Electronic Effect of Substituents on Cyclopalladation of the Solvated Palladium(II) Complexes with *N*-Benzyl Triamine [Pd(Sol){(4-$XC_6H_4CH_2$)$NH(CH_2)_3NR(CH_2)_3NH_2$}]$^{2+}$ (Sol = Solvent; R = Ph, H, and Me; X = H, Et, Me, MeO, Cl, and NO_2)

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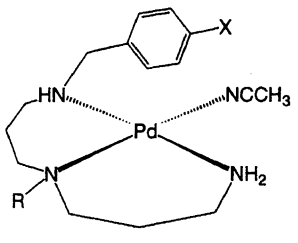
The solvated palladium(II) complexes with the potentially cyclopalladating monobenzyl triamine ligand, [Pd(CH_3CN)(BnPhdptn)]$(BF_4)_2$ (**1**) (BnPhdptn=*N*-(3-aminopropyl)-*N'*-benzyl-*N*-phenyl-1,3-propanediamine), [Pd(CH_3CN)(Bndptn)]$(BF_4)_2$(**2**) (Bndptn = *N*-(3-aminopropyl)-*N'*-benzyl-1,3-propanediamine), [Pd(CH_3CN)(4-$XC_6H_4CH_2$dptn)]$(BF_4)_2$ (4-$XC_6H_4CH_2$dptn = *N*-(3-aminopropyl)-*N'*-(4-substituted benzyl)-1,3-propanediamine; X = Me (**3**), MeO (**4**), Cl (**5**), and NO_2 (**6**)), and [Pd(CH_3CN)(4-$XC_6H_4CH_2$Medptn)]$(BF_4)_2$ (4-$XC_6H_4CH_2$Medptn = *N*-(3-aminopropyl)-*N'*-(4-substituted benzyl)-*N*-methyl-1,3-propanediamine; X = Et (**8**), Me (**9**), MeO (**10**), Cl (**11**), and NO_2 (**12**)) have been synthesized. The kinetics for the cyclopalladation of **1**—**6**, [Pd(CH_3CN)(BnMedptn)]$(BF_4)_2$ (**7**) (BnMedptn = *N*-(3-aminopropyl)-*N'*-benzyl-*N*-methyl-1,3-propanediamine), **8**—**12** in *N*,*N*-dimethylformamide (DMF), and **7**, **9**, **11**, and **12** at 25 °C in dimethyl sulfoxide (DMSO) have been investigated. The Hammett ρ values for the rate constants at 25 °C obtained by variation of the 4-substituent on the benzyl group were −0.73 for **2**—**6** and −0.87 for **7**—**12** in DMF, and −0.67 for **7**, **9**, **11**, and **12** in DMSO using the substituent constants for the *meta* position, σ_m. The difference in the rate constants for **1**, **2**, and **7** at 25 °C in DMF and the negative ρ values confirmed that the present cyclopalladation proceeds by the electrophilic attack of the palladium(II) center on the *ortho* benzyl carbon. We have also discussed the electronic effects of the solvent and the *N*-substituent of the bound triamine on the ρ values to arrive at a conclusion for the reaction mechanism of [Pd(solvent)(*N*-benzyltriamine)]-type complexes.

A great number of synthetic and stereochemical studies of cyclopalladation have been reported.[1—3] Though understanding the reaction mechanism of the cyclopalladation can aid these studies, to date there have been only a few kinetic studies,[4—9] where the reaction mechanism via the three-coordinate 14-electron intermediate has been proposed.[2—4] On the contrary, we have proved that the cyclopalladation proceeds without pre-dissociation of the coordinated solvent for the solvated palladium(II) complexes with terdentate *N*-benzyl triamine ligands in *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).[9] Furthermore, the results of the solvent effect, kinetic isotope effect, and steric effect on the cyclopalladation have indicated that the cyclopalladation proceeds via a concerted mechanism involving the *ortho* C–H bond cleavage promoted by the electrophilic attack of the palladium(II) center on the *ortho* benzyl carbon and the nucleophilic attack of the basic solvent in the bulk on the *ortho* proton. However, the contribution of the electrophilic reaction to the cyclopalladation has not yet been clarified in detail. In order to complete our mechanistic study of cyclopalladation, we have carried out a kinetic study for elucidation of the electronic effect by changing the electron density on the palladium(II) center and the benzene ring.

In the present work, we have synthesized the solvated palladium(II) complexes with monobenzyl triamine ligands having different substituents at the central amine and benzene ring (Chart 1). The kinetics of the cyclopalladation of these complexes in DMF and DMSO have been investigated. The electronic effect on the electrophilic reaction of



	R	X
1	Ph	H
2	H	H
3	H	Me
4	H	OMe
5	H	Cl
6	H	NO_2
7	Me	H
8	Me	Et
9	Me	Me
10	Me	OMe
11	Me	Cl
12	Me	NO_2

Chart 1.

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the palladium(II) center in the cyclopalladation is discussed on the basis of the kinetic parameters and Hammett's ρ values for the rate constants. We have arrived at a conclusion for the reaction mechanism of the cyclopalladation from our previous and present investigations.

Experimental

Materials. DMF and DMSO were dried over activated 4A molecular sieves and then purified by distillation under reduced pressure. *N*,*N*-Bis(3-aminopropyl)aniline (Phdptn) was prepared as the starting material for the preparation of *N*-(3-aminopropyl)-*N*′-benzyl-*N*-phenyl-1,3-propanediamine (BnPhdptn) by the hydrogenation reaction of *N*,*N*-bis(2-cyanoethyl)aniline[10] with BH_3·tetrahydrofuran complex according to the procedure reported by D. Chen et al.[11] *N*-(3-Aminopropyl)-*N*′-(4-substituted benzyl)-*N*-methyl-1,3-propanediamine (4-$XC_6H_4CH_2$Medptn; X=Et, MeO, NO_2) and *N*-(3-aminopropyl)-*N*′-(4-substituted benzyl)-1,3-propanediamine (4-$XC_6H_4CH_2$dptn, X=Me, MeO, Cl, and NO_2) were prepared by a procedure similar to that for *N*-(3-aminopropyl)-*N*′-benzyl-1,3-propanediamine (Bndptn) as described below using the corresponding 4-substituted benzaldehyde and bis(3-aminopropyl)-methylamine or bis(3-aminopropyl)amine, respectively. The other two 4-$XC_6H_4CH_2$Medptn (X=Me and Cl) were prepared by a procedure similar to that previously described for *N*-(3-aminopropyl)-*N*′-benzyl-*N*-methyl-1,3-propanediamine (BnMedptn).[9] The other chemicals were the highest grade commercially available.

Preparation of Ligands. *N*-(3-Aminopropyl)-*N*′-benzyl-*N*-phenyl-1,3-propanediamine (BnPhdptn). A solution containing Phdptn (3.40 g, 16.4 mmol) and benzaldehyde (1.72 g, 16.2 mmol) in ethanol (100 cm^3) was stirred for 15 h at room temperature. The solution to which $NaBH_4$ (1.35 g, 35.7 mmol) was added drop by drop was stirred for 9 h at room temperature and then acidified with concd HCl. The solvent was removed under reduced pressure using a rotary evaporator, and the residue was dissolved in water. After the solution was alkalified with aqueous NaOH, the free amine was extracted into a $CHCl_3$ phase. The $CHCl_3$ solution was concentrated and then chromatographed on an SiO_2 column by elution with a $CHCl_3$/methanol/concd aqueous NH_3 (10 : 4 : 1) solution. A fraction of the eluate was checked by thin-layer chromatography. The appropriate fractions were combined and the solvent was evaporated. The oily residue was dissolved in $CHCl_3$ and washed with aqueous NaOH. The $CHCl_3$ solution was dried over anhydrous Na_2SO_4 for 1 d, followed by filtration. The yellow oily product of BnPhdptn was obtained from the filtrate by removing the solvent by evaporation. Yield: 28.5%. ^{1}H NMR ($CDCl_3$) δ = 1.2 (s, 3H, NH and NH_2), 1.7 (quin, 2H, J = 7.2 Hz, $CH_2CH_2CH_2NBn$), 1.7 (quin, 2H, J = 7.2 Hz, $CH_2CH_2CH_2NH_2$), 2.6 (t, 2H, J = 7.0 Hz, CH_2NH_2), 2.7 (t, 2H, J = 7.0 Hz, CH_2NBn), 3.3 (m, 4H, CH_2NPh), 3.7 (s, 2H, CH_2Ph), 6.6—6.7 (m, 3H, NPh), 7.2—7.3 (m, 7H, NPh and CH_2Ph).

Bndptn. An ethanol solution (200 cm^3) containing bis(3-aminopropyl)amine (26.3 g, 0.200 mol) and benzaldehyde (10.9 g, 0.103 mol) was stirred for 14 h at room temperature. The solution to which $NaBH_4$ (7.95 g, 0.210 mol) was added drop by drop was stirred for 9 h at room temperature and then acidified with concd HCl. The solvent was removed under reduced pressure with a rotary evaporator, and the residue was dissolved in water. The colorless oily product of Bndptn was obtained from the resultant solution by a procedure similar to that previously described for BnPhdptn. Yield: 47.8%. ^{1}H NMR ($CDCl_3$) δ = 1.1 (s, 4H, NH and NH_2), 1.6 (quin, 2H, J = 7.0 Hz, $CH_2CH_2CH_2NBn$), 1.7 (quin, 2H, J = 7.0 Hz, $CH_2CH_2CH_2NH_2$), 2.6 (m, 4H, CH_2NH), 2.7 (t, 2H, J = 7.0 Hz, CH_2NH_2), 2.7 (t, 2H, J = 7.0 Hz, CH_2NBn), 3.8 (s, 2H, CH_2Ph), 7.2—7.3 (m, 5H, Ph).

4-$MeC_6H_4CH_2$dptn. Yield 70.6%. ^{1}H NMR ($CDCl_3$) δ = 1.2 (s, 4H, NH and NH_2), 1.6 (quin, 2H, J = 6.9 Hz, $CH_2CH_2CH_2NCH_2$), 1.7 (quin, 2H, J = 6.9 Hz, $CH_2CH_2CH_2NH_2$), 2.3 (s, 3H, CH_3), 2.6 (m, 4H, CH_2NH), 2.7 (t, 2H, J = 6.7 Hz, CH_2NH_2), 2.7 (t, 2H, J = 6.7 Hz, $CH_2NCH_2C_6H_4$), 3.7 (s, 2H, $CH_2C_6H_4$), 7.1 (d, 2H, J = 7.6 Hz, C_6H_4), 7.2 (d, 2H, J = 7.6 Hz, C_6H_4).

4-$MeOC_6H_4CH_2$dptn. Yield 67.1%. ^{1}H NMR ($CDCl_3$) δ = 1.2 (s, 4H, NH and NH_2), 1.6 (quin, 2H, J = 7.0 Hz, $CH_2CH_2CH_2NCH_2$), 1.7 (quin, 2H, J = 7.0 Hz, $CH_2CH_2CH_2NH_2$), 2.6 (m, 4H, CH_2NH), 2.7 (t, 2H, J = 6.8 Hz, CH_2NH_2), 2.7 (t, 2H, J = 7.0 Hz, $CH_2NCH_2C_6H_4$), 3.7 (s, 2H, $CH_2C_6H_4$), 3.7 (s, 3H, OCH_3), 6.8 (d, 2H, J = 8.5 Hz, C_6H_4), 7.2 (d, 2H, J = 8.5 Hz, C_6H_4).

4-$ClC_6H_4CH_2$dptn. Yield 67.8%. ^{1}H NMR ($CDCl_3$) δ = 1.2 (s, 4H, NH and NH_2), 1.6 (quin, 2H, J = 7.0 Hz, $CH_2CH_2CH_2NCH_2$), 1.7 (quin, 2H, J = 6.8 Hz, $CH_2CH_2CH_2NH_2$), 2.6 (m, 6H, CH_2NH and CH_2NH_2), 2.7 (t, 2H, J = 6.8 Hz, $CH_2NCH_2C_6H_4$), 3.7 (s, 2H, $CH_2C_6H_4$), 7.2 (m, 4H, C_6H_4).

4-$NO_2C_6H_4CH_2$dptn. Yield 29.0%. ^{1}H NMR ($CDCl_3$) δ = 1.6 (quin, 2H, J = 7.0 Hz, $CH_2CH_2CH_2NCH_2$), 1.7 (quin, 2H, J = 6.8 Hz, $CH_2CH_2CH_2NH_2$), 1.9 (s, 4H, NH and NH_2), 2.7 (m, 6H, CH_2NH and CH_2NH_2), 2.7 (t, 2H, J = 7.0 Hz, $CH_2NCH_2C_6H_4$), 3.9 (s, 2H, $CH_2C_6H_4$), 7.5 (d, 2H, J = 8.5 Hz, C_6H_4), 8.1 (d, 2H, J = 8.5 Hz, C_6H_4).

4-$EtC_6H_4CH_2$Medptn. Yield 38.2%. ^{1}H NMR ($CDCl_3$) δ = 1.2 (t, 3H, J = 7.6 Hz, CH_2CH_3), 1.3 (s, 3H, NH and NH_2), 1.6 (quin, 2H, J = 7.2 Hz, $CH_2CH_2CH_2NCH_2$), 1.7 (quin, 2H, J = 7.2 Hz, $CH_2CH_2CH_2NH_2$), 2.2 (s, 3H, NCH_3), 2.4 (m, 4H, CH_2NCH_3), 2.6 (q, 2H, J = 7.6 Hz, CH_2CH_3), 2.7 (t, 2H, J = 6.9 Hz, CH_2NH_2), 2.7 (t, 2H, J = 6.9 Hz, $CH_2NCH_2C_6H_4$), 3.7 (s, 2H, $CH_2C_6H_4$), 7.1 (d, 2H, J = 7.9 Hz, C_6H_4), 7.2 (d, 2H, J = 7.9 Hz, C_6H_4).

4-$MeC_6H_4CH_2$Medptn. Yield 34.5%. ^{1}H NMR ($CDCl_3$) δ = 1.3 (s, 3H, NH and NH_2), 1.6 (quin, 2H, J = 7.0 Hz, $CH_2CH_2CH_2NCH_2$), 1.7 (quin, 2H, J = 7.0 Hz, $CH_2CH_2CH_2NH_2$), 2.2 (s, 3H, NCH_3), 2.3 (s, 3H, $CH_3C_6H_4$), 2.4 (m, 4H, CH_2NCH_3), 2.6 (t, 2H, J = 7.0 Hz, CH_2NH_2), 2.7 (t, 2H, J = 7.0 Hz, $CH_2NCH_2C_6H_4$), 3.7 (s, 2H, $CH_2C_6H_4$), 7.1 (d, 2H, J = 7.9 Hz, C_6H_4), 7.2 (d, 2H, J = 7.9 Hz, C_6H_4).

4-$MeOC_6H_4CH_2$Medptn. Yield 50.9%. ^{1}H NMR ($CDCl_3$) δ = 1.4 (s, 3H, NH and NH_2), 1.6 (quin, 2H, J = 7.1 Hz, $CH_2CH_2CH_2NCH_2$), 1.7 (quin, 2H, J = 7.0 Hz, $CH_2CH_2CH_2NH_2$), 2.2 (s, 3H, NCH_3), 2.4 (m, 4H, CH_2NCH_3), 2.6 (t, 2H, J = 7.0 Hz, CH_2NH_2), 2.7 (t, 2H, J = 6.9 Hz, $CH_2NCH_2C_6H_4$), 3.7 (s, 2H, $CH_2C_6H_4$), 3.8 (s, 3H, OCH_3), 6.9 (d, 2H, J = 8.7 Hz, C_6H_4), 7.2 (d, 2H, J = 8.7 Hz, C_6H_4).

4-$ClC_6H_4CH_2$Medptn. Yield 40.1%. ^{1}H NMR ($CDCl_3$) δ = 1.3 (s, 3H, NH and NH_2), 1.6 (quin, 2H, J = 7.2 Hz, $CH_2CH_2CH_2NCH_2$), 1.7 (quin, 2H, J = 7.0 Hz, $CH_2CH_2CH_2NH_2$), 2.2 (s, 3H, NCH_3), 2.4 (m, 4H, CH_2NCH_3), 2.6 (t, 2H, J = 7.0 Hz, CH_2NH_2), 2.7 (t, 2H, J = 7.0 Hz, $CH_2NCH_2C_6H_4$), 3.7 (s, 2H, $CH_2C_6H_4$), 7.2—7.3 (m, 4H, C_6H_4).

4-$NO_2C_6H_4CH_2$Medptn. Yield 37.1%. ^{1}H NMR ($CDCl_3$) δ = 1.4 (s, 3H, NH and NH_2), 1.6 (quin, 2H, J = 7.2 Hz, $CH_2CH_2CH_2NCH_2$), 1.7 (quin, 2H, J = 6.9 Hz, $CH_2CH_2CH_2NH_2$), 2.2 (s, 3H, NCH_3), 2.4 (m, 4H, CH_2NCH_3), 2.7 (t, 2H, J = 6.7 Hz, CH_2NH_2), 2.7 (t, 2H, J = 6.9 Hz, $CH_2NCH_2C_6H_4$), 3.9 (s, 2H, $CH_2C_6H_4$), 7.5 (d, 2H, J = 8.7 Hz, C_6H_4), 8.1 (d, 2H, J = 8.7 Hz, C_6H_4).

Preparation of Complexes. The palladium(II) complexes

with acetonitrile and terdentate *N*-benzyl triamine ligand were prepared by a procedure similar to that previously reported for **7**[9] using tetrakis(acetonitrile)palladium(II) tetrafluoroborate with the corresponding triamine ligand.

[Pd(CH$_3$CN)(BnPhdptn)](BF$_4$)$_2$ (1). Yield 18.0%. Anal. Found: C, 41.07; H, 5.02; N, 8.66%. Calcd for $C_{21}H_{30}B_2F_8N_4Pd$: C, 40.78; H, 4.89; N, 9.06%. ^{1}H NMR (CD_3NO_2) δ = 2.0—3.6 (m, $(CH_2)_3$), 2.4 (s, CH_3CN), 3.8 and 4.2 (m, CH_2Ph), 4.0 and 4.8 (s(br), NH and NH_2), 7.4—7.8 (m, Ph). ^{13}C NMR (CD_3NO_2) δ = 3.6 (q, J = 138 Hz, CH_3CN) at room temperature and 3.9 (q, J = 139 Hz, CH_3CN) at −30 °C.

[Pd(CH$_3$CN)(Bndptn)](BF$_4$)$_2$ (2). Yield 30.1%. Anal. Found: C, 32.88; H, 4.69; N, 9.97%. Calcd for $C_{15}H_{26}B_2F_8N_4Pd$: C, 33.21; H, 4.83; N, 10.33%. ^{1}H NMR (CD_3NO_2) δ = 1.9—3.1 (m, $(CH_2)_3$), 2.2 (s, CH_3CN), 3.7 and 4.3 (m, CH_2Ph), 3.6 and 4.8 (s(br), NH and NH_2), 7.5—7.8 (m, Ph). ^{13}C NMR (CD_3NO_2) δ = 3.1 (q, J = 139 Hz, CH_3CN) at room temperature and 3.3 (q, J = 139 Hz, CH_3CN) at −30 °C.

[Pd(CH$_3$CN)(4-MeC$_6$H$_4$CH$_2$dptn)](BF$_4$)$_2$ (3). Yield 15.4%. Anal. Found: C, 34.03; H, 5.37; N, 9.82%. Calcd for $C_{16}H_{28}B_2F_8N_4Pd$: C, 34.54; H, 5.07; N, 10.07%. ^{1}H NMR (CD_3NO_2) δ = 1.9—3.1 (m, $(CH_2)_3$), 2.2 (s, CH_3CN), 2.4 (s, $C_6H_4CH_3$), 3.7 and 4.2 (m, $CH_2C_6H_4$), 3.6 and 4.8 (s(br), NH and NH_2), 7.4 and 7.7 (d, J = 8.1 Hz, C_6H_4).

[Pd(CH$_3$CN)(4-MeOC$_6$H$_4$CH$_2$dptn)](BF$_4$)$_2$ (4). Yield 32.3%. Anal. Found: C, 33.08; H, 4.85; N, 9.49%. Calcd for $C_{16}H_{28}B_2F_8N_4OPd$: C, 33.57; H, 4.93; N, 9.79%. ^{1}H NMR (CD_3NO_2) δ = 1.9—3.1 (m, $(CH_2)_3$), 2.3 (s, CH_3CN), 3.7 and 4.2 (m, $CH_2C_6H_4$), 3.6 and 4.8 (s(br), NH and NH_2), 3.9 (s, OCH_3), 7.1 and 7.7 (d, J = 8.6 Hz, C_6H_4).

[Pd(CH$_3$CN)(4-ClC$_6$H$_4$CH$_2$dptn)](BF$_4$)$_2$ (5). Yield 16.7%. Anal. Found: C, 30.97; H, 4.14; N, 9.48%. Calcd for $C_{15}H_{25}B_2ClF_8N_4Pd$: C, 31.23; H, 4.37; N, 9.71%. ^{1}H NMR (CD_3NO_2) δ = 1.9—3.1 (m, $(CH_2)_3$), 2.3 (s, CH_3CN), 3.7 and 4.2 (m, $CH_2C_6H_4$), 3.6 and 4.8 (s(br), NH and NH_2), 7.6 and 7.8 (d, J = 8.2 Hz, C_6H_4).

[Pd(CH$_3$CN)(4-NO$_2$C$_6$H$_4$CH$_2$dptn)](BF$_4$)$_2$ (6). Yield 25.4%. Anal. Found: C, 29.92; H, 4.07; N, 11.44%. Calcd for $C_{15}H_{25}B_2F_8N_5O_2Pd$: C, 30.67; H, 4.29; N, 11.92%. ^{1}H NMR (CD_3NO_2) δ = 1.9—3.1 (m, $(CH_2)_3$), 2.3 (s, CH_3CN), 3.9 and 4.4 (m, $CH_2C_6H_4$), 3.6 and 5.0 (s(br), NH and NH_2), 8.1 and 8.4 (d, J = 8.5 Hz, C_6H_4).

[Pd(CH$_3$CN)(BnMedptn)](BF$_4$)$_2$ (7).[9] ^{13}C NMR (CD_3NO_2) δ = 3.4 (q, J = 139 Hz, CH_3CN) at room temperature and 3.7 (q, J = 139 Hz, CH_3CN) at −30 °C.

[Pd(CH$_3$CN)(4-EtC$_6$H$_4$CH$_2$Medptn)](BF$_4$)$_2$ (8). Yield 31.3%. Anal. Found: C, 36.61; H, 5.23; N, 9.45%. Calcd for $C_{18}H_{32}B_2F_8N_4Pd$: C, 36.99; H, 5.52; N, 9.59%. ^{1}H NMR (CD_3NO_2) δ = 1.3 (t, J = 7.5 Hz, CH_2CH_3), 2.0—3.4 (m, $(CH_2)_3$), 2.3 (s, CH_3CN), 2.7 (q, J = 7.7 Hz, CH_2CH_3), 2.9 (s, NCH_3), 3.8 and 4.4 (m, $CH_2C_6H_4$), 3.4 and 4.7 (s(br), NH and NH_2), 7.4 and 7.7 (d, J = 8.1 Hz, C_6H_4).

[Pd(CH$_3$CN)(4-MeC$_6$H$_4$CH$_2$Medptn)](BF$_4$)$_2$ (9). Yield 28.9%. Anal. Found: C, 35.04; H, 4.82; N, 9.62%. Calcd for $C_{17}H_{30}B_2F_8N_4Pd$: C, 35.79; H, 5.30; N, 9.82%. ^{1}H NMR (CD_3NO_2) δ = 2.0—3.4 (m, $(CH_2)_3$), 2.3 (s, CH_3CN), 2.4 (s, $C_6H_4CH_3$), 2.9 (s, NCH_3), 3.6 and 4.4 (m, $CH_2C_6H_4$), 3.5 and 4.7 (s(br), NH and NH_2), 7.4 and 7.6 (d, J = 7.9 Hz, C_6H_4).

[Pd(CH$_3$CN)(4-MeOC$_6$H$_4$CH$_2$Medptn)](BF$_4$)$_2$ (10). Yield 39.3%. Anal. Found: C, 34.10; H, 4.73; N, 9.42%. Calcd for $C_{17}H_{30}B_2F_8N_4OPd$: C, 34.82; H, 5.16; N, 9.55%. ^{1}H NMR (CD_3NO_2) δ=2.0—3.4 (m, $(CH_2)_3$), 2.3 (s, CH_3CN), 3.0 (s, NCH_3), 3.8 and 4.3 (m, $CH_2C_6H_4$), 3.8 and 4.7 (s(br), NH and NH_2), 3.9 (s, OCH_3), 7.1 and 7.7 (d, J = 8.5 Hz, C_6H_4).

[Pd(CH$_3$CN)(4-ClC$_6$H$_4$CH$_2$Medptn)](BF$_4$)$_2$ (11). Yield 45.4%. Anal. Found: C, 32.04: H, 4.22; N, 9.38%. Calcd for $C_{16}H_{27}B_2ClF_8N_4Pd$: C, 32.52; H, 4.61; N, 9.48%. ^{1}H NMR (CD_3NO_2) δ=2.0—3.4 (m, $(CH_2)_3$), 2.3 (s, CH_3CN), 3.0 (s, NCH_3), 3.8 and 4.4 (m, $CH_2C_6H_4$), 3.8 and 4.8 (s(br), NH and NH_2), 7.6—7.8 (m, C_6H_4).

[Pd(CH$_3$CN)(4-NO$_2$C$_6$H$_4$CH$_2$Medptn)](BF$_4$)$_2$ (12). Yield 15.3%. Anal. Found: C, 31.69; H, 4.26; N, 11.38%. Calcd for $C_{16}H_{27}B_2F_8N_5O_2Pd$: C, 31.95; H, 4.53; N, 11.64%. ^{1}H NMR (CD_3NO_2) δ=2.0—3.4 (m, $(CH_2)_3$), 2.3 (s, CH_3CN), 3.0 (s, NCH_3), 4.0 and 4.5 (m, $CH_2C_6H_4$), 4.0 and 4.9 (s(br), NH and NH_2), 7.9—8.0 (m, C_6H_4), 8.4 (d, J = 8.8 Hz, C_6H_4).

Sample Preparations and Measurements. Sample preparations for NMR measurements were carried out in a glovebox. ^{1}H and ^{13}C NMR measurements were preformed on a Bruker AMX-400WB NMR spectrometer operating at 400.13 and 100.62 MHz, respectively.

The samples for the kinetic measurements of the cyclopalladation of each complex in DMF and DMSO were prepared on a vacuum line by distilling the purified solvent on the complex in twice-fused quartz cuvettes that were then flame-sealed. The kinetic measurements at various temperatures were performed with a Shimadzu UV-265FW spectrophotometer. The temperature of the reaction solution was held constant within ±0.1 K. The reactions were followed by a change in absorbance at 296 nm for **1**, at 283 nm for **2**, at 281 nm for **3**, at 288 nm for **4**, at 283 nm for **5**, at 301 nm for **6**, at 281 nm for **8**, at 282 nm for **9**, at 289 nm for **10**, at 284 nm for **11**, and at 340 nm for **12** in DMF, and at 283 nm for **9**, at 285 nm for **11**, and at 306 nm for **12** in DMSO. The rate constants were determined by a least-squares analysis using the data up to several half-lives.

Results and Discussion

Characterization and Kinetics. The results of the elemental analyses for the present solvated *N*-benzyl triamine complexes are in acceptable agreement with the proposed formulations (see Experimental). Each ^{1}H NMR peak assignment is consistent with that for the *N*-benzyl triamine complexes previously described.[9] The absorption spectra of the present complexes in DMF and DMSO change with isosbestic points. The change in absorbance as a function of the reaction time fits well to the exponential curve for at least several half-lives. The observed first-order rate constants are essentially the same as those obtained by the ^{1}H NMR spectral changes, which correspond to the cyclopalladation reaction.[9,12] The rate constants, obtained under the conditions of various concentrations of the palladium(II) complexes with the counter ions (BF_4^-), are independent of the concentrations. Therefore, we can judge that the present cyclopalladation proceeds quantitatively without the influence of the counter anion. The temperature dependence of the rate constants for each complex in DMF was fitted well to the Eyring equation to give the values of activation enthalpy ($\Delta H^\ddagger$) and activation entropy ($\Delta S^\ddagger$). The activation parameters and the calculated rate constants at 25 °C in DMF are summarized in Table 1, together with the observed rate constants at 25 °C in DMSO.

Table 1. Activation Parameters and Rate Constants at 25 °C for Cyclopalladation of Palladium(II) Complexes in DMF and DMSO

Complex	Solvent	Temperature range/K	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$10^6\ k^{298}$/s^{-1}
1	DMF	299.1—312.6	82.3±1.0	−36.3±3.2	303
2	DMF	308.7—332.0	97.5±1.4	−15.3±4.5	8.24
3	DMF	307.3—327.2	93.8±1.7	−25.9±5.5	10.2
4	DMF	307.5—327.5	97.1±2.7	−19.1±8.4	6.09
5	DMF	308.6—328.9	97.2±2.0	−21.3±6.2	4.49
6	DMF	309.3—333.7	100.1±2.3	−15.1±7.2	2.94
7[a)]	DMF	298.8—317.9	81.2±0.5	−47.0±1.8	130
8	DMF	299.2—319.5	88.0±2.4	−22.6±7.7	157
9	DMF	300.7—316.2	84.8±1.6	−34.1±5.3	143
10	DMF	300.2—319.9	89.3±2.0	−23.1±6.5	87.5
11	DMF	300.0—326.5	89.5±0.8	−25.7±2.5	59.1
12	DMF	303.2—323.8	94.8±1.5	−13.2±4.7	31.3
7[a)]	DMSO				1760
9	DMSO				1700
11	DMSO				1050
12	DMSO				523

a) Ref. 9.

Effect of *N*-Substituent Groups. The only difference in the structure of the palladium(II) complexes, **1**, **2**, and **7**, is the substituent group on the central amine nitrogen of the triamine ligand, i.e., Ph, H, and Me, respectively. This position is expected to be the most suitable for estimating the electronic effect on the palladium(II) atom, because the central amine is in the *trans* position to the substitutional site. Consequently, the substituent group on the central amine nitrogen has less steric influence than that on the terminal amine nitrogen, whose steric effect has been previously described.[9)] The order of the upfield shift of the methyl carbon of the bound acetonitrile molecule in the palladium(II) complexes, **1** (δ = 3.9 ppm at −30 °C) < **7** (δ = 3.7) < **2** (δ = 3.3), indicates that the electron density on the palladium(II) center increases in that order. The rate constants of these complexes for cyclopalladation in DMF at 25 °C (see Table 1) increase in the reverse order, **2** < **7** < **1**. This reactivity is consistent with the mechanism in which the cyclopalladation proceeds via the electrophilic attack of the palladium(II) center on the *ortho* carbon of the benzyl group.

The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, however, change in a different order: **7** < **1** < **2**. This order of the values of the activation parameters is maintained for the corresponding 4-substituted *N*-benzyl triamine complexes, **3**—**6** and **9**—**12**, respectively. Considering only the electronic effect, we assumed that the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ decrease in the same order as the electron density on the palladium(II) center because the electron-poor palladium(II) center favors the electrophilic Pd–C bond making in the transition state. The discrepancy in the order of the activation parameters can be explained by the steric effect of the *N*-phenyl group in **1**. The stable chair conformation for the six-membered chelate rings of the triamine ligand causes the phenyl ring to be axially oriented above the palladium(II) atom as observed for the *N*-methyl group in the crystal structure of [Pd(CH$_3$CN)(Bn$_2$Medptn)](BF$_4$)$_2$.[9)] Therefore, the relatively great steric hindrance of the *N*-phenyl group may block the Pd–C bond making and/or the attack of the proton-attracting solvent molecule in the bulk on the *ortho* proton in the transition state. Furthermore, it is possible that the interaction of the palladium(II) center with the *ortho* carbon on the side opposite to the phenyl group accompanied by the conformation change of the six-membered chelate ring is required in order to avoid the steric hindrance. These steric effects give more positive $\Delta H^{\ddagger}$ and less negative $\Delta S^{\ddagger}$ values than those expected from only the electronic effect. In addition, the vacant nonbonding p_z orbital of the palladium(II) center perpendicular to the square plane of the complex probably initially interacts with the *ortho* carbon, as proposed for the square-planar d^8 complexes.[13)] The electron density of such an outer p orbital is not much affected by the electron donation into the d orbitals of the palladium(II) center. Accordingly, the steric effect of the bulky *N*-substituent may predominate over the electronic effect.

Electronic Effect of 4-Substituent. Figure 1 shows the change in the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of the cyclopalladation in DMF for 4-XC$_6$H$_4$CH$_2$dptn and 4-XC$_6$H$_4$CH$_2$Medptn complexes (**2**—**6** (a) and **7**—**12** (b)), respectively; each plot displays relatively good correlation between the activation parameters. Such an isokinetic relationship indicates that the cyclopalladation proceeds via a similar reaction mechanism in which the activated state changes with the variation of the 4-substituent on the benzyl group. Considering that the 4-substituents are remote enough from the reaction site, the change in the steric factor of the 4-substituents is negligible. Thus, we can regard the electronic effect as the main factor which changes the reactivity of the cyclopalladating complexes. Consequently, it is meaningful to apply Hammett's rule to the rate constants of the cyclopalladation.

Hammett's equation is expressed by Eq. 1 using the reaction constant (ρ) and the substituent constant for the *meta* position (σ_m):

$$\log k^{298} = \rho\sigma_m + \log k_0 \quad (1)$$

where k^{298} is the rate constant at 25 °C for the 4-

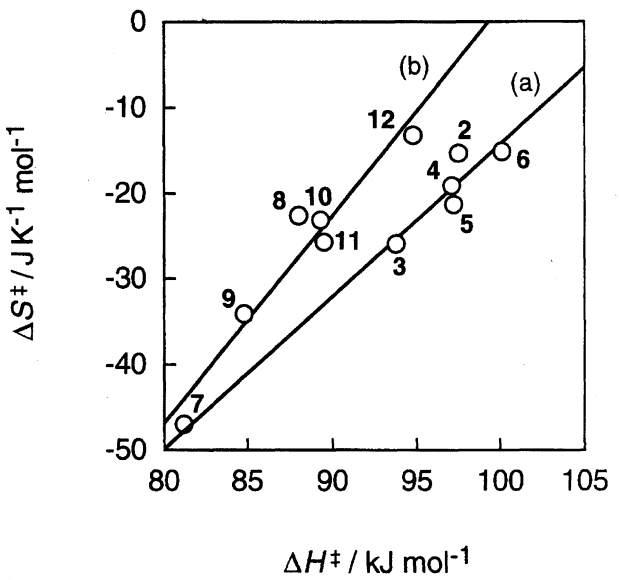


Fig. 1. Correlation between the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for cyclopalladation of **2**—**6** (a) and **7**—**12** (b) in DMF.

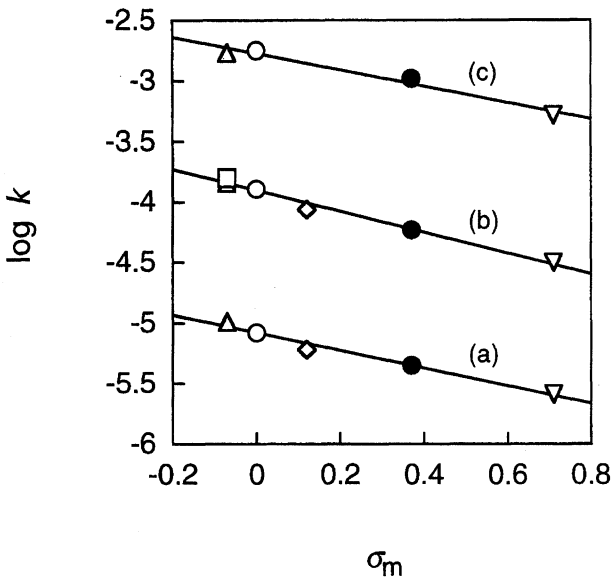
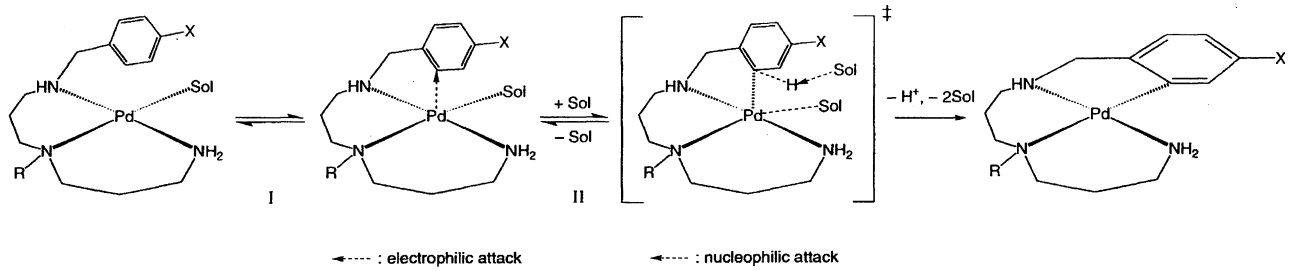


Fig. 2. Hammett's plot of log k versus σ_m for **2**—**6** in DMF (a), **7**—**12** in DMF (b), and **7**,**9**,**11**, and **12** in DMSO (c). Respective 4-substituents on the benzyl group are denoted as follows: H (○), Et (□), Me (△), MeO (◇), Cl (●), and NO_2 (▽).

$XC_6H_4CH_2$dptn and 4-$XC_6H_4CH_2$Medptn complexes with the 4-substituted benzyl group (**3**—**6** and **8**—**12**) and k_0 is that with the non-substituted benzyl group (**2** and **7**), respectively. Good linear relationships of the logarithmic values of the rate constants in DMF and DMSO with the σ_m values were observed, as shown in Fig. 2, while no correlation was found for the substituent constants for the *para* position (σ_p). The ρ values were determined to be -0.73 ± 0.06 for **2**—**6** and -0.87 ± 0.05 for **7**—**12** in DMF and -0.67 ± 0.08 for **7**, **9**, **11**, and **12** in DMSO by least-squares fitting. The negative ρ values obtained from σ_m indicate the electrophilic attack of the palladium(II) center on the *ortho* carbon. Additionally, the electronic effect from the *para* carbon through the bound ligand on the palladium(II) center is negligible in contrast with such an electronic effect on the cyclopalladation of the palladium(II) acetate with *N*,*N*-dimethylbenzylamine in acetic acid mentioned by Ryabov et al.[4]

The difference in the ρ value is attributable to the electronic effects resulting from the *N*-substituent on the amine nitrogen and the basic solvent. The less negative ρ value for **2**—**6** compared with **7**—**12** signifies that the higher electron density on the palladium(II) center causes the weaker substituent effect of the 4-substituent on the benzyl group; it concurrently indicates that, in the case of the palladium(II) center with higher electron density, the contribution of the electrophilic attack to the activation of the *ortho* C–H bond is relatively slight. On the other hand, the ρ value for **7**, **9**, **11**, and **12** in DMSO is less negative than that for **7**—**12** in DMF. Considering that DMSO is more basic than DMF,[14] the *ortho* proton abstraction by DMSO is preferable and shifts the ρ value more positively due to the contribution of the nucleophilic reaction to the *ortho* proton. In addition, the more electron donation of the bound DMSO compared with that of the bound DMF results in higher electron density on the palladium(II) center and gives the less negative ρ value. Though both of the above two electronic factors of the solvent are consistent with the difference in the ρ value in DMF and DMSO, we suggest that the *ortho*-proton abstracting ability of the bulk solvent mainly affects the ρ value because the rate constants in DMSO are more than 10-fold larger than those in DMF for the respective complexes. If the effect of the bound solvent on the electrophilic attack is predominant over the electronic effect of the bulk solvent on the proton-abstraction, an electron-donating solvent such as DMSO rather than DMF would decrease the rate constant be-



Scheme 1. Reaction mechanism for cyclopalladation of the solvated palladium(II) complexes (Sol=basic solvent). Charge on palladium(II) complexes is omitted.

cause of increasing the electron density on the palladium(II) center, which is unfavorable to the electrophilic interaction. These differences in the rate constants show that the basicity for the *ortho* proton abstraction of the basic solvent is the important factor for the kinetics, as previously reported.[9)]

Reaction Mechanism. We have clarified the electronic effect of the substituents on cyclopalladation. The results have confirmed that the electrophilic reaction of the palladium(II) center participates in the cyclopalladation and are consistent with the reaction previously proposed where the nucleophilic attack of the basic solvent in the bulk is essential to the cleavage of the *ortho* C–H bond. Finally, we have concluded from the present and previous kinetic studies[9,15)] that cyclopalladation for the solvated palladium(II) complexes with monobenzyl triamine ligands proceeds by the concerted mechanism described in Scheme 1 without a 14-electron intermediate, where the electrophilic attack of the palladium(II) center on the *ortho* benzyl carbon initiates the cyclopalladation at step I, and at step II the Pd–C bond making with the activation of the C–H bond by the basic solvent and the bond breaking of the bound solvent are concomitant to give the transition state.

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