

Preparation and Properties of New Dinitrogen Osmium(II) Complexes

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Received May 25, 1995

Introduction

A number of studies on the synthesis and the properties of dinitrogen complexes has been reported over the past 25 years¹ and these studies have been motivated by the fact that the coordination of the N₂ 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 N₂ 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 studies³ 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 dinitrogen⁴ 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 (N₂, H₂, 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 PPh₂OR (R = OMe, OEt, OⁱPr) 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, ¹³C, ³¹P) were obtained on a Bruker AC200 spectrometer at temperatures varying between –90 and +30 °C, unless otherwise noted. ¹H and ¹³C spectra are referred to internal tetramethylsilane, while ³¹P{¹H} chemical shifts are reported with respect to 85% H₃PO₄, with downfield shifts considered positive. T₁'s were determined by the inversion recovery method between +30 and –90 °C in CD₂Cl₂ with a standard 180°–τ–90° pulse sequence. Errors are ±10% in T₁ values. The conductivity of 10^{–3} M solutions of the complexes in CH₃NO₂ at 25 °C was measured with a Radiometer CDM 83 instrument.

Synthesis of Complexes. The hydride specie OsH₂[PPh(OEt)₂]₄ (**1d**) was prepared following the method previously reported,⁷ and the related OsH₂P₄ (**1a–1c**) by a modification of this method, as reported here.

OsH₂(PPh₂OEt)₄ (1b**).** An excess of PPh₂OEt (20 mmol, 4.6 mL) was added to a suspension of (NH₄)₂OsCl₆ (2 mmol, 0.88 g) in 30 mL of ethanol and the reaction mixture warmed to reflux. A solution of NaBH₄ (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 CH₂Cl₂ 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 (C₆D₆), δ: 7.70–6.90 (m, 40 H, Ph), 3.19 (m), 3.05 (m) (8 H, CH₂), 1.15 (t), 0.91 (t) (12 H, CH₃), –9.88 to –10.09 (m, 2 H, hydride). ³¹P{¹H} NMR (C₆D₆), δ: spin system A₂B₂, δ_A = 101.9, δ_B = 101.2, J_{AB} = 15.6 Hz.

OsH₂(PPh₂OR)₄ (R = Me, **1a; ⁱPr, **1c**).** A 100-mL, three-necked round bottomed flask was charged with 0.88 g (2 mmol) of (NH₄)₂OsCl₆, 2 g (53 mmol) of NaBH₄, 30 mL of THF, and 20 mmol of the appropriate phosphite PPh₂OR. The resulting mixture was refluxed for about 7 h, and then 20 mL of ethanol containing 0.8 g (21 mmol) of NaBH₄ 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 CH₂Cl₂ 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 (C₆D₆), δ: 7.76–7.00 (m, 40 H, Ph), 3.02 (t), 2.77 (d) (12 H, CH₃), –9.77 to –10.25 (m, 2 H, hydride). ³¹P{¹H} NMR (C₆D₆), δ: spin system A₂B₂, 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 [$\nu(\text{OsH})$, KBr]: 2014 (m), 1987 (m) cm^{-1} . ^1H NMR ($\text{CD}_3\text{C}_6\text{D}_5$), 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). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CD}_3\text{C}_6\text{D}_5$), δ : spin system A_2B_2 , $\delta_{\text{A}} = 99.3$, $\delta_{\text{B}} = 97.9$, $J_{\text{AB}} = 15.0$ Hz.

[OsH(N₂)P₄]CF₃SO₃ (2) [P = PPh₂OMe, **a; PPh₂OEt, **b**; PPh(OEt)₂, **d**].** To a solution of the appropriate hydride OsH₂P₄ (0.5 mmol) in 20 mL of diethyl ether cooled to –80 °C was added under nitrogen an equivalent amount of CF₃SO₃Me (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 $\geq 80\%$.

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. $\Lambda_{\text{M}} = 78.2 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$.

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. $\Lambda_{\text{M}} = 83.6 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$.

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. $\Lambda_{\text{M}} = 80.5 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$.

[OsH(η^2 -H₂)(PPh₂OR)₄]BF₄ (3) (R = Me, **a; Et, **b**; ⁱPr, **c**).** These complexes can be prepared from the dinitrogen compounds **2** by substitution of the N₂ ligand with H₂ as follows: an appropriate amount of [OsH(N₂)P₄]CF₃SO₃ (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 NaBF₄ (0.2 mmol, 22 mg) giving a white solid which was filtered and dried under vacuum; yield $\geq 80\%$.

However, the dihydrogen complexes **3** can also be easily prepared with good yield by reacting the dihydride OsH₂P₄ with HBF₄·Et₂O. A typical preparation involves the addition of a slight excess of HBF₄·Et₂O (0.25 mmol, 36 μL of 54% solution in Et₂O) to a solution of the appropriate hydride OsH₂P₄ (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 $\geq 80\%$.

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

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

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

[OsH(η^2 -H₂)(PPh(OEt)₂)₄]BPh₄ (3d). This compound was prepared as previously described.⁸

[OsH(η^2 -HD)(PPh₂OR)₄]BPh₄ (3') (R = Me, **a; Et, **b**).** An excess of CF₃COOD (0.3 mmol, 23 μL) was added to a solution of the appropriate hydride OsH₂P₄ (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 C₂H₅OD containing an excess of NaBPh₄ (0.3 mmol, 103 mg), giving a white solid which was filtered, washed with C₂H₅OD (3 mL), and dried; yield $\geq 70\%$.

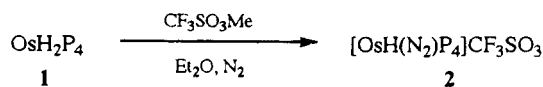
[OsH(CO)(PPh₂OMe)₄]BF₄ (4a) and [OsH(CO)(PPh₂OEt)₄]BPh₄ (4b). A solution of the appropriate dinitrogen complexes **2** (0.1 mmol) in 5 mL of CH₂Cl₂ was stirred at room temperature under a CO atmosphere (1 atm) for 2 h. The removal of the solvent gave a brown oil which was treated with 3 mL of ethanol. From the resulting solution the complexes were precipitated by adding a solution of NaBF₄ (0.4 mmol, 44 mg) in 2 mL of ethanol (**4a**) or a solution of NaBPh₄ (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. $\Lambda_{\text{M}} = 92.4 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$.

Anal. Calcd for **4b**: C, 66.66; H, 5.59. Found: C, 66.73; H, 5.43. $\Lambda_{\text{M}} = 49.7 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$.

[OsH(4-CH₃C₆H₄NC)(PPh₂OR)₄]BPh₄ (5) (R = Me, **a; Et, **b**).** A slight excess of *p*-tolyl isocyanide (0.15 mmol, 18 μL) was added to a

Scheme 1



P = PPh₂OMe, **a**; PPh₂OEt, **b**; PPh(OEt)₂, **d**

solution of the appropriate [OsH(N₂)P₄]CF₃SO₃ complex (**2**) (0.1 mmol) in 5 mL of CH₂Cl₂ 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 NaBPh₄ (0.2 mmol, 68 mg). A yellow solid slowly separated out which was filtered and crystallized from CH₂Cl₂ (2 mL) and ethanol (5 mL); yield $\geq 80\%$.

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. $\Lambda_{\text{M}} [(\text{CH}_3)_2\text{CO}] = 99.8 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$.

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. $\Lambda_{\text{M}} = 51.3 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$.

[Os{CH=C(H)CO₂Me}(PPh₂OR)₄]CF₃SO₃ (6) (R = Me, **a; Et, **b**) and [Os{CH=C(H)CO₂Et}(PPh₂OEt)₄]CF₃SO₃ (7b).** An excess of the appropriate alkyne HC≡CCO₂Me or HC≡CCO₂Et (0.4 mmol) was added to a cooled (–80 °C) solution of the dinitrogen complex [OsH(N₂)P₄]CF₃SO₃ (**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 CH₂Cl₂ (2 mL) and diethyl ether (7 mL); yield $\geq 70\%$.

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

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

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

Results and Discussion

The reaction of the dihydride complexes⁹ OsH₂P₄ (**1**) with methyl triflate under N₂ proceeds with evolution of CH₄ (by ^1H NMR) and formation of dinitrogen derivatives [OsH(N₂)P₄]CF₃SO₃ (**2**) which were separated as white solids and characterized (Scheme 1).

Under an N₂ 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 N₂ 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 $\nu(\text{N}\equiv\text{N})$ as a strong band at 2168–2197 cm^{-1} , values which result to be among the highest observed for the stretching of the N₂ ligand in mononuclear osmium complexes.⁴ The ^1H 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 $^{31}\text{P}\{^1\text{H}\}$ 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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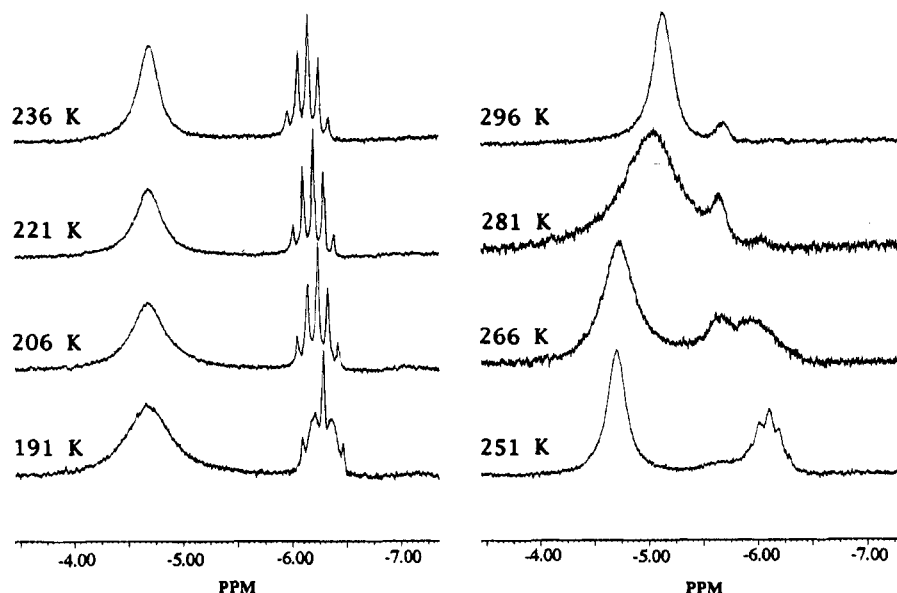
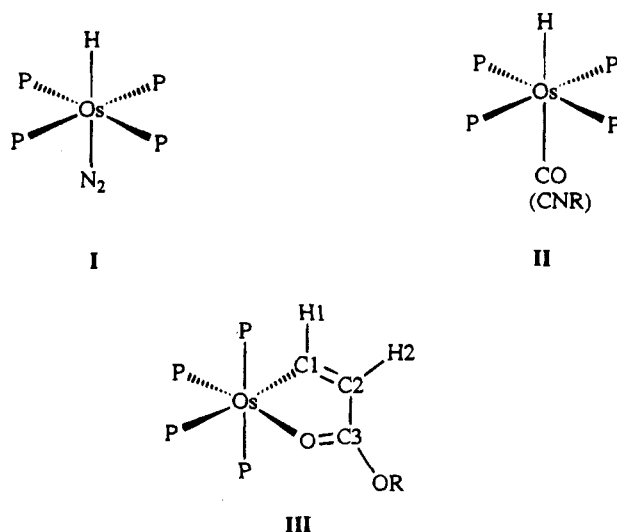
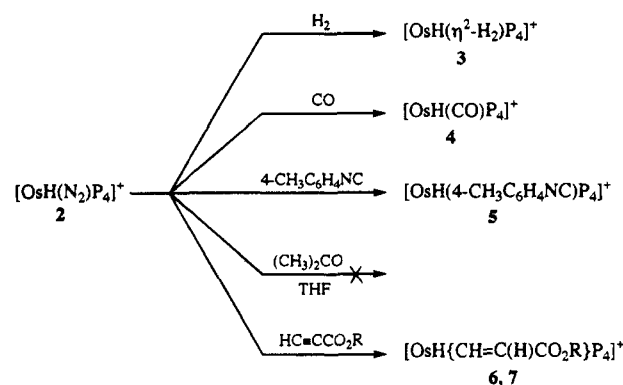


Figure 1. Variable temperature 200 MHz ^1H NMR spectra in the hydridic region of compound $[\text{OsH}(\eta^2\text{-H}_2)(\text{PPh}_2\text{OEt})_4]\text{BF}_4$ (**3b**) in CD_2Cl_2 .



Scheme 2



R = Me, Et

as the central metal. Furthermore, the good π -acceptor properties of these ligands¹¹ prompted us to attempt to prepare related Os(0) complexes by reduction or by deprotonation with bases of **2**, but the instability 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 $\text{HC}\equiv\text{CCO}_2\text{R}$ allows new chelate vinyl complexes to be prepared. The results are summarized in Scheme 2.

The molecular hydrogen complexes¹² **3** can also be prepared by reacting the dihydrides **1** with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ 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 electrolytes¹⁰ are reported in Tables 1 and 2.

The IR spectra of **3** reveals the presence of a terminal stretching mode $\nu(\text{M}-\text{H})$ at $2043\text{--}2026\text{ cm}^{-1}$ but no $\nu(\text{H}-\text{H})$ or $\nu(\text{Os}-\text{H}_2)$ absorption.^{12a,13} Most significant for the characterization of **3a**–**3c** as hydrido-dihydrogen complexes are the variable-temperature ^1H NMR spectra reported for the hydridic region in Table 2. The 200 MHz spectrum of the $[\text{OsH}(\eta^2\text{-H}_2)(\text{PPh}_2\text{OEt})_4]^+$ 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 $^2J_{\text{PH}}$ of 20 Hz is attributed to the hydride resonance whereas the broad signal at -4.6 to -5.2 ppm to the $\eta^2\text{-H}_2$ ligand. Variable-temperature T_1 measurements carried out at 200 MHz in $\text{CD}_2\text{-Cl}_2$ on these signals give a $T_1(\text{min})$ 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 $\eta^2\text{-H}_2$ ligand.¹⁴ For the quintet at -5.48 to -6.44 ppm, instead, a $T_1(\text{min})$ 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

no.	compound formula	IR ^a		¹ H NMR ^{b,c}		³¹ P{ ¹ H} NMR ^{b,d}		¹³ C NMR ^{b,e}	
		ν , cm ⁻¹	assign	δ	assign	spin syst	δ , J (Hz)	δ	assign
2a	[OsH(N ₂)(PPh ₂ OMe) ₄]CF ₃ SO ₃	2197 s	ν (N ₂)	2.53 m -11.85 qi (J_{PH} = 20 Hz)	OCH ₃ OsH	A ₄	105.3 s		
2b	[OsH(N ₂)(PPh ₂ OEt) ₄]CF ₃ SO ₃	2168 s	ν (N ₂)	3.04 m 0.32 t -11.98 qi (J_{PH} = 20 Hz)	OCH ₂ CH ₃ OCH ₂ CH ₃ OsH	A ₄	101.5 s		
2d	[OsH(N ₂){PPh(OEt) ₂ } ₂]CF ₃ SO ₃	2175 s	ν (N ₂)	3.80 m ^e 1.12 t -13.23 qi (J_{PH} = 20 Hz)	OCH ₂ CH ₃ OCH ₂ CH ₃ OsH	A ₄ ^e	108.5 s		
3a	[OsH(η^2 -H ₂)(PPh ₂ OMe) ₄]BF ₄	2026 vw	ν (OsH)	2.61 m -5.18 br	OCH ₃ OsH(H ₂)	A ₄	109.1 s		
3b	[OsH(η^2 -H ₂)(PPh ₂ OEt) ₄]BF ₄	2030 vw	ν (OsH)	2.96 m 0.21 t -4.92 br	OCH ₂ CH ₃ OCH ₂ CH ₃ OsH(H ₂)	A ₄ A ₂ B ₂ ^f	108.3 s δ_A = 110.6 δ_B = 107.7 J_{AB} = 27.2		
3c	[OsH(η^2 -H ₂)(PPh ₂ O ⁱ Pr) ₄]BF ₄	2043 vw	ν (OsH)	3.61 m 0.18 d -5.28 br	OCH(CH ₃) ₂ OCH(CH ₃) ₂ OsH(H ₂)	A ₄ A ₂ B ₂ ^f	104.1 s δ_A = 116.5 δ_B = 104.7 J_{AB} = 27.1		
4a	[OsH(CO)(PPh ₂ OMe) ₄]BF ₄	2008 s 1920 w	ν (CO) ν (OsH)	2.60 m ^g -5.85 qi (J_{PH} = 20 Hz)	OCH ₃ OsH	A ₄ ^g	102.9 s		
4b	[OsH(CO)(PPh ₂ OEt) ₄]BPh ₄	2005 s 1910 w	ν (CO) ν (OsH)	3.02 m ^g 0.37 t -5.95 qi	OCH ₂ CH ₃ OCH ₂ CH ₃ OsH	A ₄ ^g	101.3 s		
5a	[OsH(4-CH ₃ C ₆ H ₄ NC)(PPh ₂ OMe) ₄]BPh ₄	2090 s	ν (NC)	2.37 s ^g 2.52 m, br -6.95 qi (J_{PH} = 20 Hz)	4-CH ₃ C ₆ H ₄ OCH ₃ OsH	A ₄ ^g	105.2 s		
5b	[OsH(4-CH ₃ C ₆ H ₄ NC)(PPh ₂ OEt) ₄]BPh ₄	2089 s	ν (NC)	3.02 m ^g 2.52 s 0.34 t -7.15 qi	OCH ₂ CH ₃ 4-CH ₃ C ₆ H ₄ OCH ₂ CH ₃ OsH	A ₄ ^g	102.8 s		
6a	[Os{CH=C(H)CO ₂ Me}(PPh ₂ OMe) ₄]CF ₃ SO ₃	1564 s	ν (CO)	9.85, 6.37 m 2.83 s 3.08 t, 3.09 d, 2.98 d	CH CO ₂ CH ₃ OCH ₃	AB ₂ C	δ_A = 98.0 δ_B = 95.9 δ_C = 83.7 J_{AB} = 25.4 J_{AC} = 14.8 J_{BC} = 24.9	208.4 dm ^h 186.3 m 60-50 m 15.4 q	C ₁ CO OCH ₃ CO ₂ CH ₃
6b	[Os{CH=C(H)CO ₂ Me}(PPh ₂ OEt) ₄]CF ₃ SO ₃	1559 s	ν (CO)	9.89, 6.15 m 3.45, 2.98 m 3.19 s 1.42-1.25 m	CH OCH ₂ CH ₃ CO ₂ CH ₃ OCH ₂ CH ₃	AB ₂ C	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 CO OCH ₂ CH ₃ OCH ₂ CH ₃ CO ₂ CH ₃
7b	[Os{CH=C(H)CO ₂ Et}(PPh ₂ OEt) ₄]CF ₃ SO ₃	1558 s	ν (CO)	9.82, 6.11 m 3.48, 2.98 m 1.41-1.25 m 0.91 t	CH OCH ₂ CH ₃ OCH ₂ CH ₃ CO ₂ CH ₂ CH ₃	AB ₂ C	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 CD₂Cl₂. ^c Phenyl resonances are omitted. ^d Positive shift downfield from 85% H₃PO₄. ^e In (CD₃)₂CO. ^f At -90 °C. ^g In CDCl₃. ^h $^1J_{CH}$ = 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 [OsH(η^2 -HD)(PPh₂OR)₄]⁺ (R = Me, **3a'**; Et, **3b'**) and found by ¹H NMR spectra ¹ J_{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 -H₂ 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 calculated¹⁶ 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 PPh₂OⁱPr 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 -H₂ resonance, which corresponds to a H–H distance of 1.21 Å (slow spinning). With this phosphite, moreover, the dinitrogen complex is too unstable

(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. ^1H NMR Data in the Hydride Region for the Complexes

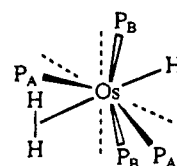
no.	compound formula	T, K	$\delta(\text{M}-\text{H})$	$T_1(\text{min}), \text{ms}$	$\delta(\text{M}-\text{H}_2)$	$T_1(\text{min}), \text{ms}$	$r_{\text{H}-\text{H}}, \text{\AA}^a$		J_{HD}, Hz
							slow rotation	fast rotation	
3a	$[\text{OsH}(\eta^2\text{-H}_2)(\text{PPh}_2\text{OMe})_4]\text{BF}_4$	199			−4.6 br	11	1.13	0.90	
3b	$[\text{OsH}(\eta^2\text{-H}_2)(\text{PPh}_2\text{OEt})_4]\text{BF}_4$	193	−6.44 qi ^b	240	−4.6 br				
		215			−4.7 br	10	1.12	0.89	
3c	$[\text{OsH}(\eta^2\text{-H}_2)(\text{PPh}_2\text{O}^i\text{Pr})_4]\text{BF}_4$	210	−6.21 qi ^b	186					
		221			−5.2 br	16	1.21	0.96	
3d	$[\text{OsH}(\eta^2\text{-H}_2)\{\text{PPh}(\text{OEt})_2\}_4]\text{BF}_4$	193	−5.48 qi ^b	180 ^c	−5.2 br				
		209			−7.0 br	32	1.35	1.07	
3'a	$[\text{OsH}(\eta^2\text{-HD})(\text{PPh}_2\text{OMe})_4]\text{BF}_4$	193	−6.60 br	88 ^c	−7.0 br				21 ^d
3'b	$[\text{OsH}(\eta^2\text{-HD})(\text{PPh}_2\text{OEt})_4]\text{BF}_4$	253	−6.40 br		−4.5 br				20 ^d
		193	−6.2 m	220	−4.7 br	31			
2b	$[\text{OsH}(\text{N}_2)(\text{PPh}_2\text{OEt})_4]\text{CF}_3\text{SO}_3$	217	11.65 qi	116 ^c	−4.6 br				
1b	$[\text{OsH}_2(\text{PPh}_2\text{OEt})_4]$	220	−10.5 m	153					

^a For calculations see ref 16. ^b $J_{\text{PH}} = 20 \text{ Hz}$. ^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 $\eta^2\text{-H}_2$ complexes **3a–3c** with those of the corresponding complex containing the $\text{PPh}(\text{OEt})_2$ ligand **3d**, previously prepared by us⁸ (Table 2). Although the J_{HD} values can not be determined for $[\text{OsH}(\eta^2\text{-H}_2)\{\text{PPh}(\text{OEt})_2\}_4]^+$ (**3d**), its $T_1(\text{min})$ value of 32 ms at 200 MHz is far higher than the others, in agreement with a more trihydridic character of the $\text{PPh}(\text{OEt})_2$ derivative **3d** as compared with the related **3a–3c**. The chemical reactivity confirms such a hypothesis, showing the substitution of the $\eta^2\text{-H}_2$ ligand by CO (1 atm) and 4- $\text{CH}_3\text{C}_6\text{H}_4\text{NC}$ to be easy in **3a** and **3b** (20 °C, 3 h) while reflux conditions⁸ 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 $[\text{OsH}(\eta^2\text{-H}_2)\{\text{PPh}(\text{OEt})_2\}_4]^+$ 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 $\text{PPh}(\text{OEt})_2$ 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 d⁶ complexes confirm the criterion¹⁹ that stable $\eta^2\text{-H}_2$ complexes can be obtained when the corresponding N_2 complexes have $\nu(\text{N}_2)$ in the range 2060–2180 cm^{-1} . On the basis of $\nu(\text{N}=\text{N})$ of our $[\text{OsH}(\text{N}_2)\text{P}_4]^+$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3a** is a sharp singlet suggesting a mutually *trans* position of the hydride and the $\eta^2\text{-H}_2$ 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 proposed⁸ 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 $\eta^2\text{-H}_2$ ligands.

Substitution reactions with CO or 4- $\text{CH}_3\text{C}_6\text{H}_4\text{NC}$ of the N_2 ligand in **2** (see Scheme 2) give the new hydride cations $[\text{OsH}(\text{CO})\text{P}_4]^+$ (**4**) and $[\text{OsH}(4\text{-CH}_3\text{C}_6\text{H}_4\text{NC})\text{P}_4]^+$ (**5**), respectively, which can be isolated and characterized. Also the $\eta^2\text{-H}_2$ ligand²⁰ in **3** can be substituted by CO or 4- $\text{CH}_3\text{C}_6\text{H}_4\text{NC}$ 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 $\nu(\text{OsH})$ at 1910–1920 cm^{-1} and the $\nu(\text{CO})$ at 2005–2008 cm^{-1} for the carbonyls **4**, while for the isocyanides **5** reveal only the $\nu(\text{CN})$ absorption at 2089–2090 cm^{-1} . In the ^1H 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 $^{31}\text{P}\{^1\text{H}\}$ 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 $\eta^2\text{-H}_2$ complexes are unreactive also using a large excess of acetylenes and reflux conditions, the related N_2 derivatives $[\text{OsH}(\text{N}_2)\text{P}_4]^+$ (**2**) quickly reacted with the activated

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- (20) Apart the substitution reaction, the $\eta^2\text{-H}_2$ complexes **3** can be easily deprotonated with triethylamine at room temperature to give the dihydride OsH_2P_4 .
- (21) (a) Albertin, G.; Amendola, P.; Antoniutti, S.; Ianelli, S.; Pelizzi, G.; Bordignon, E. *Organometallics* **1991**, *10*, 2876. (b) Albertin, G.; Antoniutti, S.; Del Ministro, E.; Bordignon, E. *J. Chem. Soc., Dalton Trans.* **1992**, 3203. (c) Albertin, G.; Antoniutti, S.; Bordignon, E.; Cazzaro, F.; Ianelli, S.; Pelizzi, G. *Organometallics* **1995**, *14*, 4114.

alkynes $\text{HC}\equiv\text{CCO}_2\text{R}$ ($\text{R} = \text{Me, Et}$) to give the new alkenyl²² $[\text{Os}\{\text{CH}=\text{C}(\text{H})\text{CO}_2\text{R}\}\text{P}_4]^+$ (**6**, **7**) derivatives which were isolated as CF_3SO_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 $1558\text{--}1564\text{ cm}^{-1}$ attributed to $\nu(\text{CO})$ of coordinate carbonyl group. In the temperature range between -90 and $+30\text{ }^\circ\text{C}$ the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **6** and **7** are AB_2C multiplets whose simulation give the J and δ parameters reported in Table 1. Furthermore, the ^1H NMR spectra show, apart from the signal of the phosphites and of the Me or Et group of the $-\text{CH}=\text{C}(\text{H})\text{CO}_2\text{R}$ ligand, two multiplets at $9.89\text{--}9.82\text{ ppm}$ and $6.37\text{--}6.11\text{ ppm}$. These multiplets are due to two protons coupled between them and with the phosphorus atoms of the phosphite ligand as shown

- (22) For vinyl osmium complexes see: Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, *12*, 663. Werner, H.; Weinand, R.; Knaup, W.; Peters, K.; von Schnering H. G. *Organometallics* **1991**, *10*, 3967. Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. Bruce, M. I.; Cifuentes, M. P.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1989**, *359*, 379. Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.

by decoupling experiments and can reasonably be attributed to the two vinyl protons H1 and H2 of the $-\text{CH}=\text{C}(\text{H}_2)\text{CO}_2\text{R}$ 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 $^1J_{\text{CH}}$ 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 $186.1\text{--}186.3\text{ ppm}$. Finally, the methyl resonance of the $-\text{CO}_2\text{Me}$ substituent is also present as a sharp quartet at $\delta\ 15.4\text{ ppm}$ in the ^{13}C spectra together with the ethyl and methyl signals of the phosphite ligands.

Acknowledgment. The financial support of Ministero dell'Università e della Ricerca Scientifica e Tecnologica is gratefully acknowledged.

IC950655E