1552 *Organometallics* **1998,** *17,* 1552−1557

Polyazolyl Chelate Chemistry. 6.[1] Bidentate Coordination of $HB(pz)_3$ (pz = Pyrazol-1-yl) to Ruthenium and Osmium: Crystal Structure of $[RuH(CO)(PPh_3)_2\{\kappa^2\text{-}HB(pz)_3\}]$

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Received November 13, 1997

$[RuHCl(CO)(PPh_3)_3]$, $[Ru(SnPh_3)Cl(CO)(PPh_3)_2]$, or $[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$ reacts with $K[HB(pz)_3]$ (pz = pyrazol-1-yl) to provide $[RuH(CO)(PPh_3)_2\{\eta^2\text{-}HB(pz)_3\}]$, thermolysis of which proceeds via loss of phosphine and formation of $[RuH(CO)(PPh_3)\{\eta^3\text{-}HB(pz)_3\}]$. The thiocarbonyl analogue $[RuH(CS)(PPh_3)_2\{\eta^2\text{-}HB(pz)_3\}]$ is obtained from $[RuHCl(CS)(PPh_3)_3]$ and $K[HB(pz)_3]$, thermolysis of which provides $[RuH(CS)(PPh_3)\{\eta^3\text{-}HB(pz)_3\}]$. In chloroform, this species provides $[RuCl(CS)(PPh_3)\{\eta^3\text{-}HB(pz)_3\}]$. $[RuH(CS)(PPh_3)_2\{\eta^2\text{-}H_2B(bta)_2\}]$ (bta = benzotriazolyl) results from the reaction of $[RuHCl(CS)(PPh_3)_3]$ with $K[H_2B(bta)_2]$. The hydride-bridged dinuclear complex $[RuCu(\mu\text{-}H)(CO)(PPh_3)_2\{\eta^3\text{-}HB(pz)_3\}]PF_6$ results in high yield from the reaction of $[RuH(CO)(PPh_3)_2\{\eta^2\text{-}HB(pz)_3\}]$, with $[Cu(NCMe)_4]BF_4$. $[Os(C_6H_5)(CO)(PPh_3)_2\{\eta^2\text{-}HB(pz)_3\}]$ (from $[Os(C_6H_5)Cl(CO)(PPh_3)_2]$ and $K[HB(pz)_3]$) converts on heating to $[Os(C_6H_5)(CO)(PPh_3)\{\eta^3\text{-}HB(pz)_3\}]$.

Introduction

We have recently been concerned with the development of poly(azolyl)borate chemistry within group 8.[1,3] The chemistry of such ligands is rich for group 6 metals and to a lesser extent for those in groups 7 and 9.[4] In contrast, group 8, the birthplace of η^5-cyclopentadienyl chemistry, has seen comparatively little of the notionally related hydrotris(pyrazol-1-yl)borate ligand (Chart 1)[4] until recently.[3,5] The tendency for this ligand to adopt a facially tridentate coordination mode is very strong, and reduced denticity is usually only observed in cases where it is disfavored by the electronic nature of the metal, e.g., d^8-ML_4 square-planar geometry.[6] A particularly elegant illustration of this situation has been provided by Connelly, who showed that the *bidentate* coordination of the $HB(pzMe_2\text{-}3,5)_3$ scorpionate in $[Rh(CO)(PPh_3)\{\eta^2\text{-}HB(pzMe_2\text{-}3,5)_3\}]$ could be closed by a one-electron-oxidation process which removed the stabilizing effect associated with the d^8 square-planar geometry.[7]

Very recently, Esteruelas has discussed the formation of complexes formulated as $[MH(CO)(P^iPr_3)_2\{\eta^2\text{-}HB(pz)_3\}]$ (M = Ru, Os) on the basis of spectroscopic data and the thermolysis of these compounds to provide the conventional η^3 complexes $[MH(CO)(P^iPr_3)\{\eta^3\text{-}HB(pz)_3\}]$,[8] which are analogues of the complexes $[RuH(CO)(PR_3)\{\eta^3\text{-}HB(pz)_3\}]$ (R = Ph,[9] Cy[10]) described previously. These observations have prompted us to report results from our ongoing study which further illustrate bidentate coordination of the $HB(pz)_3$ ligand within group 8,

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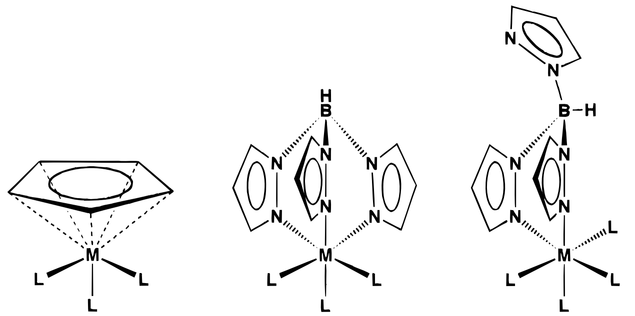
S0276-7333(97)00991-6 CCC: $15.00

Chart 1. η^5-Cyclopentadienyl and η^3- and η^2-Hydrotris(pyrazolyl)borate Coordination



including crystallographic confirmation for one example. Furthermore, we show that the pendance of one pyrazolyl group may be exploited in bridge-assisted metal–metal bond formation.

Experimental Section

General Comments. All manipulations were carried out under aerobic ambient conditions using solvents as received from commercial sources unless otherwise indicated (procedures for **6** and **7**). None of the new compounds showed marked air sensitivity during workup or subsequent spectroscopic characterization. The salts K[HB(pz)$_3$],[11] [Cu(NCMe)$_4$]PF$_6$,[12] and [RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$]BF$_4$[13] and the complexes [RuHCl(CO)(PPh$_3$)$_3$][14] and [RuHCl(CS)(PPh$_3$)$_3$][15] were prepared according to published procedures. The complex [Ru(SnPh$_3$)Cl(CO)(PPh$_3$)$_2$] was prepared from triphenylvinylstannane and [RuHCl(CO)(PPh$_3$)$_3$] according to the method described by Roper for the analogous complex [Ru(SnMe$_3$)Cl(CO)(PPh$_3$)$_2$].[16] ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded with a JEOL JNM EX270 NMR spectrometer and calibrated against internal SiMe$_4$ (^{1}H), internal CDCl$_3$ (^{13}C), or external H$_3$PO$_4$ (^{31}P) reference. In many cases the signals due to H^{3,5}(pz) and C^{3,5}(pz) could not be unequivocally assigned. "t^v" refers to virtual triplet resonances characteristic of *trans*-bis(phosphine) complexes, with apparent coupling constants. ^2J(P$_A$P$_B$) values are as observed and are not corrected for "roof" effects. 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 the salt **7**, for which it refers to the cationic complex. Elemental analysis was carried out by the Imperial College Microanalytical Service. In the case of partial solvates, the stoichiometry was confirmed by ^{1}H NMR integration.

Preparation of [RuH(CO)(PPh$_3$)$_2${η^2-HB(pz)$_3$}] (1a). (a) A suspension of [RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$]BF$_4$ (1.00 g, 1.22 mmol) and K[HB(pz)$_3$] (0.34 g, 1.33 mmol) in dichloromethane (30 mL) was stirred for 20 h and the mixture filtered through diatomaceous earth. The filtrate was freed of volatiles, and the residue was crystallized from a mixture of dichloromethane and ethanol. Yield: 0.73 g (66%). (b) [RuHCl(CO)(PPh$_3$)$_3$] (0.50 g, 0.53 mmol) and K[HB(pz)$_3$] (0.15 g, 0.60 mmol) were dissolved in dichloromethane (20 mL) and stirred for 20 h. A further quantity of dichloromethane (20 mL) was added and contaminants removed by filtration through diatomaceous earth. Ethanol (30 mL) was then added and the solvent volume reduced by rotary evaporation, resulting in crystallization of the colorless product. This was isolated by filtration and washed with ethanol (20 mL) and petroleum ether (20 mL) and dried in vacuo. Yield: 0.36 g (79%). IR (CH$_2$Cl$_2$): 2361, 2341 [ν(BH)], 1975 [ν(RuH)], 1931 [ν(CO)] cm^{-1}. IR (Nujol): 2330, 2405 [ν(BH)], 1982 [ν(RuH)], 1926 [ν(CO)], 1586, 1571, 1299, 1286, 1127, 1120, 1054, 1038, 984, 955, 920, 876, 844 cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ −11.73 [dd, 1 H, RuH, ^2J(PH) = 19.2, 23.8 Hz], 3.8 [s(br), 1 H, BH], 5.23, 5.84, 6.16, [t × 3, 3 × 1 H, H^4(pz), J(HH) ≈ 2.0 Hz], 6.41, 6.51, 6.83, 6.90 [d × 4, 4 × 1 H, H^{3,5}(pz), J(HH) ≈ 2.0 Hz], 7.09−7.32 ppm [m, 31 H, C$_6$H$_5$ and obscured H^{3,5}(pz)], 7.80 [d, 1 H, C^{3,5}(pz)] ppm; ^{13}C{^{1}H}, δ 205.2 [t, RuCO, ^{2}J(PC) = 16.1 Hz], 146.9, 144.8, 141.7 [C^3(pz)], 136.1, 135.3, 135.0 [C^5(pz)], 134.0−127.9 [C$_6$H$_5$], 105.4 (2 C), 104.1 (1 C) [C^4(pz)] ppm; ^{31}P{^{1}H}: 47.6, 42.3 ppm [AB, ^2J(AB) = 301.8 Hz]. **FAB-MS**: *m/z* (%) 869 (4) [M]$^+$, 840 (2) [M − CO − H]$^+$, 801 (80) [M − pz]$^+$, 691 (74) [Ru(pz)(PPh$_3$)$_2$]$^+$, 655 (17) [M − HB(pz)$_3$]$^+$, 625 (23) [Ru(PPh$_3$)$_2$]$^+$, 605 (36) [M − H − PPh$_3$]$^+$, 576 (10) [M − CO − H − PPh$_3$]$^+$, 537 (50) [M − pz − PPh$_3$]$^+$, 363 (68) [RuPPh$_3$]$^+$, 263 (100) [HPPh$_3$]$^+$. Anal. Found: C, 62.2; H, 5.0; N, 9.4. Calcd for C$_{46}$H$_{41}$BN$_6$OP$_2$Ru·0.33CH$_2$Cl$_2$: C, 62.0; H, 4.7; N, 9.4.

Preparation of [RuH(CS)(PPh$_3$)$_2${η^2-HB(pz)$_3$}] (1b). [RuHCl(CS)(PPh$_3$)$_3$] (0.20 g, 0.21 mmol) and K[HB(pz)$_3$] (0.05 g, 0.20 mmol) were dissolved in dichloromethane (20 mL), and the mixture was stirred for 24 h. A further quantity of dichloromethane (20 mL) was added and the precipitate of KCl removed by filtration through diatomaceous earth. Ethanol (30 mL) was then added to the filtrate and the solvent volume reduced (rotary evaporator), causing crystallization of the off-white product which was isolated by filtration, washed with petroleum ether (20 mL) and dried in vacuo. Yield: 0.10 g (78%). **IR** (CH$_2$Cl$_2$): 2435 [ν(BH)], 1982 [ν(RuH)] cm^{-1}. IR (Nujol): 2440, 2420, [ν(BH)], 1983 [ν(RuH)], 1920, 1586, 1572, 1385, 1299, 1262 [ν(CS)], 1224, 1216, 1206, 1129, 1118, 1055, 1038, 983, 954, 918, 884, 877, 849, 838 cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ −9.23 [t, 1 H, RuH, ^2J(PH) = 21.8 Hz], 3.7 [s(br), 1 H, BH], 5.18, 5.88, 6.04 [s × 3, 3 × 1 H, H^4(pz)], 6.29, 6.48, 6.85, 7.03 [s × 4, 4 × 1 H, H^{3,5}(pz)], 7.14−7.34 [m, 31 H, C$_6$H$_5$ and obscured H^{3,5}(pz)], 7.74 [d, 1 H, H^{3,5}(pz), ^3J(HH) = 2.0 Hz] ppm; ^{13}C{^{1}H}, δ 304.0 [t, RuCS, ^2J(PC) = 17.0 Hz], 146.3, 143.9, 141.5 [C^3(pz)], 136.2, 135.5, 135.0 [C^5(pz)], 134.5−127.8 [C$_6$H$_5$], 105.5 (2 C), 104.0 (1 C)[C^4(pz)] ppm; ^{31}P{^{1}H}, 45.2, 41.4 ppm [AB, ^2J(AB) = 301.8 Hz]. FAB-MS: *m/z* (%) 885 (1) [M]$^+$, 817 (62) [M − pz]$^+$, 707 (40) [M(pz)(PPh$_3$)$_2$]$^+$, 671 (12) [M − {HB(pz)$_3$}]$^+$, 621 (25) [M − PPh$_3$]$^+$, 554 (50) [Ru(pz)(PPh$_3$)]$^+$, 407 (28) [M − {HB(pz)$_3$} − PPh$_3$]$^+$. Anal. Found: C, 60.9; H, 4.8; N, 8.7. Calcd for C$_{46}$H$_{41}$BN$_6$P$_2$RuS·0.33CH$_2$Cl$_2$: C, 61.0; H, 4.6; N, 9.2.

Preparation of [RuH(CS)(PPh$_3$){η^3-HB(pz)$_3$}] (2b). [RuH(CS)(PPh$_3$)$_2${η^2−HB(pz)$_3$}] (**1b**; 0.20 g, 0.23 mmol) was stirred in benzene (10 mL) for 3 days. Ethanol (20 mL) was then added, and crystals were obtained by slow concentration. These were isolated by filtration, washed with petroleum ether (10 mL), and dried in vacuo. The off-white product can be purified by column chromatography (silica gel, benzene eluant). Yield: 0.12 g (85%). IR (CH$_2$Cl$_2$): 2480 [ν(BH)], 1981 [ν(RuH)] cm^{-1}. IR (Nujol): 2472 [ν(BH)], 1979 [ν(RuH)], 1931, 1498, 1405, 1393, 1308, 1269 [ν(CS)], 1212, 1115, 1046, 979, 955, 922, 882, 847, 813 cm^{-1}. NMR (C$_6$D$_6$, 25 °C): ^{1}H δ −8.96 [d, 1 H, RuH, ^2J(PH) = 28.4 Hz], 3.5 [s(br), 1 H, BH], 5.38,

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5.77, 5.80 [t × 3, 3 × 1 H, H^4(pz), ^3J(HH) = 2.0 Hz], 6.37, 7.25, 7.30, 7.47 [d × 4, 4 × 1 H, H^{3,5}(pz), ^3J(HH) = 2.0 Hz], 6.58−7.54 [m, 31 H, C$_6$H$_5$ obscured H^{3,5}(pz)], 8.27 [s, 1 H, H^{3,5}(pz)] ppm; ^{13}C{^{1}H}, δ 305.1 [d, RuCS, ^2J(PC) = 19.6 Hz], 144.4, 143.7, 143.0 [C^3(pz)], 134.9, 134.5, 134.4, 134.0, 129.7, 127.8, 127.7, 127.3 [C^5(pz) and C$_6$H$_5$ unequivocal assignments not made], 105.3, 105.2, 104.5 [C^4(pz)] ppm; ^{31}P{^{1}H}, 62.4 ppm. FAB-MS: *m/z* (%) 621 (65) [M]$^+$, 577 (24) [M − CS − H]$^+$, 553 (51) [M − pz]$^+$, 509 (3) [M − H − pz − CS]$^+$, 485 (7) [M − 2pz]$^+$, 407 (14) [M − HB(pz)$_3$]$^+$, 363 (10) [M − H − HB(pz)$_3$ − CS]$^+$. Anal. Found: C, 54.7; H, 4.2; N, 12.7. Calcd for C$_{28}$H$_{26}$BN$_6$PRuS: C, 54.1; H, 4.2; N, 13.5.

Preparation of [RuCl(CS)(PPh$_3$){η^3-HB(pz)$_3$}] (3). [RuH(CS)(PPh$_3$){η^3−HB(pz)$_3$}] (**2b**; 0.20 g, 0.23 mmol) was heated under reflux in chloroform (10 mL) for 5 h. Ethanol (20 mL) was then added and crystals obtained by slow concentration. The bright yellow product was purified by column chromatography (silica gel, 1:4 hexane/dichloromethane eluant). The first fraction to elute contained the desired product, which was crystallized from dichloromethane and ethanol. Yield: 0.10 g (67%). IR (CH$_2$Cl$_2$): 2489 [ν(BH)] cm^{-1}. IR (Nujol): 2516 [ν(BH)], 1509, 1499, 1392, 1310, 1290 [ν(CS)], 1221, 1210, 1190, 1112, 1049, 1028, 986, 925, 892, 856 cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ 4.6 [s(br), 1 H, BH], 5.79 [t, 2 H, H^4(pz), ^3J(HH) not resolved], 6.19 [t, 1 H, H^4(pz), ^3J(HH) not resolved], 6.29, 6.58 [d × 2, 2 × 1 H, H^{3,5}(pz), ^3J(HH) = 2.0 Hz], 7.26, 7.38, 7.63 [d × 3, 3 × 1 H, H^{3,5}(pz), ^3J(HH) = 2.0 Hz], 7.28−7.60 [m, 15 H, C$_6$H$_5$], 8.03 [d, 1 H, H^{3,5}(pz), ^3J(HH) = 2.0 Hz] ppm; ^{13}C{^{1}H}, δ 307.9 [d, RuCS, ^2J(PC) = 17.8 Hz], 144.6, 143.5, 142.4 [C^3(pz)], 136.6, 135.2, 131.8 [C^5(pz)], 134.7, 131.1, 130.2, 128.1 [C$_6$H$_5$], 106.0 (2 C), 105.5 (1 C) [C^4(pz)] ppm; ^{31}P{^{1}H}, 38.6 ppm. FAB-MS: *m/z* (%) 656 (62) [M]$^+$, 621 (67) [M − Cl]$^+$, 589 (3) [M − pz]$^+$, 576 (3) [M − Cl − CS]$^+$, 553 (7) [M − Cl − pz]$^+$, 407 (6) [M − Cl − HB(pz)$_3$]$^+$, 359 (6) [M − Cl − PPh$_3$]$^+$. Anal. Found: C, 50.7; H, 3.8; N, 12.8. Calcd for C$_{28}$H$_{25}$BClN$_6$PRuS: C, 51.3; H, 3.8; N, 12.8.

Preparation of [RuH(CS)(PPh$_3$)$_2${η^2-H$_2$B(bta)$_2$}] (4). [RuHCl(CS)(PPh$_3$)$_3$] (0.15 g, 0.16 mmol) was dissolved in dichloromethane (10 mL) and a solution of K[H$_2$B(bta)$_2$] (0.05 g, 0.17 mmol) in acetone (2 mL) added. The reaction mixture was stirred for 30 min, followed by the removal of volatiles under reduced pressure. The crude product was dissolved in dichloromethane (15 mL) and the solution filtered through diatomaceous earth. Ethanol (20 cm^3) was added to the filtrate and the solvent volume reduced at low pressure until precipitation was complete. The pale green-yellow product was filtered, washed with ethanol (10 mL) and hexane (10 mL), and dried in vacuo. Yield: 0.12 g (84%). IR (Nujol): 2431, 2421 [ν(BH)], 1282 [ν(CS)], 1209, 1146, 1077, 970, 870 cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ −9.26 [t, 1 H, RuH, *J*(PH) = 20.2 Hz], 3.7 [s(v br), 2 H, BH$_2$], 6.94−7.82 [m, 38 H, C$_6$H$_5$ + C$_6$H$_4$N$_3$] ppm; ^{13}C{^{1}H}, 305.2 [t, RuCS, *J*(PC) = 16.1 Hz], 134.0 [s(br), C^{2,6}(C$_6$H$_5$)], 132.5 [t^v, C^1(C$_6$H$_5$), *J*(PC) = 21.5 Hz], 129.4 [s, C^4(C$_6$H$_5$)], 127.4 [C^{3,5}(C$_6$H$_5$)], 146.3, 146.1, 138.4, 138.2, 125.9, 125.8 [1 C × 6, bta], 122.9, 117.8, 112.5 [2 C(br) × 3, bta] ppm. ^{31}P{^{1}H}, 43.5 ppm. FAB-MS: *m/z* (%) 919 (4) [M]$^+$, 671 (8) [M − H$_2$B(bta)$_2$]$^+$, 657 (1) [M − PPh$_3$]$^+$, 625 (0.3) [Ru(PPh$_3$)$_2$]$^+$, 407 (3) [M − PPh$_3$ − H$_2$B(bta)$_2$]$^+$, 263 (100) [HPPh$_3$]$^+$. Anal. Found: C, 63.9; H, 4.5; N, 8.9. Calcd for C$_{49}$H$_{41}$BN$_6$P$_2$RuS: C, 64.0; H, 4.5; N, 9.1%.

Preparation of [Os(C$_6$H$_5$)(CO)(PPh$_3$)$_2${η^2-HB(pz)$_3$}] (5). [Os(C$_6$H$_5$)Cl(CO)(PPh$_3$)$_2$] (0.25 g, 0.29 mmol) was stirred with K[HB(pz)$_3$] (0.08 g, 0.32 mmol) in dichloromethane (20 mL) for 1 h. Propan-2-ol (20 mL) was added and the solvent volume reduced until precipitation of the colorless product was complete. The solid was washed with ethanol and hexane and dried. Yield: 0.17 g (57%). The product can be recrystallized from a mixture of dichloromethane and ethanol. IR (CH$_2$Cl$_2$): 2478 [ν(BH)], 1920 [ν(CO)] cm^{-1}. IR (Nujol): 2476 [ν(BH)], 1920 [ν(CO)], 1569, 1297, 1130, 1058, 952, 877 cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ 5.67, 5.76 [t × 2, 1 H × 2, H^4(pz)], 6.23 [m = t + d, 2 H, H^4(pz) + H^{3,5}(pz)], 6.3−7.3 [m, 38 H, C$_6$H$_5$ + 3H^{3,5}(pz)], 7.39, 7.84 [d × 2, 1 H × 2, H^{3,5}(pz)] ppm; ^{31}P{^{1}H}, 2.34, −2.62 ppm [AB, ^2J(AB) = 301.8 Hz]. FAB-MS: *m/z* (%) 1034 (23) [M]$^+$, 967 (23) [M − pz]$^+$, 956 (3) [M − HPh]$^+$, 889 (2) [M − HPh − pz]$^+$, 772 (100) [M − PPh$_3$]$^+$. Anal. Found: C, 59.2; H, 3.6; N, 7.4. Calcd for C$_{52}$H$_{45}$BN$_6$OOsP$_2$·0.25CH$_2$Cl$_2$: C, 59.5; H, 4.4; N, 8.0.

Preparation of [Os(C$_6$H$_5$)(CO)(PPh$_3$){η^3-HB(pz)$_3$}] (6). [Os(C$_6$H$_5$)(CO)(PPh$_3$)$_2${η^2-HB(pz)$_3$}] (5; 0.07 g, 0.07 mmol) was dissolved in dry, degassed toluene (30 mL). The mixture was heated under reflux for 4 h. All solvent was removed under reduced pressure (rotary evaporation) and a small amount of ethanol (5 mL) added. Ultrasonic trituration provided a colorless product, which was washed with hexane (20 mL) and dried. Yield: 0.05 g (96%). The product can be recrystallized from a mixture of dichloromethane and ethanol. IR (CH$_2$Cl$_2$): 2487 [ν(BH)], 1922 [ν(CO)] cm^{-1}. IR (Nujol): 2478 [ν(CO)], 1914 [ν(CO)], 1569, 1307, 1214, 1116, 1049, 985, 923, 890 cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ 4.5 [s(br), 1 H, BH], 5.88, 5.89, 6.00 [t × 3, 1 H × 3, H^4(pz)], 6.60−7.34 [23 H, C$_6$H$_5$ + 3H^{3,5}(pz)], 7.58, 7.65, 7.71 [d × 3, 1 H × 3, H^{3,5}(pz)] ppm; ^{31}P{^{1}H}, 10.8 ppm. FAB-MS: *m/z* (%) 722 (100) [M]$^+$, 695 (16) [M − Ph]$^+$, 664 (6) [M − Ph − CO]$^+$, 510 (4) [M − PPh$_3$]$^+$.

Preparation of [RuCu(μ-H)(CO)(PPh$_3$)$_2${η^3-HB(pz)$_3$}]PF$_6$ (7). [RuH(CO)(PPh$_3$)$_2${η^2-HB(pz)$_3$}] (**1a**; 0.20 g, 0.23 mmol) and [Cu(NCMe)$_4$]PF$_6$ (0.09 g, 0.24 mmol) were placed in a Schlenk tube under nitrogen. Freshly degassed dichloromethane (10 mL) was then added and the mixture stirred under nitrogen for 12 h. Subsequent addition of ethanol (20 mL) and slow concentration provided off-white crystals, which were isolated by filtration, washed with light petroleum ether (20 mL), and dried in vacuo. Yield: 0.15 g (60%). IR (CH$_2$Cl$_2$): 2492 [ν(BH)], 1967 (br) [ν(CO)]/[ν(Ru−H−Cu)] cm^{-1}. IR (Nujol): 2480 [ν(BH)], 1955 [ν(CO)], 1932 [ν(Ru−H−Cu)], 1309, 1213, 1119, 1050, 926, 921, 837 [PF$_6$] cm^{-1}. NMR (CDCl$_3$, 25 °C) ^{1}H: δ −12.78 [s(br), 1 H, RuCuH, J(PH) not resolved], 4.6 [s(br), 1 H, BH], 5.83, 5.96 [t × 2, 3 H, H^4(pz), ^3J(HH) = 2.0 Hz], 6.75 [s, 2 H, H^{3,5}(pz)], 7.03−7.56 [m, 32 H, C$_6H_5$ and obscured H^{3,5}(pz), 7.73, 7.76 [s × 2, 2 H, H^{3,5}(pz)] ppm. ^{31}P{^{1}H}, 51.9, 3.4 ppm. FAB-MS: *m/z* (%) 931 (26) [M]$^+$, 669 (30) [M − PPh$_3$]$^+$, 640 (22) [M − CO − PPh$_3$]$^+$, 605 (100) [M − CuPPh$_3$]$^+$, 577 (32) [M − CO − CuPPh$_3$]$^+$, 538 (45) [M − pz − CuPPh$_3$]$^+$, 363 (21) [M − H − CO − {HB(pz)$_3$} − CuPPh$_3$]$^+$. Anal. Found: C, 49.0; H, 3.5; N, 10.1. Calcd for C$_{46}$H$_{41}$BCuF$_6$N$_6$OP$_3$Ru·CH$_2$Cl$_2$: C, 48.6; H, 3.7; N, 7.2.

Crystal Data for [RuH(CO)(PPh$_3$)$_2${η^2-HB(pz)$_3$}] (1a): C$_{46}$H$_{41}$BN$_6$OP$_2$Ru, M_r = 867.7, monoclinic, space group $P2_1/c$ (No. 14), a = 10.247(2) Å, b = 16.765(2) Å, c = 24.172(2) Å, β = 98.52(2)°, V = 4106.8(8) Å^3, Z = 4, D_c = 1.40 g cm^{-3}, μ(Mo Kα) = 5.0 cm^{-1}, F(000) = 1784. A pale brown prismatic block of dimensions 0.47 × 0.43 × 0.27 mm was used. A total of 7237 independent reflections were measured on a Siemens P4/PC diffractometer with graphite-monochromated Mo Kα radiation using ω scans. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F to give R = 0.034, R_w = 0.036 for 5691 independent observed reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 45°$) and 518 parameters. The Ru−H hydrogen atom was located from a ΔF map and refined isotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Selected bond lengths and angles are given in Table 1.

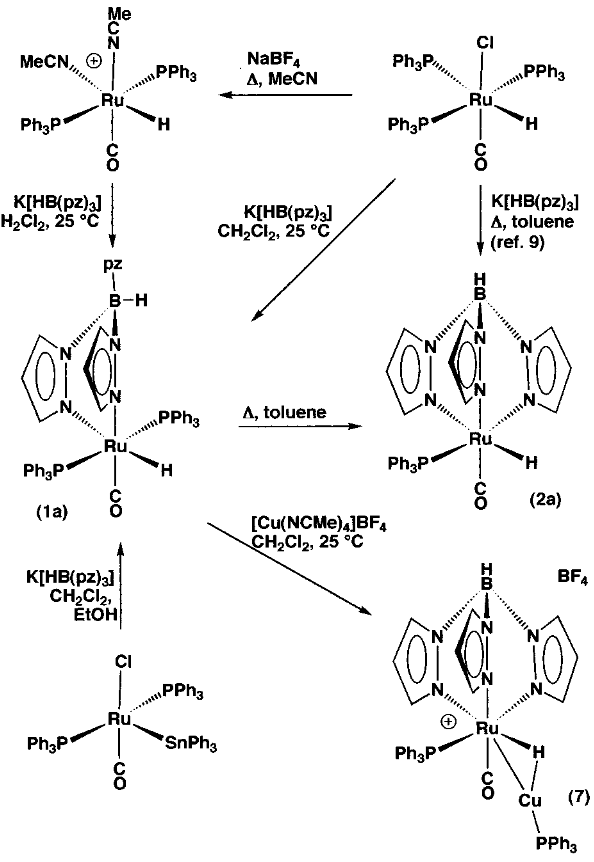
Results and Discussion

The preparation of [RuH(CO)(PPh$_3$){HB(pz)$_3$}] from K[HB(pz)$_3$] and [RuHCl(CO)(PPh$_3$)$_3$] under forcing conditions (refluxing toluene) has been reported[9] (Scheme 1). The extreme conditions reportedly required contrast

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex [RuH(CO)(PPh$_3$)$_2${η^2-HB(pz)$_3$}] (1a)

Bond Lengths			
Ru−H(1a)	1.494(35)	Ru−N(1)	2.196(2)
Ru−C(17)	1.827(3)	Ru−P(38)	2.363(1)
Ru−N(6)	2.141(2)	Ru−P(19)	2.378(1)
C(17)−O(18)	1.150(4)		
Interbond Angles			
H(1A)−Ru−N(6)	84.5(13)	H(1a)−Ru−C(17)	90.8(13)
N(1)−Ru−P(19)	89.6(1)	C(17)−Ru−P(19)	90.0(1)
N(1)−Ru−P(38)	96.7(1)	C(17)−Ru−P(38)	86.6(1)
N(1)−Ru−N(6)	88.0(1)	N(1)−Ru−C(17)	96.7(1)
H(1A)−Ru−P(19)	91.3(13)	N(6)−Ru−P(19)	88.2(1)
N(6)−Ru−P(38)	94.6(1)	Ru−N(6)−N(7)	126.2(2)
Ru−N(1)−N(2)	124.7(2)	N(2)−B(11)−N(7)	111.5(3)
N(2)−B(11)−N(12)	108.6(2)	N(7)−B(11)−N(12)	108.4(3)

Scheme 1. Synthesis of η^3- and η^2-Hydrotris(pyrazolyl)borate Carbonyl Complexes of Ruthenium



with those for the formation of the related complexes [RuH(CA)(PPh$_3$){[9]aneS$_3$}]$^+$ at room temperature.[17] Similarly, K[H$_2$B(bta)$_2$] (bta = benzotriazolyl) and [NMe$_4$][B$_3$H$_8$] react with [RuHCl(CO)(PPh$_3$)$_3$] or [RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$]ClO$_4$ to provide [RuH(CO)(PPh$_3$)$_2${κ^2-H$_2$B(bta)$_2$}][18] and [RuH(η^2-B$_3$H$_8$)(CO)(PPh$_3$)$_2$],[19] respectively, also at room temperature. Furthermore, the organometallic complexes [Ru(R)Cl(CO)(PPh$_3$)$_2$] (R = aryl, vinyl) react rapidly with K[HB(pz)$_3$] at room temperature to provide the complexes [Ru(R)(CO)(PPh$_3$){HB(pz)$_3$}].[3d]

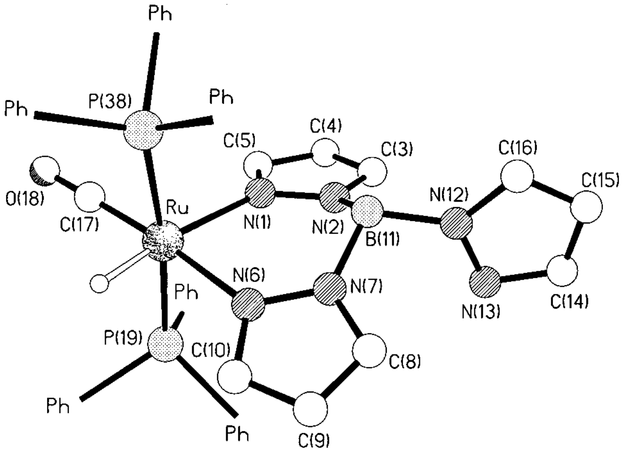


Figure 1. Molecular geometry of [RuH(CO)(PPh$_3$)$_2${η^2-HB(pz)$_3$}] (**1a**). Phenyl groups are omitted for clarity.

The reaction of [RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$]BF$_4$ with K[HB(pz)$_3$] at room temperature provides a complex formulated as [RuH(CO)(PPh$_3$)$_2${κ^2-HB(pz)$_3$}] (**1a**) (Scheme 1) on the basis of spectroscopic data and a single-crystal X-ray diffraction study (Figure 1, and Table 1, vide infra). The complex may also be prepared via the reaction of [RuHCl(CO)(PPh$_3$)$_3$] with K[HB(pz)$_3$] (CH$_2$Cl$_2$, 25 °C). Somewhat surprisingly, the reaction of [Ru(SnPh$_3$)Cl(CO)(PPh$_3$)$_2$] with K[HB(pz)$_3$] in a mixture of dichloromethane and ethanol also provides good yields of **1a**. This latter result is unusual in that the precursor stannyl complex may be recrystallized unchanged from the same solvent mixture, suggesting that alcoholysis of the ruthenium stannyl bond occurs after coordination of the HB(pz)$_3$ ligand, although we have not yet detected any intermediates in this process.

The gross formulation of **1a** follows from spectroscopic data (Experimental Section), which are comparable to those for Esteruelas' complex [RuH(CO)(P^{i}Pr$_3$)$_2${η^2-HB(pz)$_3$}][8] and [RuH(CO)(PPh$_3$)$_2${κ^2-H$_2$B(bta)$_2$}].[18] Final confirmation of the formulation is given by the thermolysis of the complex in refluxing toluene to provide [RuH(CO)(PPh$_3$){κ^3-HB(pz)$_3$}] (**2a**) and PPh$_3$. The η^2 derivative **1a** is however quite stable under mild conditions: crystals used for the X-ray diffraction study were grown over a five-day period at room temperature. The complex is indefinitely stable in the solid state.

Thiocarbonyl Complexes. Given the facile formation of [RuH(CS)(PPh$_3$)([9]aneS$_3$)]Cl from the reaction of [RuHCl(CS)(PPh$_3$)$_3$] with 1,4,7-trithiacyclononane,[17] the synthesis of the complex [RuH(CS)(PPh$_3$){HB(pz)$_3$}] (**2b**) was attempted. Treating a dichloromethane solution of [RuHCl(CS)(PPh$_3$)$_3$] with K[HB(pz)$_3$] leads to the rapid formation of [RuH(CS)(PPh$_3$)$_2${η^2-HB(pz)$_3$}] (**1b**) in good yield (Scheme 2). The spectroscopic data for **1b** differ only slightly from those for **1a**, primarily in those features associated with the thiocarbonyl ligand (^{13}C NMR: 304.5 ppm [t, ^2J(PC) = 17.0 Hz]; ν(CS) = 1262 cm^{-1}). Stirring a solution of **1b** at room temperature in dichloromethane or benzene leads to the formation of the thiocarbonyl analogue of **2a**, viz., [RuH(CS)(PPh$_3$){η^3-HB(pz)$_3$}] (**2b**). Although this transformation is slow (3 days), it is noteworthy that it ensues under ambient temperatures while the carbonyl analogue **1a** requires refluxing toluene for conversion to **2a**. Spectroscopic data for **2b** are comparable to those for **2a** and

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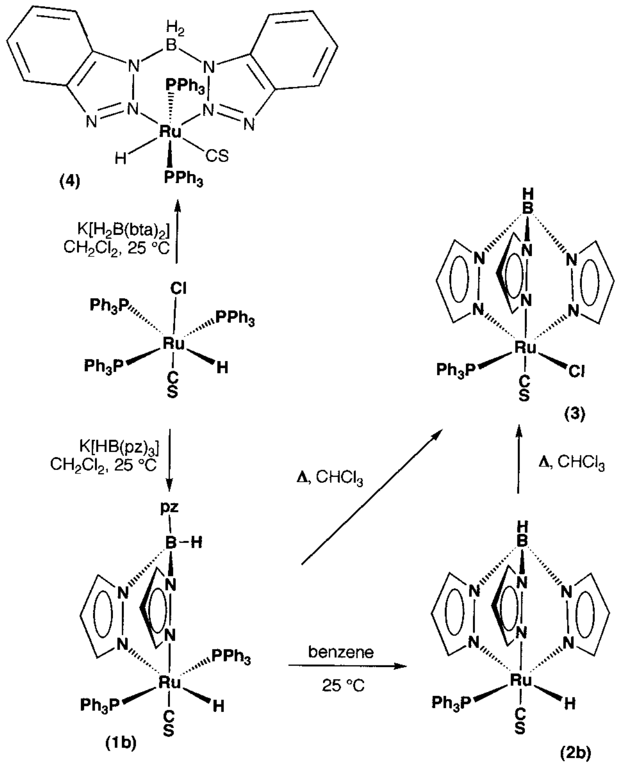
(17) Cannadine, J.; Hector, A.; Hill, A. F. *Organometallics* **1992**, *11*, 2323.

(18) Cartwright, J.; Hill, A. F. *J. Organomet. Chem.* **1992**, *429*, 229.

(19) Burns, I. D.; Hill, A. F.; Thompsett, A. R.; Alcock, N. W.; Claire, K. *J. Organomet. Chem.* **1992**, *425*, C8.

Scheme 2. Synthesis of η^3- and η^2-Poly(azolyl)borate Thiocarbonyl Complexes of Ruthenium

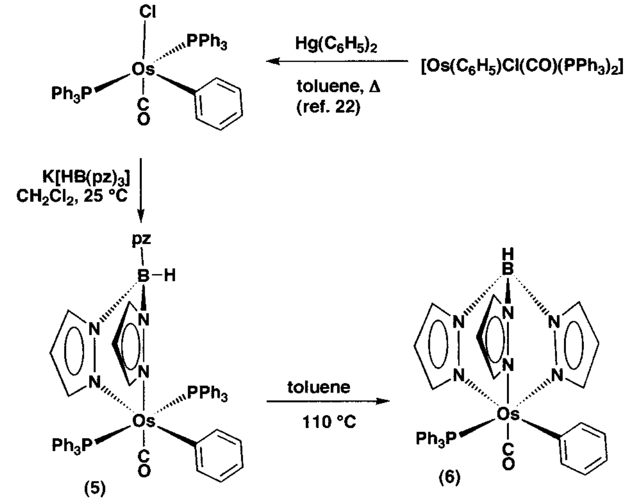


unremarkable, other than to confirm that both the thiocarbonyl (^{13}C, 305.1 ppm, d, ^2J(PC) = 19.6 Hz; IR, 1269 cm^{-1}) and the hydride ligand (^{1}H, δ −8.96, d, ^2J(PH) = 28.4 Hz) have retained their integrity. Heating **2b** in refluxing chloroform leads to hydride/chloride metathesis and formation of [RuCl(CS)(PPh$_3$){HB(pz)$_3$}] (**3**). Although the reaction of [RuCl$_2$(CS)(OH$_2$)(PPh$_3$)$_2$] with [9]aneS$_3$ provides [RuCl(CS)(PPh$_3$)([9]aneS$_3$)]Cl, this same precursor does not react cleanly with K[HB(pz)$_3$] to provide **3**. Rather, the major product is the pyrazole complex [RuCl$_2$(CS)(Hpz)(PPh$_3$)$_2$], resulting from cleavage of the HB(pz)$_3$ ligand.

The cis disposition of thiocarbonyl and hydride ligands raises the question of migratory insertion of these two ligands. Roper has illustrated that such processes are quite facile in the chemistry of osmium thiocarbonyls.[20] The complexes **1b** and **2b** therefore appear ideally constructed for such a coupling. Both the thermal conversion of **1b** to **2b** and the photolysis of **2b** lead to blue-green side products; however, these have not yet been obtained in sufficiently large amounts for complete characterization (^{13}C NMR, analysis), although these almost certainly involve thioformyl groups, given the absence of characteristic terminal thiocarbonyl infrared absorptions.

Lalor has described a series of ligands related to the pyrazolylborates but based on benzotriazole,[21] and we have shown that the dihydrobis(benzotriazolyl)borate ligand readily coordinates to ruthenium, rhodium, and iridium.[1,3c,18] The reaction of [RuHCl(CS)(PPh$_3$)$_3$] with K[H$_2$B(bta)$_2$] (bta = benzotriazolyl) readily provides the complex [RuH(CS)(PPh$_3$)$_2${η^2-H$_2$B(bta)$_2$}] (**4**), spectroscopic data for which are comparable to those for **1b** and the carbonyl analogue [RuH(CO)(PPh$_3$)$_2${η^2-H$_2$B(bta)$_2$}].[18] (^{13}C NMR, 305.2 ppm [t, ^2J(PC) = 16.1 Hz]; ν(CS) 1282 cm^{-1}). While the boat conformation of the H$_2$B(bta)$_2$ ligand would in principle render the two phosphines chemically inequivalent in a static structure, inversion of the metallacycle must be rapid on the NMR time scale. This is also suggested by the triplet multiplicity of the hydride resonance apparent in the ^{1}H NMR spectrum of **4** (−9.26 ppm, ^2J(PH) = 20.2 Hz) and the singlet ^{31}P NMR resonance (43.5 ppm).

Scheme 3. Synthesis of η^3- and η^2-Hydrotris(pyrazolyl)borate Phenyl Complexes of Osmium



Osmium Complexes. We have shown that the complex [Ru(C$_6$H$_4$Me-4)(CO)(PPh$_3$){η^3-HB(pz)$_3$}] forms rapidly from the reaction of [Ru(C$_6$H$_4$Me-4)Cl(CO)(PPh$_3$)$_2$], with no intermediates being observed.[3d,e] Reaction rates for ligand exchange reactions typically decrease down a transition-metal triad. We have therefore investigated the preparation of a related osmium complex to identify any intermediates in the coordination of the HB(pz)$_3$ ligand which might be related to **1**. Treating a dichloromethane solution of [Os(C$_6$H$_5$)Cl(CO)(PPh$_3$)$_2$][22] with K[HB(pz)$_3$] results in the smooth formation of the colorless complex [Os(C$_6$H$_5$)(CO)(PPh$_3$)$_2${η^2-HB(pz)$_3$}] (**5**). This complex also features bidentate coordination of the scorpionate (Scheme 3), evident from the ^{31}P NMR spectrum (2.34, −2.62 ppm, ^2J(P$_A$P$_B$) = 301.8 Hz). Furthermore, one of the H^4(pz) resonances in the ^{1}H NMR spectrum is shifted downfield from the remaining two, suggesting quite a different chemical environment for the pendant pyrazolyl group. As with **1a** and **1b**, one phosphine is labile, although refluxing toluene is required for the complete thermolysis of **5** to provide [Os(C$_6$H$_5$)(CO)(PPh$_3$){η^3-HB(pz)$_3$}] (**6**). The identity of **6** follows unequivocally from spectroscopic data.

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The possibility that the pendant nature of one pyrazolyl group in **2a** could be used for bridge-assisted metal−metal bond formation was briefly investigated. The reaction of **1a** with $[Cu(NCMe)_4]PF_6$ resulted in a colorless complex formulated as $[RuCu(\mu\text{-}H)(CO)(PPh_3)_2\{\kappa^3\text{-}HB(pz)_3\}]$ (**7**) being isolated (Scheme 1). A very broad resonance in the ^1H NMR spectrum at −12.78 ppm indicated the presence of a bridging hydride, although appropriate infrared activity could not be unequivocally identified. Apart from the heptet resonance due to the PF_6 counteranion, the $^{31}P\{^1H\}$ NMR spectrum clearly showed two different phosphorus environments at 51.9 and 3.4 ppm. The latter, being broad, is attributed to the phosphine attached to the copper center, while that to lower field is assigned to the ruthenium-bound phosphine. The presence of the hydrotris(pyrazol-1-yl)borate ligand was confirmed by pyrazole resonances apparent in the ^1H NMR spectrum (δ 5.83, 5.96, 6.75, 7.73, 7.76). The FAB mass spectrum proved most diagnostic, clearly showing a molecular ion at m/z 931 in addition to a range of assignable fragmentations. Unfortunately, we have been unable to obtain crystallographic grade crystals to confirm the structural formulation. It is noteworthy that, as already indicated above, the conversion of **1a** to **2a** does not proceed under the conditions of the formation of **7**. This suggests that the reaction proceeds by direct combination of the copper reagent with **1a**, presumably via coordination to the pendant pyrazolyl arm, followed by rearrangement to the final product.

Discussion of the Structure of $[RuH(CO)(PPh_3)_2\{\eta^2\text{-}HB(pz)_3\}]$ (1a). The compound forms pale brown prismatic blocks when crystallized by diffusion of ethanol into a dichloromethane solution of the complex. The X-ray analysis confirmed the cis-bidentate coordination of the $HB(pz)_3$ ligand and the *trans*-bis(phosphine) disposition suggested by spectroscopic data. The hydride hydrogen atom was clearly located in the X-ray study and freely refined. The coordination geometry at ruthenium (Figure 1) is approximately octahedral. The ruthenium phosphorus bonds are close to collinear (P(19)−Ru−P(38) = 173.1(1)°), and the atoms in the equatorial coordination sites (C(17), H(1A), N(1), N(6)) are essentially coplanar (maximum deviation 0.028 Å by H(1A)). The features of interest center on the Ru-$(\mu\text{-}pz)_2BH(pz)$ moiety. There is the expected asymmetry in the Ru−N bond distances, that trans to H(1A) (2.196(2) Å) being substantially longer than that trans to the carbonyl ligand (2.141(2) Å). In the absence of chelation by the N(12)-based pyrazolyl group, the six-membered ring comprising Ru, N(6), N(7), B(11), N(2), and N(1) has a slightly flattened boat conformation. The two noncoordinating nitrogen atoms lie only slightly out of the coordination plane by approximately 0.23 Å; cf. 0.91 Å for B(11). The pendant pyrazolyl ring is oriented approximately orthogonal to the chelate ring, rotation being hindered by the C(3) and C(8) pyrazolyl hydrogen atoms. While this ring protrudes from the molecule somewhat, there are no intermolecular contacts of any note. The only (barely) noteworthy intramolecular interaction involves a probably weak alignment of the pyrazolyl ring based on N(7) with a proximal phosphine phenyl ring (centroid-centroid separation 3.49 Å).

Acknowledgment. We are grateful to the EPSRC (U.K.) for the award of studentships (to I.D.B. and J.D.E.T.W.-E) and for the financial support of diffractometry facilities. We are grateful to Johnson Matthey Ltd for a generous loan of ruthenium salts. 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 positional parameters, intramolecular distances and angles, calculated H coordinates, anisotropic and equivalent anistropic displacement coefficients, and crystallographic procedural details (10 pages). Ordering information is given on any current masthead page.

OM970991Y