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PALLADIUM POLYPYRAZOLYLBORATE COMPLEXES CONTAINING A Pd-C BOND

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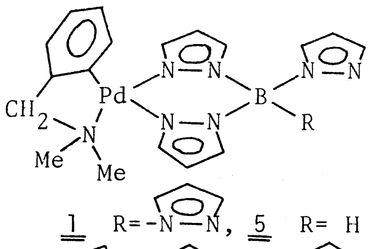
(N,N-Dimethylbenzylamine,2-C,N)(BPz_4)Pd(II) (Pz=1-pyrazolyl), (2-phenylpyridine,2'-C,N)(BPz_4)Pd(II), (azobenzene,2-C,N)(BPz_4)Pd(II), [benzo(h)quinoline,2-C,N](BPz_4)Pd(II), and (N,N-dimethylbenzylamine, 2-C,N)($HBPz_3$)Pd(II) were prepared. Pyrazolyl groups of these complexes were found to show a fluxional behavior on the basis of ^{1}H-NMR spectra.

Recently halogen-bridged dimeric complexes of palladium(II) containing a metal-carbon bond have been prepared by the intramolecular aromatic ortho-metalation reaction, and been found to be very stable.[1)] Ligands such as pyridine and phosphines cleave the halogen-bridge bonds of these complexes and form the mononuclear complexes.[1)] Interest in this cleavage reaction led us to investigate the reactions of the halogen-bridged complexes with polypyrazolylborate anions. Polypyrazolylborate anions, which were discovered by Trofimenko, are particularly interesting in their symmetrical coordination and fluxionality.[2)]

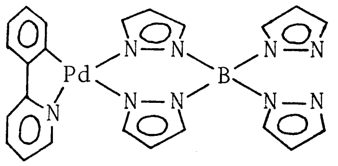
A few palladium polypyrazolylborate complexes containing π-allyl groups have been reported.[3,4)] The present paper describes the first examples of the palladium polypyrazolylborate complexes containing a phenyl-palladium σ-bond.

Di-μ-chloro-bis(N,N-dimethylbenzylamine,2-C,N)dipalladium(II)[5)] was mixed with sodium tetrakis(1-pyrazolyl)borate ($NaBPz_4$) in absolute THF. The suspension was stirred for 8 hrs. at 50°C till the yellow color disappeared. The precipitate was removed and the filtrate evaporated to dryness. The residue was recrystallized from benzene and n-hexane to give white powder of (N,N-dimethylbenzylamine,2-C,N)-[tetrakis(1-pyrazolyl)borato]palladium(II) **1**.

(2-Phenylpyridine,2′-C,N)[tetrakis(1-pyrazolyl)borato]palladium(II) 2, (azobenzene,2-C,N)[tetrakis(1-pyrazolyl)borato]palladium(II) 3 and [benzo(h)quinoline,2-C,N][tetrakis(1-pyrazolyl)borato]palladium(II) 4 were obtained by similar reactions between $NaBPz_4$ and the corresponding halogen-bridged ortho-palladation complexes.[6-8] Bis[tetrakis(1-pyrazolyl)borato]palladium(II) was a major product in the reaction of di-μ-chloro-bis(benzylideneaniline,2-C,N)dipalladium(II)[9] with $NaBPz_4$. The reaction of sodium hydrotris(1-pyrazolyl)borate ($NaHBPz_3$) with di-μ-chloro-bis(N,N-dimethylbenzylamine,2-C,N)dipalladium(II) at room temperature gave a mononuclear white complex 5 [ν(BH); 2430cm^{-1}].



1 R=-N—N, 5 R= H



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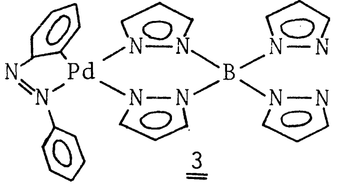

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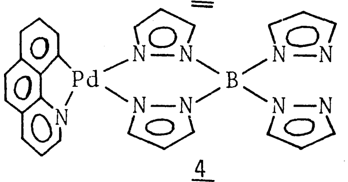

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Table 1. Yields and Properties of the New Palladium Complexes

No.	Yield %	Color	M.P.[a)] °C	^{1}H-NMR of 4-H[b)] δ-Value from TMS, ppm
1	80	White	222-223(dec)	6.22(t, coord.) 6.32(t, uncoord.)
2	31	White	>300	6.22
3	37	Yellow	241-244	6.21
4	58	Pale yellow	292-296	6.25
5	39	White	160-162(dec)	6.17(t, coord.) 6.25(t, uncoord.)

a) Melting points were determined on a microstage apparatus and uncorrected.
b) NMR spectra were recorded on a JNM-MH-100 by use of deuterated $CHCl_3$ solution at room temperature.

Yields and characteristic values of the new palladium complexes are presented in Table 1. Satisfactory elemental analyses were obtained for all polypyrazolylborate complexes.

In each of ^{1}H-NMR spectra of **2**, **3** and **4**, 4-H's of the pyrazolyl groups show only one peak, indicating a stereochemical nonrigidity at ambient temperature. At -5°C, the 4-H signal of the pyrazolyl groups of **2** splits as shown in Fig. 1. This indicates that 4-H's of coordinated pyrazoles and of uncoordinated pyrazoles show different chemical shifts and that the coordination of the pyrazolyl groups is stereochemically rigid at this temperature. Similarly, at 51°C the 4-H NMR spectrum of **1** shows only one peak (δ=6.29ppm), which splits into two signals at room temperature as shown in Table 1. That is, the coordination of the pyrazolyl groups is fluxional at 51°C and stereochemically rigid at room temperature. There is an obvious difference between the limiting temperatures for the stereochemical rigidity of **1** and **2**.

Fig. 2 shows a proposal for the geometrical arrangement in the stereochemically rigid coordination of these complexes, which have a square-planar structure about the central Pd atom and a boat conformation of Pd-(N-N)$_2$-B six-membered ring. The fluxional behavior is possibly due to a tumbling process, which involves the coordination of the uncoordinated pyrazolyl group near the palladium atom, accompanied instantaneously by the dissociation of the previously coordinated group and by inversion. This process averages the environments of all the pyrazolyl groups and results in the spectroscopic equivalence.

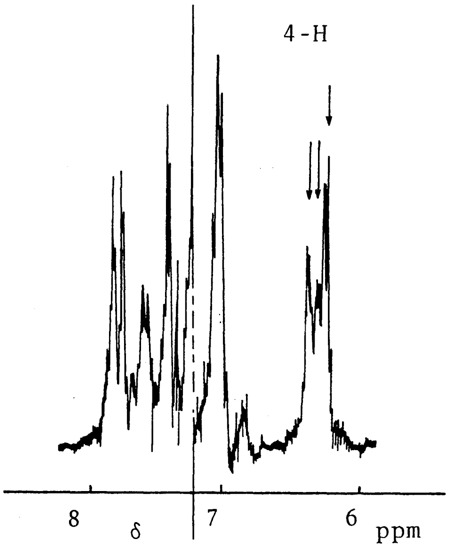

Fig. 1. ^{1}H-NMR spectrum of **2** at -5 °C.

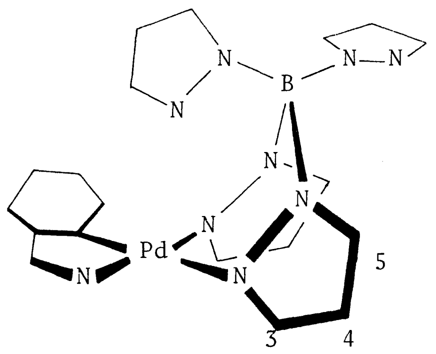

Fig. 2. The proposed geometrical arrangement.

In consideration of the bulkiness of the aromatic intramolecular metalation moiety, the methyl groups in **1** and **5** probably restrict the tumbling process of the polypyrazolyl groups because of their steric hindrance.

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