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Preparation of imine complexes of ruthenium and osmium stabilised by $[MCl(\eta^6\text{-}p\text{-cymene})(PR_3)]^+$ fragments

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ABSTRACT

Imine complexes $[MCl(\eta^6\text{-}p\text{-cymene})\{\eta^1\text{-}NH{=}C(H)Ar\}(PR_3)]BPh_4$ (**1**–**3**) [M = Ru, Os; PR_3 = $PPh(OEt)_2$, PPh_2OEt; Ar = Ph, *p*-tolyl] were prepared by reacting $MCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)$ precursors with benzyl azide $ArCH_2N_3$ in the presence of $NaBPh_4$. Benzophenone-imine complexes $[MCl(\eta^6\text{-}p\text{-cymene})\{\eta^1\text{-}NH{=}CPh_2\}(PR_3)]BPh_4$ (**4**–**6**) [M = Ru, Os; PR_3 = $PPh(OEt)_2$, PPh_2OEt] were also prepared by allowing $MCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)$ to react with $Ph_2C{=}NH$ in the presence of $NaBPh_4$. The complexes were characterised spectroscopically (IR, ^1H, ^{13}C, ^{31}P, ^{15}N NMR) and by X-ray crystal structure determination of $[RuCl(\eta^6\text{-}p\text{-cymene})\{\eta^1\text{-}NH{=}C(H)\text{-}p\text{-tolyl}\}\{PPh(OEt)_2\}]BPh_4$ (**1b**).

1. Introduction

Reaction of organic azides RN_3 toward transition metal complexes have attracted considerable attention in recent years due to the rich chemistry of these systems and the variety of complexes which can be obtained [1–8]. In the first step of the interaction between RN_3 and the metal fragment, organic azide is believed to η^1-coordinate to the metal centre and, in some cases, the corresponding complexes have been isolated and characterised [6–8]. Extrusion of N_2 from these intermediates gave terminal metal imido complexes, a common final product from reactions of organic azide with transition metal complexes [1,2d,4a,d,6]. Metal imine species [M]–NH=C(H)Ar have also recently been obtained from coordinate benzyl azide [M]–N_3CH_2Ar [9], after loss of N_2. Insertion of azide into a metal-hydride bond to give stable triazenide [M]–N(H)NNR derivatives has been observed in tungsten and hafnium complexes [2a,4c], and the insertion of RN_3 into M–CO bonds to give isocyanate is also known [1d,2d,f]. Lastly, tetraazabutadiene [M]–RN=N–N=NR complexes have been prepared from reaction of a metal fragment and an excess of organic azide [2c,3a,b,4a,b].

We are interested in the chemistry of "diazo" and "triazo" complexes of transition metals [10] and have recently reported the reactivity of Mn, Re, and Ir derivatives toward organic azides, which yielded azide, imine, and tetraazabutadiene complexes [9]. Now we have extended these studies to include half-sandwich complexes of ruthenium and osmium, in order to test the behaviour of organic azide towards this class of compounds. The results, which allowed the synthesis of unprecedented N-protio imine complexes stabilised by *p*-cymene metal fragments, are reported here.

2. Experimental

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. $RuCl_3{\cdot}3H_2O$ and $(NH_4)_2OsCl_6$ salts were Pressure Chemical Co. (USA) products, used as received. Phosphites $PPh(OEt)_2$ and PPh_2OEt were prepared by the method of Rabinowitz and Pellon [11]. Benzyl and phenyl azides [12] were prepared following methods previously reported. The labelled $C_6H_5CH_2{}^{15}N_3$ azide was prepared following the same method, by reacting $Na[^{15}NNN]$ (98% enriched, CIL) with benzyl bromide, $C_6H_5CH_2Br$. Equimolar mixtures of $C_6H_5CH_2{}^{15}NNN$ and $C_6H_5CH_2NN^{15}N$ were obtained. 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 (^1H, ^{31}P, ^{13}C, ^{15}N) were obtained on AC200 or AVANCE

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300 Bruker spectrometers at temperatures between −80 and +30 °C, unless otherwise noted. ^{1}H and ^{13}C{^{1}H} spectra are referred to internal tetramethylsilane; ^{31}P{^{1}H} chemical shifts are reported with respect to 85% H_3PO_4, while ^{15}N with respect to $CH_3{}^{15}NO_2$, in both cases with downfield shifts considered positive. The COSY, HMQC and HMBC NMR experiments were performed using their standard programs. The SwaNMR and iNMR software packages [13] were used to treat NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C 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 precursor complexes

Complexes $MCl_2(\eta^6$-*p*-cymene)(PR_3) [M = Ru, Os; PR_3 = $PPh(OEt)_2$, PPh_2OEt] were prepared following the reported method [14].

2.3. Synthesis of complexes

2.3.1. [RuCl(η^6-*p*-cymene){η^1-NH=C(H)Ar}(PR_3)]BPh_4 (**1**, **2**) [PR_3 = $PPh(OEt)_2$ (**1**), PPh_2OEt (**2**); Ar = C_6H_5 (**a**), 4-$CH_3C_6H_4$ (**b**)]

An excess of the benzyl azide $ArCH_2N_3$ (1.2 mmol, 0.8 mL of a 1.5 M solution in ethanol) was added to a solution of the appropriate complex $RuCl_2(\eta^6$-*p*-cymene)(PR_3) (0.4 mmol) in ethanol (10 mL) containing a slight excess of $NaBPh_4$ (0.6 mmol, 0.205 g). The reaction mixture was stirred for 24 h and then the solution concentrated to about 4 mL by evaporation of the solvent under reduced pressure. By slow cooling to −25 °C of the resulting solution, a yellow solid separated out which was filtered and crystallised from CH_2Cl_2 and ethanol. Suitable crystals for X-ray analysis of **1b** were obtained by slow diffusion of ethanol into a CH_2Cl_2 solution of the complex. Yield: 236 mg (66%) for **1a**, 258 mg (71%) for **1b**, 255 mg (68%) for **2b**.

Compound **1a**: IR (KBr pellet) ν_{NH}: 3252 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 8.72 (d, br, 1H, NH), 8.15 (d, 1H, =CH), 7.58–6.85 (m, 30H, Ph), 5.58, 5.56, 5.47, 5.23 (d, 4H, Ph *p*-cym), 4.18, 4.04, 4.00 (m, 4H, CH_2), 2.72 (m, 1H, CH *p*-cym), 2.06 (s, 3H, CH_3 *p*-cym), 1.42, 1.41 (t, 6H, CH_3 phos), 1.26, 1.24 (d, 6H, CH_3 ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 147.0 ppm. Λ_M = 53.8 Ω^{-1} mol^{-1} cm^2. Anal. Calc. for $C_{51}H_{56}BClNO_2PRu$ (893.30): C, 68.57; H, 6.32; Cl, 3.97; N, 1.57. Found: C, 68.49; H, 6.42; Cl, 3.75; N, 1.69%. Compound **1b**: IR (KBr pellet) ν_{NH}: 3247 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 8.51 (d, br, 1H, NH), 8.08 (d, 1H, J_{HH} = 21 Hz, =CH), 7.58–6.86 (m, 29H, Ph), 5.59, 5.54, 5.44, 5.23 (d, 4H, Ph *p*-cym), 4.18, 4.01 (m, 4H, CH_2), 2.69 (m, 1H, CH *p*-cym), 2.41 (s, 3H, CH_3 *p*-tol), 2.04 (s, 3H, CH_3 *p*-cym), 1.41, 1.40 (t, 6H, CH_3 phos), 1.25, 1.23 (d, 6H, CH_3 ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 147.1 ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 176.2 (s, =CH), 165–122 (m, Ph), 115.3 (s, C1), 106.2 (s, C4), 92.39, 92.32, 89.09 (s, C3), 90.12, 90.09, 88.69 (s, C2), 65.2, 64.7 (d, CH_2), 31.24 (s, CH *p*-cym), 22.3, 22.2 (s, CH_3 ^{i}Pr), 21.89 (d, CH_3 *p*-tol), 18.64 (s, CH_3 *p*-cym), 16.4 (d, CH_3 phos) ppm. Λ_M = 52.5 Ω^{-1} mol^{-1} cm^2. Anal. calc. for $C_{52}H_{58}BClNO_2PRu$ (907.33): C, 68.83; H, 6.44; Cl, 3.91; N, 1.54. Found: C, 68.66; H, 6.36; Cl, 3.72; N, 1.39%. Compound **2b**: IR (KBr pellet) ν_{NH}: 3269 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 10.06 (d, br, 1H, NH), 8.61 (d, 1H, J_{HH} = 21 Hz, =CH), 7.65–6.87 (m, 34H, Ph), 5.77, 5.65, 5.45, 5.39 (d, 4H, Ph *p*-cym), 3.90–3.75 (m, 2H, CH_2), 2.62 (m, 1H, CH *p*-cym), 2.45 (s, 3H, CH_3 *p*-tol), 2.07 (s, 3H, CH_3 *p*-cym), 1.29, 1.26 (t, 3H, CH_3 phos), 1.24, 1.21 (d, 6H, CH_3 ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 123.4 ppm. Λ_M = 55.0 Ω^{-1} mol^{-1} cm^2. Anal. Calc. for $C_{56}H_{58}BClNOPRu$ (939.37): C, 71.60; H, 6.22; Cl, 3.77; N, 1.49. Found: C, 71.73; H, 6.12; Cl, 3.59; N, 1.40%.

2.3.2. [RuCl(η^6-*p*-cymene){η^1-^{15}NH=C(H)C_6H_5}$(PPh(OEt)_2)$]BPh_4 (**1a$_1$**)

This complex was prepared exactly like the related unlabelled compound **1a**, using $C_6H_5CH_2{}^{15}N_3$ as a reagent; yield 215 mg (60%). IR (KBr pellet) ν_{NH}: 3242 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: ABXY spin system (A = ^{31}P, B = ^{15}N, X, Y = ^{1}H), δ_X 8.71 (1H, NH), δ_Y 8.15 (1H, =CH), J_{AB} = 7.8, J_{AX} = 2.3, J_{AY} = 0.1, J_{BX} = 72.7, J_{BY} = 0.94, J_{XY} = 21.8 Hz, 7.57–6.87 (m, 30H, Ph), 5.58, 5.56, 5.48, 5.23 (d, 4H, Ph *p*-cym), 4.18, 4.05, 4.00 (m, 4H, CH_2), 2.72 (m, 1H, CH *p*-cym), 2.06 (s, 3H, CH_3 *p*-cym), 1.42, 1.41 (t, 6H, CH_3 phos), 1.26, 1.24 (d, 6H, CH_3 ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: AB spin system, δ_A 147.1 ppm, J_{AB} = 7.8 Hz. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 177.0 (d, $J_{13_C15_N}$ = 72.5 Hz, =CH), 165–122 (m, Ph), 115.34 (s, C1), 106.15 (s, C4), 92.48, 92.34, 89.01 (s, C3), 89.97, 89.91, 88.61, 88.50 (s, C2), 65.35, 64.8 (d, CH_2), 31.23 (s, CH *p*-cym), 22.4, 22.3 (s, CH_3 ^{i}Pr), 18.6 (s, CH_3 *p*-cym), 16.4 (d, CH_3 phos) ppm. ^{15}N NMR (CD_2Cl_2, 25 °C) δ: −177.6 (dd) ppm, $J_{^{15}N^{31}P}$ = 7.8, $J_{^{15}N^1H}$ = 72.7 Hz.

2.3.3. [OsCl(*p*-cymene){η^1-NH=C(H)C_6H_4-4-CH_3}$(PPh(OEt)_2)$]BPh_4 (**3b**)

An excess of 4-$CH_3C_6H_4CH_2N_3$ (0.74 mmol, 0.62 mL of a 1.2 M solution in ethanol) was added to a solution of complex $OsCl_2(\eta^6$-*p*-cymene)$[PPh(OEt)_2]$ (0.15 g, 0.25 mmol) in 5 mL of ethanol containing an excess of $NaBPh_4$ (0.35 mmol, 0.12 g). The reaction mixture was stirred for 36 h and then the solvent removed under reduced pressure to about 2.5 mL. By slow cooling to −25 °C of the resulting solution, a yellow solid separated out which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 162 mg (65%). IR (KBr pellet) ν_{NH}: 3253 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 9.16 (d, br, 1H, NH), 8.04 (d, 1H, =CH), 7.55–6.87 (m, 29H, Ph), 5.81, 5.75, 5.73, 5.52 (d, 4H, Ph *p*-cym), 4.16, 4.01, 3.98, 3.92 (m, 4H, CH_2), 2.69 (m, 1H, CH *p*-cym), 2.44 (s, 3H, CH_3 *p*-tol), 2.20 (s, 3H, CH_3 *p*-cym), 1.43, 1.38 (t, 6H, CH_3 phos), 1.29, 1.27 (d, 6H, CH_3 ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 99.2 ppm. Λ_M = 49.6 Ω^{-1} mol^{-1} cm^2. Anal. Calc. for $C_{52}H_{58}BClNO_2OsP$ (996.49): C, 62.68; H, 5.87; Cl, 3.56; N, 1.41. Found: C, 62.50; H, 5.99; Cl, 3.37; N, 1.34%.

2.3.4. [RuCl(η^6-*p*-cymene)(η^1-NH=CPh_2)(PR_3)]BPh_4 (**4**, **5**) [PR_3 = $PPh(OEt)_2$ (**4**), PPh_2OEt (**5**)]

In a 25-mL three-necked round-bottomed flask were placed 0.25 mmol of $RuCl_2(\eta^6$-*p*-cymene)(PR_3), an excess of $NaBPh_4$ (0.4 mmol, 137 mg), and 4 mL of ethanol. An excess of benzophenone-imine Ph_2C=NH (0.5 mmol, 84 μL) was added to the resulting suspension, which was stirred for 24 h. A yellow solid separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol. Yield: 213 mg (88%) for **4**, 218 mg (87%) for **5**.

Compound **4**: IR (KBr pellet) ν_{NH}: 3239 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 8.80 (s, br, 1H, NH), 7.72–6.86 (m, 35H, Ph), 5.22, 5.21, 5.06, 5.05 (d, 4H, Ph *p*-cym), 4.25, 4.13 (m, 4H, CH_2), 2.63 (m, 1H, CH *p*-cym), 1.98 (s, 3H, CH_3 *p*-cym), 1.47, 1.46 (t, 6H, CH_3 phos), 1.15, 1.14 (d, 6H, CH_3 ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 145.2 ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 185.24 (s, =CH), 165–118 (m, Ph), 118.09 (s, C1), 104.43 (s, C4), 91.34, 91.25, 89.36 (s, C3), 89.97, 89.94, 88.08 (s, C2), 65.96, 65.76 (d, CH_2), 31.3 (s, CH *p*-cym), 22.69, 21.57 (s, CH_3 ^{i}Pr), 18.72 (s, CH_3 *p*-cym), 16.5 (d, CH_3 phos) ppm. Λ_M = 52.5 Ω^{-1} mol^{-1} cm^2. Anal. Calc. for $C_{57}H_{60}BClNO_2PRu$ (969.40): C, 70.62; H, 6.24; Cl, 3.66; N, 1.44. Found: C, 70.44; H, 6.35; Cl, 3.37; N, 1.56%. Compound **5**: IR (KBr pellet) ν_{NH}: 3244 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 8.64 (s, br, 1H, NH), 7.67–6.87 (m, 40H, Ph), 5.42, 5.37, 4.99, 4.36 (d, 4H, Ph *p*-cym), 4.09, 3.77 (m, 2H, CH_2), 2.67 (m, 1H, CH *p*-cym), 2.12 (s, 3H, CH_3 *p*-cym), 1.43 (t, 3H, CH_3 phos), 1.23, 1.19 (d, 6H, CH_3 ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 128.3 ppm. Λ_M = 53.6 Ω^{-1} mol^{-1} cm^2. Anal. Calc. for $C_{61}H_{60}BClNOPRu$

(1001.44): C, 73.16; H, 6.04; Cl, 3.54; N, 1.40. Found: C, 72.97; H, 6.13; Cl, 3.68; N, 1.31%.

*2.3.5. [OsCl(η^6-p-cymene)(η^1-NH=CPh$_2$){PPh(OEt)$_2$}]BPh$_4$ (**6**)*

This complex was prepared exactly like the related ruthenium complexes **4**, **5** and was crystallised from CH_2Cl_2 and ethanol; yield 214 mg (81%). IR (KBr pellet) ν_{NH}: 3216 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 9.78 (s, br, 1H, NH), 7.64–6.87 (m, 35H, Ph), 5.88, 5.79, 5.23, 5.20 (d, 4H, Ph *p*-cym), 4.13, 4.09 (m, 4H, CH_2), 2.54 (m, 1H, CH *p*-cym), 2.11 (s, 3H, CH_3 *p*-cym), 1.45 (t, 6H, CH_3 phos), 1.18, 1.10 (d, 6H, CH_3 ^{i}Pr) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ: 99.5 ppm. Λ_M = 50.1 Ω^{-1} mol^{-1} cm^2. Anal. Calc. for $C_{57}H_{60}BClNO_2OsP$ (1058.56): C, 64.67; H, 5.71; Cl, 3.35; N, 1.32. Found: C, 64.45; H, 5.61; Cl, 3.16; N, 1.44%.

2.4. X-ray crystallography

Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) using graphite monochromated Mo Kα radiation (λ = 0.71073 Å), and were corrected for Lorentz and polarisation effects. The software SMART [15] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT [16] for integration of intensity of reflections and scaling, and SADABS [17] for empirical absorption correction.

The structure was solved and refined with the Oscail program [18] by direct methods and refined by a full-matrix least-squares based on F^2 [19]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. Details of crystal data and structural refinement are given in Table 1.

Table 1
Crystal data and structure refinement for **1b**.

Empirical formula	$C_{52}H_{58}BClNO_2PRu$
Formula weight	907.29
Temperature (K)	293(2)
Wavelength (Å^3)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 9.9778(10) Å b = 11.1865(11) Å c = 12.1480(12) Å α = 90.174(2)° β = 106.724(2)° γ = 112.967(2)°
Volume (Å^3)	1185.4(2)
Z	1
$D_{calc.}$	1.271 Mg/m^3
Absorption coefficient	0.460 mm^{-1}
F(0 0 0)	474
Crystal size	0.21 × 0.19 × 0.16 mm
θ range for data collection	1.77 to 28.06°
Index ranges	$-13 \leqslant h \leqslant 13$; $-14 \leqslant k \leqslant 14$; $-815 \leqslant l \leqslant 16$
Reflections collected	10 803
Independent reflections	9683 [R(int) = 0.0282]
Reflections observed (>2σ)	5542
Data completeness	0.971
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.828
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9683/3/538
Goodness-of-fit on F^2	0.870
Final i indices [I > 2σ(I)]	R_1 = 0.0496 wR_2 = 0.0723
R indices (all data)	R_1 = 0.1043 wR_2 = 0.0861
Absolute structure parameter	−0.03(2)
Largest diff. peak and hole (e Å^{-3})	0.527 and −0.547

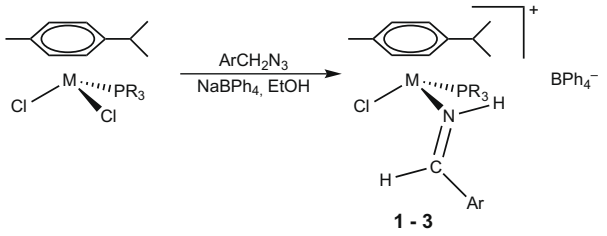
3. Results and discussion

p-Cymene complexes MCl$_2$(η^6-*p*-cymene)(PR$_3$) react with benzyl azide, ArCH$_2$N$_3$, in the presence of NaBPh$_4$, to give yellow solids which were characterised as the imine derivatives [MCl(η^6-*p*-cymene){η^1-NH=C(H)Ar}(PR$_3$)]BPh$_4$ (**1**–**3**) (Scheme 1).

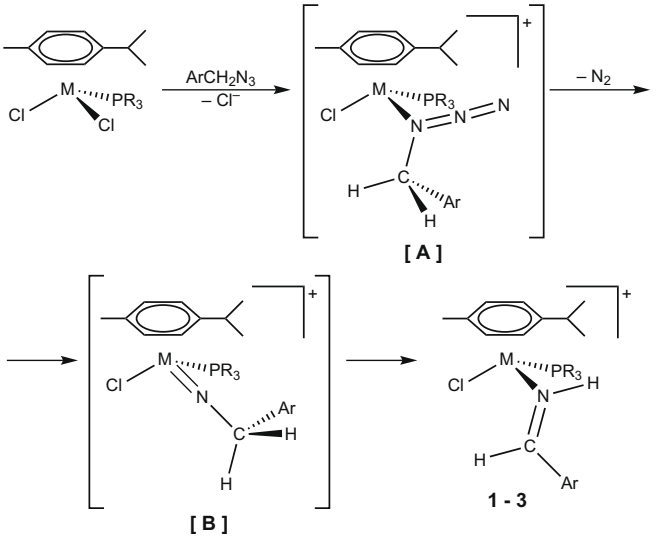
The formation of imine complexes was somewhat unexpected, but may be explained as due to the initial coordination of the benzyl azide with the metal centre [9], to give an unstable azide derivative [**A**] (Scheme 2).

Extrusion of N$_2$ in the coordinate azide species [**A**] may give the benzyl imido intermediate [**B**], which undergoes tautomerisation (1,2-H shift) to afford the final imine derivatives **1**–**3**. In order to support the pathway of Scheme 2, we attempted either to isolate the azide intermediate [**A**] or, at least, to obtain spectroscopic data supporting its formation. Unfortunately, no evidence of coordination of ArCH$_2$N$_3$ was obtained by monitoring the progress of the reaction by NMR spectra, and the only signals observed, in the case of ruthenium, were those of the final imine complexes **1** and **2**. Instead, in the case of osmium, when the reaction was carried out at 0 °C, we did isolate a raw product, the IR spectrum of which showed a band at 2190 cm^{-1}, attributable to the ν_{N_3} of the coordinate azide [9a]. The ^{1}H NMR spectrum in CD_2Cl_2 revealed the presence not only of imine complex **3** as major product, but also of a new species, slowly transforming into the imine, which may be the hypothesised azide intermediate [**A**].

We also studied the reaction of MCl$_2$(η^6-*p*-cymene)(PR$_3$) with phenyl azide, C$_6$H$_5$N$_3$, but no stable complex could be isolated. Phenyl azide, like benzyl, is probably not stabilised by the



Scheme 1. M = Ru (**1**, **2**), Os (**3**); PR$_3$ = PPh(OEt)$_2$ (**1, 3**), PPh$_2$OEt (**2**); Ar = Ph (**a**), *p*-tolyl (**b**).



Scheme 2.

p-cymene fragment [MCl(η^6-*p*-cymene)(PR_3)]$^+$ and, as in this case imine formation is prevented, it does not give isolable complexes.

Imine complexes of ruthenium and osmium are rare and, apart from Taube's pentaamine [$Os(NH_3)_5${NH=C(H)CH_3}]$^+$ complex [20a], only a few examples are known [20b,c] and none contains a half-sandwich fragment. The reaction of benzyl azide with phosphite-containing *p*-cymene precursors MCl_2(η^6-*p*-cymene)(PR_3) (M = Ru, Os) allows the easy synthesis of stable mono-substituted imine derivatives **1**–**3**.

N-Protio imine complexes **1**–**3** were isolated as yellow solids, stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes [21]. The complexes were characterised spectroscopically (IR and ^{1}H, ^{31}P, ^{13}C, ^{15}N NMR) and by X-ray crystal structure determination of [RuCl(η^6-*p*-cymene){η^1-NH=C(H)C_6H_4-4-CH_3}{PPh$(OEt)_2$}]BPh_4 (**1b**), whose ORTEP is shown in Fig. 1. The structure of the complex consists of a ruthenium atom η^6-coordinated to a *p*-cymene molecule, one chlorine atom, one diethoxyphenylphosphine bonded through the phosphorus atom and one benzylideneamine (bonded through the nitrogen atom: η^1-NH=C(H)C_6H_5) leading to the formation of a "three-legged piano stool" structure.

The geometry of the complex is octahedral and marked by near 90° values for angles N(11)–Ru–P(3), 87.7(1); Cl–Ru–P(3), 85.22(6) and N(11)–Ru–Cl; 81.2(1)°. This last value may be surprisingly short, but there are more than twenty compounds in the CCDC database (CSD version 5.30 with February 2009 updates) [22] containing a RuCl(*p*-cymene)LL′ residue, where L and L′ are not chelating ligand, with Cl–Ru–L angles below 82°. In at least seven of these, L is a monodentated N-donor ligand [23].

The average Ru–C bond distance is 2.235(7) Å (Table 2). These bond lengths are close to those in other related complexes [14,23,24] and also show the different *trans* effect of the other ligands. Ru–C(4) and Ru–C(3), *trans* to the phosphorus atom, are the longer ones. The Ru–C(1) bond involving the isopropyl-substituted carbon atom is also remarkably elongated. In any case, the longer one corresponds to the methyl substituted carbon atom, a feature described in the literature as the expected [25]. The distance from the ruthenium atom to the centroid of the benzene ring of the cymene ligand (Ct) is 1.738(14) Å, virtually the same value as that found between the best cymene plane and the metal atom, 1.737(2) Å. The rms value for this plane is 0.030, with maximum deviation of C(2) by 0.040(4) Å. This atom, labelled as C(2), is a non-substituted carbon atom, may be considered *trans* to the chloride atom, and is the shorter R–C bond found in the compound. The orientation of the *p*-cymene ligand is such that the phosphorus and chlorine atoms may be viewed as eclipsed with the Ru–C bonds (see Fig. S1) and the P–Ru–Ct–C(6) and Cl–Ru–Ct–C(4) torsion angles of 15.6(3)° and 16.4(3)°, respectively, and, consequently, the Ru–P and Ru–Cl bonds are *trans* to Ru–C bonds. However, the Ru–N are not eclipsed with Ru–C(2) bond, and the N–Ru–Ct–C(2) and N–Ru–Ct–C(3) torsion angles are 25.4(3)° and −35.3(4)°, respectively.

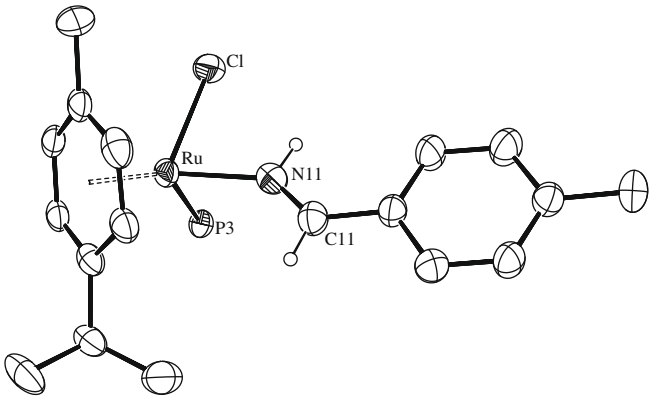


Fig. 1. ORTEP drawn of the cation of **1b**. Hydrogen atoms and the substituents on the phosphorus atom are omitted for clarity. Thermal ellipsoids are drawn at 30% probability level.

Table 2
Selected bond lengths [Å] and angles [°] for **1b**.

Ru–P(3)	2.2933(17)	Ru–Cl	2.3929(17)
Ru–N(11)	2.059(5)	Ru–Ct01	1.738(14)
Ru–C(1)	2.259(6)	Ru–C(2)	2.186(5)
Ru–C(3)	2.252(7)	Ru–C(4)	2.298(5)
Ru–C(5)	2.202(5)	Ru–C(6)	2.213(5)
N(11)–C(11)	1.260(7)	C(11)–C(12)	1.458(7)
N(11)–Ru–P(3)	87.72(13)	Cl–Ru–P(3)	85.22(6)
N(11)–Ru–Cl	81.19(14)	Ct01–Ru–P(3)	130.7(5)
Ct01–Ru–Cl	126.6(6)	Ct01–Ru–N(11)	129.0(7)
C(11)–N(11)–Ru	138.7(4)	N(11)–C(11)–C(12)	128.6(6)

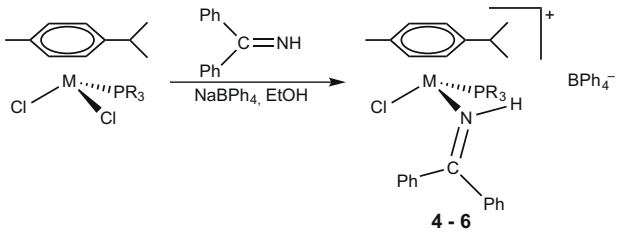
Ct represents the centroid of the benzene ring of the *p*-cymene ligand.

The Ru–N bond length is 2.059(5) Å, significantly shorter than the values found, for example, for complexes $RuCl_2$(*p*-cymene)(*p*-NH_2–C_6H_4–Cl), 2.173(2) Å [23c] or $RuCl_2$(*p*-cymene)(*p*-NH_2–$CH_2C_6H_5$), 2.144(2) Å [23e]. Such values are found in ruthenium-*p*-cymene complexes when the nitrogen atom is involved in delocalised systems, such as azides or polypyridines [26]. The C=N bond distance of the benzylideneamidate ligand, 1.260(7) Å, is the same as that found in an iridium complex [9a] and slightly shorter than that found in a tungsten complex [27]. For the time being, at the best of our knowledge, those two complexes are the only transition metal η^1-benzylideneamidate complexes crystallographically described in the literature. Again, the C–N–metal angle, 138.7(4)°, and N–C–C angle, 128.6(6)°, are surprisingly large for an sp^2-hybridised N atom, but similar values have been found for the above-mentioned complexes.

The Ru–Cl bond length is 2.393(2) Å, matching literature values well [14,23,24], and does not require further comment. The Ru–P bond length, 2.293(2) Å, is slightly shorter than lengths found for other phosphine RuCl(*p*-cymene) complexes [24a,28], but longer than that of the phosphito compound [Ru(η^6-*p*-cymene)(-P{OPh}$_3$)Cl_2], 2.2642(8) Å [29]. The disposition of the substituents of the phosphorus atoms in the phosphonite ligand is such that the phenyl ring is situated over the position occupied by the NH group. The dihedral angle N(11)–Ru–P(3)–C(21) is only −10.2(3)° (see Fig. S2).

The IR spectra of imine complexes [RuCl(η^6-*p*-cymene){η^1-NH=C(H)Ar}{PPh$(OEt)_2$}]BPh_4 (**1**–**3**) show a medium-intensity band at 3269–3247 cm^{-1}, attributed to the ν_{NH} of the imine ligand. The ^{1}H NMR spectra confirm the presence of this ligand, showing a slightly broad doublet between 10.04 and 8.50 ppm, attributed to the =NH imine proton, and a sharp doublet at 8.63–8.04 ppm due to the =CH imine resonance. In the spectrum of the labelled complex [RuCl(η^6-*p*-cymene){η^1-^{15}NH=C(H)C_6H_5}{PPh$(OEt)_2$}]BPh_4 (**1a$_1$**) the NH broad doublet splits into a multiplet, due to coupling with both ^{15}N and ^{31}P of the phosphite. The spectrum can be simulated using an AXBY model (A = ^{31}P, X = ^{1}H, B = ^{15}N, Y = CH) with the parameters reported in the Section 2. The $J_{^{15}N^1H}$ value of 72.7 Hz is as expected for imine, whereas $J_{^1H^1H}$ of 21.8 Hz suggests a *trans* arrangement of the imine ligand, like those observed in the solid state.

Also diagnostic for the presence of the ArC(H)=^{15}NH ligand is the proton-coupled ^{15}N NMR spectrum, which appears as a doublet of doublets at −177.6 ppm, owing to coupling with both ^{1}H and ^{31}P nuclei, fitting the presence of the imine ligand.



Scheme 3. M = Ru (**4, 5**), Os (**6**); PR_3 = $PPh(OEt)_2$ (**4, 6**), PPh_2OEt (**5**).

The ^1H and ^{13}C spectra show the characteristic signals of both *p*-cymene and phosphite ligands; the $^{31}P\{^1H\}$ NMR spectra appear as a sharp singlet, fitting the proposed formulation for the complexes.

The synthesis of the mono-substituted N-protio imine complexes $[MCl(\eta^6\text{-}p\text{-cymene})\{\eta^1\text{-}NH{=}C(H)Ar\}(PR_3)]BPh_4$ (**1**–**3**) of ruthenium and osmium prompted us to test whether disubstituted imine can also be stabilised by the *p*-cymene fragment $[MCl(\eta^6\text{-}p\text{-cymene})(PR_3)]^+$. Results show that dichloro complexes $MCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)$ react with benzophenone-imine $Ph_2C{=}NH$ in the presence of $NaBPh_4$ to give imine complexes $[MCl(\eta^6\text{-}p\text{-cymene})\{\eta^1\text{-}NH{=}CPh_2\}(PR_3)]BPh_4$ (**4**–**6**), which were separated and characterised (Scheme 3).

Also in this case, the reaction proceeds with the substitution of one chloride by the benzophenone-imine, giving the related complexes **4**–**6** in good yield.

Compounds **4**–**6** are yellow solids stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes [21]. Analytical and spectroscopic (IR, ^1H, ^{13}C, ^{31}P NMR) data support the proposed formulation.

The IR spectra show a medium-intensity band at 3244–3216 cm^{-1}, attributed to the ν_{NH} of the imine ligand. The presence of this ligand was confirmed by the ^1H NMR spectra, which show the characteristic slightly broad signal of the NH proton at 9.78–8.64 ppm. In the ^1H spectra, the signals of *p*-cymene, the substituents of the phosphite, and the BPh_4 anion are also present. The $^{31}P\{^1H\}$ NMR spectra appear as a singlet. In the $^{13}C\{^1H\}$ NMR spectrum of **4**, a singlet at 185.24 ppm was attributed to the iminic $HN{=}CPh_2$ carbon resonance, fitting the proposed formulation for the complexes.

4. Conclusions

This paper describes an easy route for the synthesis of mono-substituted imine complexes of Ru and Os, stabilised by half-sandwich fragments, involving the reaction of benzyl azide $ArCH_2N_3$ with dichloro precursors $MCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)$. The structural parameters of the N-protio imine complex of ruthenium $[RuCl(\eta^6\text{-}p\text{-cymene})\{\eta^1\text{-}NH{=}C(H)\text{-}p\text{-tolyl}\}\{PPh(OEt)_2\}]BPh_4$ are discussed. The synthesis of benzophenone-imine complexes of Ru and Os, stabilised by *p*-cymene fragments, is also reported.

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Appendix A. Supplementary material

CCDC 747367 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.11.008.

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