

Azo Complexes of Osmium(II): Preparation and Reactivity of Organic Azide and Hydrazine Derivatives

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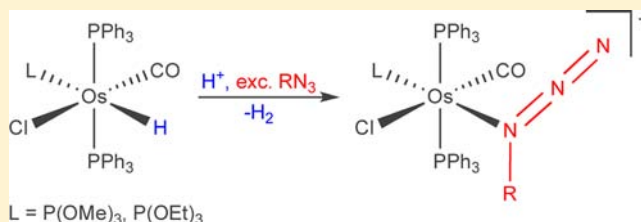
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Supporting Information

ABSTRACT: Mixed-ligand hydride complexes $\text{OsHCl}(\text{CO})(\text{PPh}_3)_2\text{L}$ (**2**) [$\text{L} = \text{P}(\text{OMe})_3, \text{P}(\text{OEt})_3$] were prepared by allowing $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ (**1**) to react with an excess of phosphite $\text{P}(\text{OR})_3$ in refluxing toluene. Dichloro compounds $\text{OsCl}_2(\text{CO})(\text{PPh}_3)_2\text{L}$ (**3**, **4**) were also prepared by reacting **1**, **2** with HCl . Treatment of hydrides $\text{OsHCl}(\text{CO})(\text{PPh}_3)_2\text{L}$ (**2**), first with triflic acid and then with an excess of RN_3 afforded organic azide complexes $[\text{OsCl}(\eta^1\text{-N}_3\text{R})(\text{CO})(\text{PPh}_3)_2\text{L}]\text{BPh}_4$ (**5–7**) [$\text{R} = 4\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2, \text{C}_6\text{H}_5\text{CH}_2, \text{C}_6\text{H}_5$; $\text{L} = \text{P}(\text{OEt})_3$].

Benzylazide complexes react in CH_2Cl_2 /ethanol solution, leading to the imine derivative $[\text{OsCl}(\text{CO})\{\eta^1\text{-NH}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{-4-CH}_3\}(\text{PPh}_3)_2\{\text{P}(\text{OEt})_3\}]\text{BPh}_4$ (**8b**). Hydrazine complexes $[\text{OsCl}(\text{CO})(\text{RNHNH}_2)(\text{PPh}_3)_2\text{L}]\text{BPh}_4$ (**9–11**) [$\text{R} = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5$; $\text{L} = \text{P}(\text{OMe})_3, \text{P}(\text{OEt})_3$] were prepared by allowing hydride species $\text{OsHCl}(\text{CO})(\text{PPh}_3)_2\text{L}$ (**2**) to react first with triflic acid and then with an excess of hydrazine. Aryldiazene derivatives $[\text{OsCl}(\text{CO})(\text{ArN}=\text{NH})(\text{PPh}_3)_2\text{L}]\text{BPh}_4$ (**12**, **13**) were also prepared following two different methods: (i) by oxidizing arylhydrazine $[\text{OsCl}(\text{C}_6\text{H}_5\text{NHNH}_2)(\text{CO})(\text{PPh}_3)_2\text{L}]\text{BPh}_4$ (**11**) with $\text{Pb}(\text{OAc})_4$ in CH_2Cl_2 at -30°C ; (ii) by allowing hydride species $\text{OsHCl}(\text{CO})(\text{PPh}_3)_2\text{L}$ (**2**) to react with aryldiazonium cations ArN_2^+ ($\text{Ar} = \text{C}_6\text{H}_5, 4\text{-CH}_3\text{C}_6\text{H}_4$) in CH_2Cl_2 . The complexes were characterized spectroscopically and by X-ray crystal structure determination of $\text{OsHCl}(\text{CO})(\text{PPh}_3)_2\{\text{P}(\text{OEt})_3\}$ (**2b**) and $[\text{OsCl}\{\eta^1\text{-NH}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{-4-CH}_3\}(\text{CO})(\text{PPh}_3)_2\{\text{P}(\text{OEt})_3\}]\text{BPh}_4$ (**8b**).

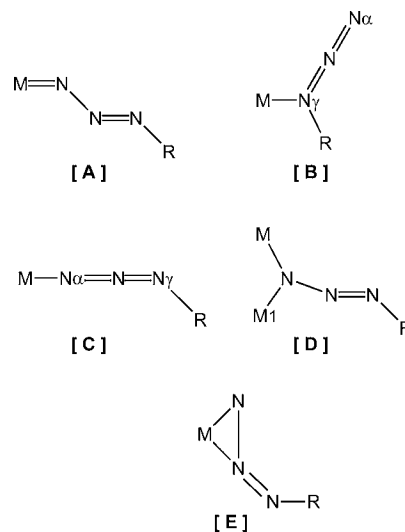


INTRODUCTION

The reaction of organic azides with transition metal complexes has attracted considerable interest in recent years, due to the variety of metal derivatives which can be prepared.^{1–9} Loss of N_2 is easy in organic azides and leads to the nitrene $\text{RN}:$ moiety, which can be incorporated either as a coordinate imido ligand or as the product of a coupling or insertion reaction between $\text{RN}:$ and another coordinate ligand.^{2–4} Imido $[\text{M}]=\text{NR}$ and tetraazabutadiene $[\text{M}](\eta^2\text{-RN}=\text{N}-\text{N}=\text{NR})$ complexes are the most common products of the reaction of RN_3 with metal complexes.^{2–4} However, in the first step of the interaction between RN_3 and a metal fragment, organic azide was believed to η^1 -coordinate to the metal center, giving an azido complex as intermediate. Although there is a significant interest in these intermediates, their isolation and characterization is difficult and stable metal complexes containing organic azide ligands are rare.^{5–8} These include $\text{V}(\text{V})$, $\text{Fe}(\text{I})$, $\text{Ta}(\text{V})$, and $\text{W}(\text{V})$ mononuclear complexes,⁵ containing the bent moiety NNN [A] (Chart 1), $\text{Cu}(\text{I})$, $\text{Ag}(\text{I})$, $\text{Pd}(\text{II})$, and $\text{Ir}(\text{III})$ derivatives,^{6,7} with “linear” organoazide ligands [B], [C], and a $\text{Ni}(\text{0})$ complex^{8a} with η^2 -coordination of the RN_3 ligand [E]. A mixed-metallic zirconium(IV)–iridium(III) complex containing a bridging PhNNN [D] group is also reported.^{8b}

We are interested in the chemistry of diazo and triazo complexes of transition metals and have reported the synthesis

Chart 1



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and reactivity of hydrazine, diazene, diazenido, and triazene derivatives of Mn¹⁰ and Fe¹¹ triads and, recently, the first benzylazide complexes of iridium⁷ stabilized by phosphites P(OR)₃ as supporting ligands. We thought of extending our studies on azo complexes with the additional aim of preparing organic azide complexes of the iron triad. As the use of metal fragments MHL₄⁺ and ML₄²⁺ containing phosphites P(OR)₃ and PPh(OR)₂ as ligands failed to stabilize organic azide complexes, we decided to try mixed-ligand complexes, to test whether coordination of RN₃ on metal fragments could take place. The results of a study on osmium, which allowed the preparation of the first organic azide complexes for this metal, are reported here.

EXPERIMENTAL SECTION

General Comments. All reactions were carried out in an inert atmosphere (argon) by means of standard Schlenk techniques or in an inert-atmosphere glovebox. Once isolated, the complexes were found to be relatively stable in air but were stored under nitrogen at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. OsO₄ was a Pressure Chemical Co. (USA) product, used as received. The phosphites P(OMe)₃ and P(OEt)₃ were Aldrich products, purified by distillation under nitrogen. Benzyl¹² and phenyl¹³ azides were prepared following methods previously reported. The labeled azide 4-CH₃C₆H₄CH₂¹⁵N₃ was prepared by following the same method,¹² by reacting Na[¹⁵NNN] (98% enriched, CIL) with 4-methylbenzylbromide 4-CH₃C₆H₄CH₂Br. Equimolar mixtures of 4-CH₃C₆H₄CH₂¹⁵NNN and 4-CH₃C₆H₄CH₂NN¹⁵N were obtained. Hydrazine (1 mol dm^{−3} solution in THF) and methyl and phenyl hydrazines were Aldrich products, used as received. Diazonium salts ArN₂⁺BF₄[−] were obtained in the usual way.¹⁴ Labeled diazonium tetrafluoroborate [C₆H₅N≡¹⁵N]BF₄ was prepared from Na¹⁵NO₂ (99% enriched, CIL) and aniline.

Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra (¹H, ³¹P, ¹⁵N) were obtained on an AVANCE 300 Bruker spectrometer at temperatures between −90 and +30 °C, unless otherwise noted. ¹H spectra are referred to internal tetramethylsilane; ³¹P{¹H} chemical shifts are reported with respect to 85% H₃PO₄, whereas ¹⁵N shifts to CH₃¹⁵NO₂; in both cases, downfield shifts are considered positive. COSY, HMQC, and HMBC NMR experiments were performed with standard programs. The iNMR software package¹⁵ was used to process NMR data. The conductivity of 10^{−3} mol dm^{−3} solutions of the complexes in CH₃NO₂ at 25 °C was measured on a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova (Italy).

Synthesis of Complexes. The complex OsCl₂(PPh₃)₃ was obtained following the method previously reported.¹⁶

OsHCl(CO)(PPh₃)₃ (1). In a 100-mL three-necked round-bottomed flask were placed 1 g of OsCl₂(PPh₃)₃ (0.95 mmol), 0.3 g (4.6 mmol) of zinc dust, and 30 mL of ethanol. The reaction mixture was refluxed for 4 h and then the volume was reduced to about 10 mL by evaporation of the solvent under reduced pressure. The orange solid which separated out was filtered and crystallized by dissolving it in toluene and, after filtration and concentration of the solution, by adding enough ethanol to precipitate the complex; yield ≥ 65%. Anal. calcd for C₅₃H₄₆ClO₄OsP₃ (1041.56): C, 63.42; H, 4.45; Cl, 3.40. Found: C, 63.18; H, 4.56; Cl, 3.23%. ¹H NMR (CD₂Cl₂, 25 °C) δ: 7.68–7.02 (m, 45 H, Ph), −6.95 ppm (dt, 1 H, OsH, J_{PH} = 87.0, J_{PH} = 25.0 Hz). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C) δ: A₂B spin syst, δ_A 8.43, δ_B −8.5, J_{AB} = 11.0 Hz. IR (KBr): ν_{OsH} 2090 (w); ν_{CO} 1910 (s) cm^{−1}.

OsHCl(CO)(PPh₃)₂L (2) [L = P(OMe)₃ (a), P(OEt)₃ (b)]. An excess of the appropriate phosphite P(OR)₃ (1.5 mmol) was added to a solution of OsHCl(CO)(PPh₃)₃ (1) (0.5 g, 0.48 mmol) in 15 mL of toluene, and the reaction mixture was refluxed for 45 min. The solvent

was removed under reduced pressure to give an oil, which was triturated with ethanol (3 mL). A white solid slowly separated out, which was filtered and crystallized from dichloromethane and ethanol; yield ≥ 85%.

Anal. Calcd for C₄₀H₄₀ClO₄OsP₃ (903.35) (2a). C, 53.18; H, 4.46; Cl, 3.92. Found: C, 53.35; H, 4.34; Cl, 4.13%. ¹H NMR (CD₂Cl₂, 25 °C) δ: 7.74, 7.36 (m, 30 H, Ph), 3.25 (d, 9 H, CH₃), −5.54 ppm (dt, 1 H, OsH, J_{PH} = 138.0, J_{PH} = 21.0 Hz). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C) δ: AB₂ spin syst, δ_A 100.9, δ_B 9.2, J_{AB} = 19.5 Hz. IR (KBr): ν_{CO} 1946 (s) cm^{−1}.

Anal. Calcd for C₄₃H₄₆ClO₄OsP₃ (945.43) (2b). C, 54.63; H, 4.90; Cl, 3.75. Found: C, 54.44; H, 5.02; Cl, 3.58%. ¹H NMR (CD₂Cl₂, 25 °C) δ: 7.76–7.34 (m, 30 H, Ph), 3.60 (qnt, 6 H, CH₂), 0.99 (t, 9 H, CH₃), −5.68 ppm (dt, 1 H, OsH, J_{PH} = 133.0, J_{PH} = 22.0 Hz). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C) δ: AB₂ spin syst, δ_A 100.7, δ_B 9.1, J_{AB} = 19.5 Hz. IR (KBr): ν_{CO} 1948 (s) cm^{−1}.

OsCl₂(CO)(PPh₃)₃ (3) and OsCl₂(CO)(PPh₃)₂L (4) [L = P(OMe)₃ (a), P(OEt)₃ (b)]. A slight excess of HCl (0.21 mmol, 0.105 mL of a 2 mol dm^{−3} solution in diethylether) was added to a solution of the appropriate carbonyl complex OsHCl(CO)(PPh₃)₃ or OsHCl(CO)(PPh₃)₂L (0.20 mmol) in dichloromethane, cooled to −196 °C. The solution was left to reach room temperature, stirred for 2 h, and then the solvent removed under reduced pressure. The oil obtained was triturated with ethanol (2 mL) until a green solid separated out, which was filtered and crystallized from toluene and ethanol; yield ≥ 80%.

Anal. Calcd for C₅₅H₄₅Cl₂O₅OsP₃ (1076.00) (3). C, 61.39; H, 4.22; Cl, 6.59. Found: C, 61.60; H, 4.09; Cl, 6.42%. ¹H NMR (CD₂Cl₂, 25 °C) δ: 7.78–7.05 ppm (m, 45 H, Ph). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C) δ: A₂B spin syst, δ_A −10.73, δ_B −17.33, J_{AB} = 12.1 Hz. IR (KBr): ν_{CO} 1954 (s); ν_{OsCl} 323, 294 (m) cm^{−1}.

Anal. Calcd for C₄₀H₃₉Cl₂O₄OsP₃ (937.79) (4a). C, 51.23; H, 4.19; Cl, 7.56. Found: C, 51.04; H, 4.31; Cl, 7.38%. ¹H NMR (CD₂Cl₂, 25 °C) δ: 7.94, 7.35 (m, 30 H, Ph), 3.25 ppm (d, 9 H, CH₃). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C) δ: AB₂ spin syst, δ_A 74.3, δ_B −8.9, J_{AB} = 23.1 Hz. IR (KBr): ν_{CO} 1969 (s); ν_{OsCl} 341, 305 (m) cm^{−1}.

Anal. Calcd for C₄₃H₄₅Cl₂O₄OsP₃ (979.87) (4b). C, 52.71; H, 4.63; Cl, 7.24. Found: C, 52.87; H, 4.72; Cl, 7.09%. ¹H NMR (CD₂Cl₂, 25 °C) δ: 7.91, 7.35 (m, 30 H, Ph), 3.55 (qnt, 6 H, CH₂), 0.99 ppm (t, 9 H, CH₃). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C) δ: AB₂ spin syst, δ_A 70.1, δ_B −6.58, J_{AB} = 23.1 Hz. IR (KBr): ν_{CO} 1982 (s) cm^{−1}.

[OsCl(η¹-N₃CH₂Ar)(CO)(PPh₃)₂][P(OEt)₃]BPh₄ (5b, 6b) [Ar = 4-CH₃C₆H₄ (5), C₆H₅ (6)] and [OsCl(η¹-N₃C₆H₅)(CO)(PPh₃)₂][P(OEt)₃]BPh₄ (7b). Triflic acid (0.12 mmol, 10.6 μL) was added to a solution of OsHCl(CO)(PPh₃)₂[P(OEt)₃] (2b) (0.12 mmol, 110 mg) in 5 mL of CH₂Cl₂ cooled to −196 °C. The reaction mixture was left to reach room temperature, stirred for 1 h, and then cooled again to −196 °C. An excess of the appropriate azide (0.4 mmol) was added to the resulting solution, which was brought to room temperature and stirred for 5 h. The solvent was removed under reduced pressure to give an oil, which was treated with ethanol (2 mL) containing an excess of NaBPh₄ (0.2 mmol, 68 mg). A pale-yellow solid slowly separated out, which was filtered and crystallized from dichloromethane and ethanol; yield ≥ 65%.

Anal. Calcd for C₇₅H₇₄BClN₃O₄OsP₃ (1410.82) (5b). C, 63.85; H, 5.29; N, 2.98; Cl, 2.51. Found: C, 63.45; H, 5.40; N, 3.09; Cl, 2.33%. Λ_M = 52.6 Ω^{−1} mol^{−1} cm². ¹H NMR (CD₂Cl₂, 25 °C) δ: 7.69–6.77 (m, 54 H, Ph), 4.23 (s, 2 H, CH₂N₃), 3.54 (qnt, 6 H, CH₂ phos), 2.37 (s, 3 H, CH₃ *p*-tolyl), 1.05 ppm (t, 9 H, CH₃ phos). ³¹P{¹H} NMR (CD₂Cl₂, −30 °C) δ: AB₂ spin syst, δ_A 65.9, δ_B −4.7, J_{AB} = 27.0 Hz. IR (KBr): ν_N 2146 (m); ν_{CO} 1952 (s) cm^{−1}.

Anal. Calcd for C₇₄H₇₂BClN₃O₄OsP₃ (1396.80) (6b). C, 63.63; H, 5.20; N, 3.01; Cl, 2.54. Found: C, 63.52; H, 5.09; N, 2.96; Cl, 2.38%. Λ_M = 55.1 Ω^{−1} mol^{−1} cm². ¹H NMR (CD₂Cl₂, 25 °C) δ: 7.95–6.87 (m, 55 H, Ph), 4.34 (s, 2 H, CH₂N₃), 3.55 (qnt, 6 H, CH₂ phos), 1.05 ppm (t, 9 H, CH₃ phos). ³¹P{¹H} NMR (CD₂Cl₂, −30 °C) δ: AB₂ spin syst, δ_A 64.9, δ_B −4.8, J_{AB} = 27.1 Hz. IR (KBr): ν_N 2141 (m); ν_{CO} 1955 (s) cm^{−1}.

Anal. Calcd for C₇₃H₇₀BClN₃O₄OsP₃ (1382.77) (7b). C, 63.41; H, 5.10; N, 3.04; Cl, 2.56. Found: C, 63.18; H, 5.22; N, 2.91; Cl, 2.43%.

$\Lambda_M = 53.9 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. $^1\text{H NMR}$ (CD_2Cl_2 , 25°C) δ : 7.92–6.87 (m, 55 H, Ph), 3.58 (qnt, 6 H, CH_2), 1.04 ppm (t, 9 H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -30°C) δ : AB_2 spin syst, δ_A 69.9, δ_B -6.7, $J_{\text{AB}} = 27.7$ Hz. IR (KBr): $\nu_{\text{N}}^{\text{N}}$ 2124 (m); ν_{CO} 1959 (s) cm^{-1} .

[OsCl(η^1 - $^{15}\text{N}_3\text{CH}_2\text{C}_6\text{H}_4$ -4- CH_3)(CO)(PPh $_3$) $_2$ [P(OEt) $_3$]]BPh $_4$ (5b $_1$). This complex was prepared exactly like the related unlabeled derivative **5b**, using 4- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2^{15}\text{N}_3$ as a reagent. $^1\text{H NMR}$ (CD_2Cl_2 , 25°C) δ : 7.69–6.77 (m, 54 H, Ph), 4.28 (s, 2 H, $\text{CH}_2^{15}\text{N}_3$), 3.55 (qnt, 6 H, CH_2 phos), 2.37 (s, 3 H, CH_3 *p*-tolyl), 1.05 ppm (t, 9 H, CH_3 phos). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -30°C) δ : AB_2X spin syst (X = ^{15}N), δ_A 65.15, δ_B -5.09, $J_{\text{AB}} = 27.2$, $J_{\text{AX}} = 55.7$, $J_{\text{BX}} = 27.7$ Hz. $^{15}\text{N NMR}$ (CD_2Cl_2 , -30°C) δ : -69.6 (s, ^{15}N), -368.4 ppm (m, ^{15}N). IR (KBr): $\nu_{^{15}\text{N}_3}$ 2118 (m); ν_{CO} 1953 (s) cm^{-1} .

[OsCl(η^1 -NH=C(H)C $_6$ H $_4$ -4- CH_3)(CO)(PPh $_3$) $_2$ [P(OEt) $_3$]]BPh $_4$ (8b). A solution of the complex **[OsCl(η^1 -N $_3$ CH $_2$ C $_6$ H $_4$ -4- CH_3)(CO)-(PPh $_3$) $_2$ [P(OEt) $_3$]]BPh $_4$ (**5b**) (100 mg, 0.07 mmol) in CH_2Cl_2 (5 mL) and EtOH (7 mL) was stirred at room temperature in the daylight for 10 h. The solvent was then removed under reduced pressure to give an oil, which was treated with ethanol (2 mL) containing NaBPh $_4$ (0.1 mmol, 34 mg). A white solid slowly separated out, which was filtered and crystallized from dichloromethane and ethanol; yield $\geq 60\%$. Anal. calcd for $\text{C}_{75}\text{H}_{74}\text{BClNO}_4\text{OsP}_3$ (1382.81): C, 65.14; H, 5.39; N, 1.01; Cl, 2.56. Found: C, 64.98; H, 5.51; Cl, 2.42%. $\Lambda_M = 53.0 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. $^1\text{H NMR}$ (CD_2Cl_2 , 25°C) δ : 8.29 (d br, 1 H, NH, $J_{\text{HH}} = 22.0$), 7.75 (d, 1 H, N=CH, $J_{\text{HH}} = 22.0$ Hz), 7.91–6.87 (m, 54 H, Ph), 3.55 (qnt, 6 H, CH_2 phos), 2.39 (s, 3 H, CH_3 *p*-tolyl), 0.99 ppm (t, 9 H, CH_3 phos). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C) δ : AB_2 spin syst, δ_A 70.0, δ_B -6.5, $J_{\text{AB}} = 23.0$ Hz. IR (KBr): ν_{NH} 3289 (m); ν_{CO} 1952 (s) cm^{-1} .**

[OsCl(RNHNH $_2$)(CO)(PPh $_3$) $_2$ L]BPh $_4$ (9–11) [R = H (9), CH $_3$ (10), C $_6$ H $_5$ (11); L = P(OMe) $_3$ (a), P(OEt) $_3$ (b)]. Triflic acid (0.11 mmol, 9.7 μL) was added to a solution of the appropriate complex OsHCl(CO)(PPh $_3$) $_2$ L (**2**) (0.1 mmol) in 5 mL of CH_2Cl_2 cooled to -196°C . The reaction mixture was brought to room temperature, stirred for 1 h, and then cooled again to -196°C . An excess of the appropriate hydrazine (0.22 mmol) was added to the resulting solution, which was brought to room temperature and stirred for 3 h. The solvent was removed under reduced pressure to give an oil, which was treated with ethanol (2 mL) containing an excess of NaBPh $_4$ (0.2 mmol, 68 mg). A white solid slowly separated out, which was filtered and crystallized from dichloromethane and ethanol; yield $\geq 75\%$.

Anal. Calcd for $\text{C}_{64}\text{H}_{63}\text{BClIN}_2\text{O}_4\text{OsP}_3$ (1253.61) (9a). C, 61.32; H, 5.07; N, 2.23; Cl, 2.83. Found: C, 61.07; H, 5.20; N, 2.11; Cl, 2.96%. $\Lambda_M = 54.6 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. $^1\text{H NMR}$ (CD_2Cl_2 , 20°C) δ : 7.96–6.80 (m, 50 H, Ph), 4.00 (br, 2 H, NH_2), 3.18 (d, 9 H, CH_3), 2.68 ppm (m br, 2 H, NH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C) δ : AB_2 spin syst, δ_A 76.9, δ_B -5.02, $J_{\text{AB}} = 26.7$ Hz. IR (KBr): ν_{NH} 3367, 3278, 3216 (w); ν_{CO} 1963 (s) cm^{-1} .

Anal. Calcd for $\text{C}_{67}\text{H}_{69}\text{BClIN}_2\text{O}_4\text{OsP}_3$ (1295.69) (9b). C, 62.11; H, 5.37; N, 2.16; Cl, 2.74. Found: C, 62.29; H, 5.24; N, 2.24; Cl, 2.52%. $\Lambda_M = 53.6 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. $^1\text{H NMR}$ (CD_2Cl_2 , 20°C) δ : 7.90–6.86 (m, 50 H, Ph), 3.55 (m, 6 H, CH_2), 3.13, 2.70 (m br, 4 H, NH_2), 1.00 ppm (t, 9 H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C) δ : AB_2 spin syst, δ_A 68.2, δ_B 7.83, $J_{\text{AB}} = 22.0$ Hz. IR (KBr): ν_{NH} 3339 (w), 3272 (m), 3253 (w); ν_{CO} 1967 (s) cm^{-1} .

Anal. Calcd for $\text{C}_{65}\text{H}_{65}\text{BClIN}_2\text{O}_4\text{OsP}_3$ (1267.64) (10a). C, 61.59; H, 5.17; N, 2.21; Cl, 2.80. Found: C, 61.36; H, 5.04; N, 2.30; Cl, 2.68%. $\Lambda_M = 51.4 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. $^1\text{H NMR}$ (CD_2Cl_2 , 20°C) δ : 7.79–6.88 (m, 50 H, Ph), 3.87 (m br, 2 H, NH_2), 3.14 (d, 9 H, CH_3 phos), 2.71 (m, 1 H, NH), 1.50 ppm (d, 3 H, NCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C) δ : AB_2 spin syst, δ_A 77.2, δ_B -4.39, $J_{\text{AB}} = 26.7$ Hz. IR (KBr): ν_{NH} 3310 (w), 3254 (m), 3183 (w); ν_{CO} 1964 (s) cm^{-1} .

Anal. Calcd for $\text{C}_{68}\text{H}_{71}\text{BClIN}_2\text{O}_4\text{OsP}_3$ (1309.72) (10b). C, 62.36; H, 5.46; N, 2.14; Cl, 2.71. Found: C, 62.13; H, 5.34; N, 2.06; Cl, 2.82%. $\Lambda_M = 55.7 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. $^1\text{H NMR}$ (CD_2Cl_2 , 20°C) δ : 7.81–6.84 (m, 50 H, Ph), 3.74 (br, 2 H, NH_2), 3.38 (qnt, 6 H, CH_2), 2.75 (m, 1 H, NH), 1.52 (d, 3 H, NCH_3), 0.97 ppm (t, 9 H, CH_3 phos). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C) δ : AB_2 spin syst, δ_A 73.8, δ_B -4.83, $J_{\text{AB}} = 26.7$ Hz. IR (KBr): ν_{NH} 3310 (w), 3258 (m), 3183 (w); ν_{CO} 1962 (s) cm^{-1} .

Anal. Calcd for $\text{C}_{70}\text{H}_{67}\text{BClIN}_2\text{O}_4\text{OsP}_3$ (1329.71) (11a). C, 63.23; H, 5.08; N, 2.11; Cl, 2.67. Found: C, 63.01; H, 5.17; N, 2.00; Cl, 2.54%. $\Lambda_M = 53.4 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. $^1\text{H NMR}$ (CD_2Cl_2 , 20°C) δ : 7.73–6.87 (m, 55 H, Ph), 4.78 (t br, 1 H, NH), 4.46 (m br, 2 H, NH_2), 3.27 ppm (d, 9 H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C) δ : AB_2 spin syst, δ_A 73.35, δ_B -4.60, $J_{\text{AB}} = 26.7$ Hz. IR (KBr): ν_{NH} 3379 (w), 3355 (m); ν_{CO} 1964 (s) cm^{-1} .

Anal. Calcd for $\text{C}_{73}\text{H}_{73}\text{BClIN}_2\text{O}_4\text{OsP}_3$ (1371.79) (11b). C, 63.92; H, 5.36; N, 2.04; Cl, 2.58. Found: C, 63.72; H, 5.25; N, 2.13; Cl, 2.50%. $\Lambda_M = 52.5 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. $^1\text{H NMR}$ (CD_2Cl_2 , 20°C) δ : 7.75–6.87 (m, 55 H, Ph), 4.83 (t br, 1 H, NH), 4.31 (m br, 2 H, NH_2), 3.61 (qnt, 6 H, CH_2), 1.14 ppm (t, 9 H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C) δ : AB_2 spin syst, δ_A 78.9, δ_B 5.0, $J_{\text{AB}} = 26.7$ Hz. IR (KBr): ν_{NH} 3249 (w), 3318 (m); ν_{CO} 1956 (s) cm^{-1} .

[OsCl(C $_6$ H $_5$ N=NH)(CO)(PPh $_3$) $_2$ L]BPh $_4$ (12) [L = P(OMe) $_3$ (a), P(OEt) $_3$ (b)]. **Method A:** A solid sample of the appropriate phenylhydrazine complex **[OsCl(C $_6$ H $_5$ NHNH $_2$)(CO)(PPh $_3$) $_2$ L]BPh $_4$ (**11**)** (0.1 mmol) was placed in a 25-mL three-necked round-bottomed flask fitted with a solid-addition side arm containing a slight excess of Pb(OAc) $_4$ (0.11 mmol, 49 mg). Dichloromethane (8 mL) was added, the solution cooled to -30°C and Pb(OAc) $_4$ portionwise was added over 20–30 min to the cold stirring solution. The solution was brought to 0°C , stirred for 5 min, and then the solvent was removed at 0°C under reduced pressure. The oil obtained was triturated with ethanol (2 mL) containing NaBPh $_4$ (0.1 mmol, 34 mg), and the resulting solution was stirred at 0°C until a pale-yellow solid separated out, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield $\geq 55\%$.

Anal. Calcd for $\text{C}_{70}\text{H}_{65}\text{BClIN}_2\text{O}_4\text{OsP}_3$ (1327.69) (12a). C, 63.32; H, 4.93; N, 2.11; Cl, 2.67. Found: C, 63.11; H, 5.02; N, 2.17; Cl, 2.55%. $\Lambda_M = 51.1 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. $^1\text{H NMR}$ (CD_2Cl_2 , 20°C) δ : 12.46 (d br, 1 H, NH, $J_{\text{PH}} = 12.0$ Hz), 7.94–6.66 (m, 55 H, Ph), 3.25 ppm (d, 9 H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C) δ : AB_2 spin syst, δ_A 80.56, δ_B -7.40, $J_{\text{AB}} = 27.9$ Hz. IR (KBr): ν_{CO} 1982 (s) cm^{-1} .

Anal. Calcd for $\text{C}_{73}\text{H}_{71}\text{BClIN}_2\text{O}_4\text{OsP}_3$ (1369.77) (12b). C, 64.01; H, 5.22; N, 2.05; Cl, 2.59. Found: C, 63.83; H, 5.38; N, 2.17; Cl, 2.45%. $\Lambda_M = 52.7 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. $^1\text{H NMR}$ (CD_2Cl_2 , 20°C) δ : 12.34 (d br, 1 H, NH, $J_{\text{PH}} = 12.7$ Hz), 7.92–6.65 (m, 55 H, Ph), 3.50 (qnt, 6 H, CH_2), 1.04 ppm (t, 9 H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C) δ : AB_2 spin syst, δ_A 77.1, δ_B -7.9, $J_{\text{AB}} = 27.3$ Hz. IR (KBr): ν_{CO} 1974 (s) cm^{-1} .

[OsCl(ArN=NH)(CO)(PPh $_3$) $_2$ L]BPh $_4$ (12, 13) [Ar = C $_6$ H $_5$ (12), 4- $\text{CH}_3\text{C}_6\text{H}_4$ (13); L = P(OMe) $_3$ (a), P(OEt) $_3$ (b)]. **Method B:** in a 25-mL three-necked round-bottomed flask were placed solid samples of the appropriate carbonyl complex OsHCl(CO)(PPh $_3$) $_2$ L (**2**) (0.1 mmol), an excess of the appropriate aryldiazonium cation **[ArN $_2$]BF $_4$** (0.25 mmol), and 10 mL of CH_2Cl_2 . The reaction mixture was stirred at room temperature for 4 h, and then, the solvent was removed under reduced pressure. The oil obtained was treated with ethanol (2 mL) containing an excess of NaBPh $_4$ (0.2 mmol, 68 mg). The resulting solution was stirred until a pale-yellow solid separated out, which was filtered and crystallized from CH_2Cl_2 and EtOH; yield ≥ 80 .

Anal. Calcd for $\text{C}_{71}\text{H}_{67}\text{BClIN}_2\text{O}_4\text{OsP}_3$ (1341.72) (13a). C, 63.56; H, 5.03; N, 2.09; Cl, 2.64. Found: C, 63.34; H, 4.92; Cl, 2.75; N, 1.98%. $\Lambda_M = 54.4 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. $^1\text{H NMR}$ (CD_2Cl_2 , 20°C) δ : 12.22 (d br, 1 H, NH), 7.92–6.59 (m, 54 H, Ph), 3.25 (d, 9 H, CH_3 phos), 2.39 ppm (s, 3 H, CH_3 *p*-tolyl). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C) δ : AB_2 spin syst, δ_A 80.9, δ_B -7.25, $J_{\text{AB}} = 27.0$ Hz. IR (KBr): ν_{CO} 1970 (s) cm^{-1} .

Anal. Calcd for $\text{C}_{74}\text{H}_{73}\text{BClIN}_2\text{O}_4\text{OsP}_3$ (1383.80) (13b). C, 64.23; H, 5.32; N, 2.02; Cl, 2.56. Found: C, 64.01; H, 5.43; N, 2.12; Cl, 2.43%. $\Lambda_M = 53.6 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. $^1\text{H NMR}$ (CD_2Cl_2 , 20°C) δ : 12.11 (d br, 1 H, NH, $J_{\text{PH}} = 8.0$ Hz), 7.80–6.57 (m, 54 H, Ph), 3.50 (m, 6 H, CH_2), 2.39 (s, 3 H, CH_3 *p*-tolyl), 1.04 ppm (d, 9 H, CH_3 phos). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C) δ : AB_2 spin syst, δ_A 77.41, δ_B -7.78, $J_{\text{AB}} = 26.7$ Hz. IR (KBr): ν_{CO} 1969 (s) cm^{-1} .

[OsCl(CO)(C $_6$ H $_5$ N= ^{15}N H)(PPh $_3$) $_2$ [P(OEt) $_3$]]BPh $_4$ (12b $_1$). This complex was prepared exactly like the related unlabeled derivative **12b** (method B), using **[C $_6$ H $_5$ N= ^{15}N] $^+\text{BF}_4^-$** as a reagent. $^1\text{H NMR}$ (CD_2Cl_2 , 20°C) δ : 12.34 (dd, 1 H, NH, $J_{\text{H}^{15}\text{N}} = 65.11$, $J_{\text{H}^{31}\text{P}} = 12.7$ Hz), 7.91–6.65 (m, 55 H, Ph), 3.50 (qnt, 6 H, CH_2), 1.04 ppm (t, 9

H, CH₃). ³¹P{¹H} NMR (CD₂Cl₂, 25 °C) δ: AB₂X spin syst (X = ¹⁵N), δ_A 77.1, δ_B -7.96, J_{AB} = 27.2, J_{AX} = 66.5, J_{BX} = 3.1 Hz. ¹⁵N NMR (CD₂Cl₂, 25 °C) δ: AB₂X spin syst, δ_X -20.4, J_{AX} = 66.5, J_{BX} = 3.1 Hz. IR (KBr): ν_{CO} 1974 (s) cm⁻¹.

X-ray Crystallography. Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and were corrected for Lorentz and polarization effects. The software SMART¹⁷ was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT¹⁸ for integration of intensity of reflections and scaling, and SADABS¹⁹ for empirical absorption correction.

The structure of **2b** was solved by direct methods using SIR92²⁰ implemented in the WingX package.²¹ The structure of **8b** was solved by Patterson methods. Both were refined by full-matrix least-squares on all F² using SHELXL97²² by using the Oscale suite.²³ Non-hydrogen atoms were refined with anisotropic displacement parameters, but some restraints were included in the model of **8b** in order to maintain the toluene ring atoms fitted to a regular hexagon. The carbonyl and Cl sites are probably disordered over two positions (as found for other structures containing Cl trans to CO), but the quality of the crystal does not allow us to find the other counterpart. The hydrogen atoms were included in idealized positions except that bonded to the osmium metal, which was found in the density map. All hydrogen atoms were refined with isotropic displacement parameters. Details of crystal data and structural refinement are given in Table 1, selected bond lengths and angles are shown in Table 2, and more data are in the Supporting Information.

RESULTS AND DISCUSSION

Preparation of Hydride Precursors. The hydridocarbonyl complex OsHCl(CO)(PPh₃)₃ (**1**) was first prepared by Vaska²⁴ by treating (NH₄)₂OsCl₆ with PPh₃ in high-boiling alcohols. We found that **1** can also be prepared in good yield by refluxing the dichloro compound OsCl₂(PPh₃)₃ in ethanol in the presence of zinc dust or magnesium turnings. The addition of the metal, Zn or Mg, is crucial for successful synthesis; otherwise only traces of the hydridocarbonyl complex **1** are obtained.

Complex **1** reacts with an excess of phosphites P(OR)₃ in toluene to give mixed-ligand derivatives OsHCl(CO)(PPh₃)₂L (**2**), which were isolated in good yield and characterized (Scheme 1).

The reaction proceeds with the substitution of only one PPh₃ ligand, affording the new hydridocarbonyl derivative **2**, containing two PPh₃ and one phosphite as supporting ligands.

Hydridocarbonyl complexes OsHCl(CO)(PPh₃)₂L (**1**, **2**) [L = PPh₃ or P(OR)₃] react at low temperature (-80 °C) with Brønsted acids HY with the evolution of H₂ and the formation of either pentacoordinate cations [OsCl(CO)(PPh₃)₂L]⁺ or neutral compounds Os(Y)Cl(CO)(PPh₃)₂L, which were stable in solution but decomposed on attempts at separating them in the solid state (Scheme 2).

The progress of the reaction between complexes **1**, **2** and Brønsted acids was monitored by NMR measurements at -80 °C. As 1 equiv of HY was added to the solution of **1** and **2** in CD₂Cl₂, the ¹H NMR spectra showed the disappearance of the signals between -6.95 and -5.54 ppm of the hydride ligands and the appearance of a new signal at about 4.6 ppm, which decreased on shaking and was attributed to free H₂.²⁵ No new signals attributable to a η²-H₂ complex²⁶ formed by protonation were observed in the spectra, according to the reaction shown in Scheme 2.

Hydrogen chloride HCl can also be used as a Brønsted acid in the reaction with OsHCl(CO)(PPh₃)₂L (**1**, **2**) leading to the

Table 1. Crystal Data and Structure Refinement

identification code	2b	8b
empirical formula	C ₄₃ H ₄₆ ClO ₄ P ₃ Os	C ₇₅ H ₇₄ BClNO ₄ P ₃ Os
formula weight	945.43	1382.81
temperature	293(2) K	293(2) K
wavelength	0.71073 Å	0.71073 Å
crystal system	monoclinic	monoclinic
space group	P2 ₁ /c	P2 ₁ /n
unit cell dimensions	a = 17.808(6) Å b = 10.058(4) Å c = 24.423(9) Å β = 110.671(5)°	a = 22.554(3) Å b = 12.7270(19) Å c = 23.939(4) Å β = 94.797(3)°
volume	4093(2) Å ³	6847.5(17) Å ³
Z	4	4
density (calculated)	1.534 Mg/m ³	1.341 Mg/m ³
absorption coefficient	3.338 mm ⁻¹	2.020 mm ⁻¹
F(000)	1896	2824
crystal size	0.52 × 0.48 × 0.37 mm	0.43 × 0.14 × 0.06 mm
theta range for data collection	1.77–28.06°	1.19–28.05°
index ranges	-23 ≤ h ≤ 23; -13 ≤ k ≤ 13; -31 ≤ l ≤ 32	-29 ≤ h ≤ 29; -16 ≤ k ≤ 16; -21 ≤ l ≤ 31
reflections collected	37532	44460
independent reflections	9831 [R(int) = 0.0321]	16271 [R(int) = 0.1398]
reflections observed (>2σ)	7951	5946
data completeness	0.989	0.980
absorption correction	semiempirical from equivalents	semiempirical from equivalents
max and min transmission	0.7456 and 0.4466	0.7456 and 0.6554
refinement method	full-matrix least-squares on F ²	full-matrix least-squares on F ²
data/restraints/parameters	9831/0/476	16271/17/758
goodness-of-fit on F ²	1.031	0.966
final R indices [I > 2σ(I)]	R ₁ = 0.0301 wR ₂ = 0.0691	R ₁ = 0.0714 wR ₂ = 0.1637
R indices (all data)	R ₁ = 0.0453 wR ₂ = 0.0778	R ₁ = 0.2350 wR ₂ = 0.2400
largest diff. peak and hole	1.493 and -1.564 e Å ⁻³	1.719 and -0.787 e Å ⁻³

dichloro derivatives OsCl₂(CO)(PPh₃)₂L (**3**, **4**), as shown in Scheme 3.

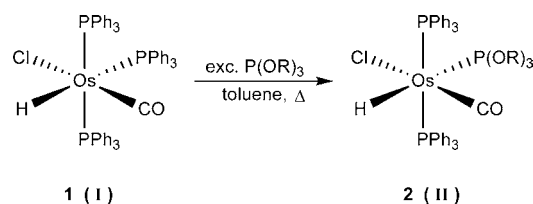
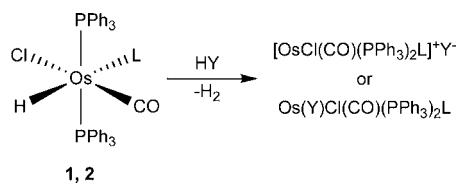
The reaction proceeds with the evolution of dihydrogen and coordination of Cl⁻, giving the dichlorocarbonyl derivatives **3**, **4**, which were isolated and characterized.

The new carbonyl complexes **1**–**4** were all separated as yellow (**1**, **3**) or white (**2**, **4**) solids, very stable in air and in solution of common organic solvents, where they behave as nonelectrolytes. Their characterization is supported by analytical and spectroscopic (IR, NMR) data and by the X-ray crystal structure determination of complex OsHCl(CO)(PPh₃)₂{P(OEt)₃} (**2b**), whose ORTEP is shown in Figure 1.

In compound **2b**, the osmium(II) atom is hexacoordinated by a hydride atom, a chloride atom, a carbonyl ligand, and three phosphorus atoms of three phosphane groups, two triphenylphosphines and one triethylphosphite, in such a way that the

Table 2. Selected Bond Lengths [Å] and Angles [deg]

2b		8b	
lengths			
Os–H(1)	1.59(5)	Os–N(1)	2.136(10)
Os–P(1)	2.3392(12)	Os–P(1)	2.295(3)
Os–P(2)	2.3672(13)	Os–P(2)	2.427(3)
Os–P(3)	2.3835(12)	Os–P(3)	2.431(3)
Os–C(1)	1.839(4)	Os–C(1)	1.901(17)
Os–Cl	2.4739(11)	Os–Cl	2.429(3)
C(1)–O(1)	1.154(5)	C(1)–O(1)	1.058(15)
		N(1)–C(2)	1.194(18)
		C(2)–C(3)	1.48(2)
angles			
H(1)–Os–C(1)	89.2(16)	N(1)–Os–C(1)	91.9(5)
H(1)–Os–Cl	87.8(16)	N(1)–Os–Cl	85.1(3)
H(1)–Os–P(1)	176.0(17)	N(1)–Os–P(1)	176.6(3)
H(1)–Os–P(2)	78.3(16)	N(1)–Os–P(2)	84.8(2)
H(1)–Os–P(3)	82.4(16)	N(1)–Os–P(3)	87.7(2)
C(1)–Os–P(1)	88.39(13)	C(1)–Os–P(1)	85.2(4)
C(1)–Os–P(2)	90.36(12)	C(1)–Os–P(2)	92.5(4)
C(1)–Os–P(3)	92.97(13)	C(1)–Os–P(3)	91.8(4)
C(1)–Os–Cl	176.99(13)	C(1)–Os–Cl	177.0(4)
P(1)–Os–Cl	94.60(5)	P(1)–Os–Cl	97.79(11)
P(1)–Os–P(2)	98.50(4)	P(1)–Os–P(2)	93.51(11)
P(1)–Os–P(3)	101.00(4)	P(1)–Os–P(3)	94.18(11)
P(2)–Os–P(3)	160.30(3)	P(2)–Os–P(3)	171.46(10)
P(2)–Os–Cl	88.78(4)	P(2)–Os–Cl	87.51(11)
P(3)–Os–Cl	86.84(3)	P(3)–Os–Cl	87.77(11)
Os–C(1)–O(1)	179.0(4)	Os–C(1)–O(1)	177.8(16)
		N(1)–C(2)–C(3)	135(2)
		Os–N(1)–C(2)	133.9(13)

Scheme 1^a^aR = Me (a), Et (b).Scheme 2^a^aY⁻ = CF₃SO₃⁻; L = PPh₃ (1), P(OMe)₃ (2a), P(OEt)₃ (2b).

PPh₃ ligands are mutually trans and the P(OEt)₃ one is trans to the hydride ligand. The environment of the osmium atom is a slightly distorted octahedron, in which the most important source of distortion comes from bending of the axis P–Os–P, with angle value of 160.30(3)^o.^{28,11k} The Os–C carbonyl bond length, 1.839(4) Å, and that of the Os–Cl (trans to former), 2.474(1) Å, are both comparable with other trans compounds and do not deserve further comment.²⁹ The mutually trans Os–P_(phosphine) bond lengths [average 2.375(1) Å] are only

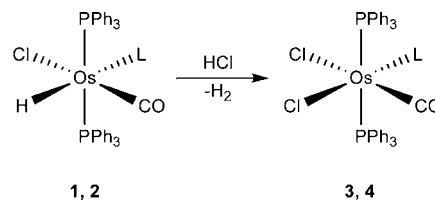
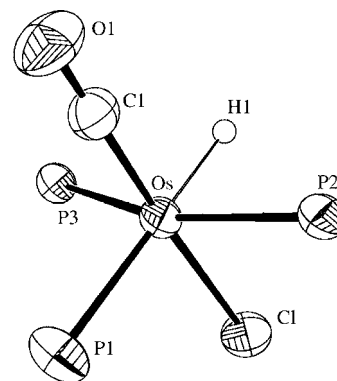
Scheme 3^a^aL = PPh₃ (1, 3), P(OMe)₃ (2a, 4a), P(OEt)₃ (2b, 4b).

Figure 1. ORTEP²⁷ view (50% probability level) of complex **2b**. The ethoxy groups of the P(OEt)₃ [P1] and the phenyl groups of the PPh₃ [P2 and P3] were not drawn for clarity.

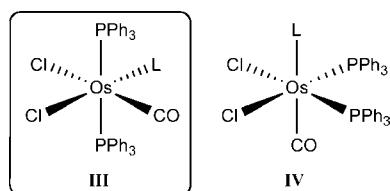
slightly longer than that of Os–P_(phosphite) [2.339(1) Å]. The difference between the two types of Os–P bond lengths is smaller than expected but is probably due to the different trans influence exerted on these ligands.^{30–32} The values for Os–P_(phosphine) bond lengths in **2b** are identical to those found in the compound [OsCl{bis(quinoliny)amidate}(PPh₃)₂].³³ Incidentally, Os–P_(phosphite) bond values in **2b** are longer than those found in the [Os(NH₂NH₂)₂{P(OEt)₃}₄]²⁺ cation^{11d} or in [Os(SnH₃)(Tp){P(OMe)₃}(PPh₃)₃].³¹

The IR spectrum of OsHCl(CO)(PPh₃)₃ (**1**) shows a strong band at 1910 cm⁻¹ attributed to the ν_{CO} of the carbonyl ligand. The spectrum also shows a weak band at 2090 cm⁻¹, attributed to the ν_{OsH} of the hydride ligand. The presence of this ligand is confirmed by the ¹H NMR spectrum, which shows a doublet of triplets at –6.95 ppm due to the resonance of the H⁻ coupled with the three phosphine ligands. The value of 87 Hz found for one J_{PH}, compared with the value of 25 Hz for the other two J_{PH}, suggests that the hydride is in trans position with respect to one PPh₃ and in cis with respect to the other two. The ³¹P NMR spectrum is an A₂B multiplet, indicating that the two phosphines are magnetically equivalent and different from the third. On this basis, mer geometry **I** may be proposed in solution for the carbonyl compound **1**.

The IR spectra of mixed-ligand complexes OsHCl(CO)(PPh₃)₂L (**2**) show the ν_{CO} as a strong band at 1946 (**2a**) and 1948 (**2b**) cm⁻¹, which falls at a value slightly higher than in the related complex **1**, according to the better π-acceptor properties of phosphites P(OR)₃ with respect to PPh₃. Instead, no bands attributable to ν_{OsH} were observed in the spectra. However, the presence of the hydride ligand is supported by the proton NMR spectra, which show a doublet of triplets at –5.54 (**2a**) and –5.68 (**2b**) ppm, due to the coupling of H⁻ with the ³¹P nuclei of phosphines. In addition, comparison of the two J_{PH} values suggests that the hydride is trans to one phosphine and in cis with respect to the other two. The ³¹P NMR spectra appear as

AB_2 multiplets, suggesting that the two phosphines are magnetically equivalent and different from the phosphite. On the basis of these data, a mer geometry **II** (Scheme 1), like that found in the solid state (Figure 1), may be proposed in solution for the mixed-ligand species **2**.

The ν_{CO} band of dichloro complex $OsCl_2(CO)(PPh_3)_3$ (**3**) appears at 1954 cm^{-1} , whereas those of the related derivatives $OsCl_2(CO)(PPh_3)_2L$ (**4**) fall at 1969 (**4a**) and 1982 (**4b**) cm^{-1} . In the far region of the spectra, two medium-intensity absorptions were also observed at 323 and 294 cm^{-1} for **3** and at 341 and 305 cm^{-1} for **4a**, and were attributed to ν_{OsCl} of two chloride ligands in a mutually cis position. The ^{31}P NMR spectra are either A_2B (**3**) or AB_2 (**4**) multiplets and can be simulated with the parameters reported in the Experimental Section, indicating that the two phosphines are magnetically equivalent and different from the third. These spectroscopic data alone do not allow us to decide unambiguously between mer (**III**) and fac (**IV**) geometry for dichloro complexes **3**, **4** (Chart 2).

Chart 2^a

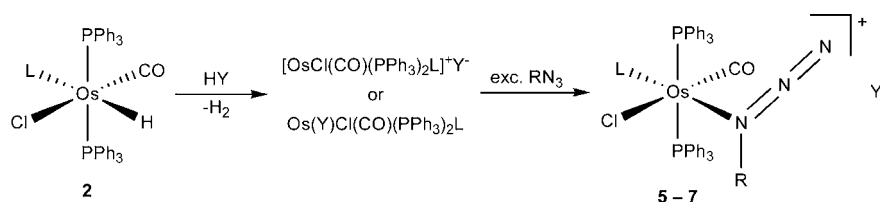
^aL = PPh_3 (**3**), $P(OMe)_3$ (**4a**), $P(OEt)_3$ (**4b**).

However, comparison of their spectroscopic properties with those of the related hydride-carbonyl complexes $OsHCl(CO)(PPh_3)_2L$ (**1**, **2**), containing the CO trans to the chloride ligand, suggests that mer geometry **III** is the most plausible for **3** and **4**.

Azide Complexes. Unsaturated mixed-ligand complexes formed by protonation of hydrides $OsHCl(CO)(PPh_3)_2L$ (**2**) with Brønsted acids reacted with an excess of organic azide RN_3 to give azide cations $[OsCl(\eta^1-N_3R)(CO)(PPh_3)_2L]^+$ (**5–7**), which were separated as BPh_4^- salts and characterized (Scheme 4).³⁴

Instead, the related hydride $OsHCl(CO)(PPh_3)_3$ (**1**) did not give azide complexes, after treatment first with Brønsted acid and then with an excess of RN_3 . Similarly, the reaction of dichloro complexes $OsCl_2(CO)(PPh_3)_2L$ (**3**, **4**) with organic azide did not afford the related complexes, and it seems that only the mixed-ligand fragments $[OsCl(CO)(PPh_3)_2\{P(OR)_3\}]^+$, containing CO, PPh_3 , and phosphites, can stabilize $[Os]-\eta^1-N_3R$ derivatives.

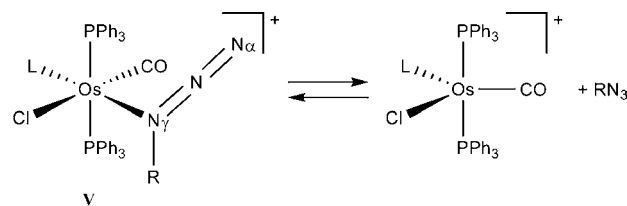
Azide complexes $[OsCl(\eta^1-N_3R)(CO)(PPh_3)_2L]^+$ (**5–7**) are pale-yellow solids stable in air but slightly unstable in solution

Scheme 4^a

^aL = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**); R = $4-CH_3C_6H_4CH_2$ (**5**), $C_6H_5CH_2$ (**6**), C_6H_5 (**7**); $Y^- = CF_3SO_3^-$.

of polar organic solvents, where they behave as 1:1 electrolytes.³⁵ Analytical and spectroscopic data (IR, 1H , ^{15}N , ^{31}P NMR) support the proposed formulation, which was further confirmed by X-ray crystal structure determination of the imine complex $[OsCl\{\eta^1-NH=C(H)C_6H_4-4-CH_3\}(CO)(PPh_3)_2\{P(OEt)_3\}]BPh_4$ (**8b**), formed from the azide derivative **5b** (see below, Figure 2).

The IR spectra of azide complexes **5–7** show a strong band at $1952–1959\text{ cm}^{-1}$, due to the ν_{CO} of the carbonyl group, and a medium-intensity one at $2146–2124\text{ cm}^{-1}$, attributed to the ν_{N_3} of the azide ligand. Support for this attribution came from the spectra of the labeled compound $[OsCl(\eta^1-^{15}N_3CH_2C_6H_4-4-CH_3)(CO)(PPh_3)_2\{P(OEt)_3\}]BPh_4$ (**5b**), which showed the $\nu^{15}N_3$ at 2118 cm^{-1} , shifted to a lower wavenumber by 28 cm^{-1} with respect to the unlabeled **5b** (Supporting Information Figure S2). The high ν_{N_3} values of our complexes, compared with those of azide complexes whose X-ray structures are known,^{6,7} suggest the η^1 -diazoamino coordination mode [**B**] (Chart 1) of the azide ligand (Scheme 5).

Scheme 5^a

^aL = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**).

Variable-temperature NMR spectra of azide complexes **5–7** showed that the compounds are fluxional. The two broad signals observed at room temperature in the ^{31}P NMR spectra, already at $-30\text{ }^\circ\text{C}$, resolved into one triplet and one doublet, which could be simulated with an AB_2 model, indicating that the two phosphine ligands are magnetically equivalent and different from the third. In addition, the ^{15}N NMR spectrum of the labeled complex $[OsCl(\eta^1-^{15}N_3CH_2C_6H_4-4-CH_3)(CO)(PPh_3)_2\{P(OEt)_3\}]BPh_4$ (**5b**) may be used as a diagnostic tool for the coordinate azide molecule. A singlet at -69.6 and a multiplet at -368.4 ppm were observed in the spectrum at $-30\text{ }^\circ\text{C}$ and attributed to the N_α and N_γ nuclei, respectively, of the coordinate $4-CH_3C_6H_4CH_2-^{15}N_3$ group. Further support to the coordination of the azide came from the ^{31}P spectrum of the labeled complex **5b**, showing two broad signals at room temperature, which resolved (at $-30\text{ }^\circ\text{C}$) into two multiplets, simulable with an AB_2X model ($X = ^{15}N$) with the parameters reported in the Experimental Section. The good fit between the calculated and experimental spectra (Supporting Information

Figure S1) strongly supports coupling of the ^{31}P nuclei of phosphines with the ^{15}N nuclei of the coordinate azide group. However, although spectroscopic data alone do not allow us to assign unambiguously a geometry in solution for complexes **5**–**7**, comparison with the data of carbonyl precursor **2** and imine complex $[\text{OsCl}\{\eta^1\text{-NH}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{-4-CH}_3\}(\text{CO})(\text{PPh}_3)_2\{\text{P}(\text{OEt})_3\}]\text{BPh}_4$ (**8b**) (see below) allow us to propose geometry **V** (Scheme 5) for our azide complexes **5**–**7**.

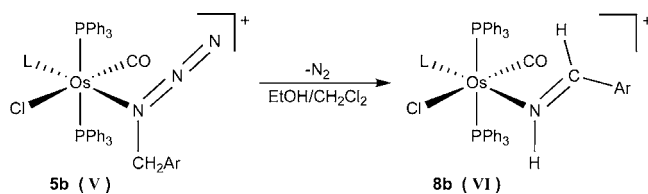
The fluxional behavior shown by azide complexes $[\text{OsCl}(\eta^1\text{-N}_3\text{R})(\text{CO})(\text{PPh}_3)_2\text{L}]\text{BPh}_4$ (**5**–**7**) may be explained by an intermolecular process involving dissociation of the azide ligand, as shown in Scheme 5. Strong support for such a dissociation equilibrium of the azide ligand in the complexes was obtained by adding free ^{15}N -labeled azide $4\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2^{15}\text{N}_3$ to the unlabeled compound **5a** in an NMR tube and observing that exchange between labeled and unlabeled azide does take place. On the basis of these results, the dissociation process of Scheme 5 may plausibly be proposed to explain the VT-NMR behavior of our azide derivatives.

Transition metal complexes containing organic azide as a ligand are rare^{5–8} and, to the best of our knowledge, there are no reports of organoazide osmium complexes in the literature. The use of the mixed-ligand precursors $\text{OsHCl}(\text{CO})(\text{PPh}_3)_2\text{L}$ (**2**) allows easy synthesis of the first RN_3 complexes for this metal. Unfortunately, the bonding mode of the azide in our compounds **5**–**7** could not be established by X-ray determination and only IR data can give some information, suggesting linear $\text{N}\gamma$ coordination [**B**] (Chart 1). Values for ν_{N_3} ($2146\text{--}2124\text{ cm}^{-1}$) higher than those of the free RN_3 ligand were found in our complexes **5**–**7** and in those^{6,7} of Ag, Pd, Cu, and Ir, in which $\text{N}\gamma$ coordination has been confirmed by X-ray determination. Such a coordination through substituted $\text{N}\gamma$ is favored by the greater Lewis basicity³⁶ of the site and is probably the most common type of azide complex with linear NNN geometry. However, one example of $\text{N}\alpha$ coordination of the azide was also observed in complex^{6b} $\text{HB}[3,5\text{-(CF}_3)_2\text{Pz}]_3\text{CuNNN}(1\text{-Ad})$ (Pz = pyrazolyl; 1-Ad = adamantyl) but, according to theoretical calculations, was attributed to Cu(I), which exhibits “enough π -donating ability to favor binding through the terminal nitrogen”.

It is worth noting that organic azide complexes are probably involved as intermediates in the metal-catalyzed cycloaddition of alkyne and organic azides to give triazole.⁹ Therefore, the preparation of new RN_3 complexes and information on the coordination chemistry of RN_3 may help to clarify the mechanism of reaction and to find new catalysts.

Benzylazide complexes $[\text{OsCl}(\eta^1\text{-N}_3\text{CH}_2\text{Ar})(\text{CO})(\text{PPh}_3)_2\{\text{P}(\text{OEt})_3\}]\text{BPh}_4$ (**5**) are stable as solids, but slowly react in solution to give a new compound, characterized as the imine species $[\text{OsCl}\{\eta^1\text{-NH}=\text{C}(\text{H})\text{Ar}\}(\text{CO})(\text{PPh}_3)_2\{\text{P}(\text{OEt})_3\}]\text{BPh}_4$ (**8**) (Scheme 6).

Scheme 6^a



^aAr = $4\text{-CH}_3\text{C}_6\text{H}_4$; L = $\text{P}(\text{OEt})_3$.

Extrusion of N_2 in coordinate azide **5**, followed by 1,2-shift of one hydrogen atom, may lead to the formation of imine derivative **8**. It should be noted that slow diffusion of ethanol into a CH_2Cl_2 solution of **5b** at $5\text{ }^\circ\text{C}$ yielded crystals of imine complex $[\text{OsCl}\{\eta^1\text{-NH}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{-4-CH}_3\}(\text{CO})(\text{PPh}_3)_2\{\text{P}(\text{OEt})_3\}]\text{BPh}_4$ (**8b**) the structure of which is shown in Figure 2.

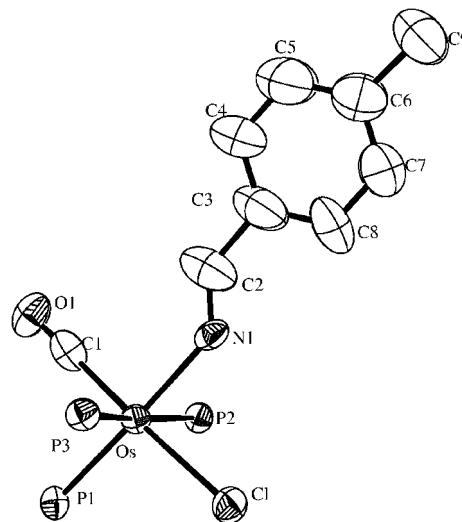


Figure 2. ORTEP²⁷ view (20% probability level) of **8b**. The ethoxy groups of the $\text{P}(\text{OEt})_3$ [P1] and the phenyl groups of the PPh_3 [P2 and P3] were not drawn for clarity.

N-protio imine complexes of osmium are rare,³⁷ and the reaction of our benzylazide complex **5** allows a new example of such imine species to be prepared.

Analytical and spectroscopic data support the proposed formulation for imine complex **8b**, which is a white solid stable in air and in solution of polar organic solvents, where it behaves as a 1:1 electrolyte.³⁵ The IR spectrum shows a strong band at 1952 cm^{-1} , attributed to the ν_{CO} of the carbonyl group, and a medium-intensity absorption at 3289 cm^{-1} , attributed to the ν_{NH} of the imine ligand. Its presence is confirmed by the ^1H NMR spectrum, which shows a slightly broad doublet at 8.29 ppm ($J_{\text{HH}} = 22\text{ Hz}$) attributed to the NH imine resonance. In a COSY experiment, this signal was correlated with a doublet at 7.75 ppm , attributed to the $=\text{CH}$ signal of the imine. In the temperature range $+20$ to $-80\text{ }^\circ\text{C}$, the ^{31}P NMR spectra of the imine complex **8b** appear as AB_2 multiplets, indicating the magnetic equivalence of the two phosphines, different from the third. Although these data do not allow to assign unambiguously a geometry in solution to **8b**, they are not in contrast with a type **VI** geometry, like that found in the solid state.

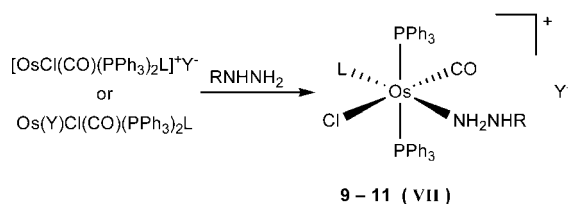
Conclusive support for the formulation of **8b** came from X-ray crystal structure determination. The asymmetric unit contains both an anion BPh_4^- and a cation complex. An ORTEP view of the cation is shown in Figure 2.

The Os(II) atom is coordinated by the nitrogen atom of a 4-methylbenzylideneamidate ligand [bonded through the nitrogen atom: $\eta^1\text{-NH}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{CH}_3$] trans to a phosphorus atom of a triethoxyphosphine ligand. There is also a chloride atom trans to a carbonyl ligand. The octahedron is completed by two mutually trans phosphorus atoms of two triphenylphosphine ligands. As stated in the Experimental Section, the carbonyl and Cl sites are probably disordered over two

positions (as found for other structures containing Cl trans to a carbonyl ligand),^{38,39} but the poor quality of the crystal did not allow us to find the other counterpart. The presence of the disorder limits discussion of the metrical parameters. Within these margins, some features may be mentioned, as follows. The environment of the osmium atom is a slightly distorted octahedron, with cis angles ranging from 84.8(2) to 97.8(1)°. The 4-methylbenzylideneamidate ligand is spatially arranged in such a way that an interaction between N–H and the Cl ligand is allowed.⁴⁰ This means that the ligand plane is parallel to the Cl–Os–carbonyl vector. Unfortunately, the parameters of this interaction or planarity are very imprecise and cannot be commented on further. The Os–N_(amidate) bond distance, 2.14(1) Å, is shorter than those found for other single nitrogen osmium bonds such as the hydrazine cation [Os(NH₂NH₂)₂{P(OEt)₃}₄]⁺, 2.20(2) Å,^{11d} or the aniline cation [Os(NH₂Ph)-H₂(κ²-acetate)P₂]⁺, 2.258(4) Å,³² but comparable with the value found for neutral or cationic osmium imine complexes [OsCl_{2-n}(=C=CHPh)(NH=CMe₂)(H₂O)_n(PⁱPr₃)₂]ⁿ⁺ (n = 0, 1) [average 2.07(1) Å].⁴⁰ This fact, together with the parameters found around the N(3) atom discussed below, suggests substantial delocalization in this ligand. The C=N bond distance, 1.19(2) Å, is also shorter than that found for other benzylideneamido complexes with W,⁴¹ Re,⁴² Fe,⁴³ Ru,^{37d} or Ir.⁷ The C(1)–N(3)–Os angle, 134(1)°, and the N(3)–C(1)–C(2) angle, 135(2)°, are also very imprecise and also surprisingly large for an sp²-hybridized N atom, but similar values have been found for the above-mentioned W, Re, Fe, Ru, and Ir complexes. The Os–P bond lengths are in two sets. The bond length of Os–P_(phosphite) is shorter [2.295(3) Å] than the mutually trans Os–P_(phosphine) one [average 2.429(3) Å]. It is noteworthy that the former is shorter than that found in **2b**, as expected for the trans influence of hydride ligand versus an amidate ligand. In contrast, Os–P_(phosphine) bond lengths are longer than those found in **2b**.

Hydrazine and Diazene Complexes. Unsaturated species, formed by protonation of OsHCl(CO)(PPh₃)₂L with the Brønsted acids HY, also react with hydrazines RNHNH₂ to give the related complexes [OsCl(CO)(RNHNH₂)(PPh₃)₂L]BPh₄ (**9–11**), which were isolated in good yield and characterized (Scheme 7).

Scheme 7^a

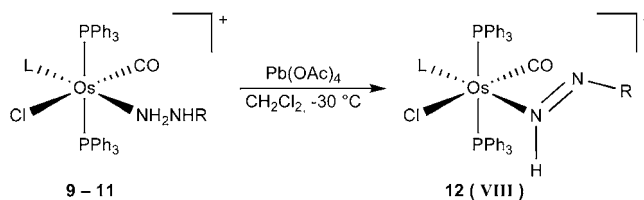


^aR = H (**9**), CH₃ (**10**), C₆H₅ (**11**); L = P(OMe)₃ (**a**), P(OEt)₃ (**b**); Y⁻ = CF₃SO₃⁻.

Hydrazine complexes **9–11** reacted with Pb(OAc)₄ at –30 °C to give the diazene derivative [OsCl(CO)(RN=NH)(PPh₃)₂L]⁺ (**12**) which, in the case of the phenyldiazene, was isolated as a solid and characterized (Scheme 8).

Instead, in the case of hydrazine NH₂NH₂ and methylhydrazine CH₃NHNH₂ derivatives, the solids obtained contained only little amounts of 1,2-diazene⁴⁴ NH=NH or methyl-diazene CH₃N=NH complexes, which decomposed during crystallization. However, even traces of the diazene ligand

Scheme 8^a

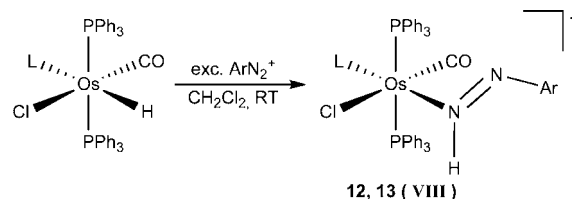


^aR = C₆H₅; L = P(OMe)₃ (**a**), P(OEt)₃ (**b**).

suggest that the selective oxidation of hydrazine to diazene does occur in any case, but the instability of the compounds often prevents their separation. Only the phenyl substituent therefore seems to be able to stabilize the diazene derivative [OsCl(CO)(C₆H₅N=NH)(PPh₃)₂L]BPh₄ (**12**). It is worth noting that the previously reported complex⁴⁵ [OsCl(NH₂NH₂)(CO)₂(PPh₃)₂]OTf reacted with Pb(OAc)₄ to give the stable and isolable derivative [OsCl(η¹-NH=NH)(CO)₂(PPh₃)₂]OTf.

This result prompted us to test a different way of preparing the same aryldiazene species by inserting aryldiazonium cations into the Os–H bond. We therefore treated hydride OsHCl(CO)(PPh₃)₂L (**2**) with aryldiazonium cations and did observe the formation of aryldiazene complexes [OsCl(CO)(ArN=NH)(PPh₃)₂L]BPh₄ (**12, 13**), which were isolated in good yield and characterized (Scheme 9).

Scheme 9^a



^aAr = C₆H₅ (**12**), 4-CH₃C₆H₄ (**13**); L = P(OMe)₃ (**a**), P(OEt)₃ (**b**).

The results highlight how aryldiazene complexes stabilized by the carbonyl fragment [OsCl(CO)(PPh₃)₂L]⁺ may be prepared either by oxidation of coordinate arylhydrazine or by insertion of aryldiazonium cations into the Os–H bond. Over the past thirty years, a number of hydrazine and aryldiazene complexes have been reported for several transition metals^{11j,46} and have been studied as models of the dinitrogen fixation process. Hydrazine has also been shown to be a substrate of nitrogenase⁴⁷ and has been trapped as an intermediate during enzyme turnover. However, although several hydrazine complexes⁴⁸ of various metals have been reported, relatively few contain osmium. The use of the mixed-ligand hydride OsHCl(CO)(PPh₃)₂L (**2**) as a precursor allows the synthesis of new hydrazine and aryldiazene osmium derivatives.

Both hydrazine [OsCl(CO)(RNHNH₂)(PPh₃)₂L]BPh₄ (**9–11**) and aryldiazene complexes [OsCl(CO)(ArN=NH)(PPh₃)₂L]BPh₄ (**12, 13**) were isolated as white or pale-yellow solids stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes.³⁵ Analytical and spectroscopic data support the proposed formulation.

The IR spectra of hydrazine complexes **9–11** showed three bands of medium intensity at 3379–3183 cm⁻¹, attributed to the ν_{NH} of the coordinate group. The spectra also show a strong absorption at 1967–1956 cm⁻¹, due to the ν_{CO} of the carbonyl

ligand. The ^1H NMR spectra confirm the presence of the hydrazine, showing one slightly broad multiplet at 4.00–3.13 ppm due to the metal-bonded NH_2 group of NH_2NH_2 and CH_3NHNH_2 ligands and another multiplet at 2.75–2.68 ppm of the NH_2 or NH protons of the hydrazine. A doublet at 1.52–1.50 ppm of the methyl group of CH_3NHNH_2 also appears in the spectra of **10**. In addition, the signals of the phenylhydrazine fall to 4.46–4.31 (NH_2) and 4.83–4.78 ppm (NH), indicating the presence of the diazo ligand.

In the temperature range +20 to -80 $^\circ\text{C}$, the ^{31}P NMR spectra appear as AB_2 multiplets indicating the magnetic equivalence of the two phosphines PPh_3 , different from the phosphite. These spectroscopic data support the proposed formulation for the hydrazine complexes **9–11** but do not allow us to assign them unambiguously a geometry in solution. However, by comparison with the data of both azide complex $[\text{OsCl}\{\eta^1\text{-NH}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{-4-CH}_3\}(\text{CO})(\text{PPh}_3)_2\{\text{P}(\text{OEt})_3\}]\text{-BPh}_4$ (**8b**), whose structure is known, and aryldiazene derivatives $[\text{OsCl}(\text{CO})(\text{ArN}=\text{NH})(\text{PPh}_3)_2\text{L}]\text{BPh}_4$ (**12**, **13**), mer geometry **VII** (Scheme 7) may plausibly be proposed for the hydrazine complexes.

The IR spectra of aryldiazene derivatives $[\text{OsCl}(\text{CO})(\text{ArN}=\text{NH})(\text{PPh}_3)_2\text{L}]\text{BPh}_4$ (**12**, **13**) show the characteristic ν_{CO} at 1982–1969 cm^{-1} , but no bands attributable to the aryldiazene group were observed. However, its presence is confirmed by the ^1H NMR spectra, which show a slightly broad doublet at 12.46–12.11 ppm, attributed to the NH diazene proton. Support for this attribution also comes from the ^1H spectrum of the ^{15}N -labeled complex $[\text{OsCl}(\text{CO})(\text{C}_6\text{H}_5\text{N}=\text{NH})\text{-}(\text{PPh}_3)_2\{\text{P}(\text{OEt})_3\}]\text{-BPh}_4$ (**12b**), which shows a doublet of doublets centered at the same chemical shift of **12b**, due to coupling with both the ^{15}N and the ^{31}P of one phosphine ($J_{\text{H}^{15}\text{N}} = 65.11$, $J_{\text{H}^{31}\text{P}} = 12.7$ Hz). The $J_{\text{H}^{31}\text{P}}$ values of the other phosphine was very low and was not observed. In the temperature range +20 to -80 $^\circ\text{C}$, the ^{31}P NMR spectrum is an AB_2X multiplet ($\text{X} = ^{15}\text{N}$) simulable with the parameters reported in the Experimental Section. The high values of $J_{\text{PA}^{15}\text{N}}$ compared with $J_{\text{PB}^{15}\text{N}}$ suggest that the aryldiazene $\text{C}_6\text{H}_5\text{N}=\text{NH}$ is in a trans position with respect to the phosphite $\text{P}(\text{OR})_3$. On the basis of these data, mer geometry **VIII** may plausibly be proposed for the aryldiazene derivatives.

CONCLUSIONS

In this report we demonstrate that the mixed-ligand fragment $[\text{OsCl}(\text{CO})(\text{PPh}_3)_2\{\text{P}(\text{OR})_3\}]^+$ allows us to prepare unprecedented organic azide complexes of osmium $[\text{OsCl}(\eta^1\text{-N}_3\text{R})\text{-}(\text{CO})(\text{PPh}_3)_2\{\text{P}(\text{OR})_3\}]\text{BPh}_4$. The spectroscopic data suggest the η^1 -diazoamino coordination mode of the azide ligand. The imine complex $[\text{OsCl}\{\eta^1\text{-NH}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{-4-CH}_3\}(\text{CO})\text{-}(\text{PPh}_3)_2\{\text{P}(\text{OR})_3\}]\text{BPh}_4$ was also prepared from the benzylazide derivative. In addition, the fragment $[\text{OsCl}(\text{CO})\text{-}(\text{PPh}_3)_2\{\text{P}(\text{OR})_3\}]^+$ can stabilize both hydrazine $[\text{OsCl}(\text{RNHNH}_2)(\text{CO})(\text{PPh}_3)_2\{\text{P}(\text{OR})_3\}]\text{BPh}_4$ and aryldiazene derivatives $[\text{OsCl}(\text{C}_6\text{H}_5\text{N}=\text{NH})(\text{CO})(\text{PPh}_3)_2\{\text{P}(\text{OR})_3\}]\text{-BPh}_4$.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data for compounds **2b** and **8b** (cif); spectroscopic NMR and IR data for the labeled **5b**₁ and unlabeled **5b** compound (Figure S1–S2, pdf). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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DEDICATION

J.C. dedicates this publication to Prof. Antonio Sousa (USC, Galicia, Spain) In Memoriam.

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