served in the final difference Fourier map, but a short C3–C3′ distance (1.35 (1) Å) is present; $R = 0.044$, and $R_w = 0.054$.

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Registry No. $CpVBr_3$, 60530-27-0; $CpVI_3$, 131322-14-0; $(MeCp)VI_3$, 131297-75-1; $CpV(CO)_4$, 12108-04-2; $(MeCp)V(CO)_4$, 63339-27-5.

Supplementary Material Available: Tables of magnetic susceptibility data, crystal data and refinement, and position and thermal parameters (6 pages); a table of final and observed structure factors (4 pages). Ordering information is given on any current masthead page.

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Synthesis and Structures of Rhodium Isocyanide Complexes Containing an η^2-Hydrotris(3,5-dimethylpyrazolyl)borate Ligand

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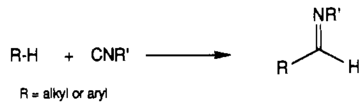
Complexes of the general type $HB(Pz^*)_3Rh(CNR)_2$ (Pz^* = 3,5-dimethylpyrazol-1-yl, R = neopentyl, 2,6-xylyl, methyl) were prepared by reaction of an isocyanide and $K[HB(Pz^*)_3]$ with $[RhCl(C_2H_4)_2]_2$ in benzene. The complexes with R = neopentyl (**1a**) and R = 2,6-xylyl (**1b**) have been structurally characterized. Complex **1a** crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.882$ (5) Å, $b = 12.740$ (6) Å, $c = 18.836$ (7) Å, $\beta = 101.11$ (3)°, $V = 3033$ (4) Å^3, and $Z = 4$. Complex **1b** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.179$ (4) Å, $b = 13.415$ (4) Å, $c = 14.792$ (9) Å, $\alpha = 67.06$ (3)°, $\beta = 75.61$ (4)°, $\gamma = 75.47$ (3) °, $V = 1775$ (3) Å^3, and $Z = 2$. The $HB(Pz^*)_3$ ligand in both **1a** and **1b** is bidentate, with the noncoordinated pyrazole ring lying roughly cofacial with the square plane formed by the metal, two-coordinated isocyanides, and two-coordinated pyrazole rings with $HB(Pz^*)_3$. A comparison of the infrared and NMR spectra of **1a** in solution (C_6D_6) and the solid state (KBr pellet) with the corresponding solution and solid-state spectra of $H_2B(Pz^*)_2Rh(CNR)_2$ (**2**) (R = neopentyl) indicates that complex **1a** remains square planar in solution and possesses a rapidly fluxional bidentate $HB(Pz^*)_3$ ligand. Complex **1a** reacts with HBF_4 to give the metal hydride salt $[HB(Pz^*)_3Rh(H)(CNR)_2]BF_4$ (**3**) (R = neopentyl), which has been structurally characterized. Complex **3** crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.028$ (9) Å, $b = 26.234$ (6) Å, $c = 12.298$ (14) Å, $\beta = 100.13$ (5)°, $V = 3820$ (8) Å^3, and $Z = 4$, displaying an octahedral geometry in which the $HB(Pz^*)_3$ ligand is tridentate.

Introduction

Since its original synthesis by Trofimenko,[1] hydrotris(pyrazolyl)borate ($HB(Pz)_3$) has been widely used as a ligand in the synthesis of novel transition-metal complexes.[2] The $HB(Pz)_3$ ligand is normally tridentate and has been considered to be both sterically and electronically similar to the cyclopentadienyl anion (Cp).[3] Complexes containing the $HB(Pz)_3$ ligand often display fluxional behavior which can vary depending on the hapticity and coordination environment of the $HB(Pz)_3$ ligand.[4]

Recently, Ghosh and Graham reported that the complex $HB(Pz^*)_3Rh(CO)_2$ (Pz^* = 3,5-dimethylpyrazol-1-yl) was capable of forming metal alkyl hydrides of the type $HB(Pz^*)_3Rh(H)(R)(CO)$ (R = alkyl) upon photolysis in alkane solution.[5] They also presented infrared spectral evidence suggesting that $HB(Pz^*)_3Rh(CO)_2$ exists in solution as a mixture of isomers in which the $HB(Pz^*)_3$ ligand is either bidentate or tridentate.[6] Recently, they have also obtained a crystal structure for the related complex $HB(F_6\text{-}Pz^*)_3Rh(CO)_2$ (F_6-Pz^* = 3,5-bis(trifluoromethyl)pyrazo-1-yl), which shows bidentate coordination of the $HB(F_6\text{-}Pz^*)_3$ ligand.[7]

We prepared the isocyanide complexes $HB(Pz^*)_3Rh(CNR)_2$ (**1a–c**), analogous to our previously studied $(C_5Me_5)Rh(CNR)_2$,[8] in the hope that they would be active as catalysts for hydrocarbon functionalization[9] (eq 1). X-ray crystal structures were obtained



(1)

for two analogues, both of which show that the $HB(Pz^*)_3$ ligand is bound in the uncommon bidentate mode.[10] Infrared and NMR spectral data are presented which indicate that the structures of these complexes in solution contain a fluxional bidentate $HB(Pz^*)_3$ ligand.

Results

Complexes **1a–c** are prepared by slow addition of the appropriate isocyanide to a benzene solution of $[RhCl(C_2H_4)_2]_2$, during which time the original orange suspension of the rhodium dimer becomes black. The black intermediate(s) has (have) not been

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Table I. Positional Parameters and *B*(eq) Values for $HB(Pz^*)_3Rh(CN(neopentyl))_2$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Rh	0.13158 (2)	0.28484 (2)	0.36437 (1)	1.79 (1)
N1	0.0458 (2)	0.0670 (3)	0.3226 (2)	2.5 (1)
N2	0.2732 (3)	0.2372 (3)	0.2568 (2)	2.7 (1)
N3	0.0457 (2)	0.3138 (2)	0.4451 (2)	2.0 (1)
N4	0.0972 (2)	0.3578 (2)	0.5087 (1)	2.0 (1)
N5	0.2106 (2)	0.4255 (2)	0.3957 (2)	1.8 (1)
N6	0.2528 (2)	0.4390 (2)	0.4673 (2)	1.9 (1)
N7	0.2745 (2)	0.2629 (2)	0.5289 (2)	2.2 (1)
N8	0.3789 (2)	0.2657 (2)	0.5217 (2)	2.5 (1)
C1	0.0737 (3)	0.1521 (3)	0.3392 (2)	2.0 (2)
C2	0.0422 (3)	−0.0441 (3)	0.3106 (2)	2.4 (2)
C4	0.2332 (3)	−0.0539 (4)	0.3051 (3)	4.0 (2)
C5	0.1296 (4)	−0.2141 (3)	0.3242 (3)	3.9 (2)
C6	0.1745 (4)	−0.0826 (4)	0.4225 (2)	3.8 (2)
C7	0.2184 (3)	0.2583 (3)	0.2965 (2)	2.1 (2)
C8	0.3566 (3)	0.2067 (3)	0.2206 (2)	2.7 (2)
C9	0.4654 (3)	0.2345 (3)	0.2638 (2)	3.0 (2)
C10	0.4760 (4)	0.3533 (4)	0.2719 (3)	4.6 (2)
C11	0.4853 (4)	0.1827 (5)	0.3371 (3)	5.7 (3)
C12	0.5440 (4)	0.1954 (4)	0.2191 (3)	4.3 (2)
C13	0.0254 (3)	0.3813 (3)	0.5506 (2)	2.1 (2)
C14	−0.0713 (3)	0.3503 (3)	0.5138 (2)	2.5 (2)
C15	−0.0567 (3)	0.3083 (3)	0.4492 (2)	2.3 (2)
C16	0.0542 (3)	0.4296 (3)	0.6234 (2)	3.0 (2)
C17	−0.1369 (3)	0.2631 (3)	0.3897 (2)	3.3 (2)
C18	0.3227 (3)	0.5188 (3)	0.4753 (2)	2.3 (2)
C19	0.3238 (3)	0.5591 (3)	0.4080 (2)	2.4 (2)
C20	0.2527 (3)	0.4996 (3)	0.3595 (2)	2.1 (1)
C21	0.3863 (3)	0.5503 (3)	0.5469 (2)	3.3 (2)
C22	0.2215 (3)	0.5125 (3)	0.2800 (2)	2.6 (2)
C23	0.4155 (3)	0.1690 (3)	0.5369 (2)	2.6 (2)
C24	0.3369 (3)	0.1042 (3)	0.5542 (2)	2.7 (2)
C25	0.2487 (3)	0.1663 (3)	0.5493 (2)	2.4 (2)
C26	0.5269 (3)	0.1428 (3)	0.5337 (2)	3.7 (2)
C27	0.1436 (3)	0.1371 (3)	0.5647 (2)	3.6 (2)
B1	0.2188 (3)	0.3712 (3)	0.5261 (2)	2.2 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

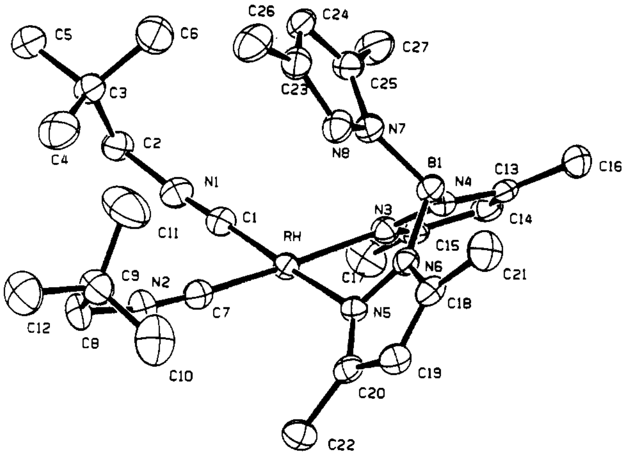

Figure 1. ORTEP drawing of **1a**. Ellipsoids are shown at the 50% probability level.

Table II. Positional Parameters and *B*(eq) Values for $HB(Pz^*)_3Rh(CN(2,6\text{-}xylyl))_2$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Rh	−0.10777 (9)	0.10154 (7)	0.14632 (6)	1.49 (5)
N1	0.0660 (8)	0.2808 (7)	0.0674 (5)	2.6 (7)
N2	−0.2087 (8)	0.2103 (6)	−0.0522 (6)	2.4 (7)
N3	−0.2421 (7)	−0.0101 (6)	0.2025 (5)	1.6 (6)
N4	−0.3100 (7)	−0.0364 (6)	0.3014 (5)	1.9 (6)
N5	−0.0287 (7)	0.0185 (6)	0.2785 (5)	1.6 (6)
N6	−0.1139 (7)	−0.0193 (6)	0.3670 (5)	1.8 (6)
N7	−0.3165 (7)	0.1327 (6)	0.3428 (5)	2.1 (6)
N8	−0.2575 (8)	0.1858 (6)	0.3817 (5)	2.2 (6)
C1	0.003 (1)	0.2092 (8)	0.0985 (6)	2.0 (8)
C2	0.1305 (9)	0.3707 (7)	0.0354 (6)	2.1 (7)
C3	0.157 (1)	0.4283 (7)	−0.0658 (7)	2.3 (8)
C4	0.222 (1)	0.5184 (8)	−0.0972 (7)	3.1 (9)
C5	0.260 (1)	0.5487 (9)	−0.0286 (9)	4 (1)
C6	0.233 (1)	0.4893 (9)	0.0710 (9)	4 (1)
C7	0.166 (1)	0.4002 (8)	0.1070 (7)	2.8 (8)
C8	0.123 (1)	0.390 (1)	−0.1400 (8)	4 (1)
C9	0.126 (1)	0.339 (1)	0.2157 (7)	4 (1)
C10	−0.172 (1)	0.1696 (7)	0.0241 (6)	2.0 (8)
C11	−0.267 (1)	0.2613 (7)	−0.1398 (6)	1.9 (7)
C12	−0.408 (1)	0.2980 (7)	−0.1278 (7)	2.5 (8)
C13	−0.463 (1)	0.3505 (8)	−0.2142 (8)	3 (1)
C14	−0.382 (1)	0.3636 (9)	−0.3062 (8)	4 (1)
C15	−0.243 (1)	0.3247 (8)	−0.3151 (7)	3.2 (9)
C16	−0.182 (1)	0.2705 (7)	−0.2303 (7)	2.5 (8)
C17	−0.494 (1)	0.279 (1)	−0.0284 (7)	4 (1)
C18	−0.029 (1)	0.2268 (9)	−0.2375 (7)	3 (1)
C19	−0.399 (1)	−0.1024 (8)	0.3194 (7)	2.5 (8)
C20	−0.391 (1)	−0.1221 (8)	0.2329 (7)	2.6 (8)
C21	−0.2939 (9)	−0.0639 (7)	0.1642 (6)	2.0 (7)
C22	−0.491 (1)	−0.141 (1)	0.4178 (7)	4 (1)
C23	−0.245 (1)	−0.0581 (8)	0.0572 (6)	2.9 (9)
C24	−0.038 (1)	−0.0825 (7)	0.4381 (6)	2.4 (8)
C25	0.099 (1)	−0.0842 (8)	0.3961 (7)	2.6 (8)
C26	0.099 (1)	−0.0194 (7)	0.2960 (7)	2.2 (8)
C27	−0.098 (1)	−0.1373 (8)	0.5443 (6)	3.3 (9)
C28	0.225 (1)	0.0021 (8)	0.2168 (7)	3.2 (9)
C29	−0.331 (1)	0.2863 (7)	0.3612 (6)	2.4 (8)
C30	−0.434 (1)	0.3020 (8)	0.3082 (7)	3.1 (9)
C31	−0.424 (1)	0.2041 (8)	0.2988 (6)	2.5 (8)
C32	−0.294 (1)	0.3670 (8)	0.3965 (8)	4 (1)
C33	−0.518 (1)	0.1724 (8)	0.2523 (7)	3 (1)
B1	−0.270 (1)	0.008 (1)	0.3714 (7)	2.2 (9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

characterized, but addition of $K[HB(Pz^*)_3]$ results in the transformation of the reaction mixture into a bright orange-yellow solution. The time required for this transformation to occur depends on the isocyanide used in the reaction. Filtration of this solution followed by evaporation of solvent from the filtrate gives the crude products as yellow solids in approximately 60% yield. The crude products can be recrystallized from toluene at −20 °C and have been fully characterized by ^1H NMR, ^{13}C NMR, IR, and UV-vis spectroscopy. At the present time it has not been possible to obtain proper analyses for complexes **1a–c**. However, ^{13}C NMR spectra of the complexes show resonances that can be assigned to toluene. The toluene content in the final products has been found to be nonstoichiometric in most cases and can vary from one sample to the next. It is possible that the entrapped toluene is related to the cause for the poor quality of the elemental analyses although there have been previous reports of trouble with the analysis of compounds containing hydrotris(pyrazol-1-yl)borate ligands.[11]

The solid-state structures for **1a,b** were obtained by single-crystal X-ray diffraction (Figures 1 and 2, respectively). Positional parameters as well as selected bond angles and distances for **1a,b** are listed in Tables I–III. In both complexes the geometry about the rhodium atom (formally d^8, Rh(I)) is square planar with the noncoordinated pyrazole ring of the $HB(Pz^*)_3$ roughly cofacial with and over the N_2RhC_2 square plane. Inspection of the intramolecular contacts indicates that there is no π-bonding interaction present between the rhodium atom and noncoordinated pyrazole ring of the $HB(Pz^*)_3$ ligand (*d*(Rh–Pz* centroid) = 3.93 and 3.87 Å for **1a** and **1b**, respectively). The isocyanide ligands in **1a** are slightly bent (C–N–C angles = 163.8 and 168.4°), as has been observed for other complexes containing this ligand.[9a] The bend is oriented so as to force C2 and C8 out of the square plane containing the rhodium atom and its neighboring coordinated atoms and places the sterically bulky *tert*-butyl groups of the isocyanides on the same side of the square plane as the nonco-

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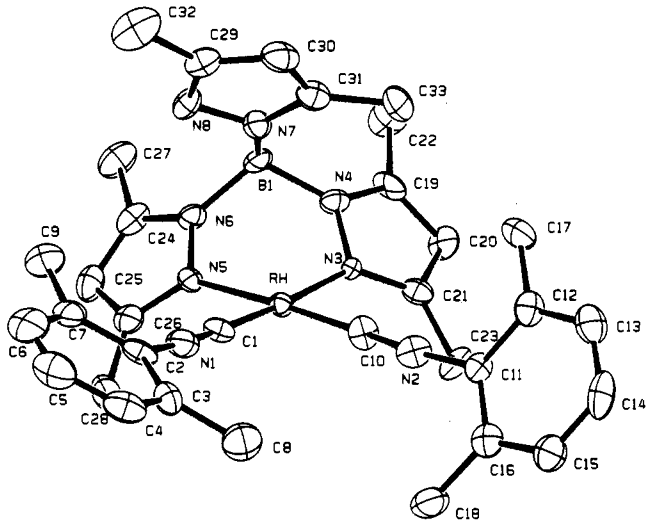

Figure 2. ORTEP drawing of **1b**. Ellipsoids are shown at the 50% probability level.

Table III. Selected Distances (Å) and Angles (deg) for $HB(Pz^*)_3Rh(CN(neopentyl))_2$ and $HB(Pz^*)_3Rh(CN(2,6\text{-}xylyl))_2$

$HB(Pz^*)_3Rh(CN(neopentyl))_2$		$HB(Pz^*)_3Rh(CN(2,6\text{-}xylyl))_2$	
	Angles		
C1–Rh–C7	85.7 (2)	C1–Rh–C10	86.3 (4)
C1–Rh–N3	95.9 (1)	C1–Rh–N3	175.9 (3)
C1–Rh–N5	174.3 (1)	C1–Rh–N5	94.4 (4)
C7–Rh–N3	175.8 (1)	C10–Rh–N3	93.2 (4)
C7–Rh–N5	91.4 (1)	C10–Rh–N5	176.4 (4)
N3–Rh–N5	86.6 (1)	N3–Rh–N5	86.4 (3)
C1–N1–C2	163.8 (4)	C1–N1–C2	174.5 (9)
C7–N2–C8	168.4 (4)	C10–N2–C11	174.3 (8)
N1–C1–Rh	174.4 (3)	N1–C1–Rh	176.5 (8)
N2–C7–Rh	176.4 (3)	N2–C10–Rh	178.5 (8)
N1–C2–C3	112.5 (3)		
N2–C8–C9	112.4 (3)		
	Distances		
Rh–C1	1.872 (4)	Rh–C1	1.86 (1)
Rh–C7	1.884 (4)	Rh–C10	1.879 (9)
Rh–N3	2.079 (3)	Rh–N3	2.072 (8)
Rh–N5	2.089 (3)	Rh–N5	2.085 (7)
N2–C7	1.156 (5)	N2–C10	1.16 (1)
N2–C8	1.432 (5)	N2–C11	1.41 (1)
N1–C1	1.165 (5)	N1–C1	1.17 (1)
N1–C2	1.433 (5)	N1–C2	1.38 (1)

ordinated pyrazole of the $HB(Pz^*)_3$ ligand. The stronger π-acceptor xylyl isocyanides in **1b** adopt the more commonly observed linear geometry (C–N–C angles = 174.5 and 174.3°), and the xylyl rings are oriented in a less sterically congested manner. The square-planar geometry in both complexes is slightly distorted with the N3–Rh–N5 and C–Rh–C angles being approximately 4° less than ideal. This contraction, undoubtedly caused by the bidentate $HB(Pz^*)_3$ ligand, is compensated for by a corresponding increase in the other two angles in the square plane.

The ^1H NMR spectrum of **1a** in THF-d_8 shows resonances at δ 2.103, 2.240, and 5.627 in a ratio of 3:3:1, which are assigned to the two methyl groups and ring proton, respectively, of three equivalent 3,5-dimethylpyrazole rings of the $HB(Pz^*)_3$ ligand. The ^1H NMR spectrum of **1a** obtained in THF-d_8 at −100 °C is identical with that of the room-temperature spectrum. The variable-temperature ^{13}C NMR spectra of **1a** show no temperature dependence of the $HB(Pz^*)_3$ ligand carbon resonances.[12] The corresponding variable-temperature ^1H and ^{13}C NMR spectra of **1b** are similar to those of **1a** in regard to the $HB(Pz^*)_3$ ligand resonances. All attempts to obtain the variable-temperature ^{14}N or ^{15}N NMR spectra of **1a** were unsuccessful.

Table IV. Positional Parameters and B(eq) for $[HB(Pz^*)_3Rh(H)(CN(neopentyl))_2]BF_4$[a]

atom	x	y	z	B, Å^2
Rh	0.11297 (4)	0.09494 (2)	0.23997 (4)	1.82 (2)
N1	0.0593 (4)	0.1810 (2)	0.3913 (4)	2.7 (2)
N2	0.2784 (4)	0.1682 (2)	0.1548 (4)	2.5 (2)
N3	0.2350 (4)	0.0608 (2)	0.3727 (4)	1.9 (2)
N4	0.2333 (4)	0.0089 (2)	0.3796 (4)	2.2 (2)
N5	0.1414 (4)	0.0356 (2)	0.1393 (4)	2.0 (2)
N6	0.1498 (4)	−0.0124 (2)	0.1833 (4)	2.1 (2)
N7	−0.0077 (4)	0.483 (2)	0.2845 (4)	1.8 (2)
N8	0.0239 (4)	0.0004 (2)	0.3208 (4)	1.9 (2)
C1	0.0776 (5)	0.1491 (2)	0.3337 (5)	2.2 (3)
C2	0.0514 (6)	0.2229 (2)	0.4674 (5)	3.1 (3)
C3	−0.0693 (6)	0.2360 (2)	0.4781 (5)	2.7 (3)
C4	−0.1260 (7)	0.1924 (3)	0.5264 (6)	4.4 (4)
C5	−0.1369 (6)	0.2510 (3)	0.3650 (6)	4.2 (4)
C6	−0.0606 (7)	0.2817 (3)	0.5552 (6)	4.5 (4)
C7	0.2192 (5)	0.1397 (2)	0.1870 (5)	2.1 (3)
C8	0.3452 (6)	0.2069 (2)	0.1132 (6)	3.3 (3)
C9	0.4728 (6)	0.1972 (3)	0.1430 (6)	3.9 (4)
C10	0.5099 (8)	0.1949 (6)	0.2643 (8)	11.1 (8)
C11	0.5294 (7)	0.2415 (4)	0.0946 (9)	7.2 (5)
C12	0.4997 (8)	0.1483 (4)	0.086 (1)	8.1 (6)
C13	0.3174 (5)	−0.0071 (2)	0.4607 (5)	2.2 (3)
C14	0.3727 (5)	0.0349 (2)	0.5065 (5)	2.4 (3)
C15	0.3200 (5)	0.0768 (2)	0.4495 (5)	2.2 (3)
C16	0.3366 (5)	−0.0620 (3)	0.4879 (5)	2.8 (3)
C17	0.3456 (5)	0.1319 (3)	0.4707 (5)	3.0 (3)
C18	0.1618 (5)	−0.0461 (2)	0.1039 (5)	2.7 (3)
C19	0.1598 (5)	−0.0194 (3)	0.0083 (5)	3.2 (3)
C20	0.1462 (5)	0.0310 (2)	0.0319 (5)	2.4 (3)
C21	0.1760 (6)	−0.1013 (3)	0.1261 (6)	4.3 (4)
C22	0.1368 (6)	0.0756 (3)	−0.0436 (5)	3.2 (3)
C23	−0.0646 (5)	−0.0229 (2)	0.3542 (5)	2.5 (3)
C24	−0.1537 (5)	0.0100 (2)	0.3376 (5)	2.6 (3)
C25	−0.1170 (5)	0.0541 (2)	0.2941 (5)	2.2 (3)
C26	−0.0577 (6)	−0.0757 (3)	0.4004 (6)	3.6 (3)
C28	−0.1809 (5)	0.1014 (3)	0.2567 (5)	2.8 (3)
B1	0.1397 (6)	−0.0212 (3)	0.3047 (6)	2.3 (3)
F1	0.1180 (7)	0.1784 (3)	0.8069 (8)	13.8 (5)
F2	0.2380 (6)	0.1807 (2)	0.6900 (5)	9.7 (4)
F3	0.2839 (8)	0.1692 (4)	0.8591 (6)	16.4 (7)
F4	0.2291 (9)	0.2437 (2)	0.8049 (8)	17.1 (6)
B2	0.218 (1)	0.1964 (4)	0.7859 (9)	5.7 (6)
O1	0.5641 (5)	0.0499 (2)	0.7512 (4)	5.1 (3)
C29	0.5590 (6)	−0.0000 (4)	0.7916 (7)	5.2 (4)
C30	0.4485 (8)	−0.0055 (4)	0.8284 (9)	7.1 (6)
C31	0.4119 (8)	0.0485 (4)	0.843 (1)	7.6 (6)
C32	0.500 (1)	0.0809 (4)	0.809 (1)	8.4 (6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

The IR spectrum of **1a** in the solid state contains two absorptions at 2159 and 2106 cm^{-1}, assigned as the symmetric and asymmetric stretch of the isocyanide ligands. The IR spectrum of **1a** in benzene solution is identical with that of the corresponding solid-state spectrum. Solution (C_6H_6) and solid-state (KBr pellet) IR spectra of $H_2B(Pz^*)_2Rh(CN(neopentyl))_2$ (**2**) also possess two absorptions at 2158 and 2104 cm^{-1}.

Reaction of **1a** with 1 equiv of $HBF_4{\cdot}Et_2O$ in THF leads to the formation of the salt, **3**, in quantitative yield (eq 2). The ^1H NMR spectrum of **3** contains a doublet at δ −12.58 and a total of six

(2)

resonances for the $HB(Pz^*)_3$ ligand in a ratio of 6:6:3:3:2:1. Complex **3** has been fully characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. The X-ray

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[12] The resonance assigned to the isonitrile carbon undergoes an upfield chemical shift from δ 151.8 (room temperature) to δ 148.5 (−100 °C).

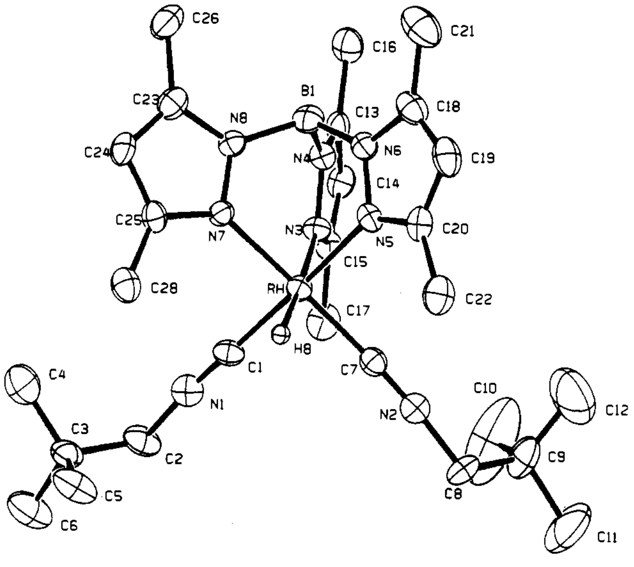

Figure 3. ORTEP drawing of the cation of **3**. Ellipsoids are shown at the 50% probability level.

Table V. Selected Angles (deg) and Distances (Å) for $[HB(Pz^*)_3Rh(H)(CN(neopentyl))_2]BF_4$

C1-Rh-C7	89.0 (2)	Rh-C1	1.924 (7)
C1-Rh-N3	92.6 (2)	Rh-C7	1.932 (7)
C1-Rh-N5	176.7 (2)	Rh-N3	2.186 (5)
C1-Rh-N7	92.2 (2)	Rh-N5	2.056 (5)
C7-Rh-N3	96.0 (2)	Rh-N7	2.045 (5)
C7-Rh-N5	93.9 (2)	N1-C1	1.144 (7)
C7-Rh-N7	175.5 (2)	N1-C2	1.457 (8)
N3-Rh-N5	88.8 (2)	N2-C7	1.149 (7)
N3-Rh-N7	88.3 (2)	N2-C8	1.444 (8)
N5-Rh-N7	84.8 (2)		
C1-N1-C2	172.6 (6)		
C7-N2-C8	175.3 (6)		

structure for the cation of **3** is shown in Figure 3. Positional parameters as well as selected bond angles and distances for **3** are listed in Tables IV and V. The cation of **3** is an octahedrally coordianted metal hydride possessing a tridentate $HB(Pz^*)_3$ ligand. The Rh-C bonds of **3** are slightly longer than for **1a** with a corresponding shortening of the isocyanide C-N bonds, an observation consistent with the decreased π-back-bonding capability of Rh(III) as well as the observed IR spectrum (ν_{CN} = 2246 and 2225 cm^{-1}). The Rh-N bond trans to the hydride is significantly longer than the other Rh-N bonds. The *tert*-butyl groups are oriented so as to place them as far apart as possible from one other.

Discussion

Table VI. Infrared Spectral Data (ν_{CNR}) for $HB(Pz^*)_3Rh(CNR)_2$ (**1a–c**) and $H_2B(Pz^*)_2Rh(CN(neopentyl))_2$ (**2**)

complex	medium	ν_1, cm^{-1}	ν_2, cm^{-1}
$HB(Pz^*)Rh(CN(neopentyl))_2$ (**1a**)	C_6H_6	2159	2106
	KBr	2158	2106
$H_2B(Pz^*)_2Rh(CN(neopentyl))_2$ (**2**)	C_6H_6	2158	2104
	KBr	2160	2105
$HB(Pz^*)_3Rh(CN(2,6\text{-xylyl}))_2$ (**1b**)	C_6H_6	2129	2064
	KBr	2128	2064
$HB(Pz^*)_3Rh(CNCH_3)_2$ (**1c**)	C_6H_6	2174	2122
	KBr	2180	2128

Although there has been much indirect evidence for the existence of η^2-coordinated hydrotris(pyrazolyl)borate[13] and tetrakis(pyrazolyl)borate[14] ligands in solution, crystallographically characterized examples of this type of ligation are less common, and only a few complexes with rhodium are known.[7,10a] We know of several other structures of transition-metal complexes containing an η^2-hydrotris(pyrazolyl)borate ligand, those of $[\eta^2\text{-}HB(Pz^*)_3]Pt(CH_3)(CO)$[10b] and its *tert*-butyl isocyanide analogue,[10c] $[\eta^2\text{-}HB(Pz)_3]Au(CH_3)_2$,[10d] $[\eta^2\text{-}HB(Pz)_3]_3Yb$,[10e] a bridging complex $[\eta^1,\eta^2\text{-}HB(Pz)_3][CuCl][Cu(C_2H_4)]$,[10f] $(\eta^2\text{-}HBPz^*_3)Sn(\eta^3\text{-}HBPz^*_3)$,[10g] $(\eta^2\text{-}HBPz_3)_2Pd$,[10h] and $(\eta^2\text{-}HBPz_3)Mo(\mu\text{-}O_2CCH_3)Mo(\eta^3\text{-}HBPz_3)$.[10i] There also exists an example by Graham in which the protonation of one of the pyrazole ring nitrogens forces the ligand to be bidentate.[15] The presence of an η^2-$HB(Pz^*)_3$ ligand in the current study highlights the strong preference for d^8 rhodium(I) to form a 16-electron square-planar complex as opposed to adopting a five-coordinate trigonal-bipyramidal or square-pyramidal geometry, as was seen in the structure of $[\eta^2\text{-}HB(Pz)_3]Rh(olefin)_2$.[10a] These latter complexes, however, were believed to be tridentate in solution. Similarly, the complex $(HBPz_3)Pt(CO)CH_3$, found to be bidentate in the solid state,[10b] was shown to be tridentate in solution.[4d]

In the present study, effort has been focused on determining if the bidentate $HB(Pz^*)_3$ ligand observed in the solid-state structure of **1a** persists in solution. The ^1H NMR (400 MHz) and ^{13}C NMR spectra of **1a** at room temperature and −100 °C show only one type of pyrazole ring which would be consistent with (1) a tridentate $HB(Pz^*)_3$ ligand undergoing rotation about the Rh-B axis that is rapid on the NMR time scale or (2) a bidentate $HB(Pz^*)_3$ ligand in which the coordinated rings and noncoordinated ring rapidly exchange on the NMR time scale.

A comparison of the solution and solid-state IR spectra of **1a** reveals that there is no shift in the isonitrile stretching frequencies in going from the solid state to benzene solution (Table VI). Furthermore, a comparison of the solution and solid-state IR spectra of **1a** with the analogous spectra of **2** (a complex in which η^2-coordination of the $H_2B(Pz^*)_2$ ligand is required, Table VI) shows the isonitrile stretching frequencies of both complexes to be identical in both the solid state and solution. Conversely, Ghosh and Graham have observed that there is a 20–30-cm^{-1} difference in the ν_{CO} stretch for an isomeric mixture of η^2- and η^3-$HB(Pz^*)_3Rh(CO)_2$ in CH_2Cl_2 solution.[6] A comparison of the solution IR spectra of η^3-$HB(Pz^*)_3Rh(CO)_2$ and $H_2B(Pz^*)_2Rh(CO)_2$ shows a similar difference of 20–30 cm^{-1} in the ν_{CO} stretch.[6] Although not conclusive, the comparison of IR data for **1a** and **2**, combined with the results obtained by Graham with the analogous carbonyl complexes, therefore suggests that the $HB(Pz^*)_3$ ligand of **1a** is fluxional and bidentate in solution.

In an attempt to stop the fluxional process, **1a** was reacted with slightly less than 1 equiv of $HBF_4\cdot Et_2O$ with the idea that protonation of the free nitrogen of the $HB(Pz^*)_3$ ligand would give $[HB(Pz^*)_2(Pz^*H^+)Rh(CNR)_2]BF_4$ (R = neopentyl), the solution IR spectrum of which could be compared with that of **1a**. However, the only product formed in the reaction was $[HB(Pz^*)_3Rh(H)(CNR)_2]BF_4$ (**3**), the result of protonation at rhodium. This result was surprising since Graham et al. have shown that protonation of the analogous carbonyl complex, $HB(Pz^*)_3Rh(CO)_2$, occurs at one of the nitrogens of the $HB(Pz^*)_3$ ligand.[15] They also found that protonation of the iridium complex occurs at the metal, as observed in the present case. While addition of triethylamine to **3** in THF solution does not result in the reformation of **1a**, the stronger base $Li[N(i\text{-}Pr)_2]$ results in an

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instantaneous deprotonation. It is possible that initial protonation occurs at one of the nitrogens of the $HB(Pz^*)_3$ ligand followed by rapid oxidative addition of the resulting N–H bond to rhodium, but at this time we have no evidence in support of any particular mechanism for this reaction.

Conclusions

A series of complexes of the general type $HB(Pz^*)_3Rh(CNR)_2$ have been prepared and characterized by single-crystal X-ray diffraction. The solid-state structures of the complexes are square planar with an η^2-$HB(Pz^*)_3$ ligand. The IR and multinuclear NMR spectra of the complexes in solution indicate that the $HB(Pz^*)_3$ ligand remains bidentate in solution and is fluxional.

Experimental Section

General Procedures. All operations and routine manipulations were performed under a nitrogen atmosphere, either on a high vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corp. dri-lab. Bis(μ-chloro)tetrakis(ethylene)dirhodium(I),[16] potassium hydrotris(3,5-dimethylpyrazolyl)borate,[17] potassium dihydrobis(3,5-dimethylpyrazolyl)borate,[17] and methyl isocyanide[18] were prepared according to published procedures. Neopentyl isocyanide was prepared according to the preparation for methyl isocyanide. The 2,6-xylyl isocyanide was purchased from Strem Chemicals, Inc. and used without further purification. All deuterated solvents were purchased from MSD Isotopes Merck Chemical Division, distilled under vacuum from dark purple solutions of benzophenone ketyl, and stored in ampules with Teflon-sealed vacuum line adapters. All other solvents were distilled from dark purple solutions of benzophenone ketyl and stored in the dry-lab.

^1H (400 MHz) NMR spectra were recorded on a Bruker AMX 400 spectrometer. ^{13}C NMR were recorded on either a Bruker AMX 400 (100 MHz) or GE 300 (75 MHz) spectrometer. ^1H NMR chemical shifts were measured in ppm (δ) relative to tetramethylsilane, using the residual ^1H resonances in the deuterated solvents as an internal reference: C_6D_6 (δ 7.15), toluene-d_8 (δ 2.09), and THF-d_8 (δ 3.58). ^{13}C NMR chemical shifts were measured in ppm relative to the deuterated solvent resonance: C_6D_6 (δ 128), THF-d_8 (δ 67.4, 25.3). Infrared spectra were recorded on a Mattson Instruments, Inc. Sirius 100 infrared spectrometer. UV–vis spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer. Elemental analysis were performed by either Desert Analytics-Organic Microanalysis Laboratory or Schwarzkopf Microanalytical Laboratory. An Enraf-Nonius CAD4 diffractometer was used for X-ray crystal structure determination.

Preparation of $HB(Pz^*)_3Rh(CN(neopentyl))_2$ (1a). To a stirred suspension of 237 mg (0.61 mmol) of bis(μ-chloro)tetrakis(ethylene)dirhodium(I) in 10 mL of benzene was added dropwise a solution of 235 mg (290 μL, 2.43 mmol) of neopentyl isocyanide in 3 mL of benzene over a 2-h period. The original orange-red suspension turned muddy red during the addition and eventually became black. The reaction mixture was stirred for 4 h at room temperature, and then 410 mg (1.22 mmol) of potassium hydrotris(3,5-dimethylpyrazolyl)borate was added all at once. Over the next 10–15 min the reaction mixture underwent a dramatic color change from black to bright orange-yellow. The reaction was stirred an additional 4 h at room temperature and was filtered to remove insoluble potassium chloride and unreacted borate salt. The filtrate was evaporated in vacuo to give 0.6 g of crude product, which contained a trace amount of an unidentified impurity. The crude product was recrystallized from toluene at −20 °C to give 211 mg (29%) of yellow microcrystals.

^1H NMR (C_6D_6): δ 0.675 (s, 18 H, $C(CH_3)_3$, 2.273 (s, 9 H, $Pz(CH_3)$), 2.510 (s, 9 H, $Pz(CH_3)$), 2.527 (s, 4 H, NCH_2), 5.841 (s, 3 H, PzH). ^{13}C NMR (C_6D_6) (75 MHz): δ 13.0 (q, J_{CH} = 124 Hz, $PzCH_3$), 15.5 (q, J_{CH} = 134 Hz, $PzCH_3$), 26.3 (q, J_{CH} = 128 Hz, $C(CH_3)_3$), 31.5 (s, $C(CH_3)_3$), 55.5 (t, J_{CH} = 146 Hz, NCH_2), 105.5 (d, J_{CH} = 171 Hz, PzCH), 144.2 (quintet, J = 8 Hz, PzC_q), 148.8 (quintet, J = 8 Hz, PzC_q), 151.5 (d, J_{CRh} = 64 Hz, isonitrile C). IR (KBr, cm^{-1}): 2463 (w, B–H), 2158 (s, CNR), 2106 (s, CNR). UV–vis (C_6H_6), nm (ϵ): 409 (2900), 373 (10000), 303 (27000). Anal. Calc (found) for $C_{27}H_{44}BN_8Rh$: C, 54.56 (49.95); H, 7.46 (7.04); N, 18.84 (17.51).

Preparation of $HB(Pz^*)_3Rh(CN(2,6\text{-xylyl}))_2$ (1b). The synthesis of **1b** was identical with that of **1a** except that 228 mg (0.590 mmol) of bis(μ-chloro)tetrakis(ethylene)rhodium(I) was used with 307 mg (2.34 mmol) of 2,6-xylyl isocyanide and 420 mg (1.24 mmol) of potassium hydrotris(3,5-dimethylpyrazolyl)borate. The crude product was recrystallized from toluene at −20 °C to yield 720 mg (92%) of the product as yellow microcrystals.

^1H NMR (C_6D_6): δ 2.169 (s, 12 H, aryl CH_3), 2.247 (s, 9 H, $PzCH_3$), 2.458 (s, 9 H, $PzCH_3$), 5.806 (s, 3 H, PzH), 6.645 (d, J = 8.0 Hz, 4 H, aryl H), 6.752 (t, J = 8.0 Hz, 2 H, aryl H). $^{13}C\{^1H\}$ NMR (THF-d_8) (100 MHz): δ 12.9 ($PzCH_3$), 15.4 ($PzCH_3$), 19.1 (aryl CH_3), 105.7 (PzCH), 127.8 (aryl CH), 128.6 (aryl CH), 130.3 (aryl C_q) 135.0 (aryl C_q), 144.7, (PzC_q), 148.8, (PzC_q), 162.1 (d, J_{CRh} = 68 Hz, isonitrile C). IR (KBr, cm^{-1}): 2465 (w, B–H), 2128 (s, CNR), 2064 (s, CNR). UV–vis (C_6H_6), nm (ϵ): 404 (2800), 327 (16700). Anal. Calc (found) for $C_{33}H_{40}BN_8Rh\cdot{}^1/_2C_7H_8$: C, 61.55 (60.32); H, 6.31 (6.27); N, 15.95 (16.18).

Preparation of $HB(Pz^*)_3Rh(CNCH_3)_2$ (1c). The synthesis of **1c** was identical with that of **1a** except that 318 mg (0.818 mmol) of bis(μ-chloro)tetrakis(ethylene)dirhodium(I) was used with 172 μL (134 mg, 3.272 mmol) of methyl isocyanide and 550 mg (1.636 mmol) of potassium hydrotris(3,5-dimethylpyrazolyl)borate. The crude product was recrystallized from toluene at −20 °C to yield 460 mg (58%) of the product as a yellow solid.

^1H NMR (C_6D_6): δ 2.105 (s, 9 H, $PzCH_3$), 2.234 (s, 9 H, $PzCH_3$), 3.168 (s, 6 H, $CNCH_3$), 5.360 (s, 3 H, PzH). $^{13}C\{^1H\}$ NMR (THF-d_8) (100 MHz): δ 12.9 ($PzCH_3$), 15.2 ($PzCH_3$), 29.0 ($CNCH_3$), 105.4 (PzCH), 144.5 (PzC_q), 148.5 (PzC_q), 151.0 (d, J_{CRh} = 66 Hz, isonitrile C). IR (KBr, cm^{-1}): 2469 (w, B–H), 2180 (s, CNR), 2128 (s, CNR). UV–vis (C_6H_6), nm (ϵ): 370 (6200), 302 (20600). Anal. Calc (found) for $C_{19}H_{28}BN_8Rh\cdot C_7H_8$: C, 54.37 (53.69); H, 6.32 (6.06): N, 19.51 (19.66).

Preparation of $H_2B(Pz^*)_2Rh(CN(neopentyl))_2$ (2). To a stirred suspension of 100 mg (0.257 mmol) of bis(μ-chloro)tetrakis(ethylene)dirhodium(I) in a 10:3 benzene:THF solvent mixture was added dropwise a solution of 123 μL (119 mg, 1.03 mmol) of neopentyl isocyanide in 3 mL of benzene. The reaction mixture turned black during the addition. The reaction mixture was stirred at room temperature for 5 h, and then 124 mg (.514 mmol) of potassium dihydrobis(3,5-dimethylpyrazolyl)borate was added all at once. The reaction mixture slowly changed color from black to dark orange over a 30-min period. After 5 h the reaction mixture was filtered to remove KCl and unreacted borate salt. The filtrate was evaporated in vacuo to give a brownish yellow solid. The crude product was recrystallized from toluene at −20 °C to yield 140 mg (54%) of a yellow, air-sensitive solid.

^1H NMR (C_6D_6): δ 0.661 (s, 18 H, $C(CH_3)_3$), 2.344 (s, 6 H, $PzCH_3$), 2.550 (s, 6 H, $PzCH_3$), 2.568 (s, 4 H, NCH_2), 5.748 (s, 2 H, PzH). $^{13}C\{^1H\}$ NMR (C_6D_6) (100 MHz): δ 8.3 ($PzCH_3$), 10.6 ($PzCH_3$), 21.8 ($C(CH_3)_3$), 26.8 ($C(CH_3)_3$, 51.0 (NCH_2), 100.1 (PzCH), 139.0 (PzC_q), 143.5 (PzC_q), 147.4 (d, J_{CRh} = 66 Hz, isonitrile C). IR (KBr, cm^{-1}): 2445 (w, B–H), 2160 (s, CNR), 2105 (s, CNR). UV–vis (C_6H_6), nm (ϵ): 372 (5800), 307 (19000). Anal. Calc (found) for $C_{22}H_{38}BN_8Rh$: C, 52.82 (51.56); H, 7.66 (7.59): N, 16.80 (16.03).

Preparation of $[HB(Pz^*)_3Rh(H)(CN(neopentyl))_2]BF_4$ (3). To a stirred solution of 74 mg (0.124 mmol) of **1a** in 5 mL of THF was added 22 μL (0.124 mmol) of $HBF_4\cdot Et_2O$ at which point the reaction solution turned colorless. The reaction mixture was stirred overnight, and then the solvent was removed in vacuo, giving the product in essentially quantitative yield as a white solid.

^1H NMR (THF-d_8): δ −12.583 (d, J_{HRh} = 12.8 Hz, 1 H, Rh–H), 1.019 (s, 18 H, $C(CH_3)_3$), 2.296 (s, 6 H, $PzCH_3$), 2.367 (s, 6 H, $PzCH_3$), 2.416 (s, 3 H, $PzCH_3$), 2.435 (s, 3 H, $PzCH_3$), 4.044 (AB quartet, J_{HH} = 15.3 Hz, J_2 = 18.0 Hz, 2 H, NCH_2), 5.893 (s, 2 H, PzH), 5.947 (s, 1 H, PzH). IR (KBr, cm^{-1}): 2552 (w, B–H str), 2246 (s, CNR), 2225 (s, CNR). Anal. Calc (found) for $C_{27}H_{45}B_2F_4N_8Rh\cdot C_7H_8$: C, 49.35 (50.43); H, 6.97 (7.24); N, 14.82 (15.17).

Solution and Refinement of Crystal Structures. $HB(Pz^*)_3Rh(CN(neopentyl))_2$ (1a). A well-formed crystal of **1a** with approximate dimensions 0.52 × 0.41 × 0.34 mm^3 was mounted on a glass fiber and placed on the diffractometer under a cold stream of nitrogen at −80 °C. The lattice constants were obtained from 25 centered reflections with values of χ between 10 and 60°. Cell reduction revealed a primative monoclinic crystal system. Data were collected in accord with the parameters in Table VII. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). The space group was uniquely assigned as $P2_1/c$ on the basis of the systematic absences, and the correctness of this choice was confirmed by successful solution of the Patterson map, showing the rhodium atom. The structure was expanded by using the DIRDIF program supplied by the Molecular Structure Corp. whose programs were used for further refinement of the structure.[19] Anisotropic refinement of all non-hydrogen atoms allowed

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Table VII. Summary of Crystallographic Data for **1a,b** and **3**

	1a	**1b**	**3**
Crystal Parameters			
empirical formula	$C_{27}H_{44}BN_8Rh$	$C_{33}H_{40}BN_8Rh\cdot{}^1/_2C_7H_8$	$C_{27}H_{45}B_2F_4N_8Rh\cdot C_4H_8O$
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$
Z	4	2	4
a, Å	12.882 (5)	10.179 (4)	12.028 (9)
b, Å	12.740 (6)	13.415 (4)	26.234 (6)
c, Å	18.836 (7)	14.792 (9)	12.298 (14)
α, deg	90	67.06 (3)	90
β, deg	101.11 (3)	75.61 (4)	100.13 (5)
γ, deg	90	75.47 (3)	90
V, Å^3	3033 (4)	1775 (3)	3820 (8)
d_{calc}, g/cm^3	1.30	1.313	1.311
t, °C	-80	-80	-80
Measurement of Intensity Data			
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
$\lambda_{Mo\,K\alpha}$ (graphite monochromated radiation)	0.71069	0.71069	0.71069
scan type	$2\theta/\omega$	$2\theta/\omega$	$2\theta/\omega$
scan rate, deg/min	2–16.5	2–16.5	2–16.5
tot background time	scan time/2	scan time/2	scan time/2
take-off angle, deg	2.6	2.6	2.6
scan range, deg	0.7 + 0.35 tan θ	0.7 + 0.35 tan θ	0.7 + 0.35 tan θ
2θ range, deg	2–44	2–50	2–44
data colled	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,\pm l$
no. of data colled	4122	6744	5187
no. of unique data $>3\sigma$	3108	3322	3429
no. of parameters varied	334	400	428
abs coeff, cm^{-1}	5.77	5.07	4.91
systematic absences	$0k0$, k odd $h0l$, l odd	none	$0k0$, k odd $h0l$, l odd
abs corrn	none	differential	differential
range of transm factors		0.78–1.13	0.92–1.07
equivalent data	$0kl$, $0k\bar{l}$	$0kl$, $0k\bar{l}$	$0kl$, $0k\bar{l}$
agrmnt of equiv data (F_o)	0.008	0.073	0.039
R_1	0.031	0.058	0.043
R_2	0.043	0.060	0.051
goodness of fit	1.36	1.45	1.96
largest peak in final E map	0.37	0.87	1.04

the use of a difference Fourier map for location of the hydrogen atoms, the coordinates of which were subsequently idealized. An empirical absorption correction was applied by using the program DIFABS. Final anisotropic refinement was carried out on all non-hydrogen atoms, with both positional and thermal parameters of the hydrogens "riding" with the atom to which they were attached.

$HB(Pz^*)_3Rh(CN(2,6\text{-xylyl}))_2\cdot{}^1/_2C_7H_8$ (1b). A crystal with approximate dimensions 0.11 × 0.11 × 0.11 mm^3 was chosen for study. The lattice constant determination, cell reduction, data collection, structure solution, and refinement of the structure for **1b** were conducted similarly to that of **1a** with the following exception. After the initial location and refinement of all of the non-hydrogen atoms, a difference Fourier map showed three significant peaks located at considerable distance from the Rh atom. A crystal packing view of the structure revealed a planar array of six atoms located on a center of symmetry. The three atoms were assigned as half of a disordered toluene molecule and were refined isotropically as a rigid group (half of a benzene molecule). Further refinement followed by inspection of the Fourier map never revealed any preference for orientation of the methyl group on the toluene molecule: hence, the fragment was left as benzene in the final refinement model.

$[HB(Pz^*)_3Rh(H)(CN(\text{neopentyl}))_2]BF_4\cdot THF$ (3). A colorless platelet of approximate dimensions 0.38 × 0.30 × 0.22 mm^3 was chosen for study. The lattice constant determination, cell reduction, data collection, structure solution, and refinement of the structure for **3** were conducted similarly to that of **1a** with the following exceptions. After initial placement of the Rh atom from the Patterson map, the remainder of the non-hydrogen atoms were located in the Fourier map, including the BF_4 fragment, a molecule of THF, and the hydrogen attached to Rh. The hydrogen attached to Rh was refined isotropically.

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Supplementary Material Available: Tables S-I–S-XV, giving bond distances and angles, anisotropic thermal parameters, coordinates of hydrogen atoms, and least-squares planes (32 pages); listings of calculated and observed structure factors (68 pages). Ordering information is given on any current masthead page.

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(19) $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$, $R_2 = [\sum w(|F_o| - |F_c|^2]^{1/2}/\sum wF_o^2$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', and f'': Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.