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RHODIUM(I) DERIVATIVES OF DIETHYLBISPYRAZOLYLBORATE

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Summary

Bis-substituted rhodium(I) polypyrazolylborates of the type $L_2RhBPz_2Et_2$ (L = CO or RNC where R = p-$CH_3C_6H_4$, t-C_4H_9 or p-$CH_3C_6H_4SO_2CH_2$) have been prepared and characterized and hence the analogous rhodium(III) derivatives by oxidative addition reactions with iodine, iodomethane, or mercury(II) chloride.

Introduction

Following Trofimenko's [1,2] initial preparation of transition metal complexes containing polypyrazolylborate ligands, other workers [3—5] have investigated reactions of polypyrazolylborates with rhodium and iridium derivatives. Boron-free products such as $[(CO)_2RhPz]_2$ or insoluble polynuclear species such as $[Rh_2(HBPz_3)_2(CO)_3]_n$, or $[Rh_2(BPz_4)_2]_n$ generally resulted, although in some cases the products could not be isolated or characterized. Recently, Bonati et al. [6] described the preparation of some new volatile complexes of the type $[(CO)_2$-$Rh(BPz_2H_2)]$ and $[Ph_3PCORh(BPz_2H_2)]$. We now describe some reactions of the ligand $BPz_2Et_2^-$ with $[Rh(CO)_2Cl]_2$ whereby bis-substituted rhodium(I) polypyrazolylborates can be prepared.

Experimental

Analyses were carried out by Mr. McKinnon of this Department or by M.H.W., Phoenix, Arizona. Infrared spectra were recorded on Beckman IR-5A or Beckman IR-12 spectrophotometers; ^1H NMR spectra were obtained on a Varian A-60 or a Bruker spectrometer operating at room temperature and 60 MC.

All reactions were carried out at room temperature. The starting materials,

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TABLE 1

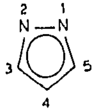
Compound [a]	State and colour [b]	M.p. (°C)	Analysis (%) Found (Calcd.)				
			C	H	N	I	Hg
$(CO)_2RhBPz_2Et_2$ (I)	yellow [c]		39.60 (39.81)	4.45 (4.42)	15.27 (15.48)		
$(C_7H_7NC)_2RhBPz_2Et_2$ (II)	greenish yellow	162–163	58.06 (57.81)	5.31 (5.56)	15.41 (15.56)		
$(CO)(C_9H_9SO_2N)RhBPz_2Et_2$ (III)	yellow	60	45.32 (45.39)	4.80 (4.73)	12.79 (13.24)		
$(C_9H_9SO_2N)_2RhBPz_2Et_2$ (IV)	pink	81 [d]	48.74 (48.30)	4.83 (4.89)	12.30 (12.07)		
$(CO)(C_4H_9NC)RhBPz_2Et_2$ (V)	yellow [c]		46.53 (46.06)	6.18 (6.00)	16.75 (16.79)		
$(C_4H_9NC)_2RhBPz_2Et_2$ (VI)	bright yellow	115	51.37 (50.85)	7.23 (7.20)	17.79 (17.80)		
$(C_7H_7NC)_2RhBPz_2Et_2I_2$ (VII)	orange brown	159	39.60 (39.32)	3.77 (3.78)	10.62 (10.59)	31.93 (31.98)	
$(C_7H_7NC)_2RhBPz_2Et_2CH_3I$ (VIII)	white	138 [d]	48.37 (48.27)	4.93 (4.92)	12.33 (12.51)	18.73 (18.91)	
$(C_7H_7NC)_2RhBPz_2Et_2HgCl_2$ (XIII)	brown	122	38.61 (38.46)	3.56 (3.70)	10.41 (10.35)		25.10 (24.72)
$(C_9H_9SO_2N)RhBPz_2Et_2I_2$ (IX)	orange	165 [d]	33.81 (33.65)	3.51 (3.42)	8.86 (8.84)	27.01 (26.75)	
$(C_9H_9SO_2N)_2RhBPz_2Et_2CH_3I$ (X)	orange	115	41.60 (41.54)	4.44 (4.42)	10.03 (10.02)	15.30 (15.15)	
$(C_9H_9SO_2N)_2RhBPz_2Et_2HgCl_2$ (XIV)	greenish yellow	153	33.87 (34.70)	3.57 (3.51)	8.38 (8.68)		21.02 (20.74)
$(C_5H_9N)_2RhBPz_2Et_2I_2$ (XI)	brick red	178	33.17 (33.07)	4.74 (4.68)	11.37 (11.57)	35.26 (34.97)	
$(C_5H_9N)_2RhBPz_2Et_2CH_3I$ (XII)	white	155	41.16 (41.05)	6.03 (6.03)	13.73 (13.68)	20.57 (20.67)	
$(C_5H_9N)_2RhBPz_2Et_2HgCl_2$ (XV)	deep yellow	190 [d]	34.52 (34.80)	4.96 (4.93)	11.82 (12.18)		29.15 (29.09)

[a] Pz = $C_3H_3N_2^-$. [b] All compounds are crystalline solids except marked. [c] Liquid. [d] Decomposed.

TABLE 2

Compound [a]	NMR data, (ppm)					
	—Et	—Me	—CH$_2$	—4 H	Phenyl—	3,5 H
$(CO)_2RhBPz_2Et_2$ [b] (I)	1.05(d) 1.3(t)			5.85(t)		7.3(d), 7.4(d)
$(C_7H_7NC)_2RhBPz_2Et_2$ [b] (II)	0.8(d) 1.17(t)	2.3(s)		6.08(t)	6.38—6.78(m)	7.53(d), 7.64(d)
$(CO)(C_9H_9SO_2N)RhBPz_2Et_2$ [b] (III)	1.00(d) 1.25(t)	1.92(s)	3.58(s)	5.9(t)	6.72—7.1(m)	7.4(d), 7.51(d)
$(C_9H_9SO_2N)_2RhBPz_2Et_2$ [b] (IV)	1.05(d) 1.45(t)	1.95(s)	3.92(s)	5.83(t)	6.77—7.15(m)	7.67(d), 7.78(d)
		—t-Bu				
$(CO)(C_4H_9NC)_2RhBPz_2Et_2$ [b] (VI)	1.25(d) 1.8(t)	0.97(s)		6.07(t)		7.60(d), 7.72(d)
$(C_4H_9NC)_2RhBPz_2Et_2$ [b] (VI)	1.1(d) 1.42(t)	0.75(s)		5.9(t)		7.42(t)
		—Me				
$(C_7H_7NC)_2RhBPz_2Et_2I_2$ [c] (VII)	1.23(t)	1.8(s)		6.33(t)	6.5—7.0(m)	7.86(d), 8.13(d)
$(C_7H_7NC)_2RhBPz_2Et_2CH_3I$ [c] (VIII)	0.7(t) Rh—CH$_3$ 1.5(d)	2.1(s)		6.33(t)	7.27—7.6(m)	7.75(d), 7.85(d)
$(C_7H_7NC)_2RhBPz_2Et_2HgCl_2$ [c] (XIII)	1.0(t)	2.4(s)		6.33(t)	7.16—7.7(m)	7.82(d), 8.10(d)
$(C_9H_9SO_2N)_2RhBPz_2Et_2I_2$ [c] (IX)	0.7(t)	2.5(s)	5.2(s)	6.3(t)	7.35—7.80(m)	8.0(d), 8.13(d)
$(C_9H_9SO_2N)_2RhBPz_2Et_2CH_3I$ [c] (X)	0.7(t) Rh—Me 1.13(d)	2.4(s)	5.15(s)	6.00(t)	7.2—7.4(m)	7.52(d), 7.65(d)
$(C_9H_9SO_2N)_2RhBPz_2Et_2HgCl_2$ [c] (XIV)	1.0(t)	2.42(s)	5.2(s)	5.8(t)	7.2—7.42(m)	7.6(d), 7.73(d)
		—t-Bu				
$(C_4H_9NC)_2RhBPz_2Et_2I_2$ [b] (XI)	0.63(t)	1.6(s)		6.25(t)		7.6(t)
$(C_4H_9NC)_2RhBPz_2Et_2CH_3I$ [c] (XII)	0.57(t) 1.15(d) Rh—CH$_3$	1.55(s)		6.13(t)		7.45(d)
$(C_4H_9NC)_2RhBPz_2Et_2HgCl_2$ [c] (XV)	0.83(t)	1.7(s)		5.7(t)		7.2(d)

[a] Pz =



. [b] Benzene-*d*. [c] Chloroform-*d*.

$Rh_2(CO)_4Cl_2$, $Zn(BPz_2Et_2)_2$ and *p*-tolyl isocyanide were prepared by available methods [7,2,8].

Preparation of $(CO)_2RhBPz_2Et_2$ *(I)*

To a solution of $Rh_2(CO)_4Cl_2$ (70 mg) in pentane $Zn[BPz_2Et_2]_2$ (1 equivalent) was added and the reaction mixture was stirred for about 15 min; $ZnCl_2$ formed and was removed by filtration. A yellow liquid was obtained in 95% yield after stripping off the pentane. Physicochemical properties and analytical data are given in Tables 1—3. Molecular weight by mass spectrum: found 363, calcd. 362.

Preparation of $(C_7H_7NC)_2RhBPz_2Et_2$ *(II)*

In a typical preparation, to a solution of $(CO)_2RhBPz_2Et_2$ (100 mg) in pentane, C_7H_7NC (2 equivalents) was added dropwise with continuous stirring; after the addition of 1 equivalent of isocyanide, a greenish yellow precipitate appeared. The reaction mixture was stirred for 30 min and filtered, and the solid obtained was washed with pentane and air-dried, yield 93%.

The products, III, IV, V and VI were prepared similarly.

Analyses and physicochemical properties of these compounds are given in Tables 1—3.

Preparation of $(C_7H_7NC)_2RhBPz_2Et_2X_2$ $(X_2 = I_2$ *or* $CH_3I)$ *(VII)*

In a typical preparation, to a solution of II (70 mg) in benzene, a solution of I_2 (1 equivalent) in benzene was added slowly with continuous stirring. The orange colour of the solution slowly changed to brown, and the progress of the reaction was followed by observing the position of bands due to $\nu(C{\equiv}N)$ in the infrared spectrum. After 2 h, the benzene was removed, and the resulting brown mass was stirred in pentane for 3—4 h and filtered. The brown shiny crystals thus obtained were filtered, washed with pentane and dried; yield 75%.

Compounds VIII, IX, X, XI and XII were prepared similarly and their physicochemical properties and analyses are given in Tables 1—3.

TABLE 3

IR DATA (cm^{-1}) IN NUJOL

I	II	III	IV	V	VI	VII	VIII
2080vs	2170vs	2160vs	2175vs	2175vs	2170vs	2220vs	2215vs
2020vs	2105vs	2010vs	2100vs	2020vs	2125vs	2200s	2200m
1500m	2040w(sh)	1595m	2050(sh)	1505m	2095(sh)	1508m	1505m
815s	1515m	1160vs	1600m	810s	1505m	820s	820s
	815s	812s	1155vs		820s		
			812s				
IX	X	XI	XII	XIII	XIV	XV	
2250vs	2220(sh)	2250vs	2220vs	2220(sh)	2220(sh)	2220vs	
2220vs	2210vs	2220(sh)	2200m	2180vs	2205vs	2190s	
1595m	1580m	1505m	1515m	1500m	1590m	1500m	
1162vs	1160s	825s	830s	812s	1160vs	840s	
815s	815s				815s		

Preparation of $(C_7H_7NC)_2RhBPz_2Et_2HgCl_2$ *(XIII)*

In a typical reaction, to a solution of II (70 mg) in diethyl ether, a solution of $HgCl_2$ (1 equivalent) in diethyl ether was added slowly. The orange colour of the solution changed to a deep brownish yellow immediately. The reaction mixture was stirred for 1 h, some turbidity which appeared was removed by filtration, and on removal of the diethyl ether yellow brown shiny crystals were obtained, yield 80%.

Compounds XIV and XV were similarly prepared and their physicochemical properties and analyses are given in Tables 1—3.

Results and discussion

The compound $(CO)_2Rh(BPz_2Et_2)$, I prepared by the reaction of $Rh_2(CO)_4Cl_2$ and $Zn(BPz_2Et_2)_2$ in pentane, is a yellow liquid which is fairly stable towards air, moisture and heat. On prolonged exposure to air, the liquid turns brown. It is very soluble in most organic solvents, and is monomeric in the vapor state (mass spectrum).

Treatment of I with *p*-tolyl isocyanide (see Scheme 1) gave $(C_7H_7NC)_2Rh(BPz_2Et_2)$, II, as a greenish-yellow crystalline solid which is quite soluble in benzene, diethyl ether and chlorinated solvents, but less soluble in aliphatic hydrocarbons. Attempts to prepare $(CO)(C_7H_7NC)Rh(BPz_2Et_2)$ using equimolar quantities of I and *p*-tolyl isocyanide, only gave mixtures of I and II.

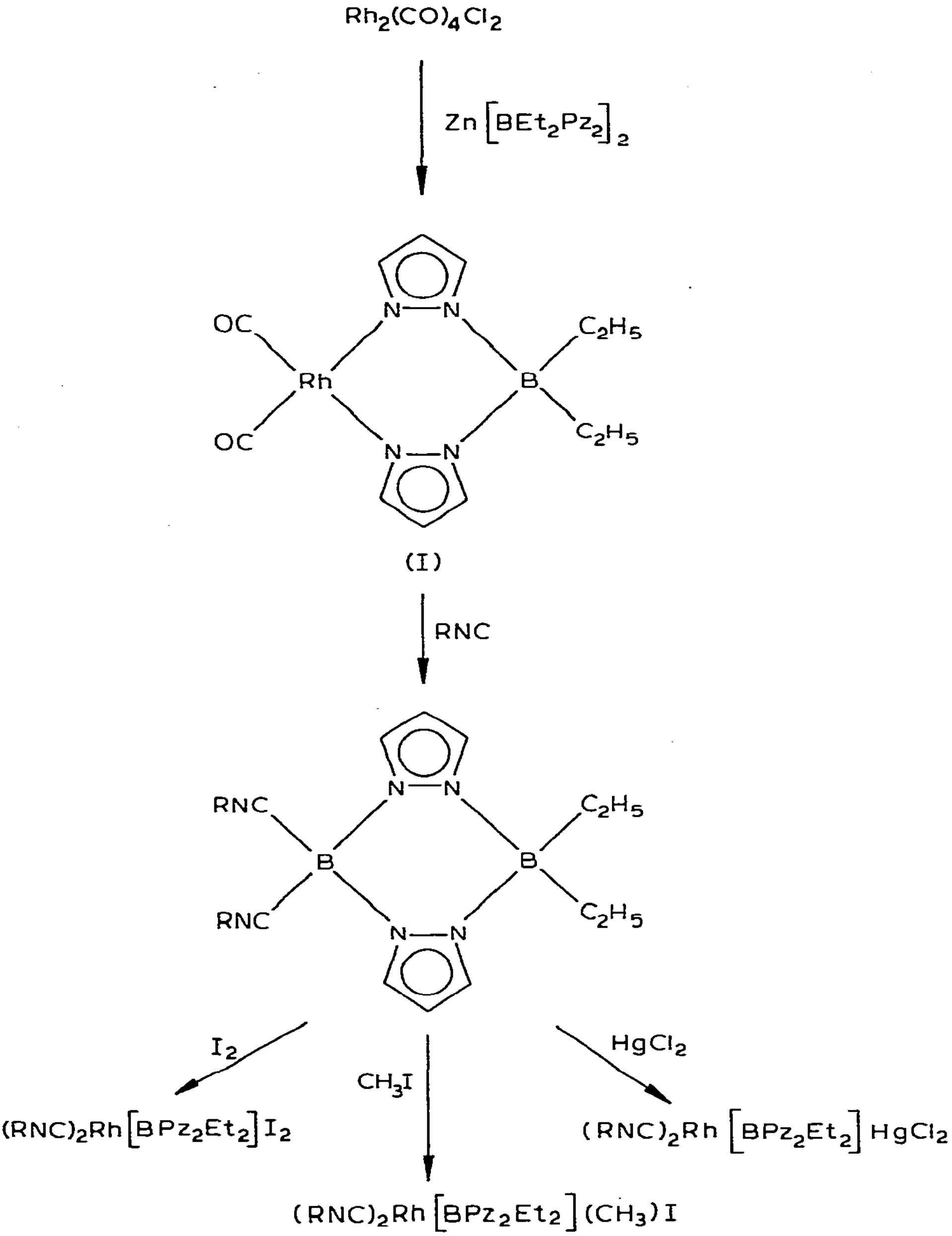
Compounds III and IV were similarly obtained by reacting $(CO)_2Rh(BPz_2Et_2)$ with one or two equivalents of $C_8H_9SO_2NC$, *p*-toluenesulphonyl isocyanide, respectively. Compounds III and IV, obtained as yellow and pink crystalline solids respectively on the evaporation of the diethyl ether solvent, dissolved readily in most organic solvents except aliphatic hydrocarbons. Compound V, a yellow liquid which crystallizes at 0°C, and compound VI, a bright yellow crystalline solid, were obtained by similar methods.

In contrast, similar reactions of I with triphenylphosphine or triphenylarsine, in attempts to obtain $(MPh_3)(CO)Rh(BPz_2Et_2)$, M = P or As, gave mixtures from which pure compounds could not be extracted. Reactions of I with 2,2-dipyridyl, bis(diphenylphosphino)ethane or acetylenes were also unsuccessful.

Oxidative addition by I_2, CH_3I or $HgCl_2$ of compounds II, IV and VI gave the new rhodium(III) compounds VII—XV. Such reactions with iodine or methyl iodide were carried out in benzene at room temperature. Removal of the benzene and recrystallization from pentane gave the iodo derivatives VII, IX and XI, as brown, orange or red crystals, respectively, or the methyl iodide products VIII or X. Reactions of II, IV and VI with mercury(II) chloride were carried out in diethyl ether, which on removal left the coloured crystalline products. All of these new products are stable in air and show good solubility in common organic solvents.

Similar reactions of II, IV and VI with acetyl chloride, trimethylchlorosilane, or triphenyltin chloride failed to yield identifiable products.

Characteristic infrared absorption bands of the new compounds are listed in Table 3. All show two distinct bands in the 815—820 cm^{-1} and 1500—1600 cm^{-1} regions due to the pyrazolyl rings. Compound I also shows two distinct, strong absorptions due to $\nu(CO)$ at 2020 and 2080 cm^{-1}, while compounds III



(R = *p*-tolyl , t-butyl and *p*-toluenesulphonyl)

and V, which contain both carbonyl and isocyanide ligands, each show two strong absorptions in the 2160—2175 cm^{-1} and 2010—2030 cm^{-1} due to ν(N≡C) and ν(CO), respectively. Products II, IV, and VI similarly display strong infrared absorptions due to ν(N≡C) in the 2100—2175 cm^{-1} region. In comparison, the octahedral rhodium(III) derivatives VII—XV show ν(N≡C) absorptions at higher frequencies in the 2180—2250 cm^{-1} region. Additionally, compounds

III, IV, IX, X and XIV each show a strong infrared absorption at ca. 1160 cm^{-1} due to the SO_2 group.

The ^1H NMR spectra of products I—VI show the expected resonances for the various types of protons (see Table 2). However, of particular note is the appearance of two distinct signals in the 0.80—1.80 ppm region, one a triplet at 1.71—1.80 ppm and the other a doublet at 0.80—1.25 ppm, both of which must arise from the $B—C_2H_5$ groups. These spectra are, however, quite different from that [2] of, for example, $Ni[B(Pz)_2(C_2H_5)_2]_2$, in which the resonances for two of the methylene groups (i.e., 4 protons) are shifted very substantially to low field. In our case, the spectra show a greater chemical shift difference between the methylene resonance (for all CH_2 groups) and the methyl resonance than is usual for C_2H_5 derivatives. Proximity to the rhodium(I) centre might well produce such greater discrimination between CH_2 and CH_3 protons. Interestingly, in the octahedral rhodium(III) compounds, VII—XV, where such proximity is not possible, only one signal (triplet) is observed in their ^1H NMR spectra, which is attributable to the $B—C_2H_5$ groups.

For the rhodium(I) derivatives, the ^1H NMR spectra might be expected to show some temperature dependence associated with conformational changes of the RhNNBNN ring. However, other than some slight broadening of signals, we observed no temperature dependence (—20 to —90°C in CD_2Cl_2) of the ^1H NMR spectra of compounds I—VI.

The resonances attributable to the pyrazolyl protons, and protons of other ligands generally are seen in the expected regions and the details are given in Table 2.

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