Preparation and Properties of New Dinitrogen Osmium(II) Complexes

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Introduction

A number of studies on the synthesis and the properties of dinitrogen complexes has been reported over the past 25 years[1] and these studies have been motivated by the fact that the coordination of the N_2 molecule to a transition metal seems to be the first stage in the nitrogen fixation process. Several auxiliary ligands have been employed to stabilize the N_2 coordination, and among these mono- and polydentate phosphine ligands have played an important role.[1] In contrast, phosphite ligands have received less attention and very scarce are the related dinitrogen complexes,[2] although some studies[3] showed the interesting ability of phosphites in stabilizing partially reduced dinitrogen ligands, such as diazene and diazenido groups.

As a part of our studies in this field,[3] we now report the synthesis and some properties of new osmium dinitrogen[4] complexes stabilized by phosphite ligands. The preparation of dihydrogen derivatives of osmium(II) with these ligands is also described along with the spectroscopic characterization of the new complexes.

Experimental Section

All synthetic work was carried out under an appropriate atmosphere (N_2, H_2, Ar) using standard Schlenk techniques or a Vacuum Atmosphere drybox. Once isolated, the complexes were found to be sufficiently air-stable and were stored under an appropriate atmosphere at −25 °C. All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. The phosphites PPh_2OR (R = OMe, OEt, O^iPr) and $PPh(OEt)_2$ were prepared by the method of Rabinowitz and Pellon.[5] Alkynes were Aldrich products, used without any further purification. *p*-Tolyl isocyanide was obtained by the method of Ziehn *et al.*[6] Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Digilab Bio-Rad FTS-40 spectrophotometer. NMR spectra (^1H, ^{13}C, ^{31}P) were obtained on a Bruker AC200 spectrometer at temperatures varying between −90 and +30 °C, unless otherwise noted. ^1H and ^{13}C 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. T_1's were determined by the inversion recovery method between +30 and −90 °C in CD_2Cl_2 with a standard 180°–τ–90° pulse sequence. Errors are ±10% in T_1 values. The conductivity of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25 °C was measured with a Radiometer CDM 83 instrument.

Synthesis of Complexes. The hydride specie $OsH_2[PPh(OEt)_2]_4$ (**1d**) was prepared following the method previously reported,[7] and the related OsH_2P_4 (**1a–1c**) by a modification of this method, as reported here.

$OsH_2(PPh_2OEt)_4$ (1b). An excess of PPh_2OEt (20 mmol, 4.6 mL) was added to a suspension of $(NH_4)_2OsCl_6$ (2 mmol, 0.88 g) in 30 mL of ethanol and the reaction mixture warmed to reflux. A solution of $NaBH_4$ (53 mmol, 2 g) in 20 mL of ethanol was added and the reflux maintained for about 4 h. The solvent was removed under reduced pressure, giving a brown solid from which the hydride was extracted first with two 20-mL portions of CH_2Cl_2 and then with three 20-mL portions of petroleum ether (40–70 °C). The extracts were mixed and the resulting solution evaporated to dryness giving an oil which was triturated with 10 mL of ethanol. A white solid slowly separated out which was crystallized from ethanol; yield ≥70%.

Anal. Calcd: C, 60.42; H, 5.61. Found: C, 60.30; H, 5.71. Mp: 168–170 °C dec. IR [ν(OsH), KBr]: 1985 (m), 1960 (m) cm^{-1}. ^1H NMR (C_6D_6), δ: 7.70–6.90 (m, 40 H, Ph), 3.19 (m), 3.05 (m) (8 H, CH_2), 1.15 (t), 0.91 (t) (12 H, CH_3), −9.88 to −10.09 (m, 2 H, hydride). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: spin system A_2B_2, δ_A = 101.9, δ_B = 101.2, J_{AB} = 15.6 Hz.

$OsH_2(PPh_2OR)_4$ (R = Me, 1a; ^{i}Pr, 1c). A 100-mL, three-necked round bottomed flask was charged with 0.88 g (2 mmol) of $(NH_4)_2OsCl_6$, 2 g (53 mmol) of $NaBH_4$, 30 mL of THF, and 20 mmol of the appropriate phosphite PPh_2OR. The resulting mixture was refluxed for about 7 h, and then 20 mL of ethanol containing 0.8 g (21 mmol) of $NaBH_4$ was added. The reflux of the reaction mixture was continued for 4 h, and then the solvent was removed under reduced pressure. From the brown solid obtained, the hydride was extracted first with two 20-mL portions of CH_2Cl_2 and then with a 20-mL portion of petroleum ether (40–70 °C). The resulting solutions were mixed, the solvent evaporated and the oil obtained triturated with 15 mL of ethanol. A white solid slowly separated out which was filtered and crystallized from ethanol: yield ≥60% for **1a**, ≥20% for **1c**.

Anal. Calcd for **1a**: C, 59.08; H, 5.15. Found: C, 58.93; H, 5.21. Mp: 142–145 °C dec. IR [ν(OsH), KBr]: 1998 (m), 1980 (m) cm^{-1}. ^1H NMR (C_6D_6), δ: 7.76–7.00 (m, 40 H, Ph), 3.02 (t), 2.77 (d) (12 H, CH_3), −9.77 to −10.25 (m, 2 H, hydride). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: spin system A_2B_2, δ_A = 108.5, δ_B = 105.5, J_{AB} = 14.7 Hz.

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Anal. Calcd for **1c**: C, 61.63; H, 6.03. Found: C, 61.78; H, 6.10. Mp: 178–180 °C dec. IR [ν(OsH), KBr]: 2014 (m), 1987 (m) cm^{-1}. ^{1}H NMR ($CD_3C_6D_5$), δ: 7.56–6.83 (m, 40 H, Ph), 4.08 (m), 3.85 (m) (4 H, CH), 0.84 (d), 0.80 (d) (24 H, CH_3), −10.20 (m, 2 H, hydride). ^{31}P{^{1}H} NMR ($CD_3C_6D_5$), δ: spin system A_2B_2, δ_A = 99.3, δ_B = 97.9, J_{AB} = 15.0 Hz.

[OsH(N_2)P_4]CF_3SO_3 (2) [P = PPh_2OMe, a; PPh_2OEt, b; PPh($OEt)_2$, d]. To a solution of the appropriate hydride OsH_2P_4 (0.5 mmol) in 20 mL of diethyl ether cooled to −80 °C was added under nitrogen an equivalent amount of CF_3SO_3Me (0.5 mmol, 55 μL) and the reaction mixture brought to room temperature. A white solid immediately began to separate out which, after 2 h, was filtered and dried under vacuum; yield ≥80%.

Anal. Calcd for **2a**: C, 51.62; H, 4.33; N, 2.27. Found: C,51.47; H, 4.24; N, 2.02. Mp: 57–60 °C dec. Λ_M = 78.2 Ω^{-1} mol^{-1} cm^2.

Anal. Calcd. for **2b**: C, 53.10; H, 4.77; N, 2.17. Found: C, 52.85; H, 4.51; N, 2.01. Mp: 82–85 °C dec. Λ_M = 83.6 Ω^{-1} mol^{-1} cm^2.

Anal. Calcd for **2d**: C, 42.41; H, 5.30; N, 2.41. Found: C, 42.57; H, 5.19; N, 2.26. Mp: 108–110 °C dec. Λ_M = 80.5 Ω^{-1} mol^{-1} cm^2.

[OsH(η^2-H_2)($PPh_2OR)_4$]BF_4 (3) (R = Me, a; Et, b; ^{i}Pr, c). These complexes can be prepared from the dinitrogen compounds **2** by substitution of the N_2 ligand with H_2 as follows: an appropriate amount of [OsH(N_2)P_4]CF_3SO_3 (0.1 mmol) was placed in a 25-mL three-necked round bottomed flask under hydrogen (1 atm) and 10 mL of dichloromethane added. The resulting solution was stirred at room temperature for 2 h and then the solvent removed under reduced pressure. The oil obtained was triturated with ethanol containing an excess of $NaBF_4$ (0.2 mmol, 22 mg) giving a white solid which was filtered and dried under vacuum; yield ≥80%.

However, the dihydrogen complexes **3** can also be easily prepared with good yield by reacting the dihydride OsH_2P_4 with HBF_4·Et_2O. A typical preparation involves the addition of a slight excess of HBF_4·Et_2O (0.25 mmol, 36 μL of 54% solution in Et_2O) to a solution of the appropriate hydride OsH_2P_4 (0.2 mmol) in diethyl ether (10 mL) cooled to −80 °C and kept under a hydrogen atmosphere (1 atm). The reaction mixture was brought to room temperature and stirred for about 1 h. A white solid separated out which was filtered and dried; yield ≥80%.

Anal. Calcd for **3a**: C, 54.55; H, 4.84. Found: C, 54.39; H, 4.89. Mp: 89–93 °C dec. Λ_M = 95.7 Ω^{-1} mol^{-1} cm^2.

Anal. Calcd for **3b**: C, 56.00; H, 5.29. Found: C, 55.76; H, 5.36. Mp: 76–78 °C dec. Λ_M = 93.8 Ω^{-1} mol^{-1} cm^2.

Anal. Calcd for **3c**: C, 57.32; H, 5.69. Found: C, 57.15; H, 5.58. Mp: 143–145 °C dec. Λ_M = 88.9 Ω^{-1} mol^{-1} cm^2.

[OsH(η^2-H_2){PPh($OEt)_2$}$_4$]BPh_4 (3d). This compound was prepared as previously described.[8]

[OsH(η^2-HD)($PPh_2OR)_4$]BPh_4 (3′) (R = Me, a; Et, b). An excess of CF_3COOD (0.3 mmol, 23 μL) was added to a solution of the appropriate hydride OsH_2P_4 (0.15 mmol) in 10 mL of diethyl ether cooled to −80 °C and kept under argon. The reaction mixture was brought at room temperature, stirred for 2 h, and then evaporated to dryness under reduced pressure. The resulting oil obtained was triturated with 5 mL of C_2H_5OD containing an excess of $NaBPh_4$ (0.3 mmol, 103 mg), giving an white solid which was filtered, washed with C_2H_5OD (3 mL), and dried; yield ≥70%.

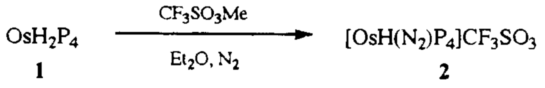
[OsH(CO)($PPh_2OMe)_4$]BF_4 (4a) and [OsH(CO)($PPh_2OEt)_4$]BPh_4 (4b). A solution of the appropriate dinitrogen complexes **2** (0.1 mmol) in 5 mL of CH_2Cl_2 was stirred at room temperature under a CO atmosphere (1 atm) for 2 h. The removal of the solvent gave a brown oil which was treated with 3 mL of ethanol. From the resulting solution the complexes were precipitated by adding or a solution of $NaBF_4$ (0.4 mmol, 44 mg) in 2 mL of ethanol **(4a)** or a solution of $NaBPh_4$ (0.2 mmol, 68 mg) in 3 mL of ethanol **(4b)**. After crystallization from ethanol the yields were about 60% for **4a** and 80% for **4b**.

Anal. Calcd for **4a**: C, 54.37; H, 4.56. Found: C, 54.30; H, 4.61. Mp: 233–235 °C dec. Λ_M = 92.4 Ω^{-1} mol^{-1} cm^2.

Anal. Calcd for **4b**: C, 66.66; H, 5.59. Found: C, 66.73; H, 5.43. Λ_M = 49.7 Ω^{-1} mol^{-1} cm^2.

[OsH(4-$CH_3C_6H_4NC$)($PPh_2OR)_4$]BPh_4 (5) (R = Me, a; Et, b). A slight excess of *p*-tolyl isocyanide (0.15 mmol, 18 μL) was added to a solution of the appropriate [OsH(N_2)P_4]CF_3SO_3 complex (**2**) (0.1 mmol) in 5 mL of CH_2Cl_2 and the reaction mixture stirred at room temperature for 2 h. The solvent was removed under reduced pressure giving an oil which was triturated with 2 mL of ethanol containing an excess of $NaBPh_4$ (0.2 mmol, 68 mg). A yellow solid slowly separated out which was filtered and crystallized from CH_2Cl_2 (2 mL) and ethanol (5 mL); yield ≥80%.

Scheme 1



$$OsH_2P_4 \ (\mathbf{1}) \xrightarrow[Et_2O,\ N_2]{CF_3SO_3Me} [OsH(N_2)P_4]CF_3SO_3 \ (\mathbf{2})$$

P = PPh_2OMe, **a**; PPh_2OEt, **b**; PPh($OEt)_2$, **d**

Anal. Calcd for **5a**: C, 67.70; H, 5.40; N, 0.94. Found: C, 67.43; H, 5.31; N, 1.02. Mp: 192–194 °C dec. Λ_M [$(CH_3)_2CO$] = 99.8 Ω^{-1} mol^{-1} cm^2.

Anal. Calcd for **5b**: C, 68.25; H, 5.73; N, 0.90. Found: C, 68.01; H, 5.64; N, 0.98. Mp: 108–110 °C dec. Λ_M = 51.3 Ω^{-1} mol^{-1} cm^2.

[Os{CH═C(H)CO_2Me}($PPh_2OR)_4$]CF_3SO_3 (6) (R = Me, a; Et, b) and [Os{CH═C(H)CO_2Et}($PPh_2OEt)_4$]CF_3SO_3 (7b). An excess of the appropriate alkyne HC≡CCO_2Me or HC≡CCO_2Et (0.4 mmol) was added to a cooled (−80 °C) solution of the dinitrogen complex [OsH(N_2)P_4]CF_3SO_3 (**2**) (0.1 mmol) in 5 mL of dichloromethane. The reaction mixture was brought to room temperature and stirred for 1 h. Removal of the solvent under reduced pressure gave a brown oil which was triturated with 5 mL of diethyl ether. After 1 h of stirring a pale-yellow solid separated out which was filtered and crystallized from CH_2Cl_2 (2 mL) and diethyl ether (7 mL); yield ≥70%.

Anal. Calcd for **6a**: C, 53.10; H, 4.46. Found C, 52.94; H, 4.50. Mp: 160–162 °C dec. Λ_M = 78.6 Ω^{-1} mol^{-1} cm^2.

Anal. Calcd for **6b**: C, 54.46; H, 4.87. Found: C, 54.28; H, 4.76. Mp: 174–176 ° C dec. Λ_M = 79.1 Ω^{-1} mol^{-1} cm^2.

Anal. Calcd for **7b**: C, 54.78; H, 4.97. Found: C, 54.86; H, 4.91. Mp: 163–165 ° C dec. Λ_M = 74.2 Ω^{-1} mol^{-1} cm^2.

Results and Discussion

The reaction of the dihydride complexes[9] OsH_2P_4 (**1**) with methyl triflate under N_2 proceeds with evolution of CH_4 (by ^{1}H NMR) and formation of dinitrogen derivatives [OsH(N_2)P_4]CF_3SO_3 (**2**) which were separated as white solids and characterized (Scheme 1).

Under an N_2 atmosphere the compounds are rather stable, both as solid and in solution of polar organic solvents where they behave as 1:1 electrolytes.[10] Instead, the loss of N_2 easily takes place in the air, also in the solid state, giving decomposition products.

Some spectroscopic properties of the dinitrogen complexes are reported in Table 1. The IR spectra reveals the ν(N≡N) as a strong band at 2168–2197 cm^{-1}, values which result to be among the highest observed for the stretching of the N_2 ligand in mononuclear osmium complexes.[4] The ^{1}H NMR spectra show, apart from the signals of phosphite, a sharp quintet between −11.85 and −13.23 ppm with J_{PH} of 20 Hz attributed to the hydride resonance. Furthermore, in the temperature range between +30 and −90 ° C the ^{31}P{^{1}H} spectra are sharp singlets (101.5–108.8 ppm) in agreement with a mutually *trans* position of hydride and dinitrogen ligands as in type **I** geometry.

Compounds **2** show that dinitrogen complexes can also be prepared with phosphite as supporting ligand using osmium(II)

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(8) Amendola, P.; Antoniutti, S.; Albertin, G.; Bordignon, E. *Inorg. Chem.* **1990**, *29*, 318.

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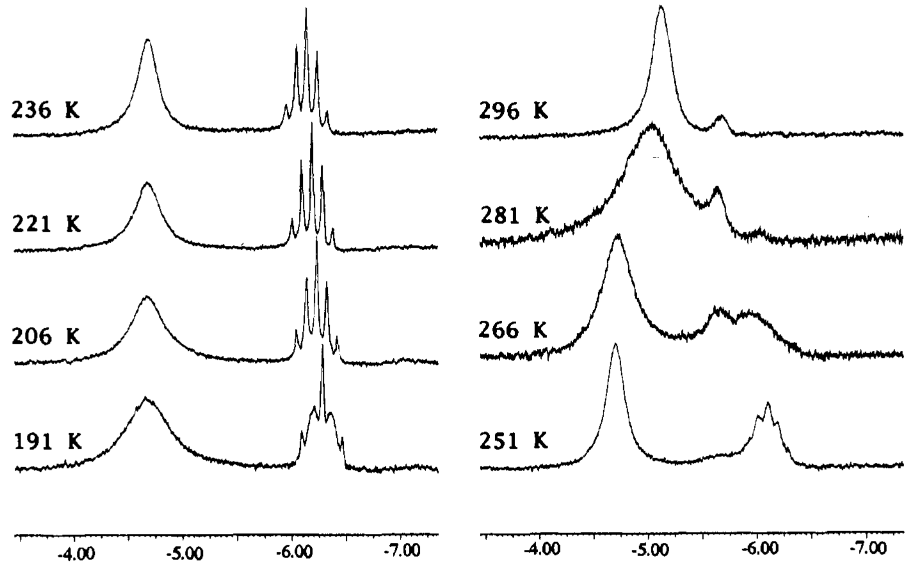
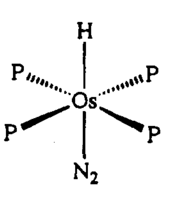


Figure 1. Variable temperature 200 MHz ^{1}H NMR spectra in the hydridic region of compound $[OsH(\eta^2\text{-}H_2)(PPh_2OEt)_4]BF_4$ (**3b**) in CD_2Cl_2.



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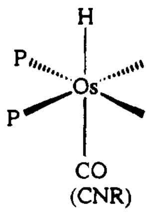

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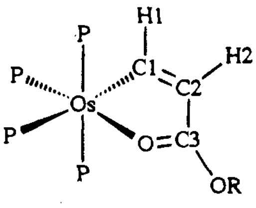


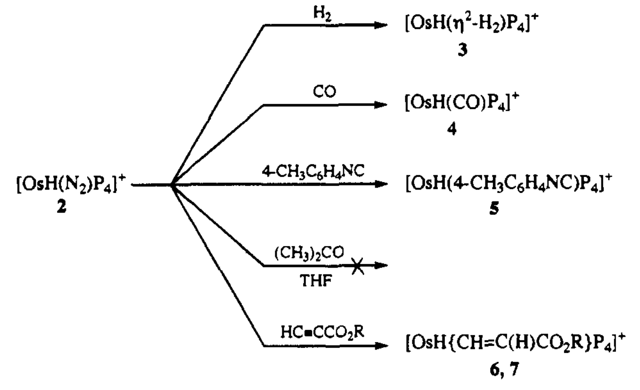
III

as the central metal. Furthermore, the good π-acceptor properties of these ligands[11] prompted us to attempt to prepare related Os(0) complexes by reduction or by deprotonation with bases of **2**, but the unstability to the loss of N_2 prevented any result.

The N_2 ligand is labile in **2** and can be substituted by several ligands including H_2, CO, and CNR affording new hydride derivatives. The substitution does not include solvents such as acetone and tetrahydrofuran, while the reaction with terminal alkynes of the type $HC{\equiv}CCO_2R$ allows new chelate vinyl complexes to be prepared. The results are summarized in Scheme 2.

The molecular hydrogen complexes[12] **3** can also be prepared by reacting the dihydrides **1** with $HBF_4{\cdot}Et_2O$ in diethyl ether under hydrogen, resulting in very stable solids, also in solutions of polar organic solvents. Selected spectroscopic properties for these complexes which are white solid, diamagnetic and 1:1 electrolytes[10] are reported in Tables 1 and 2.

Scheme 2



R = Me, Et

The IR spectra of **3** reveals the presence of a terminal stretching mode ν(M–H) at 2043–2026 cm^{-1} but no ν(H–H) or ν(Os–H_2) absorption.[12a,13] Most significant for the characterization of **3a**–**3c** as hydrido-dihydrogen complexes are the variable-temperature ^{1}H NMR spectra reported for the hydridic region in Table 2. The 200 MHz spectrum of the $[OsH(\eta^2\text{-}H_2)(PPh_2OEt)_4]^+$ cation is also shown in Figure 1. The broad signal that appears at room temperature at −4.92 to −5.28 ppm is split into two signals as the temperature is lowered, one of which is resolved into a sharp quintet already at 250 K. The well-resolved quintet at −5.48 to −6.44 ppm with $^2J_{PH}$ of 20 Hz is attributed to the hydride resonance whereas the broad signal at −4.6 to −5.2 ppm to the η^2-H_2 ligand. Variable-temperature T_1 measurements carried out at 200 MHz in CD_2Cl_2 on these signals give a T_1(min) of 11 (**3a**), 10 (**3b**), and 16 ms (**3c**) for the broad signal at −4.6 to −5.2 ppm (Table 2) in agreement with the presence of a η^2-H_2 ligand.[14] For the quintet at −5.48 to −6.44 ppm, instead, a T_1(min) range of 240–80 ms was found,[15] which is within the interval of values for an H^- resonance,[14] and well agree with those we found for the

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Table 1. Selected Infrared and NMR Data for the Osmium(II) Complexes

compound		IR[a]		^{1}H NMR[b,c]		^{31}P{^{1}H} NMR[b,d]		^{13}C NMR[b,c]	
no.	formula	ν, cm^{-1}	assign	δ	assign	spin syst	δ, J (Hz)	δ	assign
2a	$[\mathrm{OsH(N_2)(PPh_2OMe)_4]CF_3SO_3}$	2197 s	$\nu(\mathrm{N_2})$	2.53 m −11.85 qi (J_{PH} = 20 Hz)	$\mathrm{OC}H_3$ $\mathrm{Os}H$	$\mathrm{A_4}$	105.3 s		
2b	$[\mathrm{OsH(N_2)(PPh_2OEt)_4]CF_3SO_3}$	2168 s	$\nu(\mathrm{N_2})$	3.04 m 0.32 t −11.98 qi (J_{PH} = 20 Hz)	$\mathrm{OC}H_2\mathrm{CH_3}$ $\mathrm{OCH_2C}H_3$ $\mathrm{Os}H$	$\mathrm{A_4}$	101.5 s		
2d	$[\mathrm{OsH(N_2)\{PPh(OEt)_2\}_4]CF_3SO_3}$	2175 s	$\nu(\mathrm{N_2})$	3.80 m[e] 1.12 t −13.23 qi (J_{PH} = 20 Hz)	$\mathrm{OC}H_2\mathrm{CH_3}$ $\mathrm{OCH_2C}H_3$ $\mathrm{Os}H$	$\mathrm{A_4}$[e]	108.5 s		
3a	$[\mathrm{OsH(\eta^2\text{-}H_2)(PPh_2OMe)_4]BF_4}$	2026 vw	$\nu(\mathrm{OsH})$	2.61 m −5.18 br	$\mathrm{OC}H_3$ $\mathrm{OsH(H_2)}$	$\mathrm{A_4}$	109.1 s		
3b	$[\mathrm{OsH(\eta^2\text{-}H_2)(PPh_2OEt)_4]BF_4}$	2030 vw	$\nu(\mathrm{OsH})$	2.96 m 0.21 t −4.92 br	$\mathrm{OC}H_2\mathrm{CH_3}$ $\mathrm{OCH_2C}H_3$ $\mathrm{OsH(H_2)}$	$\mathrm{A_4}$ $\mathrm{A_2B_2}$[f]	108.3 s δ_{A} = 110.6 δ_{B} = 107.7 J_{AB} = 27.2		
3c	$[\mathrm{OsH(\eta^2\text{-}H_2)(PPh_2O^iPr)_4]BF_4}$	2043 vw	$\nu(\mathrm{OsH})$	3.61 m 0.18 d −5.28 br	$\mathrm{OC}H\mathrm{(CH_3)_2}$ $\mathrm{OCH(C}H_3)_2$ $\mathrm{OsH(H_2)}$	$\mathrm{A_4}$ $\mathrm{A_2B_2}$[f]	104.1 s δ_{A} = 116.5 δ_{B} = 104.7 J_{AB} = 27.1		
4a	$[\mathrm{OsH(CO)(PPh_2OMe)_4]BF_4}$	2008 s 1920 w	$\nu(\mathrm{CO})$ $\nu(\mathrm{OsH})$	2.60 m[g] −5.85 qi (J_{PH} = 20 Hz)	$\mathrm{OC}H_3$ $\mathrm{Os}H$	$\mathrm{A_4}$[g]	102.9 s		
4b	$[\mathrm{OsH(CO)(PPh_2OEt)_4]BPh_4}$	2005 s 1910 w	$\nu(\mathrm{CO})$ $\nu(\mathrm{OsH})$	3.02 m[g] 0.37 t −5.95 qi	$\mathrm{OC}H_2\mathrm{CH_3}$ $\mathrm{OCH_2C}H_3$ $\mathrm{Os}H$	$\mathrm{A_4}$[g]	101.3 s		
5a	$[\mathrm{OsH(4\text{-}CH_3C_6H_4NC)(PPh_2OMe)_4]BPh_4}$	2090 s	$\nu(\mathrm{NC})$	2.37 s[g] 2.52 m, br −6.95 qi (J_{PH} = 20 Hz)	$4\text{-}\mathrm{C}H_3\mathrm{C_6H_4}$ $\mathrm{OC}H_3$ $\mathrm{Os}H$	$\mathrm{A_4}$[g]	105.2 s		
5b	$[\mathrm{OsH(4\text{-}CH_3C_6H_4NC)(PPh_2OEt)_4]BPh_4}$	2089 s	$\nu(\mathrm{NC})$	3.02 m[g] 2.52 s 0.34 t −7.15 qi	$\mathrm{OC}H_2\mathrm{CH_3}$ $4\text{-}\mathrm{C}H_3\mathrm{C_6H_4}$ $\mathrm{OCH_2C}H_3$ $\mathrm{Os}H$	$\mathrm{A_4}$[g]	102.8 s		
6a	$[\mathrm{Os\{CH{=}C(H)CO_2Me\}(PPh_2OMe)_4]CF_3SO_3}$	1564 s	$\nu(\mathrm{CO})$	9.85, 6.37 m 2.83 s 3.08 t, 3.09 d, 2.98 d	$\mathrm{C}H$ $\mathrm{CO_2C}H_3$ $\mathrm{OC}H_3$	$\mathrm{AB_2C}$	δ_{A} = 98.0 δ_{B} = 95.9 δ_{C} = 83.7 J_{AB} = 25.4 J_{AC} = 14.8 J_{AB} = 24.9	208.4 dm[h] 186.3 m 60−50 m 15.4 q	C_1 $C\mathrm{O}$ $\mathrm{O}C\mathrm{H_3}$ $\mathrm{CO_2}C\mathrm{H_3}$
6b	$[\mathrm{Os\{CH{=}C(H)CO_2Me\}(PPh_2OEt)_4]CF_3SO_3}$	1559 s	$\nu(\mathrm{CO})$	9.89, 6.15 m 3.45, 2.98 m 3.19 s 1.42−1.25 m	$\mathrm{C}H$ $\mathrm{OC}H_2\mathrm{CH_3}$ $\mathrm{CO_2C}H_3$ $\mathrm{OCH_2C}H_3$	$\mathrm{AB_2C}$	δ_{A} = 92.0 δ_{B} = 87.5 δ_{C} = 78.9 J_{AB} = 24.7 J_{AC} = 20.6 J_{BC} = 24.2	212.8 dm[h] 186.1 n 69−61 m 16.4 m 15.4 q	C_1 $C\mathrm{O}$ $\mathrm{O}C\mathrm{H_2CH_3}$ $\mathrm{OCH_2}C\mathrm{H_3}$ $\mathrm{CO_2}C\mathrm{H_3}$
7b	$[\mathrm{Os\{CH{=}C(H)CO_2Et\}(PPh_2OEt)_4]CF_3SO_3}$	1558 s	$\nu(\mathrm{CO})$	9,82, 6.11 m 3.48, 2.98 m 1.41−1.25 m 0.91 t	$\mathrm{C}H$ $\mathrm{OC}H_2\mathrm{CH_3}$ $\mathrm{OCH_2C}H_3$ $\mathrm{CO_2CH_2C}H_3$	$\mathrm{AB_2C}$	δ_{A} = 92.1 δ_{B} = 87.7 δ_{C} = 78.9 J_{AB} = 24.7 J_{AC} = 20.4 J_{BC} = 24.2		

[a] In KBr pellets. [b] At room temperature in CD_2Cl_2. [c] Phenyl resonances are omitted. [d] Positive shift downfield from 85% H_3PO_4. [e] In $(CD_3)_2CO$. [f] At −90 °C. [g] In $CDCl_3$. [h] $^{1}J_{CH}$ = 150 Hz.

hydride resonances in the precursor compounds **1b** and **2b**, so confirming the formulation proposed.

In order to further support these assignments, we prepared the isotopomers $[\mathrm{OsH(\eta^2\text{-}HD)(PPh_2OR)_4}]^+$ (R = Me, **3a′**; Et, **3b′**) and found by ^{1}H NMR spectra $^{1}J_{\mathrm{HD}}$ values of 21 Hz for **3a′** and 20 Hz for **3b′**. As expected, the T_1(min) value of the η^2-HD isotopomer **3b′**, 31 ms, is increased with respect to the that for η^2-H_2 complex **3b**. These results seem to suggest for our complexes **3a**–**3c** the presence of a true η^2-dihydrogen ligand, but with an elongated H−H bond, as indicated by the rather low value of the J_{HD} of 20−21 Hz. From the T_1(min) a value of H−H distances of 0.90 and 0.89 Å (fast spinning) or 1.13 and 1.12 Å (slow spinning) can also be calculated[16] for **3a** and **3b**, respectively, with the 1.13−1.12 Å value as the more likely one on the base of the J_{HD} values.

The related $\mathrm{PPh_2O^iPr}$ complex **3c**, however, shows slighter differences and deserves some comments. A slightly higher T_1 value of 16 ms is found for the η^2-H_2 resonance, which corresponds to a H−H distance of 1.21 Å (slow spinning). With this phosphite, moreover, the dinitrogen complex is too unstable

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(15) In the case of compounds **3c** and **3d** as well as **2b** the T_1 measurements for the hydride signal do not give a minimum T_1 value as temperature is lowered until 183 K. The values at this temperature, however, should be near the minimum and is in the range observed for hydride resonance.

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Table 2. ^{1}H NMR Data in the Hydride Region for the Complexes

compound							r_{H-H}, Å[a]		
no.	formula	T, K	δ(M−H)	T_1(min), ms	δ(M−H_2)	T_1(min), ms	slow rotation	fast rotation	J_{HD},Hz
3a	$[OsH(\eta^2\text{-}H_2)(PPh_2OMe)_4]BF_4$	199			−4.6 br	11	1.13	0.90	
		193	−6.44 qi[b]	240	−4.6 br				
3b	$[OsH(\eta^2\text{-}H_2)(PPh_2OEt)_4]BF_4$	215			−4.7 br	10	1.12	0.89	
		210	−6.21 qi[b]	186					
3c	$[OsH(\eta^2\text{-}H_2)(PPh_2O^iPr)_4]BF_4$	221			−5.2 br	16	1.21	0.96	
		193	−5.48 qi[b]	180[c]	−5.2 br				
3d	$[OsH(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$	209			−7.0 br	32	1.35	1.07	
		193	−6.60 br	88[c]	−7.0 br				
3′a	$[OsH(\eta^2\text{-}HD)(PPh_2OMe)_4]BF_4$	193	−6.40 br		−4.5 br				21[d]
3′b	$[OsH(\eta^2\text{-}HD)(PPh_2OEt)_4]BF_4$	253			−4.7 br	31			20[d]
		193	−6.2 m	220	−4.6 br				
2b	$[OsH(N_2)(PPh_2OEt)_4]CF_3SO_3$	217	11.65 qi	116[c]					
1b	$[OsH_2(PPh_2OEt)_4$	220	−10.5 m	153					

[a] For calculations see ref 16. [b] J_{PH} = 20 Hz. [c] The minimum T_1 values have not been observed. [d] At 223 K.

and cannot be isolated. Thus the substitution of the Me or Et group with an isopropyl in our phosphite changes the properties of H_2 and N_2 complexes, confirming the important influence that the steric and electronic properties of the ancillary ligand can have on these type of compounds.[12] A further confirmation comes from a comparison of the properties of the η^2-H_2 complexes **3a**−**3c** with those of the corresponding complex containing the $PPh(OEt)_2$ ligand **3d**, previously prepared by us[8] (Table 2). Although the J_{HD} values can not be determined for $[OsH(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+$ (**3d**), its T_1(min) value of 32 ms at 200 MHz is far higher than the others, in agreement with a more trihydridic character of the $PPh(OEt)_2$ derivative **3d** as compared with the related **3a**−**3c**. The chemical reactivity confirms such a hypothesis, showing the substitution of the η^2-H_2 ligand by CO (1 atm) and 4-$CH_3C_6H_4NC$ to be easy in **3a** and **3b** (20 ° C, 3 h) while reflux conditions[8] must be used with **3d**.

A number of osmium(II) dihydrogen complexes[4a,14b,16,17] have been reported in the last years and some significant variation in the properties of the H_2 ligand by varying the ancillary phosphine ligands has already been observed in these complexes. However, the greater hydridic character of the $[OsH(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+$ derivative (**3d**) as compared with the **3a**−**3c** homologous is rather surprising in the light of recent theoretical studies,[18] which indicate that the stability of non-classical complexes increases with an increase of the π-acceptor properties of the coligands. In fact, being the $PPh(OEt)_2$ phosphite more π-acceptor than the PPh_2OR ligands,[11] it should favour the Os(II) dihydrogen−hydride form rather than an Os(IV) trihydride tautomer.

It is worth noting that our N_2 and H_2 d^6 complexes confirm the criterion[19] that stable η^2-H_2 complexes can be obtained when the corresponding N_2 complexes have $\nu(N_2)$ in the range 2060−2180 cm^{-1}. On the basis of $\nu(N{\equiv}N)$ of our $[OsH(N_2)P_4]^+$ cations (**2**) this range now widens to 2060−2197 cm^{-1} values.

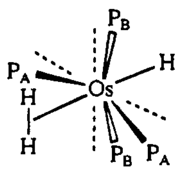

Figure 2. Distorted *trans* octahedral geometry.

In the temperature range between −90 and +30 °C the $^{31}P\{^1H\}$ NMR spectra of **3a** is a sharp singlet suggesting a mutually *trans* position of the hydride and the η^2-H_2 ligand. The related complexes **3b** and **3c** also show a sharp singlet in the ^{31}P spectra but only until −70 °C. At lower temperatures the signal broadens and at −90 °C appears as an A_2B_2 multiplet simulable with the parameter reported in Table 1. These results may be explained on the basis of a distorted *trans* octahedral geometry for **3b** and **3c** of the type shown in Figure 2 and previously proposed[8] for the related **3d** derivative. An A_2B_2 ^{31}P spectrum is in fact expected for such a structure in which two phosphorus atoms (P_A) are close to H^- and the other two (P_B) close to η^2-H_2 ligands.

Substitution reactions with CO or 4-$CH_3C_6H_4NC$ of the N_2 ligand in **2** (see Scheme 2) give the new hydride cations $[OsH(CO)P_4]^+$ (**4**) and $[OsH(4\text{-}CH_3C_6H_4NC)P_4]^+$ (**5**), respectively, which can be isolated and characterized. Also the η^2-H_2 ligand[20] in **3** can be substituted by CO or 4-$CH_3C_6H_4NC$ giving the hydrides **4** and **5**, but in this case the reaction rate is rather low, with a reaction time of about 3 h. The IR spectra of the complexes show the ν(OsH) at 1910−1920 cm^{-1} and the ν(CO) at 2005−2008 cm^{-1} for the carbonyls **4**, while for the isocyanides **5** reveal only the ν(CN) absorption at 2089−2090 cm^{-1}. In the ^{1}H NMR spectra of **4** and **5** the hydride signal appears as a well-resolved quintet between −5.85 and −7.15 ppm with J_{PH} of 20 Hz whereas in the temperature range −90 − +30 °C the $^{31}P\{^1H\}$ spectra appear as a sharp singlet suggesting a *trans* geometry (**II**) for the complexes.

The presence of both hydride and a labile ligand (N_2 and/or H_2) on an osmium(II) complex prompts us to study its reactivity toward alkyne to continue our studies on these substrates.[21]

While the η^2-H_2 complexes are unreactive also using a large excess of acetylenes and reflux conditions, the related N_2 derivatives $[OsH(N_2)P_4]^+$ (**2**) quickly reacted with the activated

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(20) Apart the substitution reaction, the η^2-H_2 complexes **3** can be easily deprotonated with triethylamine at room temperature to give the dihydride OsH_2P_4.

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alkynes HC≡CCO$_2$R (R = Me, Et) to give the new alkenyl[22] [Os{CH=C(H)CO$_2$R}P$_4$]$^+$ (**6, 7**) derivatives which were isolated as CF$_3$SO$_3$ salts and characterized. The compounds are white solids, stable in air and their formulation comes from analytical and spectroscopic data reported in Table 1. The infrared spectra reveal the presence of a strong band at 1558−1564 cm^{-1} attributed to ν(CO) of coordinate carbonyl group. In the temperature range between −90 and +30 °C the ^{31}P{^{1}H} NMR spectra of **6** and **7** are AB$_2$C multiplets whose simulation give the J and δ parameters reported in Table 1. Furthermore, the ^{1}H NMR spectra show, apart from the signal of the phosphites and of the Me or Et group of the −CH=C(H)CO$_2$R ligand, two multiplets at 9.89−9.82 ppm and 6.37−6.11 ppm. These multiplets are due to two protons coupled between them and with the phosphorus atoms of the phosphite ligand as shown by decoupling experiments and can reasonably be attributed to the two vinyl protons H1 and H2 of the −CH1=C(H2)CO$_2$R ligand.

The proton-coupled and decoupled ^{13}C spectra of **6** and **7** are consistent with the presence of the chelate vinyl ligand in the complexes and suggest a five-membered chelate ring arrangement as in type-**III** geometry. In fact the ^{13}C spectra reveal the presence of σ-bonded vinyl carbon atom C1 as a CH resonance at 208.4 ppm for **6a** and at 212.8 ppm for **6b** with a $^1J_{CH}$ values of 150 Hz. The other vinyl carbon C2 is not observable probably because it is masked by the phenyl carbon signals, whereas the carbonyl carbon atom C3 appears as a multiplet owing to the phosphorus coupling at 186.1−186.3 ppm. Finally, the methyl resonance of the −CO$_2$Me substituent is also present as a sharp quartet at δ 15.4 ppm in the ^{13}C spectra together with the ethyl and methyl signals of the phosphite ligands.

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