Ruthenium Cyclopentadienyl Aryldiazenido Complexes. Synthesis of $[Cp'Ru(PR_3)_2(N_2C_6H_4OMe)][BF_4]_2$ and $[Cp'RuCl(PPh_3)(N_2C_6H_4OMe)][BF_4]$ (Cp′ = Cp, Cp*) and X-ray Crystal Structure of $[CpRu(PPh_3)_2(N_2C_6H_4OMe)][BF_4]_2$, an Aryldiazenido Complex with a Large N−N−C(aryl) Angle and Near-Linear Ru−N−N−C(aryl) Skeleton

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The neutral ruthenium complexes $Cp'Ru(PR_3)_2Cl$ [Cp′ = Cp, PR_3 = PPh_3, PMe_3, or 1/2 dppe; Cp′ = Cp*, PR_3 = PMe_3] react with $[p\text{-}MeOC_6H_4N_2][BF_4]$ in acetone to give new cyclopentadienyl ruthenium aryldiazenido dicationic complexes $[Cp'Ru(PR_3)_2(N_2C_6H_4OMe)][BF_4]_2$ [Cp′ = Cp, PR_3 = PPh_3 (**1**), PMe_3 (**2**), or 1/2 dppe (**3**); Cp′ = Cp*, PR_3 = PMe_3 (**4**)] in good yields. The dicationic complexes **1**−**3** may also be conveniently isolated in better yield by treatment of the acetonitrile ruthenium complexes $[CpRu(PR_3)_2(NCMe)][BF_4]$ with the arenediazonium salt. When the reaction of $Cp'Ru(PPh_3)_2Cl$ (Cp′ = Cp or Cp*) with $[p\text{-}MeOC_6H_4N_2][BF_4]$ is carried out in toluene, the product is instead the cyclopentadienyl ruthenium aryldiazenido monocationic complex $[Cp'RuCl(PPh_3)(N_2C_6H_4OMe)][BF_4]$ [Cp′ = Cp (**5**) or Cp* (**6**)]. Further, if the reaction of $Cp^*Ru(PPh_3)_2Cl$ with diazonium salt is carried out in acetone, the binuclear complex $[Cp^*RuCl(N_2C_6H_4OMe)]_2[Cl]_2$ (**7**) can be isolated in low yield in addition to **6**. All new complexes **1**−**7** were fully characterized by NMR, FT-IR, and mass spectroscopies. The structure of $[CpRu(PPh_3)_2(N_2C_6H_4OMe)][BF_4]_2 \cdot 0.93CHCl_3$ (**1**·$0.93CHCl_3$) was determined by single-crystal X-ray diffraction. The structure exhibits a near-linear Ru−N−N−C geometry for the coordinated aryldiazenido group, with the NNC angle having a value of 159°, compared to the "sp^2" value of approximately 120° commonly exhibited by other "singly bent" aryldiazenido complexes. On the basis of NMR spectroscopic data, **1** reacts with $NaBH_4$ at low temperature to give an arylhydrazido(2−) complex $[CpRu(PPh_3)_2\{NN(H)C_6H_4OMe\}][BF_4]$, which readily converts to the corresponding aryldiazene complex $[CpRu(PPh_3)_2(NH{=}NC_6H_4OMe)][BF_4]$ by a hydrogen shift; at room temperature, the only product is the hydrido complex $CpRuH(PPh_3)_2$.

Introduction

The syntheses, structures, dynamic behavior, and reactions of cyclopentadienyl and pentamethylcyclopentadienyl aryldiazenido complexes of selected metals of group 7 (i.e., Mn and Re)[1−5] and group 9 (i.e., Ir)[6−9] have been studied in detail in our laboratory. Our recent interest has involved ones with triorganophosphine ligands PR_3.[4,9] The rhenium complex $[Cp^*Re(PMe_3)_2(p\text{-}N_2C_6H_4OMe)]^+$ has been shown to be dynamic on the NMR time scale, with the singly bent aryldiazenido ligand undergoing inversion or rotation at the carbon-bound nitrogen atom N_β, resulting in exchange of the inequivalent PMe_3 ligands.[4] By contrast, the corresponding iridium complex of similar formula, $[Cp^*Ir(PMe_3)_2(p\text{-}N_2C_6H_4OMe)]^+$, exhibits a doubly bent aryldiazenido ligand, as expected from the difference in electron-donating properties of these ligands (a doubly bent neutral N_2Ar ligand is a formal one-electron donor, while the neutral singly bent ligand is a formal three-electron donor).[9] While these Cp* complexes with two PMe_3 ligands could be synthesized, corresponding ones with two tri*phenyl*phosphine ligands could not be. This is undoubtedly due to the steric congestion afforded by the presence of bulky Cp* and PPh_3 ligands. To further explore the relationship between compounds of this type, we have now turned our attention to the metals of the intervening group 8, in the present case specifi-

(1) Barrientos-Penna, C. F.; Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1985**, *4*, 367.
(2) Garcia-Minsal, A.; Sutton, D. *Organometallics* **1996**, *15*, 332.
(3) Cusanelli, A.; Sutton, D. *Organometallics* **1995**, *14*, 4651.
(4) Cusanelli, A.; Batchelor, R. J.; Einstein, F. W. B.; Sutton, D. *Organometallics* **1994**, *13*, 5096.
(5) Barrientos-Penna, C. F.; Einstein, F. W. B.; Sutton, D.; Willis, A. C. *Inorg. Chem.* **1980**, *19*, 2740.
(6) Yan, X.; Batchelor, R. J.; Einstein, F. W. B.; Zhang, X.; Nagelkerke, R.; Sutton, D. *Inorg. Chem.* **1997**, *36*, 1237.
(7) Yan, X.; Batchelor, R. J.; Einstein, F. W. B.; Sutton, D. *Inorg. Chem.* **1996**, *35*, 7818.
(8) Yan, X.; Einstein, F. W. B.; Sutton, D. *Can. J. Chem.* **1995**, *73*, 939.
(9) Kim, G. C.−Y.; Batchelor, R. J.; Yan, X.; Einstein, F. W. B.; Sutton, D. *Inorg. Chem.* **1995**, *34*, 6163.

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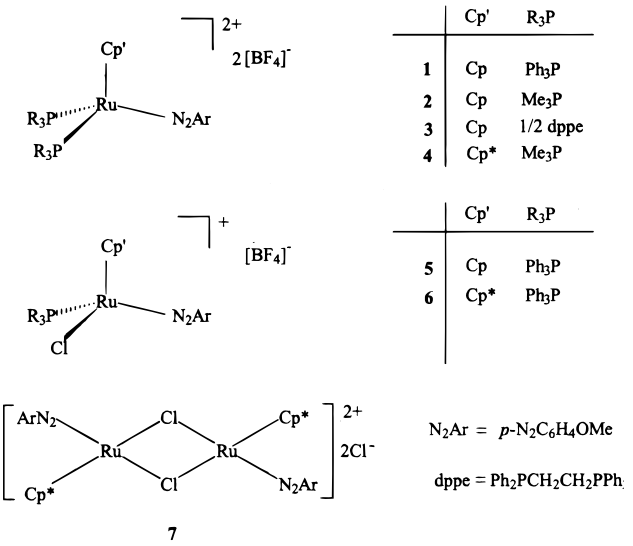
Chart 1



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cally ruthenium. Although workers in this field had an early interest in the aryldiazenido complexes of ruthenium,[10−16] it seems that cyclopentadienyl derivatives have been overlooked. One obvious question posed by the previous Re and Ir chemistry is whether one could successfully synthesize mononuclear complexes of similar composition, namely, $[Cp'Ru(PR_3)_2(p\text{-}N_2C_6H_4OMe)]^{n+}$ (where Cp′ = Cp or Cp*). For $n = 2$ the complex would presumably possess a singly bent N_2Ar ligand, but the neutral complex would have the ligand doubly bent. In this paper we report the successful synthesis of some examples of the dicationic complex and characterization of the stereochemistry of the N_2Ar ligand. Also reported are some examples of the monocationic aryldiazenido complexes $[Cp'RuCl(PR_3)(N_2Ar)]^+$ and a binuclear complex formulated to be $[Cp^*RuCl(N_2C_6H_4OMe)]_2[Cl]_2$. These new compounds are shown in Chart 1.

Experimental Section

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried over the appropriate reagents and distilled under nitrogen prior to use. Some of the routine ^{1}H NMR spectra were recorded at 100 MHz by using a Bruker SY-100 spectrometer. The remaining ^{1}H, ^{31}P{H}, ^{13}C{H}, and ^{15}N NMR spectra were obtained by M. M. Tracey in the NMR service of Simon Fraser University on a Bruker AMX-400 instrument. ^{15}N NMR chemical shifts are reported with reference to nitromethane. IR data were recorded on a Bomem Michelson model 120 FT-IR instrument. Liquid secondary ion mass spectra (LSIMS) were obtained courtesy of D. McGillivray of the MS service at the University of Victoria, Victoria, British Columbia, using a Kratos Concept H double-focusing mass spectrometer at 8 keV accelerating voltage. Scan conditions were 20−2600 amu at 8 s/d using a resolving power of 2000 at 10% V and a cesium ion beam accelerated at 12 keV. The sample matrix was *m*-nitrobenzyl alcohol. FAB mass spectra were obtained by G. Owen at SFU using a Hewlett-Packard model 5985 GCMS instrument with a fast atom bombardment probe (xenon source, Phrasor Scientific, Inc., accessory) for samples dispersed in *m*-nitrobenzyl alcohol. Masses quoted correspond to the most intense peak in the observed or calculated isotopic pattern. Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

The *p*-methoxybenzenediazonium tetrafluoroborate was prepared by the standard procedure using *p*-methoxyaniline (Aldrich) and sodium nitrite and was purified before use by recrystallization from acetone and diethyl ether. The diazonium salt substituted with ^{15}N at the terminal nitrogen atom (N_α) was prepared by using $Na^{15}NO_2$ (95% ^{15}N, MSD Isotopes) and was employed for the synthesis of ^{15}N-labeled compounds. The starting complexes $CpRu(PR_3)_2Cl$ [PR_3 = PPh_3,[17,18] PMe_3,[19,20] or 1/2 dppe[20]] and $Cp^*Ru(PR_3)_2Cl$ [R = Ph or Me][20] were synthesized according to the literature.

$[CpRu(PPh_3)_2(NCMe)][BF_4]$. This was prepared by slightly modifying the literature procedure given for the PF_6 salt.[20,21] $CpRu(PPh_3)_2Cl$ (**1**) (0.30 g, 0.41 mmol) and $NaBF_4$ (0.10 g, 0.91 mmol) were dissolved in acetonitrile (20 mL) and refluxed for 10 h. The solvent was removed in a vacuum, and the residue was extracted with dichloromethane (15 mL). Addition of diethyl ether (30 mL) precipitated a yellow solid, which was recrystallized from acetone/diethyl ether (1:5) to give $[CpRu(PPh_3)_2(NCMe)][BF_4]$ as yellow crystals in 95% yield (0.32 g). IR (KBr): ν(CN) 2280 (w) cm^{-1}, $\nu(BF_4)$ 1051 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.28 (br, 3H, NCMe), 4.50 (s, 5H, Cp), 7.00−7.60 (m, 30H, PPh_3). ^{31}P{H} NMR (acetone-d_6): δ 43.68. ^{13}C{H} NMR (acetone-d_6): δ 4.4 (NC*Me*), 84.2 (Cp), 129.2, 130.9, 132.7, 134.3 (PPh_3), 136.8 (t, *NC*Me, J_{C-P} = 22 Hz). LSIMS-MS (*m*/*z*): 691 [M(cation) − NCMe]$^+$, 429 [M(cation) − NCMe − PPh_3]$^+$. Anal. Calcd for $C_{43}H_{38}BNP_2F_4Ru$: C, 63.08; H, 4.65; N, 1.71. Found: C, 63.13; H, 4.54; N, 1.75. **$[CpRu(PMe_3)_2(NCMe)][BF_4]$** and **$[CpRu(dppe)(NCMe)][BF_4]$** have been reported previously[19,20] and were synthesized by a similar procedure.

$[CpRu(PPh_3)_2(N_2C_6H_4OMe)][BF_4]_2$ (1) and $[CpRu(PPh_3)_2(^{15}NNC_6H_4OMe)][BF_4]_2$ (1-$^{15}N_\alpha$). Method 1. From $CpRu(PPh_3)_2Cl$. Twice the stoichiometric amount of $[p\text{-}MeOC_6H_4N_2][BF_4]$ or $[p\text{-}MeOC_6H_4N^{15}N][BF_4]$ (60 mg, 0.27 mmol) was added as a solid to a stirred suspension of $CpRu(PPh_3)_2Cl$ (100 mg, 0.14 mmol) in acetone (10 mL). The mixture was heated to 40 °C for 3 h. The color of the solution changed gradually from orange to red. The volume was reduced to 5 mL, and diethyl ether (15 mL) was added to give a red oil. After recrystallization twice from acetone/diethyl ether (1:5), $[CpRu(PPh_3)_2(N_2C_6H_4OMe)][BF_4]_2$ (**1**) or $[CpRu(PPh_3)_2(^{15}NNC_6H_4OMe)][BF_4]_2$ (**1-$^{15}N_\alpha$**) was obtained as a red solid in 73% yield (100 mg). IR (KBr): ν(NN) 2074 cm^{-1}; $\nu(^{15}NN)$ 2044 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 4.00 (s, 3H, OMe), 5.93 (s, 5H, Cp), 7.16 (d, 2H C_6H_4), 7.60 (d, 2H, C_6H_4), 7.22−7.62 (m, 30H, PPh_3). ^{31}P{H} NMR (acetone-d_6): δ 34.07 (s, PPh_3, or d, PPh_3, $J_{P-^{15}N}$ = 4.5 Hz). ^{13}C{H} NMR (acetone-d_6): δ 56.7 (OMe), 96.6 (Cp), 97.4, 117.0, 130.8, 166.5 (C_6H_4), 113.9, 129.8−133.2 (m, PPh_3). ^{15}N NMR (acetone-d_6): δ −64.52 (br, $^{15}N_\alpha$). LSIMS: (*m*/*z*) 913 [M − BF_4^-]$^+$, 826 (v. weak) [M − BF_4^- − BF_4]$^+$, 691 [$CpRu(PPh_3)_2$]$^+$, 429 [$CpRu(PPh_3)$]$^+$. Anal. Calcd for $C_{48}H_{42}B_2N_2P_2OF_8Ru$: C, 57.66; H, 4.20; N; 2.80. Found: C, 57.40; H, 4.25; N, 2.98.

(10) McCleverty, J. A.; Whiteley, R. N. *J. Chem. Soc., Chem. Commun.* **1971**, 1159.
(11) McCleverty, J. A.; Seddon, D.; Whiteley, R. N. *J. Chem. Soc., Dalton Trans.* **1975**, 839.
(12) McArdle, J. V.; Schultz, A. J.; Corden, B.; Eisenberg, R. *Inorg. Chem.* **1973**, *12*, 1676.
(13) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 3060.
(14) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2784.
(15) Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 176.
(16) Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 2713.
(17) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1990**, *28*, 270.
(18) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601.
(19) Treichel, P. M.; Komar, D. A. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 205.
(20) Treichel, P. M.; Komar, D. A.; Vincenti, P. J. *Synth. React. Inorg. Met.-Org. Chem.* **1984**, *14*, 383.
(21) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A.* **1971**, 2377.

Method 2. From [CpRu(PPh$_3$)$_2$(NCMe)][BF$_4$]. The stoichiometric amount of solid [*p*-MeOC$_6$H$_4$N$_2$][BF$_4$] (15 mg, 0.068 mmol) was added to a solution of [CpRu(PPh$_3$)$_2$(NCMe)][BF$_4$] (50 mg, 0.06 mmol) in acetone (10 mL). The solution was refluxed for 5 h. The volume was reduced to 5 mL, and diethyl ether (15 mL) was added to give a red oil. Crystallization from acetone/diethyl ether gave red crystals of **1** in 88% yield (53 mg). Anal. Calcd for $C_{48}H_{42}B_2N_2P_2OF_8Ru$: C, 57.66; H, 4.20; N, 2.80. Found: C, 57.41; H, 4.40; N, 2.70.

Method 3. From CpRu(PPh$_3$)$_2$I. The stoichiometric amount of solid [*p*-MeOC$_6$H$_4$N$_2$][BF$_4$] (14 mg, 0.063 mmol) was added to CpRu(PPh$_3$)$_2$I (50 mg, 0.061 mmol) and NaBF$_4$ (13.5 mg, 0.12 mmol) in acetone (10 mL). The mixture was stirred at room temperature for 1.5 h. The solvent was removed in a vacuum, and the residue was extracted with CH_2Cl_2. Recrystallization from acetone/diethyl ether gave fine orange-red crystals of **1** in 80% yield (40 mg). Anal. Calcd for $C_{48}H_{42}B_2N_2P_2OF_8Ru$: C, 57.66; H, 4.20; N, 2.80. Found: C, 57.90; H, 4.25; N, 2.61.

[CpRu(PMe$_3$)$_2$(N$_2$C$_6$H$_4$OMe)][BF$_4$]$_2$ (2) and [CpRu(PMe$_3$)$_2$(^{15}NNC$_6$H$_4$OMe)][BF$_4$]$_2$ (2-^{15}N$_\alpha$). Method 1. From CpRu(PMe$_3$)$_2$Cl. Twice the stoichiometric amount of [*p*-MeOC$_6$H$_4$N$_2$][BF$_4$] or [*p*-MeOC$_6$H$_4$N^{15}N][BF$_4$] (65 mg, 0.29 mmol) was dissolved in acetone (5 mL) and added to the solution of CpRu(PMe$_3$)$_2$Cl (50 mg, 0.14 mmol) in acetone (10 mL) at −78 °C. The mixture was stirred at −78 °C for 1 h, and the color changed from yellow to orange-red. The solution was warmed to 0 °C, and the volume was reduced to 5 mL by vacuum. Addition of diethyl ether (15 mL) at room temperature gave the product as an orange solid, which was recrystallized from acetone/diethyl ether (1:5) to give orange-red crystals in 69% yield (60 mg). IR (KBr): ν(NN) 1877 cm^{-1}; ν(^{15}NN) 1832 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 2.07 (virtual doublet, 18H, PMe$_3$, J_{app} = 11.5 Hz), 3.95 (s, 3H, OMe), 6.39 (s, 5H, Cp), 7.23 (d, 2H C$_6$H$_4$), 7.84 (d, 2H C$_6$H$_4$). ^{31}P{H} NMR (acetone-d_6): δ 10.56 (s, PMe$_3$). ^{13}C{H} NMR (acetone-d_6): δ 20.4 (m, PMe$_3$), 56.9 (OMe), 97.2 (Cp), 116.0, 118.0, 130.6 165.7 (C$_6$H$_4$). ^{15}N NMR (acetone-d_6): δ −29.65 (s, ^{15}N$_\alpha$). LSIMS: *m*/*z* 541 [M − BF$_4^-$]$^+$, 454 [M − BF$_4^-$ − BF$_4$]$^+$ and 453 [M − BF$_4^-$ − HBF$_4$]$^+$ (overlapping, v. weak), 319 [CpRu(PMe$_3$)$_2$]$^+$, 243 [CpRu(PMe$_3$)]$^+$. Anal. Calcd for $C_{18}H_{30}B_2N_2OP_2F_8Ru$: C, 34.45; H, 4.78; N, 4.47. Found: C, 34.40; H, 4.69; N, 4.47.

Method 2. From [CpRu(PMe$_3$)$_2$(NCMe)][BF$_4$]. The stoichiometric amount of solid [*p*-MeOC$_6$H$_4$N$_2$][BF$_4$] (25 mg, 0.11 mmol) was added to a solution of [CpRu(PMe$_3$)$_2$(NCMe)][BF$_4$] (50 mg, 0.11 mmol) in acetone (10 mL). The solution was refluxed for 15 h. The volume was reduced to 5 mL, and diethyl ether (15 mL) was added to give a red oil, which was crystallized from acetone/diethyl ether to give **2** as a red solid in 87% yield (60 mg).

[CpRu(dppe)(N$_2$C$_6$H$_4$OMe)][BF$_4$]$_2$ (3) and [CpRu(dppe)(^{15}NNC$_6$H$_4$OMe)][BF$_4$]$_2$ (3-^{15}N$_\alpha$). Method 1. From CpRu(dppe)Cl. A procedure analogous to that used for **1** gave **3** or **3-^{15}N$_\alpha$** as a red solid in 86% yield. IR (KBr): ν(NN) 2066−1929 (br); ν(^{15}NN) 2038−1900 (br) cm^{-1}. ^{1}H NMR (acetone-d_6): δ 3.55 (m, 4H, CH$_2$), 3.91 (s, 3H, OMe), 6.01 (s, 5H, Cp), 6.90 (AA′BB′q, 4H, C$_6$H$_4$), 7.60−8.20 (m, 20H, Ph). ^{31}P{H} NMR (acetone-d_6): δ 71.97 (s, dppe). ^{13}C{H} NMR (acetone-d_6): δ 28.6 (t, CH$_2$, J_{C-P} = 22 Hz), 57.1 (OMe), 96.0 (Cp), 114.7, 117.2, 129.8 166.0 (C$_6$H$_4$), 129.8−134.1 (m, Ph). ^{15}N NMR (acetone-d_6): δ −58.54 (s, ^{15}N$_\alpha$). LSIMS: *m*/*z* 787 [M − BF$_4^-$]$^+$, 700 [M − BF$_4^-$ − BF$_4$]$^+$ and 699 [M − BF$_4^-$ − HBF$_4$]$^+$ (overlapping, v. weak), 565 [Ru(dppe)]$^+$. Anal. Calcd for $C_{38}H_{36}B_2N_2OP_2F_8Ru$: C, 52.23; H, 4.12; N, 3.21. Found: C, 52.21; H, 4.20; N, 3.40.

Method 2. From [CpRu(dppe)(NCMe)][BF$_4$]. A procedure analogous to that used for **2** gave **3** as a red solid in 79% yield.

[Cp*Ru(PMe$_3$)$_2$(N$_2$C$_6$H$_4$OMe)][BF$_4$]$_2$ (4) and [Cp*Ru(PMe$_3$)$_2$(^{15}NNC$_6$H$_4$OMe)][BF$_4$]$_2$ (4-^{15}N$_\alpha$). Twice the stoichiometric amount of [*p*-MeOC$_6$H$_4$N$_2$][BF$_4$] or [*p*-MeOC$_6$H$_4$N^{15}N][BF$_4$] (55 mg, 0.25 mmol) was dissolved in acetone (5 mL) and added to a solution of Cp*Ru(PMe$_3$)$_2$Cl (50 mg, 0.12 mmol) in acetone (10 mL) at −78 °C. The mixture was stirred at −78 °C for 1 h, and an orange-red solid precipitated. The solvent was removed in a vacuum at 0 °C, and the residue was recrystallized from acetone/diethyl ether (1:5) to give the product as an orange-red solid in 89% yield (75 mg). IR (KBr): ν(NN) 1815 cm^{-1}; ν(^{15}NN) 1780 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 1.99 (virtual doublet, 18H, PMe$_3$, J_{app} = 10.7 Hz), 2.21 (t, 15H, Cp*, J_{P-H} = 1.6 Hz), 3.95 (s, 3H, OMe), 7.25 (d, 2H C$_6$H$_4$), 7.77 (d, 2H C$_6$H$_4$). ^{31}P{H} NMR (acetone-d_6): δ 2.52 (s, PMe$_3$). ^{13}C{H} NMR (acetone-d_6): δ 10.8 (Cp*), 18.6 (m, PMe$_3$), 56.8 (OMe), 110.2 (Cp*), 115.0, 118.1, 130.0 166.0 (C$_6$H$_4$). ^{15}N NMR (acetone-d_6): δ −24.32 (s, ^{15}N$_\alpha$). FABMS: *m*/*z* 389 [Cp*Ru(PMe$_3$)$_2$]$^+$, 311 [Cp*Ru(PMe$_3$)]$^+$.

[CpRuCl(PPh$_3$)(N$_2$C$_6$H$_4$OMe)][BF$_4$] (5) and [CpRuCl(PPh$_3$)(^{15}NNC$_6$H$_4$OMe)][BF$_4$] (5-^{15}N$_\alpha$). Method 1. In Toluene. Twice the stoichiometric amount of solid [*p*-MeOC$_6$H$_4$N$_2$][BF$_4$] or [*p*-MeOC$_6$H$_4$N^{15}N][BF$_4$] (38 mg, 0.17 mmol) was added to a stirred suspension of CpRu(PPh$_3$)$_2$Cl (60 mg, 0.083 mmol) in toluene (10 mL). The mixture was heated to 40 °C for 3 h. The solution changed gradually from orange to yellow. The solvent was removed in a vacuum, and the residue was extracted with acetone. After recrystallization from acetone/diethyl ether (1:5) the product was obtained as a greenish solid in 88% yield (50 mg). IR (KBr): ν(NN) 1794; ν(^{15}NN) 1761 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 3.92 (s, 3H, OMe), 6.14 (d, 5H, Cp, J_{P-H} = 0.6 Hz), 7.11 (d, 2H C$_6$H$_4$), 7.39 (d, 2H C$_6$H$_4$), 7.55 (m, 15H, PPh$_3$). ^{31}P{H} NMR (acetone-d_6): δ 40.06 (s, PPh$_3$, or d, PPh$_3$, $J_{P-^{15}N}$ = 5.1 Hz). ^{13}C{H} NMR (acetone-d_6): δ 56.6 (OMe), 99.3 (Cp), 117.3, 132.9, 165.0 (C$_6$H$_4$), 129.9−137.1 (m, PPh$_3$). ^{15}N NMR (acetone-d_6): δ −18.55 (d, ^{15}N$_\alpha$, $J_{^{15}N-P}$ = 5.1 Hz). LSIMS: *m*/*z* 599 [M(cation)]$^+$, 464 [M(cation) − N$_2$C$_6$H$_4$OMe]$^+$, 429 [CpRu(PPh$_3$)]$^+$. Anal. Calcd for $C_{30}H_{27}BN_2POClF_4Ru$: C, 52.48; H, 3.94; N, 4.08. Found: C, 52.69; H, 3.94; N, 4.40.

Method 2. In Acetone. The stoichiometric amount of [*p*-MeOC$_6$H$_4$N$_2$][BF$_4$] (30 mg, 0.14 mmol) was added to a stirred suspension of CpRu(PPh$_3$)$_2$Cl (100 mg, 0.14 mmol) in acetone (10 mL). The mixture was heated to 40 °C for 3 h. The color changed from orange to red in the first 15 min and then gradually turned to yellow. The solvent was removed in a vacuum, and a ^{1}H NMR spectrum on the residue showed that [CpRuCl(PPh$_3$)(N$_2$C$_6$H$_4$OMe)][BF$_4$] (**5**) and [CpRu(PPh$_3$)$_2$(N$_2$C$_6$H$_4$OMe)][BF$_4$]$_2$ (**1**) were formed in an approximate 4:1 ratio.

[Cp*RuCl(PPh$_3$)(N$_2$C$_6$H$_4$OMe)][BF$_4$] (6), [Cp*RuCl(PPh$_3$)(^{15}NNC$_6$H$_4$OMe)][BF$_4$] (6-^{15}N$_\alpha$), [Cp*RuCl(N$_2$C$_6$H$_4$OMe)]$_2$[Cl]$_2$ (7), and [Cp*RuCl(^{15}NNC$_6$H$_4$OMe)]$_2$[Cl]$_2$ (7-^{15}N$_\alpha$). Method 1. In Toluene. Twice the stoichiometric amount of solid [*p*-MeOC$_6$H$_4$N$_2$][BF$_4$] or [*p*-MeOC$_6$H$_4$N^{15}N][BF$_4$] (55 mg, 0.25 mmol) was added to a stirred suspension of Cp*Ru(PPh$_3$)$_2$Cl (100 mg, 0.12 mmol) in toluene (10 mL). The mixture was heated to 40 °C for 3 h, and the solution changed gradually from orange to yellow. The solvent was removed in a vacuum, and the residue was extracted with dichloromethane. After recrystallization from acetone/diethyl ether (1:5), **6** or **6-^{15}N$_\alpha$** was obtained as a greenish-yellow solid in 78% yield (70 mg). IR (KBr): ν(NN) 1771; ν(^{15}NN) 1736 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.66 (d, 15H, Cp*, J_{P-H} = 1.7 Hz), 3.88 (s, 3H, OMe), 6.91 (d, 2H C$_6$H$_4$), 7.34 (d, 2H C$_6$H$_4$), 7.43 (m, 15H, PPh$_3$). ^{31}P{H} NMR (CDCl$_3$): δ 37.49 (s, PPh$_3$, or d, PPh$_3$, $J_{P-^{15}N}$ = 6.0 Hz). ^{13}C{H} NMR (CDCl$_3$): δ 9.5 (s, Cp*), 55.9 (OMe), 109.9 (Cp*), 95.1, 116.1, 131.7, 166.8 (C$_6$H$_4$), 124.3−134.8 (m, PPh$_3$). ^{15}N NMR (CDCl$_3$): δ −4.77 (d, ^{15}N$_\alpha$, $J_{^{15}N-P}$ = 6.0 Hz). LSIMS: *m*/*z* 669 [M(cation)]$^+$, 534 [M(cation) − N$_2$C$_6$H$_4$OMe]$^+$, 499 [Cp*Ru(PPh$_3$)]$^+$.

Method 2. In Acetone. The reaction was carried out as above, but in acetone at 40 °C for 3 h. The solution changed gradually from orange to yellow. The solvent was removed in a vacuum, and the residue was extracted with dichlo-

Table 1. Crystallographic Data for the Structure Determination of 1·0.93CHCl$_3$

formula	$RuP_2F_8ON_2C_{48.93}B_2H_{42.93}Cl_{2.78}$
fw	1104.5
cryst syst	triclinic
space group	$P\bar{1}$
cell dimens	*a* 10.5910(10) Å
	b 13.2210(10) Å
	c 18.8130(15) Å
	α 100.121(8)°
	β 100.126(8)°
	γ 105.461(8)°
V	2414.9(4) Å^3
Z	2
F(000)	1122.14
cryst dimens (mm)	0.42 × 0.20 × 0.16
D_{calc} (g cm^{-3})	1.527
μ (mm^{-1})	0.45
λ (Mo Kα) (Å)	0.70930
2ϑ(max) (Mo Kα)	54.0
R_F	0.041
R_{wF}	0.046
diffractometer	Nonius CCD
no. reflns measd	35 189
no. unique reflns	8606
no. reflns with $I_{net} > 2.5\sigma(I_{net})$	7601

romethane. After recrystallization from acetone/diethyl ether, [Cp*RuCl(PPh$_3$)(N$_2$C$_6$H$_4$OMe)][BF$_4$] (**6**) or [Cp*RuCl(PPh$_3$)(^{15}NNC$_6$H$_4$OMe)][BF$_4$] (**6-^{15}N$_\alpha$**) was obtained as a greenish-yellow solid in 67% yield. The mother liquid was kept at −4 °C for a week, and [Cp*RuCl(N$_2$C$_6$H$_4$OMe)]$_2$[Cl]$_2$ (**7**) or [Cp*RuCl(^{15}NNC$_6$H$_4$OMe)]$_2$[Cl]$_2$ (**7-^{15}N$_\alpha$**) was obtained as a black solid in ca. 10% yield. Data for **7** IR (KBr): ν(NN) 1753; ν(^{15}NN) 1722 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.74 (s, 15H, Cp*), 3.88 (s, 3H, OMe), 6.91 (d, 2H C$_6$H$_4$), 7.60 (d, 2H C$_6$H$_4$). ^{15}N NMR (CDCl$_3$): −24.67 (s, ^{15}N$_\alpha$,). LSIMS: *m*/*z* 851 [M − Cl]$^+$, 714 [M − Cl − N$_2$C$_6$H$_4$OMe]$^+$, 579 [Cp*RuCl$_2$(N$_2$C$_6$H$_4$OMe)$_2$]$^+$, 407 [Cp*RuCl(N$_2$C$_6$H$_4$OMe)]$^+$, 379 [Cp*RuCl(C$_6$H$_4$OMe)]$^+$.

X-ray Crystal Structure Determination for 1·0.93CHCl$_3$. Crystals were grown from chloroform−diethyl ether. A summary of the crystallographic data is given in Table 1. Complete details of the crystal data, X-ray data collection, and structure solution are provided as Supporting Information.

Reaction of [CpRu(PPh$_3$)$_2$(N$_2$C$_6$H$_4$OMe)][BF$_4$]$_2$ (1) with NaBH$_4$. (a) At 0 °C. NaBH$_4$ (25 mg, 0.63 mmol) was added to a solution of **1** (30 mg, 0.030 mmol) in acetone (20 mL) at 0 °C and stirred for 15 min. The mixture was allowed to reach room temperature and stirred for 2 h. The solvent was removed in a vacuum, and the residue was extracted with diethyl ether. Addition of hexane (30 mL) precipitated yellow CpRu(PPh$_3$)$_2$H in 43% yield (9 mg).[22] ^{1}H NMR (C$_6$D$_6$): δ −11.61 (t, 1H, J_{P-H} = 32 Hz), 4.56 (s, 5H, Cp), 7.0−7.5 (m, 30H, Ph).

(b) At −90 °C. A solution of [CpRu(PPh$_3$)$_2$(^{15}NNC$_6$H$_4$OMe)][BF$_4$]$_2$ (**1-^{15}N$_\alpha$**, 20 mg, 0.020 mmol) in acetone-*d*$_6$ (1 mL) was transferred by syringe into a 5 mm NMR tube at −80 °C which contained NaBH$_4$ (0.76 mg, 0.020 mmol). The NMR tube was then placed immediately in the NMR instrument probe, which had been cooled to −90 °C. The ^{1}H, ^{31}P{H}, and ^{15}N NMR spectra were recorded from −90 to −60 °C.

Results

1. Synthesis and Characterization of Dicationic Complexes [CpRu(PR$_3$)$_2$(N$_2$C$_6$H$_4$OMe)][BF$_4$]$_2$ (R = Ph (1), Me (2); PR$_3$ = 1/2 dppe (3)) and [Cp*Ru(PMe$_3$)$_2$(N$_2$C$_6$H$_4$OMe)][BF$_4$]$_2$ (4). Reaction of CpRu(PPh$_3$)$_2$Cl with [*p*-MeOC$_6$H$_4$N$_2$][BF$_4$] in acetone at 40 °C for 3 h gave a mixture of the new singly bent ruthenium aryldiazenido dicationic complex [CpRu(PPh$_3$)$_2$(N$_2$C$_6$H$_4$OMe)][BF$_4$]$_2$ (**1**), formed by replacement of the Cl ligand, and the new monocationic complex [CpRuCl(PPh$_3$)(N$_2$C$_6$H$_4$OMe)][BF$_4$] (**5**), formed by replacement of a PPh$_3$ ligand (Scheme 1). The ratio of the dication and the monocation formed varied with the amount of diazonium salt added. A stoichiometric amount of diazonium salt gave an approximate 1:4 ratio of **1** to **5**. This ratio increased to about 4:1 when more than 2 equiv of the diazonium salt was used. The dicationic complex **1** can be separated from **5** as a red powder by three recrystallizations from acetone/diethyl ether. Recrystallization from chloroform−diethyl ether gave orange crystals suitable for X-ray structure analysis. The dicationic complex [CpRu(PPh$_3$)$_2$(N$_2$C$_6$H$_4$OMe)][BF$_4$]$_2$ (**1**) is more conveniently formed by replacement of the MeCN ligand in [CpRu(PPh$_3$)$_2$(NCMe)][BF$_4$] with a stoichiometric amount of the diazonium salt in acetone. In this case, only **1** is formed and is isolated as orange crystals in high yield (∼90%). Thus, this is a preferred method for the preparation of the dication, although it takes a longer time to complete the reaction. The reaction of CpRu(PPh$_3$)$_2$Cl with diazonium salt was also carried out in other solvents, such as methanol, CH$_2$Cl$_2$, or THF, but neither **1** nor **5** appeared to be formed, and only a mixture of unidentified products was observed, so it seems that acetone is the ideal solvent for the preparation of these dicationic complexes from CpRu(PR$_3$)$_2$Cl.

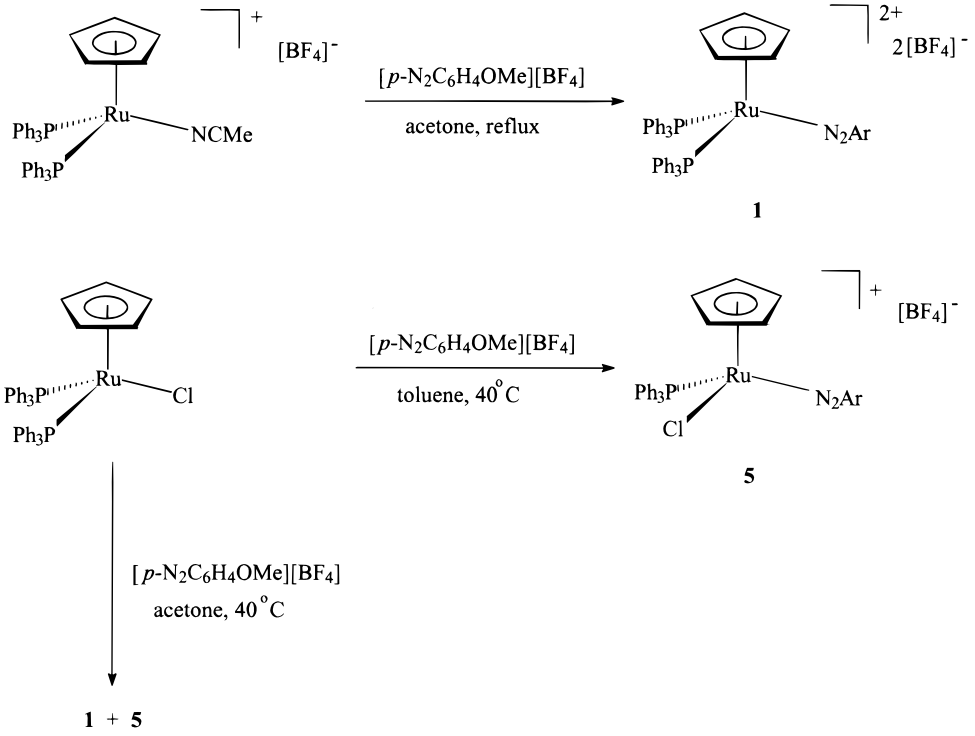
Complex **1** has been fully characterized by elemental analysis, spectroscopy, and an X-ray structure. The IR spectrum of **1** displays the expected absorption for the organic and BF$_4$ groups, and ν(NN) appears as a broad moderately strong absorption at 2074 cm^{-1}. The assignment of ν(NN) was confirmed by ^{15}N isotopic substitution at N$_\alpha$ of the diazenido ligand. A shift of this absorption to lower wavenumber by 30 cm^{-1} was observed. In the ^{1}H NMR spectrum, a singlet at δ 5.93 was observed for the Cp ligand, rather than the triplet expected if the Cp protons are observably coupled to the two equivalent phosphorus ligands. Similarly, a singlet at δ 96.6 ppm was also observed for the Cp ligand in the ^{13}C{H} NMR spectrum. The ^{31}P{H} NMR spectrum displayed a singlet resonance at room temperature and at −80 °C, in the normal region for a coordinated phosphine, and indicated the two triphenylphosphines to be equivalent on the NMR time scale at these temperatures. However, in the ^{31}P{H} NMR of **1-^{15}N$_\alpha$** the resonance was a doublet at δ 34.1 ($J_{P-^{15}N}$ = 4.5 Hz), resulting from coupling with N$_\alpha$. The ^{15}N NMR spectrum of **1-^{15}N$_\alpha$** showed a broad singlet resonance at δ −64.52 ppm, which is in the typical chemical shift range for a singly bent aryldiazenido ligand.[23] Signals due to the singly charged ion pair resulting from loss of one BF$_4^-$ anion and the fragments formed by further loss of the aryldiazenido ligand and one of the phosphines were observed in the LSIMS spectrum.

Reaction of Cp′Ru(PMe$_3$)$_2$Cl (Cp′ = Cp or Cp*) with 2 equiv of diazonium salt in acetone at −78 °C gave the dicationic complexes [Cp′Ru(PMe$_3$)$_2$(N$_2$C$_6$H$_4$OMe)][BF$_4$]$_2$ [Cp′ = Cp (**2**) or Cp* (**4**)] (Scheme 2). It should be noted that the reaction temperature is crucial to successfully

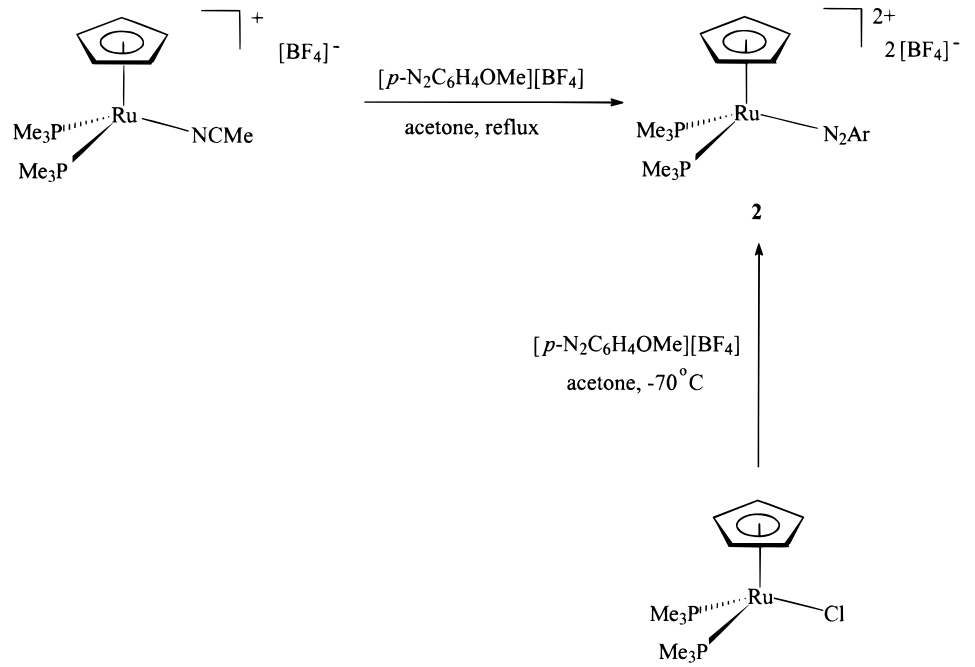
(22) Bruce, M. I.; Humphrey, M. G.; Swincer, A. G.; Wallis, R. C. *Aust. J. Chem.* **1984**, *37*, 1747.

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

Scheme 1

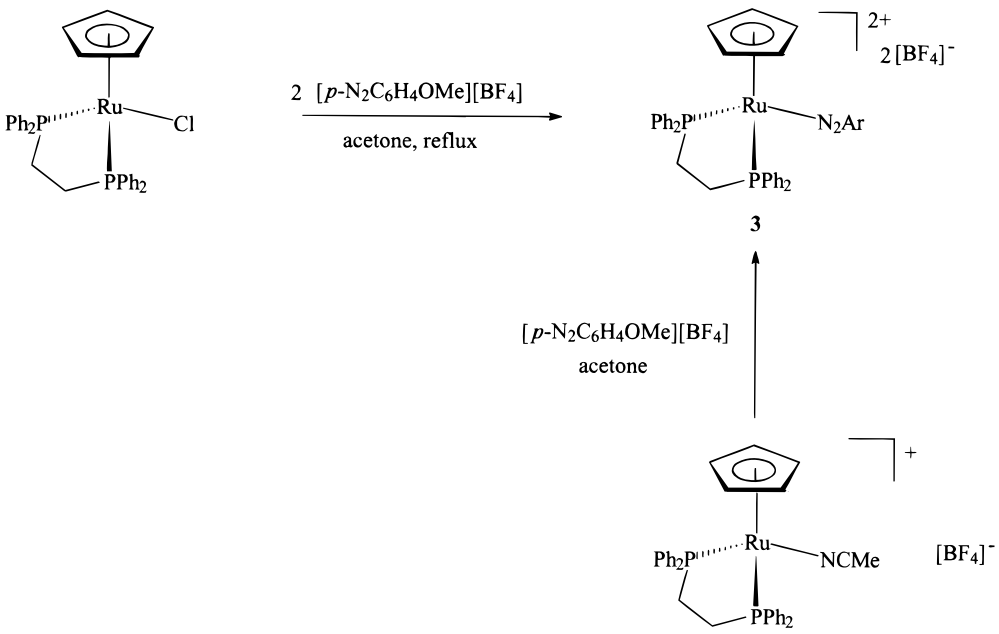


Scheme 2



synthesizing **2** and **4**. During the reaction, an orange solid precipitates at −78 °C, but as the temperature is allowed to rise, this redissolves, and the solution appears to slowly decompose (it becomes purple) when left too long at room temperature. The isolation and crystallization of the product can be successfully achieved at room temperature, if carried out quickly, but only **2** yielded a satisfactory CHN analysis. However, **2** can also be easily prepared from the reaction of [CpRu(PMe$_3$)$_2$(NCMe)][BF$_4$] with diazonium salt in acetone at refluxing temperature for 10 h with no difficulty. The IR spectra of **2** and **4** in KBr disks exhibited a strong band for ν(NN) at 1877 and 1815 cm^{-1}. Both assignments were confirmed by ^{15}N isotopic substitution at N$_\alpha$ of the aryldiazenido ligand, where significant shifts to lower wavenumbers were observed for both **2** and **4**. In the ^{1}H NMR spectrum of **2**, the Cp resonance is a singlet, but in the spectrum of **4** the Cp* resonance is a triplet from coupling to the two equivalent phosphorus atoms with $J_{H-P} = 1.6$ Hz. The resonances assigned to the PMe$_3$ ligands were observed to be virtual (filled-in) doublets. The apparent coupling constant $J_{app} = (^2J_{H-P} + {}^4J_{H-P})$, given by the separation between the two outside peaks, was 11.5 Hz in **2** and 10.7 Hz in **4**. The ^{31}P{H} NMR spectra of **2** and **4** displayed a singlet resonance at room temperature and at −90 °C, indicat-

Scheme 3



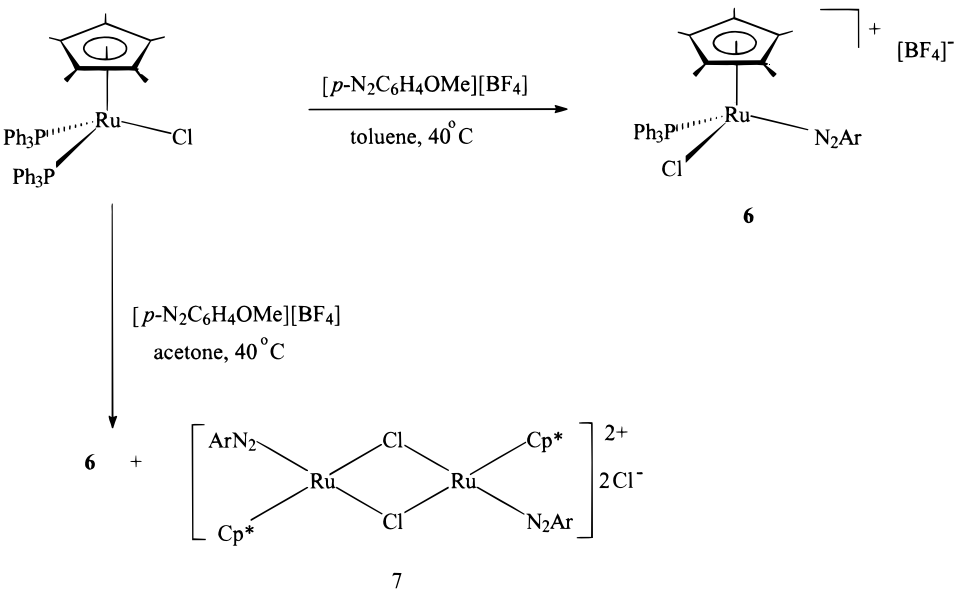
ing the phosphine ligands to remain equivalent over this temperature range. The ^{15}N NMR spectrum showed a singlet resonance at δ −29.6 for **2** and δ −24.3 for **4**, so these compounds showed no observable ^{31}P−^{15}N coupling in either the ^{15}N or the ^{31}P{H} NMR spectra. The LSIMS or FABMS spectra of **2** and **4** showed fragmentation patterns analogous to those observed for **1**.

The reaction of CpRu(dppe)Cl with 2 equiv of the diazonium salt in acetone gave [CpRu(dppe)($N_2C_6H_4$-OMe)][BF_4]$_2$ (**3**) as a red powder. There was no evidence of formation of the possible monocationic complex [CpRuCl(dppe)($N_2C_6H_4OMe$)][BF_4], which, if analogous to **5**, would necessitate a monodentate (dangling) dppe. Again, the dicationic complex can also be isolated in good yield from the reaction of [CpRu(dppe)(NCMe)]-[BF_4] with the diazonium salt in acetone at refluxing temperature (Scheme 3). The IR spectrum of **3** displays ν(NN) as a very broad absorption at 2066−1929 cm^{-1}, which is lower than that in **1**. The assignment of ν(NN) was confirmed by ^{15}N isotopic substitution at N_α, which gave a shift to lower wavenumber by 28 cm^{-1}. In the ^{1}H NMR spectrum of **3**, the Cp resonance occurred as a singlet, with no observable coupling to phosphorus, and the ^{31}P{H} NMR spectrum gave a singlet resonance at room temperature, indicating the NMR equivalence of the two phosphorus atoms at this temperature, consistent with bidentate coordination of the dppe ligand. The ^{15}N NMR spectrum of **3-^{15}N$_\alpha$** showed a singlet resonance at δ −58.54 and the absence of observable ^{31}P−^{15}N coupling.

Synthesis and Characterization of Monocationic Complexes [Cp′RuCl(PPh_3)($N_2C_6H_4OMe$)][BF_4] (Cp′ = Cp or Cp*). As stated above, the reaction of CpRu-(PPh_3)$_2$Cl with a stoichiometric amount of diazonium salt in acetone gave a mixture of the monocationic complex [CpRuCl(PPh_3)($N_2C_6H_4OMe$)][BF_4] (**5**) and the dicationic complex [CpRu(PPh_3)$_2$($N_2C_6H_4OMe$)][BF_4]$_2$ (**1**) in an approximate 4:1 ratio. It is very difficult to separate and isolate the monocation from the dication analytically pure by recrystallizations. However, when the reaction was conducted in toluene at 40 °C, only the monocationic complex **5** was formed. Recrystallization from acetone and diethyl ether gave **5** as yellow-green crystals in high yield. Similarly, Cp*Ru(PPh_3)$_2$Cl reacted with a stoichiometric amount of diazonium salt in toluene at 40 °C to give the monocationic complex [Cp*RuCl(PPh_3)($N_2C_6H_4OMe$)][BF_4] (**6**), which was isolated as a yellow-green powder. When this reaction was carried out in acetone, **6** was again the major product, but now a minor product (<10%) could also be isolated, which was formulated on the basis of spectroscopy and elemental analysis as the binuclear aryldiazenido complex [Cp*RuCl($N_2C_6H_4OMe$)]$_2$[Cl]$_2$ (**7**) (Scheme 4). Notably, by comparison with the corresponding reactions in acetone for all the other cases just described, no formation of any corresponding dicationic complex [Cp*Ru(PPh_3)$_2$($N_2C_6H_4OMe$)][BF_4]$_2$ could be detected by ^{1}H NMR spectroscopy.

For the monocationic complexes [Cp′RuCl(PPh_3)-($N_2C_6H_4OMe$)][BF_4] (**5**, **6**), the IR spectra display the expected absorption for the organic and BF_4 groups and a broad absorption at 1794 cm^{-1} (KBr disk) for **5** and 1771 cm^{-1} for **6**, which fall within the range generally associated with ν(NN) for a terminally coordinated singly bent aryldiazenido ligand. The assignment was confirmed by using their $^{15}N_\alpha$ isotopomers, which showed a shift to lower wavenumber by ∼35 cm^{-1}. In the ^{1}H NMR spectra of the monocationic complexes [Cp′RuCl-(PPh_3)($N_2C_6H_4OMe$)][BF_4], the Cp or Cp* resonances were in both cases phosphorus-coupled doublets with J_{P-H} = 0.6 Hz for **5** and 1.7 Hz for **6**. The ^{13}C{^{1}H} NMR spectrum shows a singlet resonances for the Cp in **5** or the Cp* in **6** and no coupling of these carbons to phosphorus. The ^{31}P{H} NMR spectra of **5** or **6** displayed a singlet resonance at room temperature in the normal region for a coordinated phosphine. However, for the ^{15}N-substituted compounds, the resonances in the ^{31}P{H} and ^{15} N NMR spectra were doublets with J_{P-N} = 5.1 Hz for **5** and 6.0 Hz for **6**. The LSIMS spectra of **5** and **6** exhibited very strong patterns for [M-(cation)]$^+$, and fragments formed by loss of the aryldiazenido ligand and then chlorine are observable.

Scheme 4



In the IR spectrum of the binuclear complex $[Cp^*RuCl(N_2C_6H_4OMe)]_2[Cl]_2$ (**7**), ν(NN) appeared as a broad moderately intense absorption at 1753 cm^{-1}, which indicates that the two aryldiazenide ligands are coordinated to ruthenium as terminal ligands with a singly bent geometry. The ^1H NMR spectrum of **7** showed a single peak at δ 1.74 for Cp* protons and a typical AA′BB′ pattern at δ 6.90−7.60 for the aromatic hydrogens of the diazonium ligand. Microanalysis for C, H, and N suggested the empirical formula $Cp^*Ru(N_2C_6H_4OMe)Cl_2$. However, LSIMS showed a highest mass peak at *m*/*z* 851 with an isotopic pattern matching that calculated for a dinuclear species $[Cp^*_2Ru_2(N_2C_6H_4OMe)_2Cl_3]^+$. It is difficult to formulate this as a discrete cation without violating the 18-electron rule. However, formulation as a dichloro-bridged ion pair $[Cp^*_2Ru_2(N_2C_6H_4OMe)_2Cl_2]^{2+}Cl^-$ presents no such problem. This suggests that **7** should be formulated as the dinuclear complex $[Cp^*_2Ru_2(N_2C_6H_4OMe)_2Cl_2][Cl]_2$. The LSIMS showed a fragment at *m*/*z* ca. 714−716 corresponding to further loss of $N_2C_6H_4OMe$ or Cp*, which are not distinguishable at this resolution. The fragment at *m*/*z* ca. 579 did not exhibit the correct pattern for $[Cp^*_2Ru_2Cl_3]^+$ (calcd 581) but approximately matched $[Cp^*Ru(N_2C_6H_4OMe)_2Cl_2]^+$ or $[Cp^*_2Ru(N_2C_6H_4OMe)Cl_2]^+$ (calcd 577). The patterns observed at *m*/*z* 407 and 379 closely matched the theoretical patterns for mononuclear fragments $[Cp^*RuCl(N_2C_6H_4OMe)]^+$ (or $[Cp^*_2RuCl]^+$) and $[Cp^*RuCl(C_6H_4OMe)]^+$, respectively. A dinuclear ruthenium aryldiazenido complex and a polynuclear complex given the formulas $[Ru_2Cl_3(PPh_3)_3(N_2Ar)_2][PF_6]$ and $[RuCl_2(PPh_3)(N_2Ar)]_n[PF_6]_n$ have been reported previously.[11] All the new ruthenium diazenido complexes are air-sensitive in solution but air-stable in the solid state. They are insoluble in hexane and diethyl ether, slightly soluble in acetone and chloroform, and very soluble in acetonitrile and nitromethane.

3. Crystal Structure of $[CpRu(PPh_3)_2(N_2C_6H_4OMe)][BF_4]_2\cdot 0.93CHCl_3$ (1·0.93CHCl$_3$). The structure of the dicationic complex **1** was confirmed by an X-ray structural study. The geometry of the dication is shown in Figure 1 and can be described as a three-legged pianostool structure where the N_2Ar and two PPh_3 ligands represent the legs. The Cp ligand is bonded to the ruthenium in the typical η^5 coordination mode. The N_2-Ar ligand is "singly bent", that is to say the Ru−N−N part is essentially linear (angle 175.4°) and the N−N−C(aryl) part is bent (angle 158.9°). However, this latter angle is so large that the aryldiazenide ligand adopts almost a linear coordination to ruthenium in this structure. The plane of the aryldiazenide ligand makes an angle of 35.2° with the Cp plane. Thus, there is no plane of symmetry in the dication, and the two phosphine ligands are strictly inequivalent. The bond distances and angles of interest for the dication are listed in Table 2.

4. Reactions of $[CpRu(PPh_3)_2(N_2C_6H_4OMe)][BF_4]_2$ (1). $[CpRu(PPh_3)_2(N_2C_6H_4OMe)][BF_4]_2$ reacted with an excess of $NaBH_4$ in acetone at 0 °C to give the known ruthenium hydride $CpRuH(PPh_3)_2$ in 50% yield. When this reaction was carried out at −78 °C, $CpRuH(PPh_3)_2$ was isolated in lower yield (∼20%). The low-temperature reaction was monitored by ^1H, $^{31}P\{H\}$, and ^{15}N NMR spectroscopy. The ^1H NMR spectrum at −80 °C in acetone-d_6 showed the expected triplet at δ 11.62 and singlet at δ 4.50 for the hydride and Cp protons of the hydrido complex,[22] but also a weak peak at δ 15.9, which may be assigned to N−H in an aryldiazene complex, presumably $[CpRu(PPh_3)_2(NH{=}NC_6H_4OMe)][BF_4]$.[3,24] To confirm the assignment, the reaction was repeated using **1-$^{15}N_\alpha$**. In this case the ^1H NMR spectrum was recorded more immediately at −80 °C and showed a doublet at δ 15.79 with $J_{^{15}N-H} = 67$ Hz, confirming the assignment, but now there was observed an additional singlet of comparable intensity at δ 16.65, which exhibited irreversible temperature-dependent behavior (see below and Figure 2) that suggested it should be assigned to the corresponding arylhydrazido(2−) complex $[CpRu(PPh_3)_2\{^{15}NN(H)C_6H_4OMe\}][BF_4]$.[25−27] Thus, spectra recorded 25 min and 1 h later at −80 °C showed a

(24) Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2578.
(25) Carroll, J. A.; Sutton, D. *Inorg. Chem.* **1980**, *19*, 3137.
(26) Einstein, F. W. B.; Jones, T.; Hanlan, A. J. L.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2585.
(27) Dilworth, J. R.; Harrison, S. A.; Walton, D. R. M.; Schweda, E. *Inorg. Chem.* **1985**, *24*, 2594.

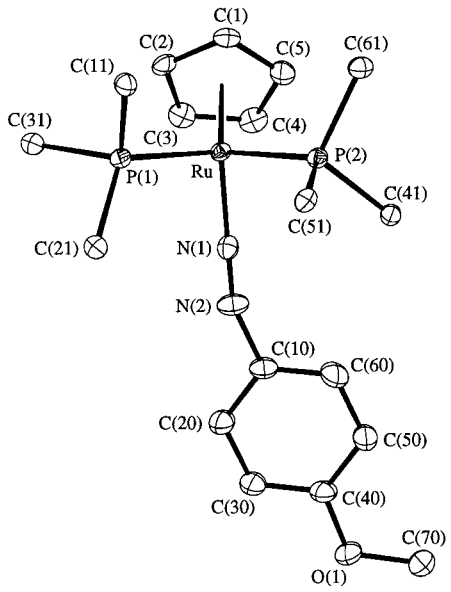


Figure 1. View of the cation $[CpRu(PPh_3)_2(N_2C_6H_4OMe)]^{2+}$ of **1**·0.93$CHCl_3$. Phenyl rings of PPh_3 groups have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Interbond Angles (deg) for 1·0.93$CHCl_3$

Ru1−P1	2.4088(10)	N2−C10	1.390(4)
Ru1−P2	2.3676(10)	C10−C20	1.389(5)
Ru1−N1	1.8561(23)	C10−C60	1.376(6)
Ru1−C1	2.225(3)	C20−C30	1.376(5)
Ru1−C2	2.257(3)	C30−C40	1.387(6)
Ru1−C3	2.259(4)	C40−C50	1.392(5)
Ru1−C4	2.246(4)	C50−C60	1.383(5)
Ru1−C5	2.243(4)	O1−C40	1.352(4)
N1−N2	1.146(3)	O1−C70	1.439(6)
Ru1−N1−N2	175.4(3)	C40−O1−C70	118.3(3)
P1−Ru1−N1	97.02(10)	C10−C20−C30	118.0(4)
P1−Ru1−P2	96.93(3)	C10−C60−C50	119.4(3)
P2−Ru1−N1	90.59(10)	C20−C10−C60	122.4(3)
N1−N2−C10	158.9(4)	C20−C30−C40	120.4(3)
O1−C40−C30	116.1(3)	C30−C40−C50	121.0(3)
O1−C40−C50	122.9(4)	C40−C50−C60	118.8(4)

decrease in the intensity of the singlet relative to the doublet, and at −70 °C the singlet had disappeared, but the doublet remained. Similarly, two unequal resonances were initially observed for the cyclopentadienyl protons assigned to the diazene (δ 4.98) and the hydrazido(2−) complex (δ 4.94), and these exhibited comparable changes. This behavior is consistent with a transformation of the hydrazido(2−) complex to the diazene complex by migration of the hydrogen from N_β to N_α. The ^{15}N NMR recorded on the same sample at −80 and −70 °C exhibited a doublet at δ −27.1 with J_{NH} = 69.8 Hz, which is clearly attributable to the diazene complex. However, the upfield peak of the doublet was somewhat more intense, and since no other resonance could be located for the hydrazido complex, it is possible that the expected singlet occurs coincident with this peak. The diazene complex was unstable, and further NMR spectra indicated complete decomposition by −60 °C. We were unable to isolate either of the postulated aryldiazene or arylhydrazido(2−) complexes.

Complex **1** reacted with KX (X = Br or I) in acetone to give the known complexes $CpRu(PPh_3)_2X$ in good yield. In this reaction, halide substitutes the N_2Ar ligand; that is, the reaction is the reverse of the method

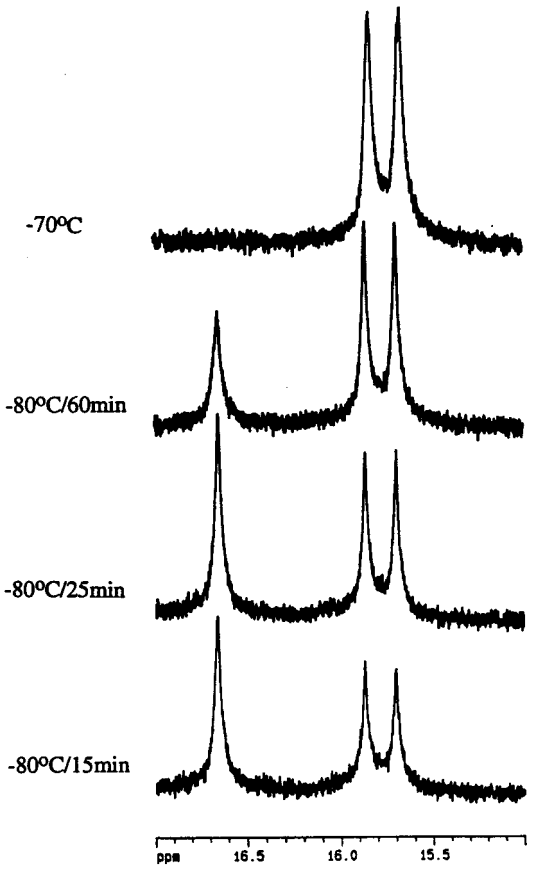


Figure 2. Variable-temperature ^1H NMR in the NH region for the low-temperature reaction of **1**-$^{15}N_\alpha$ with $NaBH_4$. The singlet at δ 16.65 is assigned to the unlabeled NH group of the arylhydrazido(2−) complex $[CpRu(PPh_3)_2\{^{15}NN(H)C_6H_4OMe\}][BF_4]$. The doublet, due to coupling with ^{15}N, is assigned to the ^{15}NH group of the aryldiazene complex $[CpRu(PPh_3)_2(^{15}NH{=}NC_6H_4OMe)][BF_4]$.

of synthesizing **1** from $CpRu(PPh_3)_2X$ and the diazonium ion. However, the reaction with NaCl afforded the aryldiazenido monocationic complex $[CpRuCl(PPh_3)(N_2C_6H_4OMe)][BF_4]$ (**5**) instead of the expected $CpRu(PPh_3)_2Cl$, so in this case Cl^- has substituted a PPh_3 group. Since **1** reacted with Cl^- or I^- in these two different ways, we were prompted to investigate the reaction of $CpRu(PPh_3)_2I$, instead of the chloride, with a stoichiometric amount of aryldiazonium salt in the presence of $NaBF_4$. The dicationic complex $[CpRu(PPh_3)_2(N_2C_6H_4OMe)][BF_4]_2$ (**1**) was isolated, and no evidence of formation of the corresponding monocationic complex $[CpRuI(PPh_3)(N_2C_6H_4OMe)][BF_4]$ was observed, in contrast to the situation when the chloride, $CpRu(PPh_3)_2Cl$, is employed.

Discussion

Synthesis of Ruthenium Aryldiazenido Complexes. The organodiazo chemistry of cyclopentadienyl ruthenium derivatives appears to be largely unexplored.[28] Specifically, we can find few previous references to reactions with arenediazonium ions. Bruce and co-workers reacted the σ-acetylide complex $CpRu(PPh_3)_2(C_2Ph)$ with ArN_2^+, but observed only electrophilic attack at the acetylide ligand, to generate an

(28) Sutton, D. *Chem. Rev.* **1993**, *93*, 995.

aryldiazovinylidene complex.[29,30] When $[CpRu(CO)_3]^+$ was reacted with hydrazines, reaction occurred at coordinated CO to give isocyanate complexes.[31] There have been a few studies of azobenzene reactions with, for example, $Cp'_2Ru_2(CO)_4$ (Cp′ = Cp, Cp*), $CpRuMe(PMe_3)_2$, or $Cp^*RuMe(CO)_2$, generally leading to cyclometalated (phenylazo)phenyl complexes.[32−35]

To our knowledge, no cyclopentadienyl ruthenium aryldiazenido complexes have previously been synthesized. As an entry into this chemistry, the complex $CpRu(PPh_3)_2Cl$ appeared to be an attractive possibility. The complex readily undergoes substitution of a PPh_3 ligand by other two-electron donors such as CO, phosphines, phosphites, and isocyanides, and furthermore it is also possible to substitute the Cl ligand.[21,36] It was encouraging to find that the *dicationic* nitrosyl complexes $[Cp'Ru(PR_3)_2(NO)]^{2+}$ (Cp′ = Cp, R = Ph or Me; Cp′ = Cp*, R = Ph) had already been prepared by substitution of chloride in the complexes $Cp'Ru(PR_3)_2Cl$ with the nitrosonium ion $[NO]^+$ by using $[NO][BF_4]$ or $[NO][PF_6]$.[19,37,38] In view of the often parallel behavior in the reactions of nitrosonium and aryldiazonium salts,[39] corresponding reactions with $[ArN_2][BF_4]$ were undertaken.

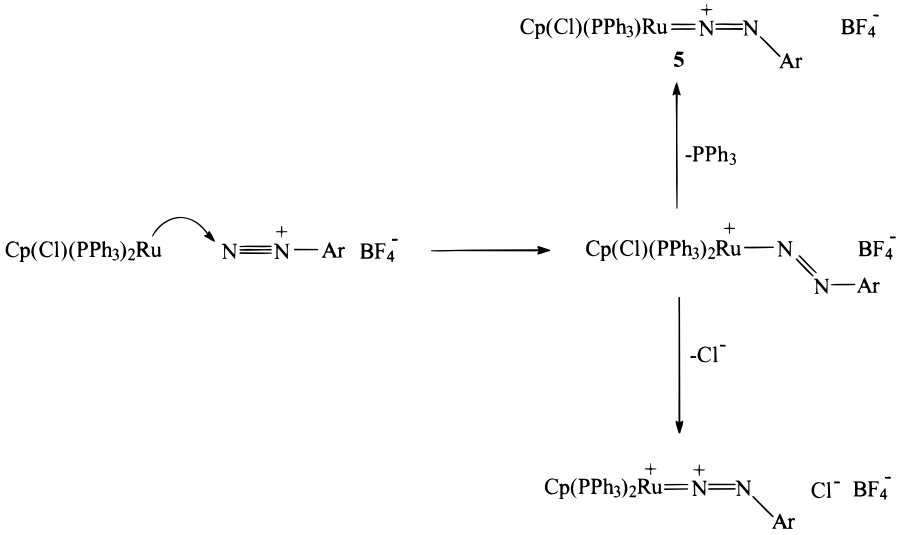
The reaction between $CpRu(PPh_3)_2Cl$ and *p*-methoxybenzenediazonium tetrafluoroborate in the polar solvent acetone gave the corresponding dicationic complex $[CpRu(PPh_3)_2(N_2C_6H_4OMe)][BF_4]_2$ (**1**) as the main product (resulting from Cl substitution), but, in addition, a minor product was the monocationic complex $[CpRu(PPh_3)(N_2C_6H_4OMe)Cl][BF_4]$ (**5**), formed by competing phosphine substitution. It is well-known that $CpRu(PPh_3)_2Cl$ (and the Cp* analogue) exhibit different substitution behavior in polar and nonpolar solvents. Polar solvents support preferential substitution of the chloride ion, whereas substitution of the bulky PPh_3 ligand is favored in nonpolar solvents.[19,40,41] Correspondingly, a high yield of **5** was obtained instead when the reaction was performed in toluene. However, the reaction of the more bulky pentamethylcyclopentadienyl analogue $Cp^*Ru(PPh_3)_2Cl$ proceeded even in acetone only with PPh_3 loss to give the monocationic complex $[Cp^*RuCl(PPh_3)(N_2C_6H_4OMe)][BF_4]$ (**6**), and no corresponding chloride-loss dicationic complex has been observed in this case. This inability to synthesize the highly crowded Cp* analogue of **1** is thus in accord with the previously mentioned results with M = Re and Ir, where the similarly crowded complexes $[Cp^*M(PPh_3)_2(N_2Ar)]^+$ could not be obtained. The additional formation of the binuclear complex $[Cp^*RuCl(N_2C_6H_4OMe)]_2[BF_4]_2$ (**7**) in this reaction can be rationalized by noting that complex **6** still has a rather crowded geometry and loss of the remaining PPh_3 ligand may occur readily to form **7**. We presume that this contamination contributes to the inability to obtain reliable microanalysis data for **6** and **7**.

The alternative synthesis of the dications **1**−**3** from the reaction of the acetonitrile complex $[CpRu(PR_3)_2(NCMe)][BF_4]$ with diazonium salt in acetone gives an improved yield but needs a longer reaction time. Indeed, the relative reaction times and temperatures required in these syntheses compare well with the known electrophilic character of the diazonium ion and its preferential reaction with relatively electron-rich metal sites in complexes.[8] The cationic complex $[CpRu(PPh_3)_2(NCMe)]^+$ is expected to be less electron-rich than neutral $CpRu(PPh_3)_2Cl$, and the reaction is slower. (No reaction was observed for the presumably even less electron-rich cationic acetone complex $[CpRu(CO)(PPh_3)(OCMe_2)][BF_4]$.) On the other hand, $CpRu(PMe_3)_2Cl$ is more electron-rich than $CpRu(PPh_3)_2Cl$,[38] and in this case the reaction is completed even at low temperatures.

The product distribution of **1** and **5** resulting from the reaction of $CpRu(PPh_3)_2Cl$ with diazonium ion in acetone was greatly dependent on the reaction stoichiometry, with a 2:1 excess of diazonium ion changing the ratio of **1**:**5** from 1:4 to 4:1, in favor of the dicationic complex **1**. In the proposed mechanism (Scheme 5), we suggest that the ruthenium atom attacks $[N_2Ar]^+$ to first give the unobserved doubly bent aryldiazenido intermediate $[CpRuCl(PPh_3)_2(N_2Ar)][BF_4]$. (This step is similar to that proposed previously to account for the rapid substitution of C_2H_4 by N_2Ar^+ in $Cp^*Ir(C_2H_4)_2$.)[8] This intermediate can then either dissociate chloride ion to give the resulting complex dication of **1** as the mixed chloride/tetrafluoroborate salt $[CpRu(PPh_3)_2(N_2C_6H_4OMe)][Cl][BF_4]$ or dissociate a PPh_3 ligand to give **5**. A further possibility is that the Cl^- counterion of the salt may reattack the dication and substitute a bulky PPh_3 ligand to give **5**, and this was indeed observed in the reaction of **1** with NaCl. Experiments conducted in an attempt to qualitatively investigate the mechanism gave the following results. (1) When the reaction of $CpRu(PPh_3)_2Cl$ with a 1:1 amount of $[p\text{-}MeOC_6H_4N_2][BF_4]$ in acetone was monitored by ^1H NMR, it was observed that the dication was formed at an early stage, but the amount of monocationic complex **5** increased relative to the dication as the reaction progressed, with complete consumption of the starting materials. This is in agreement with the idea that excess diazonium ion at an early stage promotes the formation of **1** by consuming chloride as relatively un-ionized ArN_2Cl, but as all sources of diazonium ion become depleted by reaction and the Cl^- concentration increases, the formation of **5** becomes competitive. (2) When the reaction of $CpRu(PPh_3)_2Cl$ with a stoichiometric amount of $[p\text{-}MeOC_6H_4N_2][BF_4]$ in acetone was carried out in the presence of an excess of $NaBF_4$, the relative proportion of **1**:**5** was *unchanged* at 1:4, indicating that the observed effect of additional

(29) Bruce, M. I.; Humphrey, M. G.; Liddell, M. J. *J. Organomet. Chem.* **1987**, *321*, 91.
(30) Bruce, M. I.; Dean, C.; Duffy, D. N.; Humphrey, M. G.; Koutsantonis, G. A. *J. Organomet. Chem.* **1985**, *295*, C40.
(31) Kruse, A. E.; Angelici, R. J. *J. Organomet. Chem.* **1970**, *24*, 231.
(32) Garn, D.; Knoch, F.; Kisch, H. *J. Organomet. Chem.* **1993**, *444*, 155.
(33) Bruce, M. I.; Gardner, R. C. F.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1976**, 81.
(34) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2820.
(35) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 3204.
(36) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1398.
(37) (a) Conroy-Lewis, F. M.; Simpson, S. J. *J. Organomet. Chem.* **1987**, *322*, 221. (b) Conroy-Lewis, F. M.; Redhouse, A. D.; Simpson, S. J. *J. Organomet. Chem.* **1990**, *399*, 307.
(38) Bruce, M. I.; Tomkins, I. B.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 687.
(39) Sutton, D. *Chem. Soc. Rev.* **1975**, *4*, 443.
(40) Bruce, M. I.; Hall, B. C.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1998**, 1793.
(41) Bruce, M. I.; Hall, B. C.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *522*, 307.

Scheme 5

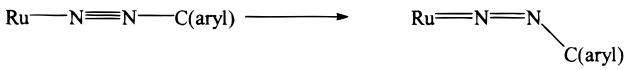


diazonium salt in increasing the relative proportion of dication **1** formed is unlikely to be simply due to the increase in $[BF_4]^-$. It therefore appears probable that the additional diazonium salt acts not just by supplying the extra $[BF_4]^-$ required for the stoichiometry of **1**. It acts to promote formation of **1** relative to **5** by consuming chloride as ArN_2Cl (which may irreversibly decompose to *p*-$MeOC_6H_4Cl$ and N_2 at the temperature of the reaction). (3) However, when the reaction with a stoichiometric amount of [*p*-$MeOC_6H_4N_2$][BF_4] in acetone was carried out in the presence of excess $NaBF_4$ *and* 1 equiv of TlOAc, chloride was consumed as TlCl, and now only the dicationic complex **1** was observed, as expected. (4) The iodo complex $CpRu(PPh_3)_2I$ is more prone to halide substitution than is the chloride, and when reacted with a stoichiometric amount of [*p*-$MeOC_6H_4N_2$]-[BF_4] in acetone in the presence of $NaBF_4$, this yielded only the dicationic complex **1**.

Molecular Structure of 1. The most interesting feature of the X-ray structure of **1** is the near-linear Ru−N−N−C skeleton, with the N−N−C angle opened up from the 120° sp^2 angle, commonly exhibited by singly bent N_2Ar ligands, to 158.9°. To our knowledge, this is the largest N−N−C angle to be observed in an aryldiazenido complex. There are other examples of aryldiazenido complexes with an opened N−N−C angle, including $RuCl_3$(*p*-$N_2C_6H_4Me$)$(PPh_3)_2$[12,13] (137°) and [$RhCl(PPh_3)_2$(*p*-$N_2C_6H_4OMe$)][BF_4]·$2CH_2Cl_2$[42] (141.3°). A compilation of the metrical details of aryldiazenido complexes reported to about 1987 has been published.[43] Although not an aryldiazenido complex, and not strictly comparable for this and other reasons, a ruthenium diazaborane derivative is known with an essentially linear Ru−N−N−B skeleton and a N−N−B angle of 173°.[44] The Ru−N bond length in **1** is somewhat longer (1.853 Å) than that in $RuCl_3$(*p*-$N_2C_6H_4Me$)$(PPh_3)_2$ (1.784 Å), as expected if the structure is tending more to the formal valence representation Ru−N≡N−C. Also, the N−N distance (1.145 Å) is correspondingly shorter than that observed in the majority of aryldiazenido complexes (near 1.25 Å),[43] though is probably not significantly different from the values in [$RhCl(PPh_3)_2$(*p*-$N_2C_6H_4OMe$)][BF_4]·$2CH_2Cl_2$ (1.157 Å) and $RuCl_3$(*p*-$N_2C_6H_4Me$)$(PPh_3)_2$. Free [*p*-$MeOC_6H_4N_2$][BF_4] has ν(NN) near 2250 cm^{-1} in the IR spectrum, and from the near-linear structure and short N−N bond length of the N_2Ar skeleton in **1** one would anticipate that ν(NN) for **1** might occur abnormally high compared with most other singly bent aryldiazenido complexes, which usually have values in the 1600−1800 cm^{-1} range.[43] And so it does. The value for **1** (2074 cm^{-1}) is far above this range and well exceeds the value in $RuCl_3$(*p*-$N_2C_6H_4Me$)$(PPh_3)_2$ (1882 cm^{-1})[14] and [$RhCl(PPh_3)_2$(*p*-$N_2C_6H_4OMe$)][BF_4]·$2CH_2Cl_2$[42] (1982 cm^{-1}). Similarly, ν(NN) for the PMe_3 complex [$Cp^*Ru(PMe_3)_2(N_2C_6H_4OMe)$][$BF_4$]$_2$ (**4**) (1780 cm^{-1}) is much greater than for the isoelectronic rhenium monocationic complex [$Cp^*Re(PMe_3)_2(N_2C_6H_4OMe)$]-[$BF_4$] ($\nu$(NN) = ca. 1620 cm^{-1}) of similar composition and structure.[4] Many years ago, a class of ruthenium aryldiazenido complexes with 2,2′-bipyridine ligands was reported having the formula [$RuCl(bipy)_2(N_2Ar)$]-[PF_6]$_2$. These complexes were remarkable at the time for displaying ν(NN) values in the region of 2080 cm^{-1}, and it was suggested that the complexes might best be considered to have the aryldiazenido ligand bound as arenediazonium $(N_2Ar)^+$.[45,46] Unfortunately, to our knowledge, no X-ray structure of these complexes has been reported. (The complex [$RuCl(NH_3)_4(N_2Ph)$]Cl_2 has been reported to have ν(NN) as high as 2121 cm^{-1}.)[47] From the result for **1**, it seems almost certain that these complexes would also display an enlarged N−N−C angle, in keeping with the high value of ν(NN). In a simplistic but nevertheless useful valence bond representation shown below it can be argued that the lowering of ν(NN), lengthening of the N−N bond length, and decrease in the N−N−C angle in the coordinated singly bent aryldiazenide ligand from the values in free

(42) Einstein, F. W. B.; Jones, R. H.; Zhang, Y.; Sutton, D. *Inorg. Chem.* **1988**, *27*, 1004.
(43) Johnson, B. F. G.; Haymore, B. L.; Dilworth, J. R. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 2, p 99.
(44) Schramm, K. D.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *16*, 3287.
(45) Bowden, W. L.; Little, W. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 5084.
(46) Bowden, W. L.; Little, W. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 4340.
(47) Yuen, C. M. C.; Lau, T. C. *Abstr. 31st Int. Conf. Coord. Chem.* **1996**, abstract 9P62.

$[N_2Ar]^+$ derives substantially from the back-bonding contribution.



It is important to note that these bipyridine and ammine complexes, and **1**−**3**, are all *dicationic* complexes. Thus, in addition to the effects of the ancillary ligands, back-bonding will be much reduced in these complexes because of the formal 2+ charge on the cation, leading to higher than usual ν(NN) values and correspondingly enlarged N−N−C angles. Indeed, there have been relatively few other examples of dicationic terminal aryldiazenido complexes synthesized.[43] A further factor that could cause the enlarged N−N−C angle in **1** is the possibility of steric crowding of the singly bent N_2Ar ligand by the sterically demanding PPh_3 groups.

The values of ν(NN) for **1**−**4** show the expected decrease as the phosphine or Cp′ becomes more basic, and values are reduced further in the monocationic complexes **5** and **6** compared to the corresponding dications. The values of $\delta(^{15}N_\alpha)$ for **1**−**4** range from −64.52 to −24.32 and may be compared with the value of −46.8 reported for $RuCl_3(PPh_3)_2(N_2Ph)$.[43] These values also become less negative systematically with increase in the basicity of the phosphine or Cp′, and **5** and **6** show still less negative values and the same trend. The values of ν(NN) and $\delta(^{15}N)$ for **7** support a structure in which the N_2Ar ligands are terminal, singly bent, rather than bridging.

The solid-state structure of the dicationic complexes **1**−**4**, exemplified by the crystal structure of **1**·0.93$CHCl_3$, follows a now familiar pattern for piano-stool geometry Cp or Cp* aryldiazenido complexes with *singly bent* aryldiazenido ligands.[2,4,8,9] The aryldiazenido ligand is oriented *unsymmetrically* with respect to a plane bisecting the P−Ru−P angle, so that the plane of the aryl ring is approximately perpendicular to that plane, and the N_2Ar ligand is bent toward one of the phosphine ligands. The rhenium complex, $[Cp^*Re(PMe_3)_2(p\text{-}N_2C_6H_4OMe)]^+$, of this type exhibits the expected two ^{31}P NMR resonances at low temperature, but these collapse to a single resonance on increasing the temperature, attributed to the singly bent aryldiazenido ligand undergoing inversion or rotation at the carbon-bound nitrogen atom N_β, resulting in exchange of the inequivalent PMe_3 ligands.[4] In the present case, the ^{31}P NMR spectra of **1**, **2**, and **4** indicated that the phosphine ligands remain equivalent down to at least −80 °C. Thus, for the two complexes where a direct comparison is possible, it seems that the ruthenium dicationic complex $[Cp^*Ru(PMe_3)_2(p\text{-}N_2C_6H_4OMe)]^{2+}$ (in **4**) has a lower barrier to rearrangement of the N_2Ar group compared with the corresponding monocationic rhenium complex $[Cp^*Re(PMe_3)_2(p\text{-}N_2C_6H_4OMe)]^+$. The origin of this difference seems likely to be related to the corresponding differences in the electronic structure and geometry of the $M-N_2Ar$ group in these two situations, which are manifested in the higher ν(NN) values and increased NNC angle exhibited by the dicationic ruthenium complexes in this study.

Conclusion

An entry into the field of cyclopentadienyl ruthenium aryldiazenido complexes has been made through the reactions of $Cp'Ru(PR_3)_2Cl$ with arenediazonium salts. Under the appropriate conditions, substitution of Cl occurs to give new dicationic complexes such as **1**−**4**, or PPh_3 substitution can occur to give monocationic complexes such as **5** and **6**. IR and NMR spectra show these complexes have a terminally coordinated singly bent N_2Ar ligand. The X-ray structure of **1** demonstrates that the N_2Ar ligand is bound to ruthenium in a near-linear geometry and has the largest known N−N−C(aryl) angle for an aryldiazenido complex to date. This geometry is compatible with the exceptionally high value of ν(NN) observed in the IR spectrum.

Acknowledgment. Financial support from NSERC Canada in the form of a research grant to D.S. is gratefully acknowledged. We thank Scott Lovell, University of Washington, Seattle, for collecting the X-ray data.

Supporting Information Available: A listing of crystal and data collection details and final parameters for **1**·0.93$CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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