidation of the coordinate CH_3NHNH_2 to methyldiazene $CH_3N{=}NH$, giving the intermediate complex [**B**] (Scheme 5).

The diazene hydrogen atom is known to be acidic [1,5e,33], and can be deprotonated by the acetate ion present in solution, giving the double-bent methyldiazenido complex [**C**]. A rearrangement of this double-bent ArN_2^- ligand to singly-bent ArN_2^+ should involve a $2e^-$ reduction of the central metal to Os(0), followed by concurrent dissociation of the chloride ligand [5e,33] to give the final cationic methyldiazenido derivative **8**.

Complexes **7** and **8** were isolated as reddish (**7**) or orange (**8**) solids, stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes [23]. Analytical and spectroscopic (IR and ^1H, ^{31}P, ^{13}C NMR) data support the proposed formulations, which were further confirmed by X-ray crystal structure determination of complex $[Ru(\kappa^2{-}O_2CCH_3)(\eta^6\text{-}p\text{-cymene})\{PPh(OEt)_2\}]BPh_4$ (**7b**), the ORTEP [24] of which is shown in Fig. 2.

Compound **7b** crystallises in the monoclinic $P2_1/n$ space group with two tetraphenylborate anions and two cationic metal complexes. In order to show the metal environment, Fig. 2 represents only one of the cationic complexes; Fig. 3 shows the two cationic complexes and their arrangement. Both cations are formed of a ruthenium atom in a classical "three-legged piano stool" structure by means of a η^6-coordinating *p*-cymene molecule, and three donor atoms as legs, a phosphorus atom for a phosphonite $PPh(OEt)_2$ ligand, and two oxygen atoms from a carboxylate anion. Selected bond lengths and angles are listed in Table 2. The geometrical anion parameters are comparable within the margin of error, but the arrangement of the ligands around the ruthenium atom is quite different in both molecules, as will be explained below. Coordination of both ruthenium atoms is best considered as octahedral, with P–Ru–O angles 85.2(1) and 88.6(1)°. The third angle between the legs corresponds to the chelating angle, with an average value of 61.4(2)°, similar to that found in other octahedral carbonate complexes, such as $[Ru(\kappa^2{-}O_2CCH_3)_2\{1,1'\text{-bis(diphenylphosphino)ferrocene}\}]$, average 61.0(2)° [34], the cationic $[Ru(N_3P)(\kappa^2{-}O_2CCH_3)]^+$, 60.61(6)° [35], or the $[Ru(\kappa^2{-}O_2CCH_3)Cl(p\text{-cymene})]$, 60.31(7)° [36].

The coordination of the acetate ligand, with differences between Ru–O bonds of only 0.006 Å (*i.e.* within the margin of error), is much more symmetrical than that found in other acetate complexes [11a,36b,37]. The Ru–O bond lengths are, on average, 2.122(4) Å and are within the limits found in the above-mentioned carboxylate complexes. The Ru–P bond length, on average 2.293(2) Å, is in fact the same value found in other pseudo-octahedral $[Ru(\eta^6\text{-}p\text{-cymene})LL'\{PPh(OEt)_2\}]^+$ cationic compounds [25] and is similar to other related compounds [38]. The average Ru–C bond distance is 2.209(6) Å for the ruthenium atom labelled as Ru(1) and slightly longer, 2.218(7) Å, for the ruthenium atom labelled as Ru(2) (Table 2). This may be an effect of the different arrangement of the ligands around the metal (see below). In any case, these values are in average slightly shorter than those found in other *p*-cymene ruthenium complexes [15,38,39]. The Ru–centroid arene ring distances are 1.7085(5) and 1.7152(5) Å, respectively, also perhaps as a consequence of the different arrangement of the ligands around the metal. These differences are clear in Fig. 3. The *p*-cymene ligand, in the molecule containing Ru(1), is much more planar than in the molecule containing Ru(2), with rms deviation of 0.009 or 0.032, respectively. In the molecule containing Ru(1), the longest Ru–C bond length is that quasi-*trans* to the phosphane ligand labelled as C(22), 2.243(5) Å and the two substituted (^{i}Pr or Me) carbon atoms are both at 2.219(6) Å from the metal. Other $Ru{-}C_{ring}$ bond lengths are shorter. But in the molecule containing Ru(2), the longest Ru–C bond length is the methyl-substituted carbon, since two influences are found at this atom, the *trans*



Scheme 4. L = $PPh(OEt)_2$ (**b**).

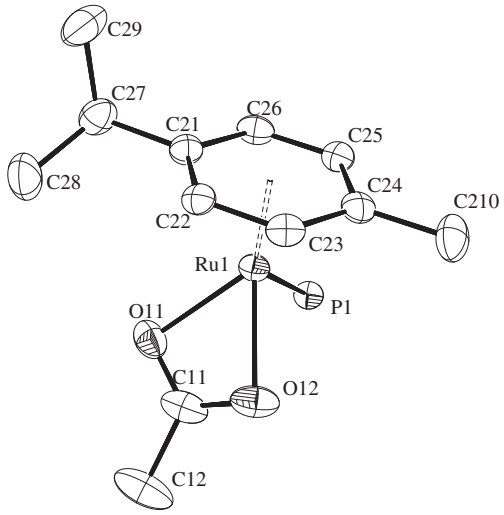


Fig. 2. ORTEP [24] view of one of the cations found in the asymmetric unit of **7b**, drawn at 20% probability level. Tetraphenylborate anion and hydrogen atoms have been omitted for clarity.

influence of the phosphane ligand and the fact of being substituted by a methyl group. The arrangement of the substituents at the phosphane ligand is also quite different, as Fig. 3 shows. In the molecule containing Ru(1), the phenyl ring is as far as possible from the acetate ligand and apparently parallel to the *p*-cymene ring, although the dihedral angle between best planes is 24.3(2)°. In the molecule containing Ru(2), the phenyl ring is as far as possible from the *p*-cymene ligand and almost perpendicular to it, with a dihedral angle between best planes of 89.6(2)°. The position of the phenyl ring and one ethoxy group are interchangeable, and this allows the different arrangement of the *p*-cymene ligand in the solid state.

Besides the signals characteristic of the *p*-cymene, phosphine and BPh_4 anion, the ^1H NMR spectrum of [Ru(κ^2–O_2CCH_3)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh_4 (**7b**) shows a doublet at 3.13 ppm, which was attributed to the methyl group of the κ^2–CH_3COO^- ligand. In a HMQC experiment, this signal was correlated with a singlet at 25.1 ppm in the ^{13}C NMR spectrum, matching the proposed assignment. The ^{13}C spectrum also shows a doublet at 185.5 ppm, due to the carbonyl carbon resonance of the acetate ligand, whereas the ^{31}P spectrum appears as a sharp singlet, as expected for a geometry in solution like that observed in the solid state.

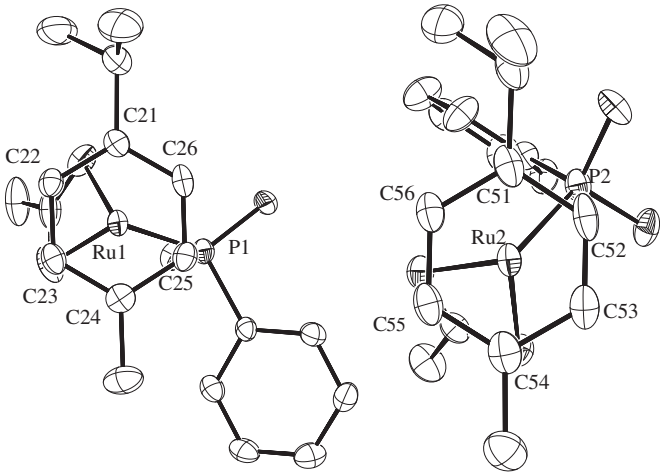


Fig. 3. The different arrangement of the ligands in the two cations found in the asymmetric unit of **7b** (drawn along the Ru-CT vector). Only labelling scheme of the *p*-cymene ligands is shown. Ethyl groups on the phosphane are not show for clarity.

Table 2
Selected bond lengths [Å] and angles [°] for **7b**.

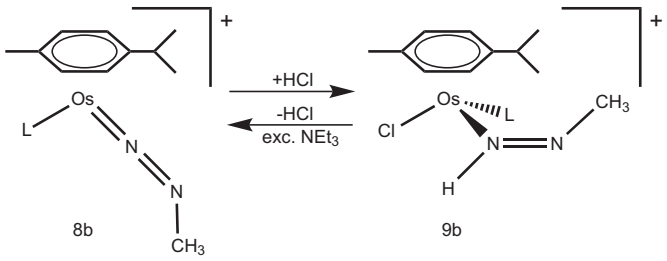
Ru(1)–CT1	1.7085(5)	Ru(2)–CT2	1.7152(5)
Ru(1)–C(21)	2.219(6)	Ru(2)–C(51)	2.248(6)
Ru(1)–C(22)	2.243(5)	Ru(2)–C(52)	2.173(6)
Ru(1)–C(23)	2.193(5)	Ru(2)–C(53)	2.179(6)
Ru(1)–C(24)	2.219(6)	Ru(2)–C(54)	2.285(7)
Ru(1)–C(25)	2.192(6)	Ru(2)–C(55)	2.243(6)
Ru(1)–C(26)	2.190(6)	Ru(2)–C(56)	2.182(6)
Ru(1)–O(12)	2.121(4)	Ru(2)–O(41)	2.117(4)
Ru(1)–O(11)	2.127(4)	Ru(2)–O(42)	2.121(4)
Ru(1)–P(1)	2.2966(15)	Ru(2)–P(2)	2.2884(16)
C(11)–O(12)	1.267(9)	C(41)–O(41)	1.245(7)
C(11)–O(11)	1.275(9)	C(41)–O(42)	1.281(7)
C(12)–C(11)	1.501(9)	C(41)–C(42)	1.484(8)
CT1–Ru(1)–O(12)	132.99(13)	CT2–Ru(2)–O(41)	132.36(11)
CT1–Ru(1)–O(11)	135.94(13)	CT2–Ru(2)–O(42)	133.20(11)
O(12)–Ru(1)–O(11)	61.7(2)	O(41)–Ru(2)–O(42)	60.99(16)
CT1–Ru(1)–P(1)	128.22(5)	CT2–Ru(2)–P(2)	131.05(5)
O(12)–Ru(1)–P(1)	88.26(13)	O(41)–Ru(2)–P(2)	88.91(11)
O(11)–Ru(1)–P(1)	86.74(12)	O(42)–Ru(2)–P(2)	85.74(12)

CT represents the centroid of the benzene ring of the *p*-cymene ligand.

The IR spectrum of methyldiazenido complex [Os(CH_3N_2)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh_4 (**8b**) shows a strong band at 1698 cm^{-1}, attributed to the ν_{NN} of the methyldiazenido ligand. A comparison of this ν_{NN} value with those of known alkyl- and aryldiazenido complexes (1730–1660 cm^{-1}) [5e,f,33,40–42], whose structures were determined by X-ray analysis, also suggests the presence of

Table 3
Crystal data and structure refinement.

Identification code	**6b**	**7b**
Empirical formula	$C_{50}H_{57}BClN_2O_2OsP$	$C_{92}H_{104}B_2O_8P_2Ru_2$
Formula weight	985.41	1623.45
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	*P*–1	$P2_1/n$
Unit cell dimensions	a = 11.6146(15) Å	a = 9.6018(9) Å
	b = 12.3314(16) Å	*b* = 20.2416(18) Å
	c = 17.946(2) Å	*c* = 43.328(4) Å
	α = 93.211(2)°	α = 90°
	β = 91.902(2)°	β = 92.398(2)°
	γ = 108.219(2)°	γ = 90°
Volume	2434.1(5) $Å^3$	8413.6(13) $Å^3$
Z	2	4
Density (calculated)	1.344 Mg/m^3	1.282 Mg/m^3
Absorption coefficient	2.745 mm^{-1}	0.451 mm^{-1}
F(000)	1000	3392
Crystal size	0.28 × 0.20 × 0.19 mm	0.46 × 0.25 × 0.19 mm
Theta range for data collection	1.74–25.03 °	1.38–25.01 °
Index ranges	$-13 \le h \le 13$; $-14 \le k \le 14$; $-21 \le l \le 21$	$-11 \le h \le 11$; $-20 \le k \le 24$; $-47 \le l \le 51$
Reflections collected	18242	44446
Independent reflections	8496 [R (int) = 0.0395]	14795 [R (int) = 0.0887]
Reflections observed (>2σ)	6625	7145
Data Completeness	0.988	0.997
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.817	1.000 and 0.857
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8496/0/532	14795/0/967
Goodness-of-fit on F^2	0.975	0.984
Final R indices [I > 2σ(I)]	R_1 = 0.0351	R_1 = 0.0510
	wR_2 = 0.0702	wR_2 = 0.1032
R indices (all data)	R_1 = 0.0533	R_1 = 0.1447
	wR_2 = 0.0763	wR_2 = 0.1419
Largest diff. peak and hole	1.256 and −0.554 e $Å^{-3}$	0.646 and −0.474 e $Å^{-3}$



Scheme 6. L = $PPh(OEt)_2$.

a singly-bent methyldiazenido ligand, formally present as $CH_3N_2^+$. The metal centre thus appears to be in a formal oxidation state of zero [Os(0)].

Besides the characteristic signals of the supporting ligands *p*-cymene and $PPh(OEt)_2$ and of the BPh_4 anion, the ^1H NMR spectrum of **8b** shows a singlet at 3.49 ppm, attributed to the methyl substituent of the methyldiazenido ligand. The ^{13}C NMR spectrum supports the presence of these ligands, showing a doublet at 37.05 ppm which, in a HMQC experiment, was correlated with the singlet at 3.49 ppm observed in the proton spectrum and attributed to the methyl carbon resonance of the diazo CH_3N_2 ligand. The spectrum also shows the signals of the *p*-cymene and phosphonite carbon resonances, whereas the ^{31}P NMR spectrum appears as a sharp singlet, fitting the proposed formulation for 16-electron methyldiazenido derivative **8b**.

Complex $[Os(CH_3N_2)(\eta^6\text{-}p\text{-cymene})\{PPh(OEt)_2\}]BPh_4$ (**8b**) reacts with Brønsted acid HCl to give the methyldiazene complex $[OsCl(CH_3N{=}NH)(\eta^6\text{-}p\text{-cymene})\{PPh(OEt)_2\}]BPh_4$ (**9b**), as shown in Scheme 6.

The reaction proceeds with protonation of the diazenido at the Nα nitrogen atom, to give the methyldiazene ligand $CH_3N{=}NH$. The reaction results in an oxidative addition, giving an osmium(II) central metal, which adds Cl^- to give the final complex $[OsCl(CH_3N{=}NH)(\eta^6\text{-}p\text{-cymene})\{PPh(OEt)_2\}]^+BPh_4^-$ (**9b**). Unfortunately, this species is quite unstable and cannot be isolated in the solid state. However, monitoring the progress of the reaction between methyldiazenido complex **8b** and HCl, by ^1H NMR, a slightly broad signal appears at 13.6 ppm, characteristic of the diazene hydrogen resonance [11c,e,f]. As the signals of the diazenido **8b** species disappear, a triplet at 3.20 ppm does appear which, in a COSY experiment, was correlated with the diazene signal at 13.6 ppm and was attributed to the methyl group of the $CH_3N{=}NH$ ligand. In the proton spectrum, new signals for the *p*-cymene and phosphonite ligands also appear, whereas a new singlet at 101.02 ppm was observed in the ^{31}P spectrum, matching the proposed formulation for **9b**. It is worth noting that the addition of an excess of NEt_3 to a solution containing methyldiazene complex $[OsCl(CH_3N{=}NH)(\eta^6\text{-}p\text{-cymene})\{PPh(OEt)_2\}]^+BPh_4^-$ (**9b**) caused the solution to change colour, with the formation of methyldiazenido derivative $[Os(CH_3N_2)(\eta^6\text{-}p\text{-cymene})\{PPh(OEt)_2\}]^+BPh_4^-$ (**8b**). NEt_3 deprotonates methyldiazene $CH_3N{=}NH$ in **9b**, with the concurrent loss of Cl^- and formation of methyldiazenido complex **8b**, as shown in Scheme 6.

These results further support the formulation of complex **9b** as containing a methyldiazene ligand, stabilised by the half-sandwich fragment $[OsCl(\eta^6\text{-}p\text{-cymene})L]$.

4. Conclusions

A facile method for the synthesis of hydrazine complexes of ruthenium and osmium, stabilised by the *p*-cymene ligand, is reported. Oxidation with $Pb(OAc)_4$ allowed acetate $[Ru(\kappa^2\text{–}O_2CCH_3)(\eta^6\text{-}p\text{-cymene})L]BPh_4$ and methyldiazenido complexes $[Os(CH_3N_2)(\eta^6\text{-}p\text{-cymene})L\}]BPh_4$ to be prepared. Half-sandwich methyldiazene cations $[OsCl(CH_3N{=}NH)(\eta^6\text{-}p\text{-cymene})L\}]^+$ were also obtained from the reaction of methyldiazenido complexes with HCl.

Acknowledgement

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Appendix A. Supplementary material

CCDC 830874 and 830875 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.ac.uk/conts/retrieving.html.

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