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REACTIONS OF A 2-PICOLYL-BRIDGED PALLADIUM(II) COMPLEX WITH SOME PYRAZOLE DERIVATIVES

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Summary

A 2-picolyl-bridged dinuclear complex, $[\{Pd(2\text{-picolyl})Cl(PPh_3)\}_2]$ (I) reacted with alkali metal salts of poly(1-pyrazolyl)borates, $Na(BPz_4)$ (Pz = 1-pyrazolyl), $Na(HBPz_3)$, and $K(H_2BPz_2)$ to afford the complexes, $[\{Pd(2\text{-picolyl})(BPz_4)\}_2]$ (II), $[Pd(2\text{-picolyl})(HBPz_3)(PPh_3)]$ (III), and $[\{Pd(2\text{-picolyl})(H_2BPz_2)\}_2]$ (V), respectively. Complexes II and V retained the 2-picolyl bridge, whereas III was mononuclear without the bridge. Complex I was treated with hydrated silver perchlorate in the presence of tris(1-pyrazolyl)methane to give $[\{Pd(2\text{-picolyl})(OH_2)(PPh_3)\}_2](ClO_4)_2$ (VI) without incorporating the neutral ligand.

Introduction

Oxidative addition of 2-picolyl chloride to $[Pd(PPh_3)_4]$ gave a 2-picolyl-bridged complex of $[\{PdCl(2\text{-picolyl})(PPh_3)\}_2]$ (I), containing two bonds from the 2-picolyl groups to the palladium atoms via a 2-picolyl methylene group and the 2-picolyl nitrogen [1]. Excellent X-ray structural analysis by Kawaguchi et al. indicated that the molecular symmetry was C_2 and that the bridge of two 2-picolyl groups stretched two palladium atoms to give a boat-form-like eight-membered ring of $Pd(2\text{-picolyl})_2Pd$ [2]. Although triphenylphosphine and 4-picoline could not cleave the bridge of 2-picolyl groups, acetylacetonate $[(acac)^-]$ and dimethyldithiocarbamate $[(Me_2NCS_2)^-]$ anions detached the 2-picolyl nitrogen from palladium to yield mononuclear complexes [1].

Our interest in coordinating properties of poly(1-pyrazolyl)borate groups [3–6] and poly(1-pyrazolyl)methane derivatives [6,7] led us to study their reactivities towards the 2-picolyl-bridged dinuclear complex I. Poly(1-pyrazolyl)borate ligands are a versatile and interesting class of uninegative ligands which have a potentiality for novel fluxionality [4–6] on the basis of NMR spectroscopy, and have been shown to confer considerable stability on organometallic complexes apparently because of their favorable electronic and geometrical properties [8].

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Experimental

General procedures

Preparative operations were performed under dry nitrogen. Complex I was obtained from oxidative addition of 2-picolyl chloride to $[Pd(PPh_3)_4]$ [1]. Sodium tetrakis(1-pyrazolyl)borate $[Na(BPz_4)]$ (Pz = 1-pyrazolyl) [3], sodium hydrotris(1-pyrazolyl)borate $[Na(HBPz_3)]$ [3], potassium dihydrobis(1-pyrazolyl)borate $[K(H_2BPz_2)]$ [3], tris(1-pyrazolyl)methane [9], and 2,2-bis(1-pyrazolyl)propane [7] were prepared by literature methods. ^1H and ^{13}C NMR, mass, and IR spectra, melting points, molar conductivities, and molecular weights were measured according to the methods described in the previous paper [1].

Reaction of I with sodium tetrakis(1-pyrazolyl)borate

A mixture of $Na(BPz_4)$ (95 mg) and I (150 mg) in benzene (15 ml) was stirred at ca. 50°C for 6 h, and the solvent was evaporated to dryness in vacuo. The resulting solid was recrystallized from dichloromethane and hexane to yield a pale yellow powder of $[\{Pd(2\text{-picolyl})(BPz_4)\}_2]$ (II), 43 mg (yield 30%).

Reaction of I with sodium hydrotris(1-pyrazolyl)borate

Complex I (100 mg) was mixed with $Na(HBPz_3)$ (51 mg) in benzene (15 ml) and the mixture was 6 h stirred at ca. 50°C. Then the mixture was concentrated in vacuo to afford a solid, which was recrystallized from dichloromethane and hexane. An off-white powder (28 mg) was collected and characterized as $[Pd(2\text{-picolyl})(HBPz_3)(PPh_3)]$ (III) (yield 21%).

Reaction of I with potassium dihydrobis(1-pyrazolyl)borate

Complex I (200 mg) in THF (15 ml) was treated with $K(H_2BPz_2)$ (78 mg) and the mixture was stirred overnight at room temperature. After removal of the solvent, the resulting solid was chromatographed on a silica-gel column under nitrogen. The first yellow fraction was eluted with deaerated benzene to give a yellow powder (IV, 5 mg) possibly $[Pd(PPh_3)_x]$ or its cyclometalation product. The second yellowish brown fraction was eluted to give a yellow powder, $[\{Pd(2\text{-picolyl})(H_2BPz_2)\}_2]$ (V), 30 mg (yield 22%).

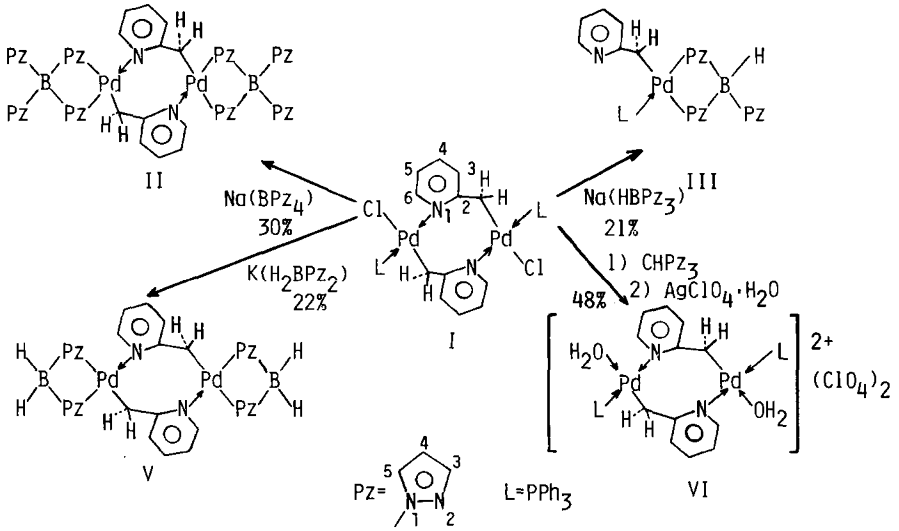
Reaction of I with hydrated silver perchlorate ($AgClO_4 \cdot H_2O$) in the presence of poly(1-pyrazolyl)methane derivatives or pyrazole

Hydrated silver perchlorate (94 mg) in benzene (15 ml) was added slowly to a benzene solution of I (200 mg) and tris(1-pyrazolyl)methane (95 mg). After stirring overnight at room temperature and evaporation to dryness in vacuo, recrystallization of the residue from acetone and ethyl ether gave a yellow powder, $[\{Pd(2\text{-picolyl})(OH_2)(PPh_3)\}_2](ClO_4)_2$ (VI) (111 mg, yield 48%). Similar reactions of I with neutral 2,2-bis(1-pyrazolyl)propane and pyrazole were carried out to afford the identical product VI. Complex VI was also obtained from a reaction of I with $AgClO_4 \cdot H_2O$ without addition of any pyrazolyl derivatives.

Results and discussion

The dinuclear complex I with the 2-picolyl-bridged structure [1,2] was treated with some poly(1-pyrazolyl)borate anions $[H_nBPz_{4-n}]^-$ ($n = 0$, 1 and 2) and poly(1-

SCHEME 1; Preparation of complexes II–V.



pyrazolyl)methane derivatives to yield new 2-picolylpalladium(II) complexes (Scheme 1), and their analytical data and physical properties are summarized in Tables 1, 2, and 3.

Sodium tetrakis(1-pyrazolyl)borate displaced triphenylphosphine in I, and gave a nonionic complex II. Determination of the molecular weight of II in CH_2Cl_2 indicated a dinuclear structure of $[\{Pd(2\text{-picolyl})(BPz_4)\}_2]$. Its ^1H NMR spectrum showed two doublets (J 7.7 Hz) at δ 3.05 and 4.45 ppm for non-equivalent methylene protons in the 2-picolyl group coupled to each other. Analogous geminal coupling of the two methylene protons was observed in I [1], and II was assumed to retain the rigid boat-form-like configuration of the 2-picolyl bridge.

In our previous papers [5,6], we reported preparation of some BPz_4-palladium(II) complexes with cyclopalladated chelate moieties bound to metal via a nitrogen donor and an aryl or alkyl group, and observed temperature-dependent ^1H NMR spectra of the BPz_4 ligand which indicated spectroscopic equivalence of four pyrazolyl groups at high temperature. A fluxional motion of the BPz_4 ligand was accounted for by a mechanism that one of the two uncoordinated pyrazolyl groups on boron underwent coordination to palladium through a vacant axial coordination-site followed by dissociation of one of the two originally coordinated pyrazolyl groups. However, the BPz_4 ligand of II did not show any fluxional behavior even at 52°C in $CDCl_3$. The boat-form-like configuration of the $Pd(2\text{-picolyl})_2Pd$ ring blocked possibly the vacant axial site, which was expected to be open to the third pyrazolyl group.

In contrast to II, nonionic complex III prepared from $Na(HBPz_3)$ has a mononuclear structure, and a characteristic $\nu(BH)$ band was observed at 2435 cm^{-1}. In the ^1H NMR spectrum in $CDCl_3$, three pyrazolyl groups were spectroscopically equivalent in the temperature range 28 to -31°C, indicating fluxional behavior of the $HBPz_3$ ligand. It is well-known that fluxional motion of the $HBPz_3$ ligand occurs more easily than that of the BPz_4 ligand [5,6]. A virtual triplet (J 2.0 Hz) at δ 6.05 ppm was attributed to three spectroscopically equivalent protons of H(4) in the

TABLE 1

ANALYSES AND PROPERTIES OF THE PALLADIUM(II) COMPLEXES

Complex	Analyses (Found (calcd.) (%))			M.p.[a] (°C)	M.W.[b]	Λ_M[f]
	C	H	N			
$[\{Pd(2\text{-picolyl})(BPz_4)\}_2]$	45.03	3.92	26.13	244–250	934[c]	0.3[c]
(II)	(45.27)	(3.80)	(26.39)		(955.2)	
$[Pd(2\text{-picolyl})(HBPz_3)(PPh_3)]$	58.65	4.69	14.70	157–161	680.5[d]	0.7[g]
(III)	(58.82)	(4.64)	(14.55)		(673.8)	
$[\{Pd(2\text{-picolyl})(H_2BPz_2)\}_2]$	42.25	4.20	19.92	144–146	[e]	[e]
(V)	(41.72)	(4.08)	(20.27)			
$[\{Pd(2\text{-picolyl})(OH_2)(PPh_3)\}_2](ClO_4)_2$	50.14	4.30	2.21	201–202	–	248[g]
(VI)	(49.85)	(4.01)	(2.42)			

[a] With decomposition. Samples were placed between two thin microscope-cover-glasses. [b] Molecular weight determined with vapor pressure osmometry. [c] In dichloromethane. [d] In benzene. [e] Not measured. [f] Molar conductivity, Ω^{-1} cm^2 mol^{-1}. Determined for 1.0×10^{-3} M solutions at 25°C. [g] In acetone.

TABLE 2

SELECTED IR BANDS OF THE PALLADIUM(II) COMPLEXES [a]

Complex	ν(CH) [b]	$\nu(\mathrm{CH_2})$ [c]	ν(BH)	ν(C=N) [c]	ν(PPh) [e]	ν(ClO)
II	3120	2952 2900	–	1595	–	–
III	3100	2965 2910	2435	1585	1425 1475	–
V	3120	2965 2920	2415 + 2435 [d] 2280	1602	–	–
VI	–	2970 2930	–	1600	1435 1477	1095

[a] In cm^{-1}, KBr disk. [b] In pyrazolyl moiety. [c] In 2-pycolyl moiety. [d] Slightly resolved doublet. [e] Characteristic bands of arylphosphines.

pyrazolyl groups, and two doublets at δ 7.33 (J 2.0 Hz) and 7.63 ppm (J 2.0 Hz) were assigned to H(3) and H(5). Moreover, the spectrum showed a doublet (J 5.0 Hz) at δ 2.91 ppm of two equivalent methylene protons in the 2-picolyl group, coupled to the ^{31}P nucleus. The coupling constant was satisfactory for *cis* configuration of the methylene group with respect to tertiary phosphine [10]. Spectroscopic equivalence of two methylene protons indicated free rotation of the 2-picolyl group around the palladium–carbon σ bond and dissociation of the 2-picolyl nitrogen from palladium.

Complex III showed a double doublet (J 5.0, and 1.8 Hz) at δ 8.28 ppm for H(6) of the 2-picolyl groups. In ^{1}H NMR spectra of similar mononuclear 2-picolyl complexes [1], [Pd(2-picolyl)(acac)(PPh$_3$)] and [Pd(2-picolyl)(PPh$_3$)(Me$_2$NCS$_2$)], H(6) protons resonated at comparable field, but H(6) resonances were not observed in neutral dinuclear complexes with 2-picolyl bridges, such as [{Pd(2-picolyl)Cl(PPh$_3$)}$_2$] [1], [{Pd(2-picolyl)(OAc)(PPh$_3$)}$_2$] (OAc = acetato) [1], and [{Pd(2-picolyl)(BPz$_4$)}$_2$], and probably overlapped with signals of some other aromatic protons in PPh$_3$ or BPz$_4$ moieties at higher field. Upfield shifts of H(6) protons in these dinuclear complexes was possibly due to anisotropic shielding effects of the PPh$_3$ ligand or 1-pyrazolyl groups.

From the reaction of I with K(H$_2$BPz$_2$), two kinds of materials were obtained

TABLE 3

^{1}H NMR DATA OF THE 2-PYCOLYL GROUP OF THE PALLADIUM(II) COMPLEXES [a]

Complex	$\delta(\mathrm{CH_2})$	δ(H(6))	δ(H(5)) or δ(H(4))	δ(H(3))
II [b]	3.05(d, 7.7) [d] 4.45(d, 7.7) [d]	[g]	[g]	[g]
III [b]	2.91(d, 5.0) [e]	8.28(dd, 5.0,1.8)	6.82(bt, 7.2) 7.02(dt, 7.2,1.8)	6.19(bd, 7.1)
VI [c]	2.72(bt, 9.3) [f] 4.38(dd, 9.3,4.5) [f]	7.76(d,5.5)	6.47(bt, 7.0) 6.99(bt, 7.0)	[g]

[a] δ(ppm), TMS; multiplicities and coupling constants in Hz are given in parentheses, d, doublet; bd, broad doublet: dd, doublet of doublets; bt, broad triplet; dt, doublet of triplets. [b] In CDCl$_3$. [c] In CD$_2$Cl$_2$. [d] Coupled to each other. [e] Coupled to ^{31}P nucleus. [f] Coupled to each other and to ^{31}P nucleus. [g] Not determined.

after column-chromatographic separation on silica gel. One of them was a yellow solid of V *. The solid slowly decomposed in deoxygenated halogenated hydrocarbons and was slightly soluble in THF, C_6H_6, and acetone. An IR spectrum of V showed many bands for 2-picolyl and H_2BPz_2 moieties, but no bands attributable to PPh_3. The H_2BPz_2 moiety gave a slightly resolved doublet at ca. 2425 and a singlet at 1060 cm^{-1}, characteristic of the H_2BPz_2 moiety coordinated to square-planar complexes [3]. These spectroscopic data and elemental analyses suggested product V to be a dinuclear complex of $[\{Pd(2\text{-picolyl})(H_2BPz_2)\}_2]$. Although the mass spectrum of V measured at 190°C did not show a parent-peak of the complex, there were some interesting signals with appropriate isotope patterns centered at *m/e* 397 assignable to $[Pd(2\text{-picolyl})_2Pd]^+$, at *m/e* 345 to $[Pd(2\text{-picolyl})(H_2BPz_2)]^+$, and at *m/e* 291 to $[Pd(2\text{-picolyl})_2]^+$. These signals were in agreement with a dinuclear structure of V and with coordination of 2-picolyl-nitrogen to palladium. It is noteworthy that the dinuclear structure of the 2-picolyl bridge in I was retained in the course of reactions with H_2BPz_2 and BPz_4 anions, but this was not the case for $HBPz_3$. However, reasons for these different reactivities are not obvious at the present stage.

The other minor product, IV, was a pale yellow air-sensitive powder, possibly a zerovalent phosphine species "$Pd(PPh_3)_x$" or its cyclometalation product [11]. Zerovalent palladium species with triphenylphosphine may be formed owing to the reducing ability of the H_2BPz_2 group and reductive elimination of the 2-picolyl group. The potassium salt of H_2BPz_2 was reported to reduce palladium(II) ions in aqueous solution to free metal [3].

Complex I was treated with hydrated silver perchlorate at room temperature in the presence of tris(1-pyrazolyl)methane, and a reaction mixture gave yellow microcrystals of VI, which were recrystallized from acetone and diethyl ether. In the ^1H and ^{13}C NMR and IR spectra of VI were no signals attributable to the pyrazolyl derivative. The IR spectra showed many bands of triphenylphosphine, the 2-picolyl group, and a non-coordinating perchlorate anion. An out-of-plane deformation mode in the 2-picolyl moiety was observed at 425 cm^{-1} and suggested coordination of 2-picolyl nitrogen, analogously to compound I [1]. The proton-decoupled ^{13}C NMR spectrum of the 2-picolyl group (CD_2Cl_2), showed a doublet at δ 164.2 ppm (J 3.7 Hz, C(2)) and three slightly broadened singlets at δ 151.1 (C(6)), 137.7 (C(4)), and 26.2 ppm (methylene carbon), whereas two singlets at δ 125.5 and 121.1 ppm were assigned to C(3) and C(5). In addition, the ^1H NMR spectra of VI showed signals of non-equivalent methylene protons (Table 3), and a H(6) proton did not resonate around δ 8.3 ppm owing to its upfield shift. These spectroscopic data indicated retention of the 2-picolyl bridge and coordination of the 2-picolyl nitrogen.

Similar reactions of I and hydrated silver perchlorate with 2,2-bis(1-pyrazolyl)propane or pyrazole failed to coordinate to palladium, and yielded VI. In spite of the potential chelate effect on complexation of poly(1-pyrazolyl)methane derivatives, they could not break the coordination of 2-picolyl nitrogen neither displace triphenylphosphine owing to the low basicity of their 2-N donors. These results of neutral poly(1-pyrazolyl)methane derivatives were very

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* As for V, measurement of a ^1H NMR spectrum and osmometric or cryoscopic determinations of molecular weights were not performed owing to its low solubility.

different from those of poly(1-pyrazolyl)borate anions, which served as strong-field ligands to form three types of 2-picolyl complexes II, III, and V. On abstraction of chlorine from I by hydrated silver perchlorate, the water molecule probably occupied the coordination-site in place of the chlorine atom. Since the ClO_4 moiety in VI gave a T_2(OClO) bending mode at 625 cm^{-1} and a T_2(ClO) stretching mode at 1095 cm^{-1} without any significant splitting, coordination of ClO_4 was unlikely.

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