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Structure and Reactivity of *trans*-Bis[2-(2-chloroethyl)pyridine]palladium Chloride (1). A Study on the Elimination Reaction of 1 and 2-(2-Chloroethyl)pyridine Induced by Quinuclidine in Acetonitrile

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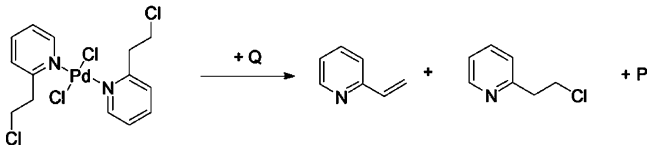

The *trans*-bis[2-(2-chloroethyl)pyridine]palladium chloride (**1**) has been prepared and structurally characterized by X-ray spectroscopy and computational study. The X-ray structure of **1** is consistent with the trans isomer (with respect to Pd). The NMR spectrum and the computational study are in agreement with an equilibrium in CD_3CN solution between two isomers of the trans structure. The reaction of the palladium complex with quinuclidine in CH_3CN, at 25 °C, leads to competing elimination and displacement reactions with formation of vinylpyridine and chloroethylpyridine in a ratio of 1.5:1. However, the rate constant for formation of uncoordinated (vinyl)pyridine monitored by HPLC ($k_Q^{HPLC} = 2.3 \times 10^{-3}$ M^{-1} s^{-1}) is nearly 3 times slower than a rate constant monitored spectrophotometrically ($k_Q = 6.5 \times 10^{-3}$ M^{-1} s^{-1}). This suggests that the initial product of elimination is a palladium complex of vinylpyridine and that displacement from this complex is partially rate determining in the formation of the uncoordinated product. A study by UV spectroscopy at $\lambda = 295$ nm of *trans*-bis[2-(2-chloroethyl)pyridine-d_2]palladium chloride with quinuclidine (Q) has shown the presence of a significant primary kinetic isotope effect, $k_Q(H)/k_Q(D) = 1.8$, for the elimination reaction within the Pd complex, **1**. The second-order rate constant for the β-elimination reaction from 2-(2-chloroethyl)pyridine induced by quinuclidine in CH_3CN at 25 °C is $k_Q^{FREE} = 6.2 \times 10^{-6}$ M^{-1} s^{-1}. It can be observed as a significant activation (about 3 orders of magnitude) of the β-elimination reaction within the complex **1** with respect to the free 2-(2-chloroethyl)pyridine. The possible mechanism in agreement with these results is discussed.

Introduction

In previous studies,[1−5] we have shown that a large activation of the β-elimination reactions, in systems activated by a pyridine ring, can be observed because of electrophilic catalysis at the nitrogen atom of the pyridine ring (Scheme 1). The proton activating factor (PAF) is defined[6] as the ratio of the rate constants for the nitrogen protonated substrate and the nitrogen unprotonated substrate, and the value of PAF for the acetohydroxamate-induced β-elimination reaction[2] with 2-(2-chloroethyl)pyridine, **2**, is 1.38×10^5. It was shown[5] that methylation of the pyridine ring in the same systems consistently produces large activation of the process (MethylAF = 6.88×10^5). Activation by Zn^{2+} is also large, for substrate *N*-[2-

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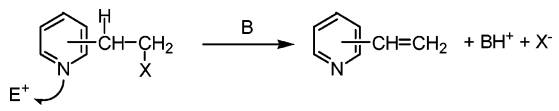

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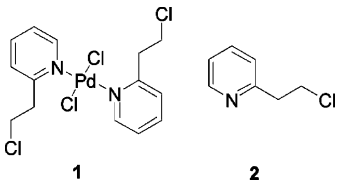

(2-pyridyl)ethyl]quinuclidinium,[7] with the metal activating factor (MetAF) being 8.1×10^4.

In this work, we have studied the comparison in reactivity between free **2** and Pd-bonded **2** within the Pd planar square complex *trans*-bis[2-(2-chloroethyl)pyridine]-palladium chloride, **1** (Scheme 2); the structure of **1** has been determined by X-ray spectroscopy, NMR study, and theoretical calculations (see Experimental Section).

Chemistry of the Pd complex is important in several applied fields,[8,9] and the quantification of the activation of the β-elimination reaction within a Pd complex adds relevant information to our previous studies.

Results and Discussion

A. Structural Characterization. The X-ray structure of **1** is consistent with the trans isomer (with respect to Pd; Scheme 2). However, a solution of **1** in CD_3CN presents an NMR spectrum consistent with the presence of an equilibrium between two isomers in a ratio of 1:0.8 (25 °C). We assume that this mixture is related to two rotamers of the trans structure (with respect to Pd), involving the chloroethyl system on the same side (trans−cis) or on the opposite side (trans−trans). In fact, an NMR study excludes the possibility of the cis−trans isomer from the NOE analysis (lack of dipolar interactions between CH_2Cl hydrogens and the 5,6-aromatic hydrogens of the pyridine ring). The cis−cis isomer should be sterically hindered. The presence of the two rotamers is in agreement with similar reported[10] compounds. An ^{1}H-EXSY study between 5 and 30 °C gave values of $\Delta H^{\ddagger} =$ 13.7 kcal/mol and $\Delta S^{\ddagger} = 12$ kcal/mol K for the conversion of the two isomers. The ΔH_0 is 0.9 kcal/mol.

To further confirm the nature of the two isomers observed in solution, DFT (B3PW91) calculations on **1** have been carried out. Three of the four possible geometries, defined by the respective positions of the pyridine rings (cis−trans) and by the relative position of the chloroethyl chains (cis−trans), were considered (Figure 1). The cis−cis geometry was not calculated because the steric strain between the two chloroethyl chains would be prohibitive. The most stable structure, **1tt**, corresponds to the geometry obtained in the X-ray crystallography study. The agreement between the calculated and experimental geometrical parameters is very good (see caption of Figure 1). The rotamer **1tc** with trans pyridyl rings but with cis chloroethyl chains is computed to be less stable by 1.8 kcal/mol, in very good agreement with the experimental value determined from NMR spectroscopy. As expected, the cis geometry of the two pyridyl rings is computed to be less stable and the isomer **1ct** lies at 13.6 kcal/mol above **1tt**, ruling out any presence of the latter in solution.

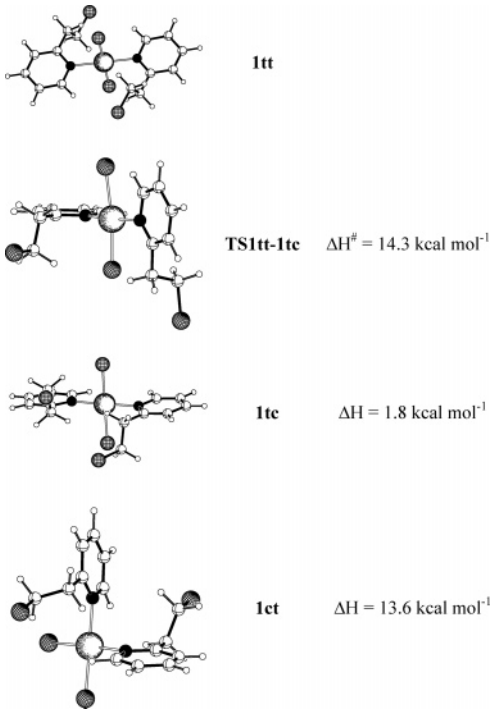

FIGURE 1. B3PW91 optimized geometries of the three isomers, **1tt**, **1tc**, and **1ct**, and of the transition state, **TS1tt**−**1tc**, connecting **1tt** and **1tc**. Selected geometrical parameters (distances in Å, angles in degrees, experimental values in parentheses) for **1tt**: Pd−N = 2.038 (2.029), Pd−Cl = 2.329 (2.298), Cl−Pd−N = 89.9 (88.8), and C−N−Pd−Cl = 79.4 (70.6).

The transition state, **TS1tt**−**1tc**, connecting the two trans isomers has been optimized, and it presents a perpendicular pyridyl ring (Figure 1). The transition-state vector consists of the rotation of this pyridyl ring, and the calculated enthalpy of this transition state (TS) (14.3 kcal/mol) is in excellent agreement with the experimental value of 13.7 kcal/mol. The calculations are thus in full agreement with the description of the observed complexes in solution as the two rotamers of the trans isomer.

B. Reaction Products and Kinetic Study. To identify the possible products of the reaction between **1** and quinuclidine, Q, in CD_3CN, an NMR tube containing 4.5 mg of **1** in 0.6 mL of CD_3CN and 0.1 M Q was left to react at 25 °C, and by recording the ^{1}H NMR spectrum, it was possible to observe the disappearance of the signals at $\delta = 4.23-4.47$ ppm related to the CH_2-CH_2-Pd system or the disappearance of the related aromatic signals. It was clear that the formation of 2-vinylpyridine unbonded with Pd by the characteristic signals at $\delta =$

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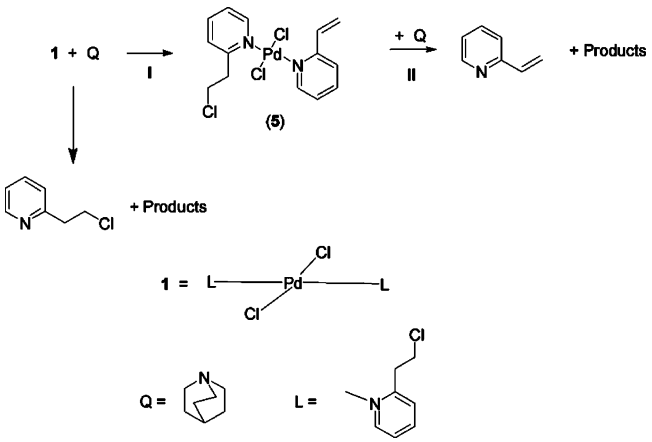
SCHEME 3



5.47 (d), 6.24 (d), and 6.84 (dd) ppm. It was also possible to observe the presence of 2-(2-chloroethyl)pyridine unbonded to Pd by comparison with the spectrum of a pure sample ($\delta = 4.00$ ppm (t); CH_2-Cl). After 2.5 h, the molar ratio of 2-vinylpyridine/2-(2-chloroethyl)pyridine, calculated by integration of signals, was 1.5:1, and from the reaction, 60% of 2-vinylpyridine and 40% of 2-(2-chloroethyl)pyridine were produced. The UV kinetic profiles showed a leveling-off after 2.5 h; however, a slow decrease of the amount of **2** was observed after this time, but this process was too slow to affect reactions of the coordinated species.

The reactivity of the system **1** + Q in CH_3CN, at 25 °C, was evaluated by following spectrophotometrically the increase in absorbance at $\lambda = 295$ nm due to products formation. The reaction followed good pseudo-first-order kinetics (excess of Q) up to at least 80% of the reaction. This result shows that the two rotamers of **1** have very similar reactivities or are rapidly interconverted on the time scale of the reaction. The average value of the second-order rate constant k_Q is 6.5×10^{-3} M^{-1} s^{-1}. A kinetic study by HPLC (UV-detector; $\lambda = 280$ nm), following the formation of 2-vinylpyridine (pseudo-first-order; [Q] = 0.1−0.17 M), gave a value of $k_Q^{HPLC} = 2.3 \times 10^{-3}$ M^{-1} s^{-1}. The difference between k_Q values obtained with the two different techniques could be explained considering the mechanism proposed below; following the reaction by UV spectroscopy at $\lambda = 295$ nm, both the Pd-bonded and free 2-vinylpyridine can be observed, whereas by HPLC, only free 2-vinylpyridine is detected. It follows that there must be a sequence of steps, and the expulsion of 2-vinylpyridine from **5** (see Scheme 3) is partially rate determining. A full kinetic analysis is not possible, owing to the probable variations of the rate constants of the various possible intermediates in the reaction paths.

To check if C−H bond breaking for the elimination reaction from **1** is rate determining, the substrate 2-(2-chloroethyl)pyridine-d_2, **3**, was synthesized and the related Pd complex was prepared (*trans*-bis[2-(2-chloroethyl)-pyridine-d_2]palladium chloride, **4**) following the same procedure as that used for the undeuterated system **1**. A kinetic study, following spectrophotometrically at $\lambda = 295$ nm the products formation from **4** in pseudo-first-order conditions ([Q] = 0.05−0.2 M), gave a second-order rate constant $k_Q(D) = 3.6 \times 10^{-3}$ M^{-1} s^{-1}. An NMR study of the products of the reaction from **4** + Q (0.1 M) in CD_3CN, at 25 °C, showed, after 5 h, the formation of 2-vinylpyridine-d_1 and 2-(2-chloroethyl)pyridine-d_2 in a ratio of alkene/chloride 0.54:1.

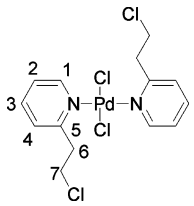
The fact that a study of the initial rate of the elimination reaction from free 2-(2-chloroethyl)pyridine (in CH_3CN at 25 °C induced by Q) gave a value of the second-order rate constant, $k_Q^{FREE} = 6.2 \times 10^{-6}$ M^{-1} s^{-1}, is relevant. This value is significantly lower than the one observed for the elimination reaction from **1**, and this result allows excluding that the process from free 2-(2-chloroethyl)pyridine can be significant in the elimination reaction from **1**.

The mechanistic interpretation of these results is complicated by the presence of two molecules of **2** (2-(2-chloroethyl)pyridine) bonded to Pd. The mechanism proposed is shown in Scheme 3; in fact, the intermediate **5** could give a second elimination or an exchange reaction with Q. The overall system is therefore complicated, but presumably, the reactivity of **5** in the elimination or substitution reactions is similar to that of **1**.

Step I is the elimination reaction of HCl by a direct attack of Q on **1**; this step must be partially rate determining owing to the presence of the primary deuterium isotope effect, $k_Q(H)/k_Q(D) = 1.8$ (this is an overall isotope effect that refers to the two overall rate constants $k_Q(H)$ and $k_Q(D)$; the term $k_Q(H)/k_Q(D)$ for the elimination reaction should be calculated from the proper rate constants, but the complexity of this system does not allow the complete dissection of the various parameters). Step II is the release of free 2-vinylpyridine, and this step must also be partially rate determining because the second-order rate constant k_Q obtained by following the formation of 2-vinylpyridine by HPLC is lower than the one obtained following product formation spectrophotometrically at $\lambda = 295$ nm. It is possible that at $\lambda = 295$ nm there is the absorption of both the Pd-bonded and free 2-vinylpyridine. In fact, an experiment following an NMR tube reaction with **1** and Q in CD_3CN, at 25 °C, at various times, showed, together with the formation of the signals related to free 2-vinylpyridine, the formation of signals at $\sigma = 6$ ppm that can be related to the vinylic hydrogens of Pd-bonded 2-vinylpyridine. This signal disappears during the reaction. We have not determined the structures of the products containing Pd (probably $PdCl_2Q_2$) because we have focused the study on the formation of 2-vinylpyridine (by elimination reaction) or free 2-(2-chloroethyl)pyridine.

The first elimination reaction of HCl must occur within the **1** complex because the rate constant for the β-elimination induced by Q from *2-(*2-chloroethyl)pyridine is $k_Q^{FREE} = 6.2 \times 10^{-6}$ M^{-1} s^{-1}. This rate constant is much lower than the one observed with **1**, so it can be excluded from the reaction of free 2-(2-chloroethyl)pyridine. The second-order rate constant (spectrophotometrically determined at $\lambda = 295$ nm) is about 1000 times larger than that of free 2-(2-chloroethyl)pyridine in the same reaction conditions (Q/CH_3CN, 25 °C). This activation can be compared[2] with that by protonation of the nitrogen atom of the pyridine ring of 2-(2-chloroethyl)pyridine ($CH_3CONHO^-/CH_3CONHOH$, H_2O, $\mu = 1$ M KCl, 50 °C), with the proton activating factor (PAF) being 1.38×10^5. Also, we have previously[5] reported the activation for the same process by methylation of the N atom, with the methyl activating factor (MethylAF) being 6.88×10^5 (OH^-/H_2O,

SCHEME 4



μ = 1 M KCl, 25 °C). We have also showed[7] that in a related system with a leaving group quinuclidine (*N*-[2-(2-pyridyl)ethyl]quinuclidinium) the activation with Zn^{2+} (by metal ion interaction with the N atom of the pyridine ring) is 8.1×10^4 (OH^-/H_2O, μ = 1 M KCl, 50 °C).

It should be considered that the mechanism of the elimination reaction from **1** can be E2 concerted or E1cb; in fact, it is not possible to distinguish between these two possibilities in this case. In previous studies,[1,2,5,7] it was shown that systems where the pyridine ring is protonated or interacts with a metal ion react by the E1cb mechanism.

It should be finally noted that the mechanism of Scheme 3 is related to two parallel processes, so the calculation for the second-order rate constant should take this fact into account. However, in this case, the second-order rate constant would be a combination of constants so we prefer to evaluate the overall activation due to Pd complexation.

Experimental Section

Materials. Quinuclidine, CH_3CN (HPLC grade), Na_2PdCl_4, D_2O, DMSO-d_6, and CD_3CN were commercial materials. 2-(2-Chloroethyl)pyridine, **2**, was prepared according to a previously described procedure.[2] One- and two-dimensional ^1H NMR spectra were recorded on 200 and 400 MHz spectrometers. Referencing is relative to TMS.

***trans*-Bis[2-(2-chloroethyl)pyridine]palladium Chloride (1).** A mixture of Na_2PdCl_4 (0.31 g, 1.05 mmol), 2-(2-chloroethyl)pyridine (0.3 g, 2.19 mmol), and acetone (20 mL) was left to react under nitrogen and magnetic stirring for 15 h. The solvent was evaporated under reduced pressure, and the residue was washed several times with CH_2Cl_2. The CH_2Cl_2 solution was taken to dryness, and the solid residue was washed with *n*-hexane and crystallized from CH_2Cl_2/*n*-hexane at room temperature. Mp: 195−199 °C dec. ^1H NMR (CD_2Cl_2, 302.6 K, 400.13 MHz, J in Hz, Scheme 4): δ 4.27 (t, $^3J_{H6^a-H7^a}$ = 6.8, H6^a), 4.32 (t, $^3J_{H6^b-H7^b}$ = 6.8, H6^b), 4.40 (t, $^3J_{H7^a-H6^a}$ = 6.8, H7^a), 4.50 (t, $^3J_{H7^b-H6^b}$ = 6.8, H7^b), 7.38 (ddd, $^3J_{H2-H1} = {}^3J_{H2-H3}$ = 7.7, $^4J_{H2-H4}$ = 1.4, H2), 7.47 (d, $^3J_{H4-H3}$ = 7.8, H4), 7.84 (ddd, $^3J_{H3-H2} = {}^3J_{H3-H4}$ = 7.7, $^4J_{H3-H1}$ = 1.4, H3), 8.94 (d, $^3J_{H1^b-H2}$ = 7.7, H1^b), 9.10 (d, $^3J_{H1^a-H2}$ = 7.7, H1^a). Anal. Calcd for $C_{14}H_{16}N_2Cl_4Pd$: C, 36.51; H, 3.50; N, 6.08. Found: C, 36.35; H, 3.44; N, 6.03.

To obtain the thermodynamic parameter of the equilibrium between the two isomers, ^1H NMR experiments were conducted at different temperatures in the range 278.9−302.6 K.

The values of the equilibrium constants at different temperatures are $K^{278.9}$ = 1.428 ± 0.001, $K^{291.0}$ = 1.333 ± 0.001, and $K^{302.6}$ = 1.266 ± 0.001. The enthalpy energy for the equilibrium was derived by plotting K as a function of $1/T$, and the value is $\Delta H_{ab}° = 0.86 \pm 0.2$ kcal/mol.

2-(2-Hydroxyethyl)pyridine-d_2 (6). 2-(2-Hydroxyethyl)-pyridine dissolved in D_2O/DSMO-d_6 (40:60, v/v) and 0.67 M OD^- was kept at 58 °C, and the deuteration, to form **6**, was checked by NMR. After 288 h, the solution was poured in DCl/D_2O and extracted with Et_2O. The organic layer was dried over Na_2SO_4, and then the solvent was removed by rotary evaporation to give 2-(hydroxyethyl)pyridine-d_2. The percent of deuteration was 97%, assigned by NMR and gas-mass analysis.

2-(2-Chloroethyl)pyridine-d_2 (3) was prepared from **6** according to a previously described procedure.[2] The percent of deuteration was 97%.

***trans*-Bis[2-(2-chloroethyl)pyridine-d_2]palladium chloride (4)** was prepared as described previously for complex **1**. The percent of deuteration was 97%.

NMR Measurements. A. T1 Measurements. The longitudinal relaxation times for the ^1H nuclei were measured by the standard inversion recovery method on solutions of complex *trans*-bis[2-(2-chloroethyl)pyridine]palladium chloride in methylene chloride-d_2 at 302.6 K. A total of 15 experiments, having a relaxation delay ranging from 0.001 to 20 s, were acquired, each of them consisting of 16 scans. The total relaxation delay between two consecutive scans was 40 s. All single experiments were Fourier transformed. Frequency domain spectra were processed with a standard T1/T2 software package available on spectrometers to extract the relaxation parameters. Important T1 values are 4.0 s for H1^a, 4.0 s for H1^b, 3.1 s for H3, 3.0 s for H4, 2.9 s for H2, 1.4 s for H7^b, 1.4 s for H7^a, and 1.1 s for H6^a and H6^b.

B. EXSY and NOE Measurements. Quantitative EXSY and NOE measurements were carried out in CD_2Cl_2 because of the higher solubility of complex **1** in this solvent; however, qualitative measurements in CD_3CN gave similar results. The 1H-NOESY[11] NMR experiments were acquired by the standard three-pulse sequence or by the PFG version.[12] The number of transients was 64, the number of data points was 256, and the "nt" values were 48. Quantitative ^1H-NOESY NMR experiments were carried out with a relaxation delay of 12 s and a mixing time of 0.4 s. The ^1H-NOESY NMR experiments were conducted at different temperatures in the range 278.9−302.6 K. The auto- and cross-peak volumes were determined using XWinNMR Bruker software after phase and baseline corrections in both dimensions. The volume uncertainty was estimated by determining the volume of noise signals in a "blank space" of the spectrum. The use of 2D-NOESY for chemical kinetics was first proposed by Jeneer and Ernst[11] and was called 2D-EXSY (exchange spectroscopy). 2D-EXSY spectra arise from noncoherent magnetization transfer that can take place by exchange of nuclei between nonequivalent sites and avoids the cross relaxation between sites with different resonance frequencies. 2D-EXSY can measure a rate constant, k, on the order of $10^{-1}-10^2$ s^{-1}.[13] The upper limit is governed by the difference in chemical shift ($k \ll \omega_a - \omega_b$), and the lower limit is dictated by the relaxation time T_1 ($k \sim 1/T_1$). For an uncoupled system of spins A and B, with the simplification of equal spin−lattice relaxation time, the rate constant k_{obs} is related to the mixing time τ_m by eq 1:

$$\ln\left(\frac{r+1}{r-1}\right) = k_{obs}\tau_m \qquad (1)$$

In eq 1, the term r is related to the volumes of the cross and diagonal signal (I) and to the molar fraction of the species A and B (X) by eq 2:

$$r = \frac{4X_aX_b(I_{aa} + I_{bb})}{(I_{ab} + I_{ab})} - (X_a - X_b) \qquad (2)$$

Because the system is in equilibrium (A ⇄ B), it is possible to determine the direct k_{a-b} and the reverse k_{b-a} rate constants by eqs 3 and 4:

$$k_{a-b} = X_b k_{obs} \qquad (3)$$

$$k_{b-a} = X_a k_{obs} \qquad (4)$$

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The rate constants k_{obs}, k_{ab}, and k_{ba} could be obtained by applying directly eqs 1, 3, and 4, respectively. The rate constants of exchange between the two isomers for complex *trans*-bis[2-(2-chloroethyl)pyridine]palladium chloride in methylene chloride-d_2 at 278.9, 291.0, and 302.6 K were determined by detecting the H1^a and H1^b resonances. The values of the rate constants at different temperatures are $k_{obs}^{278.9} = 1.6 \pm 0.1$, $k_{ab}^{278.9} = 0.7 \pm 0.1$, $k_{ba}^{278.9} = 0.9 \pm 0.1$, $k_{obs}^{291.0} = 4.7 \pm 0.3$, $k_{ab}^{291.0} = 2.0 \pm 0.3$, $k_{ba}^{291.0} = 2.7 \pm 0.3$, $k_{obs}^{302.6} = 9.5 \pm 0.5$, $k_{ab}^{302.6} = 4.2 \pm 0.5$, and $k_{ba}^{302.6} = 5.3 \pm 0.5$ s^{-1}. The thermodynamic parameters of activation for the exchange process were derived from Eyring plots and are $\Delta H_{ab}^{\ddagger} = 14 \pm 1$ kcal/mol, $\Delta S_{ab}^{\ddagger} = 12 \pm 4$ kcal/mol K, $\Delta H_{ba}^{\ddagger} = 13 \pm 1$ kcal/mol, and $\Delta S_{ba}^{\ddagger} = 10 \pm 4$ kcal/mol K.

Kinetic Studies. Kinetics of the reaction from **1** with quinuclidine in CH_3CN at 25 °C was followed spectrophotometrically at $\lambda = 295$ nm. The concentration of **1** was [**1**] = $1 \times 10^{-4} - 2 \times 10^{-4}$ M, and [Q] = 0.05−0.2 M. The pseudo-first-order rate constant k_{obs} (s^{-1}) was calculated as the slope of a plot, $\ln(A_\infty - A_0)/(A_\infty - A_t)$, against time. Good linearity was observed up to at least 80% of the reaction. The kinetics of **1** with quinuclidine was also followed by HPLC in isocratic conditions, eluent CH_3CN/ H_2O 80:20, by monitoring the 2-vinylpyridine formed with a UV detector at 280 nm. Kinetics of the elimination reaction from 2-(2-chloroethyl)pyridine, **2**, with quinuclidine in CH_3CN at 25 °C was followed by initial rates,[2] monitoring the formation of 2-vinylpyridine by UV spectroscopy at $\lambda = 278$ nm.

X-ray Crystallography. A single crystal of *trans*-bis[2-(2-chloroethyl)pyridine]palladium chloride, **1**, suitable for X-ray diffraction (a yellow block with approximate dimensions of 0.20 × 0.10 × 0.06 mm), was obtained as described previously. Data were collected on a (CCD areal) diffractometer using Mo Kα graphite monochromated radiation ($\lambda = 0.71073$ Å), and ω scans and the frame data were acquired with the CRYSALIS (CCD 169) software. The crystal to detector distance was 65.77 mm. The frames were processed using the CRYSALIS (RED 169) software to give the *hkl* file, corrected for scan speed, background, Lorentz, and polarization effects. Standard reflections, measured periodically, showed no apparent variation in intensity during data collection, and so, no correction for crystal decomposition was necessary. The data were collected for absorption using the SADABS[14] program.

The Laue symmetry was determined to be 2/*m*. The dimensions of the cell yielded a calculated density of 1.78 g cm^{-3} ($Z = 2$ and fw = 460.49) that was confirmed by the experimental value of 1.80(3) g cm^{-3}. The observed systematic absences were consistent with the monoclinic space group $P2_1/n$ (No. 14). The data were collected at room temperature. The lattice parameters found were $a = 7.641$ (5), $b = 14.915$ (5), $c = 7.965$ (5) Å, $\beta = 108.52$ (5), and $V = 860.7$ (9) Å^3. Data were collected to $2\Theta_{max}$ of 56.68° in the index range $-7 \le h \le 9$, $-19 \le k \le 19$, and $-10 \le l \le 10$ with a total of 5243 collected reflections, of which 185 were rejected, and after merging, 1989 were unique (R(int) = 0.0263).

The structure was solved by the direct method using the Sir97[15] program and refined by the full-matrix least-squares method F^2 using SHELXL-97,[16] WinGX[17] version. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added at the calculated positions and refined using a riding model.

The final cycle of full-matrix least-squares refinement against $|F|^2$ was based on 1591 observed reflections [$F_0 > 4\sigma(F_0)$] and 100 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.0377$, $R_w = 0.0584$, and GOF = 1.079.

The crystal structure is a monomeric molecule containing Pd(II) coordinated, in a square planar environment, by two trans chlorides and two nitrogen atoms in the pyridine rings. In the complex, the palladium center is coplanar with the four coordinating atoms (the N−Pd−N and the Cl−Pd−Cl angles are 180°). The X-ray diffraction spectrum of the complex corroborates the presence of a unic confomer in the solid state, in which the two carbon chains are in an anti disposition.

CCDC 244649 contains the supplementary crystallographic data for this paper.

The atomic coordinates for these structures have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by email at data_request@ccdc.cam.ac.uk, or by contacting the Director, The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

Computational Details. All calculations were performed with the Gaussian 98 set of programs[18] within the framework of hybrid DFT B3PW91.[19] The palladium[20] and chlorine[21] atoms were represented by the relativistic effective core potential (RECP) from the Stuttgart group and their associated basis set and augmented by an f (Pd)[22] or a d (Cl)[22] polarization function. A 6-31G(d,p) basis set[23] was used for all the remaining atoms of the molecules studied (C, H, and N). The geometry optimizations were performed without any symmetry constraints, and the nature of the stationary point was confirmed to be a minimum by analytical frequency calculations. The energy differences between the optimized structures were enthalpy values, as obtained after frequency calculations with Gaussian 98.

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Note Added after ASAP Publication. The ratio of vinylpyridine and chloroethylpyridine was incorrect in the Abstract in the version published ASAP November 18, 2005; the corrected version was published ASAP November 22, 2005.

Supporting Information Available: X-ray crystallographic information including a CIF table for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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