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LETTER

Syntheses and catalytic activities of new poly(1-pyrazolyl)boratoruthenium complexes containing weakly coordinating nitrile ligands

Masayoshi Onishi*, Kazuto Ikemoto
and Katsuma Hiraki
Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852 (Japan)

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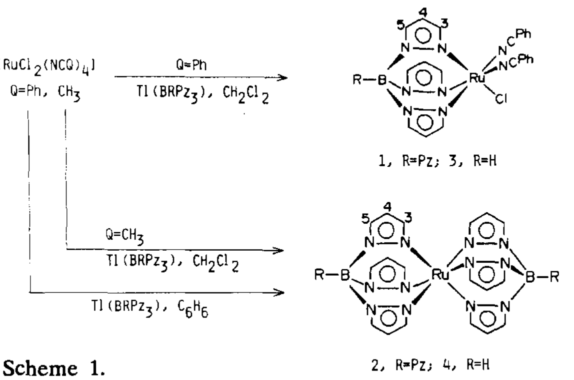
Poly(1-pyrazolyl)borato ligands $BH_nPz_{(4-n)}^-$ (Pz = 1-pyrazolyl) have become one of the most popular ligands in coordination chemistry since their introduction by Trofimenko, and the ligands especially in the tridentate coordination mode are often considered as π-cyclopentadienyl analogues in that both kinds of ligands effectively occupy three facial coordination sites around a metal ion and are six-electron donors with uni-negative charge [1]. Their complexes are known for almost every transition metal, many displaying unusual structural and chemical properties, such as stereochemical fluxionality observed in NMR spectroscopy [1]. However for ruthenium, only a few poly(1-pyrazolyl)borato complexes have been described [2], in spite of the well-known potentiality of ruthenium for affording high efficient catalytic species in a variety of homogeneous catalytic reactions [3]. To our knowledge, there have been no descriptions on catalytic reactions with transition metal poly(1-pyrazolyl)borate complexes so far, in sharp contrast to the case of the π-cyclopentadienyl analogues, on which much research has been performed in the last decade, for example for the modification of catalytic reactivities by pentamethyl introduction into the cyclopentadienyl rings [4]. As part of our objectives in developing new catalytic reaction systems with poly(1-pyrazolyl)borato ligands, we have treated dichlorotetrakis(organonitrile)ruthenium(II) with thallium salts of these anionic ligands to get chlorobis(organonitrile)[poly(1-pyrazolyl)borato]ruthenium(II), of which the organonitrile can be regarded as a weakly coordinating coexistent ligand [5].

A mixture of thallium tetrakis(1-pyrazolyl)borate and tetrakis(benzonitrile)dichlororuthenium(II) was heated in dichloromethane under reflux for 2 days. After removal of the solvent *in vacuo*, the residue was chromatographed on a silica-gel column, eluting with diethyl ether to give a yellowish green solid upon evaporation. The solid was characterized as bis(benzonitrile)chloro[tetrakis(1-pyrazolyl)borato]ruthenium(II) (**1**). On the other hand, similar reaction under benzene reflux gave a white powder of bis[tetrakis(1-pyrazolyl)borato]ruthenium(II) (**2**), i.e. a bis(π-cyclopentadienyl)ruthenium(II) (ruthenocene) analogue. Only complex **2** was obtained from reactions of tetrakis(acetonitrile)dichlororuthenium(II), and formation of bis(acetonitrile)chloro[tetrakis(1-pyrazolyl)borato]ruthenium(II) was not observed. As shown in Scheme 1, thallium hydrotris(1-pyrazolyl)borate yielded the complexes **3** and **4**, which are analogous to **1** and **2**, respectively. Table 1 summarizes some properties of these new complexes*.

In the ^{13}C NMR spectrum of the BPz_4 complex **1** in C_6D_6 at 30 °C, four pyrazolyl groups were divided into three classes by a 2:1:1 ratio. Two spectroscopically equivalent groups and one unique pyrazolyl group were tridentately coordinated to ruthenium, and the remaining one was uncoordinated. The classification of the three coordinated pyrazolyl groups in the 2:1 ratio indicates lack of rotation [1] of the tridentate BPz_4 ligand around the B–Ru axis at this temperature.

Upon addition of olefins, such as methyl acrylate to the methanol solution of **1**, a clear color change from yellowish green to reddish brown occurred immediately confirming the potential coordinative unsaturation of **1** due to facile displacement of the weakly coordinating nitrile ligands by incoming olefin



Scheme 1.

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*Author to whom correspondence should be addressed.

*Satisfactory elemental analyses were obtained for all the new complexes described in this paper.

TABLE 1. Properties of new poly(1-pyrazolyl)boratoruthenium complexes

Complex	Melting point[a] (°C)	IR[b] (cm^{-1})	^{13}C NMR of 1-pyrazolyl groups[c]		
			δ(3-C)	δ(4-C)	δ(5-C)
1 $[RuCl(BPz_4)(PhCN)_2]$	145	2200(CN)	145.32(2)	106.44(2)	135.36(2)
			141.78(1)	106.52(1)	136.25(1)
			143.88(1)	106.79(1)	136.06(1)
2 $[Ru(BPz_4)_2]$	250		143.97(6)	105.90(6)	134.98(6)
			141.79(2)	106.17(2)	136.14(2)
3 $[RuCl(BHPz_3)(PhCN)_2]$	150	2480(BH)	143.42(2)	105.90(3)	134.98(2)
		2230(CN)	142.80(1)		135.48(1)
4 $[Ru(BHPz_3)_2]$	260	2480(BH)	143.11(6)	105.32(6)	134.88(6)

[a] In evacuated capillary. [b] In KBr disk; stretching frequencies for the bond shown in parentheses. [c] In $CDCl_3$, except 1 in C_6D_6; δ value from TMS; the number of carbon atoms shown in parentheses; ^{13}C resonances of benzonitrile ligands are omitted.

TABLE 2. Olefin hydrogenation by the poly(1-pyrazolyl)borato complexes[a]

Compound	Olefin	Conversion (%)	Product[b]	TN[c]
1	$H_2C{=}CHCO_2CH_3$	100	$C_2H_5CO_2CH_3$	200
1	$C_6H_5{-}CH_2{-}CH{=}CH_2$	100	$C_6H_5{-}C_3H_7$	122
			$C_6H_5{-}CH{=}CH(CH_3)$ (*E*)	12
			$C_6H_5{-}CH{=}CH(CH_3)$ (*Z*)	65
3	$H_2C{=}CHCO_2CH_3$	100	$C_2H_5CO_2CH_3$	200
3	$C_6H_5{-}CH_2{-}CH{=}CH_2$	57	$C_6H_5{-}C_3H_7$	42
			$C_6H_5{-}CH{=}CH(CH_3)$ (*E*)	19
			$C_6H_5{-}CH{=}CH(CH_3)$ (*Z*)	52

[a] Reaction conditions: complex, 0.025 mmol; olefin, 5 mmol; methanol, 7 ml; Et_3N, 1 ml (7.17 mmol); H_2, 50 kg/cm^2 (initial pressure at r.t.); reaction temperature, 50 °C; reaction time, 16 h. [b] By GLC analysis. [c] Turnover number per catalysis.

substrates. Therefore, an attempt at the hydrogenation of methyl acrylate in methanol for 16 h with molecular hydrogen under 50 kg/cm^2 pressure, in the presence of Et_3N, was made. Methyl acrylate disappeared and was all converted to methyl propionate, as shown in Table 2. In the case of 3-phenylpropene hydrogenation, (*E*)- and (*Z*)-1-phenylpropenes were formed as by-products through an olefin double-bond migration process. Similar results were also obtained for the $BHPz_3$ complex 3. As a whole, the present study demonstrates for the first time catalytic olefin hydrogenation by use of transition metal poly(1-pyrazolyl)borate complexes with molecular hydrogen under pressure. Further studies, involving those on other related substrates for hydrogenation and on similar complexes with poly(alkyl-substituted 1-pyrazolyl)borato ligands, are now in progress and will be reported in subsequent publications.

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