Ruthenium Tris(pyrazolyl)borate Complexes. 1. Synthesis and Reactivity of $Ru(HB(pz)_3)(COD)X$ (X = Cl, Br) and $Ru(HB(pz)_3)(L_2)Cl$ (L = Nitrogen and Phosphorus Donor Ligands)

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The synthesis and catalytic reactivity of a variety of new ruthenium complexes of the tris(pyrazolyl)borate ligand ($HB(pz)_3$) are reported in this paper. From the parent complex $Ru(HB(pz)_3)(COD)X$ (X = Cl, Br) the cationic derivatives $[Ru(HB(pz)_3)(COD)L]^+$ (L = H_2O, CH_3CN, pyridine, dmso) have been obtained by treatment with 1 equiv of $AgCF_3SO_3$ in CH_2Cl_2 solutions of L. Displacement of COD from these latter complexes has been accomplished in boiling dmf solutions of ligands L_2 = $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2NMe_2$ (pn), and $Me_2NCH_2CH_2NMe_2$ (tmeda) as well as L = pyridine and 3-methylpyridine to give $Ru(HB(pz)_3)(L_2)Cl$ and $Ru(HB(pz)_3)(L)_2Cl$, respectively, each in high yield. From some of these complexes, in turn, the chloride ion has been abstracted with either $AgCF_3SO_3$, $TlCF_3SO_3$, or $NaBPh_4$ in CH_3CN as the solvent. In this way we obtained $[Ru(HB(pz)_3)(dppm)(CH_3CN)]CF_3SO_3$, $[Ru(HB(pz)_3)(pn)(CH_3CN)]BPh_4$, and $[Ru(HB(pz)_3)(tmeda)(CH_3CN)]BPh_4$. Selected X-ray structures are included. Some of the complexes synthesized are efficient catalysts for the formation of selectively C−O-coupled products from the reaction of phenylacetylene with either benzoic acid or allyl alcohols.

Introduction

The tris(pyrazolyl)borate anion ($HB(pz)_3$) as a ligand in transition metal complexes has been introduced by Trofimenko.[2] For the organoruthenium chemistry, $HB(pz)_3$ has been known as a ligand for more than 20 years.[3] Although several new ruthenium complexes containing $HB(pz)_3$ have been reported in recent years,[4] not many coligands have been used other than CO, phosphines, arenes, and C_5H_5. Very recently, also ruthenium dihydrogen complexes with $HB(pz)_3$ have become known.[5] After all, the few systematic studies hitherto done on the complexes of the $[Ru(HB(pz)_3)]^+$ fragment do not allow definite conclusions to be drawn as to the factors that determine their formation, stability, and reactivity patterns.

$HB(pz)_3$ is often compared with C_5H_5 and C_5Me_5 due to the same charge and number of electrons donated (six-electron donors). Notwithstanding, differences in size and electronic properties are obvious. Thus the cone angle of $HB(pz)_3$ close to 180° is well above the 100 and 146° calculated for C_5H_5 and C_5Me_5, respectively.[6] The steric bulk of the $HB(pz)_3$ ligand appears to disfavor higher coordination numbers of the metal center. In addition there are differences in symmetry. The $[Ru(HB(pz)_3)]^+$ fragment is strongly hybridized biased to bind preferentially three additional ligands for an octahedral six-coordinate structure to be obtained and maintained. The diffuse electron clouds of the C_5H_5 and C_5Me_5 ligands, on the other hand, are rather ineffective in promoting strongly directional frontier orbitals. As a consequence, processes involving coordination number increase, e.g., oxidative additions and associative nucleophilic substitutions at the metal center, are less likely for the $HB(pz)_3$ system. There are, to the best of our knowledge, no reports of genuine seven-coordinate ruthenium $HB(pz)_3$ compounds. Thus, polyhydride complexes of high hydrogen content favor dihydrogen rather than dihydride coordination in order to maintain octahedral geometry as in $Ru(HB(pz)_3)(\eta^2\text{-}H_2)_2H$[5a,b] and $Ru(HB(pz)_3)(PCy_3)(\eta^2\text{-}H_2)H$.[5c]

In attempt to elaborate the chemistry of ruthenium $HB(pz)_3$ complexes along more general lines we describe here new synthetic routes to a range of new mononuclear complexes of the type $[Ru(HB(pz)_3)(COD)L]^+$ (L = H_2O, CH_3CN, pyridine (py), dmso), $Ru(HB(pz)_3)(L_2)Cl$ (L = $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2NMe_2$ (pn), $Me_2NCH_2CH_2NMe_2$ (tmeda)), and $Ru(HB(pz)_3)(L)_2Cl$ (L

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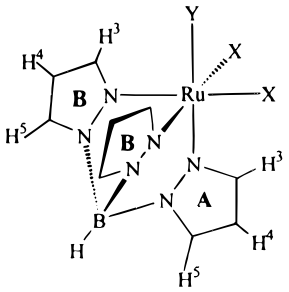
= pyridine (py), 3-methylpyridine (3-Mepy)). In addition we report on the catalytic reactivity of some of these complexes.

Experimental Section

General Information. Manipulation were performed under an inert atmosphere of purified nitrogen or argon by using Schlenk techniques and/or a glovebox. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[7] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $[Ru(COD)(NH_2NMe_2)_3H]BPh_4$ (COD = 1,5-cyclooctadiene), potassium tris(pyrazolyl)borate ($K[HB(pz)_3]$), and $Ph_2PCH_2CH_2NMe_2$ (pn) were prepared according to the literature.[8−10] ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, and were referenced to $SiMe_4$ and to H_3PO_4 (85%). Diffuse reflectance FT-IR spectra were recorded on a Mattson RS 2 spectrometer. Microanalysis were done by Microanalytical Laboratories, University of Vienna.

Synthesis. $Ru(HB(pz)_3)(COD)Cl$ (1a). A suspension of $[Ru(COD)(NH_2NMe_2)_3H]BPh_4$ (6.00 g, 8.45 mmol) and $K[HB(pz)_3]$ (2.13 g, 8.45 mmol) in acetone (70 mL) was refluxed for 2 h. To this solution was added CCl_4 (15 mL), and the mixture was refluxed for additional 30 min. The solution was then allowed to cool to −20 °C resulting in a precipitate of **1a** and KCl. The mixture was redissolved in CH_2Cl_2, and KCl was removed by filtration. Removal of the solvent gave analytically pure **1a**. Yield: 2.90 g (75%). Anal. Calcd for $C_{17}H_{22}BClN_6Ru$: C, 44.61; H, 4.84; N, 18.36. Found: C, 44.57; H, 4.91; N, 18.50. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.13 (d, 1H, J = 2.1 Hz, H_A^3), 7.79 (d, 1H, J = 2.4 Hz, H_A^5), 7.65 (d, 2H, J = 2.4 Hz, H_B^5), 7.56 (d, 2H, J = 2.1 Hz, H_B^3), 6.32 (dd, 1H, J = 2.1 Hz, J = 2.4 Hz, H_A^4), 6.21 (dd, 2H, J = 2.1 Hz, J = 2.4 Hz, H_B^4), 5.01 (m, 2H, olefinic H of COD), 3.96 (m, 2H, olefinic H of COD), 3.02 (m, 2H), 2.70 (m, 2H), 2.43 (m, 4H). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 145.7 (C_A^3), 142.4 (C_B^3), 138.2 (C_A^5), 135.5 (C_B^5), 106.8 (C_A^4, C_B^4), 95.2 (olefinic C of COD), 87.7 (olefinic C of COD), 31.1 (aliphatic C of COD), 30.4 (aliphatic C of COD).



$Ru(HB(pz)_3)(COD)Br$ (1b). This complex has been prepared analogously to **1a** except that $CHBr_3$ was used instead of CCl_4. Yield: 79%. Anal. Calcd for $C_{17}H_{22}BBrN_6Ru$: C, 40.66; H, 4.42; N, 16.73. Found: C, 40.57; H, 4.43; N, 16.80. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.17 (d, 1H, J = 2.6 Hz, H_A^3), 7.78 (d, 1H, J = 2.6 Hz, H_A^5), 7.66 (d, 2H, J = 2.6 Hz, H_B^5), 7.59 (d, 2H, J = 2.2 Hz, H_B^3), 6.32 (dd, 1H, J = 2.6 Hz, J = 2.6 Hz, H_A^4), 6.21 (m, 2H, J = 2.6 Hz, J = 2.2 Hz, H_B^4), 5.01 (m, 2H, olefinic H of COD), 3.96 (m, 2H, olefinic H of COD), 3.02 (m, 2H), 2.70 (m, 2H), 2.43 (m, 4H). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 145.5 (C_A^3), 143.4 (C_B^3), 138.2 (C_A^5), 135.7 (C_B^5), 106.8 (C_A^4), 106.7 (C_B^4), 92.5 (olefinic C of COD), 86.5 (olefinic C of COD), 31.8 (aliphatic C of COD), 30.8 (aliphatic C of COD).

$[Ru(HB(pz)_3)(COD)(H_2O)]CF_3SO_3$ (2a). To a solution of **1a** (153 mg, 0.334 mmol) in CH_2Cl_2 or acetone (3 mL) was added $AgCF_3SO_3$ (85.9 mg, 0.334 mmol). After the mixture was stirred for 1 h, the resulting precipitate of AgCl was removed by filtration. On addition of diethyl ether/pentane, a white precipitate was formed which was collected on a glass frit, washed with pentane, and dried under vacuum. Yield: 189 mg (96%). Anal. Calcd for $C_{18}H_{24}BF_3N_6O_4RuS$: C, 36.68; H, 4.10; N, 14.26. Found: C, 36.90; H, 4.24; N, 14.36. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.89 (d, 1H, J = 2.0 Hz, H_A^3), 7.80 (d, 1H, J = 2.4 Hz, H_A^5), 7.73 (d, 4H, J = 2.0 Hz, H_B^3, H_B^5), 6.30 (dd.1H, J = 2.0 Hz, J = 2.4 Hz, H_A^4), 6.26 (m, 2H, J = 2.0 Hz, J = 2.0 Hz, H_B^4), 5.15 (m, 2H, olefinic H of COD), 4.77 (s, 2H, H_2O), 4.31 (m, 2H, olefinic H of COD), 2.74−2.57 (m, 6H, aliphatic H of COD), 2.29 (m, 2H, aliphatic H of COD). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 146.6 (C_A^3, 142.9 (C_B^3), 139.3 (C_A^5), 136.9 (C_B^5), 107.6 (C_A^4), 107.4 (C_B^4), 97.9 (olefinic C of COD), 94.2 (olefinic C of COD), 31.3 (aliphatic C of COD), 28.4 (aliphatic C of COD). IR (diffuse reflectance, cm^{-1}): 3349 (s, ν_{OH}), 3235 (s, ν_{OH}), 3143(s, ν_{OH}), 2499 (m, ν_{B-H}), 1654 (s, δ_{H-O-H}).

$[Ru(HB(pz)_3)(COD)(CH_3CN)]CF_3SO_3$ (2b). This complex was synthesized analogously to **2a** with acetonitrile as the solvent. Yield: 97%. Anal. Calcd for $C_{20}H_{25}BF_3N_7O_3RuS$: C, 39.23; H, 4.11; N, 16.01. Found: C, 39.37; H, 4.05; N, 15.89. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.13 (d, 1H, J = 2.0 Hz, H_A^3), 7.81 (d, 1H, J = 2.4 Hz, H_A^5), 7.68 (d, 4H, J = 2.4 Hz, H_B^3, H_B^5), 6.39 (dd, 1H, J = 2.0 Hz, J = 2.4 Hz, H_A^4), 6.28 (dd, 2H, J = 2.4 Hz, J = 2.4 Hz, H_B^4), 5.05 (m, 2H, olefinic H of COD), 4.23 (m, 2H, olefinic H of COD), 2.87−2.65 (m, 4H, aliphatic H of COD), 2.54 (s, 3H, CH_3CN), 2.47−2.25 (m, 4H, aliphatic H on COD). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 145.9 (C_A^3), 143.0 (C_B^3), 138.9 (C_A^5), 136.6 (C_B^5), 129.9 (CH_3CN), 107.7 (C_B^4), 107.6 (C_A^4), 96.4 (olefinic C of COD), 93.2 (olefinic C of COD), 30.4 (aliphatic C of COD), 29.4 (aliphatic C of COD), 5.4 (CH_3CN). IR (diffuse reflectance, cm^{-1}): 2480 (m, ν_{B-H}), 2284 (w, ν_{CN}).

$[Ru(HB(pz)_3)(COD)(py)]CF_3SO_3$ (2c). A solution of **1a** (190 mg, 0.415 mmol) in CH_2Cl_2 (5 mL) was treated with $AgCF_3SO_3$ (106 mg, 0.415 mmol) and pyridine (ca 10 equiv). After the mixture was stirred for 8 h, AgCl formed was removed by filtration. Addition of diethyl ether resulted in the formation of a yellow precipitate which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 248.3 mg (92%). Anal. Calcd for $C_{23}H_{27}BF_3N_7O_3RuS$: C, 42.47; H, 4.18; N, 15.07. Found: C, 42.35; H, 4.08; N, 15.22. ^1H NMR (δ, nitromethane-d_3, 20 °C): 8.69 (d, 2H, J = 6.1 Hz, H_{py}^2, H_{py}^6), 8.27 (d, 1H, J = 2.5 Hz, H_A^3), 7.99 (d, 2H, J = 2.5 Hz, H_B^3), 7.88 (d, 1H, J = 2.5 Hz, H_A^5), 7.88 (m, 1H, H_{py}^4), 7.70 (d, 2H, J = 2.5 Hz, H_B^5), 7.39 (m, 2H, H_{py}^3, H_{py}^5), 6.40 (dd, 2H, J = 2.5 Hz, J = 2.5 Hz, H_B^4), 6.35 (dd, 1H, J = 2.5 Hz, J = 2.5 Hz, H_A^4), 4.99 (m, 2H, olefinic H of COD), 4.62 (m, 2H, olefinic H of COD), 2.91 (m, 2H, aliphatic H of COD), 2.69 (m, 2H, aliphatic H of COD), 2.57 (m, 2H, aliphatic H of COD), 2.36 (m, 2H, aliphatic H of COD). $^{13}C\{^1H\}$ NMR (δ, nitromethane-d_3, 20 °C): 154.8 (C_{py}^2, C_{py}^6), 147.8 (C_A^3), 143.8 (C_B^3), 140.4(C_B^5), 140.2 (C_A^5), 139.6 (C_{py}^4), 127.0 (C_{py}^3, C_{py}^5), 108.9 (C_B^4), 107.9 (C_A^4), 96.7 (olefinic C of COD), 96.6 (olefinic C of COD), 31.1 (aliphatic C of COD), 29.6 (aliphatic C of COD).

$[Ru(HB(pz)_3)(COD)(dmso)]CF_3SO_3$ (2d). A solution of **1a** (190 mg, 0.415 mmol) in CH_2Cl_2 (5 mL) was treated with $AgCF_3SO_3$ (106 mg, 0.415 mmol) and dmso (ca. 10 equiv). After the mixture was stirred for 8 h, AgCl formed was removed by filtration. Addition of diethyl ether resulted in the formation of a yellow precipitate, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 171 mg (97%). Anal. Calcd for $C_{20}H_{28}BF_3N_6O_4RuS_2$: C, 36.99; H, 4.35; N, 12.94. Found: C, 37.06; H, 4.38; N, 13.04. ^1H NMR (δ, nitromethane-d_3, 20 °C): 8.07 (d, 1H, J = 2.5 Hz, H_A^3), 8.04 (d, 2H, J = 2.3 Hz, H_B^3), 7.95 (d, 1H, J = 2.5 Hz, H_A^5), 7.79 (d, 2H, J = 2.3 Hz,

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H_B^5), 6.47 (dd, 2H, J = 2.3 Hz, J = 2.3 Hz, H_B^4), 6.36 (dd, 1H, J = 2.5 Hz, J = 2.5 Hz, H_A^4), 5.00 (m, 2H, olefinic H of COD), 4.41 (m, 2H, olefinic H of COD), 2.80−2.47 (m, 8H, aliphatic H of COD), 2.25 (s, 6H, $(CH_3)_2SO$). $^{13}C\{^1H\}$ NMR (δ, nitromethane-d_3, 20 °C): 148.2 (C_A^3), 143.8 (C_B^3), 140.4 (C_A^5), 138.4 (C_B^5), 108.4 (C_B^4), 108.2 (C_A^4), 100.4 (olefinic C of COD), 95.1 (olefinic C of COD), 38.4 ($(CH_3)_2SO$), 31.4 (aliphatic C of COD), 28.9 (aliphatic C of COD).

Ru(HB(pz)$_3$)(dppm)Cl (3a). A solution of **1a** (300 mg, 0.655 mmol) and dppm (265 mg, 0.689 mmol) in dmf (25 mL) was heated at reflux for 2 h, whereupon a yellow precipitate was formed. The solid was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 415 mg (84%). Anal. Calcd for $C_{34}H_{32}BClN_6P_2Ru$: C, 55.64; H, 4.39; N, 11.45. Found: C, 55.70; H, 4.45; N, 11.20.

[Ru(HB(pz)$_3$)(dppm)(CH$_3$CN)]CF$_3$SO$_3$ (3b). A suspension of **3a** (200 mg, 0.272 mmol) in acetontrile (15 mL) was treated with $AgCF_3SO_3$ (70 mg, 0.272 mmol) and heated at reflux for 14 h. After removal of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 and insoluble materials were filtered off. Addition of diethyl ether/pentane afforded **3b** in analytically pure form. Yield: 135 mg (75%). Anal. Calcd for $C_{37}H_{35}BF_3N_7O_3P_2RuS$: C, 50.01; H, 3.97; N, 11.03. Found: C, 49.88; H, 4.06; N, 11.23. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.90 (d, 2H, J = 2.4 Hz, H_B^5), 7.73 (d, 1H, J = 2.0 Hz, H_A^5), 7.59 (d, 2H, J = 1.9 Hz, H_B^3), 7.55 (m, 10 H, Ph), 7.28 (m, 2H, Ph), 7.13 (m, 4H, Ph), 7.00 (m, 4H, Ph), 6.40 (d, 1H, J = 1.9 Hz, H_A^3), 6.36 (dd, 2H, J = 2.4, Hz, J = 1.9 Hz, H_B^4), 5.62 (dd, 1H, J = 2.0 Hz, J = 1.9 Hz, H_A^4), 5.54 (m, 1H, PCH_2P), 4.96 (m, 1H, PCH_2P), 1.86 (s, 3H, CH_3CN). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 147.6 (C_A^3), 144.5 (C_B^3), 138.2 (C_A^5), 137.0 (C_B^5), 133.1−129.0 (m, Ph), 126.2 (CH_3CN), 106.2 (C_B^4), 104.0 (C_A^4), 50.1 (t, J_{PC} = 23.0 Hz, PCH$_2$P), 4.2 (CH_3CN). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 7.0. IR (diffuse reflectance, cm^{-1}): 2490 (m, ν_{B-H}), 2284 (w, ν_{CN}).

Ru(HB(pz)$_3$)(pn)Cl (4a). A solution of **1a** (270 mg, 0.590 mmol) and $Ph_2PCH_2CH_2NMe_2$ (153 mg, 0.595 mmol) in dmf (25 mL) was heated at reflux for 2 h. After removal of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 and diethyl ether was added. The orange precipitate formed was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 329 mg (92%). Anal. Calcd for $C_{25}H_{30}BClN_7PRu$: C, 49.48; H, 4.98; N, 16.16. Found: C, 49.70; H, 5.05; N, 16.27. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.22 (d, 1H, J = 2.4 Hz, H^3), 7.80 (d, 1H, J = 2.4 Hz, H^5), 7.62 (m, 3H, H^5, Ph), 7.59 (d, 1H, J = 2.8 Hz, H^5), 7.33−7.22 (m, 4H, Ph), 7.07 (m, 2H, Ph), 7.01 (d, 1H, J = 1.6 Hz, H^3), 6.80 (br, 2H, Ph), 6.36 (m, 1H, H^4), 6.31 (d, 1H, J = 1.6 Hz, H^3), 5.90 (m, 1H, H^4), 5.65 (m, 1H, H^4), 3.10−2.75 (m, 4H, PCH_2CH_2N), 2.93 (s, 3H, CH_3), 2.16 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 147.3 (C^3), 147.1 (C^3), 143.2 (C^3), 137.0−128.2 (C^5, Ph), 106.4 (C^4), 106.1 (C^4), 105.3 (C^4), 64.7 (d, J_{PC} = 6.2 Hz, NCH_2-CH$_2$P), 54.9 (CH_3), 53.5 (CH_3), 29.0 (d, J_{PC} = 23.4 Hz, NCH$_2$CH_2P). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 66.1.

[Ru(HB(pz)$_3$)(pn)(CH$_3$CN)]BPh$_4$ (4b). A suspension of **4a** (150 mg, 0.247 mmol) and $NaBPh_4$ (87 mg, 0.254 mmol) in CH_2Cl_2 (3 mL) containing acetonitrile (1 mL) was stirred at room temperature for 12 h. After removal of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 and NaCl was filtered off. On addition of diethyl ether a white precipitate was formed which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 136 mg (59%). Anal. Calcd for $C_{51}H_{53}B_2N_8PRu$: C, 65.75; H, 5.73; N, 12.03. Found: C, 65.82; H, 5.68; N, 12.14. ^1H NMR (δ, acetone-d_6, 20 °C): 8.26 (d, 1H, J = 2.2 Hz, H^3), 8.02 (d, 1H, J = 2.2 Hz, H^5), 7.93 (d, 1H, J = 2.4 Hz, H^5), 7.87 (d, 1H, J = 2.4 Hz, H^5), 7.54 (m, 2H, Ph), 7.48−7.31 (m, 11H, H^3, Ph, Ph(BPh$_4$)), 7.17 (m, 2H, Ph), 6.92 (m, 12H, Ph, BPh$_4$), 6.80 (m, 4H, BPh$_4$), 6.68 (d, 1H, J = 2.2 Hz, H^3), 6.49 (m, 1H, H^4), 6.08 (m, 1H, H^4), 5.91 (m, 1H, H^4), 3.39 (m, 2H, CH_2), 3.10−2.87 (m, 2H, CH_2), 3.04 (s, 3H, CH_3), 2.34 (s, 3H, CH_3CN), 2.22 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 165.6 (q, J_{BC} = 49.3 Hz, BPh_4 (C_1)), 147.9 (C^3), 145.8 (C^3), 143.6 (C^3), 138.6−129.9 (C^5, Ph), 137.7 (q, J_{BC} = 1.5 Hz, BPh_4 (C_3, C_5)) 127.4 (CH_3CN), 126.7 (J_{BC} = 2.5 Hz, BPh_4 (C_2, C_6)), 122.9 (BPh_4 (C_4)), 108.1 (C^4), 107.8 (C^4), 107.1 (C^4), 65.4 (d, J_{PC} = 6.1 Hz, NCH_2CH$_2$P), 55.1 (CH_3), 53.8 (CH_3), 28.9 (J_{PC} = 25.9 Hz, NCH$_2$CH_2P), 4.9 (CH_3-CN). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 69.4. IR (diffuse reflectance, cm^{-1}): 2501 (m, ν_{B-H}), 2272 (m, ν_{CN}).

Ru(HB(pz)$_3$)(tmeda)Cl (5a). To a solution of **1a** (300 mg, 0.655 mmol) in dmf (30 mL) was added tmeda (ca. 5 equiv) and the mixture was heated at 130 °C for 2 h. On removal of the solvent *in vacuo*, the resulting solid was dissolved in CH_2-Cl_2 and insoluble materials were removed by filtration. On addition of diethyl ether a yellow precipitate was formed which was collected on a glass frit, washed with diethyl ether, and dried in vacuum. Yield: 259.3 mg (85%). Anal. Calcd for $C_{15}H_{26}BClN_8Ru$: C, 38.68; H, 5.63; N, 24.06. Found: C, 38.74; H, 5.54; N, 23.94. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.98 (d, 2H, J = 2.0 Hz, H_B^3), 7.81 (d, 1H, J = 2.4 Hz, H_A^5), 7.78 (d, 1H, J = 2.0 Hz, H_A^3), 7.69 (d, 2H, J = 2.4 Hz, H_B^5), 6.23 (dd, 1H, J = 2.0 Hz, J = 2.4 Hz, H_A^4), 6.19 (dd, 2H, J = 2.0 Hz, J = 2.4 Hz, H_B^4), 3.06 (s, 6H, N(CH_3)$_2$), 3.07−2.87 (m, 4H, NCH_2CH_2N), 2.38 (s, 6H, N(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 147.0 (C_A^3), 146.1 (C_B^3), 137.5 (C_A^5), 136.1 (C_B^5), 106.4 (C_B^4), 105.9 (C_A^4), 63.4 (NCH_2CH_2N), 54.2 (N(CH_3)$_2$), 53.1 (N(CH_3)$_2$).

[Ru(HB(pz)$_3$)(tmeda)(CH$_3$CN)]BPh$_4$ (5b). This complex was synthesized analogously to **4b** with **5a** as starting material. Yield: 93%. Anal. Calcd for $C_{41}H_{49}B_2N_9Ru$: C, 62.29; H, 6.25; N, 15.94. Found: C, 62.35; H, 6.22; N, 16.10. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.30 (d, 1H, J = 2.3 Hz, H_A^3), 8.02 (d, 1H, J = 2.3 Hz, H_A^5), 7.93 (d, 2H, J = 2.3 Hz, H_B^3), 7.88 (d, 2H, J = 2.3 Hz, H_B^5), 7.39 (m, 8H, BPh_4), 6.94 (m, 8H, BPh_4), 6.82 (m, 4H, BPh_4), 6.42 (dd, 1H, J = 2.3 Hz, J = 2.3 Hz, H_A^4), 6.31 (dd, 2H, J = 2.3 Hz, J = 2.3 Hz, H_B^4), 3.02 (m, 4H, NCH_2CH_2N), 3.00 (s, 6H, N(CH_3)$_2$), 2.50 (s, 3H, CH_3CN), 2.33 (s, 6H, N(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 165.5 (q, J_{BC} = 49.6 Hz, BPh_4 (C_1)), 147.5 (C_A^3), 145.5 (C_B^3), 138.3 (C_A^5), 137.9 (C_B^5), 137.6 (q, J_{BC} = 1.5 Hz, BPh_4 (C_3, C_5)), 128.4 (CH_3CN), 126.7 (J_{BC} = 2.8 Hz, BPh_4 (C_2, C_6)), 122.9 (BPh_4 (C_4)), 108.0 (C_B^4), 107.5 (C_A^4), 63.9 (NCH_2CH_2N), 54.8 (N(CH_3)$_2$), 53.2 (N(CH_3)$_2$), 5.0 (CH_3CN). IR (diffuse reflectance, cm^{-1}): 2481 (m, ν_{B-H}), 2253 (m, ν_{CN}).

Ru(HB(pz)$_3$)(py)$_2$Cl (6). To a solution of **1a** (300 mg, 0.655 mmol) in dmf (30 mL) was added pyridine (10 equiv), and the mixture was heated at reflux for 1 h. The resulting solid was dissolved in CH_2Cl_2, and on addition of petroleum ether a yellow precipitate was formed and collected on a glas frit, washed with petroleum ether, and dried in vacuum. Yield: 306 mg (95%). Anal. Calcd for $C_{19}H_{20}BClN_8Ru$: C, 44.94; H, 3.97; N, 22.07. Found: C, 45.04; H, 4.09; N, 22.20. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.66 (m, 4H, H_{py}^2, H_{py}^6), 7.87 (d, 1H, J = 2.4 Hz, H_A^5), 7.75 (d, 2H, J = 2.4 Hz, H_B^5), 7.57 (m, 2H, H_{py}^4), 7.19 (d, 2H, J = 2.0 Hz, H_B^3), 7.11 (m, 4H, H_{py}^3, H_{py}^5), 6.74 (d, 1H, J = 2.0 Hz, H_A^3), 6.23 (dd, 1H, J = 2.0 Hz, J = 2.4 Hz, H_A^4), 6.13 (dd, 2H, J = 2.0 Hz, J = 2.4 Hz, H_B^4). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 156.5 (C_{py}^2, C_{py}^6), 144.6 (C_A^3), 144.3 (C_B^3), 136.7 (C_A^5), 135.9 (C_B^5), 134.5 (C_{py}^4), 124.1 (C_{py}^3, C_{py}^5), 107.4 (C_A^4), 106.6 (C_B^4).

Ru(HB(pz)$_3$)(3-Mepy)$_2$Cl (7). This complex was synthesized analogously to **6** with 3-Mepy and **1a** as the starting materials. Yield: 87%. Anal. Calcd for $C_{21}H_{24}BClN_8Ru$: C, 47.08; H, 4.51; N, 20.91. Found: C, 46.84; H, 4.45; N, 21.09. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.62 (s, 2H, H_{py}^2), 8.29 (d, 2H, J = 5.6 Hz, H_{py}^6), 7.89 (d, 1H, J = 2.2 Hz, H_A^5), 7.76 (d, 2H, J = 2.2 Hz, H_B^5), 7.36 (d, 2H, J = 7.4 Hz, H_{py}^4), 7.22 (d, 2H, J = 1.8 Hz, H_B^3), 6.96 (dd, 1H, J = 5.6 Hz, J = 7.4 Hz, H_{py}^5), 6.75 (d, 1H, J = 1.8 Hz, H_A^3), 6.22 (dd, 1H, J = 2.2 Hz, J = 1.8 Hz, H_A^4), 6.13 (dd, 2H, J = 2.2 Hz, J = 1.8 Hz, H_B^4), 2.24 (s, 6H, Me). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 156.6 (C_{py}^2), 153.8 (C_{py}^6), 144.6 (C_A^3), 144.4 (C_B^3), 136.7 (C_A^5), 135.9 (C_B^5), 135.4 (C_{py}^4), 133.5 (C_{py}^3), 123.4 (C_{py}^5), 107.3 (C_A^4), 106.6 (C_B^4), 19.2 (Me).

Table 1. Crystallographic Data

	1b	**2a**	**4b**·CH_2Cl_2	**5b**
formula	$C_{17}H_{22}BBrN_6Ru$	$C_{18}H_{24}BF_3N_6O_4RuS$	$C_{52}H_{55}B_2Cl_2N_8PRu$	$C_{41}H_{49}B_2N_9Ru$
fw	502.20	589.37	1016.60	790.58
cryst size, mm	0.18 × 0.28 × 0.32	0.07 × 0.22 × 0.29	0.08 × 0.60 × 0.70	0.14 × 0.19 × 0.30
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	8.313(2)	23.849(4)	11.071(2)	11.691(2)
b, Å	8.747(2)	14.836(3)	13.609(3)	13.400(2)
c, Å	13.474(4)	13.101(3)	17.903(4)	13.533(2)
α, deg	82.91(1)		83.91(1)	104.80(1)
β, deg	78.47(1)	93.20(1)	82.28(1)	92.55(1)
γ, deg	75.92(1)		71.97 (1)	96.12(1)
V, Å^3	928.2(4)	4628(2)	2535.7(9)	2032.4(6)
Z	2	8	2	2
ρ_{calc}, g cm^{-3}	1.797	1.692	1.331	1.292
T, K	298	297	293	296
μ, mm^{-1} (Mo Kα)	3.011	0.830	5.767	0.426
abs corr	empirical	none	analytical	none
transm factors min/max	0.89/1.10		0.80/0.96	
θ_{max}, deg	25	22	25	22
index ranges	$0 \le h \le 9$, $-9 \le k \le 10$, $-15 \le l \le 16$	$-25 \le h \le 25$, $0 \le k \le 15$, $0 \le l \le 13$	$0 \le h \le 13$, $-14 \le k \le 16$, $-20 \le l \le 21$	$-12 \le h \le 12$, $-14 \le k \le 13$, $0 \le l \le 14$
no. of rflns measd	3272	6270	8914	4962
no. of unique rflns	3272	5700	8914	4962
no. of rflns $F > 4\sigma(F)$	3092	4329	7437	3997
no. of params	248	648	601	479
$R(F)$ ($F > 4\sigma(F)$)	0.0200	0.0425	0.0396	0.0400
$R(F)$ (all data)	0.0221	0.0678	0.0525	0.0586
w$R(F^2)$ (all data)	0.0504	0.0950	0.1039	0.0924
diff Fourier peaks min/max, e Å^{-3}	−0.36/0.36	−0.56/0.50	−0.62/0.49	−0.31/0.34

Coupling of Phenylacetylene with Benzoic Acid. To a solution of benzoic acid (248 mg, 2.034 mmol) and phenylacetylene (208 mg, 2.034 mmol) in toluene (20 mL) was added 5% catalyst, and the mixture was heated at reflux for 10 h. Removal of the solvent and chromatographical purification (silica gel, petroluem ether/CH_2Cl_2 (10:1) as eluent) yields a mixture of three isomers (**Ia**−**c**) as determined by ^{1}H NMR spectroscopy. ^{1}H NMR (δ, $CDCl_3$, 20 °C): **Ia**, 8.12 (m, 2H), 7.67−7.23 (m, 9H), 5.84 (d, 1H, J = 7.5 Hz); **Ib**, 8.12 (m, 3H), 7.67−7.23 (m, 8H), 6.58 (d, 1H, J = 12.9 Hz); **Ic**, 8.25 (m, 2H), 7.73−7.08 (m, 8H), 5.61 (d, 1H, J = 1.8 Hz), 5.18 (d, 1H, J = 1.8 Hz).

Coupling of Phenylacetylene with Allyl Alcohol. To a solution of phenylacetylene (523 mg, 5.12 mmol) and allyl alcohol (2 mL, 29.4 mmol) in toluene (20 mL), 2% of **6** was added, and the mixture was heated at reflux for 24 h. The solvent was removed under vacuum. The orange residue was purified by flash chromatography (silica gel, CH_2Cl_2 as eluent) to afford 0.589 mg (72%) of an isomeric mixture of **IIa**,**b** in a 1:1 ratio. The products were separated by chromatography (silica gel, petroleum ether/CH_2Cl_2 (10:1) as eluent). Yield: **IIa** (207 mg, 25%), **IIb** (162 mg, 20%). ^{1}H NMR (δ, $CDCl_3$, 20 °C): **IIa**, 7.66 (d, 2H, J = 7.0 Hz), 7.60−7.10 (m, 3H), 6.23 (d, 1H, J = 7.3 Hz), 6.98 (m, 1H), 5.38 (m, 3H), 4.47 (d, 2H, J = 5.4 Hz); **IIb**, 9.70 (d, 1H, J = 1.8 Hz), 7.33 (m, 5H), 5.75 (m, 1H), 5.05 (m, 2H), 3.63 (m, 1H), 2.87 (m, 1H), 2.50 (m, 1H).

X-ray Structure Determination for 1b, 2a, 4b, and 5b. Crystal data and experimental details are given in Table 1. X-ray data were collected on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo Kα (λ = 0.1069 Å) radiation and the $\theta-2\theta$ scan technique. Three representative reference reflections were measured every 120 min and used to correct for crystal decay and system instability. Corrections for Lorentz and polarization effects, and, where necessary, for absorption were applied. The structures were solved by direct methods.[11] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized positions.[12] The structures were refined against F^2.

(11) Sheldrick, G. M. SHELXS86: Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1986.

(12) Sheldrick, G. M. SHELXL93: Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.

Results and Discussion

Synthesis of Ru(HB(pz)$_3$)(COD)X (X = Cl, Br) Complexes. Complexes **1a**,**b** have been prepared by following a slightly modified literature procedure.[13,14] Treatment of [Ru(COD)(NH_2NMe_2)$_3$H]BPh_4 with 1 equiv of K[HB(pz)$_3$] in boiling acetone for 2 h leads to the hydride complex Ru(HB(pz)$_3$)(COD)H. On addition of CCl_4 and $CHBr_3$ in about 10-fold excess, the hydride intermediate is transformed into complexes **1a**,**b**, respectively. It is worth noting that **1a** has been originally prepared by utilizing the PF_6^- salt of [Ru(COD) (NH_2-NMe_2)$_3$H]$^+$ which is obtained in about 50% isolated yield, whereas the BPh_4^- salt can be isolated in much higher yield, *viz* 90% yield.[13] **1a**,**b** are thermally robust orange solids which are stable to air both in the solid state and in solution. The NMR spectroscopic properties of **1a** are in agreement with the literature.[14] The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1b** are almost identical to that of **1a** and are not further discussed here. The analytical data of **1a**,**b** support the formulation given. In addition, the structure of **1b** has been confirmed by X-ray crystallography as depicted in Figure 1. Important bond distances are reported in the caption. The geometry at ruthenium is approximately octahedral. The bite angle of the HB(pz)$_3$ ligand produces an average N−Ru−N angle of 84.8° only slightly distorted from 90°. The Ru atom is bound to COD with an average Ru−C distance of 2.213(2) Å. The Ru−Br distance is 2.585(1) Å.

Synthesis of [Ru(HB(pz)$_3$)(COD)L]$^+$ (L = H_2O, CH_3CN, dmso, py) Complexes. In an attempt to prepare the coordinatively unsaturated complex [Ru-

(13) (a) Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1986**, *5*, 2199. (b) Albers, M. O.; Francesca, S.; Crosby, A.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2014.

(14) Jalon, F. A.; Otero, A.; Rodriguez, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1629.

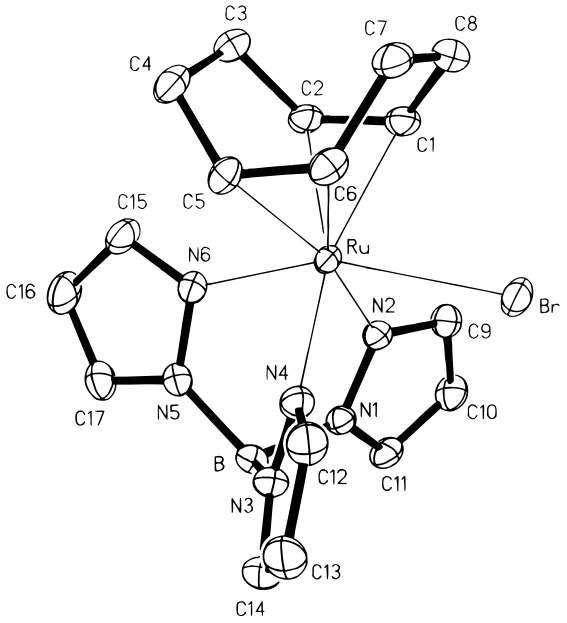
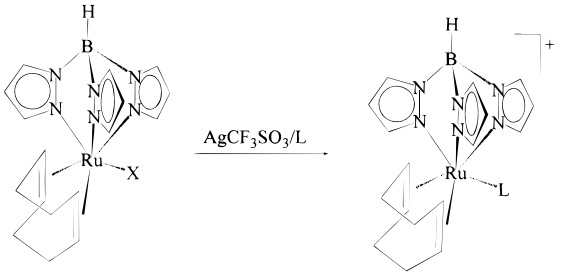


Figure 1. Structural view of Ru(HB(pz)$_3$)(COD)Br (**1b**). Selected bond lengths (Å): Ru−N(2) 2.117(2), Ru−N(4) 2.114(2), Ru−N(6) 2.164(2), Ru−C(1) 2.225(2), Ru−C(2) 2.211(2), Ru−C(5) 2.215(2), Ru−C(6) 2.209(2), Ru−Br 2.5849(6).

Scheme 1



X = Cl **1a**
X = Br **1b**

L = H_2O (**2a**), CH_3CN (**2b**), dmso (**2c**), pyridine (**2d**)

(HB(pz)$_3$)(COD)]CF_3SO_3 similar to the C_5Me_5 analogue [Ru(η^5-C_5Me_5)(nbd)]BF_4 (nbd = norbornadiene),[15] **1a** or **1b** has been treated with $AgCF_3SO_3$ (1 equiv) in CH_2Cl_2 for 2 h at room temperature. But instead of the expected product we obtained [Ru(HB(pz)$_3$)(COD)(H_2O)]CF_3SO_3 (**2a**) in 96% yield as a pale yellow air stable complex (Scheme 1). Characterization was by ^{1}H and ^{13}C{^{1}H} NMR and IR spectroscopy and elemental analysis. A structural view of **2a**, as determined by X-ray crystallography, is depicted in Figure 2. Important bond distances are reported in the caption.

The water molecule found in **2a** presumably stems from the CH_2Cl_2 solution, despite rigorous drying. In neat CD_3CN the water molecule in **2a** is quantitatively replaced within several hours forming **2b**. The proton resonance of the coordinated water molecule is observed as a sharp singlet at 4.77 ppm (2H) (*cf.* the corresponding resonance for [Ru(η^5-C_5Me_5)(nbd)(H_2O)]BF_4 is observed at 4.71 ppm[15]). IR spectroscopy shows broad ν_{OH} and δ_{H-O-H} absoroptions in the range 3349−3143 and at 1654 cm^{-1}, respectively.

The crystal structure of **2a** exhibits two crystallographically independent complexes in the asymmetric unit resulting in eight complexes per unit cell. The two independent complexes are linked via hydrogen bonds between the water ligands and the $CF_3SO_3^-$ anions to form a neutral dimeric species as shown in Figure 2. The hydrogen bond O···O distances vary from 2.714 to 2.802 Å with a mean value of 2.750 Å. The Ru(1)−O(1) and Ru(2)−O(2) distances are 2.140(4) and 2.161(4) Å, respectively. This distance is comparable to that observed in [Ru(η^5-C_5Me_5)$(CO)_2(H_2O)$]$^+$ (2.173(3) Å)[16] and [Ru(HC(pz)$_3$)$(H_2O)_3$]$^{2+}$ (HC(pz)$_3$ = tris(pyrazolyl)methane) (2.131(1) Å)[17] but is somewhat shorter than in the related complex [Ru(η^5-C_5Me_5)(nbd)(H_2O)]BF_4 (2.238(5) Å)[15] attesting to the higher lability of the water molecule in the latter.

The cationic complexes **2b**−**d** have been prepared by reacting **1a** with $AgCF_3SO_3$ (1 equiv) in either neat CH_3CN (**2b**) or in CH_2Cl_2 containing about 10 equiv of dmso (**2c**) or pyridine (**2d**) (Scheme 1). All of these reactions are essentially quantitative demonstrating the high affinity of the [Ru(HB(pz)$_3$)(COD)]$^+$ moiety toward hard donor ligands. **2b**−**d** have been characterized by a combination of elemental analysis and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. In addition, **2b** has been characterized by IR spectroscopy. The data bear no remarkable features and will not be considered further. Noteworthily, the related complexes Ru(η^5-C_5H_5)(COD)X (X = Cl, Br) do not afford stable cationic solvent complexes in contrast to Ru(η^5-C_5Me_5)(COD)X.[15,18] Thus, in this particular ligand environment, HB(pz)$_3$ appears to be related more closely to C_5Me_5 than to C_5H_5.

Attempted Conversion of 1 with Allyl Bromide. In an attempt to synthesize Ru(IV) η^3-allyl complexes of the type Ru(HB(pz)$_3$)(η^3-allyl)Br_2 a procedure well established for the synthesis of similar C_5R_5 (R = H, Me) complexes has been followed.[19−21] However, treatment of **1a** or **1b** with an excess of allyl bromide in even boiling ethanol for 24 h was unsuccessful and the starting material was nearly quantitatively recovered. The poor reactivity of **1** contrasts with the mild conditions sufficient for preparing similar compounds via oxidative addition of allyl halides to Ru(η^5-C_5R_5)(COD)X (R = H, Me; X = Cl, Br).[19−21] This is an impressive example of a coligand effect. COD, a weak ligand in the neighborhood of C_5R_5, becomes substitutionally inert in the presence of HB(pz)$_3$. Furthermore, the product of the oxidative addition will be a seven-coordinate species which is unfavorable in the case of HB(pz)$_3$ complexes, as noted in the Introduction. The steric bulk of this ligand discourages high coordination numbers, and in addition to the steric effect, the donor orbitals on the HB(pz)$_3$ ligand, localized on the N atoms, are effective in hybridizing the metal fragment into an octahedral array. Thus, we believe that predominantly steric and electronic effects, rather then lack of substitutive reactivity or any inherent instability of the Ru(IV) products, prevent oxidative additions to occur.

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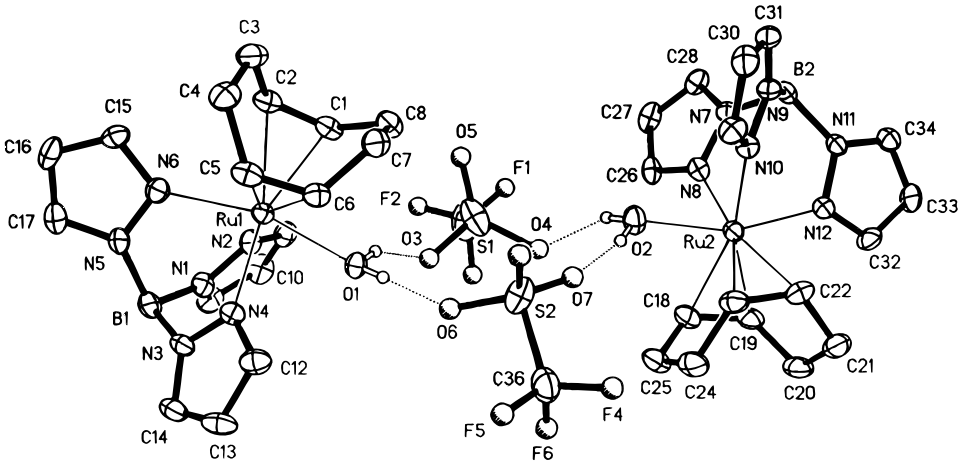
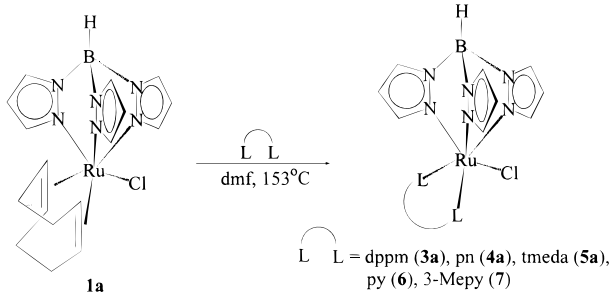


Figure 2. Structural view of $[Ru(HB(pz)_3)(COD)(H_2O)]CF_3SO_3$ (**2a**). Selected bond lengths (Å): Ru(1)−N(2) 2.108(5), Ru(1)−N(4) 2.103(5), Ru(1)−N(6) 2.123(5), Ru(1)−C(1) 2.231(6), Ru(1)−C(2) 2.238(7), Ru(1)−C(5) 2.243(6), Ru(1)−C(6) 2.219(6), Ru(1)−O(1) 2.140(4), Ru(2)−N(8) 2.130(5), Ru(2)−N(10) 2.099(5), Ru(2)−N(12) 2.120(5), Ru(2)−C(18) 2.230(7), Ru(2)−C(19) 2.253(6), Ru(2)−C(22) 2.236(7), Ru(2)−C(23) 2.223(7), Ru(2)−O(2) 2.161(4), O(1)···O(3) 2.714(6), O(1)···O(6) 2.726(7), O(2)···O(4) 2.757(10), O(2)···O(7) 2.802(7).

Scheme 2



Synthesis of $Ru(HB(pz)_3)(L_2)Cl$ (L = dppm, pn, tmeda, py, 3-Mepy) Complexes. While in $Ru(\eta^5\text{-}C_5R_5)(COD)X$ (R = H, Me; X = Cl, Br) the substitution of COD and/or halo ligands is rapid and facile under mild reaction conditions,[13,20] displacement of cyclooctadiene in **1a**,**b** is rather sluggish. Nevertheless, in boiling dmf **1a** reacts readily with the chelating ligands dppm, pn, and tmeda as well as with py and 3-Mepy to give, on workup, $Ru(HB(pz)_3)(dppm)Cl$ (**3a**), $Ru(HB(pz)_3)(pn)Cl$ (**4a**), $Ru(HB(pz)_3)(tmeda)Cl$ (**5a**), $Ru(HB(pz)_3)(py)_2Cl$ (**6**), and $Ru(HB(pz)_3)(3\text{-Mepy})_2Cl$ (**7**), respectively, each in high yields (Scheme 2). Characterization of these complexes was again by elemental analysis and by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, except for **3a** because of its poor solubility in all common solvents. **3a** is easily converted to the more soluble cationic complex $[Ru(HB(pz)_3)(dppm)(CH_3CN)]CF_3SO_3$ (**3b**) on treatment with either $AgCF_3SO_3$, $TlCF_3SO_3$, or $NaBPh_4$ in CH_3CN as the solvent. Similarly, **4a** and **5a** react readily with $NaBPh_4$ in the presence of CH_3CN to give the air-stable cationic complexes $[Ru(HB(pz)_3)(pn)(CH_3CN)]BPh_4$ (**4b**) and $[Ru(HB(pz)_3)(tmeda)(CH_3CN)]BPh_4$ (**5b**) in high yields. The NMR spectra of **3b** and **4**−**7** exhibit the resonances of $HB(pz)_3$ and the other coligands in the expected ranges. The IR spectra of **3b**, **4b**, and **5b** exhibit the ν_{CN} absorption at 2284, 2272, and 2253 cm^{-1}, respectively, very similar to that of free CH_3CN (2283 and 2246 cm^{-1}). This result suggests that back-bonding is not a prominent feature of the metal−nitrile interaction in these complexes.

Structural views of **4b** and **5b**, as determined by X-ray crystallography, are shown in Figures 3 and 4 with

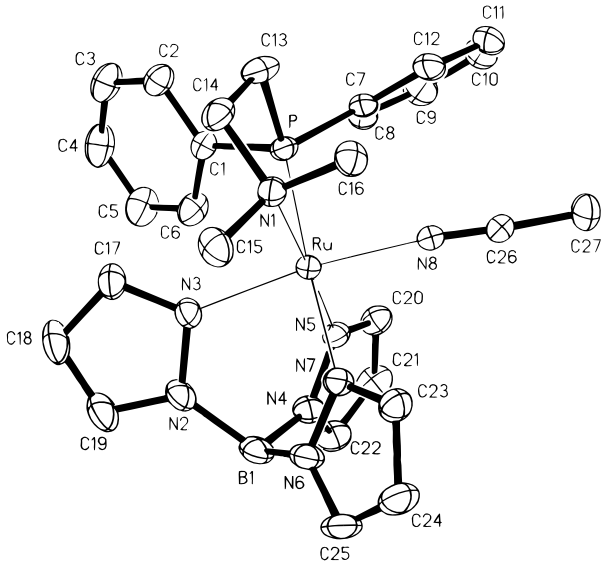


Figure 3. Structural view of $[Ru(HB(pz)_3)(pn)(CH_3CN)]BPh_4{\cdot}CH_2Cl_2$ (**4b**·CH_2Cl_2) (BPh_4^- and CH_2Cl_2 omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−N(1) 2.206(2), Ru−N(3) 2.093(2), Ru−N(5) 2.076(2), Ru−N(7) 2.137(2), Ru−N(8) 2.013(2), Ru−P 2.2695(9), N(8)−C(26) 1.128(4), Ru−N(8)−C(26) 170.3(2), N(8)−C(26)−C(27) 176.5(3).

important bond distances and angles reported in the captions. The coordination geometry of complexes **4b** and **5b** is approximately octahedral with all angles at ruthenium being between 84 and 95° and 172 and 178°. The three $Ru-N(HB(pz)_3)$ bond lengths show only minor variations and are within the range of other ruthenium $HB(pz)_3$ complexes.[4] The coordinated acetonitrile in **4b** and **5b** is almost linear being 176.5 and 174.5°, respectively. The $Ru-N(CH_3CN)$ bond distances are 2.013(2) and 1.992(4) Å. The Ru−N(pn) and Ru−P(pn) bond distances are 2.206(2) and 2.270(1) Å, respectively. The Ru−N(tmeda) bond distances are 2.192(4) and 2.180(4) Å (*cf.* in $Ru(\eta^5\text{-}C_5Me_5)(tmeda)Cl$ the Ru−N distances are significantly longer being 2.262(4) and 2.295(4) Å).[22] There are no structural features in complexes **4b** and **5b** indicating unusual deviations or distortions.

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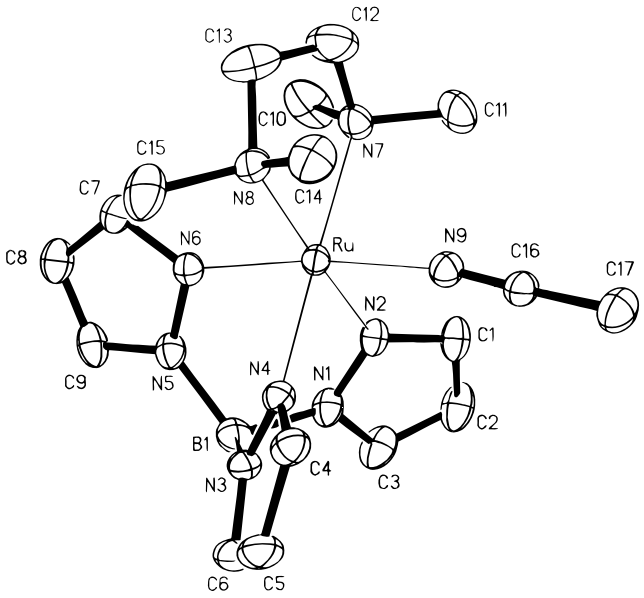
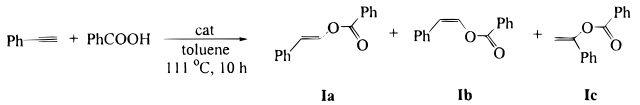


Figure 4. Structural view of $[Ru(HB(pz)_3)(tmeda)(CH_3CN)]BPh_4$ (**5b**) (BPh_4^- omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−N(2) 2.081(4), Ru−N(4) 2.070(4), Ru−N(6) 2.114(4), Ru−N(7) 2.192(4), Ru−N(8) 2.180(4), Ru−N(9) 1.992(4), N(9)−C(16) 1.130(5), Ru−N(9)−C(16) 170.4(4), N(9)−C(16)−C(17) 174.5(5).

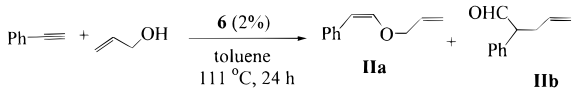
Table 2. Catalytic Coupling of Phenylacetylene with Benzoic Acid



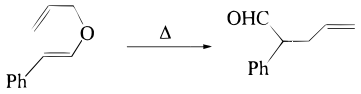
entry	catalyst	yield (%)	**Ia**:**Ib**:**Ic**
1	$Ru(HBpz_3)(COD)Cl$ (**1a**)	96	1.63:1:0
2	$Ru(HBpz_3)(py)_2Cl$ (**6**)	98	1.22:1:0
3	$Ru(HBpz_3)(tmeda)Cl$ (**5**)	99	1.38:1:0
4	$[Ru(HBpz_3)(COD)(CH_3CN)]CF_3SO_3$ (**2b**)	46	1.56:1:0.52
5	$[Ru(HBpz_3)(COD)(H_2O)]CF_3SO_3$ (**2a**)	0	

Catalytic Reactions of Ruthenium Tris(pyrazolyl)borate Complexes. Coupling of Phenylacetylene with Benzoic Acid. Heating a mixture of benzoic acid and phenylacetylene in toluene with catalyst (5%) yields, on workup, vinyl esters up to essentially quantitative yields depending on the catalyst used (Table 2). The neutral complexes $Ru(HB(pz)_3)(COD)Cl$ (**1a**), $Ru(HB(pz)_3)(tmeda)Cl$ (**5**), and $Ru(HB(pz)_3)(py)_2Cl$ (**6**) and the cationic complexes $[Ru(HB(pz)_3)(COD)(H_2O)]CF_3SO_3$ (**2a**) and $[Ru(HB(pz)_3)(COD)(CH_3CN)]CF_3SO_3$ (**2b**) have been tested as catalysts. The neutral complexes lead to selective addition of benzoic acid to the terminal carbon atom of the phenylacetylene giving exclusively isomers **Ia,b**, while the cationic catalyst **2b** gives, in addition to isomers **Ia**,**b**, isomer **Ic**. The overall yield, however, is significantly lower. With **2a** as catalyst, no coupling reaction took place. Catalytic couplings of acetylenes and carboxylic acids have also been reported by others.[23,24]

Scheme 3



Coupling of Phenylacetylene with Allyl Alcohol. Heating a mixture of phenylacetylene and excess allyl alcohol with 2% catalyst in toluene at reflux yields, on workup, a mixture of the *cis* allyl vinyl ether **IIa** and the aldehyde **IIb**, as shown by ^1H NMR spectroscopy (Scheme 3). Under these reaction conditions, **IIb** appears to be formed from the thermally unstable *trans* isomer via a Claisen rearrangement. Both products were obtained in a 1:1 ratio. This reaction does not occur in the absence of the ruthenium catalyst. It is interesting to note that ruthenium complexes of types $Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Cl$,[25a] $Ru(\eta^5\text{-}C_5H_5)(COD)Cl$,[25b,c] and $Ru(\eta^5\text{-}C_5Me_5)(COD)Cl$[26] catalyze the coupling of acetylenes and allyl alcohols to give C−C-coupling reactions in all cases. This appears to be the first time that C−O-coupling between acetylenes and allyl alcohols catalyzed by ruthenium complexes have been reported. The mechanism of this reaction can only be speculated upon at present. It seems likely, however, that a vinylidene complex is a reactive intermediate in this catalytic process. Such intermediates have been postulated in the related C−C-coupling reaction of phenylacetylene and allyl alcohol.[25a] Further work is in progress and will be reported in a forthcoming paper.



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Supporting Information Available: Listings of complete atomic coordinates and *U* values, anisotropic temperature factors, complete bond lengths and angles, and least-squares planes for complexes **1b**, **2a**, **4b**, and **5b** (53 pages). Ordering information is given on any current masthead page.

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