Kinetics and Mechanism of Cyclopalladation for $[Pd(S)(Bn_2Medptn)](BF_4)_2$ (S = Solvent, $Bn_2Medptn$ = *N,N''*-Dibenzyl-*N'*-methyl-3,3'-diaminodipropylamine) and Its Derivatives

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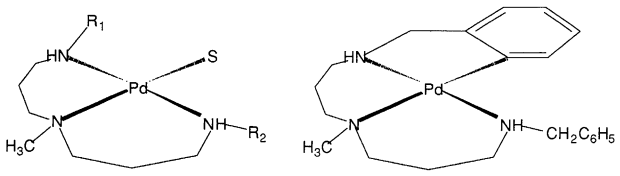
The kinetics of the cyclopalladation for $[Pd(CH_3CN)(Bn_2Medptn)](BF_4)_2$ ($Bn_2Medptn$ = *N,N''*-dibenzyl-*N'*-methyl-3,3'-diaminodipropylamine) and its derivatives confirmed the concerted mechanism where both the electrophilic attack of the palladium(II) center toward the ortho benzyl carbon and the nucleophilic interaction of the basic solvent with the ortho proton are operative in the activation process for the cyclopalladation.

The kinetic properties of square-planar palladium(II) complexes have been well established and the associative mechanism via the trigonal-bipyramidal transition state has been generally proposed.[1] On the other hand, it has been claimed that cyclopalladation proceeds by the mechanism via the three-coordinate 14-electron intermediate.[2] Accordingly, thorough kinetic studies are required for the complete understanding of the incompatibility in the reaction mechanism, and elucidation of the mechanism for cyclopalladation also gives us further insight into the reactivities of Werner-type palladium(II) complexes. However, there have so far been only a few kinetic studies on the cyclopalladation partially due to the complexity of the reaction mechanism,[2c,3] although a great number of the synthetic studies have been reported.[2f,4] For the clear-cut mechanistic study, we have performed the kinetics for the cyclopalladation of the solvated palladium(II) complexes with the potentially cyclopalladating triamine ligands having a benzyl group at each terminal amine (*N,N''*-dibenzyl-*N'*-methyl-3,3'-diaminodipropylamine, $Bn_2Medptn$) and at one terminal amine (*N*-benzyl-*N'*-methyl-3,3'-diaminodipropylamine, BnMedptn). Such a reaction system is expected not to be accompanied by any side reactions such as polymerization and dissociation of the bound ligand.

The triamine ligands, $Bn_2Medptn$, BnMedptn, and BnMedptn-d_7 which has a deuterated benzyl group were synthesized by the reaction of *N'*-methyl-3,3'-diaminodipropylamine with benzaldehyde, benzyl chloride, and benzyl chloride-d_7 in ethanol, respectively. The acetonitrile complexes with each triamine ligand, $[Pd(CH_3CN)(L)](BF_4)_2$ (L = $Bn_2Medptn$ (**1**), BnMedptn (**2**), and BnMedptn-d_7 (**3**)), were prepared from $[Pd(CH_3CN)_4](BF_4)_2$ (Aldrich, 91%) in acetonitrile. The cyclopalladated complex of **1**, $[Pd(Bn_2Medptn\text{-}C,N,N',N'')]CF_3SO_3$ (**4**), was prepared by treating $[PdCl(Bn_2Medptn)]Cl\cdot 2H_2O$ [5] with $AgCF_3SO_3$ in water. The structures of the complexes were characterized by the ^1H NMR spectra and the elemental analysis.[6]

The ^1H NMR measurements for **1** in several solvents confirmed that cyclopalladation does not proceed in acetonitrile but it does in *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and pyridine to give the same spectrum as **4**. The reaction rates are substantially different in the order: pyridine >> DMSO > DMF. The flame-sealed samples in which water was completely removed were ued for the spectrophotometric kinetic measurements; otherwise the isosbestic points were not observed in the spectral change probably due to side reactions. The reaction in pyridine was completed within 30 s. The observed first-order rate constants are independent of the concentration ($2.71–10.3\times10^{-4}$ mol kg^{-1}) of **1** in DMF, and the spectra after the termination of the reaction in DMF, DMSO, and pyridine are identical with those of the cyclopalladated complex (**4**) in the respective solvents. The findings indicate that the counter anion has no participation in the reaction mechanism and that the cyclopalladation proceeds quantitatively under the present experimental conditions. The temperature dependence of the first-order rate constants was fitted the Eyring equation to give the activation parameters for the cyclopalladation of **1** in DMF and DMSO (Table 1). If the cyclopalladation proceeds via the three-coordinate 14-electron intermediate and the solvents in the bulk have no participation in the reaction mechanism, the overall activation parameters should be affected by the pre-equilibrium of the dissociation of the coordinated solvent,[7] where the more basic or stronger donor solvent results in the larger activation enthalpy and slower rate. Accordingly, the difference in rate: pyridine >> DMSO > DMF >> acetonitrile (no reaction) which is inconsistent with the above mechanism, strongly suggests that the nucleophilic interaction of the basic solvent with the ortho proton accompanied by the electrophilic attack of the palladium(II) center toward the ortho carbon is included in the activation process.



	R_1	R_2	S
1	$CH_2C_6H_5$	$CH_2C_6H_5$	CH_3CN
2	$CH_2C_6H_5$	H	CH_3CN
3	$CD_2C_6D_5$	H	CH_3CN

4

Since it is considered that the ortho C–H bond cleavage plays a significant role in the activation process for cyclopalladation judging from the quite large values of $\Delta H^{\ddagger}$ for **1**, the kinetic measurements for **2** and **3** in DMF at various temperatures were performed to confirm the magnitude of the kinetic isotope effect (k_H/k_D). As shown in Table 1, the extremely large kinetic isotope effect of 10.3 at 25 °C which comes from the large difference in the activation enthalpy (11.6 kJ mol^{-1}), is consistent with the lower zero-point energy of the C–D bond compared with the C–H bond.[8] Consequently, the energy for the C–H bond cleavage on

Table 1. Activation parameters and rate constants at 25 ℃ for cyclopalladation of Pd(II) complexes in DMF and DMSO

complex	solvent	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	k^{298}/s^{-1}
1	DMF	104.0±1.2	3.5±3.9	5.74×10^{-6}
1	DMSO	83.8±2.6	-31.0±8.8	3.13×10^{-4}
2	DMF	81.2±0.5	-47.0±1.8	1.30×10^{-4}
3	DMF	92.8±1.4	-27.5±4.4	1.26×10^{-5}

the ortho carbon of the benzyl group is mainly reflected in the activation energy, while the proton attracting effect of the basic solvent also makes a contribution to such an activation as described above.

In conclusion, the electrophilic attack of the palladium(II) center toward the ortho carbon in the benzyl group directed to the palladium(II) center is essential to the activation of the ortho C–H bond, and further, the nucleophilic interaction of the basic solvent with the ortho proton concertedly makes a contribution to the cleavage of the ortho C–H bond which degree depends on the basicity of the solvent.

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References and Notes

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5 This complex was prepared from $K_2[PdCl_4]$ and $Bn_2Medptn$ in a water-acetonitrile mixture.

6 **1**: ^{1}H NMR (CD_3NO_2): δ 2.0-3.2 (m, $(CH_2)_3$), 2.3 (s, CH_3CN), 3.1 (s, NCH_3), 4.0 and 4.3 (m, CH_2Ph), 4.7 (s, br, NH), 7.5-7.6 (m, Ph). Anal. Found: C, 41.82; H, 5.18; N, 8.71%. Calcd for $PdF_8N_4C_{23}B_2H_{34}$: C, 42.73; H, 5.30; N, 8.67%. **2**: ^{1}H NMR (CD_3NO_2): δ 2.0-3.4 (m, $(CH_2)_3$), 2.3 (s, CH_3CN), 2.9 (s, NCH_3), 3.8 and 4.4 (m, CH_2Ph), 3.8 and 4.8 (s, br, NH and NH_2), 7.5-7.8 (m, Ph). Anal. Found: C, 34.82; H, 5.17; N, 9.68%. Calcd for $PdF_8N_4C_{16}B_2H_{28}$: C, 34.54; H, 5.07; N, 10.07%. **3**: ^{1}H NMR (CD_3NO_2): δ 2.0-3.4 (m, $(CH_2)_3$), 2.3 (s, CH_3CN), 2.9 (s, NCH_3), 3.8 and 4.8 (s, br, NH and NH_2). **4**: ^{1}H NMR (DMF-d_7): δ 1.6-3.1 (m, $(CH_2)_3$), 2.9 (s, NCH_3), 4.1 (m, CH_2Ph (pendant)), 4.5 (m, CH_2Ph (bound)), 5.4 and 6.1 (NH), 7.0-7.7 (m, Ph). Anal. Found: C, 45.97; H, 5.33; N, 7.21%. Calcd for $PdSF_3O_3N_3C_{22}H_{30}$: C, 45.56; H, 5.21; N, 7.25%.

7 It was confirmed by the ^{1}H NMR measurements that the substitution of the coordinated acetonitrile in **1** by the solvent in the bulk is rapid enough to complete the reaction during the preparation of the sample.

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