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Pentamethylcyclopentadienyl Half-Sandwich Diazoalkane Complexes of Ruthenium: Preparation and Reactivity

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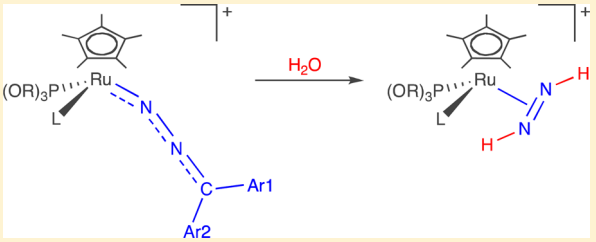
Supporting Information

ABSTRACT: The diazoalkane complexes $[Ru(\eta^5\text{-}C_5Me_5)(N_2CAr1Ar2)\{P(OR)_3\}L]BPh_4$ (**1**–**4**) [R = Me, L = $P(OMe)_3$ (**1**); R = Et, L = $P(OEt)_3$ (**2**); R = Me, L = PPh_3 (**3**); R = Et, L = PPh_3 (**4**); Ar1 = Ar2 = Ph (**a**); Ar1 = Ph, Ar2 = *p*-tolyl (**b**); Ar1Ar2 = $C_{12}H_8$ (**c**); Ar1 = Ph, Ar2 = PhC(O) (**d**)] and $[Ru(\eta^5\text{-}C_5Me_5)\{N_2C(C_{12}H_8)\}\{PPh(OEt)_2\}(PPh_3)]BPh_4$ (**5c**) were prepared by allowing chloro-compounds $RuCl(\eta^5\text{-}C_5Me_5)[P(OR)_3]L$ to react with the diazoalkane $Ar1Ar2CN_2$ in the presence of $NaBPh_4$. Treatment of complexes **1**–**4** with H_2O afforded 1,2-diazene derivatives $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}NH{=}NH)\{P(OR)_3\}L]BPh_4$ (**6**–**9**) and ketone Ar1Ar2CO. A reaction path involving nucleophilic attack by H_2O on the coordinated diazoalkane is proposed and supported by density functional theory calculations. The complexes were characterized spectroscopically (IR and ^1H, ^{31}P, ^{13}C, ^{15}N NMR) and by X-ray crystal structure determination of $[Ru(\eta^5\text{-}C_5Me_5)(N_2CC_{12}H_8)\{P(OEt)_3\}_2]BPh_4$ (**2c**) and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}NH{=}NH)\{P(OEt)_3\}_2]BPh_4$ (**7**).



INTRODUCTION

Diazoalkane complexes of transition metals continue to attract attention,[1−6] due to the various coordination modes and reactivity shown by the metal-bonded $Ar1Ar2CN_2$ group. Diazoalkanes have also been used in models of the dinitrogen fixation process.[7,8]

A number of diazoalkane complexes have been prepared[1−6] for several metals, and reactivity studies have revealed various pathways, depending on coordination mode and the nature of ancillary ligands. In η^2-C,N coordinated diazoalkane, extrusion of N_2 and carbene M=CAr1Ar2 formation was observed,[1,2b,9,10] whereas an η^1-N-bonded $Ar1Ar2CN_2$ complex can yield dinitrogen [M]−N_2 derivatives,[2g,k] or cleave the N−N bond of the $Ar1Ar2CN_2$ group.[2i] Dipolar (3 + 2) cycloaddition of coordinated diazoalkane with alkene and alkyne, yielding 3H-pyrazole derivatives, has also recently been reported.[6a,b] However, no example of hydrolysis reaction on a coordinated $Ar1Ar2CN_2$ group had ever been reported until we found that pentamethylcyclopentadienyl half-sandwich complexes $[Ru(\eta^5\text{-}C_5Me_5)(N_2CAr1Ar2)\{P(OR)_3\}(PPh_3)]BPh_4$ can undergo an unprecedented reaction with H_2O, affording side-on 1,2-diazene derivatives $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}NH{=}NH)\{P(OR)_3\}(PPh_3)]BPh_4$.[11] This interesting preliminary result prompted us to extend study to other half-sandwich complexes, in order to test whether other fragments can give rise to hydrolysis of coordinated $Ar1Ar2CN_2$ and how the nature of ancillary ligands can influence the properties of diazoalkane derivatives.

This paper reports full details of our study on the synthesis of diazoalkane complexes of pentamethylcyclopentadienyl coordinated ruthenium and their reactivity toward hydrolysis of the coordinated $Ar1Ar2CN_2$ group.

EXPERIMENTAL SECTION

General Comments. All synthetic work was carried out under Ar or N_2, with standard Schlenk techniques or in an inert atmosphere drybox. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $RuCl_3{\cdot}3H_2O$ (Pressure Chemical Co., USA) and pentamethylcyclopentadiene C_5Me_5H (STREM) were used as received. The phosphites $P(OMe)_3$ and $P(OEt)_3$ (Aldrich) were used as received, whereas phenyldiethoxyphosphine $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon.[12] Other reagents were purchased from commercial sources in the highest available purity and used as received. Diazoalkanes $Ar1Ar2CN_2$ (Ar1 = Ar2 = Ph; Ar1 = Ph, Ar2 = *p*-tolyl; Ar1Ar2 = $C_{12}H_8$) were prepared following the known methods.[13] Infrared spectra were recorded on a PerkinElmer Spectrum-One FT-IR spectrophotometer. NMR spectra (^1H, ^{13}C, ^{31}P, ^{15}N) were obtained on an AVANCE 300 Bruker spectrometer at temperatures between −90 and +25 °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, ^{15}N relative to $CH_3{}^{15}NO_2$; in both cases, downfield shifts (values in ppm) are considered positive. COSY, HMQC, and HMBC NMR spectroscopic experiments were performed with standard programs. The iNMR software package[14] was used to treat NMR spectroscopic data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C was measured on a Radiometer CDM 83. Elemental analyses

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were determined in the Microanalytical Laboratory of the Dipartimento di Scienze del Farmaco, University of Padova (Italy).

Caution. Pure diazoalkanes $N_2CAr1Ar2$ are potentially explosive; they must be handled with competence and caution.

Ethylglycine Hydrochloride.[15] In a 50 mL one-necked round-bottomed flask containing 1.0 g (9.0 mmol) of glycine hydrochloride in 10 mL of ethanol, cooled to ca. −20 °C, $SOCl_2$ was added (1.17 mL, 16 mmol); when the mixture reached room temperature, another equivalent of solid glycine (1.0 g, 9.0 mmol) was slowly added and the mixture was refluxed for 2 h. After the colorless solution was cooled to room temperature, the solvent was removed under reduced pressure leaving a white solid, which was dried under high vacuum (0.01 mmHg) for 2 h and recrystallized from ethanol; yield ≥ 90%.

Preparation of ^{15}NNC(H)COOEt. The labeled compound was prepared by slight modification of the reported method.[16] In a 50 mL three-necked round-bottomed flask, equipped with an argon inlet, septum cap, and thermometer, were placed 1.0 g (7.2 mmol) of ethylglycine hydrochloride, 2 mL of H_2O, and 4 mL of CH_2Cl_2, and the mixture was cooled to ca. −5 °C. An ice-cooled solution of labeled $Na^{15}NO_2$ (98% ^{15}N enriched, 0.6 g, 8.5 mmol) in H_2O (2 mL) was added. To the resulting mixture, cooled to ca. −10 °C, 0.65 g of H_2SO_4 5% soln. (w/w) was slowly added. As a warm up could reduce the yield, the mixture was maintained at a temperature ≤ −1 °C during addition. Thereafter, the mixture was stirred for 20 min from −10 to −1 °C and then poured into an ice-cooled separating funnel. The yellow organic layer was recovered and the water phase was extracted with dichloromethane (2 × 3 mL). The combined organic phase was washed with ice-cooled $NaHCO_3$ 5% soln. (6 mL), the organic phase was separated, and the water phase was extracted with dichloromethane (2 × 3 mL). The combined organic phase was dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure at 0 °C. The resulting yellow oil was vacuum-dried for 25 min, and the resulting product was cold-distilled under high vacuum (0.01 mmHg); yield 0.62 g, 75%. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) δ: 4.75 (s br, 1H, CHN_2), 4.18 (q, 2H, CH_2), 1.25 (t, 3H, CH_3); ^{15}N NMR (30.42 MHz, CD_2Cl_2, 25 °C) δ: 5.3 (s br, ^{15}NNC).

Synthesis of Complexes. The compound $[RuCl_2(\eta^5\text{-}C_5Me_5)]_2$ was prepared following the reported method.[17]

$RuCl(\eta^5\text{-}C_5Me_5)(PPh_3)_2$. This complex was obtained by a slight modification of the reported method.[18] A mixture of $[RuCl_2(\eta^5\text{-}C_5Me_5)]_2$ (1 g, 1.63 mmol), an excess of PPh_3 (2.62 g, 10.0 mmol), and 60 mL of anhydrous ethanol was refluxed for 72 h. The solution was then concentrated to about 30 mL by evaporation of the solvent under reduced pressure, and the solid formed was filtered, washed with ethanol, and dried under reduced pressure; yield ≥85%; ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.46−7.06 (m, 30H, Ph), 1.31 (t, 15H, CH_3 C_5Me_5); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: A_2, 41.58 (s); Anal. Calcd for $C_{46}H_{45}ClP_2Ru$ (796.32): C, 69.38; H, 5.70; Cl, 4.45; Found: C, 69.56; H, 5.61; Cl, 4.63%.

*$RuCl(\eta^5\text{-}C_5Me_5)[P(OR)_3]_2$ (**R = Me, Et**).* These complexes were prepared following two different methods. Method A: An excess of the appropriate phosphite $P(OR)_3$ (2.27 mmol) (R = Me, Et) was added to a solution of the complex $RuCl(\eta^5\text{-}C_5Me_5)(PPh_3)_2$ (0.30 g, 0.38 mmol) in 10 mL of toluene, and the reaction mixture was stirred for 4 h. The solvent and the excess of phosphine were removed under reduced pressure to give an oil, which was extracted with three 5 mL portions of petroleum ether 40−60 °C. The extracted material was evaporated to dryness, and the oil obtained was treated with methanol or ethanol (2 mL). By slow cooling of the solution to ca. −40 °C, a yellow solid separated out, which was filtered and dried under reduced pressure; yield ≥ 65%. Method B: A slight excess of the appropriate phosphite (7.2 mmol) was added to a solution of the complex $[RuCl_2(\eta^5\text{-}C_5Me_5)]_2$ (1.0 g, 1.63 mmol) in 20 mL of tetrahydrofuran (thf). Zinc dust (18.3 mmol, 1.20 g) was added to the reaction mixture, which was stirred for 2 h and then filtered on cellulose. The solvent was removed under reduced pressure to give an oil, which was triturated with methanol or ethanol (3 mL). By cooling of the resulting solution to ca. −40 °C, a yellow solid slowly separated, which was filtered and dried under reduced pressure; yield ≥75%. **R = Me:** ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 3.61 (t, 18H, CH_3 phos), 1.64 (t, 15H, CH_3 C_5Me_5); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: A_2, 158.1 (s); Anal. Calcd for $C_{16}H_{33}ClO_6P_2Ru$ (519.90): C, 36.96; H, 6.40; Cl, 6.82; Found: C, 37.08; H, 6.33; Cl, 6.75%. **R = Et:** ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 3.98 (m, 12H, CH_2), 1.63 (t, 15H, CH_3 C_5Me_5), 1.24 (t, 18H, CH_3 phos); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: A_2, 153.4 (s); Anal. Calcd for $C_{22}H_{45}ClO_6P_2Ru$ (604.06): C, 43.74; H, 7.51; Cl, 5.87; Found: C, 43.83; H, 7.60; Cl, 5.80%.

*$RuCl(\eta^5\text{-}C_5Me_5)[P(OR)_3](PPh_3)$ (**R = Me, Et**).* An excess of the appropriate phosphite $P(OR)_3$ (3.75 mmol) was added to a solution of $RuCl(\eta^5\text{-}C_5Me_5)(PPh_3)_2$ (1.0 g, 1.26 mmol) in 10 mL of toluene, and the reaction mixture was stirred for 1 h. The solvent was removed under reduced pressure to give an oil, which was triturated with methanol or ethanol (3 mL). A yellow solid was slowly precipitated by cooling of the resulting solution to ca. −25 °C, which was filtered and dried under reduced pressure; yield ≥70%. **R = Me:** ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.62−7.33 (m, 15H, Ph), 3.44 (t, 9H, CH_3 phos), 1.32 (s br, 15H, CH_3 C_5Me_5); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 146.7, δ_B 49.3, $^2J_{AX}$ = 77.4 Hz; Anal. Calcd for $C_{31}H_{39}ClO_3P_2Ru$ (658.11): C, 56.58; H, 5.97; Cl, 5.39; Found: C, 56.42; H, 6.07; Cl, 5.22%. **R = Et:** ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.65, 7.34 (m, 15H, Ph), 3.92, 3.79 (m, 6H, CH_2), 1.30 (s br, 15H, CH_3 C_5Me_5), 1.02 (t, 9H, CH_3 phos); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 142.6, δ_X 49.6, $^2J_{AX}$ = 79.3 Hz; Anal. Calcd for $C_{34}H_{45}ClO_3P_2Ru$ (700.19): C, 58.32; H, 6.48; Cl, 5.06; Found: C, 58.48; H, 6.37; Cl, 4.92%.

$RuCl(\eta^5\text{-}C_5Me_5)[PPh(OEt)_2](PPh_3)$. This complex was prepared like related phosphite compounds $RuCl(\eta^5\text{-}C_5Me_5)[P(OR)_3](PPh_3)$; yield ≥75%. ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.72−7.02 (m, 20H, Ph), 4.01, 3.65 (m, 4H, CH_2), 1.33 (s, 15H, CH_3 C_5Me_5), 1.19 (t, 6H, CH_3 phos); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 158.7, δ_X 46.75, $^2J_{AX}$ = 50.7 Hz; Anal. Calcd for $C_{38}H_{45}ClO_2P_2Ru$ (732.23): C, 62.33; H, 6.19; Cl, 4.84; Found: C, 62.49; H, 6.25; Cl, 4.54%.

*$[Ru(\eta^5\text{-}C_5Me_5)(N_2CAr1Ar2)\{P(OR)_3\}_2]BPh_4$ (**1, 2**) [R = Me (1), Et (2); Ar1 = Ph, Ar2 = p-tolyl (b); Ar1Ar2 = $C_{12}H_8$ (c); Ar1 = Ph, Ar2 = PhC(O) (d)].* In a 25 mL three-necked round-bottomed flask were placed 0.3 mmol of the complex $RuCl(\eta^5\text{-}C_5Me_5)[P(OR)_3]_2$, an excess of the appropriate diazoalkane (0.9 mmol), an excess of $NaBPh_4$ (0.6 mmol, 205 mg), and 5 mL of methanol or ethanol. The reaction mixture was stirred for 24 h and then concentrated to about 3 mL by evaporation of the solvent under reduced pressure. By cooling to ca. −25 °C of the resulting mixture a yellow-orange solid separated out, which was filtered and crystallized from dichloromethane (1 mL) and ethanol (2 mL); yield ≥80%. **1b:** IR (KBr, cm^{-1}) ν_{N_2} 1914 (s); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.499−6.87 (m, 29H, Ph), 3.51 (t, 18H, CH_3 phos), 2.41 (s, 3H, CH_3 *p*-tolyl), 1.79 (t, 15H, CH_3 C_5Me_5); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: A_2, 147.0; Anal. Calcd for $C_{53}H_{65}BN_2O_6P_2Ru$ (1011.93): C, 64.09; H, 6.47; N, 2.77; Found: C, 64.26; H, 6.33; N, 2.65%; Λ_M = 56.1 Ω^{-1} mol^{-1} cm^2. **1c:** IR (KBr, cm^{-1}) ν_{N_2} 1928 (s); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 9.08, 7.98−6.87 (m, 28H, Ph + fluorene), 3.66 (t, 18H, CH_3 phos), 1.83 (t, 15H, CH_3 C_5Me_5); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: A_2, 144.4; ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: 165−119 (m, Ph + fluorene), 100.2 (s, C_5Me_5), 82.5 (br, CN_2), 53.91 (d, CH_3 phos), 10.08 (s, CH_3 C_5Me_5); Anal. Calcd for $C_{53}H_{61}BN_2O_6P_2Ru$ (995.89): C, 63.92; H, 6.17; N, 2.81; Found: C, 63.84; H, 6.09; N, 2.70%; Λ_M = 55.5 Ω^{-1} mol^{-1} cm^2. **2b:** IR (KBr, cm^{-1}) ν_{N_2} 1930 (s); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.48−6.87 (m, 29H, Ph), 3.88 (m, 12H, CH_2), 2.41 (s, 3H, CH_3 *p*-tolyl), 1.79 (t, 15H, CH_3 C_5Me_5), 1.21 (t, 18H, CH_3 phos); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: A_2, 141.6; Anal. Calcd for $C_{60}H_{77}BN_2O_6P_2Ru$ (1096.09): C, 65.75; H, 7.08; N, 2.56; Found: C, 65.57; H, 7.20; N, 2.44%; Λ_M = 54.7 Ω^{-1} mol^{-1} cm^2. **2c:** IR (KBr, cm^{-1}) ν_{N_2} 1950 (s); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 9.10, 7.96−6.87 (m, 28H, Ph + fluorene), 4.02 (m, 12H, CH_2), 1.83 (t, 15H, CH_3 C_5Me_5), 1.28 (t, 18H, CH_3 phos); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: A_2, 138.7; Anal. Calcd for $C_{59}H_{73}BN_2O_6P_2Ru$ (1080.05): C, 65.61; H, 6.81; N, 2.59; Found: C, 65.44; H, 6.70; N, 2.68%; Λ_M = 55.1 Ω^{-1} mol^{-1} cm^2. **2d:** IR (KBr, cm^{-1}) ν_{N_2} 1952 (m), ν_{CO} 1741 (s); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.65−6.87 (m, 30H, Ph), 3.83 (m, 12H, CH_2), 1.76 (t, 15H, CH_3

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C_5Me_5), 1.20 (t, 18H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: A_2, 144.5; Anal. Calcd for $C_{60}H_{75}BN_2O_7P_2Ru$ (1110.08): C, 64.92; H, 6.81; N, 2.52; Found: C, 64.71; H, 6.70; N, 2.59%; Λ_M = 56.4 Ω^{-1} mol^{-1} cm^2.

*[Ru(η^5-C_5Me_5)(N_2CAr1Ar2){P(OR)$_3$}(PPh$_3$)]BPh$_4$ (**3, 4**) [R = Me (**3**), Et (**4**); Ar1 = Ar2 = Ph (a); Ar1 = Ph, Ar2 = p-tolyl (b); Ar1Ar2 = $C_{12}H_8$ (c)].* In a 25 mL three-necked round-bottomed flask were placed solid samples of RuCl(η^5-C_5Me_5)[P(OR)$_3$](PPh$_3$) (0.3 mmol), an excess of the appropriate diazoalkane (0.9 mmol), an excess of $NaBPh_4$ (0.6 mmol, 205 mg) and 7 mL of methanol or ethanol. The reaction mixture was stirred for 24 h after which time the solid formed, which was filtered and crystallized from dichloromethane (1 mL) and ethanol (3 mL); yield ≥ 75%. **3a:** IR (KBr, cm^{-1}) ν_{N_2} 1945 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.66−6.87 (m, 45H, Ph), 3.32 (d, 9H, CH_3 phos), 1.49 (t, 15H, CH_3 C_5Me_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 140.97, δ_X 48.63, $^2J_{AX}$ = 65.26 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 165−122 (m, Ph), 98.59 (s, C_5Me_5), 83.5 (br, CN_2), 53.98 (d, CH_3 phos), 9.99 (s, CH_3 C_5Me_5); Anal. Calcd for $C_{68}H_{69}BN_2O_3P_2Ru$ (1136.12): C, 71.89; H, 6.12; N, 2.47; Found: C, 71.70; H, 6.05; N, 2.57%; Λ_M = 56.2 Ω^{-1} mol^{-1} cm^2. **3b:** IR (KBr, cm^{-1}) ν_{N_2} 1919 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.83−6.85 (m, 44H, Ph), 3.32 (d, 9H, CH_3 phos), 2.39 (s, 3H, CH_3 *p*-tolyl), 1.47 (t, 15H, CH_3 C_5Me_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 141.15, δ_X 48.75, $^2J_{AX}$ = 65.38 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 165−122 (m, Ph), 98.47 (d, C_5Me_5), 83.88 (s, CN_2), 53.95 (d, CH_3 phos), 21.27 (s, CH_3 *p*-tolyl), 9.97 (s, CH_3 C_5Me_5); Anal. Calcd for $C_{68}H_{71}BN_2O_3P_2Ru$ (1150.14): C, 72.06; H, 6.22; N, 2.44; Found: C, 71.88; H, 6.29; N, 2.32%; Λ_M = 55.2 Ω^{-1} mol^{-1} cm^2. **3c:** IR (KBr, cm^{-1}) ν_{N_2} 1950 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 9.07, 8.00−6.87 (m, 43H, Ph), 3.47 (d, 9H, CH_3 phos), 1.56 (t, 15H, CH_3 C_5Me_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 138.30, δ_X 47.37, $^2J_{AX}$ = 63.91 Hz; Anal. Calcd for $C_{68}H_{67}BN_2O_3P_2Ru$ (1134.10): C, 72.02; H, 5.95; N, 2.47; Found: C, 72.18; H, 5.82; N, 2.53%; Λ_M = 51.9 Ω^{-1} mol^{-1} cm^2. **4b:** IR (KBr, cm^{-1}) ν_{N_2} 1942 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.81−6.87 (m, 44H, Ph), 3.70 (m, 6H, CH_2), 2.41 (s, 3H, CH_3 *p*-tolyl), 1.47 (t, 15H, CH_3 C_5Me_5), 1.12 (t, 9H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 136.76, δ_X 48.24, $^2J_{AX}$ = 64.52 Hz; Anal. Calcd for $C_{72}H_{77}BN_2O_3P_2Ru$ (1192.22): C, 72.53; H, 6.51; N, 2.35; Found: C, 72.34; H, 6.57; N, 2.26%; Λ_M = 54.2 Ω^{-1} mol^{-1} cm^2. **4c:** IR (KBr, cm^{-1}) ν_{N_2} 1928 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 9.05, 7.98−6.87 (m, 43H, Ph), 3.84 (qnt, 6H, CH_2), 1.55 (t, 15H, CH_3 C_5Me_5), 1.15 (t, 9H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 133.75, δ_X 47.27, $^2J_{AX}$ = 63.32 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 165−120 (m, Ph), 99.57 (s, C_5Me_5), 80.96 (br, CN_2), 63.73 (d, CH_2), 16.00 (d, CH_3 phos), 9.91 (s, CH_3 C_5Me_5); Anal. Calcd for $C_{71}H_{73}BN_2O_3P_2Ru$ (1176.18): C, 72.50; H, 6.26; N, 2.38; Found: C, 72.41; H, 6.18; N, 2.45%; Λ_M = 54.5 Ω^{-1} mol^{-1} cm^2.

*[Ru(η^5-C_5Me_5){N_2C($C_{12}H_8$)}{PPh(OEt)$_2$}(PPh$_3$)]BPh$_4$ (**5c**).* This complex was prepared like the related species **3** and **4**; yield ≥85%. IR (KBr, cm^{-1}) ν_{N_2} 1967 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 9.07, 7.97−6.47 (m, 48H, Ph + fluorene), 3.85−3.51 [m, 4H, CH_2; multiplets are due to the diastereotopic nature of the two OEt groups of PPh(OEt)$_2$], 1.43 (t, 15H, CH_3 C_5Me_5), 1.26, 1.19 (t, 6H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 160.67, δ_X 45.75, $^2J_{AX}$ = 52.25 Hz; Anal. Calcd for $C_{57}H_{58}BN_2O_2P_2Ru$ (976.91): C, 70.08; H, 5.98; N, 2.87; Found: C, 70.31; H, 6.05; N, 2.79%; Λ_M = 53.6 Ω^{-1} mol^{-1} cm^2.

*[Ru(η^5-C_5Me_5)(η^2-NH═NH){P(OR)$_3$}$_2$]BPh$_4$ (**6,7**) [R = Me (**6**), Et (**7**)].* An excess of H_2O (0.5 mmol, 9 μL) was added to a solution of the appropriate diazoalkane complex [Ru(η^5-C_5Me_5)(N_2CAr1Ar2){P(OR)$_3$}$_2$]BPh$_4$ (**1,2**) (0.1 mmol) in 10 mL of CH_2Cl_2, and the reaction mixture was stirred for 48 h. The solvent was removed under reduced pressure to give an oil, which was triturated with alcohol (2 mL). A yellow-orange solid slowly separated out, which was filtered and crystallized by diffusion of ethanol into a dichloromethane solution (2 mL) of the complex; yield ≥ 85%. **6**: ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.72−6.87 (m, 20H, Ph), 3.65 (t, 18H, CH_3 phos), 1.66 (t, 15H, CH_3 C_5Me_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: A_2 spin syst, 153.0; Anal. Calcd for $C_{40}H_{55}BN_2O_6P_2Ru$ (833.70): C, 57.63; H, 6.65; N, 3.36; Found: C, 57.43; H, 6.77; N, 3.24%; Λ_M = 53.2 Ω^{-1} mol^{-1} cm^2. **7**: ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.65−6.87 (t, 20H, Ph), 4.09 (m, 12H, CH_2), 1.64 (t, 15H, CH_3 C_5Me_5), 1.27 (t, 18H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: A_2 spin syst, 150.1; Anal. Calcd for $C_{46}H_{67}BN_2O_6P_2Ru$ (917.86): C, 60.19; H, 7.36; N, 3.05; Found: C, 60.02; H, 7.19; N, 3.17%; Λ_M = 54.3 Ω^{-1} mol^{-1} cm^2.

*[Ru(η^5-C_5Me_5)(η^2-^{15}NH═NH){P(OEt)$_3$}$_2$]BPh$_4$ (**7$_1$**).* This labeled complex was prepared in one step by reacting RuCl(η^5-C_5Me_5)[P(OEt)$_3$]$_2$ in ethanol first with ethyldiazoacetate ^{15}NNC(H)COOEt and then with water, as follows: in a 25 mL three-necked round-bottomed flask were placed solid samples of the chloro-complex RuCl(η^5-C_5Me_5)[P(OEt)$_3$]$_2$ (100 mg, 0.16 mmol), an excess of $NaBPh_4$ (0.32 mmol, 109 mg) and 5 mL of ethanol. An excess of ^{15}N-labeled diazoalkane (0.48 mmol, 51 μL) was added to the mixture, which was then stirred for 15 h. Dichloromethane (5 mL) and an excess of water (0.7 mmol, 13 μL) were added to the reaction mixture, which was stirred for 15 h more. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL). A yellow-orange solid slowly separated out by cooling the solution to ca. −25 °C; yield ≥ 48%. ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.63−6.88 (t, 20H, Ph), 7.14 (br, 2H, NH) (4.10 (m, 12H, CH_2), 1.65 (t, 15H, CH_3 C_5Me_5), 1.28 (t, 18H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: A_2X spin syst, 150.15 (s br); ^{15}N NMR (CD_2Cl_2, 20 °C) δ: $NYZA_2$ spin syst (N = ^{15}N; Y, Z = ^1H; A = ^{31}P), δ_N −208.3, $^1J_{NY}$ = 92.1, $^2J_{NZ}$ = < 2.0, $^2J_{NA}$ = < 1.5 Hz.

*[Ru(η^5-C_5Me_5)(η^2-NH═NH){P(OR)$_3$}(PPh$_3$)]BPh$_4$ (**8,9**) [R = Me (**8**), Et (**9**)].* These complexes were prepared like the related species **6**,**7**, starting from diazoalkane complexes **3**,**4**; yield ≥85%. **8:** ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.43, 7.31 (br), 7.02, 6.87 (t) (35H, Ph), 3.58 (d, 9H, CH_3 phos), 1.43 (t, 15H, CH_3 C_5Me_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 120.30, δ_X 37.33, $^2J_{AX}$ = 90.41 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 165−119 (m, Ph), 108.84 (s, C_5Me_5), 55.72 (d, CH_3 phos), 9.34 (s, CH_3 C_5Me_5); Anal. Calcd for $C_{55}H_{61}BN_2O_3P_2Ru$ (971.91): C, 67.97; H, 6.33; N, 2.88; Found: C, 67.82; H, 6.40; N, 2.78%; Λ_M = 53.6 Ω^{-1} mol^{-1} cm^2. **9:** ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.46, 7.31 (br), 7.02, 6.87 (t) (35H, Ph), 4.02 (m, 6H, CH_2), 1.43 (t, 15H, CH_3 C_5Me_5), 1.08 (t, 9H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 115.11, δ_X 37.71, $^2J_{AX}$ = 91.02 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 165−122 (m, Ph), 108.68 (s, C_5Me_5), 65.31 (d, CH_2), 15.97 (d, CH_3 phos), 9.38 (s, CH_3 C_5Me_5); Anal. Calcd for $C_{58}H_{67}BN_2O_3P_2Ru$ (1013.99): C, 68.70; H, 6.66; N, 2.76; Found: C, 68.62; H, 6.77; N, 2.64%; Λ_M = 55.3 Ω^{-1} mol^{-1} cm^2.

*[Ru(η^5-C_5Me_5)(η^2-^{15}NH═NH){P(OR)$_3$}(PPh$_3$)]BPh$_4$ (**8$_1$, 9$_1$**) [R = Me (**8**), Et (**9**)].* These complexes were prepared exactly like the related labeled compond **7$_1$**, by reacting chloro-compounds RuCl(η^5-C_5Me_5)-[P(OR)$_3$](PPh$_3$) first with labeled ethyldiazoacetate ^{15}NNC(H)-COOEt and then with water; yield ≥ 45%. **8$_1$**: ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.01 (br, 2H, NH); ^{15}N NMR (CD_2Cl_2, 20 °C) δ: −210.9 (dm), $^1J^{15}_{NH}$ = 92.0 Hz. **9$_1$**: ^1H NMR (CD_2Cl_2, 20 °C) δ: 6.94 (br, 2H, NH); ^{15}N NMR (CD_2Cl_2, 20 °C) δ: NYZAX spin syst (N = ^{15}N; Y, Z = ^1H; A, X = ^{31}P), δ_N −211.1, $^1J_{NY}$ = 92.4, $^2J_{NZ}$ = 2.7, $^2J_{NA}$ = 3.7, $^2J_{NX}$ = 0.9, $^3J_{YZ}$ = 17.0, $^3J_{YA}$ = 3.0, $^3J_{YX}$ = 6.6, $^3J_{ZA}$ = 3.0, $^3J_{ZX}$ = 1.0, $^2J_{AX}$ = 90.87 Hz; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AXN spin syst, δ_A 115.3, δ_X 37.9, $^2J_{AX}$ = 90.9, $^2J_{AN}$ = 3.7, $^2J_{XN}$ = 0.9 Hz.

*Reaction of [Ru(η^5-C_5Me_5){N_2C($C_{12}H_8$)}{P(OMe)$_3$}(PPh$_3$)]BPh$_4$ (**3c**) with H_2O: Separation of Fluorenone $C_{12}H_8CO$.* An excess of H_2O (0.44 mmol, 8 μL) was added to a solution of diazoalkane complex **3c** (100 mg, 0.088 mmol) in 10 mL of dichloromethane, and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL). A yellow solid, characterized as the diazene complex **8**, slowly separated by cooling the resulting solution to ca. −25 °C and was filtered and dried under reduced pressure. The mother liquor was chromatographed on a silica gel column (52 cm) using a mixture of petroleum ether (40−60 °C), dichloromethane, and ethanol in 20:5:2 ratio as eluent. The first eluted species was evaporated to dryness and

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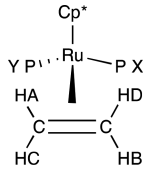
characterized as fluorenone $C_{12}H_8CO$ by GC and IR (KBr, ν_{CO} 1712 s, cm^{-1}) data by comparison with an authentic sample.

*[Ru(η^5-C_5Me_5)(CO){P(OEt)$_3$}(PPh$_3$)]BPh$_4$ (**10**).* To a solution of Ru(η^5-C_5Me_5)[P(OEt)$_3$](PPh$_3$) (100 mg, 0.14 mmol) in ethanol (5 mL) was added an excess of $NaBPh_4$ (0.28 mmol, 96 mg), and the reaction mixture was stirred under a CO atmosphere (1 atm) for 10 h. The yellow solid which precipitated was filtered and crystallized from dichloromethane (1 mL) and ethanol (2 mL); yield ≥85%. IR (KBr, cm^{-1}) ν_{CO} 1951 (s); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.55−6.86 (m, 35H, Ph), 3.85 (qnt, 6H, CH_2), 1.60 (t, 15H, CH_3 C_5Me_5), 1.13 (t, 9H, CH_3 phos); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 133.60, δ_{BX} 50.65, $^2J_{AX}$ = 53.22 Hz; Anal. Calcd for $C_{59}H_{65}BO_4P_2Ru$ (1011.97): C, 70.02; H, 6.47; Found: C, 69.81; H, 6.34%; Λ_M = 53.9 Ω^{-1} mol^{-1} cm^2.

*[Ru(η^5-C_5Me_5)(η^2-CH_2=CH_2){P(OMe)$_3$}(PPh$_3$)]BPh$_4$ (**11**).* A solution of diazoalkane complex (0.1 mmol) in 10 mL of dichloromethane was stirred under ethylene H_2C=CH_2 (1 atm) for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.15 mmol, 51 mg). A yellow-orange solid slowly separated, which was filtered and crystallized from dichloromethane (1 mL) and ethanol (2 mL); yield ≥ 75%. ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.54−6.88 (m, 35H, Ph), 3.49 (d, 9H, CH_3 phos), ABCDXY spin syst (ABCD = ^{1}H; X, Y = ^{31}P), δ_A = δ_B = 2.51, δ_C = δ_D = 2.37, $^3J_{AB}$ = $^3J_{CD}$ = 13.90, $^2J_{AC}$ = $^2J_{BD}$ = −1.10, $^3J_{AD}$ = $^3J_{BC}$ = 8.60, $^3J_{AX}$ = $^3J_{BX}$ = 5.65, $^3J_{AY}$ = $^3J_{BY}$ = 0.75, $^3J_{CX}$ = $^3J_{DX}$ = 6.00, $^3J_{CY}$ = $^3J_{DY}$ = 0.75 Hz (4H, CH_2=CH_2), 1.39 (br, 15H, CH_3 C_5Me_5); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 139.97, δ_B 49.13, $^2J_{AX}$ = 65.00 Hz; ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: 165−119 (m, Ph), 99.05 (s, C_5Me_5), 55.73 (d, CH_3 phos), 43.30 (s, =CH_2), 9.39 (s, CH_3 C_5Me_5); Anal. Calcd for $C_{57}H_{63}BO_3P_2Ru$ (969.94): C, 70.58; H, 6.55; Found: C, 70.40; H, 6.68%; Λ_M = 54.1 Ω^{-1} mol^{-1} cm^2.



*[Ru(η^5-C_5Me_5){=C=C(H)(p-tolyl)}{P(OMe)$_3$}(PPh$_3$)]BPh$_4$ (**12b**).* An excess of the terminal alkyne HC≡C(*p*-tolyl) (0.4 mmol, 52 μL) was added to a solution of the diazoalkane complex [Ru(η^5-C_5Me_5){N_2C(Ph)(*p*-tolyl)}{P(OMe)$_3$}(PPh$_3$)]BPh_4 (**3b**) (0.1 mmol) in dichloromethane (5 mL), and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.15 mmol, 51 mg). A pink solid slowly separated out, which was filtered and crystallized from dichloromethane (1 mL) and ethanol (2 mL); yield ≥80%. IR (KBr, cm^{-1}) $\nu_{Ru=C=C}$ 1634 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.60−6.87 (m, 39H, Ph), 5.52 (dd, $^4J_{PH}$ = 2.4, $^4J_{PH}$ = 6.0, 1H, =CH), 3.45 (t, 9H, CH_3 phos), 2.33 (s, 3H, CH_3 *p*-tolyl), 1.59 (t, 15H, CH_3 C_5Me_5); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 138.03, δ_X 50.46, $^2J_{AX}$ = 52.70 Hz; Anal. Calcd for $C_{64}H_{67}BO_3P_2Ru$ (1058.04): C, 72.65; H, 6.38; Found: C, 72.52; H, 6.47%; Λ_M = 52.5 Ω^{-1} mol^{-1} cm^2.

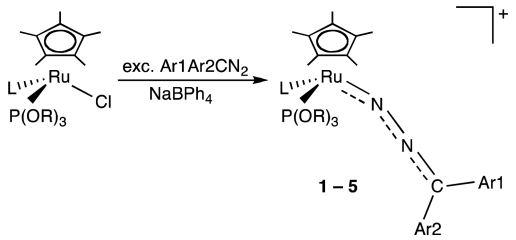
X-ray Crystallography. Crystallographic data were collected at room temperature using a Bruker Smart 6000 CCD detector and Cu−Kα radiation (λ = 1.54178 Å) generated by a Incoatec microfocus source equipped with Incoatec Quazar MX optics. The software APEX2[19] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[19] for integration of intensity of reflections, and SADABS[19] for scaling and empirical absorption correction. The crystallographic treatment was performed with the Oscail program.[20] The structure of compound **2c** was solved by direct methods and refined by a full-matrix least-squares based on F^2.[21] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. One of the ethyl groups on the P(OEt)$_3$ ligand resulted to be disordered over two position with relative abundance of 0.57(3):0.43(3). The structure of compound **7** was solved by using the SHELXT program[22] and refined by a full-matrix least-squares based on F^2, SHELXL program.[23] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. Hydrogen atoms in the diazene ligand were found in the density map, but their refinement was unsuccessful. For this reason, they were included in idealized positions by using the HFIX 23 instruction, and their site occupation factors were refined, resulting to be close to 60:40%. Only the hydrogen atoms at 60% probability were used in figures. Details of crystal data and structural refinement are given in the Supporting Information.

Computational Studies. The computational geometry optimizations were carried out without symmetry constraints, using the range-separated DFT functional ωB97X[24] in combination with the def2-SVP split-valence polarized basis set of Ahlrichs and Weigend, with relativistic ECP on the metal center.[25] The "restricted" formalism was always applied. The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections (T = 298.15 K) were obtained. The correction for BSSE to the computed dissociation energies was introduced by means of the CP approach.[26] The C-PCM implicit solvation model (ε = 9.08) was added to ωB97X calculations.[27] Gaussian '09 was used as software,[28] running on x86-64 workstations based on Intel Xeon E5 v3 multicore processors.

RESULTS AND DISCUSSION

Preparation of Diazoalkane Complexes. Pentamethylcyclopentadienyl half-sandwich complexes Ru(η^5-C_5Me_5)[P(OR)$_3$]L were reacted with an excess of diazoalkane Ar1Ar2CN_2 in the presence of $NaBPh_4$ to yield the diazoalkane derivatives [Ru(η^5-C_5Me_5)(N_2CAr1Ar2){P(OR)$_3$}L]BPh_4 (**1**−**5**), which were isolated and characterized (Scheme 1).

Scheme 1. R = Me, L = P(OMe)$_3$ (1); R = Et, L = P(OEt)$_3$ (2); R = Me, L = PPh$_3$ (3); R = Et, L = PPh$_3$ (4); P(OR)$_3$ = PPh(OEt)$_2$, L = PPh$_3$ (5); Ar1 = Ar2 = Ph (a); Ar1 = Ph, Ar2 = *p*-tolyl (b); Ar1Ar2 = $C_{12}H_8$ (c); Ar1 = Ph, Ar2 = PhC(O) (d)



The reaction proceeded with substitution of chloride by diazoalkane, affording cationic diazoalkane complexes **1**−**5**. The presence of the $NaBPh_4$ salt, which favors the substitution of Cl^-, allows easy formation of complexes **1**−**5**.

Both the bis(phosphite) [Ru(η^5-C_5Me_5){P(OR)$_3$}$_2$]$^+$ and mixed-ligand fragments [Ru(η^5-C_5Me_5){P(OR)$_3$}(PPh$_3$)]$^+$ stabilize the diazoalkane complexes **1**−**5**. This result contrasts with those obtained with the related C_5H_5 derivatives,[6a,b] which give stable diazoalkane derivatives [Ru(η^5-C_5H_5)(N_2CAr1Ar2){P(OR)$_3$}(PPh$_3$)]$^+$ only with mixed phosphine and phosphite ligands. No Ar1Ar2CN_2 complex was obtained using the bis(phosphite) [Ru(η^5-C_5H_5){P(OR)$_3$}$_2$]$^+$. The better donor properties of C_5Me_5 with respect to C_5H_5 allow diazoalkane complexes to be prepared also with two phosphites P(OR)$_3$ as coligands.

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All new complexes $[Ru(\eta^5\text{-}C_5Me_5)(N_2CAr1Ar2)\{P(OR)_3\}L]BPh_4$ (**1**–**5**) were isolated as yellow-orange solids, that are stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes.[29] Their characterization is supported by analytical and spectroscopic data (IR and NMR) and by X-ray crystal structure determination of complex $[Ru(\eta^5\text{-}C_5Me_5)\{N_2C(C_{12}H_8)\}\{P(OEt)_3\}_2]BPh_4$ (**2c**), the ORTEP[30] of which is shown in Figure 1.

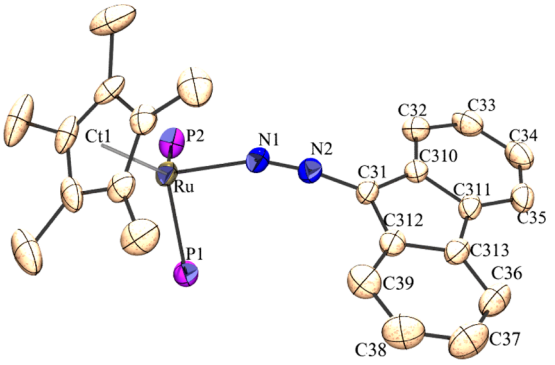

Figure 1. ORTEP view of the cation of **2c**. Ellipsoids are drawn at 30% probability. P1 and P2 represent $P(OEt)_3$ ligands. Hydrogen atoms are not shown.

Compound **2c** consists of a tetraphenylborate salt of a ruthenium cationic complex. Only the cation is shown in Figure 1. The cation contains a ruthenium atom in a half-sandwich piano-stool structure, coordinated by a η^5-pentamethylcyclopentadienyl ligand (Cp*), two phosphite ligands $[P(OEt)_3]$ as legs, and one 9-fluorenediazo ligand bound to the Ru center via the terminal nitrogen atom ligand. Selected bond lengths and angles are shown in Table 1, together with those of **7** for comparative purposes, since it is also a cationic complex of general formula $Cp^*Ru\{P(OEt)_3\}_2\}[N]$, in which [N] represents a nitrogen donor ligand (*vide infra*). The overall geometry of the half-sandwich piano-stool complex is a slightly distorted octahedral and is marked by near 90° values for P–Ru–P and N–Ru–P angles (legs of the piano-stool) or by the angles between the centroid of the Cp* ligand (Ct1) and the legs, in both compounds close to the theoretical 125.3° (Table 1). Again in all three, the η^5-coordination mode of the Cp* ligand and the coordinative behavior of the phosphites is, as usual for these ligands, with a Ru–C bond length average of about 2.26 Å and Ru–P bond distances [between 2.2504(8) and 2.2904(11) Å], i.e., in the expected range for triethylphosphite compounds [e.g., an average of 2.266(3) Å for *cis*-$H_2Ru\{P(OEt)_3\}_4$][31] and do not need further comments. The most interesting characteristic of **2c** is the coordination mode of the 9-fluorenediazo ligand. It should be noted that the Ru–N(1)–N(2) bond angle depends on the ancillary ligand, so that the tris(pyrazolyl)borate derivative (Tp) shows an angle close to 130°,[32] but η^5-indenyl or Cp derivatives have angles between 150 and 160°. The new Cp* derivative **2c** should be included in the latter group, with a Ru–N(1)–N(2) bond angle of 153.1(3)°. In fact, the value is between those found in the 9-diazofluorene ruthenium complex $(\eta^5\text{-Ind})RuP^1P^2\{NNC(C_{12}H_8)\}$ [150.5(2)°][33] or the diaryldiazo Ru complex $CpRuP^1P^2[NNC(Ph)Tol]$ [156.0(1)°].[6a] Conversely, the N(1)–N(2)–C(11) bond angle is 164.1(4)°, more acute than those found in the above-mentioned η^5-indenyl, 171.2(3)°,[33] the Cp substituted compound, 173.9(6)°,[6a] and the 9-diazofluorene ruthenium complex $Ru\{NNC(C_{12}H_8)\}(PNP)Cl_2$ [170.1(3)°].[2g] Of course, it is also far from the almost linear value found for the Tp derivative, 178.2(4)°.[32] The bond distances at the diazo moiety, Ru–N(1) of 1.950(3) Å, N(1)–N(2) of 1.161(4) Å and N(2)–C(11) of 1.296(4) Å, are virtually the same values found in the above-mentioned 9-diazofluorene ruthenium complexes $(\eta^5\text{-Ind})RuP^1P^2\{NNC(C_{12}H_8)\}$[33] and $Ru[NNC(C_{12}H_8)\}(PNP)Cl_2$,[2g] or even in $CpRuP^1P^2[NNC(Ph)Tol]$,[6a] so that a double bond between the nitrogen atoms and also N(2) and C(11) can be proposed.

Table 1. Selected Bond Lengths [Å] and Angles [°][a]

	2c	7
Ru–Ct1	1.9096(3)	1.9080(3)
Ru–N(1)	1.950(3)	2.026(3)
Ru–N(2)		2.020(3)
Ru–Ct2		1.9009(3)
Ru–P(1)	2.2541(10)	2.2904(11)
Ru–P(2)	2.2737(10)	2.2761(10)
$Ru-C_{avg}$	2.260	2.259(4)
Ru–C(1)	2.247(4)	2.265(4)
Ru–C(2)	2.256(3)	2.284(4)
Ru–C(3)	2.270(3)	2.274(4)
Ru–C(4)	2.272(3)	2.245(4)
Ru–C(5)	2.257(3)	2.229(4)
N(1)–N(2)	1.161(4)	1.385(5)
N(2)–C(31)	1.296(4)	
C(31)–C(312)	1.448(5)	
C(31)–C(310)	1.453(5)	
Ct1–Ru–P(1)	126.58(3)	119.61(3)
Ct1–Ru–P(2)	124.78(3)	125.31(3)
P(1)–Ru–P(2)	90.73(4)	87.85(4)
Ct1–Ru–N(1)	123.25(9)	121.50(12)
Ct1–Ru–N(2)		122.46(10)
N(1)–Ru–P(1)	89.63(9)	110.98(12)
N(1)–Ru–P(2)	91.26(9)	81.84(11)
N(2)–Ru–P(1)		81.10(11)
N(2)–Ru–P(2)		106.93(11)
N(1)–Ru–N(2)		40.02(14)
P(1)–Ru–Ct2		96.23(3)
P(2)–Ru–Ct2		94.53(3)
Ct1–Ru–Ct2		124.306(16)
N(1)–N(2)–Ru		70.19(19)
Ru–N(1)–N(2)	153.1(3)	69.79(19)
N(1)–N(2)–C(31)	164.1(4)	
N(2)–C(31)–C(310)	127.6(3)	
N(2)–C(31)–C(312)	123.6(3)	
C(312)–C(31)–C(310)	108.8(3)	

[a]Ct1 represents the centroid if the Cp* ligand, Ct2 represents the middle of the N=N bond.

The IR spectra of diazoalkane complexes $[Ru(\eta^5\text{-}C_5Me_5)(N_2CAr1Ar2)\{P(OR)_3\}L]BPh_4$ (**1**–**5**) show a medium-intensity band at 1967–1914 cm^{-1}, which can be attributed to the ν_{N2} of the diazoalkane ligand. Comparison of this value with literature data[1−3] also suggests an end-on η^1-coordination mode for the $Ar1Ar2CN_2$ group, like that found in the solid state for **2c**. The ^1H NMR spectra show the characteristic signals of the ancillary ligands and those of the substituents Ar1 and Ar2 of the diazo ligand. The ^{31}P NMR spectra are either singlets for bis(phosphite) derivatives **1**, **2**, or AX systems for mixed-ligand complexes **3**–**5**, fitting the proposed formulation.

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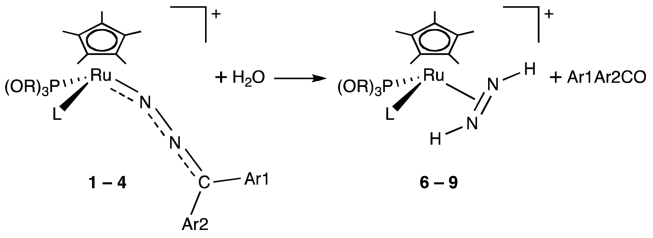
Hydrolysis Reactions. Diazoalkane complexes **1**–**4** react with H_2O at room temperature to give the η^2-diazene derivatives $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}NH{=}NH)\{P(OR)_3\}L]BPh_4$ (**6**–**9**), which were isolated in almost quantitative yield and characterized (Scheme 2).

Scheme 2. R = Me, L = $P(OMe)_3$ (6); R = Et, L = $P(OEt)_3$ (7); R = Me, L = PPh_3 (8); R = Et, L = PPh_3 (9)



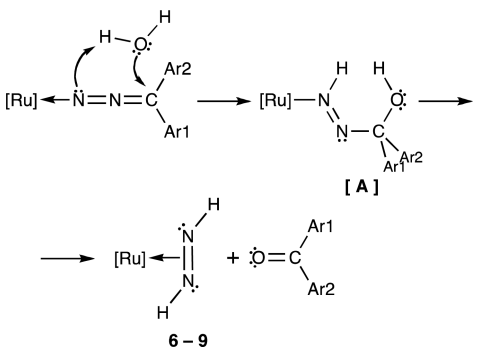
Ketone Ar1Ar2CO also forms in the reaction and was separated in good yield (>90%), indicating the stoichiometry shown in Scheme 2 for the hydrolysis reaction.

All diazoalkane complexes react with H_2O, both those containing two phosphites (**1**, **2**) and mixed-ligand $P(OR)_3$ and PPh_3 ones (**3**, **4**), affording side-on 1,2-diazene derivatives **6**–**9**. Instead, related cyclopentadienyl complexes $[Ru(\eta^5\text{-}C_5H_5)(N_2CAr1Ar2)\{P(OR)_3\}(PPh_3)]BPh_4$, recently prepared by us,[6a,b] do not undergo hydrolysis, and the starting complexes were recovered unchanged after 24 h of reaction. This result was rather unexpected, since $\eta^5\text{-}C_5Me_5$ diazo derivatives **1**–**4** react so easily with H_2O that 1,2-diazene complexes **6**–**9** slowly form, even with traces of water present in not strictly anhydrous solvents. Also unreactive to hydrolysis are the half-sandwich indenyl $[Ru(\eta^5\text{-}C_9H_7)(N_2CAr1Ar2)\{P(OR)_3\}(PPh_3)]BPh_4$[33] and tris(pyrazolyl)borate derivatives $[Ru(Tp)(N_2CAr1Ar2)\{P(OR)_3\}(PPh_3)]BPh_4$,[32] highlighting the peculiar properties of the pentamethylcyclopentadienyl ligand, which, in the half-sandwich fragment $[Ru(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}L]^+$ (L = phosphite or PPh_3), can activate the coordinated diazoalkane toward hydrolysis.

The formation of diazene ligands from hydrolysis of a coordinated diazoalkane is rather surprising, but may be explained as due to the nucleophilic attack[5a] of H_2O on the carbon atom of diazoalkane, according to the reaction path shown in Scheme 3.

In order to support this pathway, we exploited NMR spectra to follow the progress of the reaction, in an attempt to detect intermediates, but no new species were observed, apart from the reagents, final diazenes **6**–**9**, and ketone Ar1Ar2C=O.

Scheme 3. [Ru] = $[Ru(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}L]^+$



This hydrolysis reaction was therefore studied by DFT calculations on the compound $[Ru(\eta^5\text{-}C_5Me_5)(N_2CPh_2)\{P(OMe)_3\}_2]^+$.

Nucleophilic attack by water on the diazoalkane carbon atom is accompanied by protonation at N1 and affords the diazene intermediate $[Ru(\eta^5\text{-}C_5Me_5)\{NHNC(OH)Ph_2\}\{P(OMe)_3\}_2]^+$ [**A**]. The substituents on the N atoms are mutually cis, and a N–H---O intramolecular hydrogen bond stabilizes the species (see Figure 2 and Supporting Information). The LUMO of the coordinated diazoalkane is localized, among all, on the N-bonded carbon atom and has the correct orientation to interact with the electron pairs of water. The HOMO contributes to the formal lone pair on the N1 atom (see Figure 3). The frontier orbitals of the diazoalkane complex should therefore be involved in the interaction of the ligand with the water molecule. The energies of these orbitals are influenced by the presence of substituents on the cyclopentadienyl ring. In fact, calculations show a lowering of about 0.25 eV of E_{HOMO} and 0.14 eV of E_{LUMO}, caused by the replacement of the metal fragment with $[Ru(\eta^5\text{-}C_5H_5)\{P(OMe)_3\}_2]^+$. These variations can be attributed to the smaller donation of the nonsubstituted cyclopentadienyl ring.

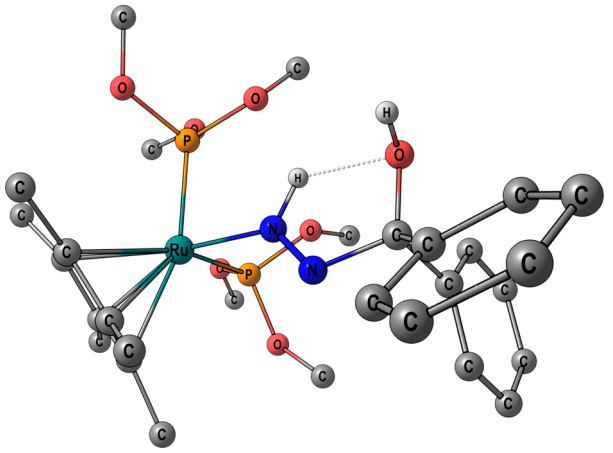


Figure 2. DFT-optimized structure of $[Ru(\eta^5\text{-}C_5Me_5)\{NHNC(OH)Ph_2\}\{P(OMe)_3\}_2]^+$. C-PCM\ωB97X\def2-SVP calculations, dichloromethane as continuous medium. Hydrogen atoms on the ancillary ligands and the phenyl rings have been omitted for clarity. Selected computed bond lengths (Å): Ru–N 2.080; N–N 1.227; N–H 1.044; NH---O 1.948; N–C 1.502; C–O 1.396; O–H 0.967; Ru–C 2.206, 2.214, 2.219, 2.227, 2.243; Ru–P 2.256, 2.259. Selected computed angles (deg): Ru–N–N 131.1; Ru–N–H 115.6; H–N–N 113.2; N–N–C 115.2; N–C–O 111.3.

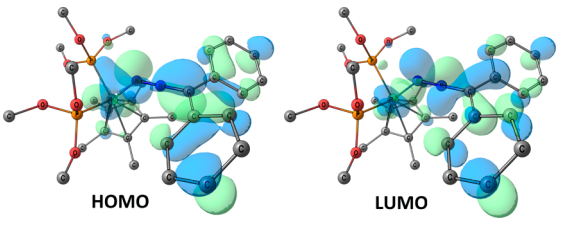


Figure 3. Frontier orbitals of $[Ru(\eta^5\text{-}C_5Me_5)(N_2CPh_2)\{P(OMe)_3\}_2]^+$. C-PCM\ωB97X\def2-SVP calculations, dichloromethane as continuous medium. Surface isovalue = 0.035 au Hydrogen atoms have been omitted for clarity.

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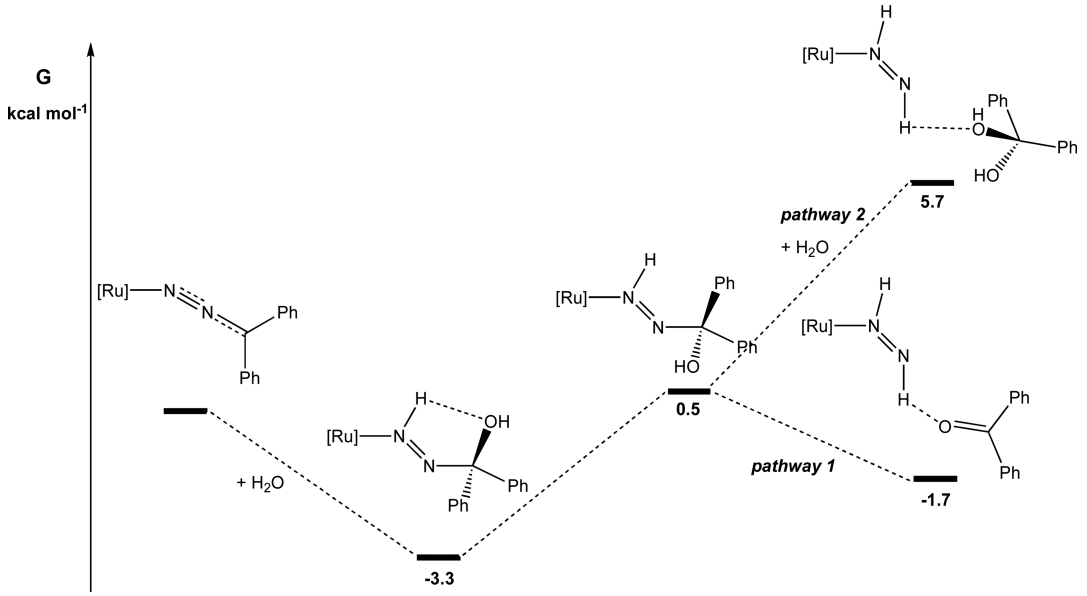
Scheme 4. Relative Gibbs Energies of Possible Intermediates in Diazoalkane Hydrolysis[a]



[a][Ru]-N_2CPh_2 + xH_2O taken as reference (G = 0 kcal mol^{-1}; x = 1, 2). [Ru] = $[Ru(\eta^5\text{-}C_5Me_5)\{P(OMe)_3\}_2]^+$. C-PCM\ωB97X\def2-SVP calculations, dichloromethane as continuous medium. Only local minima are reported.

After the addition of water, C−N bond cleavage and hydrogen transfer from the oxygen atom to N2 lead to $[Ru(\eta^5\text{-}C_5Me_5)\{NHNH\text{---}OCPh_2\}\{P(OMe)_3\}_2]^+$. It is likely that this step is preceded by a rotation around the C−N bond in the intermediate $[Ru(\eta^5\text{-}C_5Me_5)\{NHNC(OH)Ph_2\}\{P(OMe)_3\}_2]^+$, in order to reduce the distance between N2 and the hydrogen atom of the OH moiety. The relative energy of the corresponding rotamer, depicted in Scheme 4, is around 0.5 kcal mol^{-1} with respect to the reactants (see the Supporting Information for Cartesian coordinates). The conversion of $[Ru(\eta^5\text{-}C_5Me_5)\{NHNC(OH)Ph_2\}\{P(OMe)_3\}_2]^+$ to $[Ru(\eta^5\text{-}C_5Me_5)\{NHNH\text{---}OCPh_2\}\{P(OMe)_3\}_2]^+$, depicted in Scheme 4 (pathway 1), is slightly endoergonic, but additional Gibbs energy, around 5.1 kcal mol^{-1}, is subsequently given by the dissociation of benzophenone and the consequent increase in entropy.

Another mechanism for the C−N bond cleavage may involve nucleophilic attack by another water molecule on the carbon atom of [Ru]-$NHNC(OH)Ph_2$, with the formation of the intermediate $C(OH)_2Ph_2$ geminal diol, which in turn converts to benzophenone and water (pathway 2). The intermediate of the latter, $[Ru(\eta^5\text{-}C_5Me_5)\{NHNH\text{---}(OH)_2CPh_2\}\{P(OMe)_3\}_2]^+$, has higher relative Gibbs energy than that on pathway 1, as Scheme 4 shows. As in the previous case, dissociation of the organic substrate from the diazene moiety causes the Gibbs energy to fall by about 5 kcal mol^{-1}. The relative energies of the intermediates (local minima) are reported in Scheme 4. The computed data are not conclusive about the hydrolysis mechanism because we were unable to locate the transition states, and the Gibbs energy difference between the intermediates of the two pathways, summarized in Scheme 4, is not sufficient to unambiguously determine the most probable mechanism. The Cartesian coordinates of $[Ru(\eta^5\text{-}C_5Me_5)\{NHNH\text{---}OCPh_2\}\{P(OMe)_3\}_2]^+$ and $[Ru(\eta^5\text{-}C_5Me_5)\{NHNH\text{---}(OH)_2CPh_2\}\{P(OMe)_3\}_2]^+$ are available in a separated XYZ file (Supporting Information).

It is worth noting that free diazoalkanes are reported[34,35] to undergo hydrolysis, yielding alcohol and N_2. Coordination of our pentamethylcyclopentadienyl fragment $[Ru(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}L]^+$ entails novel reactivity to hydrolysis, affording diazene NH═NH and ketone.

Diazene NH═NH is one of the most reactive nitrogen hydrides,[36] undergoing disproportionation at ca. −150 °C in the condensed phase to N_2 and N_2H_4. However, it is an important molecule, useful as a reagent in stereoselective cis hydrogenation of unsaturated organic compounds[37] and of possible importance to inorganic and bioinorganic N_2 reduction processes.[38] The stability of diazene is greatly enhanced by coordination to transition metals, usually in a bimetallic (μ-HN═NH) or end-on (η^1-HN═NH) fashion, obtained by oxidation of hydrazine complexes.[39−41] Hydrolysis of a coordinated diazolkane highlights a new method of synthesizing this important nitrogen dihydride species.

The new diazene complexes $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}HN{=}NH)\{P(OR)_3\}L]BPh_4$ (**6**–**9**) were separated as yellow solids stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes.[29] Their characterization is supported by analytical and spectroscopic data (IR, ^1H, ^{31}P, ^{13}C, ^{15}N NMR) and by X-ray crystal structure determination of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}HN{=}NH)\{P(OMe)_3\}(PPh_3)]BPh_4$ (**8**)[11] and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}HN{=}NH)\{P(OEt)_3\}_2]BPh_4$ (**7**), the ORTEP[30] of which is shown in Figure 4.

In the cation of **7**, the ruthenium atom is again coordinated by one Cp*, two $P(OEt)_3$ ligands and another ligand, to achieve the half-sandwich piano-stool structure, one η^2-diazene ligand acting as one of the *legs*. The molecular structure of $[RuCp^*(\eta^2\text{-}HN{=}NH)\{P(OEt)_3\}_2]^+$ is closely related to another compound previously described by our group, $[RuCp^*(\eta^2\text{-}NH{=}NH)(PPh_3)\{P(OMe)_3\}]^+$.[11] The difference between them is the presence of differing phosphane ligands, two $P(OEt)_3$ ligands in **7** instead of one PPh_3 and one $P(OMe)_3$ ligand in the previously described compound.[11] Both compounds consist of a tetraphenylborate salt of a ruthenium complex, but **7** crystallizes in triclinic space group $P\bar{1}$, and the other crystallizes in monoclinic space group $P2_1/c$. The cation found in **7** is shown in Figure 4: its most interesting feature is,

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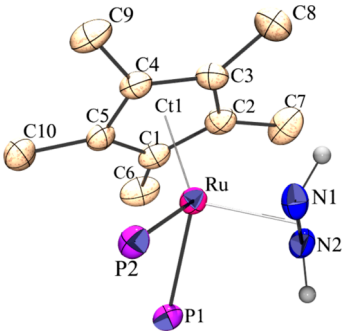

Figure 4. ORTEP view of the cation of **7**. Ellipsoids are drawn at 20% probability level. P1 and P2 represent $P(OEt)_3$ ligands.

again, the presence of one η^2-diazene (η^2-HN═NH) ligand, which is side-on bound to the metal. To the best of our knowledge, only two nonbridging side-on diazene ruthenium complexes have been crystallographically described, the above-mentioned phosphine-phosphito $[RuCp^*(\eta^2\text{-NH═NH})\{P(OMe)_3\}(PPh_3)]^+$ complex[11] and $[Ru(\eta^2\text{-NH═NH})(depe)_2]$.[41a] It should also be noted that the Ru−N distances, 2.020(3) and 2.026(3) Å, are even shorter than those found in $[RuCp^*(\eta^2\text{-NH═NH})\{P(OMe)_3\}(PPh_3)]^+$,[11] 2.030(3) and 2.038(3) Å, and clearly shorter than those in the $[Ru(\eta^2\text{-NH═NH})(depe)_2]$ complex,[41a] 2.123(4) and 2.134(3) Å. However, the N−N bond length falls between both values, being 1.385(5) Å vs 1.366(5)[11] or 1.414(5) Å;[41a] that is, all of them are clearly longer than those reported in other ruthenium diazene complexes, either terminal or bridging [about 1.28 Å]. The lengthening of the N−N bond has been ascribed[41a] to back-bonding from the filled d-orbitals of ruthenium to the antibonding π^* orbitals of the diazene ligand.

The relative position of the hydrogen atoms of the diazene moiety cannot be unambiguously determined from the X-ray crystal structure.[42] DFT calculations on the two possible isomers (see the separate XYZ file) support the relative trans orientation, which resulted in it being more stable than the corresponding cis one by about 0.9 kcal mol^{-1} (Gibbs energy difference).

The ^{1}H NMR spectra of diazene complexes **6**−**9** only show the signals of the ancillay ligands C_5Me_5, $P(OR)_3$, and PPh_3 and the anion BPh_4. No signals attributable to the diazene hydrogen atoms were observed. However, a heterocorrelated experiment (HMQC spectra, Figure 5) between the ^{15}N and ^{1}H nuclei of the labeled complexes $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}H^{15}N═NH)\{P(OR)_3\}L]BPh_4$ ($\mathbf{7_1}$, $\mathbf{8_1}$, $\mathbf{9_1}$) clearly identifies the η^2-HN═NH protons at 7.14−6.94 ppm as signals—one doublet and one broad singlet—overlapping the multiplet of the phenyl protons.

Further support for the presence of the η^2-diazene ligand comes from the proton-coupled ^{15}N NMR spectra of labeled complexes $\mathbf{7_1}$, $\mathbf{8_1}$, and $\mathbf{9_1}$, which appear as doublets of multiplets at −208.3 ($\mathbf{7_1}$), −210.9 ($\mathbf{8_1}$), and −211.1 ($\mathbf{9_1}$) ppm; they could be simulated with an NYZAX model (N = ^{15}N; Y, Z = ^{1}H; A, X = ^{31}P) for mixed-ligand complexes $\mathbf{8_1}$ and $\mathbf{9_1}$ and with an $NYZA_2$ model for phosphite derivative $\mathbf{7_1}$ (Figure 6), $^1J^{15}_{NH}$ = 92.1, $^2J^{15}_{NH}$ < 2.0 Hz. The spectra collapsed to a single multiplet (a triplet for $\mathbf{7_1}$) upon ^{1}H decoupling, confirming the presence of the NH═NH group in the complexes.

The ^{31}P NMR spectra of **8** and **9** are AX multiplets (AXN in the labeled complexes), whereas those of **6** and **7** are singlets (doublets in the labeled $\mathbf{7_1}$), fitting the proposed formulation for the complexes. However, the singlet observed (between +20 and −80 °C) in the ^{31}P NMR spectra of complexes $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-NH═NH})\{P(OR)_3\}_2]BPh_4$ (**6**, **7**), which contain a *trans* η^2-diazene ligand, is somewhat surprising because an AB system would be expected. Probably, the difference in chemical shift between the two ^{31}P nuclei is so small in these compounds that gives, within the line width of the spectrum, an apparent singlet.

Some reactivity studies on diazene complexes **6**−**9** indicated that they are robust species, in which the diazene ligand is quite stable to substitution. For example, treatment of **9** with CO (1 atm) gives rise to substitution of the NH═NH ligand and formation of the species $[Ru(\eta^5\text{-}C_5Me_5)(CO)\{P(OEt)_3\}L]BPh_4$ (**10**), but after 48 h of reaction only about 20% of the carbonyl was formed (Scheme 5). Ethylene (1 atm) also reacts

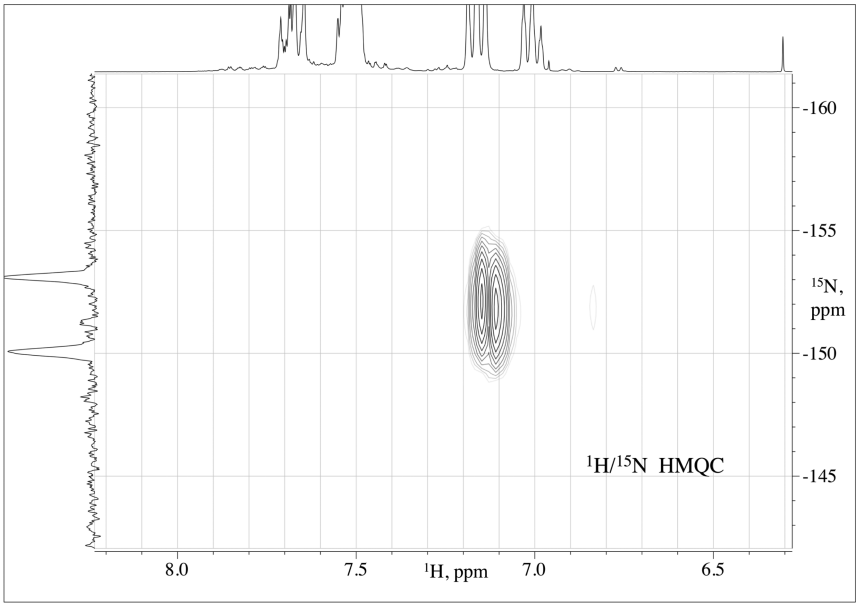

Figure 5. ^{1}H/^{15}N HMQC NMR spectrum of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}^{15}NH═NH)\{P(OEt)_3\}_2]BPh_4$ ($\mathbf{7_1}$) in CD_2Cl_2 at 243 K.

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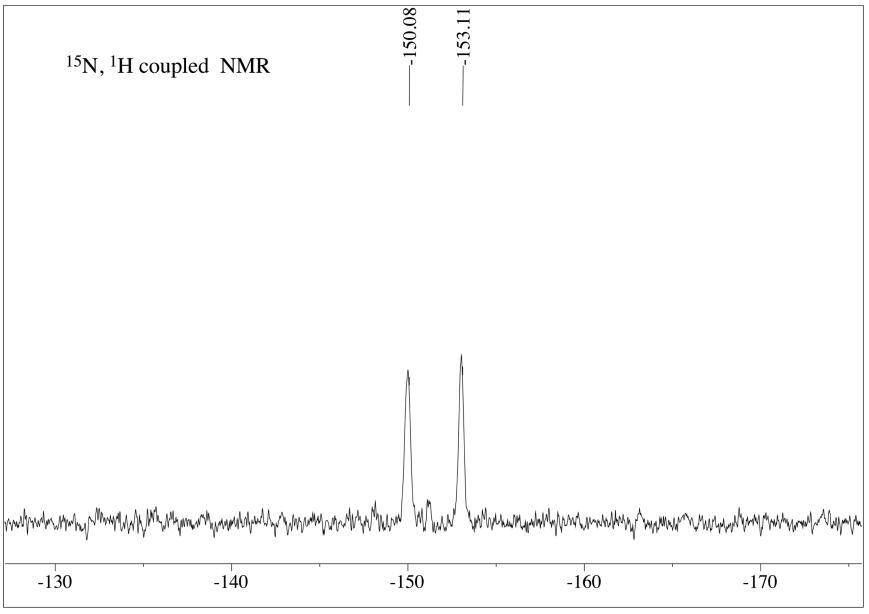
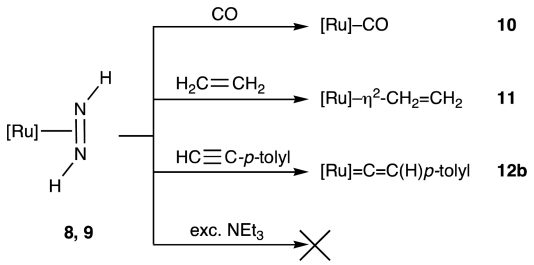


Figure 6. ^{15}N, ^{1}H coupled NMR spectrum of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}^{15}NH{=}NH)\{P(OEt)_3\}_2]BPh_4$ ($\mathbf{7_1}$) in CD_2Cl_2 at 243 K.

Scheme 5. [Ru] = $[Ru(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}(PPh_3)]^+$



with **8** to afford the ethylene complex $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}H_2C{=}CH_2)\{P(OMe)_3\}(PPh_3)]BPh_4$ (**11**), the formation of which is rather slow: only 10−15% was obtained after 24 h of reaction at room temperature. Similar behavior is shown by *p*-tolyl acetylene, which slowly substitutes the diazene ligand, affording the vinylidene complex $[Ru(\eta^5\text{-}C_5Me_5)\{{=}C{=}C\text{-}(H)(p\text{-tolyl})\}\{P(OMe)_3\}(PPh_3)]BPh_4$ (**12b**).[43]

Instead, the diazene complexes do not react with base (a large excess of NEt_3). This result is rather surprising, as the aryldiazene [M]−HN=NAr is known[7,8,44,45] to undergo deprotonation to afford aryldiazenido complexes [M]=N=NAr. The hydrogens of our η^2-HN=NH group were probably not sufficiently acidic, preventing any deprotonation reaction giving rise to new diazo species.

CONCLUSIONS

This work reports that diazoalkane molecules coordinated to the half-sandwich pentamethylcyclopentadienyl fragment $[Ru(\eta^5\text{-}C_5Me_5)\{P(OR)_3\}L]^+$ undergo unprecedented hydrolysis, affording side-on 1,2-diazene derivatives. A reaction path involving nucleophilic attack of H_2O on the diazoalkane is proposed and discussed on the basis of DFT calculations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00671.

Table S1, NMR spectroscopy data: Figures S1−S2 (PDF)

Crystallographic data (CIF1 and CIF2)

Computational data (XYZ)

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Notes

The authors declare no competing financial interest.

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(43) It is worth noting that, since the substitution of diazene in **8**, **9** is slow, the resulting complexes **10**, **11**, **12** were prepared following different methods, reported in the Experimental Section.
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