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Ruthenium Tris(pyrazolyl)borate Diazo Complexes: Preparation of Aryldiazenido, Aryldiazene, and Hydrazine Derivatives

Gabriele Albertin,*,[†] Stefano Antoniutti,[†] Marco Bortoluzzi,[†] Jesus Castro-Fojo,[‡] and Soledad Garcia-Fontán[‡]

Dipartimento di Chimica, Università Ca' Foscari di Venezia, Dorsoduro 2137,
30123 Venezia, Italy, and Departamento de Quimica Inorganica, Universidade de Vigo,
36200 Vigo, Spain

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Tris(pyrazolyl)borate aryldiazenido complexes $[RuTpLL'(ArN_2)](BF_4)_2$ (**1**–**3**) [Ar = C_6H_5, 4-$CH_3C_6H_4$; Tp = hydridotris(pyrazolyl)borate; L = $P(OEt)_3$ or $PPh(OEt)_2$, L′ = PPh_3; L = L′ = $P(OEt)_3$] were prepared by allowing dihydrogen $[RuTp(\eta^2\text{-}H_2)LL']^+$ derivatives to react with aryldiazonium cations. Spectroscopic characterization (IR, ^{15}N NMR) using the ^{15}N-labeled derivatives strongly supports the presence of a linear [Ru]—N≡N—Ar aryldiazenido group. Hydrazine complexes $[RuTp(RNHNH_2)LL']BPh_4$ (**4**–**6**) [R = H, CH_3, C_6H_5, 4-$NO_2C_6H_4$; L = $P(OEt)_3$ or $PPh(OEt)_2$, L′ = PPh_3; L = L′ = $P(OEt)_3$] were also prepared by reacting the $[RuTp(\eta^2\text{-}H_2)LL']^+$ cation with an excess of hydrazine. The complexes were characterized spectroscopically (IR and NMR) and by X-ray crystal structure determination of the $[RuTp(CH_3NHNH_2)\{P(OEt)_3\}(PPh_3)]BPh_4$ (**4d**) derivative. Tris(pyrazolyl)borate aryldiazene complexes $[RuTp(ArN{=}NH)LL']BPh_4$ (**7**–**9**) (Ar = C_6H_5, 4-$CH_3C_6H_4$) were prepared following three different methods: (i) by allowing hydride species RuHTpLL′ to react with aryldiazonium cations in CH_2Cl_2; (ii) by treating aryldiazenido $[RuTpLL'(ArN_2)](BF_4)_2$ with $LiBHEt_3$ in CH_2Cl_2; (iii) by oxidizing arylhydrazine $[RuTp(ArNHNH_2)LL']BPh_4$ complexes with $Pb(OAc)_4$ in CH_2Cl_2 at –30 °C. Methyldiazene complexes $[RuTp(CH_3N{=}NH)LL']BPh_4$ were also prepared by the oxidation of the corresponding methylhydrazine $[RuTp(CH_3NHNH_2)LL']BPh_4$ with $Pb(OAc)_4$.

Introduction

The chemistry of aryldiazenido, diazene, and hydrazine complexes has developed extensively in the past 30 years, using mainly π-acceptors such as carbonyl, phosphine, and cyclopentadienyl as ancillary ligands.[1,2] Less attention has been devoted to the use of N-donor molecules, such as bis(pyrazolyl)borate (Bp) and tris(pyrazolyl)borate[3] (Tp) as ligands, whose studies involve mainly Ti,[4] Mo,[5] and W[5] complexes. No examples of diazo compounds of the iron triad containing (pyrazolyl)borates as supporting ligands have ever been reported.

The interest for this class of compounds is motivated not only by the relationship that the diazo complexes may have with the intermediates of the dinitrogen fixation process but also by the different reactivity modes, dynamic behavior, and structural properties that these complexes may exhibit.[1,2] Of particular interest should be the geometry types (linear or singly or doubly bent) that the aryldiazenido may exhibit as a function of steric and electronic factors of the ligand set. Also, the stabilization of diazene and hydrazine on the

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* To whom correspondence should be addressed. E-mail: albertin@unive.it.

[†] Università Ca' Foscari di Venezia.

[‡] Universidade de Vigo.

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metal center and their reactivity toward oxidation and reduction are important aspects of this chemistry.

We have previously reported[6,7] on the synthesis and reactivity of aryldiazenido, diazene, and hydrazine complexes of the iron triad of the $[M(ArN_2)P_4]^+$, $[M(ArN_2)(CO)_2P_2]^+$, $[M(ArN{=}NH)_2P_4]^{2+}$, and $[M(RNHNH_2)_2P_4]^{2+}$ (M = Fe, Ru, Os; P = phosphites) types containing phosphites and carbonyls as ancillary ligands. Now, we have extended these studies with the aim of introducing tris(pyrazolyl)borate in the diazo chemistry of the iron triad, and in this paper, we report the synthesis and reactivity of unprecedented diazo complexes of ruthenium[8] stabilized by the tris(pyrazolyl)borate ligand.

Experimental Section

General Comments. All synthetic work was carried out in an appropriate atmosphere (Ar, N_2) using standard Schlenk techniques or a vacuum atmosphere drybox. Once isolated, the complexes were found to be relatively stable in air but were stored in an inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $RuCl_3 \cdot 3H_2O$ salt was a ChemPur (U.S.A.) product, used as received. Potassium hydridotris(pyrazolyl)borate (KTp) was prepared according to a published procedure.[9] Phenyldiethoxyphosphine, $PPh(OEt)_2$, was prepared by the method of Rabinowitz and Pellon,[10] while $P(OEt)_3$ was an Aldrich product purified by distillation under nitrogen. Diazonium salts were prepared in the usual way.[11] The related bis(diazonium) salt $[N_2\text{-}Ar\text{-}ArN_2](BF_4)_2$ (Ar−Ar = 4,4′-C_6H_4−C_6H_4) was prepared by treating the amine precursors $H_2NAr\text{-}ArNH_2$ with $NaNO_2$, as described in the literature for common mono(diazonium) salts. The labeled diazonium tetrafluoroborates, $(C_6H_5N{\equiv}{}^{15}N)BF_4$ and $[4,4'\text{-}{}^{15}N{\equiv}NC_6H_4\text{-}C_6H_4N{\equiv}{}^{15}N](BF_4)_2$, were prepared from $Na^{15}NO_2$ (99% enriched, CIL) and the appropriate amine. Hydrazine, NH_2NH_2, was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method.[12] High-grade (99.99%) lead(IV) acetate was purchased from Aldrich. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer. NMR spectra (^1H, ^{31}P, ^{13}C, ^{15}N) were obtained on AC200 or AVANCE 300 Bruker spectrometers at temperatures between −90 and +30 °C, unless otherwise noted. ^1H and ^{13}C spectra are referred to internal tetramethylsilane. $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, while ^{15}N is reported with respect to $CH_3{}^{15}NO_2$; in both cases, downfield shifts are considered positive. The COSY, HMQC, and HMBC NMR experiments were performed using their standard programs. The SwaN-MR software package[13] was used to treat NMR data. The conductivity of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25 °C was measured with a Radiometer CDM 83.

Synthesis of the Complexes. The hydrides RuHTpLL′ [L = $P(OEt)_3$ or $PPh(OEt)_2$; L′ = PPh_3] and $RuHTp\{P(OEt)_3\}_2$, the dihydrogen complexes $[RuTp(\eta^2\text{-}H_2)LL']BF_4$ and $[RuTp(\eta^2\text{-}H_2)\{P(OEt)_3\}_2]BF_4$, and the aquo-complex $[RuTp(H_2O)\{P(OEt)_3\}(PPh_3)]BF_4$ were prepared by following the reported methods.[14]

$[RuTpLL'(ArN_2)](BF_4)_2$ (1, 2, 3) [L = $P(OEt)_3$, L′ = PPh_3 (1); L = $PPh(OEt)_2$, L′ = PPh_3 (2); L = L′ = $P(OEt)_3$ (3); Ar = C_6H_5 (a), 4-$CH_3C_6H_4$ (b)]. Method 1: From the Hydride. An equimolar amount of $HBF_4 \cdot Et_2O$ (0.1 mmol, 14 μL of a 54% solution in Et_2O) was added to a solution of the appropriate hydride RuHTpLL′ (0.1 mmol) in CH_2Cl_2 (10 mL) which had been cooled to −196 °C. The reaction mixture was brought to 0 °C, stirred for 30 min, and then transferred by needle into a three-necked, round-bottomed 25-mL flask containing an excess of the appropriate aryldiazonium salt (0.3 mmol) cooled to −196 °C. The reaction mixture was brought to room temperature and then stirred for about 2 h. The solution was filtered to remove the unreacted diazonium salt and then concentrated under reduced pressure to about 3 mL. By slow addition of a large amount (10−20 mL) of diethyl ether, red-orange microcrystals separated out and were filtered and dried under vacuum; yield ≥ 70%.

Method 2 for $[RuTp\{P(OEt)_3\}(PPh_3)(ArN_2)](BF_4)_2$ (1): From the Aquo-Complex. Solid samples of $[RuTp(H_2O)\{P(OEt)_3\}(PPh_3)]BF_4$ (100 mg, 0.12 mmol) and of the appropriate aryldiazonium salt $[ArN_2]BF_4$ (0.36 mmol) were placed into a 25-mL three-necked, round-bottomed flask. After cooling to −196 °C, CH_2Cl_2 (10 mL) was added, and the reaction mixture, brought to room temperature, was stirred for about 4 h. The solution was filtered to remove the unreacted diazonium salt and then concentrated under reduced pressure to about 3 mL. The addition of diethyl ether (10−20 mL) under vigorous stirring caused the separation of red-orange microcrystals which were filtered and dried under vacuum; yield ≥ 70%. Found: C, 45.63; H, 4.51; N, 11.10. $C_{39}H_{45}B_3F_8N_8O_3P_2Ru$ (**1a**) requires: C, 45.87; H, 4.44; N, 10.97%. $\Lambda_M = 181.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 46.60; H, 4.49; N, 10.69. $C_{40}H_{47}B_3F_8N_8O_3P_2Ru$ (**1b**) requires: C, 46.41; H, 4.58; N, 10.82%. $\Lambda_M = 182.3\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 49.76; H, 4.37; N, 10.64. $C_{44}H_{47}B_3F_8N_8O_2P_2Ru$ (**2b**) requires: C, 49.51; H, 4.44; N, 10.50%. $\Lambda_M = 179.9\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 35.22; H, 4.78; N, 12.25. $C_{27}H_{45}B_3F_8N_8O_6P_2Ru$ (**3a**) requires: C, 35.05; H, 4.90; N, 12.11%. $\Lambda_M = 177.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 35.70; H, 4.97; N, 11.81. $C_{28}H_{47}B_3F_8N_8O_6P_2Ru$ (**3b**) requires: C, 35.81; H, 5.04; N, 11.93%. $\Lambda_M = 182.8\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[RuTp\{P(OEt)_3\}(PPh_3)(C_6H_5N{\equiv}{}^{15}N)](BF_4)_2$ ($1a_1$) and $[RuTp\{P(OEt)_3\}_2(C_6H_5N{\equiv}{}^{15}N)](BF_4)_2$ ($3a_1$). These complexes were

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prepared exactly like the related unlabeled complexes **1a** and **3a**, following method 1 and using ($C_6H_5N{\equiv}^{15}N$)BF_4 as a reagent; yield ≥ 65%.

[RuTp($RNHNH_2$)LL′]BPh_4 (4, 5, 6) [L = $P(OEt)_3$, L′ = PPh_3 (4); L = $PPh(OEt)_2$, L′ = PPh_3 (5); L = L′ = $P(OEt)_3$ (6); R = C_6H_5 (a), 4-$NO_2C_6H_4$ (c), CH_3 (d), H (e)]. To a solution of the appropriate hydride RuHTpLL′ (0.2 mmol) in 10 mL of CH_2Cl_2, cooled to −196 °C, was added an equivalent amount of CF_3SO_3H (0.2 mmol, 18 μL). The reaction mixture was brought to 0 °C and stirred for 30 min and then an excess of the appropriate hydrazine (0.6 mmol) added. After 2 h of stirring, the solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 mL) containing an excess of $NaBPh_4$ (0.4 mmol, 137 mg). A pale yellow solid separated out, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield ≥ 80%. Found: C, 64.46; H, 5.89; N, 9.44. $C_{63}H_{68}B_2N_8O_3P_2Ru$ (**4a**) requires: C, 64.68; H, 5.86; N, 9.58%. $\Lambda_M = 53.1\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 62.42; H, 5.52; N, 10.27. $C_{63}H_{67}B_2N_9O_5P_2Ru$ (**4c**) requires: C, 62.28; H, 5.56; N, 10.38%. $\Lambda_M = 54.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 62.60; H, 5.93; N, 10.26. $C_{58}H_{66}B_2N_8O_3P_2Ru$ (**4d**) requires: C, 62.88; H, 6.00; N, 10.11%. $\Lambda_M = 55.4\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 62.41; H, 5.79; N, 10.10. $C_{57}H_{64}B_2N_8O_3P_2Ru$ (**4e**) requires: C, 62.59; H, 5.90; N, 10.24%. $\Lambda_M = 50.9\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 66.70; H, 5.76; N, 9.24. $C_{67}H_{68}B_2N_8O_2P_2Ru$ (**5a**) requires: C, 66.95; H, 5.70; N, 9.32%. $\Lambda_M = 56.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 65.08; H, 5.74; N, 9.76. $C_{62}H_{66}B_2N_8O_2P_2Ru$ (**5d**) requires: C, 65.33; H, 5.84; N, 9.83%. $\Lambda_M = 49.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 65.21; H, 5.80; N, 9.79. $C_{61}H_{64}B_2N_8O_2P_2Ru$ (**5e**) requires: C, 65.08; H, 5.73; N, 9.95%. $\Lambda_M = 56.2\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 57.22; H, 6.32; N, 10.51. $C_{51}H_{68}B_2N_8O_6P_2Ru$ (**6a**) requires: C, 57.05; H, 6.38; N, 10.44%. $\Lambda_M = 58.0\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[RuTp(ArN=NH)LL′]BPh_4 (7, 8, 9) [Ar = C_6H_5 (a), 4-$CH_3C_6H_4$ (b); L = $P(OEt)_3$, L′ = PPh_3 (7); L = $PPh(OEt)_2$, L′ = PPh_3 (8); L = L′ = $P(OEt)_3$ (9)]. Method 1: From the Hydride. In a 25-mL three-necked, round-bottomed flask were placed solid samples of the appropriate hydride RuHTpLL′ (0.1 mmol) and an excess of aryldiazonium tetrafluoroborate [ArN_2]BF_4 (0.3 mmol). The flask was cooled to −196 °C and CH_2Cl_2 (7 mL) added. The reaction mixture was brought to room temperature and stirred for 2 h and then the solvent removed under reduced pressure. The oil obtained was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.2 mmol, 68 mg). A yellow-orange solid slowly separated out from the resulting solution, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield ≥ 85%. Found: C, 64.60; H, 5.66; N, 9.71. $C_{63}H_{66}B_2N_8O_3P_2Ru$ (**7a**) requires: C, 64.79; H, 5.70; N, 9.59%. $\Lambda_M = 55.0\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 65.22; H, 5.68; N, 9.37. $C_{64}H_{68}B_2N_8O_3P_2Ru$ (**7b**) requires: C, 65.04; H, 5.80; N, 9.48%. $\Lambda_M = 55.7\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 67.23; H, 5.77; N, 9.10. $C_{68}H_{68}B_2N_8O_2P_2Ru$ (**8b**) requires: C, 67.28; H, 5.65; N, 9.23%. $\Lambda_M = 56.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 56.96; H, 6.18; N, 10.35. $C_{51}H_{66}B_2N_8O_6P_2Ru$ (**9a**) requires: C, 57.15; H, 6.21; N, 10.46%. $\Lambda_M = 57.2\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 57.40; H, 6.26; N, 10.17. $C_{52}H_{68}B_2N_8O_6P_2Ru$ (**9b**) requires: C, 57.52; H, 6.31; N, 10.32%. $\Lambda_M = 58.4\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[RuTp($C_6H_5N{=}^{15}NH$){$P(OEt)_3$}(PPh_3)]BPh_4 (7a$_1$) and [RuTp($C_6H_5N{=}^{15}NH$){$P(OEt)_3$}$_2$]BPh_4 (9a$_1$). These complexes were prepared exactly like the related unlabeled **7a** and **9a** using ($C_6H_5N{\equiv}^{15}N$)BF_4 as a reagent; yield ≥ 80%.

[{RuTp[$P(OEt)_3$](PPh_3)}$_2$(μ-4,4′-NH=NC_6H_4−C_6H_4N=NH)](BPh_4)$_2$ (7f). This complex was prepared following the method used for the related compounds **7a** and **7b** by allowing the hydride RuHTp{$P(OEt)_3$}(PPh_3) (74 mg, 0.1 mmol) to react in CH_2Cl_2 (10 mL) with a half-equimolar amount of (4,4′-$N_2C_6H_4$−$C_6H_4N_2$)(BF_4)$_2$ (0.05 mmol, 19 mg) bis(aryldiazonium) salt. The reaction mixture was stirred for 4 h, and the solid obtained was crystallized from CH_2Cl_2 and ethanol; yield ≥ 75%. Found: C, 64.69; H, 5.72; N, 9.48. $C_{126}H_{130}B_4N_{16}O_6P_4Ru_2$ requires: C, 64.85; H, 5.61; N, 9.60%. $\Lambda_M = 126\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[{RuTp[$P(OEt)_3$](PPh_3)}$_2$(μ-4,4′-$^{15}NH{=}NC_6H_4{-}C_6H_4N{=}^{15}NH$)]($BPh_4$)$_2$ (7f$_1$). This complex was prepared exactly like the related unlabeled **7f** using (4,4′-$^{15}N{\equiv}NC_6H_4{-}C_6H_4N{\equiv}^{15}N$)($BF_4$)$_2$ as a reagent; yield ≥ 70%.

[RuTp(ArN=NH)LL′]BPh_4 (7, 8, 9) [L = $P(OEt)_3$, L′ = PPh_3, Ar = C_6H_5 (7a); L = $PPh(OEt)_2$, L′ = PPh_3, Ar = 4-$CH_3C_6H_4$ (8b); L = L′ = $P(OEt)_3$, Ar = C_6H_5 (9a)]. Method 2: From the Aryldiazenido. An equimolar amount of $LiBHEt_3$ (0.1 mmol, 100 μL of a 1 M solution in THF) was added to a solution of the appropriate aryldiazenido [ReTpLL′(ArN_2)](BF_4)$_2$ (0.1 mmol) in 10 mL of CH_2Cl_2 which was cooled to −196 °C. The reaction mixture was brought to 0 °C and stirred for 2 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.2 mmol, 68 mg). A yellow-orange solid slowly separated out from the resulting solution, which was filtered and crystallized twice from CH_2Cl_2 and ethanol; yield ≥ 45%. Found: C, 64.60; H, 5.67; N, 9.68. $C_{63}H_{66}B_2N_8O_3P_2Ru$ (**7a**) requires: C, 64.79; H, 5.70; N, 9.59%. $\Lambda_M = 59.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 67.21; H, 5.56; N, 9.16. $C_{68}H_{68}B_2N_8O_2P_2Ru$ (**8b**) requires: C, 67.28; H, 5.65; N, 9.23%. $\Lambda_M = 58.1\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 57.39; H, 6.14; N, 10.35. $C_{51}H_{66}B_2N_8O_6P_2Ru$ (**9a**) requires: C, 57.15; H, 6.21; N, 10.46%. $\Lambda_M = 59.7\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[RuTp(C_6H_5N=NH)LL′]BPh_4 (7a, 9a) [L = $P(OEt)_3$, L′ = PPh_3 (7); L = L′ = $P(OEt)_3$ (9)]. Method 3: Oxidation of the Hydrazine. A solid sample of the appropriate hydrazine complexes **4**, **6** (0.2 mmol) was placed in a 25-mL three-necked, round-bottomed flask fitted with a solid-addition sidearm containing a slight excess of $Pb(OAc)_4$ (0.22 mmol, 97 mg). Dichloromethane (10 mL) was added, the solution cooled to −30 °C and the $Pb(OAc)_4$ added portionwise over 20−30 min to the cold, stirring solution. The solution was warmed to room temperature and stirred for 15 min and then the solvent removed under reduced pressure. The oil obtained was treated with ethanol (3 mL) containing an excess of $NaBPh_4$ (0.4 mmol, 137 mg), and the yellow-orange solid was filtered and recrystallized from CH_2Cl_2 and ethanol; yield ≥ 65%. Found: C, 64.60; H, 5.81; N, 9.43. $C_{63}H_{66}B_2N_8O_3P_2Ru$ (**7a**) requires: C, 64.79; H, 5.70; N, 9.59%. $\Lambda_M = 56.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 57.28; H, 6.17; N, 10.32. $C_{51}H_{66}B_2N_8O_6P_2Ru$ (**9a**) requires: C, 57.15; H, 6.21; N, 10.46%. $\Lambda_M = 60.4\ \Omega^{-1}\ mol^{-1}\ cm^2$.

[RuTp(CH_3N=NH){$P(OEt)_3$}(PPh_3)]BPh_4 (7d). These complexes were prepared by oxidation of the methylhydrazine complexes with $Pb(OAc)_4$, following the method used for the related phenyldiazene **7a**, **9a** derivatives (method 3). The pale-yellow solid obtained was twice crystallized from CH_2Cl_2 and ethanol at 0 °C; yield ≥ 30%. Found: C, 62.89; H, 5.75; N, 10.27. $C_{58}H_{64}B_2N_8O_3P_2Ru$ requires: C, 63.00; H, 5.83; N, 10.13%. $\Lambda_M = 56.7\ \Omega^{-1}\ mol^{-1}\ cm^2$.

X-ray Crystal Structure Determination of [RuTp(CH_3NHNH_2){$P(OEt)_3$}(PPh_3)]BPh_4 (4d). The data were collected on a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation. Absorption correction was carried out using SADABS.[15] The structure was solved by direct methods and refined by full-matrix least squares based[16] on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions

Table 1. Crystal Data and Structure Refinement for $[RuTp(CH_3NHNH_2)\{(POEt)_3\}(PPh_3)]BPh_4$ (**4d**)

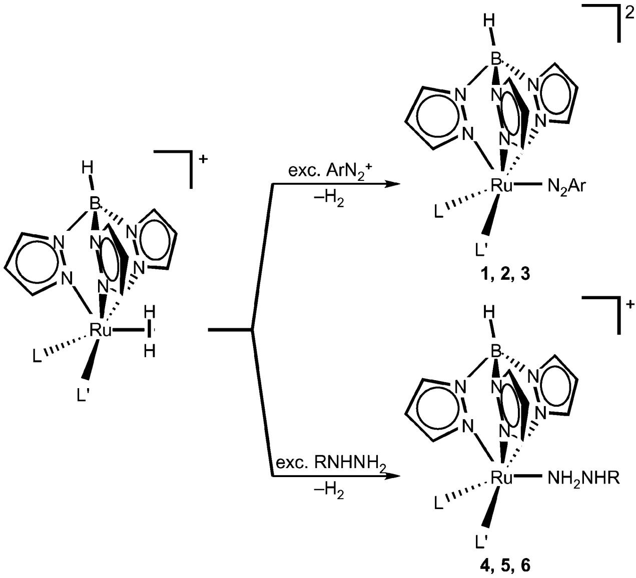
compound	$[RuTp(CH_3NHNH_2)\{(POEt)_3\}(PPh_3)]BPh_4$
empirical formula	$C_{58}H_{66}B_2N_8O_3P_2Ru$
fw	1107.82
temp	293(2) K
wavelength	0.710 73 Å
cryst syst	orthorhombic
space group	*Pbca*
unit cell dimensions	$a = 14.2119(19)$ Å $b = 27.294(4)$ Å $c = 29.490(4)$ Å
vol	114 39(3) $Å^3$
Z	8
density (calcd)	1.287 Mg/m^3
abs coeff	0.380 mm^{-1}
$F(000)$	4624
cryst size	$0.37 \times 0.22 \times 0.08$ mm^3
θ range for data collection	1.38−28.10°
index ranges	$-9 \le h \le 18, -36 \le k \le 35, -38 \le l \le 38$
reflns collected	54 280
independent reflns	13 531 [$R(int) = 0.1685$]
completeness to $\theta = 28.10°$	97.0%
abs correction	multiscan
max and min transmission	1.0000 and 0.7863
data/restraints/params	13 531/0/679
GOF on F^2	0.680
final R indices [I > 2σ(I)]	$R_1 = 0.0447$, $wR_2 = 0.0438$
R indices (all data)	$R_1 = 0.3060$, $wR_2 = 0.0839$
largest diff peak and hole	0.427 and −0.358 e $Å^{-3}$

and refined with isotropic displacement parameters, except those attached to nitrogen atoms of the hydrazine molecule, which were located and refined with isotropic displacement parameters. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from *International Tables for X-ray Crystallography*.[17] Data collection and refinement results are summarized in Table 1.

Results and Discussion

Aryldiazenido Complexes. Dihydrogen complexes[14,18] $[RuTp(\eta^2\text{-}H_2)LL']BF_4$ [L = $P(OEt)_3$ and $PPh(OEt)_2$; L′ = PPh_3] react with aryldiazonium cations in CH_2Cl_2 to give the aryldiazenido $[RuTpLL'(ArN_2)](BF_4)_2$ (**1**, **2**, **3**) derivatives (Scheme 1).

Scheme 1[a]



1, 2, 3

4, 5, 6

[a] L = $P(OEt)_3$, L′ = PPh_3 **1**, **4**; L = $PPh(OEt)_2$, L′ = PPh_3 **2**, **5**; L = L′ = $P(OEt)_3$ **3**, **6**; Ar = C_6H_5 **a**, 4-$CH_3C_6H_4$ **b**; R = C_6H_5 **a**, 4-$NO_2C_6H_4$ **c**, CH_3 **d**, H **e**.

The reaction proceeds with the replacement of the η^2-H_2 ligand, giving the dicationic complexes **1**−**3** which were isolated in good yield (≥70%) and characterized. The $[RuTp\{P(OEt)_3\}(PPh_3)(ArN_2)](BF_4)_2$ (**1**) compounds can also be prepared by substituting the H_2O ligand in the $[RuTp(H_2O)\{P(OEt)_3\}(PPh_3)]BF_4$ complex with aryldiazonium cations in CH_2Cl_2 as the solvent. The reaction is slower than that with the η^2-H_2 precursor, but it also gives the dicationic complexes **1** in good yield (Scheme 2).

Good analytical data were obtained for the crystallized samples of aryldiazenido complexes **1**−**3**, which are red-orange solids stable in air and in a solution of polar organic solvents, where they behave as 2:1 electrolytes.[19] The IR and NMR data (Table 2) support the proposed formulation. We have also obtained crystals of **1b**, but their poor quality prevented any X-ray structure determination. The IR spectra show, beside the absorptions of the Tp and the phosphine ligands, a broad medium-intensity band at 2095−2073 cm^{-1} attributed to the $\nu(N_2)$ of the aryldiazenido ligand. This assignment was confirmed by the ^{15}N isotopic substitution of the ArN_2 ligand. A shift of this absorption to lower wavenumbers, by 25−29 cm^{-1}, was observed in the labeled **1a$_1$** and **3a$_1$** derivatives. The $\nu(N_2)$ value of our complexes **1**−**3** also suggests[20] a near-linear structure (Chart 1) for the RuNNAr group when compared to literature data.[8a] The ^{15}N NMR spectra confirm this hypothesis showing a multiplet at −70.7 (**1a$_1$**) and −75.3 (**3a$_1$**) ppm, which falls in the range of linear aryldiazenido ligands.[8a,21]

The ^1H NMR spectra of **1**−**3** support their formulation, showing the characteristic signals of the Tp ligand and the phosphine groups. In the spectra of **1b**, **2b**, and **3b**, the singlet of the methyl substituent of the 4-$CH_3C_6H_4N{\equiv}N$ ligand at 2.54−2.51 ppm is also observed. In a temperature range between −80 and +20°C, the $^{31}P\{^1H\}$ NMR spectra of $[RuTpL(PPh_3)(ArN_2)](BF_4)_2$ (**1**, **2**) appear as AB quartets due to the presence of two different phosphine ligands. Coupling with ^{15}N was also observed in the spectrum of the labeled **1a$_1$** complex, which appeared as an ABX (X = ^{15}N) multiplet with the two $J_{P^{15}N}$ of 6.5 and 3.5 Hz, respectively. The spectra of the $[RuTp\{P(OEt)_3\}_2(ArN_2)](BF_4)_2$ (**3**) phosphite derivatives, instead, appear as sharp singlets due to the magnetic equivalence of the two phosphite ligands. A doublet with $J_{P^{15}N}$ of 6.7 Hz was observed in the spectra of the labeled $[RuTp\{P(OEt)_3\}_2(C_6H_5N{\equiv}^{15}N)](BF_4)_2$ (**3a$_1$**) derivative.

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(15) Sheldrick, G. M. *SADABS, An Empirical Absorption Correction Program for Area Detector Data*; University of Göttingen: Germany, 1996.

(16) Sheldrick, G. M. *SHELX-97, Program for the Solution and Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.

(17) *International Tables for X-ray Crystallography*; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.

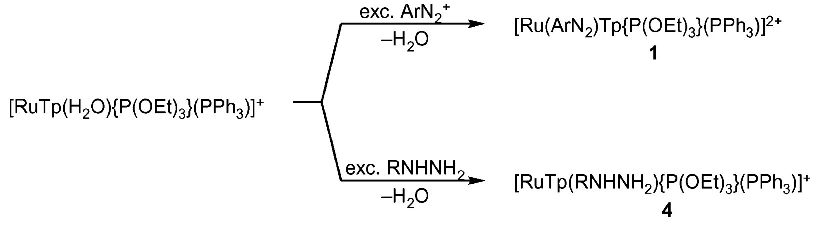
(18) The dihydrogen complexes $[RuTp(\eta^2\text{-}H_2)LL']BF_4$ used in these studies were prepared in solution by treating the hydrides RuHTpLL′ with an equimolar amount of $HBF_4 \cdot Et_2O$.

(19) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81−122.

(20) (a) Bowden, W. L.; Little, W. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 5084−5085. (b) Bowden, W. L.; Little, W. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 4340−4345.

(21) Haymore, B. L.; Hughes, M.; Mason, J.; Richards, R. C. *J. Chem. Soc., Dalton Trans.* **1988**, 2935−2940.

Scheme 2[a]



[a] Ar = C_6H_5 **a**, 4-$CH_3C_6H_4$ **b**; R = C_6H_5 **a**, 4-$NO_2C_6H_4$ **c**, CH_3 **d**, H **e**.

Chart 1

$$[Ru]-N\equiv N-Ar$$

1 - 3

On the basis of these data, a geometry of the type reported in Scheme 1 can reasonably be proposed for our aryldiazenido derivatives.

Aryldiazenido complexes of the iron triad are reported[1,2,6−8,20] with several supporting ligands such as tertiary phosphine, carbonyl, cyclopentadienyl, and 2,2′-bipyridine. With hydrido-tris(pyrazolyl)borate, instead, the chemistry of organo−diazo complexes appears to be largely unexplored, and complexes **1**−**3** are, to the best of our knowledge, the first tris(pyrazolyl)borate diazo complexes of the iron triad. The use of mixed-ligand dihydrogen $[RuTp(\eta^2\text{-}H_2)LL']BF_4$ complexes with phosphite and Tp as precursors appears to be an easy entry into this chemistry. The high value of $\nu(N_2)$ (2095−2073 cm^{-1}) and the value of δ ^{15}N (approximately −70 ppm) for **1**−**3** suggest the presence of a linear ArN_2 group in our complexes. The comparable $[RuCp(PPh_3)_2(ArN_2)](BF_4)_2$ complexes,[8a] containing cyclopentadienyl instead of Tp as supporting ligand, showed similar values for $\nu(N_2)$ and δ ^{15}N, and an X-ray crystal structure indicated a near-linear Ru−N−N−C geometry for the aryldiazenido ligand. This precedent supports the hypothesis of the geometry of our complexes **1**−**3** (Chart 1) and shows that either Cp or Tp as ancillary ligand gives the strictly comparable aryldiazenido $[RuCp(PPh_3)_2(ArN_2)](BF_4)_2$ and $[RuTpLL'(ArN_2)](BF_4)_2$ (**1**−**3**) derivatives. Although a complete comparison cannot be made for the absence of mixed-ligand $[RuCpLL'(ArN_2)]^{2+}$ species, the spectroscopic properties suggest that the introduction of phosphite ligands in RuTp chemistry makes the [RuTpLL′] fragment able to bind the aryldiazenido group and is strictly comparable to the $[RuCp(PPh_3)_2]$ one. Furthermore, as previously observed in related dicationic[8a,20] $[RuCp(PPh_3)_2(ArN_2)](BF_4)_2$ and $[RuCl(bpy)_2(ArN_2)](PF_6)_2$ compounds, the linear arrangement of the ArNN ligand seems to be strongly dependent on the formal 2+ charge of the complexes.

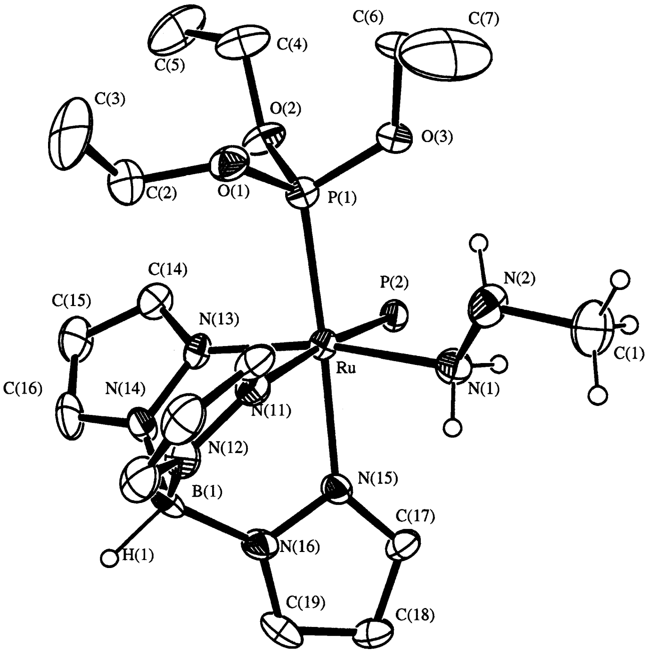


Figure 1. ORTEP diagram (30% probability level) of the cation $[RuTp(CH_3NHNH_2)\{P(OEt)_3\}(PPh_3)]^+$ (**4d**$^+$). The phenyl groups have been omitted for the sake of clarity.

Hydrazine Complexes. Hydrazine, $RNHNH_2$, can replace the dihydrogen ligand in $[RuTp(\eta^2\text{-}H_2)LL']^+$ cations to give $[RuTp(RNHNH_2)LL']^+$ (**4**, **5**, **6**) derivatives, which were isolated as BPh_4 salts and characterized (Scheme 1). The reaction easily proceeds at room temperature in CH_2Cl_2 yielding a series of hydrazine complexes of the type **4**−**6**. Also, the aquo-complex $[RuTp(H_2O)\{P(OEt)_3\}(PPh_3)]^+$ can be used as a precursor, by replacing H_2O with hydrazine, to give the final derivatives **4** (Scheme 2).

The hydrazine complexes **4**−**6** were isolated as white or pale-yellow solids stable in air and in a solution of polar organic solvents, where they behave as 1:1 electrolytes.[19] Their characterization is supported by analytical and spectroscopic data (Table 2) and by the X-ray crystal structure determination of the methylhydrazine complex **4d**. The ORTEP drawing of the $[RuTp(CH_3NHNH_2)\{P(OEt)_3\}(PPh_3)]^+$ cation (**4d**$^+$) is shown in Figure 1.

The ruthenium atom has a slightly distorted octahedral arrangement of donor atoms. Selected bond distances and angles are displayed in Table 3. The shortest angle in the octahedron is not due to the chelating effect of the scorpionate ligand Tp, but the value of the N(15)−Ru−N(1) angle is only 80.87(17)°, indicating a displacement of the hydrazine ligand. Also, the equatorial plane containing the atoms labeled as N(11), N(13), P(2), and N(1) shows both a poor planarity (rms of 0.0314) when compared with the other two planes of the octahedron (rms of 0.0125 and 0.0026) and that the N(1) atom lies 0.128(8) Å out of the plane formed by the other three donor atoms N(11), N(13), and P(2).

The Ru−P bond distances show a difference between them of 0.923 Å due to the different nature of the phosphine

Table 2. IR and NMR Data for Ruthenium Complexes

		IR[a]		^{1}H NMR[b]			^{31}P{^{1}H} NMR[b,c]
	compound	ν/cm^{-1}	assgnt	δ, J/Hz	assgnt	spin system	δ, J/Hz
1a	$[RuTp\{P(OEt)_3\}(PPh_3)(C_6H_5N{\equiv}N)](BF_4)_2$	(2523) w	ν(BH)	8.29−6.26 m	Ph + Tp	AB	δ_A 103.1
		(2079) m	ν(NN)	3.92 m	CH_2		δ_B 25.9
				3.63 m			$J_{AB} = 49.0$
				1.14 t	CH_3		
1a$_1$	$[RuTp\{P(OEt)_3\}(PPh_3)(C_6H_5N{\equiv}^{15}N)](BF_4)_2$[d]	(2523) w	ν(BH)	8.30−6.28 m	Ph + Tp	ABX	δ_A 103.8
		(2050) m	$\nu(^{15}NN)$	3.91 m	CH_2	(X = ^{15}N)	δ_B 26.2
				3.63 m			$J_{AB} = 48.9$
				1.15 t	CH_3		$J_{AX} = 6.50$
							$J_{BX} = 3.50$
1b	$[RuTp\{P(OEt)_3\}(PPh_3)(4\text{-}CH_3C_6H_4N{\equiv}N)](BF_4)_2$[e]	(2519) w	ν(BH)	8.54−6.25 m	Ph + Tp	AB	δ_A 104.2
		(2084) m	ν(NN)	3.85 m	CH_2		δ_B 26.4
				3.60 m			$J_{AB} = 49.4$
				2.54 s	CH_3 *p*-tol		
				1.14 t	CH_3 phos		
2b	$[RuTp\{PPh(OEt)_2\}(PPh_3)(4\text{-}CH_3C_6H_4N{\equiv}N)](BF_4)_2$	(2529) w	ν(BH)	8.53−6.14 m	Ph + Tp	AB	δ_A 137.2
		(2073) m	ν(NN)	4.16 m	CH_2		δ_B 26.1
				4.08 m			$J_{AB} = 41.0$
				3.62 m			
				3.08 m			
				2.52 s	CH_3 *p*-tol		
				1.54 t	CH_3 phos		
				0.96 t			
3a	$[RuTp\{P(OEt)_3\}_2(C_6H_5N{\equiv}N)](BF_4)_2$	(2490) w	ν(BH)	8.55−6.10 m	Ph + Tp	A_2	106.2 s
		(2087) m	ν(NN)	3.66 m	CH_2		
				1.19 t	CH_3		
3a$_1$	$[RuTp\{P(OEt)_3\}_2(C_6H_5N{\equiv}^{15}N)](BF_4)_2$[f]	(2492) m	ν(BH)	8.55−6.10 m	Ph + Tp	A_2X	δ_A 106.8
		(2062) m	$\nu(^{15}NN)$	3.66 m	CH_2	(X = ^{15}N)	$J_{AX} = 6.7$
				1.19 t	CH_3		
3b	$[RuTp\{P(OEt)_3\}_2(4\text{-}CH_3C_6H_4N{\equiv}N)](BF_4)_2$	(2498) m	ν(BH)	8.51−6.10 m	Ph + Tp	A_2	107.0 s
		(2095) m	ν(NN)	3.90 m	CH_2		
				2.51 s	CH_3 *p*-tol		
				1.25 t	CH_3 phos		
4a	$[RuTp(C_6H_5NHNH_2)\{P(OEt)_3\}(PPh_3)]BPh_4$	3360 sh	ν(NH)	7.98−6.11 m	Ph + Tp	AB	δ_A 132.9
		3348 m		4.91 m	$RuNH_2$		δ_B 48.7
		3283 m		3.96 m			$J_{AB} = 56$
		2493 m	ν(BH)	4.50 m	NH		
		1608 m	$\delta(NH_2)$	3.64 m	CH_2		
				3.34 m			
				1.04 t	CH_3		
4c	$[RuTp(4\text{-}NO_2C_6H_4NHNH_2)\{P(OEt)_3\}(PPh_3)]BPh_4$	3385 w	ν(NH)	8.01−6.03 m	Ph + Tp	AB	δ_A 131.4
		3327 w		5.49 m	NH		δ_B 47.0
		3267 w		4.62 m	$RuNH_2$		$J_{AB} = 55$
		2488 m	ν(BH)	3.98 m			
		1601 m	$\delta(NH_2)$	3.65 m	CH_2		
				3.35 m			
				1.03 t	CH_3		
4d	$[RuTp(CH_3NHNH_2)\{P(OEt)_3\}(PPh_3)]BPh_4$[g]	3346 m	ν(NH)	8.08−6.09 m	Ph + Tp	AB	δ_A 132.9
		3271 m		3.61 m	CH_2		δ_B 48.9
		3196 w		3.36 m			$J_{AB} = 56$
		2480 m	ν(BH)	3.56 m	$RuNH_2$		
				3.37 m			
				3.06 m	NH		
				2.11 d	NCH_3		
				$J_{HH} = 6$			
				1.04 t	CH_3 phos		
4e	$[RuTp(NH_2NH_2)\{P(OEt)_3\}(PPh_3)]BPh_4$	3374 br, m	ν(NH)	8.06−6.09 m	Ph + Tp	AB	δ_A 132.8
		3305 br, w		3.85 m	$RuNH_2$		δ_B 48.8
		3276 br, m		3.43 m			$J_{AB} = 55$
		2486 m	ν(BH)	3.64 m	CH_2		
				3.32 m			
				2.77 t, br	NH_2		
				1.05 t	CH_3		
5a	$[RuTp(C_6H_5NHNH_2)\{PPh(OEt)_2\}(PPh_3)]BPh_4$	3342 br, m	ν(NH)	8.01−5.81 m	Ph + Tp	AB	δ_A 169.7
		3283 w		5.95 m	$RuNH_2$		δ_B 47.7
		2493 m	ν(BH)	3.80 m			$J_{AB} = 51$
		1605 m	$\delta(NH_2)$	4.31 t, br	NH		
				4.15 m	CH_2		
				3.84 m			
				3.48 m			
				3.13 m			
				1.65 t	CH_3		
				0.88 t			

Table 2. (Continued)

		IR[a]		^{1}H NMR[b]			$^{31}P\{^1H\}$ NMR[b,c]
	compound	ν/cm^{-1}	assgnt	δ, J/Hz	assgnt	spin system	δ, J/Hz
5d	$[RuTp(CH_3NHNH_2)\{PPh(OEt)_2\}(PPh_3)]BPh_4$[h]	3340 m	ν(NH)	7.99−5.81 m	Ph + Tp	AB	δ_A 169.5
		3267 m		4.11 m	CH_2		δ_B 49.2
		3248 sh		3.85 m			$J_{AB} = 52$
		2482 m	ν(BH)	3.46 m			
				3.08 m			
				3.69 m	NH		
				3.58 m	$RuNH_2$		
				3.18 m			
				2.23 d	NCH_3		
				$J_{HH} = 6$			
				1.58 t	CH_3 phos		
				0.86 t			
5e	$[RuTp(NH_2NH_2)\{PPh(OEt)_2\}(PPh_3)]BPh_4$	3364 m	ν(NH)	7.96−5.83 m	Ph + Tp	AB	δ_A 169.5
		3294 w		4.02 m	CH_2		δ_B 49.0
		3284 m		3.76 m			$J_{AB} = 52$
		2488 m	ν(BH)	3.44 m			
				3.06 m			
				3.48 m	$RuNH_2$		
				3.08 m	NH_2		
				1.52 t	CH_3		
				0.88 t			
6a	$[RuTp(C_6H_5NHNH_2)\{P(OEt)_3\}_2]BPh_4$	3356 m, br	ν(NH)	7.87−6.19 m	Ph + Tp	A_2	135.6 s
		3288 w		5.29 m, br	NH		
		2478 m	ν(BH)	4.94 t, br	$RuNH_2$		
		1601 m	$\delta(NH_2)$	3.62 m	CH_2		
				1.17 t	CH_3		
7a	$[RuTp(C_6H_5N{=}NH)\{P(OEt)_3\}(PPh_3)]BPh_4$	2488 m	ν(BH)	13.87 s, br	NH	AB	δ_A 128.8
				8.00−6.08 m	Ph + Tp		δ_B 41.9
				3.68 m	CH_2		$J_{AB} = 55$
				3.38 m			
				1.06 t	CH_3		
7a$_1$	$[RuTp(C_6H_5N{=}^{15}NH)\{P(OEt)_3\}(PPh_3)]BPh_4$[i]	2486 m	ν(BH)	ABXY spin syst	NH	ABX	δ_A 129.1
				(Y = H, X = ^{15}N)			δ_B 41.9
				δ_Y 13.86			$J_{AB} = 55$
				$J_{AX} = 4.40$			$J_{AX} = 4.40$
				$J_{BX} = 2.80$			$J_{BX} = 2.80$
				$J_{XY} = 64.9$			
				$J_{AY} = 3.68$			
				$J_{BY} = 1.26$			
				8.02−6.08 m	Ph + Tp		
				3.69 m	CH_2		
				3.40 m			
				1.07 t	CH_3		
7b	$[RuTp(4\text{-}CH_3C_6H_4N{=}NH)\{P(OEt)_3\}(PPh_3)]BPh_4$[j]			13.70 s, br	NH	AB	δ_A 128.7
				8.00−6.05 m	Ph + Tp		δ_B 41.5
				3.68 m	CH_2		$J_{AB} = 56$
				3.35 m			
				2.38 s	CH_3 *p*-tol		
				1.06 t	CH_3 phos		
7d	$[RuTp(CH_3N{=}NH)\{P(OEt)_3\}(PPh_3)]BPh_4$			13.52 s, br	NH	AB	δ_A 132.9
				8.00−5.95 m	Ph + Tp		δ_B 47.5
				3.62 m	CH_2		$J_{AB} = 55$
				3.30 m			
				3.04 s	NCH_3		
				1.02 t	CH_3 phos		
7f	$[\{RuTp[P(OEt)_3](PPh_3)\}_2$ $(\mu\text{-}4,4'\text{-}NH{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_2$	2488 m	ν(BH)	13.98 m, br	NH	AB	δ_A 128.8
				8.00−6.08 m	Ph + Tp		δ_B 41.7
				3.68 m	CH_2		$J_{AB} = 55$
				3.38 m			
				1.08 t	CH_3		
7f$_1$	$[\{RuTp[P(OEt)_3](PPh_3)\}_2$ $(\mu\text{-}4,4'\text{-}^{15}NH{=}NC_6H_4{-}C_6H_4N{=}^{15}NH)](BPh_4)_2$[k]	2486 m	ν(BH)	ABXY spin syst	NH	ABX	δ_A 128.7
				(Y = H, X = ^{15}N)			δ_B 41.8
				δ_Y 14.00			$J_{AB} = 55.0$
				$J_{AX} = 4.80$			$J_{AX} = 4.80$
				$J_{BX} = 2.60$			$J_{BX} = 2.60$
				$J_{XY} = 64.8$			
				$J_{AY} = 3.45$			
				$J_{BY} = 0.81$			
				8.05−6.10 m	Ph + Tp		
				3.75 m	CH_2		
				3.42 m			
				1.11 t	CH_3		

Table 2. (Continued)

	compound	IR[a] ν/cm^{-1}	IR[a] assgnt	^{1}H NMR[b] δ, J/Hz	^{1}H NMR[b] assgnt	spin system	$^{31}P\{^1H\}$ NMR[b,c] δ, J/Hz
8b	$[RuTp(4\text{-}CH_3C_6H_4N{=}NH)\{PPh(OEt)_2\}(PPh_3)]BPh_4$	2484 m	ν(BH)	13.46 s, br	NH	AB	δ_A 161.3
				8.01−5.92 m	Tp + Ph		δ_B 38.9
				3.77 qnt	CH_2		$J_{AB} = 45$
				3.33 qnt			
				2.38 s	CH_3 *p*-tol		
				1.32 t	CH_3 phos		
				0.89 t			
9a	$[RuTp(C_6H_5N{=}NH)\{P(OEt)_3\}_2]BPh_4$	2478 m	ν(BH)	14.44 s, br	NH	A_2	130.5 s
				8.01−6.28 m	Ph + Tp		
				3.65 m	CH_2		
				1.19 t	CH_3		
9a₁	$[RuTp(C_6H_5N{=}^{15}NH)\{P(OEt)_3\}_2]BPh_4$[l]	2478 m	ν(BH)	A_2XY spin syst	NH	A_2X	δ_A 130.3
				(Y = H, X = ^{15}N)			$J_{AX} = 5.2$
				δ_Y 14.47			
				$J_{AX} = 5.2$			
				$J_{AY} = 3.6$			
				$J_{XY} = 66.0$			
				8.04−6.28 m	Ph + Tp		
				3.68 m	CH_2		
				1.19 t	CH_3		
9b	$[RuTp(4\text{-}CH_3C_6H_4N{=}NH)\{P(OEt)_3\}_2]BPh_4$	2492 m	ν(BH)	14.30 t, br	NH	A_2	130.9 s
				$J_{PH} = 4.0$			
				8.51−6.26 m	Ph + Tp		
				3.68 m	CH_2		
				2.40 s	CH_3 *p*-tol		
				1.17 t	CH_3 phos		

[a] In KBr pellets and (CH_2Cl_2). [b] In CD_2Cl_2 at 25 °C, unless otherwise noted. [c] Positive shift downfield from 85% H_3PO_4. [d] ^{15}N NMR: ABX spin system (X = ^{15}N), δ_X −70.7, $J_{AX} = 6.50$, $J_{BX} = 3.50$ Hz. [e] ^{13}C NMR: 151−108 m Ph + Tp, 66.1 d CH_2, 22.7 s CH_3 *p*-tolyl, 15.9 d CH_3 phos. [f] ^{15}N NMR: A_2X spin system (X = ^{15}N), δ_X −75.3, $J_{AX} = 6.7$ Hz. [g] ^{13}C NMR: 165−127 m Ph + Tp, 62.4 d CH_2, 42.3 s NCH_3, 16.1 d CH_3 phos. [h] ^{13}C NMR: 165−106 m Ph + Tp, 66.0 d, 65.9 d CH_2, 42.5 s NCH_3, 16.9 d, 16.1 d CH_3 phos. [i] ^{15}N NMR: ABXY spin system (X = ^{15}N, Y = ^{1}H), δ_X −10.9, $J_{AX} = 4.40$, $J_{BX} = 2.80$, $J_{AY} = 3.68$, $J_{BY} = 1.26$, $J_{XY} = 64.9$ Hz. [j] ^{13}C NMR: 165−106 m Ph + Tp, 62.7 d CH_2, 21.5 s CH_3 *p*-tolyl, 16.1 d CH_3 phos. [k] ^{15}N NMR: ABXY spin system (X = ^{15}N, Y = ^{1}H), δ_X −12.1, $J_{AX} = 4.80$, $J_{BX} = 2.60$, $J_{AY} = 3.45$, $J_{BY} = 0.81$, $J_{XY} = 64.8$ Hz. [l] ^{15}N NMR: A_2XY spin system (X = ^{15}N, Y = ^{1}H), δ_X −15.2, $J_{AX} = 5.2$, $J_{AY} = 3.6$, $J_{XY} = 66.0$ Hz.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for **4d**

Ru−N(13)	2.085(4)	Ru−N(11)	2.111(4)
Ru−N(15)	2.123(4)	Ru−N(1)	2.154(3)
Ru−P(1)	2.2348(16)	Ru−P(2)	2.3271(15)
N(1)−N(2)	1.437(5)	N(2)−C(1)	1.461(6)
N(13)−Ru−N(11)	87.0(2)	N(13)−Ru−N(15)	89.00(18)
N(11)−Ru−N(15)	82.18(17)	N(13)−Ru−N(1)	168.00(19)
N(11)−Ru−N(1)	85.31(18)	P(1)−Ru−P(2)	94.57(6)
N(13)−Ru−P(1)	91.28(13)	N(11)−Ru−P(1)	91.29(13)
N(15)−Ru−P(1)	173.44(13)	N(1)−Ru−P(1)	98.05(12)
N(13)−Ru−P(2)	92.19(14)	N(11)−Ru−P(2)	174.09(14)
N(15)−Ru−P(2)	91.96(13)	N(1)−Ru−P(2)	94.55(12)
N(2)−N(1)−Ru	123.2(3)	N(1)−N(2)−C(1)	110.8(4)
N(14)−B(1)−N(12)	108.1(6)	N(14)−B(1)−N(16)	110.1(6)
N(16)−B(1)−N(12)	107.0(6)	O(1)−P(1)−O(2)	103.1(2)
O(1)−P(1)−O(3)	98.9(2)	O(2)−P(1)−O(3)	107.2(2)
C(61)−P(2)−C(71)	97.9(3)	C(61)−P(2)−C(81)	102.3(3)
C(81)−P(2)−C(71)	103.6(3)		

Table 4. Selected Hydrogen Bonds[a]

	D−H	H···A	D···A	∠(DHA)
N(2)−H(2)···O(3)	1.01(6)	2.01(6)	2.926(7)	150(6)
N(1)−H(1A)···N(15)	0.90	2.50	2.775(6)	98.2
N(1)−H(1B)···Cg[b]	0.90	2.71	3.590(4)	166.5
C(6)−H(6A)···O(1)	0.97	2.44	2.837(7)	104.4
C(14)−H(14)···O(2)	0.93	2.53	3.091(7)	119.5
C(66)−H(66)···N(15)	0.93	2.48	3.093(7)	124.0

[a] With esd's except riding H. [b] Cg represents the centroid of the phenyl ring labeled as 8.

ligands.[22b] The Ru−N bond distances from the Tp ligand in trans orientation to the phosphine ligands are slightly shorter than the values expected under a trans influence of the phosphine ligands.[22] The Ru−N(13) bond length is shorter, because the hydrazine ligand is in the trans position.

The dihedral angles between the pyrazolyl rings are 120.6(2)°, 125.7(2)°, and 113.7(2)° (expected 120°), and a similar distortion can be found in the angles around the boron atom (N−B−N angles) (Table 3). We can infer from these values that the pyrazolyl ring containing N(15) and N(16) atoms is deviated from its natural position, probably because of the hydrogen bonds in which this ring(s) is implied (vide infra).

Although there are not substantial intermolecular interactions, the molecular arrangement is stabilized by some intramolecular classic and nonclassic hydrogen bonds. Classic ones involve both nitrogen atoms of the hydrazine ligand with N(15) of one pyrazolyl ligand and O(3) of the phosphite ligand (Table 4). The nonclassic ones involve both C−H···N or C−H···O as well as N−H···π. This last one involves the NH_2 group of the hydrazine ligand and the π-cloud of a phenyl ring of the phosphine ligand (Figure 2). The mean values of these bond distances fall within the range previously observed.[23]

All other structural parameters in the ligands, as well as in the BPh_4^- anion, are in the normal range.

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(22) (a) Jiménez Tenorio, M. A.; Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Dalton Trans.* **1998**, 3601−3607. (b) Conner, D.; Jayaprakash, K. N.; Gunoe, T. B.; Boyle, P. D. *Inorg. Chem.* **2002**, *41*, 3042−3049. (c) Buriez, B.; Burns, I. D.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1999**, *18*, 1504−1516.

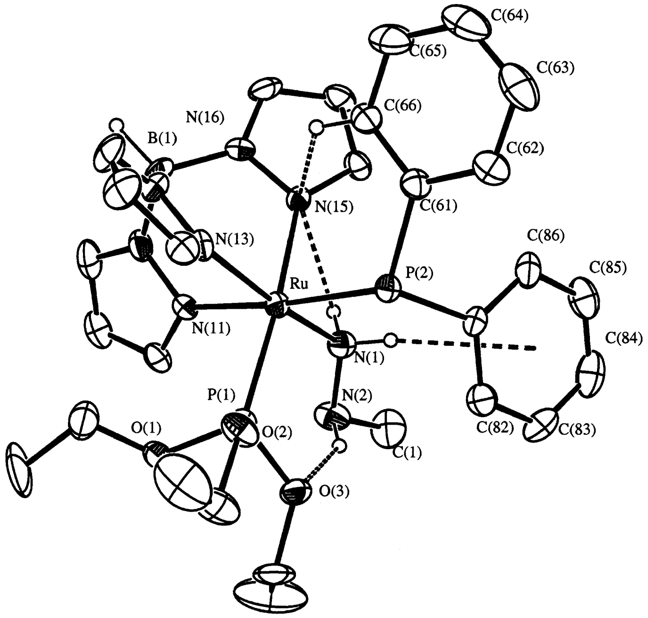

Figure 2. View of the cation **4d**$^+$ showing the intramolecular H-bonds. One of the phenyl groups has been omitted.

The IR spectra of all the complexes **4**−**6** show the characteristic absorptions of the Tp, the phosphine ligands, and the BPh_4^- anion. In the 3385−3196 cm^{-1} region, furthermore, three or four weak bands are present, attributed to the ν(NH) of the hydrazine ligands. The presence of the $RNHNH_2$ group is confirmed by ^{1}H NMR spectra, which show the NH and NH_2 resonances as slightly broad multiplets between 5.95 and 2.77 ppm (Table 2).

Unexpectedly, for the mixed-ligand phosphine−phosphite $[RuTp(RNHNH_2)L(PPh_3)]BPh_4$ (**4**, **5**) complexes, three NH resonances were observed for the coordinated $RNHNH_2$ ligands, with 1:1:1 intensity ratio (1:1:2 ratio for NH_2NH_2 in **4a** and **5a**). The attributions were confirmed by homodecoupling experiments and ^{1}H COSY spectra, which indicated that the two hydrogens of the coordinated NH_2 group fall at different chemical shift values. This is probably due to the coordination of the NH_2 group of hydrazine to the $[RuTpL(PPh_3)]$ fragment, which makes the two NH_2 hydrogen atoms prochiral, with different chemical shift values. Values of 8−10 Hz for the $^2J_{HH}$ of the two prochiral NH_2 protons were also determined.[24]

The ^{1}H NMR spectra of the phosphite $[RuTp(C_6H_5NHNH_2)\{P(OEt)_3\}_2]BPh_4$ (**6a**) derivative, however, show only one broad multiplet for the NH_2 as well as one for the NH protons of the coordinated hydrazine ligand.

In the temperature range between +20 and −80 °C, the $^{31}P\{^1H\}$ NMR spectra of the $[RuTp(RNHNH_2)L(PPh_3)]BPh_4$ (**4**, **5**) complexes appear as AB quartets, while only one singlet is present in the spectra of the $[RuTp(C_6H_5NHNH_2)\{P(OEt)_3\}_2]BPh_4$ (**6a**) derivative. On the basis of these data, a geometry like the one determined in the solid state for **4d** can be proposed for all the hydrazine derivatives.

Hydrazine complexes of ruthenium are reported with several supporting ligands, such as arene, diene, phosphine, phosphite, and isocyanide.[7b,25−29] Attempts were also made to prepare complexes with cyclopentadienyl (Cp), by reacting $[CpRu(CO)_3]^+$ with hydrazines, but the reaction occurred at the coordinated CO to give isocyanate complexes.[30]

The use of $[RuTp(\eta^2\text{-}H_2)L(PPh_3)]^+$ and $[RuTp(\eta^2\text{-}H_2)\{P(OEt)_3\}_2]^+$ as precursors allows the first tris(pyrazolyl)borate ruthenium hydrazine complexes to be prepared.

Aryldiazene Complexes. Aryldiazene complexes $[RuTp(ArN{=}NH)L(PPh_3)]BPh_4$ (**7**, **8**) [L = $P(OEt)_3$ and $PPh(OEt)_2$] and $[RuTp(ArN{=}NH)\{P(OEt)_3\}_2]BPh_4$ (**9**) can be prepared following three different methods: (i) the insertion of aryldiazonium cations, ArN_2^+, into the [Ru]−H bond of the RuHTpLL′ hydride, (ii) the reduction of aryldiazenido [Ru]−N≡NAr (**1**−**3**) with $LiBHEt_3$, (iii) the oxidation of arylhydrazine $[Ru]{-}NH_2NHR$ (**4**−**6**) with $Pb(OAc)_4$, as shown in Scheme 3.

Both the $RuHTpL(PPh_3)$ and $RuHTp\{P(OEt)_3\}_2$ hydrides react quickly with aryldiazonium cations in CH_2Cl_2 to give the $[RuTp(ArN{=}NH)L(PPh_3)]BPh_4$ (**7**, **8**) and $[RuTp(ArN{=}NH)\{P(OEt)_3\}_2]BPh_4$ (**9**) aryldiazene derivatives, which were separated as BPh_4 salts and characterized. The reaction was also extended to bis(aryldiazonium) $[N_2Ar{-}ArN_2](BF_4)_2$ cations leading to the binuclear bis(aryldiazene) $[\{RuTp[P(OEt)_3](PPh_3)\}_2(\mu\text{-}4,4'\text{-}NH{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_2$ (**7f**) derivative (Scheme 4). The same aryldiazene complexes **7**−**9** were obtained by reacting the aryldiazenido $[RuTpL(PPh_3)(ArN_2)](BF_4)_2$ (**1**, **2**) and $[RuTp\{P(OEt)_3\}_2(ArN_2)](BF_4)_2$ (**3**) with $LiBHEt_3$ in CH_2Cl_2 at 0 °C. Studies using the labeled $[Ru]{-}^{15}N{\equiv}NPh$ (**1a$_1$**) complex confirm that the reduction takes place on the N(1) nitrogen atom, giving the aryldiazene $[Ru]{-}^{15}NH{=}NPh$ (**7a$_1$**) derivatives. Furthermore, the reaction of arylhydrazine $[RuTp(ArNHNH_2)L(PPh_3)]BPh_4$ (**4a**) and $[RuTp(ArNHNH_2)\{P(OEt)_3\}_2]BPh_4$ (**6a**) complexes with $Pb(OAc)_4$ at −30 °C leads to the selective oxidation of the $ArNHNH_2$ group to give the corresponding aryldiazene [Ru]−NH=NAr (**7**, **9**) derivatives.

These results highlight one of the important properties that the Tp ligand may have in diazo chemistry, namely, being able to stabilize aryldiazenido, aryldiazene, and arylhydrazine molecules bonded to the same [RuTpLL′] fragment. The facile synthesis of aryldiazene complexes through three different reactions is also an interesting and novel result in this chemistry, which includes the mixed-ligand [RuTpLL′]

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[23] Braga, D.; Grepioni, F.; Tedesco, E. *Organometallics* **1998**, *17*, 2669−2672 and references therein.

[24] For prochiral CH_2 protons, the $^2J_{HH}$ values fall in the 10−15 Hz range. See: (a) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York, 1969. (b) Abraham, R. J.; Loftus, P. *Proton and carbon-13 NMR spectroscopy*; Heyden: London, 1980.

[25] Crabtree, R. H.; Pearman, A. *J. Organomet. Chem.* **1977**, *141*, 325−333.

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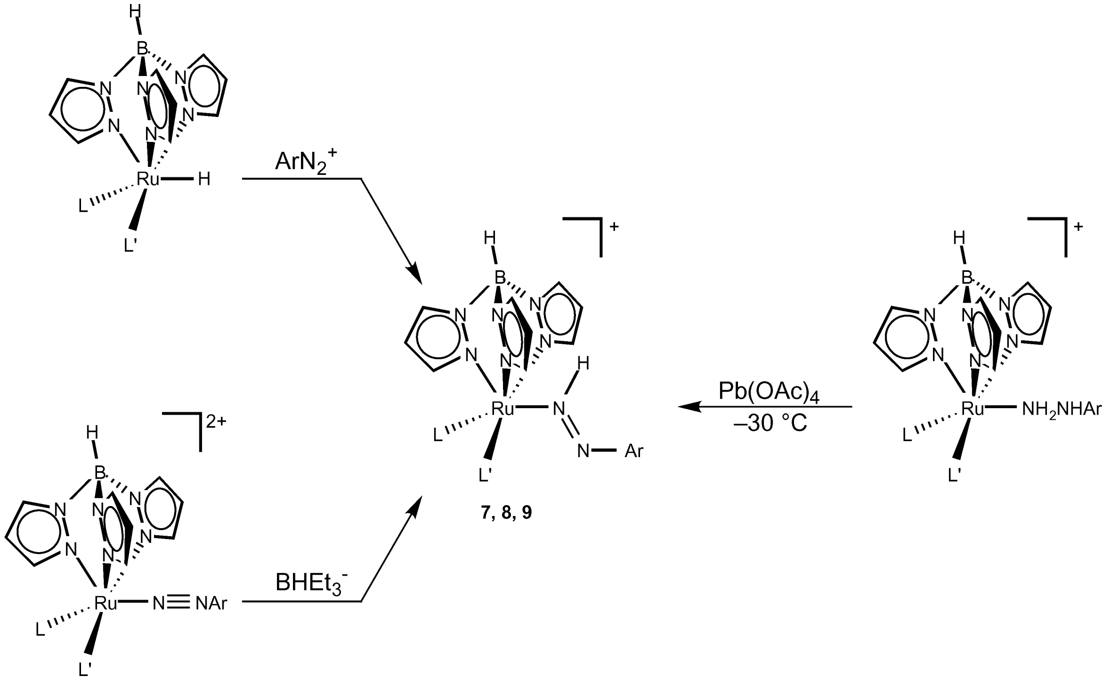
[29] Singleton, E.; Swanepoel, H. E. *Inorg. Chim. Acta* **1982**, *57*, 217−221.

[30] Kruse, A. E.; Angelici, R. J. *J. Organomet. Chem.* **1970**, *24*, 231−239.

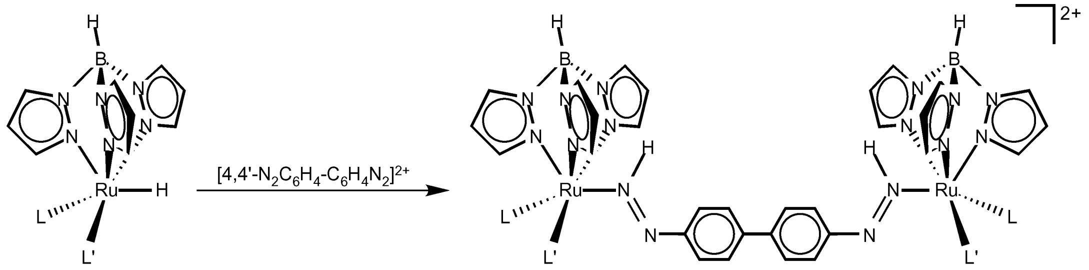
Scheme 3[a]



7, 8, 9

[a] L = P(OEt)$_3$, L′ = PPh$_3$ **7**; L = PPh(OEt)$_2$, L′ = PPh$_3$ **8**; L = L′ = P(OEt)$_3$ **9**; Ar = C_6H_5 **a**, 4-$CH_3C_6H_4$ **b**.

Scheme 4[a]



7f

[a] L = P(OEt)$_3$, L′ = PPh$_3$.

fragment with Tp and phosphite. A comparison with the related ruthenium−cyclopentadienyl [RuCp(PPh$_3$)$_2$] fragment[8a] shows that, also in this case, an aryldiazene cation of the [RuCp(PPh$_3$)$_2$(NH=NC$_6$H$_4$OMe)]$^+$ type can be obtained from the reaction of the aryldiazenido with BH$_4^-$, but it is stable only at −80 °C. Our tris(pyrazolyl)borate aryldiazene complexes **7**−**9**, instead, are very stable and can be isolated in the solid state. The ability of our [RuTpLL′] fragment to stabilize the diazo complexes, however, may be due to the peculiar properties of the Tp ligand and also to the presence of the phosphite, which contributes to making the RuTpLL′ group suitable for diazo chemistry.

The result of the oxidation of arylhydrazine complexes prompted us to extend the study to the other hydrazines, and the results are shown in Scheme 5.

The methylhydrazine complexes (**4d**, **5d**) react with Pb(OAc)$_4$ at −30 °C to give the methyldiazene [RuTp(CH$_3$N=NH)LL′]$^+$ cations which, in the case of **7d**, can be isolated as BPh$_4$ salts in pure form and characterized. The related NH$_2$NH$_2$ complexes (**4e**, **5e**), instead, did not give any stable complexes from the reaction with Pb(OAc)$_4$. A color change of the solution was observed, but only an intractable oil was separated, which (by NMR) contained neither the starting NH$_2$NH$_2$ complex nor the expected 1,2-diazene [RuTp(NH=NH)LL′]BPh$_4$ derivatives. Probably, the oxidation of the hydrazine takes place in this case as well, but the instability of the 1,2-diazene [Ru]−NH=NH formed prevents the isolation of stable species.

All the diazene complexes **7**−**9** were isolated as stable white or yellow solids, stable in air and in a solution of polar organic solvents, where they behave as 1:1 electrolytes.[19] The analytical and spectroscopic data (Table 2) support the proposed formulation. In particular, the presence of the diazene ligand is indicated by the characteristic high-frequency (13−15 ppm), slightly broad signal of the NH

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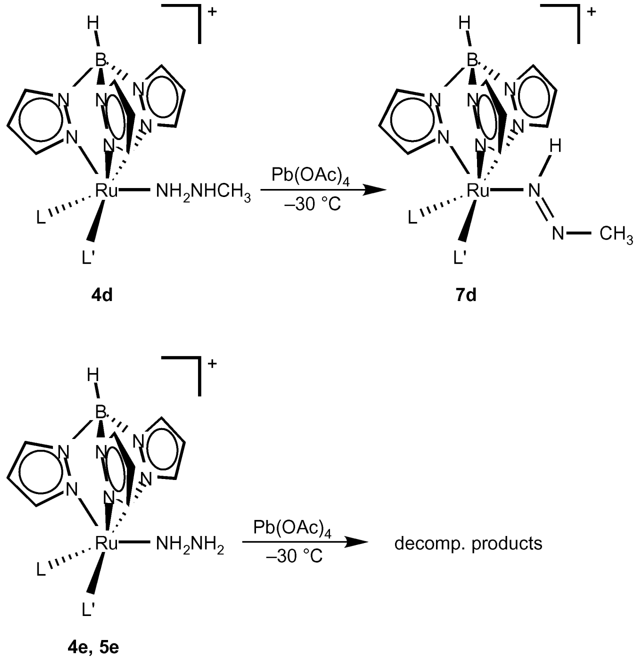
(31) (a) Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 2713−2722. (b) Carrol, J. A.; Sutton, D.; Xiaoheng, Z. *J. Organomet. Chem.* **1982**, *244*, 73−86.

Scheme 5



diazene proton. This attribution is confirmed, in the case of the aryldiazene species, by the spectra of the labeled [Ru]$-^{15}$NH$=$NAr (**7a$_1$**, **7f$_1$**, **9a$_1$**) complexes, which show the split of the NH signal into one well-resolved doublet of multiplets with the value for $^1J_{^{15}\mathrm{NH}}$ of 64−66 Hz, in agreement with the presence of the diazene group.[1,2,7,8,31] Further support comes from the ^{15}N NMR spectra of **7a$_1$**, **7f$_1$**, and **9a$_1$**, which appear as ABXY (**7a$_1$**, **7f$_1$**) and A$_2$XY (**9a$_1$**) (X $=$ ^{15}N, Y $=$ ^{1}H) multiplets and which were simulated with the parameters reported in Table 2 confirming the proposed formulation for the complexes.

The ^{1}H NMR spectra of the diazene complexes **7**−**9** also show the signals of the methyl substituent of the CH$_3$N$=$NH and 4-CH$_3$C$_6$H$_4$N$=$NH groups, beside the characteristic resonaces of Tp and phosphine ligands and those of the BPh$_4$ anion. In the temperature range between +20 and −80 °C, the ^{31}P{^{1}H} NMR spectra of [RuTp(RN$=$NH){P(OEt)$_3$}(PPh$_3$)]BPh$_4$ (**7**, **8**) appear as an AB quartet, while only one singlet is observed in the spectra of the [RuTp(C$_6$H$_5$N$=$NH){P(OEt)$_3$}$_2$]BPh$_4$ (**9a**) derivative. On the basis of these data, a geometry like those reported in Schemes 3−5 can reasonably be proposed for our diazene derivatives.

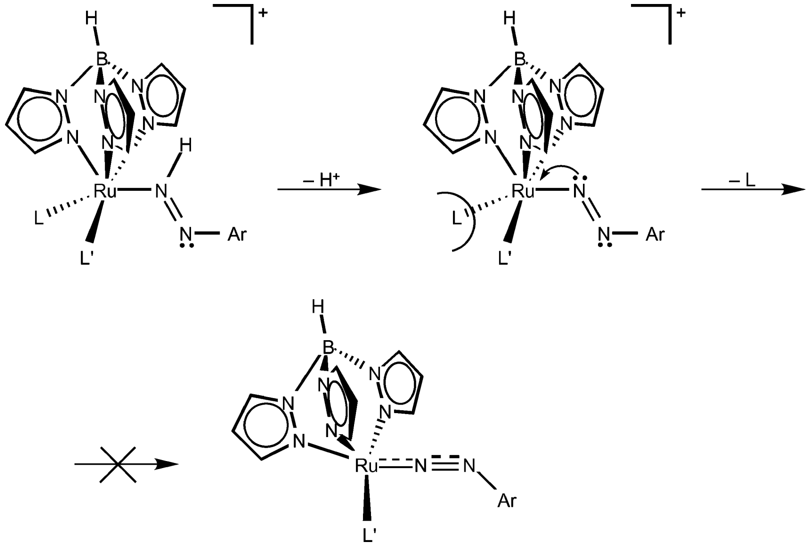
Reactivity studies on ArN$=$NH complexes **7**−**9** were performed toward deprotonation and reduction reactions, and the results showed that the aryldiazenes are robust complexes which do not react either with bases (NEt$_3$ or OH$^-$) or with reducing agents such as H$_2$ (1 atm) or BHEt$_3^-$ and BH$_4^-$. The stability toward a base of [M]$-$NH$=$NAr group is somewhat unexpected, owing to the known acidity of the coordinate diazene which often undergoes deprotonation giving the aryldiazenido [M]$-$N$_2$Ar complexes.[1a,6a,7a] However, the unreactivity of our diazene complexes may be explained by taking into account that a doubly bent aryldiazenido (ArN$_2^-$) complex should be formed by first deprotonating a [Ru]$-$NH$=$NAr species (Scheme 6).

A rearrangement of this doubly bent ArN$_2^-$ ligand to singly bent ArN$_2^+$ should involve a 2e$^-$ reduction of the central metal to Ru(0), followed by the concurrent dissociation of one ligand to give a final pentacoordinate aryldiazenido complex.[6a,b,7a,d] The reluctance to dissociate any ligands in the [RuTpLL′] fragment probably prevents the formation of aryldiazenido derivatives by deprotonation of the corresponding aryldiazene.

Conclusions

A facile route for the synthesis of tris(pyrazolyl)borate diazo complexes of ruthenium has been developed using classical and nonclassical RuHTpLL′ and [RuTp(η^2-H$_2$)LL′]$^+$ hydrides as precursors. The exceptionally high value of ν(N$_2$) and the ^{15}N NMR data for the dicationic aryldiazenido [RuTpLL′(ArN$_2$)](BF$_4$)$_2$ complexes strongly suggest a near-linear arrangement of the Ru-bonded ArN$_2$ ligand. The structural parameters for a tris(pyrazolyl)borate methylhydrazine complex are also reported. Finally, the synthesis of stable aryldiazene [RuTp(ArN$=$NH)LL′]BPh$_4$ complexes has been achieved through three different paths, involving one

Scheme 6



of the following types of reactions: insertion, reduction, or oxidation.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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