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Mono- and Bis(hydrazine) Complexes of Osmium(II): Synthesis, Reactions, and X-ray Crystal Structure of the $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$ Derivative

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Reaction of OsH_2P_4 [$P = P(OEt)_3$, $PPh(OEt)_2$, PPh_2OEt] with methyl triflate followed by the treatment with hydrazines gave the $[OsH(RNHNH_2)P_4]BPh_4$ (**1**−**3**) ($R = H$, CH_3, C_6H_5, 4-$NO_2C_6H_4$) derivatives. Instead, the reaction of OsH_2P_4 first with methyl triflate, then with triflic acid, and finally with an excess of the appropriate hydrazine afforded the bis(hydrazine) $[Os(RNHNH_2)_2P_4](BPh_4)_2$ (**4**, **5**) ($R = H$, CH_3, C_6H_5) complexes. Also the $[Os(NH_2NH_2)\{P(OEt)_3\}_5](BPh_4)_2$ (**7**) derivative was prepared. All the hydrazine complexes were fully characterized by IR and ^1H and ^{31}P NMR spectra, and a single-crystal X-ray structure determination of the complex $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4](BPh_4)_2\cdot C_2H_5OH$ (**4a**) is reported. The compound crystallizes in the space group $P2_1/c$ with $a = 20.550(4)$ Å, $b = 19.663(4)$ Å, $c = 20.843(4)$ Å, $\beta = 99.84(9)°$, and $Z = 4$. The coordination around the osmium atom is octahedral and the orientation of the ligands in the $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4]^{2+}$ cation is determined by several strong hydrogen bonds involving hydrazine nitrogen and phosphite oxygen atoms. Amidrazone complexes $[Os\{\eta^2\text{-}NH{=}C(R1)N(R)NH_2\}\{P(OEt)_3\}_4](BPh_4)_2$ (**8**, **9**) ($R = H$, CH_3; $R1 = CH_3$, 4-$CH_3C_6H_4$) were prepared by allowing nitrile complexes $[Os(R1CN)_2P_4](BPh_4)_2$ to react with hydrazine NH_2NH_2 or methylhydrazine CH_3NHNH_2. Reaction of complexes containing substituted hydrazine ligands of the type $[OsH(RNHNH_2)P_4]BPh_4$ and $[Os(RNHNH_2)_2P_4](BPh_4)_2$ [$P = P(OEt)_3$; $R = CH_3$, C_6H_5] with $Pb(OAc)_4$ at −30 °C results in the selective oxidation of the hydrazine affording the corresponding diazene $[OsH(RN{=}NH)P_4]BPh_4$ (**10**) and $[Os(RN{=}NH)_2P_4](BPh_4)_2$ (**11**) derivatives. The first bis(methyldiazene) complex $[Os(CH_3N{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ (**11b**) was thus prepared.

Introduction

The chemistry of transition metal complexes containing diazenido RN_2, diazene $RN{=}NH$, hydrazine $RNHNH_2$, and other partially reduced dinitrogen ligands continues to arouse interest not only for their relationship with the intermediates of the dinitrogen fixation process but also for the diverse reactivity modes and structural properties that the diazo complexes exhibit.[1,2] However, although a large number of studies have been reported over the past 25 years, relatively few of them are concerned with hydrazine or substituted hydrazine complexes.[1−3] Furthermore, the osmium compounds containing NH_2NH_2 or $RNHNH_2$ ligands are rare[3b,4,5] and include, apart from the pioneering work on $[OsCl_2(RNHNH_2)P_3]$ and $[OsCl_2P_2]_2(\mu\text{-}NH_2NH_2)_2$ ($R = H$, Ph; P = tertiary phosphine) derivatives,[4] only two papers on the cycloocta-1,5-diene (COD) complexes[5] $[OsCl(COD)(NH_2NH_2)_3]BPh_4$ and $[Os(COD)(NH_2NH_2)_4](BPh_4)_2$ and on the carbonyl compound[3b] $[OsBr(CO)_2(NH_2NH_2)(PPh_3)_2]CF_3SO_3$.

Coordinate hydrazine NH_2NH_2 has been proposed as a possible intermediate in the nitrogen fixation process, has been shown to be a substrate[6] as well as a product of functioning nitrogenase, and has been isolated by quenching the enzyme.[7] In this context, however, much remains to be known about the chemistry of coordinate hydrazine and therefore it should be of interest to report some new results on the synthesis and on the reactivity of hydrazine derivatives.

In previous papers[8] we have reported on the synthesis and on the properties of both mono and bis forms of aryldiazene

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and aryldiazenido complexes of the iron family of the type $[MH(ArN{=}NH)P_4]^+$, $[M(ArN{=}NH)_2P_4]^{2+}$, $[M(ArN_2)P_4]^+$, and $[M(ArN_2)_2P_3]^{2+}$ (M = Fe, Ru, Os; P = phosphite).[8] Now, we have extended[9] these studies to include hydrazine and substituted hydrazines as ligands, and in this paper we report the synthesis and the characterization of mono- and bis(hydrazine) complexes of osmium(II) together with some reactivity studies and an X-ray crystal structure determination.

Experimental Section

All synthetic work was carried out under an appropriate atmosphere (Ar, H_2) using standard Schlenk techniques or a Vacuum Atmosphere drybox. 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 vacuumtight storage flasks. The $(NH_4)_2OsCl_6$ salt was a Johnson Matthey product, used as received. Triethyl phosphite, $P(OEt)_3$ (Aldrich), was purified by distillation under nitrogen, while $PPh(OEt)_2$ and the PPh_2OEt were prepared by the method of Rabinowitz and Pellon.[10] The hydrazines CH_3NHNH_2, $C_6H_5NHNH_2$, 4-$NO_2C_6H_4$-$NHNH_2$, $C_6H_5CONHNH_2$, and $(CH_3)_2NNH_2$ were Aldrich products used as received. Hydrazine, NH_2NH_2, was prepared by decomposition of hydrazine cyanurate (Fluka) by following the reported method.[11] 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) were obtained on a Bruker AC200 spectrometer at temperatures varying between −90 and +30 °C, unless otherwise noted. ^1H spectra are referred to internal tetramethylsilane, while $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The SwaN-MR software package[12] has been used in treating the NMR data. The conductivities of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83 instrument.

Synthesis of Complexes. The hydrides OsH_2P_4 [P = $P(OEt)_3$, $PPh(OEt)_2$, PPh_2OEt] were prepared as previously reported.[8f,13]

$[OsH(RNHNH_2)P_4]BPh_4$ (1, 2) [P = $P(OEt)_3$ (1), $PPh(OEt)_2$ (2); R = H (a), CH_3 (b), C_6H_5 (c), 4-$NO_2C_6H_4$ (d)]. Methyl triflate (0.10 mmol, 11 μL) was added to a solution of the appropriate hydride OsH_2P_4 (0.10 mmol) in 10 mL of toluene cooled to −196 °C. The reaction mixture was brought to room temperature and stirred for 90 min, and then an excess of the appropriate hydrazine (0.15 mmol) was added. After 1 h of stirring, the solvent was removed under reduced pressure giving an oil which was treated with 2 mL of ethanol containing an excess of $NaBPh_4$ (0.30 mmol, 0.10 g). A white or pale-yellow solid slowly separated out from the resulting solution, which was filtered out and crystallized from CH_2Cl_2 (1 mL) and ethanol (3 mL); yield ≥70%. Anal. Calcd for **1a**: C, 47.76; H, 7.10; N, 2.32. Found: C, 47.34; H, 7.18; N, 2.20. $\Lambda_M = 60.2\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **1b**: C, 48.20; H, 7.18; N, 2.29. Found: C, 48.40; H, 6.92; N, 2.12. $\Lambda_M = 55.7\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **1c**: C, 50.54; H, 6.99; N, 2.18. Found: C, 50.25; H, 7.01; N, 2.12. $\Lambda_M = 53.0\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for **1d**: C, 48.83; H, 6.68; N, 3.16. Found: C, 48.66; H, 6.80; N, 3.06. $\Lambda_M = 54.7\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **2a**: C, 57.57; H, 6.42; N, 2.10. Found: C, 57.36; H, 6.55; N, 1.99. $\Lambda_M = 54.0\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **2b**: C, 57.86; H, 6.50; N, 2.08. Found: C, 57.51; H, 6.60; N, 2.03. $\Lambda_M = 58.4\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **2c**: C, 59.57; H, 6.36; N, 1.98. Found: C, 59.70; H, 6.26; N, 1.90. $\Lambda_M = 56.3\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[OsH\{(CH_3)_2NNH_2\}P_4]BPh_4$ [P = $P(OEt)_3$ (1e), $PPh(OEt)_2$ (2e)]. These complexes were prepared exactly like the related compounds **1** and **2** using an excess of $(CH_3)_2NNH_2$ as a reagent; yield ≥65%. Anal. Calcd for **1e**: C, 48.62; H, 7.26; N, 2.27. Found: C, 48.79; H, 7.30; N, 2.15. $\Lambda_M = 54.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **2e**: C, 58.15; H, 6.58; N, 2.05. Found: C, 58.40; H, 6.45; N, 2.12. $\Lambda_M = 55.6\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[OsH(RNHNH_2)(PPh_2OEt)_4]BPh_4$ (3) [R = CH_3 (b), C_6H_5 (c)]. These complexes may be prepared by reacting the dihydride $OsH_2(PPh_2OEt)_4$ first with methyl triflate and then with the appropriate hydrazine as reported for the related $P(OEt)_3$ (**1**) and $PPh(OEt)_2$ (**2**) derivatives. However, in order to obtain larger yields and pure compounds, an alternative procedure can be used, such as the following. An excess of the appropriate hydrazine (1 mmol) was added to a solution of the $[OsH(\eta^2\text{-}H_2)(PPh_2OEt)_4]BPh_4$ complex[13] (0.10 mmol, 0.14 g) in 10 mL of CH_2Cl_2, and the reaction mixture was stirred at room temperature for about 24 h. The solvent was removed under reduced pressure giving an oil which was treated with 2 mL of ethanol containing an excess of $NaBPh_4$ (0.2 mmol, 0.07 g). The resulting solution was cooled to −10 °C and vigorously stirred until a white solid separated out, which was filtered out and crystallized from CH_2Cl_2 (1 mL) and ethanol (3 mL); yield ≥50%. Anal. Calcd for **3b**: C, 65.85; H, 5.94; N, 1.90. Found: C, 66.02; H, 5.90; N, 1.85. $\Lambda_M = 57.0\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **3c**: C, 67.09; H, 5.83; N, 1.82. Found: C, 66.88; H, 5.76; N, 1.70. $\Lambda_M = 56.1\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[Os(RNHNH_2)_2P_4](BPh_4)_2$ (4, 5) [P = $P(OEt)_3$ (4), $PPh(OEt)_2$ (5); R = H (a), CH_3 (b), C_6H_5 (c)]. To a solution of the appropriate hydride OsH_2P_4 (0.10 mmol) in 10 mL of toluene cooled to about −196 °C was added an equimolar amount of methyl triflate (0.10 mmol, 11 μL) and the reaction mixture brought to room temperature. After about 90 min of stirring, the solution was cooled again to −196 °C and a slight excess of triflic acid (0.11 mmol, 9.7 μL) added. The reaction mixture was then brought to room temperature and stirred for about 5 h. An excess of the appropriate hydrazine (1 mmol) was added to the solution, which was stirred for 24 h and then evaporated to dryness under reduced pressure. The oil obtained was dissolved in 2 mL of ethanol, and an excess of $NaBPh_4$ (0.40 mmol, 0.14 g) in 2 mL of ethanol was added. A white solid immediately separated out which was filtered out and crystallized from CH_2Cl_2 (2 mL) and ethanol (3 mL); yield ≥80%. Anal. Calcd for **4a**: C, 55.53; H, 6.99; N, 3.60. Found: C, 55.68; H, 7.03; N, 3.49. $\Lambda_M = 104.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **4b**: C, 56.06; H, 7.12; N, 3.53. Found: C, 56.20; H, 7.15; N, 3.40. $\Lambda_M = 101.7\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **4c**: C, 59.02; H, 6.84; N, 3.28. Found: C, 59.21; H, 6.69; N, 3.19. $\Lambda_M = 107.2\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **5a**: C, 62.71; H, 6.46; N, 3.32. Found: C, 62.53; H, 6.40; N, 3.23. $\Lambda_M = 112.9\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **5b**: C, 63.08; H, 6.59; N, 3.27. Found: C, 62.88; H, 6.35; N, 3.36. $\Lambda_M = 115.4\ \Omega^{-1}\ mol^{-1}\ cm^2$. Anal. Calcd for **5c**: C, 65.36; H, 6.36; N, 3.05. Found: C, 65.35; H, 6.29; N, 3.01. $\Lambda_M = 109.6\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[Os\{(CH_3)_2NNH_2\}_2\{P(OEt)_3\}_4](BPh_4)_2$ (4e). This compound was prepared exactly like **4** and **5**; yield ≥55%. Anal. Calcd: C, 56.58; H, 7.25; N, 3.47. Found: C, 56.69; H, 7.11; N, 3.34. $\Lambda_M = 116.3\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[Os(\eta^2\text{-}C_6H_5CONHNH_2)\{P(OEt)_3\}_4](BPh_4)_2$ (6). This complex was prepared by a slight modification to the method used for **4** and **5**, as follows. Methyl triflate (0.10 mmol, 11 μL) was added to a cooled solution (−196 °C) of $OsH_2[P(OEt)_3]_4$ (0.10 mmol, 0.086 g) in 10 mL of toluene, and the reaction mixture brought to room temperature and then stirred for about 90 min. Triflic acid (0.10 mmol, 8.8 μL) was then added to the solution cooled again to about −196 °C, and the resulting mixture was brought to room temperature and stirred for 5 h. The flask was open to the air and an excess of solid $C_6H_5CONHNH_2$ (0.5 mmol, 0.067 g) added to the solution together with 5 mL of CH_2Cl_2. The suspension was stirred for 24 h and then filtered to remove

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the excess benzoylhydrazine. The resulting solution was evaporated to dryness giving an oil which was treated with 2 mL of ethanol containing an excess of $NaBPh_4$ (0.4 mmol, 0.14 g). A white solid slowly separated out, which was filtered out and crystallized from CH_2Cl_2 (2 mL) and ethanol (3 mL); yield ≥55%. Anal. Calcd: C, 58.23; H, 6.68; N, 1.72. Found: C, 58.40; H, 6.52; N, 1.70. $\Lambda_M = 108.2$ Ω^{-1} mol^{-1} cm^2.

$[Os(\eta^2\text{-}O_2SOCF_3)\{PPh(OEt)_2\}_4]BPh_4$. To a solution of $OsH_2[PPh(OEt)_2]_4$ (0.32 mmol, 0.32 g) in 5 mL of toluene cooled to about −196 °C was added an equimolar amount of $CF_3SO_3CH_3$ (0.32 mmol, 36 μL), and the reaction mixture was brought to room temperature and stirred for 90 min. An excess of CF_3SO_3H (0.96 mmol, 86 μL) was then added to the resulting solution previously cooled to about −196 °C. After the reaction mixture was brought to 20 °C, it was stirred for 3 h and then the solvent removed under reduced pressure. The oil obtained was treated with ethanol (4 mL), and then an excess of $NaBPh_4$ (1 mmol, 0.34 g) in 3 mL of ethanol was added to the resulting solution. A white solid slowly separated out, which was filtered out and crystallized fractionally from ethanol to separate the triflate complex $[Os(\eta^2\text{-}O_2SOCF_3)P_4]BPh_4$ from the dihydrogen $[OsH(\eta^2\text{-}H_2)P_4]BPh_4$ compound present in the solid obtained; yield ≥40%. Anal. Calcd: C, 53.79; H, 5.56. Found: C, 53.49; H, 5.80. $\Lambda_M = 53.4$ Ω^{-1} mol^{-1} cm^2. ^1H NMR (CD_2Cl_2, 25 °C; δ): 7.60−6.70 (m, 40 H, Ph), 3.88 (m, br, 16 H, CH_2), 1.24 (t, 24 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): spin system A_2B_2, $\delta_A = 118.1$, $\delta_B = 77.8$, $J_{AB} = 31$ Hz.

$[Os(RCN)_2P_4](BPh_4)_2$ [R = CH_3, 4-$CH_3C_6H_4$; P = $P(OEt)_3$ and $PPh(OEt)_2$]. To a solution of the appropriate hydride OsH_2P_4 (0.5 mmol) in 10 mL of toluene cooled to about −196 °C was added an equimolar amount of methyl triflate (0.5 mmol, 55 μL) and the reaction mixture, brought to room temperature, stirred for 90 min. An excess of the appropriate nitrile (25 mmol) and then an excess of triflic acid (1.5 mmol, 132 μL) were added to the solution cooled again to −196 °C, which was brought to room temperature and stirred for 24 h. The solvent was removed under reduced pressure giving an oil which was treated with 5 mL of ethanol. The addition of an excess of $NaBPh_4$ (2 mmol, 0.68 g) in 3 mL of ethanol caused the precipitation of a white solid, which was filtered out and crystallized from CH_2Cl_2 (4 mL) and ethanol (5 mL); yield ≥80%. Anal. Calcd for R = CH_3 and P = $P(OEt)_3$: C, 57.94; H, 6.78; N, 1.78. Found: C, 58.10; H, 6.63; N, 1.70. $\Lambda_M = 115.2$ Ω^{-1} mol^{-1} cm^2. ^1H NMR (CD_2Cl_2, 25 °C; δ): 7.40−6.80 (m, 40 H, Ph), 4.15−3.90 (m, 24 H, CH_2), 1.72 (s, 6 H, CH_3 nitrile), 1.29, 1.26 (t, 36 H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): spin system A_2B_2, $\delta_A = 81.0$, $\delta_B = 73.4$, $J_{AB} = 44.1$ Hz. Anal. Calcd for R = CH_3 and P = $PPh(OEt)_2$: C, 64.86; H, 6.27; N, 1.64. Found: C, 64.80; H, 6.31; N, 1.68. $\Lambda_M = 117.7$ Ω^{-1} mol^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$, 25 °C; δ]: 7.90−6.70 (m, 60 H, Ph), 4.25−4.00 (m, 16 H, CH_2), 1.75 (s, 6 H, CH_3 nitrile), 1.45, 1.44 (t, 24 H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): spin system A_2B_2, $\delta_A = 112.5$, $\delta_B = 107.4$, $J_{AB} = 33.6$ Hz. Anal. Calcd for R = 4-$CH_3C_6H_4$ and P = $P(OEt)_3$: C, 61.18; H, 6.65; N, 1.62. Found: C, 60.94; H, 6.41; N, 1.58. $\Lambda_M = 108.4$ Ω^{-1} mol^{-1} cm^2. IR (KBr): 2263 [m, ν(CN)] cm^{-1}. ^1H NMR [$(CD_3)_2CO$, 25 °C; δ]: 7.85−6.70 (m, 48 H, Ph), 4.45−4.20 (m, 24 H, CH_2), 2.44 (s, 6 H, CH_3 nitrile), 1.37, 1.34 (t, 36 H, CH_3 phos). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C; δ]: spin system A_2B_2, $\delta_A = 84.0$, $\delta_B = 77.4$, $J_{AB} = 44.0$ Hz. Anal. Calcd for R = 4-$CH_3C_6H_4$ and P = $PPh(OEt)_2$: C, 67.31; H, 6.19; N, 1.51. Found: C, 67.55; H, 6.03; N, 1.55. $\Lambda_M = 110.0$ Ω^{-1} mol^{-1} cm^2. IR (KBr): 2258 [m, ν(CN)] cm^{-1}. ^1H NMR [$(CD_3)_2CO$, 25 °C; δ]: 8.00−6.70 (m, 68 H, Ph), 4.20−3.90 (m, 16 H, CH_2), 2.40 (s, 6 H, CH_3 nitrile), 1.45, 1.38 (t, 24 H, CH_3 phos). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C; δ]: spin system A_2B_2, $\delta_A = 108.9$, $\delta_B = 104.3$, $J_{AB} = 33.4$ Hz.

$[OsH\{P(OEt)_3\}_5]BPh_4$ and $OsCl_2[P(OEt)_3]_4$. A 50-mL three-necked round-bottomed flask was charged with 0.5 g (1.2 mmol) of $(NH_4)_2OsCl_6$, 20 mL of anhydrous ethanol, 3.7 mL (24 mmol) of $P(OEt)_3$, and about 1 g (15 mmol) of zinc dust. The reaction mixture was refluxed for 14 h and filtered, and then the solvent was removed under reduced pressure. The oil obtained was treated with ethanol (5 mL) giving a pale-yellow solution which separated a small amount (about 7−8%) of a yellow solid characterized as $OsCl_2[P(OEt)_3]_4$. After filtration, an excess of $NaBPh_4$ (2 mmol, 0.68 g) in 2 mL of ethanol was added and the resulting solid formed was filtered out and crystallized from ethanol; yield ≥55%. Anal. Calcd for $[OsH\{P(OEt)_3\}_5]BPh_4$: C, 48.36; H, 7.21. Found: C, 48.41; H, 7.15. $\Lambda_M = 51.5$ Ω^{-1} mol^{-1} cm^2. IR (KBr): 1990 [m, ν(OsH)] cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C; δ): 7.30−6.70 (m, 20 H, Ph), 3.96 (m, 30 H, CH_2), 1.25 (t, 45 H, CH_3), −11.16 to −11.92 (m, 1 H, hydride). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C; δ): spin system AB_4, $\delta_A = 105.7$, $\delta_B = 99.3$, $J_{AB} = 34$ Hz. Anal. Calcd for $OsCl_2[P(OEt)_3]_4$: C, 31.14; H, 6.53. Found: C, 31.16; H, 6.84. ^1H NMR (CD_2Cl_2, 25 °C; δ): 4.19 (m, 24 H, CH_2), 1.22 (t, 36 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C; δ): 83.5 s ($J_{^{31}P^{187}Os} = 293.4$ Hz).

$[Os(NH_2NH_2)\{P(OEt)_3\}_5](BPh_4)_2$ (7). To a solution under hydrogen (1 atm) of $[OsH\{P(OEt)_3\}_5]BPh_4$ (0.10 mmol, 0.134 g) in 10 mL of CH_2Cl_2 was added an equimolar amount of $HBF_4{\cdot}Et_2O$ (0.10 mmol, 15 μL of a 54% solution in Et_2O) and the reaction mixture stirred for 24 h. An excess of NH_2NH_2 (1 mmol, 32 μL) was added, and after the H_2 atmosphere was replaced with an argon one, the solution was stirred for about 3 h. The solvent was removed under reduced pressure giving an oil which was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.20 mmol, 0.068 g). A white solid slowly separated out, which was filtered out and crystallized from CH_2Cl_2 (2 mL) and ethanol (3 mL); yield ≥60%. Anal. Calcd: C, 55.39; H, 7.09; N, 1.66. Found: C, 55.54; H, 6.91; N, 1.58. $\Lambda_M = 108.0$ Ω^{-1} mol^{-1} cm^2.

$[Os\{\eta^2\text{-}NH{=}C(R1)N(R)NH_2\}\{P(OEt)_3\}_4](BPh_4)_2$ (8, 9) [R1 = CH_3 (8), 4-$CH_3C_6H_4$ (9); R = H (a), CH_3 (b)]. An excess of the appropriate hydrazine (1.2 mmol) was added to a solution of $[Os(R1CN)_2P_4](BPh_4)_2$ (0.15 mmol) in 15 mL of 1,2-dichloroethane and the reaction mixture refluxed for 3 h. The solvent was removed under reduced pressure giving an oil which was treated with 3 mL of ethanol. The addition of a slight excess of $NaBPh_4$ (0.2 mmol, 68 mg) to the resulting solution caused the precipitation of a white solid, which was filtered out and crystallized from CH_2Cl_2 (2 mL) and ethanol (4 mL); yield ≥50%. Anal. Calcd for **8a**: C, 56.74; H, 6.89; N, 2.68. Found: C, 56.64; H, 6.65; N, 2.50. $\Lambda_M = 112.5$ Ω^{-1} mol^{-1} cm^2. Anal. Calcd for **8b**: C, 57.00; H, 6.95; N, 2.66. Found: C, 57.13; H, 6.90; N, 2.54. $\Lambda_M = 116.6$ Ω^{-1} mol^{-1} cm^2. Anal. Calcd for **9a**: C, 58.50; H, 6.81; N, 2.56. Found: C, 58.72; H, 6.67; N, 2.40. $\Lambda_M = 121.4$ Ω^{-1} mol^{-1} cm^2. Anal. Calcd for **9b**: C, 58.73; H, 6.88; N, 2.54. Found: C, 58.48; H, 6.71; N, 2.49. $\Lambda_M = 113.9$ Ω^{-1} mol^{-1} cm^2.

$[Os(CH_3N{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ (11b). A sample of $[Os(CH_3NHNH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$ (0.10 mmol, 0.16 g) was placed in a three-necked 25-mL round-bottomed flask fitted with a solid-addition side arm containing an excess of $Pb(OAc)_4$ (0.30 mmol, 0.14 g). Dichloromethane (10 mL) was added, the solution cooled to −30 °C, and the $Pb(OAc)_4$ added portionwise over 20−30 min to the cold stirred solution. The solution was then brought to room temperature and filtered, and the solvent was removed under reduced pressure giving an oil. The addition of ethanol (3 mL) containing an excess of $NaBPh_4$ (0.2 mmol, 0.068 g) caused the separation of an orange solid, which was filtered out and crystallized from CH_2Cl_2 (2 mL) and ethanol (3 mL); yield ≥60%. Anal. Calcd: C, 56.20; H, 6.88; N, 3.54. Found: C, 56.32; H, 6.93; N, 3.44. $\Lambda_M = 114.2$ Ω^{-1} mol^{-1} cm^2.

$[OsH(C_6H_5N{=}NH)\{P(OEt)_3\}_4]BPh_4$ (10c) and $[Os(C_6H_5N{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ (11c). These complexes were prepared by oxidation with an excess of $Pb(OAc)_4$ of the corresponding hydrazine complexes $[OsH(C_6H_5NHNH_2)\{P(OEt)_3\}_4]BPh_4$ and $[Os(C_6H_5NHNH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$, respectively, following the same procedure reported for the methylhydrazine $[Os(CH_3NHNH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$ derivative; yield ≥65%. Anal. Calcd for **10c**: C, 50.62; H, 6.84; N, 2.19. Found: C, 50.86; H, 6.89; N, 2.11. $\Lambda_M = 53.5$ Ω^{-1} mol^{-1} cm^2. Anal. Calcd for **11c**: C, 59.16; H, 6.62; N, 3.28. Found: C, 59.41; H, 6.49; N, 3.17. $\Lambda_M = 107.1$ Ω^{-1} mol^{-1} cm^2.

$[Os(\eta^2\text{-}O_2CCH_3)\{P(OEt)_3\}_4]BPh_4$ (12). This complex was obtained by the oxidation reaction with $Pb(OAc)_4$ of both the hydrazine $[OsH(NH_2NH_2)\{P(OEt)_3\}_4]BPh_4$ and $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$ derivatives. In a typical preparation a solution of $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$ (0.10 mmol, 0.16 g) in 10 mL of CH_2Cl_2 cooled to −30 °C is oxidized with solid $Pb(OAc)_4$ (0.20 mmol, 0.089 g) added portionwise over a 20−30 min period. The solution was then filtered and the solvent removed under reduced pressure giving an oil. This oil was treated with 4 mL of ethanol containing an excess of $NaBPh_4$ (0.2 mmol, 0.068

Table 1. Crystal and Structure Refinement Data for $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4](BPh_4)_2 \cdot C_2H_5OH$ (**4a**)

empirical formula	$C_{74}H_{114}B_2N_4O_{13}OsP_4$
fw	1603.45
temp	20(2) °C
wavelength	1.541 84 Å
cryst system	monoclinic
space group	$P2_1/c$
unit cell dimens	$a = 20.550(4)$ Å $b = 19.663(4)$ Å, $\beta = 99.84(9)°$ $c = 20.843(4)$ Å
V	8298(3) Å^3
Z	4
D(calcd)	1.283 g/cm^3
abs coeff	4.096 mm^{-1}
F(000)	3344
θ range for data collcn	3−70°
index ranges	$-25 \leq h \leq 24$, $0 \leq k \leq 23$, $0 \leq l \leq 25$
reflcns collcd	16 177
indepdt reflcns	15 738 [R(int) = 0.1307]
refinement method	full-matrix least-squares on F^2
data/restraints/params	15738/927/815
goodness-of-fit on F^2	0.842
final R indices[a] [$I > 2\sigma(I)$]	R1 = 0.0909, wR2 = 0.2168
R indices (all data)	R1 = 0.3598, wR2 = 0.3906
largest ΔF peak and hole	0.548 and −1.903 e/Å^3

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $w = 1/\{\sigma^2(F_o^2) + [0.17(2F_c^2 + F_o^2)/3]^2\}$.

Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^4) (One-Third Trace of the Diagonalized Matrix), with Esd's in Parentheses for Relevant Non-Hydrogen Atoms

atom	x/a	y/b	z/c	U_{eq}
Os	2164.5(4)	60.7(4)	2244.3(5)	912(4)
P1	2802(3)	−22(3)	1442(3)	971(23)
P2	2886(3)	779(3)	2809(3)	923(24)
P3	1442(3)	185(3)	2976(3)	972(26)
P4	2614(3)	−886(3)	2753(4)	1045(30)
N1	1471(7)	−572(8)	1576(8)	1054(77)
N2	786(11)	−569(10)	1653(10)	1523(119)
N3	1685(8)	925(7)	1689(9)	1095(81)
N4	1167(12)	787(10)	1168(12)	1592(119)
O1	2717(6)	626(7)	958(8)	1230(73)
O2	3556(6)	−111(7)	1642(7)	1178(66)
O3	2565(7)	−612(8)	947(8)	1448(84)
O4	3304(8)	1193(8)	2419(8)	1713(94)
O5	2602(8)	1345(8)	3164(10)	1808(110)
O6	3388(8)	372(11)	3350(8)	1993(101)
O7	1034(8)	−455(7)	3054(7)	1331(77)
O8	907(6)	773(6)	2725(7)	1179(67)
O9	1669(8)	467(9)	3684(10)	1551(93)
O10	2625(7)	−919(6)	3491(8)	1301(76)
O11	2150(6)	−1513(6)	2456(7)	1304(72)
O12	3281(8)	−1160(8)	2623(10)	1581(93)

g), and the resulting solution was vigorously stirred at 0 °C until a white solid separated out, which was filtered out and crystallized from ethanol; yield ≥65%. Anal. Calcd: C, 48.70; H, 6.78. Found: C, 48.92; H, 6.60. $\Lambda_M = 50.7\ \Omega^{-1}\ mol^{-1}\ cm^2$.

X-ray Crystallography. The X-ray diffractometric analysis was performed on a colorless crystal with a CAD4 diffractometer. Cu Kα radiation ($\lambda = 1.541\ 84$ Å) was used because the crystal was expected to diffract poorly, even in the presence of heavy scatters, due to possible radiation damage and solvent loss. Automatic peak search, centering, and indexing procedures established a monoclinic primitive lattice, and systematic extinctions together with centric intensities statistics identified unambiguously the space group as $P2_1/c$. The intensity of a reference reflection was measured periodically throughout data collection to monitor crystal decay. Intensity loss of more than 50% was detected, and data were rescaled accordingly. Table 1 reports crystal data and details of data collection and structure refinement. The intensity data were processed with a peak-profile procedure and corrected for Lorentz and polarization effects. The phase problem was solved by direct methods, using SIR92,[14] which allowed one to retrieve all non-hydrogen atoms. Neutral atomic scattering factors were employed, those for non-hydrogen atoms being corrected for anomalous dispersion. Hydrogen atoms were placed at idealized positions, riding on their carrier atoms, with the exception of those belonging to hydrazine, whose presence and geometry were to be confirmed experimentally. Several cycles of full-matrix least-squares refinement were performed on F^2 till the isotropic model had reached convergence, using SHELXL96.[15] A total of 12 anisotropic scaling factors were then refined to model an empirical absorption surface according to the method of Parkin, Moezzi, and Hope,[16] as implemented in SHELXL96. The validity of this absorption correction was supported by the improvement of the rms R factor (wR2) from 0.468 to 0.452 upon the introduction of the 12 parameters. This was also checked with the cross-validation method implemented in SHELXPRO[17] by refining the 12 parameters of the absorption model on a set of about 14 000 reflections and calculating the consequent R-factor drop on the remaining 1600 "unbiased free reflections". The resultant "local free-R" dropped from 0.379 to 0.363 confirming the significance of the correction. The values of the 12 anisotropic scaling factors refined with the isotropic model on all reflections were held fixed in the subsequent structure refinements to prevent instability due to their correlation with atomic anisotropic thermal motion. Anisotropic thermal displacement parameters were introduced and refined for all non-hydrogen atoms; at this stage a careful inspection of the Fourier density map allowed us to locate the hydrazinic hydrogens, which were restrained to maintain correct geometry and realistic thermal factors during the subsequent refinements. In order to improve the observation to parameter ratio, phenyl rings were constrained to rigid group behavior, and rigid bond and isotropicity restraints were applied on the thermal motion of all carbons. The final model includes also a highly mobile ethanol molecule, which was detected in the last stages of the refinement. The final geometry was analyzed by the program PARST95,[18] and the drawings were made with ZORTEP.[19] All the calculations were performed on ENCORE91 computer at the Centro di Studio per la Strutturistica Diffrattometrica del CNR in Parma, Italy. Besides the use of data from the original literature, data for comparison with other compounds were retrieved and analyzed by the software packages of the Cambridge Structural Database.[20] Table 2 reports final fractional atomic coordinates for non-hydrogen atoms.

Results and Discussion

Mono- and Bis(hydrazine) Complexes. Hydride−hydrazine complexes $[OsH(RNHNH_2)P_4]BPh_4$ (**1**−**3**) were prepared by treating hydride species OsH_2P_4 first with methyl triflate and then with an excess of the appropriate $RNHNH_2$ ligand. Bis(hydrazine) derivatives $[Os(RNHNH_2)_2P_4](BPh_4)_2$ (**4**, **5**), instead, can be obtained by sequential reaction of the hydrides OsH_2P_4 first with methyl triflate, then with triflic acid and, finally, with an excess of the appropriate hydrazine as shown in Scheme 1. The reaction of the hydride species OsH_2P_4 with $CF_3SO_3CH_3$ proceeds with evolution of CH_4 (by ^1H NMR) and the probable formation of the triflate complex[21] $OsH(\eta^1\text{-}OSO_2CF_3)P_4$ which affords, by substitution of the $CF_3SO_3^-$ ligand, the final hydrazine complexes **1**−**3**. Compounds **3**, containing the PPh_2-

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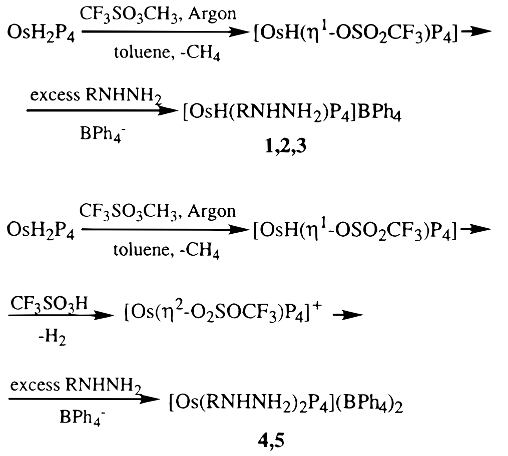
Scheme 1



P = P(OEt)$_3$ (**1**,**4**), PPh(OEt)$_2$ (**2**,**5**), PPh$_2$OEt (**3**); R = H (**a**), CH$_3$ (**b**), C$_6$H$_5$ (**c**), 4-NO$_2$C$_6$H$_4$ (**d**).

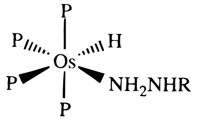
OEt phosphine ligand, can also be obtained by substitution with hydrazines of the η^2-H$_2$ ligand in [OsH(η^2-H$_2$)(PPh$_2$OEt)$_4$]$^+$ cations.[13]

Treatment of the η^1-triflate OsH(η^1-OSO$_2$CF$_3$)P$_4$ complex with triflic acid may result in a protonation reaction giving the dihydrogen intermediate [Os(η^2-H$_2$)(η^1-OSO$_2$CF$_3$)P$_4$]$^+$ CF$_3$SO$_3^-$ which, by loss of H$_2$, affords the η^2-triflate [Os(η^2-O$_2$SOCF$_3$)P$_4$]$^+$-CF$_3$SO$_3^-$ derivative. Although the presence of a dihydrogen complex was not detected in the reaction mixture, its formation is plausible on the basis of the known properties[8g,13] of the osmium hydrides containing phosphite ligands. Furthermore, the achievement and the characterization of the η^2-triflate [Os(η^2-O$_2$SOCF$_3$){PPh(OEt)$_2$}$_4$]BPh$_4$ complex seems to support the proposed reaction path. Substitution of the η^2-triflate with RNHNH$_2$ is easy and gives the bis(hydrazine) [Os(RNHNH$_2$)$_2$P$_4$]$^{2+}$ cations which can be separated as BPh$_4$ salts and characterized. It is worth noting that also the *N*,*N*-dimethylhydrazine complexes [OsH{(CH$_3$)$_2$NNH$_2$}P$_4$]BPh$_4$ (**1e**, **2e**) and [Os{(CH$_3$)$_2$NNH$_2$}$_2$P$_4$](BPh$_4$)$_2$ (**4e**) can be obtained by following the method reported in Scheme 1.

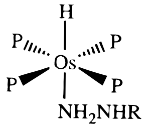
Good analytical data were obtained for all the hydrazine complexes **1**−**5**, which are white solids stable in the air and in solutions of polar organic solvents, where they behave as 1:1 (**1**−**3**) or 2:1 (**4**, **5**) electrolytes.[22] The IR and NMR data (Table 3) support the proposed formulation and allow a geometry in solution to be established.

The presence of the hydrazine ligand in all the complexes **1**−**5** is confirmed by the IR spectra, which show the characteristic ν(NH) and δ(NH$_2$) bands at 3386−3219 and at 1618−1593 cm^{-1}, respectively. Furthermore, in the [OsH(RNHNH$_2$)-P$_4$]BPh$_4$ (**1**−**3**) derivatives the absorption due to the ν(OsH) is also observed at 2078−1926 cm^{-1}.

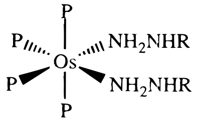
The ^{1}H NMR spectra confirm the presence of the hydrazine ligand showing the characteristic NH and NH$_2$ signals, which were clearly assigned by accurate integration and homodecoupling experiments and are reported in Table 3. The spectra also show that, in the case of NH$_2$NH$_2$ complexes, two NH$_2$ proton signals are present for all the mono- and bis(hydrazine) complexes suggesting the presence of a η^1-coordination for the hydrazine ligand. Furthermore, the ^{31}P{^{1}H} NMR spectra allow one to assign a geometry in solution for all the osmium compounds. In particular, the ^{31}P spectra of the [OsH(RNHNH$_2$)P$_4$]$^+$ (**1**−**3**) cations appear, for all the complexes except **2a**,**b**, as A$_2$BC or AB$_2$C multiplets, which can be simulated with the parameters reported in Table 3 and suggest the existence of a *cis* geometry **I**. This geometry is also confirmed by the presence, in the ^{1}H NMR spectra, of a complicated multiplet between −7.36 and −9.72 ppm for the hydride ligand. Surprisingly, in the temperature range between +30 and −90 °C, the ^{31}P NMR spectra of the [OsH(NH$_2$NH$_2$)-{PPh(OEt)$_2$}$_4$]BPh$_4$ (**2a**) and [OsH(CH$_3$NHNH$_2$){PPh(OEt)$_2$}$_4$]-BPh$_4$ (**2b**) derivatives appear as sharp singlets, suggesting that the hydride and the hydrazine ligands are in a mutually *trans* position as in type **II** structure. This different geometry observed in the two compounds **2a**,**b** with respect to the other monohydrazine compounds is, in some aspects, rather difficult to explain taking also into account that the two compounds were prepared exactly as the other derivatives **1**−**3** and that no isomerization was observed in solution for all the monohydrazine derivatives. A steric influence of the ancillary phosphite ligands in determining the geometry of the two complexes **2a**,**b** seems to be unprobable, because the steric hindrance (cone angle)[23] of the PPh(OEt)$_2$ ligand is just intermediate between those of the P(OEt)$_3$ and of the PPh$_2$OEt, whose related hydrazine and methylhydrazine [OsH(RNHNH$_2$)P$_4$]$^+$ (**1a**, **3a**; **1b**, **3b**) derivatives show a *cis* geometry. However, also the electronic properties[23] of the PPh(OEt)$_2$ ligand are intermediate between those of P(OEt)$_3$ and PPh$_2$OEt, while, instead, NH$_2$-NH$_2$ and CH$_3$NHNH$_2$ are different from the other arylhydrazines. Probably, a combination of steric and electronic factors of both the phosphite and the hydrazine ligands favor a *cis* or a *trans* arrangement of the ligands, as observed in our hydrazine derivatives. As a result, both the *N*,*N*-dimethylhydrazine complexes [OsH{(CH$_3$)$_2$NNH$_2$}P$_4$]BPh$_4$ (**1e**, **2e**) containing the P(OEt)$_3$ and the PPh(OEt)$_2$ ligands show a type-**I** *cis* geometry. Furthermore, on the basis of the A$_2$B$_2$ multiplets observed in the ^{31}P{^{1}H) NMR spectra, a *cis* arrangement (**III**) of the two RNHNH$_2$ ligands can also be proposed in solution for all the bis(hydrazine) [Os(RNHNH$_2$)$_2$P$_4$](BPh$_4$)$_2$ (**4**, **5**) complexes, except for **5a**,**b**. Such a *cis* geometry was also observed in the solid state (X-ray, see below) for the [Os(NH$_2$NH$_2$)$_2${P(OEt)$_3$}$_4$]-(BPh$_4$)$_2$ (**4a**) derivative and is shown in Figure 1.



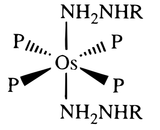
I



II



III



IV

For the related [Os(NH$_2$NH$_2$)$_2${PPh(OEt)$_2$}$_4$](BPh$_4$)$_2$ (**5a**) and [Os(CH$_3$NHNH$_2$)$_2${PPh(OEt)$_2$}$_4$](BPh$_4$)$_2$ (**5b**) complexes, instead, the ^{31}P NMR spectra indicate the presence of a *trans* geometry (**IV**) (sharp singlet at 108.1 and 108.2 ppm) in agreement with the presence, for the bis(hydrazine) derivative

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(22) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(23) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Rahman, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1.

Table 3. IR and NMR Spectroscopic Data for the Osmium Complexes

compound		IR^a (cm^{-1})	assgnt	^{1}H NMR^{b,c} (ppm)	assgnt	spin syst	^{31}P{^{1}H} NMR^{b,d} (ppm; J, Hz)
no.	formula						
1a	$[OsH(NH_2NH_2)\{P(OEt)_3\}_4]BPh_4$	3374 m	ν(NH)	4.67 m, br	$OsNH_2$	A_2BC	$\delta_A = 103.6$
		3330 m		3.33 m, br	NH_2		$\delta_B = 103.6$
		3273 m		4.20−3.75 m	CH_2		$\delta_C = 97.5$
		1956 m	ν(OsH)	1.30, 1.25, 1.21 t	CH_3		$J_{AB} = 34.0$
		1593 m	$\delta(NH_2)$	−8.55 to −9.54 m	H hydride		$J_{AC} = 42.6$
							$J_{BC} = 27.3$
1b	$[OsH(CH_3NHNH_2)\{P(OEt)_3\}_4]BPh_4$	3348 m	ν(NH)	4.59 m, br	$OsNH_2$	A_2BC	$\delta_A = 103.7$
		3314 m		2.77 m, br	NH		$\delta_B = 103.5$
		1927 m	ν(OsH)	4.15−3.75 m	CH_2		$\delta_C = 98.0$
				2.44 d, br	CH_3NH		$J_{AB} = 34.1$
				1.29, 1.25, 1.21 t	CH_3		$J_{AC} = 43.0$
				−8.73 to −9.72 m	H hydride		$J_{BC} = 27.7$
1c	$[OsH(C_6H_5NHNH_2)\{P(OEt)_3\}_4]BPh_4$	3363 m	ν(NH)	5.35 m, br	$OsNH_2$	AB_2C	$\delta_A = 102.8$
		3314 w		4.85 br	NH		$\delta_B = 102.6$
		3301 m		4.18−3.80 m	CH_2		$\delta_C = 96.4$
		1930 m	ν(OsH)	1.28, 1.24, 1.19 t	CH_3		$J_{AB} = 34.8$
		1604 m	$\delta(NH_2)$	−8.54 to −9.53 m	H hydride		$J_{AC} = 27.5$
							$J_{BC} = 43.1$
1d	$[OsH(4\text{-}NO_2C_6H_4NHNH_2)\{P(OEt)_3\}_4]BPh_4{}^e$	3386 m	ν(NH)	6.33 m, br	NH	AB_2C	$\delta_A = 104.1$
		3365 m		5.79 m, br	$OsNH_2$		$\delta_B = 103.7$
		3301 m		4.32−3.93 m	CH_2		$\delta_C = 96.7$
		1926 m	ν(OsH)	1.35, 1.28, 1.22 t	CH_3		$J_{AB} = 34.9$
		1601 m	$\delta(NH_2)$	−8.21 to −9.21 m	H hydride		$J_{AC} = 28.2$
							$J_{BC} = 43.4$
1e	$[OsH\{(CH_3)_2NNH_2\}\{P(OEt)_3\}_4]BPh_4$	3308 m	ν(NH)	4.63 m, br	$OsNH_2$	A_2BC	$\delta_A = 102.7$
		1963 m	ν(OsH)	4.13−3.80 m	CH_2		$\delta_B = 101.4$
				2.41 s	$(CH_3)_2N$		$\delta_C = 97.8$
				1.27, 1.25, 1.21 t	CH_3		$J_{AB} = 36.1$
				−8.55 to −9.31 m	H hydride		$J_{AC} = 43.0$
							$J_{BC} = 25.2$
2a	$[OsH(NH_2NH_2)\{PPh(OEt)_2\}_4]BPh_4$	3370 m	ν(NH)	4.80 m, br	$OsNH_2$		125.8 s
		3334 m		3.14 m, br	NH_2		
		3317 m		4.02−3.47 m	CH_2		
		3259 w		1.14, 1.12 t	CH_3		
		2063 m	ν(OsH)	−18.07 qi	H hydride		
		1603 m	$\delta(NH_2)$	$J_{PH} = 18$ Hz			
2b	$[OsH(CH_3NHNH_2)\{PPh(OEt)_2\}_4]BPh_4$	3328 m	ν(NH)	4.64 m, br	$OsNH_2$		125.9 s
		3304 w		3.19 m	NH		
		3256 w		4.02−3.40 m	CH_2		
		2078 m	ν(OsH)	2.42 d	CH_3NH		
		1611 m	$\delta(NH_2)$	$J_{HH} = 6.4$ Hz			
				1.13 t	CH_3		
				−18.02 qi	H hydride		
				$J_{PH} = 18$ Hz			
2c	$[OsH(C_6H_5NHNH_2)\{PPh(OEt)_2\}_4]BPh_4{}^e$	3375 w	ν(NH)	5.39 t, br	NH	AB_2C	$\delta_A = 126.3$
		3293 m		5.04 m, br	$OsNH_2$		$\delta_B = 124.7$
		3219 w		4.10−3.30 m	CH_2		$\delta_C = 115.9$
		1983 m	ν(OsH)	1.26, 1.15, 1.13,			$J_{AB} = 23.6$
		1600 m	$\delta(NH_2)$	1.03, 0.97 t	CH_3		$J_{AC} = 21.0$
				−7.98 to −8.70 m	H hydride		$J_{BC} = 28.4$
2e	$[OsH\{(CH_3)_2NNH_2\}\{PPh(OEt)_2\}_4]BPh_4$	3326 m	ν(NH)	4.35 br	$OsNH_2$	A_2BC	$\delta_A = 124.8$
		3282 m		4.00−3.50 m	CH_2		$\delta_B = 122.7$
		2005 m	ν(OsH)	2.35 s	$(CH_3)_2N$		$\delta_C = 116.2$
		1607 m	$\delta(NH_2)$	1.27, 1.20, 1.13,			$J_{AB} = 25.6$
				0.95 t	CH_3		$J_{AC} = 28.7$
				−8.06 to −8.79 m	H hydride		$J_{BC} = 15.0$
3b	$[OsH(CH_3NHNH_2)(PPh_2OEt)_4]BPh_4$	3334 w	ν(NH)	3.70−2.90 m	CH_2	A_2BC	$\delta_A = 98.7$
		3268 m		2.41 m	NH		$\delta_B = 94.9$
		2045 m	ν(OsH)	1.53 d	CH_3NH		$\delta_C = 91.9$
				1.22, 1.10, 1.03,			$J_{AB} = 17.7$
				0.64 t	CH_3		$J_{AC} = 22.0$
				−8.02 to −8.75 m	H hydride		$J_{BC} = 19.0$
3c	$[OsH(C_6H_5NHNH_2)(PPh_2OEt)_4]BPh_4{}^e$	3359 m	ν(NH)	5.20 br	NH	A_2BC	$\delta_A = 100.7$
		3327 w		4.60 m, br	$OsNH_2$		$\delta_B = 97.4$
		3259m		3.40−3.00 m	CH_2		$\delta_C = 93.0$
		2045 m	ν(OsH)	0.85, 0.76, 0.59 t	CH_3		$J_{AB} = 16.1$
		1611 m	$\delta(NH_2)$	−7.36 to −8.09 m	H hydride		$J_{AC} = 22.4$
							$J_{BC} = 17.9$
4a	$[Os(NH_2NH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$	3372 m	ν(NH)	4.81 br	$OsNH_2$	A_2B_2	$\delta_A = 84.6$
		3315 m		4.15−3.90 m	CH_2		$\delta_B = 77.9$
		3299 m		2.97 br	NH_2		$J_{AB} = 43.2$
		3266 m		1.33, 1.28 t	CH_3		
		1617 m	$\delta(NH_2)$				
4b	$[Os(CH_3NHNH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$	3345 m	ν(NH)	5.03 br	$OsNH_2$	A_2B_2	$\delta_A = 83.6$
		3304 m		4.20−3.90 m	CH_2		$\delta_B = 77.0$
		3290 m		2.57 d	CH_3NH		$J_{AB} = 43.2$
		1596 m	$\delta(NH_2)$	$J_{HH} = 6$ Hz			
				1.34, 1.29 t	CH_3		

Table 3 (Continued)

compound		IR[a]		^{1}H NMR[b,c]		spin	^{31}P{^{1}H} NMR[b,d]
no.	formula	(cm^{-1})	assgnt	(ppm)	assgnt	syst	(ppm; *J*, Hz)
4c	$[Os(C_6H_5NHNH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$[e]	3309 m	ν(NH)	6.38 br	$OsNH_2$	A_2B_2	$\delta_A = 85.8$
		3285 m		4.55−3.30 m	CH_2		$\delta_B = 76.7$
		3229 m		1.40, 1.38 t	CH_3		$J_{AB} = 42.9$
		1601 m	$\delta(NH_2)$				
4e	$[Os\{(CH_3)_2NNH_2\}_2\{P(OEt)_3\}_4](BPh_4)_2$[e]	3326 m	ν(NH)	5.45 br	$OsNH_2$	A_2B_2	$\delta_A = 83.2$
		3301 m		4.43−4.20 m	CH_2		$\delta_B = 77.6$
		1607 m	$\delta(NH_2)$	2.67 s	$(CH_3)_2N$		$J_{AB} = 44.1$
				1.41, 1.37 t	CH_3		
5a	$[Os(NH_2NH_2)_2\{PPh(OEt)_2\}_4](BPh_4)_2$	3349 m	ν(NH)	4.80 m, br	$OsNH_2$		108.1 s
		3313 w		3.90−3.60 m	CH_2		
		3289 w		2.26 m, br	NH_2		
		3259 m		1.25, 1.22 t	CH_3		
		1616 m	$\delta(NH_2)$				
5b	$[Os(CH_3NHNH_2)_2\{PPh(OEt)_2\}_4](BPh_4)_2$	3350 m	ν(NH)	5.01 m, br	$OsNH_2$		108.2 s
		3314 m		4.10−3.70 m	CH_2		
		3260 m		3.85 br	NH		
		1618 m	$\delta(NH_2)$	2.32 d	CH_3NH		
				$J_{HH} = 6$			
				1.27 t	CH_3		
5c	$[Os(C_6H_5NHNH_2)_2\{PPh(OEt)_2\}_4](BPh_4)_2$	3326 m	ν(NH)	6.37 br	NH	A_2B_2	$\delta_A = 113.9$
		3297 m		5.45 br	$OsNH_2$		$\delta_B = 102.9$
		3273 m		3.80−3.20 m	CH_2		$J_{AB} = 31.9$
		1601 m	$\delta(NH_2)$	1.21, 1.10 t	CH_3		
6	$[Os(\eta^2\text{-}C_6H_5CONHNH_2)\{P(OEt)_3\}_4](BPh_4)_2$	3271 m	ν(NH)	7.30 br	NH	A_2BC	$\delta_A = 88.9$
		3206 w		6.12 m	$OsNH_2$		$\delta_B = 84.2$
		1633 m	ν(CO)	4.17−3.96 m	CH_2		$\delta_C = 71.3$
		1601 w	$\delta(NH_2)$	1.32, 1.30, 1.17 t	CH_3		$J_{AB} = 40.6$
							$J_{AC} = 41.1$
							$J_{BC} = 42.0$
7	$[Os(NH_2NH_2)\{P(OEt)_3\}_5](BPh_4)_2$	3366 w	ν(NH)	4.90 br	$OsNH_2$	AB_4	$\delta_A = 81.9$
		3318 w		3.52 m, br	NH_2		$\delta_B = 79.0$
		3270 w		4.20 m	CH_2		$J_{AB} = 40.3$
				1.50, 1.45 t	CH_3		
8a	$[Os\{\eta^2\text{-}NH{=}C(CH_3)NHNH_2\}\{P(OEt)_3\}_4](BPh_4)_2$	3395 m	ν(NH)	6.40 br	$NH{=}C$	AB_2C	$\delta_A = 85.4$
		3333 m		5.58 br	NH_2 and NH		$\delta_B = 83.0$
		3290 m		3.98 m	CH_2		$\delta_C = 81.0$
		1647 m	$\delta(NH_2)$	1.35 s	$C(CH_3)$		$J_{AB} = 41.5$
				1.29, 1.26 t	CH_3		$J_{AC} = 42.9$
				9.29 br [e]	$NH{=}C$		$J_{BC} = 43.4$
				7.08 br	$OsNH_2$		
				4.20 m	CH_2		
				2.24 s	$C(CH_3)$		
				1.35, 1.34, 1.32 t	CH_3		
8b	$[Os\{\eta^2\text{-}NH{=}C(CH_3)N(CH_3)NH_2\}\{P(OEt)_3\}_4](BPh_4)_2$	3399 m	ν(NH)	6.26 m, br	$OsNH_2$	ABC_2	$\delta_A = 84.8$
		3313 w		5.76 br	$NH{=}C$		$\delta_B = 81.7$
		3264 m		4.10−3.90 m	CH_2		$\delta_C = 81.6$
		1640 m	$\delta(NH_2)$	2.57, 1.67 s	CH_3		$J_{AB} = 40.3$
				1.31, 1.27, 1.26 t	CH_3 phos		$J_{AC} = 39.2$
							$J_{BC} = 42.8$
9a	$[Os\{\eta^2\text{-}NH{=}C(4\text{-}CH_3C_6H_4)NHNH_2\}\{P(OEt)_3\}_4](BPh_4)_2$[e]	3395 m	ν(NH)	9.79 br	$NH{=}C$	AB_2C	$\delta_A = 86.0$
		3330 m		7.42	$OsNH_2$		$\delta_B = 84.8$
		3292 m		4.24 br	CH_2		$\delta_C = 84.1$
		1636 m	$\delta(NH_2)$	2.38 s	$CH_3C_6H_4$		$J_{AB} = 41.1$
				1.37, 1.36, 1.32 t	CH_3		$J_{AC} = 43.8$
							$J_{BC} = 42.8$
9b	$[Os\{\eta^2\text{-}NH{=}C(4\text{-}CH_3C_6H_4)N(CH_3)NH_2\}\{P(OEt)_3\}_4](BPh_4)_2$	3397 m	ν(NH)	6.49 m, br	$OsNH_2$	AB_2C	$\delta_A = 84.9$
		3273 m		6.06 m, br	$NH{=}C$		$\delta_B = 81.7$
		3230 w		4.04 m	CH_2		$\delta_C = 81.1$
		1625 m	$\delta(NH_2)$	2.63, 2.45 s	CH_3		$J_{AB} = 40.8$
				1.34, 1.30, 1.27 t	CH_3 phos		$J_{AC} = 42.7$
							$J_{BC} = 43.3$
11b	$[Os(CH_3N{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$			14.0 s,br	NH	A_2B_2	$\delta_A = 82.7$
				3.97 m	CH_2		$\delta_B = 76.5$
				3.71 s	CH_3N		$J_{AB} = 43.3$
				1.30, 1.23 t	CH_3		
12	$[Os(\eta^2\text{-}O_2CCH_3)\{P(OEt)_3\}_4]BPh_4$	1523 m	ν(CO)	4.04 m	CH_2	A_2B_2	$\delta_A = 100.4$
				1.78 s	CCH_3		$\delta_B = 78.0$
				1.29, 1.25 t	CH_3		$J_{AB} = 38.7$

[a] In KBr. [b] In CD_2Cl_2 at 25 °C. [c] Phenyl proton resonances are omitted. [d] Positive shift downfield from 85% H_3PO_4. [e] In $(CD_3)_2CO$ at 25 °C.

too, of a *trans* arrangement of the NH_2NH_2 and the CH_3NHNH_2 ligands in complexes containing the $PPh(OEt)_2$ as an ancillary ligand.

Treatment of the dihydride OsH_2P_4 first with methyl triflate, then with triflic acid, and finally with an excess of benzoylhydrazine gives the $[Os(\eta^2\text{-}C_6H_5CONHNH_2)\{P(OEt)_3\}_4]^{2+}$ (**6**) cation, which was separated as BPh_4 salt and characterized. As for the related hydrazine complexes, the infrared spectrum shows the bands due to the ν(NH) at 3271 and 3206 cm^{-1} and that due to the $\delta(NH_2)$ at 1601 cm^{-1} of the $NHNH_2$ group. At 1633 cm^{-1} is also present a medium-intensity band attributed to the coordinated carbonyl group of the benzoylhydrazine. The ^{1}H NMR spectrum confirms the proposed formulation showing, apart from the resonances of the $P(OEt)_3$ and the BPh_4^- protons,

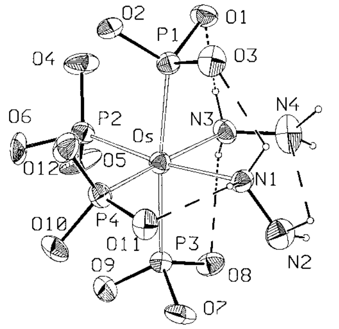
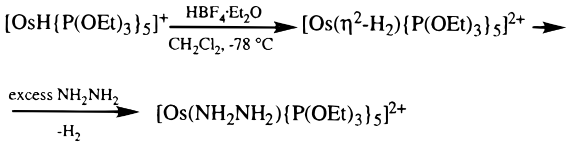


Figure 1. ORTEP view of the $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4]^{2+}$ cation of **4a**. Ethyl groups are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Intramolecular hydrogen bonds are evidenced as dashed lines.

Scheme 2



$$[OsH\{P(OEt)_3\}_5]^+ \xrightarrow[CH_2Cl_2,\ -78\ ^\circ C]{HBF_4\cdot Et_2O} [Os(\eta^2\text{-}H_2)\{P(OEt)_3\}_5]^{2+} \longrightarrow \xrightarrow[-H_2]{\text{excess } NH_2NH_2} [Os(NH_2NH_2)\{P(OEt)_3\}_5]^{2+}$$

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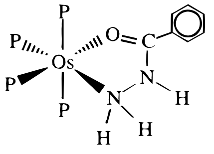
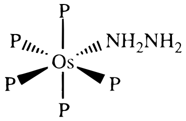
Table 4. Most Relevant Bond Distances (Å) and Angles (deg) with Esd's in Parentheses

	Distances		
Os−P1	2.300(6)	P3−O7	1.536(16)
Os−P2	2.232(6)	P3−O8	1.620(13)
Os−P3	2.316(7)	P3−O9	1.57(2)
Os−P4	2.260(6)	P4−O10	1.536(19)
P1−O1	1.615(16)	P4−O11	1.615(14)
P1−O2	1.544(13)	P4−O12	1.538(19)
P1−O3	1.573(17)	Os−N1	2.200(14)
P2−O4	1.516(19)	Os−N3	2.193(15)
P2−O5	1.507(19)	N1−N2	1.446(28)
P2−O6	1.607(18)	N3−N4	1.412(27)
	Angles		
N1−Os−N3	85.4(6)	Os−P1−O3	112.2(7)
P4−Os−N3	175.3(4)	Os−P1−O2	118.7(6)
P4−Os−N1	90.0(4)	Os−P1−O1	112.6(6)
P3−Os−N3	89.2(5)	Os−P2−O6	110.1(7)
P3−Os−N1	93.4(4)	Os−P2−O5	116.6(7)
P3−Os−P4	92.0(2)	Os−P2−O4	116.3(7)
P2−Os−N3	89.2(4)	Os−P3−O9	122.4(8)
P2−Os−N1	172.6(4)	Os−P3−O8	109.8(5)
P2−Os−P4	95.3(2)	Os−P3−O7	113.9(7)
P2−Os−P3	91.6(2)	Os−P4−O12	120.7(7)
P1−Os−N3	86.0(5)	Os−P4−O11	106.3(5)
P1−Os−N1	83.5(4)	Os−P4−O10	116.0(6)
P1−Os−P4	92.6(2)	Os−N1−N2	117.7(12)
P1−Os−P3	174.4(2)	Os−N3−N4	118.0(13)
P1−Os−P2	91.1(2)		

one broad signal at 6.12 ppm and one, partially masked by the phenyl protons, at 7.30 ppm attributed to the NH_2 and NH protons, respectively, of the $C_6H_5CONHNH_2$ ligand. Finally, the ^{31}P NMR spectrum appears as a A_2BC multiplet, in agreement with the presence of a chelate benzoylhydrazine ligand of the type schematized in geometry **V**.



V



VI

Monohydrazinepentakis(phosphite)$[Os(NH_2NH_2)\{P(OEt)_3\}_5]$-$(BPh_4)_2$ (**7**) complex was also prepared by reacting the hydride $[OsH\{P(OEt)_3\}_5]BPh_4$ first with an equivalent amount of $HBF_4\cdot Et_2O$ and then with an excess of hydrazine, as shown in Scheme 2. Protonation reaction of $[OsHP_5]^+$ with $HBF_4\cdot Et_2O$ results in the formation of an η^2-H_2 complex which is thermally unstable and cannot be isolated. The ^1H NMR spectra of the CD_2Cl_2 solution, however, confirm the presence of the dihydrogen complex showing a broad signal at −7.0 ppm with a T_1(min)[24] of 8 ms (210 K) at 200 MHz. Substitution of the labile η^2-H_2 ligand with hydrazine affords the $[Os(NH_2NH_2)\{P(OEt)_3\}_5]^{2+}$ derivative which was isolated as the BPh_4^- salt and characterized (Table 3). The ^1H NMR spectrum shows two NH_2 signals at 4.90 and 3.52 ppm in agreement with a η^1-coordination of the NH_2NH_2 ligand. Furthermore, the IR spectrum confirms the presence of the hydrazine group showing the characteristic ν(NH) bands at 3366−3270 cm^{-1}. Finally, the $^{31}P\{^1H\}$ NMR spectrum appears as an AB_4 multiplet in agreement with the presence of a type-**VI** geometry for the complex.

X-ray Crystal Structure of $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4]$-$(BPh_4)_2$ (4a). The asymmetric unit contains one $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4]^{2+}$ cation, displayed in Figure 1, two BPh_4^- anions, and one ethanol molecule. Relevant parameters regarding the cation geometry are listed in Table 4. The metal coordination is octahedral and involves four phosphorus atoms and two nitrogens, the latter in *cis* each other. The two Os−P bonds situated in *trans* to the hydrazine ligands (Os−P2 = 2.232(6) Å, Os−P4 = 2.260(6) Å) are slightly shorter than those involving P1 and P3 (Os−P1 = 2.300(6) Å, Os−P3 = 2.316(7) Å), which are in *trans* to each other, due to different electronic influence of the two kinds of ligands. The angles between *cis* phosphorus atoms fall in the range 91.1−95.3°, while the angles between phosphorus and nitrogens are smaller, ranging from 83.5 to 93.4°, due to the steric hindrance of the $P(OEt)_3$ groups and to intramolecular hydrogen bonds, as discussed later on. The average Os−N bond length is 2.196 Å, slightly longer than the one found in $[OsBr(NH_2NH_2)(CO)_2(PPh_3)_2]CF_3SO_3$,[3b] where the nitrogen atom is placed at 2.181 Å from the metal and *trans* to a carbonyl group. This is the only other osmium−hydrazine complex whose crystal structure has been determined so far. In both compounds hydrazine approaches the metal at an angle very close to 120°, while the remaining angles on N1 and N3 are close to tetrahedral values, reflecting the sp^3 hybridization of the nitrogen atoms bonded to the metal. Hydrazines form a network of intramolecular hydrogen bonds: N2···N4 = 3.00(3) Å, N2−H···N4 = 105(8)°, N1···O3 = 2.79(2), N1−H···O3 = 104(3)°, N1···O11 = 2.80(2) Å, N1−H···O11 = 144(6)°, N3···O1 = 2.87(2), N3−H···O1 = 129(9)°, N3···O8 = 2.91(2), N3−H···O8 = 101(9)°. As a result, the approximate directions of the lone pairs belonging to N2 (lp2) and N4 (lp4) are differently oriented with respect to the Os−N bond, with Os−N1−N2−lp2 = −60° and Os−N3−N4−lp4 = 20°.

Nitrogens are not involved in any intermolecular contact shorter than 3.8 Å. The ethanol molecule found in the crystal does not participate in any close contact with either cations or anions; this justifies its high thermal mobility and suggests that the crystal decomposition observed during data collection is due to solvent loss.

Amidrazone complexes. The results obtained on the synthesis of mono- and bis(hydrazine) complexes of osmium(II) **1**−**7** prompted us to extend these studies to other osmium

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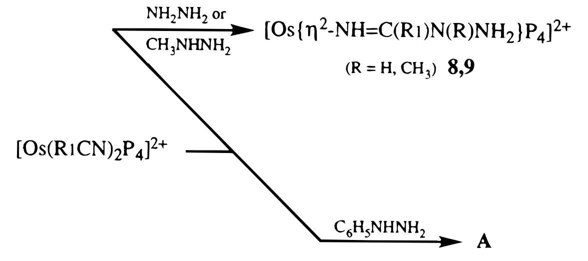
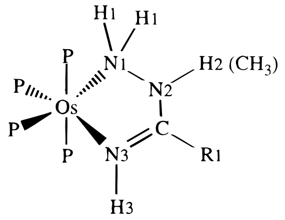
(24) Albertin, G.; Antoniutti, S.; Bordignon, E. Manuscript in preparation.

Scheme 3



R1 = CH_3, 4-$CH_3C_6H_4$; P = $P(OEt)_3$, $PPh(OEt)_2$; A = mixture of unidentified products.

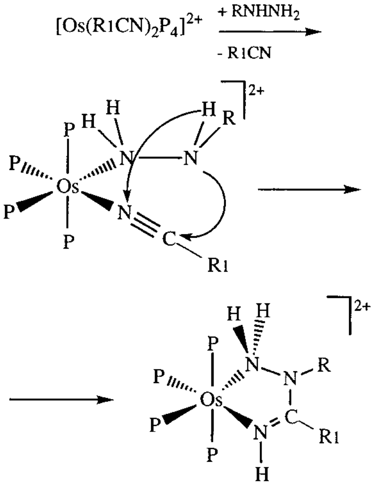
derivatives with the aim to verify whether new hydrazine derivatives may be prepared. We therefore prepared the new bis(nitrile) derivatives $[Os(R1CN)_2P_4](BPh_4)_2$ and studied their reaction with hydrazines $RNHNH_2$ observing that the same reaction depends on the nature of the substituent R on the hydrazines, as shown in Scheme 3. While with arylhydrazines such as $C_6H_5NHNH_2$ the reaction proceeds in reflux conditions to give a mixture of unidentified products, with hydrazine NH_2-NH_2 or methylhydrazine CH_3NHNH_2, instead, the reaction afforded a white solid which was characterized as an amidrazone[25] complex of the type $[Os\{\eta^2\text{-}NH{=}C(R1)N(R)NH_2\}P_4]$-$(BPh_4)_2$ (**8**, **9**) whose geometry is schematized in **VII**. However, only with the $P(OEt)_3$ ligand the amidrazone complexes were prepared in pure form, while with the related $PPh(OEt)_2$ compounds only intractable oils or mixtures of difficult separation were always obtained. The compounds **8** and **9** are white solids stable in the air and in solution of polar organic solvents where they behave as 2:1 electrolytes.[22] The elemental analyses and the IR and NMR spectra (Table 3) support the proposed formulation. In particular, the infrared shows the ν(NH) and the $\delta(NH_2)$ bands of the amidrazone ligand as weak- or medium-intensity absorptions at 3399−3230 cm^{-1} and at 1647−1625 cm^{-1}, respectively. The ^1H NMR spectra show, apart from the signals of the phosphites and of the BPh_4^-, two or three NH signals which were assigned, by homodecoupling experiments and accurate integration, to the H1, H2, and H3 protons (Table 3) of the chelate amidrazone ligand of the type of geometry **VII**. The $^{31}P\{^1H\}$ NMR spectra confirm such a geometry showing for all the compounds an AB_2C or ABC_2 multiplet which can be easily simulated with the parameters reported in Table 3.



VII

The formation of an amidrazone complex from the reaction of a coordinated nitrile with an hydrazine or methylhydrazine molecule is not surprising taking into account the well-known reaction[25] of nucleophilic attack of hydrazine on activated nitriles giving, as primary product, an amidrazone molecule. Furthermore, nucleophilic attack upon coordinated nitrile by alcohols, amines, and carbanions to give iminoethers, amidines, and imines is well established,[26−28] and therefore, a similar reaction is expected to take place also with hydrazine as a nucleophilic reagent.[29] Finally, related amidrazone complexes $[Fe\{\eta^2\text{-}NH{=}C(R1)NHNH_2\}P_4](BPh_4)_2$ were previously obtained by us[9] from hydrazine−nitrile $[Fe(NH_2NH_2)(R1CN)P_4]^{2+}$ cations, probably through a nucleophilic attack of an end of coordinated NH_2-NH_2 to the cyanide carbon atom of the coordinated nitrile, followed by a H-shift, giving a five-membered metallacycle. On these bases, the formation of an amidrazone complex by reacting a bis(nitrile) complex of osmium with hydrazine or methylhydrazine is plausible, although doubt remains on the probable reaction path. Treatment of $[Os(R1CN)_2P_4]^{2+}$ with $RNHNH_2$ (R = H, CH_3) can result in the substitution of only one R1CN ligand affording the $[Os(RNHNH_2)(R1CN)P_4]^{2+}$ intermediate. By nucleophilic attack of one end of the coordinated $RNHNH_2$ on the nitrile carbon atom of the coordinate nitrile followed by a H-shift, the amidrazone complexes may be obtained (Scheme 4). Since excess of hydrazine is used, base-catalyzed proton transfer can also be a reasonable mechanism for the intramolecular H-shift.

Scheme 4



R = H, CH_3; R1 = 4-$CH_3C_6H_4$, CH_3; P = $P(OEt)_3$, $PPh(OEt)_2$.

However, the hydrazine can also react directly (without being bonded to the osmium) with the coordinated R1CN group of $[Os(R1CN)_2P_4]^{2+}$ giving the η^1-amidrazone ligand which, by substitution of the other R1CN, can then give the final chelate

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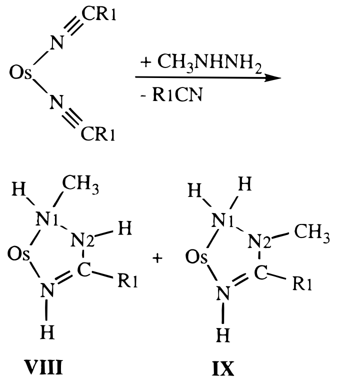
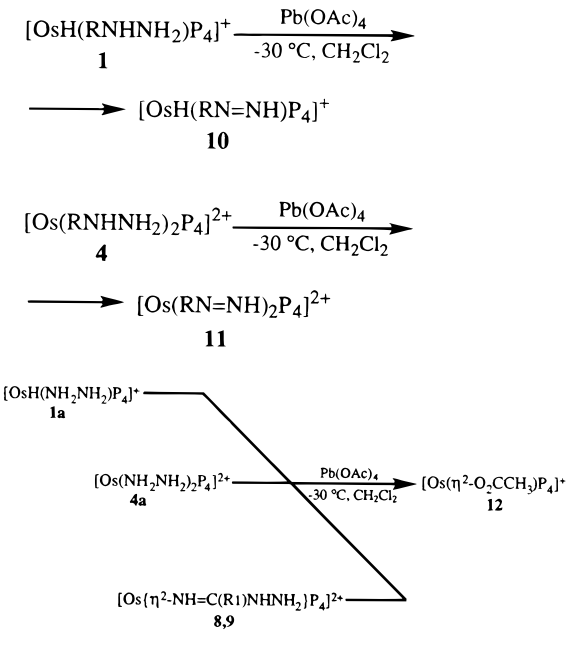
Scheme 5



Scheme 6



P = $P(OEt)_3$; R = CH_3 (**b**), C_6H_5 (**c**); R1 = CH_3 (**8**), 4-$CH_3C_6H_4$ (**9**).

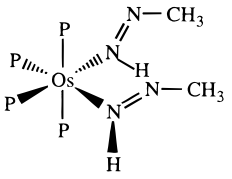
complex. In this case the reaction with methylhydrazine, which possesses two possible sites for an attack, might give the two compounds **VIII** and **IX** (Scheme 5). Furthermore, if the reaction on coordinated nitrile parallels that of free R1CN, the N1-substituted amidrazone **VIII** would be the predominant product. The exclusive formation of the compound **IX** (geometry **VII**) in our case seems, therefore, to suggest a reaction path that involves the substitution of one R1CN followed by the nucleophilic attack as shown in Scheme 4. Although a nitrile−hydrazine $[Os(RNHNH_2)(R1CN)P_4]^{2+}$ intermediate was not detected, such a mechanism is also supported by the results previously reported on the reaction of the related bis(nitrile)-iron(II) complexes[9] with hydrazine.

Oxidation Reactions. Hydrazine complexes of osmium(II) **1**−**5** react with $Pb(OAc)_4$ at −30 °C in CH_2Cl_2 to give, in some cases, the corresponding diazene derivatives and in other the acetate complex $[Os(\eta^2\text{-}O_2CCH_3)P_4]BPh_4$, as shown in Scheme 6. Studies on these reactions showed, first of all, that only the Os complexes containing the $P(OEt)_3$ phosphite ligand react with $Pb(OAc)_4$ to give the diazene or the acetate complexes. The $PPh(OEt)_2$ or PPh_2OEt derivatives, instead, do not react with $Pb(OAc)_4$ at low temperature (−30 °C) and the use of different conditions [large excess of $Pb(OAc)_4$ or higher temperature] lead only to decomposition products.

Both the mono $[OsH(RNHNH_2)P_4]^+$ and the bis $[Os(RNHNH_2)_2P_4]^{2+}$ derivatives of osmium(II) containing substituted hydrazine can be easily oxidized by $Pb(OAc)_4$ to give the corresponding substituted diazene complexes **10** and **11**, which were isolated and characterized. Confirmation of the presence of the diazene ligand in these complexes is given by the high-frequency signal of the NH groups at 12−15 ppm observed in the ^1H NMR spectra. However, the formulation of the phenyldiazene complexes **10c** and **11c** is also confirmed by a comparison of their spectroscopic properties with those of the same derivatives $[OsH(C_6H_5N{=}NH)P_4]BPh_4$ and $[Os(C_6H_5N{=}NH)_2P_4](BPh_4)_2$ previously prepared by us from the reaction of hydride species OsH_2P_4 with the phenyldiazonium cation.[8f]

Interesting, in this context, is the reaction of the methylhydrazine derivative with $Pb(OAc)_4$ which allows the synthesis of a rare example[30] of methyldiazene complex which, of course, cannot be obtained from the reaction of a methyldiazonium cation. Oxidation of $[Os(CH_3NHNH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$ afforded, in fact, $[Os(CH_3N{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ (**11b**), which was isolated as a yellow-orange solid and characterized. Also the hydride $[OsH(CH_3NHNH_2)P_4]BPh_4$ can be oxidized by $Pb(OAc)_4$ to give an orange solid whose ^1H NMR spectrum shows a NH signal at 14.4 ppm suggesting the presence of a diazene ligand. The thermal unstability of the complex, however, prevented its complete characterization. Oxidation of hydrazine complexes giving stable diazene derivatives is reported in a few cases[3b,c,30,31] and often involves dinuclear complexes with a diazene bridging unit.

The bis(methyldiazene) complex $[Os(CH_3N{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ (**11b**) is stable both as a solid and in solutions of polar organic solvents where it behaves as a 2:1 electrolyte.[22] Good analytical data were obtained for the compound whose ^1H NMR spectrum shows the characteristic, slightly broad diazene signal at 14.0 ppm (Table 3). In the proton spectrum also the signal of the methyl substituent of the $CH_3N{=}NH$ ligand is present as a sharp singlet at 3.71 ppm together with the $P(OEt)_3$ and BPh_4 signals. Furthermore, the ^{31}P spectrum appears as a symmetric A_2B_2 multiplet suggesting that the two diazene ligands are in a mutually *cis* position as in a type-**X** geometry.



X

The results obtained on the reaction of substituted hydrazine with $Pb(OAc)_4$ prompted us to extend these studies to the related NH_2NH_2 complexes in an attempt to prepare the 1,2-diazene $OsNH{=}NH$ derivative. Unfortunately, the reaction of both the $[OsH(NH_2NH_2)P_4]^+$ (**1a**) and $[Os(NH_2NH_2)_2P_4]^{2+}$ (**4a**) cations with an excess of $Pb(OAc)_4$ proceeds to give a pale-yellow

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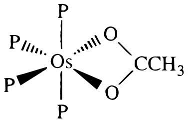
solution from which no diazene derivative was separated but only a white solid characterized as the acetate [Os(η^2-O_2CCH_3)-{P(OEt)$_3$}$_4$]BPh_4 (**12**) complex (Scheme 6). The use of an equimolar amount of $Pb(OAc)_4$ instead of an excess results in the formation only of a mixture of starting materials and of the acetate complex **12**. As the starting compounds **1a** and **4a** are unreactive toward the substitution of the NH_2NH_2 ligand by the acetate ion, it is probable that also in this case the reaction with $Pb(OAc)_4$ proceeds with the oxidation of the NH_2NH_2 group to give the corresponding diazene NH═NH ligand. This ligand, however, must be rather labile in cations of the type [OsH(NH═NH)P_4]$^+$, [Os(NH═NH)$_2P_4$]$^{2+}$, or [Os(NH═NH)(NH_2-NH_2)P_4]$^{2+}$ and can be easily substituted by the acetate ion affording the found chelate [Os(η^2-O_2CCH_3)P_4]BPh_4 derivative.

We also attempted to oxidize the NH_2NH_2 ligands in **1a** and **4a** with different reagents such as O_2, H_2O_2, or $(CH_3)_3COOH$, but we obtained either the starting complexes or decomposition products which did not show any diazene compound. Furthermore, it can be noted that the acetate complex **12** was also obtained by treating the amidrazone complexes **8** and **9** with $Pb(OAc)_4$. Finally, the formulation of the complex **12** as an acetate complex comes from the analytical and the spectroscopic data. In particular, the infrared spectrum shows the ν(CO) of the CH_3COO ligand as a medium-intensity band at 1523 cm^{-1}, while in the ^{1}H NMR spectrum the methyl protons of CH_3COO^- group appear as a sharp singlet at 1.78 ppm in CD_2Cl_2 at 25 °C. Furthermore, the $^{31}P\{^1H\}$ NMR spectrum shows an A_2B_2 multiplet, in agreement with the formulation proposed and schematized in **XI**.



XI

Conclusions. In this contribution we have reported a method for the facile synthesis of mono- and bis(hydrazine) derivatives of osmium of the type [OsH($RNHNH_2$)P_4]$^+$, [Os($RNHNH_2$)-P_5]$^{2+}$, and [Os($RNHNH_2$)$_2P_4$]$^{2+}$ stabilized by phosphite ligands. The first structural parameters for a bis(hydrazine) complex, [Os(NH_2NH_2){P(OEt)$_3$}$_4$](BPh_4)$_2$, are also reported. The reaction of nitrile complexes with hydrazine also allows amidrazone [Os{η^2-NH═C(R1)N(R)NH_2}{P(OEt)$_3$}$_4$](BPh_4)$_2$ derivatives to be prepared. Among the properties shown by the new osmium hydrazine complexes we can emphasize the easy oxidation of the substituted hydrazine $RNHNH_2$ ligand by lead tetraacetate to give the corresponding substituted diazene [OsH(RN═NH)-P_4]$^+$ and [Os(RN═NH)$_2P_4$]$^{2+}$ cations, including the first [Os-(CH_3N═NH)$_2P_4$](BPh_4)$_2$ bis(methyldiazene) derivative.

Acknowledgment. The financial support of MURST and the CNR, Rome, is gratefully acknowledged. We thank Daniela Baldan for technical assistance.

Supporting Information Available: X-ray crystallographic files, in CIF format, for compound **4a** are available on the Internet only. Access information is given on any current masthead page.

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