Polyazolyl Chelate Chemistry. 7.[1] Reactivity of the Complexes [MCl(PPh$_3$)$_2${HB(pz)$_3$}] (M = Ru, Os; pz = Pyrazol-1-yl)

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The substitution chemistry of the complex [RuCl(PPh$_3$)$_2${HB(pz)$_3$}] (**1**) is reported. Treating **1** with the phosphines bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)-ethane (dppe), or 1,1′-bis(diphenylphosphino)ferrocene (dppf) provides the complexes [RuCl(dppm){HB(pz)$_3$}] (**2**), [RuCl(dppe){HB(pz)$_3$}] (**3**), or [RuCl(dppf){HB(pz)$_3$}] (**4**), respectively. Reactions of **1** with pivaloisonitrile (CNCMe$_3$) are solvent dependent: In neat dichloromethane or tetrahydrofuran the reaction of **1** with CNCMe$_3$ provides the neutral complex [Ru(CNCMe$_3$)Cl(PPh$_3${HB(pz)$_3$}] (**5**), while the salt [Ru(CNCMe$_3$)(PPh$_3$)$_2${HB(pz)$_3$}]PF$_6$ (**6·PF$_6$**) is obtained when the reaction is carried out in dichloromethane/methanol mixtures in the presence of NH$_4$PF$_6$. The reaction of **4** with CNCMe$_3$ and NH$_4$PF$_6$ provides the salt [Ru(CNCMe$_3$)(dppf){HB(pz)$_3$}]PF$_6$ (**7·PF$_6$**). The bis(isonitrile) salt [Ru(CNCMe$_3$)$_2$(PPh$_3${HB(pz)$_3$}]-PF$_6$ (**8·PF$_6$**) results from the reaction of **1**, **5**, or **6·PF$_6$** with excess CNCMe$_3$ in thf/methanol. The reaction of **1** with Na[S$_2$CNMe$_2$] provides the complex [Ru(S$_2$CNMe$_2$)(PPh$_3${HB(pz)$_3$}] (**9**); however similar reaction of **1** or [Ru(NCMe)$_2$(PPh$_3${HB(pz)$_3$}]PF$_6$ with Na[O$_2$CH] failed to cleanly provide [Ru(O$_2$CH)(PPh$_3${HB(pz)$_3$}] (**10**), although this could be characterized spectroscopically. Rather, the ultimate product of these reactions was the hydrido complex [RuH(PPh$_3$)$_2${HB(pz)$_3$}] (**11**), which could also be obtained in high yield from the reaction of **1** with NaOMe. In a similar manner, reaction of **4** with methanolic NaOMe provided [RuH(dppf){HB(pz)$_3$}] (**12**). The reactions of **1** and **4** with alkynes are solvent dependent: Treating **1** with HC≡CR (R = C$_6$H$_4$Me-4, CPh$_2$OH) in thf provides, respectively, the vinylidene complex [RuCl(=C=CHC$_6$H$_4$Me-4)(PPh$_3${HB(pz)$_3$}] (**13**) and the allenylidene complex [RuCl(=C=C=CPh$_2$)(PPh$_3${HB(pz)$_3$}] (**14**), while the reaction of **1** with HC≡CC$_6$H$_4$Me-4 in a mixture of thf and methanol provides the alkynyl complex [Ru(C≡CC$_6$H$_4$Me-4)(PPh$_3$)$_2${HB(pz)$_3$}] (**15**). The reaction of **1** with HC≡CCPh$_2$OH in the presence of AgPF$_6$ provides the allenylidene salt [Ru(=C=C=CPh$_2$)(PPh$_3$)$_2${HB(pz)$_3$}]PF$_6$ (**16·PF$_6$**), and similar treatment of **4** provides [Ru(=C=C=CPh$_2$)(dppf){HB(pz)$_3$}]PF$_6$ (**17·PF$_6$**). The reaction of **4** with HC≡CC$_6$H$_4$Me-4 and AgPF$_6$ provides the vinylidene salt [Ru(=C=CHC$_6$H$_4$Me-4)(dppf){HB(pz)$_3$}]PF$_6$ (**18·PF$_6$**), deprotonation of which (NaOMe) provides [Ru(C≡CC$_6$H$_4$Me-4)(dppf){HB(pz)$_3$}] (**19**). The allenylidene salt (**16·PF$_6$**) with NaOMe provides the γ-alkoxyalkynyl complex [Ru(C≡CCPh$_2$-OMe)(PPh$_3$)$_2${HB(pz)$_3$}] (**20**). The complex [OsCl(PPh$_3$)$_2${HB(pz)$_3$}] (**21**) is obtained from the reaction of [OsCl$_2$(PPh$_3$)$_3$] with K[HB(pz)$_3$] and is converted by KOH in reluxing 2-methoxyethanol to the hydride complex [OsH(PPh$_3$)$_2${HB(pz)$_3$}] (**22**). The vinylidene complex **13** reacts with [Et$_2$NH$_2$][S$_2$CNEt$_2$] to provide the metallacyclic vinyl complex [Ru{C(=CHC$_6$H$_4$-Me-4)SC(NEt$_2$)S}(PPh$_3${HB(pz)$_3$}] (**23**). Similarly the complex **14** and the salt **16·PF$_6$** react with Na[S$_2$CNMe$_2$] to both provide the metallacyclic allenyl complex [Ru{C(=C=CPh$_2$)SC-(NMe$_2$)S}(PPh$_3${HB(pz)$_3$}] (**24**). These reactions represent the first examples of the coupling of dithiocarbamates with vinylidene and allenylidene ligands. The complexes **5** and [RuCl(CS)(PPh$_3${HB(pz)$_3$}] (**25**) and the salt (**16·PF$_6$**) were characterized crystallographically.

Introduction

The development of hydrotris(pyrazolyl)borate chemistry[3] within group 8 has accelerated in recent times.[4−12] In particular the chemistry of divalent ruthenium has received considerable attention including the isolation of "Ru{HB(pz)$_3$}" (pz = pyrazol-1-yl) complexes featuring hydride,[1,4−7] dihydrogen,[5,6] vinyl,[8] aryl,[8] alkyl,[7] thiocar-

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bonyl,[1] vinylidene,[9] triboronate,[10] and very recently allenylidene[11] ligands. We have previously reported the simple preparation (and structural characterization) of the complex $[RuCl(PPh_3)_2\{HB(pz)_3\}]$ (**1**) from the reaction of $[RuCl_2(PPh_3)_3]$ and $K[HB(pz)_3]$.[12] In the interim, undeterred by Simpson's erroneous claim[4] that such a procedure fails to give a well-defined product, other groups have exploited this complex (**1**),[6,7,9,11] demonstrating its utility and prompting us to report the results of our ongoing study of its reactivity. A feature that emerges is the increased reactivity of **1** relative to the well-known and notionally related complex $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$.[13] This may be traced to (i) the increased donor capacity of the $HB(pz)_3$ scorpionate relative to the cyclopentadienyl ligand, which contributes to the lability of the chloride ligand in polar solvents, and (ii) the increased steric profile of the $HB(pz)_3$ ligand relative to $\eta\text{-}C_5H_5$, which favors dissociation of one phosphine ligand. These factors are central to the chemistry that follows. In addition to the syntheses of diphosphine, hydride, alkynyl, vinylidene, and allenylidene complexes, the novel coupling of vinylidene and allenylidene ligands with dithiocarbamate salts is reported, leading to unusual metallacyclic vinyl and allenyl complexes. Aspects of this work have formed the basis of a preliminary report.[11b]

Experimental Section

General Comments. All manipulations were carried out under aerobic, ambient conditions using solvents as received from commercial sources unless otherwise indicated. None of the new compounds showed marked air-sensitivity during workup or subsequent spectroscopic characterization. The complex $[RuCl(PPh_3)_2\{HB(pz)_3\}]$ was prepared according to the published procedure.[12] $[Et_2NH_2][S_2CNEt_2]$ was prepared by the reaction of diethylamine and carbon disulfide in diethyl ether. All other reagents were used as received from commercial sources. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded with a JEOL JNM EX270 NMR spectrometer and calibrated against internal $SiMe_4$ (^1H), internal $CDCl_3$ (^{13}C), or external H_3PO_4 (^{31}P) references. In many cases the signals due to $H^{3,5}$(pz) and $C^{3,5}$(pz) could not be unequivocally differentiated. Although the doublet or triplet multiplicity of the ^1H NMR resonances associated with the pyrazolyl groups were invariably discernible, occasionally these were not resolved at 270 MHz, and accordingly J(HH) values (typically 1.5−2.5 Hz) are not always given. Infrared spectra were recorded both as dichloromethane solutions and Nujol mulls using Perkin-Elmer 1720-X or Mattson Series 1 FT-IR spectrometers. Characteristic "fingerprint" bands for PPh_3 are omitted. FAB-mass spectrometry was carried out using an Autospec Q instrument with 3-nitrobenzyl alcohol as a matrix. Compositional assignments are based on simulation of isotopic distributions; "M" refers to the molecular ion with the exception of salts, for which it refers to the cationic complex. FAB-MS data are reported in the form *m*/*z* (% abundance) [assignment]. Elemental analysis was carried out by the Imperial College Microanalytical Service. In the case of partial solvates, the stoichiometry was confirmed by ^1H NMR integration.

Preparation of [RuCl(dppm){HB(pz)$_3$}] (2). $[RuCl(PPh_3)_2\{HB(pz)_3\}]$ (**1**) (0.30 g, 0.34 mmol) and bis(diphenylphosphino)methane (0.15 g, 0.39 mmol) were degassed under vacuum. Degassed benzene (25 mL) was introduced and the solution heated under reflux for 1 h. The resulting yellow precipitate was filtered and washed with benzene (10 mL) and hexane (10 mL) and dried in vacuo. Yield: 0.14 g (56%). IR CH_2Cl_2: 2468 [ν(BH)] cm^{-1}. Nujol: 2470 [ν(BH)], 1311, 1213, 1114, 1047, 981, 881, 846, 813 cm^{-1}. NMR insufficiently soluble. FAB-MS: 734 (60) $[M]^+$, 699 (31) $[M - Cl]^+$. Anal. Found: C, 56.4; H, 4.3; N, 11.0. $C_{34}H_{32}BClN_6P_2Ru\cdot 0.25C_6H_6$ requires C, 56.6; H, 4.5; N, 11.2.

Preparation of [RuCl(dppe){HB(pz)$_3$}] (3). $[RuCl(PPh_3)_2\{HB(pz)_3\}]$ (**1**) (0.50 g, 0.57 mmol) and 1,2-bis(diphenylphosphino)ethane (0.23 g, 0.58 mmol) were degassed under vacuum. Degassed benzene (50 mL) was added and the solution heated at reflux for 3 h. The resulting yellow/green precipitate was filtered, washed with benzene (15 mL), diethyl ether (15 mL), and hexane (15 mL), and dried in vacuo. Yield: 0.25 g (58%). IR Nujol: 2472 [ν(BH)], 1307, 1213, 1112, 1076, 1045, 979, 917 881, 867, 848, 811 cm^{-1}. NMR insufficiently soluble. FAB-MS: 748 (5) $[M]^+$, 713 (2) $[M - Cl]^+$, 614 (3) $[M - 2pz]^+$, 535 (2) $[M - HB(pz)_3]^+$, 507 (2) $[M - C_2H_4HB(pz)_3]^+$. Anal. Found: C, 55.7; H, 4.3; N, 10.8. $C_{35}H_{34}BClN_6P_2Ru$ requires C, 56.2; H, 4.6; N, 11.2.

Preparation of [RuCl(dppf){HB(pz)$_3$}] (4). $[RuCl(PPh_3)_2\{HB(pz)_3\}]$ (**1**) (0.30 g, 0.34 mmol) and 1,1′-bis(diphenylphosphino)ferrocene (0.19 g, 0.34 mmol) were degassed under vacuum and dissolved in degassed benzene (30 mL), and the solution was heated under reflux for 40 min. The resulting orange solution was taken to dryness and a pale yellow product obtained by ultrasonic trituration in hexane (15 mL). This was washed with diethyl ether (10 mL) and hexane (10 mL) and dried in vacuo. Yield: 0.24 g (77%). This product may be recrystallized from dichloromethane and hexane. IR CH_2Cl_2: 2480 [ν(BH)] cm^{-1}. Nujol: 2491 [ν(BH)], 1307, 1211, 1118, 1043, 981, 887, 838, 813 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ 4.50, 4.54, 4.59 [s × 3, C_5H_4], 4.97 [t, 1 H, H^4(pz), J(HH) = 2.2 Hz], 5.32 [s, 2 H, $H^{3,5}$(pz)], 5.72 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz], 5.84 [t, 2 H, H^4(pz), J(HH) = 2.2 Hz], 6.55−7.30 [m, 20 H, PC_6H_5], 7.35 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz], 7.61 [d, 2 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz] ppm. $^{31}P\{^1H\}$: 35.7 ppm. FAB-MS: 904 (100) $[M]^+$, 869 (83) $[M - Cl]^+$, 835 (8) $[M - pz]^+$, 733 (12) $[M - Cl\text{-}2pz]^+$, 655 (18) $[M - ClHB(pz)_3]^+$, 351 (55) $[M - dppf]^+$. Anal. Found: C, 55.6; H, 4.3; N, 9.4. $C_{43}H_{58}BClFeN_6P_2Ru\cdot 0.33CH_2Cl_2$ requires C, 55.8; H, 4.2; N, 9.0.

Preparation of [RuCl(CN^{t}Bu)(PPh$_3$){HB(pz)$_3$}] (5). $[RuCl(PPh_3)_2\{HB(pz)_3\}]$ (**1**) (0.20 g, 0.22 mmol) was degassed under vacuum and dissolved in degassed tetrahydrofuran (10 mL). Pivaloisocyanide ($CNCMe_3$, 0.05 mL, 0.04 g, 0.44 mmol) was added, and the reaction heated under reflux for 1 h. Ethanol (10 mL) was then added and a pale yellow solid precipitated by rotary evaporation. The product was filtered, washed with ethanol (10 cm^3) and petroleum ether (10 cm^3),

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and dried. Yield: 0.10 g (62%). The product can be recrystallized from dichloromethane and ethanol. IR CH_2Cl_2: 2483 [ν(BH)], 2115 [ν(CN)] cm^{-1}. Nujol: 2473 [ν(BH)], 2117 [ν(CN)], 1497, 1407, 1398, 1313 1248, 1208, 1114, 1045, 982, 924, 878, 847, 818, 789 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 1.40 [s, 9 H, CH_3], 5.66, 5.83, 6.15 [t × 3, 3 × 1 H, H^4(pz), J(HH) = 2.3 Hz], 6.20, 6.83 [d × 2, 2 × 1 H, $H^{3,5}$(pz), J(HH) = 2.0 Hz], 7.58, 7.63 [d × 2, 2 × 1 H, $H^{3,5}$(pz), J(HH) = 2.5 Hz], 7.20−7.44 [m, 15 H, PC_6H_5], 7.54, 7.99 [d × 2, 2 × 1 H, $H^{3,5}$(pz), J(HH) = 0.99 Hz] ppm. ^{13}C{^{1}H}: δ 161.6 [m, CN, J(PC) = unresolved], 145.7, 143.7, 142.5 [s × 3, 3 × C^3(pz)], 135.7, 134.7 [s × 2, 2 × C^5(pz)], 134.3 [d, $C^{2,3,5,6}(C_6H_5)$, J(PC) = 9.0 Hz], 135−127 [1 × C^5(pz) + $C^1(C_6H_5)$], 129.7 [s, $C^4(C_6H_5)$], 127.6 [d, $C^{2,3,5,6}(C_6H_5)$, J(PC) = 8.9 Hz], 105.1, 105.3 [s × 2, 3 × C^4(pz)], 56.8 [s, $NCMe_3$], 31.2 [s, CH_3] ppm. ^{31}P{^{1}H}: 50.5 ppm. FAB-MS: 695 (100) $[M]^+$, 660 (92) $[M - Cl]^+$, 576 (23) $[M - ClCN^tBu]^+$, 507 (3) $[M - ClCN^tBu\text{-}pz]^+$, 431 (6) $[M - ClCN^tBuHB(pz)_2]^+$, 314 (12) $[Ru - HB(pz)_3]^+$. Anal. Found: C, 53.9; H, 4.7; N, 13.9. $C_{32}H_{34}BClN_7PRu\cdot 0.25CH_2Cl_2$ requires C, 54.1; H, 4.9; N, 13.7. The complex was also characterized crystallographically (vide infra).

Preparation of [Ru(CN^{t}Bu)(PPh$_3$)$_2${HB(pz)$_3$}]PF$_6$ (6·PF$_6$). [RuCl(PPh$_3$)$_2${HB(pz)$_3$}] (**1**) (0.30 g, 0.34 mmol) and NH_4PF_6 (0.12 g, 0.74 mmol) were degassed under vacuum and dissolved in degassed dichloromethane (10 mL) and methanol (10 mL). The solution was treated with $CNCMe_3$ (0.05 mL, 0.04 g, 0.44 mmol) and stirred for 2 h. The solution was taken to dryness and the crude product dissolved in dichloromethane (15 mL) and passed through diatomaceous earth. The filtrate was freed of solvent in vacuo, and a colorless product was obtained by ultrasonic trituration in diethyl ether (25 mL). This was washed with diethyl ether (10 mL) and petroleum ether (10 mL) and dried in vacuo. Yield: 0.25 g (68%). Recrystallization from a mixture of dichloromethane and ether provided the dichloromethane monosolvate confirmed by ^{1}H NMR integration. IR CH_2Cl_2: 2489 [ν(BH)], 2132 [ν(NC)] cm^{-1}. Nujol: 2487 [ν(BH)], 2130 [ν(NC)], 1646, 1587, 1309, 1230, 1211, 1124, 1051, 985, 921, 840 [PF_6^-] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 1.49 [s, 9 H, CH_3], 5.39 [d, 1 H, $H^{3,5}$(pz)], 5.42 [t, 1 H, H^4(pz)], 5.73 [t, 2 H, H^4(pz)], 6.31 [d, 2 H, $H^{3,5}$(pz), J(HH) = 1.7 Hz], 6.88−7.35 [m, 30 H, C_6H_5], 7.59 [d, 2 H, $H^{3,5}$(pz), J(HH) = 2.0 Hz], 7.70 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz] ppm. ^{31}P{^{1}H}: 43.4 ppm. FAB-MS: 922 (27) $[M]^+$, 660 (100) $[M - PPh_3]^+$, 604 (6) $[M - CMe_3PPh_3]^+$, 363 (6) $[RuPPh_3]^+$. Anal. Found: C, 52.8; H, 4.2; N, 8.4. $C_{50}H_{49}BF_6N_7P_3Ru\cdot CH_2Cl_2$ requires C, 53.2; H, 4.5; N, 8.5.

Preparation of [Ru(CN^{t}Bu)(dppf){HB(pz)$_3$}]PF$_6$ (7·PF$_6$). [RuCl(dppf){HB(pz)$_3$}] (**4**) (0.30 g, 0.33 mmol) was dissolved in dichloromethane (10 mL) and treated with $AgPF_6$ (0.16 g, 0.63 mmol), causing the color of the solution to become deep green. Pivaloisocyanide ($CNCMe_3$, 0.08 mL, 0.06 g, 0.72 mmol) was added and the reaction stirred for 1 h. The suspension was filtered through a plug of diatomaceous earth, and all solvent were removed from the filtrate. The crude product was triturated ultrasonically in diethyl ether (25 mL) to give a yellow solid, which was filtered off, washed with diethyl ether (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.30 g (95%). This product may be recrystallized from chloroform and diethyl ether to provide a chloroform monosolvate. IR CH_2Cl_2: 2485 [ν(BH)], 2210 [ν(NC)] cm^{-1}. Nujol: 2480 [ν(BH)], 1307, 1213, 1133, 1114, 1085, 981, 836 [PF_6^-] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 1.53 [s, 9 H, CH_3], 4.31, 4.42, 4.57, 5.02 [s × 4, 8 H, C_5H_4], 5.85 [t, 1 H, H^4(pz), J(HH) = 2.0 Hz], 5.95 [t, 2 H, H^4(pz), J(HH) = 2.1 Hz], 6.68 [d, 2 H, $H^{3,5}$-(pz), J(HH) = 1.5 Hz], 6.22, 6.86, 7.12, 7.57 [m × 4, 20 H, C_6H_5], 7.40 [s, 1 H, $H^{3,5}$(pz)], 7.78 [d, 2 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz], 7.91 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz] ppm. ^{31}P{^{1}H}: 40.8 ppm. FAB-MS: 952 (100) $[M]^+$, 869 (2) $[M - CN^tBu]^+$, 733 (4) $[M - CN^tBu\text{-}2pz]^+$. Anal. Found: C, 47.9; H, 4.0; N, 8.1. $C_{48}H_{47}BF_6FeN_7P_3Ru\cdot CHCl_3$ requires C, 48.4; H, 4.1; N, 8.3.

[Ru(CN^{t}Bu)$_2$(PPh$_3$){HB(pz)$_3$}]ClO$_4$/PF$_6$ (8·PF$_6$/ClO$_4$). (a) [RuCl(CN^{t}Bu)(PPh$_3$)$_2${HB(pz)$_3$}] (**5**) (0.25 g, 0.36 mmol) was dissolved in dichloromethane (10 mL) and $AgClO_4$ (0.25 g, 1.2 mmol) added. The solution was stirred for 30 min and then all solvent removed. The residue was dissolved in dichloromethane (10 cm^3) and the AgCl removed by filtration through diatomaceous earth. The filtrate was then treated with pivaloisonitrile (0.08 mL, 0.059 g, 0.71 mmol) and stirred for 1 h. All volatiles were then removed and the residual solid triturated in hexane (25 mL) in an ultrasound bath. The colorless product was filtered off, washed with hexane (10 mL) and diethyl ether (10 mL), and dried in vacuo. Yield: 0.30 g (99%). (b) [RuCl(PPh$_3$)$_2${HB(pz)$_3$}] (**1**) (0.30 g, 0.34 mmol) was dried in vacuo, dissolved in degassed tetrahydrofuran (20 mL), and heated at reflux with pivaloisonitrile (0.04 cm^3, 0.03 g, 0.35 mmol) for 20 min. A solution of NH_4PF_6 (0.11 g, 0.68 mmol) dissolved in degassed methanol (10 mL) was then added along with further pivaolisonitrile (0.08 mL, 0.06 g, 0.71 mmol) and the solution heated under reflux for a further hour until colorless. All solvent was then removed and the crude product dissolved in chloroform (25 mL) and filtered through diatomaceous earth. The filtrate was freed of solvent and a colorless product obtained by ultrasonic trituration in hexane (25 mL). This was washed with hexane (20 mL) and dried in vacuo. Yield: 0.26 g (86%). The product can be recrystallized from dichloromethane and hexane. IR CH_2Cl_2: 2493 [ν(BH)], 2169, [ν(CN)], 2134 [ν(CN)] cm^{-1}. Nujol: 2494 [ν(BH)], 2247, 2171 [ν(CN)], 2132 [ν(CN)], 1501, 1408, 1397, 1310, 1237, 1204, 1090 [ClO_4^-], 985, 928, 899, 845, 816, 790 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 1.42 [s, 18 × 9 H, CH_3], 5.94 [apparent "q" (t × 2), 2 H, H^4(pz), J(HH) = 2.2 Hz], 6.28 [s, 1 H, H^4(pz)], 6.59 [s, 2 H, $H^{3,5}$(pz)], 7.0−7.7 [m, 15 H + 2 H, PC_6H_5 + 2$H^{3,5}$(pz)], 7.73 [s, 2 H, $H^{3,5}$(pz)] ppm. ^{13}C{^{1}H}: δ 149.1, [d(br), CN, J(PC) = 19.2 Hz], 144.0, 142.4, 142.2 [s × 3, 3 × C^3(pz)], 136.4, 136.3, 135.6 [s × 3, 3 × C^5(pz)], 133.4 [d, $C^{2,6}(C_6H_5)$, J(PC) = 8.9 Hz], 131.5 [d, $C^1(C_6H_5)$, J(PC) = 46.4 Hz], 130.8 [s, $C^4(C_6H_5)$], 128.6 [d, $C^{3,5}(C_6H_5)$], 106.5 [s, C^4(pz)], 106.3 [s, 2C^4(pz)], 58.5, 58.2 [s × 2, 2 × $NCMe_3$], 30.6, 29.8 [s × 2, 2 × CH_3] ppm. ^{31}P{^{1}H}: 47.6 ppm. FAB-MS: 743 (100) $[M]^+$, 660 (7) $[M - CN^tBu]^+$, 576 (3) $[M - 2CN^tBu]^+$, 481 (18) $[M - PPh_3]^+$, 315 (9) $[M - 2CN^tBuPPh_3]^+$. Anal. Found: C, 52.6; H, 4.3; N, 13.9. $C_{37}H_{43}BClN_8O_4PRu$ requires C, 52.8; H, 5.2; N, 13.3.

Preparation of [Ru(S$_2$CNMe$_2$)(PPh$_3$){HB(pz)$_3$}] (9). [RuCl(PPh$_3$)$_2${HB(pz)$_3$}] (**1**) (0.30 g, 0.34 mmol) and sodium dimethyldithiocarbamate (0.24 g, 1.3 mmol) were degassed under vacuum and dissolved in a degassed mixture of tetrahydrofuran (20 mL) and methanol (10 mL). The solution was stirred and heated at reflux for 50 min. The solution was taken to dryness and the crude product dissolved in dichloromethane (10 mL) and methanol (10 mL). Yellow/orange crystals precipitated on slow rotary evaporation and were filtered off and washed with methanol (15 mL) and hexane (10 mL) and dried in vacuo. Yield: 0.18 g (75%). The product can be recrystallized from dichloromethane/diethyl ether mixtures as an ether solvate; however, the crystals partially desolvate on attempted drying. IR CH_2Cl_2: 2478 [ν(BH)] cm^{-1}. Nujol: 2485 [ν(BH)], 1398, 1384, 1309, 1263, 1209, 1116, 1041, 1017, 869, 811 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 3.07 [s, 6 H, CH_3], 5.75 [t, 2 H, H^4(pz), J(HH) = 2.1 Hz], 6.18 [t, 1 H, H^4(pz), J(HH) = 2.0 Hz], 6.74 [d, 2 H, $H^{3,5}$(pz), J(HH) = 1.7 Hz], 7.15−7.34 [m, 16 H, C_6H_5 + $H^{3,5}$(pz)], 7.66 [d, 2 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz], 7.80 [d, 1 H, $H^{3,5}$(pz), J(HH) = 1.7 Hz] ppm. ^{31}P{^{1}H}: 58.8 ppm. FAB-MS: 697 (12) $[M]^+$, 575 (2) $[M - S_2CNMe_2]^+$, 435 (11) $[M - PPh_3]^+$, 371 (11) $[M - pz\text{-}PPh_3]^+$. Anal. Found: C, 52.5; H, 4.4; N, 13.1. $[C_{30}H_{34}N_7PRuS_2]\cdot 0.33(C_2H_5)_2O$ requires C, 52.2; H, 4.8; N, 13.6.

Preparation of [Ru(O$_2$CH)(PPh$_3$){HB(pz)$_3$}] (10). [RuCl-(PPh$_3$)$_2${HB(pz)$_3$}] (**1**) (0.30 g, 0.34 mmol) and sodium formate (0.09 g, 1.33 mmol) were degassed under vacuum and dissolved in a degassed mixture of dichloromethane (20 mL) and methanol (10 mL). The solution was stirred and heated gently for 20 min. All solvent was evaporated, the crude product was

dissolved in dichloromethane (10 mL) and passed through diatomaceous earth, and hexane (30 mL) was added to the filtrate. The green/yellow product that precipitated was filtered, washed with hexane (20 mL), and dried in vacuo. Yield: 0.15 g (71%). Attempts to purify the crude product resulted in slow decomposition. IR CH_2Cl_2: 2478 [ν(BH)] 1612 [ν(OCO)] cm^{-1}. Nujol: 2468 [ν(BH)], 1621, 1608 [ν(OCO)], 1500, 1409, 1376, 1305, 1213, 1120, 1045, 981, 921, 889, 850 cm^{-1}. NMR ($CDCl_3$, 25 °C) $^{31}P\{^1H\}$: 66.0 ppm. FAB-MS: 839 (41) $[(\mathbf{11})]^+$, 622 (21) $[M]^+$, 576 (100) $[M - CO_2]^+$.

Preparation of [RuH(PPh$_3$)$_2${HB(pz)$_3$}] (11). Sodium metal (0.20 g, 8.70 mmol) was added to degassed methanol (30 mL) under nitrogen and the solution stirred for 20 min. [RuCl(PPh$_3$)$_2${HB(pz)$_3$}] (1.00 g, 1.15 mmol) was added and the solution heated under reflux for 3 h. A bright yellow precipitate was filtered from the solution, washed with methanol (15 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.70 g (73%). IR Nujol: 2447 [ν(BH)], 2007 [ν(RuH)], 1585, 1571, 1496, 1405, 1394, 1301, 1211, 1116, 1043, 973, 919, 844 cm^{-1}. ^1H and ^{31}P NMR data were indentical to those reported previously for **11** prepared via an alternative route.[7]

Preparation of [RuH(dppf){HB(pz)$_3$}] (12). [RuCl(dppf)-{HB(pz)$_3$}] (**4**) (0.20 g, 0.22 mmol) was added to a solution of sodium methoxide prepared by dissolving sodium metal (0.1 g) in degassed methanol (15 mL). The suspension was heated under reflux for 4 h and the yellow precipitate filtered, washed with methanol (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.16 g (83%). This product may be recrystallized from dichloromethane/methanol mixtures. IR CH_2Cl_2: 2462 [ν(BH)], 1984 [ν(RuH)], 1972 cm^{-1}. Nujol: 2456 [ν(BH)], 2024 [ν(RuH)], 1309, 1297, 1268, 1230, 1209, 1189, 1157, 1120, 1089, 1041, 1024, 998, 970, 923, 881, 842, 815 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ −14.71 [t, 1 H, RuH, J(HH) = 29.7 Hz], 4.15, 4.19, 4.28, 4.57 [s × 4, 8 H, C_5H_4], 5.59 [s, 2 H, H^4(pz)], 5.71 [s, 1 H, H^4(pz)], 6.64 [s, 2 H, $H^{3,5}$(pz)], 6.98−7.24 [m, 15 H + 1 H, PC_6H_5 + $H^{3,5}$(pz)], 7.44 [d, 2 H, $H^{3,5}$(pz)], 7.58 [d, 1 H, $H^{3,5}$(pz)] ppm. $^{31}P\{^1H\}$: 65.0 ppm. FAB-MS: 869 (100) $[M]^+$, 802 (7) $[M - pz]^+$, 733 (11) $[M - 2pz]^+$, 655 (7) $[M - HB(pz)_3]^+$. Anal. Found: C, 58.6; H, 4.2; N, 10.2. $C_{43}H_{59}BFeN_6P_2Ru$ requires C, 58.1; H, 6.7; N, 9.5.

Preparation of [RuCl(=C=CHC$_6$H$_4$Me-4)(PPh$_3$){HB(pz)$_3$}] (13). [RuCl(PPh$_3$)$_2${HB(pz)$_3$}] (**1**) (1.20 g, 1.37 mmol) was degassed under vacuum and dissolved in degassed tetrahydrofuran (10 mL). 4-Ethynyltoluene (0.70 mL, 0.64 g, 5.52 mmol) was added and the reaction stirred for 36 h. All solvent was removed from the red solution, the crude product was dissolved in dichloromethane (5 mL), and diethyl ether (30 mL) was added to precipitate the pale red complex. This was filtered, washed with diethyl ether (20 mL) and hexane (20 mL), and dried in vacuo. Yield: 0.75 g (75%). IR CH_2Cl_2: 2487 [ν(BH)], 1972, 1637 [ν(C=C)] cm^{-1}. Nujol: 2476 [ν(BH)], 1965, 1637 [ν(C=C)], 1606, 1506, 1309, 1214, 1155, 1116, 1047, 983, 887, 842, 815 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ 2.33 [s, 3 H, CH_3], 4.89 [d, 1 H, C=CH, J(HP) = 4.0 Hz], 5.73, 5.90 [t × 2, 2 × 1 H, H^4(pz), J(HH) = 2.0 Hz], 5.94 [m, 1 H, H^4(pz)], 6.08 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2 Hz], 6.73 [d, 1 H, $H^{3,5}$(pz), J(HH) = 1.7 Hz], 6.96, 7.01 [$(AB)_2$, 4 H, C_6H_4, J(AB) = 8.28 Hz], 7.17 [d, 1 H, $H^{3,5}$(pz), J(HH) = 1.7 Hz], 7.16−7.55 [m, 15 H, PC_6H_5], 7.61 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz], 7.65 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.0 Hz], 7.85 [d, 1 H, $H^{3,5}$(pz), J(HH) = 1.5 Hz] ppm. $^{13}C\{^1H\}$: δ 370.0 [d, Cα, J(PC) = 19.4 Hz], 145.0 [s, C^3(pz)], 143.5 [s, 2 × C^3(pz)], 136.5, 134.2 [s × 2, 2 × C^5(pz)], 134.8 [d, $C^{2,3,5,6}(C_6H_5)$, J(PC) = 9.7 Hz], 132.2 [d, $C^1(C_6H_5)$, J(PC) = 45.3 Hz], 129.9 [s, $C^4(C_6H_5)$], 129.4 [s, $C^{2,3,5,6}(C_6H_4)$], 128.0 [d, $C^{2,3,5,6}$-(C_6H_5), J(PC) = 9.7 Hz], 126.6 [s, $C^{1,4}(C_6H_5)$], 126.0 [s, $C^{2,3,5,6}$-(C_6H_4)], 112.0 [s, Cβ], 105.9, 105.8, 105.6 [s × 3, 3 × C^4(pz)], 65.9 [$C^1(C_6H_4)$], 21.3 [s, CH_3] ppm. $^{31}P\{^1H\}$: 37.6 ppm. FAB-MS: 729 (13) $[M]^+$, 693 (15) $[M - Cl]^+$, 612 (100) $[M - HCCR]^+$, 576 (100) $[M - ClHCCR]^+$. Anal. Found: C, 58.8; H, 4.1; N, 11.2. $C_{36}H_{33}BClN_6PRu$ requires C, 59.4; H, 4.6; N, 11.5.

Preparation of [RuCl(=C=C=CPh$_2$)(PPh$_3$){HB(pz)$_3$}] (14). [RuCl(PPh$_3$)$_2${HB(pz)$_3$}] (0.35 g, 0.40 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.24 g, 1.15 mmol) were degassed under vacuum and dissolved in degassed tetrahydrofuran (25 mL). The reaction was heated at reflux for 4 h. All solvent was removed, the crude product was dissolved in dichloromethane (5 mL), and hexane was added (10 mL). The solvent volume was reduced to ca. 5 mL by rotary evaporation and this solution stored at −20 °C for 18 h. The resulting purple precipitate was filtered off, washed with cold hexane (10 mL), and dried in vacuo. Yield: 0.21 g (66%). IR CH_2Cl_2: 2483 [ν-(BH)], 1920 [ν(C=C=C)] cm^{-1}. Nujol: 2476 [ν(BH)], 1914 [ν-(C=C=C)], 1718, 1587, 1309, 1278, 1213, 1116, 1047, 983, 925, 889, 846, 815 cm^{-1}. NMR ($CDCl_3$, 25°C) ^1H: δ 5.69 [t, 1 H, H^4(pz), J(HH) = 2.2 Hz], 5.84 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.0 Hz], 6.09 [t, 1 H, H^4(pz), J(HH) = 2.0 Hz], 6.16 [t, 1 H, H^4(pz), J(HH) = unresolved], 7.04 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.0 Hz], 7.15−7.89 [m, 15 H + 10 H + 4 H, PC_6H_5 + C_6H_5 + $H^{3,5}$(pz)] ppm. $^{13}C\{^1H\}$: δ 313.6 [d, Cα, J(PC) = 22.7 Hz], 230.6 [s, Cβ], 146.4 [s, 2 × C^3(pz)], 146.3 [s, CPh_2], 144.7 [s, C^3(pz)], 143.5 [d, $C^1(PC_6H_5)$, J(PC) = 28.1 Hz], 136.3 [s, C^5(pz)], 134.9 [d, $C^{2,3,5,6}(PC_6H_5)$, J(PC) = 8.6 Hz], 134.4−126.1 [$C^4(PC_6H_5)$ + C_6H_5 + 2C^5(pz)], 127.9 [d, $C^{2,3,5,6}(PC_6H_5)$, J(PC) = 9.7 Hz], 106.0 [s, C^4(pz)], 105.4 [s, 2 × C^4(pz)] ppm. $^{31}P\{^1H\}$: 38.1 ppm. FAB-MS: 1029 (36) $[Ru\{HB(pz)_3\}(C_3Ph_2)(PPh_3)_2]^+$, 802 (43) $[M]^+$, 767 (100) $[M - Cl]^+$, 699 (11) $[M - Cl\text{-}pz]^+$, 633 (16) $[M - Cl\text{-}2pz]^+$, 576 (60) $[M - ClC_3Ph_2]^+$, 553 (43) $[M - ClHB(pz)_3]^+$, 540 (17) $[M - PPh_3]^+$. Anal. Found: C, 63.6; H, 4.6; N, 8.1. $C_{42}H_{35}BClN_6PRu\cdot 0.25C_6H_{14}$ requires C, 63.4; H, 4.7; N, 10.2.

Preparation of [Ru(C≡CC$_6$H$_4$Me-4)(PPh$_3$)$_2${HB(pz)$_3$}] (15). [RuCl(PPh$_3$)$_2${HB(pz)$_3$}] (**1**) (0.50 g, 0.57 mmol) was degassed under vacuum and dissolved in a degassed mixture of tetrahydrofuran (10 mL) and methanol (20 mL). The solution was treated with 4-ethynyltoluene (0.30 mL, 0.27 g, 2.29 mmol) and the reaction heated at reflux for 4 h. The resulting yellow precipitate was filtered off, washed with methanol (20 mL) and hexane (20 mL), and dried in vacuo. Yield: 0.21 g (39%). The product can be recrystallized from a mixture of dichloromethane and methanol as the dichloromethane hemisolvate as indicated by ^1H NMR integration. IR CH_2Cl_2: 2476 [ν(BH)], 2075 [ν(C≡C)] cm^{-1}. Nujol: 2462 [ν(BH)], 2069 [ν(C≡C)], 1305, 1213, 1122, 1112, 1045, 979, 921, 844, 815 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ 2.33 [s, 3 H, CH_3], 4.5 [s(br), 1 H, BH], 5.57 [t, 1 H, H^4(pz)], 5.65 [t, 2 H, H^4(pz)], 6.86 [d, 2 H, $H^{3,5}$(pz)], 6.94−7.36 [m, 34 H, C_6H_5 + C_6H_4], 7.43 [d, 1 H, $H^{3,5}$(pz), J(HH) = 1.7 Hz], 7.51 [d, 2 H, $H^{3,5}$(pz), J(HH) = 2.0 Hz], 7.55 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.0 Hz] ppm. ^{13}C: 148.5 (1 × C), 145.6 [t^v, $C^1(C_6H_5)$ J(PC) = 18.3 Hz], 145.3 (2 × C) [C^3(pz)], 135.7, 135.4, 135.2, 135.0, 130.5 128.6 [C_6H_4 + C^5-(pz), unequivocal assignments not attempted], 134.6 [t^v, $C^{2,6}$-(C_6H_5)], 128.8 [$C^4(C_6H_5)$], 127.5 [t^v, $C^{3,5}(C_6H_5)$], 111.0 [Cβ], 105.1 (2C) [C^4(pz)], 104.9 (1 × C) [C^4(pz)], 104.6 [t, RuC≡, J(PC) = 20.5 Hz], 21.4 [CH_3] ppm. $^{31}P\{^1H\}$: 42.6 ppm. FAB-MS: 954 (4) $[M]^+$, 874 (8) $[M - pz\text{-}BH]^+$, 839 (20) $[M - CCR]^+$, 692 (6) $[M - PPh_3]^+$, 612 (32) $[M - pz\text{-}BHPPh_3]^+$, 576 (41) $[M - CCRPPh_3]^+$. Anal. Found: C, 65.4; H, 4.9; N, 8.4. $C_{54}H_{47}BN_6P_2Ru\cdot 0.5CH_2Cl_2$ requires C, 65.7; H, 4.9; N, 8.4.

Preparation of [Ru(=C=C=CPh$_2$)(PPh$_3$)$_2${HB(pz)$_3$}]-PF$_6$ (16·PF$_6$). [RuCl(PPh$_3$)$_2${HB(pz)$_3$}] (**1**) (0.35 g, 0.40 mmol) and $AgPF_6$ (0.20 g, 0.79 mmol) were degassed under vacuum, and dichloromethane (20 mL) was added. The reaction was stirred for 25 min and 1,1-diphenyl-2-propyn-1-ol (0.23 g, 1.11 mmol) added. The reaction was stirred for a further 3 h and then filtered through diatomaceous earth to remove precipitated AgCl. All solvent was removed, the crude product was dissolved in dichloromethane (3 mL), and hexane (35 mL) was added in order to precipitate the purple salt. This was washed with hexane (30 mL) and dried. Yield: 0.42 g (89%). The product can be recrystallized from chloroform/hexane mixtures as a chloroform solvate. IR CH_2Cl_2: 2489 [ν(BH)], 1943 [ν(C=C=C)] cm^{-1}. Nujol: 2487 [ν(BH)], 1941 [ν(C=C=C)], 1587,

1309, 1284, 1211, 1126, 1051, 1022, 982, 921, 840 [PF_6^-] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ 5.59 [t, 2 H, H^4(pz)], 5.64 [t, 1 H, H^4(pz), J(HH) = 2.1 Hz], 5.68 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.0 Hz], 6.10 [d, 2 H, $H^{3,5}$(pz)], 6.91−7.71 [m, 42 H, C_6H_5 + 2$H^{3,5}$-(pz)], 7.88 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.0 Hz] ppm. $^{13}C\{^1H\}$: δ 316.6 [t, C_α, J(PC) = 17.8 Hz], 208.9 [s, C^β], 160.9 [s, CPh_2], 146.5 [s, C^3(pz)], 145.0 [s, 2 × C^3(pz)], 144.2 [s, C_6H_5], 137.0 [s, 2 × C^5(pz)], 136.7 [s, C^5(pz)], 133.8 [s, $C^{3,5}(PC_6H_5)$], 132.7 [s, $C^4(PC_6H_5)$], 132.3−129.5 [$C^1(PC_6H_5)$ + CC_6H_5], 128.4 [$C^{2,6}$-(PC_6H_5), J(PC) = 4.3 Hz], 106.8 [s, C^4(pz)], 105.8 [s, 2 × C^4-(pz)] ppm. $^{31}P\{^1H\}$: 36.6 ppm. FAB-MS: 1029 (34) $[M]^+$, 839 (4) $[M - C_3Ph_2]^+$, 767 (100) $[M - PPh_3]^+$, 699 (11) $[M - pz\text{-}PPh_3]^+$, 631 (14) $[M - 2pz\text{-}PPh_3]^+$, 577 (30) $[M - C_3Ph_2PPh_3]^+$, 553 (24) $[M - HB(pz)_3PPh_3]^+$. Anal. Found: C, 56.3; H, 4.2; N, 6.2. $C_{60}H_{50}BF_6N_6P_3Ru\cdot CHCl_3$ requires C, 56.7; H, 4.0; N, 6.5. The salt was also characterized crystallographically (vide infra).

Preparation of [Ru(=C=C=CPh$_2$)(dppf){HB(pz)$_3$}]PF$_6$ (17·PF$_6$). [RuCl(dppf){$HB(pz)_3$}] (**4**) (0.25 g, 0.28 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.17 g, 0.82 mmol) were degassed under vacuum along with $AgPF_6$ (0.14 g, 0.55 mmol) and then dissolved in degassed tetrahydrofuran (15 mL). The reaction was stirred for 40 min, the color of the solution becoming an intense purple. All solvent was removed, the crude product was dissolved in dichloromethane and passed through diatomaceous earth, and the filtrate volume was concentrated to ca. 10 mL. Hexane was slowly added, and the purple solid that precipitated was filtered off, washed with hexane (10 mL), and dried in vacuo. Yield: 0.35 g (99%). IR CH_2Cl_2: 2491 [ν(BH)], 1940 [ν(C=C=C)] cm^{-1}. Nujol: 2487 [ν(BH)], 1936 [ν(C=C=C)], 1587, 1309, 1213, 1124, 1083, 1051, 998, 840 [PF_6^-] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ 4.79, 4.81, 4.85, 5.12 [s × 4, 8 H, C_5H_4], 5.42 [t, 1 H, H^4(pz), J(HH) = 2.2 Hz], 5.77 [t, 2 H, H^4-(pz), J(HH) = 2.1 Hz], 6.08 [d, 2 H, $H^{3,5}$(pz), J(HH) = 1.7 Hz], 6.39 [d, 1 H, $H^{3,5}$(pz), J(HH) = 1.7 Hz], 6.43−7.74 [m, 32 H, C_6H_5 + 2$H^{3,5}$(pz)], 7.60 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz] ppm. $^{13}C\{^1H\}$: δ 316.2 [t, C_α, J(PC) = 17.3 Hz], 208.3 [s, C_β], 161.3 [s, CPh_2], 145.0 [s, C^3(pz)], 144.4 [s, 2 × C^3(pz)], 137.2 [s, 2 × C^5(pz)], 135.4 [s, C^5(pz)], 134.9 [$C^1(PC_6H_5)$, J(PC) = 22.7 Hz], 132.5 [$C^{3,5}(PC_6H_5)$], 131.0−129.5 [C_6H_5 + $C^4(PC_6H_5)$], 128.2 [$C^{2,6}(PC_6H_5)$], 106.6 [s, C^4(pz)], 106.1 [s, 2 × C^4(pz)], 75.4, 75.0, 73.8, 70.7 [s × 4, C_5H_4] ppm. $^{31}P\{^1H\}$: 30.2 ppm. FAB-MS: 1059 (100) $[M]^+$, 869 (12) $[M - C_3Ph_2]^+$, 845 (3) $[M - HB(pz)_3]^+$, 655 (11) $[M - C_3Ph_2HB(pz)_3]^+$. Anal. Found: C, 57.6; H, 3.8; N, 6.7. $C_{58}H_{48}BF_6FeN_6P_3Ru$ requires C, 57.9; H, 4.0; N, 7.0.

Preparation of [Ru(=C=CHC$_6$H$_4$Me-4)(dppf){HB(pz)$_3$}]-PF$_6$ (18·PF$_6$). [RuCl(dppf){$HB(pz)_3$}] (**4**) (0.50 g, 0.55 mmol) was dried under vacuum and dissolved in degassed tetrahydrofuran (30 mL). Silver hexafluorophosphate (0.28 g, 1.11 mmol) was added and the reaction stirred for 20 min until the color of solution had darkened considerably. 4-Ethynyltoluene (0.20 mL, 0.18 g, 1.55 mmol) was added by syringe and the reaction heated at reflux for 1 h under nitrogen. After cooling, the suspension was filtered through a plug of diatomaceous earth and the dark red filtrate taken to dryness by rotary evaporation. The crude product was triturated ultrasonically in diethyl ether (25 mL) to give a green solid, which was filtered, washed with diethyl ether (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.53 g (85%). IR CH_2Cl_2: 2493 [ν(BH)], 2003, 1982, 1639, 1604 [ν(C=C)] cm^{-1}. Nujol: 2489 [ν(BH)], 1639 [ν(C=C)], 1600, 1309, 1214, 1162, 1120, 1085, 1051, 1000, 985, 840 [PF_6^-] cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: low resolution due to inseparable paramagnetic contaminants prevented useful data from being acquired. $^{31}P\{^1H\}$: 29.8 ppm. FAB-MS: 985 (12) $[M]^+$, 915 (3) $[M - pz]^+$, 869 (4) $[M - CCHTol]^+$, 771 (3) $[M - HB(pz)_3]^+$, 655 (6) $[M - CCHTol\text{-}HB(pz)_3]^+$.

Preparation of [Ru(C≡CC$_6$H$_4$Me-4)(dppf){HB(pz)$_3$}] (19). [Ru(=C=CHC$_6$H$_4$Me-4)(dppf){$HB(pz)_3$}]PF_6 (**18·PF$_6$**) (0.20 g, 0.18 mmol) was added to a solution of NaOMe generated in situ by reaction of sodium (0.1 g, excess) with methanol (15 mL). The reaction was stirred for 1 h, and the resulting precipitate was filtered off, redissolved in dichloromethane (10 mL), and diluted with methanol (15 mL). Slow concentration by rotary evaporation provided brick-red crystals, which were washed with cold methanol (1 mL) and hexane (5 mL) and dried in vacuo. Yield: 0.11 g (63%). The product is sparingly soluble in methanol, and a further crop of crystals could be obtained by concentration of the filtrate. The complex could be recrystallized from a mixture of dichloromethane and hexane as a dichloromethane monosolvate, as indicated by ^1H NMR integration. IR CH_2Cl_2: 2476 [ν(BH)], 2075 [ν(C≡C)] cm^{-1}. Nujol: 2460 [ν(BH)], 2071 [ν(C≡C)], 1992, 1606, 1502, 1307, 1226, 1211, 1160, 1120, 1085, 1043, 979, 887, 836, 813 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ 2.16 [s, 3 H, CH_3], 4.43, 4.49, 4.55 [s × 3, C_5H_4], 5.12 [t, 1 H, H^4(pz), J(HH) = 2.1 Hz], 5.78 [t, 2 H, H^4(pz), J(HH) = 2.1 Hz], 5.83 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.0 Hz], 6.56 [m, 4 H, C_6H_4], 6.53−7.32 [m, 22 H, C_6H_5 + 2$H^{3,5}$(pz)], 7.38 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz], 7.55 [t, 2 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz] ppm. $^{31}P\{^1H\}$: 41.1 ppm. FAB-MS: 984 (41) $[M]^+$, 868 (9) $[M - CCR]^+$, 772 (4) $[M - HB(pz)_3]^+$, 655 (3) $[M - CCRHB(pz)_3]^+$. Anal. Found: C, 59.3; H, 4.4; N, 7.7. $C_{53}H_{45}BFeN_6P_2Ru\cdot CH_2Cl_2$ requires C, 59.6; H, 4.4; N, 7.9.

Preparation of [Ru(C≡CCPh$_2$OMe)(PPh$_3$)$_2${HB(pz)$_3$}] (20). [Ru(=C=C=CPh$_2$)(PPh$_3$)$_2${$HB(pz)_3$}]PF_6 (**16·PF$_6$**) (0.20 g, 0.17 mmol) was added to a solution of sodium metal (0.1 g) in methanol (10 mL), and an instant reaction was observed. The mixture was stirred for 30 min, resulting in the formation of a red precipitate. The crude product was filtered off and redissolved in dichloromethane (10 mL), and methanol (10 mL) was added. Slow reduction in solvent volume caused the precipitation of a brick-red product. This was filtered off, washed with methanol (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.12 g (66%). The product can be recrystallized from chloroform and ethanol as a chloroform solvate, as indicated by ^1H NMR integration. IR CH_2Cl_2: 2468 [ν(BH)], 2061 [ν(C≡C)] cm^{-1}. Nujol: 2460 [ν(BH)], 2061 [ν(C≡C)], 1955, 1664, 1307, 1211, 1170, 1122, 1043, 979, 933, 887, 846, 813 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ 3.23 [s, 3 H, OCH_3], 4.5 [s(br), 1 H, BH], 5.13 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.0 Hz], 5.31 [t, 1 H, H^4(pz), J(HH) = 2.2 Hz], 5.57 [t, 2 H, H^4(pz), J(HH) = 2.2 Hz], 6.90 [d, 2 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz], 6.81−7.62 [m, 41 H, C_6H_5 + $H^{3,5}$(pz)], 7.46 [d, 2 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz] ppm. $^{31}P\{^1H\}$: 48.5 ppm. FAB-MS: 1060 (1) $[M]^+$, 1029 (5) $[M - OMe]^+$, 839 (4) $[M - CCR]^+$, 813 (3) $[M - OMeHB(pz)_3]^+$, 797 (6) $[M - PPh_3]^+$, 783 (8) $[M - MePPh_3]^+$, 766 (70) $[M - OMePPh_3]^+$, 699 (12) $[M - OMe\text{-}pz\text{-}HB(pz)_3]^+$, 631 (11) $[M - OMe\text{-}2pz\text{-}HB(pz)_3]^+$, 576 (100) $[M - CCRPPh_3]^+$, 554 (84) $[M - OMeHB(pz)_3PPh_3]^+$, 506 (12) $[M - PhHB(pz)_3PPh_3]^+$, 476 (29) $[M - OMePhHB(pz)_3PPh_3]^+$. Anal. Found: C, 56.7; H, 3.6; N, 6.1. $C_{61}H_{53}BN_6OP_2Ru\cdot 2.5CHCl_3$ requires C, 56.2; H, 4.1; N, 6.2.

Preparation of [OsCl(PPh$_3$)$_2${HB(pz)$_3$}] (21). [$OsCl_2$-$(PPh_3)_3$] (0.60 g, 0.57 mmol) and K[$HB(pz)_3$] (0.17 g, 0.68 mmol) were dissolved in degassed dichloromethane (10 mL) and stirred for 40 min. The yellow/green solution was passed through diatomaceous earth and all solvent evaporated. The crude product was triturated ultrasonically in diethyl ether (25 mL), and the yellow product filtered, washed with diethyl ether (20 cm^3) and hexane (20 cm^3), and dried. The product could be recrystallized from a mixture of dichloromethane and hexane. Yield: 0.43 g (78%). IR CH_2Cl_2: 2481 [ν(BH)] cm^{-1}. Nujol: 2466 [ν(BH)], 1305, 1213, 1157, 1120, 1043, 981, 919, 887, 846, 815 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^1H: δ 4.5 [s(br), 1 H, BH], 5.13 [t + d, 2 H, H^4(pz) + $H^{3,5}$(pz), J(HH) = 2.4 Hz], 5.63 [t, 2 H, H^4(pz), J(HH) = 2.1 Hz], 6.80 [d, 2 H, $H^{3,5}$(pz), J(HH) = 1.7 Hz], 6.97−7.16 [m, 30 H, PC_6H_5], 7.45 [d, 2 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz], 7.47 [d, 1 H, $H^{3,5}$(pz), J(HH) = 2.2 Hz] ppm. $^{31}P\{^1H\}$: −7.5 ppm. FAB-MS: 964 (38) $[M]^+$, 929 (41) $[M - Cl]^+$, 715 (3) $[M - ClHB(pz)_3]^+$, 702 (100) $[M - PPh_3]^+$, 666 (74) $[M - ClPPh_3]^+$, 633 (5) $[M - pz\text{-}PPh_3]^+$, 598 (6) $[M - Cl$-

pz-PPh_3]$^+$. Anal. Found: C, 55.9; H, 4.2; N, 8.7. $C_{45}H_{40}BClN_6OsP_2$ requires C, 56.1; H, 4.2; N, 8.7.

Preparation of [OsH(PPh_3)$_2${HB(pz)$_3$}] (22). Potassium hydroxide (1 pellet) and [OsCl(PPh_3)$_2${HB(pz)$_3$}] (**21**) (0.15 g, 0.16 mmol) were added to degassed 2-methoxyethanol (5 mL) under nitrogen, and the mixture was heated under reflux for 20 min to give a yellow solution. The solvent was removed in vacuo at 60 °C. The residue was extracted with dichloromethane, and the combined extracts were filtered through diatomaceous earth to remove potassium salts. The filtrate was concentrated to ca. 5 mL and then diluted with ethanol (10 mL). Slow concentration (rotary evaporator) provided pale yellow crystals. Yield: 0.10 g (69%). IR CH_2Cl_2: 2476 [ν(BH)], 2030 [ν(OsH)] cm^{-1}. Nujol: 2483 [ν(BH)], 2024 [ν(OsH)], 1585, 1307, 1216, 1207, 1120, 1043, 875 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ −15.61 [t, 1 H, J(P$_2$H) = 18.5 Hz, OsH], 5.46 [, 2 H, H^4(pz), J(HH) = 2.0 Hz], 5.71 [t, 1 H, H^4(pz), J(HH) = 2.0 Hz], 6.27 [d, 1 H, H^{3,5}(pz)], 6.81 [d, 1 H, H^{3,5}(pz)], 6.92−7.69 [m, 34 H, H^{3,5}(pz) = C_6H_5] ppm. ^{31}P{^{1}H}: 17.3 ppm. FAB-MS: 930 (53) [M]$^+$, 666 (36) [M − PPh_3]$^+$.

Preparation of [Ru{C(=CHC$_6$H$_4$Me-4)S$_2$CNEt$_2$}(PPh_3)-{HB(pz)$_3$}] (23). [RuCl(=C=CHC$_6$H$_4$Me-4)(PPh_3){HB(pz)$_3$}] (0.20 g, 0.28 mmol) was dissolved in tetrahydrofuran (10 mL) and treated with [Et_2NH_2][S_2CNEt_2] (0.12 g, 0.54 mmol), and the reaction was stirred for 1.5 h, during which time the solution became bright yellow. All solvent was removed and the crude product triturated ultrasonically in ethanol (10 mL) to provide a yellow complex. This was filtered off, washed with ethanol (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.09 g (40%). The product can be recrystallized from chloroform and ethanol as a chloroform partial solvate. IR Nujol: 2464 [ν(BH)], 1529, 1349, 1309, 1265, 1213, 1147, 1114, 1074, 1043, 977, 921, 865, 844, 813 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 1.0 [s(br), 6 H, NCCH_3], 2.36 [s, 3 H, CH_3], 3.3 [s(br), 4 H, NCH_2], 4.2 [s(br), 1 H, BH], 5.88, 5.91, 6.08 [t × 3, 3 × 1 H, H^4(pz), J(HH) = not resolved], 6.10 [s, 1 H, CH=C], 6.63 [d, 1 H, H^{3,5}(pz), J(HH) = not resolved], 7.11−7.30 [m, 15 H + 4 H + 2 H, PC_6H_5 + C_6H_4 + H^{3,5}(pz)], 7.62 [d, 1 H, H^{3,5}(pz), J(HH) = not resolved], 7.73 [d, 1 H, H^{3,5}(pz), J(HH) = 1.7 Hz], 7.77 [d, 1 H, H^{3,5}(pz), J(HH) = 1.7 Hz] ppm. ^{13}C{^{1}H}: δ 206.0 [s, S_2C], 173.2 [d, C$_\alpha$, J(PC) = 11.9], 144.8, 144.6, 142.1 [s × 3, 3 × C^3(pz)], 135.5, 135.3, 135.0 [s × 3, 3 × C^5(pz)], 134.5 [d, C^{2,6}-(C_6H_5), J(PC) = 9.7], 127.2 [d, C^{3,5}(C_6H_5), J(PC) = 8.6 Hz], 138.3−128.2 [C_6H_4 + C=CH + C^4(C_6H_5) + C^1(C_6H_5)], 105.1 (2C) [C^4(pz)], 104.7 (1C) [C^4(pz)], 52.5, 47.1 [s(br) × 2, CH_2], 21.2 [$C_6H_4CH_3$], 12.1 [s, 2 × CH_2CH_3] ppm. ^{31}P{^{1}H}: 58.6 ppm. FAB-MS: m/z (%) = 841 (75) [M]$^+$, 577 (14) [M − PPh_3]$^+$, 463 (100) [M − C=C$HC_6H_4MePPh_3$]$^+$, 630 (4) [M − S_2CNMe_2-PPh_3]$^+$. Anal. Found: C, 53.9; H, 4.5; N, 10.4. Calcd for $C_{41}H_{43}$-BN_7PRuS_2·0.75$CHCl_3$: C, 53.9; H, 4.7; N, 10.5.

Preparation of [Ru{C(=C=CPh$_2$)S$_2$CNMe$_2$}(PPh_3){HB-(pz)$_3$}] (24). [RuCl(=C=C=CPh$_2$)(PPh_3){HB(pz)$_3$}] (0.30 g, 0.37 mmol) and Na[S_2CNMe_2] (0.11 g, 0.78 mmol) were dissolved in tetrahydrofuran (15 mL). The reaction was heated at reflux for 2 h to give a yellow solution. All solvent was removed and the product dissolved in dichloromethane (5 mL) and hexane (10 mL). The solvent volume was reduced in vacuo to ca. 5 mL, and during cooling for 10 h at −20 °C, crystals formed. These were filtered off, washed with cold hexane (2 mL), and dried in vacuo. Yield: 0.25 g (75%). IR Nujol: 2458 [ν(BH)], 1951, 1594, 1307, 1261, 1211, 1114, 1043, 979, 919, 887, 846 cm^{-1}. NMR ($CDCl_3$, 25 °C) ^{1}H: δ 3.26 [s, 6 H, CH_3], 4.6 [s(br), 1 H, BH], 5.67, 5.88, 5.91, 5.94, 6.09, 6.67, 7.66, 7.70, 7.73 [s × 9, 9 × 1 H, H^{3,4,5}(pz), J(HH) = not resolved], 6.74−7.45 [m, 15 H + 10 H, PC_6H_5 + C_6H_5] ppm. ^{13}C{^{1}H}: δ 207.9 [s, S_2C], 201.2 [s, C$_\alpha$], 145.8, 145.0 [s × 2, 2 × C^3(pz)], 141.9 [d, C^3(pz), J(PC)= 3.2], 140.8 [s, C$_\beta$], 135.9, 135.4, 135.0 [s × 3, C^5(pz)], 134.3 [d, C^{2,6}(PC_6H_5), J(PC) = 9.7], 130.2 [C^4-(PC_6H_5)], 127.7 [d, C^1(PC_6H_5), J(PC) = 18.3], 127.1 [d, C^{3,5}-(PC_6H_5), J(PC) = 8.6 Hz], 124.6−134.8, 118.5 [C_6H_5 + CPh_2], 105.7 [d, C^4(pz), J(PC) = 6.5 Hz], 105.1, 104.9 [C^4(pz)], 45.5 [s(br), CH_3] ppm. ^{31}P{^{1}H}: 56.2 ppm. FAB-MS: m/z (%) = 887 (15) [M]$^+$, 767 (3) [M − S_2CNMe_2]$^+$, 625 (17) [M − PPh_3]$^+$, 433 (3) [M − $C_3Ph_2PPh_3$]$^+$. Anal. Found: C, 58.3; H, 4.8; N, 10.4. Calcd for $C_{45}H_{26}BN_7PRuS_2$·0.5CH_2Cl_2: C, 58.8; H, 4.6; N, 10.6.

Crystallographic Analyses. Table 1 provides a summary of the crystal data and data collection and refinement parameters for **5**, **16·PF$_6$**, and **25**. The structures were solved by direct methods and were refined by full-matrix least-squares based on F^2. The partial occupancy solvent molecule in **16·PF$_6$** was found to be distributed over two sites, and in **25** an 80:20 exchange disorder was found in the positions of the chlorine atom and the thiocarbonyl group: in each case only the major occupancy non-hydrogen atoms were refined anisotropically. The remaining non-hydrogen atoms in all three structures were refined anisotropically. In all three structures the pendant phenyl rings were refined as optimized rigid bodies and the hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, U(H) = 1.2U_{eq}(C/B) [U(H) = 1.5U_{eq}(C−Me)], and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system (version 5.03, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1994).

The crystallographic data (excluding structure factors) for the structures reported in Table 1 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-116639, -116640, and -116641. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB12 1EZ, U.K. (Fax Int. code +(1223)336-033; e-mail teched@chemcrys.cam.ac.uk). Selected bond lengths and angles are given in Tables 2, 3, and 4 for compounds **5**, **16·PF$_6$**, and **25**, respectively.

Results and Discussion

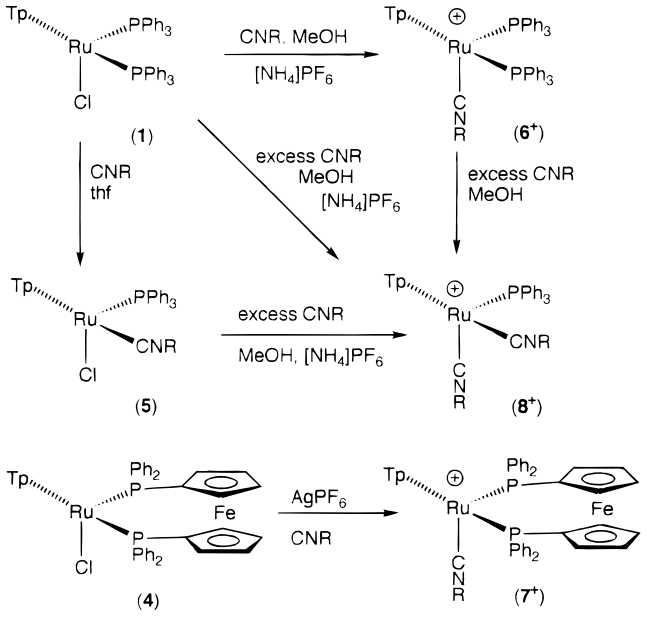
Reactions with Diphosphines. The steric encumbrance associated with the hydrotris(pyrazolyl)borate ligand can be expected to labilize one or both of the triphenylphosphine ligands in **1**. The related complex [RuCl(PPh_3)$_2$(η-C_5H_5)] reacts with a variety of phosphines when heated in toluene under reflux.[13] The reactions of **1** with a range of chelating diphosphines were therefore investigated and found to proceed under somewhat milder conditions. Thus the reaction of **1** with bis(diphenylphosphino)methane (dppm) was found to be complete within 1 h in refluxing benzene. Unfortunately, the complex proved too insoluble for useful NMR data to be obtained, although the gross formulation as [RuCl(dppm){HB(pz)$_3$}] (**2**) was confirmed by FAB-mass spectrometry, which revealed a molecular ion (60%) in addition to fragmentation due to loss of the chloride ligand (31%). In a similar manner the reaction of **1** with 1,2-bis(diphenylphosphino)ethane (dppe) provided the sparingly soluble complex [RuCl(dppe){HB(pz)$_3$}] (**3**). Due to the insolubility of both **2** and **3**, a more soluble derivative was sought for subsequent chemistry. The reaction of **1** with 1,1′-bis(diphenylphosphino)ferrocene (dppf) was therefore investigated and found to proceed within 40 min in refluxing benzene to provide the complex [RuCl(dppf){HB(pz)$_3$}] (**4**) in 77% yield. This complex was considerably more soluble and accordingly more completely characterized, spectroscopically. The base peak for the FAB-mass spectrum was attributable to the molecular ion, in addition to a major fragmentation (83%) due to loss of the halide. The ^{1}H NMR spectrum of **4** included two triplets [δ 4.97, 5.84] in the intensity ratio of 1:2 due to the H^4(pz) protons, reflecting the time-averaged plane of symmetry within the molecule. This was further indicated by the appearance of

Table 1. Crystal Data, Data Collection, and Refinement Parameters[a]

data	5	16·PF_6	25
formula	$C_{32}H_{34}N_7BPClRu$	$C_{60}H_{50}N_6BP_2Ru\cdot PF_6$	$C_{28}H_{25}N_6BPSClRu$
solvent		$0.75Et_2O$	
fw	695.0	1229.4	655.9
color, habit	orange/yellow blocks	deep red tabular prisms	yellow prismatic needles
cryst size/mm	0.40 × 0.33 × 0.13	0.73 × 0.38 × 0.33	0.83 × 0.37 × 0.10
cryst syst	monoclinic	triclinic	monoclinic
space group symbol, number	$P2_1/c$, 14	$P\bar{1}$, 2	$C2/c$, 15
cell dimensions			
a/Å	9.918(1)	12.643(4)	31.881(4)
b/Å	16.581(2)	16.112(2)	9.6809(2)
c/Å	19.807(2)	16.515(2)	18.591(2)
α/deg		94.72(1)	
β/deg	96.88(1)	101.70(2)	94.11(1)
γ/deg		111.63(1)	
V/Å^3	3233.8(6)	3016(1)	5723(1)
Z	4	2	8
D_c/g cm^{-3}	1.427	1.354	1.523
F(000)	1424	1263	2656
radiation used	Mo Kα	Mo Kα	Cu Kα
μ/mm^{-1}	0.65	0.40	6.74
θ range/deg	2.1−25.0	1.8−25.0	2.8−60.0
no. of unique reflections			
measured	5687	10577	4247
observed, $\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$	4700	8956	4059
abs corr	semiempirical		semiempirical
max., min. transmission	0.82, 0.77		0.12, 0.02
no. of variables	352	663	329
R_1[b]	0.036	0.039	0.066
wR_2[c]	0.089	0.115	0.182
weighting factors a, b[d]	0.046, 1.494	0.079, 0.369	0.094, 29.331
largest diff peak, hole/e Å^{-3}	0.39, −0.29	0.64, −0.30	0.82, −0.90

[a] Details in common: graphite-monochromated radiation, ω-scans, Siemens P4/PC diffractometer, 293 K, refinement based on F^2. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \sqrt{\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}}$. [d] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Scheme 1. Reactions with Isonitriles (R = CMe_3)



a singlet resonance (35.7 ppm) in the $^{31}P\{^1H\}$ NMR spectrum. It is noteworthy that in the syntheses of compounds **2**−**4** the reactions proceed under considerably milder conditions than those of the cyclopentadienyl analogues.

Reactions with Isonitriles (Scheme 1). Bruce has shown that the reactions of [$RuCl(PPh_3)_2(\eta$-$C_5H_5)$] with pivaloisonitrile ($CNCMe_3$) proceed in refluxing toluene or xylene to provide [$RuCl(CNCMe_3)(PPh_3)(\eta$-$C_5H_5)$].[14]

(14) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1981**, *34*, 209.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex [$RuCl(CNCMe_3)(PPh_3)\{HB(pz)_3\}$] (5)

Bond Lengths

Ru−C(1)	1.920(3)	Ru−Cl(7)	2.4257(9)	C(1)−N(2)	1.153(4)
Ru−N(8)	2.114(3)	Ru−N(13)	2.080(3)	Ru−N(18)	2.118(3)
Ru−P(24)	2.3447(8)	N(2)−C(3)	1.448(4)		

Interbond Angles

Ru−C(1)−N(2)	174.6(3)	N(18)−Ru−P(24)	173.31(7)
N(13)−Ru−P(24)	91.32(7)	N(8)−Ru−P(24)	91.08(7)
C(1)−Ru−Cl(7)	89.15(10)	C(1)−Ru−P(24)	93.74(9)
C(1)−Ru−N(13)	92.77(12)	C(1)−Ru−N(18)	90.83(12)
N(8)−Ru−N(13)	89.88(10)	N(13)−Ru−N(18)	83.56(10)
N(8)−Ru−N(18)	84.62(10)	C(1)−N(2)−C(3)	170.8(4)

[a] Angle sum of N_x−Ru−N_y − 270° = −11.9°.

In contrast, the reaction of **1** with $CNCMe_3$ in dichloromethane at room temperature is complete within 10 h at room temperature to provide [$RuCl(CNCMe_3)(PPh_3)\{HB(pz)_3\}$] (**5**). More conveniently, heating **1** and $CNCMe_3$ in refluxing thf provides **5** in 62% yield within 1 h. The infrared spectrum of **5** features an intense absorption due to the single isonitrile ligand at 2115 cm^{-1} (CH_2Cl_2), while the ^{13}C NMR spectrum includes a multiplet resonance at 161.6 ppm due to the isonitrile carbon. The chirality at ruthenium is reflected in the appearance of three resonances (145.7, 143.7, and 142.5 ppm) due to the C^3(pz) carbons of the chemically distinct pyrazolyl rings, and this is also apparent in the ^1H NMR spectrum of **5**, wherein three triplet resonances (δ 5.66, 5.83, and 6.15, J(HH) = 2.3 Hz) are observed for the H^4(pz) protons. The complex **5** was characterized crystallographically, and the results are summarized in Tables 1 and 2 and Figure 1 and are discussed below.

As in the case of [$RuCl(PPh_3)_2(\eta$-$C_5H_5)$], an alternative mode of ligand substitution is available to **1**, i.e., that

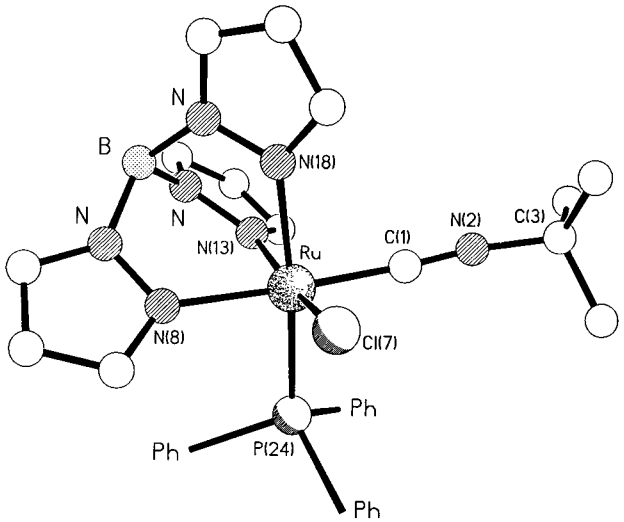


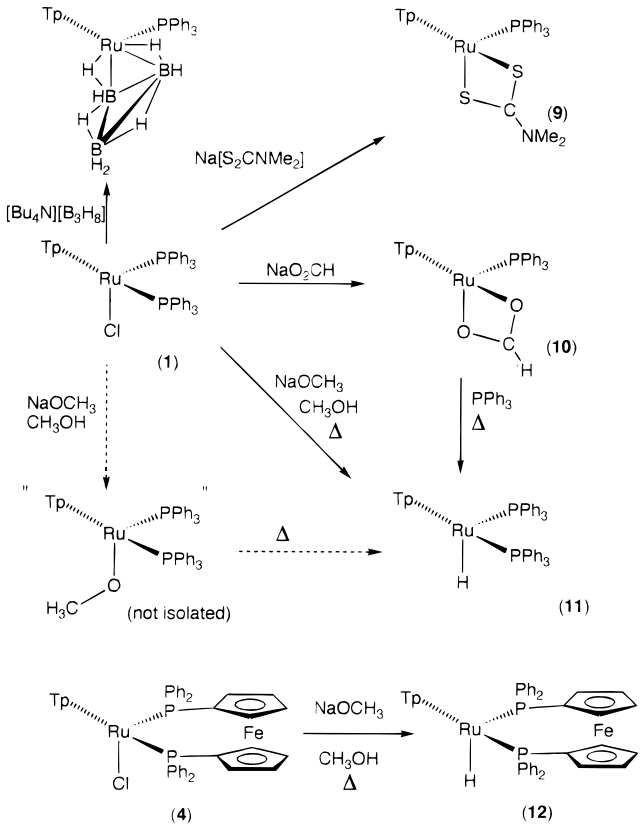
Figure 1. Molecular geometry of [RuCl(CNCMe$_3$)(PPh$_3$)-{HB(pz)$_3$}] (**5**). Phenyl groups omitted for clarity.

involving ionization of the ruthenium chloride bond. This is favored by polar solvents, and the reaction of **1** with CNCMe$_3$ in a mixture of dichloromethane and methanol in the presence of NH_4PF_6 provides the salt [Ru(CNCMe$_3$)(PPh$_3$)$_2${HB(pz)$_3$}]PF$_6$ (**6·PF$_6$**). The gross formulation follows from the appearance of an intense molecular ion for the cationic complex, in addition to fragmentations due to loss of PPh$_3$ and isobutene. The infrared absorption for the isonitrile ligand appears at 2132 cm^{-1} (CH_2Cl_2) to slightly higher frequency of that for **5**. The formulation is further confirmed by the appearance of corresponding pyrazolyl resonances in the ^{1}H NMR spectrum in the intensity ratio of 1:2, indicating the presence of a molecular plane of symmetry. The chloride ligand of **4** is also labile and readily replaced by CNCMe$_3$ to provide the salt [Ru(CNCMe$_3$)(dppf){HB(pz)$_3$}]PF$_6$ (**7·PF$_6$**). A bis(isonitrile) complex [Ru(CNCMe$_3$)$_2$(PPh$_3$){HB(pz)$_3$}]PF$_6$ (**8·PF$_6$**) may be obtained from the reaction of the monoisonitrile complex **5** with excess CNCMe$_3$ in dichloromethane/methanol mixtures, or alternatively it may be obtained directly from **1** with an excess of isonitrile and NH_4PF_6 in tetrahydrofuran/methanol mixtures. The cis disposition of the two isonitriles (imposed by the geometric constraints of the facial HB(pz)$_3$ ligand) is indicated by the appearance of two isonitrile absorbances [2169, 2134 cm^{-1} (CH_2Cl_2)] in the infrared spectrum of **8·PF$_6$** and one doublet ^{13}C NMR resonance [149.1 ppm, J(PC) = 13.6 Hz] for the isonitrile carbon and a single resonance for the methyl resonance at 1.42 ppm in the ^{1}H NMR spectrum.

Reactions with Bidentate Anions (Scheme 2). We have previously shown that **1** provides an entry into ruthenatetraboranes via reaction with [Bu$_4$N][B$_3$H$_8$].[10] The reactions of other potentially chelating anions were briefly investigated. First, simple halide and phosphine replacement occurs on treating **1** with Na[S$_2$CNMe$_2$] to provide the expected dithiocarbamate complex [Ru(S$_2$CNMe$_2$)(PPh$_3$){HB(pz)$_3$}] (**9**). The symmetrical nature of the dithiocarbamate coordination is reflected in the appearance of a singlet resonance (δ 3.07 ppm) due to the NMe$_2$ group and the 1:2 intensity ratios of the respective pyrazolyl resonances in the ^{1}H NMR spectrum.

The reaction of **1** with sodium formate was next

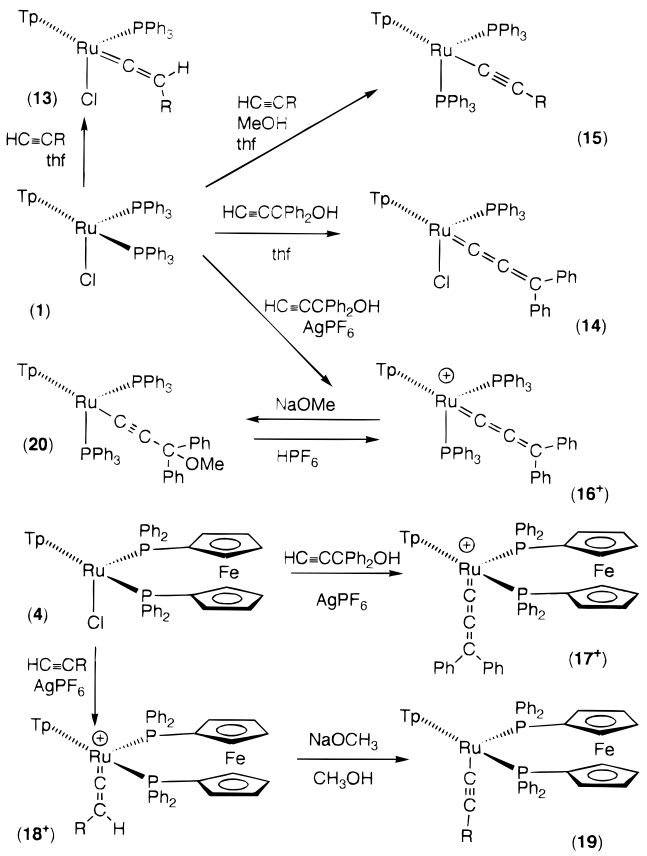
Scheme 2. Reactions with Anions



investigated in the hope of preparing the complex [Ru(O$_2$CH)(PPh$_3$){HB(pz)$_3$}] (**10**). Jia has recently described the synthesis and reactivity of the hydrido complexes [RuH(PPh$_3$)(L){HB(pz)$_3$}] [L = PPh$_3$ (**11**), NCMe] derived from **1** via reaction with NaBH$_4$.[6] The reactivity of the two hydrido complexes differs due to the different labilities of the ligands L. We envisaged that the formato complex **10** could serve as a "masked" version of the coordinatively unsaturated complex "RuH(PPh$_3$){HB(pz)$_3$}" by virtue of the often facile thermal decarboxylation of bidentate formato ligands. An example of such a process is the formation of [RuHCl(CS)(PPh$_3$)$_3$] from the reaction of [RuCl(O$_2$CH)(CS)(PPh$_3$)$_2$] with triphenylphosphine described by Roper.[15] Indeed such a decarboxylation proved to be particularly facile, complicating the preparation of **10** from **1**. A slow reaction ensues at room temperature in dichloromethane/methanol mixtures to provide a complex formulated as [Ru(O$_2$CH)(PPh$_3$){HB(pz)$_3$}] (**10**) in 71% yield; however, the compound is thermolabile and difficult to purify. In a similar manner the reaction of [Ru(NCMe)$_2$(PPh$_3$){HB(pz)$_3$}]PF$_6$[7] with sodium formate also leads to impure samples of **10**. While the FAB-mass spectrum features an isotope pattern attributable to the molecular ion (21%), the base peak corresponds to decarboxylation and a further pattern is observed due to formation in the matrix of **11** (41%). The bidentate formato ligand gives rise to infrared absorbances at 1608 and 1500 cm^{-1}. Heating **10** in the presence of triphenylphosphine leads to smooth formation of **11**. In a similar manner, heating **1** in the presence of triphenylphosphine and sodium formate provides good yields of **11**, greatly simplifying

(15) Brothers, P. J.; Roper, W. R. *J. Organomet. Chem.* **1983**, *258*, 73.

Scheme 3. Reactions with Alkynes (R = C_6H_4Me-4)



its preparation. An alternative preparation of **13** was however developed based on the reaction of **1** with methanolic sodium methoxide: Heating **1** in methanolic suspension with excess sodium methoxide for 3 h results in formation of **13** in 73% isolated yield. The mechanism whereby a metal chloride is metathesized to a hydride by basic alcohols is usually thought to involve β-metal-hydride elimination from an alkoxide intermediate. The formation of **11** from **1**, which has a labile phosphine, is therefore unremarkable, other than for its convenience. It is however somewhat surprising that a similar reaction ensues readily between **4** and methanolic sodium methoxide to provide [RuH(dppf){HB(pz)$_3$}] (**12**). A vacant coordination site is presumed to be required cis to the putative methoxide ligand, and we had not expected either of the ligands dppf or HB(pz)$_3$ to dissociate a chelate under these comparatively mild conditions. The spectroscopic data for **12** are generally unremarkable other than for the appearance of a high-field triplet resonance at δ −14.71 ppm showing coupling to the two chemically equivalent phosphorus nuclei of the chelating diphosphine [J(HH) = 29.7 Hz].

Reactions with Alkynes (Scheme 3). Perhaps the most significant field to emerge from the chemistry of the complex [RuCl(PPh$_3$)$_2$(η-C$_5$H$_5$)] is that of vinylidenes and allenylidenes.[16] Bruce has comprehensively investigated the reactions of terminal alkynes (HC≡CR) with this complex and shown that depending on the conditions employed, alkynyl complexes [Ru(C≡CR)(PPh$_3$)$_2$(η-C$_5$H$_5$)],[17,18] vinylidene complexes [RuCl(=C=CHR)(PPh$_3$)(η-C$_5$Me$_5$)],[19] or salts [Ru(=C=CHR)(PPh$_3$)$_2$(η-C$_5$H$_5$)]PF$_6$[17,18] may be obtained, and these compounds have been central to the development of the chemistry of vinylidenes.[16] Furthermore, Selegue has shown that propargylic alcohols are dehydrated by the complex [RuCl(PMe$_3$)$_2$(η-C$_5$H$_5$)] to provide the allenylidene salt [Ru(=C=C=CPh$_2$)(PMe$_3$)$_2$(η-C$_5$H$_5$)]PF$_6$.[20] Such dehydration processes of 1-propynols by divalent ruthenium complexes have subsequently become the focus of much recent attention.[21−25] It therefore seemed reasonable to anticipate a similar chemistry for the "Ru{HB(pz)$_3$}" fragment.

During our studies, Kirchner reported the reaction of **1** with ethynylbenzene, which provided the neutral vinylidene complex [RuCl(=C=CHPh)(PPh$_3$){HB(pz)$_3$}].[9] We have similarly obtained the complex [RuCl(=C=CHC$_6$H$_4$Me-4)(PPh$_3$){HB(pz)$_3$}] (**13**), which is completely analogous to Kirchner's complex. In the case of 1,1-diphenylpropynol, however, rather than the vinylidene complex [RuCl(=C=CHCPh$_2$OH)(PPh$_3$){HB(pz)$_3$}], the allenylidene complex [RuCl(=C=C=CPh$_2$)(PPh$_3$){HB(pz)$_3$}] (**14**) is obtained. Despite the rapid recent growth in the chemistry of ruthenium allenylidenes, the majority of complexes are cationic, and neutral examples remain rare.[25] Although this intensely colored species forms in spectroscopically quantitative yield, the isolated yields are frustratingly lower (ca. 66%) due to its high solubility in all organic solvents. The compound gives rise to a strong infrared absorption at 1914 cm^{-1}, typical of the allenylidene ligand. Carbon-13 resonances attributable to the carbon nuclei α [313.6 ppm, J(PC) = 22.7 Hz] and β [230.6 ppm] to the ruthenium were clearly identified; however that due to the γ-carbon was not unambiguously differentiated from those due to the pyrazolyl and phenyl carbons. For comparative purposes, Table 5 collects carbon-13 and infrared data for complexes of the form [RuCl(CA)(PPh$_3$){HB(pz)$_3$}] (A = O, S, NR, CHR, CCPh$_2$). The FAB-mass spectrum included an isotope pattern attributable to the molec-

(16) For reviews on the chemistry of vinylidenes and allenylidenes, see: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem*. **1983**, *22*, 59. (b) Bruce, M. I. *Chem. Rev*. **1991**, *91*, 197. (c) Bruce, M. I. *Pure Appl. Chem*. **1990**, *62*, 1021. (d) For a recent review of the chemistry of these ligands bound to divalent ruthenium, see: Hill, A. F. In *Comprehensive Organometallic Chemistry II*, Vol. 7; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995.

(17) Bruce, M. I.; Swincer, A. G. *Aust. J. Chem*. **1980**, *33*, 1471.

(18) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem*. **1979**, *32*, 1471.

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Complex [RuCl(CS)(PPh$_3$){HB(pz)$_3$}] (25)[a]

Bond Lengths					
Ru−C	1.768(11)	Ru−Cl	2.430(2)	C−S	1.569(11)
Ru−N(1)	2.096(6)	Ru−N(6)	2.103(6)	Ru−N(11)	2.182(6)
Ru−P	2.373(2)				

Interbond Angles			
Ru−C−S	170.2(6)	N(6)−Ru−P	175.1(2)
C−Ru−Cl	87.9(13)	C−Ru−P	95.1(3)
C−Ru−N(6)	88.0(3)	C−Ru−N(11)	171.5(3)
N(6)−Ru−Cl	87.3(2)	N(1)−Ru−N(6)	84.5(2)
N(6)−Ru−N(11)	84.8(2)	N(1)−Ru−N(11)	87.2(2)

[a] Angle sum of N_x−Ru−N_y − 270° = −13.5°.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for the Complex [Ru(C═C═CPh$_2$)(PPh$_3$)$_2$){HB(pz)$_3$}] (16$^+$)[a]

Bond Lengths					
Ru−C(1)	1.889(3)	C(1)−C(2)	1.248(4)	C(2)−C(3)	1.357(4)
Ru−N(16)	2.179(2)	Ru−N(21)	2.132(2)	Ru−N(26)	2.144(2)
Ru−P(32)	2.3779(7)	Ru−P(51)	2.4327(11)	C(3)−C(9)	1.477(3)
C(3)−C(15)	1.481(3)				

Interbond Angles			
Ru−C(1)−C(2)	167.6(3)	C(1)−C(2)−C(3)	169.0(3)
C(9)−C(3)−C(15)	121.8(2)	C(1)−Ru−N(16)	171.76(10)
C(1)−Ru−N(21)	86.95(10)	C(1)−Ru−P(32)	90.18(8)
C(1)−Ru−P(51)	98.52(9)	P(32)−Ru−P(51)	100.11(3)
N(16)−Ru−N(21)	87.01(9)	N(21)−Ru−N(26)	81.88(9)
N(16)−Ru−N(26)	85.34(9)		

[a] Angle sum of N_x−Ru−N_y − 270° = −15.8°.

Table 5. Selected Spectrocopic Data for the Complexes [RuCl(CA)(PPh$_3$){HB(pz)$_3$}]

complex A =	δ(^{31}P) (ppm)	δ(^{13}C$_{CA}$) (ppm)	J(PC$_A$) (Hz)	ν(CA)[a] (cm^{-1})
NCMe$_3$	50.5	161.6	*b*	2117
O[c]	40.5	203.5	16	1965
S	38.6	307.9	17.8	1290
C═CPh$_2$	38.1	313.6	22.7	1920
CHC$_6$H$_4$Me	37.6	370.0	19.4	1637

[a] Nujol mull. [b] Not resolved. [c] See ref 4.

ular ion in addition to the base peak which corresponded to loss of the halide ligand.

In contrast to the formation of **13**, treating **1** with 4-ethynyltoluene in a mixture of methanol and tetrahydrofuran under reflux provides an alternative product, the σ-alkynyl complex [Ru(C≡CC$_6$H$_4$Me-4)(PPh$_3$)$_2${HB(pz)$_3$}] (**15**), the formulation of which rests on spectroscopic data: The alkynyl group is manifest in an infrared absorption at 2075 cm^{-1} (CH_2Cl_2) attributable to ν(C≡C). The molecular ion is only weakly apparent (4%), in contrast to that due to elimination of the alkynyl ligand (20%).

Treating **1** with HC≡CCPh$_2$OH in the presence of $AgPF_6$ also leads to an allenylidene complex; however, in this case it is the salt [Ru(═C═C═CPh$_2$)(PPh$_3$)$_2${HB(pz)$_3$}]PF_6 (**16·PF$_6$**). This salt was characterized spectroscopically and by a single-crystal X-ray structure determination, the results of which are summarized in Figure 3 and Tables 1 and 4 and are discussed below. The spectroscopic data of note for **16·PF$_6$** include a characteristic intense infrared absorption at 1943 cm^{-1}, to higher frequency of that observed for the neutral complex **14**. Presumably the same arguments used to relate metal π-basicity to the ν(CO), ν(CN), or ν(CS) frequency of carbonyl, isonitrile, and thiocarbonyl ligands

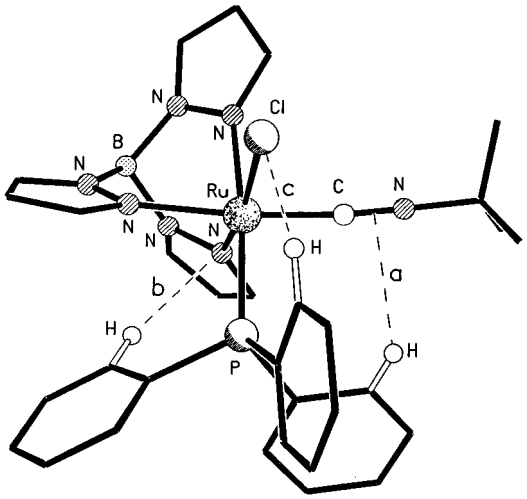


Figure 2. Schematic representation of the intramolecular C−H···π (a and b) and C−H···Cl (c) stabilizing interactions present in the structure of **5**.

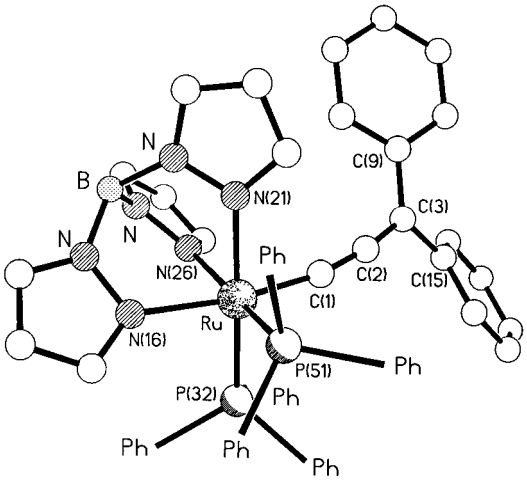


Figure 3. Molecular geometry of [Ru(C═C═CPh$_2$)(PPh$_3$)$_2$-{HB(pz)$_3$}] (**16**$^+$). Phosphine phenyl groups omitted for clarity.

can also be employed for this mode of allenylidene vibration. As with complex **14** the C_α and C_β carbons give clearly identifiable ^{13}C NMR resonances at 316.6 and 208.9 ppm, the former showing cis coupling to the two chemically equivalent phosphorus nuclei [J(PC) = 17.8 Hz]. Thus on proceeding from the neutral **14** to the cationic **16**$^+$, C_α appears to become marginally more deshielded [accompanied by a minimal decrease in J(PC)], while there is an upfield shift for the C_β resonance. These observations might be loosely interpreted in terms of more cationic character for C_α as a result of poorer retrodonation from ruthenium.

The related allenylidene salt [Ru(═C═C═CPh$_2$)(dppf)-{HB(pz)$_3$}]PF_6 (**17·PF$_6$**) is obtained in quantitative yield from the reaction of **4** with HC≡CCPh$_2$OH and $AgPF_6$. Spectroscopic data pertaining to the allenylidene ligand are remarkably similar to those for **16·PF$_6$**. The only notable difference in the spectroscopic data in general, and perhaps as expected, is that while the base peak for **16**$^+$ corresponds to loss of PPh$_3$ from the molecular ion (24% relative abundance), it is the molecular ion that constitutes the base peak in the spectrum of **17**$^+$, reflecting the chelation of the dppf ligand. During this

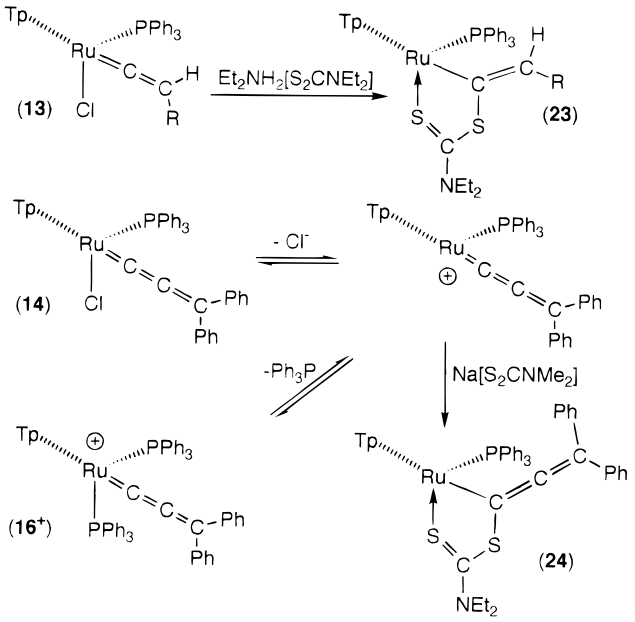
work the closely related complex [Ru(=C=C=CPh_2)(dippe){$HB(pz)_3$}]$^+$ was described.[11]

Treating **4** with 4-ethynyl toluene in the presence of $AgPF_6$ results in the formation of the vinylidene salt [Ru(=C=CHC_6H_4Me-4)(dppf){$HB(pz)_3$}]PF_6 (**18·PF$_6$**). The presence of the vinylidene ligand follows from the appearance of a strong absorption at 1604 cm^{-1} (CH_2Cl_2) in the infrared spectrum of **18·PF$_6$**. Unfortunately the salt was not obtained in pure form, and the contaminant(s) appeared to be paramagnetic in nature (ferrocenium?), precluding useful ^{1}H NMR data from being obtained. Nevertheless a singlet resonance (29.8 ppm) was observed in the ^{31}P{^{1}H} NMR spectrum. A well-resolved molecular ion was identified in the FAB mass spectrum, in addition to an isotope pattern attributable to loss of alkyne. The formulation of **18·PF$_6$** was further supported by its subsequent reaction with methanolic sodium methoxide, which resulted in the formation of the alkynyl complex [Ru(C≡CC_6H_4Me-4)(dppf){$HB(pz)_3$}] (**19**). This species is directly analogous to the complex [Ru(C≡CC_6H_4Me-4)$(PPh_3)_2${$HB(pz)_3$}] (**15**), and accordingly the spectroscopic data are directly comparable. Thus the alkynyl ligand gives rise to a weak infrared absorption at 2075 cm^{-1} (CH_2Cl_2). Deprotonation of **18·PF$_6$** to form **19** is accompanied by a shift in the singlet ^{31}P NMR resonance from 29.8 to 41.1 ppm. The FAB mass spectrum reveals a molecular ion in addition to fragmentations due to loss of pyrazol and the alkynyl ligand.

A final example of an alkynyl complex analogous to **15** and **19** is provided by the product of the reaction of **16·PF$_6$** with sodium methoxide. Rather than attack at C_α, to provide an allenyl-ether, attack is observed to occur exclusively at C_γ to provide [Ru(C≡$CCPh_2$OMe)$(PPh_3)_2${$HB(pz)_3$}] (**20**). In a similar reaction, Esteruelas has recently reported attack by methoxide at the γ-carbon of an osmium allenylidene,[26] and precedent for ruthenium comes from the reactions of [Ru(=C=C=CPh_2)L$(PPh_3)(\eta^5$-$C_9H_7)$]PF_6 (L = CO, PPh_3)[27] and [Ru(=C=C=CPh_2)(CO)(P^{i}Pr$_3$)(η-C_5H_5)]PF_6[28] with various nucleophiles. In all these cases, attack occurs regioselectively at C_γ, results that are consistent with theoretical calculations for the model complex [Ru(=C=C=CH_2)(CO)$(PH_3)(\eta$-$C_5H_5)$]$^+$.[28] The alkynyl ligand gives rise to the characteristic infrared absorption at 2061 cm^{-1} (CH_2Cl_2) in addition to strong bands in the region attributable to ν(C−O) (1211−1043 cm^{-1}). While a molecular ion is clearly visible in the FAB-mass spectrum, it is noteworthy that a predominant peak is observed due to loss of methoxide, perhaps reflecting the mechanism by which **16**$^+$ is formed from **1**. This chemistry is also reflected in solution, in that treating **20** with HPF_6 regenerates **16·PF$_6$**.

Osmium Complexes. While the chemistry of the $HB(pz)_3$Ru fragment has grown considerably in the previous 2−3 years, the corresponding osmium chemistry remains in its infancy. Key compounds include the binuclear complex [$Os_2(CO)_4${$HB(pz)_3$}$_2$],[29] the hydrido complexes [OsH(CO)$(PR_3)_x${η^{4-x}-$HB(pz)_3$}] (x = 1, 2; R = ^{i}Pr,[5] Ph[1]), the aryl complexes [Os(C_6H_5)(CO)$(PPh_3)_x$-{η^{4-x}-$HB(pz)_3$}],[1] and the osmium neopentylidyne [Os(≡$CCMe_3$)$(CH_2CMe_3)_2${$HB(pz)_3$}].[30] Although not studied in detail, preliminary results indicate that a similar chemistry to that of **1** can be anticipated for osmium. Thus treating [$OsCl_2(PPh_3)_3$] with K[$HB(pz)_3$] leads to the formation of the yellow complex [OsCl$(PPh_3)_2${$HB(pz)_3$}] (**21**) in 78% yield. Spectroscopic data are comparable in all respects to those for **1**. The conversion of **21** to the hydrido complex [OsH$(PPh_3)_2${$HB(pz)_3$}] (**22**) may be achieved by heating **21** with potassium hydroxide in 2-methoxyethanol under reflux. While the mechanism of formation is clearly similar to the formation of **11** from **1**, the sequence requires considerably higher temperatures. Thus heating **21** with NaOMe in refluxing methanol for 5 h results in only approximately 5% conversion to **22**. This observation is consistent with the general decrease in reaction rates on proceeding from ruthenium to osmium. Since the original submission of this paper, Jia and Lau have reported similar syntheses of the complexes **21** and **22**.[32]

Scheme 4. Dithiocarbamate Coupling Reactions (R = C_6H_4Me-4)



Dithiocarbamate Coupling Reactions (Scheme 4). As described above, the reaction of **1** with Na[S_2CNMe_2] proceeds by conventional displacement of the chloride and one phosphine ligand to provide **9**. The reactions of the complexes **13** and **14** with dithiocarbamates are however quite unique. Treating the vinylidene complex **13** with 1 equiv of [Et_2NH_2][S_2CNEt_2] results in the formation of a yellow complex formulated as [Ru{C(=CHC_6H_4Me-4)S_2CNEt_2}(PPh_3){$HB(pz)_3$}] (**23**) on the

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basis of spectroscopic and elemental analytical data. The gross formulation is suggested by the appearance of an intense molecular ion (75%) in the FAB-mass spectrum, in addition to a smaller peak due to phosphine elimination. The $^{13}C\{^1H\}$ NMR spectrum is devoid of resonances in the region typical of either vinylidene or alkynyl groups, but contains peaks at 206.0 ppm, due to the dithiocarbamate carbon, and at 173.2 ppm. This latter resonance appears as a doublet showing coupling to one phosphorus nucleus [J(PC) = 11.9 Hz] and is toward the low-field end of the range typical of the α-carbon of vinyl ligands. The β-carbon is not unequivocally distinguished from resonances due to the aryl groups; however, the ^1H NMR spectrum includes a peak at δ 6.10, which is typical of the β-proton of vinyl ligands and is shifted to low field of the corresponding resonance in the precursor **13** [δ 4.89]. Notably, the resonances due to the methylene groups of the NEt_2 substituent are broadened in both the ^{13}C and ^1H NMR spectra, suggesting the onset of a fluxional process, possibly involving rotation about the C−N multiple bond. Such rotation is uncommon in simple chelated dithiocarbamates.

A similar reaction ensues between the allenylidene complex **14** to provide the metallacyclic allenyl complex [Ru{C(=C=CPh$_2$)S$_2$CNMe$_2$}(PPh$_3$){HB(pz)$_3$}] (**24**). The formulation follows from spectroscopic data which are comparable to those for the metallacycle in the complex [Ru{C(=C=CPh$_2$)S$_2$CNMe$_2$}(S$_2$CNMe$_2$)(CO)(PPh$_3$)], which we have recently reported.[11b] Specifically, an abundant molecular ion is observed in the FAB-mass spectrum, while $^{13}C\{^1H\}$ NMR data include resonances due to the dithiocarbamate and allenyl C_α and C_β carbon nuclei (207.9, 201.2, and 140.8 ppm, respectively). The resonances due to the dithiocarbamate substituents appear as singlets in both the ^1H (δ 3.26) and $^{13}C\{^1H\}$ (45.5 ppm) NMR spectra, suggesting, as in the previous example (**23**), that rotation about the C−N mutliple bond is facile. The salt **16·PF$_6$** also reacts with Na[S$_2$CNMe$_2$] to provide **24** in high yields; however, the reaction is considerably slower, despite the charge on the complex, which should activate it toward nucleophilic attack. We therefore suspect that both species provide the same 16-electron cationic intermediate [Ru(=C=C=CPh$_2$)(PPh$_3$){HB(pz)$_3$}]$^+$ in solution, but that **16**$^+$ does this more slowly.

We have recently reported the novel coupling reactions of dithiocarbamates with alkylidene[33] and propenylidene complexes.[34] Roper has described the synthesis of a metallacycle [Ru{C(=CC$_3$H$_3$N)S$_2$CNMe$_2$}Cl(CO)(PPh$_3$)$_2$], related to **23**, which arises from the reaction of a chloro(pyrollyl)carbene complex with dithiocarbamate salts.[35] Furthermore Hogarth has provided an "inorganic" example of such a process with the insertion of nitrenes into coordinated dithiocarbamates of copper.[36] The present results therefore add to the growing range of metallacyles derived from the coupling of dithiocarbamates with co-ligands.

Discussion of the Structures of [RuCl(CA)(PPh$_3$){HB(pz)$_3$}] [A = NCMe$_3$ (5); S (25)] and [Ru(=C=C=CPh$_2$)(PPh$_3$)$_2$){HB(pz)$_3$}]PF$_6$ (16·PF$_6$). The complex [RuCl(CS)(PPh$_3$){HB(pz)$_3$}] (**25**) has been described recently;[1] however, structural data were not then available.

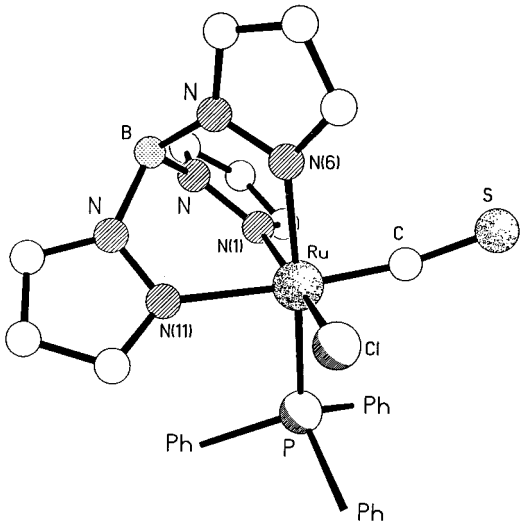

Figure 4. Molecular geometry of [RuCl(CS)(PPh$_3$){HB(pz)$_3$}] (**25**). Phenyl groups omitted for clarity.

(a) [RuCl(CNCMe$_3$)(PPh$_3$){HB(pz)$_3$}] (5). The molecular geometry of one enantiomer of **5** is depicted in Figure 1. The ruthenium center has a slightly distorted octahedral arrangement of donor atoms with interligand angles in the range 83.73(7)−101.21(3)°. The smaller of these are due to the N−Ru−N angles, which are, however, unremarkable given the constraints of the chelation of the HB(pz)$_3$ "scorpionate", while the largest separates the chloride and phosphine ligands [Cl(7)−Ru−P(24) = 101.21(3)°]. The Ru−P(24) and Ru−Cl(7) distances at 2.3447(8) and 2.4257(9) Å are also typical of these ligands bound to divalent ruthenium, although the latter lies to the longer end of this range, perhaps reflecting a trans influence which contributes to the lability of this ligand. The isonitrile ligand with a short Ru−C(1) separation of 1.920(3) Å is, as expected, essentially linear at both C(1) [174.6(3)°] and N(2) [170.8(4)°] such that the Ru−C(1) and N(2)−C(3) vectors subtend an angle of 11.2°. There are no substantial intermolecular interactions; however, the molecular conformation is stabilized by a combination of internal C−H···π and C−H···Cl hydrogen-bonding interactions. All of these involve the ortho hydrogen atom from each of the three phenyl rings. The C−H···π interactions (Figure 2) are (i) to the C=N multiple bond of the isonitrile ligand [H···π = 2.74 Å, C−H···π 119°] and (ii) to the center of the pyrazolyl ring based on N(13) [H···π = 2.72 Å, C−H···π = 170°]. The C−H···Cl(7) hydrogen bond has C(35)···C(7) and H···Cl(7) distances of 3.26 and 2.33 Å, respectively, and a C−H···Cl(7) angle of 164°.

(b) [RuCl(CS)(PPh$_3$){HB(pz)$_3$}] (25). The molecular geometry of one enantiomer of the complex **25** is shown in Figure 4. In contrast to **5**, some positional disorder occurs between the chloride and thiocarbonyl ligands [ca. 80:20]. Such disorder would in effect convert between the two enantiomers; however, as the space group is centrosymmetric, there are equal numbers of enantiomers throughout the crystal. This effect does however limit detailed interpretation of bond lengths associated

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with these ligands, and only the geometry involving the major conformer will be discussed. The geometry of the molecule is, as expected, very similar to that of **5** with essentially octahedral angles at ruthenium lying in the range 84.5(2)−96.55(8)°, and once again the largest of these is between the chloride and phosphine ligands. Refinement of a disordered model suggests that the Ru−Cl and Ru−C bond lengths of 2.430(2) and 1.768(11) Å are typical of these ligands bound to divalent ruthenium. The remaining donor atoms N(1), N(6), N(11), and P all have unremarkable bond lengths to ruthenium, although it may be noted that the pyrazolyl group trans to the thiocarbonyl ligand has significantly (13σ) the longest Ru−N bond length, with Ru−N(11) = 2.182(6) Å. As with **5**, there is an analogous pattern of C−H···π and C−H···Cl hydrogen-bonding interactions involving one ortho hydrogen of each phenyl group, although in this instance the C−H···Cl interaction is noticeably weaker. The geometries of the C−H···π interactions are (i) to the C═S multiple bond [H···π = 2.73 Å, C−H···π = 131°] and (ii) to the pyrazolyl ring based on N(1) [H···π = 2.74 Å, C−H···π = 173°]. The C···Cl and H···Cl distances are 3.21 and 2.68 Å, respectively, with a C−H···π angle of 116°.

(c) [Ru(═C═C═CPh$_2$)(PPh$_3$)$_2${HB(pz)$_3$}]PF$_6$ (16·PF$_6$). As there are no significant intermolecular cation−anion contacts (other than very weak C−H···F interactions), the molecular geometry of **16**$^+$ is shown in Figure 3. Despite the cationic charge on the complex, the three ruthenium−nitrogen bond lengths are longer than those in the previous two neutral structures. Of these, it is that which is trans to the allenylidene ligand [Ru−N(16)] at 2.179(2) Å which is the longest (ca. 17σ). Steric factors (two cis phosphine ligands) might be expected to cause this to be elongated; however, the allenylidene ligand can also be assumed to exert a substantial trans influence. The ruthenium phosphorus bond lengths of 2.3779(7) and 2.4327(11) Å are somewhat longer than those in **1** [2.332(3), 2.349(3) Å] and **5** [2.3447(8) Å] but comparable to that in **25** [2.373(2) Å]. The allenylidene ligand is bowed somewhat along its spine, with angles at C(1) and C(2) both being less than 180°, culminating in the Ru−C(1) and C(2)−C(3) bonds lying at an angle of 23° to each other. The bond lengths along the allenylidene spine each reflect the conjugation of multiple bond character. In common with the preceding two structures, there are C−H···π interactions involving ortho C−H groups of two of the phenyl rings attached to P(51). Both of these interactions have relatively short H···π distances, with that to the C(1)−C(2) multiple bond being 2.54 Å [C−H···π = 142°] while the other to one of the pyrazolyl rings (that containing N(10)) has a H···π distance of 2.61 Å and a C−H···π angle of 169°. The "third" phenyl ortho C−H group is directed into the face of one of the phenyl rings of the other phosphine ligand, though here the H···π distance is long at 3.04 Å, although the approach is nearly linear with a C−H···π angle of 172°.

Concluding Remarks. The above results taken together indicate that a rich chemistry is accessible from the complex **1**, much of which has parallels in the chemistry of [RuCl(PPh$_3$)$_2$(η-C$_5$H$_5$)].[13] Two points of contrast should however be noted in favor of the pursuit of "Ru{HB(pz)$_3$}" vs "Ru(η-C$_5$H$_5$)" chemistry. First, while the NMR characteristics of the cyclopentadienyl ligand are endearing (a singlet resonance in ^{1}H and ^{13}C NMR spectra), they give little information about the nature of the substitution at the metal center other than chemical shift fingerprinting. The number of resonances due to the pyrazolyl groups of the HB(pz)$_3$ ligand immediately indicate the number of identical co-ligands. Second, the conditions under which **1** enters into ligand exchange processes are considerably milder than those of [RuCl(PPh$_3$)$_2$(η-C$_5$H$_5$)]. Finally, much of the character of the chemistry of the "Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)" fragment can be traced to the strongly π-basic nature of the ruthenium center. Replacing η-C$_5$H$_5$ with HB(pz)$_3$ increases the basicity of the metal center further, and it has been argued that it also leads to more ideally octahedral hybridization.[31] These factors should contribute to the further development of poly(pyrazolyl)-borate chemistry within group 8.

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Supporting Information Available: ORTEP representations, tables of positional parameters, intramolecular distances and angles, calculated H-coordinates, anisotropic and equivalent anisotropic displacement coefficients, and crystallographic procedural details. This material is available free of charge via the Internet at http://pubs.acs.org.

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