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Coordination-Site Exchange of Azaheterocyclic Ligands in Five-Coordinate Palladium(II) Complexes. Bis(4,7-dimethyl-1,10-phenanthroline)(triphenylphosphine)palladium(II) Tetrafluoroborate and the 4,7-Diphenyl Derivative

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Synopsis. Variable-Temperature ^{1}H NMR suggests that the fluxional motion of a potentially five-coordinate complex $[Pd(PPh_3)(4,7\text{-}R_2\text{-phen})_2][BF_4]_2$ (R=Me, Ph) is frozen at lower temperatures, where the complex is in a rigid configuration (an unusual trigonal bipyramid). The fluxional motion is explained by two synchronous rearrangement systems, and an activation parameter, ΔG*, for the site exchange is given.

For the ligand rearrangement systems of five-coordinate Pd(II) complexes,[1–6] most of the isolated complexes determined by means of X-ray diffraction and the discernible species in a solution detected by means of the spectra have been found to be in the form of a square pyramid, and their dynamic behavior in solution appears to proceed via the transition state of a trigonal bipyramid.

Previously, the crystal structure of the potentially five-coordinate Pd(II) complex $[PdCl(PPh_3)_2(phen)]^+$ has been described by the present author[6] as a very distorted square pyramid in which one nitrogen atom from the phen occupies the apical position, with a relatively long Pd–N distance (the two phosphines are mutually trans). Its solution structure[7] with a stereochemical non-rigidity, which has been explained by an oscillation of the apical phen, interestingly seems to be rather close to a square planar structure, with an anamalous unidentate phen. It should, however, be noticed that an analogous Pt(II) complex $[PtCl(PEt_3]_2(phen)]^+$,[3] with two phosphines mutually cis displays no dissociation processes in spite of the fact that the phen bite is loosened, in contrast to the Pd(II) complex.

This paper will deal with the dynamic motion of $[Pd(PPh_3)(phen)_2][BF_4]_2$ (R=Me, Ph) as evidenced by variable-temperature ^{1}H NMR spectroscopy.

Experimental

Preparation of Complexes-$[Pd(PPh_3)(4,7\text{-}Me_2\text{-phen})_2][BF_4]_2$. This complex was prepared by a procedure analogous to that used for the corresponding phen complex.[8] Found: C, 56.93; H, 3.89; N, 5.40%. Calcd for $C_{46}H_{39}N_4B_2F_8PPd$: C, 57.62; H, 4.10; N, 5.84%. Conductance (acetone solution of ca. 10^{-3} M.): Λ_M, 288 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (CDCl$_3$). vide infra.

$[Pd(PPh_3)(4,7\text{-}Ph_2\text{-phen})_2][BF_4]_2$. This complex was prepared as above. Found: C, 64.86; H, 4.16; N, 4.36%. Calcd for $C_{69}H_{53}N_4B_2F_8OPPd$: C, 65.50; H, 4.22; N, 4.42%. IR (nujol mulls): ν(CO)(an acetone of solvation), 1710 cm^{-1}. ^{1}H NMR (CDCl$_3$): vide infra. Conductance (acetone solution of ca. 7.8×10^{-4} M.): Λ_M, 203 Ω^{-1} cm^2 mol^{-1}.

Physical Measurements. The conductivities were measured using a Denki Kagaku Keiki AO-6 instrument in dried acetone solutions. The lower-temperature ^{1}H NMR spectra were recorded, using JEOL FX-90A (89.55 MHz) in the region of 193—303 K in CDCl$_3$, at the NMG Applied Research Center of JEOL Ltd., Akishima, Tokyo.

Results and Discussion

The ^{1}H NMR spectra of $[Pd(PPh_3)(4,7\text{-}R_2\text{-phen})_2][BF_4]_2$ (R=Me, Ph), which are dependent on the temperature, are shown in Fig. 1.

The lower-temperature ^{1}H NMR of the complex with R=H, as has been described elsewhere,[7] shows that its dynamic motion is not effectively frozen; only resonance broardening and overlapping were observed over a wide range of temperatures (173—303 K). Therefore, 4,7-Me$_2$ and Ph$_2$-phen were used as azaheterocyclic ligands, because a relatively simple spectrum with a small number of coupling patterns can then be expected.

At ambient temperatures, $[Pd(PPh_3)(4,7\text{-}R_2\text{-phen})_2]^{2+}$ is stereochemically non-rigid, but it becomes

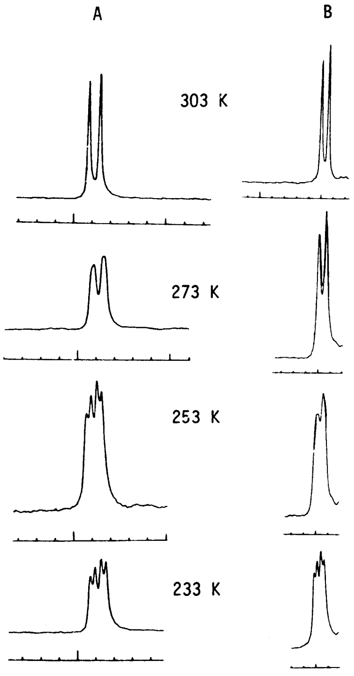


Fig. 1. Variable-temperature ^{1}H NMR(resonances due to 2,9-protons) of: A, $[Pd(PPh_3)(4,7\text{-}Ph_2\text{-phen})_2][BF_4]_2$ B, $[Pd(PPh_3)(4,7\text{-}Me_2\text{-phen})_2][BF_4]_2$ in CDCl$_3$.

Table 1. Temperature-Dependent ^{1}H NMR Data of $[Pd(PPh_3)(4,7\text{-}R_2\text{-phen})_2]^{2+}$ (R=Me, Ph)

Complex	T/°K	δ/ppm$^{b)}$	$\delta\nu^{c)}$	ΔG^*(kcal mol^{-1})$^{d)}$
R=Me	303	8.472		
	253(T_c)$^{a)}$	8.477		
	233	8.477 8.450	2.415	13.88
R=Ph	303	8.892		
	273(T_c)$^{a)}$	8.892		
	253	8.902 8.872	2.635	14.97

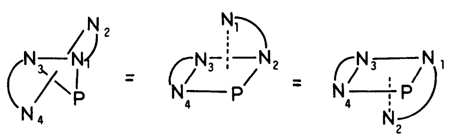
a) Coalescence temperature. b) Chemical shifts due to 2,9-protons, which are relative to Me_4Si at δ 0.00. c) Observed spacing between the two resonances due to 2 and 9-H of the azaheterocyclic ligand. d) Calculated by the use of $\Delta G^*/RT_c = 22.96 + \ln(T_c/\delta\nu)$,[10] where ΔG^* is an activation parameter for the site exchange of the azaheterocyclic ligand.

stereochemically rigid at lower temperatures. At 253 K, resonances due to 2,9-H in the 4,7-Ph$_2$-phen complex (Fig. 1A) were observed as two separate signals, each with coupling with the 3,8-H of the azaheterocyclic rings. The NMR spectrum at this temperature is consistent with the formation of an unsymmetrical structure (stereochemically rigid) in which two 4,7-Ph$_2$-phen are equivalent, while each azaheterocyclic ligand is unsymmetrically bound to the metal. Only a trigonal bipyramidal structure, with its axial positions occupied with nitrogen atoms, fits this requirement. Above 253 K, the resonance lines due to 2,9-H of the 4,7-Ph$_2$-phen complex become broadened, and at 273 K they coalesce into one resonance. The lines sharpen with an increase in the temperature. The ^{1}H NMR of the corresponding 4,7-Me$_2$-phen complex, which is dependent on the temperature, shows a pattern analogous to that observed for the 4,7-Ph$_2$-phen complex.

Even at lower temperatures, resonance patterns due to the CH_3 group (4,7-Me$_2$-phen complex) and 5,6-H (both complexes) were observed as a single resonance. These observations may not be unusual, for the 4,7-CH_3 and 5,6-H of the phen derivative may be too distant from the metal to be magnetically influenced.[9]

These NMR data are consistent with a site exchange between two nitrogen atoms of the azaheterocyclic ligand, and the fluxional motion may well be explained by means of two synchronous rearrangement systems: One a twist motion from a trigonal bipyramid to a tetragonal pyramid, and the other a concurrent oscillation of the apical 4,7-R$_2$-phen, which may average the magnetical environment around its two halves,[11] as is indicated in Scheme 1.

The activation parameters (ΔG^*) for the site exchange were estimated to be 13.9 kcal mol^{-1} for the 4,7-Me$_2$-phen complex and 15.0 kcal mol^{-1} for the 4,7-Ph$_2$-phen complex. The other activation parameters could not be obtained because of the relatively large $J/\delta\nu(\approx 2)$ ratio.



Scheme 1.

Although the conductivity data indicate that the association of the BF_4^- anion does not occur, it is still uncertain whether or not the fluxional motion of the complexes proceeds via dissociation processes. It should, however, be noticed that the fluxional behaviour of an analogous Pt(II) complex $[Pt(PPh_3)(phen)_2][BF_4]_2$ does not proceeds via a dissociation processes; to its ^{13}C NMR spectrum shows ^{195}Pt-C coupling at the 2,9-positions of the azaheterocyclic ligand.[12]

For the fluxional motion of $[Pd(PPh_3)(4,7\text{-}R_2\text{-phen})_2]^{2+}$, the trigonal bipyramid is unusually the ground state, while the square pyramid is an intermediate. These findings rather resemble the dissociation processes proposed for $[Ni(CN)_2(PMe_3)_3]$,[13] the intermediate of which has been supposed to be square pyramid. In most of the five-coordinate Pt(II) and Pd(II) complexes {i.e. $[PdCl_2(PMe_3)_3]$[4] and $[Pt(CN)(phen)_2][NO_3]$[2]}, the fluxional motion has, on the other hand, been supposed to proceed via the transition state or the intermediate of the trigonal bipyramid.

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