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

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#### Abstract

Chloro-complexes [OsCl(N–N)P<sub>3</sub>]BPh<sub>4</sub> (1, 2) [N–N = 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen);  $P = P(OEt)_3$  and PPh(OEt)<sub>2</sub>] were prepared by allowing OsCl<sub>4</sub>(N–N) to react with zinc dust in the presence of phosphites. Treatment of the chloro-complexes 1, 2 with NaBH<sub>4</sub> yielded, in the case of bpy, the hydride [OsH(bpy)P<sub>3</sub>]BPh<sub>4</sub> (4) derivatives. Mono-phosphite [OsCl(bpy)<sub>2</sub>P]BPh<sub>4</sub> (3) complexes were also prepared by reacting the [OsCl<sub>2</sub>(bpy)<sub>2</sub>]Cl compound with zinc dust in the presence of phosphite. Protonation reaction of the hydride [OsH(bpy)P<sub>3</sub>]<sup>+</sup> (4) cations with Brønsted acid was studied and led to thermally unstable (above 0 °C) dihydrogen [Os( $\eta^2$ -H<sub>2</sub>)(bpy)P<sub>3</sub>]<sup>2+</sup> (4\*) derivatives. The presence of the H<sub>2</sub> ligand is supported by variable-temperature NMR spectra and *T*<sub>1min</sub> measurements. Carbonyl [Os(CO)(bpy){P(OEt)<sub>3</sub>}](BPh<sub>4</sub>)<sub>2</sub> (5), nitrile [Os(CH<sub>3</sub>CN) (bpy){P(OEt)<sub>3</sub>}](BPh<sub>4</sub>)<sub>2</sub> (6), and hydrazine [Os(bpy)(NH<sub>2</sub>NH<sub>2</sub>){P(OEt)<sub>3</sub>}](BPh<sub>4</sub>)<sub>2</sub> (7) complexes were prepared by substituting the H<sub>2</sub> ligand in the  $\eta^2$ -H<sub>2</sub> (4\*) derivatives. Aryldiazene complex [Os(C<sub>6</sub>H<sub>5</sub>N=NH)(bpy){P(OEt)<sub>3</sub>}](BPh<sub>4</sub>)<sub>2</sub> (8) was also obtained by allowing the hydride [OsH(bpy)P<sub>3</sub>]BPh<sub>4</sub> to react with phenyldiazonium cation. © 2004 Elsevier B.V. All rights reserved.

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  $\pi$ -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] [OsH(N–N)(CO)(PR<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and [OsH(N–N)<sub>2</sub>(CO)]<sup>+</sup> complexes (N–N = bpy, phen) and the phosphine [3a] [OsH(N–N)(P–P)PR<sub>3</sub>]<sup>+</sup> [P–P = *cis*-1, 2-bis(diphenylphosphine)ethylene; PR<sub>3</sub> = PPh<sub>3</sub>, PPh<sub>2</sub>-Me, PMe<sub>3</sub>] derivatives (for nitrogen-donor osmium hydrides see [4]). No example of such a type of complexes

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with phosphite  $[P(OR)_3, PPh(OR)_2, etc.]$  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  $[OsX(\eta^2-H_2)P_4]^+$  (X = H, Cl, Br, I, N<sub>3</sub>, etc.) containing phosphite  $[P = P(OR)_3$ , PPh(OR)<sub>2</sub>, PPh<sub>2</sub>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

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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 (NH<sub>4</sub>)<sub>2</sub>OsCl<sub>6</sub> was a Johnson Matthey (USA) product, used as received. Triethylphosphite P(OEt)<sub>3</sub> (Aldrich) was purified by distillation under nitrogen, while PPh(OEt)<sub>2</sub> was prepared by the method of Rabinowitz and Pellon [6]. Diazonium salt [C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>]BF<sub>4</sub> was obtained in the usual way, as described in the literature [7]. Labeled diazonium tetrafluoroborate  $[C_6H_5N\equiv^{15}N]BF_4$  was prepared from  $Na^{15}NO_2$  (99% enriched, CIL) and the appropriate amine. Hydrazine (NH<sub>2</sub>NH<sub>2</sub>) was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method [8]. 2,2'-Bipyridine (bpy), 1,10-phenanthroline (phen), triffic acid and CF<sub>3</sub>SO<sub>3</sub>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 (<sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C, <sup>15</sup>N) were obtained on a Bruker AC200 or an AVANCE 300 spectrometers at temperatures varying between -90 and +30 °C, unless otherwise noted. <sup>1</sup>H and <sup>13</sup>C spectra are referred to internal tetramethylsilane, while  ${}^{31}P{}^{1}H{}$ chemical shifts are reported with respect to 85% H<sub>3</sub>PO<sub>4</sub>, with downfield shifts considered positive. The <sup>15</sup>N spectra were referred to external CH<sub>3</sub><sup>15</sup>NO<sub>2</sub> 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<sub>3</sub>NO<sub>2</sub> at 25 °C were measured with a Radiometer CDM 83 instrument.

#### 2.2. Synthesis of complexes

The  $OsCl_4(N-N)$  [N-N=2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen)] and  $[OsCl_2(bpy)_2]Cl$  complexes were prepared following the methods previously reported [10].

2.2.1.  $[OsCl(N-N)P_3]BPh_4$  (1, 2) [N-N=bpy (1), phen (2);  $P=P(OEt)_3$  (a),  $PPh(OEt)_2$  (b)]

In a 25-cm<sup>3</sup> three-necked round-bottomed flask were placed 0.6 mmol of solid  $OsCl_4(N-N)$  compound, an excess of zinc dust (0.4 g, 6.1 mmol) and 10 cm<sup>3</sup> 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 cm<sup>3</sup>) containing an excess of NaBPh<sub>4</sub> (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  $\ge 65\%$ ;  $\Lambda_M$  (S cm<sup>2</sup> mol<sup>-1</sup>) = 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.  $C_{52}H_{73}BClN_2O_9OsP_3$  (**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.  $C_{64}H_{73}BClN_2O_6OsP_3$  (**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.  $C_{54}H_{73}BClN_2O_9OsP_3$  (**2a**) requires C, 53.01; H, 6.01; N, 2.29; Cl, 2.90%.

## 2.3. $[OsCl(bpy)_2P]BPh_4$ (3) $[P = P(OEt)_3$ (a), $PPh(OEt)_2$ (b)]

These complexes were prepared following the method used for the related tris(phosphite) **1**, **2** complexes by treating the  $[OsCl_2(bpy)_2]Cl$  compound with an excess of both zinc dust and the appropriate phosphite in refluxing ethanol; yield  $\geq 75\%$ ;  $\Lambda_M$  (S cm<sup>2</sup> mol<sup>-1</sup>) = 50.9 for **3a**, 54.2 for **3b**. Found: C, 58.56; H, 5.16; N, 5.34; Cl, 3.60. C<sub>50</sub>H<sub>51</sub>BClN<sub>4</sub>O<sub>3</sub>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. C<sub>54</sub>H<sub>51</sub>BClN<sub>4</sub>O<sub>2</sub>OsP (**3b**) requires C, 61.45; H, 4.87; N, 5.31; Cl, 3.36%.

# 2.4. $[OsH(bpy)P_3]BPh_4$ (4) $[P = P(OEt)_3$ (a), $PPh(OEt)_2$ (b)]

In a 50-cm<sup>3</sup> three-necked round-bottomed flask were placed 300 mg (0.61 mmol) of  $OsCl_4(bpy)$ , 15 cm<sup>3</sup> of ethanol and an excess of the appropriate phosphite (8 mmol). A solution of NaBH<sub>4</sub> (12 mmol, 0.45 g) in 15 cm<sup>3</sup> 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-cm<sup>3</sup> portions of CH<sub>2</sub>Cl<sub>2</sub>. The extracts were evaporated to dryness leaving an oil which was treated with ethanol (2 cm<sup>3</sup>). The addition of an excess of NaBPh<sub>4</sub> (0.86 g, 2.5 mmol) in 2 cm<sup>3</sup> 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**;  $\Lambda_{\rm M}$  (S cm<sup>2</sup> mol<sup>-1</sup>) = 55.6 for 4a, 54.6 for 4b. Found: C, 53.49; H, 6.51; N, 2.34.  $C_{52}H_{74}BN_2O_9O_8P_3$  (4a) requires C, 53.61; H, 6.40; N, 2.40%. IR, cm<sup>-1</sup> (KBr) 2065 (w), 2026 (w) v(OsH). Found: C, 60.83; H, 5.80; N, 2.08. C<sub>64</sub>H<sub>74</sub>BN<sub>2</sub>O<sub>6</sub>OsP<sub>3</sub> (4b) requires C, 60.95; H, 5.91; N, 2.22%. IR, cm<sup>-1</sup> (KBr) 2025 (w) v(OsH).

# 2.4.1. $[Os(\eta^2 - H_2)(bpy)P_3]^{2+}$ (4\*) $[P = P(OEt)_3$ (a), PPh(OEt)<sub>2</sub> (b)]

These complexes were prepared in solution by reacting the  $[OsH(bpy)P_3]BPh_4$  hydride with an excess of  $CF_3SO_3H$  or  $HBF_4 \cdot Et_2O$ . A typical experiment involves the preparation of a solution of the appropriate hydride G. Albertin et al. | Journal of Organometallic Chemistry 689 (2004) 1639-1647

(0.02 mmol) in 0.5 cm<sup>3</sup> of CD<sub>2</sub>Cl<sub>2</sub> in a 5-mm screw-cap NMR tube. The tube is cooled to -80 °C and an excess of CF<sub>3</sub>SO<sub>3</sub>H (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. $[Os(CO)(bpy) \{P(OEt)_3\}_3](BPh_4)_2$ (5a)

An excess of triflic acid (0.43 mmol, 38 µl) was added to a solution of  $[OsH(bpy){P(OEt)_3}_3]BPh_4$  (100 mg, 0.086 mmol) in 10 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> 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 cm<sup>3</sup>) containing an excess of NaBPh<sub>4</sub> (0.060 g, 0.17 mmol). A yellow solid slowly separated out which was filtered and crystallised from CH<sub>2</sub>Cl<sub>2</sub> and ethanol; yield  $\ge 35\%$ .  $\Lambda_{\rm M}$  (S cm<sup>2</sup> mol<sup>-1</sup>) = 119. Found: C, 61.06; H, 6.33; N, 1.74. C<sub>77</sub>H<sub>93</sub>B<sub>2</sub>N<sub>2</sub>O<sub>10</sub>OsP<sub>3</sub> requires C, 61.19; H, 6.20; N, 1.85%. IR, cm<sup>-1</sup> (KBr) 2025 (s)  $\nu$ (CO).

# 2.4.3. $[Os(CH_3CN)(bpy) \{P(OEt)_3\}_3](BPh_4)_2$ (6a)

To a solution of  $[OsH(bpy){P(OEt)_3}_3]BPh_4$  (100 mg, 0.086 mmol) in 5 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> was added an excess of CH<sub>3</sub>CN (2 cm<sup>3</sup>, 38 mmol) and the mixture cooled to -196 °C. An excess of CF<sub>3</sub>SO<sub>3</sub>H (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 cm<sup>3</sup>) containing an excess of NaBPh<sub>4</sub> (0.17 mmol, 0.060 g). A yellow solid slowly separated out which was filtered and crystallised from CH<sub>2</sub>Cl<sub>2</sub> and ethanol; yield  $\geq$ 55%.  $\Lambda_{\rm M}$  (S cm<sup>2</sup> mol<sup>-1</sup>) = 124. Found: C, 61.38; H, 6.45; N, 2.71. C<sub>78</sub>H<sub>96</sub>B<sub>2</sub>N<sub>3</sub>O<sub>9</sub>OsP<sub>3</sub> requires C, 61.46; H, 6.35; N, 2.76%.

## 2.4.4. $[Os(bpy)(NH_2NH_2) \{P(OEt)_3\}_3](BPh_4)_2$ (7a)

An excess of CF<sub>3</sub>SO<sub>3</sub>H (122 µl, 1.38 mmol) was added to a solution of [OsH(bpy){P(OEt)<sub>3</sub>}<sub>3</sub>]BPh<sub>4</sub> (200 mg, 0.172 mmol) in 10 cm<sup>3</sup> of  $CH_2Cl_2$  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 NH<sub>2</sub>NH<sub>2</sub> (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 cm<sup>3</sup>) containing an excess of NaBPh<sub>4</sub> (0.35 mmol, 0.12 g). A pale-yellow solid slowly separated out which was filtered and crystallised from ethanol; CH<sub>2</sub>Cl<sub>2</sub> and yield ≥ 35%.  $\Lambda_{\rm M}$  $(S \text{ cm}^2 \text{ mol}^{-1}) = 118$ . Found: C, 59.98; H, 6.52; N, 3.57. C<sub>72</sub>H<sub>72</sub>BN<sub>3</sub>O<sub>4</sub>P<sub>3</sub>Re requires C, 60.24; H, 6.45; N, 3.70%. IR, cm<sup>-1</sup> (KBr) 3354 (w), 3310 (w), 3269 (w), 3231 (w) v(NH).

## 2.4.5. $[Os(C_6H_5N=NH)(bpy) \{P(OEt)_3\}_3](BPh_4)_2$ (8a)

In a 25-cm<sup>3</sup> three-necked round-bottomed flask were placed solid samples of  $[OsH(bpy){P(OEt)_3}_3]BPh_4$  (100 mg, 0.086 mmol) and of an excess the phenyldiazonium tetrafluoroborate (C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>)BF<sub>4</sub> (0.26 mmol, 50 mg) and the flask was cooled to -196 °C. Dichloromethane (10 cm<sup>3</sup>) 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  $(2 \text{ cm}^3)$  containing an excess of NaBPh<sub>4</sub> (60 mg, 0.17 mmol). A yellow solid slowly separated out which was filtered and crystallised from  $CH_2Cl_2$  and ethanol; yield ≥80%. *Λ*<sub>M</sub>  $(\text{S cm}^2 \text{ mol}^{-1}) = 126$ . Found: C, 62.16; H, 6.39; N, 3.45. C<sub>82</sub>H<sub>99</sub>B<sub>2</sub>N<sub>4</sub>O<sub>9</sub>OsP<sub>3</sub> requires C, 61.97; H, 6.28; N, 3.52%.

2.4.6.  $[Os(C_6H_5N=^{15}NH)(bpy) \{P(OEt)_3\}_3](BPh_4)_2$ (8*a*<sub>1</sub>)

This complex was prepared exactly like the related unlabelled compound **8a** using  $(C_6H_5N\equiv^{15}N)BF_4$  as a reagent; yield  $\ge 75\%$ .

#### 3. Results and discussion

Zinc dust reduction of  $OsCl_4(N-N)$  (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  $[OsCl(N-N)P_3]^+$  (1,2) which were isolated as  $BPh_4$  salts and characterised (Scheme 1).

Treatment of the chloro-complexes 1, 2 with NaBH<sub>4</sub> in ethanol gives the hydride  $[OsH(bpy)P_3]^+$  (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  $[OsH(bpy)P_3]^+$  (4) were also obtained by one-pot synthesis by reacting  $OsCl_4(bpy)$ 

OsCl<sub>4</sub>(N-N) 
$$\xrightarrow{\text{Zn dust}}$$
 [OsCl(N-N)P<sub>3</sub>]<sup>+</sup>  
**1**, 2

Scheme 1. N–N = bpy 1, phen 2;  $P = P(OEt)_3$  (a),  $PPh(OEt)_2$  (b).

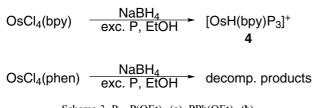
$$[OsCl(bpy)P_3]^+ \xrightarrow{exc. NaBH_4} [OsH(bpy)P_3]^+$$

$$1 \qquad 4$$

$$[OsCl(phen)P_3]^+ \xrightarrow{exc. NaBH_4}$$

$$EtOH, reflux \qquad 4$$

Scheme 2.  $P = P(OEt)_3$  (a),  $PPh(OEt)_2$  (b).



Scheme 3.  $P = P(OEt)_3$  (a),  $PPh(OEt)_2$  (b).

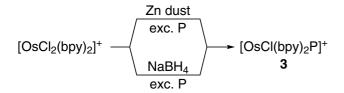
with NaBH<sub>4</sub> in refluxing ethanol in the presence of an excess of phosphite, as shown in Scheme 3.

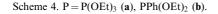
Instead, the reaction of the related phenanthroline OsCl<sub>4</sub>(phen) complex does not give any hydridic species, but only decomposition products.

The different behaviour of the two nitrogenous ligands bpy and phen in the chemistry of mixed-ligand complexes with phosphites and polypyridyls is rather unexpected in light of the comparable properties shown by bpy and phen as ligands in related  $[RuH(N-N)P_3]^+$ complexes [11] which can be obtained with both bpy and phen as supporting groups. The absence of reactivity of both the phenanthroline complexes OsCl<sub>4</sub>(phen) and  $[OsCl(phen)P_3]^+$  towards the formation of hydride with NaBH<sub>4</sub> prompted us to extend the studies to other reagents such as LiAlH<sub>4</sub>, NaBH<sub>3</sub>CN, LiBHEt<sub>3</sub>, KH or H<sub>2</sub> in the presence of base in an attempt to prepare the related H<sup>-</sup> species. In any case, no formation of hydride complexes was observed and therefore it seems that only with bpy can mixed-ligand hydrides with phosphites and polypyridyls be prepared. With phenanthroline, instead, substitution of the Cl ligand with hydride does not take place.

We have also studied the reaction of  $OsCl_4(bpy)$  with phosphite and  $NaBH_4$  in different conditions, i.e. changing the ratio between the reagents and the reaction time, in an attempt to prepare hydride species with a different stoichiometry of the type  $OsH_2(bpy)_2P_2$  or  $OsHCl(bpy)_2P_2$ . The only obtained result, however, was a decrease of the yield of  $[OsH(bpy)P_3]^+$  (4a) complex which seems to be the only hydride containing phosphite and polypyridyl ligands obtained from the  $OsCl_4(bpy)$ used as a precursor.

Bis(bipyridine)  $[OsCl_2(bpy)_2]Cl$  react with zinc dust in the presence of phosphite to give the chloro-cations  $[OsCl(bpy)_2P]^+$  (3) which were isolated as BPh<sub>4</sub> salts and characterised (Scheme 4).





The reaction of  $[OsCl_2(bpy)_2]Cl$  with phosphites was also studied in the presence of NaBH<sub>4</sub>, but exclusively the chloro-complexes **3** were obtained (Scheme 4). The absence of any hydride species in this reaction prompted us to extend the studies of both the chloro-cations  $[OsCl_2(bpy)_2]^+$  and  $[OsCl(bpy)_2P]^+$  (**3**) towards other reagents such as LiAlH<sub>4</sub>, LiBHEt<sub>3</sub> and KH in an attempt to prepare hydride complexes. Unfortunately, no complex containing the H<sup>-</sup> ligand was separated from the reaction and either the chloro-complexes **3** or decomposition products were the only obtained products.

It seems, therefore, that osmium hydride species with bis(bipyridine) and phosphites as supporting ligands cannot be obtained using the  $[OsCl_2(bpy)_2]Cl$  as a precursor.

These results contrast with those previously obtained [3] with carbon monoxide, which allows the easy synthesis of bis(bipyridine) hydride  $[OsH(bpy)_2(CO)]^+$  derivatives. Differences were also observed by a comparison with the related ruthenium complexes [11], whose  $[RuH(bpy)_2P]^+$  (P = phosphite) hydride derivatives can be prepared by reacting  $RuCl_2(bpy)_2$  with NaBH<sub>4</sub> in the presence of phosphites.

The coordination of any hydride ligand to mixed-ligand osmium(II) complexes with polypyridyls and phosphites seems therefore to be rather difficult and only the tris(phosphite)  $[OsH(bpy)P_3]BPh_4$  (4) derivatives can be obtained.

Good analytical data were obtained for all the osmium complexes, which are stable in air and in solution of polar organic solvents in which they behave as 1:1 electrolytes [12]. The IR and NMR data (Table 1) support the proposed formulation. The <sup>1</sup>H NMR spectra of the  $[OsCl(N-N)P_3]BPh_4$  (1,2) complexes show the characteristic signals of both the phosphite and the nitrogenous ligands (bpy and phen) beside those of the BPh<sub>4</sub> anion. The  ${}^{31}P{}^{1}H$  NMR spectra appear as AB<sub>2</sub> multiplets suggesting the magnetic equivalence of two phosphines, different from the third. These data do not allow to unambiguously distinguish between a mer or a fac geometry for the complexes (Chart 1). However, the methylene proton signals of the P(OEt)<sub>3</sub> ligands in 1a and **2a** appear as one quintet and one multiplet between 4.36 and 3.65 ppm. The presence of the multiplet should be due to the coupling [13] of two phosphites in a mutually *trans* position. On this basis a *mer* geometry (I) can be reasonably proposed.

The <sup>1</sup>H NMR spectra confirm the presence of the ligands in the bis(bipyridine)  $[OsCl(bpy)_2P]^+$  (3) complex whose <sup>31</sup>P spectra appear as one sharp singlet at 67.5 (3a) and 97.6 (3b) ppm. The spectroscopic data, however, do not allow to distinguish between a *cis* or a *trans* geometry (Chart 1) of the complexes.

The IR spectra of the hydride  $[OsH(bpy){PPh (OEt)_2}_3]BPh_4$  (4b) show a weak band at 2025 cm<sup>-1</sup> attributed to  $v_{OsH}$  of the hydride ligand. The presence of

Table 1	
IR and NMR data for the osmium	complexes

$ \begin{bmatrix} 14 \\ 13 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10$		Compound	<sup>1</sup> H NMR <sup>a,b</sup> $\delta$ ( <i>J</i> , Hz)	Assignment	Spin system	<sup>31</sup> P{ <sup>1</sup> H}NMR <sup>a</sup> $\delta$ (J, Hz)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1a	$[OsCl(bpy){P(OEt)_3}_3]BPh_4$	4.30 m 3.76 m 1.36 t	CH <sub>2</sub>	$AB_2$	$\delta_{\rm B}$ 77.5
	1b	[OsCl(bpy){PPh(OEt) <sub>2</sub> } <sub>3</sub> ]BPh <sub>4</sub>	4.11 m 3.72 m 1.42 t 1.07 t	CH <sub>2</sub>	AB <sub>2</sub>	$\delta_{\rm B}$ 104.4
	2a	[OsCl(phen){P(OEt) <sub>3</sub> } <sub>3</sub> ]BPh <sub>4</sub>	4.36 qnt 3.65 m 1.40 t	CH <sub>2</sub>	AB <sub>2</sub>	$\delta_{\rm B}$ 77.2
	3a	$[OsCl(bpy)_2 \{P(OEt)_3\}]BPh_4$	3.87 qnt	$CH_2$	А	67.5 s
	3b	$[OsCl(bpy)_2\{PPh(OEt)_2\}]BPh_4$	3.89 m	CH <sub>2</sub>	A	97.6 s
	<b>4</b> a	$[OsH(bpy){P(OEt)_3}_3]BPh_4^c$	4.03 qnt 3.65 m	CH <sub>2</sub>	$AB_2$	$\delta_{\rm B}$ 101.4
$ \begin{aligned} \delta_{X} - 6.76 & J_{AB} = 45 \\ J_{AX} = 112 & J_{BX} = 22 \\ A_{2}BX spin system & H^{-} \\ \delta_{X} - 15.87 & J_{AX} = J_{BX} = 22 \end{aligned} \\ \mathbf{4^{*}a} & [Os(\eta^{2}-H_{2})(bpy)\{P(OEt)_{3}\}_{3}]^{2^{+d}} & 9.30-6.81 m & bpy + Ph & A_{2}B & \delta_{A} 84.9 \\ 3.76 m & CH_{2} & \delta_{B} 79.2 \\ 3.37 m & J_{AB} = 41 \\ 1.36 t & CH_{3} & J_{AB} = 41 \\ 1.36 t & CH_{3} & J_{AB} = 41 \\ 1.36 t & CH_{3} & J_{AB} = 41 \\ 1.36 t & CH_{3} & J_{AB} = 41 \\ 1.36 t & CH_{3} & J_{AB} = 20 \\ \end{aligned} \\ \mathbf{4b} & [OsH(bpy)\{PPh(OEt)_{2}\}_{3}]BPh_{4} & 8.84-6.38 m & bpy + Ph & A_{2}B & \delta_{A} 125.7 \\ 3.80-3.26 m & CH_{2} & \delta_{B} 123.3 \\ 1.29 t & CH_{3} & J_{AB} = 30 \\ 1.21 t & J_{AB} = 20 \\ \end{bmatrix} \\ \mathbf{4^{*b}} & [Os(\eta^{2}-H_{2})(bpy)\{PPh(OEt)_{2}\}_{3}]^{2^{+}} & 9.30-6.85 m^{\circ} & bpy + Ph & A_{2}B^{\circ} & \delta_{A} 113.0 \\ 3.74 m & CH_{2} & \delta_{B} 103.6 \\ 1.09 m & CH_{3} & J_{AB} = 32 \\ -9.34 br & H_{2} & J_{AB} = 32 \\ \end{bmatrix} $			1.27 t 0.93 t		$A_2B$	
$ \begin{aligned} \mathbf{4^*a} & [Os(\eta^2-H_2)(bpy)\{P(OEt)_3\}_3]^{2+d} & 9.30-6.81 m & bpy+Ph & A_2B & \delta_A 84.9 \\ 3.76 m & CH_2 & J_{AB} = 41 \\ 3.37 m & J_{AB} = 41 \\ 1.36 t & CH_3 & J_{AB} = 41 \\ 1.36 t & CH_3 & J_{AB} = 41 \\ 1.12 t & A_2B & \delta_A 81.6 \\ 0.34 m & -9.17 br & H_2 & \delta_B 80.2 \\ J_{AB} = 20 \end{aligned} $			$\delta_{\rm X} - 6.76$ $J_{\rm AX} = 112$ $J_{\rm BX} = 22$ $A_2 B X \text{ spin system}$ $\delta_{\rm X} - 15.87$			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						
		$[Os(\eta^2-H_2)(bpy)\{P(OEt)_3\}_3]^{2+d}$	3.76 m	1.	$A_2B$	$\delta_{\rm B}$ 79.2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			1.12 t	CH <sub>3</sub>	$A_2B$	δ <sub>A</sub> 81.6
$3.80-3.26 \text{ m} \qquad CH_2 \qquad \delta_B \ 123.3 \\ 1.29 \text{ t} \qquad CH_3 \qquad J_{AB} = 30 \\ 1.21 \text{ t} \\ 1.15 \text{ t} \\ A_2BX \text{ spin system} \qquad H^- \\ \delta_X \ -15.35 \\ J_{AX} = J_{BX} = 20 \\ 4*b \qquad [Os(\eta^2-H_2)(bpy)\{PPh(OEt)_2\}_3]^{2+} \qquad 9.30-6.85 \text{ m}^e \qquad bpy + Ph \qquad A_2B^e \qquad \delta_A \ 113.0 \\ 3.74 \text{ m} \qquad CH_2 \qquad \delta_B \ 103.6 \\ 1.09 \text{ m} \qquad CH_3 \qquad J_{AB} = 32 \\ -9.34 \text{ br} \qquad H_2 \\ 5a \qquad [Os(bpy)(CO)\{P(OEt)_3\}_3](BPh_4)_2^{f} \qquad 9.37-6.85 \text{ m} \qquad bpy + Ph \qquad AB_2 \qquad \delta_A \ 83.7 \\ \end{cases}$				H <sub>2</sub>		
$A_2BX spin system$ $\delta_X -15.35$ $J_{AX} = J_{BX} = 20$ $H^ 4*b$ $[Os(\eta^2-H_2)(bpy)\{PPh(OEt)_2\}_3]^{2+}$ $9.30-6.85 \text{ m}^e$ $3.74 \text{ m}$ $1.09 \text{ m}$ $-9.34 \text{ br}$ $bpy + Ph$ $H_2$ $A_2B^e$ $\delta_B 103.6$ $J_{AB} = 32$ $-9.34 \text{ br}$ 5a $[Os(bpy)(CO)\{P(OEt)_3\}_3](BPh_4)_2^{f}$ $9.37-6.85 \text{ m}$ $bpy + Ph$ $H_2$ $AB_2$ $\delta_A 83.7$		$[OsH(bpy){PPh(OEt)_2}_3]BPh_4$	3.80–3.26 m 1.29 t 1.21 t	$CH_2$	$A_2B$	$\delta_{\rm B}$ 123.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			$A_2BX$ spin system $\delta_X$ -15.35	H-		
<b>5a</b> $[Os(bpy)(CO){P(OEt)_3}_3](BPh_4)_2^f$ 9.37–6.85 m bpy + Ph AB <sub>2</sub> $\delta_A$ 83.7	4*b	$[Os(\eta^2\text{-}H_2)(bpy)\{PPh(OEt)_2\}_3]^{2+}$	3.74 m 1.09 m	CH <sub>2</sub> CH <sub>3</sub>	$A_2B^e$	$\delta_{\rm B}$ 103.6
	5a	$[Os(bpy)(CO)\{P(OEt)_3\}_3](BPh_4)_2{}^f$	9.37–6.85 m 4.18 m		AB <sub>2</sub>	$\begin{array}{c} \delta_{\rm A} 83.7 \\ \delta_{\rm B} 75.5 \end{array}$

Table 1 (continued)

	Compound	<sup>1</sup> H NMR <sup>a,b</sup> $\delta$ (J, Hz)	Assignment	Spin system	<sup>31</sup> P{ <sup>1</sup> H}NMR <sup>a</sup> $\delta$ (J, Hz)
		3.60 qnt 1.41 t 0.94 t	CH <sub>3</sub>		$J_{\rm AB} = 42$
6a	$[Os(CH_3CN)(bpy){P(OEt)_3}_3](BPh_4)_2$	9.37–6.85 m 4.12 m 3.61 qnt 1.28 s 1.37 t 0.94 t	bpy + Ph CH <sub>2</sub> CH <sub>3</sub> CN CH <sub>3</sub>	$A_2B$	$\delta_{A} 76.9$ $\delta_{B} 72.4$ $J_{AB} = 49$
7a	$[Os(bpy)(NH_2NH_2){P(OEt)_3}_3](BPh_4)_2$	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 <sub>2</sub>	$\delta_{A} 79.5$ $\delta_{B} 77.8$ $J_{AB} = 46$
8a	$[Os(C_6H_5N=NH)(bpy){P(OEt)_3}_3](BPh_4)_2$	15.24 s, br 14.04 s, br 9.12–6.83 m 4.20 m 3.68 m 1.36 m	NH bpy + Ph CH <sub>2</sub> CH <sub>3</sub>	$AB_2$ $A_2B$	$\delta_{A} 81.6$ $\delta_{B} 75.7$ $J_{AB} = 46$ $\delta_{A} 78.4$
		0.99 m			$\frac{\delta_{\rm B}}{J_{\rm AB}} = 45$
8a <sub>1</sub>	$[Os(C_6H_5N=^{15}NH)(bpy){P(OEt)_3}_3](BPh_4)_2$	15.25 dm $J_{15\rm NH} = 66$ 14.06 dm $J_{15\rm NH} = 66$	NH	AB <sub>2</sub>	$\delta_{A} 81.6$ $\delta_{B} 75.8$ $J_{AB} = 46$
		9.12–6.83 m 4.20 m 3.67 m	bpy + Ph CH <sub>2</sub>	$A_2B$	$\delta_{\rm A}$ 78.4 $\delta_{\rm B}$ 75.5
		1.36 m 0.98 m	CH <sub>3</sub>		$J_{AB} = 45$

<sup>a</sup> In CD<sub>2</sub>Cl<sub>2</sub> at 25 °C.

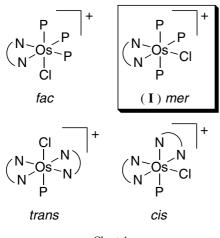
<sup>b</sup> Positive shift downfield from 85% H<sub>3</sub>PO<sub>4</sub>.

<sup>c</sup> T<sub>1 min</sub> (200 MHz) at 213 K: 181 ms.

 $^{d}$ At -30 °C.

<sup>e</sup>At −70 °C.

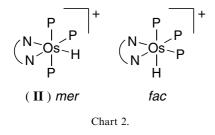
<sup>f13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$ : 232.5 (dt, CO,  $J_{CPcis} = J_{CPtrans} = 30$  Hz), 165–122 (m, Ph + bpy), 65.2 (m, CH<sub>2</sub>), 16.1 (m, CH<sub>3</sub>).





this ligand, however, is confirmed by the <sup>1</sup>H 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 <sup>31</sup>P{<sup>1</sup>H} NMR spectra appear as an A<sub>2</sub>B multiplet, this hydridic quartet can be simulated using an A<sub>2</sub>BX (X = H) model with the parameters reported in Table 1. These parameters highlight how the two J<sub>PH</sub> 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 <sup>1</sup>H NMR spectra of the related [OsH(bpy)  $\{P(OEt)_3\}_3$ ]BPh<sub>4</sub> (4a) show, in contrast with 4b, two multiplets in the hydride region at -6.76 and at -15.87

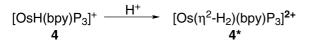


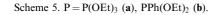
ppm, respectively, suggesting the presence of two isomers. This is confirmed by the  ${}^{31}P{}^{1}H$  NMR spectra which show two multiplets simulated using one AB<sub>2</sub> and one  $A_2B$  model with the parameters reported in Table 1. Also the two hydride multiplets of the <sup>1</sup>H NMR spectrum can be simulated using an  $AB_2X (X = H)$  model in one case, and an A<sub>2</sub>BX model in the other. The values for the two  $J_{\rm PH}$  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  $J_{\rm PH}$ 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  $[OsH(N-N)P_3]^+$  complexes can be protonated with  $CF_3SO_3H$  to give the dihydrogen  $[Os(\eta^2-H_2)(bpy)P_3]^{2+}$  (4\*) derivatives, as shown in Scheme 5.

The reaction was followed by NMR spectra and showed that, in the case of the  $[OsH(bpy){PPh (OEt)_2}_3]^+$  (4b) cation, the addition of CF<sub>3</sub>SO<sub>3</sub>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  $\eta^2$ -H<sub>2</sub> ligand of the  $[Os(\eta^2-H_2)(bpy)P_3]^{2+}$  dication. Measurements of  $T_1$  (200 MHz) on these signals gave values of  $T_{1\min}$  of 7.5 ms, in agreement [14] with the presence of the dihydrogen ligand.

The protonation of the related [OsH (bpy)  $\{P(OEt)_3\}_3]^+$  (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 <sup>1</sup>H NMR spectra. *T*<sub>1</sub> 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 <sup>31</sup>P{<sup>1</sup>H} NMR spectra, however, show the presence of two multiplets simulable using AB<sub>2</sub> and A<sub>2</sub>B spin systems (Table 1) and suggesting that the protonation should afford two different  $\eta^2$ -H<sub>2</sub> isomers, probably with *fac* and *mer* geometry, as the hydride precursor. The





presence of only one proton  $\eta^2$ -H<sub>2</sub> 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  $\eta^2$ -H<sub>2</sub>, the triflate complex.

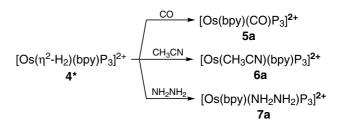
We have also prepared the isotopomer  $[Os(\eta^2 -$ HD)(bpy) $P_3$ ]<sup>+</sup> by protonation of the hydride 4 with  $CF_3SO_3D$  in an attempt to determine the values of  $J_{HD}$ . Unfortunately, the  $\eta^2$ -HD signal of the isotopomers results rather broad and does not allow a reasonable value of  $J_{\rm HD}$  to be measured. The values of the  $T_{1\,\rm min}$ measurements on the broad signal near -9 ppm, however, strongly support [14,15] the presence of an  $\eta^2$ -H<sub>2</sub> ligand. From the  $T_{1 \min}$  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  $[Os(\eta^2 H_2$ )(bpy)(CO)(PPh\_3)<sub>2</sub>]<sup>2+</sup> derivative [3c].

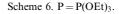
The influence of the three phosphite ligands bonded to the Os(bpy)P<sub>3</sub> fragment (**4**\*) on the  $\eta^2$ -H<sub>2</sub> seems therefore to be very similar to that of one carbonyl and two PPh<sub>3</sub> ligands in the [Os( $\eta^2$ -H<sub>2</sub>)(bpy)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> derivative.

The new dihydrogen complexes  $4^*$  are thermally unstable and the <sup>1</sup>H NMR spectra showed that the evolution of H<sub>2</sub> 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 mixedligand  $\eta^2$ -H<sub>2</sub> 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  $\eta^2$ -H<sub>2</sub> ligand in the  $[Os(\eta^2-H_2)(bpy)P_3]^{2+}$  derivatives prompted us to test these complexes as precursors for the synthesis of new osmium derivatives. The results show that the substitution of  $\eta^2$ -H<sub>2</sub> proceeds with several types of ligands affording the corresponding complexes. Some examples are shown in Scheme 6.





The new carbonyl **5a**, nitrile **6a** and hydrazine **7a** complexes were isolated as yellow or orange solids stable in air and in solution of polar organic solvents, where they behave as 2:1 electrolytes [12]. Analytical and spectroscopic data (Table 1) support the proposed formulations.

The IR spectra of the carbonyl compound **5a** show, beside the absorptions of the bpy, the phosphites and the BPh<sub>4</sub>, a strong absorption at 2025 cm<sup>-1</sup> due to  $v_{CO}$  of the carbonyl ligand. The <sup>13</sup>C spectra confirm the presence of CO showing a doublet of triplets at 232.5 ppm, attributed to the carbonyl carbon resonances coupled with the phophorus nuclei of the phosphines. The two  $J_{PC}$  show the same value of 30 Hz, suggesting that the CO is in a mutual *cis* position with all the phosphite ligands. Taking into account that, in the temperature range between +20 and -80 °C, the <sup>31</sup>P spectrum is an AB<sub>2</sub> multiplet, a *mer*-type geometry (**III**, Chart 3) can be reasonably proposed for the carbonyl derivative.

The IR spectra of the nitrile  $[Os(CH_3CN)(bpy) P_3](BPh_4)_2$  (**6a**) complex do not show any band attributable to  $v_{CN}$ , probably owing to its very low intensity [18]. However, the presence of this ligand is confirmed by the <sup>1</sup>H NMR spectra which show the singlet at 1.28 ppm of the methyl group of the CH<sub>3</sub>CN. In the temperature range between +20 and -80 °C the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the nitrile complex **6a** appears as an A<sub>2</sub>B multiplet which was simulated with the parameters reported in Table 1. These data, however, do not allow to unambiguously assign a geometry in solution to the complex.

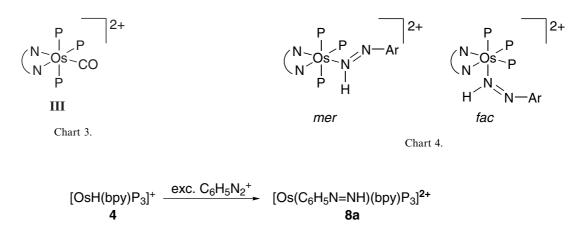
The presence of the hydrazine ligand in [Os  $(NH_2NH_2)(bpy)P_3$ ]<sup>2+</sup> (**7a**) derivative is confirmed by the IR spectra which show the characteristic [19] mediumintensity bands at 3354–3231 cm<sup>-1</sup> due to the  $v_{NH}$  of the  $NH_2NH_2$  ligand. Further support comes from the <sup>1</sup>H NMR spectrum which shows two slightly broad signals at 4.02 and 1.69 ppm, attributed to the hydrogen of the NH<sub>2</sub> groups of hydrazine. The <sup>1</sup>H COSY confirms these attributions. The proton spectrum also shows the signals of the other ligands, while the <sup>31</sup>P spectrum appears as an AB<sub>2</sub> multiplet. Also in this case, however, any geometry in solution cannot be unambiguously proposed.

Insertion reaction into the Os–H bond of the hydride  $[OsH(bpy)P_3]^+$  was studied with several unsaturated molecules such as terminal alkynes RC=CH, heteroallenes (CO<sub>2</sub>, CS<sub>2</sub>) and aryldiazonium cations ArN<sub>2</sub><sup>+</sup>. The results showed that at room temperature only the aryldiazonium cations react with the hydride 4 to give the corresponding aryldiazene complex **8a**, which was isolated as an orange solid and characterised (Scheme 7).

In the high-frequency region, the <sup>1</sup>H NMR spectra of **8a** show two slightly broad signals at 15.24 and 14.04 ppm, each of which is split into one doublet of multiplets  $(J_{15\text{NH}} = 66 \text{ Hz})$  in the spectra of the labelled [Os  $(C_6H_5\text{N}=^{15}\text{NH})(\text{bpy})\text{P}_3]^{2+}$  (**8a**\_1) derivative, in agreement [20,21] with the presence of two different diazene ligands. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra show two multiplets which can be simulated using one AB<sub>2</sub> and one A<sub>2</sub>B model with the parameters reported in Table 1. The elemental analysis agrees with the presence of only one aryldiazene ligand in the complex, so the two diazene signals in the proton spectra and the two multiplets in the <sup>31</sup>P ones can be interpreted on the basis of the presence of two isomers of the type reported in Chart 4.

The insertion of  $ArN_2^+$  into the Os-H bond of the two isomers of **4** is not followed by any isomerisation reaction affording, as in the hydride precursor, the *fac* and *mer* isomers of the aryldiazene derivatives.

Aryldiazene complexes of osmium(II) are known [21], but contain only phosphine or carbonyl as supporting ligands. The preparation of the complex **8a** shows that also bipyridyl is able to stabilise aryldiazene derivatives of osmium(II).



Scheme 7.  $P = P(OEt)_3$ .

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