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Rotamers of 1-Phenylethylamine Ligands in (*R, S*)- and (*S, S*)-*trans*-Bis(succinimidato)-bis(1-phenylethylamine)palladium(II) Complexes

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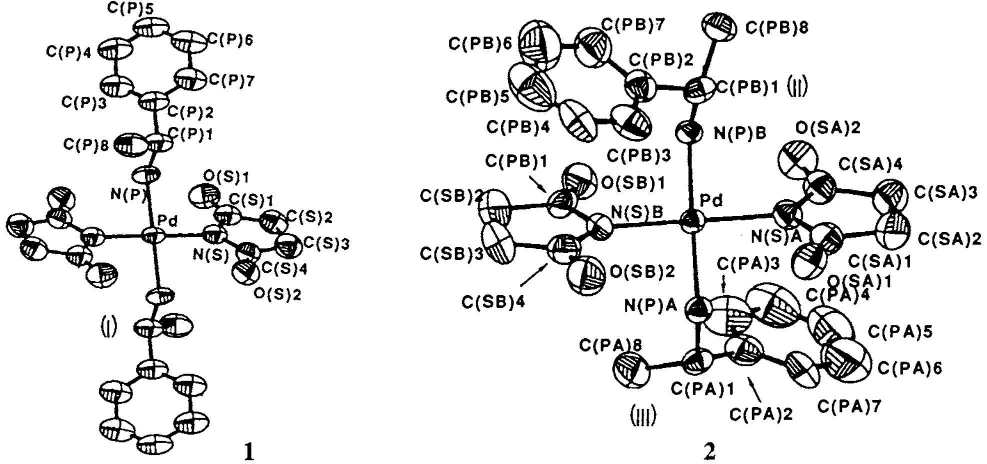
Both *trans*-[Pd(succim)$_2$(*R*-phenea)(*S*-phenea)] and *trans*-[Pd(succim)$_2$(*S*-phenea)$_2$] (succim=succinimidate, phenea=1-phenylethylamine) were prepared and their crystal structures were determined by X-ray analysis. Three different *staggered* rotamers around N-C bond of the phenea ligands have been found.

The structural difference between *meso* and *optically active* forms of the metal complexes sometimes plays a crucial role in chemical reactions. Indeed, Noyori et al. recently reported those zinc complexes with chiral amino alcohols in relation to the chiral amplification reaction.[1)] We wish to report here the conformational change of 1-phenylethylamine ligands in *meso* and *optically active* palladium(II) complexes with monodentate succinimidate ligands.

Two new complexes *trans*-[Pd(succim)$_2$(*R*-phenea)(*S*-phenea)] **1** and *trans*-[Pd(succim)$_2$(*S*-phenea)$_2$] **2** were prepared following the reported method using the *racemic* or *optically active* phenea ligand.[2)] Suitable crystals were obtained from chloroform/hexane (1 : 1) mixture, and X-ray structure determinations of **1** and **2** were performed.[3)] ORTEP drawings of **1** and **2** are shown in Fig. 1.



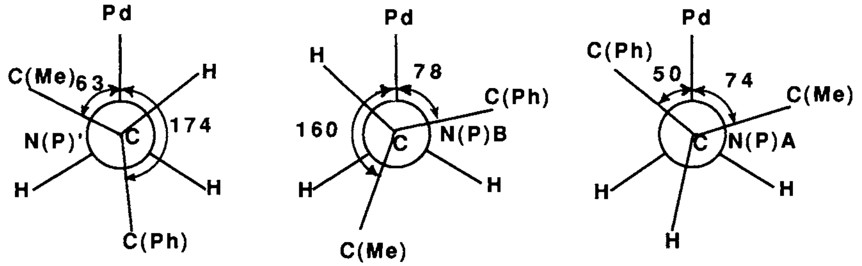
1 **2**

Fig. 1. View of the structures of **1** and **2**. Selected bond lengths(Å) and angles (°): Pd-N(S) 2.048(5), Pd-N(P) 2.067(5), N(S)-Pd-N(P) 89.7(2), for **1**; Pd-N(S)A 2.077(9), Pd-N(P)A 2.060(8), Pd-N(S)B 2.013(8), Pd-N(P)B 2.042(8), N(S)A-Pd-N(S)B 179.5(4), N(S)A-Pd-N(P)A 90.4(3), N(S)A-Pd-N(P)B 88.0(3), N(S)B-Pd-N(P)A 90.0(3), N(S)B-Pd-N(P)B 91.5(3), N(P)A-Pd-N(P)B 176.3(4), for **2**.

In **1**, the palladium atom is located on a special position $\bar{1}$. The dihedral angle between the PdN$_4$ and the imidate CNC planes is 41°. Intramolecular hydrogen bonds between the phenea NH$_2$ and succim carbonyl oxygen are N-H...O 2.83(1) Å, N-H-O 141(4)° and 2.86(1) Å, 140(4)° respectively.

In **2**, the geometry around the palladium atom is still nearly centrosymmetric except the methyl groups of *S*-phenea. Moreover, phenyl planes of both S-phenea are situated nearly parallel to succim planes. This arrangement forces two methyl groups to have different orientations. The corresponding dihedral angles are 42° and 45°. Intramolecular hydrogen bonds N-H...O 2.85(1) -2.94(1) Å, N-H-O 131(7) - 140(7)° resemble those found in **1**.

The most remarkable feature of the molecular structures of **1** and **2** is the presence of three different possible *staggered* rotamers of phenea. The projections of phenea along the N-C(chiral center) bond are shown in Fig. 2. Three types of the rotamer appear ; those are *staggered*-(I) for **1**, *staggered*-(II) and *staggered*-(III) for **2** respectively. (I) is so called opened form and (II) and (III) correspond to the closed form.[4] The Pd-N(phenea) distances suggest that the steric repulsions between phenea and succim in (I) and (III) are larger than that in (II).[5] Therefore, it can be mentioned that the repulsion caused by the methyl group is larger than that of the phenyl group.



staggered-(I) (**1**) *staggered*-(II) (**2**) *staggered*-(III) (**2**)

Fig. 2. Three *staggered* rotamers around N-C(chiral center) of phenea.

The investigations of the isomerization reaction in the solution state are now in progress.

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References

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2) S. Komorita and S. Yamada, *Synth. React. Inorg. Met-org. Chem.*, **14**, 485 (1984).
Elemental analysis : Found (Calcd for $C_{24}H_{30}N_4O_4Pd$): C, 53.03(52.90); H, 5.54(5.55); N, 10.32(10.28) % for **1**, and C, 52.17(52.90); H, 5.53(5.55); N, 10.10(10.28) % for **2**.

3) Crystal data of **1**: F.W.=544.94, triclinic, $P\bar{1}$, a=11.478(2), b=8.483(3), c=7.129(1) Å α=102.15(2), β=106.17(1), γ=67.14(1) °, U=610.2(2) Å^3, Z=1, Dc=1.48, Dm=1.47 g cm^{-3}, μ(Cu $K\alpha$)=65.7 cm^{-1}. R=0.056, Rw=0.065. The absorption effects were corrected. Total 1834 independent reflections with $|F\mathrm{o}|>3\sigma(F\mathrm{o})$ (2θ max=125°) were used. Crystal data of **2** : F.W.=544.94, monoclinic, $P2_1$, a=12.080(3), b=7.854(1), c=13.254(2) Å β=99.77(2) °, U=1239.3(4) Å^3, Z=2, Dc=1.46, Dm=1.45 g cm^{-3}, μ(Mo $K\alpha$)=7.71 cm^{-1}. R=0.033, Rw=0.066. Total 2434 independent reflections with $|F\mathrm{o}|>3\sigma(F\mathrm{o})$ (2θ max=60°) were used.

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5) The averaged value of Pd-N (primary amine) is 2.041(22) Å: A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, and R. Taylor, *J. Chem. Soc., Dalton Trans.*, **1989**, S36.

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