

Preparation and reactivity with azo-species of hydride and dihydrogen complexes of osmium stabilised by tris(pyrazolyl)borate and phosphite ligands

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Abstract

Mixed-ligand $\text{OsCl}(\text{Tp})\text{L}(\text{PPh}_3)$ complexes **1** [Tp = hydridotris(pyrazolyl)borate; L = $\text{P}(\text{OMe})_3$, $\text{P}(\text{OEt})_3$ and $\text{PPh}(\text{OEt})_2$] were prepared by allowing $\text{OsCl}(\text{Tp})(\text{PPh}_3)_2$ to react with an excess of phosphite. Treatment of chlorocomplexes **1** with NaBH_4 in ethanol afforded hydride $\text{OsH}(\text{Tp})\text{L}(\text{PPh}_3)$ derivatives **2**. Stable dihydrogen $[\text{Os}(\eta^2\text{-H}_2)(\text{Tp})\text{L}(\text{PPh}_3)]\text{BPh}_4$ derivatives **3** were prepared by protonation of hydrides **2** with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ at -80°C . The presence of the $\eta^2\text{-H}_2$ ligand is supported by short $T_{1\text{min}}$ values and J_{HD} measurements on the partially deuterated derivatives. Treatment of the hydride $\text{OsH}(\text{Tp})[\text{P}(\text{OEt})_3](\text{PPh}_3)$ complex with the aryldiazonium salt $[4\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2]\text{BF}_4$ afforded aryldiazene $[\text{Os}(4\text{-CH}_3\text{C}_6\text{H}_4\text{N}=\text{NH})(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$ derivative **4**. Instead, aryldiazenido $[\text{Os}(4\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2)(\text{Tp})[\text{P}(\text{OEt})_3](\text{PPh}_3)](\text{BF}_4)_2$ derivative **5** was obtained by reacting the hydride $\text{OsH}(\text{Tp})[\text{P}(\text{OEt})_3](\text{PPh}_3)$ first with methyltriflate and then with aryldiazonium $[4\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2]\text{BF}_4$ salt. Spectroscopic characterisation (IR, ^{15}N NMR) by the ^{15}N -labelled derivative strongly supports the presence of a near-linear $\text{Os}-\text{N}\equiv\text{N}-\text{Ar}$ aryldiazenido group. Imine $[\text{Os}\{\eta^1\text{-NH}=\text{C}(\text{H})\text{Ar}\}(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$ complexes **6** and **7** (Ar = C_6H_5 , $4\text{-CH}_3\text{C}_6\text{H}_4$) were also prepared by allowing the hydride $\text{OsH}(\text{Tp})[\text{P}(\text{OEt})_3](\text{PPh}_3)$ to react first with methyltriflate and then with alkylazides.

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1. Introduction

Dihydrogen complexes of transition metals are an important class of compounds which have been extensively studied in the last twenty years, both from a fundamental point of view and in an attempt to provide insights into the stoichiometric and catalytic activation of H_2 by coordination [1–3]. Numerous examples of stable $\eta^2\text{-H}_2$ complexes have been prepared for several transition metals with a wide range of ancillary ligands, including mono and polydentate tertiary phosphines, carbonyl, nitrosyl and cyclopentadienyl species [1–3].

Less attention has been paid to the tris(pyrazolyl)borate (Tp) ligand, whose dihydrogen chemistry has led to relatively few papers with respect to the other ligands [4,5], and only two examples of stable $\eta^2\text{-H}_2$ complexes have been reported for osmium [6].

We are interested in the chemistry of classical and non-classical metal hydride complexes, and have reported the synthesis and reactivity of several $\eta^2\text{-H}_2$ derivatives of manganese and iron triads stabilised by phosphite ligands [7,8]. We have also focused attention on the use of these hydrides as precursors in “organometallic” diazo chemistry, which allows the preparation of numerous examples of aryldiazene, aryldiazenido and hydrazine derivatives [9]. Recently, we have extended these studies to polypyridine [10] and tris(pyrazolyl)borate as supporting ligands, and have reported the synthesis and reactivity of classical

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and non-classical hydride complexes of ruthenium stabilised by the Ru(Tp)L(PPh₃) fragment [11].

Now, as part of ongoing studies, we report the synthesis and reactivity towards azo-species of new hydride and dihydrogen complexes of osmium containing Tp and phosphite as ancillary ligands.

2. Experimental

2.1. General considerations

All synthetic work was carried out in an appropriate atmosphere (Ar, H₂) 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. (NH₄)₂OsCl₆ salt was a Pressure Chem (USA) product, used as received. Potassium hydridotris(pyrazolyl)borate (KTp) was prepared according to a published procedure [12]. Phosphite PPh(OEt)₂ was prepared by the method of Rabinowitz and Pellon [13], while P(OMe)₃ and P(OEt)₃ were Aldrich products, purified by distillation under nitrogen. Diazonium salts were prepared in the usual way [14]. The related labelled salt (4-CH₃C₆H₄N¹⁵N)BF₄ was prepared from Na¹⁵NO₂ (99% enriched, CIL, CH) and *p*-toluidine. Alkyl [15] and aryl [16] azides were prepared following methods previously reported. The labelled 4-CH₃C₆H₄CH₂¹⁵N₃ azide was obtained by reacting Na(¹⁵NNN) (98% enriched, CIL, CH) with 4-CH₃C₆H₄CH₂Br. Equimolar amounts of R¹⁵NNN and RNN¹⁵N were obtained. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer. NMR spectra (¹H, ³¹P, ¹³C, ¹⁵N) were obtained on AC200 or AVANCE 300 Bruker spectrometers at temperatures between –90 and +30 °C, unless otherwise noted. ¹H and ¹³C spectra are referred to internal tetramethylsilane; ³¹P{¹H} chemical shifts are reported with respect to 85% H₃PO₄ and ¹⁵N ones to CH₃¹⁵NO₂, in both cases with downfield shifts considered positive. The COSY, HMQC and HMBC NMR experiments were performed using their standard programs. The SwaN-MR and iNMR software packages [17] were used to treat NMR data. Proton T₁ values were measured in CD₂Cl₂ at 200 MHz with a standard 180-τ-90° pulse sequence. The conductivity of 10^{–3} mol dm^{–3} solutions of the complexes in CH₃NO₂ at 25 °C were measured with a Radiometer CDM 83. Elemental analyses were determined in the Micro-analytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova (Italy).

2.2. Synthesis of complexes

The OsCl₂(PPh₃)₂ and OsCl(Tp)(PPh₃)₃ complexes were prepared following the method previously reported [6b,18].

2.2.1. OsCl(Tp)L(PPh₃) (1) [L = P(OMe)₃ (a), P(OEt)₃ (b), PPh(OEt)₂ (c)]

An excess of the appropriate phosphite (10.0 mmol) was added to a solution of OsCl(Tp)(PPh₃)₂ (1.0 mmol, 0.96 g) in 40 mL of toluene and the reaction mixture was refluxed for 4 h in the case of P(OMe)₃ and 10 h with the other phosphites. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 mL). A yellow solid slowly separated out which was filtered and crystallised from ethanol; yield ≥85%. **1a**: C₃₀H₃₄BClN₆O₃OsP₂ (825.05): calcd. C, 43.67; H, 4.15; N, 10.19; Cl, 4.30. Found: C, 43.83; H, 4.26; N, 10.08; Cl, 4.41%. **1b**: C₃₃H₄₀BClN₆O₃OsP₂ (867.13): calcd. C, 45.71; H, 4.65; N, 9.69; Cl, 4.09. Found: C, 45.67; H, 4.80; N, 9.54; Cl, 4.22%. **1c**: C₃₇H₄₀BClN₆O₂OsP₂ (899.17): calcd. C, 49.42; H, 4.48; N, 9.35; Cl, 3.94. Found: C, 49.56; H, 4.53; N, 9.33; Cl, 4.06%.

2.2.2. OsH(Tp)L(PPh₃) (2) [L = P(OMe)₃ (a), P(OEt)₃ (b), PPh(OEt)₂ (c)]

To a solution of the appropriate OsCl(Tp)L(PPh₃) (**1**) complex (0.39 mmol) in 10 mL of ethanol was added an excess of NaBH₄ (8 mmol, 0.30 g) in 10 mL of ethanol and the reaction mixture refluxed for 1 h. The solvent was removed under reduced pressure leaving a white solid from which the hydride was extracted with three 5-mL portions of benzene. The extracts were evaporated to dryness and the obtained oil triturated with ethanol (2 mL). A pale-yellow solid slowly separated out, which was filtered and crystallized from ethanol; yield ≥70%. **2a**: C₃₀H₃₅BN₆O₃OsP₂ (790.60): calcd. C, 45.58; H, 4.46; N, 10.63. Found: C, 45.49; H, 4.37; N, 10.78%. **2b**: C₃₃H₄₁BN₆O₃OsP₂ (832.68): calcd. C, 47.60; H, 4.96; N, 10.09. Found: C, 47.41; H, 5.04; N, 9.96%. **2c**: C₃₇H₄₁BN₆O₂OsP₂ (864.73): calcd. C, 51.39; H, 4.78; N, 9.72. Found: C, 51.51; H, 4.75; N, 9.66%.

2.2.3. [Os(η²-H₂)(Tp)L(PPh₃)]BPh₄ (3) [L = P(OMe)₃ (a), P(OEt)₃ (b), PPh(OEt)₂ (c)]

A slight excess of HBF₄ · Et₂O (0.12 mmol, 17 μL of a 54% solution in diethylether) was added to a suspension, under a dihydrogen atmosphere, of the appropriate OsH(Tp)L(PPh₃) (**2**) hydride (0.11 mmol) in ethanol (5 mL) cooled to –80 °C. The reaction mixture was left to reach room temperature and stirred for 2 h. An excess of NaBPh₄ (0.22 mmol, 75 mg) in 2 mL of ethanol was added to the resulting solution which was stirred until a white solid separated out. The solid was filtered and crystallised under an H₂ atmosphere from CH₂Cl₂ and ethanol; yield ≥80%. **3a**: C₅₄H₅₆B₂N₆O₃OsP₂ (1110.84): calcd. C, 58.39; H, 5.08; N, 7.57. Found: C, 58.55; H, 4.99; N, 7.71%. *A*_M = 53.6 S cm² mol^{–1}. **3b**: C₅₇H₆₂B₂N₆O₃OsP₂ (1152.92): calcd. C, 59.38; H, 5.42; N, 7.29. Found: C, 59.17; H, 5.49; N, 7.20%. *A*_M = 51.3 S cm² mol^{–1}. **3c**: C₆₁H₆₂B₂N₆O₂OsP₂ (1184.97): calcd. C, 61.83; H, 5.27; N, 7.09. Found: C, 61.65; H, 5.35; N, 6.96%. *A*_M = 52.8 S cm² mol^{–1}.

2.2.4. $[Os(\eta^2-HD)(Tp)L(PPh_3)]^+CF_3CO_2^-$ (**3₁**)
 $[L = P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**), $PPh(OEt)_2$ (**c**)]

These complexes were prepared in solution at $-80^\circ C$ using CF_3COOD as the protonating agent. A typical experiment involves the preparation, in a vacuum-atmosphere dry-box, of a CD_2Cl_2 solution (0.5 mL) of the appropriate $OsH(Tp)L(PPh_3)$ (**2**) hydride (0.01 mmol) in a NMR tube. The tube was sealed by the screw-cap, cooled to $-80^\circ C$, and then a slight excess of CF_3COOD (0.011 mmol, 0.85 μL) added. After transferring the tube into the probe of the NMR instrument, pre-cooled to $-80^\circ C$, the spectra were recorded in the temperature range from -80 to $20^\circ C$.

2.2.5. $[Os(4-CH_3C_6H_4N=NH)(Tp)\{P(OEt)_3\}(PPh_3)]-BPh_4$ (**4b**)

Solid samples of $OsH(Tp)\{P(OEt)_3\}(PPh_3)$ (**2b**) (100 mg, 0.12 mmol) and of the $[4-CH_3C_6H_4N_2]BF_4$ diazonium salt (0.24 mmol, 49 mg) were placed in a 25-mL three-necked round-bottomed flask. The flask was cooled to $-196^\circ C$ and CH_2Cl_2 (7 mL) was added. The reaction mixture was brought to room temperature, stirred for 1 h and then the solvent was removed under reduced pressure. The solid obtained was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.26 mmol, 89 mg). A yellow solid separated out from the resulting solution which was filtered and crystallized from CH_2Cl_2 and ethanol; yield $\geq 85\%$. $C_{64}H_{68}B_2N_8O_3OsP_2$ (1271.06): calcd. C, 60.48; H, 5.39; N, 8.82. Found: C, 60.36; H, 5.50; N, 8.91%. $A_M = 55.6 S cm^2 mol^{-1}$.

2.2.6. $[Os(4-CH_3C_6H_4N=^{15}NH)(Tp)\{P(OEt)_3\}(PPh_3)]-BPh_4$ (**4b₁**)

This complex was prepared exactly like the related unlabelled complex **4b** using the $[4-CH_3C_6H_4N\equiv^{15}N]BF_4$ salt as a reagent; yield $\geq 75\%$.

2.2.7. $[Os(4-CH_3C_6H_4N_2)(Tp)\{P(OEt)_3\}(PPh_3)](BF_4)_2$ (**5b**)

An equimolar amount of CH_3OTf (14 μL , 0.12 mmol) was added to a solution of $OsH(Tp)\{P(OEt)_3\}(PPh_3)$ (**2b**) (100 mg, 0.12 mmol) in 5 mL of diethylether cooled to $-196^\circ C$. The reaction mixture was left to reach the room temperature, stirred for 2 h and then transferred by *cannula* into a 25-mL three-necked flask containing an excess of $[4-CH_3C_6H_4N_2]BF_4$ (0.48 mmol, 99 mg) in CH_2Cl_2 (5 mL) cooled to $-196^\circ C$. The reaction mixture was brought to room temperature, stirred for 24 h and then the solvent was removed under reduced pressure. The oil obtained was triturated with diethylether (5 mL) until a gummy solid separated out which was filtered and crystallized from CH_2Cl_2 and ethanol; yield $\geq 55\%$. $C_{40}H_{47}B_3F_8N_8O_3OsP_2$ (1124.43): calcd. C, 42.73; H, 4.21; N, 9.97. Found: C, 42.95; H, 4.33; N, 9.84%. $A_M = 177 S cm^2 mol^{-1}$.

2.2.8. $[Os(4-CH_3C_6H_4N\equiv^{15}N)(Tp)\{P(OEt)_3\}(PPh_3)]-(BF_4)_2$ (**5b₁**)

This complex was prepared exactly like the related unlabelled complex **5b** using the $[4-CH_3C_6H_4N\equiv^{15}N]BF_4$ salt as a reagent; yield $\geq 50\%$.

2.2.9. $[Os(ArCH=NH)(Tp)\{P(OEt)_3\}(PPh_3)]BPh_4$ (**6b**, **7b**) [$Ar = C_6H_5$ (**6**), $4-CH_3C_6H_4$ (**7**)]

An equimolar amount of CH_3OTf (14 μL , 0.12 mmol) was added to a solution of $OsH(Tp)\{P(OEt)_3\}(PPh_3)$ (**2b**) (100 mg, 0.12 mmol) in 5 mL of toluene cooled to $-196^\circ C$. The reaction mixture was left to reach the room temperature, stirred for 2 h and then an excess of the appropriate benzyl azide RN_3 (0.36 mmol) ($R = C_6H_5CH_2$ or $4-CH_3C_6H_4CH_2$) was added. The resulting solution was stirred for 24 h and then the solvent was removed under reduced pressure. The oil obtained was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.24 mmol, 82 mg). A green solid slowly separated out from the resulting solution which was filtered and crystallized from CH_2Cl_2 and ethanol; yield $\geq 65\%$. **6b**: $C_{64}H_{67}B_2N_7O_3OsP_2$ (1256.05): calcd. C, 61.20; H, 5.38; N, 7.81. Found: C, 61.08; H, 5.28; N, 7.75%. $A_M = 54.1 S cm^2 mol^{-1}$. **7b**: $C_{65}H_{69}B_2N_7O_3OsP_2$ (1270.07): calcd. C, 61.47; H, 5.48; N, 7.72. Found: C, 61.59; H, 5.55; N, 7.59%. $A_M = 52.5 S cm^2 mol^{-1}$.

2.2.10. $[Os(4-CH_3C_6H_4CH\equiv^{15}NH)(Tp)\{P(OEt)_3\}(PPh_3)]-(BPh_4)_2$ (**7b₁**)

This complex was prepared exactly like the related unlabelled complex **7b** using the $4-CH_3C_6H_4CH_2^{15}N_3$ azide as a reagent; yield $\geq 65\%$.

3. Results and discussion

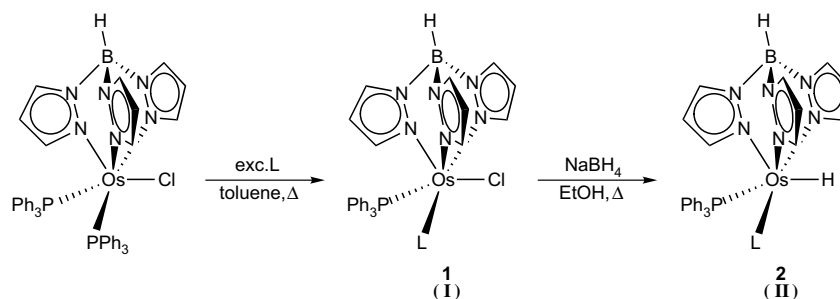
3.1. Synthesis of hydride complexes

The triphenylphosphine $OsCl(Tp)(PPh_3)_2$ complex [**6b**] reacts with phosphites in toluene to give mixed-ligand $OsCl(Tp)L(PPh_3)$ (**1**) derivatives in good yields (Scheme 1).

The reaction proceeds with the substitution of only one PPh_3 ligand, exclusively giving phosphine–phosphite complexes **1**. A higher temperature of reaction with xylene as solvent or a longer reaction time only result in a lower yield for compounds **1**, owing to some decomposition.

Treatment of chloro-complexes **1** with $NaBH_4$ in refluxing ethanol yields hydride $OsH(Tp)L(PPh_3)$ (**2**) complexes, which were isolated as white solids and characterized.

Both complexes **1** and **2** were isolated as yellow (**1**) or white (**2**) solids stable in air and in solution of polar organic solvents, where they behave as non-electrolytes [19]. Analytical and spectroscopic data (IR and 1H , ^{31}P NMR; Tables 1 and 2) support the proposed formulations. IR spectra showed the bands characteristic of phosphite and Tp ligands and, in the case of hydrides **2**, medium-intensity absorption at $2049-2079 cm^{-1}$, due to ν_{OSH} . 1H NMR spectra confirm the presence of the Tp and phosphite ligands, showing the characteristic signals of pyrazolate proton atoms between 8.10 and 5.5 ppm and those of the methoxy and ethoxy substituents of the phosphites. A multiplet near -15 ppm is also present in the spectra of the $OsH(Tp)L(PPh_3)$ (**2**) complexes and was attributed to the hydride ligand. As the ^{31}P spectra appear as an AB pattern,

Scheme 1. L = P(OMe)₃ (a), P(OEt)₃ (b), PPh(OEt)₂ (c).

hydride signals can be simulated using an ABX ($X = {}^1\text{H}$) model with the parameters listed in Table 1. On the basis of the spectroscopic data, therefore, the formulations of complexes **1** and **2**, with geometry of types **I** and **II**, respectively (Scheme 1), are confirmed.

Hydrides OsH(Tp)L(PPh₃) (**2**) quickly react with Brønsted acid HX ($X = \text{BF}_4^-$, OTf^-) to give dihydrogen $[\text{Os}(\eta^2\text{-H}_2)(\text{Tp})\text{L}(\text{PPh}_3)]^+$ (**3**) cations, which were separated as tetraphenylborate salts and characterised (Scheme 2).

The synthesis of dihydrogen complexes **3** was carried out with both ethanol and dichloroethane as solvents, and provided white microcrystals in high yields. Crucial for successful preparation was an H₂ atmosphere (1 atm) and beginning protonation at low temperature (-80°C). Otherwise, oily products with low yields in dihydrogen complexes are obtained.

The $[\text{Os}(\eta^2\text{-H}_2)(\text{Tp})\text{L}(\text{PPh}_3)]\text{BPh}_4$ (**3**) derivatives are white solids very stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes [19]. The loss of dihydrogen was not observed at room temperature either in solid state or in solution, and the complexes can be conserved unchanged for a long time. This stability of osmium complexes **3** contrasts with those of the related ruthenium $[\text{Ru}(\eta^2\text{-H}_2)(\text{Tp})\text{L}(\text{PPh}_3)]^+$ cations (L = phosphites) [11b], which lose H₂ even at 5°C , preventing their separation in the solid state.

Good analytical data were obtained for the $[\text{Os}(\eta^2\text{-H}_2)(\text{Tp})\text{L}(\text{PPh}_3)]\text{BPh}_4$ (**3**) complexes, whose spectroscopic data (IR and ${}^1\text{H}$, ${}^{31}\text{P}$ NMR; Table 1) strongly support the proposed formulation. Besides the signals of Tp, phosphine and the BPh₄ anion, ${}^1\text{H}$ NMR spectra show a slightly broad triplet at -7.52 to -7.57 ppm, attributed to the $\eta^2\text{-H}_2$

H₂ ligand. Variable-temperature T_1 measurements on this signal gave $T_{1\text{min}}$ values of 8.3–9.5 ms (Table 2), fitting the presence of a dihydrogen derivative [20]. Further support for the occurrence of the $\eta^2\text{-H}_2$ ligand came from measuring the J_{HD} values of the isotopomer $[\text{Os}(\eta^2\text{-HD})(\text{Tp})\text{L}(\text{PPh}_3)]^+$ derivatives. The HD complexes were prepared by addition of deuterated trifluoroacetic acid CF_3COOD to hydrides **2** in CD_2Cl_2 . Their ${}^1\text{H}$ NMR spectra appear as a complicated multiplet, which resolves into a sharp triplet of intensity ratio 1:1:1 in the ${}^1\text{H}\{{}^{31}\text{P}\}$ spectra. A J_{HD} value of 25.2–25.0 Hz was measured from this triplet, confirming the formation of the dihydrogen derivatives. The ${}^1\text{H}\{{}^{31}\text{P}\}$ spectra also show a small, relatively broad signal, due to the low amount of H₂ species resulting from uncompleted deuteration of the acid. Comparisons between the phosphorus-coupled and decoupled proton spectra revealed values between 10.45 and 7.75 Hz for ${}^2J_{\text{PH}(\text{HD})}$ (Table 1), as deduced by simulations.

The H–H distances of the H₂ ligand in complexes **3** were calculated [21] from the J_{HD} values, and are listed in Table 2. Values between 1.020 and 1.017 Å were observed for our $\eta^2\text{-H}_2$ complexes **3**, which are consistent with “elongated” dihydrogen complexes [22]. The H–H distances of **3** are in fact intermediate between those of dihydrogen complexes ($\text{H–H} \leq 1 \text{ \AA}$) and the distances usually associated with dihydride complexes ($\text{H–H} \geq 1.5 \text{ \AA}$), indicating a strong mutual metal–H₂ interaction.

Instead, the related ruthenium $[\text{Ru}(\eta^2\text{-H}_2)(\text{Tp})\text{L}(\text{PPh}_3)]^+$ complexes [11b] are thermally unstable species, which lose H₂ even at $5\text{--}10^\circ\text{C}$ and have shorter H–H distances (about 0.9 Å) than derivatives **3**.

The H–H bond length of the H₂ ligand may also be calculated [23] from the $T_{1\text{min}}$ values, and the results (Table 2) show that there is general agreement between the distances calculated from the J_{HD} values and those determined by the T_1 method by means of a static rotation model. This fits recent analysis [24] of J_{HD} and $T_{1\text{min}}$ data of known dihydrogen complexes, and suggests that H–H distances should be calculated by a static rotation model, to obtain reasonable H–H distances in the $\eta^2\text{-H}_2$ ligand.

The ${}^{31}\text{P}\{{}^1\text{H}\}$ NMR spectra of $[\text{Os}(\eta^2\text{-H}_2)(\text{Tp})\text{L}(\text{PPh}_3)]\text{BPh}_4$ (**3**) complexes appear as an AB multiplet, fitting the geometry shown in Scheme 2. A comparison of our complexes **3** with related $\eta^2\text{-H}_2$ complexes of osmium containing

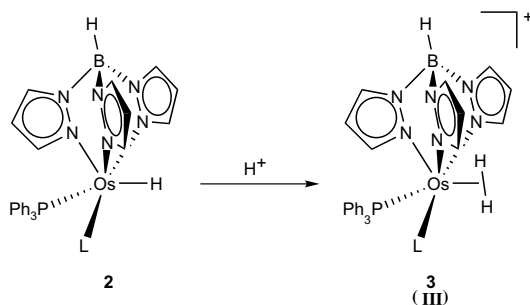
Scheme 2. L = P(OMe)₃ (a), P(OEt)₃ (b), PPh(OEt)₂ (c).

Table 1
Infrared, ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR data for osmium complexes

	Compound	IR ^a		^1H NMR ^b		$^{31}\text{P}\{^1\text{H}\}$ NMR ^{b,c}	
		(cm^{-1})	assgnt	(ppm; J , Hz)	assgnt	spin syst	(ppm; J , Hz)
1a	$\text{OsCl}(\text{Tp})\{\text{P}(\text{OMe})_3\}(\text{PPh}_3)$	2471 m	ν_{BH}	8.08–5.78 m 3.25d $J_{\text{PH}} = 10$	Ph + Tp CH ₃	AB	δ_{A} 79.0 δ_{B} -1.7 $J_{\text{AB}} = 30.0$
1b	$\text{OsCl}(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)$	2487 m	ν_{BH}	8.04–5.63 m 3.51 m 0.97 t	Ph + Tp CH ₂ CH ₃	AB	δ_{A} 76.4 δ_{B} -2.0 $J_{\text{AB}} = 31.2$
1c	$\text{OsCl}(\text{Tp})\{\text{PPh}(\text{OEt})_2\}(\text{PPh}_3)$	2483 m	ν_{BH}	7.80–5.68 m 3.84 m 3.45 m 1.12 t 0.90 t	Ph + Tp CH ₂ CH ₃	AB	δ_{A} 103.1 δ_{B} -5.6 $J_{\text{AB}} = 22.2$
2a	$\text{OsH}(\text{Tp})\{\text{P}(\text{OMe})_3\}(\text{PPh}_3)$	2489 m 2049 m	ν_{BH} ν_{OsH}	7.88–5.54 m 3.02 d $J_{\text{PH}} = 10$ ABX spin syst (X = ^1H) $\delta_{\text{X}} -15.00$ $J_{\text{AX}} = 18$ $J_{\text{BX}} = 24$	Ph + Tp CH ₃ OsH	AB	δ_{A} 107.6 δ_{B} 24.1 $J_{\text{AB}} = 33.6$
2b	$\text{OsH}(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)$	2456 m 2063 m	ν_{BH} ν_{OsH}	7.93–5.15 m 3.60 m 3.35 m 0.86 t ABX $\delta_{\text{X}} -15.30$ $J_{\text{AX}} = 24$ $J_{\text{BX}} = 18$	Ph + Tp CH ₂ CH ₃ OsH	AB	δ_{A} 103.1 δ_{B} 25.2 $J_{\text{AB}} = 32.5$
2c	$\text{OsH}(\text{Tp})\{\text{PPh}(\text{OEt})_2\}(\text{PPh}_3)$	2492 m 2079 m	ν_{BH} ν_{OsH}	7.81–5.51 m 3.90 m 3.47 m 3.23 m 1.03 t 0.71 t ABX $\delta_{\text{X}} -15.23$ $J_{\text{AX}} = 24$ $J_{\text{BX}} = 18$	Ph + Tp CH ₂ CH ₃ OsH	AB	δ_{A} 121.8 δ_{B} 22.9 $J_{\text{AB}} = 30.0$

3a	$[\text{Os}(\eta^2\text{-H}_2)(\text{Tp})\{\text{P}(\text{OMe})_3\}(\text{PPh}_3)]\text{BPh}_4$	2485 m	ν_{BH}	7.93–5.70 m 3.20d $J_{\text{PH}} = 12$ –7.52 t, br ABX^{d} $\delta_{\text{X}} -7.58$ $J_{\text{AX}} = 10.45$ $J_{\text{BX}} = 8.0$	Ph + Tp CH ₃ $\eta^2\text{-H}_2$	AB	$\delta_{\text{A}} 80.0$ $\delta_{\text{B}} 2.55$ $J_{\text{AB}} = 29.2$
3b	$[\text{Os}(\eta^2\text{-H}_2)(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	2496 m	ν_{BH}	7.92–5.80 m 3.66 m 3.35 m 1.05 t –7.57 t, br ABX^{d} $\delta_{\text{X}} -7.56$ $J_{\text{AX}} = 10.4$ $J_{\text{BX}} = 7.75$	Ph + Tp CH ₂ CH ₃ $\eta^2\text{-H}_2$	AB	$\delta_{\text{A}} 74.8$ $\delta_{\text{B}} 3.50$ $J_{\text{AB}} = 31.0$
3c	$[\text{Os}(\eta^2\text{-H}_2)(\text{Tp})\{\text{PPh}(\text{OEt})_2\}(\text{PPh}_3)]\text{BPh}_4$	2496 m	ν_{BH}	7.95–5.60 m 3.45 m 3.00 m 1.08 t 0.85 t –7.55 t, br ABX^{d} $\delta_{\text{X}} -7.60$ $J_{\text{AX}} = 9.48$ $J_{\text{BX}} = 8.0$	Ph + Tp CH ₂ CH ₃ $\eta^2\text{-H}_2$	AB	$\delta_{\text{A}} 103.1$ $\delta_{\text{B}} 3.30$ $J_{\text{AB}} = 26.1$
4b	$[\text{Os}(4\text{-CH}_3\text{C}_6\text{H}_4\text{N}=\text{NH})(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	2492 m	ν_{BH}	14.97d, br 7.90–6.00 m 3.68 m 3.35 m 2.34 s 1.05 t	NH Ph + Tp CH ₂ CH ₃ <i>p</i> -tol CH ₃ phos	AB	$\delta_{\text{A}} 68.5$ $\delta_{\text{B}} -2.17$ $J_{\text{AB}} = 31.6$
4b₁	$[\text{Os}(4\text{-CH}_3\text{C}_6\text{H}_4\text{N}=\text{N}^{15}\text{NH})(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$	2496 m	ν_{BH}	ABXY (X = ¹ H, Y = ¹⁵ N) $\delta_{\text{X}} 14.98$ $J_{\text{AX}} = 3.43$ $J_{\text{BX}} = 0.78$ $J_{\text{XY}} = 68.1$ 7.90–6.05 m 3.69 m 3.35 m 2.34 s 1.06 t	NH Ph + Tp CH ₂ CH ₃ <i>p</i> -tol CH ₃ phos	ABY	$\delta_{\text{A}} 68.9$ $\delta_{\text{B}} -2.17$ $J_{\text{AB}} = 31.6$ $J_{\text{AY}} = 2.6$ $J_{\text{BY}} = 0.75$

(continued on next page)

Table 1 (continued)

Compound	IR ^a		¹ H NMR ^b		³¹ P{ ¹ H} NMR ^{b,c}	
	(cm ⁻¹)	assgnt	(ppm; <i>J</i> , Hz)	assgnt	spin syst	(ppm; <i>J</i> , Hz)
5b [Os(4-CH ₃ C ₆ H ₄ N≡N)(Tp){P(OEt) ₃ }(PPh ₃)](BF ₄) ₂	2502 m	<i>v</i> _{BH}	8.50–5.95 m	Ph + Tp	AB	δ_A 54.8
	1938 m	<i>v</i> _{N≡N}	3.87 m	CH ₂		δ_B -12.7
			3.62 m			J_{AB} = 29.8
			2.33 s	CH ₃ <i>p</i> -tol		
			1.12 t	CH ₃ phos		
5b₁ [Os(4-CH ₃ C ₆ H ₄ N≡ ¹⁵ N)(Tp){P(OEt) ₃ }(PPh ₃)](BF ₄) ₂	2498 m	<i>v</i> _{BH}	8.50–6.00 m	Ph + Tp	ABY	δ_A 54.9
	1894 m	<i>v</i> _{N≡¹⁵N}	3.85 m	CH ₂		δ_B -12.7
			3.60 m			J_{AB} = 29.8
			2.33 s	CH ₃ <i>p</i> -tol		J_{AY} = 5.64
			1.13 t	CH ₃ phos		J_{BY} = 2.55
6b [Os{C ₆ H ₅ C(H)=NH}(Tp){P(OEt) ₃ }(PPh ₃)]BPh ₄	3323 w	<i>v</i> _{NH}	10.70 d, br	NH	AB	δ_A 71.6
	2492 m	<i>v</i> _{BH}	7.90–5.98 m	Ph + Tp		δ_B 0.84
			7.02 d	=CH		J_{AB} = 31.5
			3.65 m	CH ₂		
			3.33 m			
			1.02 t	CH ₃		
7b [Os{4-CH ₃ C ₆ H ₄ C(H)=NH}(Tp){P(OEt) ₃ }(PPh ₃)]BPh ₄	3336 w	<i>v</i> _{NH}	10.52 d, br	NH	AB	δ_A 72.5
	2462 m	<i>v</i> _{BH}	J_{HH} = 21.7			δ_B 1.95
			7.98–6.05 m	Ph + Tp		J_{AB} = 32.2
			7.04 d	=CH		
			3.65 m	CH ₂		
			3.30 m			
			2.38 s	CH ₃ <i>p</i> -tol		
			1.02 t	CH ₃ phos		
7b₁ [Os{4-CH ₃ C ₆ H ₄ C(H)= ¹⁵ NH}(Tp){P(OEt) ₃ }(PPh ₃)]BPh ₄	3330 w	<i>v</i> _{NH}	10.53 dd	NH	ABY	δ_A 72.61
	2462 m	<i>v</i> _{BH}	$J^{15\text{NH}}$ = 72.4			δ_B 1.98
			J_{HH} = 21.7			J_{AB} = 32.2
			7.95–6.05 m	Ph + Tp		J_{AY} = 2.23
			7.04 d	=CH		J_{BY} ≤ 1.60
			3.65 m	CH ₂		
			3.32 m			
			2.38 s	CH ₃ <i>p</i> -tol		
			1.02 t	CH ₃ phos		

^a In KBr pellets.^b In CD₂Cl₂ at 25 °C, unless otherwise noted.^c Positive shifts downfield from 85% H₃PO₄.^d At -70 °C.

Table 2
 $T_{1\text{min}}$ (200 MHz) and J_{HD} NMR data for some dihydrogen and hydride complexes and calculated H–H distances

Compound	T (K)	δ (ppm)	$T_{1\text{min}}$ (ms)	J_{HD} (Hz)	$r_{\text{H-H}}$ (Å)		
					From J_{HD}^{a}	From $T_{1\text{min}}$ slow rotation ^b	From $T_{1\text{min}}$ fast rotation ^c
3a $[\text{Os}(\eta^2\text{-H}_2)(\text{Tp})\{\text{P}(\text{OMe})_3\}(\text{PPh}_3)]^+$	200	–7.60 m	8.8	25.2	1.017	1.093	0.866
3b $[\text{Os}(\eta^2\text{-H}_2)(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]^+$	202	–7.59 m	8.3	25.0	1.020	1.082	0.858
3c $[\text{Os}(\eta^2\text{-H}_2)(\text{Tp})\{\text{PPh}(\text{OEt})_2\}(\text{PPh}_3)]^+$	212	–7.58 m	9.5	25.2	1.017	1.107	0.877
2b $\text{OsH}(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)$	211	–14.92 q	189	–	–	–	–

^a H–H distances were calculated (from the J_{HD} values for the HD complexes) using the equation [21]: $r_{\text{H-H}} = 1.44 - 0.0168 (J_{\text{HD}})$.

^{b,c} The H–H distances were calculated [23] (from $T_{1\text{min}}$ values) for fast rotation^c or static regimes^b of the H_2 ligand.

the Tp ligand [6] shows that stable, isolable complexes were obtained in all cases. In the $[\text{Os}(\eta^2\text{-H}_2)\text{Tp}(\text{CO})\text{-}(\text{P}^i\text{Pr}_3)]\text{BF}_4$ complex [6a], an H–H distance of 0.99 Å was calculated (from J_{HD} values), which is only slightly shorter than those of our complexes **3**. In the triphenylphosphine $[\text{Os}(\eta^2\text{-H}_2)\text{Tp}(\text{PPh}_3)_2]\text{BPh}_4$ derivative, the H–H distance was not calculated, but the J_{HD} value of 24.8 Hz is clearly comparable with those of our complexes **3**. These results indicate that the influence of the phosphite ligand on the H–H distance of the $\eta^2\text{-H}_2$ ligand in Tp complexes is rather restricted, resulting in the fact that all the Tp–osmium dihydrogen complexes have very similar properties.

3.2. Reactivity with azo-molecules

The reactivity of classical (**2**) and non-classical (**3**) hydride complexes were studied, and the results are shown in Schemes 3 and 4.

Classical hydride $\text{OsH}(\text{Tp})\text{L}(\text{PPh}_3)$ (**2**) complexes react with the *p*-tolyl diazonium cation to give the corresponding

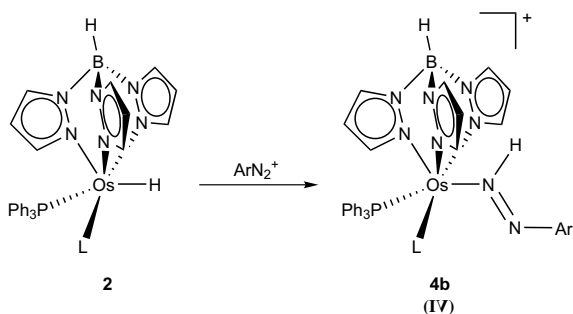
aryldiazene [25] $[\text{Os}(\text{ArN}=\text{NH})(\text{Tp})\text{L}(\text{PPh}_3)]\text{BPh}_4$ (**4**) derivative, which was isolated as the BPh_4 salt and characterised (Scheme 3).

The reaction proceeds with the insertion of the ArN_2^+ cation into the Os–H bond, to give the aryldiazene complex. In contrast, the related dihydrogen $[\text{Os}(\eta^2\text{-H}_2)(\text{Tp})\text{L}(\text{PPh}_3)]^+$ (**3**) cations do not react with aryldiazonium cations, and the starting complexes can be recovered unchanged after several hours of reaction. This unreactivity may be attributed to the stability towards the substitution of the $\eta^2\text{-H}_2$ ligand, which prevents the formation of an aryldiazenido $[\text{Os}]\text{-N}\equiv\text{NAr}$ complex. In the related ruthenium $[\text{Ru}(\eta^2\text{-H}_2)(\text{Tp})\text{L}(\text{PPh}_3)]^+$ derivatives [11a], easy substitution of the $\eta^2\text{-H}_2$ ligand did allow the synthesis of $[\text{Ru}(\text{ArN}_2)(\text{Tp})\text{L}(\text{PPh}_3)](\text{BF}_4)_2$ derivatives.

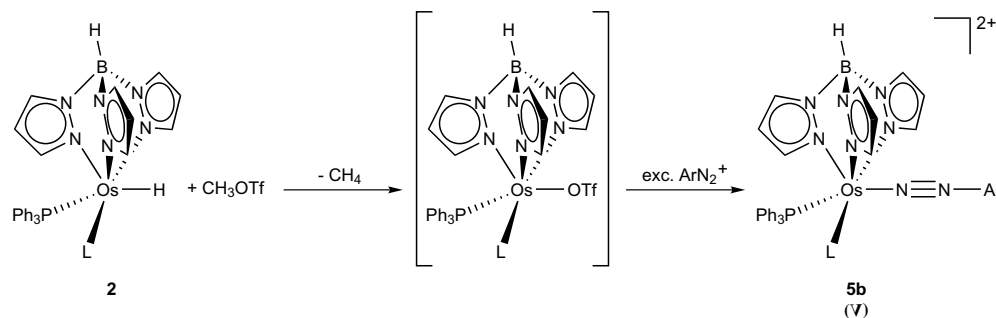
We therefore used a different strategy to prepare osmium aryldiazenido complexes, involving treating hydrides $\text{OsH}(\text{Tp})\text{L}(\text{PPh}_3)$ (**2**) first with methyltriflate and then with aryldiazonium cations, as shown in Scheme 4.

The reaction of **2** with methyltriflate proceeds with the evolution of CH_4 and formation of the triflate $\text{Os}(\kappa^1\text{-OTf})(\text{Tp})\text{L}(\text{PPh}_3)$ intermediate, which was not isolated. Substitution of the labile OTf^- ligand with ArN_2^+ gave the aryldiazenido $[\text{Os}(\text{ArN}_2)(\text{Tp})\text{L}(\text{PPh}_3)]^{2+}$ (**5**) cation, which was isolated as the BF_4 salt and characterised.

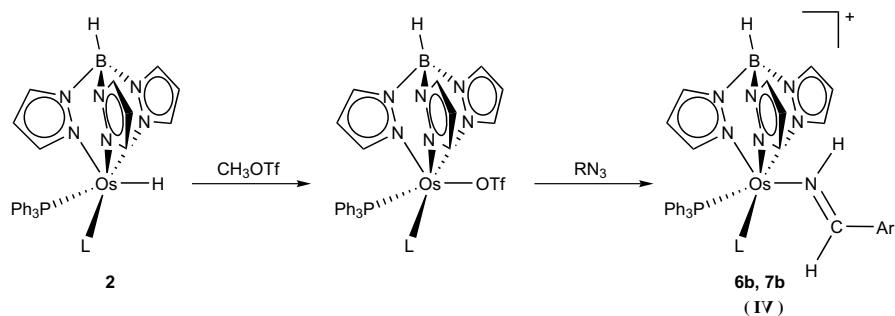
The easy substitution of the triflate ligand in $\text{Os}(\kappa^1\text{-OTf})(\text{Tp})\text{L}(\text{PPh}_3)$ prompted us to extend the reactivity to organic azide RN_3 , with the aim of coordinating this molecule [26] to the osmium fragment. Surprisingly, treatment of hydride $\text{OsH}(\text{Tp})\text{L}(\text{PPh}_3)$ (**2**) first with methyltriflate and then with alkylazide RN_3 gave as final product imine $[\text{Os}\{\eta^1\text{-NH}=\text{C}(\text{H})\text{Ar}\}(\text{Tp})\text{L}(\text{PPh}_3)]^+$ (**6, 7**) cations, which were isolated as BPh_4 salts and characterised (Scheme 5).



Scheme 3. L = P(OEt)₃; Ar = 4-CH₃C₆H₄.



Scheme 4. L = P(OEt)₃; OTf⁻ = CF₃SO₃⁻; Ar = 4-CH₃C₆H₄.

Scheme 5. L = P(OEt)₃; R = C₆H₅CH₂ (**6**), 4-CH₃C₆H₄CH₂ (**7**).

The reaction was also studied with phenylazide C₆H₅N₃, but no stable complex was isolated.

The formation of imine in the reaction of the $[\text{Os}]\text{-}\kappa^1\text{-OTf}$ complex with organic azide may be explained on the basis of the reaction path shown in Scheme 6, which involves first the coordination of azide to give the $[\text{Os}(\text{N}_3\text{R})(\text{Tp})\text{L}(\text{PPh}_3)]^+$ intermediate **[A]**. Extrusion of N₂ from the coordinated RN₃ gives the imide $[\text{Os}(\text{NR})(\text{Tp})\text{L}(\text{PPh}_3)]^+$ derivative **[B]** (transient species), leading to the formation of imine $[\text{Os}\{\eta^1\text{-NH}=\text{C}(\text{H})\text{Ar}\}(\text{Tp})\text{L}(\text{PPh}_3)]^+$ (**6, 7**) derivatives through the 1,2-shift of one hydrogen atom.

For information on the reaction path, we studied the reaction of $\text{Os}(\kappa^1\text{-OTf})(\text{Tp})\text{L}(\text{PPh}_3)$ with organic azide, in an attempt to isolate some intermediates like **[A]** and **[B]** or, at least, to detect them in solution from the ¹⁵N NMR spectra using labelled R¹⁵N₃ as a reagent. Unfortunately, no conclusive finding supported the presence of either azide complex **[A]** or imide species **[B]**, although their formation is plausible and is in fact suggested by several precedents [26,27]. In every case, although the path of Scheme 6 is only tentative, it may explain the synthesis of a rare example of a monosubstituted imine derivative.

The new azo-complexes **4–7** are yellow (**4, 6, 7**) or red-orange (**5**) solids stable in air and in solution of polar organic solvents, where they behave as 1:1 (**4, 6, 7**) or 2:1 (**5**) electrolytes [19]. Analytical and spectroscopic data (IR and ¹H, ³¹P, ¹³C, ¹⁵N NMR; Tables 1 and 3) support the proposed formulation.

The IR spectrum of the aryldiazene $[\text{Os}(4\text{-CH}_3\text{C}_6\text{H}_4\text{N}=\text{NH})(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$ (**4b**) complex shows the bands characteristic of Tp and phosphine ligands, but none attributable to $\nu_{\text{N}=\text{N}}$ or ν_{NH} of the diazene ligand. However, the presence of the ArN=NH group was confirmed by the ¹H NMR spectrum, which shows the characteristic, slightly broad signal of the diazene hydrogen atom at

14.97 ppm. A singlet of the methyl substituent of the 4-CH₃C₆H₄N=NH ligand at 2.34 ppm is also visible in the proton NMR spectrum. In addition, in the spectrum of the labelled $[\text{Os}(4\text{-CH}_3\text{C}_6\text{H}_4\text{N}=\text{NH})(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)]\text{BPh}_4$ (**4b**₁) complex, a doublet of multiplets appears at 14.98 ppm, with $J^{15\text{NH}}$ of 68.1 Hz, due to ¹⁵NH proton resonance, fitting the presence of the diazene group [9,10,25,28]. We also recorded the ¹⁵N NMR spectrum of the labelled complex, which appears as a doublet of multiplets, due to coupling with the hydrogen and with the phosphorus nuclei of phosphines. As the ³¹P NMR spectrum is an AB multiplet, the ¹⁵N spectrum of **4b**₁ was simulated using an ABY (Y = ¹⁵N) model with the parameters reported in Table 3, fitting geometry IV (Scheme 3) for aryldiazene complex **4b**.

The IR spectrum of aryldiazenido $[\text{Os}(4\text{-CH}_3\text{C}_6\text{H}_4\text{N}\equiv\text{N})(\text{Tp})\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)](\text{BF}_4)_2$ (**5b**) shows a medium-intensity band at 1938 cm⁻¹, attributed to the $\nu_{\text{N}=\text{N}}$ of the aryldiazenido ligand. This assignment was confirmed by the ¹⁵N isotopic substitution of the aryl ArN₂ ligand. A shift of this absorption to 1894 cm⁻¹, with a wavenumber lowering of 44 cm⁻¹, was observed in labelled derivative **5b**₁. The ν_{N_2} of **5b** falls at a higher value than those observed for singly-bent aryldiazenido complexes, which usually have values in the 1800–1600 cm⁻¹ range [25]. Therefore, the $\nu_{\text{N}=\text{N}}$ value of 1938 cm⁻¹ found in our complex **5b** suggests the near-linear structure of the Os–N–N–Ar group.

Linear aryldiazenido complexes have previously been reported for ruthenium [11b,29] and show ν_{N_2} in the 2095–2073 cm⁻¹ range, which is higher than the value of **5b**. However, the ¹⁵N NMR spectrum of our aryldiazenido complex appears as a ABY (Y = ¹⁵N) multiplet centred at –76.0 ppm (Table 3), which falls in the range generally observed for linear aryldiazenido ligands [29a,30]. On the basis of these data, therefore, we hypothesise the presence of a near-linear structure Os–N–N–Ar for our complex **5b**.

The ¹H NMR spectrum supports the proposed formulation for complex **5b**, showing the characteristic signals of Tp and phosphine ligands, and a singlet at 2.33 ppm of the methyl substituent of the 4-CH₃C₆H₄N≡N group. In the temperature range between +20 and –80 °C, the ³¹P NMR spectrum appears as an AB multiplet, due to the presence of two different phosphine ligands. Coupling with the

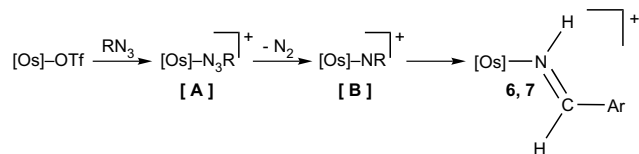
Scheme 6. [Os] = Os(Tp)L(PPh₃); L = P(OEt)₃ (**b**); R = C₆H₅CH₂ (**6**), 4-CH₃C₆H₄CH₂ (**7**).

Table 3
 $^{13}\text{C}\{^1\text{H}\}$ and $^{15}\text{N}\{^1\text{H}\}$ NMR data for some osmium complexes

Compound	$^{13}\text{C}\{^1\text{H}\}$ NMR ^a		$^{15}\text{N}\{^1\text{H}\}$ NMR ^a	
	(ppm/ <i>J</i> , Hz)	assgnt	Spin system	(ppm/ <i>J</i> , Hz)
4b₁ [Os(4-CH ₃ C ₆ H ₄ N= ¹⁵ NH)(Tp){P(OEt) ₃ }(PPh ₃)]BPh ₄			ABY (Y = ¹⁵ N)	$\delta_{\text{Y}} -27.5$ $J_{\text{AY}} = 2.60$ $J_{\text{BY}} = 0.75$
5b₁ [Os(4-CH ₃ C ₆ H ₄ N= ¹⁵ N)(Tp){P(OEt) ₃ }(PPh ₃)](BF ₄) ₂			ABY	$\delta_{\text{Y}} -76.0$ $J_{\text{AY}} = 5.64$ $J_{\text{BY}} = 2.55$
7b [Os{4-CH ₃ C ₆ H ₄ C(H)=NH}(Tp){P(OEt) ₃ }(PPh ₃)]BPh ₄	170.7 s 165–106 m 62.1 d 21.7 s 16.2 d	=CH Ph + Tp CH ₂ CH ₃ <i>p</i> -tol CH ₃ phos		
7b₁ [Os{4-CH ₃ C ₆ H ₄ C(H)= ¹⁵ NH}(Tp){P(OEt) ₃ }(PPh ₃)]BPh ₄	170.9 d $J_{^{13}\text{C}^{15}\text{N}} = 3.8$ 165–106 m 62.0 d 21.7 s 16.2 d	=CH Ph + Tp CH ₂ CH ₃ <i>p</i> -tol CH ₃ phos	ABY	$\delta_{\text{Y}} -177.8$ $J_{\text{AY}} = 2.23$ $J_{\text{BY}} \leq 1.60$

^a In CD₂Cl₂ at 25 °C, unless otherwise noted.

¹⁵N of the aryldiazenido was also observed in the spectrum of labelled complex **5b₁**, which appears as a ABY (Y = ¹⁵N) multiplet, simulable with the parameters listed in Table 3. On the basis of these data, a geometry of type V may reasonably be proposed for our aryldiazenido derivative.

Aryldiazene and aryldiazenido complexes of osmium are reported with several ligands [8a–10c,31] such as phosphine, carbonyl and 2,2'-bipyridine, but no complexes with tris(pyrazolyl)borate have ever been reported [25]. The use of the hydride OsH(Tp)L(PPh₃) complex as a precursor allows the preparation of the first diazo-complexes of osmium with tris(pyrazolyl)borate as supporting ligand.

The IR spectra of imine [Os{η¹-NH=C(H)Ar}(Tp){P(OEt)₃}(PPh₃)]BPh₄ (**6**, **7**) complexes show, not only the absorption of the Tp and phosphine ligands, but also one medium-intensity band at 3336–3323 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 a slightly broad doublet at 10.70–10.52 ppm (³J_{HH} = 21.7 Hz), due to the =NH proton of the imine group. Support for this attribution came from the spectra of labelled complex **7b₁**, which showed the split of the NH signal into one well-resolved doublet of doublets, with ¹J¹⁵NH at 72.4 Hz, fitting the proposed attribution. Also, in the COSY spectra, the doublet at 10.70–10.52 ppm was correlated with another doublet at 7.04–7.02 ppm, attributed to the =CH methine proton of the imine group. Lastly, the proton-coupled ¹⁵N NMR spectrum of labelled **7b₁** shows a doublet of multiplets at -177.8 ppm, due to coupling with the imine proton and with the phosphorus nuclei of phosphines. As the ³¹P NMR spectrum is an AB multiplet, the ¹⁵N{¹H} spectrum was simulated using an ABY (Y = ¹⁵N) model with the parameters listed in Table 3, as

expected for a η¹-coordinated 4-CH₃C₆H₄C(H) = ¹⁵NH molecule.

The ¹³C NMR spectrum of [Os{η¹-NH=C(H)Ar}(Tp){P(OEt)₃}(PPh₃)]BPh₄ (**7b**) complex shows, not only the signals of the Tp and phosphine ligands and the BPh₄ anion, but also one singlet at 170.7 ppm, which was correlated, in an HMQC experiment, with the proton signal at 7.04 ppm and attributed to the methine =CH carbon resonance of the imine group. On the basis of these data, the presence of the imine ligand in a geometry of type VI is proposed.

Imine complexes of osmium are rare [32], and generally prepared from the reaction of free imine with an appropriate metal fragment. Our reaction of a benzylazide ArCH₂N₃ with the triflate Os(κ¹-OTf)(Tp)L(PPh₃) complex allows complexes containing unusual monosubstituted ArC(H)=NH imine ligands to be prepared.

4. Conclusions

This report describes the synthesis of classical and non-classical hydride complexes of osmium, stabilised by phosphite, triphenylphosphine and tris(pyrazolyl)borate as supporting ligands. *T*₁ measurements and *J*_{HD} values give information on the H–H distance of the η²-H₂ ligand, with values consistent with “elongated” dihydrogen complexes. The hydride OsH(Tp)L(PPh₃) derivatives behave as precursors of the first tris(pyrazolyl)borate diazo complexes of osmium, allowing an easy route for the synthesis of aryldiazene [Os]-NH=N-Ar and aryldiazenido [Os]-N=N-Ar derivatives. Infrared (ν_{N2}) and ¹⁵N NMR data of the aryldiazenido [Os(ArN₂)(Tp){P(OEt)₃}(PPh₃)](BF₄)₂ complex suggest the near-linear arrangement of the Os-bonded ArN₂ ligand. Lastly, the synthesis of mono-substituted

imine[Os]–NH=C(H)Ar complexes was also achieved, with alkylazide as a reagent.

Acknowledgement

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