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Hydrotripyrazolylborate Complexes of Rhodium and Iridium

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The complexes $HB(3,5\text{-}Me_2pz)_3RhCl_2(MeOH)$ (**2**) and $[HBpz_3RhCl_2]_2$ (**41**) have been prepared from the reaction of the appropriate sodium pyrazolylborate with $RhCl_3 \cdot xH_2O$ in refluxing methanol. **41** reacts with acetonitrile to give $HBpz_3RhCl_2(MeCN)$ (**42**). The complexes **2** and **42** are convenient starting materials for a variety of derivatives. Many neutral donor ligands readily displace the coordinated solvent molecules to give derivatives of the type $(HBpz_3)RhCl_2L$ (L = PR_3, AsR_3, pyridine, NR_3, RNC, CO; $HBpz_3$ = hydrotripyrazolylborato). Reactions with the appropriate silver or thallium salt gave complexes of the type $(HBpz_3)RhCl(Y)$ (Y = acac, hfac, S_2CNEt_2) and $(HBpz_3)RhY_2L$ (Y = acetate, no L; Y = CF_3CO_2, L = H_2O). A hydrido complex, $Et_3NH[HB(3,5\text{-}Me_2pz)_3RhCl_2H]$ (**25**), is obtained when **2** is reacted with H_2/Et_3N in refluxing toluene. Similar anionic complexes were obtained from the reaction of $(R_4N)X$ or $(AsPh_4)Cl$ with **2**. Reaction of $Na[HB(3,5\text{-}Me_2pz)_3]$ with $[(al)_2RhCl]_2$ gave $HB(3,5\text{-}Me_2pz)_3Rh(\eta^1\text{-al})(\eta^3\text{-al})$ (al = allyl). A few iridium(III) complexes containing the $HB(3,5\text{-}Me_2pz)_3$ ligand have also been prepared.

Introduction

The chemistry of the pentamethylcyclopentadienyl complexes of rhodium(III) and iridium(III) has been extensively developed during recent years by Maitlis and co-workers.[1] The parent complexes, $[(C_5Me_5)MCl_2]_2$, derived from the reaction of hexamethylbicyclo[2.2.0]hexadiene with $RhCl_3 \cdot 3H_2O$ or 1-(1-chloroethyl)pentamethylcyclopentadiene with $RhCl_3 \cdot 3H_2O$ and $IrCl_3 \cdot 5H_2O$ have inert $\eta^5\text{-}C_5Me_5$–metal bonds[1] but relatively labile and reactive metal–chlorine bonds. Of particular interest is the reaction of the chloro-bridged derivatives with molecular hydrogen in the presence of a base to give hydrido derivatives[1] (e.g., eq 1 and 2). In the presence

$$[(C_5Me_5)MCl_2]_2 + H_2/Et_3N \xrightarrow[20\ ^\circ C,\ CH_2Cl_2]{1\ h} [(C_5Me_5)M]_2HCl_3 \quad (1)$$

$$[(C_5Me_5)IrCl_2]_2 + H_2/Et_3N \xrightarrow[i\text{-PrOH/acetone/water}]{24\ h,\ 20\ ^\circ C} [(C_5Me_5)Ir]_2H_3Cl \quad (2)$$

of H_2 and base the complexes $[(C_5Me_5)MCl_2]_2$ or their hydrido derivatives $[(C_5Me_5)M]_2HCl_3$ and $[(C_5Me_5)IrHCl]_2$ exhibit catalytic activity with respect to the hydrogenation of olefins and acetylene.[1] Furthermore, dienes and trienes such as 1,3-butadiene and heptatriene were found to react with $[(C_5Me_5)MCl_2]_2$ in EtOH in the presence of Na_2CO_3 via a hydrido intermediate to yield η^3-allyl–metal(III) complexes, while 1,5-cyclooctadiene, norbornadiene, and ethylene gave $(C_5Me_5)Rh^I$ diene complexes[1] (e.g., eq 3).

$$[(C_5Me_5)RhCl_2]_2 + 1,5\text{-COD} \xrightarrow[Na_2CO_3]{EtOH} (C_5Me_5)Rh^I(1,5\text{-COD}) \quad (3)$$

It is well established in the literature that from a structural point of view the complex chemistry of the tripyrazolylborate anion frequently resembles that of cyclopentadienyl (or pentamethylcyclopentadienyl) complexes.[2] However, as might be expected for a tridentate N-donor ligand, the tripyrazolylborate complexes are kinetically less labile than their cyclopentadienyl analogues. This paper describes the synthesis and structural characterization of tris(3,5-dimethylpyrazolyl)borate and tripyrazolylborate complexes of rhodium(III) and iridium(III). The complexes obtained are, in many cases, structural analogues of known η^5-pentamethylcyclopentadienyl complexes. Previously reported pyrazolylborate complexes of rhodium and iridium are all complexes of the +1 oxidation state with the exception of $RB(pz)_3Rh(CO)I_2$.[3] This Rh(III) complex was synthesized by the I_2 oxidation of $(RB(pz)_3)_2Rh_2(CO)_3$.

Experimental Section

The sodium hydrotris(1-pyrazolyl)borate and sodium tris(3,5-dimethylpyrazolyl)borate salts were prepared according to Trofimenko.[4] $RhCl_3 \cdot 3H_2O$ and $H_2IrCl_6 \cdot xH_2O$ were utilized as obtained from Johnson Matthey Chemicals Ltd. The compound $[(al)_2RhCl]_2$ (al = allyl) was synthesized according to Powell and Shaw.[5] All other reagents and solvents were used as received except for the ACS toluene which was dried and distilled over sodium metal (N.B. the 0.01% water present in ACS toluene was found to be sufficient to convert **2** to **3**; see below). Proton magnetic resonance spectra were obtained on a Varian Associates T-60 nuclear magnetic resonance spectrophotometer unless stated otherwise, and infrared spectra were obtained on a Perkin-Elmer 337 grating infrared spectrophotometer.

Analytical and spectroscopic data for all new compounds are given in Tables I–IV. Difficulty was encountered in obtaining good analyses for some of these pyrazolylborate complexes even after repeated preparations and recrystallizations. Consequently a considerable number of the compounds reported in Tables I–IV have rather unsatisfactory analytical data. All of these complexes, however, had ^1H NMR spectra that were fully consistent with the formulation given. Elemental analyses were done by Microanalyses Laboratory, Toronto, and Canadian Analytical Services Ltd.

$HB(3,5\text{-}Me_2pz)_3$ Complexes. μ-Dichloro-bis[[hydrotris(3,5-dimethylpyrazolyl)borato]chlororhodium(III)] (1). $NaHB(3,5\text{-}Me_2pz)_3$ (0.774 g) was dissolved in 30 mL of methanol and added slowly to a stirred solution of $RhCl_3 \cdot 3H_2O$ (0.616 g) in 25 mL of methanol. The resulting mixture was refluxed for 1.5 h, the volume of the solution was reduced on a rotary evaporator, and the flask was placed in a refrigerator for a few hours. The product (**1**) crystallized from methanol as dark gold plates, 30% yield (0.331 g).

[Hydrotris(3,5-dimethylpyrazolyl)borato]dichloro(methanol)rhodium(III) (2). $NaHB(3,5\text{-}Me_2pz)_3$ (4.34 g), dissolved in 30 mL of methanol, was slowly added to a stirred solution of $RhCl_3 \cdot 3H_2O$ (3.56 g) in 10 mL of methanol. The resulting mixture was refluxed for 0.5 h and then filtered hot to remove metallic rhodium (N.B. occasionally, residual $NaBH_4$ present in the ligand in its impure form results in a small amount of reduction of $RhCl_3 \cdot 3H_2O$ to metallic rhodium). The filtrate was then refluxed for another 3 h and the first crop of crystals filtered from the hot solution. A second crop of crystals was recovered on reduction of the volume of filtrate. The combined product was recrystallized from methanol as golden yellow crystals, 68% yield (4.63 g).

[Hydrotris(3,5-dimethylpyrazolyl)borato]dichloroaquorhodium(III) (3). $NaHB(3,5\text{-}Me_2pz)_3$ (0.635 g) was refluxed in 25 mL of 95% EtOH for 2 h. When the mixture cooled, the product precipitated out as pale yellow prisms, 100% yield (0.551 g). The same product **3** is obtained if **2** is refluxed in ACS toluene straight from the bottle.

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(2) S. Trofimenko, *Acc. Chem. Res.*, **4**, 17 (1971).
(3) D. O'Sullivan and F. J. Lalor, *J. Organomet. Chem.*, **65**, C-47 (1974).
(4) S. Trofimenko, *J. Am. Chem. Soc.*, **88**, 1842 (1966).
(5) J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 583 (1966).

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Table I. Physical Data for Hydrotris(3,5-dimethylpyrazolyl)borate Complexes of Rhodium

				elemental analysis, %							
				calcd				found			
compd	characteristics	mp, °C	% yield	C	H	N	Cl	C	H	N	Cl
1	dark gold plates	228–233	30	38.3	4.7	17.8	15.0	39.7	5.2	16.6	14.9
2	gold prisms	296–298	69.5	38.2	5.2	16.7	14.1	37.8	4.9	17.5	15.2
3	pale yellow prisms	315	100	37.2	4.9			37.8	5.0		
4	yellow plates	259–262	72	39.9	4.9	19.1	13.8	40.2	5.2	18.1	13.4
5	bright yellow needles	298	65	46.0	4.7	17.1		45.9	4.6	16.8	
6	pale yellow needles	355	79	43.7	4.9	17.8		42.1	5.1	18.2	
7	pale yellow prisms	168	53	44.7	5.1	17.4		44.3	5.1	18.4	
8	gold prisms	280–282	56	44.1	6.5			43.0	5.6		
9	yellow prisms	226–230	55	46.9	7.1	16.0	11.5	47.2	6.9	15.6	11.4
10	pale yellow prisms	>350	76	35.7	5.6	22.1		35.1	5.3	21.4	
11	dark gold prisms	165	72	42.4	5.2	19.9		40.5	5.3	18.4	
12	dark gold needles	352–355 dec	81	43.8	4.8	17.9	12.9	43.5	4.7	17.4	12.5
13	gold microprisms	304–306	94	38.5	4.4			39.6	4.4		
14	bright gold needles	293	61	43.4	5.6	17.7		43.5	5.5	17.4	
15	gold tetragonal prisms	>360	65	47.0	5.0	16.7	12.1	43.4	4.5	17.0	12.4
16	dark gold needles	199–201	74	54.0	5.0	11.5	9.7	53.6	4.5	11.2	9.6
17	dark orange needles	222	71	50.1	5.2			49.0	5.5		
18	orange prisms	232	77	45.3	5.4	13.8	11.7	45.3	5.6	13.4	11.7
19	dark yellow prisms	162	55	47.5	5.3			48.3	5.7		
20	bright gold prisms	339	66	52.7	4.7	9.4	12.0	53.2	4.9	9.0	11.6
21	dark gold plates	341 dec	91	36.5	5.5	15.7	11.3	36.3	5.6	15.4	11.3
22	dark yellow plates	261–300 dec	93	40.4	6.1	17.4	12.6	39.9	5.9	17.0	12.2
23	orange needles	266–267	75	43.4	6.6	15.4	16.7	44.6	6.6	14.5	16.7
24	bright gold prisms	332–342 dec	80	43.4	6.7			42.7	7.2		
25	dark gold prisms	258	78	43.9	6.8	17.1		44.8	5.6	16.5	
26	pale yellow needles	171–175	66	56.7	5.4	12.0	5.1	55.1	5.4	11.9	4.7
27	dark gold prisms	221–224	68	48.3	5.3	11.6		50.0	5.5	12.1	
28	gold prisms	172–175	74	48.3	6.0	14.6		47.3	6.5	13.8	
29	bright yellow prisms	230–235	75	45.5	6.7	15.2		45.3	6.6	15.0	
30	bright yellow prisms	129–133	57	50.5	5.6			51.2	5.7		
31	bright orange prisms	231–235	69	44.6	5.5	13.6	5.7	44.6	5.6	13.5	5.6
32	pale yellow plates	229–231	80	44.9	5.4	15.7	6.6	44.9	5.4	15.7	6.7
33	bright yellow plates	255–258	80	37.4	3.6	13.4		38.2	3.8	12.6	
34	pale gold needles	350–353	91	41.2	5.5			39.8	5.1		
35	pale yellow plates	297	92	44.0	5.4			43.6	5.6		
36	pale yellow plates	231–233	91	36.6	3.5	13.4		37.1	3.9	12.7	
37	pale yellow needles	234–236	43	36.7	3.4	12.8		35.6	3.9	10.8	
38	pale yellow prisms	232–233	56	35.1	3.6	13.0		36.2	3.5	14.1	
39	pale yellow needles	263–265	62	41.0	5.3	12.4	4.5	40.8	5.2	12.2	4.6
40	pale yellow plates	209	36	42.8	5.4			42.7	5.4		

[Hydrotris(3,5-dimethylpyrazolyl)borato]dichloro(L)rhodium(III). Simple displacement of the coordinated methanol from **2** by a neutral donor ligand, L, gives the series of complexes of the type HB(3,5-$Me_2pz)_3RhCl_2L$, e.g., **4–19** and **32–34**, in yields varying from 61 to 94% (after recrystallization). These complexes were prepared as follows. The appropriate reagent (slight excess) and **2** were refluxed together in dry toluene for 3 h. (An exception is **4** which was obtained from refluxing **2** in neat acetonitrile.) The products were recrystallized from CH_2Cl_2/hexanes; their physical properties are listed in Table I.

Tetraphenylarsonium [Hydrotris(3,5-dimethylpyrazolyl)borato]-trichlororhodate(III) (20). Compound **2** (0.160 g), dissolved in a minimum amount of CH_2Cl_2, was mixed with Ph_4AsCl (0.100 g) dissolved in CH_2Cl_2. The solution was filtered and reduced in volume, and hexanes were added. The product was isolated as bright gold prisms, 66% yield (0.186 g).

R_4N [Hydrotris(3,5-dimethylpyrazolyl)borato]dichloro(X)-rhodate(III) [R_4N = Me_4N, X = Br (21) or F (22); R_4N = Et_3NH, X = Cl (23); R_4N = Et_4N, X = Cl (24)]. The above four complex salts were prepared by refluxing the appropriate salt (e.g., Et_3NHCl for **23**) in dry toluene with an equimolar amount of **2**, filtering off the resulting solid, and recrystallizing it from CH_2Cl_2/hexane. The yields ranged from 75 to 93% (see Table I).

Triethylammonium [Hydrotris(3,5-dimethylpyrazolyl)borato]di-chlorohydridorhodate(III) (25). Compound **2** (0.274 g) was refluxed in 50 mL of dry toluene with 0.1 mL of Et_3N while H_2 was bubbled through the solution for 5 h. The resulting dull gold crystals were filtered to give a 78% yield (0.315 g).

[Hydrotris(3,5-dimethylpyrazolyl)borato]chlorohydrido(PR_3)rho-dium(III) [PR_3 = PPH_3 (26), PPh_2Me (27), $PPhMe_2$ (28), PEt_3 (29), $PMe(o\text{-tol})_2$ (30), $AsMe_2Ph$ (31)]. $Et_3NH[HCl_2Rh(3,5\text{-}Me_2pz)_3BH]$ (**25**) was refluxed with an equimolar amount of the appropriate phosphine or arsine under N_2 in dry toluene for 2 h. The resulting solutions were filtered, the filtrates reduced to dryness, and the residues extracted with CH_2Cl_2. Hexanes were added to the CH_2Cl_2 solutions and the products filtered as yellow crystals. Yields ranged from 57 to 75% (see Table I).

[Hydrotris(3,5-dimethylpyrazolyl)borato][$(RCO_2)_2L$]rhodium(III) [R = CH_3, No L (35); R = CF_3, L = H_2O (36)]. Compound **2** was refluxed in dry toluene with equimolar amounts of the appropriate silver salt in each case. After 3 h the AgCl was filtered off and the solution reduced to dryness. The residue was extracted with CH_2Cl_2, and the products were precipitated out of the extract with hexanes. Yields of pale yellow plates were 92 and 91%, respectively.

Bis(trifluoroacetato)[hydrotris(3,5-dimethylpyrazolyl)borato]-carbonylrhodium(III) (37). HB(3,5-$Me_2pz)_3Rh(CF_3CO_2)_2H_2O$ (**36**, 0.693 g) was refluxed in 50 mL of dry toluene for 2 h while CO was bubbled through the solution. A pale yellow solution resulted, from which off-white crystals were deposited on standing. The product was recrystallized from CH_2Cl_2/hexanes in 43% yield (0.298 g).

Bis(trifluoroacetato)[hydrotris(3,5-dimethylpyrazolyl)borato]-(acetonitrile)rhodium(III) (38). Compound **36** (0.148 g) was refluxed in 25 mL of dry toluene with 2 mL of CH_3CN for 1 h. The product was isolated from the toluene solution and recrystallized from CH_2Cl_2/hexanes as pale yellow prisms in 56% yield (0.086 g).

Tetraethylammonium Bis(trifluoroacetato)[hydrotris(3,5-di-methylpyrazolyl)borato]chlororhodate(III) (39). $Et_4N[Cl_3Rh(3,5\text{-}Me_2pz)_3BH]$ (**24**, 0.372 g) was refluxed in dry toluene with Ag-(O_2CCF_3) (0.258 g) for 2 h. The solution was filtered and the precipitate extracted with acetone. The product was obtained as pale yellow needles (0.480 g, 62% yield) upon reducing the volume of the acetone extract.

Table II.[g] ^{1}H NMR and IR Data for Hydrotris(3,5-dimethylpyrazolyl)borate Complexes of Rhodium

no.	compd	^{1}H NMR data for $HB(3,5\text{-}Me_2pz)_3$: 4-H,[a,e] δ[b]	int[c]	3,5 CH_3's,[a,e] δ[b]	int[d]	other ^{1}H NMR data[a,e]: δ[b]	int[c]	other relevant data
1	$[HB(3,5\text{-}Me_2pz)_3RhCl_2]_2$	5.9 m	3	2.45 s, 2.40 s, 2.21 s, 1.85 s	2:1:1:2			
2	$HB(3,5\text{-}Me_2pz)_3RhCl_2MeOH$	6.0 s, 5.9 s	2:1	2.6 s, 2.5 s, 2.4 s	1:2:3	CH_3, 3.55 d; OH, 7.45 q	3:1	
3	$HB(3,5\text{-}Me_2pz)_3RhCl_2H_2O$	5.9 s, 5.8 s	2:1	2.8 s, 2.7 s, 2.4 s	1:2:3	H_2O, 6.5 br	2	
4	$HB(3,5\text{-}Me_2pz)_3RhCl_2CH_3CN$	5.9 s, 5.8 s	2:1	2.8 s, 2.7 s, 2.4 s	1:2:3	CH_3, 2.6 s	3	IR ν(C≡N) = 2300 cm^{-1}
5	$HB(3,5\text{-}Me_2pz)_3RhCl_2PhCN$	5.8 br	3	2.8 s, 2.7 s, 2.4 s	1:2:3	Ph, 7.9–7.4	5	IR ν(C≡N) = 2260 cm^{-1}
6	$HB(3,5\text{-}Me_2pz)_3RhCl_2py$	5.9 s, 5.8 s	1:2	2.9 s, 2.5 s, 1.7 s	1:3:2	py, 9.9 d, 8.0–7.0 m	5	
7	$HB(3,5\text{-}Me_2pz)_3RhCl_2(4\text{-pic})$[h]	5.85 s, 5.8 s	1:2	2.9 s, 2.5 s, 1.7 s	1:3:2	CH_3, 1.5 (s, Ar), 8.3 d, 7.3 d	3:4	
8	$HB(3,5\text{-}Me_2pz)_3RhCl_2N(CH_2CH_3)_3$	5.8 s	3	2.8 s, 2.4 s	3:3	CH_3, 1.5 t; CH_2, 3.4 q	9:6	
9	$HB(3,5\text{-}Me_2pz)_3RhCl_2N(CH_2CH_2CH_3)_3$	5.8 s	3	2.8 s, 2.4 s	3:3	CH_3, 1.05 t; CH_2, 3.3 q, 2.0 m	9:6:6	
10	$HB(3,5\text{-}Me_2pz)_3RhCl_2NH_3$[f]	6.0 d	3	2.45 s, 2.4 s, 2.2 s	2:3:1	NH_3, 4.6 br	3	
11	$HB(3,5\text{-}Me_2pz)_3RhCl_2(3,5\text{-}Me_2pyr)$[i]	5.9 br	3	2.4 s, 1.8 s	3:3	4-H, 5.9 s; CH_3, 2.35 s, 2.15 s	1:3:3	
12	$[HB(3,5\text{-}Me_2pz)_3RhCl_2]_2bpy$	6.0 s, 5.7 s	1:2	2.9 s, 2.6–2.3 br	2:4	bpy, 9.8 d, 8.8–8.2 m, 7.5 m	5	
13	$HB(3,5\text{-}Me_2pz)_3RhCl_2CO$	5.85 s	3	2.8 s, 2.6 s, 2.4 s	1:2:3			IR ν(CO) = 2100 cm^{-1}
14	$HB(3,5\text{-}Me_2pz)_3RhCl_2C{\equiv}N\text{-}n\text{-}Bu$	5.8 m	3	2.8 s, 2.5 s, 2.35 s	1:2:3	N-CH_2, 4.2 t; N-R, 2.2–0.8	2:7	IR ν(C≡N) = 2203 cm^{-1}
15	$HB(3,5\text{-}Me_2pz)_3RhCl_2C{\equiv}NCH_2Ph$	5.85 s, 5.75 s	2:1	2.8 s, 2.45 s, 2.35 s	1:2:3	Ph, 7.5 s; CH_2, 5.2 s	5:2	IR ν(C≡N) = 2230 cm^{-1}
16	$HB(3,5\text{-}Me_2pz)_3RhCl_2PPh_3$	5.8 s, 5.5 s	1:2	3.0 s, 2.5 s, 2.3 s, 1.7 s	1:2:1:2	Ph, 7–8	15	
17	$HB(3,5\text{-}Me_2pz)_3RhCl_2PPh_2Me$	5.8 s, 5.5 s	1:2	2.8 s, 2.4 s, 2.3 s, 1.65 s	1:2:1:2	Ph, 7.5–7.0; CH_3, 2.6 d	10:3	
18	$HB(3,5\text{-}Me_2pz)_3RhCl_2PPhMe_2$	5.75 s, 5.55 s	1:2	2.8 s, 2.4 s, 2.3 s, 2.25 s	1:2:1:2	Ph, 6.8–7.3; CH_3, 2.05 d	5:6	
19	$HB(3,5\text{-}Me_2pz)_3RhCl_2PMe(o\text{-}tol)_2\cdot CH_2Cl_2$	5.8 s, 5.6 s	1:2	2.8 s, 2.4 s, 2.3 s, 1.7 s	1:2:1:2	Ph, 7.5–6.5; CH_3, 2.9, 2.4 d	8:6:3	
20	$Ph_4As[HB(Me_2pz)_3RhCl_3]$	5.6 s	3	2.7 s, 2.4 s	3:3	Ph, 7.8 s	20	
21	$(CH_3)_4N[HB(3,5\text{-}Me_2pz)_3RhCl_2Br]$	5.85 s	3	2.6 d, 2.4 s	3:3	CH_3, 3.2 s	12	
22	$(CH_3)_4N[HB(3,5\text{-}Me_2pz)_3RhCl_2F]$	5.8 s	3	2.7 s, 2.4 s	3:3	CH_3, 3.1 s	12	
23	$(CH_3CH_2)_3NH[HB(3,5\text{-}Me_2pz)_3RhCl_3]$	5.8 s	3	2.75 s, 2.35 s	3:3	CH_3, 1.45; CH_2, 3.3 q	9:6	
24	$(CH_3CH_2)_4N[HB(3,5\text{-}Me_2pz)_3RhCl_3]$	5.8 s	3	2.6 s, 2.4 s	3:3	CH_3, 1.2 t; CH_2, 3.1 q	12:8	
25	$(CH_3CH_2)_3NH[HB(3,5\text{-}Me_2pz)_3RhCl_2H]$	5.8 s, 5.6 s	1:2	2.6 s, 2.4 s, 2.25 s	1:3:2	CH_3, 1.4 t; CH_2, 3.3 q H^-, −14.45 dd	9:6:1	$^1J_{Rh-H}$ = 4.4 Hz IR ν(H^-) = 2070 cm^{-1}
26	$HB(3,5\text{-}Me_2pz)_3RhClH(PPh_3)$	5.7 s, 5.0 s	2:1	2.7 s, 2.5 s, 2.25 s, 1.4 s, 1.2 s	1:1:2:1:1	Ph, 7.8–7.0 H^-, −14.25 dd	15:1	$^1J_{Rh-H}$ = 8.0 Hz, $^2J_{P-H}$ = 20 Hz IR ν(H^-) = 2135 cm^{-1}
27	$HB(3,5\text{-}Me_2pz)_3RhClH(PPh_2Me)\cdot CH_2Cl_2$	5.65 s, 5.4 s	2:1	2.6 s, 2.5 s, 2.4 s, 1.65 s, 1.55 s	1:1:2:1:1	Ph, 7.5–7.0; CH_3, 2.2 d H^-, −15.2 dd	10:3:1	$^1J_{Rh-H}$ = 10 Hz, $^2J_{P-H}$ = 24 Hz IR ν(H^-) = 2070 cm^{-1}
28	$HB(3,5\text{-}Me_2pz)_3RhClH(PPhMe_2)$	5.9 s, 5.7 s, 5.45 s	1:1:1	2.6 s, 2.3 s, 1.65 s	3:2:1	Ph, 7.6–7.4; CH_3 2.0 d H^-, −15.84 dd	5:6:1	$^1J_{Rh-H}$ = 10 Hz, $^2J_{P-H}$ = 20 Hz IR ν(H^-) = 2175 cm^{-1}
29	$Hb(3,5\text{-}Me_2pz)_3RhClH[P(CH_2CH_3)_3]$	5.8 s, 5.7 s, 5.6 s	1:1:1	2.6 s, 2.55 s, 2.45 s, 2.4 s, 2.3 s	1:1:1:1:2	CH_3, 0.09 dt; CH_2, 1.9 dd H^-, −16.2 dd	9:6:1	$^1J_{Rh-H}$ = 10 Hz, $^2J_{P-H}$ = 24 Hz
30	$HB(3,5\text{-}Me_2pz)_3RhClH[PMe(o\text{-}tol)_2]\cdot CH_2Cl_2$	5.6 s, 5.4 s	2:1	2.6 s, 2.5 s, 2.3 s, 1.8 s, 1.3 s	2:1:1:1:1	Ph, 7.4–6.8; CH_3, 2.2 m H^-, −14.66 dd	8:6:1	$^1J_{Rh-H}$ = 7 Hz, $^2J_{P-H}$ = 23 Hz
31	$HB(3,5\text{-}Me_2pz)_3RhClH[As(CH_3)_2Ph]$	5.85 s, 5.7 s, 5.5 s	1:1:1	2.6 s, 2.5 s, 2.3 s, 1.65 s	1:2:2:1	Ph, 7.5–7.0; CH_3, 1.8 s, 1.5 s H^-, −15.48 d	5:6:1	$^1J_{Rh-H}$ = 6 Hz
32	$HB(3,5\text{-}Me_2pz)_3RhCl(CH_3COCHCOCH_3)$	5.8 s	3	2.6 s, 2.3 s, 1.9 s	2:3:1	CH_3, 2.1 s; CH, 5.8 s	6:1	
33	$HB(3,5\text{-}Me_2pz)_3RhCl(CF_3COCHCOCF_3)$	5.9 s	3	2.6 s, 2.45 s, 1.9 s	2:3:1	CH, 6.6 s	1	
34	$HB(3,5\text{-}Me_2pz)_3RhCl(Et_2NCS_2)$	5.8 s, 5.6 s	2:1	2.5 d, 2.3 d	3:3	CH_3, 1.35 t; CH, 3.7 q	6:4	
35	$HB(3,5\text{-}Me_2pz)_3Rh(CH_3CO_2)_2$	5.9 s, 5.8 s	1:2	2.6 s, 2.4 s, 2.15 s	1:3:2	CH_3, 2.35 s	6	
36	$HB(3,5\text{-}Me_2pz)_3Rh(CF_3CO_2)_2H_2O$	6.0 s, 5.9 s	2:1	2.5 s, 2.2 s, 2.05 s	3:2:1	H_2O, 7.9 s	2	
37	$HB(3,5\text{-}Me_2pz)_3Rh(CF_3CO_2)_2CO$	5.95 s, 5.9 s	1:2	2.45 s, 2.35 s, 2.25 s	3:1:2			IR ν(CO) = 2130 cm^{-1}
38	$HB(3,5\text{-}Me_2pz)_3Rh(CF_3CO_2)_2CH_3CN$	5.9 s, 5.8 s	2:1	2.4 s, 2.3 s, 2.2 s	3:2:1	CH_3, 2.6 s	3	
39	$(CH_3CH_2)_4N[HB(3,5\text{-}Me_2pz)_3Rh(CF_3CO_2)_2Cl]$	5.8 s	3	2.5 s, 2.0 s	3:3	CH_3, 1.2 t; CH_2, 3.25 q	12:8	
40	$(CH_3CH_2)_3NH[HB(3,5\text{-}Me_2pz)_3Rh(CH_3CO_2)_2H]$	5.8 s, 5.7 s	1:2	2.45 s, 2.3 s, 2.05 s	1:2:3	CH_3, 1.1 t; CH_2, 3.15 q H^-, −20.8 d	9:6:1	J_{Rh-H} = 7 Hz IR ν(H^-) = 2050 cm^{-1}

[a] Solvent used was $CDCl_3$ unless marked otherwise. [b] δ's relative to Me_4Si. [c] Intensities are in number of protons per rhodium atom. [d] Intensities are in numbers of methyl groups per rhodium atom. [e] Solvent used for ^{1}H NMR was $Me_2SO\text{-}d_6$. [f] The ^{1}H NMR is consistent with the presence of two NH_3 groups. Whether both of these are coordinated to the Rh(III) center with one anionic chloride or whether there are two chloro ligands with one coordinated NH_3 and one NH_3 molecule of crystallization has yet to be determined. [g] d is doublet, m is multiplet, q is quartet, s is singlet, t is triplet, br is broad. [h] 4-Pic = 4-picoline. [i] 3,5-Me_2pyr = 3,5-dimethylpyrazole.

Table III. Physical Data for Hydrotripyrazolylborate Complexes of Rhodium and Iridium

				elemental analysis, %							
				calcd				found			
compd	characteristics	mp, °C	% yield	C	H	N	Cl	C	H	N	Cl
41	dark gold plates	293–297	70	27.9	2.6	21.7	18.3	25.5	2.9	20.1	17.5
42	dull gold prism	>360	62	31.5	3.5			32.0	3.2		
43	dark gold prisms	206–211	65	39.2	3.1	20.0	14.4	35.7	3.2	19.7	14.7
44	bright yellow prisms	331–332	69	36.0	3.0	21.0	15.2	35.9	3.2	19.9	15.0
45	dull yellow prisms	239–241	46	36.9	5.1	20.0	14.5	34.6	5.7	18.9	13.8
46	dull gold prisms	>350	65	31.6	2.9	21.5	15.6	31.7	3.3	18.2	16.4
47	bright yellow prisms	148–150	45	35.8	4.1	20.9	15.1	36.0	4.3	20.7	15.0
48	pale gold prisms	275–278	76	50.0	3.9	12.9	10.9	50.2	4.0	12.6	11.0
49	bright gold prisms	273–275	75	48.4	4.3	13.3		48.8	3.9	13.1	
50	bright gold prisms	291	78	38.9	4.0	16.0	13.5	38.0	4.4	15.7	13.8
51	bright gold prisms	287	63	35.9	5.0	16.6	14.0	35.4	5.0	16.5	13.9
52	dark gold prisms	110–111	84	46.8	3.6	12.1	10.2	46.5	3.8	12.0	10.2
53	pale yellow needles	290	85	35.9	3.7	14.8	12.4	36.2	3.6	14.5	12.0
54	pale yellow prisms	>350	65	28.9	4.1	18.1	13.1	28.5	4.3	17.6	12.9
55	dull yellow prisms	>350	42	37.3	3.8	18.7	7.9	35.7	4.6	16.9	8.4
56	bright yellow needles	191–192	51	30.1	2.0	15.0	6.4	30.4	2.1	14.8	6.6
57	pale yellow plates	178–180	64	27.9	2.2	15.0		27.7	2.3	14.7	
58	pale yellow prisms	132–137	52	30.9	2.3	16.8		30.4	2.3	16.1	
59	pale yellow needles	132–135	13	52.3	6.6	17.4		51.7	6.4	17.0	
60	pale orange prisms	245–255	62	32.2	5.0			30.4	4.6		
61	pale orange prisms	240–245	57	37.2	4.5			38.8	4.7		
62	pale yellow needles	166–167	58	31.1	3.3	11.5		31.4	4.0	11.1	
63	pale orange prisms	237–240	57	38.6	4.5	13.5		33.6	4.9	12.4	
64	bright yellow prisms		75	44.8	4.9	18.4		41.6	5.0	17.7	
65	dark red crystals		70	28.3	3.2	12.3	37.2[a]	28.2	3.6	12.1	37.0[a]

[a] This value is for iodine.

Triethylammonium Bis(trifluoroacetato)[hydrotris(3,5-dimethylpyrazolyl)borato]hydridorhodate(III) (40). Compound **36** (0.316 g) was refluxed in 50 mL of dry toluene for 4 h with H_2 bubbling through the solution. Et_3N (0.150 mL) was added 0.5 h after the beginning of the reaction. The required product was filtered as pale yellow plates in 36% yield (0.240 g).

$HB(1\text{-}pz)_3$ Complexes. μ-Dichloro-bis[[hydrotris(1-pyrazolyl)borato]chlororhodium(III)] (41). $NaHB(1\text{-}pz)_3$ (2.20 g) dissolved in 30 mL of methanol was added slowly to a stirred solution of $RhCl_3\cdot 3H_2O$ (2.46 g) in 10 mL of methanol. The resulting solution was refluxed for 4 h and then filtered hot. The filtrate volume was reduced on a rotary evaporator and a second crop of product collected. The combined yield was 70% (2.59 g) of dull gold crystals.

(Hydrotripyrazolylborato)dichloro(acetonitrile)rhodium(III) (42). $[HB(pz)_3RhCl_2]_2$ (**41**, 2.59 g) was refluxed in 25 mL of acetonitrile for 24 h. The solution was filtered hot, the volume of filtrate was reduced, and the filtrate was cooled to 0 °C and left to stand overnight. A second crop of bright yellow crystals was combined with the first precipitate to give a 62% yield of desired product (1.78 g).

[Hydrotris(1-pyrazolyl)borato]dichloro(L)rhodium(III) [L = PhCN (43); L = $AsPh(CH_3)_2$ (53)]. The appropriate reagent (slight excess) and **42** were refluxed together in dry toluene for 24 h. The products were recrystallized from dry toluene; their physical properties are listed in Table III.

Tetramethylammonium [Hydrotris(1-pyrazolyl)borato]bromodichlororhodate (III) (54). Compound **42** (0.165 g) was refluxed with $(CH_3)_4NBr$ (0.067 g) in 10 mL of dry toluene for 24 h and worked up as for **43** to give **54** as pale yellow prisms in 65% yield (0.136 g).

[Hydrotris(1-pyrazolyl)borato](β-diketonate)chlororhodium(III) [β-diketonate = acac (55) or hfac (56)]. Equimolar amounts of **42** and the thallium salt of the β-diketonate were reacted together following the same procedure as for **43** to give the products as yellow crystals in 51 and 42% yields, respectively.

[Hydrotris(1-pyrazolyl)borato]bis(trifluoroacetato)rhodium(III) (57). Compound **42** (0.523 g) was refluxed with AgO_2CCF_3 (0.548 g) in 20 mL of dry toluene for 4 h. The AgCl was filtered hot and the product isolated from the filtrate as pale yellow plates in 64% yield (0.450 g).

[Hydrotris(1-pyrazolyl)borato]bis(trifluoroacetato)(acetonitrile)rhodium(III) (58). Compound **57** (0.111 g) was refluxed in 10 mL of dry toluene with 2 mL of CH_3CN for 8 h. The solution was filtered hot and the product isolated from the filtrate as pale yellow prisms in 52% yield (0.060 g).

$HB(3,5\text{-}Me_2pz)_3al_2Rh$ Complex. [Hydrotris(3,5-dimethylpyrazolyl)borato]diallylrhodium(III) (59). $NaHB(3,5\text{-}Me_2pz)_3$ (0.703 g), dissolved in 5 mL of CH_2Cl_2, was stirred with μ-dichloro-bis[diallylrhodium(III)] (0.473 g) suspended in 10 mL of CH_2Cl_2 at room temperature for 4 h. Pale green crystals were isolated from the solution to give 0.137 g of product (13.3% yield).

$HB(3,5\text{-}Me_2pz)_3Ir$ Complexes. μ-Dichloro-bis[[hydrotris(3,5-dimethylpyrazolyl)borato]chloroiridium(III)] (60). $NaHB(3,5\text{-}Me_2pz)_3$ (1.89 g) dissolved in 20 mL of 95% EtOH was slowly added to a stirred ethanolic solution of H_2IrCl_6 (1.96 g). The mixture was refluxed for 24 h and then filtered hot. The volume of the filtrate was reduced in vacuo, and the resulting mixture was then cooled to 0 °C and left overnight. A second crop of pale orange crystals was isolated and combined with the first precipitate to give a total yield of **60** of 62% (2.03 g).

[Hydrotris(3,5-dimethylpyrazolyl)borato]dichloro(dimethylphenylarsine)iridium(III) (61). Compound **60** (0.126 g) was refluxed with $As(Me)_2Ph$ (0.032 mL) in 10 mL of dry toluene for 3 h. The clear solution was filtered hot and the filtrate cooled to 0 °C and left overnight. The product was isolated as pale orange prisms in 57% yield (0.095 g).

[Hydrotris(3,5-dimethylpyrazolyl)borato]bis(trifluoroacetato)iridium(III) (62). Compound **60** (0.265 g) was refluxed with $Ag(O_2CCF_3)$ (0.249 g) in 15 mL of dry toluene for 24 h. The solution was filtered and the product isolated from the filtrate in the usual way as pale yellow needles in 58% yield (0.202 g).

[Hydrotris(3,5-dimethylpyrazolyl)borato]chloro(acetylacetonato)iridium(III) (63). Equimolar amounts of **60** and the appropriate β-diketone thallium(I) salt were refluxed in dry toluene for 24 h. The solution was filtered and **63** isolated from the filtrate in 57% yield.

Bis[dicarbonyl[hydrotris(3,5-dimethylpyrazolyl)borato]rhodium(I)] and Derivatives. [Hydrotris(3,5-dimethylpyrazolyl)borato]dicarbonylrhodium(I) (64). $[(CO)_2RhCl]_2$[6] (0.400 g) was stirred in dry benzene with $KHB(3,5\text{-}Me_2pz)_3$ (0.650 g) for 0.5 h at room temperature. The solution was filtered to remove KCl and unreacted materials, and the product was isolated as yellow crystals in 75% yield (0.704 g).

[Hydrotris(3,5-dimethylpyrazolyl)borato]diiodocarbonylrhodium(III) (65). Compound **64** (0.100 g) dissolved in 5 mL of CH_2Cl_2 was stirred under N_2 while I_2 (0.61 g) dissolved in 5 mL of CH_2Cl_2 was slowly added dropwise. The mixture was stirred 2.5 h at room temperature

(6) Prepared according to the method of McCleverty and Wilkinson.[7]

(7) J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, **8**, 211 (1967).

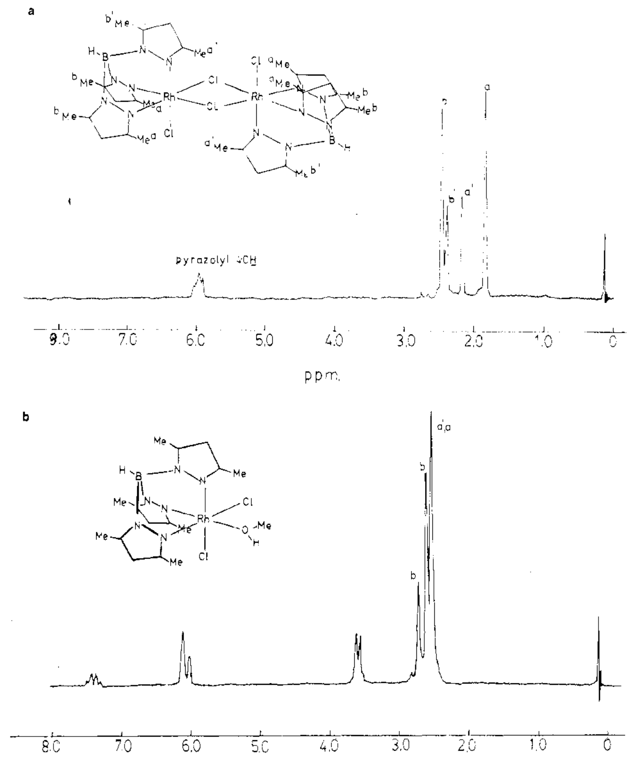


Figure 1. ^{1}H NMR spectra of (a) $[HB(3,5\text{-}Me_2pz)RhCl_2]_2$ (**1**) and (b) $HB(3,5\text{-}Me_2pz)_3RhCl_2MeOH$ (**2**) in $CDCl_3$ with Me_4Si as an internal reference. The insets are the proposed structures based on ^{1}H NMR. The assignments of methyl resonances in both cases are arbitrary.

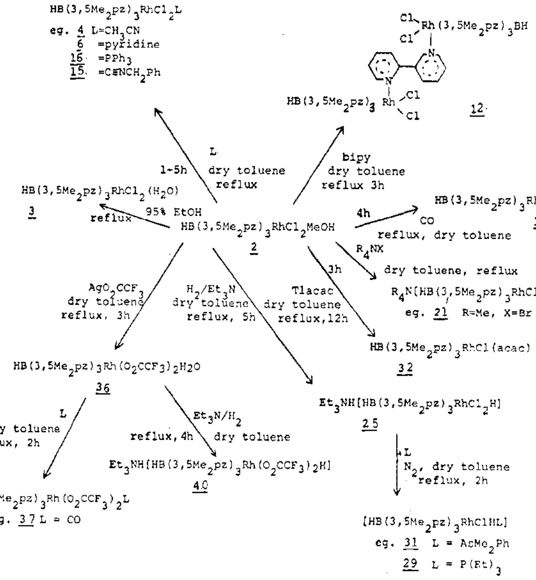
and filtered, and the product was isolated as dark red crystals in 70% yield (0.105 g).

Results and Discussion

The reaction of equimolar amounts of sodium hydrotris(3,5-dimethylpyrazolyl)borate and rhodium trichloride trihydrate in refluxing methanol yields two types of complex, depending on the conditions used. Dilute solutions and a short reflux time of approximately 1 h gave, upon work up, dark gold crystals of the chloro-bridged dimeric complex $[HB(3,5\text{-}Me_2pz)_3RhCl_2]_2$ (**1**), isolated in 30% yield. With a more concentrated solution of starting materials and longer reflux times, or when **1** was refluxed in methanol for 4 h, the less soluble monomeric methanol solvate $HB(3,5\text{-}Me_2pz)_3RhCl_2MeOH$ (**2**) was obtained in high yield. Shorter reflux times gave mixtures of **1** and **2**. The structures assigned to **1** and **2** are based primarily on elemental microanalyses and their ^{1}H NMR spectra shown in Figure 1a and Figure 1b, respectively. The ^{1}H NMR spectrum of **1** shows four different methyl proton resonances in a ratio of 2:1:1:2. This is consistent with a dimeric structure with bridging chlorides as shown in Figure 1a. The ^{1}H NMR of **2** shows a 1:2:3 pattern for the six methyl groups of the pyrazolylborate ligand together with a 1:1 doublet of relative intensity 3 and a 1:3:3:1 quartet of relative intensity 1 which can be assigned to the coordinated MeOH (CH_3 and OH, respectively). The spectrum is consistent with the structure proposed for **2** (Figure 1b), assuming accidental overlap of two of the "3,5-dimethylpyrazolyl" methyl resonances (expect four resonances in a ratio of 1:1:2:2, observe three in a ratio of 1:2:3).

The preferred formation of the methanol complex **2** in more concentrated methanolic solutions than those used to obtain the chloro-bridged dimer **1** can be ascribed to the relative solubilities of the two complexes. The dimer **1** is very soluble in methanol and is difficult to recover from a methanol solution. On the other hand, the methanol complex **2** is only moderately soluble in methanol.

Scheme I. Hydrotris(3,5-dimethylpyrazolyl)borate Complexes of Rhodium(III)



A plausible reaction sequence for the formation of **1** and **2** is given in eq 4.

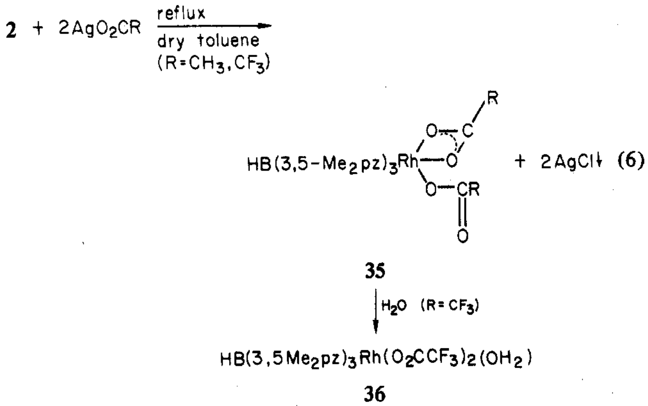
$$\mathrm{Na[HB(3,5\text{-}Me_2pz)_3] + RhCl_3{\cdot}xH_2O \rightarrow \underset{A}{Na[HB(3,5\text{-}Me_2pz)_3RhCl_3]} \rightarrow \underset{\mathbf{2}}{HB(3,5\text{-}Me_2pz)_3RhCl_2MeOH} \xrightleftharpoons{-MeOH} \underset{\mathbf{1}}{[HB(3,5\text{-}Me_2pz)_3RhCl_2]_2}} \quad (4)$$

When the methanolic solution is very concentrated, the methanol complex **2** precipitates as soon as it is formed. After a while when most of the $HB(3,5\text{-}Me_2pz)_3RhCl_2$ entity has precipitated out as **2**, the solution is sufficiently dilute that the chloro-bridged dimer **1** can be formed. Support for this reasoning can be found in the fact that the yield of the methanol complex **2** never gets above 70%. (Complexes similar to A can be prepared quite easily from the reaction of **2** with tetraalkylammonium halides (see Scheme I). If 95% ethanol or absolute ethanol is used as the solvent in place of methanol, an ethanol complex analogous to **2** is not obtained. Instead, the hydrated complex $HB(3,5\text{-}Me_2pz)_3RhCl_2(OH_2)$ (**3**) is obtained in quantitative yield. When **3** is refluxed in methanol for 7 h, it is fully converted to **2**. Likewise, when **2** is refluxed in 95% ethanol, it is converted back to **3**.

The complex **2** is a suitable starting point for the preparation of various derivatives. The coordinated methanol can be readily displaced by monodentate donor ligands such as acetonitrile, amines, pyridine, tertiary phosphines, tertiary arsines, isocyanides, and carbon monoxide to give complexes of the type $HB(3,5\text{-}Me_2Pz)_3RhCl_2L$. In most cases higher yields were obtained by using the methanol complex **2** as starting material rather than the aquo complex **3**. A typical reaction would be to take an equimolar amount of **2** and ligand in dry toluene and reflux the mixture for 1–5 h. A representative number of such reactions are summarized in Scheme I. The complexes are structurally characterized on the basis of their ^{1}H NMR spectra and microanalytical data, given in Tables I and II. The reaction of **2** with 2,2′-bipyridyl (excess) gave only the bpy-bridged product **12**. The absence of a chelating bipyridyl complex suggests that displacement of the chloride ligands is considerably more difficult than displacement of methanol. Substitution of the chloro ligands can be achieved by metathesis using silver(I) or thallium(I) salts. Reaction of **2** with equimolar amounts of Tl(acac), Tl(hfac), or AgS_2CNEt_2 in refluxing toluene gave the complexes **32**, **33**, and **34**, respectively (eq 5). Reaction of **2** with 2 equiv of AgO_2CCF_3 or

$$[HB(3,5\text{-}Me_2pz)_3RhCl_2(MeOH)] + Tl(acac) \rightarrow HB(3,5\text{-}Me_2pz)_3RhCl(acac) + MeOH + TlCl\downarrow \quad (5)$$

AgO_2CCH_3 gave complexes containing one bidentate and one unidentate carboxylate ligand (eq 6).



Direct evidence for the bidentate and monodentate dicarboxylate structure of **35** was not obtained. The carboxylate methyl groups of **35** gave only one identifiable resonance in the ^1H NMR of relative intensity 6 (presumably due to accidental overlap), and the evidence for the presence of both types of carboxylate in the infrared spectrum of **35** was not conclusive due to a multitude of absorptions in the region between 1600 and 1300 cm^{-1} (i.e., both carboxylate ν_{CO}'s and pyrazolylborate ν_{CN}'s). However, the fact that the ^1H NMR spectrum of **35** shows a 1:3:2 pattern in the "3,5-dimethylpyrazolyl" methyl region characteristic of the $HB(3,5\text{-}Me_2pz)_3$ ligand in an environment where two of the other three sites on the metal center are equivalent and one is different (cf. Figure 1b) suggested structure **35**, especially since there was no sign of the presence of a coordinated water molecule as in **36**. Bidentate and monodentate dicarboxylate structures similar to **35** have been reported by Robinson et al.[8] for the series of complexes $Ru(O_2CR)_2(PPh_3)_2CO$. The bidentate and monodentate carboxylate groups in these Ru(II) complexes may exchange rapidly on the ^1H NMR time scale. The fact that only one singlet assignable to the acetato methyl groups can be found in the tripyrazolylborate rhodium complex could indicate that the same type of exchange as observed by Robinson is occurring in **35**. However, this possibility can be ruled out by observation of the ^1H NMR resonances of the $HB(3,5\text{-}Me_2pz)_3$ ligand. If the carboxylate groups in **35** were exchanging rapidly on the ^1H NMR time scale, only two singlets would appear for the 3- and 5-methyls on the pyrazolylborate group; instead the pattern elucidated above is seen, indicating that the carboxylates on **35** are static on the ^1H NMR time scale. The bis(trifluoroacetate) complex was never obtained in a pure form, as it readily picked up one molecule of water to give the aquo complex **36**. The water molecule in the aquo complex **36** can be readily displaced by (i) neutral donor ligands (L) to give $HB(3,5\text{-}Me_2pz)_3Rh(O_2CCF_3)_2L$ [e.g., L = CO (**37**), CH_3CN (**38**)] and (ii) by anionic ligands X^- to give $M^+[HB(3,5\text{-}Me_2pz)_3Rh(O_2CCF_3)_2X]^-$ (e.g., $M^+ = R_4N^+$; $X^- = Cl^-, H^-$). The hydrido derivative $Et_3NH[HB(3,5\text{-}Me_2pz)_3Rh(O_2CCF_3)_2H]$ (**40**) was obtained from the direct reaction of **36** with molecular hydrogen in refluxing toluene in the presence of a slight excess of triethylamine (see Scheme I).

(8) S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1912 (1973).

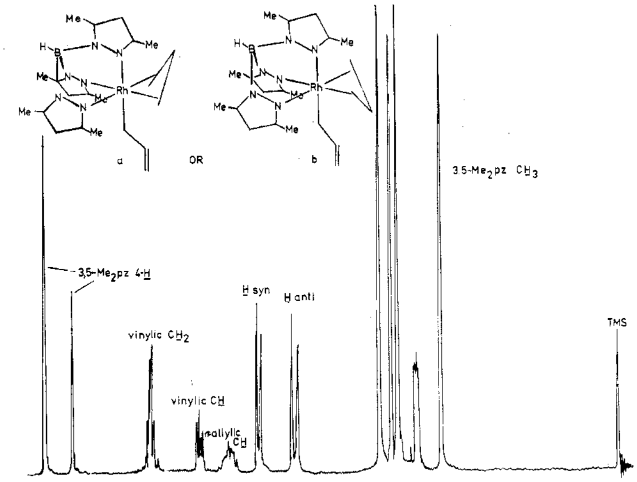


Figure 2. ^1H NMR spectrum (220 MHz) of freshly prepared $HB(3,5\text{-}Me_2pz)_3Rh(\eta^1\text{-al})(\eta^3\text{-al})$ (**59**) in $CDCl_3$ with Me_4Si as an internal reference. Inset shows two possible isomeric structures of **59**. Only one of these is formed initially.[9]

Anionic and hydrido complexes structurally analogous to **40** can be prepared directly from the methanol complex **2**. Thus reaction of **2** with tetraalkylammonium halides or $AsPh_4Cl$ in refluxing toluene gave a series of complexes (**20** to **24**; see Scheme I), and direct reaction of **2** with molecular hydrogen in the presence of triethylamine gave the anionic hydride derivative $Et_3NH[HB(3,5\text{-}Me_2pz)_3RhCl_2H]$ (**25**). The presence of a hydrido ligand in complexes **25** and **40** was confirmed by the characteristic high-field resonance in the ^1H NMR at −14.4 ppm (J_{Rh-H} = 4.8 Hz) and −20.8 ppm (J_{Rh-H} = 7 Hz), respectively, and by typical hydrido stretching frequencies in the infrared spectra at 2070 and 2075 cm^{-1}, respectively. A series of neutral hydrido complexes of the type $HB(3,5\text{-}Me_2pz)_3RhClHL$ (**26–31**) was prepared from the reaction of the anionic hydrido complex **25** with tertiary phosphine and arsine ligands in refluxing toluene (see Scheme I). The ^1H NMR spectra of the phosphine complexes **26–30** all contain a high-field doublet of doublets of relative intensity 1 assignable to the hydrido ligand ($^2J_{P-H}$ = 24; $^1J_{Rh-H}$ = 10 Hz; see Table II).

The complexes **26–31** could not be obtained from the direct reaction of $HB(3,5\text{-}Me_2pz)_3RhCl_2L$ (L = PR_3 or AsR_3) with H_2 in the presence of triethylamine (no reaction in refluxing toluene). None of the hydrido derivatives prepared showed any stoichiometric reactivity with respect to dienes or any catalytic activity with respect to olefin hydrogenation in refluxing toluene.

An interesting complex was obtained from the reaction of $[(al)_2RhCl]_2$ with $Na[HB(3,5\text{-}Me_2pz)_3]$. After the reaction

Scheme II. Hydrotris(1-pyrazolyl)borate Complexes of Rhodium(III)

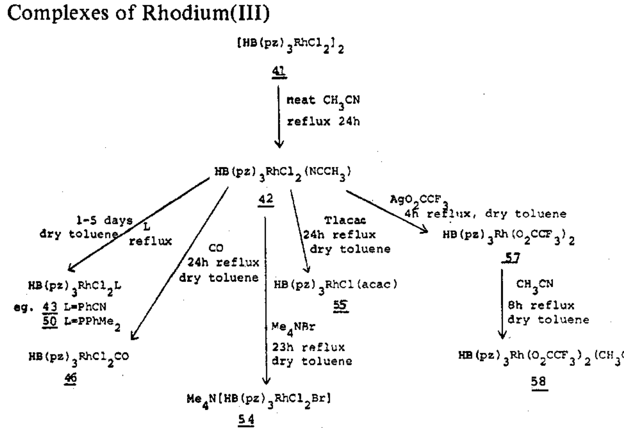
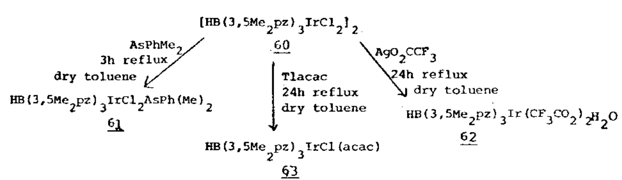


Table IV.[a,g] Tripyrazolylborate Complexes of Rhodium and Iridium: ^{1}H NMR[a] (δ) and IR Data (cm^{-1})

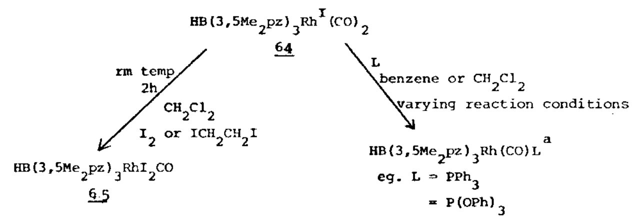
no.	compd	NMR data[b] for $HB(1\text{-}pz)_3$ and $HB(3,5\text{-}Me_2pz)_3$: 4-H	int[c]	3,5 H's	int	other NMR data	int[e]	IR data
41	$[HB(pz)_3RhCl_2]_2$	6.35 t[e]	3	7.9 d, 7.75 d	3:3[c]			
42	$HB(pz)_3RhCl_2CH_3CN\cdot CH_3CN$	6.3 t[e]	3	8.0 d, 7.7 m	3:3[c]	CH_3, 2.5 s	3	
43	$HB(pz)_3RhCl_2PhCN$	6.4 dt	3	8.1 d, 8.0 d, 7.7 d	1:2:3[c]	Ph, 7.8–7.3	5	
44	$HB(pz)_3RhCl_2$ pyridine	6.25 q[e]	3	7.8 d, 7.35 d	3:3[c]	py, 8.5 d, 8.1 d, 8.0–7.6 m, 7.1 m	2:1:1:1	
45	$HB(pz)_3RhCl_2(CH_3CH_2)_3N$	6.6 d, 6.3[f]	1:2	8.0 m, 7.8 m, 7.6 m	2:2:2[c]	CH_3, 1.5 t; CH_2, 3.3 q	9:6	
46	$HB(pz)_3RhCl_2CO\cdot CH_3CN$	6.4–6.1	3	8.1 m, 7.7 m, 7.45 d	1:3:2[c]			ν(CO) 2120
47	$HB(pz)_3RhCl_2C{\equiv}N\text{-}n\text{-}Bu$	6.3 t	3	8.15 m, 7.85 d, 7.65 m	1:1:4[c]	n-Bu: N–CH_2, 4.0 t; $CH_2CH_2CH_3$, 2.1–0.8 m	2:7	ν(C≡N) 2240
48	$HB(pz)_3RhCl_2PPh_3$	6.25 t, 5.8 t	1:2	8.2 d, 7.7 m, 6.6 d	1:3:2[c]	Ph, 7.9–7.1 m	15	
49	$HB(pz)_3RhCl_2PPh_2Me\cdot{}^1/_2tol$[h]	6.2 t, 5.8 t	1:2	8.1 d, 7.8 m, 6.6 d	1:3:2[c]	Ph, 7.4–7.1 m; CH_3, 2.7 d	10:3	
50	$HB(pz)_3RhCl_2PPhMe_2$	6.2 t, 6.0 t	1:2	8.1 d, 7.65 m, 7.1 d	1:3:2[c]	Ph, 7.4–7.1; CH_3, 2.15 d	5:3:3	
51	$HB(pz)_3RhCl_2P(CH_2CH_3)_3$	6.2 m	3	8.05 m, 7.7 m, 7.5 m	1:4:1[c]	CH_3, 1.1–0.5 dt; CH_2, 2.5–1.9 dq	9:6	
52	$HB(pz)_3RhCl_2AsPh_3$	6.3 t, 5.9 t	1:2	8.2 d, 7.5 m, 6.9 d	1:3:2[c]	Ph, 7.2–7.7	15	
53	$HB(pz)_3RhCl_2AsPh(CH_3)_2$	6.2 t, 6.0 t	1:2	8.05 m, 7.7 m, 7.1 m	1:4:1[c]	Ph, 7.1 m; CH_3, 2.4 s, 2.0 s	5:3:3	
54	$(CH_3)_4N[BH(pz)_3RhCl_2Br]$	6.35 t	3	7.9 d, 7.8 s	3:3[c]	CH_3, 3.2 s	12	
55	$HB(pz)_3Rh(CH_3COCHCOCH_3)Cl$	6.3 m	3	7.9 m, 7.6 m	2:4[c]	CH_3, 2.5 s, 2.0 s; CH, 5.6 s	3:3:1	
56	$HB(pz)_3Rh(CF_3COCHCOCF_3)Cl$	6.3 m	3	7.9 m	6[c]	CH, 6.55 s	1	
57	$HB(pz)_3Rh(CF_3CO_2)_2$	6.4 t	3	7.8 d	6[c]			
58	$HB(pz)_3Rh(CF_3CO_2)_2CH_3CN$	6.3 m	3	8.1 d, 7.75 d	6[c]	CH_3, 2.5 s	3	ν(C≡N) 2340
60	$[HB(3,5\text{-}Me_2pz)_3IrCl_2]_2$	5.8 m, 5.7 d[e]	1:2	2.35 s, 2.3 s, 2.1 s, 1.7 s	2:1:1:2[d]			
61	$HB(3,5\text{-}Me_2pz)_3IrCl_2\phi AsMe_2$	5.8 m	3	2.4 s, 2.15 s, 1.8 s, 1.6 s	2:1:2:1[d]	Ph, 7.2–7.3 m; CH_3, 2.45 s	5:6	
62	$HB(3,5\text{-}Me_2pz)_3Ir(CF_3CO_2)_2H_2O$	5.8 br	3	2.45 s, 2.4 s, 1.95 s, 1.6 s	2:1:1:2[d]	H_2O, 7.2 s	1:5	
63	$HB(3,5\text{-}Me_2pz)_3Ir(acac)Cl$	5.9 br	3	2.4 s, 2.2 s, 2.0 s, 1.8 s	2:1:1:2[d]	CH_3, 2.45 s, 2.35 s; CH, 5.9	6:1	
64	$HB(3,5\text{-}Me_2pz)_3Rh(CO)_2$	5.77	3	2.36 s, 2.42 s	3:3[d]			ν(CO) 2045
65	$HB(3,5\text{-}Me_2pz)_3RhI_2(CO)$	6.0 s, 5.9 s	1:2	2.9 s, 2.7 s, 2.45 s, 2.4 s	2:1:1:2[d]			ν(CO) 2090

[a] See footnotes of Table II for footnotes a–g. [h] The $^1/_2$tol indicates that the ^{1}H NMR shows the presence of toluene as a solvent of crystallization in the ratio of 1 mol of toluene for every 2 mol of product.

Scheme III. Hydrotris(3,5-dimethylpyrazolyl)borate Complexes of Iridium(III)



Scheme IV. Hydrotris(3,5-dimethylpyrazolyl)borate Complexes of Rhodium(I) and -(III)



[a] These complexes were never definitively characterized. NMR spectra were broad and ill-defined.

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mixture was stirred for 4 h at room temperature, $HB(3,5\text{-}Me_2pz)_3Rh(al)_2$ (**59**) was obtained and was assigned the structure **59** shown in Figure 2 on the basis of its 220-MHz ^1H NMR spectrum and from elemental analysis (see Table III). The structure of **59** which contains both an η^1- and an η^3-allyl group is very similar to the product $[Rh(\eta^1\text{-al})(\eta^3\text{-al})(\eta^5\text{-}C_5H_5)]$ derived from the reaction of $[Rh(al)_2Cl]_2$ and TlC_5H_5.[5] Compound **59** may occur in two isomeric forms, a or b (Figure 2), but only one of these appeared initially.[9]

Hydrotris(1-pyrazolyl)borate Rhodium(III) Complexes. Slow addition of a concentrated methanolic solution of sodium hydrotris(1-pyrazolyl)borate to an equimolar amount of $RhCl_3\cdot xH_2O$ in methanol followed by 24 h of reflux gave dull gold crystals of **41** which is assigned the dimeric structure $[HB(pz)_3RhCl_2]_2$ on the basis of its ^1H NMR spectrum and microanalytical data (see Tables III and IV). At no time was a methanol complex or an aquo complex, analogous to **2** or **3**, observed. The chloro bridges of **41** are, however, readily cleaved by a variety of ligands and strongly coordinating solvents. Thus, for example, when **41** was refluxed in neat acetonitrile for 24 h, the complex $HB(pz)_3RhCl_2(MeCN)$ (**42**) was obtained in (62%) yield. Complex **42** is a particularly useful starting material for the preparation of a variety of hydrotris(1-pyrazolyl)borate rhodium(III) complexes, with product yields being considerably higher than those obtained when the dimer **41** is used. Typical reactions are summarized in Scheme II, and analytical and spectroscopic data of the complexes prepared are given in Tables III and IV. While the chemistry observed is very similar to that of [hydrotris(3,5-dimethylpyrazolyl)borato]rhodium(III) complexes, attempts to prepare $Et_3NH[HB(pz)_3RhX_2H]$ complexes structurally analogous to complexes **25** and **40** were unsuccessful (methods tried included H_2/Et_3N and KOH–EtOH plus $LiAlH_4$).

Hydrotris(3,5-dimethylpyrazolyl)borate Iridium(III) Complexes. A few iridium(III) complexes, structural analogues of complexes in Schemes I and II, have been prepared (see Tables III and IV). The starting material for the complexes prepared is the dimeric complex $[HB(3,5\text{-}Me_2pz)_3IrCl_2]_2$ (**60**), obtained from the reaction of H_2IrCl_6 with $NaHB(3,5\text{-}Me_2pz)_3$ in refluxing 95% EtOH (24 h). The ^1H NMR spectrum of **60** is very similar to that of its rhodium analogue **1** (see Figure 1a). Compound **60** was found to be very unreactive toward both coordinating solvents and tertiary phosphine ligands in refluxing toluene. However, reaction with $AsPhMe_2$ in refluxing toluene was successful as were several reactions with silver(I) and thallium(I) salts. These reactions are summarized in Scheme III. It is noteworthy that of the iridium complexes prepared, none exhibited a ν_{B-H} mode in the region ~2500 cm^{-1}, in contrast to their rhodium analogues, all of which exhibited a stretch in this region, albeit a fairly weak absorption. However, the ^1H NMR spectra of the iridium complexes confirm the presence of the tripyrazolylborate ligands.

(9) When the sample was allowed to stand more than 4 h in $CDCl_3$, resonances assignable to another η^3-allylic complex began to appear in the NMR. This complex could conceivably be the isomer **61b**, but since no new resonances which could be assigned to the η^1-allyl in **61b** appeared, the new resonances could also be due to a chloro complex formed from the replacement of the η^1-allylic moiety by a chloride from $CDCl_3$. The integration suggests that the latter possibility is the more likely!

[Hydrotris(3,5-dimethylpyrazolyl)borato]dicarbonylrhodium(I) and Some of Its Reactions. The rhodium(I) complex $HB(3,5\text{-}Me_2pz)_3Rh(CO)_2$ (**64**) was first made by Trofimenko[10] from $[(OC)_2RhCl]_2$ and $K[HB(3,5\text{-}Me_2pz)_3]$ stirred overnight in DMF at room temperature, followed by a tedious workup procedure. We found that when the two reagents are stirred together for 0.5 h in dry benzene, the product **64** can be easily isolated from solution after filtering off the KCl. Reaction of **64** with a stoichiometric amount of I_2 in CH_2Cl_2 gave the rhodium(III) complex $HB(3,5\text{-}Me_2pz)_3RhI_2(CO)$ (**65**). Complex **65** was structurally characterized by its ^1H NMR and IR spectra which are similar to those of $HB(3,5\text{-}Me_2pz)_3RhCl_2(CO)$ (**13**) (see Tables II and IV). Previously, Lalor et al.[3] have reported that hydrotris(1-pyrazolyl)borates react with $[(OC)_2RhCl]_2$ to give $[HB(pz)_3]_2Rh_2(CO)_3$ with bridging carbonyls. In contrast Bruce and Borkett[11] reported that $[(OC)_2RhCl]_2$ reacts with $K[HB(Me_2pz)_3]$ to give $[(OC)_2Rh(Me_2pz)]_2$ while King and Bond[12] reported that the same reaction results in decomposition to elemental rhodium. We have observed both kinds of reactions, the former when the $K[HB(Me_2pz)_3]$ is contaminated with unreacted 3,5-dimethylpyrazole and the latter when the $K[HB(3,5\text{-}Me_2pz)_3]$ is contaminated with unreacted borohydride. It is also of interest to note that an excess of $K[HB(3,5\text{-}Me_2pz)_3]$ is required in the preparation of $HB(3,5\text{-}Me_2pz)_3Rh(CO)_2$. When a 1:1 ratio of reactants is used, other ν_{CO} bands in the region of 1835 cm^{-1} are observed in the IR spectra of the products, although the exact spectral details were not reproducible from one preparation to another. The reaction of **64** with tertiary phosphines and arsines gave compounds which were isolated as yellow glasses. Their analytical and IR data are consistent with the formulation $HB(3,5\text{-}Me_2pz)_3Rh(CO)PR_3$. Their ^1H NMR spectra, however, are broad, complex, and irreproducible, and we have not as yet been able to fully characterize these systems.

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Registry No. **1**, 73117-94-9; **2**, 73117-95-0; **3**, 73117-96-1; **4**, 73117-97-2; **5**, 73117-98-3; **6**, 73117-99-4; **7**, 73118-00-0; **8**, 73118-01-1; **9**, 73118-02-2; **10**, 73118-03-3; **11**, 73118-04-4; **12**, 73118-05-5; **13**, 73118-06-6; **14**, 73118-07-7; **15**, 73118-08-8; **16**, 73117-74-5; **17**, 73117-75-6; **18**, 73117-76-7; **19**, 73117-77-8; **20**, 73117-79-0; **21**, 73117-81-4; **22**, 73117-83-6; **23**, 73117-85-8; **24**, 73117-86-9; **25**, 73117-88-1; **26**, 73117-89-2; **27**, 73117-90-5; **28**, 73117-91-6; **29**, 73117-92-7; **30**, 73117-93-8; **31**, 73117-59-6; **32**, 73117-60-9; **33**, 73117-61-0; **34**, 73117-62-1; **35**, 73117-63-2; **36**, 73117-64-3; **37**, 73117-65-4; **38**, 73117-66-5; **39**, 73117-68-7; **40**, 73117-70-1; **41**, 73137-31-2; **42**, 73137-32-3; **43**, 73117-71-2; **44**, 73117-72-3; **45**, 73117-73-4; **46**, 73117-44-9; **47**, 73117-45-0; **48**, 73117-46-1; **49**, 73117-47-2; **50**, 73117-48-3; **51**, 73117-49-4; **52**, 73117-50-7; **53**, 73117-51-8; **54**, 73117-53-0; **55**, 73117-54-1; **56**, 73117-55-2; **57**, 73117-56-3; **58**, 73117-57-4; **59**, 73137-30-1; **60**, 73117-58-5; **61**, 73137-28-7; **62**, 73117-36-9; **63**, 73117-37-0; **64**, 33790-49-7; **65**, 73117-38-1; μ-dichloro-bis[diallylrhodium(III)], 12090-11-8; $[(CO)_2RhCl]_2$, 14523-22-9; H_2IrCl_6, 16941-92-7.

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