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METAL POLYPYRAZOLYLBORATE COMPLEXES

IV*. SOME REACTIONS OF ORGANOMETALLIC RHODIUM(I) CHLORIDE DERIVATIVES WITH POLYPYRAZOLYLBORATES

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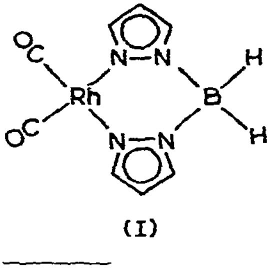
Summary

Reactions of the 1,5-cyclooctadiene complex $[C_8H_{12}RhCl]_2$ with the potassium polypyrazolylborates $K[H_{4-n}BPz_n]$ (Pz = pyrazolyl, n = 2, 3 and 4; Pz = 3,5-dimethylpyrazolyl, n = 2 and 3) in ethereal solvents give the corresponding complexes $C_8H_{12}RhPz_nBH_{4-n}$ as stable yellow solids. Reaction of $[Rh(CO)_2Cl]_2$ with potassium bis(pyrazolyl)borate in hexane gives yellow $H_2B(C_3H_3N_2)_2Rh(CO)_2$, but similar reactions of $[Rh(CO)_2Cl]_2$ with the other polypyrazolylborates lead only to decomposition at room temperature. The tris- and tetrakis(pyrazolyl)borate rhodium 1,5-cyclooctadiene complexes all appear stereochemically non-rigid at room temperature.

Polypyrazolylborate metal carbonyl complexes are known for chromium [2], molybdenum [2], tungsten [2], manganese [2], iron [1,3—5] and ruthenium [3]. We have now found that the reaction of $[Rh(CO)_2Cl]_2$ with potassium bis(pyrazolyl)borate in hexane at room temperature proceeds rapidly to give a yellow solution from which a nearly quantitative yield of yellow crystalline $H_2B(C_3H_3N_2)_2Rh(CO)_2$ can be isolated. The obvious formulation of this product as the square planar rhodium(I) derivative (I) is supported by the observation of two sharp ν(CO) frequencies at 2088 and 2022 cm^{-1} and by the equivalence of both pyrazolyl rings from the proton NMR spectrum.



(I)

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[*] For paper III of this series see ref.1.

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All similar attempts to prepare stable identifiable rhodium carbonyl derivatives of other polypyrazolylborate ligands [6,7] were unsuccessful. Reactions of $[Rh(CO)_2Cl]_2$ with potassium tris(pyrazolyl)borate and potassium tetrakis(pyrazolyl)borate in hexane gave yellow crystalline products of similar appearance to $H_2B(C_3H_3N_2)_2Rh(CO)_2$. However, these products decomposed rapidly at room temperature to red solids. Presumably a complex analogous to I is formed using two pyrazolyl rings of the tris- or tetrakis(pyrazolyl)borate ligand but a further reaction involving the uncomplexed pyrazolyl ring(s) and displacement of the carbonyl groups on the rhodium atom leads to decomposition of this complex. Reactions of $[Rh(CO)_2Cl]_2$ with potassium bis(3,5-dimethylpyrazolyl)borate and potassium tris(3,5-dimethylpyrazolyl)borate under similar conditions gave no evidence for the formation of a rhodium carbonyl complex but instead resulted in immediate complete decomposition to give a black precipitate, presumably rhodium metal. This contrasts with the reported [8] preparation of the stable boron-free bridging 3,5-dimethylpyrazolide complex $[Me_2C_3HN_2Rh(CO)_2]_2$. Attempts to prepare iridium carbonyl polypyrazolylborates by reactions of commercial iridium tricarbonyl chloride (Strem Chemical Co.) with the potassium polypyrazolylborates $K[H_{4-n}B(C_3H_3N_2)_n]$ in 10/3 benzene—tetrahydrofuran failed to give any tractable products.

The instability of the complex obtained from $[Rh(CO)_2Cl]_2$ and trispyrazolylborate contrasts with the reported [2] isolation by Trofimenko of a stable yellow complex $HB(C_3H_3N_2)_3Rh(C_2H_4)_2$ from the ethylene complex $[(C_2H_4)_2RhCl]_2$ and potassium trispyrazolylborate. We have now found that reactions of the 1,5-cyclooctadiene complex $[C_8H_{12}RhCl]_2$ with the three polypyrazolylborates $K[H_{4-n}B(C_3H_3N_2)_n]$ (n = 2, 3 and 4) and the two poly(3,5-dimethylpyrazolyl)borates $K[H_{4-n}B(Me_2C_3HN_2)_n]$ (n = 2 and 3) all give stable yellow complexes of the general type 1,5-$C_8H_{12}RhPz_nBH_{4-n}$ (Pz = pyrazolyl, n = 2, 3 and 4; Pz = 3,5-dimethylpyrazolyl, n = 2 and 3); the compound $HB(C_3HMe_2N_2)_3RhC_8H_{12}$ was previously [8] obtained by Trofimenko under somewhat different reaction conditions*. The proton NMR spectrum of each of these five complexes (Table 2) indicates all of the pyrazolyl or 3,5-dimethylpyrazolyl rings in a given complex to be equivalent on the NMR time-scale at room temperature. Stereochemical nonrigidity is therefore suggested for the tris- and tetrakis(pyrazolyl)borate complexes; such stereochemical non-rigidity was previously established for the rhodium complex [3] $HB(C_3H_3N_2)_3Rh(C_2H_4)_2$ as well as for polypyrazolylborate complexes of molybdenum [9], tungsten [9], palladium [2] and platinum [10].

Experimental

The rhodium complexes $[Rh(CO)_2Cl]_2$ [11] and $[C_8H_{12}RhCl]_2$ [12] and the polypyrazolylborates $K[H_{4-n}B(C_3H_3N_2)_n]$ (n = 2, 3 and 4) [13] and $K[H_{4-n}B(3,5\text{-}Me_2C_3HN_2)_n]$ (n = 2 [14] and 3 [15]) were prepared by the cited published procedures. Other general aspects of the experimental techniques are given in previous papers of this series.

Analytical, yield, and melting point data on the new rhodium complexes are given in Table 1. Their proton NMR spectra are given in Table 2.

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* *Note added in proof.* After this paper was accepted for publication, the complexes $H_2B(C_3H_3N_2)_2$

TABLE 1

NEW RHODIUM(I) POLYPYRAZOLYLBORATE DERIVATIVES[a]

Compound[b]	Yield (%)	M.p. (°C)[c]	Analyses found (calcd.) (%)[d]		
			C	H	N
$H_2B(C_3H_3N_2)_2Rh(CO)_2$[e]	92	71	31.3 (31.4)	2.5 (2.6)	18.6 (18.3)
$H_2B(C_3H_3N_2)_2RhC_8H_{12}$	59	101	47.1 (46.9)	5.6 (5.6)	15.6 (15.7)
$HB(C_3H_3N_2)_3RhC_8H_{12}$	61	167	47.1 (48.1)	5.2 (5.2)	18.6 (19.8)
$B(C_3H_3N_2)_4RhC_8H_{12}$	56	208	48.7 (49.0)	5.1 (4.9)	21.5 (22.8)
$H_2B(C_3HMe_2N_2)_2RhC_8H_{12}$	24	145 (dec.)	52.4 (52.2)	6.9 (6.8)	13.4 (13.5)

[a] All of these compounds were yellow solids. [b] $C_3HMe_2N_2$ refers to the 3,5-dimethylpyrazolyl system; C_8H_{12} refers to 1,5-cyclooctadiene. [c] Melting points were taken in capillaries and are uncorrected. [d] Analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia 30308. [e] Infrared spectrum: ν(CO) in hexane: 2088 s and 2022 s cm^{-1}.

TABLE 2

PROTON NMR SPECTRA OF RHODIUM(I) POLYPYRAZOLYLBORATE DERIVATIVES[a]

Compound[b]	Proton NMR spectrum, τ (ppm)[c]				
	Pyrazolyl ring[d]			Olefin ligand	
	5 Position	4 Position	3 Position	Complexed olefinic	Saturated CH_2
$H_2B(C_3H_3N_2)_2Rh(CO)_2$[e]	2.88 d (2.5)	4.21 t (2.5)	2.67 d (2.5)		
$H_2B(C_3H_3N_2)_2RhC_8H_{12}$	2.76 d (3)	3.95 t (3)	2.56 d (3)	5.78	~7.5 (br), ~8.1 m
$HB(C_3H_3N_2)_3Rh(C_2H_4)_2$[f]	2.38 d (1.9)	3.83 t (2.1)	2.20 dd (2.3, 0.5)	7.46	
$HB(C_3H_3N_2)_3RhC_8H_{12}$	2.44 d (2.0)	3.83 t (2.3)	2.28 d (2.4)	6.07	~7.5 (br), 8.16 m
$B(C_3H_3N_2)_4RhC_8H_{12}$	2.91 d (2.4)	3.74 t (2.2)	2.41 d (1.9)	6.03	~7.8 (br), ~8.3 m
$H_2B(C_3HMe_2N_2)_2RhC_8H_{12}$	7.79 s (CH_3)	4.50 s	7.73 s (CH_3)	5.74 (br)	~7.6 (br), 8.26 m
$HB(C_3HMe_2N_2)_3RhC_8H_{12}$	7.86 s (CH_3)	4.22 s	7.63 s (CH_3)	5.85 (br)	~7.7 (br), ~8.4 m

[a] These proton NMR spectra were taken in $CDCl_3$ solution (unless otherwise indicated) and recorded on a Varian HA-100 spectrometer at 100 MHz. [b] C_8H_{12} = 1,5-Cyclooctadiene, $C_3H_3N_2$ = pyrazolyl, $C_3HMe_2N_2$ = 3,5-dimethylpyrazolyl. [c] s = Singlet, d = doublet, t = triplet, dd = double doublet, m = multiplet, (br) = broad. Coupling constants in Hz are given in parentheses. [d] For the numbering of the positions of the pyrazolyl ring see ref. 2. [e] C_6D_6 solution. [f] Data from ref. 2.

Reaction of [Rh(CO)$_2$Cl]$_2$ with potassium bis(pyrazolyl)borate

A mixture of 1.86 g (10 mmoles) of potassium bis(pyrazolyl)borate, 1.0 g (1.7 mmoles) of $[Rh(CO)_2Cl]_2$, and ≈ 100 ml of hexane was stirred for 15 min at room temperature. The reaction mixture was then filtered and solvent removed from the filtrate at ≈ 25°/35 mmHg. Low temperature crystallization of the residue from hexane gave 0.94 g (92% yield) of yellow crystalline $H_2B(C_3H_3N_2)_2Rh(CO)_2$, m.p. 71°.

General procedure for the reactions of $[C_8H_{12}RhCl]_2$ with the potassium polypyrazolylborates

A mixture of 3 mmoles of the potassium polypyrazolylborate, 0.493 g (1 mmole) of $[C_8H_{12}RhCl]_2$, 30 ml of diethyl ether and 10 ml of tetrahydrofuran was stirred for 45 min at room temperature. Solvent was then removed at ≈ 60°/25 mmHg. The bis(pyrazolyl)borate complexes $H_2B(C_3H_3N_2)_2RhC_8H_{12}$ and $H_2B(C_3HMe_2N_2)_2RhC_8H_{12}$ were purified by low temperature crystallization from hexane. The tris(pyrazolyl)borate complexes $HB(C_3H_3N_2)_3RhC_8H_{12}$ and $HB(C_3HMe_2N_2)_3RhC_8H_{12}$ were purified by low temperature crystallization from mixtures of diethyl ether and dichloromethane. The tetrakis(pyrazolyl)borate complex $B(C_3H_3N_2)_4RhC_8H_{12}$ was purified by chromatography on alumina in a mixture of dichloromethane and hexane followed by low temperature crystallization from a mixture of dichloromethane and hexane.

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