

Polyazolyl Chelate Chemistry. 8.¹ Organometallic Dihydridobis(pyrazol-1-yl)borato Complexes of Ruthenium(II)

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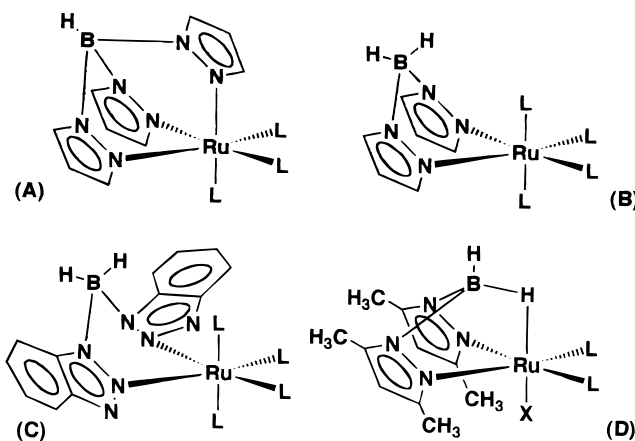
Received May 12, 1998

Treatment of either $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ or $[\text{RuH}(\text{CO})(\text{NCMe})_2(\text{PPh}_3)_2]\text{BF}_4$ with $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ (pz = pyrazol-1-yl) provides $[\text{RuH}(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (**1**), which is also the product of the reaction of $[\text{Ru}(\text{SnPh}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ or $[\text{Ru}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ with $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ in the presence of ethanol. The complexes $[\text{RuHCl}(\text{CS})(\text{BTD})(\text{PPh}_3)_2]$ (BTD = 2,1,3-benzothiadiazole) and $[\text{RuHCl}(\text{CS})(\text{BSD})(\text{PPh}_3)_2]$ (BSD = 2,1,3-benzoselenadiazole) are obtained from the reactions of $[\text{RuHCl}(\text{CS})(\text{PPh}_3)_3]$ and BTD or BSD . $[\text{RuH}(\text{CS})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (**2**) is obtained in a manner similar to that for **1** from either $[\text{RuHCl}(\text{CS})(\text{PPh}_3)_3]$ or $[\text{RuHCl}(\text{CS})(\text{BTD})(\text{PPh}_3)_2]$ and $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$. The σ -aryl complexes $[\text{RuPh}(\text{CA})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (A = O (**3**), S (**4**)) result from the reactions of $[\text{RuPhCl}(\text{CA})(\text{PPh}_3)_2]$ with $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$. The σ -vinyl complexes $[\text{Ru}(\text{CR}^1=\text{CHR}^2)\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ ($\text{R}^1 = \text{R}^2 = \text{H}$ (**5**), $\text{C}_6\text{H}_4\text{Me-4}$ (**6**); $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{C}_6\text{H}_4\text{Me-4}$ (**7**), CPh_2OH) react with $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ to provide $[\text{Ru}(\text{CR}^1=\text{CHR}^2)(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ ($\text{R}^1 = \text{R}^2 = \text{C}_6\text{H}_4\text{Me-4}$ (**8**); $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{C}_6\text{H}_4\text{Me-4}$ (**9**), H (**10**), CPh_2OH (**11**)). Treating $[\text{Ru}(\text{CPh}=\text{CHPh})\text{Cl}(\text{CS})(\text{PPh}_3)_2]$ with $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ provides $[\text{Ru}(\text{CPh}=\text{CHPh})(\text{CS})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (**13**), which reacts rapidly with carbon monoxide to give the thioacyl complex $[\text{Ru}(\eta^2\text{-SCCPh}=\text{CHPh})(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (**14**) by loss of phosphine. The alkynyl derivatives $[\text{Ru}(\text{C}\equiv\text{CR})(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$ (**15**), CPh_2OH (**16**)) were prepared from the reaction of $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (**9**) with excess $\text{HC}\equiv\text{CR}$ or alternatively from the reaction of **1** with $[\text{Hg}(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})_2]$. The crystal structure of **10** is also reported.

Introduction

Within group 8, the chemistry of the hydridotris-(pyrazol-1-yl)borate ligand (**A**, Chart 1) has recently begun to attract attention^{1,3–10} after many years of

Chart 1



intense study in other triads.^{11,12} Prior to this work, however, ruthenium complexes of the related dihydridobis(pyrazol-1-yl)borate ligand (**B**, Chart 1) had yet to be described, although two very closely related ligands

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have been investigated briefly: we have reported the synthesis of dihydridobis(benzotriazolyl)borate complexes (**C**, Chart 1),¹³ and Singleton has reported the syntheses of dihydridobis(dimethylpyrazolyl)borate complexes $[\text{RuX}(\text{L}_2)\{\text{H}_2\text{B}(\text{pzMe}_2)_2\}]$ ($\text{X} = \text{H, Me; L}_2 = \text{cod, dppb}$),¹⁴ which feature agostic coordination of one B–H bond to ruthenium (**D**, Chart 1). Very recently, the first example of a ruthenium complex of the $\text{H}_2\text{B}(\text{pz})_2$ ligand was reported: the reaction of $[\text{Ru}(\text{CH}_3\text{I}(\text{CO})_2(\text{PMe}_3)_2)]$ with $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ results in migratory insertion of the methyl and carbonyl ligands to provide the acyl complex $[\text{Ru}\{\text{C}(\text{=O})\text{CH}_3\}(\text{CO})(\text{PMe}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$.¹⁰ We were intrigued by Singleton's compounds in that a potentially hemilabile agostic B–H...Ru interaction can in principle mask a vacant coordination site. We report herein the synthesis of novel examples of ruthenium complexes of the $\text{H}_2\text{B}(\text{pz})_2$ ligand, including derivatives bearing hydride, alkenyl, alkynyl, carbonyl, thiocarbonyl, and thioacyl coligands and the structural characterization of one such complex, viz. $[\text{Ru}(\text{CH}=\text{CH}_2)(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$.

Experimental Section

The complexes $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$,¹⁵ $[\text{RuH}(\text{CO})(\text{NCMe})_2(\text{PPh}_3)_2]\text{BF}_4$,¹⁶ $[\text{RuHCl}(\text{CS})(\text{PPh}_3)_3]$,¹⁷ $[\text{RuPhCl}(\text{CO})(\text{PPh}_3)_2]$,¹⁸ $[\text{RuPhCl}(\text{CS})(\text{PPh}_3)_2]$,¹⁹ $[\text{Ru}(\text{CH}=\text{CH}_2\text{Cl}(\text{CO})(\text{PPh}_3)_2)]$,²⁰ and $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ ²¹ have been described elsewhere. The complexes $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ (**7**), $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$, and $[\text{Ru}\{\text{C}(\text{C}_6\text{H}_4\text{Me-4})=\text{CHC}_6\text{H}_4\text{Me-4}\}\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ (**6**) were prepared in a manner analogous to that for the previously reported BSD (2,1,3-benzoselenadiazole) derivatives.^{22,23} The species $[\text{Ru}(\text{CPh}=\text{CHPh})\text{Cl}(\text{CS})(\text{PPh}_3)_2]$ was obtained by reaction of $[\text{RuHCl}(\text{CS})(\text{PPh}_3)_3]$ or $[\text{Ru}(\text{O}_2\text{CH})\text{Cl}(\text{CS})(\text{PPh}_3)_2]$ with diphenylacetylene.²³ Infrared, NMR, and FAB-MS data were obtained using Matteson Research Series IR, JEOL JNM-EX270, and Autospec Q instruments, respectively. Characteristic phosphine-associated infrared data are not reported. "tv" indicates a virtual triplet ^{13}C NMR signal indicating a trans disposition of phosphine ligands. On occasion, as indicated by "n.r.", the multiplicity of the $^1\text{H}(\text{pz})$ and $^{13}\text{C}[\text{C}^{2-6}(\text{PC}_6\text{H}_5)]$ resonances was apparent, though not resolved. Typically, ^1H NMR signals for the BTD and BSD ligands were obscured by phosphine resonances. Microanalytical data were obtained from the Imperial College and University of North London Microanalytical services. Crystal solvates were confirmed by ^1H NMR

integration for dichloromethane; however, this was not always possible for chloroform solvates due to overlap with phosphine resonances.

Preparation of $[\text{RuHCl}(\text{CS})(\text{BSD})(\text{PPh}_3)_2]$. $[\text{RuHCl}(\text{CS})(\text{PPh}_3)_3]$ (0.31 g, 0.32 mmol) was dissolved in tetrahydrofuran (30 mL) and 2,1,3-benzoselenadiazole (BSD: 0.12 g, 0.66 mmol) added. The mixture was heated to 60 °C for 1 h, cooled, and diluted with ethanol (30 mL). The solvent volume was then reduced (rotary evaporator), providing olive green crystals. These were filtered and washed with ethanol (20 mL) and hexane (20 mL) and dried in vacuo. Yield: 0.27 g (95%). IR (Nujol): 2052, 2027 $[\nu(\text{RuH})]$, 1716, 1585, 1570, 1266 $[\nu(\text{CS})]$ cm^{-1} . NMR (CDCl_3 , 25 °C): ^1H , δ –10.46 [t, 1 H, RuH, $J(\text{HP}) = 19.3$ Hz], 6.87–7.68 [m, 34 H, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4$] ppm; $^{31}\text{P}\{^1\text{H}\}$ 43.6 ppm. FAB-MS: m/z (%) 836 (2) $[\text{M} - \text{C}_4\text{H}_4]^+$, 705 (2) $[\text{M} - \text{H} - \text{BSD}]^+$, 669 (2) $[\text{M} - \text{H} - \text{Cl} - \text{BSD}]^+$. Anal. Found: C, 58.0; H, 4.0; N, 2.9. Calcd for $\text{C}_{43}\text{H}_{35}\text{ClN}_2\text{P}_2\text{RuSSe}$: C, 58.1; H, 4.0; N, 3.2.

Preparation of $[\text{RuHCl}(\text{CS})(\text{BTD})(\text{PPh}_3)_2]$. $[\text{RuHCl}(\text{CS})(\text{PPh}_3)_3]$ (0.41 g, 0.41 mmol) and 2,1,3-benzothiadiazole (BTD: 0.12 g, 0.88 mmol) were dissolved in dichloromethane (30 mL). The mixture was stirred for 1 h and then diluted with ethanol (10 mL). The solvent volume was reduced to ca. 10 mL, resulting in precipitation of the product. The yellow product was filtered off, washed with ethanol (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.34 g (98%). IR (Nujol): 2042 $[\nu(\text{RuH})]$, 1719, 1525, 1280, 1266 $[\nu(\text{CS})]$, 898, 881, 832 cm^{-1} . NMR (CDCl_3 , 25 °C): ^1H , δ –10.20 [t, 1 H, RuH, $J(\text{HP}) = 19.2$ Hz], 7.0–7.8 [m, 34 H, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4$] ppm; $^{31}\text{P}\{^1\text{H}\}$, 43.8 ppm. FAB-MS: m/z (%) 705 (6) $[\text{M} - \text{BTD}]^+$, 670 (15) $[\text{M} - \text{Cl} - \text{BTD}]^+$, 407 (5) $[\text{M} - \text{Cl} - \text{BTD} - \text{PPh}_3]^+$, 363 (2) $[\text{RuPPh}_3]^+$. Anal. (recrystallized from chloroform and ethanol as chloroform hemisolvate) Found: C, 57.8; H, 2.9; N, 3.0. Calcd for $\text{C}_{43}\text{H}_{35}\text{ClN}_2\text{P}_2\text{RuS}_2 \cdot 0.5\text{CHCl}_3$: C, 57.9; H, 4.0; N, 3.1.

Preparation of $[\text{RuH}(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (1**).** (a) $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (0.30 g, 0.32 mmol) and $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ (0.06 g, 0.32 mmol) were dissolved in a mixture of dichloromethane (15 mL) and ethanol (1 mL). The mixture was stirred for 2 h and then all solvent removed under reduced pressure. The crude product was dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth. Ethanol (10 mL) was added to the filtrate and the solvent volume reduced (rotary evaporator) until precipitation was complete. The crude product was extracted with dichloromethane and the combined extracts filtered through diatomaceous earth. The colorless product was obtained by dilution with ethanol and slow concentration under reduced pressure, washed with ethanol (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.20 g (79%).

(b) $[\text{RuH}(\text{NCMe})_2(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ (0.20 g, 0.24 mmol) and $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ (0.05 g, 0.27 mmol) were dissolved in a mixture of dichloromethane (15 mL) and ethanol (1 mL). The mixture was stirred for 2 h and then all solvent removed under reduced pressure. The crude product was isolated and purified as described in (a) above. Yield: 0.16 g (82%). IR (CH_2Cl_2): 2402, 2293 $[\nu(\text{BH}_2)]$, 2150 $[\nu(\text{RuH})]$, 1930 $[\nu(\text{CO})]$ cm^{-1} . IR (Nujol): 2405, 2293 $[\nu(\text{BH}_2)]$, 2179 $[\nu(\text{RuH})]$, 1933 $[\nu(\text{CO})]$, 1406, 1302, 1211, 1160, 1055, 920, 877, 830 cm^{-1} . NMR (CDCl_3 , 25 °C): ^1H , δ –11.69 [t, 1 H, RuH, $J(\text{PH}) = 21.8$], 3.1 [s(br), 2 H, BH_2], 5.29, 5.89 [t \times 2, 2 \times 1 H, $\text{H}^4(\text{pz})$, $J(\text{HH}) = 2.0$], 6.53 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH})$ n.r.], 6.84 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 1.3$], 7.13–7.33 [m, 31 H, $\text{C}_6\text{H}_5 + \text{H}^{3,5}(\text{pz})$], 7.46 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 1.32$ Hz] ppm; $^{13}\text{C}\{^1\text{H}\}$, δ 205.6 [t, CO, $J(\text{PC}) = 16.1$], 144.2, 144.1 [s \times 2, 2 \times $\text{C}^3(\text{pz})$], 135.4, 135.3 [s \times 2, 2 \times $\text{C}^5(\text{pz})$], 134.8 [t v , $\text{C}^1(\text{C}_6\text{H}_5)$, $J(\text{PC}) = 20.5$ Hz], 134.0 [t v , $\text{C}^{2,6}(\text{C}_6\text{H}_5)$, $J(\text{PC})$ n.r.], 129.2 [$\text{C}^4(\text{C}_6\text{H}_5)$], 127.8 [t v , $\text{C}^{3,5}(\text{C}_6\text{H}_5)$, $J(\text{PC})$ n.r.], 105.0, 104.8 [s \times 2, $\text{C}^4(\text{pz})$] ppm; $^{31}\text{P}\{^1\text{H}\}$, 45.1 ppm. FAB-MS: m/z (%) 801 (6) $[\text{M}]^+$, 655 (1) $[\text{M} - \text{H}_2\text{B}(\text{pz})_2]^+$, 537 (6) $[\text{M} - 2\text{H} - \text{PPh}_3]^+$, 509 (2) $[\text{M} - 2\text{H} - \text{CO} - \text{PPh}_3]^+$, 471 (1) $[\text{M} - 2\text{H} - \text{pz} - \text{PPh}_3]^+$, 441 (4) $[\text{M} - 2\text{H} - \text{pz} - \text{CO} - \text{PPh}_3]^+$, 363 (5)

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[RuPPh₃]⁺. Anal. Found: C, 63.8; H, 4.5; N, 6.9. Calcd for C₄₃H₃₉BN₄OP₂Ru: C, 64.4; H, 4.9; N, 7.0.

Reaction of [Ru(SnPh₃)Cl(CO)(PPh₃)₂] with K[H₂B(pz)₂]. [Ru(SnPh₃)Cl(CO)(PPh₃)₂] (0.28 g, 0.26 mmol) and K[H₂B(pz)₂] (0.06 g, 0.32 mmol) were dissolved in a mixture of dichloromethane (15 mL) and ethanol (1 mL). The mixture was stirred for 1 h and then all solvent removed under reduced pressure. The crude product was extracted with dichloromethane (2 × 10 mL), and the combined extracts were filtered through diatomaceous earth, diluted with ethanol, and concentrated under reduced pressure to provide colorless crystals. The product was identified as **1** by comparison of spectroscopic data with those described above. Yield: 0.15 g (72%).

Reaction of [Ru(SiMe₃)Cl(CO)(PPh₃)₂] with K[H₂B(pz)₂]. [Ru(SiMe₃)Cl(CO)(PPh₃)₂] (0.20 g, 0.26 mmol) and K[H₂B(pz)₂] (0.06 g, 0.32 mmol) were dissolved in a mixture of dichloromethane (15 mL) and ethanol (1 mL). The mixture was stirred for 1 h and then all solvent removed under reduced pressure. The crude product was isolated and purified as described in (b) above. The product was identified as **1** by comparison of spectroscopic data with those described above. Yield: 0.15 g (71%).

Preparation of [RuH(CS)(PPh₃)₂{H₂B(pz)₂}] (2). (a) [RuHCl(CS)(PPh₃)₃] (0.19 g, 0.20 mmol) and K[H₂B(pz)₂] (0.04 g, 0.22 mmol) were dissolved in a mixture of dichloromethane (15 mL) and ethanol (1 mL). The mixture was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and the solution filtered through diatomaceous earth. Ethanol (10 mL) was added and the solvent volume reduced on the rotary evaporator until precipitation was complete. The colorless product was filtered off, washed with ethanol (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.13 g (81%).

(b) [RuHCl(CS)(BTD)(PPh₃)₂] (0.20 g, 0.24 mmol) and K[H₂B(pz)₂] (0.05 g, 0.27 mmol) were dissolved in a mixture of dichloromethane (15 mL) and ethanol (1 mL). The reaction was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and the solution filtered through diatomaceous earth. Ethanol (10 mL) was added to the filtrate and the solvent volume slowly reduced on the rotary evaporator until precipitation was complete. The colorless product was filtered off, washed with ethanol (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.16 g (79%). The product can be recrystallized from cold chloroform/ethanol mixtures. IR (CH₂Cl₂): 2402, 2292 [ν(BH₂)], 1977 [ν(RuH)] cm⁻¹. IR (Nujol): 2377, 2286 [ν(BH₂)], 1952 [ν(RuH)], 1434, 1299, 1264 [ν(CS)], 1210, 1158, 1054, 922, 878, 824 cm⁻¹. NMR (CDCl₃, 25 °C): ¹H, δ -9.11 [t, 1 H, RuH, J(PH) = 21.8], 3.0 [s(br), 2 H, BH₂], 5.26 [t, 1 H, H⁴(pz), J(HH) n.r.], 5.93 [t, 1 H, H⁴(pz), J(HH) = 2.0 Hz], 6.33, 7.09 [d × 2, 1 H × 2, H^{3,5}(pz), J(HH) n.r.], 7.14–7.32 [m, 31 H, C₆H₅ + H^{3,5}(pz)], 7.50 [d, 1 H, H^{3,5}(pz), J(HH) n.r.] ppm; ³¹P{¹H}, 43.6 ppm. FAB-MS: *m/z* (%) 817 (4) [M]⁺, 707 (3) [M - CS - pz]⁺, 669 (2) [M - H₂B(pz)₂]⁺, 554 (3) [M - PPh₃]⁺, 407 (3) [M - H₂B(pz)₂ - PPh₃]⁺. Anal. Found: C, 61.4; H, 4.7; N, 6.6. Calcd for C₄₃H₃₉BN₄P₂RuS·0.25CHCl₃: C, 61.3; H, 4.4; N, 6.6.

Preparation of [Ru(C₆H₅)(CO)(PPh₃)₂{H₂B(pz)₂}] (3). [Ru(C₆H₅)Cl(CO)(PPh₃)₂] (0.31 g, 0.41 mmol) and K[H₂B(pz)₂] (0.08 g, 0.43 mmol) were dissolved in a mixture of dichloromethane (15 mL) and ethanol (1 mL). The reaction mixture was stirred for 30 min and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and the solution filtered through diatomaceous earth. Ethanol (10 mL) was added to the filtrate and the solvent volume reduced on the rotary evaporator until precipitation of the cream-colored product was complete. This was filtered off, washed with ethanol (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.28 g (79%). The product can be recrystallized from chloroform/ethanol mixtures. IR (CH₂Cl₂): 2420, 2294 [ν(BH₂)], 1937 [ν(CO)] cm⁻¹. IR (Nujol): 2421, 2357, 2301 [ν(BH)], 1935 [ν(CO)], 1567, 1433, 1301, 1225, 1163, 1054, 890, 878 cm⁻¹.

NMR (CDCl₃, 25 °C): ¹H, δ 3.2 [s(br), 2 H, BH₂], 5.79 [m, 4 H, 2 × H⁴(pz) + H^{2,4}(RuC₆H₅)], 6.5–7.0 [m, 1 H × 2, 2 × H^{3,5}(pz), obscured], 6.61 [t, 2 H, H^{3,5}(RuC₆H₅), J(HH) = 7.6], 6.87 [t, 1 H, H⁴(C₆H₅), J(HH) = 7.3], 7.15 [d, 1 H, H^{3,5}(pz), J(HH) = 2.0], 6.95–7.40 [m, 30 H, PC₆H₅], 7.70 [d, 1 H, H^{3,5}(pz), J(HH) = 2.0 Hz] ppm; ³¹P{¹H}, 28.7 ppm. FAB-MS: *m/z* (%) 877 (4) [M]⁺, 849 (1) [M - CO]⁺, 801 (2) [M - Ph]⁺, 614 (5) [M - PPh₃]⁺, 538 (26) [M - Ph - PPh₃]⁺, 509 (7) [M - CO - Ph - PPh₃]⁺, 363 (12) [RuPPh₃]⁺. Anal. Found: C, 65.3; H, 4.3; N, 5.7. Calcd for C₄₉H₄₃BN₄OP₂RuS·0.25CHCl₃: C, 65.2; H, 4.8; N, 6.2.

Preparation of [Ru(C₆H₅)(CS)(PPh₃)₂{H₂B(pz)₂}] (4). [Ru(C₆H₅)Cl(CS)(PPh₃)₃] (0.20 g, 0.26 mmol) and K[H₂B(pz)₂] (0.05 g, 0.27 mmol) were dissolved in a mixture of dichloromethane (10 mL) and ethanol (10 mL). The reaction mixture was stirred for 30 min and all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and the solution filtered through diatomaceous earth. Ethanol (10 mL) was added to the filtrate and the solvent volume slowly reduced on the rotary evaporator until precipitation was complete. The pale yellow product was filtered, washed with ethanol (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.14 g (61%). IR (Nujol): 2428, 2343 [ν(BH₂)], 1265 [ν(CS)], 1184, 1163, 1116, 1053, 922, 891, 876 cm⁻¹. NMR (CDCl₃, 25 °C): ¹H, δ 3.2 [s(br), 2 H, BH₂], 5.72, 5.86 [t × 2, 1 H × 2, H⁴(pz), J(HH) = 2.1], 6.70 [d, 1 H, H^{3,5}(pz), J(HH) = 2.0], 7.02–7.24 [m, 30 H, PC₆H₅], 6.90–7.95 [m, 5 H, RuC₆H₅], 7.34 [d, 1 H, H^{3,5}(pz), J(HH) = 1.3], 7.67 [d, 1 H, H^{3,5}(pz), J(HH) = 2.0], 7.78 [d, 1 H, H^{3,5}(pz), J(HH) = 1.7 Hz] ppm; ³¹P{¹H}, 26.3 ppm. FAB-MS: *m/z* (%) 893 (1) [M]⁺, 783 (10) [M - CS - pz]⁺, 716 (2) [M - CS - pz]⁺, 631 (6) [M - PPh₃]⁺, 554 (6) [M - Ph - PPh₃]⁺, 521 (8) [M - CS - pz - PPh₃]⁺, 414 (6) [M - CS - Ph - H₂B(pz)₂]⁺. Anal. Found: C, 65.6; H, 4.7; N, 6.2. Calcd for C₅₀H₄₃BN₄P₂RuS: C, 65.9; H, 4.9; N, 6.3.

Preparation of [Ru(CR=CHR)Cl(CO)(BTD)(CO)(PPh₃)₂] (6) (R = C₆H₄Me-4). [RuHCl(CO)(BTD)(PPh₃)₂] (0.20 g, 0.24 mmol) and di-*p*-tolylacetylene (0.10 g, 0.49 mmol) were dissolved in tetrahydrofuran (20 mL), and the mixture was heated under reflux for 20 min. Ethanol (20 mL) was added and a brown product obtained by slow concentration. This was filtered off, washed with ethanol (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.18 g (72%). IR (CH₂Cl₂): 1921 [ν(CO)] cm⁻¹. IR (Nujol): 1913 [ν(CO)], 1585, 1556, 1508, 1307, 1272, 892, 846 cm⁻¹. NMR (CDCl₃, 25 °C): ¹H, δ 2.18, 2.22 [s × 2, 3 H × 2, CH₃], 5.28 [s, 1 H, =CHR], 6.36, 6.45, 6.67, 6.75 [(AB)₂ × 2, 8 H, J(AB) = 7.92 Hz, (C₆H₄) × 2], 7.14–7.55 [m, 34 H, C₆H₅ + C₆H₄N₂S] ppm; ³¹P{¹H}, 33.1 ppm. FAB-MS *m/z* (%) 861 (1) [M - Cl - BTD]⁺, 830 (0.5) [M - Cl - CO - BTD]⁺, 689 (2) [RuCl(CO)(PPh₃)₂]⁺, 654 (9) [Ru(CO)(PPh₃)₂]⁺, 625 (3) [Ru(PPh₃)₂]⁺, 599 (4) [M - Cl - PPh₃ - BTD]⁺, 570 [M - Cl - CO - PPh₃ - BTD]⁺, 363 (6) [RuPPh₃]⁺.

Preparation of [Ru(CH=CHC₆H₄Me-4)Cl(CO)(BTD)(CO)(PPh₃)₂] (7). [RuHCl(CO)(BTD)(PPh₃)₂] (0.40 g, 0.48 mmol) was dissolved in dichloromethane (40 mL) and 4-ethynyltoluene (0.12 mL, 0.11 g, 0.95 mmol) added, causing an immediate red coloration to develop. The mixture was stirred for 10 min and then diluted with ethanol (35 mL). An orange-red product was obtained upon reduction in solvent volume to ca. 10 mL. This was filtered off, washed with ethanol (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.39 g (85%). The complex was only partially characterized, being a simple analogue of the previously reported complex [Ru-(CH=CHC₆H₄Me-4)Cl(CO)(BSD)(CO)(PPh₃)₂]. IR (CH₂Cl₂): 1928 [ν(CO)] cm⁻¹. IR (Nujol): 1915 [ν(CO)], 1573, 1546, 1527, 1506, 1313, 1265, 980, 924, 874, 845, 827 cm⁻¹. NMR (CDCl₃, 25 °C): ¹H, δ 2.26 [s, 3 H, CH₃], 5.74 [d, 1 H, =CHR, J(HH) = 16.5], 6.79, 6.94, [(AB)₂, 4 H, J(AB) = 7.5 Hz, C₆H₄], 7.05–7.46 [m, 32 H, C₆H₅ + H_{5,6}(C₆H₄N₂S)], 7.89 [d(br), 2 H, H^{4,7}(C₆H₄N₂S)], 8.61 [dt, 1 H, RuCH, J(HH) = 16.5, J(PH) =

3.0 Hz] ppm; $^{31}\text{P}\{^1\text{H}\}$, 26.8 ppm. Anal. Found: C, 66.0; H, 4.8; N, 3.0. Calcd for $\text{C}_{52}\text{H}_{43}\text{ClN}_2\text{OP}_2\text{RuS}$: C, 66.3; H, 4.6; N, 3.0.

Preparation of $[\text{Ru}(\text{CR}=\text{CHR})(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (8, $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$). $[\text{Ru}(\text{CR}=\text{CHR})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ (6; 0.15 g, 0.15 mmol) and $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ (0.03 g, 0.16 mmol) were degassed under vacuum and dissolved in a degassed mixture of dichloromethane (15 mL) and ethanol (3 mL). The mixture was stirred for 2 h and all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth. All solvent was again removed and the crude solid triturated ultrasonically in hexane (10 mL). The pale green product was filtered off, washed with cold ethanol (1 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.09 g (60%). The product is slightly soluble in ethanol but can be recrystallized from cooled chloroform/ethanol mixtures as a chloroform monosolvate. IR (CH_2Cl_2): 2418, 2294 [$\nu(\text{BH}_2)$], 1937 [$\nu(\text{CO})$] cm^{-1} . (Nujol): 2410, 2297 [$\nu(\text{BH})$], 1945 [$\nu(\text{CO})$], 1572, 1543, 1505, 1433, 1298, 1265, 1207, 1160, 1055, 977, 875, 838 cm^{-1} . NMR (CDCl_3 , 25 $^\circ\text{C}$): ^1H , δ 2.18, 2.28 [s \times 2, 3 H \times 3, CH_3], 3.1 [s(br), 2 H, BH_2], 6.48, 6.51, 6.53, 6.57, 6.79, 6.82, 6.87, 6.90 [s \times 8, 11 H, $\text{C}_6\text{H}_4 + 2\text{H}^4(\text{pz}) + =\text{CH}$, unequivocal assignment not possible], 7.23–7.45 [m, 31 H, $\text{C}_6\text{H}_5 + \text{H}^{3,5}(\text{pz})$], 7.36 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 1.7$], 7.39 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 1.5$], 7.42 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 2.2$ Hz] ppm; $^{31}\text{P}\{^1\text{H}\}$, 28.7 ppm. FAB-MS: m/z (%) 918 (7) $[\text{M}]^+$, 801 (2) $[\text{M} - \text{CRCHR}]^+$, 655 (8) $[\text{M} - \text{PPh}_3]^+$, 625 (4) $[\text{M} - \text{CO} - \text{PPh}_3]^+$, 538 (100) $[\text{M} - \text{CRCHR} - \text{PPh}_3]^+$, 509 (24) $[\text{M} - \text{H}_2\text{B}(\text{pz})_2 - \text{PPh}_3]^+$, 363 (12) $[\text{RuPPh}_3]^+$. Anal. Found: C, 64.3; H, 5.2; N, 7.1. Calcd for $\text{C}_{59}\text{H}_{53}\text{BN}_4\text{OP}_2\text{Ru} \cdot \text{CHCl}_3$: C, 63.9; H, 4.8; N, 5.0.

Preparation of $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (9). $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ (7; 0.19 g, 0.20 mmol) and $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ (0.04 g, 0.22 mmol) were degassed under vacuum and dissolved in a degassed mixture of dichloromethane (5 mL) and ethanol (1 mL). The mixture was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and the solution filtered through diatomaceous earth. Ethanol (10 mL) was added and the solvent volume reduced on the rotary evaporator until precipitation of the yellow product was complete. This was filtered off, washed with ethanol (1 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.13 g (70%). The product is slightly soluble in ethanol. IR (CH_2Cl_2): 2418, 2294 [$\nu(\text{BH})$], 1937 [$\nu(\text{CO})$] cm^{-1} . IR (Nujol): 2410, 2297 [$\nu(\text{BH}_2)$], 1945 [$\nu(\text{CO})$], 1572, 1543, 1505, 1433, 1298, 1265, 1207, 1160, 1055, 977, 875, 838 cm^{-1} . NMR (CDCl_3 , 25 $^\circ\text{C}$): ^1H , δ 2.34 [s, 3 H, CH_3], 3.1 [s(br), 2 H, BH_2], 5.76, 5.83 [t \times 2, 1 H \times 2, $\text{H}^4(\text{pz})$, $J(\text{HH}) = 2.1$], 5.85 [d, 1 H, $=\text{CHR}$, $J(\text{HH}) = 16.8$ Hz], 6.82 [(AB) $_2$, 2 H, C_6H_4 , $J(\text{AB}) = 7.92$; second doublet of (AB) $_2$ system obscured], 6.92 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 2.0$], 6.97–7.30 [m, 34 H, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4(\text{AB}) + \text{H}^{3,5}(\text{pz})$], 7.50 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 2.0$], 7.97 [dt, 1 H, RuCH , $J(\text{HH}) = 17.2$ Hz, $J(\text{HP}) = 3.0$ Hz] ppm; $^{13}\text{C}\{^1\text{H}\}$, δ 206.9 [t, CO, $J(\text{PC}) = 15.2$], 155.5 [m, RuC , $J(\text{PC}) = 7.1$], 144.1, 144.0, 142.8, 142.7 [s \times 4 (see Results and Discussion), 2 \times $\text{C}^3(\text{pz})$], 140.4 [s, CHR], 138.7 [s, $\text{C}^1(\text{C}_6\text{H}_4)$], 137.2, 137.0, 135.5, 135.4 [s \times 4, 2 \times $\text{C}^5(\text{pz})$], 134.1 [t v , $\text{C}^{2,6}(\text{C}_6\text{H}_5)$, $J(\text{PC})$ n.r.], 133.1 [s, $\text{C}^4(\text{C}_6\text{H}_4)$], 132.7 [t v , $\text{C}^1(\text{C}_6\text{H}_5)$, $J(\text{PC}) = 20.6$ Hz], 129.2 [s, $\text{C}^4(\text{C}_6\text{H}_5)$], 128.7 [s, $\text{C}^{2,6}(\text{C}_6\text{H}_4)$], 127.5 [t v , $\text{C}^{3,5}(\text{C}_6\text{H}_5)$, $J(\text{PC})$ n.r.], 124.4 [s, $\text{C}^{3,5}(\text{C}_6\text{H}_4)$], 105.5, 105.4, 104.7, 104.6 [s \times 4, 2 \times $\text{C}^4(\text{pz})$], 21.1 [s, CH_3] ppm; $^{31}\text{P}\{^1\text{H}\}$, 28.7 ppm. FAB-MS: m/z (%) 918 (7) $[\text{M}]^+$, 801 (2) $[\text{M} - \text{CHCHR}]^+$, 655 (8) $[\text{M} - \text{PPh}_3]^+$, 625 (4) $[\text{M} - \text{CO} - \text{PPh}_3]^+$, 538 (100) $[\text{M} - \text{CHCHR} - \text{PPh}_3]^+$, 509 (24) $[\text{M} - \text{H}_2\text{B}(\text{pz})_2 - \text{PPh}_3]^+$, 363 (12) $[\text{RuPPh}_3]^+$. Anal. Found: C, 67.8; H, 4.9; N, 6.0. Calcd for $\text{C}_{52}\text{H}_{47}\text{BN}_4\text{OP}_2\text{Ru}$: C, 68.1; H, 5.2; N, 6.1.

Preparation of $[\text{Ru}(\text{CH}=\text{CH}_2)(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (10). $[\text{Ru}(\text{CH}=\text{CH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ (0.23 g, 0.32 mmol) and $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ (0.07 g, 0.38 mmol) were degassed under vacuum and dissolved in a degassed mixture of dichloromethane (10

mL) and ethanol (2 mL). The reaction mixture was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and the solution filtered through diatomaceous earth. Ethanol (10 mL) was added and the solvent volume reduced on the rotary evaporator until precipitation of the product was complete. The pale yellow crystalline product was filtered off, washed with ethanol (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.20 g (75%). IR (CH_2Cl_2): 2417, 2295 [$\nu(\text{BH}_2)$], 1935 [$\nu(\text{CO})$] cm^{-1} . IR (Nujol): 2419, 2358, 2348, 2296 [$\nu(\text{BH}_2)$], 1947 [$\nu(\text{CO})$], 1924, 1434, 1304, 1291, 1270, 1246, 1160, 1053, 978, 930, 884 cm^{-1} . NMR (CDCl_3 , 25 $^\circ\text{C}$): ^1H , δ 3.0 [s(br), 2 H, BH_2], 4.85 [dt, 1 H, H_β , $J(\text{H}_\alpha\text{H}_\beta) = 18.5$, $J(\text{H}_\beta\text{H}_\gamma) = 1.3$], 5.72, 5.79 [t \times 2, 1 H \times 2, $\text{H}^4(\text{pz})$, $J(\text{HH}) = 2.2$], 5.79 [m, 1 H, H_β], 6.99 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 2.0$], 7.04–7.28 [m, 33 H, $\text{C}_6\text{H}_5 + \text{H}_\alpha + 2 \text{H}^{3,5}(\text{pz})$], 7.45 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 2.0$ Hz] ppm; $^{13}\text{C}\{^1\text{H}\}$ ($\text{CH}_2\text{Cl}_2/\text{CDCl}_3$ 10:1), δ 207.0 [t, CO, $J(\text{PC}) = 15.2$], 161.0 [t, RuC , $J(\text{PC}) = 12.5$], 144.0, 143.9, 142.7, 142.6 [s \times 4 (see Results and Discussion), 2 \times $\text{C}^3(\text{pz})$], 137.0, 136.9, 135.3, 135.2 [s \times 4, 2 \times $\text{C}^5(\text{pz})$], 134.1 [t v , $\text{C}^{2,6}(\text{C}_6\text{H}_5)$, $J(\text{PC})$ n.r.], 132.8 [t v , $\text{C}^1(\text{C}_6\text{H}_5)$, $J(\text{PC}) = 21.0$ Hz], 129.1 [s, $\text{C}^4(\text{C}_6\text{H}_5) + =\text{CH}_2$], 127.3 [t v , $\text{C}^{3,5}(\text{C}_6\text{H}_5)$, $J(\text{PC})$ n.r.], 105.4, 105.3, 104.4, 104.3 [s \times 4, 2 \times $\text{C}^4(\text{pz})$] ppm; $^{31}\text{P}\{^1\text{H}\}$, 28.7 ppm. FAB-MS: m/z (%) 827 (4) $[\text{M}]^+$, 801 (2) $[\text{M} - \text{CO}]^+$, 565 (6) $[\text{M} - \text{PPh}_3]^+$, 537 (31) $[\text{M} - \text{CO} - \text{PPh}_3]^+$, 509 (8) $[\text{M} - \text{CHCH}_2 - \text{CO} - \text{PPh}_3]^+$, 363 (13) $[\text{RuPPh}_3]^+$. Anal. Found: C, 65.0; H, 5.0; N, 6.5. Calcd for $\text{C}_{45}\text{H}_{41}\text{BN}_4\text{OP}_2\text{Ru}$: C, 65.3; H, 5.0; N, 6.8. The complex was also characterized crystallographically (vide infra).

Preparation of $[\text{Ru}(\text{CH}=\text{CHCPh}_2\text{OH})(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (11). $[\text{Ru}(\text{CH}=\text{CHCPh}_2\text{OH})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ (0.60 g, 0.58 mmol) and $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ (0.13 g, 0.70 mmol) were dissolved in a mixture of dichloromethane (15 mL) and ethanol (3 mL). The reaction mixture was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and the solution filtered through diatomaceous earth. All solvent was again removed and the crude solid triturated ultrasonically in hexane (10 mL). The pale green product was filtered off, washed with ethanol (5 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.45 g (77%). IR (CH_2Cl_2): 3052 [$\nu(\text{OH})$], 2420, 2294 [$\nu(\text{BH})$], 1934 [$\nu(\text{CO})$] cm^{-1} . IR (Nujol): 3050 [$\nu(\text{OH})$], 2424, 2402, 2358, 2343 [$\nu(\text{BH}_2)$], 1947, 1934 [$\nu(\text{CO})$], 1301, 1214, 1186, 1160, 1056, 925, 892, 877 cm^{-1} . NMR (CDCl_3 , 25 $^\circ\text{C}$): ^1H , δ 1.47 [s, 1 H, OH], 3.0 [s(br), 2 H, BH_2], 5.52, 5.75 [t \times 2, 1 H \times 2, $\text{H}^4(\text{pz})$, $J(\text{HH}) = 2.1$], 6.02 [d, 1 H, $\text{RuC}=\text{CH}$, $J(\text{HH}) = 16.6$], 6.66 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 2.0$ Hz], 6.89–7.32 [m, 44 H, $\text{C}_6\text{H}_5 + \text{RuCH} + \text{H}^{3,5}(\text{pz})$] ppm; $^{31}\text{P}\{^1\text{H}\}$, 29.9 ppm. FAB-MS: m/z (%) 1010 (2) $[\text{M}]^+$, 993 (3) $[\text{M} - \text{OH}]^+$, 747 (2) $[\text{M} - \text{PPh}_3]^+$, 730 (4) $[\text{M} - \text{OH} - \text{PPh}_3]^+$, 538 (33) $[\text{M} - \text{vinyl} - \text{PPh}_3]^+$, 509 (11) $[\text{M} - \text{CO} - \text{vinyl} - \text{PPh}_3]^+$. Anal. Found: C, 69.0; H, 5.1; N, 5.5. Calcd for $\text{C}_{58}\text{H}_{51}\text{BN}_4\text{O}_2\text{P}_2\text{Ru}$: C, 69.0; H, 5.1; N, 5.6.

Preparation of $[\text{Ru}(=\text{CHCH}=\text{CPh}_2)\{\kappa^2\text{-H}_2\text{B}(\text{pz})_2\}(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ (12). $[\text{Ru}(\text{CH}=\text{CHCPh}_2\text{OH})(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (11; 0.10 g, 0.10 mmol) was dissolved in dichloromethane (10 mL) and 85% tetrafluoroboric acid diethyl ether solution (1 drop) added. An instantaneous color change to red was observed and, after stirring for 2 min., all solvent was removed. The resulting red oil was washed with hexane (3 \times 10 mL) and dried under vacuum overnight. Yield: 0.08 g (76%). Repeated attempts to induce crystallization failed. The following limited spectroscopic data were obtained from the crude material. IR (CH_2Cl_2): 2308, 2296 [$\nu(\text{BH}_2)$], 1982 [$\nu(\text{CO})$], 1712 [$\text{CH}=\text{CPh}_2$] cm^{-1} . IR (KBr): 2360, 2343 [$\nu(\text{BH}_2)$], 1955 [$\nu(\text{CO})$], 1619, 1481, 1434, 1297, 1224, 1064 (br) [$\nu(\text{BF}_4)$], 919, 813 cm^{-1} . NMR (CDCl_3 , 25 $^\circ\text{C}$): ^1H , δ 6.03, 6.06 [t \times 2, 1 H \times 2, $\text{H}^4(\text{pz})$, $J(\text{HH}) = 2.1$], 6.69–7.82 [m, 42 H, $\text{C}_6\text{H}_5 + 2\text{H}^{3,5}(\text{pz})$], 7.86, 7.89 [s(br) \times 2, 1 H \times 2, $\text{H}^{3,5}(\text{pz})$], 8.23 [d, 1 H, $=\text{CH}_\beta$, $J(\text{H}_\alpha\text{H}_\beta) = 14.1$], 15.72 [dt, 1 H, $\text{Ru}=\text{CH}_\alpha$, $J(\text{H}_\alpha\text{H}_\beta) = 13.9$; $J(\text{P}_2\text{H}_\alpha) = 2.1$ Hz] ppm; $^{31}\text{P}\{^1\text{H}\}$, 24.2 ppm. FAB-MS: m/z (%) 993 (16) $[\text{M}]^+$, 731 (55) $[\text{M} - \text{PPh}_3]^+$, 585 (12) $[\text{M} -$

$\text{H}_2\text{B}(\text{pz})_2 - \text{PPh}_3]^+$, 555 (21) $[\text{M} - \text{CO} - \text{H}_2\text{B}(\text{pz})_2 - \text{PPh}_3]^+$, 538 (28) $[\text{M} - \text{CHR} - \text{PPh}_3]^+$, 510 (11) $[\text{M} - \text{CHR} - \text{CO} - \text{PPh}_3]^+$.

Preparation of $[\text{Ru}(\text{CPh}=\text{CHPh})(\text{CS})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (13). $[\text{Ru}(\text{CPh}=\text{CHPh})\text{Cl}(\text{CS})(\text{PPh}_3)_2]$ (0.26 g, 0.31 mmol) and $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ (0.06 g, 0.32 mmol) were degassed in vacuo and dissolved in a degassed mixture of dichloromethane (10 mL) and ethanol (1 mL). The mixture was stirred for 35 min and then freed of all volatiles. The crude product was dissolved in dichloromethane (10 mL) and the solution filtered through diatomaceous earth. Ethanol (5 mL) was added and the solvent volume reduced (rotary evaporator) until precipitation was complete (ca. 2 mL). The ochre product was filtered off, washed with cold ethanol (1 mL) and hexane (5 mL), and dried in vacuo. Yield: 0.16 g (54%). IR (Nujol): 2465, 2421 $[\nu(\text{BH}_2)]$, 1592, 1584, 1557, 1312, 1276 $[\nu(\text{CS})]$, 1202, 1120, 974, 922, 880 cm^{-1} . NMR (CDCl_3 , 25 °C): ^1H , δ 3.5 [s(br), 2 H, BH_2], 5.94 [m, 2 H, $\text{H}^4(\text{pz})$], 6.61 [d, 2 H, $\text{H}^{2,6}(\text{C}_6\text{H}_5)$, $J(\text{HH}) = 6.7$], 6.72 [d, 2 H, $\text{H}^{2,6}(\text{C}_6\text{H}_5)$, $J(\text{HH}) = 6.7$], 6.86 [s, 1 H, CHPh], 6.88–6.97 [m, $\text{C}_6\text{H}_5 + \text{H}^{3,5}(\text{pz})$], 7.02 [t, 2 H, $\text{H}^{3,5}(\text{C}_6\text{H}_5)$, $J(\text{HH}) = 7.3$ Hz], 7.07–7.53 [m, $\text{PC}_6\text{H}_5 + \text{H}^{3,5}(\text{pz})$] ppm; $^{31}\text{P}\{^1\text{H}\}$, 47.0 ppm. FAB-MS: m/z (%) 1041 (0.25) $[\text{M}]^+$, 973 (0.5) $[\text{M} - \text{pz}]^+$, 908 (1) $[\text{M} - 2\text{pz}]^+$, 889 (0.5) $[\text{M} - \text{H}_2\text{B}(\text{pz})_2]^+$, 778 (3) $[\text{M} - \text{PPh}_3]^+$, 670 (12) $[\text{M} - \text{vinyl} - \text{H}_2\text{B}(\text{pz})_2]^+$, 623 (6) $[\text{M} - \text{vinyl} - \text{CS} - \text{H}_2\text{B}(\text{pz})_2]^+$, 554 (45) $[\text{M} - \text{vinyl} - \text{PPh}_3]^+$, 407 (30) $[\text{M} - \text{vinyl} - \text{H}_2\text{B}(\text{pz})_2 - \text{PPh}_3]^+$, 363 (19) $[\text{RuPPh}_3]^+$. Anal. Found: C, 63.2; H, 4.7; N, 7.2. Calcd for $\text{C}_{57}\text{H}_{49}\text{BN}_4\text{P}_2\text{RuS}$: 1.25(CH_2Cl_2): C, 63.5; H, 4.7; N, 5.1.

Preparation of $[\text{Ru}(\eta^2\text{-SCCPh}=\text{CHPh})(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (14). $[\text{Ru}(\text{CPh}=\text{CHPh})(\text{CS})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (13: 0.10 g, 0.10 mmol) was dissolved in dichloromethane (5 mL) and a stream of carbon monoxide passed through the solution for 15 s, prompting an immediate red coloration. The flask was stoppered and stirred for 2 min and then ethanol (10 mL) added. The solvent volume was reduced (rotary evaporator) until precipitation of the product was complete. Ultrasonic trituration can be employed to initialize crystallization. The red product was filtered off, washed with ethanol (2 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.07 g (68%). IR (CH_2Cl_2): 2414, 2354 $[\nu(\text{BH}_2)]$, 1926 $[\nu(\text{CO})]$, cm^{-1} . IR (Nujol): 2419, 2279 $[\nu(\text{BH}_2)]$, 1925 $[\nu(\text{CO})]$, 1582, 1561, 1328, 1314, 1298, 1261, 1205, 1147, 1055, 984, 948, 883, 844, 812 cm^{-1} . NMR (CDCl_3 , 25 °C): ^1H , δ 3.9 [s(br), 2 H, BH_2], 5.99 [t, 1 H, $\text{H}^4(\text{pz})$, $J(\text{HH}) = 2.2$], 6.02 [m, 1 H, $\text{H}^4(\text{pz})$], 6.63 [m, C_6H_5], 6.84, 6.97 [d \times 2, 2 \times 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 2.0$], 7.08 [d, 2 H, $\text{H}^{2,6}(\text{C}_6\text{H}_5)$, $J(\text{HH})$ n.r.], 7.11 [s, 1 H, CHPh], 7.18 [t, 2 H, $\text{H}^{3,5}(\text{C}_6\text{H}_5)$, $J(\text{HH}) = 7.6$ Hz], 7.28–7.44 [m, C_6H_5], 7.60 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH})$ n.r.], 7.75 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 2.0$ Hz] ppm; $^{13}\text{C}\{^1\text{H}\}$, δ 311.4 [d, SC, $J(\text{PC}) = 9.7$], 208.5 [d, CO, $J(\text{PC}) = 17.3$], 154.0 [s, SCC], 146.5, 144.5 [2 \times s, 2 \times $\text{C}^3(\text{pz})$], 140.8–127.8 [$\text{C}_6\text{H}_5 + 2 \text{C}^5(\text{pz}) + \text{CHPh}$], 134.3 [d, $\text{C}^{2,6}(\text{C}_6\text{H}_5)$, $J(\text{PC}) = 9.7$], 132.5 [d, $\text{C}^1(\text{PC}_6\text{H}_5)$, $J(\text{PC}) = 47.5$], 130.5 [s, $\text{C}^4(\text{PC}_6\text{H}_5)$], 128.4 [d, $\text{C}^{3,5}(\text{PC}_6\text{H}_5)$, $J(\text{PC}) = 10.8$ Hz], 104.8, 104.3 [s \times 2, 2 \times $\text{C}^4(\text{pz})$] ppm; $^{31}\text{P}\{^1\text{H}\}$, 42.9 ppm. FAB-MS: m/z (%) 762 (5) $[\text{M}]^+$, 614 (1) $[\text{M} - \text{H}_2\text{B}(\text{pz})_2]^+$, 587 (3) $[\text{M} - \text{CO} - \text{H}_2\text{B}(\text{pz})_2]^+$, 537 (3) $[\text{M} - \text{thioacyl}]^+$, 509 (1) $[\text{M} - \text{CO} - \text{thioacyl}]^+$, 472 (3) $[\text{M} - \text{thioacyl} - \text{pz}]^+$, 443 (3) $[\text{M} - \text{CO} - \text{thioacyl} - \text{pz}]^+$, 363 (3) $[\text{RuPPh}_3]^+$. Anal. Found: C, 62.3; H, 4.4; N, 7.8. Calcd for $\text{C}_{40}\text{H}_{34}\text{BN}_4\text{OPRuS}$: C, 63.1; H, 4.5; N, 7.4.

Preparation of $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (15). (a) $[\text{Ru}(\text{CH}=\text{CHR})(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (9: 0.15 g, 0.16 mmol) and 4-ethynyltoluene (0.04 mL, 0.04 g, 0.32 mmol) were dissolved in tetrahydrofuran (15 mL) and the mixture heated under reflux for 5 h. All solvent was removed and the crude product dissolved in dichloromethane (10 mL) and ethanol (10 mL) added. On slow concentration under reduced pressure a colorless product precipitated. This was filtered off, washed with ethanol (5 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.08 g (53%).

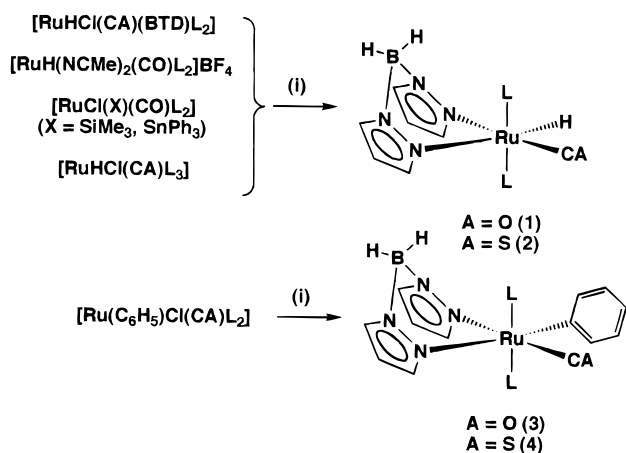
(b) A mixture of $[\text{RuH}(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (1: 0.20 g, 0.25 mmol) and $[\text{Hg}(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})_2]$ (0.16 g, 0.38 mmol) in tetrahydrofuran (30 mL) was heated under reflux for 1 h. The mixture was cooled and filtered through diatomaceous earth to remove elemental mercury. The filtrate was diluted with ethanol and the mixture concentrated slowly under reduced pressure to provide colorless crystals of the product. This was identified by comparison of spectroscopic data with those for a sample of 15 obtained in (a) above. Yield: 0.12 g (53%). IR (CH_2Cl_2): 2404, 2296 $[\nu(\text{BH}_2)]$, 2103 $[\nu(\text{C}\equiv\text{C})]$, 1951 $[\nu(\text{CO})]$ cm^{-1} . IR (Nujol): 2379, 2296 $[\nu(\text{BH}_2)]$, 2107 $[\nu(\text{C}\equiv\text{C})]$, 1943 $[\nu(\text{CO})]$, 1299, 1216, 1164, 985, 881, 817 cm^{-1} . NMR (CDCl_3 , 25 °C): ^1H , δ 2.28 [s, 3 H, CH_3], 3.0 [s(br), 2 H, BH_2], 5.48, 5.66 [t \times 2, 1 H \times 2, $\text{H}^4(\text{pz})$, $J(\text{HH}) = 2.1$], 6.77, 6.93 [(AB)₂, 4 H, C_6H_4 , $J(\text{AB}) = 7.9$], 6.82 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 2.0$ Hz], 7.06–7.33 [m, 33 H, $\text{C}_6\text{H}_5 + \text{H}^{3,5}(\text{pz})$], 7.43 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH})$ n.r.] ppm; $^{31}\text{P}\{^1\text{H}\}$, 30.9 ppm. FAB-MS: m/z (%) 1066 (11) $[\text{M} + \text{nba}]^+$, 801 (11) $[\text{M}]^+$, 653 (15) $[\text{M} - \text{PPh}_3]^+$. Anal. Found: C, 66.7; H, 4.7; N, 6.0. Calcd for $\text{C}_{52}\text{H}_{45}\text{BN}_4\text{OP}_2\text{Ru}$: 0.25(CH_2Cl_2): C, 67.0; H, 4.9; N, 6.0.

Preparation of $[\text{Ru}(\text{C}\equiv\text{CCPh}_2\text{OH})(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (16). $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (9: 0.13 g, 0.14 mmol) and $\text{HC}\equiv\text{CCPh}_2\text{OH}$ (0.07 g, 0.34 mmol) were dissolved in tetrahydrofuran (15 mL), and the mixture was heated under reflux for 4 h. All solvent was removed, and the crude product was dissolved in dichloromethane (10 mL) and ethanol (10 mL) added. On slow concentration under reduced pressure a colorless product precipitated. This was filtered off, washed with ethanol (5 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.07 g (49%). The complex can be recrystallized from chloroform–ethanol mixtures. IR (CH_2Cl_2): 2402, 2310 $[\nu(\text{BH}_2)]$, 2105 $[\nu(\text{C}\equiv\text{C})]$, 1951 $[\nu(\text{CO})]$ cm^{-1} . IR (Nujol): 2370, 2343 $[\nu(\text{BH}_2)]$, 2291, 2113 $[\nu(\text{C}\equiv\text{C})]$, 1953 $[\nu(\text{CO})]$, 1301, 1160, 917, 879, 846 cm^{-1} . NMR (CDCl_3 , 25 °C): ^1H , δ 1.75 [s, 1 H, OH], 3.0 [s(br), 2 H, BH_2], 5.38, 5.64 [t \times 2, 1 H \times 2, $\text{H}^4(\text{pz})$, $J(\text{HH}) = 2.1$], 6.70 [d, 1 H, $\text{H}^{3,5}(\text{pz})$, $J(\text{HH}) = 1.7$], 7.01–7.56 [m, 43 H, $\text{C}_6\text{H}_5 + \text{H}^{3,5}(\text{pz})$] ppm; $^{13}\text{C}\{^1\text{H}\}$ ($\text{CDCl}_3/\text{CH}_2\text{Cl}_2$ 10:1, 25 °C), δ 205.3 [t, CO, $J(\text{PC}) = 15.1$], 147.5 [$\text{C}^1(\text{CC}_6\text{H}_5)$], 145.5, 144.1 [2 \times s, 2 \times $\text{C}^3(\text{pz})$], 136.3, 135.7 [2 \times s, 2 \times $\text{C}^5(\text{pz})$], 134.2 [t^v, $\text{C}^{2,6}(\text{PC}_6\text{H}_5)$, $J(\text{PC}) = 5.4$], 132.8 [t^v, $\text{C}^1(\text{PC}_6\text{H}_5)$, $J(\text{PC}) = 21.6$], 129.3 [$\text{C}^4(\text{PC}_6\text{H}_5)$], 127.6 [t^v, $\text{C}^{3,5}(\text{PC}_6\text{H}_5)$, $J(\text{PC})$ n.r.], 133.5, 129.2, 127.4, 126.3, 126.1, 124.2 [C_6H_5], 115.9 [$\text{RuC}\equiv\text{C}$], 108.2 [t, $\text{Ru}-\text{C}\equiv$, $J(\text{PC}) = 17.3$ Hz], 105.7, 104.8 [s \times 2, 2 \times $\text{C}^4(\text{pz})$], 75.2 [COH] ppm; $^{31}\text{P}\{^1\text{H}\}$, 31.9 ppm. FAB-MS: m/z (%) 991 (26) $[\text{M} - \text{OH}]^+$, 729 (45) $[\text{M} - \text{OH} - \text{PPh}_3]^+$, 701 (16) $[\text{M} - \text{OH} - \text{CO} - \text{PPh}_3]^+$. Anal. Found: C, 67.3; H, 4.6; N, 5.3. Calcd for $\text{C}_{58}\text{H}_{49}\text{BN}_4\text{O}_2\text{P}_2\text{Ru}$: 0.25(CHCl_3): C, 67.4; H, 4.8; N, 5.4.

Crystal Data, X-ray Data Collection, and Structural Determination of $[\text{Ru}(\text{CH}=\text{CH}_2)(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (10). The complex forms yellow prisms by diffusion of ethanol into a saturated solution of the complex in chloroform. That chosen for data collection had dimensions $0.47 \times 0.30 \times 0.13$ mm. Crystal data for $[\text{Ru}(\text{CH}=\text{CH}_2)(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (10): $\text{C}_{45}\text{H}_{41}\text{BN}_4\text{OP}_2\text{Ru}$, $M_r = 827.6$, monoclinic, space group $P2_1/c$ (No. 14), $a = 9.376(1)$ Å, $b = 38.542(3)$ Å, $c = 11.277(1)$ Å, $\beta = 103.18(1)^\circ$, $V = 3967.7(6)$ Å³, $Z = 4$, $D_c = 1.386$ g cm^{-3} , $\mu(\text{Cu K}\alpha) = 42.7$ cm^{-1} , $F(000) = 1704$, $T = 293$ K.

Data were measured on a Siemens P4/PC diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å, graphite monochromator) using ω scans. Independent reflections (5898) were measured ($2\theta \leq 120^\circ$), of which 4280 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors, and a semiempirical absorption correction was applied; the maximum and minimum transmission factors were 0.34 and 0.23, respectively.

The structure was solved by direct methods, and all of the non-hydrogen atoms were refined anisotropically. The pendant phenyl rings were refined as optimized rigid bodies. The hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters ($U(\text{H}) = 1.2 U_{\text{eq}}(\text{C/B})$), and allowed to ride on their parent atoms. Refinements were by full-

Scheme 1^a

^a Abbreviations: L = PPh₃, BTD = 2,1,3-benzothiadiazole, pz = pyrazol-1-yl, A = O, S. Legend: (i) K[H₂B(pz)₂], CH₂Cl₂, EtOH.

matrix least squares based on F^2 to give $R1 = 0.057$ and $wR2 = 0.127$ for the observed data and 416 parameters. The maximum and minimum residual electron densities in the final ΔF map were 0.90 and $-0.70 \text{ e } \text{\AA}^{-3}$, respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.000 and -0.001 , respectively. Computations were carried out using the SHELXTL PC program system (Version 5.03, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994).

Results and Discussion

The complex [RuHCl(CO)(PPh₃)₃] reacts in dichloromethane with dihydrobis(pyrazol-1-yl)borate at room temperature within 1 h to provide a complex formulated as [RuH(CO)(PPh₃)₂{η²-H₂B(pz)₂}] (**1**) in good yield (Scheme 1). The same product also results from the reaction of K[H₂B(pz)₂] with [RuH(CO)(NCMe)₂(PPh₃)₂]BF₄. A triplet resonance in the ¹H NMR spectrum at -11.69 ppm ($J(\text{PH}) = 21.8 \text{ Hz}$) and an absorption in the infrared spectrum (Nujol) attributed to $\nu(\text{RuH})$ at 2179 cm^{-1} confirm the retention of the hydride ligand. This peak is accompanied by a more intense $\nu(\text{CO})$ absorption at 1933 cm^{-1} . Five resonances derived from the pyrazolyl protons of the borate ligand are observed in the ¹H NMR spectrum, the sixth being obscured by phosphine resonances. Two of these at 5.29 and 5.89 ppm are resolved as triplets ($J(\text{HH}) = 1.98 \text{ Hz}$) and are assigned to the H⁴(pz) protons. The remainder appear as doublets at 6.53, 6.84, and 7.46 ($J(\text{HH}) = 1.32 \text{ Hz}$) ppm arising from the H^{3,5}(pz) protons. A very broad resonance was noted for the BH₂ protons at approximately 3.1 ppm, and this group also gives rise to a pair of $\nu(\text{BH}_2)$ infrared absorbances at 2405 and 2293 cm^{-1} . The mutually *trans* geometry of the two triphenylphosphine ligands was confirmed by the sharp singlet resonance at 45.1 ppm in the ³¹P{¹H} NMR spectrum. This feature was shared by all the complexes to follow, and thus it can be assumed that the boat-shaped geometry of the pyrazolylborate chelate inverts rapidly on the ³¹P{¹H} NMR time scale, chemically equilibrating the phosphine environments. This may be contrasted with the AB pattern observed for [RuH(CO)(PPh₃)₂{η²-HB(pz)₃}], where such an inversion cannot occur.^{3b} The gross molecular composition of the complex was further confirmed by the FAB mass spectrum, which includes

a prominent molecular ion isotopic envelope at m/z 801 as well as fragmentations due to loss of the carbonyl and phosphine ligands. The coordinatively unsaturated stannyl and silyl complexes [RuCl(SnPh₃)(CO)(PPh₃)₂]²⁴ and [RuCl(SiMe₃)(CO)(PPh₃)₂]²⁵ were prepared by literature routes. After reaction with dihydridobis(pyrazol-1-yl)borate, however, the only product isolated in both cases was the hydride compound **1**. This suggests that ligation of the pyrazolylborate ligand enhances the susceptibility of the silyl and stannyl ligands to hydrolysis, a feature which we have recently remarked upon for HB(pz)₃ ligands in this system.^{3b}

Treatment of [RuHCl(CS)(PPh₃)₃]¹⁷ with K[H₂B(pz)₂] proceeds in a similar manner to provide the thiocarbonyl complex [RuH(CS)(PPh₃)₂{η²-H₂B(pz)₂}] (**2**). Alternatively, the complex [RuHCl(CS)(BTD)(PPh₃)₂] (BTD = 2,1,3-benzothiadiazole, obtained from [RuHCl(CS)(PPh₃)₃] and BTD; see Experimental Section), may be employed, utilizing the lability of the BTD ligand which has been demonstrated for the related carbonyl analogue [RuHCl(CO)(BTD)(PPh₃)₂].²⁶ Apart from the features arising from the thiocarbonyl ligand ($\nu(\text{CS})$ 1264 cm^{-1}), spectroscopic data for **2** were found to be comparable to those obtained for the carbonyl analogue **1**. On treatment with carbon monoxide, no migratory insertion of the hydride and thiocarbonyl ligands in this complex was observed, although such processes are well-established for osmium *cis*-hydrido-thiocarbonyl complexes.²⁷

The σ -aryl species [RuPh(CO)(PPh₃)₂{η²-H₂B(pz)₂}] (**3**) was prepared by treating the 16-electron complex [RuPhCl(CO)(PPh₃)₂]¹⁸ with K[H₂B(pz)₂] in dichloromethane. The $\nu(\text{CO})$ associated infrared absorption for **3** was observed at 1937 cm^{-1} (Nujol). Multiplet resonances due to the phenyl group were noted in the ¹H NMR spectrum at 6.61 and 6.87 ppm, distinct from those due to the PPh₃ coligands. The gross formulation was confirmed by a molecular ion at m/z 877 in the FAB-MS spectrum. The thiocarbonyl analogue [RuPh(CS)(PPh₃)₂{η²-H₂B(pz)₂}] (**4**) could also be prepared in a similar manner from K[H₂B(pz)₂] and [RuPhCl(CS)(PPh₃)₂]¹⁹ and displayed spectroscopic features almost identical with those of the carbonyl analogue **3**, with the exception of the appearance of an intense $\nu(\text{CS})$ absorption at 1265 cm^{-1} (Nujol).

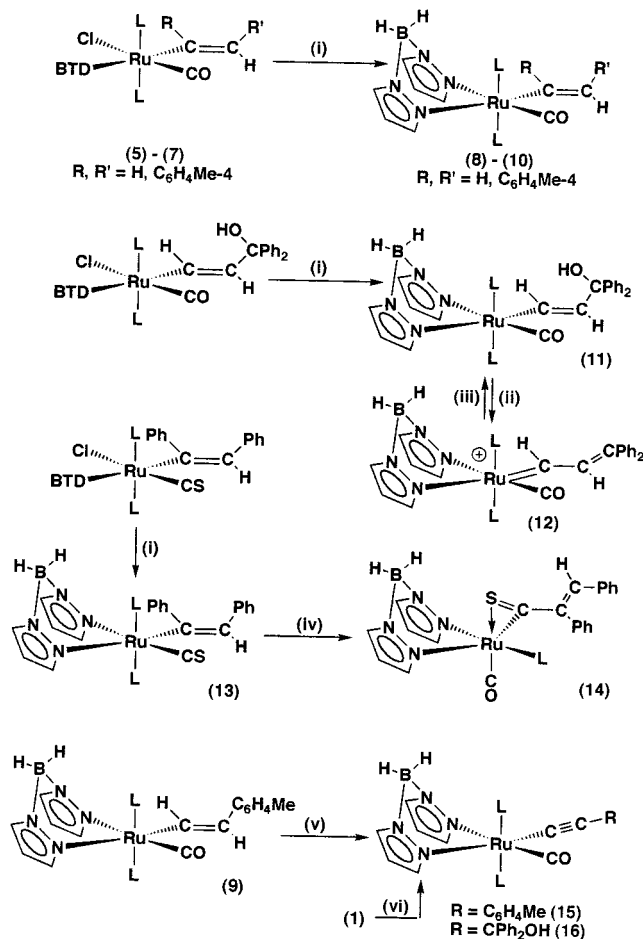
Since our original report on the synthesis of the range of vinyl complexes [Ru(CH=CHR)Cl(CO)(BSD)(PPh₃)₂] (R = H, C₆H₅, C₆H₄Me-4, CH₂SiMe₂⁺, CH₂PO₃Et₂),²² 2,1,3-benzoselenadiazole (BSD) has ceased to be commercially available. This class of compound has been particularly useful in that both the chloride ligand and

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Scheme 2^a

^a Abbreviations as in Scheme 1. Legend: (i) $K[H_2B(pz)_2]$; (ii) HBF_4 ; (iii) KOH ; (iv) CO ; (v) $HC\equiv CR$; (vi) $[Hg(C\equiv CC_6H_4Me-4)_2]$.

the selenium heterocycle are labile. We have therefore prepared the related class of compounds based on the commercially available 2,1,3-benzothiadiazole (BTD) ligand via the reactions of $[RuHCl(CO)(BTD)(PPh_3)_2]$ ²⁶ with a range of alkynes. The derived σ -vinyl complexes are in all respects comparable to those based on BSD. Similar chemistry can be developed from $[RuHCl(CO)(py)(PPh_3)_2]$; however, the compounds are colorless while those bearing the BSD or BTD ligand are typically brightly colored. This feature offers practical (and aesthetic) advantages for monitoring reaction progress by visual means and by TLC. Thus, the complexes $[Ru(CR=CHR)Cl(CO)(BTD)(PPh_3)_2]$ ($R = H$, (**5**), C_6H_4Me-4 (**6**)) and $[Ru(CH=CHC_6H_4Me-4)Cl(CO)(BTD)(PPh_3)_2]$ (**7**) are readily obtained from the reactions of $[RuHCl(CO)(BTD)(PPh_3)_2]$ with the appropriate alkyne.

Treating **6** with $K[H_2B(pz)_2]$ results in the formation of $[Ru(CR=CHR)(CO)(PPh_3)_2\{H_2B(pz)_2\}]$ (**8**; $R = C_6H_4Me-4$) (Scheme 2). Methyl resonances for the chemically distinct tolyl groups were observed at 2.20 and 2.29 ppm in the 1H NMR spectrum. The $(AB)_2$ resonances for the aromatic tolyl protons were found to partially overlap with those for the dihydridobis(pyrazol-1-yl)borate ligand, precluding unequivocal assignment. The carbonyl ligand gave rise to a single intense $\nu(CO)$ absorption at 1945 cm^{-1} (Nujol). Positive ion FAB mass spectrometry showed the presence of a molecular ion at m/z 918, confirming the gross molecular formulation. In a simi-

lar manner, treatment of $[Ru(CH=CHC_6H_4Me-4)Cl(CO)(BTD)(PPh_3)_2]$ (**7**) with $K[H_2B(pz)_2]$ yielded the complex $[Ru(CH=CHC_6H_4Me-4)(CO)(PPh_3)_2\{H_2B(pz)_2\}]$ (**9**). In addition to the pyrazolyl resonances, one doublet of the tolyl $(AB)_2$ system (6.82 ppm, $J(AB) = 7.92$ Hz) could be distinguished in the 1H NMR spectrum. The vinylic proton α to the metal exhibited coupling with both the *trans*- β -vinylic proton and the phosphorus nuclei of the chemically equivalent phosphines to give a doublet of triplets at δ 7.97 ($J(H_\alpha H_\beta) = 17.2$, $J(HP) = 3.0$ Hz). The carbonyl and α -vinyl carbons both gave rise to triplet resonances in the $^{13}C\{^1H\}$ NMR spectrum at 206.9 ($J(PC) = 15.2$) and 155.5 ppm ($J(PC) = 7.1$ Hz), respectively. Resonances for all six carbon environments of the pyrazolyl rings were identified in the $^{13}C\{^1H\}$ NMR spectrum. However, it was found that instead of a single resonance, each pyrazolyl carbon gave rise to a pair of singlets at almost identical chemical shift. The resonances at 144.1, 144.0, 142.8, and 142.7 ppm were attributed to the two $C^3(pz)$ carbons and those at 137.2, 137.0, 135.5, and 135.4 ppm to the $C^5(pz)$ carbons. At higher field, the $C^4(pz)$ carbons gave rise to singlet resonances at 105.5, 105.4, 104.7, and 104.6 ppm. The presumed origin of this splitting can perhaps be traced to the results of the crystallographic study of the parent vinyl complex (**10**; vide infra), which revealed that in the solid state the vinyl ligand lies out of the equatorial coordination plane and experiences some restrictions to free rotation about the $Ru-C$ bond. This effect is expected to be further enhanced for the more sterically cumbersome vinyl ligand in **9**. The $^{31}P\{^1H\}$ NMR spectrum was also found to show broadening of the singlet at 28.7 ppm at room temperature, perhaps indicating the onset of such a dynamic process. The pyrazolyl resonances in the 1H NMR spectrum were also found to be discernably broadened. The parent vinyl complex $[Ru(CH=CH_2)(CO)(PPh_3)_2\{H_2B(pz)_2\}]$ (**10**) could be prepared from $[Ru(CH=CH_2)Cl(CO)(BTD)(PPh_3)_2]$ or in high yield directly from $[Ru(CH=CH_2)Cl(CO)(PPh_3)_2]$. The α -proton resonance of the ethenyl ligand in the 1H NMR spectrum was obscured by phosphine resonances; however, a multiplet resonance for the *trans*- β' -proton was observed centered at δ 5.79 ppm. The *cis*- β -proton appeared as a well-defined doublet of triplets at 4.85 ($J(H_\alpha H_\beta) = 18.5$, $J(H_\beta H_{\beta'}) = 1.3$ Hz) ppm. The $^{13}C\{^1H\}$ NMR spectrum included a triplet resonance at 207.0 ($J(PC) = 15.2$ Hz) ppm for the carbonyl carbon and second triplet showing smaller coupling at 161.0 ppm ($J(PC) = 12.5$ Hz) for the α -vinyl carbon. Crystallographic grade crystals of **10** were obtained, and the results of the crystallographic study are summarized in Tables 1 and 2 and Figure 1; these results are discussed below.

The complex $[Ru(CH=CHCPh_2OH)(CO)(PPh_3)_2\{H_2B(pz)_2\}]$ (**11**) was prepared in order to investigate the potential for further reactivity of γ -functionalized σ -vinyl ligands, while supported by the $H_2B(pz)_2$ coligand. We have previously shown that γ -hydroxy vinyl ligands are prone to dehydroxylation by Lewis acids,^{22b} and more recently this approach has proven useful for the synthesis of alkenylalkylidene complexes.²⁸⁻³⁰ The above species forms as the only organometallic product from the reaction of $K[H_2B(pz)_2]$ with $[Ru(CH=CHCPh_2OH)Cl(CO)(BTD)(PPh_3)_2]$. This colorless complex dis-

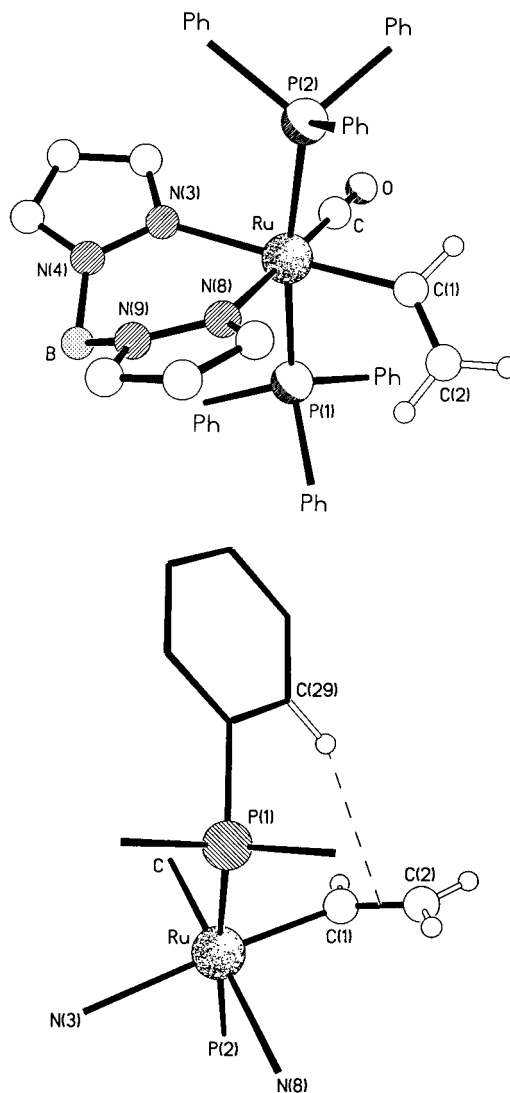
Table 1. Crystal Data and Data Collection and Solution and Refinement Details for $[\text{Ru}(\text{CH}=\text{CH}_2)(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (**10**)

Crystal Data	
emp formula	$\text{C}_{45}\text{H}_{41}\text{BN}_4\text{OP}_2\text{Ru}$
M_r	827.6
a, b, c (Å)	9.376(1), 38.542(3), 11.277(1)
α, β, γ (deg)	90, 103.18(1), 90
V (Å ³)	3967.7(6)
space grp	$P2_1/c$
Z	4
D_{calc} (g cm ⁻³)	1.386
cryst size (mm)	$0.47 \times 0.30 \times 0.13$
Data Collection	
T (K)	293
diffractometer	Siemens P4/PC
wavelength	Cu K α , 1.541 78 Å
scan type	ω -scans ($4.58 \leq 2\theta \leq 120^\circ$)
abs cor	semiempirical
max, min transmission	0.34, 0.23
no. of data	5898 unique; 4280 with $F > 4\sigma(F)$ retained
Solution and Refinement	
method	direct and difference Fourier
program	SHELXTL PC version 5.03
residuals	$R1 = 0.057$, $wR2 = 0.127$ (416 params)
e density (e Å ⁻³)	max 0.90, min -0.70

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **10**

Ru-C	1.848(7)	Ru-C(1)	2.080(7)
Ru-N(8)	2.178(6)	Ru-N(3)	2.194(5)
Ru-P(1)	2.410(2)	Ru-P(2)	2.433(2)
C-O	1.142(9)	C(1)-C(2)	1.345(11)
C-Ru-C(1)	88.7(3)	C-Ru-N(8)	179.4(3)
C(1)-Ru-N(8)	91.8(3)	C-Ru-N(3)	92.7(3)
C(1)-Ru-N(3)	176.3(2)	N(8)-Ru-N(3)	86.7(2)
C-Ru-P(1)	84.4(2)	C(1)-Ru-P(1)	87.2(2)
N(8)-Ru-P(1)	95.5(2)	N(3)-Ru-P(1)	96.3(2)
C-Ru-P(2)	92.0(2)	C(1)-Ru-P(2)	85.6(2)
N(8)-Ru-P(2)	88.2(2)	N(3)-Ru-P(2)	91.0(2)
Ru-C-O	178.7(6)	Ru-C(1)-C(2)	131.1(6)

plays a strong $\nu(\text{CO})$ infrared absorption 1934 cm^{-1} (Nujol). Three clear resonances (two triplets and one doublet) were observed in the ^1H NMR spectrum for the pyrazolyl protons, with the remainder being obscured by the aromatic phosphine resonances. The α -vinyl proton was also obscured within this region, whereas the β -vinyl proton was visible as a doublet resonance at δ 6.02 showing a $J(\text{H}_\alpha\text{H}_\beta)$ coupling of 16.6 Hz consistent with the (*E*)-vinyl regiochemistry arising from *cis*-hydrometalation. The hydroxyl proton gave rise to a singlet resonance at 1.47 ppm. On dissolution of the product in deuteriochloroform, a red coloration was observed but was found not to affect the subsequent NMR spectrum appreciably. This observation was taken to indicate conversion of **11** to the vinyl carbene complex $[\text{Ru}(\text{=CHCH}=\text{CPh}_2)(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]\text{Cl}$ (**12**), since the vinyl carbene ligand is an intense

**Figure 1.** Molecular geometry of $[\text{Ru}(\text{CH}=\text{CH}_2)(\text{CO})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}]$ (**10**). Phenyl groups and pyrazolyl hydrogen atoms have been removed for clarity.

chromophore. This transformation was attempted on a preparative scale with $\text{HBF}_4 \cdot \text{OEt}_2$ in dichloromethane, resulting in an instant deep red coloration. Unfortunately, the product was found to be highly soluble even in hexane and has not been isolated in pure form. The solution infrared spectrum (CH_2Cl_2) showed a new absorption at 1978 cm^{-1} consistent with the cationic complex formulation. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of the solution gave a singlet at 27.0 ppm. The ^1H NMR exhibited unresolved doublet resonances at 6.55 and 9.47 ppm attributable to, respectively, the β - and α -protons of the $\text{Ru}=\text{CHCH}=\text{CPh}_2$ group. FAB mass spectroscopy revealed a molecular ion at m/z 933 for the complex and fragmentation due to loss of phosphine and carbonyl ligands. Furthermore, treatment with KOH regenerated the precursor complex **11**.

Though complexes of the type $[\text{RuR}(\text{CO})(\text{PPh}_3)\{\text{HB}(\text{pz})_3\}]$ ($\text{R} = \text{vinyl}$) are known,^{3c,d} no thiocarbonyl analogue has been reported. Reaction between $[\text{Ru}(\text{CR}'=\text{CHPh})\text{Cl}(\text{CS})(\text{PPh}_3)_2]$ ($\text{R}' = \text{H}, \text{Ph}$)²³ and $\text{K}[\text{HB}(\text{pz})_3]$ results in an intractable mixture of products, though some evidence suggests the coordination of a fragmented pyrazolyl ring. However, with $\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ the complex $[\text{Ru}(\text{CPh}=\text{CHPh})\text{Cl}(\text{CS})(\text{PPh}_3)_2]$ reacts cleanly to give

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[Ru(CPh=CHPh)(CS)(PPh₃)₂{H₂B(pz)₂}] **13**. In addition to resonances attributed to the pyrazolyl protons, a singlet was observed in the ¹H NMR spectrum at 6.86 ppm for the vinylic proton. An intense absorption in the infrared spectrum at 1276 cm⁻¹ (Nujol) indicated the retention of the thiocarbonyl ligand.

The cis disposition of the thiocarbonyl and stilbenyl ligands in **13** should predispose the complex toward migratory insertion. Such processes are well-established in the chemistry of osmium thiocarbonyls;^{24,27} e.g., the complex [Os(CPh=CHPh)Cl(CS)(PPh₃)₂] reacts with carbon monoxide to provide the thioacyl species [Os(η²-SCCPh=CHPh)Cl(CO)(PPh₃)₂].³¹ A rapid reaction also ensues between **13** and carbon monoxide to provide a red complex formulated as [Ru(η²-SCCPh=CHPh)(CO)(PPh₃)₂{H₂B(pz)₂}] (**14**). The characteristic ν(CS) absorption was conspicuously absent. Rather, a ν(CO) absorption was visible at 1925 cm⁻¹ (Nujol), suggesting that migratory insertion of the vinyl and thiocarbonyl ligands had taken place. The ¹H NMR spectrum showed typical resonances for the pyrazolyl protons as well as a singlet at 7.11 ppm attributed to the vinylic proton, moved to lower field with respect to **13**, consistent with its new position remote from the ruthenium center. The gross formulation was further confirmed as the monophosphine species **14** by FAB-mass spectroscopic data. Thus, although the formation of the bis(phosphine) monodentate thioacyl species [Ru{η¹-C(=S)CPh=CHPh}(CO)(PPh₃)₂{H₂B(pz)₂}] is plausible, subsequent loss of phosphine allows ruthenium-sulfur bond formation to provide the favorable ruthenathiirene^{19,24,25,32} structural motif. It is worth noting that complexes containing monodentate vinyl thioacyl ligands are unknown for group 8 metal systems.

In recent times a number of ruthenium alkenyl complexes have been found to react with terminal alkynes to provide σ-alkynyl derivatives.³³ For example, Santos and co-workers have reported the conversion of vinyl complexes of the form [Ru(CH=CHR)Cl(CO)L(PPh₃)₂] (L = Me₂Hpz, py) and [Ru(CH=CHR)Cl(CO)L(dppf)] (L = Me₂Hpz, PPh₃) into the acetylide species [Ru(C≡CR)Cl(CO)L(PPh₃)₂]³⁴ and [Ru(C≡CR)Cl(CO)L(dppf)]³⁵ respectively. Presumably, a labile ligand (Me₂Hpz, py, PPh₃) dissociates, leaving a vacant site for oxidative addition of the incoming alkyne, followed by alkene reductive elimination and recoordination of the labile ligand. At first glance, it might appear that the complex [Ru(CH=CHC₆H₄Me-4)(CO)(PPh₃)₂{H₂B(pz)₂}] (**9**) is precluded from such a sequence by virtue of the strong borate chelation. This was, however, found not to be the case: the complex [Ru(C≡CC₆H₄Me-4)(CO)(PPh₃)₂{H₂B(pz)₂}] (**15**) could be isolated in high yield from the reaction of **9** with 4-ethynyltoluene in refluxing tetrahydrofuran. We have recently employed alkynyl mercurials for the facile conversion of metal hydrides

into metal alkynyls,³⁶ and such a process may also be employed for the preparation of **15**. Thus, treating **1** with bis(4-tolylethynyl)mercury in refluxing tetrahydrofuran provides elemental mercury and good yields of **15**. The infrared spectrum (Nujol) proved diagnostic, displaying a ν(C≡C) absorption at 2107 cm⁻¹ and a ν(CO) absorption at 1943 cm⁻¹ in addition to the characteristic fingerprint bands due to the pyrazolyl rings (1320 and 1100 cm⁻¹). The FAB mass spectrum displayed a molecular ion at *m/z* 801 (11% abundance) and a fragmentation for loss of a phosphine at *m/z* 653 (15% abundance). Microanalysis of the chloroform monosolvate was found to agree well with the formulation given above. The γ-hydroxyacetylide species [Ru(C≡CCPh₂-OH)(CO)(PPh₃)₂{H₂B(pz)₂}] (**16**) was also prepared in an identical manner to the tolylalkynyl derivative from **9** and 1,1-diphenyl-2-propynol. Spectroscopic data for **16** were essentially comparable to those for **15**, with the exception that the hydroxyl proton was apparent as a singlet resonance (δ 1.75) in the ¹H NMR spectrum. The ¹³C{¹H} NMR spectrum gave a well-defined triplet at 205.3 (*J*(PC) = 5.1 Hz) ppm for the carbonyl carbon. The acetylenic carbons were observed at 108.2 (C_α, *J*(PC) = 17.3 Hz) and 115.9 ppm (C_β). The FAB mass spectrum contained no molecular ion but gave instead a substantially abundant [M - OH]⁺ peak at *m/z* 991. Dissolution of the colorless complex in deuteriochloroform led to an immediate color change to purple. This protonation by traces of HCl in the deuterated solvent was accomplished on a preparative scale with HBF₄·OEt₂ to give a salt presumed to be [Ru(=C=C=CPh₂)(CO)(PPh₃)₂{H₂B(pz)₂}]BF₄. As with the presumed salt [Ru(=CHCH=CPh₂)(CO)(PPh₃)₂{H₂B(pz)₂}]Cl (**12**), however, difficulties were encountered in isolating the deep purple product. This intense color is characteristic of the chromophore associated with the allenylidene ligand, and a solution infrared spectrum (CH₂Cl₂) revealed two intense bands at 2001 and 1955 cm⁻¹ attributed to ν(CO) and ν(C=C=C) absorptions, respectively. On treatment with potassium hydroxide the purple coloration dispersed to regenerate the precursor alkynyl complex **16** (confirmed by spectroscopy).

Discussion of the Molecular Structure of [Ru(CH=CH₂)(CO)(PPh₃)₂{H₂B(pz)₂}] (10**).** The molecular structure of **10** is shown in Figure 1, and Table 1 contains selected bond lengths and angles for the molecule. The geometry at ruthenium is essentially octahedral with cis interligand angles in the range 84.4(2)–96.3(2)°. The two phosphine ligands are mutually trans with P(1)–Ru–P(2) at 172.05(6)°, this deviation from linearity primarily involving displacement of P(1) away from the BH₂ group. The vinyl ligand is unremarkable, with the Ru–C(1) (2.080(7) Å) and C(1)–C(2) (1.345(11) Å) bond lengths being comparable to those for [Ru(CH=CH₂)(CO)(PPh₃)₂][9]aneS₃]PF₆ ([9]aneS₃ = 1,4,7-trithiacyclononane; 2.097(5) and 1.292(7) Å, respectively).^{20a} There is a noticeable enlargement of the angle at C(1) (131.1(6)°). The vinylic C(1)–C(2) bond is rotated 38° out of the equatorial coordination plane so as to satisfy the steric constraints of the proximal pyrazolyl ring. The extent of rotation, however, is larger than that required purely to satisfy these

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steric restraints. Inspection of intramolecular contacts reveals a stabilizing C–H $\cdots\pi$ interaction between one of the ortho hydrogens of one phosphine phenyl group to the vinylic π -system (H $\cdots\pi$ = 2.57 Å, C–H $\cdots\pi$ = 148°). The ligand of interest in this work is the H₂B-(pz)₂ chelate, which clearly adopts a boat conformation such that B and Ru lie respectively 0.59 and 0.47 Å above the plane defined by the four nitrogen atoms. The two Ru–N bond lengths are very similar (2.178(6), 2.194(5) Å) and, hence, no differential trans influence is manifest for the vinyl and carbonyl ligands. There are no intermolecular contacts of note.

Conclusions

A variety of new dihydridobis(pyrazol-1-yl)borate ruthenium complexes have been described. This has involved a broad range of organometallic functional groups and ligands, including aryl, carbonyl, alkynyl, alkenyl, thiocarbonyl, hydride, and thioacyl coligands. Limited evidence also suggests the formation of alkylidene and allenylidene complexes which are in need of further study. Furthermore, the processes of migratory insertion and alkenyl–alkynyl σ -metathesis (presumably via oxidative-addition/reductive-elimination sequences) have been supported by this ligand. In all

cases the dihydridobis(pyrazol-1-yl)borate ligand was found to adopt a bidentate coordination, although these processes typically involve intermediates of reduced coordination number. It remains to be established whether the facility of these reactions is due to dissociation of one arm of the chelate or whether phosphine dissociation is assisted by the assumption of tridentate coordination of the borate. Such a mode of coordination has been previously demonstrated for the bulkier H₂B-(pzMe₂)₂ ligand.¹⁴

Acknowledgment. We are grateful to the EPSRC (U.K.) for the award of a studentship (to J.D.E.T.W.-E.) and for the financial support of diffractometry facilities. Ruthenium salts were generously provided by Johnson Matthey Ltd. A.F.H. gratefully acknowledges the award of a Senior Research Fellowship by the Leverhulme Trust and The Royal Society.

Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters and an ORTEP drawing for [Ru(CH=CH₂){ η^2 -H₂B(pz)₂}(CO)(PPh₃)₂] (**10**) (8 pages). Ordering information is given on any current masthead page.

OM980374P