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Preparation and reactivity of *p*-cymene complexes of ruthenium and osmium incorporating 1,3-triazenide ligands

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ABSTRACT

p-Cymene complexes $MCl_2(\eta^6$-*p*-cymene)L [M = Ru, Os; L = $P(OEt)_3$, $PPh(OEt)_2$, $(CH_3)_3CNC$] were prepared by allowing $[MCl(\mu$-Cl)$(\eta^6$-*p*-cymene)$]_2$ to react with phosphites or *tert*-butyl isocyanide. Treatment of $MCl_2(\eta^6$-*p*-cymene)L complexes with 1,3-ArN=NN(H)Ar triazene and an excess of NEt_3 gave the cationic triazenide derivatives $[M(\eta^2$-1,3-ArNNNAr$)(\eta^6$-*p*-cymene)L$]BPh_4$ (Ar = Ph, *p*-tolyl). Neutral triazenide complexes $MCl(\eta^2$-1,3-ArNNNAr$)(\eta^6$-*p*-cymene) (M = Ru, Os) were also prepared by allowing $[MCl(\mu$-Cl$)(\eta^6$-*p*-cymene$)]_2$ to react with 1,3-diaryltriazene in the presence of triethylamine. *p*-Cymene complexes $MCl_2(\eta^6$-*p*-cymene)L reacted with equimolar amounts of 1,3-ArN=NN(H)Ar triazene to give both triazenide complexes $[M(\eta^2$-1,3-ArNNNAr$)(\eta^6$-*p*-cymene)L$]BPh_4$ and amine derivatives $[MCl(ArNH_2)(\eta^6$-*p*-cymene)L$]BPh_4$. A reaction path for the formation of the amine complex is also reported. The complexes were characterised by spectroscopy and X-ray crystallography of $RuCl_2(\eta^6$-*p*-cymene)[PPh(OEt)$_2$] and $[Ru(\eta^2$-1,3-*p*-tolyl-NNN-*p*-tolyl$)(\eta^6$-*p*-cymene$)\{CNC(CH_3)_3\}]BPh_4$. Selected triazenide complexes were studied as catalysts in the hydrogenation of 2-cyclohexen-1-one and cinnamaldehyde.

1. Introduction

The chemistry of half-sandwich η^6-arene complexes of ruthenium(II) and osmium(II) have been extensively developed in recent years [1–3], due to both their interesting coordination properties and their potential applications as precursors in catalytic reactions [3], including hydrogen transfer [4], alkene polymerisation [5] and olefin oxidation [6]. Ruthenium(II)-arene derivatives are also attracting current interest for use as anticancer agents [7].

The η^6-arene molecule is very stable to the substitution in half-sandwich d^6 complexes, allowing facile synthesis of a large number of η^6-arene complexes of Ru and Os containing a variety of supporting ligands such as mono- and bi-dentate phosphines [2d–f], aliphatic and aromatic amines [4e–g], β-diketones [8a], tris(pyrazolyl)borate [8b–d], bis- and tris-(pyrazolyl)alkane [2a,8e], *N*-heterocyclic carbene [2b,c], 1,2-bipyridine [7a], *etc.* However, despite numerous studies, only a brief note on the compound RuCl$(ClC_6H_4N_3C_6H_4Cl)$(*p*-cymene) [9] has been reported on half-sandwich complexes containing the diaryltriazenide species [1,3-ArNNNAr]$^-$ as a supporting ligand.

This anion is a "small-bite" ligand which can act as a monodentate, chelate or bridging ligand, providing many examples of transition-metal complexes [10–12]. However, its use in the chemistry of half-sandwich η^6-arene complexes is practically unexplored [9], although this bidentate N-donor ligand may potentially confer interesting chemical and catalytic properties on this class of complexes.

We previously reported [13] the synthesis and reactivity of triazene and triazenide complexes of Ru and Os of the type $[M(\eta^2$-1,3-ArNNNAr$)L_4]BPh_4$ and $[MH\{\eta^1$-1,3-ArN=NN(H)Ar$\}L_4]BPh_4$ (M = Ru, Os; L = phosphite) and have now extended these studies to include half-sandwich η^6-arene complexes, with the aim of testing whether triazenide ligands can be introduced into the chemistry of arene complexes and how they can modify their chemical and catalytic properties. The results of these studies, which allowed the synthesis and some reactivity of unprecedented η^6-*p*-cymene complexes of Ru and Os incorporating either triazenide and phosphite or triazenide and isocyanide mixed ligands, are reported here.

2. Experimental section

2.1. General comments

All synthetic work was carried out under Ar using standard Schlenk techniques or an inert atmosphere dry-box. All solvents

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were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $RuCl_3 \cdot 3H_2O$ and OsO_4 were Pressure Chemical Co. (USA) products, used as received. Phosphite $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon [14], while $P(OEt)_3$ was an Aldrich product purified by distillation under nitrogen. 1,3-Diaryltriazene 1,3-ArN=NN(H)Ar (Ar = Ph, *p*-tolyl) were prepared following the literature method [15]. The labeled triazene1,3-$Ph^{15}N{=}N^{15}N(H)Ph$ was prepared from labeled aniline $Ph^{15}NH_2$ (99% enriched, CIL) and $NaNO_2$. Other reagents, including $(CH_3)_3CNC$, were purchased from commercial sources in the highest available purity and used as received. Infrared spectra (KBr pellets) were recorded on Perkin–Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra (^1H, ^{31}P, ^{13}C, ^{15}N) were obtained on AVANCE 300 Bruker spectrometer (300 MHz) at temperatures between −90 and +30 °C, unless otherwise noted. ^1H and $^{13}C\{^1H\}$ spectra are referred to internal tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4 and ^{15}N to $CH_3^{15}NO_2$, and in both cases downfield shifts are considered positive. *J* values are given in Hz. For the OCH_2CH_3 substituents of the phosphites: CH_2 (multiplet), $J_{HH} = 7$ Hz; CH_3 (triplet), $J_{HH} = 7$ Hz. For *p*-cymene 4-$CH_3C_6H_4CH(CH_3)_2$: CH (multiplet), $J_{HH} = 6.8$ Hz; CH_3 (doublet), $J_{HH} = 6.8$ Hz. COSY, HMQC and HMBC NMR experiments were performed with standard programs. The SwaNMR and iNMR software packages [16] 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 was measured on a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova (Italy).

2.2. Synthesis of precursor complexes

Complexes $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ and $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ were prepared following the previously reported methods [17].

2.3. Synthesis of complexes

2.3.1. $RuCl_2(\eta^6\text{-}p\text{-cymene})L$ (**1**) and $OsCl_2(\eta^6\text{-}p\text{-cymene})L$ (**2**) [L = P(OEt)$_3$ (**a**), PPh(OEt)$_2$ (**b**)]

An excess of the appropriate phosphite (3.5 mmol) was added to a solution of the dimeric complex $[MCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (M = Ru, Os) (0.7 mmol) in CH_2Cl_2 (10 mL) and the reaction mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure to give an oil which was triturated with *n*-hexane (10 mL). A yellow solid slowly separated out which was filtered and crystallised from dichloromethane and hexane; yield: ≥90%. **1a**: ^1H NMR (CD_2Cl_2, 25 °C) δ: 5.50, 5.24 (d, 4H, Ph), 4.11 (qnt, 6H, CH_2), 2.83 (m, 1H, CH), 2.10 (s, 3H, CH_3 *p*-cym), 1.27 (*t*, 9H, CH_3 phos), 1.21 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 114.2 (s) ppm. $C_{16}H_{29}Cl_2O_3PRu$ (472.35): calcd. C 40.68, H 6.19, Cl 15.01; found C 40.46, H 6.11, Cl 14.88%. **1b**: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.75, 7.45 (m, 5H, Ph phos), 5.33, 5.24 (d, 4H, Ph *p*-cym), 4.16, 4.04 (m, 4H, CH_2), 2.68 (m, 1H, CH), 1.91 (s, 3H, CH_3 *p*-cym), 1.32 (*t*, 6H, CH_3 phos), 1.09 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 138.2 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 138–128 (m, Ph phos), 108.9, 98.9, 90.9, 88.8 (s, Ph *p*-cym), 64.4 (d, CH_2), 30.5 (s, CH), 21.9 (s, CH_3 Pr^i), 17.9 (s, CH_3 *p*-cym), 16.4 (d, CH_3 phos) ppm. $C_{20}H_{29}Cl_2O_2PRu$ (504.39): calcd. C 47.62, H 5.80, Cl 14.06; found C 47.48, H 5.72, Cl 14.23%. **2a**: ^1H NMR (CD_2Cl_2, 25 °C) δ: 5.64, 5.50 (d, 4H, Ph), 4.12 (qnt, 6H, CH_2), 2.82 (m, 1H, CH), 2.22 (s, 3H, CH_3 *p*-cym), 1.29 (*t*, 9H, CH_3 phos), 1.26 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 69.5 (s) ppm. $C_{16}H_{29}Cl_2O_3OsP$ (561.51): calcd. C 34.22, H 5.21, Cl 12.63; found C 34.11, H 5.30, Cl 12.78%. **2b**: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.65, 7.43 (m, 5H, Ph phos), 5.51, 5.39 (d, 4H, Ph *p*-cym), 4.10, 3.96 (m, 4H, CH_2), 2.64 (m, 1H, CH), 2.06 (s, 3H, CH_3 *p*-cym), 1.32 (*t*, 6H, CH_3 phos), 1.16 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 92.4 (s) ppm. $C_{20}H_{29}Cl_2O_2OsP$ (593.55): C 40.47, H 4.92, Cl 11.95; found: C 40.32, H 5.04, Cl 11.80%.

2.3.2. $RuCl_2(\eta^6\text{-}p\text{-cymene})(PPr^i{}_3)$ (**1c**)

This complex was prepared exactly like the related complexes **1**; yield ≥90%. ^1H NMR (CD_2Cl_2, 25 °C) δ: 5.61, 5.55 (d, 4H, Ph), 2.71 (m, 4H, CH), 2.05 (s, 3H, CH_3 *p*-cym), 1.33, 1.29, 1.27 (d, 24H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 36.7 (s) ppm. $C_{19}H_{35}Cl_2Pru$ (466.43): calcd. C 48.93, H 7.56, Cl 15.20; found C 49.08, H 7.66, Cl 14.97%.

2.3.3. $RuCl_2(\eta^6\text{-}p\text{-cymene})(CNBu^t)$ [18] (**3**) and $OsCl_2(\eta^6\text{-}p\text{-cymene})(CNBu^t)$ (**4**)

An excess of *tert*-butyl isocyanide (2.1 mmol, 0.24 mL) was added to a solution of the appropriate dimeric complex $[MCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (M = Ru, Os) (0.7 mmol) in toluene (10 mL) and the reaction mixture was stirred at room temperature for 5 h. The solvent was removed under reduced pressure to give an oil which was triturated with *n*-hexane (8 mL). A pale yellow solid slowly separated out which was filtered and crystallised from dichloromethane and hexane; yield ≥85%. **3**: IR (KBr pellet) ν_{CN}: 2191 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 5.53, 5.35 (d, 4H, Ph), 2.76 (m, 1H, CH), 2.21 (s, 3H, CH_3 *p*-cym), 1.51 (s, 9H, CH_3 Bu^t), 1.26 (d, 6H, CH_3 Pr^i) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 138.5 (s, CN), 107.8, 106.4, 87.7, 87.5 (s, Ph *p*-cym), 58.6 (s, C Bu^t), 31.5 (s, CH), 30.6 (s, CH_3 Bu^t), 22.4 (s, CH_3 Pr^i), 18.7 (s, CH_3 *p*-cym) ppm. $C_{15}H_{23}Cl_2NRu$ (389.33): calcd. C 46.27, H 5.95, Cl 18.21, N 3.60; found C 46.33, H 5.83, Cl 18.09, N 3.73%. **4**: IR (KBr pellet) ν_{CN}: 2185 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 5.65, 5.45 (d, 4H, Ph), 2.73 (m, 1H, CH), 2.28 (s, 3H, CH_3 *p*-cym), 1.53 (s, 9H, CH_3 Bu^t), 1.27 (d, 6H, CH_3 Pr^i) ppm. $C_{15}H_{23}Cl_2NOs$ (478.49): C 37.65, H 4.84, Cl 14.82, N 2.93; found C 37.74, H 4.92, Cl 14.68, N 2.99%.

2.3.4. $[Ru(\eta^2\text{-}1,3\text{-}ArNNNAr)(\eta^6\text{-}p\text{-cymene})L]BPh_4$ (**5**, **6**) [Ar = Ph (**5**), *p*-tolyl (**6**); [L = P(OEt)$_3$ (**a**), PPh(OEt)$_2$ (**b**)]

In a 25-mL three-necked round-bottomed flask were placed solid samples of the complex $RuCl_2(\eta^6\text{-}p\text{-cymene})L$ (**1**) (0.4 mmol), of the appropriate 1,3-diaryltriazene (0.5 mmol), of the salt $NaBPh_4$ (0.82 mmol, 0.28 g) and 6 mL of ethanol. An excess of triethylamine (4.0 mmol, 0.55 mL) was added to the resulting suspension, which was stirred for 12 h. An orange solid separated out from the reaction mixture which was filtered and crystallised from dichloromethane and ethanol; yield ≥80%. **5b**: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.35–6.89 (m, 35H, Ph), 5.96, 5.50 (d, 4H, Ph *p*-cym), 3.88 (m, 4H, CH_2), 2.73 (m, 1H, CH), 2.16 (s, 3H, CH_3 *p*-cym), 1.19 (d, 6H, CH_3 Pr^i), 1.18 (*t*, 6H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 148.1 (s) ppm. $\Lambda_M = 53.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. $C_{56}H_{59}BN_3O_2PRu$ (948.94): calcd. C 70.88, H 6.27, N 4.43; found C 70.67, H 6.38, N 4.30%. **6a**: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.36–6.89 (m, 28H, Ph), 5.91, 5.49 (d, 4H, Ph *p*-cym), 3.85 (m, 6H, CH_2), 2.65 (m, 1H, CH), 2.36 (s, 6H, CH_3 *p*-tol), 2.19 (s, 3H, CH_3 *p*-cym), 1.17 (d, 6H, CH_3 Pr^i), 1.12 (*t*, 9H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 117.6 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 165–187 (m, Ph), 64.6 (d, CH_2), 32.4 (s, CH), 22.6 (s, CH_3 Pr^i), 21.0 (s, CH_3 *p*-tol), 19.6 (s, CH_3 *p*-cym), 16.0 (d, CH_3 phos) ppm. $\Lambda_M = 51.7\ \Omega^{-1}\ mol^{-1}\ cm^2$. $C_{54}H_{63}BN_3O_3PRu$ (944.95): calcd. C 68.64, H 6.72, N 4.45; found C 68.73, H 6.63, N 4.34%. **6b**: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.35–6.82 (m, 33H, Ph), 5.96, 5.46 (d, 4H, Ph *p*-cym), 3.87 (m, 4H, CH_2), 2.73 (m, 1H, CH), 2.37 (s, 6H, CH_3 *p*-tol), 2.14 (s, 3H, CH_3 *p*-cym), 1.20 (*t*, 6H, CH_3 phos), 1.18 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 148.2 (s) ppm. $\Lambda_M = 55.2\ \Omega^{-1}\ mol^{-1}\ cm^2$. $C_{58}H_{63}BN_3O_2PRu$ (976.99): calcd. C 71.30, H 6.50, N 4.30; found C 71.14, H 6.62, N 4.18%.

*2.3.5. [Ru(η^2-1,3-p-tolyl-NNN-p-tolyl)(η^6-p-cymene)(PPr^i_3)]BPh_4 (**6c**)*

This complex was prepared exactly like the related complexes **5**, **6**; yield ≥80%. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.34–6.84 (m, 28H, Ph), 6.01, 5.40 (d, 4H, Ph *p*-cym), 2.65 (m, 4H, CH), 2.36 (s, 6H, CH_3 *p*-tol), 2.11 (s, 3H, CH_3 *p*-cym), 1.17, 1.13, 1.12 (d, 24H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 49.2 (s) ppm. Λ_M = 56.5 Ω^{-1} mol^{-1} cm^2. $C_{57}H_{69}BN_3PRu$ (939.03): calcd. C 72.91, H 7.41, N 4.47; found C 72.72, H 7.52, N 4.36%.

*2.3.6. [Os(η^2-1,3-ArNNNAr)(η^6-p-cymene)L]BPh_4 (**7**, **8**) [Ar = Ph (**7**), p-tolyl (**8**); L = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**)]*

These complexes were prepared like the related ruthenium derivatives **5**, **6**, but using a reaction time of 24 h; yield ≥85%. **7a**: ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.38–6.86 (m, 30H, Ph), 6.03, 5.69 (d, 4H, Ph *p*-cym), 3.84 (qnt, 6H, CH_2), 2.60 (m, 1H, CH), 2.39 (s, 3H, CH_3 *p*-cym), 1.13 (d, 6H, CH_3 Pr^i), 1.08 (*t*, 9H, CH_3 phos) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 75.7 (s) ppm. Λ_M =54.9 Ω^{-1} mol^{-1} cm^2. $C_{52}H_{59}BN_3O_3OsP$ (1006.06): calcd. C 62.08, H 5.91, N 4.18; found C 62.23, H 5.80, N 4.06%. **7b**: ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.34–6.87 (m, 35H, Ph), 6.07, 5.71 (d, 4H, Ph *p*-cym), 3.86 (m, 4H, CH_2), 2.67 (m, 1H, CH), 2.38 (s, 3H, CH_3 *p*-cym), 1.18 (*t*, 6H, CH_3 phos), 1.14 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 105.8 (s) ppm. Λ_M = 56.5 Ω^{-1} mol^{-1} cm^2. $C_{56}H_{59}BN_3O_2OsP$ (1038.10): calcd. C 64.79, H 5.73, N 4.05; found C 64.56, H 5.86, N 3.93%. **8a**: ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.34–6.87 (m, 28H, Ph), 6.00, 5.64 (d, 4H, Ph *p*-cym), 3.83 (m, 6H, CH_2), 2.60 (m, 1H, CH), 2.37 (s, 3H, CH_3 *p*-cym), 2.36 (s, 6H, CH_3 *p*-tol), 1.12 (*t*, 9H, CH_3 phos), 1.08 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 76.3 (s) ppm. Λ_M = 51.8 Ω^{-1} mol^{-1} cm^2. $C_{54}H_{63}BN_3O_3OsP$ (1034.11): calcd. C 62.72, H 6.14, N 4.06; found C 62.55, H 6.27, N 4.19%. **8b**: ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.35–6.87 (m, 33H, Ph), 6.05, 5.66 (d, 4H, Ph *p*-cym), 3.84 (m, 4H, CH_2), 2.67 (m, 1H, CH), 2.36 (s, 3H, CH_3 *p*-cym), 2.35 (s, 6H, CH_3 *p*-tol), 1.18 (*t*, 6H, CH_3 phos), 1.13 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 106.0 (s)ppm. Λ_M = 54.4 Ω^{-1} mol^{-1} cm^2. $C_{58}H_{63}BN_3O_2OsP$ (1066.15): calcd. C 65.34, H 5.96, N 3.94; found C 65.13, H 6.06, N 3.81%.

*2.3.7. [Os(η^2-1,3-$Ph^{15}NN^{15}NPh$)(η^6-p-cymene){$PPh(OEt)_2$}]BPh_4 (**7b***)*

This complex was prepared exactly like the related unlabeled compound **7b** by using 1,3-$Ph^{15}N{=}N^{15}N(H)Ph$ as a reagent; yield ≥70%. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.36–6.88 (m, 35H, Ph), 6.06, 5.70 (d, 4H, Ph *p*-cym), 3.85 (m, 4H, CH_2), 2.67 (m, 1H, CH), 2.37 (s, 3H, CH_3 *p*-cym), 1.18 (*t*, 6H, CH_3 phos), 1.14 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AX_2 spin syst (X = ^{15}N), δ_A 105.9 ppm, J_{Ax} 5.2 Hz. $^{15}N\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: X_2A spin syst (A = ^{31}P), δ_x −188.9 ppm, J_{xA} 5.2 Hz.

*2.3.8. [M(η^2-1,3-ArNNNAr)(η^6-p-cymene)($CNBu^t$)]BPh_4 (**9**–**12**) [M = Ru (**9**, **10**), Os (**11**, **12**); Ar = Ph (**9**, **11**), p-tolyl (**10**, **12**)]*

In a 25-mL three-necked round-bottomed flask were placed solid samples of the complex MCl_2(η^6-*p*-cymene)($CNBu^t$) (**3**, **4**) (M = Ru, Os) (0.2 mmol), a slight excess of the appropriate 1,3-diaryltriazene (0.24 mmol), an excess of solid $NaBPh_4$ (0.40 mmol, 137 mg) and 5 mL of ethanol. An excess of triethylamine (2.4 mmol, 0.33 mL) was added to the resulting suspension, which was stirred for 12 h, in the case of ruthenium, or 24 h, for osmium. The yellow solid that separated out was filtered and crystallised from dichloromethane and ethanol; yield ≥80%. **9**: IR (KBr pellet) ν_{CN}: 2189 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.39–6.89 (m, 30H, Ph), 5.81, 5.44 (d, 4H, Ph *p*-cym), 2.66 (m, 1H, CH), 2.14 (s, 3H, CH_3 *p*-cym), 1.28 (s, 9H, CH_3 Bu^t), 1.23 (d, 6H, CH_3 Pr^i) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 165–116 (m, Ph), 142.5 (s, br, CN), 113.9, 107.5, 89.4, 86.6 (s, Ph *p*-cym), 60.1 (s, C Bu^t), 32.5 (s, CH), 30.3 (s, CH_3 Bu^t), 22.9 (s, CH_3 Pr^i), 20.0 (s, CH_3 *p*-cym) ppm. Λ_M = 58.6 Ω^{-1} mol^{-1} cm^2. $C_{51}H_{53}BN_4Ru$ (833.87): calcd. C 73.46, H 6.41, N 6.72; found C 73.29, H 6.54, N 6.60%. **10**: IR (KBr pellet) ν_{CN}: 2191 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.37–6.86 (m, 28H, Ph), 5.79, 5.42 (d, 4H, Ph *p*-cym), 2.66 (m, 1H, CH), 2.37 (s, 6H, CH_3 *p*-tol), 2.13 (s, 3H, CH_3 *p*-cym), 1.29 (s, 9H, CH_3 Bu^t), 1.22 (d, 6H, CH_3 Pr^i) ppm. Λ_M = 55.6 Ω^{-1} mol^{-1} cm^2. $C_{53}H_{57}BN_4Ru$ (861.93): calcd. C 73.85, H 6.67, N 6.50; found C 73.66, H 6.55, N 6.38%. **11**: IR (KBr pellet) ν_{CN}: 2181 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.41–6.86 (m, 30H, Ph), 6.00, 5.63 (d, 4H, Ph *p*-cym), 2.63 (m, 1H, CH), 2.31 (s, 3H, CH_3 *p*-cym), 1.30 (s, 9H, CH_3 Bu^t), 1.19 (d, 6H, CH_3 Pr^i) ppm. Λ_M = 56.5 Ω^{-1} mol^{-1} cm^2. $C_{51}H_{53}BN_4Os$ (923.03): calcd. C 66.36, H 5.79, N 6.07; found C 66.47, H 5.66, N 6.15%. **12**: IR (KBr pellet) ν_{CN}: 2183 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.35–6.86 (m, 28H, Ph), 5.97, 5.60 (d, 4H, Ph *p*-cym), 2.62 (m, 1H, CH), 2.37 (s, 6H, CH_3 *p*-tol), 2.29 (s, 3H, CH_3 *p*-cym), 1.30 (s, 9H, CH_3 Bu^t), 1.18 (d, 6H, CH_3 Pr^i) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 165–116 (m, Ph), 136.6 (s, CN), 100.8, 100.6, 82.4, 78.8 (s, Ph *p*-cym), 60.1 (s, C Bu^t), 32.5 (s, CH), 30.6 (s, CH_3 Bu^t), 23.2 (s, CH_3 Pr^i), 21.0 (s, CH_3 *p*-tol), 19.7 (s, CH_3 *p*-cym) ppm. Λ_M = 53.1 Ω^{-1} mol^{-1} cm^2. $C_{53}H_{57}BN_4Os$ (951.09): calcd. C 66.93, H 6.04, N 5.89; found C 66.71, H 5.93, N 5.98%.

*2.3.9. [Os(η^2-1,3-$Ph^{15}NN^{15}NPh$)(η^6-p-cymene)($CNBu^t$)]BPh_4 (**11***)*

This complex was prepared exactly like the related unlabeled compound **11** by using 1,3-$Ph^{15}N{=}N^{15}N(H)Ph$ as a reagent; yield ≥75%. IR (KBr pellet) ν_{CN}: 2179 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.40–6.86 (m, 30H, Ph), 6.01, 5.65 (d, 4H, Ph *p*-cym), 2.63 (m, 1H, CH), 2.31 (s, 3H, CH_3 *p*-cym), 1.30 (s, 9H, CH_3 Bu^t), 1.18 (d, 6H, CH_3 Pr^i) ppm. $^{15}N\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: X_2 spin syst, δ_x −186.9 ppm.

*2.3.10. RuCl(η^2-1,3-ArNNNAr)(η^6-p-cymene) (**13**, **14**) [Ar = Ph (**13**), p-tolyl (**14**)] and OsCl(η^2-1,3-p-tolyl-NNN-p-tolyl)(η^6-p-cymene) (**15**)*

In a 25-mL three-necked round-bottomed flask were placed solid samples of the appropriate dimeric complex [MCl_2(η^6-*p*-cymene)]$_2$ (M = Ru, Os) (0.3 mmol), a slight excess of 1,3-diaryltriazene (0.7 mmol) and 10 mL of toluene. An excess of triethylamine (3 mmol, 0.42 mL) was added to the resulting solution, which was stirred for 24 h. The solvent was removed under reduced pressure to give an oil which was triturated with *n*-hexane. An orange solid slowly separated out which was filtered and crystallised from dichloromethane and ethanol; yield ≥85%. **13**: ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.32, 7.10 (m, 10H, Ph), 5.80, 5.38 (d, 4H, Ph *p*-cym), 2.74 (m, 1H, CH), 2.30 (s, 6H, CH_3 Pr^i), 1.20 (d, 3H, CH_3 *p*-cym) ppm. $C_{22}H_{24}ClN_3Ru$ (466.97): calcd. C 56.59, H 5.18, Cl 7.59, N 9.00; found C 56.44, H 5.27, Cl 7.45, N 9.13%. **14**: ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.20–7.12 (m, 8H, Ph), 5.79, 5.36 (d, 4H, Ph *p*-cym), 2.74 (m, 1H, CH), 2.34 (s, 6H, CH_3 *p*-tol), 2.29 (s, 6H, CH_3 Pr^i), 1.21 (d, 3H, CH_3 *p*-cym) ppm. $C_{24}H_{28}ClN_3Ru$ (495.02): calcd. C 58.23, H 5.70, Cl 7.16, N 8.49; found C 58.40, H 5.82, Cl 7.01, N 8.58%. **15**: ^{1}H NMR (CD_2Cl_2, 25 °C) δ: 7.38–6.90 (8H, m, Ph), 6.14, 5.62 (4H, d, Ph *p*-cym), 2.59 (1H, m, CH), 2.36 (3H, s, CH_3 *p*-cym), 2.34 (6H, s, CH_3 *p*-tol), 1.13 (6H, d, CH_3 Pr^i) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 144.2, 134.5, 129.8, 116.8 (s, Ph), 97.3, 94.2, 73.1, 69.0 (s, Ph *p*-cym), 32.6 (s, CH), 23.1 (s, CH_3 Pr^i), 21.0 (s, CH_3 *p*-tol), 19.2 (s, CH_3 *p*-cym) ppm. $C_{24}H_{28}ClN_3Os$ (584.18): calcd. C 49.34, H 4.83, Cl 6.07, N 7.19; found C 49.15, H 4.71, Cl 6.26, N 7.03%.

*2.3.11. [MCl($ArNH_2$)(η^6-p-cymene)L]BPh_4 (**16**–**19**) [M = Ru (**16**, **17**), Os (**18**, **19**); Ar = Ph (**16**, **18**), p-tolyl (**17**, **19**); L = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**)]*

In a 25-mL three-necked round-bottomed flask were placed solid samples of the appropriate complex MCl_2(η^6-*p*-cymene)L (**1**,

2) (M = Ru, Os) (0.2 mmol), an equimolar amount of 1,3-diaryltriazene (0.2 mmol), an equimolar amount of $NaBPh_4$ (0.2 mmol, 68 mg) and 5 mL of ethanol. The reaction mixture was stirred for 24 h and the yellow solid which separated out was filtered and dried under vacuum. The amine complex was separated from the mixture by fractional crystallisation from +20 to −20 °C using a mixture of CH_2Cl_2 and ethanol as solvent. The first separated products contained mainly the compounds [M(η^2-1,3-ArNNNAr)(η^6-*p*-cymene)L]BPh_4, while the third fraction contained the amine derivatives **16**–**19**; yield ≥20%. **16b**: IR (KBr pellet) ν_{NH}: 3293, 3216 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.90–6.86 (m, 25H, Ph), 5.40, 4.48 (br d, 2H, NH_2), 5.34, 5.18 (m, 5H, Ph amine), 5.25, 5.14, 4.80, 4.77 (d, 4H, Ph *p*-cym), 4.14, 4.06 (m, 4H, CH_2), 2.57 (m, 1H, CH), 1.88 (s, 3H, CH_3 *p*-cym), 1.48, 1.46 (*t*, 6H, CH_3 phos), 1.11, 1.09 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 144.7 (s) ppm. Λ_M = 54.3 Ω^{-1} mol^{-1} cm^2. $C_{50}H_{56}BClNO_2PRu$ (881.29): calcd. C 68.14, H 6.40, Cl 4.02, N 1.59; found C 67.96, H 6.53, Cl 3.91, N 1.68%. **17a**: IR (KBr pellet) ν_{NH}: 3289, 3215 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.34–6.88 (m, 24H, Ph), 5.34, 5.30, 4.80, 4.68 (d, 4H, Ph *p*-cym), 4.75 (br, 2H, NH_2), 4.23 (m, 6H, CH_2), 2.64 (m, 1H, CH), 2.38 (s, 3H, CH_3 *p*-tol), 1.97 (d, 6H, CH_3 Pr^i), 1.39 (*t*, 9H, CH_3 phos), 1.16 (d, 3H, CH_3 *p*-cym) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 114.0 (s) ppm. Λ_M = 57.2 Ω^{-1} mol^{-1} cm^2. $C_{47}H_{58}BClNO_3PRu$ (863.28): calcd. C 65.39, H 6.77, Cl 4.11, N 1.62; found C 65.16, H 6.91, Cl 3.94, N 1.70%. **17b**: IR (KBr pellet) ν_{NH}: 3318, 3237 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.64–6.85 (m, 25H, Ph), 5.97, 5.47 (d, 4H, Ph amine), 5.28, 5.13, 4.79, 4.75 (d, 4H, Ph *p*-cym), 5.30, 4.42 (br d, 2H, NH_2), 4.05, 3.85 (m, 4H, CH_2), 2.61 (m, 1H, CH), 2.35 (m, 3H, CH_3 *p*-tol), 1.87 (s, 3H, CH_3 *p*-cym), 1.46, 1.45 (*t*, 6H, CH_3 phos), 1.13, 1.10 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 145.1 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 165–116.5 (m, Ph), 118.1, 105.9, 88.2, 87.5 (s, Ph amine), 116.1, 105.6, 92.5, 90.0, 88.3, 84.6 (s, Ph *p*-cym), 66.3, 65.2 (s, CH_2), 30.9 (s, CH), 22.4, 22.0 (s, CH_3 Pr^i), 21.1 (s, CH_3 *p*-tol), 21.0 (s, CH_3 *p*-cym), 16.4 (m, CH_3 phos) ppm. Λ_M = 58.6 Ω^{-1} mol^{-1} cm^2. $C_{51}H_{58}BClNO_2PRu$ (895.32): calcd. C 68.42, H 6.53, Cl 3.96, N 1.56; found C 68.22, H 6.67, Cl 4.14, N 1.43%. **18b**: IR (KBr pellet) ν_{NH}: 3273, 3220 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.68–6.86 (m, 25H, Ph), 5.25, 4.64 (br d, 2H, NH_2), 5.53, 5.27, 5.13, 5.06 (d, 4H, Ph *p*-cym), 5.40–5.10 (m, 5H, Ph amine), 4.10, 3.95 (m, 4H, CH_2), 2.56 (m, 1H, CH), 2.05 (s, 3H, CH_3 *p*-cym), 1.43, 1.42 (*t*, 6H, CH_3 phos), 1.18, 1.16 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 105.8 (s) ppm. Λ_M = 55.7 Ω^{-1} mol^{-1} cm^2. $C_{50}H_{56}BClNO_2OsP$ (970.45): calcd. C 61.88, H 5.82, Cl 3.65, N 1.44; found C 61.75, H 5.68, Cl 3.83, N 1.31%. **19b**: IR (KBr pellet) ν_{NH}: 3269, 3218 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.62–6.88 (m, 25H, Ph), 6.05, 5.65 (d, 4H, Ph amine), 5.30, 5.13, 5.11, 5.03 (d, 4H, Ph *p*-cym), 5.22, 4.56 (br d, 2H, NH_2), 4.11, 3.99 (m, 4H, CH_2), 2.59 (m, 1H, CH), 2.37 (m, 3H, CH_3 *p*-tol), 2.00 (s, 3H, CH_3 *p*-cym), 1.44, 1.43 (*t*, 6H, CH_3 phos), 1.27, 1.17 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 100.4 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 165–116 (m, Ph), 112.0, 98.5, 81.8, 79.6 (s, Ph amine), 109.9, 101.1, 84.5, 81.7, 77.9, 75.2 (s, Ph *p*-cym), 65.6, 64.8 (s, CH_2), 30.7 (s, CH), 22.6, 22.1 (s, CH_3 Pr^i), 20.9 (s, CH_3 *p*-cym), 18.4 (s, CH_3 *p*-tol), 16.3 (m, CH_3 phos) ppm. Λ_M = 56.9 Ω^{-1} mol^{-1} cm^2. $C_{51}H_{58}BClNO_2OsP$ (984.48): calcd. C 62.22, H 5.94, Cl 3.60, N 1.42; found C 62.00, H 5.82, Cl 3.77, N 1.54%.

2.3.12. [RuCl($Ph^{15}NH_2$)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh_4 (**16b***) [OsCl($Ph^{15}NH_2$)(η^6-*p*-cymene)-{PPh(OEt)$_2$}]BPh_4 (**18b***)

These complexes were prepared exactly like the related unlabeled compounds **16b** and **18b** by using 1,3-$Ph^{15}N{=}N^{15}N(H)Ph$ as a reagent; yield ≥18%. **16b***: IR (KBr pellet) ν^{15}_{NH}: 3288, 3212 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.90–6.86 (m, 25H, Ph), 5.38, 4.49 (ddd, 2H, NH_2, J^{151}_{NH} 72.8 Hz), 5.34, 5.18 (m, 5H, Ph amine), 5.25, 5.13, 4.78, 4.76 (d, 4H, Ph *p*-cym), 4.14, 4.08 (m, 4H, CH_2), 2.59 (m, 1H, CH), 1.87 (s, 3H, CH_3 *p*-cym), 1.47, 1.46 (*t*, 6H, CH_3 phos), 1.11, 1.08 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AX spin syst (X = ^{15}N), δ_A 144.8 ppm, J_{Ax} 3.9 Hz. ^{15}N NMR (CD_2Cl_2, 25 °C) δ: XAY_2 spin syst (A = ^{31}P, Y = ^1H), δ_x −366.6 ppm, J_{Ax} 3.9, J_{xY} 72.8 Hz. **18b***: IR (KBr pellet) ν^{15}_{NH}: 3260, 3215 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.63–6.86 (m, 25H, Ph), 5.25, 4.63 (ddd, 2H, NH_2), 5.52, 5.28, 5.13, 5.06 (d, 4H, Ph *p*-cym), 5.43–5.10 (m, 5H, Ph amine), 4.11, 3.95 (m, 4H, CH_2), 2.58 (m, 1H, CH), 2.05 (s, 3H, CH_3 *p*-cym), 1.44, 1.43 (*t*, 6H, CH_3 phos), 1.18, 1.16 (d, 6H, CH_3 Pr^i) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: AX spin syst (X = ^{15}N), δ_A 100.2 ppm, J_{Ax} 2.7 Hz. ^{15}N NMR (CD_2Cl_2, 25 °C) δ: XAY_2 spin syst (A = ^{31}P, Y = ^1H), δ_x −377.4 ppm, J_{xA} 2.7, J_{xY} 72.9 Hz.

2.3.13. [OsCl($ArNH_2$)(η^6-*p*-cymene)($CNBu^t$)]BPh_4 (**20**, **21**) [Ar = Ph (**20**), *p*-tolyl (**21**)]

These complexes were prepared exactly like the related phosphite complexes **18**, **19** by using $OsCl_2$(η^6-*p*-cymene)($CNBu^t$) (**4**) as a precursor; yield ≥25%. **20**: IR (KBr pellet): ν_{NH} 3256, 3206 (m); ν_{CN} 2178 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.35–6.72 (m, 20H, Ph), 5.61, 4.63 (br d, 2H, NH_2), 5.32–5.04 (m, 9H, Ph amine + *p*-cym), 2.45 (m, 1H, CH), 2.11 (s, 3H, CH_3 *p*-cym), 1.33 (s, 9H, CH_3 Bu^t), 1.19, 1.16 (d, 6H, CH_3 Pr^i) ppm. Λ_M = 55.9 Ω^{-1} mol^{-1} cm^2. $C_{45}H_{50}BClN_2Os$ (855.39): calcd. C 63.19, H 5.89, Cl 4.14, N 3.27; found C 63.33, H 5.76, Cl 4.32, N 3.18%. **21**: IR (KBr pellet): ν_{NH} 3256, 3193 (m); ν_{CN} 2174 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.35–6.65 (m, 20H, Ph), 5.98, 5.61 (d, 4H, Ph amine), 5.75, 4.74 (br d, 2H, NH_2), 5.26–5.07 (m, 4H, Ph *p*-cym), 2.48 (m, 1H, CH), 2.30 (s, 3H, CH_3 *p*-tol), 2.10 (s, 3H, CH_3 *p*-cym), 1.34 (s, 9H, CH_3 Bu^t), 1.17, 1.11 (d, 6H, CH_3 Pr^i) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 165–116 (m, Ph), 106.7, 100.8, 82.4, 78.8 (s, Ph amine), 103.9, 98.1, 78.1, 76.0 (s, Ph *p*-cym), 102.4 (s, CN), 59.4 (s, C Bu^t), 31.9 (s, CH), 30.5 (s, CH_3 Bu^t), 23.2 (s, CH_3 Pr^i), 21.5 (s, CH_3 *p*-tol), 18.2 (s, CH_3 *p*-cym) ppm. Λ_M = 54.4 Ω^{-1} mol^{-1} cm^2. $C_{46}H_{52}BClN_2Os$ (869.41): calcd. C 63.55, H 6.03, Cl 4.08, N 3.22; found C 63.34, H 6.15, Cl 3.92, N 3.29%.

2.3.14. [OsCl($Ph^{15}NH_2$)(η^6-*p*-cymene)($CNBu^t$)]BPh_4 (**20***)

This complex was prepared exactly like the related unlabeled compound **20** by using 1,3-$Ph^{15}N{=}N^{15}N(H)Ph$ as a reagent; yield ≥20%. IR (KBr pellet): ν^{15}_{NH} 3246, 3203 (m); ν_{CN} 2178 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.36–6.73 (m, 20H, Ph), 5.61, 4.63 (dd, 2H, NH_2), 5.30–5.03 (m, 9H, Ph amine + *p*-cym), 2.45 (m, 1H, CH), 2.11 (s, 3H, CH_3 *p*-cym), 1.33 (s, 9H, CH_3 Bu^t), 1.19, 1.16 (d, 6H, CH_3 Pr^i) ppm. $^{15}N\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: −387.6 (s) ppm.

2.4. Crystal structure determination

Crystallographic data were collected for **10** on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) and for **1b** on Bruker SMART APEX 2 CCD diffractometer at RIAIDT-CACTUS (Universidade de Santiago de Compostela) using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), and were corrected for Lorentz and polarisation effects. The software SMART [19] and SAINT [20] (**10**) or APEX2 [21] (**1b**) was used for collecting frames of data, indexing reflections, determination of lattice parameters, integration of intensity of reflections and scaling, and SADABS [22] for empirical absorption correction. Both structures were solved and refined with the Oscail program [23] by Patterson (**10**) or by direct (**1b**) methods and refined by a full-matrix least-squares based on F^2 [24]. 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. CCDC 762672 and 762673 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

2.5. General procedure for the hydrogenation experiments

A 150-mL stainless steel reaction vessel was charged, under a nitrogen purge, with 2.6 mmol of substrate, 0.0052 mmol of the catalytic precursor and 5 mL of toluene. The reactor was then pressurised at 50 atm of hydrogen, heated at 60–100 °C for the due time, then cooled to rt and the gas vented off. Conversions were determined by GC analysis carried out on an Agilent 6850 Series gas chromatograph, using an HP1 column (30 m × 0.32 mm × 0.25 μm). For analytical purposes, the target products were recovered from the reaction mixture by flash silica gel chromatography (*n*-hexane/ether, 8/2). NMR measurements were used to test the stability of the complexes in the catalytic reactions. The osmium complexes [Os(1,3-ArNNNAr)(η^6-*p*-cymene)L]BPh_4 were recovered unchanged at the end of the hydrogenation reactions, whereas only traces of the precursor complexes [Ru(1,3-ArNNNAr)(η^6-*p*-cymene)L]BPh_4 were found in the case of ruthenium.

2.5.1. Homogeneity test

When transition-metal complexes are used as precatalysts in hydrogenation processes, an important question is to establish the nature of the active species. The true catalyst may be either a homogeneous transition-metal complex or active metallic particles, present in solution as metal powder or metal nanoclusters, formed under reaction conditions [25–28]. Visual homogeneity of the solution is not enough to assess the absence of suspended or colloidal metal, therefore we carried out some hydrogenation experiments in the presence of Hg(0), according to a procedure described in the literature [28]. It is known that Hg(0) is able to poison metal(0) heterogeneous catalysts by amalgamating the metal catalyst or adsorbing on its surface but it does not deactivate homogeneous systems. We chose as model reactions the hydrogenation of styrene **IX** (Scheme 10) in the presence of the osmium precatalyst **8a** and the reduction of 2-cyclohexen-1-one **I** (Scheme 8) catalysed by ruthenium complex **5b**, respectively: both experiments were carried out at 80 °C and 50 atm of H_2 for 22 h. In the case of the osmium catalyst, no effect of Hg(0) on the catalysis was observed, so confirming the homogeneity of the reaction; on the contrary, the suppression of catalysis by Hg(0) towards the ruthenium complex was the evidence for a heterogeneous catalyst.

Table 1
Crystal data and structure refinement.

Identification code	**1b**	**10**
Empirical formula	$C_{20}H_{29}Cl_2O_2PRu$	$C_{53}H_{57}BN_4Ru$
Formula weight	504.37	861.91
Temperature	296(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\text{-}1$
Unit cell dimensions	$a = 11.9383(5)$ Å $b = 14.4755(7)$ Å $c = 12.8598(5)$ Å $\beta = 96.331(2)°$	$a = 11.1198(11)$ Å $b = 14.9589(15)$ Å $c = 15.4090(15)$ Å $\alpha = 98.707(2)°$ $\beta = 110.891(2)°$ $\gamma = 96.135(2)°$
Volume	2208.79(17) Å^3	2330.9(4) Å^3
Z	4	2
Density (calculated)	1.517 Mg/m^3	1.228 Mg/m^3
Absorption coefficient	1.036 mm^{-1}	0.375 mm^{-1}
$F(000)$	1032	904
Crystal size	0.29 × 0.20 × 0.14 mm	0.36 × 0.22 × 0.14 mm
Theta range for data collection	2.13–26.43°	1.40–28.02°
Index ranges	$-14 \le h \le 14$; $-18 \le k \le 18$; $-16 \le l \le 16$	$-14 \le h \le 13$; $-19 \le k \le 18$; $-20 \le l \le 20$
Reflections collected	26325	15310
Independent reflections	4523 [R(int) = 0.0530]	10652 [R(int) = 0.0399]
Reflections observed ($>2\sigma$)	3597	5863
Data completeness	0.996	0.943
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.831	1.000 and 0.925
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4523/0/240	10652/0/540
Goodness-of-fit on F^2	1.064	1.051
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0312$ $wR_2 = 0.0598$	$R_1 = 0.0685$ $wR_2 = 0.1683$
R indices (all data)	$R_1 = 0.0458$ $wR_2 = 0.0632$	$R_1 = 0.1293$ $wR_2 = 0.2103$
Largest diff. peak and hole	0.443, −0.457 eÅ^{-3}	1.113, −1.445 eÅ^{-3}

3. Results and discussion

3.1. Preparation of phosphite and isocyanide complexes

Reaction of dinuclear *p*-cymene complexes of ruthenium and osmium [MCl(μ-Cl)(η^6-*p*-cymene)]$_2$ with an excess of phosphite (L) in CH_2Cl_2 afforded mononuclear half-sandwich derivatives $MCl_2(\eta^6$-*p*-cymene)L (**1**, **2**) in excellent yield (Scheme 1).

tert-Butyl isocyanide [18] also reacts with dimeric compounds [MCl(μ-Cl)(η^6-*p*-cymene)]$_2$ in CH_2Cl_2 to yield half-sandwich isocyanide derivatives $MCl_2(\eta^6$-*p*-cymene)(CNR) (**3**, **4**), which were isolated and characterised (Scheme 1).

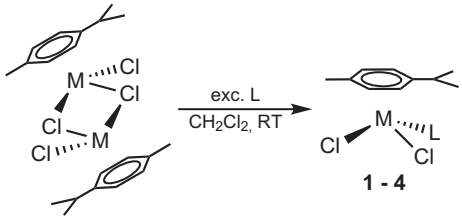
The reaction parallels that reported with common tertiary phosphines [1,2,17b] and allows mononuclear complexes to be prepared.

p-Cymene complexes **1**–**4** were separated as red or orange solids, stable in air and in solution of common organic solvents, in which they behave as non-electrolytes [29]. Analytical and spectroscopic data (IR and NMR) support the proposed formulation for the compounds.

The ^{1}H NMR spectra of phosphite complexes **1**, **2** show the characteristic signals of *p*-cymene hydrogen atoms and those of phosphite substituents; a singlet appears between 138 and 69 ppm in the $^{31}P\{^1H\}$ NMR spectra.

The IR spectra of isocyanide complexes **3**, **4** show a strong band at 2191–2185 cm^{-1}, attributable to ν_{CN} of the isocyanide ligand. ^{1}H and $^{13}C\{^1H\}$ NMR spectra confirm the presence of both isocyanide and *p*-cymene ligands, showing their characteristic signals (see Experimental).

To further support the formulation of phosphite complexes, we determined the X-ray crystal structure of $RuCl_2(\eta^6$-*p*-cymene)[PPh(OEt)$_2$] (**1b**), whose ORTEP is shown in Fig. 1. The complex adopts a typical 'piano-stool' geometry with the pseudo-tetrahedral arrangement of the *p*-cymene and other three ligands around the metal center ruthenium. Bond angles subtended by the ligands forming the legs and the ruthenium atom are all close to 90°



Scheme 1. M = Ru (**1**, **3**), Os (**2**, **4**); L = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b) (**1**, **2**); Bu^tNC (**3**, **4**).

(Table 2) and attest to the overall octahedral coordination of the metal atom. The distance from the ruthenium atom to the centroid of the planar *p*-cymene ring is 1.7102(2) Å (Table 2), value within the range found in the literature for Ru(*p*-cymene) complexes [9,30–34]. The ruthenium to carbon distances show some differences, with an average Ru–C 2.218(3) Å but in a wide range of 2.174 (3)–2.280(2) Å. Longer values correspond to those *trans* to the phosphorus atom and the shorter Ru–C bond corresponds to those "over" the phosphorus atom, and consequently *trans* to chloro ligands. The complex completes its coordination sphere with two chlorine atoms and a diethoxyphenylphosphine ligand, and this structure is usual in the literature, where *p*-cymene dihalo ruthenium(II) complexes have been extensively studied [30–33], and do not require further comment.

3.2. Half-sandwich triazene complexes

Half-sandwich phosphite complexes $MCl_2(\eta^6$-*p*-cymene)L (**1**, **2**) react with 1,3-diaryltriazene 1,3-ArN=NN(H)Ar in the presence of triethylamine to give triazenide complex cations $[M(\eta^2$-1,3-ArNNNAr$)(\eta^6$-*p*-cymene)L$]^+$ (**5**–**8**), which were isolated as BPh_4^- salts and characterised (Scheme 2).

Related isocyanide complexes $MCl_2(\eta^6$-*p*-cymene)(CNR) (**3**, **4**) also react with 1,3-ArN = NN(H)Ar in the presence of NEt_3 to give triazenide-isocyanide derivatives $[M(\eta^2$-1,3-ArNNNAr$)(\eta^6$-*p*-cymene)(CNR)$]^+$ (**9**–**12**), which were separated as BPh_4^- salts in good yield (Scheme 2). Crucial for successful synthesis is carrying out the reaction in ethanol as solvent containing one equivalent of $NaBPh_4$ and adding an excess of NEt_3 later. Otherwise, the result is an impure material, containing small amounts of triazenide complex.

The reaction of the the *p*-cymene complexes $MCl_2(\eta^6$-*p*-cymene)L (**1**–**4**) (L = phosphite or isocyanide) with 1,3-triazene probably proceeds with initial η^1-coordination of the triazene to the metal center through substitution of one Cl^- to give the intermediate [**A**] (Scheme 3).

Deprotonation of η^1-triazene [35] in intermediate [**A**] by NEt_3 allowed η^2-coordination of the triazenide $ArNNNAr^-$ anion and yielded the final complexes **5**–**12**.

The preparation of triazenide complexes **5**–**12** with phosphites or isocyanides also prompted us to study the reaction of dimeric

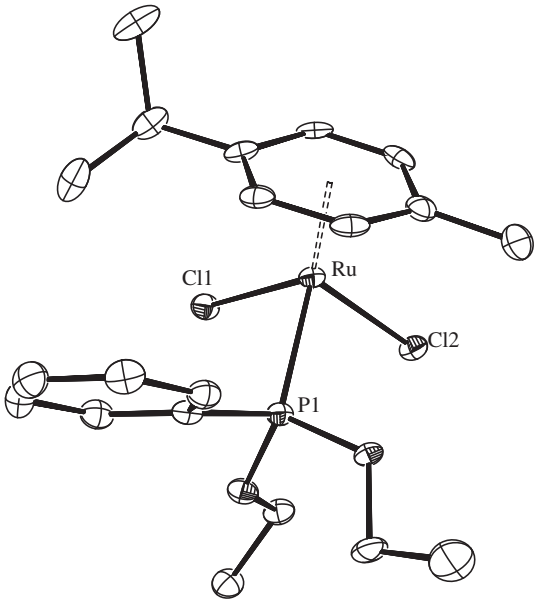


Fig. 1. The compound **1b** drawn at 50% probability level.

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

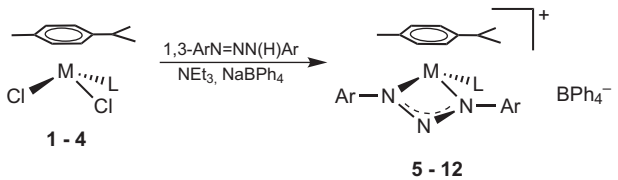
Ru–P(1)	2.2807(7)	Ru–Cl(2)	2.4038(7)
Ru–Cl(1)	2.4171(7)	Ru–CT[a]	1.7102(2)
CT–Ru–P(1)	127.71(2)	CT–Ru–Cl(2)	124.793(19)
P(1)–Ru–Cl(2)	87.89(2)	CT–Ru–Cl(1)	127.287(19)
P(1)–Ru–Cl(1)	87.59(2)	Cl(2)–Ru–Cl(1)	88.81(2)

[a] CT represents the centroid of the benzene ring for the *p*-cymene ligand.

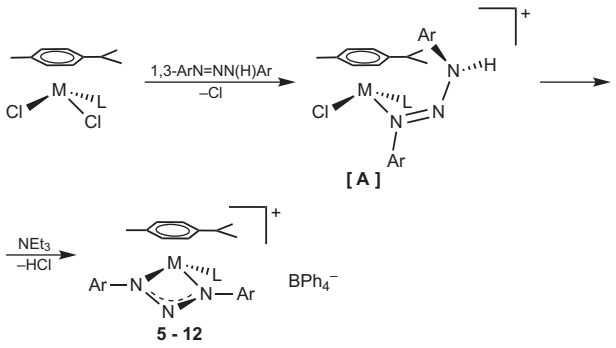
species $[MCl(\mu$-Cl$)(\eta^6$-*p*-cymene$)]_2$ with 1,3-triazene. Results show that, in the presence of triethylamine, the reaction proceeds to give triazenide complexes $MCl(\eta^2$-1,3-ArNNNAr$)(\eta^6$-*p*-cymene) (**13**–**15**), which were isolated in good yield and characterised (Scheme 4).

Initial coordination of the 1,3-ArN=NN(H)Ar molecule to the central metal is probably followed by deprotonation (NEt_3), giving the η^2-coordination of the 1,3-$ArNNNAr^-$ ligand. The triazenide therefore splits the chloro bridge of the starting materials to give the final monomeric derivatives **13**–**15**. Treatment of these complexes with phosphite or isocyanide in the presence of $NaBPh_4$ led to the complexes $[M(\eta^2$-1,3-ArNNNAr$)(\eta^6$-*p*-cymene)L$]BPh_4$ (**5**–**12**) (Scheme 5) [5–12].

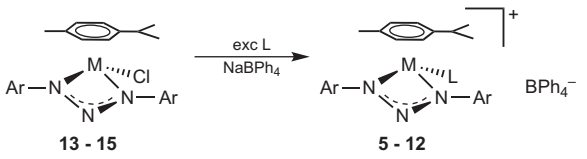
The new half-sandwich triazenide complexes **5**–**15** were separated as yellow or orange solids, stable in air and in solution of polar organic solvents in which they behave as 1:1 electrolytes **5**–**12** or non-electrolytes **13**–**15** [29]. Their formulation is supported by analytical and spectroscopic data (IR and NMR spectra) and X-ray crystal structure determination of $[Ru(\eta^2$-1,3-*p*-tolyl-NNN-*p*-tolyl$)(\eta^6$-*p*-cymene$\{CNC(CH_3)_3\}]BPh_4$ (**10**), whose ORTEP is shown in Fig. 2. The complex consists of a tetraphenylborate salt of a cation complex with a ruthenium atom coordinated by a η^6-*p*-cymene ligand, a 1,3-di-*p*-tolyltriazenide, and a carbon atom from a *tert*-butyl isocyanide group. This complex also adopts the typical 'piano-stool' geometry. Bond angles subtended by the ligands forming the legs and the ruthenium atom are all close to 90° (Table 3) and attest to the overall octahedral coordination of the metal atom, except chelate angle N(1)–Ru–N(2), with a value of 59.63(16)° due the small-bite of the triazenide ligand. The distance from the ruthenium atom to the centroid of the planar *p*-cymene ring is 1.7332 (4) Å, value within the range found in the literature for Ru(*p*-cymene) complexes [9,30–34]. The Ru–C distances range from 2.210(6) to 2.281(5) Å [average Ru–C 2.236(6) Å, and differences of only 0.07 Å]. It is noteworthy that the longest Ru–C bond involves the *iso*-propyl substituted carbon atom and not the methyl-substituted one, as observed for many cymene ruthenium complexes [34]. The complex completes its coordination sphere with a two nitrogen atoms from a bidentated 1,3-di-*p*-tolyl-triazenide-κ(*N,N″*) and a carbon atom from a *tert*-butyl isocyanide group. The small-bite of the triazene conditions the bond angles around the metal, but only those affecting this ligand, in such a way that the centroid–Ru–$C_{isocyanide}$ angle has a value of 126.6 (5)° (close to the theoretically expected 125.26°) and the N–Ru–$C_{isocyanide}$ angles are close to the expected 90°. The chelate angle of 59.6(2) is only slightly larger than those found for similar



Scheme 2. M = Ru (**5**, **6**, **9**, **10**), Os (**7**, **8**, **11**, **12**); Ar = Ph (**5**, **7**, **9**, **11**), *p*-tolyl (**6**, **8**, **10**, **12**); L = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b) (**5**–**8**), Bu^tNC (**9**–**12**).



Scheme 3. M = Ru, Os; Ar = Ph, *p*-tolyl; L = phosphite or isocyanide.



Scheme 5.

complexes by the Strähle group [9]. The N–N bond lengths in the triazenide molecule are also only slightly longer than those mentioned by the Strähle group, and are considered as a double bond. Those values are also comparable to those obtained previously by our group [13], with the expected differences due the different environment of the metal atom, and also to other triazene complexes with ruthenium [36] or with other metals [37]. The *tert*-butyl isocyanide group acts as a typical σ–donor ligand, with N(4)–C(41)–Ru angle of 177.6(5)° and C(41)–N(4)–C(42) of 178.4(8)°, close to the characteristic linearity of the poor d → p π-back-bonding [38]. However, the C(41)–N(4) bond length, 1.161(8) Å, is quite long, but still consistent with a triple bond between both atoms. The Ru–C bond length of 1.967(7) Å is in the range of Ru-*tert*-butyl isocyanide complexes [39].

The ^{1}H NMR spectra of complexes [M(η^2-1,3-ArNNNAr)(η^6-*p*-cymene)L]BPh$_4$ (**5-8**) show the characteristic signals of *p*-cymene and phosphite ligands and, in the case of the *p*-tolyl triazenide, there is also a singlet at 2.38–2.35 ppm of the methyl substituents. However, support for the presence of the triazenide group comes from the ^{15}N{^{1}H} NMR spectrum of the labeled complex [Os(η^2-1,3-Ph^{15}NN^{15}NPh)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh$_4$ (**7b***), which appears as a doublet at −188.9 ppm ($J_{^{15}N^{31}P}$ = 5.2 Hz) due to coupling with the phosphorus nucleus of the phosphite. The ^{31}P{^{1}H} NMR spectra of all phosphite complexes are singlets, fitting the proposed formulation.

The infrared spectra of isocyanide complexes [M(η^2-1,3-ArNNNAr)(η^6-*p*-cymene){CNC(CH$_3$)$_3$}]BPh$_4$ (**9**–**12**) show a strong band at 2191–2181 cm^{-1} due to ν_{CN} of the Bu^{t}NC ligand. ^{1}H NMR data confirm the presence of *tert*-butyl isocyanide showing not only the signals of the *p*-cymene and triazenide ligands, but also a singlet at 1.30–1.28 ppm of the *tert*-butyl substituents. The ^{15}N{^{1}H} NMR spectrum of [Os(η^2-1,3-Ph^{15}NN^{15}NPh)(η^6-*p*-cymene)(CNBu^{t})]BPh$_4$ (**11***) appears as a singlet at −186.9 ppm, confirming the proposed formulation for the complexes.

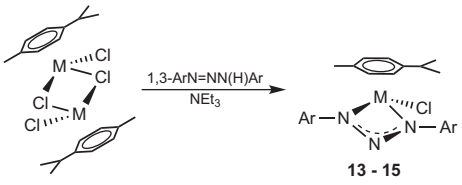
3.3. Preparation of amine derivatives

With the aim of synthesizing half-sandwich 1,3-triazene complexes like complex [**A**] and thus supporting the reaction path proposed in Scheme 3, we reacted precursors MCl$_2$(η^6-*p*-cymene)L (L = phosphites or isocyanides) with equimolar amounts of 1,3-triazene in the absence of NEt$_3$. Surprisingly, the reaction, in ethanol containing NaBPh$_4$, proceeds to give a mixture of triazenide-[M(η^2-1,3-ArNNNAr)(η^6-*p*-cymene)L]BPh$_4$ (**5**–**12**) and amine complexes [MCl(ArNH$_2$)(η^6-*p*-cymene)L]BPh$_4$ (**16**–**21**), which were separated by fractional crystallisation and characterised (Scheme 6).

The reaction was also carried out in the absence of NaBPh$_4$ but, in this case, was very slow and gave only traces of triazenide complexes. The presence of NaBPh$_4$ is crucial for the progress of the reaction, probably because it favors substitution of the chloride in precursor MCl$_2$(η^6-*p*-cymene)L, but does not allow preparation of 1,3-triazene complexes of the type [MCl(η^1-1,3-ArN=NN(H)Ar)(η^6-*p*-cymene)L]BPh$_4$ [**A**]. Instead, amine complexes **16**–**21** are formed together with the known triazenide derivatives **5**–**12**. This result is not completely unexpected, taking into account both the plausible path of the reaction between MCl$_2$(η^6-*p*-cymene)L and 1,3-ArN=NN(H)Ar (Scheme 3) and the properties of the free 1,3-triazene molecule.

The triazenic hydrogen atom NH of complex [MCl(η^1-1,3-ArN=NN(H)Ar)(η^6-*p*-cymene)L]$^{+}$ [**A**], initially formed, is probably deprotonated either by the BPh$_4^-$ anion, or by traces of water in the solvent, giving triazenide derivatives **5**–**12**. As a result, the acidity of the solution increases (HBPh$_4$, H$_3$O^{+}) during the reaction course, and this may cause protonation of the aminic nitrogen atom of free triazene ArN=NN(H)Ar (Scheme 7), leading to cleavage of the N–N bond and formation of amine ArNH$_2$ and aryldiazonium cation ArN$_2^+$.

In addition, amine ArNH$_2$ can substitute one chloride in the starting complex MCl$_2$(η^6-*p*-cymene)L to give the half-sandwich



Scheme 4. M = Ru (**13**, **14**), Os (**15**); Ar = Ph (**13**), *p*-tolyl (**14**, **15**).

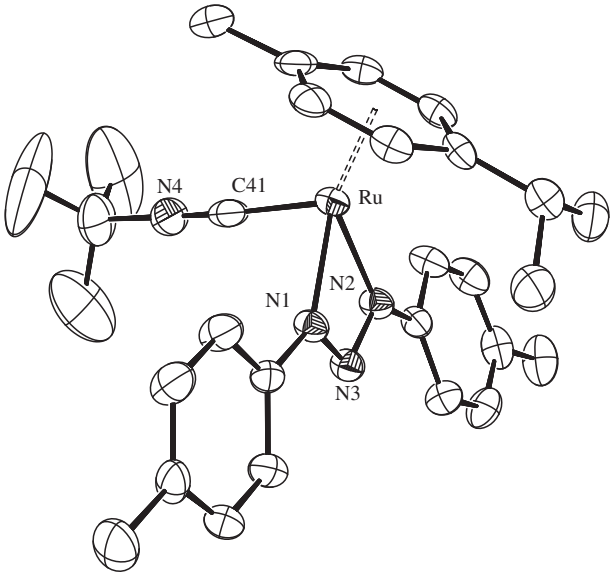


Fig. 2. The cation **10** drawn at 30% probability level.

Table 3
Selected bond lengths [Å] and angles [°] for **10**.

Ru–C(41)	1.967(7)	Ru–N(1)	2.063(4)
Ru–N(2)	2.064(4)	Ru–CT	1.7332(4)
C(11)–N(1)	1.396(6)	N(1)–N(3)	1.327(6)
N(3)–N(2)	1.299(5)	N(2)–C(21)	1.413(7)
C(41)–N(4)	1.161(8)		
CT–Ru–C(41)	126.65(15)	CT–Ru–N(1)	135.91(13)
C(41)–Ru–N(1)	87.62(19)	CT–Ru–N(2)	136.01(12)
C(41)–Ru–N(2)	87.9(2)	N(1)–Ru–N(2)	59.63(16)
N(3)–N(1)–C(11)	119.1(4)	N(2)–N(3)–N(1)	102.8(4)
N(3)–N(2)–C(21)	118.5(4)	N(4)–C(41)–Ru	177.6(5)
C(41)–N(4)–C(42)	178.4(8)		

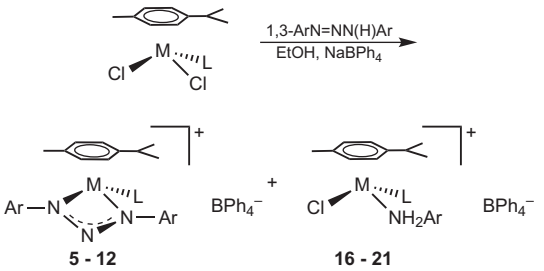
amine derivatives **16**–**21**. Support for this reaction path came from the reaction with 1,3-Ph^{15}N=N^{15}N(H)Ph, which afforded both the ^{15}N-labeled triazenide complexes [M(η^2-1,3-Ph^{15}NN^{15}NPh)(η^6-*p*-cymene)L]BPh_4 (**7b***, **11***) and the ^{15}N-amine derivatives [MCl(Ph^{15}NH$_2$)(η^6-*p*-cymene)L]BPh_4 (**16b***, **18b***, **20***).

Amine complexes [MCl($ArNH_2$)(η^6-*p*-cymene)L]BPh_4 were also prepared by reacting MCl_2(η^6-*p*-cymene)L with the appropriate arylamine $ArNH_2$ in ethanol containing $NaBPh_4$.

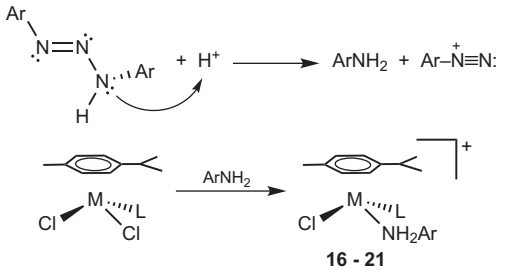
Complexes [MCl($ArNH_2$)(η^6-*p*-cymene)L]BPh_4 (**16**–**21**) are yellow solids, stable in air and in solution of polar organic solvents, in which they behave as 1:1 electrolytes [29]. Analytical and spectroscopic data (IR, NMR) support the proposed formulation.

The IR spectra show two medium-intensity bands at 3318–3193 cm^{-1} attributed to ν_{NH} of the amine group $ArNH_2$. A strong band at 2178–2174 cm^{-1}, due to ν_{CN} of the $(CH_3)_3CNC$ ligand, is also present in the isocyanide complexes **20** and **21**.

The ^{1}H NMR spectra support the proposed formulation, showing either the signals of the *p*-cymene and phosphite or isocyanide ligand, and two slightly broad doublets between 5.75 and 4.42 ppm attributed to the two hydrogens of the amine ligand. The stereogenic nature of the central metal causes splitting of the NH_2 signals into the two observed multiplets. In the spectra of labeled complexes [OsCl(Ph^{15}NH$_2$)(η^6-*p*-cymene)L]BPh_4 (**16b***, **18b***, **20***), the two broad doublets are replaced by two doublets of doublets (of doublets, **16b***, **18b***), owing to the coupling with the ^{15}N nucleus ($J_{^1H^{15}N}$ = 72.8 Hz), fitting the proposed assignment. The proton-coupled ^{15}N NMR spectra also support the presence of the amine ligand showing a doublet of triplets at −366.6 ppm ($J_{^{15}N^1H}$ = 72.8 Hz) for **16b***, due to coupling with both the NH_2 hydrogen atoms and the ^{31}P{^{1}H} nucleus of the phosphite, while only one triplet, at −387.6 ppm, appears for isocyanide complex **20***. The ^{31}P{^{1}H} NMR spectra of the phosphite complexes are sharp singlets, whereas the ^{13}C{^{1}H} spectra of the isocyanide complexes **21** show a singlet of the isocyanide carbon atom near 102 ppm, fitting the proposed formulation for the amine derivatives.



Scheme 6. M = Ru (**16**, **17**), Os (**18**–**21**); Ar = Ph (**16**, **18**, **20**), *p*-tolyl (**17**, **19**, **21**); L = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b) (**16**–**19**), Bu^{t}NC (**20**, **21**).



Scheme 7.

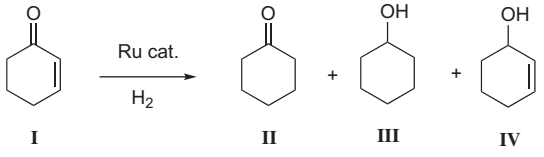
3.4. Catalytic activity

3.4.1. Hydrogenation with ruthenium complexes

Ruthenium compounds are known to reduce a great variety of substrates such as unfunctionalised or functionalised olefins, ketones, aldehydes, esters, acids, imines, *etc.* [40–42]. In this context, we tested some of our η^6-*p*-cymene complexes, of the types RuCl(η^2-1,3-ArNNNAr)(η^6-*p*-cymene) and [Ru(η^2-1,3-ArNN-NAr)(η^6-*p*-cymene)L]BPh_4 (L = phosphite or isocyanide) in the hydrogenation of α,β-unsaturated substrates such as 2-cyclohexen-1-one **I** and cinnamaldehyde **V**, in order to study the activity of these catalytic systems toward the reduction of the carbon–carbon and carbon-oxygen double bond, respectively. A first set of experiments was carried out on 2-cyclohexen-1-one **I** in toluene, (Scheme 8) with a substrate-to-catalyst molar ratio of 500, at 60–80 °C and 50 atm of hydrogen pressure for 22 h (Table 4).

The two η^6-*p*-cymene catalytic precursors containing only the triazenide ligand, RuCl(η^2-1,3-*p*-tolyl-NNN-*p*-tolyl)(η^6-*p*-cymene) (**14**) and RuCl(η^2-1,3-PhNNNPh)(η^6-*p*-cymene) (**13**), respectively, showed quite low activity and selectivity. After 22 h at 80 °C, conversions were only about 30–35%: both cyclohexanone **II** and cyclohexanol **III** were produced, but the saturated ketone **II** was the main reaction product, obtained with about 70% selectivity (items 1 and 2, Table 4). When the triazenide-phosphite complexes **6b**, **6a** and **5b** were employed as catalysts for the hydrogenation of **I** at 80 °C, complete substrate conversions were obtained and cyclohexanol **III**, was the prevailing reaction product (run 3, 5 and 7, Table 4). By performing the same reaction at 60 °C revealed a lower reaction rate, but the selectivity was now strongly shifted toward cyclohexanone **II** (about 94%) (run 4, 6 and 8, Table 4).

Very surprisingly, catalytic precursor [Ru(η^2-1,3-*p*-tolyl-NNN-*p*-tolyl)(η^6-*p*-cymene)(P^iPr_3)]BPh_4 (**6c**), containing the *iso*-propyl phosphine moiety, was practically inactive at 60 °C; when the hydrogenation experiment was carried out at 80 °C, cyclohexenone was totally converted into a mixture of the corresponding saturated ketone **II** (88.1%) and alcohol **III** (11.9%) (runs 9 and 10, Table 4). Lastly, isocyanide derivative [Ru(η^2-1,3-*p*-tolyl-NNN-*p*-tolyl)(η^6-*p*-cymene)(^{t}BuNC)}]BPh_4 (**10**) was used as catalytic precursor: in this case, at both 80 and 60 °C, substrate conversion was complete, with the formation of a mixture of **II** and **III**: depending on reaction temperature, we observed complete inversion of selectivity (runs 11 and 12, Table 4).



Scheme 8.

Table 4
Hydrogenation of 2-cyclohexen-1-one **I** catalysed by ruthenium complexes.

Run	Cat.	T (°C)	Conv. (%)	**II** (%) selectivity	**III** (%) selectivity
1	**14**	80	30.2	72.2	27.8
2	**13**	80	35.6	72.7	27.3
3	**6b**	80	100	27.5	72.5
4	**6b**	60	87.2	94.1	5.9
5	**6a**	80	100	23.9	76.1
6	**6a**	60	91.7	93.2	6.8
7	**5b**	80	100	37.9	62.1
8	**5b**	60	75.8	94.5	5.5
9	**6c**	80	100	88.1	11.9
10	**6c**	60	2.7	2.7	–
11	**10**	80	100	39.2	60.8
12	**10**	60	100	63.9	36.1

Substrate = 2.6 mmol; Cat. = 0.0052 mmol; toluene = 3 mL; t = 22 h; p(H2) = 50 atm.

Interesting results were also obtained in the hydrogenation of cinnamaldehyde **V** (Scheme 9). Hydrogenation of α,β-unsaturated aldehydes, particularly *trans*-cinnamaldehyde, is in fact an important step in the production of some useful fine chemicals as intermediates in the synthesis of pharmaceuticals, additives for food flavours, and valuable building block for fragrances [43]. The catalytic chemoselective hydrogenation of the carbonyl group is a challenging task [40–42]: for example, *bis*-phosphine-ruthenium (II)-(*p*-cymene) complexes have been used in the chemoselective reduction of the carbonyl moiety of *trans*-cinnamaldehyde [44] and, more recently, the dinuclear complex $[Ru(PhBP_3)(\mu\text{-}Cl)]_2$, containing the tripodal phosphonoborate ligand $[PhB(CH_2PPh_2)_3]^-$, turned out to be very active and selective in the hydrogenation of cinnamaldehyde to the corresponding unsaturated alcohol **VIII** [45]. Although cinnamyl alcohol **VIII** is highly desirable, reduction of the carbon–carbon double bond is generally thermodynamically favoured over carbonyl reduction and 3-phenylpropanal **VI** and/or 3-phenylpropanol **VII** therefore formed.

By analogy with the experiments carried out on 2-cyclohexen-1-one **I**, first, we evaluated the activity of the two catalytic precursors not containing any phosphorus ligand, **14** and **13**, respectively: as was observed in the hydrogenation of **I**, their activity was quite low, giving only about 50% substrate conversion after 24 h at 100 °C and 50 atm of H_2 pressure. These catalysts showed good capability to hydrogenate both C=C and C=O double bonds, affording a mixture of the saturated aldehyde **VI**, corresponding alcohol **VII**, and cinnamyl alcohol **VIII**: in both cases, **VI** was the main reaction product (runs 1 and 2, Table 5). Ruthenium–phosphite complexes **6b**, **6a** and **6c**, after 17 h at 100 °C, gave high substrate conversions: in all cases 3-phenylpropanol **VII** was the main reaction product (runs 3–5, Table 5). Ruthenium complex **6c**, modified with *iso*-propylphosphine, was much less active, furnishing only about 34% of substrate conversion, and cinnamyl alcohol **VIII**, the main reaction product, was obtained with 55% selectivity (run 6, Table 5). Lastly, compound **10**, containing the isocyanide ligand, was employed as catalytic precursor: its activity, like that observed in 2-cyclohexen-1-one hydrogenation, was very high, affording 100% of substrate conversion. The good hydrogenating capability of this catalyst was confirmed by the good formation of saturated alcohol **VII**, obtained with about 80% selectivity. In general, these *p*-cymene-diaryltriazene ruthenium complexes show fairly good activities, with TONs ranging from 150 to 500, comparable with other ruthenium(II)-*p*-cymene compounds such as those described by Dyson and Chaplin [44]. These last complexes, however, work well also at 50 °C, show higher TOFs and are more selective for the reduction of carbonyl groups in the presence of olefinic bonds. We can suppose that this difference in activity and selectivity is probably due to the great steric hindrance of the ligands bound to metal center of our catalytic systems.

Table 5
Hydrogenation of cinnamaldehyde **V** catalysed by ruthenium complexes.

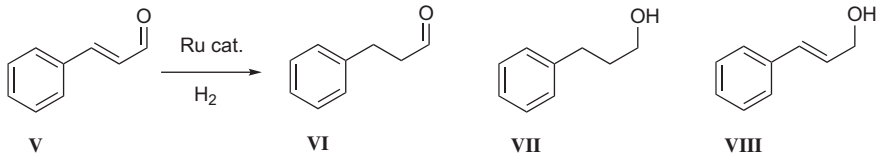
Run	Cat.	T (°C)	t (h)	Conv. (%)	**VI** (%) selectivity	**VII** (%) selectivity	**VIII** (%) selectivity
1	**14**	100	24	50.2	56.6	18.1	25.5
2	**13**	100	24	56.0	58.0	19.6	22.4
3	**6b**	100	17	95.9	27.7	52.6	19.7
4	**6a**	100	17	83.9	29.4	48.6	22.0
5	**5b**	100	17	90.8	25.0	53.1	21.9
6	**6c**	100	17	33.7	35.9	9.1	55.0
7	**10**	100	17	100	20.6	79.4	–

Substrate = 2.6 mmol; Cat. = 0.0052 mmol; toluene = 5 mL; $p(H_2)$ = 50 atm.

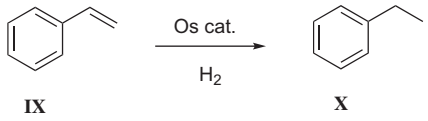
3.4.2. Hydrogenation with osmium complexes

Analogous complexes of osmium were also employed in the hydrogenation process. Osmium derivatives are known to be active in the hydrogenation of unfunctionalised olefins and α,β-unsaturated compounds [25,46–52]. For example, styrene had been efficiently hydrogenated to ethylbenzene by using tetranuclear osmium clusters at ambient pressure and 140 °C: these complexes are effective homogeneous catalysts even if they probably undergo fragmentation to produce lower nuclearity species responsible for the activity [25]. Also mononuclear osmium complexes modified with phosphino ligands were employed in the hydrogenation of styrene under ambient hydrogen pressure at 60 °C [25,46–48]. In this context, we first carried out some hydrogenation experiments on styrene **IX** at 80 °C and 50 atm of H_2 for 22 h, by using a substrate-to-catalyst molar ratio of 500/1 (Scheme 10).

All the catalytic precursors employed were very active, affording ethylbenzene **X** in very good yields (80–100%) (see Table 6). We then carried out hydrogenation experiments on 2-cyclohexen-1-one **I**. The hydrogenation of 2-cyclohexen-1-one was efficiently carried out by Sanchez-Delgado et al. in the presence of the homogeneous catalyst $OsH(Br)(CO)(PPh_3)_3$: under H_2 atmospheric pressure at 100 °C, the α,β-unsaturated substrate was reduced to cyclohexanone with 100% yield; by increasing the reaction temperature to 150 °C and H_2 pressure to 5 atm, conversion was complete but, in this case, a mixture of cyclohexanone (69%) and cyclohexanol (31%) was obtained [49]. More recently, 2-cyclohexen-1-one has been hydrogenated in the presence of the cationic complex $[OsH(CO)(NCMe)_2(PPh_3)_2]BF_4$ at 100 °C and 4 atm of H_2: cyclohexanone was selectively produced by allowing the reaction



Scheme 9.



Scheme 10.

to occur in 2-methoxyethanol, as well as in toluene solution [50]. We carried out our hydrogenation experiments on 2-cyclohexen-1-one at 80 °C and 50 atm of H_2 for 22 h, by using a substrate/catalyst molar ratio of 500/1.

Cationic complexes [Os(η^2-1,3-*p*-tolyl-NNN-*p*-tolyl)(η^6-*p*-cymene){P(OEt)$_3$}]BPh_4 (**8a**), [Os(η^2-1,3-PhNNNPh)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh_4 (**7b**) and [Os(η^2-1,3-*p*-tolyl-NNN-*p*-tolyl)(η^6-*p*-cymene){PPh(OEt)$_2$}]BPh_4 (**8b**) gave low substrate conversions, affording a mixture of cyclohexanone **II** and cyclohexanol **III**: ketone **II**, the main reaction product, was obtained with 80–85% selectivity (see Table 7). The neutral osmium derivative OsCl(η^2-1,3-*p*-tolyl-NNN-*p*-tolyl)(η^6-*p*-cymene) (**15**), not containing any phosphorus ligand, was even less active (10% conversion) and afforded cyclohexanone **II** as the only reaction product. A better result was obtained by performing the reaction in the presence of the isocyanide derivative [OsCl($PhNH_2$)(η^6-*p*-cymene)(Bu^tNC)]BPh_4 (**20**) which, after 22 h at 80 °C, gave a substrate conversion of about 77%. Again, a mixture of **II** and **III** was produced and cyclohexanone **II** was the prevailing reaction product (84.2% selectivity). In order to increase the catalytic activity of the above osmium complexes, the reaction temperature was taken to 100 °C. Very interestingly, as shown in Table 7, the temperature not only brought substrate conversion to 100%, but also enhanced the capacity for hydrogenation of the C=O double bond. All the cationic osmium complexes containing a phosphite ligand did afford alcohol **III** in about 40% yield (runs 2, 4 and 6, Table 7) and the most active isocyanide complex **20** produced cyclohexanol at a yield as high as 100% (run 10, Table 7).

When these osmium-based catalytic precursors were used to hydrogenate cinnamaldehyde at 100 °C and 50 atm of H_2 for 22 h, very disappointing results were obtained: in all cases, 3-phenylpropanal **VI**, the only reaction product, was obtained in practically negligible amounts (2–3%). This result was quite surprising, as cinnamaldehyde had been efficiently hydrogenated by Sanchez-Delgado et al. in the presence of osmium complexes modified with PPh_3 at 100 °C and 30 atm of H_2. Very interestingly, complex $OsCl_2(PPh_3)_3$ produced an almost equimolar mixture of the saturated aldehyde and the saturated alcohol, whereas complexes $OsH_4(PPh_3)_3$ and $OsHCl(CO)(PPh_3)_3$ were more selective for the formation of cinnamyl alcohol [47]. Korean authors have also reported the hydrogenation of cinnamaldehyde with hydridocarbonyl osmium complexes containing diphosphine ligands, and observed that the C=O bond was more easily reduced than the C=C bond [51]. In our case, the lack of catalytic activity was probably due to the great steric hindrance of our catalytic precursors, hindering the coordination of the substrate to the osmium center.

Table 6
Hydrogenation of styrene **IX** catalysed by osmium complexes.

Run	Cat.	*T* (°C)	***X*** yield (%)
1	**8b**	80	84.3
2	**8a**	100	95.0
3	**7b**	80	80.5
4	**15**	100	100
5	**20**	80	100

Substrate = 2.6 mmol; Cat. = 0.0052 mmol.
Toluene = 5 mL; $p(H_2)$ = 50 atm; t = 22 h.

Table 7
Hydrogenation of 2-cyclohexen-1-one **I** catalysed by osmium complexes.

Run	Cat.	*T* (°C)	Conv. (%)	**II** (%) selectivity	**III** (%) selectivity
1	**8a**	80	19.2	88.5	11.5
2	**8a**	100	100	57.8	42.2
3	**8b**	80	17.5	85.1	14.9
4	**8b**	100	100	61.3	38.7
5	**7b**	80	20.9	80.0	20.0
6	**7b**	100	100	58.4	41.6
7	**15**	80	10.1	100	–
8	**15**	100	100	81.3	28.7
9	**20**	80	76.6	84.2	15.8
10	**20**	100	100	–	100

Substrate = 2.6 mmol; Cat. = 0.0052 mmol; toluene = 5 mL; $p(H_2)$ = 50 atm; t = 22 h.

4. Conclusions

In this paper we report the synthesis of half-sandwich complexes of ruthenium and osmium containing 1,3-triazenide as a supporting ligand of the types [M(η^2-1,3-ArNNNAr)(η^6-*p*-cymene)L]BPh_4 (L = phosphite or isocyanide) and MCl(η^2-1,3-ArNNNAr)(η^6-*p*-cymene). A new reaction of the *p*-cymene complexes MCl_2(η^6-*p*-cymene)L, which yielded the amine derivative [MCl($ArNH_2$)(η^6-*p*-cymene)L]BPh_4 when treated with equimolar amounts of diaryltriazene 1,3-ArN=NN(H)Ar, is also reported. Characterisation of new compounds by spectroscopic (^{1}H, ^{31}P, ^{13}C, ^{15}N NMR) and crystallographic (X-ray) data is discussed. Triazenide complexes [M(η^2-1,3-ArNNNAr)(η^6-*p*-cymene)L]BPh_4 are active catalysts in the hydrogenation of both substrates 2-cyclohexen-1-one and cinnamaldehyde, and isocyanide complexes show better hydrogenation capability than phosphite ones.

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