

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'(ArN₂)](BF₄)₂ (1–3) [Ar = C₆H₅, 4-CH₃C₆H₄; Tp = hydridotris-(pyrazolyl)borate; L = P(OEt)₃ or PPh(OEt)₂, L' = PPh₃; L = L' = P(OEt)₃] were prepared by allowing dihydrogen [RuTp(η^2 -H₂)LL']⁺ derivatives to react with aryldiazonium cations. Spectroscopic characterization (IR, ¹⁵N NMR) using the ¹⁵N-labeled derivatives strongly supports the presence of a linear [Ru]—N=N—Ar aryldiazenido group. Hydrazine complexes [RuTp(RNHNH₂)LL']BPh₄ (4–6) [R = H, CH₃, C₆H₅, 4-NO₂C₆H₄; L = P(OEt)₃ or PPh(OEt)₂, L' = PPh₃; L = L' = P(OEt)₃] were also prepared by reacting the [RuTp(η^2 -H₂)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(CH₃NHNH₂){P(OEt)₃}(PPh₃)]BPh₄ (4d) derivative. Tris(pyrazolyl)borate aryldiazene complexes [RuTp(ArN=NH)LL']BPh₄ (7–9) (Ar = C₆H₅, 4-CH₃C₆H₄) were prepared following three different methods: (i) by allowing hydride species RuHTpLL' to react with aryldiazonium cations in CH₂Cl₂; (ii) by treating aryldiazenido [RuTpLL'(ArN₂)](BF₄)₂ with LiBHEt₃ in CH₂Cl₂; (iii) by oxidizing arylhydrazine [RuTp(ArNHNH₂)LL']BPh₄ were also prepared by the oxidation of the corresponding methylhydrazine [RuTp(CH₃NHNH₂)LL']BPh₄ 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)borate³ (Tp) as

 (1) (a) Sutton, D. Chem. Rev. 1993, 93, 995–1022. (b) Kisch, H.; Holzmeier, P. Adv. Organomet. Chem. 1992, 34, 67–109. ligands, whose studies involve mainly Ti,⁴ Mo,⁵ and W⁵ 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

 $[\]ast$ 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 ruthenium⁸ stabilized by the tris(pyrazolyl)borate ligand.

Experimental Section

General Comments. All synthetic work was carried out in an appropriate atmosphere (Ar, N₂) 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 vacuumtight storage flasks. RuCl₃·3H₂O 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 [N₂- $Ar-ArN_2|(BF_4)_2$ (Ar-Ar = 4,4'-C₆H₄-C₆H₄) was prepared by treating the amine precursors H₂NAr-ArNH₂ with NaNO₂, 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'- $^{15}N \equiv NC_6H_4 - C_6H_4N \equiv ^{15}N (BF_4)_2$, were prepared from $Na^{15}NO_2$ (99% enriched, CIL) and the appropriate amine. Hydrazine, NH₂-NH₂, was prepared by decomposition of hydrazine cyanurate (Fluka)

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(11) Vogel, A. I. Practical Organic Chemistry, 3rd ed.; Longmans, Green and Co.: New York, 1956. 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, ³¹P, ¹³C, ¹⁵N) were obtained on AC200 or AVANCE 300 Bruker spectrometers at temperatures between -90 and +30 °C, unless otherwise noted. ¹H and ¹³C spectra are referred to internal tetramethylsilane. ³¹P-(¹H) chemical shifts are reported with respect to 85% H₃PO₄, while ¹⁵N is reported with respect to CH₃¹⁵NO₂; 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 package¹³ was used to treat NMR data. The conductivity of 10^{-3} M solutions of the complexes in CH₃-NO₂ 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 [$RuTp(\eta^2-H_2)LL'$]BF₄ and [$RuTp(\eta^2-H_2)-$ { $P(OEt)_3$ }_2]BF₄, and the aquo-complex [$RuTp(H_2O)$ { $P(OEt)_3$ }-(PPh_3)]BF₄ 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 HBF4·Et2O (0.1 mmol, 14 µL of a 54% solution in Et₂O) was added to a solution of the appropriate hydride RuHTpLL' (0.1 mmol) in CH₂Cl₂ (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, roundbottomed 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 \geq 70%.

Method 2 for $[RuTp{P(OEt)_3}(PPh_3)(ArN_2)](BF_4)_2$ (1): From the Aquo-Complex. Solid samples of [RuTp(H₂O){P(OEt)₃}-(PPh₃)]BF₄ (100 mg, 0.12 mmol) and of the appropriate aryldiazonium salt [ArN2]BF4 (0.36 mmol) were placed into a 25-mL threenecked, round-bottomed flask. After cooling to -196 °C, CH₂Cl₂ (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 \geq 70%. Found: C, 45.63; H, 4.51; N, 11.10. C₃₉H₄₅B₃F₈N₈O₃P₂-Ru (1a) requires: C, 45.87; H, 4.44; N, 10.97%. $\Lambda_{\rm M} = 181.5 \ \Omega^{-1}$ mol⁻¹ cm². Found: C, 46.60; H, 4.49; N, 10.69. C₄₀H₄₇B₃F₈N₈O₃P₂-Ru (1b) requires: C, 46.41; H, 4.58; N, 10.82%. $\Lambda_{\rm M} = 182.3 \ \Omega^{-1}$ mol⁻¹ cm². Found: C, 49.76; H, 4.37; N, 10.64. C₄₄H₄₇B₃F₈N₈O₂P₂-Ru (**2b**) requires: C, 49.51; H, 4.44; N, 10.50%. $\Lambda_{\rm M} = 179.9 \ \Omega^{-1}$ mol⁻¹ cm². Found: C, 35.22; H, 4.78; N, 12.25. C₂₇H₄₅B₃F₈N₈O₆P₂-Ru (**3a**) requires: C, 35.05; H, 4.90; N, 12.11%. $\Lambda_{\rm M} = 177.8 \ \Omega^{-1}$ mol⁻¹ cm². Found: C, 35.70; H, 4.97; N, 11.81. C₂₈H₄₇B₃F₈N₈O₆P₂-Ru (**3b**) requires: C, 35.81; H, 5.04; N, 11.93%. $\Lambda_{\rm M} = 182.8 \ \Omega^{-1}$ $mol^{-1} cm^2$.

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

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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 $\geq 65\%$.

 $[RuTp(RNHNH_2)LL']BPh_4 (4, 5, 6) [L = P(OEt)_3, L' = PPh_3]$ (4); $L = PPh(OEt)_2$, $L' = PPh_3$ (5); $L = L' = P(OEt)_3$ (6); R = C_6H_5 (a), 4-NO₂ C_6H_4 (c), CH_3 (d), H (e)]. To a solution of the appropriate hydride RuHTpLL' (0.2 mmol) in 10 mL of CH₂Cl₂, cooled to -196 °C, was added an equivalent amount of CF₃SO₃H (0.2 mmol, 18 μ L). 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 NaBPh₄ (0.4 mmol, 137 mg). A pale yellow solid separated out, which was filtered and crystallized from CH₂Cl₂ and ethanol; yield \geq 80%. Found: C, 64.46; H, 5.89; N, 9.44. C₆₃H₆₈B₂N₈O₃P₂Ru (4a) requires: C, 64.68; H, 5.86; N, 9.58%. $\Lambda_{\rm M} = 53.1 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. Found: C, 62.42; H, 5.52; N, 10.27. C₆₃H₆₇B₂N₉O₅P₂Ru (4c) requires: C, 62.28; H, 5.56; N, 10.38%. $\Lambda_{\rm M} = 54.5 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. Found: C, 62.60; H, 5.93; N, 10.26. C₅₈H₆₆B₂N₈O₃P₂Ru (**4d**) requires: C, 62.88; H, 6.00; N, 10.11%. $\Lambda_{\rm M} = 55.4 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. Found: C, 62.41; H, 5.79; N, 10.10. C₅₇H₆₄B₂N₈O₃P₂Ru (4e) requires: C, 62.59; H, 5.90; N, 10.24%. $\Lambda_{\rm M} = 50.9 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. Found: C, 66.70; H, 5.76; N, 9.24. C₆₇H₆₈B₂N₈O₂P₂Ru (5a) requires: C, 66.95; H, 5.70; N, 9.32%. $\Lambda_{\rm M} = 56.8 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. Found: C, 65.08; H, 5.74; N, 9.76. C₆₂H₆₆B₂N₈O₂P₂Ru (**5d**) requires: C, 65.33; H, 5.84; N, 9.83%. $\Lambda_{\rm M} = 49.6 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. Found: C, 65.21; H, 5.80; N, 9.79. C₆₁H₆₄B₂N₈O₂P₂Ru (**5e**) requires: C, 65.08; H, 5.73; N, 9.95%. $\Lambda_{\rm M} = 56.2 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. Found: C, 57.22; H, 6.32; N, 10.51. C₅₁H₆₈B₂N₈O₆P₂Ru (6a) requires: C, 57.05; H, 6.38; N, 10.44%. $\Lambda_{\rm M} = 58.0 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$.

 $[RuTp(ArN=NH)LL']BPh_4$ (7, 8, 9) $[Ar = C_6H_5$ (a), 4-CH₃C₆H₄ (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 [ArN₂]-BF₄ (0.3 mmol). The flask was cooled to -196 °C and CH₂Cl₂ (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 NaBPh₄ (0.2 mmol, 68 mg). A yelloworange solid slowly separated out from the resulting solution, which was filtered and crystallized from CH_2Cl_2 and ethanol; yield $\geq 85\%$. Found: C, 64.60; H, 5.66; N, 9.71. C₆₃H₆₆B₂N₈O₃P₂Ru (7a) requires: C, 64.79; H, 5.70; N, 9.59%. $\Lambda_{\rm M} = 55.0 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. Found: C, 65.22; H, 5.68; N, 9.37. C₆₄H₆₈B₂N₈O₃P₂Ru (7b) requires: C, 65.04; H, 5.80; N, 9.48%. $\Lambda_{\rm M} = 55.7 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. Found: C, 67.23; H, 5.77; N, 9.10. C₆₈H₆₈B₂N₈O₂P₂Ru (8b) requires: C, 67.28; H, 5.65; N, 9.23%. $\Lambda_{\rm M} = 56.6 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. Found: C, 56.96; H, 6.18; N, 10.35. C₅₁H₆₆B₂N₈O₆P₂Ru (9a) requires: C, 57.15; H, 6.21; N, 10.46%. $\Lambda_{\rm M} = 57.2 \ \Omega^{-1} \ {\rm mol}^{-1}$ cm². Found: C, 57.40; H, 6.26; N, 10.17. C₅₂H₆₈B₂N₈O₆P₂Ru (9b) requires: C, 57.52; H, 6.31; N, 10.32%. $\Lambda_M = 58.4 \ \Omega^{-1} \ mol^{-1}$ cm^2 .

[RuTp(C₆H₅N=¹⁵NH){P(OEt)₃}(PPh₃)]BPh₄ (7a₁) and [RuTp-(C₆H₅N=¹⁵NH){P(OEt)₃}₂]BPh₄ (9a₁). These complexes were prepared exactly like the related unlabeled 7a and 9a using (C₆H₅N≡¹⁵N)BF₄ as a reagent; yield ≥ 80%.

[{**RuTp**[**P**(**OEt**)₃](**PPh**₃)}₂(*µ*-4,4'-N**H**=**NC**₆**H**₄-**C**₆**H**₄**N**=**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}(PPh₃) (74 mg, 0.1 mmol) to react in CH₂Cl₂ (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 CH₂Cl₂ and ethanol; yield \geq 75%. Found: C, 64.69; H, 5.72; N, 9.48. C₁₂₆H₁₃₀B_4N_{16}O_6P_4Ru_2 requires: C, 64.85; H, 5.61; N, 9.60%. $\Lambda_M = 126 \ \Omega^{-1} \ mol^{-1} \ cm^2$.

 $[\{\mathbf{RuTp}[\mathbf{P}(\mathbf{OEt})_3](\mathbf{PPh}_3)\}_2(\mu-4,4'\cdot^{15}\mathbf{NH}=\mathbf{NC}_6\mathbf{H}_4-\mathbf{C}_6\mathbf{H}_4\mathbf{N}=^{15}\mathbf{NH})]-(\mathbf{BPh}_4)_2 \ (\mathbf{7f}_1). \text{ This complex was prepared exactly like the related unlabeled$ **7f** $using <math>(4,4'\cdot^{15}\mathbf{N}\equiv\mathbf{NC}_6\mathbf{H}_4-\mathbf{C}_6\mathbf{H}_4\mathbf{N}\equiv^{15}\mathbf{N})(\mathbf{BF}_4)_2$ as a reagent; yield $\geq 70\%$.

[RuTp(ArN=NH)LL']BPh₄ (7, 8, 9) [L = P(OEt)₃, L' = PPh₃, $Ar = C_6H_5$ (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 LiBHEt₃ (0.1 mmol, 100 μ L of a 1 M solution in THF) was added to a solution of the appropriate aryldiazenido [ReTpLL'(ArN2)](BF4)2 (0.1 mmol) in 10 mL of CH₂Cl₂ 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 NaBPh₄ (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 \geq 45%. Found: C, 64.60; H, 5.67; N, 9.68. C₆₃H₆₆B₂N₈O₃P₂Ru (7a) requires: C, 64.79; H, 5.70; N, 9.59%. $\Lambda_{\rm M} = 59.5 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. Found: C, 67.21; H, 5.56; N, 9.16. C₆₈H₆₈B₂N₈O₂P₂Ru (8b) requires: C, 67.28; H, 5.65; N, 9.23%. $\Lambda_{\rm M} = 58.1 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. Found: C, 57.39; H, 6.14; N, 10.35. C₅₁H₆₆B₂N₈O₆P₂Ru (9a) requires: C, 57.15; H, 6.21; N, 10.46%. $\Lambda_{\rm M} = 59.7 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$.

 $[RuTp(C_6H_5N=NH)LL']BPh_4$ (7a, 9a) $[L = P(OEt)_3, L' =$ PPh₃ (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, roundbottomed 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 NaBPh₄ (0.4 mmol, 137 mg), and the yellow-orange solid was filtered and recrystallized from CH_2Cl_2 and ethanol; yield \geq 65%. Found: C, 64.60; H, 5.81; N, 9.43. C₆₃H₆₆B₂N₈O₃P₂Ru (7a) requires: C, 64.79; H, 5.70; N, 9.59%. $\Lambda_{\rm M} = 56.8 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$. Found: C, 57.28; H, 6.17; N, 10.32. C₅₁H₆₆B₂N₈O₆P₂Ru (9a) requires: C, 57.15; H, 6.21; N, 10.46%. $\Lambda_{\rm M} = 60.4 \ \Omega^{-1} \ {\rm mol}^{-1}$ cm².

[**RuTp(CH₃N=NH){P(OEt)₃}(PPh₃)]BPh₄ (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 CH₂Cl₂ and ethanol at 0 °C; yield ≥ 30%. Found: C, 62.89; H, 5.75; N, 10.27. C₅₈H₆₄B₂N₈O₃P₂-Ru requires: C, 63.00; H, 5.83; N, 10.13%. Λ_M = 56.7 Ω⁻¹ mol⁻¹ cm².

X-ray Crystal Structure Determination of [RuTp(CH₃NHNH₂)-{P(OEt)₃}(PPh₃)]BPh₄ (4d). The data were collected on a SI-EMENS Smart CCD area-detector diffractometer with graphitemonochromated Mo K α radiation. Absorption correction was carried out using SADABS.¹⁵ The structure was solved by direct methods and refined by full-matrix least squares based¹⁶ 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(CH₃NHNH₂){(POEt)₃}(PPh₃)]BPh₄ (4d)

compound empirical formula fw temp wavelength cryst syst space group unit cell dimensions	[RuTp(CH ₃ NHNH ₂){(POEt) ₃ }(PPh ₃)]BPh ₄ C ₅₈ H ₆₆ B ₂ N ₈ O ₃ P ₂ Ru 1107.82 293(2) K 0.710 73 Å orthorhombic <i>Pbca</i> a = 14.2119(19) Å b = 27.294(4) Å a = 20,400(4) Å
vol	114 39(3) A^3
Z	8
density (calcd)	1.287 Mg/m ³
abs coeff	0.380 mm ⁻¹
F(000)	4624
cryst size	0.37 × 0.22 × 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 [<i>R</i> (int) = 0.1685]
completeness to $\theta = 28.10^{\circ}$	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 <i>R</i> indices [I > 2 α (D)]	$R_{1} = 0.0447$ w $R_{2} = 0.0438$
<i>R</i> indices (all data)	$R_1 = 0.3060, wR_2 = 0.0839$
largest diff peak and hole	0.427 and $-0.358 \text{ e} \text{ Å}^{-3}$

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(η^2 -H₂)LL']BF₄ [L = P(OEt)₃ and PPh(OEt)₂; L' = PPh₃] react with aryldiazonium cations in CH₂Cl₂ to give the aryldiazenido [RuTpLL'(ArN₂)](BF₄)₂ (**1**, **2**, **3**) derivatives (Scheme 1).

The reaction proceeds with the replacement of the η^2 -H₂ ligand, giving the dicationic complexes **1**-**3** which were isolated in good yield (\geq 70%) and characterized. The [RuTp-{P(OEt)₃}(PPh₃)(ArN₂)](BF₄)₂ (**1**) compounds can also be prepared by substituting the H₂O ligand in the [RuTp(H₂O)-{P(OEt)₃}(PPh₃)]BF₄ complex with aryldiazonium cations in CH₂Cl₂ as the solvent. The reaction is slower than that with the η^2 -H₂ 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 redorange 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.



^{*a*} L = P(OEt)₃, L' = PPh₃ **1**, **4**; L = PPh(OEt)₂, L' = PPh₃ **2**, **5**; L = L' = P(OEt)₃ **3**, **6**; Ar = C₆H₅ **a**, 4-CH₃C₆H₄ **b**; R = C₆H₅ **a**, 4-NO₂C₆H₄ **c**, CH₃ **d**, H **e**.

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 ¹⁵N isotopic substitution of the ArN₂ 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 suggests²⁰ a near-linear structure (Chart 1) for the RuNNAr group when compared to literature data.^{8a} The ¹⁵N 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-CH₃C₆H₄N \equiv N ligand at 2.54-2.51 ppm is also observed. In a temperature range between -80 and +20°C, the ³¹P{¹H} NMR spectra of [RuTpL(PPh₃)(ArN₂)](BF₄)₂ (1, 2) appear as AB quartets due to the presence of two different phosphine ligands. Coupling with ¹⁵N 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 $J_{\rm P^{15}N}$ 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.

(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.

⁽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(η²-H₂)LL']BF₄ used in these studies were prepared in solution by treating the hydrides RuHTpLL' with an equimolar amount of HBF₄•Et₂O.

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

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

Scheme 2^a



a
 Ar = C₆H₅ **a**, 4-CH₃C₆H₄ **b**; R = C₆H₅ **a**, 4-NO₂C₆H₄ **c**, CH₃ **d**, H **e**.

Chart 1

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(η^2 -H₂)LL']BF₄ complexes with phosphite and Tp as precursors appears to be an easy entry into this chemistry. The high value of ν - (N_2) (2095–2073 cm⁻¹) and the value of δ ¹⁵N (approximately -70 ppm) for 1-3 suggest the presence of a linear ArN₂ group in our complexes. The comparable [RuCp-(PPh₃)₂(ArN₂)](BF₄)₂ complexes,^{8a} containing cyclopentadienyl instead of Tp as supporting ligand, showed similar values for $\nu(N_2)$ and δ ¹⁵N, and an X-ray crystal structure indicated a near-linear Ru-N-N-C geometry for the



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.

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(PPh₃)₂(ArN₂)](BF₄)₂ and [RuTpLL'(ArN₂)](BF₄)₂ (**1**–**3**) derivatives. Although a complete comparison cannot be made for the absence of mixed-ligand [RuCpLL'(ArN₂)]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(PPh₃)₂] one. Furthermore, as previously observed in related dicationic^{8a,20} [RuCp(PPh₃)₂(ArN₂)](BF₄)₂ and [RuCl-(bpy)₂(ArN₂)](PF₆)₂ compounds, the linear arrangement of the ArNN ligand seems to be strongly dependent on the formal 2+ charge of the complexes.

Hydrazine Complexes. Hydrazine, RNHNH₂, can replace the dihydrogen ligand in [RuTp(η^2 -H₂)LL']⁺ cations to give [RuTp(RNHNH₂)LL']⁺ (**4**, **5**, **6**) derivatives, which were isolated as BPh₄ salts and characterized (Scheme 1). The reaction easily proceeds at room temperature in CH₂Cl₂ yielding a series of hydrazine complexes of the type **4**–**6**. Also, the aquo-complex [RuTp(H₂O){P(OEt)₃}(PPh₃)]⁺ can be used as a precursor, by replacing H₂O 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(CH₃NHNH₂){P(OEt)₃}-(PPh₃)]⁺ 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 $80.87(17)^\circ$, 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 [1H] NMR ^{b,c}
	compound	ν/cm^{-1}	assgnt	<i>δ</i> , <i>J</i> /Hz	assgnt	spin system	δ , J/Hz
1a	$[RuTp{P(OEt)_3}(PPh_3)(C_6H_5N \equiv N)](BF_4)_2$	(2523) w (2079) m	$ \nu(BH) $	8.29-6.26 m 3.92 m 3.63 m	Ph + Tp CH_2	AB	$\delta_{A} 103.1 \\ \delta_{B} 25.9 \\ J_{AB} = 49.0$
1a ₁	$[RuTp{P(OEt)_3}(PPh_3)(C_6H_5N \equiv {}^{15}N)](BF_4)_2{}^d$	(2523) w (2050) m	$\nu(BH)$ $\nu(^{15}NN)$	1.14 t 8.30–6.28 m 3.91 m 3.63 m 1.15 t	CH_3 Ph + Tp CH_2 CH_3	$\begin{array}{l} ABX\\ (X = {}^{15}N) \end{array}$	$\delta_{A} \ 103.8$ $\delta_{B} \ 26.2$ $J_{AB} = 48.9$ $J_{AX} = 6.50$
1b	$[RuTp{P(OEt)_3}(PPh_3)(4-CH_3C_6H_4N=N)](BF_4)_2^{e}$	(2519) w (2084) m	$ \nu(BH) $ $ \nu(NN) $	8.54-6.25 m 3.85 m 3.60 m 2.54 s	Ph + Tp CH ₂ CH ₃ p -tol	AB	$J_{\rm BX} = 3.50$ $\delta_{\rm A} \ 104.2$ $\delta_{\rm B} \ 26.4$ $J_{\rm AB} = 49.4$
2b	$[RuTp{PPh(OEt)_2}(PPh_3)(4-CH_3C_6H_4N\equiv N)](BF_4)_2$	(2529) w (2073) m	ν(BH) ν(NN)	1.14 t 8.53-6.14 m 4.16 m 4.08 m 3.62 m 3.08 m 2.52 s 1.54 t 0.96 t	$CH_3 pnos$ Ph + Tp CH_2 $CH_3 p-tol$ $CH_3 phos$	AB	$\delta_{A} 137.2$ $\delta_{B} 26.1$ $J_{AB} = 41.0$
3a	$[RuTp{P(OEt)_3}_2(C_6H_5N\equiv N)](BF_4)_2$	(2490) w (2087) m	$ \nu(BH) $ $ \nu(NN) $	8.55-6.10 m 3.66 m 1.19 t	Ph + Tp CH_2 CH_2	A ₂	106.2 s
3a1	$[RuTp{P(OEt)_3}_2(C_6H_5N \equiv {}^{15}N)](BF_4)_2^{f}$	(2492) m (2062) m	$ \frac{\nu(BH)}{\nu(^{15}NN)} $	8.55–6.10 m 3.66 m 1.19 t	Ph + Tp CH_2 CH_3	A_2X (X = ¹⁵ N)	$\delta_{\rm A} 106.8$ $J_{\rm AX} = 6.7$
3b	$[RuTp{P(OEt)_3}_2(4-CH_3C_6H_4N\equiv N)](BF_4)_2$	(2498) m (2095) m	$ \nu(BH) $ $ \nu(NN) $	8.51-6.10 m 3.90 m 2.51 s 1.25 t	Ph + Tp CH ₂ CH ₃ p -tol CH ₂ phos	A ₂	107.0 s
4a	[RuTp(C ₆ H ₅ NHNH ₂){P(OEt) ₃ }(PPh ₃)]BPh ₄	3360 sh 3348 m 3283 m 2493 m 1608 m	$ u(NH) $ $ u(BH) $ $ \delta(NH_2) $	7.98 - 6.11 m 4.91 m 3.96 m 4.50 m 3.64 m 3.34 m	Ph + Tp RuNH ₂ NH CH ₂	AB	$\delta_{A} 132.9$ $\delta_{B} 48.7$ $J_{AB} = 56$
4c	[RuTp(4-NO ₂ C ₆ H ₄ NHNH ₂){P(OEt) ₃ }(PPh ₃)]BPh ₄	3385 w 3327 w 3267 w 2488 m 1601 m	$ u(NH) $ $ u(BH) $ $ \delta(NH_2) $	1.04 t 8.01-6.03 m 5.49 m 4.62 m 3.98 m 3.65 m 3.35 m	CH_3 Ph + Tp NH $RuNH_2$ CH_2 CH_2	AB	$\delta_{A} 131.4$ $\delta_{B} 47.0$ $J_{AB} = 55$
4d	[RuTp(CH ₃ NHNH ₂){P(OEt) ₃ }(PPh ₃)]BPh ₄ ^g	3346 m 3271 m 3196 w 2480 m	ν(NH) ν(BH)	$\begin{array}{c} 1.03 \text{ t} \\ 8.08 - 6.09 \text{ m} \\ 3.61 \text{ m} \\ 3.36 \text{ m} \\ 3.56 \text{ m} \\ 3.56 \text{ m} \\ 3.37 \text{ m} \\ 3.06 \text{ m} \\ 2.11 \text{ d} \\ J_{\text{HH}} = 6 \\ 1.04 \text{ cm} \end{array}$	CH_3 $Ph + Tp$ CH_2 $RuNH_2$ NH NCH_3	AB	$\delta_{A} 132.9$ $\delta_{B} 48.9$ $J_{AB} = 56$
4 e	[RuTp(NH ₂ NH ₂){P(OEt) ₃ }(PPh ₃)]BPh ₄	3374 br, m 3305 br, w 3276 br, m 2486 m	ν(NH) ν(BH)	1.04 t 8.06-6.09 m 3.85 m 3.43 m 3.64 m 3.32 m 2.77 t br	$CH_3 \text{ phos}$ Ph + Tp $RuNH_2$ CH_2 NH_2	AB	$\delta_{A} 132.8$ $\delta_{B} 48.8$ $J_{AB} = 55$
5a	[RuTp(C ₆ H ₅ NHNH ₂){PPh(OEt) ₂ }(PPh ₃)]BPh ₄	3342 br, m 3283 w 2493 m 1605 m	$ u(\rm NH) $ $ u(\rm BH) $ $ \delta(\rm NH_2) $	2, t, or 1.05 t 8.01–5.81 m 5.95 m 3.80 m 4.31 t, br 4.15 m 3.84 m 3.48 m 3.48 m 3.13 m 1.65 t 0.88 t	CH ₃ Ph + Tp RuNH ₂ NH CH ₂ CH ₃	AB	$\delta_{A} 169.7$ $\delta_{B} 47.7$ $J_{AB} = 51$

Ruthenium Tris(pyrazolyl)borate Diazo Complexes

Table 2. (Continued)

		IR ^a		¹ H NMR ^b			
	compound	ν/cm^{-1}	assgnt	δ, J/Hz	assgnt	spin system	$\delta, J/Hz$
5d	[RuTp(CH ₃ NHNH ₂){PPh(OEt) ₂ }(PPh ₃)]BPh ₄ ^h	3340 m 3267 m 3248 sh 2482 m	ν(NH) ν(BH)	7.99-5.81 m 4.11 m 3.85 m 3.46 m 3.08 m 2.60 m	Ph + Tp CH ₂	AB	$\delta_{A} 169.5$ $\delta_{B} 49.2$ $J_{AB} = 52$
				3.58 m 3.58 m 3.18 m 2.23 d $J_{\text{HH}} = 6$ 1.58 t 0.86 t	NH RuNH ₂ NCH ₃ CH ₃ phos		
5e	$[RuTp(NH_2NH_2)\{PPh(OEt)_2\}(PPh_3)]BPh_4$	3364 m 3294 w 3284 m 2488 m	ν(NH) ν(BH)	7.96–5.83 m 4.02 m 3.76 m 3.44 m	$Ph + Tp \\ CH_2$	AB	$\delta_{A} 169.5$ $\delta_{B} 49.0$ $J_{AB} = 52$
				3.06 m 3.48 m 3.08 m 1.52 t 0.88 t	RuNH ₂ NH ₂ CH ₃		
6a	[RuTp(C ₆ H ₅ NHNH ₂){P(OEt) ₃ } ₂]BPh ₄	3356 m, br 3288 w 2478 m 1601 m	$ u(\text{NH}) $ $ u(\text{BH}) $ $ \delta(\text{NH}_2) $	7.87-6.19 m 5.29 m, br 4.94 t, br 3.62 m 1.17 t	Ph + Tp NH $RuNH_2$ CH_2 CH_2	A ₂	135.6 s
7a	[RuTp(C ₆ H ₅ N=NH){P(OEt) ₃ }(PPh ₃)]BPh ₄	2488 m	ν(BH)	13.87 s, br 8.00-6.08 m 3.68 m 3.38 m 1.06 t	$ \frac{NH}{Ph + Tp} CH_2 $ $ CH_2 $	AB	$\delta_{A} 128.8$ $\delta_{B} 41.9$ $J_{AB} = 55$
7a ₁	$[RuTp(C_6H_5N=15NH){P(OEt)_3}(PPh_3)]BPh_4^i$	2486 m	ν(BH)	ABXY spin syst (Y = H, X = 15 N) δ_Y 13.86 J_{AX} = 4.40 J_{BX} = 2.80 J_{XY} = 64.9 J_{AY} = 3.68 J_{BY} = 1.26 8.02-6.08 m	NH Ph + Tp	ABX	δ_{A} 129.1 δ_{B} 41.9 $J_{AB} = 55$ $J_{AX} = 4.40$ $J_{BX} = 2.80$
7b	$[RuTp(4-CH_3C_6H_4N=NH){P(OEt)_3}(PPh_3)]BPh_4^{j}$			3.69 m 3.40 m 1.07 t 13.70 s, br 8.00-6.05 m 3.68 m 3.35 m 2.38 s	CH_2 CH_3 NH $Ph + Tp$ CH_2 $CH_3 n-tol$	AB	$\delta_{A} 128.7$ $\delta_{B} 41.5$ $J_{AB} = 56$
7d	[RuTp(CH ₃ N=NH){P(OEt) ₃ }(PPh ₃)]BPh ₄			1.06 t 13.52 s, br 8.00-5.95 m 3.62 m 3.30 m 3.04 s	$CH_3 phos$ NH Ph + Tp CH_2 NCH_3	AB	$\delta_{A} 132.9$ $\delta_{B} 47.5$ $J_{AB} = 55$
7f	$[\{RuTp[P(OEt)_3](PPh_3)\}_2 \\ (\mu-4,4'-NH=NC_6H_4-C_6H_4N=NH)](BPh_4)_2$	2488 m	ν(BH)	1.02 t 13.98 m, br 8.00-6.08 m 3.68 m 3.38 m	$CH_3 phos$ NH Ph + Tp CH_2	AB	$\delta_{A} 128.8$ $\delta_{B} 41.7$ $J_{AB} = 55$
7f ₁	$[\{RuTp[P(OEt)_3](PPh_3)\}_2 \\ (\mu-4,4'-^{15}NH=NC_6H_4-C_6H_4N=^{15}NH)](BPh_4)_2^k$	2486 m	ν(BH)	1.08 t ABXY spin syst (Y = H, X = 15 N) δ_Y 14.00 $J_{AX} = 4.80$ $J_{BX} = 2.60$ $J_{XY} = 64.8$ $J_{AY} = 3.45$ $J_{BY} = 0.81$ 8.05-6.10 m	CH ₃ NH	ABX	$ \begin{aligned} & \delta_{\rm A} \ 128.7 \\ & \delta_{\rm B} \ 41.8 \\ & J_{\rm AB} = 55.0 \\ & J_{\rm AX} = 4.80 \\ & J_{\rm BX} = 2.60 \end{aligned} $
				3.75 m 3.42 m 1.11 t	CH ₂ CH ₃		

		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
8b	$[RuTp(4-CH_3C_6H_4N=NH){PPh(OEt)_2}(PPh_3)]BPh_4$	2484 m	ν(BH)	13.46 s, br 8.01-5.92 m 3.77 qnt 3.33 qnt 2.38 s 1.32 t 0.89 t	$\begin{array}{c} \mathrm{NH} \\ \mathrm{Tp} + \mathrm{Ph} \\ \mathrm{CH}_2 \\ \\ \mathrm{CH}_3 p\text{-tol} \\ \mathrm{CH}_3 p\text{hos} \end{array}$	AB	$\delta_{A} 161.3$ $\delta_{B} 38.9$ $J_{AB} = 45$
9a	$[RuTp(C_6H_5N=NH){P(OEt)_3}_2]BPh_4$	2478 m	ν(BH)	14.44 s, br 8.01–6.28 m 3.65 m 1.19 t	$egin{array}{c} \mathrm{NH} & \mathrm{Ph} + \mathrm{Tp} & \mathrm{CH}_2 & \mathrm{CH}_3 & \end{array}$	A ₂	130.5 s
9a ₁	$[RuTp(C_6H_5N=^{15}NH){P(OEt)_3}_2]BPh_4^{\prime}$	2478 m	v(BH)	A ₂ XY spin syst (Y = H, X = 15 N) δ_Y 14.47 $J_{AX} = 5.2$ $J_{AY} = 3.6$ $J_{XY} = 66.0$ 8.04-6.28 m 3.68 m	NH Ph + Tp CH ₂	A ₂ X	$\delta_{A} 130.3$ $J_{AX} = 5.2$
9b	$[RuTp(4-CH_{3}C_{6}H_{4}N=NH){P(OEt)_{3}}_{2}]BPh_{4}$	2492 m	ν(BH)	1.19 t 14.30 t, br $J_{PH} = 4.0$ 8.51-6.26 m 3.68 m 2.40 s 1.17 t	$\begin{array}{c} \mathrm{CH}_{3}\\ \mathrm{NH}\\ \\ \mathrm{Ph}+\mathrm{Tp}\\ \mathrm{CH}_{2}\\ \mathrm{CH}_{3} \ p\text{-tol}\\ \mathrm{CH}_{3} \ p\text{hos} \end{array}$	A ₂	130.9 s

^{*a*} In KBr pellets and (CH₂Cl₂). ^{*b*} In CD₂Cl₂ at 25 °C, unless otherwise noted. ^{*c*} Positive shift downfield from 85% H₃PO₄. ^{*d*} ¹⁵N NMR: ABX spin system (X = ¹⁵N), $\delta_X - 70.7$, $J_{AX} = 6.50$, $J_{BX} = 3.50$ Hz. ^{*e*} ¹³C NMR: 151–108 m Ph + Tp, 66.1 d CH₂, 22.7 s CH₃ *p*-tolyl, 15.9 d CH₃ phos. ^{*f*} ¹⁵N NMR: A₂X spin system (X = ¹⁵N), $\delta_X - 75.3$, $J_{AX} = 6.7$ Hz. ^{*s*} ¹³C NMR: 165–127 m Ph + Tp, 62.4 d CH₂, 42.3 s NCH₃, 16.1 d CH₃ phos. ^{*h*} ¹³C NMR: 165–106 m Ph + Tp, 66.0 d, 65.9 d CH₂, 42.5 s NCH₃, 16.9 d, 16.1 d CH₃ phos. ^{*i*} ¹⁵N NMR: ABXY spin system (X = ¹⁵N), $Y = ^{1}$ H), $\delta_X - 10.9$, $J_{AX} = 4.40$, $J_{BX} = 2.80$, $J_{AY} = 3.68$, $J_{BY} = 1.26$, $J_{XY} = 64.9$ Hz. ^{*i*} ¹³C NMR: 165–106 m Ph + Tp, 62.7 d CH₂, 21.5 s CH₃ *p*-tolyl, 16.1 d CH₃ phos. ^{*k*} ¹⁵N NMR: ABXY spin system (X = ¹⁵N, Y = ¹H), $\delta_X - 10.9$, $J_{AX} = 4.40$, $J_{BX} = 2.80$, $J_{AY} = 3.68$, $J_{BY} = 1.26$, $J_{XY} = 64.9$ Hz. ^{*i*} ¹³C NMR: 165–106 m Ph + Tp, 62.7 d CH₂, 21.5 s CH₃ *p*-tolyl, 16.1 d CH₃ phos. ^{*k*} ¹⁵N NMR: ABXY spin system (X = ¹⁵N, Y = ¹H), $\delta_X - 12.1$, $J_{AX} = 4.80$, $J_{BX} = 2.60$, $J_{AY} = 3.45$, $J_{BY} = 0.81$, $J_{XY} = 64.8$ Hz. ^{*l*} ¹⁵N NMR: A₂XY spin system (X = ¹⁵N, Y = ¹H), $\delta_X - 15.2$, $J_{AX} = 5.2$, $J_{AY} = 3.6$, $J_{XY} = 66.0$ 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)		

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- $(2)^{\circ}$, 125.7 $(2)^{\circ}$, and 113.7 $(2)^{\circ}$ (expected 120°), and a similar

Table 4. Selected Hydrogen Bonds^a

	D-H	Н•••А	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
$N(1)-H(1B)\cdots Cg^{b}$	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.

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 NH₂ 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.

^{(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 BPh₄⁻ 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 RNHNH₂ group is confirmed by ¹H NMR spectra, which show the NH and NH₂ resonances as slightly broad multiplets between 5.95 and 2.77 ppm (Table 2).

Unexpectedly, for the mixed-ligand phosphine-phosphite [RuTp(RNHNH₂)L(PPh₃)]BPh₄ (**4**, **5**) complexes, three NH resonances were observed for the coordinated RNHNH₂ ligands, with 1:1:1 intensity ratio (1:1:2 ratio for NH₂NH₂ in **4a** and **5a**). The attributions were confirmed by homodecoupling experiments and ¹H COSY spectra, which indicated that the two hydrogens of the coordinated NH₂ group fall at different chemical shift values. This is probably due to the coordination of the NH₂ group of hydrazine to the [RuTpL(PPh₃)] fragment, which makes the two NH₂ hydrogen atoms prochiral, with different chemical shift values. Values of 8–10 Hz for the ²J_{HH} of the two prochiral NH₂ protons were also determined.²⁴

The ¹H NMR spectra of the phosphite $[RuTp(C_6H_5-NHNH_2){P(OEt)_3}_2]BPh_4$ (**6a**) derivative, however, show only one broad multiplet for the NH₂ as well as one for the NH protons of the coordinated hydrazine ligand.

In the temperature range between +20 and -80 °C, the ${}^{31}P{}^{1}H{}$ NMR spectra of the [RuTp(RNHNH₂)L(PPh₃)]BPh₄ (**4**, **5**) complexes appear as AB quartets, while only one singlet is present in the spectra of the [RuTp(C₆H₅NHNH₂)-{P(OEt)₃}₂]BPh₄ (**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 $[RuTp(\eta^2-H_2)L(PPh_3)]^+$ and $[RuTp(\eta^2-H_2)-{P(OEt)_3}_2]^+$ as precursors allows the first tris(pyrazolyl)-borate ruthenium hydrazine complexes to be prepared.

Aryldiazene Complexes. Aryldiazene complexes [RuTp-(ArN=NH)L(PPh₃)]BPh₄ (7, 8) [L = P(OEt)₃ and PPh-(OEt)₂] and [RuTp(ArN=NH){P(OEt)₃}]BPh₄ (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 LiBHEt₃, (iii) the oxidation of arylhydrazine [Ru]-NH₂NHR (4-6) with Pb(OAc)₄, as shown in Scheme 3.

Both the RuHTpL(PPh₃) and RuHTp{ $P(OEt)_3$ } hydrides react quickly with aryldiazonium cations in CH₂Cl₂ to give the [RuTp(ArN=NH)L(PPh₃)]BPh₄ (7, 8) and [RuTp(ArN= NH){P(OEt)₃}₂]BPh₄ (9) aryldiazene derivatives, which were separated as BPh₄ salts and characterized. The reaction was also extended to bis(aryldiazonium) [N₂Ar-ArN₂]- $(BF_4)_2$ cations leading to the binuclear bis(aryldiazene) $[{RuTp[P(OEt)_3](PPh_3)}_2(\mu-4,4'-NH=NC_6H_4-C_6H_4N=NH)]$ - $(BPh_4)_2$ (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 $[RuTp{P(OEt)_3}_2 (ArN_2)$](BF₄)₂ (**3**) with LiBHEt₃ in CH₂Cl₂ at 0 °C. Studies using the labeled [Ru] $-^{15}N \equiv$ NPh (1a₁) complex confirm that the reduction takes place on the N(1) nitrogen atom, giving the aryldiazene [Ru]-¹⁵NH=NPh (7a₁) derivatives. Furthermore, the reaction of arylhydrazine [RuTp(ArNHNH₂)L- (PPh_3)]BPh₄ (4a) and [RuTp(ArNHNH₂){P(OEt)₃}]BPh₄ (6a) complexes with $Pb(OAc)_4$ at -30 °C leads to the selective oxidation of the ArNHNH₂ 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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⁽²⁴⁾ For prochiral CH₂ 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.

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^{*a*} L = P(OEt)₃, L' = PPh₃ **7**; L = PPh(OEt)₂, L' = PPh₃ **8**; L = L' = P(OEt)₃ **9**; Ar = C₆H₅ **a**, 4-CH₃C₆H₄ **b**.

Scheme 4^a



 a L = P(OEt)₃, L' = PPh₃.

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 $[RuCp(PPh_3)_2(NH=NC_6H_4OMe)]^+$ type can be obtained from the reaction of the aryldiazenido with BH₄⁻, 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(CH₃N= NH)LL']⁺ cations which, in the case of **7d**, can be isolated as BPh₄ salts in pure form and characterized. The related NH_2NH_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_2NH_2 complex nor the expected 1,2-diazene [RuTp(NH= NH)LL']BPh₄ 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 highfrequency (13–15 ppm), slightly broad signal of the NH

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diazene proton. This attribution is confirmed, in the case of the aryldiazene species, by the spectra of the labeled [Ru]— ¹⁵NH=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 ¹*J*¹⁵_{NH} of 64–66 Hz, in agreement with the presence of the diazene group.^{1,2,7,8,31} Further support comes from the ¹⁵N NMR spectra of **7a**₁, **7f**₁, and **9a**₁, which appear as ABXY (**7a**₁, **7f**₁) and A₂XY (**9a**₁) (X = ¹⁵N, Y = ¹H) multiplets and which were simulated with the parameters reported in Table 2 confirming the proposed formulation for the complexes.

The ¹H NMR spectra of the diazene complexes **7**–**9** also show the signals of the methyl substituent of the CH₃N= NH and 4-CH₃C₆H₄N=NH groups, beside the characteristic resonaces of Tp and phosphine ligands and those of the BPh₄ anion. In the temperature range between +20 and -80 °C, the ³¹P{¹H} NMR spectra of [RuTp(RN=NH){P(OEt)₃}-

Scheme 6

(PPh₃)]BPh₄ (**7**, **8**) appear as an AB quartet, while only one singlet is observed in the spectra of the [RuTp(C₆H₅N=NH)- $\{P(OEt)_3\}_2$]BPh₄ (**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 (NEt₃ or OH⁻) or with reducing agents such as H₂ (1 atm) or BHEt₃⁻ and BH₄⁻. 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]-N₂Ar complexes.^{1a,6a,7a} However, the unreactivity of our diazene complexes may be explained by taking into account that a doubly bent aryldiazenido (ArN₂⁻) 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 $[RuTp(\eta^2-H_2)LL']^+$ hydrides as precursors. The exceptionally high value of $\nu(N_2)$ and the ¹⁵N NMR data for the dicationic aryldiazenido [RuTpLL'(ArN₂)](BF₄)₂ complexes strongly suggest a nearlinear arrangement of the Ru-bonded ArN₂ ligand. The structural parameters for a tris(pyrazolyl)borate methylhydrazine complex are also reported. Finally, the synthesis of stable aryldiazene [RuTp(ArN=NH)LL']BPh₄ complexes has been achieved through three different paths, involving one



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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