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Molecular Hydrogen Complexes. Preparation and Reactivity of New Ruthenium(II) and Osmium(II) Derivatives and a Comparison along the Iron Triad

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Molecular hydrogen complexes [$MH(\eta^2\text{-}H_2)P_4$]BF_4 [M = Ru, Os; P = $PhP(OEt)_2$, $P(OEt)_3$, $P(OMe)_3$] were prepared by allowing the MH_2P_4 hydrides to react with $HBF_4{\cdot}Et_2O$ at -80 °C in ethanol or diethyl ether. Their characterization by variable-temperature ^1H and ^{31}P NMR data, T_1 measurements, and J_{HD} values is reported. The influence of the phosphite ligand and the central metal (Fe, Ru, Os) on the properties of the complexes is also discussed. Monohydrido complexes of the type [$MHLP_4$]BPh_4 [L = CO, 4-$CH_3C_6H_4NC$, 4-$CH_3C_6H_4CN$; P = $PhP(OEt)_2$, $P(OEt)_3$] were obtained by substitution of dihydrogen with the appropriate ligand. The reactions of arenediazonium cations with the molecular hydrogen and dihydride RuH_2P_4 complexes were examined, and the syntheses of pentacoordinate [$Ru(ArN{=}NH)P_4$]$(BPh_4)_2$ and [$Ru(ArN_2)P_4$]BPh_4 complexes and octahedral [$RuH(ArN{=}NH)P_4$]BPh_4 and [$Ru(ArN{=}NH)_2P_4$]$(BPh_4)_2$ derivatives were achieved. The characterization of the complexes by IR and ^1H and ^{31}P NMR spectra is reported.

Introduction

Molecular hydrogen complexes of transition metals continue to be reported, and some data on their chemical properties are being established.[1-11] However, neither the factors determining the stability of dihydrogen coordination nor the influence of the central metal and/or steric and electronic properties of the coligands adjacent to the η^2-H_2 ligand in determining the properties of these complexes are completely understood. For example, it has been demonstrated[2b,d] that in the series of complexes of the type MH_4P_3 (M = Fe, Ru, Os; P = tertiary phosphine) only the first two (Fe, Ru) contain the η^2-H_2 ligand, whereas osmium shows a classical hydride structure. On the other hand, dihydrogen ligands are always present in the triad [$MH(\eta^2\text{-}H_2)(depe)_2$]$^+$ (M = Fe, Ru, Os; depe = $Et_2PCH_2CH_2PEt_2$).[3b] In $MoH_2(CO)(R_2PC_2H_4PR_2)_2$ derivatives it has been observed[1e] that the dihydrogen vs dihydride equilibrium strongly depends on the basicity of the ancillary phosphine ligands.

In a previous paper[12] we reported the synthesis of new iron(II) molecular hydrogen complexes containing monodentate phosphite ligands, and we have now extended these studies to the ruthenium and osmium complexes, with the aim of studying the influence of the central metal on the properties of the dihydrogen complexes in the iron triad. Furthermore, a study on the reactivity of these η^2-H_2 complexes with arenediazonium cations was undertaken in order to compare the results with those previously obtained with "classical" dihydride MH_2P_4 derivatives, which allow the synthesis of bis(aryldiazene) complexes.[13] The results of these studies are also presented here.

Experimental Section

General Comments. Unless otherwise noted, all manipulations were carried out in H_2 and/or argon atmosphere by using standard Schlenk and syringe techniques or a Vacuum Atmosphere drybox. All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Diethoxyphenylphosphine was prepared by the method of Rabinowitz and Pellon;[14] triethyl and trimethyl phosphite were Ega Chemie products purified by distillation under nitrogen. Deuterium was obtained[15] from D_2O and Na; high-purity HD was prepared from $LiAlH_4$ and D_2O (99.8%) by following the reported method.[16] Diazonium salts were obtained in the usual way described in the literature.[17] Labeled diazonium salts [$C_6H_5N{\equiv}^{15}N$]BF_4 and [$C_6H_5{}^{15}N{\equiv}N$]BF_4 were prepared from $Na^{15}NO_2$ (99% enriched, Stohler Isotope Chemicals) and the arylamine (or $NaNO_2$ and labeled arylamine $C_6H_5{}^{15}NH_2$). Substituted phenyl isocyanides were obtained by the phosgene method of Ugi et al.[18] Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer Model 683 spectrophotometer. Solution ^1H NMR spectra were obtained by using Varian EM-390 and Varian FT-80A spectrometers. Spectra were recorded at temperatures varying between -85 and +34 °C, unless otherwise noted, and are referred to internal tetramethylsilane. Fourier-mode, proton-noise-decoupled ^{31}P NMR spectra were collected on a Varian FT-80A spectrometer operating at 32.203 MHz. All 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 -80 °C in CD_2Cl_2 with a standard 180°-τ-90° pulse sequence. Errors are ±10% in T_1 values. Conductivities of 10^{-3} M solutions of the complexes in acetone at 25 °C were measured with

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a Radiometer CDM 83 instrument. Solution susceptibilities were determined by the Evans method.[19]

Synthesis of the Complexes. The hydrides RuH_2P_4 [P = $PhP(OEt)_2$, $P(OEt)_3$, $P(OMe)_3$][20a,b] and OsH_2P_4 [P = $PhP(OEt)_2$, $P(OEt)_3$][20c] were prepared according to the procedures previously reported.

$[RuH(\eta^2\text{-}H_2)P_4]BF_4$ [P = $PhP(OEt)_2$ (1a′), $P(OMe)_3$ (1b′)]. A slight excess of $HBF_4 \cdot Et_2O$ (54% solution) (ca. 0.6 mmol, 87 μL) was added to a solution of RuH_2P_4 (0.5 mmol) in diethyl ether cooled to −80 °C. The reaction mixture was slowly brought to 0 °C under vigorous stirring until a white solid separated after 10–15 min. This was filtered out and recrystallized from CH_2Cl_2 (5 mL) and diethyl ether (30 mL); yield ≥85% for **1a′**, ≥60% for **1b′**.

Data for **1a′**: Λ_M = 146 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2; δ), 7.47 (m, 20 H, Ph), 3.45, 3.14 (m, 16 H, CH_2), 1.02 (t, 24 H, CH_3).

Data for **1b′**: Λ_M = 142 Ω^{-1} M^{-1} cm^2; ^1H NMR (CD_2Cl_2 at 0 °C; δ), 3.47 (m, 36 H, CH_3).

$[RuH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]BF_4$ (1c′). This compound may be prepared in the same way as the related **1a′** and **1b′**. However, as the solid obtained is thermally unstable, the complex was prepared in a NMR tube by adding a slight excess of $HBF_4 \cdot Et_2O$ to a dichloromethane solution of $RuH_2[P(OEt)_3]_4$.

$[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BPh_4$ (1a). A slight excess of $HBF_4 \cdot Et_2O$ (54% solution) (ca. 0.6 mmol, 87 μL) was added to a suspension of RuH_2P_4 (0.5 mmol, 0.45 g) in ethanol cooled to −80° C. The reaction mixture was brought to 0 °C in 10–15 min and stirred until a colorless solution was obtained (5–10 min). The addition of $NaBPh_4$ (0.5 mmol, 0.17 g) afforded a white precipitate, which was filtered out and recrystallized by dissolving in CH_2Cl_2 (3–4 mL) and, after filtration, adding ethanol in excess (20–30 mL); yield ≥80%.

Λ_M = 82.4 Ω^{-1} M^{-1} cm^2. IR (Nujol; cm^{-1}): 2028 w (ν_{MH}). ^1H NMR (CD_2Cl_2; δ): 7.57, 7.35, 6.87 (m, 40 H, Ph), 3.30 (m, 16 H, CH_2), 1.01 (t, 24 H, CH_3), −3.6 (br, 2 H, η^2-H_2), −8.17 (qi, 1 H, hydride). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ): A_2B_2, δ_A 165.8, δ_B 162.6 (J_{AB} = 46.8 Hz).

$[RuD(\eta^2\text{-}D_2)P_4]BF_4$ [P = $PhP(OEt)_2$ (1a′$_1$), $P(OMe)_3$ (1b′$_1$)]. These complexes were prepared by D_2 exchange of a dichloromethane solution of **1a′** or **1b′**. In a typical preparation, 0.5 g of $[RuH(\eta^2\text{-}H_2)P_4]BF_4$ compound in 10 mL of CH_2Cl_2 was allowed to stand under D_2 (1 atm) at 0 °C for 60 min. The solvent was removed under reduced pressure to give a pale yellow oil, which was triturated with diethyl ether. The white solid obtained was filtered out and dried under vacuum; yield ≥90%.

Data for **1a′$_1$**: ^1H NMR (CD_2Cl_2; δ), 7.47 (m, 20 H, Ph), 3.46, 3.14 (m, 16 H, CH_2), 1.02 (t, 24 H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ), 163.5 (s).

Data for **1b′$_1$**: ^1H NMR (CD_2Cl_2; δ), 3.47 (m, 36 H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ), 150.0 (s).

$[RuH(\eta^2\text{-}HD)P_4]BF_4$. These compounds were prepared together with the other isotopomers $[RuD(\eta^2\text{-}HD)P_4]^+$, $[RuH(\eta^2\text{-}D_2)P_4]^+$, and $[RuD(\eta^2\text{-}H_2)P_4]^+$ by HD exchange of **1a′** and **1b′** for 60 min at 0 °C by following the method reported above.

$[OsH(\eta^2\text{-}H_2)P_4]BF_4$ [P = $PhP(OEt)_2$ (1*a′), $P(OEt)_3$ (1*c′)]. A slight excess of $HBF_4 \cdot Et_2O$ (54% solution) (ca. 0.24 mmol, 35 μL) was added to a solution of OsH_2P_4 (0.2 mmol) in 5 mL of diethyl ether cooled to −80 °C. The solution was stirred for 5–10 min and then warmed to about −20 °C in 5–10 min. The white solid that separated out was filtered out and recrystallized from CH_2Cl_2 (3 mL) and diethyl ether (15 mL) at 0 °C; yield ≥85%.

Data for **1*a′**: Λ_M = 151 Ω^{-1} M^{-1} cm^2; ^1H NMR (CD_2Cl_2; δ), 7.44 (m, 20 H, Ph), 3.35 (m, 16 H, CH_2), 1.04 (t, 24 H, CH_3).

Data for **1*c′**: Λ_M = 153 Ω^{-1} M^{-1} cm^2; ^1H NMR (CD_2Cl_2; δ), 3.93 (m, 24 H, CH_2), 1.29 (t, 36 H, CH_3).

$[OsH(\eta^2\text{-}H_2)P_4]BPh_4$ [P = $PhP(OEt)_2$ (1*a), $P(OEt)_3$ (1*c)]. To a suspension of OsH_2P_4 (0.2 mmol) in 10 mL of ethanol was slowly added an excess of $HBF_4 \cdot Et_2O$ (54% solution) (ca. 0.35 mmol, 50 μL) at −80 °C. The reaction mixture was brought to 0 °C and stirred for 30 min. The addition of $NaBPh_4$ (0.22 mmol, 0.076 g) to the resulting solution afforded a white solid, which was recrystallized by dissolving in CH_2Cl_2 (5 mL) and, after filtration, by adding ethanol until the solid separated out; yield ≥75%.

Data for **1*a**: Λ_M = 86.3 Ω^{-1} M^{-1} cm^2; ^1H NMR (CD_2Cl_2; δ), 7.37, 6.92 (m, 40 H, Ph), 3.28 (m, 16 H, CH_2), 0.97 (t, 24 H, CH_3).

Data for **1*c**: Ω_M = 90.1 Ω^{-1} M^{-1} cm^2; IR (KBr; cm^{-1}), 1958 vw (ν_{MH}); ^1H NMR (CD_2Cl_2; δ), 7.30, 6.98 (m, 20 H, Ph), 3.94 (m, 24 H, CH_2), 1.27 (t, 36 H, CH_3), −8.36 (qi, 3 H, hydride and η^2-H_2, $J_{PH_{app}}$ = 3 Hz) [at −70 °C, −7.9 (br, 3 H, hydride and η^2-H_2)]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ), 99.9 (s) [at −70 °C, 103.5 (s)].

$[RuH(CO)\{PhP(OEt)_2\}_4]BPh_4$ (2a). A solution of $[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$ (0.2 mmol, 0.2 g) in 10 mL of dichloromethane was stirred at room temperature under CO (1 atm) for 10 min and the solvent evaporated to dryness. The oil obtained was treated with ethanol containing $NaBPh_4$ (0.22 mmol, 0.076 g) to give a white solid, which was filtered out and recrystallized from CH_2Cl_2 (5 mL) and ethanol (20 mL); yield ≥90%.

Λ_M = 84.7 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2; δ): 7.48, 7.37, 6.97 (m, 40 H, Ph), 3.53 (m, 16 H, CH_2), 1.10 (t, 24 H, CH_3).

$[RuH(4\text{-}CH_3C_6H_4NC)\{PhP(OEt)_2\}_4]BPh_4$ (3a). 4-Tolyl isocyanide (0.24 mmol, 29 μL) was added to a solution of $[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$ (0.2 mmol, 0.2 g) in 10 mL of CH_2Cl_2 and the reaction mixture stirred for 10 min. Removal of the solvent gave a pale yellow oil, which was treated with ethanol (10 mL). The addition of $NaBPh_4$ (0.25 mmol, 0.086 g) to the resulting solution caused the separation of a white solid, which was recrystallized from ethanol; yield ≥90%.

Λ_M = 83.8 Ω^{-1} M^{-1} cm^2. ^1H NMR [$(CD_3)_2CO$; δ]: 7.59, 7.35, 6.88 (m, 44 H, Ph), 3.66 (m, 16 H, CH_2), 2.41 (s, 3 H, CH_3), 1.14 (t, 24 H, phosphine CH_3).

$[OsH(4\text{-}CH_3C_6H_4NC)\{PhP(OEt)_2\}_4]BF_4$ (3*a′). A slight excess of 4-tolyl isocyanide (0.1 mmol, 12 μL) was added to a solution of $[OsH(\eta^2\text{-}H_2)P_4]BF_4$ (0.075 mmol, 0.080 g) in 5 mL of 1,2-dichloroethane and the reaction mixture refluxed for 3 h. The solvent was removed under reduced pressure, giving an oil that was triturated with ethanol (10 mL), affording a white solid that was filtered out and recrystallized from CH_2Cl_2 (5 mL) and ethanol (20 mL); yield ≥90%.

Λ_M = 150 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2; δ): 7.43, 7.29 (m, 24 H, Ph), 3.58 (m, 16 H, CH_2), 2.43 (s, 3 H, CH_3), 1.13 (t, 24 H, phosphine CH_3).

$[OsH(4\text{-}CH_3C_6H_4NC)\{P(OEt)_3\}_4]BPh_4$ (3*c). This complex was prepared exactly like compound **3*a′**, starting from the $[OsH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]BPh_4$ derivative; yield ≥85%.

Λ_M = 92.9 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2; δ): 7.26, 6.97 (m, 24 H, Ph), 4.00 (m, 24 H, CH_2), 2.35 (s, 3 H, CH_3), 1.25 (t, 36 H, phosphine CH_3).

$[RuH(4\text{-}CH_3C_6H_4CN)\{PhP(OEt)_2\}_4]BPh_4$ (4a). A slight excess of 4-tolunitrile (0.26 mmol, 30 μL) was added to a solution of $[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$ (0.2 mmol, 0.2 g) in 10 mL of $ClCH_2CH_2Cl$ and the reaction mixture refluxed for 1 h. The solvent was evaporated to dryness, giving a pale yellow oil that was triturated with ethanol (10 mL). The addition of $NaBPh_4$ (0.3 mmol, 0.1 g) to the resulting solution gave a white solid, which was filtered out and recrystallized from CH_2Cl_2 (5 mL) and ethanol (10 mL); yield ≥75%.

Λ_M = 82.7 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2; δ): 7.29, 6.96 (m, 44 H, Ph), 3.86 (m, 16 H, CH_2), 2.39 (s, 3 H, CH_3), 1.28 (t, 24 H, phosphine CH_3).

$[RuHP_5]BPh_4$ (5a) and $[RuH\{P(OEt)_3\}P_4]BPh_4$ (6a) [P = $PhP(OEt)_2$]. The appropriate phosphite (0.22 mmol) was added to a solution of $[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$ (0.2 mmol, 0.2 g) in 10 mL of CH_2Cl_2. The reaction mixture was stirred for 3 h at room temperature and the solvent evaporated to dryness. The resulting oil was triturated with ethanol (10 mL) containing $NaBPh_4$ (0.25 mmol, 0.086 g) to afford a white solid, which was recrystallized from CH_2Cl_2 (5 mL) and ethanol (20 mL); yield ≥80%.

Data for **5a**: Λ_M = 80.9 Ω^{-1} M^{-1} cm^2; ^1H NMR [$(CD_3)_2CO$; δ], 7.63, 7.40, 6.87 (m, 45 H, Ph), 3.54 (m, 20 H, CH_2), 1.18, 1.13 (t, 30 H, CH_3).

Data for **6a**: Λ_M = 84.2 Ω^{-1} M^{-1} cm^2; ^1H NMR (CD_2Cl_2, δ), 7.57, 7.32, 6.96 (m, 40 H, Ph), 3.59 (m, 22 H, CH_2), 1.14, 1.02 (t, 33 H, CH_3).

$[OsH\{P(OEt)_3\}\{PhP(OEt)_2\}_4]BF_4$ (6*a′). An excess of the appropriate phosphite, $P(OEt)_3$ (0.25 mmol, 42 μL), was added to a solution of $[OsH(\eta^2\text{-}H_2)P_4]BF_4$ (0.17 mmol) in 10 mL of $ClCH_2CH_2Cl$ and the reaction mixture refluxed for 3 h. The solvent was removed under reduced pressure to give an oil, which was treated with ethanol (5 mL). The resulting solution was stirred for 1 h and then cooled to 5 °C to afford light blue mirocrystals of the complex; yield ≥70%.

Λ_M = 148 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2; δ): 7.56, 7.33 (m, 20 H, Ph), 3.62 (m, 22 H, CH_2), 1.17, 1.03 (t, 33 H, CH_3).

$[OsH\{PhP(OEt)_2\}\{P(OEt)_3\}_4]BPh_4$ (6*c). This complex was prepared exactly like **6*a′**, starting from the $[OsH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]BPh_4$ derivative; yield ≥70%.

Λ_M = 95.6 Ω^{-1} M^{-1} cm^2. ^1H NMR (CD_2Cl_2; δ): 7.96, 7.37, 6.88 (m, 25 H, Ph), 4.03 (m, 28 H, CH_2), 1.33, 1.26, 1.17 (t, 42 H, CH_3).

$[Ru(4\text{-}CH_3C_6H_4N{=}NH)\{PhP(OEt)_2\}_4]Y_2$ [Y = BF_4^- (7a′), BPh_4^- (7a)]. A solution of $[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$ (0.2 mmol, 0.2 g) in 10 mL of anhydrous acetone was cooled to 0 °C and transferred into

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a reaction flask containing 0.2 mmol (0.042 g) of the $[4\text{-}CH_3C_6H_4N_2]BF_4$ arenediazonium salt. The reaction mixture was stirred at 0 °C for 3.5 h and the solution brought to dryness at reduced pressure. The oil obtained was triturated with ethanol, giving, after 10 min, orange microcrystals of $[Ru(4\text{-}CH_3C_6H_4N{=}NH)P_4](BF_4)_2$, which were filtered out and dried under vacuum. The addition of $NaBPh_4$ (0.2 mmol, 0.07 g) to the remaining solution caused the separation of $[Ru(4\text{-}CH_3C_6H_4N{=}NH)P_4](BPh_4)_2$ as a yellow-orange solid, which was filtered out. Both of the complexes were recrystallized by dissolving the solid in CH_2Cl_2 (5 mL) and, after filtration, by adding ethanol drop by drop until the solid separated out; yield for **7a′** ≥20%, for **7a** ≥65%.

Data for **7a′**: $\Lambda_M = 293\ \Omega^{-1}\ M^{-1}\ cm^2$; ^1H NMR (CD_2Cl_2; δ), 12.4 (br, 1 H, NH), 7.63, 7.27, 6.85 (m, 24 H, Ph), 3.91 (m, 16 H, CH_2), 2.42 (s, 3 H, CH_3), 1.41, 1.18 (t, 24 H, phosphine CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ), ABC_2, δ_A 160.9, δ_B 157.8, δ_C 146.3 ($J_{AB} = 58.4$, $J_{AC} = 47.0$, $J_{BC} = 47.0$ Hz).

Data for **7a**: $\Lambda_M = 173\ \Omega^{-1}\ M^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2; δ), 12.4 (br, 1 H, NH), 7.57, 7.30, 6.91 (m, 64 H, Ph), 3.85 (m, 16 H, CH_2), 2.42 (s, 3 H, CH_3), 1.37, 1.15, 1.07 (t, 24 H, phosphine CH_3).

$[Ru(C_6H_5N{=}^{15}NH)\{PhP(OEt)_2\}_4](BPh_4)_2$ (7a$_1$) and $[Ru(C_6H_5{}^{15}N{=}NH)\{PhP(OEt)_2\}_4](BPh_4)_2$ (7a$_2$). These complexes were prepared exactly like **7a** by using respectively the labeled $[C_6H_5N{\equiv}^{15}N]BF_4$ and $[C_6H_5{}^{15}N{\equiv}N]BF_4$ diazonium salts; yield ≥65%.

Data for **7a$_1$**: $\Lambda_M = 171\ \Omega^{-1}\ M^{-1}\ cm^2$; ^1H NMR (CD_2Cl_2; δ), 12.4 (d of m, 1 H, NH; $^1J_{^{15}NH} = 66$ Hz), 7.57, 7.31, 6.91 (m, 65 H, Ph), 3.80 (m, 16 H, CH_2), 1.31, 1.07, 1.03 (t, 24 H, CH_3).

Data for **7a$_2$**: $\Lambda_M = 176\ \Omega^{-1}\ M^{-1}\ cm^2$; ^1H NMR (CD_2Cl_2; δ), 12.5 (m, 1 H, NH), 7.57, 7.28, 6.92 (m, 65 H, Ph), 3.80 (m, 16 H, CH_2), 1.33, 1.10, 1.08 (t, 24 H, CH_3).

$[Ru(4\text{-}CH_3C_6H_4N{=}NH)\{P(OMe)_3\}_4](BPh_4)_2$ (7b). This compound was prepared by following the method reported above for **7a**, starting from $[RuH(\eta^2\text{-}H_2)\{P(OMe)_3\}_4]BF_4$; yield ≥75%.

$\Lambda_M = 178\ \Omega^{-1}\ M^{-1}\ cm^2$. ^1H NMR (CD_2Cl_2; δ): 13.7 (br, 1 H, NH), 7.33, 6.97 (m, 44 H, Ph), 3.59 (m, 36 H, phosphine CH_3), 2.45 (s, 3 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ): ABC_2, δ_A 134.2, δ_B 132.3, δ_C 120.8 ($J_{AB} = 77.0$, $J_{AC} = 60.0$, $J_{BC} = 61.2$ Hz).

$[RuH(4\text{-}CH_3C_6H_4N{=}NH)P_4]BPh_4$ [P = $PhP(OEt)_2$ (8a), $P(OMe)_3$ (8b)]. A solution of RuH_2P_4 (0.2 mmol) in 10 mL of CH_2Cl_2 was cooled to −80 °C and quickly transferred into a reaction flask containing 0.2 mmol (0.041 g) of $[4\text{-}CH_3C_6H_4N_2]BF_4$ arenediazonium salt. The reaction mixture was brought to room temperature and stirred for 2 h. The solvent was removed under reduced pressure, leaving an oil that was triturated with ethanol or methanol (10 mL) to give a yellow solution. The addition of $NaBPh_4$ (0.25 mmol, 0.086 g) afforded a yellow solid, which was filtered out, dissolved in alcohol to saturation at 25 °C, and then crystallized by slow cooling to −30 °C; yield ≥85%.

Data for **8a**: $\Lambda_M = 92.0\ \Omega^{-1}\ M^{-1}\ cm^2$; ^1H NMR (CD_2Cl_2; δ), 13.67 (m, 1 H, NH), 7.23, 6.97 (m, 44 H, Ph), 3.65 (m, 16 H, CH_2), 2.42 (s, 3 H, CH_3).

Data for **8b**: $\Lambda_M = 91.7\ \Omega^{-1}\ M^{-1}\ cm^2$; ^1H NMR [$(CD_3)_2CO$; δ], 13.8 (br, 1 H, NH), 7.34, 6.89 (m, 24 H, Ph), 3.72 (d), 3.66 (t), 3.58 (d, 36 H, phosphine CH_3), 2.36 (s, 3 H, CH_3).

$[Ru(4\text{-}CH_3C_6H_4N{=}NH)_2P_4](BPh_4)_2$ [P = $PhP(OEt)_2$ (9a), $P(OMe)_3$ (9b)]. A solution of RuH_2P_4 (0.3 mmol) in 20 mL of CH_2Cl_2 was cooled to −80 °C and quickly transferred into a reaction flask containing an excess of the arenediazonium salt $[4\text{-}CH_3C_6H_4N_2]BF_4$ (0.9 mmol, 0.185 g). The reaction mixture, brought to room temperature, was stirred for 3 h and then filtered to separate the unreacted diazonium salt. The solution was evaporated to dryness to give a yellow oil, which was treated with ethanol or methanol (10 mL). The addition of $NaBPh_4$ (0.7 mmol, 0.24 g) to the resulting solution afforded a yellow solid, which was filtered out and recrystallized from CH_2Cl_2 (5 mL) and ethanol or methanol (15–20 mL). In some cases, the ^1H NMR spectra of the $PhP(OEt)_2$ derivative **9a** showed the presence of a small amount of the pentacoordinate mono(diazene) $[Ru(ArN{=}NH)P_4](BPh_4)_2$ complex, which could be removed by repeated crystallization. For example, the slow cooling to −30 °C of a saturated solution of the complex in ethanol/dichloromethane (15/3 mL) afforded yellow crystals of pure $[Ru(4\text{-}CH_3C_6H_4N{=}NH)_2\{PhP(OEt)_2\}_4](BPh_4)_2$ derivative; yield ≥65%.

Data for **9b**: $\Lambda_M = 171\ \Omega^{-1}\ M^{-1}\ cm^2$; ^1H NMR (CD_2Cl_2; δ), 13.74 (m, 2 H, NH), 7.42, 7.25, 6.94 (m, 48 H, Ph), 3.73, 3.50 (t, 36 H, phosphine CH_3), 2.47 (s, 6 H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ), A_2B_2, δ_A 131.1, δ_B 120.8 ($J_{AB} = 60.1$ Hz).

$[Ru(4\text{-}CH_3C_6H_4N_2)P_4]BPh_4$ [P = $PhP(OEt)_2$ (10a), $P(OMe)_3$ (10b)]. Triethylamine (0.3 mmol, 45 μL) was added to a solution of the appropriate bis(diazene) complex $[Ru(ArN{=}NH)_2P_4](BPh_4)_2$ (0.2 mmol) in dichloromethane (5 mL) and the reaction mixture stirred for 2 h. A white solid $[(Et_3NH)BPh_4]$ began to separate out after 30 min and, at the end of the reaction, was separated by filtration. The remaining solution was evaporated to dryness and the oil obtained treated with ethanol or methanol (10 mL) to give a yellow solution, which was cooled to −4 °C. The separated solid was filtered off, and further cooling to −30 °C yielded yellow microcrystals of the $[Ru(ArN_2)P_4]BPh_4$ compound; yield ≥75%.

Data for **10a**: $\Lambda_M = 82.6\ \Omega^{-1}\ M^{-1}\ cm^2$; ^1H NMR [$(CD_3)_2CO$, δ], 7.16, 6.75 (m, 44 H, Ph), 3.58 (m, 16 H, CH_2), 2.28 (s, 3 H, CH_3), 1.18 (t, 24 H, phosphine CH_3).

Data for **10b**: $\Lambda_M = 83.3\ \Omega^{-1}\ M^{-1}\ cm^2$; IR ($CH_2Cl_2$; cm^{-1}), 1652 m (ν_{NN}); ^1H NMR [$(CD_3)_2CO$; δ], 7.33, 6.90 (m, 24 H, Ph), 3.64 (m, 36 H, phosphine CH_3), 2.39 (s, 3 H, CH_3); $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$ at −50 °C; δ], ABC_2, δ_A 153.9, δ_B 151.5, δ_C 135.9 ($J_{AB} = 85.9$, $J_{AC} = 51.3$, $J_{BC} = 53.3$ Hz).

Results and Discussion

The reactions of the hydride complexes MH_2P_4 [M = Ru, Os; P = $PhP(OEt)_2$, $P(OEt)_3$, $P(OMe)_3$] with $HBF_4{\cdot}Et_2O$ in diethyl ether at low temperature (−60 °C) gave the molecular hydrogen complexes $[MH(\eta^2\text{-}H_2)P_4]BF_4$ (**1′**, **1*′**). The reactions were also carried out in alcohol as the solvent from which the complexes were isolated as BPh_4^- salts. The osmium compounds $[OsH(\eta^2\text{-}H_2)P_4]^+$ (**1***) are very stable both as solids and in organic polar solutions, and evolution of H_2 does not take place either at room temperature or at +80 °C. On the other hand, the stability of the ruthenium complexes depends on the phosphite used. While $PhP(OEt)_2$ derivative $[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$ (**1a′**) shows stability similar to that of the osmium compound, the analogous $[RuH(\eta^2\text{-}H_2)\{P(OMe)_3\}_4]BF_4$ (**1b′**) is rather unstable (loss of H_2) and can only be handled at +20 °C for a short time. The $[RuH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]BF_4$ (**1c′**) derivative, which is also thermally unstable, decomposes with evolution of H_2 even at −30 °C, both as a solid and in solution, and its characterization is only given by the ^1H NMR spectra. The exchange of the H_2 ligand with D_2 gas in solution is fast for the ruthenium complexes, and pure samples of the $[RuD(\eta^2\text{-}D_2)P_4]^+$ derivatives can be obtained after 1 h of exchange reaction at 0 °C. In contrast, exchange with D_2 gas was not observed for the osmium derivatives $[OsH(\eta^2\text{-}H_2)P_4]BPh_4$ (**1*a**, **1*c**) even after 48 h at reflux in hexadeuterioacetone.

Selected spectroscopic properties of the dihydrogen complexes, which are white solids, diamagnetic, and 1:1 electrolytes, are reported in Table I. The infrared spectra of the ruthenium complexes show weak bands at 2030–2028 cm^{-1}, which disappear in the deuterated $[MD(\eta^2\text{-}D_2)P_4]^+$ compounds. These ν_{MH} bands for the osmium derivatives are in the 2040–1950-cm^{-1} range. No other absorption bands due to the modes of most interest, ν_{HH} and ν_{MH_2}, or ν_{HD} in the mixture of isotopomers containing $[MH(\eta^2\text{-}HD)P_4]^+$, were observed, probably because these bands either are too weak to be seen or are obscured by the more intense ν_{CC} and ν_{CH} absorptions.[1d]

The ^1H NMR spectra of the $[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$ (**1a′**) complex at room temperature show a broad signal at δ −3.6 and a quintet at δ −8.17 in the high-field region. Decreasing the sample temperature does not change the broad signal, but the quintet appears as a well-resolved multiplet at −70 °C (Figure 1). Measurements of the relaxation time[21] of these signals give at −70 °C a mean value of 90 ms for the multiplet, attributed to the hydride resonance, whereas a very short T_1 value of 5 ms characteristic of $\eta^2\text{-}H_2$ ligands[1d,2b–d] is found for the broad signal at δ −3.8. To support these assignments further, we recorded the ^1H NMR spectra of the isotopomer $[RuH(\eta^2\text{-}HD)\{PhP(OEt)_2\}_4]^+$ and observed the $^1J_{HD}$ coupling of 32 Hz to be ca. a 1:1:1 triplet in the position we had previously identified with the dihydrogen resonance (δ −3.8). This value, which is close to those reported for other HD complexes,[1–5] confirms the proposed assignment. Moreover, as expected,[1b] we also found that the T_1 value for $\eta^2\text{-}H_2$ resonance increases when HD is substituted by H_2, i.e. 20 ms for η^2-HD and 5 ms for $\eta^2\text{-}H_2$ at −70 °C. Finally, the relaxation times for the H^- and H_2 resonances begin to average on warming, owing to proton exchange[3b] between the lone hydride with the two hy-

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(21) T_1's were measured between +30 and −80 °C, and no minimum values[2d] for T_1 were observed in this temperature range at 80 MHz. Measurements at different frequencies (200 and 400 MHz) are in progress.

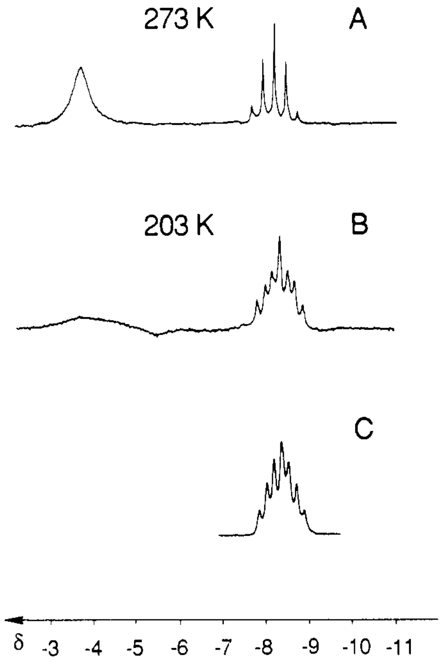


Figure 1. Observed ^1H NMR spectra in the hydride region of $[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$ (**1a′**) at 0 °C (A) and at −70 °C (B) in CD_2Cl_2. The simulated spectrum (C) was obtained with the following parameters: spin system A_2B_2X (X = H), δ_A 165.9, δ_B 162.7, δ_X −8.39, J_{AB} = 47.0, J_{AX} = −28.1, J_{BX} = −13.0; line width at half-height 8 Hz.

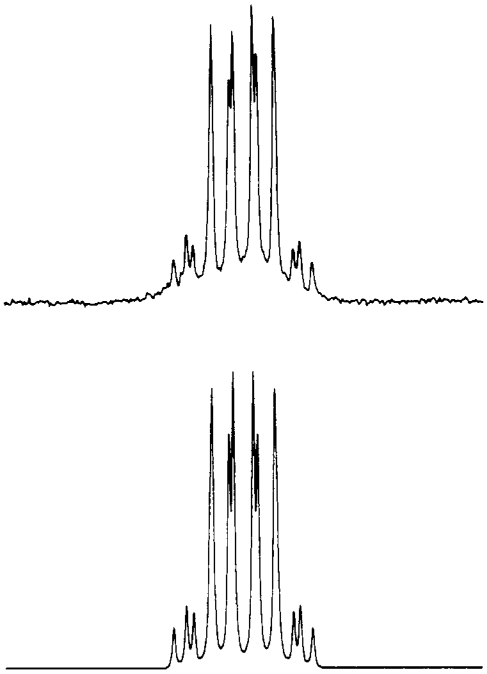
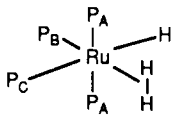


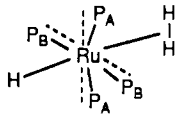
Figure 2. Observed (top) and calculated (bottom) $^{31}P\{^1H\}$ NMR spectra of $[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$ (**1a′**) at −70 °C in CD_2Cl_2. The simulated spectrum was obtained with parameters given in Table I.

drogen atoms,[22] and values of 18 ms for $\eta^2\text{-}H_2$ and 47 ms for H^- are found at +30 °C.

At room temperature the $^{31}P\{^1H\}$ NMR spectrum of complex $[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BPh_4$ (**1a**) consists of a broad singlet at δ 163.4. Lowering the sample temperature produces a complex sequence of changes until at −70 °C an A_2B_2 multiplet appears (Figure 2), which can be simulated with the parameters reported in Table I. An octahedral structure with the H^- and H_2 ligands in a trans position for the complex in solution, having a sharp singlet, should be excluded. On the other hand, for cis geometry (I), an A_2BC spectrum would be expected. However, the difference in chemical shifts of the two phosphorus nuclei trans to H^- and H_2 may be so small that, within the experimental line width, an A_2B_2 pattern consistent with cis geometry (I) is observed. An alternative explanation involves the existence of a distorted octahedral structure with trans geometry (II) in which, for example, trans-phosphorus atoms P_A are closer to the H_2 ligand and trans-phosphorus atoms P_B are closer to the H^- ligand. For such a structure an A_2B_2 ^{31}P spectrum is expected, as previously observed in the $RuHCl(P\text{-}P)_2$ complex,[23] whose X-ray structure indicates trans geometry with inequivalent phosphorus atoms. ^1H NMR spectra are also consistent with a distorted trans geometry, showing an A_2B_2X multiplet at −70 °C for the hydride resonance (Figure 1). Furthermore, the presence of well-separated resonances for H^- and $\eta^2\text{-}H_2$ seems to indicate slow exchange of H atoms between H_2 and H^- ligands, as expected for the mutually trans positions of these two ligands. The X-ray structure of the complex was not determined due to the poor quality of the crystals obtained, and in the absence of other data, any further discussion is purely speculative.



I



II

At 0 °C, in the high-field region of its ^1H NMR spectrum, the $[RuH(\eta^2\text{-}H_2)\{P(OMe)_3\}_4]^+$ (**1b**) derivative also shows a broad signal at δ −4.5 attributed to the $\eta^2\text{-}H_2$ resonance and a sharp quintet at δ −9.69 assigned to the hydride ligand. This spectrum does not change on cooling the sample, and T_1 measurements at −70 °C, which give a mean value of 4 ms for the broad signal ($\eta^2\text{-}H_2$) and 180 ms for the quintet (H^-), confirm the proposed formulation. Furthermore, the isotopomer $[RuH(\eta^2\text{-}HD)\{P(OMe)_3\}_4]BF_4$ shows a 1:1:1 triplet at δ −4.40 with $^1J_{HD}$ = 31 Hz, in agreement with the existence of a molecular hydrogen ligand in **1b**.[1-5] In the temperature range between +30 and −85 °C, the $^{31}P\{^1H\}$ NMR spectra show only one sharp singlet, suggesting a trans geometry for these complexes. The $[RuH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]BF_4$ (**1c′**) derivative is thermally unstable and cannot be isolated in pure form. However, the ^1H NMR spectra, which show a broad signal at δ −4.9 (T_1 = 3 ms at −70 °C) attributed to $\eta^2\text{-}H_2$ and a quintet at δ −9.50 (T_1 = 195 ms at −70 °C) due to an H^- resonance, confirm its formulation. Furthermore, the observation of a sharp singlet in the $^{31}P\{^1H\}$ NMR spectra between −30 and −80 °C provides evidence of a trans geometry for this compound.

A slightly different feature is shown by the ^1H NMR spectra of the osmium complexes $[OsH(\eta^2\text{-}H_2)P_4]BPh_4$ (**1*a**, **1*c**). At room temperature, in the high-field region, the $PhP(OEt)_2$ compound **1*a** exhibits only one quintet at δ −6.86, which collapses at about 0 °C to a broad signal. Further lowering of the temperature changes the spectrum. At −70 °C a sharp multiplet at δ −6.50 with T_1 = 44 ms due to the hydride ligand and a broad singlet at δ −7.0 with the short T_1 value of 8 ms due to the $\eta^2\text{-}H_2$ ligand are observed. The $P(OEt)_3$ derivative **1*c** also shows, at +30 °C, one quintet at δ −8.36, which collapses at about 0 °C to a broad signal. However, further lowering of the temperature does not change the profile of the spectra and even at −85 °C only one broad signal is present. T_1 measurements at this temperature give a mean value of 10 ms, in agreement with the formulation as a molecular hydrogen rather than a trihydride complex. Further reduction of the temperature below −85 °C would probably show both the hydride and $\eta^2\text{-}H_2$ resonances in the ^1H NMR spectra, as observed in the related $PhP(OEt)_2$ derivative.

At room temperature both complexes $[OsH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BPh_4$ and $[OsH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]BPh_4$ (**1*a**, **1*c**) show

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[22] However, this exchange should be rather slow at room temperature on the NMR time scale, because the two H^- and $\eta^2\text{-}H_2$ resonances are well separated, and the hydride signal is not broad but appears as a quintet. It may also be noted that the coalescence of the two H^- and $\eta^2\text{-}H_2$ resonances was not observed until the sample temperature was increased to +70 °C.

[23] Ball, R. G.; James, B. R.; Trotter, J.; Wang, D. K. W.; Dixon, K. R. *J. Chem. Soc., Chem. Commun.* **1979**, 460.

Table I. Selected Infrared and NMR Data for Ruthenium and Osmium Complexes

		IR^a		^{1}H NMR^{b,c}	^{31}P{^{1}H} NMR^{b-d}	
no.	compd	ν, cm^{-1}	assignt	δ(H hydride) (coupling const)	spin syst	δ(P) (coupling const)
1a′	$[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$	2030 w^e	ν_{MH}	+30 °C: −8.17 qi (H hydr), −3.6 br (η^2-H_2)		163.4 s
				−70 °C: −8.39 m (H hydr), −3.8 br (η^2-H_2)	A_2B_2	δ_A 165.9, δ_B 162.7 (J_{AB} = 47.0)
1b′	$[RuH(\eta^2\text{-}H_2)\{P(OMe)_3\}_4]BF_4$			0 °C: −9.69 qi (H hydr) (J_{PH} = 19), −4.5 br (η^2-H_2)		149.8 s
				−70 °C: −9.69 qi (H hydr) (J_{PH} = 19), −4.6 br (η^2-H_2)		152.4 s
1c′	$[RuH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]BF_4$			−70 °C: −9.50 qi (H hydr) (J_{PH} = 19), −4.9 br (η^2-H_2)		144.9 s
1*a′	$[OsH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$	(2040 w)	ν_{MH}	+30 °C: −6.78 qi ($J_{PH_{app}}$ = 7)		122.2 s
				−70 °C: −6.48 m (H hydr), −6.9 br (η^2-H_2)		121.0 m
1*a	$[OsH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BPh_4$			+30 °C: −6.86 qi ($J_{PH_{app}}$ = 7)		119.6 s
				−70 °C: −6.50 m (H hydr), −7.0 br (η^2-H_2)	$A_2B_2{}^f$	δ_A 124.9, δ_B 119.2 (J_{AB} = 32.5)
1*c′	$[OsH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]BF_4$	(1955 w)	ν_{MH}	+30 °C: −8.34 qi ($J_{PH_{app}}$ = 3)		99.8 s
				−70 °C: −7.9 br		103.2 s
2a	*trans*-$[RuH(CO)\{PhP(OEt)_2\}_4]BPh_4$	2001 s (1999 s)	ν_{CO}	−6.36 qi (J_{PH} = 21)		158.2 s
3a	*trans*-$[RuH(4\text{-}CH_3C_6H_4NC)\{PhP(OEt)_2\}_4]BPh_4$	2102 s (2103 s)	ν_{CN}	−7.43 qi^g (J_{PH} = 20)		161.8 s^g
3*a′	*trans*-$[OsH(4\text{-}CH_3C_6H_4NC)\{PhP(OEt)_2\}_4]BF_4$	2095 s (2103 s)	ν_{CN}	−8.58 qi (J_{PH} = 20)		118.6 s
3*c	*cis*-$[OsH(4\text{-}CH_3C_6H_4NC)\{P(OEt)_3\}_4]BPh_4$	(1970 w) 2134 s, (2142 s)	ν_{MH} ν_{CN}	−10.74 m	ABC_2	δ_A 101.8, δ_B 100.1, δ_C 98.4 (J_{AB} = 39.5, J_{AC} = 47.0, J_{BC} = 32.0)
4a	*trans*-$[RuH(4\text{-}CH_3C_6H_4CN)\{PhP(OEt)_2\}_4]BPh_4$	2256 m	ν_{CN}	−13.96 qi (J_{PH} = 20)		162.7 s
5a	$[RuH\{PhP(OEt)_2\}_5]BPh_4$	(1955 w)	ν_{MH}	−9.15 m^g	A_4B^g	δ_A 161.2, δ_B 158.0 (J_{AB} = 35.0)
6a	*trans*-$[RuH\{P(OEt)_3\}\{PhP(OEt)_2\}_4]BPh_4$	(1943 w)	ν_{MH}	−8.13 qi, −9.51 qi ($J_{PH_{cis}}$ = 19.4, $J_{PH_{trans}}$ = 110)	A_4B	δ_A 162.9, δ_B 133.7 (J_{AB} = 38.0)
6*a′	*trans*-$[OsH\{P(OEt)_3\}\{PhP(OEt)_2\}_4]BF_4$	(2000 w)	ν_{MH}	−9.88 qi, −10.87 qi ($J_{PH_{cis}}$ = 19.85, $J_{PH_{trans}}$ = 79.1)	A_4B	δ_A 118.7, δ_B 93.6 (J_{AB} = 25.8)
6*c	*cis*-$[OsH\{PhP(OEt)_2\}\{P(OEt)_3\}_4]BPh_4$	(2000 w)	ν_{MH}	−11.16 m^g		116.5 m, 96.4 m^g
7a	$[Ru(4\text{-}CH_3C_6H_4N{=}NH)\{PhP(OEt)_2\}_4](BPh_4)_2$				ABC_2	δ_A 160.1, δ_B 157.6, δ_C 145.7 (J_{AB} = 58.8, J_{AC} = 47.0, J_{BC} = 45.0)
7a$_1$	$[Ru(C_6H_5N{=}^{15}NH)\{PhP(OEt)_2\}_4](BPh_4)_2$				ABC_2N	δ_A 160.2, δ_B 156.9, δ_C 145.7 (J_{AB} = 58.4, J_{AC} = 47.0, J_{BC} = 47.0, J_{AN} = 3.5, J_{BN} = 1.0, J_{CN} = 4.8)
7a$_2$	$[Ru(C_6H_5{}^{15}N{=}NH)\{PhP(OEt)_2\}_4](BPh_4)_2$				ABC_2N	δ_A 159.8, δ_B 157.3, δ_C 145.5 (J_{AB} = 58.4, J_{AC} = 47.0, J_{BC} = 47.0, J_{AN} = 0.5, J_{BN} = 4.3, J_{CN} = 1.3)
8a	*trans*-$[RuH(4\text{-}CH_3C_6H_4N{=}NH)\{PhP(OEt)_2\}_4]BPh_4$	(1960 w)	ν_{MH}	−12.86 qi, −12.87 qi (J_{PH} = 19.5, J_{HH} = 1.0^h)		161.7 s
8b	*cis*-$[RuH(4\text{-}CH_3C_6H_4N{=}NH)\{P(OMe)_3\}_4]BPh_4$	(1895 w)	ν_{MH}	−7.28 m^g	AB_2C^g	δ_A 154.2, δ_B 146.2, δ_C 141.6 (J_{AB} = 63.0, J_{AC} = 43.4, J_{BC} = 42.0)
9a	*cis*-$[Ru(4\text{-}CH_3C_6H_4N{=}NH)_2\{PhP(OEt)_2\}_4](BPh_4)_2$				A_2B_2	δ_A 156.5, δ_B 145.7 (J_{AB} = 45.3)
10a	$[Ru(4\text{-}CH_3C_6H_4N_2)\{PhP(OEt)_2\}_4]BPh_4$	1640 m, (1638 m)	ν_{NN}		$ABC_2{}^i$	δ_A 167.5, δ_B 164.9, δ_C 151.5 (J_{AB} = 49.3, J_{AC} = 40.5, J_{BC} = 43.0)

[a] In CH_2Cl_2 and (KBr). [b] At room temperature in CD_2Cl_2, unless otherwise noted. [c] Coupling constants in Hz. [d] Positive shift downfield from 85% H_3PO_4. [e] In nujol mull. [f] ^{31}P{^{1}H} parameters obtained at −85 °C. [g] At room temperature in $(CD_3)_2CO$. [h] Coupling constant between H hydride and H diazene. [i] At −50 °C in $(CD_3)_2CO$.

a sharp singlet in their ^{31}P{^{1}H} NMR spectra. However, at lower temperatures a different behavior is observed for the two complexes. At −80 °C a sharp singlet persists for the $P(OEt)_3$ complex, in agreement with a trans geometry for **1*c**, while an A_2B_2 multiplet appears in the spectrum for the $PhP(OEt)_2$ derivative. As previously discussed for the related ruthenium complex **1a**, the presence of inequivalent phosphorus atoms may be interpreted on the basis of the existence of cis geometry or, more probably, of a distorted octahedral structure with trans geometry for **1a**.

The NMR spectra of our complexes do not indicate any evidence of the existence of an equilibrium between classical and nonclassical structures. The formation of a trihydride species of the type $[MH_3P_4]^+$ should in fact give a new hydride signal. The η^2-H_2 and H^- resonances in the high-field region of the ^{1}H NMR due to the $[MH(\eta^2\text{-}H_2)P_4]^+$ derivatives were observed at all temperatures in our study. This feature was expected, because H–H bond scission should be favored by basic ligands.[1d,e,11] Our phosphites are more acidic than the bidentate tertiary phosphine $R_2PCH_2CH_2PR_2$, for which exclusively nonclassical structures are observed for the related $[RuH(\eta^2\text{-}H_2)(P\text{-}P)_2]^+$ and $[OsH(\eta^2\text{-}H_2)(P\text{-}P)_2]^+$ derivatives.[3]

The NMR properties (^{1}H and T_1) of the three molecular hydrogen complexes $[MH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]^+$ (M = Fe, Ru, Os) are provided in Table II. The data show that while for the iron and ruthenium complexes the chemical shift differences between η^2-H_2 and H^- resonances are large (+3.1 and +4.5 ppm), the difference of −0.5 ppm for the osmium complex is small. Furthermore, the T_1 values (in milliseconds) for the η^2-H_2 resonance

Table II. Comparison between ^{1}H NMR Data for Fe, Ru, and Os Dihydrogen Complexes

compd	resonance	chem shift, δ^{a}	$\Delta\delta$	T_1,[a] ms	$T_1(H^-)/T_1(H_2)$
$[FeH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BPh_4$[b]	H^-	−10.30 m	+3.1	65	16
	$\eta^2\text{-}H_2$	−7.2 br		4	
$[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BPh_4$[c]	H^-	−8.30 m	+4.5	90	18
	$\eta^2\text{-}H_2$	−3.8 br		5	
$[OsH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BPh_4$	H^-	−6.50 m	−0.5	44	5.5
	$\eta^2\text{-}H_2$	−7.0 br		8	

[a] Values at −70 °C in CD_2Cl_2 obtained at 80 MHz. [b] Reference 12. [c] $^{1}J_{HD}$ = 32 Hz. For the Fe and Os derivatives the J_{HD} value had not been obtained.

increase in the order Fe (4) < Ru (5) < Os (8). The $H^-/\eta^2\text{-}H_2$ T_1 ratios are comparable for Fe and Ru (16 and 18) and similar to those previously reported for other dihydrogen complexes,[2,3,10b] whereas a very low value (about 5) was observed for the osmium complex. We can thus hypothesize a longer H–H bond and hence a greater hydridic character of the $\eta^2\text{-}H_2$ ligand in the osmium complexes as compared to the Fe and Ru analogues. Although the absence of the J_{HD} value[24] for the osmium complexes does not confirm this hypothesis, the different reactivities of the complexes support our proposal. It may also be noted that a longer H–H bond in osmium complexes,[3f] as well as the occasional breaking of the H–H bond to give a classical structure[2b] has been observed.

Studies on the chemical properties of dihydrogen complexes $[MH(\eta^2\text{-}H_2)P_4]^+$ (**1**, **1***) showed that they can easily be deprotonated with triethylamine at room temperature to give the MH_2P_4 dihydride precursors. Furthermore, the H_2 ligand in **1** and **1*** may be substituted by several ligands such as CO, CNR, phosphite, etc., affording new monohydrides of the type $[MHLP_4]^+$ (eq 1). Substitution of dihydrogen is fast at room temperature

$$[MH(\eta^2\text{-}H_2)P_4]^+ + L \rightarrow [MHLP_4]^+ + H_2 \qquad (1)$$

$$L = CO, CNR, P(OEt)_3, PhP(OEt)_2;\ M = Ru, Os$$

for the ruthenium complexes, whereas reflux conditions are required for the osmium complexes. The slow substitution of dihydrogen in the osmium compound therefore fits the ^{1}H NMR data, which seem to indicate some hydridic character of the H_2 ligand. It can also be observed that the substitution of the $P(OMe)_3$ ligand in the $[RuH(\eta^2\text{-}H_2)\{P(OMe)_3\}_4]BF_4$ complex **1b′** by CO or CNR is also fast at room temperature to always give mixtures of $[RuHLP_4]^+$ and $[RuHL_2P_3]^+$ derivatives. Similarly, pure $[OsH(CO)P_4]BPh_4$ compounds could not be isolated because of the presence of the dicarbonyl species in the final product.

Some spectroscopic properties of the new $[MHLP_4]BPh_4$ monohydrides, which are stable, diamagnetic, and 1:1 electrolytes, are shown in Table I. The $^{31}P\{^{1}H\}$ NMR spectra between +30 and −80 °C, which show only one singlet for the carbonyl **2a**, isocyanide **3a**, and nitrile **4a** compounds, indicate the existence in solution of the trans geometry for the $[RuHLP_4]^+$ complexes, whereas an A_4B multiplet appears in the spectrum of the pentakis(phosphite) $[RuHLP_4]^+$ (**5a**, **6a**) derivatives. On the other hand, the geometry in solution for the osmium complexes depends on the nature of the phosphite ligand. While the structure for $PhP(OEt)_2$ is trans, the cis geometry can be proposed for the $P(OEt)_3$ compounds in solution on the basis of the complicated multiplets that appear in their $^{31}P\{^{1}H\}$ NMR spectra.

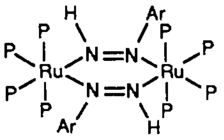
Monohydrido complexes of ruthenium containing phosphite ligands are rather rare,[13b] and monohydrido phosphite complexes have not been reported for osmium.[20c] The use of dihydrogen complexes as precursors represents a convenient method of synthesis of the new series of ruthenium(II) and osmium(II) phosphite monohydride derivatives.

Reactivity with Arenediazonium Cations. The $[RuH(\eta^2\text{-}H_2)P_4]BF_4$ compounds **1a′** and **1b′** rapidly react with arenediazonium cations in acetone or dichloromethane to give the mono(diazene) pentacoordinate $[Ru(ArN{=}NH)P_4]^{2+}$ (cations of **7**), which can be isolated as both BF_4^- or BPh_4^- salts. In contrast, the osmium derivatives $[OsH(\eta^2\text{-}H_2)P_4]^+$ are unreactive toward ArN_2^+ and can be recovered unchanged after 24 h of stirring at room temperature. It may be noted that when the reaction between the dihydrogen complexes and the arenediazonium cations is carried out in nonrigorously anhydrous solvents (acetone or CH_2Cl_2), the final product contains not only **7** but also the bis(aryldiazene) $[Ru(ArN{=}NH)_2P_4]^{2+}$ cation, whose presence was deduced from the ^{1}H and ^{31}P NMR spectra of the mixture. The formation of such a compound under these conditions may tentatively be explained (Scheme I) on the basis of a deprotonation reaction of the dihydrogen complex due to traces of water in the solvent, giving the dihydride species RuH_2P_4, which is known (see Scheme I) to react with ArN_2^+ to afford the bis(aryldiazene) derivatives.

Scheme I

$$[RuH(\eta^2\text{-}H_2)P_4]^+ \xrightarrow{-H^+} RuH_2P_4 \xrightarrow{ArN_2^+} [Ru(ArN{=}NH)_2P_4]^{2+}$$

Some spectroscopic properties of the diazene $[Ru(ArN{=}NH)P_4]Y_2$ complexes, which are orange-yellow solids, diamagnetic, and 2:1 electrolytes, are reported in Table I. The ^{1}H NMR spectra show a broad singlet at δ 12.45 attributed to the NH resonance, which is split into two multiplets in the labeled ^{15}N compounds ($J_{^{15}NH}$ = 65 Hz), in agreement with the proposed formulation. In the temperature range between +30 and −80 °C the $^{31}P\{^{1}H\}$ NMR spectra of the $[Ru(ArN{=}NH)P_4]^{2+}$ derivatives appear as a multiplet, which can be readily simulated by using an ABC_2 model with the parameters reported in Table I. These data, however, do not allow assignment of an unambiguous geometry in solution for the diazene complexes, and the only reasonable assumption we can make is the exclusion of a regular TBP geometry for which an A_2B_2 or AB_3 spectra would be expected. The ABC_2 spectra would suggest both a square-pyramidal structure and a TBP distorted toward SP geometry for **7**. Furthermore, an octahedral geometry with two diazene bridges should also give such ^{31}P spectra. In order to test this possibility, we prepared ^{15}N-labeled compounds $[Ru(C_6H_5N{\equiv}{}^{15}NH)\{PhP(OEt)_2\}_4]^{2+}$ (**7a**$_1$) and $[Ru(C_6H_5{}^{15}N{\equiv}NH)\{PhP(OEt)_2\}_4]^{2+}$ (**7a**$_2$) and recorded the corresponding ^{31}P spectra. The different spectra with a change in the coupling constants between the ^{15}N and phosphorus atoms for the two compounds (Table I) exclude the existence of a dimeric species of type III because similar ^{31}P spectra would be expected for **7a**$_1$ and **7a**$_2$.



III

We have previously reported[12] that the reaction of the related iron $[FeH(\eta^2\text{-}H_2)P_4]BPh_4$ complexes with arenediazonium cations affords the bis(aryldiazenido) derivatives $[Fe(ArN_2)_2P_3](BPh_4)_2$ as final products. The formation of diazene intermediates was demonstrated, which by further reaction gave the $[Fe(ArN_2)_2P_3]^{2+}$

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(24) Since in $[OsH(\eta^2\text{-}H_2)P_4]^+$ derivatives the exchange of the H_2 ligand with D_2 or HD is too slow to be observed, we tried to prepare the isotopomer $[OsH(\eta^2\text{-}HD)P_4]^+$ by reacting hydride OsH_2P_4 with CF_3COOD in diethyl ether. Unfortunately, the compound obtained did not reveal the J_{HD} value because, here too, the $\eta^2\text{-}H_2$ resonance appeared as a broad signal even at −80 °C and not as a 1:1:1 triplet.

final product. In contrast, no evidence for the formation of an analogous bis(diazenido) compound was detected by using different solvents and excess of arenediazonium salt. The different nature and/or properties of the diazene intermediate in iron and ruthenium complexes probably result in different final products in the reaction of η^2-H_2 derivatives with arenediazonium cations.

We also studied the reactivity of the dihydride precursor RuH_2P_4 toward arenediazonium cations in order to compare these results with those obtained with the dihydrogen complexes. We also wished to clarify the influence of the phosphite ligand on the reaction by comparison of our findings with our previous data[13b] on the hydride $RuH_2[P(OEt)_3]_4$. While the $RuH_2[P(OMe)_3]_4$ derivative reacts in CH_2Cl_2 or acetone with arenediazonium cations in a 1:1 ratio or in excess to give six-coordinate $[RuH(ArN{=}NH)P_4]^+$ (**8b**) and $[Ru(ArN{=}NH)_2P_4]^{2+}$ (**9b**) derivatives, respectively, the hydride $RuH_2[PhP(OEt)_2]_4$ reacts in both acetone or CH_2Cl_2 solution with an excess of ArN_2^+ to give a mixture of bis(diazene) $[Ru(ArN{=}NH)_2\{PhP(OEt)_2\}_4]^{2+}$ (**9a**) and the pentacoordinate $[Ru(ArN{=}NH)\{PhP(OEt)_2\}_4]^{2+}$ (**7a**) derivatives (ratio 5:1), from which the bis(diazene) can be separated in pure form by fractional crystallization. The same mixture was also obtained by reacting the $[RuH(ArN{=}NH)\{PhP(OEt)_2\}_4]^+$ compound with arenediazonium cations.

Since we observed that solutions of bis(aryldiazene) in acetone or dichloromethane slowly give the pentacoordinate $[Ru(ArN{=}NH)P_4]^{2+}$ complexes by dissociation of one of the diazene ligands, it is probable that the reaction between RuH_2P_4 and ArN_2^+ proceeds first to give the bis(diazene), which by slow dissociation affords the pentacoordinate $[Ru(ArN{=}NH)P_4]^{2+}$ derivatives found in the final reaction mixture. The dissociation of one diazene ligand from $[Ru(ArN{=}NH)_2\{PhP(OEt)_2\}_4]^{2+}$ complexes were observed, but not from the corresponding $P(OMe)_3$ and $P(OEt)_3$ compounds. This observation may reasonably be explained on the basis of the large steric hindrance of $PhP(OEt)_2$ as compared with the $P(OMe)_3$ and $P(OEt)_3$ ligands.

Some spectroscopic properties of both the mono- and bis(diazene) complexes are provided in Table I. These compounds have properties similar to those of the closely related $P(OEt)_3$ derivatives previously reported by us.[13b] The deprotonation reactions of both the $[Ru(ArN{=}NH)_2P_4]^{2+}$ and $[Ru(ArN{=}NH)P_4]^{2+}$ derivatives with NEt_3 proceed to give the pentacoordinate aryldiazenido $[Ru(ArN_2)P_4]BPh_4$ (**10**) complexes, which were isolated and characterized. The ν_{NN} at 1640 cm^{-1} (1624 cm^{-1} in the labeled ^{15}N compounds) in the IR spectra suggest for **10a** a singly bent ArN_2 group. The ABC_2 multiplets in the $^{31}P\{^1H\}$ NMR spectra like those in the spectra of the related iron derivatives[13a] indicate the existence in solution of a TBP geometry distorted toward SP. However, this result contrasts with those found for the $P(OEt)_3$ derivatives,[13b] in which the A_2B_2-type ^{31}P spectra suggest a regular TBP structure. Finally, it may be observed that the mono(aryldiazenido) complexes can easily be protonated by $HBF_4{\cdot}Et_2O$ to give the pentacoordinate $[Ru(ArN{=}NH)P_4](BPh_4)_2$ derivatives.

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Registry No. **1a**, 123752-69-2; **1a′**, 123752-68-1; **1a′**$_1$, 123753-16-2; **1*a**, 123752-74-9; **1*a′**, 123752-73-8; **1b′**, 123752-71-6; **1b′**$_1$, 123753-18-4; **1c′**, 123753-14-0; **1*c**, 123808-88-8; **1*c′**, 123752-76-1; **2a**, 86494-67-9; **3a**, 123752-78-3; **3*a′**, 123752-80-7; **3*c**, 123752-82-9; **4a**, 123752-84-1; **5a**, 123752-85-2; **6a**, 123752-87-4; **6*a**, 123752-89-6; **6*c**, 123752-91-0; **7a**, 123752-93-2; **7a′**, 123752-94-3; **7a**$_1$, 123752-96-5; **7a**$_2$, 123752-98-7; **7b**, 123753-00-4; **8a**, 123753-02-6; **8b**, 123753-04-8; **9a**, 123753-06-0; **9b**, 123753-08-2; **10a**, 123753-10-6; **10b**, 123753-12-8; $RuH_2[PhP(OEt)_2]_4$, 123877-52-1; $RuH_2[P(OMe)_3]_4$, 38784-31-5; $RuH_2[P(OEt)_3]_4$, 53495-34-4; $OsH_2[PhP(OEt)_2]_4$, 123753-19-5; $OsH_2[P(OEt)_3]_4$, 123753-20-8.

Supplementary Material Available: Melting point data and elemental analyses for the complexes (Table S1) (3 pages). Ordering information is given on any current masthead page.

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Electrophilic Addition Reactions of Ag^+ with $Pt(AuPPh_3)_8^{2+}$ and $Pt(CO)(AuPPh_3)_8^{2+}$. Crystal Structures of $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$ and $[Pt(CO)(AgNO_3)(AuPPh_3)_8](NO_3)_2$

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$Pt(AuPPh_3)_8^{2+}$ (**1**) and $Pt(CO)(AuPPh_3)_8^{2+}$ (**2**) react with Ag^+, forming the addition products $PtAg(AuPPh_3)_8^{3+}$ (**3**) and $Pt(CO)Ag(AuPPh_3)_8^{3+}$ (**4**), respectively. Compound **3** is characterized by conductivity measurements, elemental analysis, IR and ^{31}P and ^{195}Pt NMR spectroscopy, and single-crystal X-ray diffraction of its nitrate (monoclinic, space group $P2/a$, $a = 28.007$ (18) Å, $b = 17.748$ (3) Å, $c = 28.216$ (4) Å, $\beta = 99.12$ (3)°, $V = 13848$ Å^3, $Z = 4$, residuals $R = 0.048$ and $R_w = 0.071$ for 3722 observed reflections and 495 variables, Mo Kα radiation). Compound **4** is characterized by elemental analysis, IR and ^{31}P, ^{13}C, and ^{195}Pt NMR spectroscopy, and single-crystal X-ray diffraction of its nitrate (triclinic, space group $P\bar{1}$, $a = 17.4363$ (24) Å, $b = 20.358$ (7) Å, $c = 20.500$ (3) Å, $\alpha = 94.18$ (2)°, $\beta = 93.20$ (1)°, $\gamma = 99.64$ (2)°, $V = 7138$ Å^3, $Z = 2$, residuals $R = 0.065$ and $R_w = 0.086$ for 8383 observed reflections and 475 variables, Mo Kα radiation). In the metal clusters **3** and **4** the central Pt atom is surrounded by eight Au atoms and one Ag atom. The phosphines are attached to the Au atoms, and one nitrate is attached to the Ag atom. CO is μ_1-bonded to Pt in **4**. Both reactions show the electrophilic addition of a Ag^+ ion. The alternative synthesis of **4** by addition of CO to **3** shows the amphoteric behavior of the central Pt atom in this cluster compound.

Introduction

The addition of nucleophiles to centered gold or mixed platinum-gold clusters is well-known. In reactions 1 and 2 CO and

$$Pt(AuPPh_3)_8^{2+} + CO \rightarrow Pt(CO)(AuPPh_3)_8^{2+} \tag{1}$$

$$Au(AuPPh_3)_7^{2+} + PPh_3 \rightarrow Au(PPh_3)(AuPPh_3)_7^{2+} \tag{2}$$

PPh_3 are added to the central platinum and gold atoms, respectively.[1,2] These reactions can be described as Lewis base additions to the central metal atoms of the clusters. The electron configurations change, in both cases, from $(S^\sigma)^2(P^\sigma)^4$ to $(S^\sigma)^2(P^\sigma)^6$.[3,4]

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