

Preparation and reactivity of osmium(II) hydride complexes with phosphites and polypyridyls

Gabriele Albertin ^{*}, Stefano Antoniutti, Sonia Pizzol

Dipartimento di Chimica, Università Ca' Foscari di Venezia, Dorsoduro 2137, 30123 Venezia, Italy

Received 11 December 2003; accepted 17 February 2004

Abstract

Chloro-complexes $[\text{OsCl}(\text{N-N})\text{P}_3]\text{BPh}_4$ (**1, 2**) [$\text{N-N} = 2,2'$ -bipyridine (bpy) and 1,10-phenanthroline (phen); $\text{P} = \text{P}(\text{OEt})_3$ and $\text{PPh}(\text{OEt})_2$] were prepared by allowing $\text{OsCl}_4(\text{N-N})$ to react with zinc dust in the presence of phosphites. Treatment of the chloro-complexes **1, 2** with NaBH_4 yielded, in the case of bpy, the hydride $[\text{OsH}(\text{bpy})\text{P}_3]\text{BPh}_4$ (**4**) derivatives. Mono-phosphite $[\text{OsCl}(\text{bpy})_2\text{P}]\text{BPh}_4$ (**3**) complexes were also prepared by reacting the $[\text{OsCl}_2(\text{bpy})_2]\text{Cl}$ compound with zinc dust in the presence of phosphite. Protonation reaction of the hydride $[\text{OsH}(\text{bpy})\text{P}_3]^+$ (**4**) cations with Brønsted acid was studied and led to thermally unstable (above 0 °C) dihydrogen $[\text{Os}(\eta^2\text{-H}_2)(\text{bpy})\text{P}_3]^{2+}$ (**4***) derivatives. The presence of the H_2 ligand is supported by variable-temperature NMR spectra and $T_{1\text{min}}$ measurements. Carbonyl $[\text{Os}(\text{CO})(\text{bpy})\{\text{P}(\text{OEt})_3\}_3](\text{BPh}_4)_2$ (**5**), nitrile $[\text{Os}(\text{CH}_3\text{CN})(\text{bpy})\{\text{P}(\text{OEt})_3\}_3](\text{BPh}_4)_2$ (**6**), and hydrazine $[\text{Os}(\text{bpy})(\text{NH}_2\text{NH}_2)\{\text{P}(\text{OEt})_3\}_3](\text{BPh}_4)_2$ (**7**) complexes were prepared by substituting the H_2 ligand in the $\eta^2\text{-H}_2$ (**4***) derivatives. Aryldiazene complex $[\text{Os}(\text{C}_6\text{H}_5\text{N}=\text{NH})(\text{bpy})\{\text{P}(\text{OEt})_3\}_3](\text{BPh}_4)_2$ (**8**) was also obtained by allowing the hydride $[\text{OsH}(\text{bpy})\text{P}_3]\text{BPh}_4$ to react with phenyldiazonium cation.
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Keywords: Osmium; Hydride; Dihydrogen complexes; Polypyridyl; Phosphite ligands

1. Introduction

The chemistry of classical and non-classical osmium hydride complexes has been developed extensively in the past 20 years using mainly π -acceptors such as phosphine, carbonyl or cyclopentadienyl as supporting ligands [1,2]. Less attention has been paid to the use of nitrogen-donor ligands such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) in stabilizing osmium hydrides. A glance through the literature shows that the only hydride complexes containing polypyridyl ligands are the carbonyl [3] $[\text{OsH}(\text{N-N})(\text{CO})(\text{PR}_3)_2]^+$ and $[\text{OsH}(\text{N-N})_2(\text{CO})]^+$ complexes ($\text{N-N} = \text{bpy}, \text{phen}$) and the phosphine [3a] $[\text{OsH}(\text{N-N})(\text{P-P})\text{PR}_3]^+$ [$\text{P-P} = \text{cis-1, 2-bis}(\text{diphenylphosphine})\text{ethylene}$; $\text{PR}_3 = \text{PPh}_3, \text{PPh}_2\text{-Me}, \text{PMe}_3$] derivatives (for nitrogen-donor osmium hydrides see [4]). No example of such a type of complexes

with phosphite [$\text{P}(\text{OR})_3, \text{PPh}(\text{OR})_2$, etc.] ligands has even been prepared.

We have previously reported on the synthesis and reactivity of classical and non-classical hydride complexes of osmium [5] of the type OsH_2P_4 and $[\text{OsX}(\eta^2\text{-H}_2)\text{P}_4]^+$ ($\text{X} = \text{H}, \text{Cl}, \text{Br}, \text{I}, \text{N}_3$, etc.) containing phosphite [$\text{P} = \text{P}(\text{OR})_3, \text{PPh}(\text{OR})_2, \text{PPH}_2\text{OR}$] as ancillary ligands. We have now extended these studies with the aim of introducing nitrogen-donor ligands such as 2,2'-bipyridine and 1,10-phenanthroline in the osmium hydride chemistry with phosphite ligands. The results of these studies, which allow the synthesis and the reactivity of new mixed-ligand classical and non-classical osmium hydride complexes, are reported here.

2. Experimental

2.1. General considerations and physical measurements

All synthetic work was carried out under an appropriate atmosphere (Ar, H_2) using standard Schlenk

^{*} Corresponding author. Tel.: +39-041-234-8555; fax: +39-041-234-8917.

E-mail address: albertin@unive.it (G. Albertin).

techniques or a Vacuum Atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored under 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. The $(\text{NH}_4)_2\text{OsCl}_6$ was a Johnson Matthey (USA) product, used as received. Triethylphosphite $\text{P}(\text{OEt})_3$ (Aldrich) was purified by distillation under nitrogen, while $\text{PPh}(\text{OEt})_2$ was prepared by the method of Rabinowitz and Pellon [6]. Diazonium salt $[\text{C}_6\text{H}_5\text{N}_2]\text{BF}_4$ was obtained in the usual way, as described in the literature [7]. Labeled diazonium tetrafluoroborate $[\text{C}_6\text{H}_5\text{N}\equiv^{15}\text{N}]\text{BF}_4$ was prepared from $\text{Na}^{15}\text{NO}_2$ (99% enriched, CIL) and the appropriate amine. Hydrazine (NH_2NH_2) was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method [8]. 2,2'-Bipyridine (bpy), 1,10-phenanthroline (phen), triflic acid and $\text{CF}_3\text{SO}_3\text{D}$ were Aldrich products used without any further purification. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer. NMR spectra (^1H , ^{31}P , ^{13}C , ^{15}N) were obtained on a Bruker AC200 or an AVANCE 300 spectrometers at temperatures varying between -90 and $+30^{\circ}\text{C}$, unless otherwise noted. ^1H and ^{13}C spectra are referred to internal tetramethylsilane, while $^{31}\text{P}\{^1\text{H}\}$ chemical shifts are reported with respect to 85% H_3PO_4 , with downfield shifts considered positive. The ^{15}N spectra were referred to external $\text{CH}_3^{15}\text{NO}_2$ with downfield shifts considered positive. The COSY, HMQC and HMBC NMR experiments were performed using standard Bruker programs. The SwaN-MR software package [9] has been used in treating the NMR data. The conductivity of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25°C were measured with a Radiometer CDM 83 instrument.

2.2. Synthesis of complexes

The $\text{OsCl}_4(\text{N}-\text{N})$ [$\text{N}-\text{N}=2,2'$ -bipyridine (bpy) and 1,10-phenanthroline (phen)] and $[\text{OsCl}_2(\text{bpy})_2]\text{Cl}$ complexes were prepared following the methods previously reported [10].

2.2.1. $[\text{OsCl}(\text{N}-\text{N})\text{P}_3]\text{BPh}_4$ (**1**, **2**) [$\text{N}-\text{N}=\text{bpy}$ (**1**), phen (**2**); $\text{P}=\text{P}(\text{OEt})_3$ (**a**), $\text{PPh}(\text{OEt})_2$ (**b**)]

In a 25-cm³ three-necked round-bottomed flask were placed 0.6 mmol of solid $\text{OsCl}_4(\text{N}-\text{N})$ compound, an excess of zinc dust (0.4 g, 6.1 mmol) and 10 cm³ of ethanol. An excess of the appropriate phosphite (6 mmol) was added to the resulting suspension which was refluxed for 4 h and then filtered. The solution was evaporated to dryness leaving a brown oil which was triturated with ethanol (2 cm³) containing an excess of NaBPh_4 (1.8 mmol, 0.62 g). A red-brown solid slowly

separated out which was filtered and crystallised from CH_2Cl_2 and ethanol; yield $\geq 65\%$; A_M ($\text{S cm}^2 \text{ mol}^{-1}$) = 53.3 for **1a**, 49.5 for **1b**, 55.1 for **2a**. Found: C, 52.29; H, 6.25; N, 2.20; Cl, 3.17. $\text{C}_{52}\text{H}_{73}\text{BClN}_2\text{O}_9\text{OsP}_3$ (**1a**) requires C, 52.07; H, 6.13; N, 2.34; Cl, 2.96%. Found: C, 59.08; H, 5.74; N, 1.99; Cl, 2.69. $\text{C}_{64}\text{H}_{73}\text{BClN}_2\text{O}_6\text{OsP}_3$ (**1b**) requires C, 59.33; H, 5.68; N, 2.16; Cl, 2.74%. Found: C, 52.85; H, 6.12; N, 2.16; Cl, 3.11. $\text{C}_{54}\text{H}_{73}\text{BClN}_2\text{O}_9\text{OsP}_3$ (**2a**) requires C, 53.01; H, 6.01; N, 2.29; Cl, 2.90%.

2.3. $[\text{OsCl}(\text{bpy})_2\text{P}]\text{BPh}_4$ (**3**) [$\text{P}=\text{P}(\text{OEt})_3$ (**a**), $\text{PPh}(\text{OEt})_2$ (**b**)]

These complexes were prepared following the method used for the related tris(phosphite) **1**, **2** complexes by treating the $[\text{OsCl}_2(\text{bpy})_2]\text{Cl}$ compound with an excess of both zinc dust and the appropriate phosphite in refluxing ethanol; yield $\geq 75\%$; A_M ($\text{S cm}^2 \text{ mol}^{-1}$) = 50.9 for **3a**, 54.2 for **3b**. Found: C, 58.56; H, 5.16; N, 5.34; Cl, 3.60. $\text{C}_{50}\text{H}_{51}\text{BClN}_4\text{O}_3\text{OsP}$ (**3a**) requires C, 58.68; H, 5.02; N, 5.47; Cl, 3.46%. Found: C, 61.28; H, 4.72; N, 5.23; Cl, 3.44. $\text{C}_{54}\text{H}_{51}\text{BClN}_4\text{O}_2\text{OsP}$ (**3b**) requires C, 61.45; H, 4.87; N, 5.31; Cl, 3.36%.

2.4. $[\text{OsH}(\text{bpy})\text{P}_3]\text{BPh}_4$ (**4**) [$\text{P}=\text{P}(\text{OEt})_3$ (**a**), $\text{PPh}(\text{OEt})_2$ (**b**)]

In a 50-cm³ three-necked round-bottomed flask were placed 300 mg (0.61 mmol) of $\text{OsCl}_4(\text{bpy})$, 15 cm³ of ethanol and an excess of the appropriate phosphite (8 mmol). A solution of NaBH_4 (12 mmol, 0.45 g) in 15 cm³ of ethanol was added to the resulting suspension and the reaction mixture was refluxed for 4 h. The solvent was removed under reduced pressure to give a brown solid from which the hydride was extracted with three 10-cm³ portions of CH_2Cl_2 . The extracts were evaporated to dryness leaving an oil which was treated with ethanol (2 cm³). The addition of an excess of NaBPh_4 (0.86 g, 2.5 mmol) in 2 cm³ of ethanol caused the separation of a yellow solid which was filtered and crystallised from CH_2Cl_2 and ethanol; yield $\geq 60\%$ for **4a**, and about 20% for **4b**; A_M ($\text{S cm}^2 \text{ mol}^{-1}$) = 55.6 for **4a**, 54.6 for **4b**. Found: C, 53.49; H, 6.51; N, 2.34. $\text{C}_{52}\text{H}_{74}\text{BN}_2\text{O}_9\text{OsP}_3$ (**4a**) requires C, 53.61; H, 6.40; N, 2.40%. IR, cm^{-1} (KBr) 2065 (w), 2026 (w) $\nu(\text{OsH})$. Found: C, 60.83; H, 5.80; N, 2.08. $\text{C}_{64}\text{H}_{74}\text{BN}_2\text{O}_6\text{OsP}_3$ (**4b**) requires C, 60.95; H, 5.91; N, 2.22%. IR, cm^{-1} (KBr) 2025 (w) $\nu(\text{OsH})$.

2.4.1. $[\text{Os}(\eta^2\text{-H}_2)(\text{bpy})\text{P}_3]^{2+}$ (**4***) [$\text{P}=\text{P}(\text{OEt})_3$ (**a**), $\text{PPh}(\text{OEt})_2$ (**b**)]

These complexes were prepared in solution by reacting the $[\text{OsH}(\text{bpy})\text{P}_3]\text{BPh}_4$ hydride with an excess of $\text{CF}_3\text{SO}_3\text{H}$ or $\text{HBF}_4\cdot\text{Et}_2\text{O}$. A typical experiment involves the preparation of a solution of the appropriate hydride

(0.02 mmol) in 0.5 cm³ of CD₂Cl₂ in a 5-mm screw-cap NMR tube. The tube is cooled to –80 °C and an excess of CF₃SO₃H (0.03 mmol) added by microsyringe through the cap. The probe of the NMR instrument was pre-cooled to –80 °C, the tube introduced and the spectra were recorded between –80 and +20 °C.

2.4.2. [Os(CO)(bpy){P(OEt)₃}₃](BPh₄)₂ (**5a**)

An excess of triflic acid (0.43 mmol, 38 μl) was added to a solution of [OsH(bpy){P(OEt)₃}₃]BPh₄ (100 mg, 0.086 mmol) in 10 cm³ of CH₂Cl₂ cooled to –196 °C. The reaction mixture, brought to room temperature, was allowed to stand under a CO atmosphere (1 atm) for about 24 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 cm³) containing an excess of NaBPh₄ (0.060 g, 0.17 mmol). A yellow solid slowly separated out which was filtered and crystallised from CH₂Cl₂ and ethanol; yield ≥ 35%. *M*_M (S cm² mol^{–1}) = 119. Found: C, 61.06; H, 6.33; N, 1.74. C₇₇H₉₃B₂N₂O₁₀OsP₃ requires C, 61.19; H, 6.20; N, 1.85%. IR, cm^{–1} (KBr) 2025 (s) ν(CO).

2.4.3. [Os(CH₃CN)(bpy){P(OEt)₃}₃](BPh₄)₂ (**6a**)

To a solution of [OsH(bpy){P(OEt)₃}₃]BPh₄ (100 mg, 0.086 mmol) in 5 cm³ of CH₂Cl₂ was added an excess of CH₃CN (2 cm³, 38 mmol) and the mixture cooled to –196 °C. An excess of CF₃SO₃H (38 μl, 0.43 mmol) was added and the solution, brought to room temperature, was stirred for 3 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 cm³) containing an excess of NaBPh₄ (0.17 mmol, 0.060 g). A yellow solid slowly separated out which was filtered and crystallised from CH₂Cl₂ and ethanol; yield ≥ 55%. *M*_M (S cm² mol^{–1}) = 124. Found: C, 61.38; H, 6.45; N, 2.71. C₇₈H₉₆B₂N₃O₉OsP₃ requires C, 61.46; H, 6.35; N, 2.76%.

2.4.4. [Os(bpy)(NH₂NH₂){P(OEt)₃}₃](BPh₄)₂ (**7a**)

An excess of CF₃SO₃H (122 μl, 1.38 mmol) was added to a solution of [OsH(bpy){P(OEt)₃}₃]BPh₄ (200 mg, 0.172 mmol) in 10 cm³ of CH₂Cl₂ cooled to –196 °C. The reaction mixture was brought to room temperature, stirred for 3 h and then again cooled to –196 °C. An excess of NH₂NH₂ (82 μl, 2.6 mmol) was added and the reaction mixture, brought to room temperature, was stirred for about 18 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 cm³) containing an excess of NaBPh₄ (0.35 mmol, 0.12 g). A pale-yellow solid slowly separated out which was filtered and crystallised from CH₂Cl₂ and ethanol; yield ≥ 35%. *M*_M (S cm² mol^{–1}) = 118. Found: C, 59.98; H, 6.52; N, 3.57. C₇₂H₇₂BN₃O₄P₃Re requires C, 60.24; H, 6.45; N, 3.70%. IR, cm^{–1} (KBr) 3354 (w), 3310 (w), 3269 (w), 3231 (w) ν(NH).

2.4.5. [Os(C₆H₅N=NH)(bpy){P(OEt)₃}₃](BPh₄)₂ (**8a**)

In a 25-cm³ three-necked round-bottomed flask were placed solid samples of [OsH(bpy){P(OEt)₃}₃]BPh₄ (100 mg, 0.086 mmol) and of an excess the phenyldiazonium tetrafluoroborate (C₆H₅N₂)BF₄ (0.26 mmol, 50 mg) and the flask was cooled to –196 °C. Dichloromethane (10 cm³) was added, the reaction mixture was left to reach the room temperature and was stirred for 5 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 cm³) containing an excess of NaBPh₄ (60 mg, 0.17 mmol). A yellow solid slowly separated out which was filtered and crystallised from CH₂Cl₂ and ethanol; yield ≥ 80%. *M*_M (S cm² mol^{–1}) = 126. Found: C, 62.16; H, 6.39; N, 3.45. C₈₂H₉₉B₂N₄O₉OsP₃ requires C, 61.97; H, 6.28; N, 3.52%.

2.4.6. [Os(C₆H₅N=¹⁵NH)(bpy){P(OEt)₃}₃](BPh₄)₂ (**8a₁**)

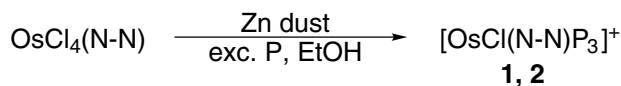
This complex was prepared exactly like the related unlabelled compound **8a** using (C₆H₅N≡¹⁵N)BF₄ as a reagent; yield ≥ 75%.

3. Results and discussion

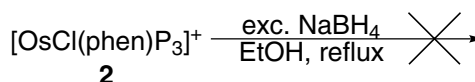
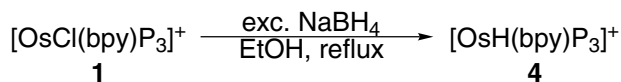
Zinc dust reduction of OsCl₄(N–N) (N–N = bpy and phen) complexes in the presence of the phosphite P(OEt)₃ or PPh(OEt)₂ gives the mixed-ligand chloro cations [OsCl(N–N)P₃]⁺ (**1**, **2**) which were isolated as BPh₄ salts and characterised (Scheme 1).

Treatment of the chloro-complexes **1**, **2** with NaBH₄ in ethanol gives the hydride [OsH(bpy)P₃]⁺ (**4**) cations only in the case of the 2,2′-bipyridine ligand (Scheme 2) while with the 1,10-phenanthroline no reaction was observed and the chloro-complex **2** was recovered in almost quantitative yield.

The hydride derivatives [OsH(bpy)P₃]⁺ (**4**) were also obtained by one-pot synthesis by reacting OsCl₄(bpy)



Scheme 1. N–N = bpy **1**, phen **2**; P = P(OEt)₃ (**a**), PPh(OEt)₂ (**b**).



Scheme 2. P = P(OEt)₃ (**a**), PPh(OEt)₂ (**b**).

Table 1
IR and NMR data for the osmium complexes

Compound	¹ H NMR ^{a,b} δ (J, Hz)	Assignment	Spin system	³¹ P{ ¹ H}NMR ^a δ (J, Hz)
1a [OsCl(bpy){P(OEt) ₃] ₃]BPh ₄	9.78–6.88 m 4.30 m 3.76 m 1.36 t 0.91 t	bpy + Ph CH ₂ CH ₃	AB ₂	δ _A 81.2 δ _B 77.5 J _{AB} = 47
1b [OsCl(bpy){PPh(OEt) ₂] ₃]BPh ₄	9.27–6.70 m 4.11 m 3.72 m 1.42 t 1.07 t 0.98 t	bpy + Ph CH ₂ CH ₃	AB ₂	δ _A 111.5 δ _B 104.4 J _{AB} = 36
2a [OsCl(phen){P(OEt) ₃] ₃]BPh ₄	10.0–6.84 m 4.36 qnt 3.65 m 1.40 t 0.75 t	phen + Ph CH ₂ CH ₃	AB ₂	δ _A 81.0 δ _B 77.2 J _{AB} = 44
3a [OsCl(bpy) ₂ {P(OEt) ₃ }]BPh ₄	9.65–6.83 m 3.87 qnt 1.01 t	bpy + Ph CH ₂ CH ₃	A	67.5 s
3b [OsCl(bpy) ₂ {PPh(OEt) ₂ }]BPh ₄	9.90–6.57 m 3.89 m 1.28 t	bpy + Ph CH ₂ CH ₃	A	97.6 s
4a [OsH(bpy){P(OEt) ₃] ₃]BPh ₄ ^c	9.75–6.83 m 4.03 qnt 3.65 m 1.31 t 1.27 t 0.93 t AB ₂ X spin system δ _X –6.76 J _{AX} = 112 J _{BX} = 22 A ₂ BX spin system δ _X –15.87 J _{AX} = J _{BX} = 22	bpy + Ph CH ₂ CH ₃ H ⁻ H ⁻	AB ₂ A ₂ B	δ _A 103.9 δ _B 101.4 J _{AB} = 26 δ _A 105.5 δ _B 97.2 J _{AB} = 45
4*a [Os(η ² -H ₂)(bpy){P(OEt) ₃] ₃] ²⁺ ^d	9.30–6.81 m 3.76 m 3.37 m 1.36 t 1.12 t 0.34 m –9.17 br	bpy + Ph CH ₂ CH ₃ H ₂	A ₂ B A ₂ B	δ _A 84.9 δ _B 79.2 J _{AB} = 41 δ _A 81.6 δ _B 80.2 J _{AB} = 20
4b [OsH(bpy){PPh(OEt) ₂] ₃]BPh ₄	8.84–6.38 m 3.80–3.26 m 1.29 t 1.21 t 1.15 t A ₂ BX spin system δ _X –15.35 J _{AX} = J _{BX} = 20	bpy + Ph CH ₂ CH ₃ H ⁻	A ₂ B	δ _A 125.7 δ _B 123.3 J _{AB} = 30
4*b [Os(η ² -H ₂)(bpy){PPh(OEt) ₂] ₃] ²⁺	9.30–6.85 m ^e 3.74 m 1.09 m –9.34 br	bpy + Ph CH ₂ CH ₃ H ₂	A ₂ B ^e	δ _A 113.0 δ _B 103.6 J _{AB} = 32
5a [Os(bpy)(CO){P(OEt) ₃] ₃](BPh ₄) ₂ ^f	9.37–6.85 m 4.18 m	bpy + Ph CH ₂	AB ₂	δ _A 83.7 δ _B 75.5

Table 1 (continued)

Compound	^1H NMR ^{a,b} δ (J, Hz)	Assignment	Spin system	$^{31}\text{P}\{^1\text{H}\}$ NMR ^a δ (J, Hz)
	3.60 qnt 1.41 t 0.94 t	CH ₃		$J_{\text{AB}} = 42$
6a	[Os(CH ₃ CN)(bpy){P(OEt) ₃ } ₃](BPh ₄) ₂	9.37–6.85 m 4.12 m 3.61 qnt 1.28 s 1.37 t 0.94 t	bpy + Ph CH ₂ CH ₃ CN CH ₃	A ₂ B δ_{A} 76.9 δ_{B} 72.4 $J_{\text{AB}} = 49$
7a	[Os(bpy)(NH ₂ NH ₂){P(OEt) ₃ } ₃](BPh ₄) ₂	9.26–6.81 m 4.18 m 3.51 qnt 4.02 br 1.69 br 1.38 t 0.92 t	bpy + Ph CH ₂ OsNH ₂ NH ₂ CH ₃	AB ₂ δ_{A} 79.5 δ_{B} 77.8 $J_{\text{AB}} = 46$
8a	[Os(C ₆ H ₅ N=NH)(bpy){P(OEt) ₃ } ₃](BPh ₄) ₂	15.24 s, br 14.04 s, br 9.12–6.83 m 4.20 m 3.68 m 1.36 m 0.99 m	NH bpy + Ph CH ₂ CH ₃	AB ₂ δ_{A} 81.6 δ_{B} 75.7 $J_{\text{AB}} = 46$ A ₂ B δ_{A} 78.4 δ_{B} 75.5 $J_{\text{AB}} = 45$
8a₁	[Os(C ₆ H ₅ N= ¹⁵ NH)(bpy){P(OEt) ₃ } ₃](BPh ₄) ₂	15.25 dm $J_{15\text{NH}} = 66$ 14.06 dm $J_{15\text{NH}} = 66$ 9.12–6.83 m 4.20 m 3.67 m 1.36 m 0.98 m	NH bpy + Ph CH ₂ CH ₃	AB ₂ δ_{A} 81.6 δ_{B} 75.8 $J_{\text{AB}} = 46$ A ₂ B δ_{A} 78.4 δ_{B} 75.5 $J_{\text{AB}} = 45$

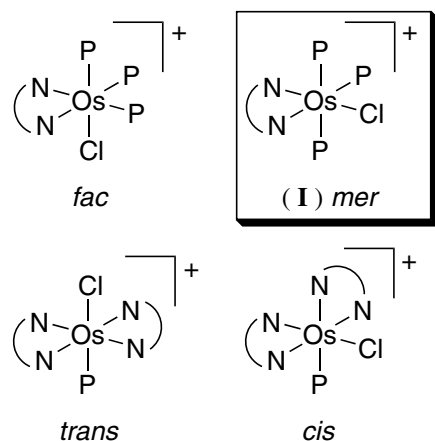
^a In CD₂Cl₂ at 25 °C.^b Positive shift downfield from 85% H₃PO₄.^c $T_{1\text{min}}$ (200 MHz) at 213 K: 181 ms.^d At –30 °C.^e At –70 °C.^f $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂, 25 °C) δ : 232.5 (dt, CO, $J_{\text{Cp}is} = J_{\text{Cp}trans} = 30$ Hz), 165–122 (m, Ph + bpy), 65.2 (m, CH₂), 16.1 (m, CH₃).

Chart 1.

this ligand, however, is confirmed by the ^1H NMR spectra, which show a quartet at –15.35 ppm attributed to the hydride ligand coupled with the phosphorus nuclei. Taking into account that in the temperature range between +30 and –80 °C the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra appear as an A₂B multiplet, this hydridic quartet can be simulated using an A₂BX (X=H) model with the parameters reported in Table 1. These parameters highlight how the two J_{PH} have the same value of 20 Hz, in agreement with the same mutual *cis* position of the hydride with all the phosphite ligands. On the basis of these data, a *mer* geometry (II, Chart 2) can reasonably be proposed for the hydride **4b**.

The ^1H NMR spectra of the related [OsH(bpy){P(OEt)₃}₃](BPh₄) (**4a**) show, in contrast with **4b**, two multiplets in the hydride region at –6.76 and at –15.87

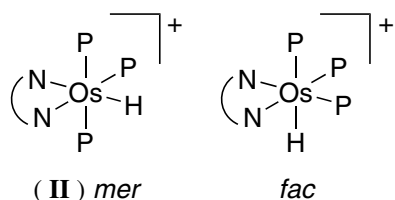


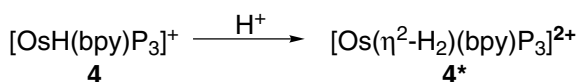
Chart 2.

ppm, respectively, suggesting the presence of two isomers. This is confirmed by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra which show two multiplets simulated using one AB_2 and one A_2B model with the parameters reported in Table 1. Also the two hydride multiplets of the ^1H NMR spectrum can be simulated using an AB_2X ($\text{X} = \text{H}$) model in one case, and an A_2BX model in the other. The values for the two J_{PH} are the same (22 Hz) for the multiplet at -15.87 ppm of one isomer in which the hydride should be in the same *cis* position with all the phosphite ligands, as in a *mer* geometry (II). In the other isomer the J_{PH} show two different values of 22 and 112 Hz, respectively, suggesting that the hydride should be *trans* to one phosphite and *cis* with respect to the other two, as in a *fac* geometry. On the basis of these data, the presence of two isomers with a *mer* and a *fac* geometry (Chart 2) can be reasonably proposed for the hydride **4a**.

The mixed-ligand phosphite-bipyridine osmium $[\text{OsH}(\text{N}-\text{N})\text{P}_3]^+$ complexes can be protonated with $\text{CF}_3\text{SO}_3\text{H}$ to give the dihydrogen $[\text{Os}(\eta^2\text{-H}_2)(\text{bpy})\text{P}_3]^{2+}$ (**4***) derivatives, as shown in Scheme 5.

The reaction was followed by NMR spectra and showed that, in the case of the $[\text{OsH}(\text{bpy})\{\text{PPh}(\text{OEt})_2\}_3]^+$ (**4b**) cation, the addition of $\text{CF}_3\text{SO}_3\text{H}$ caused the disappearance of the hydride multiplet at -15.35 ppm in the proton spectra and the appearance of one broad signal at -9.1 ppm attributed to the $\eta^2\text{-H}_2$ ligand of the $[\text{Os}(\eta^2\text{-H}_2)(\text{bpy})\text{P}_3]^{2+}$ dication. Measurements of T_1 (200 MHz) on these signals gave values of $T_{1\text{min}}$ of 7.5 ms, in agreement [14] with the presence of the dihydrogen ligand.

The protonation of the related $[\text{OsH}(\text{bpy})\{\text{P}(\text{OEt})_3\}_3]^+$ (**4b**) cation, which contains two hydride multiplets due to both the *fac* and the *mer* isomers, proceeds with the formation of only one broad signal at -9.0 ppm in the ^1H NMR spectra. T_1 measurements (200 MHz) on the broad proton signal at -9.0 ppm give a value of 9.5 ms, in agreement with the existence of a dihydrogen complex. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, however, show the presence of two multiplets simulable using AB_2 and A_2B spin systems (Table 1) and suggesting that the protonation should afford two different $\eta^2\text{-H}_2$ isomers, probably with *fac* and *mer* geometry, as the hydride precursor. The

Scheme 5. P = P(OEt)₃ (a), PPh(OEt)₂ (b).

presence of only one proton $\eta^2\text{-H}_2$ signal may be due either to overlapping of the signals of the two isomers due to their broadness, or to decomposition of one isomer giving, by loss of $\eta^2\text{-H}_2$, the triflate complex.

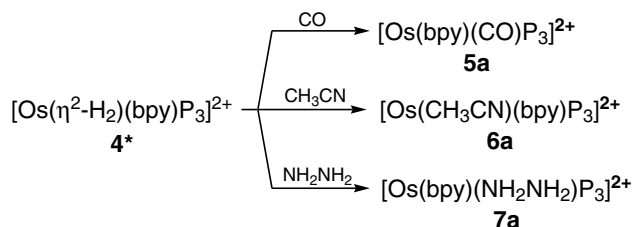
We have also prepared the isotopomer $[\text{Os}(\eta^2\text{-HD})(\text{bpy})\text{P}_3]^+$ by protonation of the hydride **4** with $\text{CF}_3\text{SO}_3\text{D}$ in an attempt to determine the values of J_{HD} . Unfortunately, the $\eta^2\text{-HD}$ signal of the isotopomers results rather broad and does not allow a reasonable value of J_{HD} to be measured. The values of the $T_{1\text{min}}$ measurements on the broad signal near -9 ppm, however, strongly support [14,15] the presence of an $\eta^2\text{-H}_2$ ligand. From the $T_{1\text{min}}$ values the H–H distances were calculated [16] and fall in the range 0.88 (**4*a**)–0.84 Å (**4*b**) for a fast rotation model and in the range 1.11 (**4*a**)–1.06 Å (**4*b**) for a static one. These values, which do not seem to be influenced by the nature of the phosphite ligands, are comparable with those calculated for known [17] dicationic dihydrogen complexes and very similar to those of the related osmium $[\text{Os}(\eta^2\text{-H}_2)(\text{bpy})(\text{CO})(\text{PPh}_3)_2]^{2+}$ derivative [3c].

The influence of the three phosphite ligands bonded to the $\text{Os}(\text{bpy})\text{P}_3$ fragment (**4***) on the $\eta^2\text{-H}_2$ seems therefore to be very similar to that of one carbonyl and two PPh_3 ligands in the $[\text{Os}(\eta^2\text{-H}_2)(\text{bpy})(\text{CO})(\text{PPh}_3)_2]^{2+}$ derivative.

The new dihydrogen complexes **4*** are thermally unstable and the ^1H NMR spectra showed that the evolution of H_2 began above 0°C . This prevented the isolation of the compounds in the solid state. The thermal instability of **4*** is somewhat unexpected, because the dihydrogen complexes of osmium are usually more stable than the related ruthenium derivatives [11]. Probably, this trend is not followed in dicationic mixed-ligand $\eta^2\text{-H}_2$ complexes with phosphites and polypyridyls and a comparable thermal instability is expected for all the iron triad derivatives.

3.1. Reactivity

The lability of the $\eta^2\text{-H}_2$ ligand in the $[\text{Os}(\eta^2\text{-H}_2)(\text{bpy})\text{P}_3]^{2+}$ derivatives prompted us to test these complexes as precursors for the synthesis of new osmium derivatives. The results show that the substitution of $\eta^2\text{-H}_2$ proceeds with several types of ligands affording the corresponding complexes. Some examples are shown in Scheme 6.

Scheme 6. P = P(OEt)₃.

Acknowledgements

The financial support of MIUR (Rome) – Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 2002–2003 – is gratefully acknowledged. We thank Daniela Baldan for technical assistance.

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