geometry, only three reasonable structures meet the above requirements. The possibilities include (Figure 6) one 4:3 geometry and two PBP's.[11]

Of the structures shown in Figure 6, the least likely is III (4:3), which requires a large amount of structural reorganization relative to the PBP's (I and II). We prefer structure II because the PPh_3–Os bond need elongate only slightly and protonation would result in expansion of the square plane containing three sterically nondemanding ligands, i.e., the two hydrides and a CO. In isomer I, expansion of the square plane would force the phosphines toward the bpy π cloud, and therefore I is a less satisfactory structure.

Concluding Remarks

Seven-coordination is unusual in the chemistry of Os(IV), as are high-oxidation-state Os polyhydrides. In this work we have described examples where both features are present in the same molecule. In a reactivity sense an important inference that can be drawn from our results is that seven-coordinate intermediates may play an important role in the formation of trifluoromethanesulfonate derivatives of octahedral precursors such as those shown in eq 1 and 2.

A striking contrast in behavior exists between the complexes discussed here and $[Os(bpy)_2(CO)H]^+$, where the reactivity with H^+ involves irreversible loss of H_2, presumably via initial protonation at Os.[12] Considered in that light, the reactions described here provide a conceptual link between electrophilic attack on low-spin d^6 metal centers and oxidative-addition reactions, both of which are uncommon for coordinatively saturated, octahedral precursors.

There is a final point to consider. The dihydrido complexes are thermally stable under ambient conditions so that the equilibrium in eq 7 *must* exist and might be observable if S is, for

$$[Os(bpy)(L)_2(CO)S]^{2+} + H_2 \rightleftharpoons [Os(bpy)(L)_2(CO)H_2]^{2+} + S \quad (7)$$

example, a weakly bound solvent molecule. The importance of reaction 7 is that it could provide a mechanistic basis for the activation of H_2 by d^6 octahedral metal complexes.[13]

Acknowledgment. We wish to acknowledge the Gas Research Institute (Grant No. 5083-260-0827) for support of this work.

Registry No. *mer*-$Os(PPh_3)_3(CO)HCl$, 36007-23-5; *trans*-$[Os(PPh_3)_2(bpy)(CO)H](PF_6)$, 84117-37-3; *trans*-$[Os(PPh_3)_2(4,4'\text{-}Me_2bpy)(CO)H](PF_6)$, 106252-49-7; *trans*-$[Os(PPh_3)_2(5,5'\text{-}Me_2bpy)(CO)H](PF_6)$, 106252-51-1; *trans*-$[Os(PPh_3)_2(bpy\text{-}d_8)(CO)H](PF_6)$, 106252-53-3; *trans*-$[Os(PPh_3)_2(bpy)(CO)H_2]^{2+}$, 106267-39-4; *trans*-$[Os(PPh_3)_2(4,4'\text{-}Me_2bpy)(CO)H_2]^{2+}$, 106252-54-4; *trans*-$[Os(PPh_3)_2(5,5'\text{-}Me_2bpy)(CO)H_2]^{2+}$, 106252-55-5; *trans*-$[Os(PPh_3)_2(bpy\text{-}d_8)(CO)H_2]^{2+}$, 106252-56-6.

(11) We wish to thank a reviewer for a useful discussion of alternate structures.

(12) The electronic and steric features of metal hydrides that influence the base strength of the central metal, or even the hydridic vs. protonic character of the bond, have recently been discussed. See: Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.

(13) Brothers, P. J. *Prog. Inorg. Chem.* **1981**, *28*, 1-57 and references therein.

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Thermodynamics, Kinetics, and Mechanism of Exchange of Cyclopalladated Ligands

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The exchange between cyclopalladated complexes and free ligands has been studied in acetic acid. An equilibrium study of the system based on *N,N*-dimethylbenzylamine derivatives $[PdX(YZC_6H_2CH_2NMe_2)]_2 + 2C_6D_5CD_2NMe_2 \rightleftharpoons [PdX(C_6D_4CD_2NMe_2)]_2 + 2YZC_6H_2DCH_2NMe_2$ (K_1) has revealed that Pd(II) binds preferably with the electron-poorest ligand at equilibrium; K_1 is 114, 0.59, 0.125, 0.008, and 0.0034 for 4-Y (5-Z) = MeO (MeO), H (Me), H (H), H (Cl), and H (NO_2), respectively, at 55 °C in $D_3CCOOD/CDCl_3$, X = $MeCO_2^-$. A procedure for regioselective ortho palladation of "bifunctional" derivatives such as 1-(3,4-dimethoxyphenyl)-2-methyl-3-(4-nitrophenyl)-2-azapropane (**7**) is put forward. In aprotic chloroform, Pd(II) acetate metalates the electron-rich ring of **7** to yield **8a**, but the electron-poor ring is ortho palladated in acetic acid to yield **9a**. A dissociative exchange mechanism is proposed on the basis of a kinetic study of reactions between $[PdX(YZC_6H_2CH_2NMe_2)]_2$ and 2-phenylpyridine or azobenzene to afford the corresponding cyclopalladated complexes. Preequilibrium measurements have indicated that in the former case the reactive species are monomers formed via acetate-bridge cleavage by 2-phenylpyridine but in the latter case the complexes react as dimers. Despite this, all of the reactions are first order in complex and zero order in entering ligand. The rate constants of the 2-phenylpyridine case at 75 °C are (10^4k) 12.6, 3.9, 2.35, 2.6, 0.44, and 0.0225 s^{-1} for 4-Y (5-Z) = MeO (MeO), H (Me), H (H), H (MeO), H (Cl), and H (NO_2), respectively. On the basis of substituent and solvent kinetics isotope effects, values of activation parameters, and data obtained previously, it has been suggested that cleavage of the Pd–N bond of the leaving ligand occurs first, followed by acidolysis of the Pd–C bond. Both steps can contribute to the overall rate. The two are followed by the rapid activation of the C–H bond of the incoming ligand. Reasons for the pseudonucleophilic behavior of Pd(II) toward C–H bonds of benzylamines in acetic acid have been evaluated on the basis of the proposed mechanism.

Introduction

In the course of our study of vinylation of the ortho-palladated *N,N*-dimethylbenzylamine complex $[PdCl(C_6H_4CH_2NMe_2)]_2$ by styrenes, we found ortho-palladated *o*-((dimethylamino)methyl)stilbene derivatives.[1] The latter were formed due to a ligand exchange between the starting palladocycle and *o*-((dimethylamino)methyl)stilbene in the presence of acetic acid as cosolvent. Further efforts[2-7] have shown that ligand exchange may serve as an elegant synthetic procedure for the preparation of novel palladocycles (see Scheme I). In all cases the reactions are triggered by an addition of acetic acid to a solution of complex

(1) Ryabov, A. D.; Polyakov, V. A.; Yatsimirsky, A. K. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1503.
(2) Ryabov, A. D.; Yatsimirsky, A. K. *Inorg. Chem.* **1984**, *23*, 789.
(3) Ryabov, A. D.; Kazankov, G. M. *J. Organomet. Chem.* **1984**, *268*, 85.
(4) Ryabov, A. D. *Koord. Khim.* **1985**, *11*, 1532.
(5) (a) Ryabov, A. D.; Kazankov, G. M. *Koord. Khim.* **1986**, *12*, 540. (b) Ceder, R. M.; Granell, J.; Sales, J. *J. Organomet. Chem.* **1986**, *307*, C44. (c) Granell, J.; Sainz, D.; Sales, J.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1785.
(6) Ryabov, A. D.; Usatov, A. V.; Kalinin, V. N.; Zakharkin, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 2790.
(7) Ryabov, A. D.; Usatov, A. V.; Kalinin, V. N.; Zakharkin, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 1212.

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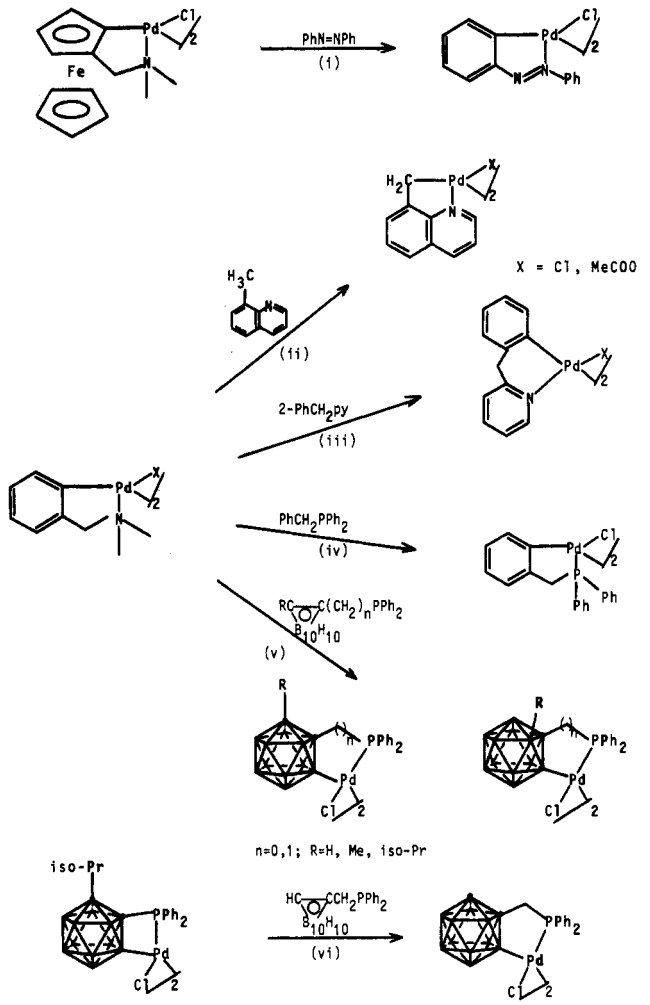
Scheme I



and ligand. The exchange may involve two N-donor ligands (eq i–iii)[2-5] and a leaving N- and an entering P-donor ligand (eq iv and v),[6] as well as two P-donor ligands (eq vi).[7] Pd(II) can cleave not only sp^3 (eq ii) and sp^2 C–H bonds (eq i, iii, and iv) of entering ligands to afford Pd–C bonds but also B–H bonds of carboranes (eq v and vi). Bonds to be cleaved are Pd–C (eq i–v) and Pd–B (eq vi). Chloro (eq i–vi) and acetato-bridged (eq ii and iii)[5] complexes with four- (eq v), five- (eq i, ii, iv, vi), and six-membered (eq iii) palladocycles can be produced. It has been already pointed out,[2,3] and supported by recent works,[4-7] that the ligand exchange is especially advantageous when a chloro-bridged cyclopalladated dimer should be obtained in one step. A simplicity of performing the reaction and isolating products makes the procedure very attractive.

The present work is an attempt to understand the mechanism of the reactions shown in Scheme I. These must involve both a protolytic cleavage of palladium–carbon bonds and a metal-assisted activation of carbon–hydrogen bonds. Mechanistic aspects of both processes have been intensively investigated in recent years.[8,9] The

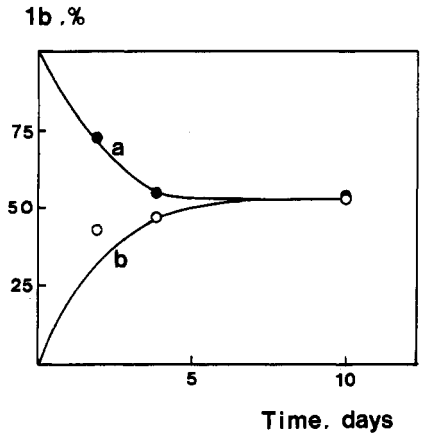
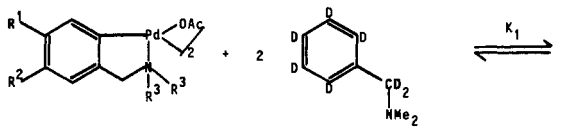
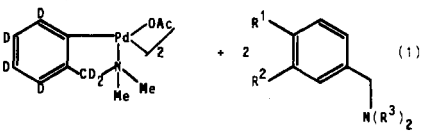


Figure 1. Interaction of (a) **1b** with **2** and (b) **3** with **4b**. For conditions see Table I.

present study consists of three parts. The first is a thermodynamic investigation of the model system shown in eq 1. These exper-

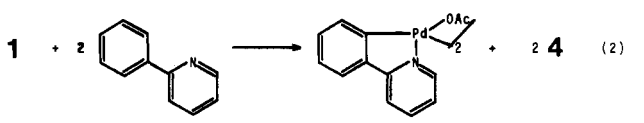


1 2

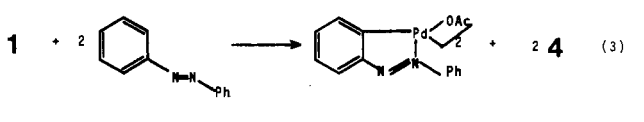


3 4 (1)

	R^1	R^2	R^3
a	MeO	MeO	Me
b	Me	H	Me
c	H	H	Me
d	MeO	H	Me
e	Cl	H	Me
f	NO_2	H	Me
g	H	H	Et



5 (2)



6 (3)

iments have been dictated by an earlier observation[2] that the exchange is reversible and were undertaken to determine the general features of the reaction. The results obtained in combination with those obtained previously[10] have allowed the formulation of principles of regioselective palladation of "bifunctional"

(8) For the reviews of mechanisms of transition-metal–carbon bond cleavages see: Belucco, U.; Michelin, P.; Uguagliati, P.; Crociani, B. *J. Organomet. Chem.* **1983**, *250*, 565. Johnson, M. D. In *The Chemistry of the Metal-Carbon Bond*; Hartley, R. F., Patai, S., Eds.; Wiley: Chichester, England, 1985; Vol. 2, p 513.

(9) Mechanistic aspects of the C–H bond cleavage in the course of cyclometalation are discussed, for example, in: Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713. Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620. Bruno, J. W.; Smyth, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40. Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502. Reference 10.

(10) Ryabov, A. D.; Sakodinskaya, I. K.; Yatsimirsky, A. K. *J. Chem. Soc., Dalton Trans.* **1985**, 2629.

Table I. Equilibrium Data of Reaction 1[a]

syst			starting	entering	reacn			
R^1	R^2	R^3	complex	ligand	time, h	$\alpha = c_4/2c_1$	α(av)	$K_1 = \alpha^3$
MeO	MeO	Me	**1a**	**2**	41	4.7	4.85	114
				3	**4a**	41	5.0	
Me	H	Me	**1b**	**2**	240	0.82	0.84	0.59
				3	**4b**	240	0.86	
H	H	Me	**1c**	**2**	240	0.54	0.50	0.125
				3	**4c**	240	0.46	
Cl	H	Me	**1e**	**2**	170	0.20		0.008
NO_2	H	Me	**3**	**4f**	216	0.15		0.0034
H	H	Et	**1g**	**2**	360	2.04	2.1	9.3
				3	**4g**	360	2.14	

[a] Conditions: 55 °C; 0.10 mL of D_3CCOOD; 0.25 mL of $CDCl_3$; 0.055 mmol of **1**; 0.11 mmol of **2**.

benzylamine derivatives bearing electron-rich and electron-poor aromatic rings. The second part of the present study deals with the solution behavior of the complexes **1** chosen for a kinetic study in the presence or in the absence of incoming ligands, i.e. 2-phenylpyridine (PP) and azobenzene (AB). The third part of this study is devoted to the kinetics of Pd(II) transfer from **1** to PP and AB (reactions 2 and 3, respectively).

Results

Thermodynamics of the Ligand Exchange. Reaction 1, run in a $D_3CCOOD/CDCl_3$ mixture at 55 °C, was used to study electronic and steric effects in the exchange. The latter was followed by integrating ^1H NMR signals from NCH_2 protons of free and palladated *N,N*-dimethylbenzylamine. No resonances from species other than those shown in eq 1 were observed. Reaction 1 is a truly reversible process. Figure 1 shows the relative content of **1b** as a function of time, when the reaction has been run from the left or right sides of eq 1. To characterize the equlibria quantitatively, the ratio α has been measured at equilibrium (Table I). When stoichiometric amounts of reagents are used, the equilibrium constant K_1 is equal to α^3. In fact, if c_1–c_4 are equilibrium concentrations of **1**–**4**, respectively, with the mass balance equations $[Pd(II)]_t = 2c_1 + 2c_3$, $[L]_t = 2c_1 + c_4$, and $[D]_t = c_2 + 2c_3$ taken into account, where $[Pd(II)]_t$, $[L]_t$, and $[D]_t$ are total concentrations of Pd(II) and ligands **4** and **2**, respectively, and $[Pd(II)]_t = [L]_t = [D]_t$, one obtains that at the equilibrium $2c_1 = c_2$ and $2c_3 = c_4$. Consequently

$$K_1 = \frac{c_3 c_4^2}{c_1 c_2^2} = \frac{\frac{1}{2}c_4 c_4^2}{2^2 c_1^2 c_1} = \left(\frac{c_4}{2c_1}\right)^3 = \alpha^3 \qquad (4)$$

if $\alpha = c_4/2c_1$. The values of K_1 are presented in Table I. Values of K_1 can be correlated with σ^+ constants: $\log K_1 = -(1.4 \pm 0.2) - (3.6 \pm 0.4)\sigma^+$. The values for K_1 for sterically similar ligands (R^3 = Me) demonstrate that eq 1 is shifted to the right for electron-rich ligands but to the left for electron-poor ones. Thus, when two benzylamine ligands are reacted with palladium(II) in acetic acid, Pd(II) will ortho metalate preferably a ligand with a stronger electron-releasing group. This result seems to be rather surprising, since it is generally accepted that Pd(II) behaves as a typical electrophile in cyclopalladation.[10] Our recent kinetic study of direct ortho palladation of ring-substituted *N,N*-dimethylbenzylamines has shown that under certain conditions, namely in acetic acid, where $Na_2Pd_2(OAc)_6$ is a reactive species, Pd(II) assumes pseudonucleophilic properties (the slope of the Hammett plot is +1.4) but behaves as an electrophile in chloroform (the slope is −1.6).[10] Evidently, both kinetic and thermodynamic control will provide ortho palladation of electron-poor aromatic nuclei of benzylamine derivatives. In contrast, in nonprotic media, such as chloroform for example, electron-rich nuclei should be activated in accordance with the electrophilic nature of Pd(II). To verify this statement, the "bifunctional" benzylamine **7** has been prepared and its reactions with palladium(II) acetate have been investigated in the two media. The corresponding chemistry is depicted in Scheme II. Treatment of **7** by palladium(II) acetate in chloroform results in the predicted activation of the C–H bond of the electron-rich "MeO" nucleus to afford the acetato-bridged complex **8a**. When the reaction is carried out in acetic acid, an isomer of **8a** is obtained in which Pd(II) is bound to the nitro-substituted ring, i.e. **9a**. Interaction of **8a** and **9a** with KCl provides chloro-bridged complexes **8b** and **9b**, respectively. Low-field parts of their 100-MHz ^1H NMR spectra recorded in the presence of pyridine-d_5 (py-d_5)[11] are presented in Figure 2. These spectral patterns clearly show to which of the two rings the palladium is σ bound. The spectrum of **8b** contains an intense singlet at δ 8.21, ascribed to four equivalent protons of the nonmetalated "NO_2" ring, and two strongly separated singlets at δ 6.52 and 5.39 ascribed to H^3 and H^6 protons of the metalated "MeO" ring, respectively. The spectrum of **9b** is more complex and consists of the two resolved ABX patterns from metalated and nonmetalated rings. Signals from H^6 and H^3 appear as two doublets at δ 6.69 and 6.82, respectively. A doublet of doublets from H^4 is partly overlapped with a signal from $H^{2'}$ of the nonmetalated ring, while $H^{5'}$ and $H^{6'}$ are seen as a doublet (δ 7.03) and a doublet of doublets (δ 7.07), respectively. An indicated weak signal at δ 8.21, arising from **8b**, allows us to estimate the ratio **[9b]/[8b]** = 77.6, which can be compared with the ratio $\alpha_{\mathbf{1a}}/\alpha_{\mathbf{1f}}$ = 32.3. The ratios show a reasonable agreement, if one takes into account a difference in a donor strength of N in **1a** and **1f**. The formation of **8** and **9** suggests also that a product distribution in reaction 1 is not governed by a change in basicity of N donors of the ligands but rather by a change in electron density of aromatic nuclei.

When the corresponding solutions are heated, a thermodynamic preference of Pd(II) for electron-poor rings in acetic acid is additionally demonstrated by the isomerization of **8** into **9**. This is a simple intramolecular ligand exchange. Note, as in the above case (eq 1), no other species except those in Scheme II were observed by ^1H NMR.[12]

Returning to the data in Table I, one can see that K_1 values for **1c** and **1g** suggest that Pd(II) metalates preferably the less sterically branched substrate when the electronic properties of two ligands are similar. Another curious observation is that α differs from unity for **1c** (α = 0.50). This formally means that deuteriated *N,N*-dimethylbenzylamine is more basic than its protic analogue. It is difficult to rationalize this phenomenon; however, thermodynamic H/D isotope effects in organo transition metal chemistry have been observed previously.[13]

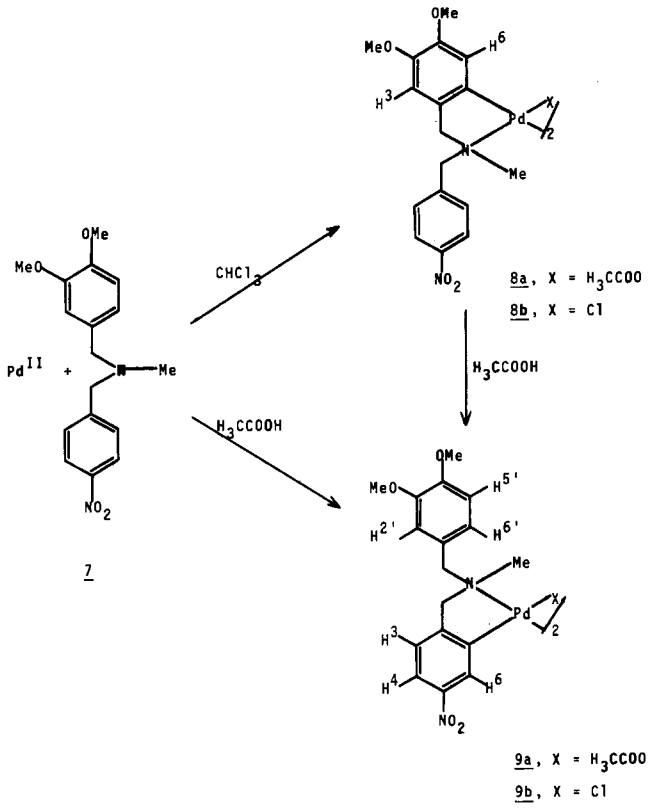
Solution Behavior of Complexes 1. Cyclopalladated acetato-bridged dimers have a boat-type conformation in the solid state.[14]

(11) py provides profound simplification of ^1H NMR spectra of dimeric acetato-bridged palladocycles by converting them into monomers; see ref 10, for example.

(12) One could expect the formation of a complex with both rings palladated. Such species were not observed. It should be noted that attempts of other authors to prepare similar doubly palladated aryl complexes were unsuccessful; see: (a) Selbin, J.; Abboud, K. Watkins, S. F.; Gutierrez, M. A.; Fronczek, F. R. *J. Organomet. Chem.* **1983**, *241*, 259. (b) Selbin, J.; Gutierrez, M. A. *J. Organomet. Chem.* **1983**, *246*, 95. At the same time Newkome reported on syntheses of doubly palladated alkyl complexes; see: Newkome, G. R.; Kawato, T.; Kohli, D. K.; Puckett, W.; Oliver, B. D.; Chiari, G.; Fronczek, F. R.; Deutsch, W. A. *J. Am. Chem. Soc.* **1981**, *103*, 3423. Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451.

(13) Brainard, R.; Whitesides, G. M. *Organometallics* **1985**, *4*, 1550.

Scheme II



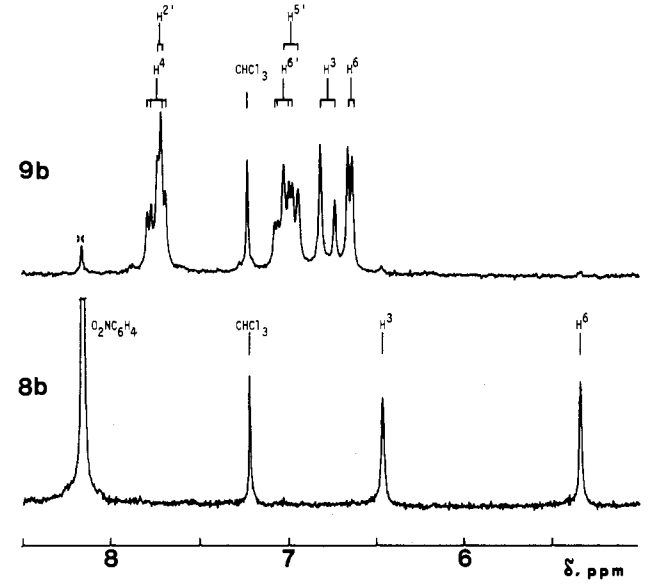
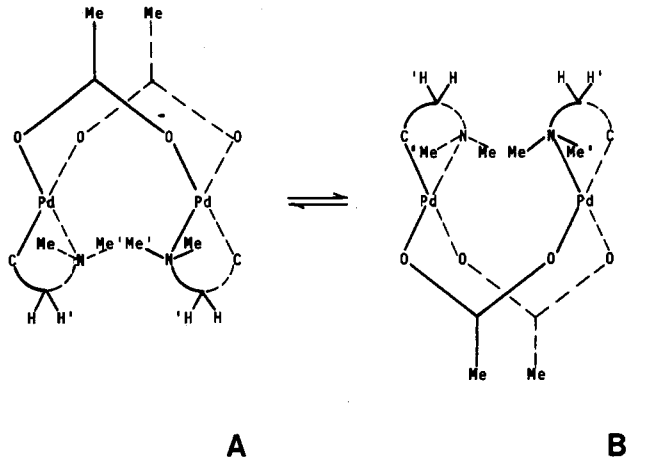


Figure 2. Low-field parts of ^1H NMR Spectra of **8b** and **9b** recorded in $CDCl_3$ in the presence of py-d_5.

^1H and ^{13}C NMR data of complexes of the type **1** indicate[15] that such a conformation is preserved in solution, providing an AB quartet from NCH_2 protons and two singlets from NCH_3 groups in proton spectra of **1c** in $CDCl_3$. In D_3CCOOD at 30 °C, these signals appear as a pair of very broad doublets centered at δ 3.30 and 2.40, respectively. At 60 °C they transform into broad singlets, which sharpen upon increasing the temperature. Cooling provides the reverse changes. Thus, a dynamic process occurs, which is probably an exchange between equally populated states A and B in Scheme III. Similar inversions across acetato bridges

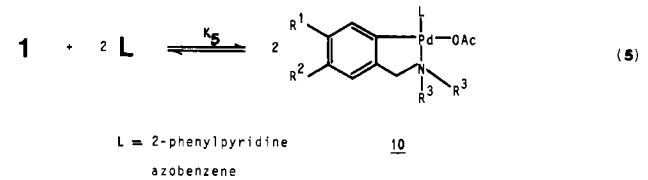
Scheme III



were studied in detail by Powell[16] in carboxylato phosphine Pd(II) complexes and were observed by Deeming[17] in cyclopalladated complexes. In the present case a full line-shape analysis of the NCH_3 signals[18,19] gives the rate constants for inversion k_{inv} = 208, 417, 1000, and 1500 s^{-1} at 50, 60, 80, and 100 °C, respectively, in D_3CCOOD. When the shape of the NCH_2 signal was analyzed at 60 °C, k_{inv} = 476 s^{-1}. The similar values of k_{inv} obtained by treating different signals confirms that they both reflect the same dynamic process shown in Scheme III. Another explanation of the dynamic behavior could involve a Pd–N bond cleavage followed by rotation across the Ar–CH_2N and CH_2–NMe_2 bonds; however, different values of rate constants from NCH_2 and NCH_3 signals should be expected.[20]

Analysis of the temperature dependence of k_{inv} gave the following activation parameters: $\Delta H^{\ddagger}$ = 8.4 ± 0.9 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −21 ± 3 cal K^{-1} mol^{-1}. These fall in the range reported[16b] for other complexes, for which a partial acetate bridge cleavage mechanism was proposed. This coincidence suggests the same mechanism in the present case and argues against an alternative one via Pd–N bond cleavage.

Bridge-Splitting Equilibria. Addition of a stoichiometric amount of 2-phenylpyridine (PP) to a solution of the dimer **1c** in D_3CCOOD leads immediately to the expected monomerization of the dimer according to eq 5.[21] As a result, broad doublets at δ 3.30



(5)

(NCH_2) and 2.40 (NCH_3) transform into slightly broadened singlets appearing at δ 3.77 and 2.63, respectively. At the same time a pattern from aromatic protons changes markedly. A signal from H^6 (ortho to the Pd–C bond) drifts upfield and is seen as a doublet at δ 5.8 (J = 8 Hz). All spectral changes are consistent with eq 5.[21] Further, a doublet at δ 9.28 (J = 5 Hz) refers to H^{α} of coordinated PP. It is well-separated from that of free PP (δ 8.83) at 30 °C. These signals broaden and coalesce at higher temperatures, indicative of an intermolecular exchange between the free and coordinated ligand. Other dimeric complexes **1** behave in a similar way. Compound **1g**, possessing diastereotopic[22]

(14) Churchill, M. R.; Wasserman, H. J.; Young, G. J. *Inorg. Chem.* **1980**, *19*, 762. See also ref 12a,b.
(15) Van der Ploeg, A. F. M. G.; Van Koten, G.; Vriese, K. *J. Organomet. Chem.* **1981**, *222*, 155.
(16) (a) Powell, J. *J. Am. Chem. Soc.* **1969**, *91*, 4311. (b) Powell, J.; Jack, T. *Inorg. Chem.* **1972**, *11*, 1039. (c) Jack, T. R.; Powell, J. *Can. J. Chem.* **1975**, *53*, 2558.
(17) Deeming, A. J.; Rothwell, I. P. *J. Organomet. Chem.* **1981**, *205*, 117.
(18) Bintch, G. *Top. Stereochem.* **1968**, *3*, 97.
(19) Polyakov, V. A.; Ryabov, A. D. *J. Chem. Soc., Dalton Trans.* **1986**, 589.
(20) Van Koten, G.; Noltes, J. *J. Am. Chem. Soc.* **1976**, *98*, 5393.
(21) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Dalton Trans.* **1978**, 1490.

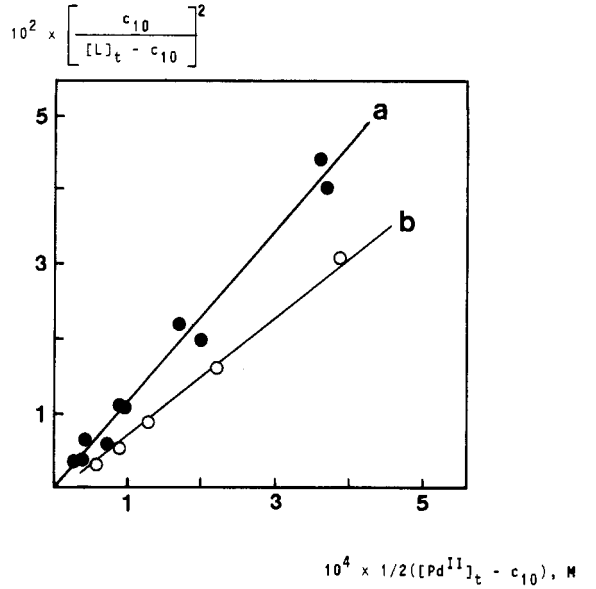


Figure 3. Evaluation of equilibrium constants K_5 according to eq 8 for **1a** at 25 (a) 25 °C and (b) 40 °C.

NCH_2Me hydrogens, was probed to establish the Pd–N bond cleavage in the monomeric complex **10g**, which would lead to topomerization[23] and collapse of the NCH_2Me signal into a quartet. It has been found, however, that the diastereotopy is preserved even at 100 °C, and 11 lines are well-resolved at 60 MHz. We thus conclude that no reversible Pd–N bond rupture takes place according to ^1H NMR data.

It is difficult to measure equilibrium constants K_5 by NMR, since the equilibria are shifted too far to the right in the concentration region employed. Spectrophotometric studies, operating with more dilute solutions, are now of use. Stepwise addition of PP to H_3CCOOH solutions of **1** (ca. 0.5×10^{-3} M) decreases absorbance systematically at 370–450 nm, the largest change being at 400 nm. The decrease stops at [PP] = ca. 4×10^{-2} M, when the dimer is completely converted into the monomer. At transient [PP] the absorbance is given by eq 6, where c_1 and c_{10} are con-

$$A = c_1\epsilon_1 + c_{10}\epsilon_{10} \qquad (6)$$

centrations of **1** and **10**, respectively, while ϵ_1 and ϵ_{10} are the corresponding molar absorptivities. Taking into account a mass balance equation ($[Pd(II)]_t = 2c_1 + c_{10}$) and that in the absence of added ligand $A_0 = c_1\epsilon_1$ (but when the latter is in great excess $A_\infty = c_{10}\epsilon_{10}$), eq 7 can be written. If c_L stands for the concen-

$$c_{10} = \frac{A_0 - A}{A_0 - A_\infty}[Pd(II)]_t \qquad (7)$$

trations of PP, $K_5 = c_{10}^2/c_L^2c_1$. Since $[L]_t = c_L + c_{10}$, final substitution gives eq 8, which allows confirmation of eq 5. If the

$$\left[\frac{c_{10}}{[L]_t - c_{10}}\right]^2 = K_5\left[\frac{[Pd(II)]_t - c_{10}}{2}\right] \qquad (8)$$

latter equilibrium is valid, the plot of $[c_{10}/([L]_t - c_{10})]^2$ against $^1/_2([Pd(II)]_t - c_{10})$ should be a straight line passing through an origin, the slope being equal to K_5. Such dependences are presented in Figure 3, where data for **1a** are included. Similarly derived values of K_5 together with corresponding thermodynamic parameters $\Delta H°$ and $\Delta S°$ are summarized in Table II.

A systematic variation in K_5 with a change in ring substituents is worth mentioning. Figure 4 shows the corresponding Hammett plot, the analytical form of which is $\log K_5 = (2.09 \pm 0.03) + (1.22 \pm 0.08)\sigma_m$. A positive slope indicates that complexation is governed by a ligand-to-metal charge transfer. A moderate

Table II. Equilibrium Constants K_5 and Corresponding Thermodynamic Parameters in Acetic Acid

complex ($R^{1,2}$)	T, °C	K_5, $dm^3\ mol^{-1}$	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal $K^{-1}\ mol^{-1}$
		L = 2-Phenylpyridine		
1a ($[MeO]_2$)	25	115 ± 6	−3.6 ± 0.8	−2.6 ± 2.5
	40	86 ± 1		
	50	75[a]		
1b (Me)	25	244 ± 10	−7.4 ± 0.6	−14 ± 2
	50	92 ± 4		
1c (H)	25	214 ± 12	−4.4 ± 0.6	−4.2 ± 2.2
	50	120 ± 4		
1d (MeO)	25	433 ± 11	−5.2 ± 0.6	−5.4 ± 1.8
	50	219 ± 11		
1e (Cl)	25	1014 ± 32	−7.6 ± 0.5	−11.7 ± 1.8
	50	376 ± 15		
1f (NO_2)	25	2700	−8.4 ± 0.5	−12.7 ± 1.5
	50	831[a]		
	70	413 ± 5		
1g (H)	25	445 ± 30		
5	25	138 ± 4	−6.3 ± 0.4	−6.5 ± 1.2
	70	33 ± 2		
		L = Azobenzene		
1c (H)	30	0.15 ± 0.01[a]	−3.2 ± 0.7	−14.3 ± 2.3
	60	0.093 ± 0.004[b]		

[a] Calculated values. [b] In D_3CCOOD.

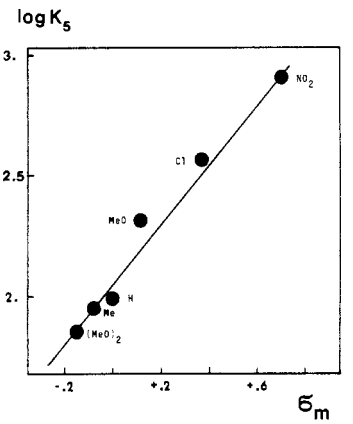


Figure 4. Hammett plot of log K_5 against σ_m for complexes **1a–f**.

value of ρ (+1.22) may be due to the contribution of back-donation from a d_{xy} orbital to a pyridine π system.

Absolute values of K_5 can be compared with those of Deeming et al.[21] for the complexation of the chloro analogue of **1c** with py and 2-Mepy in toluene at 30 °C (2.2×10^4 and 0.77×10^4 dm^3 mol^{-1}, respectively). Data from Table II indicate that the stability of the acetato monomers **10** is a factor of ca. 10^2 lower compared with that of the chloro monomers. This difference accounts for earlier observations[24] that chloro monomers are more stable than acetato monomers.

Spectrophotometry provides no information for calculation of K_5 in the case of azobenzene (AB), but the ^1H NMR technique does. A stepwise increase in [AB] in a D_3CCOOD solution of **1c** results in a development of new broad NCH_2 and NCH_3 signals at δ 3.75 and 2.72, respectively, for the monomeric complex **10**, which are observed alongside resonances from the dimer. At higher [AB], when eq 5 is shifted to the right, a signal from the aromatic H^6 proton is distinctly seen at δ 6.00. A very broad signal is observed at δ 8.57, corresponding to four protons. This is probably due to a downfield shift[21] of the 2-, 6-, 2′- and 6′-hydrogens of AB, which experience "agostic" interactions[25] with axial coodination sites of the Pd(II) plane. A similar observation had been reported[26] for N-coordinated *N,N*-dimethylbenzylamine, but

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(23) Ōki, M.; Ohira, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3117.
(24) Ryabov, A. D.; Polyakov, V. A.; Yatsimirsky, A. K. *Inorg. Chim. Acta* **1984**, *91*, 59.
(25) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

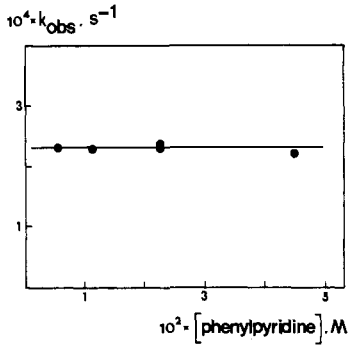
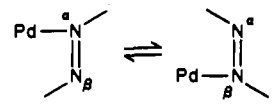


Figure 5. Dependence of k_{obsd} on 2-phenylpyridine concentration in the case of **1c** at 75 °C.

only two protons showed agostic contacts. Involvement of four protons in the present case suggests that the perpendicular coordination of AB to the palladium plane provides agostic interactions of the C–H bonds with the fifth and sixth axial sites, on the one hand, while the ligand experiences either rapid rotation around the nitrogen–phenyl bonds or pseudorotation as a result of an exchange between the N-donor sites, on the other:



A rotation around the nitrogen–phenyl bonds seems to be probable in the case of coordinated AB, since a double-bond character of the azo function, which hinders the rotation due to conjugation with phenyl rings, can be significantly lowered on binding with Pd(II).

The ratio $\beta = c_{10}/2c_1$ was obtained in this case by comparing the areas under NCH_2 signals from the monomer and dimer. When a similar approach is applied, the following equation, which binds β with K_5, can be derived[27]

$$2[Pd(II)]_t(\beta + 1) = K_5\beta\{[L]_t(\beta + 1) - [Pd(II)]_t\}^2 \quad (9)$$

where all symbols are as above. A plot of the left side of eq 9 against $\beta\{[L]_t(\beta + 1) - [Pd(II)]_t\}^2$ has been found to be linear, the slope corresponding to K_5 (see Table II).

Kinetics of Reaction 2. The majority of runs have been performed with **1c** at 75 °C. In excess PP, pseudo-first-order rate constants, k_{obsd}, are virtually independent of [**1c**] in the range (0.15–0.55) × 10^{-3} M. A dependence of k_{obsd} on [PP] is presented in Figure 5. As seen, the reaction is zero order in the incoming ligand in the range (0.56–4.5) × 10^{-2} M. Therefore, the rate expression is given by

$$\text{rate} = k[\mathbf{1}] \quad (10)$$

with $k_{obsd} = k$. A solvent kinetic isotope effect, measured in H_3CCOOD and D_3CCOOD, k_H/k_D, is 1.80. The leaving *N*,*N*-dimethylbenzylamine has no effect on reaction rate at early stages of the reaction (up to 40–50% completion). These good first-order portions were followed by very complicated non-first-order traces, which were not studied in detail. The rate constants k are strongly temperature-dependent and are equal to 1.5 × 10^{-4}, 2.35 × 10^{-4}, 5.6 × 10^{-4}, and 8.5 × 10^{-4} s^{-1} at 68, 75, 82.5, and 89 °C, respectively. Calculated activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are summarized in Table III.

The remaining complexes **1** follow the same kinetic behavior but show different reactivities depending on the nature of ring substituents. k_{obsd} for **1a** is independent of [**1a**] in the range (0.16–0.56) × 10^{-3} M and [PP] in the range (0.56–2.25) × 10^{-2} M. k_H/k_D is 1.54 in this case. Activation parameters are in Table III. Equation 10 has been confirmed for complexes **1b,d**. Assuming the same rate law also for **1f–h**, the rate constants k have been evaluated; the data are summarized in Table III.

Table III. Rate Constants k (75 °C) and Corresponding Activation Parameters of Reactions 2 and 3 in Acetic Acid

complex ($R^{1,2}$)	10^4k, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
Entering Ligand = 2-Phenylpyridine			
1a ($[MeO]_2$)	12.6	17.7 ± 0.6	−20.9 ± 1.8
1b (Me)	3.9	19.5 ± 0.5	−18.1 ± 1.3
1c (H)	2.35	19.2 ± 1.4	−20.0 ± 4.4
1d (MeO)	2.6	22.0 ± 0.3	−12.0 ± 1.0
1e (Cl)	0.44	24.7 ± 1.7	−8 ± 5
1f (NO_2)	0.0225[a]	35.0 ± 4.1	16 ± 11
1g (H)	0.30	30.3 ± 5.0	4 ± 14
Entering Ligand = Azobenzene			
1c (H)	1.6	23.0 ± 0.5	−5.0 ± 1.3

[a] Extrapolated from higher temperatures.

Kinetics of Reaction 3. Reactions between **1c** and azobenzene were in most instances run at 85 °C. The exchange was again first order in the complex and zero order in the entering ligand. Thus, eq 10 holds; $k_H/k_D = 1.08$. The values for k are 1.6 × 10^{-4}, 2.6 × 10^{-4}, 4.3 × 10^{-4}, and 6.7 × 10^{-4} s^{-1} at 75, 80, 85, and 90.5 °C, respectively. The values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are given in Table III.

Rates of Palladation of 2-Phenylpyridine by Palladium(II) Acetate. Rates of the formation of **5** were measured in acetic acid in the temperature range 45–65 °C. At $[Pd(II)]_t$ = 0.2 × 10^{-2} M k_{obsd} was independent of [PP] in the range (0.52–2.08) × 10^{-2} M, and the rate constant was 0.001 25 s^{-1} at 50 °C. The enthalpy and entropy of activation $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 15.1 ± 0.7 kcal mol^{-1} and −25.2 ± 0.2 cal K^{-1} mol^{-1}, respectively, were obtained from the temperature dependence of the rate constant.

Evidence for Reversibility of Ortho Palladation of *N*,*N*-Dimethylbenzylamine in Acetic Acid. When *N*,*N*-dimethylbenzylamine is thermostated at 70 °C in a H_3CCOOD solution of palladium(II) acetate (5% with respect to the amine), a gradual enrichment of the aromatic ring with deuterium is observed by NMR. Two deuterium atoms are incorporated into the ring after a fortnight. The H/D exchange is complicated by metal reduction, but this can be suppressed by addition of copper(II) acetate. No more than two protons are exchanged even after increasing the reaction time, suggesting that only 2- and 6-H atoms are involved.

Discussion

The data from Table II show that the abilities of PP and AB to monomerize dimers **1** differ by a factor of 10^3. As a result, under the kinetic conditions of reactions 2 and 3, complexes **1** exist in monomeric and dimeric forms, respectively. In fact, K_5 for **1c** and PP extrapolated to 75 °C is 71.3 dm^3 mol^{-1}. When $[Pd(II)]_t$ = 1.0 × 10^{-3} M and [PP] = 2.2 × 10^{-2} M, the concentration of the monomer **10** is 0.95 × 10^{-3} M (95%). A reverse tendency is observed in the case of AB. K_5 is 0.067 dm^3 mol^{-1} at 85 °C. Assuming it to be the same in D_3CCOOD and H_3CCOOH, at $[Pd(II)]_t$ = 1.0 × 10^{-3} M and [AB] = 1.0 × 10^{-2} M the molar fraction of the dimer **1c** is 94%, but at [AB] = 2.0 × 10^{-2} M it is 87%. A remarkable feature is that rate law 10 holds in this concentration range. Therefore, at least at [AB] < 2 × 10^{-2} M the transition state of the exchange reaction does not contain an AB molecule, suggesting a purely "dissociative" mechanism. Zero order in PP, when reaction 2 is concerned, may be also a result of the "dissociative" mechanism, in which the monomeric species **10** is involved. We define the mechanism as "dissociative" to indicate that the cleavage of starting palladocycles occurs in the transition state but not the formation of new M–C bonds. The cleavage is induced by acetic acid, since no exchange takes place without the solvent.[2] The monomerization of the dimers to produce monomeric solvento species[16c] cannot be rate-determining in reaction 3, since the reaction rate should be comparable with the

(26) Jones, T. C.; Nielson, A. J.; Rickard, C. E. *Aust. J. Chem.* **1984**, *37*, 2179.

(27) The algebra is as follows: $K_5 = c_{10}^2/c_1c_L^2 = (c_{10}/2c_1)^2(4c_1/c_L^2) = \beta^2(4c_1/c_L^2)$. Since $[Pd(II)]_t = 2c_1 + c_{10}$, one obtains $4c_1 = 2\beta[Pd(II)]_t/(\beta + 1)$. At the same time $[L]_t = c_L + c_{10}$, and therefore $c_L = [L]_t - [Pd(II)]_t/(\beta + 1)$. Substitution of $4c_1$ and c_L^2 into the last expression for K_5 gives eq 9.

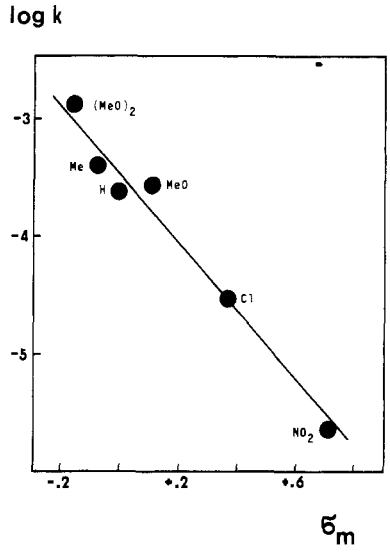


Figure 6. Hammett plot of log k against σ_m for reaction 2.

rate of inversion of the dimer **1c**, which proceeds via the partial bridge cleavage mechanism. But a rate difference of 4×10^6 at 80 °C is too large to accept such a possibility. A mechanism with a rapid dissociation of **1** followed by rate-limiting palladation of PP by liberated palladium(II) acetate can also be discarded for the same reason. Indeed, the rate of direct palladation of PP is 4.0×10^{-3} s^{-1} at 65 °C, whereas between **1c** and PP the rate is 0.15×10^{-3} s^{-1} at 68 °C; at the same time the $\Delta H^{\ddagger}$ values of the former and the latter are 15.1 and 19.2 kcal mol^{-1}, respectively.

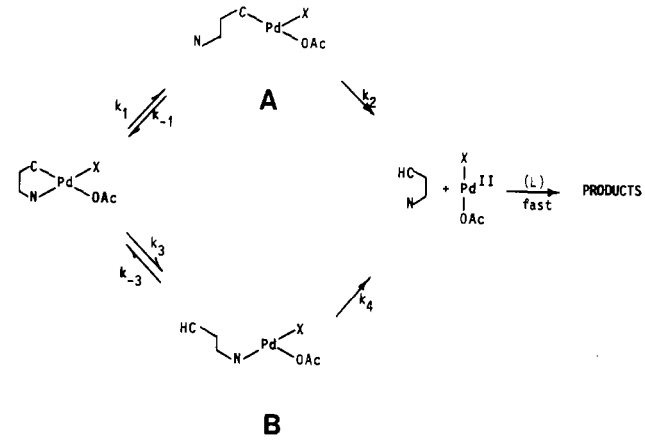
The slowest step in the dissociative mechanism may be a cleavage of either the Pd–C or Pd–N bond. Between the extremes, a transient situation may be realized, when both processes have close rates. A moderate solvent kinetic isotope effect k_H/k_D of 1.80 and 1.54 in reaction 2 for **1c** and **1a**, respectively, clearly shows that the Pd–C bond breaking plays a role. The values, however, are much lower than those reported for an acid cleavage of nonchelated platinum–carbon bonds.[28] This may be a result of a contribution of the Pd–N bond breaking, since no significant solvent kinetic isotope effect should be expected in the latter case. Pd–N bond breaking seems to be more important for slower reactions, (3) in particular, for which k_H/k_D is only 1.08.

Consider the kinetic parameters in Table III; the rate constants drop monotonously on going from electron-rich to electron-poor complexes. The corresponding Hammett plot is shown in Figure 6, and eq 11 is its analytical form; the slope of −2.93 is remarkable.

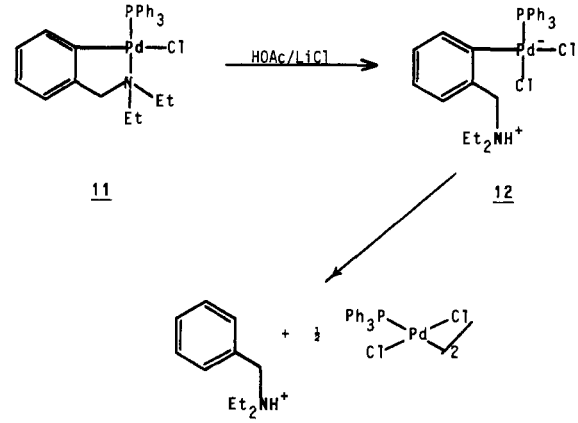
$$\log k = -(3.44 \pm 0.08) - (2.93 \pm 0.25)\sigma_m \qquad (11)$$

One can hardly find a reaction involving palladium complexes so sensitive to electronic effects,[29] suggesting a very polar transition state. The negative ρ is in accord with both mechanistic proposals. A removal of electron density from palladium would slow down the proton-assisted heterolytic cleavage and strengthen the coordinative Pd–N bond toward dissociation. The Hammett correlation with σ_m constants suggests that the electronic density at palladium plays a crucial role. The $\Delta H^{\ddagger}$ values also vary systematically; as one goes from the dimethoxy to the nitro complex, $\Delta H^{\ddagger}$ increases by 17.3 kcal mol^{-1} from 18.7 to 35.0 kcal mol^{-1}, respectively. It is tempting to connect $\Delta H^{\ddagger}$ with Pd–C bond breaking in the case of **1a** (ordered transition state, large and negative $\Delta S^{\ddagger}$) and with Pd–N bond breaking in the case of **1f** (small and positive $\Delta S^{\ddagger}$). But the real mechanism is obviously more complicated. Its pathways are shown in Scheme IV, where X stands for either the incoming ligand and the remaining part

Scheme IV



Scheme V



of the dimer for reactions 2 and 3, respectively. The exchange is considered here as irreversible. This is a simplification, but a reasonable one under the initial reaction conditions of reactions 2 and 3. In fact, even when stoichiometric amounts of reagents are employed, yields of isolated products are close to 80%.[5] Yields are even higher when the entering ligands are in large excess.

There are two pathways in Scheme IV, which differ in the sequence of the cleavage of Pd–C/Pd–N bonds. The kinetics do not allow discrimination between the two. The preferred pathway is A, since it is in accord with our previous findings on a lithium chloride induced acidolysis of **11** (Scheme V).[30] Isolated and characterized intermediate **12** was shown to transform into the final products.

In terms of the pathway chosen and with consideration of a mass balance equation, the rate constant k is given by the expression $k = k_1k_2/(k_1 + k_2 + k_{-1})$. If the dissociation of the Pd–N bond is the slowest step, the expression transforms to $k = k_1k_2/(k_2 + k_{-1})$. But if $k_{-1} \ll k_2$, one obtains $k = k_1$. The latter assumption seems to be correct, since nucleophilic properties of tertiary amines are significantly lowered in acetic acid due to N-protonation.[10] Characteristic features of the k_1-limited pathway (low values of k_H/k_D, high $\Delta H^{\ddagger}$, zero or positive $\Delta S^{\ddagger}$) are manifested in reaction 3 and in reaction 2 for electron-poor complexes. Reactions of electron-rich complexes are characterized by lower values of $\Delta H^{\ddagger}$, more negative $\Delta S^{\ddagger}$ values, and k_H/k_D exceeding unity. This indicates the increasing of the kinetic importance of the k_2 step, which would have a much more ordered transition state due to involvement of an acetic acid molecule. Note that the Pd–N bond dissociation should not be considered as a rapid preequilibrium. The k_2 step results in a complete departure of the leaving ligand. We believe that only after this step can palladation of the incoming ligand take place. There are several supporting observations. First, ortho palladation is known[10] to be most effective when only one

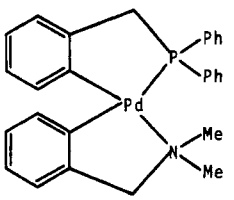
(28) Romeo, R.; Minniti, D.; Lanza, S.; Uguagliati, P.; Belucco, U. *Inorg. Chem.* **1978**, *17*, 1813. Romeo, R.; Minniti, D.; Lanza, S. *J. Organomet. Chem.* **1979**, *165*, C36.

(29) An example is the cleavage of aryl–thallium(III) bonds by Pd(II), where ρ is −3.0; see: Yatsimirsky, A. K.; Deiko, S. A.; Ryabov, A. D. *Tetrahedron* **1983**, *39*, 2381.

(30) Ryabov, A. D. *J. Organomet. Chem.* **1984**, *268*, 91.

ligand suitable for metalation is bound to the metal. Second, a chiral leaving ligand does not induce asymmetric induction, when an incoming ligand is a prochiral one.[31]

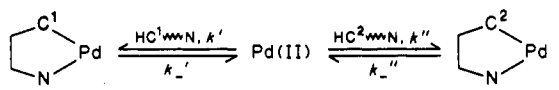
A few comments can be made concerning an alternative "associative" mechanism that would involve the formation of doubly palladated species of the type $[\overline{Pd(C\sim N)}(\overline{C'\sim N})]$.[5c] It had already been mentioned that such species were not observed during a study of equilibrium 1 or conversions of **8** into **9**. Kinetics also disfavors the associative mechanism. It is difficult to rationalize the negative ρ in reaction 2 with a closure of the second ring (such a process is known to be electrophilic[10]). Zero order in AB is also inconsistent with the associative pathway. Moreover, such doubly palladated species are highly reactive toward acetic acid. For example, **13** instantaneously decomposes into a mixture



13

of the cyclopalladated acetato-bridged phosphine complex and free *N,N*-dimethylbenzylamine on addition of acetic acid[32] (cf. (iv) in Scheme I). In view of all these facts, the associative mechanism does not seem acceptable.

It is not difficult now to account for a thermodynamic preference of Pd(II) for electron-poor benzylamines (as well as benzylideneanilines[5c]) in acetic acid. The key points here are a reversibility of palladation and the dissociative mechanism of the exchange. Consider the simplified scheme



Let $HC^1\sim N$ and $HC^2\sim N$ be similar electron-rich and electron-poor ligands, the concentrations of which are equal and much higher than that of Pd(II). In this case the ratio of *monomeric* cyclopalladated complexes is given by $Q = [\overline{Pd(C^2\sim N)}]/[\overline{Pd(C^1\sim N)}] = K'K'' = k_{-}'k''/k'k_{-}''$. We do know[10] that if $Pd_3(OAc)_6$ is a reactive species (a solution of palladium(II) acetate in glacial acetic acid), $k' \simeq k''$ and, therefore, $Q = k_{-}'/k_{-}''$; i.e., the equilibrium is determined by the rates of dissociation of the palladocycles involved. Using the rate constants in Table III, one can obtain Q equal to 1.7 and 560 for the pairs **1c**/**1b** and **1a**/**1f**, respectively. At the same time it is possible to calculate Q from the data in Table I. In this case $Q = (\alpha'/\alpha'')^2$, since complexes are considered here as monomeric for clarity. The resulting values are 2.8 and 1040 for the same pairs, respectively. The surprisingly good agreement provides additional evidence in favor of the mechanisms proposed in this work.

Conclusion. The thermodynamic and kinetic results clearly show that the exchange of cyclopalladated ligands takes place due to acidolysis of the starting palladocycles in acetic acid. The first step of this slow process is probably the cleavage of the palladium–nitrogen bond followed by protonolysis of the palladium–carbon bond. The driving force of the palladium(II) transfer from one ligand to another for structurally related ligands is determined by different resistances of the two palladocycles toward acidolysis: palladium(II) will migrate to the ligand that forms the palladocycle less susceptible to acidolysis.

Experimental Section

Instrumentation. Electronic spectra were recorded on a Hitachi 356 spectrophotometer and IR spectra for KBr disks on a JASCO 200 spectrophotometer. ^1H NMR spectra were run on Tesla BS 467 or Bruker CXP 100 instruments. Measurements were made with hexamethyldisiloxane as internal standard. All chemical shifts are given on the δ scale relative to tetramethylsilane; J values are in Hz.

Reagents. Cyclopalladated complexes **1**, ring-substituted derivatives of bis(μ-acetato)bis[{2-((dimethylamino)methyl)phenyl-C^1,N}palladium(II)] (**1c**), were prepared as described previously.[10] 2-Phenylpyridine (Aldrich) was vacuum-distilled before use. Azobenzene (Reakhim) was recrystallized from ethanol. Cyclopalladated derivatives of 2-phenylpyridine and azobenzene were synthesized via the ligand-exchange procedure reacting the ligands with **1c** in acetic acid.[5a] Yields of bis(μ-acetato)bis[{2-(2-pyridyl)phenyl-C^1,N}palladium(II)] (**5**) and bis(μ-acetato)bis[{2-(phenylazo)phenyl-C^1,N}palladium(II)] (**6**) were 74 and 83%, respectively. Acetic acid of the highest available purity (Reakhim) was used for kinetic and equilibrium measurements. It was additionally purified by distillation over 3–5% $KMnO_4$ to remove all possible reducing impurities. A fraction with boiling point 117.5–118 °C was taken for spectrophotometric experiments. Deuterated solvents $CDCl_3$ and D_3C-COOD (Izotop) were used as received, while H_3CCOOD was prepared from acetic anhydride and D_2O. Chloroform (Kiev Khimfarmzavod) was purified according to the standard procedure.[33]

1-(3,4-Dimethoxyphenyl)-2-methyl-3-(4-nitrophenyl)-2-azapropane (7). (3,4-Dimethoxybenzyl)amine (Merck) and 4-nitrobenzaldehyde (Fluka) were condensed in benzene to afford the corresponding Schiff base. This was reduced with $NaBH_4$ in EtOH into the corresponding secondary amine and then N-methylated with a HCOOH/HCOH mixture. The details are given elsewhere.[34] Data are as follow: mp 187 °C (hydrochloride); IR 1520 and 1345 cm^{-1} (NO_2); ^1H NMR ($CDCl_3$, free base) δ 7.42–8.22 (AA'BB', $ArNO_2$), 6.80 (m, ArOMe), 3.85 (m, OCH_3, C^3H_2), 3.72 (s, C^1H_2), 2.24 (s, NCH_3).

Study of Equilibrium 1 (Exemplified by Interaction between 1c and 2). A solution of **1c** (32 mg, 55 μmol) in 0.25 mL of $CDCl_3$ was mixed with *N,N*-dimethylbenzylamine-d_7 (**2**; 0.016 mL, 0.11 mmol), 0.10 mL of D_3CCOOD, and 0.06 mL of hexamethyldisiloxane. The solution was filtered directly into a 5-mm NMR tube and its ^1H NMR spectrum recorded. The spectrum contained a pair of broad doublets from the NCH_2 and NCH_3 protons of **1c** (see above), the shape of which was found to be unaffected by **2**. After the "zero-time" spectrum was recorded, the solution was transferred into a stoppered 5-mL tube and thermostated in the dark at 55 °C. After appropriate time intervals (usually days), the solution was again passed through a capillary cotton filter to remove traces of palladium metal formed and its ^1H NMR spectrum was recorded. As the exchange proceeded, new signals from dissociated, primarily palladated *N,N*-dimethylbenzylamine began to develop. A sharp NCH_2 singlet of **4c** is seen in a weaker field compared with the NCH_2 signal of **1c**, in particular. Integration of both signals makes it possible to determine the ratio of **4** (c_4) and **1** (c_1), defined as $\alpha = c_4/2c_1$. It is more convenient to evaluate α at 75 °C, when the signal from **1c** is much sharper. The product distribution was assumed to be at equilibrium, when α became independent of time. In the case of **1a** α was obtained by integrating resonances from OCH_3 protons of the palladated and free ligand (palladation induces a high-field shift). It was confirmed that the ratios obtained from the NCH_2 and OCH_3 signals were identical.

Palladation of 1-(3,4-Dimethoxyphenyl)-2-methyl-3-(4-nitrophenyl)-2-azapropane (7): Bis(μ-acetato)bis[{2-((methyl((4-nitrophenyl)-methyl)amino)methyl)-4,5-dimethoxyphenyl-C^1,N}palladium(II)] (8a). A solution of **7** (419 mg, 1.32 mmol) in chloroform (8 mL) was mixed with a solution of palladium(II) acetate (297 mg, 1.32 mmol) in 8 mL of chloroform and allowed to stand at 20 °C for 24 h. The solution was then separated from palladium metal precipitate, and H_2O (20 mL) was added. The aqueous layer was extracted with chloroform (10 mL) and the organic fractions were combined, washed twice with water, and dried over $MgSO_4$. After filtration, the solution was concentrated under vacuum, the final volume being ca. 13 mL. Hexane (15 mL) was added and the solution stirred (magnetic bar) to induce precipitation of a yellow solid. The latter was filtered, washed with hexane, and vacuum-dried to afford 405 mg of **8a** (64%). Complex **8a** is only sparingly soluble in organic solvents ($CHCl_3$, C_6H_6), and this complicates its purification by column chromatography. Anal. Calcd for $C_{38}H_{44}N_4O_{12}Pd_2$: C, 47.5; H, 4.6. Found: C, 48.2; H, 4.7. Data are as follows: mp 170–172 °C

(31) Ryabov, A. D.; Kazankov, G. M., submitted for publication. The reaction involved ortho-palladated (*R*)- or (S)-dimethyl-1-phenethylamine and 8-ethylquinoline.
(32) Ryabov, A. D., Abicht, H.-P.; Yatsimirsky, A. K., submitted for publication in *Polyhedron*.
(33) Perrin, D. D.; Armagero, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, England, 1980; p 167.
(34) Ryabov, A. D.; Polyakov, V. A.; Talebarovskaya, I. K.; Katkova, V. A.; Yatsimirsky, A. K.; Berezin, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.*, in press.

dec; IR 1570 and 1415 (bridging H_3CCOO),[35] 1520 and 1350 cm^{-1} (NO_2); ^1H NMR ($CDCl_3$, in the presence of py-d_5) δ 8.26, 8.17, 8.07, and 7.98 (AA'BB', $ArNO_2$), 6.45 (s, H^3), 5.45 (s, H^6), 4.59, 4.46, 3.92, and 3.79 (q, J = 13, C^3H_2), 4.15, 4.02, 3.76, and 3.55 (q, J = 13, C^1H), 3.78 (s, O^4CH_3), 3.45 (s, O^5CH_3), 3.03 (s, NCH_3), 1.91 (s, H_3CCOO).

Bis(μ-chloro)bis[{2-((methyl((4-nitrophenyl)methyl)amino)methyl)-4,5-dimethoxyphenyl-C^1,N}palladium(II)] (8b). To a solution of **8a** (218 mg, 0.45 mmol) in acetone (15 mL) was added concentrated aqueous KCl (10 mL). The yellow precipitate that formed was filtered, washed with water, and dried over NaOH to afford 153 mg of **8b** (69%). Anal. Calcd for $C_{34}H_{38}N_4O_8Cl_2Pd_2 \cdot 4H_2O$: C, 41.4; H, 4.7; N, 5.7. Found: C, 41.2; H, 5.0; N, 5.6. Data are as follows: mp 119–121 °C dec; IR 1520 and 1350 cm^{-1} (NO_2); ^1H NMR δ 8.21 (s, $ArNO_2$), 6.52 (s, H^3), 5.39 (s, H^6), 4.91, 4.78, 3.86, and 3.73 (q, J = 13, C^3H_2), 4.26, 4.12, 3.66, and 3.52 (q, J = 14, C^1H_2), 3.74 (s, O^4CH_3), 3.43 (s, O^5CH_3), 3.13 (s, NCH_3).

Bis(μ-acetato)bis[{2-((methyl((3,4-dimethoxyphenyl)methyl)amino)-methyl)-5-nitrophenyl-C^1,N}palladium(II)] (9a). A. palladium(II) acetate (328 mg, 1.46 mmol) was dissolved in H_3CCOOH (15 mL) with gentle heating, and the solution was filtered. **7** (463 mg, 1.46 mmol) in $CHCl_3$ (15 mL) was then added, and the mixture was kept at 70 °C for 4 h. Some reduction of Pd(II) was observed. The mixture was filtered, and $CHCl_3$ (15 mL) and water (15 mL) were added. The aqueous layer was washed with $CHCl_3$ (15 mL) and the organic layers were combined, washed twice with water (20 mL), and dried over $MgSO_4$. After evaporation of the solvent under vacuum, the residue was column-chromatographed on SiO_2 ($CHCl_3$ eluent) to yield 340 mg of **9a** (49%). In contrast to the case for **8a**, the complex **9a** is soluble in common organic solvents. Anal. Calcd for $C_{38}H_{44}N_4O_{12}Pd_2$: C, 47.5; H, 4.6; N, 5.8. Found: C, 47.0; H, 4.5; N, 5.7. Data: mp 144–151 °C dec; IR 1575 and 1420 (bridging H_3CCOO), 1515 and 1340 cm^{-1} (NO_2); ^1H NMR δ 7.75 (dd, J = 8 and 2, H^4), 6.81 (d, J = 8, H^3), 6.78 (d, J = 2, H^6), 7.44 (d, J = 2, $H^{2'}$), 6.99 (dd, J = 8 and 2, $H^{6'}$), 6.93 (d, J = 8, $H^{5'}$), 4.49, 4.37, 3.75, and 3.62 (q, J = 12, C^3H_2), 4.34, 4.19, 3.69, and 3.54 (q, J = 15, C^1H_2), 3.88 and 3.85 (s, OCH_3), 2.96 (s, NCH_3), 1.93 (s, H_3CCOO).

B. To the dimeric complex **8a** (100 mg, 0.105 mmol) dissolved on heating in benzene (5 mL) was added H_3CCOOH (5 mL). The solution was thermostated at 70 °C for 4 h and then developed as in A to afford 51 mg of **9a** (51%).

Bis(μ-chloro)bis[{2-((methyl((3,4-dimethoxyphenyl)methyl)amino)-methyl)-5-nitrophenyl-C^1,N}palladium(II)] (9b). This complex can be prepared either by treating a solution of **9a** in acetone with aqueous KCl or thermostating a suspension of **8b** in a H_3CCOOH/C_6H_6 mixture at 70 °C according to the procedures presented above. Anal. Calcd for $C_{34}H_{38}N_4O_8Cl_2Pd_2$: C, 44.7; H, 4.2; N, 6.1. Found: C, 45.0; H, 4.3; N, 6.1. Data: mp 126–129 °C dec; IR 1515 and 1340 cm^{-1} (NO_2); ^1H NMR δ 7.78 (dd, J = 8 and 2, H^4), 6.82 (d, J = 8, H^3), 6.69 (d, J = 2, H^6), 7.74 (d, J = 2, $H^{2'}$), 7.06 (dd, J = 8 and 2, $H^{6'}$), 7.03 (d, J = 8, $H^{5'}$), 4.85, 4.72, 3.75, and 3.62 (q, J = 13, C^3H_2), 4.34, 4.19, 3.69, and 3.54 (q, J = 15, C^1H_2), 3.87 and 3.86 (s, OCH_3), 3.07 (s, NCH_3).

Measurements of Equilibria 5. Stock solutions of complexes **1** in $CHCl_3$ (ca. 0.017 M) were added to H_3CCOOH (ca. 3.0 mL) in a 10-mm quartz cell, which was placed into the thermostated cell compartment of a spectrophotometer. Solutions of 2-phenylpyridine in H_3CCOOH were added. Spectra were recorded after not less than 5 min to ensure proper equilibration at a given temperature.

Kinetic Studies of Reactions 2 and 3. The former reaction was followed at 400 nm by monitoring an increase in absorbance due to the formation of the ortho-palladated 2-phenylpyridine complex **5** (λ_{max} 304 nm, ϵ 9200 dm^3 mol^{-1} cm^{-1} in H_3CCOOH). Stock solutions of **1** in $CHCl_3$ and 2-phenylpyridine in H_3CCOOH were mixed with glacial acetic acid in 10-mm cells to achieve **1** concentrations of (0.15–0.56) × 10^{-3} M and ligand concentrations of (0.56–4.5) × 10^{-2} M. The content of $CHCl_3$ in the system did not exceed 5%. At such concentrations, $CHCl_3$ had no effect on reaction rates. The ligand exchange was initiated by placing the solutions into the compartment of a spectrophotometer thermostated at 58.5–96 °C. The reactions were accompanied by an increase in absorbance at 380–460 nm, and final spectra were similar to those of **5** under the same conditions. Yields were usually not less than 90%. In most cases kinetic curves were biphasic. The first faster process, where the absorbance decreased, was completed within 5 min, followed by a gradual increase in absorbance due to accumulation of final products. The first step is probably because of conversion of the dimers into the corresponding monomeric complexes. An attempt was made to follow this process by ^1H NMR, but his was not successful. Only the slower parts of the kinetic curves were analyzed graphically by plotting log $[A_\infty/(A_\infty - A)]$ against time, where A and A_∞ are absorbances at time t and $t = \infty$, respectively. Linearity was commonly observed for 2–3 half-lives, and pseudo-first-order rate constants (k_{obsd}) were calculated from the slopes of these plots. Slower reactions were analyzed by the Guggenheim method. The rates of reaction 3 were measured in a similar way except absorbance was registered at 600 nm. The Eyring equation was used to evaluate ΔH^* and ΔS^* from the rate constants.

The kinetics of direct palladium of 2-phenylpyridine by palladium(II) acetate in acetic acid was measured as previously described for *N*,*N*-dimethylbenzylamine.[10]

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Registry No. **1a**, 103903-71-5; **1b**, 103903-70-4; **1c**, 103958-60-7; **1d**, 103903-72-6; **1e**, 103903-73-7; **1f**, 103903-74-8; **1g**, 107035-13-2; **2**, 106988-36-7; **3**, 106988-35-6; **4a**, 65495-21-8; **4b**, 4052-88-4; **4c**, 103-83-3; **4f**, 15184-96-0; **4g**, 772-54-3; **5**, 107035-14-3; **6**, 107035-15-4; **7**, 106977-06-4; **7**·HCl, 107009-82-5; **8a**, 106977-07-5; **8b**, 106977-08-6; **9a**, 106977-05-3; **9b**, 106977-09-7; **10c**, 106987-66-0; **10g**, 106977-10-0; $Pd^{II}(OAc)_2$, 3375-31-3; PP, 1008-89-5; AB, 103-33-3; D_2, 7782-39-0; (3,4-dimethoxybenzyl)amine, 5763-61-1; 4-nitrobenzaldehyde, 555-16-8.

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