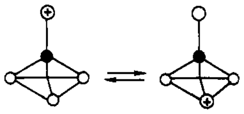
to migrate to the apical position and become the pentacarbonyl portion of the molecule. Close examination of the X-ray structure of $[Cr_4(CO)_{17}S]^{2-}$ reveals that the appended $Cr(CO)_5$ unit is bent down toward the chromium triangle. Hence, the above mentioned motion is not unrealistic.

Further evidence for this metal atom migration is provided by the $[Cr_3W(CO)_{17}S]^{2-}$ cluster. When $[Cr_3(CO)_{12}S]^{2-}$ is reacted with $W(CO)_5$·THF, the infrared spectrum displays a pattern identical with that of $[Cr_4(CO)_{17}S]^{2-}$. However a complex pattern emerges in the ^{13}C NMR spectra. An identical pattern is obtained when $[Cr_2W(CO)_{12}S]^{2-}$ is reacted with $Cr(CO)_5$·THF. This suggest the presence of two isomers, $[(\mu_2\text{-}CO)_3(CO)_9Cr_3(\mu_4\text{-}S)W(CO)_5]^{2-}$ and $[(\mu_2\text{-}CO)_3(CO)_9Cr_2W(\mu_4\text{-}S)Cr(CO)_5]^{2-}$ (eq 6).



(6)

Comparing the intensities of the resonance assigned to the $Cr(CO)_5$ unit (215.9 ppm) to that assigned to the $W(CO)_5$ unit (198.1 ppm) reveals that the two isomers are present in a 1:3 ratio. This ratio represents the statistical distribution of the metal atoms about the cluster.

Conclusions

We have exploited the coordinating ability of a naked sulfur atom and utilized it as a template to construct a variety of group 6 cluster compounds. By careful control of the reaction conditions, selective aggregation of metal fragments can be achieved. This provides us with the synthetic methodology to construct mixed-metal clusters, such as the chiral cluster $[CrMoW(CO)_{12}S][PPN]_2$. The technique of metal atom aggregation should provide a general route to the synthesis of discrete transition-metal clusters containing a chiral metal framework. These new sulfur-capped cluster systems display very facile carbonyl migration processes. Variable-temperature NMR studies indicate that these CO scrambling processes cannot be explained by existing migration mechanisms; alternative fluxional processes are proposed.

Acknowledgment. The financial support of the Robert A. Welch Foundation is greatly appreciated.

Registry No. $[Cu_3(CO)_{12}S][PPN]_2$, 112680-67-8; $[Mo_3(CO)_{12}S][PPN]_2$, 112680-70-3; $[W_3(CO)_{12}S][PPN]_2$, 112680-72-5; $[Cr_2W(CO)_{12}S][PPN]_2$, 112680-74-7; $[Mo_2W(CO)_{12}S][PPN]_2$, 112680-77-0; $[CrMoW(CO)_{12}S][PPN]_2$, 112680-79-2; $Cr(CO)_6$, 13007-92-6; $Cr(CO)_5THF$, 15038-41-2; $Mo(CO)_6$, 13939-06-5; $Mo(CO)_5THF$, 53248-43-4; $W(CO)_6$, 14040-11-0; $W(CO)_5THF$, 36477-75-5; $[Cr(CO)_5SH][PPN]$, 71688-47-6; $[Mo(CO)_5SH][PPN]$, 71688-49-8; $[W(CO)_5SH][PPN]$, 71771-28-3; $[Cr_2(CO)_{10}SH][PPN]$, 77310-17-9; $[Mo_2(CO)_{10}SH][PPN]$, 112680-80-5; $[W_2(CO)_{10}SH][PPN]$, 112680-81-6; $[CrMo(CO)_{10}SH][PPN]$, 112680-83-8; $[CrW(CO)_{10}SH][PPN]$, 112680-85-0; $[WMo(CO)_{10}SH][PPN]$, 112680-87-2; $[Mo_2Cr(CO)_{12}S][PPN]_2$, 112680-89-4; $[Cr_4(CO)_{17}S][PPN]_2$, 87050-04-2; $[Mo_4(CO)_{17}S][PPN]_2$, 112680-93-0; $[(\mu_2\text{-}CO)_3(CO)_9Cr_2W(\mu_4\text{-}S)Cr(CO)_5][PPN]_2$, 112680-95-2; $[(\mu_2\text{-}CO)_3(CO)_9Cr_3(\mu_4\text{-}S)W(CO)_5][PPN]_2$, 112680-91-8.

Supplementary Material Available: Complete listings of atomic coordinates and temperature factors for both cation and anion and anisotropic temperature factors and low-temperature ^{13}C NMR spectra of an equimolar mixture of $[Cr_3(CO)_{12}S][PPN]_2$ and $[Mo_3(^{13}CO)_{12}S][PPN]_2$ and ^{13}C NMR spectra of $[Cr_3W(CO)_{17}S][PPN]_2$ (14 pages); tables of observed and calculated structure factors (82 pages). Ordering information is given on any current masthead page.

Contribution from the Dipartimento di Chimica dell'Università di Venezia, 30123 Venice, Italy, and Istituto di Chimica Generale, Centro Strutturistica CNR, Università di Parma, 43100 Parma, Italy

Bis(aryldiazene)- and Related Mono(aryldiazenido)ruthenium Complexes: Preparation, Characterization, and Reactivity. Crystal Structure of $[Ru(4\text{-}CH_3C_6H_4N{=}NH)_2\{P(OEt)_3\}_4](PF_6)_2$

Gabriele Albertin,[1a] Stefano Antoniutti,[1a] Giancarlo Pelizzi,[1b] Francesca Vitali,[1b]
and Emilio Bordignon*[1a]

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Complexes $[Ru(ArN{=}NH)_2L_4](BPh_4)_2$ (**1**) and $[RuH(ArN{=}NH)L_4]BPh_4$ (**2**) [$L = P(OEt)_3$; Ar = C_6H_5, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 4-FC_6H_4, 2,6-$Cl_2C_6H_3$, 2,3-$Cl_2C_6H_3$] were synthesized by allowing the hydride $RuH_2[P(OEt)_3]_4$ to react with aryldiazonium cations; their characterization by ^1H and $^{31}P\{^1H\}$ NMR (with ^{15}N isotopic substitution) is reported. Atom connectivity in the cation $[Ru(4\text{-}CH_3C_6H_4N{=}NH)_2\{P(OEt)_3\}_4]^{2+}$ is determined by a low-precision X-ray structure determination of its PF_6^- salt. Crystals are monoclinic, space group $P2_1/n$, with unit cell dimensions $a = 23.319$ (3) Å, $b = 22.328$ (3) Å, $c = 11.513$ (2) Å, $\beta = 91.93$ (1)°, and $Z = 4$. The structure was solved by heavy-atom methods and refined by least squares to an R index of 0.0969. The geometry around the ruthenium atom is essentially octahedral with the two diazene ligands in cis positions. The reaction of the bis(aryldiazene) derivatives **1** with NEt_3 leads to new pentacoordinate aryldiazenido $[Ru(ArN_2)\{P(OEt)_3\}_4]^+$ (**3**; Ar = C_6H_5, 4-$CH_3C_6H_4$, 4-FC_6H_4) complexes. Protonation reactions with HBF_4 and CF_3COOH of these aryldiazenido compounds **3** afforded $[Ru(ArN{=}NH)\{P(OEt)_3\}_4](BPh_4)_2$ and $[Ru(CF_3COO)(ArN{=}NH)\{P(OEt)_3\}_4]BPh_4$ (Ar = 4-$CH_3C_6H_4$) derivatives, respectively. Lastly, a new series of ruthenium(II) complexes of the types *trans*-$[Ru(ArN{=}NH)(CO)L_4]^{2+}$, *cis*- and *trans*-$[RuCl(CO)L_4]^+$, $[Ru(ArN{=}NH)L_5]^{2+}$, $[RuCl(4\text{-}CH_3C_6H_4NC)_2L_3]^+$, $[Ru(4\text{-}CH_3C_6H_4NC)_3L_3]^{2+}$, and *cis*-$[RuCl(4\text{-}CH_3C_6H_4N{=}NH)L_4]^+$ (Ar = 4-$CH_3C_6H_4$) were prepared by ligand-substitution reaction of both **1** and **2** derivatives. Their characterization by infrared and ^1H and $^{31}P\{^1H\}$ NMR spectra is also reported.

Introduction

We recently reported[2] the synthesis of the first example of a bis(diazene) complex, $[Fe(ArN{=}NH)_2\{P(OEt)_3\}_4]^{2+}$, obtained by the "apparent" insertion of two aryldiazonium groups into the Fe-H bond of the FeH_2L_4 hydride. Since polyhydrides of Ru, Os, Rh, Ir, W, and Re are known to react with diazonium salt to give mono(diazene) or mono(hydrazido) complexes in any case,[3] we extended this reaction to other dihydrides in order to test whether the formation of bis(diazene) complexes is a general

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(1) (a) Università di Venezia. (b) Università di Parma.

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reaction of dihydrides MH_2L_4 containing phosphite ligand or whether it is a property peculiar to iron. In this paper we describe the reaction of the dihydride $RuH_2[P(OEt)_3]_4$ with aryldiazonium cations, which permitted the synthesis of the first bis(aryldiazene) complexes of ruthenium to be achieved. Furthermore, since aryldiazene and aryldiazenido complexes may be considered as conceptual models for an initial stage of N_2 binding and reduction, an extensive study on their reactivity was carried out; the results are also reported here. Lastly, in view of the relatively few reported X-ray crystal structures of aryldiazene derivatives[2,4,5] and the absence of data on bis(diazene) complexes, the structural characterization of $[Ru(4\text{-}CH_3C_6H_4N{=}NH)_2\{P(OEt)_3\}_4](PF_6)_2$ was also undertaken.

Experimental Section

Solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuumtight storage flasks. $RuCl_3\cdot 1\text{-}3H_2O$ (Alfa Ventron) was used as supplied. Triethyl phosphite was purified by distillation under nitrogen. Diazonium salts were obtained in the usual way, as described in the literature.[6] The labeled diazonium salts $[C_6H_5{}^{14}N{\equiv}{}^{15}N]BF_4$ and $[C_6H_5{}^{15}N{\equiv}{}^{14}N]BF_4$ were prepared by using the appropriate $Na^{15}NO_2$ and $C_6H_5{}^{15}NH_2$ (99% enriched, Stohler Isotope Chemicals) as reagents. 4-Tolyl isocyanide was obtained by the phosgene method of Ugi et al.[7] Triethylamine was distilled from CaH_2. 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 instrument. Solid-state spectra were obtained by using potassium bromide pellets; solution spectra were obtained from KBr solution cells (path length 0.5 mm). Proton magnetic resonance spectra were recorded on Varian EM390 or Varian FT-80A instruments, with tetramethylsilane as an internal standard. 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, downfield shifts being considered positive. The conductivities of 10^{-3} M solutions of the complexes in acetone at 25 °C were measured with a "Halosis" bridge. Solution susceptibilities were determined by the Evans method.[8]

Synthesis of the Complexes. All preparative work was performed under an inert atmosphere by using standard Schlenk techniques. The hydride $RuH_2[P(OEt)_3]_4$ was prepared according to the procedure previously reported.[9]

$[Ru(ArN{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ (1; Ar = C_6H_5 (a), 4-$CH_3C_6H_4$ (b), 4-$CH_3OC_6H_4$ (c), 4-FC_6H_4 (d), 2,6-$Cl_2C_6H_3$ (e), 2,3-$Cl_2C_6H_3$ (f)). A solution of $RuH_2[P(OEt)_3]_4$ (0.77 g, 1 mmol) in CH_2Cl_2 (20 mL) was cooled to −10 °C and quickly transferred into a reaction flask containing an excess of the appropriate diazonium salt (4 mmol). The reaction mixture, brought to room temperature, was stirred for 60-80 min and then filtered to separate the unreacted diazonium salt. Removal of the solvent under reduced pressure gave a yellow oil, which was triturated with ethanol (25 mL). The addition of $NaBPh_4$ (0.75 g, 2.2 mmol) to the resulting solution caused the precipitation of a yellow solid, which was filtered and crystallized from CH_2Cl_2 (5 mL) and ethanol (30 mL); yield ≥80%. Physical constants and elemental analyses follow. Anal. Calcd for **1a**: C, 62.41; H, 6.98; N 3.47. Found: C, 62.14; H, 6.95; N, 3.26. Mp 143 °C dec. $\Lambda_M = 187.0\ cm^2\ \Omega^{-1}\ M^{-1}$. ^1H NMR (δ): 14.34 [app (apparent) t, 2 H, NH]; 7.72, 7.33, 6.88 (m, 50 H, Ph); 4.34, 4.08 (m, 24 H, CH_2); 1.39, 1.09 (t, 36 H, CH_3). Anal. Calcd for **1b**: C, 62.81; H, 7.11; N, 3.41. Found: C, 62.53; H, 7.19; N, 3.45. Mp 146 °C dec. $\Lambda_M = 182.2\ cm^2\ \Omega^{-1}\ M^{-1}$. ^1H NMR (δ): 14.21 (app t, 2 H, NH); 7.60, 7.32, 6.88 (m, 48 H, Ph); 4.37, 4.09 (m, 24 H, CH_2); 2.43 (s, 6 H, CH_3 diazene); 1.41, 1.11 (t, 36 H, CH_3). Anal. Calcd for **1c**: C, 61.61; H, 6.97; N, 3.34. Found: C, 61.47; H, 6.99; N, 3.38. Mp 142 °C dec. $\Lambda_M = 179.5\ cm^2\ \Omega^{-1}\ M^{-1}$. ^1H NMR (δ): 13.88 (app t, 2 H, NH); 7.85, 7.30, 6.88 (m, 48 H, Ph); 4.34, 4.05 (m, 24 H, CH_2); 3.82 (s, 6 H, CH_3 diazene); 1.40, 1.10 (t, 36 H, CH_3). Anal. Calcd for **1d**: C, 61.06; H, 6.71; N, 3.39. Found: C, 59.84; H, 6.66; N, 3.35. Mp 140 °C dec. $\Lambda_M = 181.1\ cm^2\ \Omega^{-1}\ M^{-1}$. ^1H NMR (δ): 14.26 (app t, 2 H, NH); 7.93, 7.32, 6.88 (m, 48 H, Ph); 4.38, 4.11 (m, 24 H, CH_2); 1.41, 1.12 (t, 36 H, CH_3). Anal. Calcd for **1e**: C, 57.51; H, 6.21; N, 3.19; Cl, 8.08. Found: C, 57.30; H, 6.01; N, 3.41; Cl, 8.30. Mp 97 °C dec. $\Lambda_M = 181.1\ cm^2\ \Omega^{-1}\ M^{-1}$. ^1H NMR (δ): 15.00 (app t, 2 H, NH); 7.58, 7.33, 6.88 (m, 46 H, Ph); 4.34, 4.16 (m, 24 H, CH_2); 1.41, 1.17 (t, 36 H, CH_3). Anal. Calcd for **1f**: C, 57.51; H, 6.21; N, 3.19; Cl, 8.08. Found: C, 57.60; H, 6.07; N, 3.22; Cl, 7.97. Mp 113 °C dec. $\Lambda_M = 173.8\ cm^2\ \Omega^{-1}\ M^{-1}$. ^1H NMR (δ): 14.67 (app t, 2 H, NH); 7.75, 7.33, 6.87 (m, 46 H, Ph); 4.41, 4.18 (m, 24 H, CH_2); 1.42, 1.17 (t, 36 H, CH_3).

$[Ru(C_6H_5{}^{14}N{=}{}^{15}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ ($1a_1$) and $[Ru(C_6H_5{}^{15}N{=}{}^{14}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ ($1a_2$). These labeled ^{15}N complexes were prepared as for **1** by using the $C_6H_5{}^{14}N{\equiv}{}^{15}N^+BF_4^-$ and $C_6H_5{}^{15}N{\equiv}{}^{14}N^+BF_4^-$ aryldiazonium salts, respectively; yield ≥80%. Anal. Calcd for **$1a_1$**: C, 62.34; H, 6.98; N, 3.59. Found: C, 62.22; H, 7.07; N, 3.37. Mp 143 °C dec. $\Lambda_M = 205.2\ cm^2\ \Omega^{-1}\ M^{-1}$. ^1H NMR (δ): 14.36 (d of m, 2 H, NH); 7.73, 7.33, 6.88 (m, 50 H, Ph); 4.35, 4.09 (m, 24 H, CH_2); 1.40, 1.10 (t, 36 H, CH_3). Anal. Calcd for **$1a_2$**: C, 62.34; H, 6.98; N, 3.59. Found: C, 62.30; H, 7.12; N, 3.41. Mp 143 °C dec. $\Lambda_M = 200.8\ cm^2\ \Omega^{-1}\ M^{-1}$. ^1H NMR (δ): 14.36 (app q, 2 H, NH); 7.74, 7.33, 6.88 (m, 50 H, Ph); 4.36, 4.09 (m, 24 H, CH_2); 1.41, 1.10 (t, 36 H, CH_3).

$[Ru(4\text{-}CH_3C_6H_4N{=}NH)_2\{P(OEt)_3\}_4](PF_6)_2$ (1g). The complex was prepared by following the method reported above, with NH_4PF_6 as precipitating agent; yield ≥70%. Anal. Calcd: C, 35.22; H, 5.91; N, 4.32. Found: C, 34.97; H, 5.88; N, 4.26. Mp 162 °C dec. $\Lambda_M = 305.2\ cm^2\ \Omega^{-1}\ M^{-1}$. ^1H NMR (δ): 14.26 (app t, 2 H, NH); 7.73 (m, 8 H, Ph); 4.44, 4.17 (m, 24 H, CH_2); 2.49 (s, 6 H, CH_3 diazene); 1.46, 1.17 (t, 36 H, CH_3).

$[RuH(ArN{=}NH)\{P(OEt)_3\}_4]BPh_4$ (2; Ar = C_6H_5 (a), 4-$CH_3C_6H_4$ (b), 4-$CH_3OC_6H_4$ (c), 4-FC_6H_4 (d)). A solution of $RuH_2[P(OEt)_3]_4$ (0.77 g, 1 mmol) in 20 mL of CH_2Cl_2 was cooled to −80 °C and quickly transferred, at the same temperature, into a reaction flask containing the appropriate diazonium salt (1 mmol, ratio 1:1). The temperature of the reaction mixture was brought slowly to 20 °C, and the solution was stirred for 2 h. The solvent was removed under reduced pressure, leaving an oil, which was treated with ethanol (10 mL) to give a light yellow solution. The addition of $NaBPh_4$ (0.69 g, 2 mmol) afforded a yellow precipitate, which was filtered and dried under vacuum. The crystals of these complexes could be obtained by slow cooling to −30 °C of their saturated solutions in ethanol prepared at 25 °C; yield ≥75%. Physical constants and elemental analyses for the monodiazene complexes follow. Anal. Calcd for **2a**: C, 53.92; H, 7.29; N, 2.33. Found: C, 53.81; H, 7.33; N, 2.29. Mp 105 °C dec. $\Lambda_M = 91.6\ cm^2\ \Omega^{-1}\ M^{-1}$. IR ($cm^{-1}$, KBr): 1895 m ($\nu_{MH}$). ^1H NMR (δ): 14.04 (app t, 1 H, NH); 7.36, 6.89 (m, 25 H, Ph); 4.11 (m, 24 H, CH_2); 1.30, 1.26, 1.17 (t, 36 H, CH_3); −7.34 (m, 1 H, hydride; see Table I). Anal. Calcd for **2b**: C, 54.77; H, 7.44; N, 2.32. Found: C, 54.69; H, 7.53; N, 2.32. Mp 120 °C dec. $\Lambda_M = 89.0\ cm^2\ \Omega^{-1}\ M^{-1}$. IR ($cm^{-1}$, KBr): 1898 m ($\nu_{MH}$). ^1H NMR (δ): 13.88 (app t, 1 H, NH); 7.33 , 6.88 (m, 24 H, Ph); 4.03 (m, 24 H, CH_2); 2.31 (s, 3 H, CH_3 diazene); 1.28, 1.24, 1.15 (t, 36 H, CH_3); −7.35 (m, 1 H, hydride; $J_{AY} = -130.0$ Hz, $J_{BY} = -23.0$ Hz, $J_{CY} = -17.0$ Hz, $J_{XY} = 0.1$ Hz; Y part of AB_2CXY spectrum for Y = H). Anal. Calcd for **2c**: C, 54.05; H, 7.34; N, 2.29. Found: C, 54.08; H, 7.42; N, 2.28. Mp 122 °C dec. $\Lambda_M = 86.2\ cm^2\ \Omega^{-1}\ M^{-1}$. IR ($cm^{-1}$, KBr): 1927 m ($\nu_{MH}$). ^1H NMR (δ): 13.66 (app. t, 1 H, NH); 7.33, 6.88 (m, 24 H, Ph); 4.10 (m, 24 H, CH_2); 3.80 (s, 3 H, CH_3 diazene); 1.31, 1.26, 1.17 (t, 36 H, CH_3); −7.33 (m, 1 H, hydride; $J_{AY} = -128.0$ Hz, $J_{BY} = -23.5$ Hz, $J_{CY} = -16.5$ Hz, $J_{XY} = 0.1$ Hz; Y part of AB_2CXY spectrum for Y = H). Anal. Calcd for **2d**: C, 53.60; H, 7.16; N, 2.32. Found: C, 53.22; H, 7.23; N, 2.24. Mp 119 °C dec. $\Lambda_M = 86.9\ cm^2\ \Omega^{-1}\ M^{-1}$. IR ($cm^{-1}$, KBr): 1886 m ($\nu_{MH}$). ^1H NMR (δ): 13.99 (app t, 1 H, NH); 7.37, 6.88 (m, 24 H, Ph); 4.11 (m, 24 H, CH_2); 1.31, 1.27, 1.19 (t, 36 H, CH_3); −7.33 (m, 1 H, hydride; $J_{AY} = -128.0$ Hz, $J_{BY} = -23.0$ Hz, $J_{CY} = -17.5$ Hz, $J_{XY} = 0.1$ Hz; Y part of AB_2CXY spectrum for Y = H).

$[RuH(C_6H_5{}^{14}N{=}{}^{15}NH)\{P(OEt)_3\}_4]BPh_4$ ($2a_1$) and $[RuH(C_6H_5{}^{15}N{=}{}^{14}NH)\{P(OEt)_3\}_4]BPh_4$ ($2a_2$). These complexes were prepared as for the nonlabeled compound **2a** by using $C_6H_5{}^{14}N{\equiv}{}^{15}N^+BF_4^-$ and $C_6H_5{}^{15}N{\equiv}{}^{14}N^+BF_4^-$ aryldiazonium salts, respectively; yield ≥75%. Anal. Calcd for **$2a_1$**: C, 53.87; H, 7.28; N, 2.42. Found: C, 53.83; H, 7.32; N, 2.25. Mp 104 °C dec. $\Lambda_M = 91.6\ cm^2\ \Omega^{-1}\ M^{-1}$. IR ($cm^{-1}$, KBr): 1894 m ($\nu_{MH}$). ^1H NMR (δ): 14.03 (d of m, 1 H, NH); 7.34, 6.88 (m, 25 H, Ph); 4.10 (m, 24 H, CH_2); 1.30, 1.26, 1.17 (t, 36 H, CH_3); −7.33 (m, 1 H, hydride; see Table I). Anal. Calcd for **$2a_2$**: C, 53.87; H, 7.28; N, 2.42. Found: C, 53.80; H, 7.25; N, 2.47. Mp 96 °C dec. $\Lambda_M = 91.4\ cm^2\ \Omega^{-1}\ M^{-1}$. IR ($cm^{-1}$, KBr): 1891 m ($\nu_{MH}$). ^1H NMR (δ): 14.03 (m, 1 H, NH); 7.33, 6.88 (m, 25 H, Ph); 4.11 (m, 24 H, CH_2); 1.30, 1.26, 1.18 (t, 36 H, CH_3); −7.33 (m, 1 H, hydride; see Table I).

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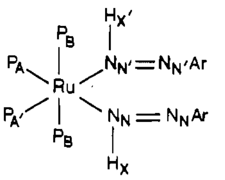
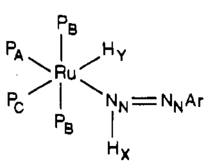
Table I. ^{1}H NMR Data for Nonaromatic Diazene Protons and Hydride Protons of Selected Ruthenium(II) Complexes





			chem shift, δ (coupling constant, Hz)[a]	
no.	cation	spectrum type	X part of spectrum (X = diazene H)	Y part of spectrum (Y = hydride)
1a	$[Ru(C_6H_5{}^{14}N{=}{}^{14}NH)_2L_4]^{2+}$	AA′B$_2$XX′	$\delta_X = \delta_{X'} = 14.34$ ($J_{AX} = J_{A'X'} = 8.0$, $J_{AX'} = J_{A'X} = 2.60$, $J_{BX} = J_{BX'} = 1.4$)	
1a$_1$	$[Ru(C_6H_5{}^{14}N{=}{}^{15}NH)_2L_4]^{2+}$	AA′B$_2$NN′XX′	$\delta_X = \delta_{X'} = 14.36$ ($J_{AX} = J_{A'X'} = 8.0$, $J_{AX'} = J_{A'X} = 3.0$, $J_{BX} = J_{BX'} = 1.4$, $J_{NX} = J_{N'X'} = 65.3$, $J_{NX'} = J_{N'X} = 0.3$)	
1a$_2$	$[Ru(C_6H_5{}^{15}N{=}{}^{14}NH)_2L_4]^{2+}$	AA′B$_2$NN′XX′	$\delta_X = \delta_{X'} = 14.36$ ($J_{AX} = J_{A'X'} = 8.0$, $J_{AX'} = J_{A'X} = 2.50$, $J_{BX} = J_{BX'} = 1.4$, $J_{NX} = J_{N'X'} = 4.7$, $J_{NX'} = J_{N'X} = 0.2$)	
1e	$[Ru(2,6\text{-}Cl_2C_6H_3{}^{14}N{=}{}^{14}NH)_2L_4]^{2+}$	AA′B$_2$XX′	$\delta_X = \delta_{X'} = 15.00$ ($J_{AX} = J_{A'X'} = 8.0$, $J_{AX'} = J_{A'X} = 2.54$, $J_{BX} = J_{BX'} = 1.4$)	
2a	$[RuH(C_6H_5{}^{14}N{=}{}^{14}NH)L_4]^+$	AB$_2$CXY	$\delta_X = 14.04$ ($J_{AX} = 7.5$, $J_{BX} = 2.0$, $J_{CX} = 5.5$, $J_{XY} = 0.1$)	$\delta_Y = -7.34$ ($J_{AY} = -128.5$, $J_{BY} = -23.0$, $J_{CY} = -17.0$)
2a$_1$	$[RuH(C_6H_5{}^{14}N{=}{}^{15}NH)L_4]^+$	AB$_2$CNXY	$\delta_X = 14.03$ ($J_{AX} = 7.5$, $J_{BX} = 2.0$, $J_{CX} = 5.5$, $J_{NX} = 63.3$, $J_{XY} = 0.1$)	$\delta_Y = -7.34$ ($J_{AY} = -128.5$, $J_{BY} = -23.0$, $J_{CY} = -17.0$, $J_{NY} = 1.4$)
2a$_2$	$[RuH(C_6H_5{}^{15}N{=}{}^{14}NH)L_4]^+$	AB$_2$CNXY	$\delta_X = 14.03$ ($J_{AX} = 7.5$, $J_{BX} = 2.0$, $J_{CX} = 5.5$, $J_{NX} = 3.8$, $J_{XY} = 0.1$)	$\delta_Y = -7.34$ ($J_{AY} = -128.5$, $J_{BY} = -23.0$, $J_{CY} = -17.0$, $J_{NY} = 2.8$)
9	$[Ru(4\text{-}CH_3C_6H_4{}^{14}N{=}{}^{14}NH)L_5]^{2+}$	AB$_4$X	$\delta_X = 13.57$ ($J_{AX} = 8.8$, $J_{BX} = 2.0$)	

[a] At room temperature in $(CD_3)_2CO$.

$[Ru(4\text{-}CH_3OC_6H_4N{=}NH)(4\text{-}FC_6H_4N{=}NH)\{P(OEt)_3\}_4](BPh_4)_2$ (1h). An excess of $[4\text{-}FC_6H_4N_2]BF_4$ (0.26 g, 1.25 mmol) was added at 0 °C to a solution of $[RuH(4\text{-}CH_3OC_6H_4N{=}NH)\{P(OEt)_3\}_4]BPh_4$ (0.61 g, 0.5 mmol) in 20 mL of CH_2Cl_2. The reaction mixture was stirred for 70 min and then filtered to remove the unreacted diazonium salt. Evaporation of the solvent under reduced pressure gave an oil, which was triturated with ethanol (15 mL). The addition of $NaBPh_4$ (0.24 g, 0.7 mmol) to the resulting yellow solution yielded a yellow solid, which was collected and crystallized from CH_2Cl_2 (5 mL) and ethanol (25 mL); yield ≥80%. Anal. Calcd: C, 61.34; H, 6.84; N, 3.32. Found: C, 61.27; H, 6.90; N, 3.20. Mp 140 °C dec. $\Lambda_M = 177.4$ cm^2 Ω^{-1} M^{-1}. ^{1}H NMR (δ): 14.28 (app t, 1 H, NH), 13.81 (app t, 1 H, NH); 7.82, 7.33, 6.88 (m, 48 H, Ph); 4.33, 4.05 (m, 24 H, CH_2); 3.79 (s, 3 H, CH_3 diazene); 1.40, 1.38, 1.09 (t, 36 H, CH_3).

$[Ru(ArN_2)\{P(OEt)_3\}_4]BPh_4$ (3; Ar = C_6H_5 (a), 4-$CH_3C_6H_4$ (b), 4-FC_6H_4 (d)). Triethylamine (0.15 mL, 1 mmol) was added to a solution of the appropriate $[Ru(ArN{=}NH)_2L_4]^{2+}$ complex (0.5 mmol) in 10 mL of CH_2Cl_2, and the reaction mixture was stirred for 2 h. A white precipitate of $(Et_3NH)BPh_4$ began to separate out after 5–10 min and was finally filtered off, and the solvent was evaporated to dryness. The orange oil obtained was treated with ethanol (10 mL) to give an orange solution, which was cooled to +5 °C. The solid obtained was removed by filtration and, by further cooling of the remaining orange solution at −30 °C, crystals of $[Ru(ArN_2)L_4]^+$ were obtained, which were recrystallized from ethanol; yield ≥60%. Physical constants and elemental analyses follow. Anal. Calcd for **3a**: C, 54.50; H, 7.20; N, 2.35. Found: C, 54.71; H, 7.11; N, 2.24. $\Lambda_M = 92.1$ cm^2 Ω^{-1} M^{-1}. IR (cm^{-1}, CH_2Cl_2 solution): 1646 s (ν_{NN}). ^{1}H NMR (δ): 7.75, 6.92 (m, 25 H, Ph); 4.09 (m, 24 H, CH_2); 1.35, 1.19 (t, 36 H, CH_3). Anal. Calcd for **3b**: C, 54.86; H, 7.28; N, 2.33. Found: C, 54.90; H, 7.21; N, 2.29. $\Lambda_M = 91.7$ cm^2 Ω^{-1} M^{-1}. IR (cm^{-1}, CH_2Cl_2 solution): 1647 s (ν_{NN}). ^{1}H NMR (δ): 7.35, 6.87 (m, 24 H, Ph); 4.11 (m, 24 H, CH_2); 2.37 (s, 3 H, CH_3 diazenido); 1.32, 1.17 (t, 36 H, CH_3). Anal. Calcd for **3d**: C, 53.69; H, 7.01; N, 2.32. Found: C, 53.90; H, 7.12; N, 2.25. $\Lambda_M = 100.6$ cm^2 Ω^{-1} M^{-1}. IR (cm^{-1}, CH_2Cl_2 solution): 1644 s (ν_{NN}). ^{1}H NMR (δ): 7.32, 6.87 (m, 24 H, Ph); 4.08 (m, 24 H, CH_2); 1.33, 1.17 (t, 36 H, CH_3).

$[Ru(C_6H_5N{\equiv}{}^{15}N)\{P(OEt)_3\}_4]BPh_4$ (3a$_1$). This complex was prepared by following the method reported above for **3**, starting from the $[Ru(C_6H_5N{=}{}^{15}NH)_2L_4]^{2+}$ **1a$_1$** derivative. Anal. Calcd: C, 54.45; H, 7.19; N, 2.44. Found: C, 54.60; H, 7.10; N, 2.41. $\Lambda_M = 89.5$ cm^2 Ω^{-1} M^{-1}. IR (cm^{-1}, CH_2Cl_2 solution): 1626 s (ν_{NN}). ^{1}H NMR (δ): 7.75, 6.92 (m, 25 H, Ph); 4.09 (m, 24 H, CH_2); 1.31, 1.15 (t, 36 H, CH_3).

$[Ru(4\text{-}CH_3C_6H_4N{=}NH)\{P(OEt)_3\}_4](BPh_4)_2$ (4). A slight excess of HBF_4 (54 μL of a ca. 54% Et_2O solution, ca. 0.37 mmol) was slowly added to a cooled solution (0 °C) of $[Ru(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_3\}_4]BPh_4$ (0.41 g, 0.25 mmol) in 10 mL of dichloromethane. The reaction mixture was stirred for 20 min and then evaporated to dryness to give a red oil, which was triturated with ethanol (10 mL). The addition of $NaBPh_4$ (0.17 g, 0.5 mmol) caused the precipitation of a white product, which was filtered and crystallized from CH_2Cl_2/ethanol (5 mL/20 mL); yield ≥75%. Anal. Calcd: C, 62.25; H, 7.14; N, 1.84. Found: C, 62.59; H, 6.99; N, 1.96. Mp 118 °C dec. $\Lambda_M = 168.4$ cm^2 Ω^{-1} M^{-1}. ^{1}H NMR (δ): 13.95 (m, 1 H, NH); 7.59, 7.35, 6.88 (m, 44 H, Ph); 4.22 (m, 24 H, CH_2); 2.42 (s, 3 H, CH_3 diazene); 1.38, 1.35, 1.26 (t, 36 H, CH_3).

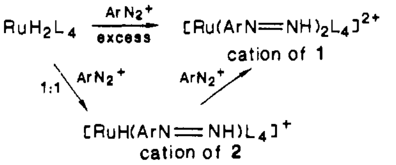
$[Ru(CF_3COO)(4\text{-}CH_3C_6H_4N{=}NH)\{P(OEt)_3\}_4]BPh_4$ (5). Trifluoroacetic acid (37 μL, 0.5 mmol) was added to a dichloromethane solution (10 mL) of $[Ru(4\text{-}CH_3C_6H_4N_2)\{P(OEt)_3\}_4]BPh_4$ (0.41 g, 0.25 mmol), and the solution was stirred for 30 min. The solvent was removed under reduced pressure, giving a yellow oil, which was treated with ethanol (10 mL). The addition of $NaBPh_4$ (0.17 g, 0.5 mmol) to the resulting solution afforded a yellow solid, which was crystallized from CH_2Cl_2/ethanol (5 mL/20 mL); yield ≥70%. Anal. Calcd: C, 55.95; H, 6.17; N, 1.95. Found: C, 56.02; H, 6.20; N, 1.88. Mp 128 °C dec. $\Lambda_M =$ 90.3 cm^2 Ω^{-1} M^{-1}. IR (cm^{-1}, KBr): 1673 s (ν_{COO}). ^{1}H NMR (δ): 16.57 (m, 1 H, NH); 7.50, 7.35, 6.88 (m, 24 H, Ph); 4.21 (m, 24 H, CH_2); 2.41 (s, 3 H, CH_3 diazene); 1.35, 1.31, 1.19 (t, 36 H, CH_3).

***trans*-$[Ru(4\text{-}CH_3C_6H_4N{=}NH)(CO)\{P(OEt)_3\}_4](BPh_4)_2$ (6).** A solution of $[Ru(4\text{-}CH_3C_6H_4N{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ (0.82 g, 0.5 mmol) in 25 mL of acetone was refluxed under CO (1 atm) for 3 h. The solvent was removed under vacuum to give an oil, which was triturated with ethanol (10 mL). The pale yellow solid that slowly formed was crystallized from acetone/ethanol (5 mL/30 mL); yield ≥75%. Anal. Calcd: C, 61.90; H, 7.01; N, 1.80. Found: C, 61.94; H, 7.13; N, 1.63. Mp 167 °C dec. $\Lambda_M = 187.3$ cm^2 Ω^{-1} M^{-1}. IR (cm^{-1}, CH_2Cl_2 solution): 2040 s (ν_{CO}). ^{1}H NMR (δ): 13.20 (qi, 1 H, NH; $J_{PH} = 3.3$ Hz); 7.52, 7.33, 6.88 (m, 44 H, Ph); 4.27 (m, 24 H, CH_2); 2.38 (s, 3 H, CH_3 diazene); 1.33 (t, 36 H, CH_3).

***cis*-$[RuCl(CO)\{P(OEt)_3\}_4]BPh_4$ (7).** A solution of $[Ru(4\text{-}CH_3C_6H_4N{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ (0.82 g, 0.5 mmol) in 30 mL of 1,2-dichloroethane was allowed to stand at room temperature under CO (1 atm) for 9 days. The solution was then evaporated to dryness, and the oil obtained was stirred with ethanol (10 mL) to give a white solid, which was filtered and dried under vacuum. The compound was crystallized by slow cooling to −30 °C of its saturated solution at room temperature in ethanol (20 mL) and dichloromethane (ca. 7 mL); yield ≥60%. Anal. Calcd: C, 51.25; H, 7.02; Cl, 3.09. Found: C, 51.13; H, 7.02; Cl, 3.07. $\Lambda_M = 93.1$ cm^2 Ω^{-1} M^{-1}. IR (cm^{-1}, CH_2Cl_2 solution): 2053 s (ν_{CO}). ^{1}H NMR (δ): 7.32, 6.88 (m, 20 H, Ph); 4.25 (m, 24 H, CH_2); 1.34 (t, 36 H, CH_3).

***trans*-$[RuCl(CO)\{P(OEt)_3\}_4]BPb_4$ (8).** A solution of $[Ru(4\text{-}CH_3C_6H_4N{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ (0.82 g, 0.5 mmol) in 30 mL of 1,2-dichloroethane was heated to reflux under a CO atmosphere for 8 h. The solvent was removed under reduced pressure and the oil obtained triturated with ethanol (20 mL). After 30 min a white solid separated

Scheme I



L = P(OEt)$_3$; Ar = C_6H_5 (**a**), 4-$CH_3C_6H_4$ (**b**), 4-$CH_3OC_6H_4$ (**c**), 4-FC_6H_4 (**d**), 2,6-$Cl_2C_6H_3$ (**e**), 2,3-$Cl_2C_6H_3$ (**f**)

out, which was filtered and crystallized from ethanol; yield ≥65%. Anal. Calcd: C, 51.25; H, 7.02; Cl, 3.09. Found: C, 50.66; H, 7.03; Cl, 3.20. Mp 196 °C dec. Λ_M = 91.6 cm^2 Ω^{-1} M^{-1}. IR (cm^{-1}, CH_2Cl_2 solution): 2006 s (ν_{CO}). ^{1}H NMR (δ): 7.33, 6.88 (m, 20 H, Ph); 4.30 (m, 24 H, CH_2); 1.34 (t, 36 H, CH_3).

[Ru(4-$CH_3C_6H_4$NC)$_3${P(OEt)$_3$}$_3$](BPh$_4$)$_2$ (9). 4-Tolyl isocyanide (0.3 mL, 2.5 mmol) was added to a solution of [Ru(4-$CH_3C_6H_4$N=NH)$_2${P(OEt)$_3$}$_4$](BPh$_4$)$_2$ (0.82 g, 0.5 mmol) in 30 mL of 1,2-dichloroethane, and the reaction mixture was heated under reflux for 5 h. The solvent was removed and the oil obtained treated with ethanol (10 mL) to give a white solid, which was filtered and crystallized in ethanol; yield ≥70%. Anal. Calcd: C, 68.01; H, 6.72; N, 2.64. Found: C, 67.81; H, 6.67; N, 2.71. Mp 183 °C dec. Λ_M = 165.0 cm^2 Ω^{-1} M^{-1}. IR (cm^{-1}, CH_2Cl_2 solution): 2204 m, 2176 s (ν_{CN}). ^{1}H NMR (δ): 7.38, 6.88 (m, 52 H, Ph); 4.36 (m, 18 H, CH_2); 2.36 (s, 9 H, CH_3 isocyanide); 1.37 (t, 27 H, CH_3).

[Ru(4-$CH_3C_6H_4$N=NH){P(OEt)$_3$}$_5$](BPh$_4$)$_2$ (10). An excess of triethyl phosphite (0.42 g, 2.5 mmol) was added to a solution of [Ru(4-$CH_3C_6H_4$N=NH)$_2${P(OEt)$_3$}$_4$](BPh$_4$)$_2$ (0.82 g, 0.5 mmol) in 20 mL of acetone, and the reaction mixture was heated to reflux for 10 h. Evaporation of the solvent under reduced pressure gave an oil, which was treated with ethanol (15 mL). The pale yellow solid that slowly formed was crystallized from acetone/ethanol (5 mL/25 mL); yield ≥60%. Anal. Calcd: C, 60.39; H, 7.33; N, 1.66. Found: C, 59.98; H, 7.32; N, 1.53. Mp 162 °C dec. Λ_M = 182.9 cm^2 Ω^{-1} M^{-1}. ^{1}H NMR (δ): 13.57 (app d of t, 1 H, NH); 7.50, 7.33, 6.88 (m, 44 H, Ph); 4.26 (m, 30 H, CH_2); 2.38 (s, 3 H, CH_3 diazene); 1.39, 1.30 (t, 45 H, CH_3).

***cis*-[RuCl(4-$CH_3C_6H_4$N=NH){P(OEt)$_3$}$_4$]BPh$_4$ (11).** Lithium chloride (0.026 g, 0.6 mmol) was added to a solution of [Ru(4-$CH_3C_6H_4$N=NH)$_2${P(OEt)$_3$}$_4$](BPh$_4$)$_2$ (0.5 g, 0.3 mmol) in 20 mL of acetone, and the reaction mixture was refluxed for 4.5 h. After filtration, the solvent was removed by evaporation, giving an oil which was triturated with ethanol (10 mL). The resulting pale yellow solid was filtered and crystallized by ethanol; yield ≥65%. Anal. Calcd: C, 53.25; H, 7.15; N, 2.26; Cl, 2.86. Found: C, 53.40; H, 7.04; N, 2.08; Cl, 3.01. Mp 135 °C dec. Λ_M = 85.4 cm^2 Ω^{-1} M^{-1}. ^{1}H NMR (δ): 14.08 (app d, 1 H, NH); 7.49, 7.33, 6.88 (m, 24 H, Ph); 4.21 (m, 24 H, CH_2); 2.40 (s, 3 H, CH_3 diazene); 1.31, 1.28 (t, 36 H, CH_3).

[RuCl(4-$CH_3C_6H_4$NC)$_2${P(OEt)$_3$}$_3$]BPh$_4$ (12). 4-Tolyl isocyanide (0.18 g, 1.5 mmol) was added to a solution of [RuH(4-$CH_3C_6H_4$N=NH){P(OEt)$_3$}$_4$]BPh$_4$ (0.6 g, 0.5 mmol) in 20 mL of 1,2-dichloroethane. The reaction mixture was stirred at room temperature for 5 days, and the solvent was then removed at reduced pressure. The resulting brown oil was treated with ethanol, affording a white solid, which was crystallized by ethanol; yield ≥35%. Anal. Calcd: C, 58.61; H, 6.70; N, 2.36. Found: C, 58.48; H, 6.78; N, 2.22. Mp 185 °C dec. Λ_M = 86.3 cm^2 Ω^{-1} M^{-1}. IR (cm^{-1}, CH_2Cl_2 solution): 2181 s, 2157 s (ν_{CN}). ^{1}H NMR (δ): 7.36, 6.88 (m, 28 H, Ph); 4.21, 4.29 (qi, 18 H, CH_2); 2.38 (s, 6 H, CH_3 isocyanide); 1.30, 1.31 (t, 27 H, CH_3).

X-ray Structure of [Ru(4-$CH_3C_6H_4$N=NH)$_2${P(OEt)$_3$}$_4$](PF$_6$)$_2$ (1g). Details are given in the supplementary material. A determination of only low precision was obtained, due to the low diffracting power of the crystal.

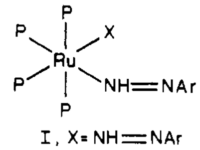
Results and Discussion

Preparation and Characterization of Diazene Complexes. The dihydride RuH$_2$[P(OEt)$_3$]$_4$ quickly reacts in CH_2Cl_2 with an excess of aryldiazonium cations to afford the bis(aryldiazene) complexes [Ru(ArN=NH)$_2$L$_4$]$^{2+}$ (cation of **1**). However, with a 1:1 stoichiometry of ArN$_2^+$BF$_4^-$ at −80 °C, the mono(diazene) derivatives [RuH(ArN=NH)L$_4$]$^+$ (cation of **2**) were also prepared, and these may further react with aryldiazonium cation to yield the bis(diazene) compounds **1** as final products (Scheme I). Some spectroscopic properties (IR and ^{31}P{^{1}H} NMR data) of the new Ru(II) complexes, which are yellow crystalline solids, stable both in the solid state and in solution, are available as supplementary material (Table S1). The compounds are diamagnetic, and the conductivity values[10] for **1** and **2** agree with those reported for 1:2 and 1:1 electrolytes, respectively. The ^{31}P{^{1}H} NMR spectra of the bis(diazene) complexes **1** are A$_2$B$_2$ multiplets between −70 and +40 °C, in agreement with the existence in solution of a cis geometry (I) for the compounds, as observed in the solid state.

Table II. Crystallographic Details for [Ru(4-$CH_3C_6H_4$N=NH)$_2${P(OEt)$_3$}$_4$](PF$_6$)$_2$

formula	$C_{38}H_{76}F_{12}N_4O_{12}P_6Ru$
fw	1295.93
cryst syst	monoclinic
color and habit	parallelepipedic yellow cryst
cryst dimens, mm	0.39 × 0.44 × 0.83
space group	$P2_1/n$[a]
a, Å	23.319 (3)
b, Å	22.328 (3)
c, Å	11.513 (2)
β, deg	91.93 (1)
V, Å^3	5991 (1)
Z	4
radiation (λ, Å)	graphite-monochromated Mo Kα (λ = 0.71069)
d_{calcd}, g cm^{-3}	1.437
μ(Mo Kα), cm^{-1}	5.01
data collection range	$\pm h,+k,+l$
scan mode	$\omega-2\theta$
scan speed, deg s^{-1}	0.100
scan width, deg	1.40
2θ limits, deg	6.0–49.0
no. of data collected[b]	10293
no. of unique data	9473
R_{int}	0.0276
no. of obsd data	4431 [$I > 3\sigma(I)$]
no. of unique data used (last cycle)	3735
params refined	468
data-to-variable ratio	8.0/1
max and min heights in final ΔF map, e Å^{-3}	+1.40, −0.91
R[c]	0.0969
R_w[d]	0.1035
R_g[e]	0.1391
GOF	0.374

[a] A nonstandard setting of $P2_1/c$, C_{2h}^5 (No. 14), with equivalence positions: $\pm(x, y, z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$. [b] Including 274 systematically absent reflections. [c] $R = \sum|\Delta F|/\sum|F_o|$. [d] $R_w = \sum(\Delta F)w^{1/2}/\sum w^{1/2}F_o$. [e] $R_g = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$.



I, X = NH=NAr
II, X = H

In the nonaromatic diazene proton region[11] (δ 11.6–15.1) the ^{1}H NMR spectra of **1** appear as triplets. This signal is split into two multiplets when the ^{15}N-labeled complex [Ru(ArN=^{15}NH)$_2$L$_4$]$^{2+}$ (cation of **1a**$_1$) is used. The ^{14}NH resonance for all the previously reported aryldiazene derivatives is described as a singlet, which, though generally broad,[3a,11] in some cases appears as a sharp resonance,[4b] presumably because of the rapid quadrupolar relaxation of the ^{14}N nucleus as a result of coordination to the metal. In our case, the presence of a triplet in the ^{14}N complex may be explained on the basis of weak coupling between the diazene protons and the four phosphorus nuclei. In fact, when we take into account the A$_2$B$_2$-type ^{31}P spectra, the ^{1}H experimental spectra can be simulated as the X part of an AA′B$_2$XX′ model[12]

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(10) In 10^{-3} M acetone solution at 25 °C. See: Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(11) (a) Sutton, D. *Chem. Soc. Rev.* **1975**, *4*, 443. (b) Carroll, J. A.; Sutton, D.; Xiaoheng, Z. *J. Organomet. Chem.* **1982**, *244*, 73.

(12) The ^{1}H diazene nuclei (and the ^{31}P nuclei trans to the ArNNH ligand, i.e. P$_A$ in Table I), although chemically equivalent, are not magnetically equivalent, because the cis J_{PH} values are different from the trans J_{PH} coupling constants. An AA′B$_2$XX′ (X = H of diazene) instead of an A$_2$B$_2$X$_2$ model must therefore be used.

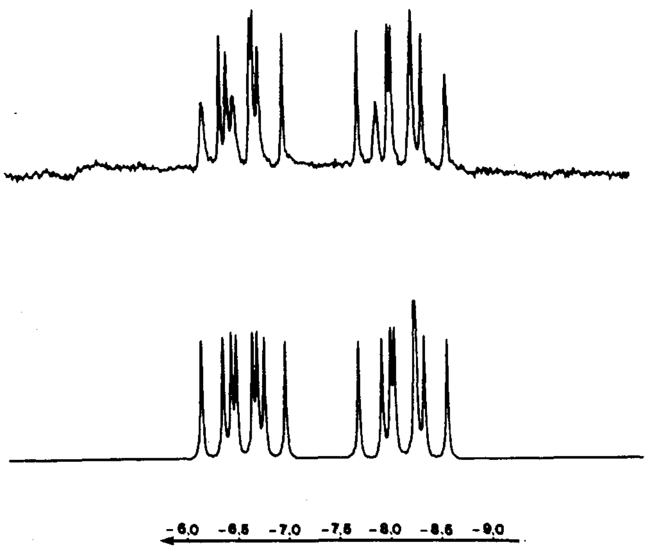

Figure 1. Observed (upper) and calculated (lower) ^1H NMR spectra of the hydride proton of the mono(diazene) $[RuH(C_6H_5N{=}NH)L_4]^+$ complex. The simulated spectrum was obtained with parameters given in Tables I and S1.

by using the values listed in Table I, and the good fit between the observed and calculated spectra supports this assignment. The observed and calculated spectra are available as supplementary material (Figure S1). In effect, the one-bond coupling between ^1H and ^{15}N ($^1J_{^{15}NH}$ = 65.3 Hz) in the labeled complex $\mathbf{1a}_1$ splits the signal into two multiplets, which can be simulated as the X part of an $AA'B_2NN'XX'$ model (parameters in Table I). The two-bond $^2J_{^{15}NH}$ coupling constant for the phenyldiazene complexes was also determined from the ^1H NMR spectra of the $[Ru(Ar^{15}N{=}^{14}NH)_2L_4]^{2+}$ complex, and its value of 4.7 Hz agrees with those previously reported[3a] for other mono(diazene) derivatives. An alternative explanation for the appearance as a triplet of the diazene proton signal of **1** may involve coupling between the diazene and the aromatic protons of the phenyl ring attached to the same diazene ligand. However, the J_{HH} values across four bonds are expected to be smaller than those observed in our case (8.0–1.4 Hz, Table I). Furthermore, the spectra of the 2,6-$Cl_2C_6H_3N{=}NH$ and 2,3-$Cl_2C_6H_3N{=}NH$ bis(diazene) derivatives **1e** and **1f** always show triplets in the NH region, reasonably excluding coupling with the phenyl protons.

Mono(diazene) complexes **2** show an AB_2C pattern in their $^{31}P\{^1H\}$ NMR spectra (between −70 and +40 °C) as may be expected for type II geometry in solution in which the hydride and the diazene ligand are in mutually cis positions. On the other hand, the ^1H NMR spectra of **2** show a triplet at δ 14.04–13.66 in the NH region, interpreted as a result of coupling between the diazene hydrogen atom and the four P nuclei (Table I). In effect, in the ^{15}N-labeled derivative $[RuH(C_6H_5N{=}^{15}NH)L_4]^+$ (cation of $\mathbf{2a}_1$) the signal at δ 14.04 (**2a**) is replaced by two multiplets ($^1J_{^{15}NH}$ = 63.3 Hz), thus confirming the existence of the diazene ligand. Furthermore, in the hydride region, the ^1H NMR spectra of mono(diazenes) **2** appear as multiplets (Figure 1), which may be simulated as the Y part of an AB_2CXY spin system (Table I), in agreement with the proposed geometry (II) for the complexes.

The reaction of the ruthenium dihydride $RuH_2(CO)(PPh_3)_3$ with aryldiazonium cations had been previously studied,[3a] but the insertion of only one ArN_2^+ group to give the mono(aryldiazene) $[RuH(ArN{=}NH)(CO)(PPh_3)_3]^+$ had been observed. In our case, the formation of the bis(diazene) compounds should be attributed to the presence of the phosphite ligand, which makes the Ru–H bond of the mono(diazene) **2** susceptible to further insertion by ArN_2^+ to give **1** as the final product. Polyhydrides of Os, Rh, Ir, W, and Re were also reacted with aryldiazonium cations to give, however, monoinsertion products.[3] In the case of Cp_2WH_2, the reaction with $ArN_2^+BF_4^-$ was studied extensively[3c–f] and shows a "double insertion" of the ligand, with formation first of the arylhydrazido(2−) $[Cp_2WH(NNHAr)]X$ ($X = BF_4^-$ or PF_6^-) complex, which isomerizes to the diinserted product $[Cp_2W(H_2NNAr)]X$. The absence of the reaction with the second ArN_2^+ ligand in this complex may be attributed to the initial formation of an arylhydrazido(2−) derivative instead of an aryldiazene, which contained the N1 atom susceptible to facile reaction with the nearby hydride to give the stable hydrazido(1−) $[CpW(H_2NNAr)]X$ as final product.

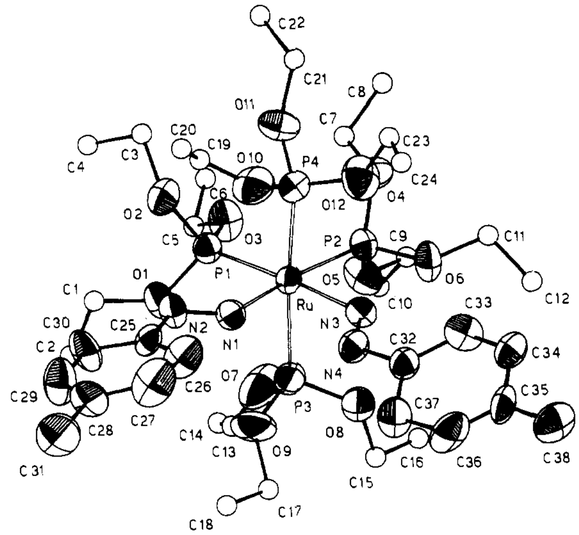

Figure 2. ORTEP diagram and atom-labeling scheme for the $[Ru(4\text{-}CH_3C_6H_4N{=}NH)_2\{P(OEt)_3\}_4]^{2+}$ cation. Thermal ellipsoids are drawn at the 40% probability level. Anisotropic parameters were used only for shaded atoms. Ethyl carbon atoms are shown artificially small.

In contrast, our monoinsertion product, the diazene $[RuH(ArN{=}NH)L_4]^+$, is very stable and does not show any tendency to rearrange to an arylhydrazido(2−) complex, even after 8 h of refluxing in 1,2-dichloroethane. The synthesis of bis(diazene) complexes from the reaction of dihydride with aryldiazonium cations therefore seems to be attributable to the nature and stability of the first insertion product as well as the reactivity of its M–H bond toward the ArN_2^+ ligand.

A view of the molecular structure of the complex cation $[Ru(4\text{-}CH_3C_6H_4N{=}NH)_2\{P(OEt)_3\}_4]^{2+}$ is shown in Figure 2, together with the atom-labeling scheme. The ruthenium atom is in an octahedral environment, coordinated to four phosphite groups and two diazene molecules. Due to low precision of the refinement (see the supplementary material) no significance beyond connectivity of the atoms may be attributed at this time.

Aryldiazenido Derivatives. Bis(diazene) complexes **1** slowly react in CH_2Cl_2 solution, in both stoichiometric and excess amounts of triethylamine, to afford the aryldiazenido complexes $[Ru(ArN_2)L_4]^+$ (cation of **3**), which were isolated and characterized. When the progress of the reaction is monitored by

$$\underset{\text{cation of }\mathbf{1}}{[Ru(ArN{=}NH)_2L_4]^{2+}} \xrightarrow{NEt_3} \underset{\text{cation of }\mathbf{3}}{[Ru(ArN_2)L_4]^+}$$

$$Ar = C_6H_5\ (\mathbf{a}),\ 4\text{-}CH_3C_6H_4\ (\mathbf{b}),\ 4\text{-}FC_6H_4\ (\mathbf{d})$$

infrared spectra, it may be observed that no different aryldiazenido compounds beyond **3** are detected, the 1644–1647-cm^{-1} band of **3** being the only observed ν_{NN} absorption. On the other hand, the NMR spectra of the reaction mixture do not show the formation of new diazenes, i.e. possible intermediates $[Ru(ArN{=}NH)(ArN_2)L_4]^+$, but only the disappearance of starting compound **1**. Since aryldiazenido complexes **3** can be recovered in good yield (≥80%), and the hydrocarbon ArH was also detected[13] in the reaction mixture, as observed for homologous iron,[2] we may hypothesize that the reaction with NEt_3 involves deprotonation of

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(13) It was previously shown that the hydrocarbon ArH is, together with N_2, the decomposition product of the free diazene ligand: Albertin, G.; Antoniutti, S.; Lanfranchi, M.; Pelizzi, G.; Bordignon, E. *Inorg. Chem.* **1986**, *25*, 950.

only one diazene group of **1**, with concurrent dissociation of the other ArN=NH ligand to give **3** as the final product.

The infrared spectra of the $[Ru(ArN_2)L_4]^+$ complexes show only one band at 1642–1647 cm^{-1} in the ν(NN) region, both in the solid state and in CH_2Cl_2 solution. In the case of the $C_6H_5N_2$ derivative **3a**, this band at 1646 cm^{-1} (CH_2Cl_2) shifts to 1626 and 1628 cm^{-1} on labeling with ^{15}N (using respectively labeled diazonium salts $Ar^{14}N{\equiv}{}^{15}N^+BF_4^-$ and $Ar^{15}N{\equiv}{}^{14}N^+BF_4^-$). These values seem to indicate a singly bent aryldiazenido group for our derivatives **3**, as may be deduced by a comparison of ν_{NN} with those values for aryldiazenido complexes whose crystal structures are known, e.g., $[Fe(ArN_2)\{P(OEt)_3\}_4]BPh_4$,[2] $[Fe(C_6H_5N_2)(CO)_2(PPh_3)_2]BF_4$,[14] $[RuCl_3(4\text{-}CH_3C_6H_4N_2)(PPh_3)_2]$,[15,16] and $[Mn(CO)_2(\eta^5\text{-}C_5H_4\text{-}CH_3)(2\text{-}CF_3C_6H_4N_2)]BF_4$.[17] This assignment also agrees with the empirical rules proposed by Haymore and Ibers.[15]

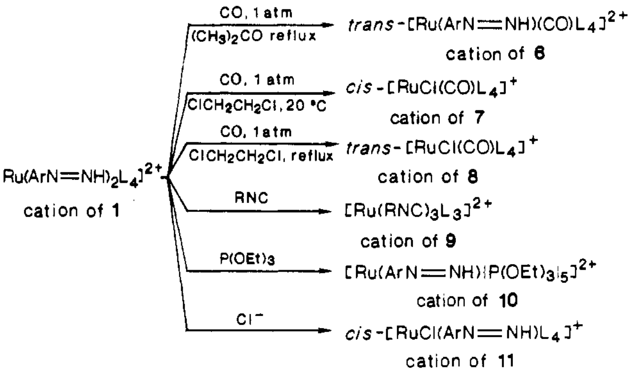
The previously reported pentacoordinate $[Ru(ArN_2)(CO)_2(PPh_3)_2]^+$ complexes[18] show complicated infrared spectra in the ν_{NN} region, interpreted on the basis of the existence of two isomers with "singly bent" and "doubly bent" aryldiazenido ligands, respectively. However, a lower ν'_{NN} value at 1556 cm^{-1}, as compared to that for **3**, was calculated for the singly bent isomers[18] of $[Ru(ArN_2)(CO)_2(PPh_3)_2]^+$, which seems to indicate the lower π-bonding character of the ArN_2 ligand in our derivatives.

The $^{31}P\{^1H\}$ NMR spectra of complexes **3** show a broad pattern at room temperature. Lowering the sample temperature to −50 °C, however, produces an A_2B_2 multiplet for all the complexes. Trigonal-bipyramidal geometry with a singly bent aryldiazenido group in an equatorial position may therefore reasonably be proposed in solution for these complexes. For the related iron complexes[2] $[Fe(ArN_2)\{P(OEt)_3\}_4]^+$, a slightly distorted TBP geometry in the solid state, which seems to be present also in solution, was observed, as may be deduced from their ABC_2 type ^{31}P spectra. In contrast, although the X-ray crystal structures of ruthenium compounds **3** were not determined, the ^{31}P spectra seem to indicate that no appreciable distortion from TBP geometry occurs in solution for these derivatives.

Aryldiazenido derivatives **3** react with trifluoroacetic acid in CH_2Cl_2 to give the hexacoordinate aryldiazene complexes $[Ru(CF_3COO)(ArN{=}NH)L_4]BPh_4$ (**5**, Ar = 4-$CH_3C_6H_4$), which were isolated and characterized. Compound **5** is a 1:1 electrolyte [Λ_M = 90.3 Ω^{-1} M^{-1} cm^2 in $(CH_3)_2CO$], and its ^1H NMR spectrum shows an NH resonance at δ 16.57, in agreement with the proposed formulation. Furthermore, in order to determine the nitrogen site of the protonation, we studied the reaction of both $[Ru(Ar^{15}N{\equiv}{}^{14}N)L_4]^+$ and $[Ru(Ar^{14}N{\equiv}{}^{15}N)L_4]^+$ complexes toward CF_3COOH and observed that protonation takes place at the N1 atom[19] (bonded to the Ru), affording the proposed aryldiazene complex **5**. Lastly, the $^{31}P\{^1H\}$ NMR spectra of **5** appear as an ABC_2 multiplet, indicating the mutually cis positions of the diazene and trifluoroacetate ligands.

Fluoroboric acid, HBF_4, in slight excess also reacts with aryldiazenido compounds **3** in CH_2Cl_2 at 0 °C to yield the white, diamagnetic, 1:2 electrolyte $[Ru(ArN{=}NH)L_4](BPh_4)_2$ (**4**, Ar = 4-$CH_3C_6H_4$), after further addition of $NaBPh_4$. The ^1H NMR spectra of ^{15}N-labeled and unlabeled complexes confirm the proposed diazene formulation for **4** (δ_{NH} at 13.95, $^1J_{^{15}NH}$ = 65.0 Hz), in agreement with protonation of the N1 atom of the ArN-N-Ru moiety. At room temperature the $^{31}P\{^1H\}$ NMR spectrum of **4** in $(CD_3)_2CO$ appears as a slightly broad pattern. However, already at +5 °C a static spectrum is observed, which remains unchanged down to −80 °C. A computer simulation using an ABC_2 model agrees well with the experimental spectrum. In this temperature range (from +34 to −80 °C) no resonance due to free $P(OEt)_3$ were detected. Furthermore, the use of CD_2Cl_2 as solvent instead of acetone does not change the profile of the spectra. These data do not allow the unambiguous assignment of a geometry to the mono(diazene) complex **4**, in solution. In effect, the ABC_2 ^{31}P spectra could be interpreted on the basis of the existence of a square-pyramidal geometry for **4**, also in agreement with previous theoretical[20] and structural[21] studies on pentacoordinated d^6 complexes. However, a distorted TBP toward SP geometry should still give ABC_2 ^{31}P spectra, as well as a diazene-bridged dimer with two octahedral ruthenium atoms. The only certain assumption is therefore exclusion of regular trigonal-bipyramidal geometry with the ArNNH group in an equatorial position for **4** because, in such a case, an A_2B_2 spectrum would be expected.

Scheme II

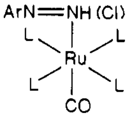


L = $P(OEt)_3$; Ar = 4-$CH_3C_6H_4$

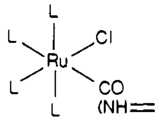
Reactivity. The reaction of the bis(diazene) complexes **1** with several ligands such as CO, RNC, $P(OEt)_3$, and Cl^- proceeds with the substitution of one or two diazene groups to give a new series of Ru(II) derivatives, as shown in Scheme II.

Carbon monoxide (1 atm) reacts with **1** in boiling acetone to give the mono(diazene) $[Ru(ArN{=}NH)(CO)L_4]^{2+}$ (cation of **6**), which was isolated and characterized. Further substitution of the ArNNH or $P(OEt)_3$ ligand by CO in **6**, however, does not take place even if the reaction mixture is refluxed by 24 h.

The infrared spectrum of compound **6** shows the ν_{CO} band at 2040 cm^{-1} (CH_2Cl_2), and the $^{31}P\{^1H\}$ NMR spectrum appears (between +40 and −70 °C) as a singlet, in agreement with the ArNNH and CO ligands in mutually trans positions in complex III.



III



IV

If 1,2-dichloroethane instead of acetone is used as solvent, the reaction of the bis(diazene) derivatives toward CO proceeds at room temperature to give *cis*-$[RuCl(CO)L_4]^+$ (cation of **7**), whereas under reflux conditions *trans*-$[RuCl(CO)L_4]^+$ (cation of **8**) is obtained.[22] Monitoring the progress of the reaction by infrared spectra shows that the mono(diazene) $[Ru(ArN{=}NH)(CO)L_4]^{2+}$ is not detected in this solvent. In fact, at room temperature only the 2053-cm^{-1} band of cis complex **7** is observed in the spectrum of the reaction mixture, whereas under reflux

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[14] Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 1369.

[15] Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 3060.

[16] McArdle, J. V.; Schultz, A. J.; Corden, B. J.; Eisenberg, R. *Inorg. Chem.* **1973**, *12*, 1676.

[17] Barrientos-Penna, C. F.; Einstein, F. W. B.; Sutton, D.; Willis, A. C. *Inorg. Chem.* **1980**, *19*, 2740.

[18] Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2784.

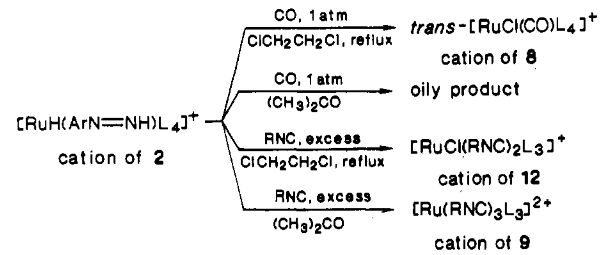
[19] A $^1J_{^{15}NH}$ value of 66.5 Hz was determined from the $[Ru(CF_3COO)(ArN{=}{}^{15}NH)L_4]^+$ derivative.

[20] (a) Pearson, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 4947. (b) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365. (c) Burdett, J. K. *Inorg. Chem.* **1975**, *14*, 375, 931. (d) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

[21] (a) Hoffman, P. R.; Caulton, K. G. *J. Am Chem. Soc.* **1975**, *97*, 4221. (b) Holmes, R. R. *Prog. Inorg.* Chem. **1984**, *32*, 119 and references therein.

[22] The chlorine ion in the ruthenium complex comes from the $ClCH_2CH_2Cl$ solvent.

Scheme III



conditions both the 2053- and 2006-cm^{-1} absorptions due respectively to the cis (**7**) and trans (**8**) compounds are present. Because the cis–trans isomerization of the carbonyl takes place in boiling solvent, only the band at 2006 cm^{-1} of the trans compound **8** is observed, in the latter case, at the end of the reaction. It may be noted that, in the absence of CO, while the bis(diazene) **1** is unreactive in 1,2-dichloroethane, the mono(diazene) $[\mathrm{Ru(ArN{=}NH)(CO)L_4}]^{2+}$ (cation of **6**) quickly reacts with this solvent to give *cis*-$[\mathrm{RuCl(CO)L_4}]^+$ (cation of **7**). Therefore, the different behavior of **1** toward CO in acetone and 1,2-dichloroethane should be attributed to the reactivity of **6**, which probably also formed as an intermediate in the carbonylation of **1** in 1,2-dichloroethane.

Both carbonyls were isolated as stable, diamagnetic $\mathrm{BPh_4}^-$ salts and were found to be 1:1 electrolytes. Their ^{31}P{^{1}H} NMR spectra (between +40 and −70 °C) consist of an ABC_2 pattern for the cis derivative **7**, whereas only one peak is observed for the trans complex **8**, in agreement with geometries of types IV and III, respectively, for the two compounds. The IR spectra of both isomers show in the ν_{CO} region only one band at 2053 cm^{-1} (cis) and 2006 cm^{-1} (trans), respectively, in CH_2Cl_2 solution. The lowering of ν_{CO} by ca. 50 cm^{-1} in the trans compound is attributable to the position of the halogen ligand, which increases the M–CO π-back-bonding when it is trans to the CO ligand. Monocarbonyl complexes of Ru(II) are rare and, apart from the hydrides,[23] the only reported ones are of the type $[\mathrm{RuCl_2(CO)L_3}]$ (L = phosphine).[24]

The reaction of bis(diazene) complexes with 4-tolyl isocyanide proceeds slowly, and when excess RNC was used in boiling solvents, $[\mathrm{Ru(RNC)_3L_3}]^{2+}$ (cation of **9**) was isolated as the final product.[25] A singlet at 117.3 ppm in the ^{31}P{^{1}H} NMR spectrum suggests a *fac* structure for the complex.

Triethyl phosphite substitutes only one diazene ligand in **1** to afford the new mono(diazene) $[\mathrm{Ru(ArN{=}NH)\{P(OEt)_3\}_5}]^{2+}$ (cation of **10**). Halogenide ion (Cl$^-$) also substitutes only one ArNNH ligand in **1** to yield $[\mathrm{RuCl(ArN{=}NH)L_4}]^+$ (cation of **11**), whose ^{31}P{^{1}H} NMR spectrum (AB_2C multiplet) suggests cis positions of the halogenide and diazene groups (IV).

We also studied the reactivity of the mono(diazene) $[\mathrm{RuH(ArN{=}NH)L_4}]^+$ (cation of **2**) toward CO and RNC. The results obtained (Scheme III) show that not only is the diazene group substituted by CO or RNC in these complexes but also the hydride ligand. Ruthenium(II) complexes similar to those prepared from the bis(diazene) derivatives can therefore be obtained.

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Registry No. **1a**, 111959-58-1; **1b**, 111959-60-5; **1c**, 111959-62-7; **1d**, 111959-64-9; **1e**, 111959-66-1; **1f**, 111959-68-3; **1g**, 111959-69-4; **1h**, 111959-79-6; **2a**, 111959-71-8; **2b**, 111959-73-0; **2c**, 111959-75-2; **2d**, 111959-77-4; **3a**, 111959-81-0; **3b**, 111959-83-2; **3d**, 111959-85-4; **4**, 111959-87-6; **5**, 111975-18-9; **6**, 111959-89-8; **7**, 112019-34-8; **8**, 110982-24-6; **9**, 111959-91-2; **10**, 111959-93-4; **11**, 111959-95-6; **12**, 111017-97-1; $\mathrm{RuH_2[P(OEt)_3]_4}$, 38720-12-6; ^{15}N, 14390-96-6; 1,2-dichloroethane, 107-06-2.

Supplementary Material Available: Infrared and ^{31}P{^{1}H} NMR data (Table S1), observed and simulated ^{1}H NMR spectra for complexes **1a**, **1a**$_1$, and **1a**$_2$ (Figure S1), a full description of the structure determination, fractional atomic coordinates (Table S2), a table of thermal parameters, and a full list of bond lengths and bond angles (11 pages); a listing of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

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(23) (a) Parshall, G. W.; Knoth, W. H.; Schunn, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 4990. (b) Couch, D. A.; Robinson, S. D. *Inorg. Chem.* **1974**, *13*, 456; *Inorg. Chim. Acta* **1974**, *9*, 39. (c) Creswell, C. J.; Robinson, S. D.; Sahajpal, A. *Polyhedron* **1983**, *2*, 517.

(24) (a) Couch, D. A.; Robinson, S. D.; Wingfield, J. N. *J. Chem. Soc., Dalton Trans.* **1974**, 1309. (b) Levison, J. J.; Robinson, S. D. *J. Chem. Soc. A* **1970**, 639.

(25) Further studies on this reaction are in progress and will be reported in a forthcoming paper.