(which arose from the attack of ClF on the methyl groups) were found. Chlorine, SOF_2 (resulting from hydrolysis of SF_4), and CF_3NCl_2 were identified by molecular weight and infrared spectra, respectively.

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Menschutkin Type Amine Alkylations Involving Ethyl Transfer from Platinum(II) Chelate Complexes of *o*-(Diphenylphosphino)thiophenetole

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The compound *o*-$Ph_2PC_6H_4SEt$ has been used as a chelate ligand to synthesize the platinum(II) complexes *cis*-[Pt(*o*-$Ph_2PC_6H_4SEt)_2](BF_4)_2$ and *cis*-[Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt$)]BF_4. The complex *cis*-Pt(*o*-$Ph_2PC_6H_4SEt)_2^{2+}$ reacts with amines to give *cis*-Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt)^+$ and then Pt(*o*-$Ph_2PC_6H_4S)_2$. The rate laws are first order in both platinum complex and amine. In acetonitrile solvent the rate constants and thermodynamic parameters (ΔH^* and ΔS^*) have been obtained for the first reaction step with dibenzylamine, butylamine, dibutylamine, tributylamine, diethylamine, and triethylamine. In DMF solvent the analogous data have been measured for the second step by using butylamine, dibutylamine, and tributylamine. The ΔH^* (13–18 kcal mol^{-1}) and ΔS^* (−12 to −31 cal K^{-1} mol^{-1}) values are in the range expected for a Menschutkin type S_N2 alkylation reaction. The reaction rates decrease in the amine sequence primary > secondary > tertiary, but for benzylamines the rate only differs by a factor of 5 from benzylamine to tribenzylamine.

Introduction

Methyl transfer is a topic of considerable significance in biological chemistry. One of the most important compounds that has been implicated in such reactions is *S*-adenosylmethionine.[1] This compound is widely involved as an in vivo carbonium ion type methylating agent. Carbonium ion alkylation by *S*-adenosylmethionine is an important route for the methylation of ethanolamine and noradrenaline, and the methylation of DNA may eventually be proven to be of significance to cancer mechanisms.[2]

Methyl transfer from methylthioether groups complexed to transition-metal ions is a well-documented reaction,[3] and we have recently shown that such a transfer to thiocyanate or iodide ion or to benzylamine can be explained on the basis of a S_N2 type nucleophilic displacement at the electrophilic methyl carbon.[4] These previous rate data were collected with a complex having a methylthioether moiety coordinated to palladium(II), and the reaction was complicated by the presence of a side reaction which resulted in substitution of the complexed methylthioether ligand by the incoming nucleophile. Since the electrophilicity orders for carbon and palladium(II) appear to be closely similar,[5] it is difficult to achieve selectivity to attack at carbon rather than at palladium(II) by judicious choice of nucleophile. In this paper we report that we can achieve this regioselectivity by complexation of the thioether group to the kinetically inert platinum(II) center, rather than with the labile palladium(II) ion. Finally, we use our data to compare the reactivity of coordinated thiomethyl and thioethyl ligands.

Experimental Section

The compound *o*-(diphenylphosphino)thioanisole (*o*-$Ph_2PC_6H_4SMe$) and the complexes [Pd(*o*-$Ph_2PC_6H_4SMe)_2](BF_4)_2$ and Pd(*o*-$Ph_2PC_6H_4S)_2$ were prepared by published procedures.[3] Sodium tetrachloropalladate(II) and potassium tetrachloroplatinate(II) were purchased from Johnson Mathey, Inc. The solvents DMF and CH_3CN used in the kinetic measurements were spectral grade purity from Aldrich Chemical Co. These solvents were dried over phosphorus pentoxide in the manner proposed by Burfield.[6] Triethylamine and tributylamine were purchased from Matheson Coleman and Bell; benzylamine, butylamine, and dibutylamine were purchased from Aldrich. All amines were dried over 4 Å molecular sieves prior to distillation. Tetraethylammonium bromide was purified by recrystallization from a mixture of dichloromethane and diethyl ether. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer Model 683 spectrophotometer. ^{31}P NMR data were collected on a JEOL FX 60 FTNMR spectrometer operating at 24.15 MHz and referenced to external trimethyl phosphite (δ 140). ^1H NMR data were collected on a Varian EM 390 spectrometer operating at 90 MHz and referenced to internal Me_4Si. $CDCl_3$ was purchased from Aldrich, and CD_3CN from Stohler Isotope Co. Photochemical experiments were carried out by using a 200-W mercury lamp purchased from Illumination Industries enclosed in a fan-cooled Ealing Corp. housing. A Pyrex glass cutoff filter ($\lambda > 320$ nm) was used. Electronic absorption spectra were measured on a Hewlett-Packard Model 8451A diode-array spectrometer. Microanalyses were carried out by Galbraith Laboratories, Knoxville, TN. Conductivity measurements were made with an Industrial Instruments conductivity unit incorporating a cell with a platinized electrode.

***o*-(Diphenylphosphino)thiophenetole (*o*-$Ph_2PC_6H_4SEt$).** To a solution of *o*-aminobenzenethiol (100 g, 0.8 mol) in absolute alcohol (300 mL) was added sodium metal (18.4 g) in chunks while the temperature of the mixture was maintained at 0 °C with an ice bath. After completion of the reaction, ethyl iodide (125 g, 0.8 mol) was added from a dropping

(1) (a) Coward, J. K. In *The Biochemistry of Adenosylmethionine*; Salvatore, F., Borek, E., Zappia, V., Williams-Ashman, H. G., Schlenk, F., Eds.; Columbia University Press: New York, 1977; pp 127–144. (b) Stekol, J. N. In *Transmethylation and Methionine Biosynthesis*; Shapiro, S. K., Schlenk, F., Eds.; University of Chicago Press: Chicago, 1965; Chapter 14. (c) Lederer, E. In *The Biochemistry of Adenosylmethionine*; Salvatore, F., Borek, E., Zappia, V., Williams-Ashman, H. G., Schlenk, F., Eds.; Columbia University Press: New York, 1977; pp 89–126.

(2) Feinberg, A. P.; Vogelstein, B. *Nature (London)* **1983**, *301*, 89–92.

(3) (a) Lindoy, L. F.; Livingstone, S. E.; Lockyer, T. N. *Aust. J. Chem.* **1966**, *19*, 1391–1400. (b) Lindoy, L. F.; Livingstone, S. E.; Lockyer, T. N. *Inorg. Chem.* **1967**, *6*, 652–656. (c) Lindoy, L. F.; Livingstone, S. E.; Lockyer, T. N. *Aust. J. Chem.* **1967**, *20*, 471–478. (d) Livingstone, S. E.; Lockyer, T. N. *Aust. J. Chem.* **1974**, *27*, 259–267. (f) Eller, P. G.; Riker, J. M.; Meek, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 3540–3548. (g) Meek, D. W. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 235–238. (h) Boorman, P. M.; Chivers, T.; Mahadev, K. N. *J. Chem. Soc., Chem. Commun.* **1974**, 502–503. (i) Boorman, P. M.; Chivers, T.; Mahadev, K. N. *Can. J. Chem.* **1977**, *55*, 869–877. (j) Boorman, P. M.; Chivers, T.; Mahadev, K. N. *Can. J. Chem.* **1975**, *53*, 383–388. (k) Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 3386–3392. (l) Hiraki, K.; Fuchita, Y.; Murata, T. *Inorg. Chim. Acta* **1980**, *45*, L205–L206. (m) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *Organometallics* **1982**, *1*, 235–239.

(4) (a) Roundhill, D. M.; Beaulieu, W. B.; Bagchi, U. *J. Am. Chem. Soc.* **1979**, *101*, 5428–5430. (b) Roundhill, D. M.; Roundhill, S. G. N.; Beaulieu, S. B.; Bagchi, U. *Inorg. Chem.* **1980**, *19*, 3365–3373. (c) Benefiel, A.; Roundhill, D. M.; Fultz, W. C.; Rheingold, A. L. *Inorg. Chem.* **1984**, *23*, 3316–3324.

(5) Basolo, F.; Pearson, B. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967; pp 399, 417.

(6) Burfield, D. R.; Herlee, K.; Smithers, R. H. *J. Org. Chem.* **1977**, *42*, 3060–3065.

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funnel over a period of 40 min. The solution was heated at reflux for 90 min. The reaction mixture was added to water (2 L) to give the product as a yellow oil. The mixture was extracted with diethyl ether (6 × 100 mL) and the organic layer dried over $MgSO_4$. After removal of diethyl ether on a rotary evaporator, the oil was vacuum-distilled to give *o*-aminothiophenetole (101 g, 82% yield). To this compound was added aqueous hydrogen bromide (200 mL, 48%). The amine hydrobromide salt that precipitated was mechanically pulverized and the slurry cooled in an ice bath at 0 °C. A solution of sodium nitrite (45.5 g, 0.66 mol) in water (81 mL) was added to the slurry, and the temperature was maintained below 10 °C. A mixture of cuprous bromide (52 g) in aqueous hydrogen bromide (48 mL, 48%) was heated in a 1-L three-necked flask fitted with a distilling head and condenser, separatory funnel, and connection to a steam line. The brown diazonium mixture was added in four equal portions to the boiling solution of CuBr in HBr. After the addition was complete, concentrated hydrochloric acid (50 mL) was added and the mixture steam-distilled for 6 h. The separated organic layer was washed with aqueous sodium hydroxide (2 × 25 mL, 5%). Following extraction with diethyl ether the product was dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the yellow oil vacuum-distilled. To the formed *o*-bromothiophenetole (19 g) in dry diethyl ether (100 mL) was added *n*-butyllithium (48.6 mL, 1.8 M) over a period of 2 h while the temperature was maintained at 0 °C under a nitrogen atmosphere. Freshly distilled chlorodiphenylphosphine (15.7 mL, 0.088 mol) was added over a period of 3 h while the reaction mixture was maintained at 0 °C. The mixture was hydrolyzed with hydrochloric acid (70 mL, 0.2 N). The organic layer was separated and concentrated to give an oil. Trituration of the oil in ethyl alcohol gave a white solid that was recrystallized from hot ethyl alcohol. Yield: 23 g (74%). NMR: δ(H) 1.30 (CH_3), 2.97 (CH_2) (^3J(HH) = 7.2 Hz); δ(P) −15.0. Anal. Calcd for $C_{20}H_{19}PS$: C, 74.5; H, 5.94. Found: C, 74.2; H, 6.33.

***cis*-Bis(*o*-(diphenylphosphino)thiophenetole)platinum(II) Tetrafluoroborate (*cis*-[Pt(*o*-$Ph_2PC_6H_4SEt)_2$]$(BF_4)_2$).** A solution containing potassium tetrachloroplatinate(II) (131 mg, 0.32 mmol) and sodium tetrafluoroborate (1 g) in water (20 mL) was added via dropping funnel over a period of several minutes to a boiling solution containing *o*-(diphenylphosphine)thiophenetole (200 mg, 0.62 mmol) in acetone (35 mL). After the mixture was boiled for 5 min, the pink color faded and a white precipitate formed. After cooling, the filtered complex was washed with aqueous acetone and then diethyl ether. The compound was recrystallized from an acetonitrile/methyl alcohol mixed solvent. Yield: 368 mg (88%). Anal. Calcd for $C_{40}H_{38}B_2F_8P_2PtS_2$: C, 47.4; H, 3.78. Found: C, 47.5; H, 4.00. NMR δ(H) 1.30 (CH_3), 3.37 (CH_2), 3.70 (CH_2); δ(P) 40.3 (^1J(PtP) = 3105 Hz). Λ_M = 226 Ω^{-1} cm^{-1} mol^{-1} (2.2 × 10^{-4} M solution in CH_3CN at 25 °C).

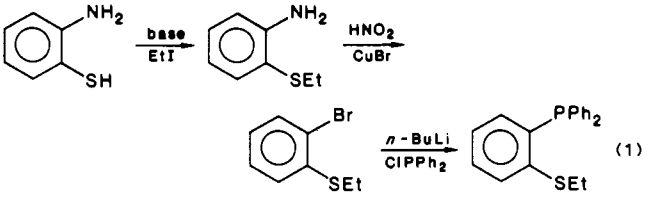
***cis*-(*o*-(Diphenylphosphino)benzenethiolato)(*o*-(diphenylphosphino)thiophenetole)platinum(II) Tetrafluoroborate (*cis*-[Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt$)]BF_4).** A solution containing potassium tetrachloroplatinate(II) (96 mg, 0.23 mmol) in water (15 mL) was added dropwise to a refluxing solution of *o*-(diphenylphosphino)thiophenetole (150 mg, 0.46 mmol) in acetone (30 mL). The solution was refluxed for 12 h and then filtered into a mixed solution containing sodium tetrafluoroborate (1 g) dissolved in a solvent containing equal portions of acetone and water. The solution was concentrated by boiling, and the filtered yellow complex was washed with water and aqueous ethyl alcohol. Yield: 140 mg (68%). The compound was recrystallized by adding benzene to a solution of the complex in chloroform. Anal. Calcd for $C_{38}H_{33}BF_4P_2PtS_2$: C, 50.8; H, 3.76. Found: C, 49.8; H, 3.86. The product is slightly contaminated with *cis*-[Pt(*o*-$Ph_2PC_6H_4SEt)_2$]$(BF_4)_2$. NMR: $\delta(P_A)$ 37.6, $\delta(P_B)$ 35.6 ($^1J(PtP_A)$ = 2735 Hz, $^1J(PtP_B)$ = 3271 Hz, $^2J(P_AP_B)$ = 10 Hz). Λ_M = 134 Ω^{-1} cm^{-1} mol^{-1} (4.7 × 10^{-4} M solution in CH_3CN at 25 °C).

Bis(*o*-(diphenylphosphino)thiophenetole)palladium(II) Tetrafluoroborate ([Pd(*o*-$Ph_2PC_6H_4SEt)_2$]$(BF_4)_2$). To a refluxing solution of *o*-(diphenylphosphino)thiophenetole (210 mg, 0.65 mmol) in acetone (20 mL) was added sodium tetrachloropalladate(II) (103 mg, 0.35 mmol) in water (10 mL) by means of a dropping funnel. After the resulting orange solution turned yellow, it was filtered into a solution of sodium tetrafluoroborate (0.5 g) in aqueous acetone (10 mL of a 40% solution). The solution was cooled to 0 °C, and the white solid that precipitated was filtered and washed with aqueous ethanol (50% solution). Yield: 75%. The complex was recrystallized from a mixed acetone and benzene solvent. Anal. Calcd for $C_{40}H_{38}B_2F_8P_2PtS_2$: C, 52.1; H, 4.38. Found: C, 51.9; H, 4.14. NMR: δ(H) 1.35 (CH_3), 3.35 (CH_2); δ(P) 54.1.

Kinetic Measurements. All kinetic measurements were performed in a closed quartz cell thermostated to ±0.5 °C by using a Brinkman Lauda Model T2 temperature controller. The cell was placed inside the cell compartment of a Hewlett-Packard Model 8451A diode-array spectrophotometer. The cell compartment was equipped with a magnetic stirrer, and the spectrophotometer was fitted with an external disk drive, plotter, and kinetics software package. The solution of the platinum complex was introduced into the quartz cell with a Sigma Corp. single-delivery 1000-μL pipet. The amine reagents were added directly to the stirred solution of the complex in either solution or pure form with a Pipetman P-200 microliter syringe. When pure amine was added, a density to weight conversion was used to calculate the amine concentration. The absorbance vs. time curves, monitored at 362 nm for reactions with *cis*-Pt(*o*-$Ph_2PC_6H_4SEt)_2^{2+}$ in CH_3CN and at 396 nm for reactions with *cis*-Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt)^+$ in DMF, were obtained under pseudo-first-order conditions in the presence of a large excess of amine. For data collected with Et_4NBr present in DMF solution the ionic strength was held constant by adding a large excess of this compound or $NaClO_4$. The ln (absorbance) plots were linear in all cases for a minimum of 3 half-lives, and the slopes obtained from the $-\ln(A_\infty - A_t)$ plots were determined from least-squares treatment of the data. Typically, between 30 and 120 data points defined each line, and the least-squares data treatment estimated the errors in the slopes.

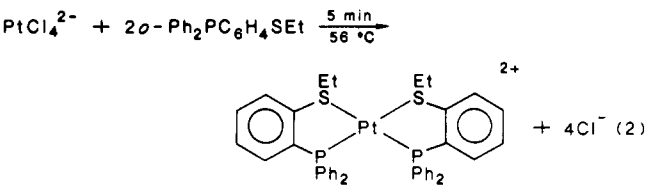
Results and Discussion

Synthesis. The compound *o*-$Ph_2PC_6H_4SEt$ has been prepared by a procedure similar to that previously used for *o*-$Ph_2PC_6H_4SMe$. The reaction sequence, outlined in eq 1, involves



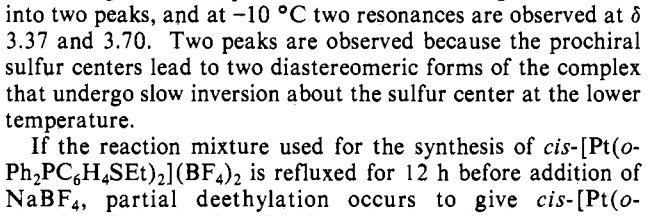
(1)

S-ethylation of *o*-$Ph_2PC_6H_4SH$, followed by a Sandmeyer replacement of the amine functionality by bromide, and final replacement of the bromo group by the diphenylphosphino moiety. The compound reacts with $PtCl_4^{2-}$ in the presence of tetrafluoroborate ion to give the bis chelate complex *cis*-[Pt(*o*-$Ph_2PC_6H_4SEt)_2$]$(BF_4)_2$ (eq 2). The observed value of 3105 Hz



for ^1J(PtP) correlates with a cis stereochemistry for the complex.[7] Coordination of the thioether moiety is confirmed by the downfield shift of the methylenic hydrogens. At 25 °C in CD_3CN solvent these resonances are observed as a broad band centered at δ 3.5, a downfield shift of 0.5 ppm from the position in the free ligand. On cooling of the sample to 17 °C, this band begins to resolve into two peaks, and at −10 °C two resonances are observed at δ 3.37 and 3.70. Two peaks are observed because the prochiral sulfur centers lead to two diastereomeric forms of the complex that undergo slow inversion about the sulfur center at the lower temperature.

If the reaction mixture used for the synthesis of *cis*-[Pt(*o*-$Ph_2PC_6H_4SEt)_2$]$(BF_4)_2$ is refluxed for 12 h before addition of $NaBF_4$, partial deethylation occurs to give *cis*-[Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt)$]BF_4 (eq 3). The cis stereochem-



istry is confirmed by the small value of 9.8 Hz for ^2J(PP). Photochemical irradiation of a chloroform solution of *cis*-[Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt)$]BF_4 gives a small amount of the

(7) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: New York, 1979; p 94.

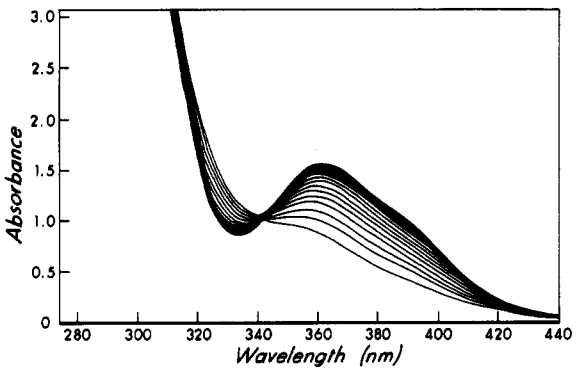


Figure 1. Overlay of electronic spectra from the reaction of *cis*-Pt(*o*-$Ph_2PC_6H_4SEt)_2^{2+}$ with triethylamine.

trans compound (δ(P) 44.5, 44.6). Complete deethylation leads to the formation of the complex Pt(*o*-$Ph_2PC_6H_4S)_2$, the stereochemistry of which cannot be unambiguously assigned from the ^1J(PtP) value of 2909 Hz.[8] This neutral complex can be prepared from *cis*-Pt(*o*-$Ph_2PC_6H_4SEt)_2^{2+}$ by refluxing for 10 h in acetonitrile solvent with benzylamine, dibutylamine, or NaSCN.

Kinetics and Mechanism. Reaction rates have been measured for the deethylation of both *cis*-Pt(*o*-$Ph_2PC_6H_4SEt)_2^{2+}$ and *cis*-Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt)^+$ with benzylamine, dibenzylamine, triethylamine, diethylamine, tributylamine, butylamine, and dibutylamine. The complex Pt(*o*-$Ph_2PC_6H_4SEt)_2^{2+}$ in acetonitrile solvent shows only a low-energy shoulder on the intense $\pi \rightarrow \pi^*$ aromatic bands, but the product complexes *cis*-Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt)^+$ and Pt(*o*-$Ph_2PC_6H_4S)_2$ show resolved low-energy chromophores at 362 nm (ϵ = 2300 dm^3 mol^{-1} cm^{-1}) and 396 nm (ϵ = 3700 dm^3 mol^{-1} cm^{-1}), respectively. We assign these bands to thiolato→platinum(II) charge-transfer transitions. In Figure 1 we show the spectral overlay obtained for the deethylation reactions shown in eq 4 using triethylamine

$$cis\text{-Pt}(o\text{-}Ph_2PC_6H_4SEt)_2^{2+} \xrightarrow[-Et_2NH_2^+]{EtNH_2\ (k_1)} cis\text{-Pt}(o\text{-}Ph_2PC_6H_4S)(o\text{-}Ph_2PC_6H_4SEt)^+ \xrightarrow[-EtNH_2^+]{EtNH_2\ (k_2)} Pt(o\text{-}Ph_2PC_6H_4S)_2 \quad (4)$$

under pseudo-first-order conditions. Analogous reactions are found with the other amines. Rate data have been collected by following the changes in absorbance at 362 nm with time. Plots of ln ($A_\infty - A_t$) against time are linear over 3 half-lives, the value of A_∞ used being an experimental number optimized to give the best linear fit. Although the reaction consists of two consecutive alkyl transfers, k_1 for the first step is readily obtained from a first-order plot since it is significantly greater than k_2. The rate constant data for k_1 are collected in Table I. These data have been measured from the linear plots of k_{obsd} vs. [amine], which show a small intercept. The rate law for the first step is shown in eq 5. The values of k_s obtained from the intercept range from 1

$$\text{rate} = (k_s + k_1[\text{amine}])[cis\text{-Pt}(o\text{-}Ph_2PC_6H_4SEt)_2^{2+}] \quad (5)$$

$\times 10^{-5}$ to 5×10^{-5} s^{-1} and represent a homolytic or solvent-induced deethylation pathway. The activation parameters obtained from Eyring plots of ln (k_1/T) vs. $1/T$ are given in Table II. These data assume that the dominant pathway is the bimolecular one, and no correction is made for changes in the contributions from k_s over the temperature range. This simplified treatment of the data as two distinctly separable consecutive reactions is reinforced by the fortuitous circumstance that both *cis*-Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt)^+$ and the product *cis*-Pt(*o*-$Ph_2PC_6H_4S)_2$ have closely similar ϵ values (2300 and 2500, respectively) at 362 nm (Figure 2). If data for two consecutive reactions are measured at an isosbestic point, a linear first-order plot will result, allowing measurement of k_1. Our data collected at 362 nm give a good approximation to this situation.

The rate data for the second (k_2) step were measured in DMF solvent because of the low solubility of the product Pt(*o*-$Ph_2PC_6H_4S)_2$ in acetonitrile. In DMF solvent the biphasic nature of the reaction sequence is again readily apparent, leading to the facile separate evaluation of k_1 and k_2. The rate constant for the second step has been evaluated by extrapolating the linear second

(8) Lai, R. D.; Shaver, A. *Inorg. Chem.* **1981**, *20*, 477–480.

Table I. Rate Constant Data k_1 for Ethyl Group Transfer from *cis*-Pt(*o*-$Ph_2PC_6H_4SEt)_2^{2+}$ to Amine Nucleophiles at Different Temperatures in Acetonitrile Solvent

amine	temp, °C	k_1, M^{-1} s^{-1}
benzylamine (0.22 M)	59	5.3 (2) × 10^{-3}
dibenzylamine (0.473 M)	60.0	1.69 (9) × 10^{-3}
	50.1	7.8 (3) × 10^{-4}
	40.8	3.26 (9) × 10^{-4}
	33.0	1.49 (1) × 10^{-4}
butylamine (0.482 M)	55.9	6.0 (4) × 10^{-3}
	45.5	2.6 (1) × 10^{-3}
	36.0	1.35 (22) × 10^{-3}
	31.6	7.8 (4) × 10^{-4}
	26.5	4.3 (1) × 10^{-4}
dibutylamine (0.414 M)	58.7	9.0 (4) × 10^{-3}
	54.4	7.1 (2) × 10^{-3}
	50.8	5.3 (4) × 10^{-3}
	45.1	3.1 (1) × 10^{-3}
	41.0	1.9 (1) × 10^{-3}
	31.0	7.7 (3) × 10^{-4}
tributylamine (0.293 M)	60.0	2.8 (1) × 10^{-3}
	56.3	2.00 (7) × 10^{-3}
	46.0	7.99 (5) × 10^{-4}
	40.9	4.33 (7) × 10^{-4}
	25.0	8.2 (1) × 10^{-5}
diethylamine (0.673 M)	38.4	1.49 (3) × 10^{-3}
	35.8	1.2 (1) × 10^{-3}
	32.0	1.0 (4) × 10^{-3}
	31.0	8.6 (2) × 10^{-4}
	25.4	5.69 (1) × 10^{-4}
	22.0	4.24 (12) × 10^{-4}
trimethylamine (0.501 M)	63.6	2.93 (5) × 10^{-3}
	55.0	1.50 (4) × 10^{-3}
	45.7	6.8 (1) × 10^{-4}
	35.4	2.5 (2) × 10^{-4}

Table II. Activation Parameters (ΔH^* and ΔS^*) for Ethyl Group Transfer from *cis*-Pt(*o*-$Ph_2PC_6H_4SEt)_2^{2+}$ to Amine Nucleophiles in Acetonitrile Solvent

amine	ΔH^*, kcal mol^{-1}	ΔS^*, cal K^{-1} mol^{-1}
dibenzylamine	17.7 (3)	−18 (3)
butylamine	16.6 (7)	−18 (3)
dibutylamine	17.9 (6)	−14 (2)
tributylamine	19.4 (4)	−13 (4)
diethylamine	13.2 (5)	−29 (5)
triethylamine	16.7 (7)	−21 (5)

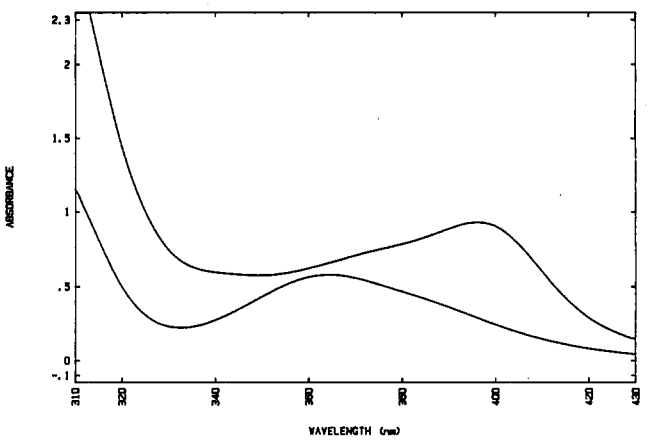


Figure 2. Electronic spectra of *cis*-Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt$) (λ_{max} = 362 nm) and Pt(*o*-$Ph_2PC_6H_4S)_2$ (λ_{max} = 396 nm).

Table III. Rate Constant Data for Ethyl Group Transfer from *cis*-Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt$)$^+$ to Amine Nucleophiles at Different Temperatures in DMF Solvent

amine	temp, °C	k_2, M^{-1} s^{-1}
butylamine (0.706 M)	71.0	8.1 (2) × 10^{-4}
	63.6	4.89 (2) × 10^{-4}
	55.4	2.78 (9) × 10^{-4}
	50.3	1.80 (2) × 10^{-4}
dibutylamine (0.283 M)	73.8	7.5 (3) × 10^{-4}
	65.1	3.9 (4) × 10^{-4}
	58.5	2.5 (2) × 10^{-4}
	48.0	9.8 (2) × 10^{-5}
tributylamine (0.293 M)	72.4	2.10 (7) × 10^{-4}
	63.9	1.0 (1) × 10^{-4}
	55.0	5.74 (9) × 10^{-5}

Table IV. Activation Parameters (ΔH^* and ΔS^*) for Ethyl Group Transfer from *cis*-Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt$)$^+$ to Amine Nucleophiles in DMF Solvent

amine	ΔH^*, kcal mol^{-1}	ΔS^*, cal K^{-1} mol^{-1}
butylamine	15.9 (2)	−29
dibutylamine	16.7 (1)	−25
tributylamine	15.7 (8)	−30

portion of a ln ($A_\infty - A_t$) vs. time plot back to $t = 0$. The intercept gives B for eq 6, which when used in eq 7 allows the measurement

$$A_\infty - A_t = xe^{-k_{1(obsd)}t} + ye^{-k_{2(obsd)}t} \quad (6)$$

$$\ln \Delta = \ln (A_\infty - A_t - ye^{-k_{2(obsd)}t}) = xe^{-k_{1(obsd)}t} \quad (7)$$

of k_1 from a plot of ln Δ vs. time. Although there is frequently much ambiguity in the unequivocal identification of k_1 and k_2 with respect to their relative rates in biphasic reactions, in this case the isolation of the intermediate complex and the determination of its molar extinction coefficient eliminate this uncertainty. From such biphasic analyses for the deethylation reactions of *cis*-Pt(*o*-$Ph_2PC_6H_4SEt)_2^{2+}$ with dibutylamine (0.414 M) in DMF solvent, we find that the pseudo-first-order rate constants are, at 49.4 °C, $k_1 = 1.12 \times 10^{-3}$ s^{-1} and $k_2 = 4.79 \times 10^{-5}$ s^{-1} and, at 58.0 °C, $k_1 = 2.19 \times 10^{-3}$ s^{-1} and $k_2 = 8.13 \times 10^{-5}$ s^{-1}.

Since the intermediate complex *cis*-Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt$)$^+$ is readily isolable, it is preferable to avoid this biphasic analysis method by carrying out the second reaction as a single step using this monodealkylated complex as initially added reagent. The reaction can be monitored from the disappearance of the band at 362 nm due to *cis*-Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt$)$^+$ and also from the growth of the band at 396 nm due to Pt(*o*-$Ph_2PC_6H_4S)_2$. Plots of ln ($A_\infty - A_t$) vs. time for the reactions with butylamine, dibutylamine, and tributylamine are linear, and k_{obsd} values are constant for different concentrations of *cis*-Pt(*o*-$Ph_2PC_6H_4S$)(*o*-$Ph_2PC_6H_4SEt$) with constant amine concentrations. Since these plots intersect close to the origin, we observe the second-order rate law shown in eq 8. The rate constants are shown in Table III, and the activation parameters in Table IV.

$$\text{rate} = (k'_s + k_2[\text{amine}])[\text{Pt}(o\text{-}Ph_2PC_6H_4S)(o\text{-}Ph_2PC_6H_4SEt)^+] \quad (8)$$

Mechanistically, these reactions show many of the salient features found in the Menschutkin reaction, which is the bimolecular alkylation of amines by alkyl halides. In agreement with such an S_N2 type mechanism we find that the reactions between these palladium complexes and amines have rate laws that are first order in both the palladium complex and amine. In all cases the entropies of activation are negative, ranging from −12 to −31 cal K^{-1} mol^{-1} for ΔS^*. These values correlate with an associative pathway, although changes in solvation between the ground and transition states will be influencing the individual magnitude of the entropies. The activation enthalpies range from 13 to 20 kcal mol^{-1}, which correspond with those expected for an S_N2 reaction.[9]

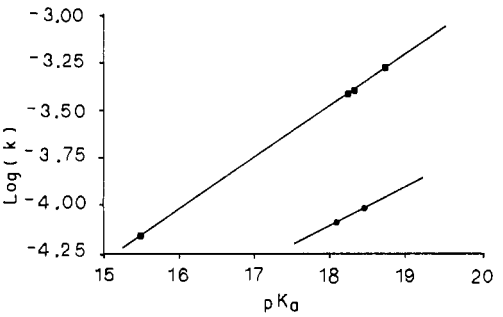


Figure 3. Brønsted plot for the reaction of amines with *cis*-Pt(*o*-$Ph_2PC_6H_4SEt)_2^{2+}$ using data from Table V.

Table V. Experimental Values of log k_1 and pK_a for the Range of Bases Used in the Menschutkin Type Reaction with *cis*-Pt(*o*-$Ph_2PC_6H_4SEt)_2^{2+}$ at 25 °C in Acetonitrile Solvent

amine	log k_1	pK_a[a]
diethylamine	−3.26	18.75
dibutylamine	−3.385	18.31
butylamine	−3.386	18.26
dibenzylamine	−4.16	15.5[b]
tributylamine	−4.09	18.09
triethylamine	−4.01	18.46

[a] Taken from ref 13. [b] Taken from ref 14. The value was extrapolated from linear plots of pK_a in acetonitrile against pK_a in nitromethane solvent.

Table VI. Comparative Rate Data (M^{-1} s^{-1}) for Amine Alkylation[a]

	n-$BuNH_2$	$(n\text{-Bu})_2NH$	$(n\text{-Bu})_3N$
MeI (30 °C)[b]	5.5 × 10^{-4}	1.5 × 10^{-4}	6.9 × 10^{-5}
EtI (35 °C)	1.3 × 10^{-3}	3.6 × 10^{-4}	5.6 × 10^{-5}
cis-Pt(*o*-$Ph_2PC_6H_4SEt)_2^{2+}$ (25 °C)	4.1 × 10^{-4}	4.1 × 10^{-4}	8.2 × 10^{-5}
cis-Pt(*o*-$Ph_2PC_6H_4S$)-(*o*-$Ph_2PC_6H_4SEt)^+$ (25 °C)	2.3 × 10^{-5}	1.3 × 10^{-5}	4.5 × 10^{-6}
p-$ClC_6H_4SMe_2^+$ (25 °C)	3.3 × 10^{-3}		

[a] Acetonitrile solvent. [b] Benzene solvent.

The observed rate law shows that the slow step is bimolecular, but we cannot prove whether the initial amine attack occurs at palladium or carbon. Replacement of a complexed thioether moiety does not, however, reasonably represent a step along the reaction path since the uncomplexed compound *o*-$Ph_2PC_6H_4SEt$ does not itself undergo ethyl group transfer to an amine. Our kinetic data do not allow us to exclude an $S_{RN}1$ pathway. Such a mechanism has been found in the electrochemical reductive cleavage of sulfonium salts.[10] In this context the complex *cis*-[Pt(*o*-$Ph_2PC_6H_4SEt)_2](BF_4)_2$ shows no reversible electrochemistry, but [Pd(*o*-$Ph_2PC_6H_4SEt)_2](BF_4)_2$ in DMF solvent reversibly reduces at −0.41 V (vs. Ag/AgCl).

The range of amines studied allows us to estimate both electronic and steric effects in this Menschutkin reaction. In Figure 3 we show a Brønsted plot of log k_1 against the pK_a of the amine bases in Table V, and in Table VI we show comparative rate data for the alkylation of amines with alkyl halides, sulfonium ions, and thiophenetole complexes of platinum(II). It is apparent from

(9) (a) Menschutkin, N. *Z. Phys. Chem., Stoechim. Verwandtschaftsl.* **1890**, *5*, 589. (b) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1953; pp 349, 412. (c) Pickles, N. J. T.; Hinshelwood, C. N. *J. Chem. Soc.* **1936**, 1353–1357. (d) Laidler, K. J. *J. Chem. Soc.* **1938**, 1786–1789. (e) Matsui, T.; Tohura, N. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1751–1762. (f) Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1980**, *102*, 5892–5902. (g) Abraham, M. H.; Nasehzadeh, A. *J. Chem. Soc., Chem. Commun.* **1981**, 905–906. (h) Kevill, D. N. *J. Chem. Soc., Chem. Commun.* **1981**, 421–422.

(10) Saeva, F. D.; Morgan, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 4121–4125.

Table VII. Rate Constants for the Menschutkin Type Reaction between Tetraethylammonium Bromide and *cis*-$[Pt(o\text{-}Ph_2PC_6H_4SEt)_2](BF_4)_2$ or *cis*-$[Pt(o\text{-}Ph_2PC_6H_4S)(o\text{-}Ph_2PC_6H_4SEt)]BF_4$ in DMF Solvent

$[Et_4NBr]$, mM	$[NaClO_4]$, mM	T, °C	k_{obsd}, s^{-1}	k_1, s^{-1}
		cis-$Pt(o\text{-}Ph_2PC_6H_4SEt)_2^{2+}$		
7.0	14.0	71	9.2×10^{-5}	1.3×10^{-2}
10.5	10.5	71	1.5×10^{-4}	1.4×10^{-2}
12.6	8.4	71	1.7×10^{-4}	1.3×10^{-2}
16.0	5.0	71	1.75×10^{-4}	1.1×10^{-2}
19.0	2.0	71	1.55×10^{-4}	0.8×10^{-2}
21	21	71	1.2×10^{-4}	0.6×10^{-2}
38.3	0	58	5.34×10^{-4}	$1.39\ (7) \times 10^{-2}$
29.0	9.6	58	4.20×10^{-4}	$1.45\ (7) \times 10^{-2}$
19.1	19.0	58	2.91×10^{-4}	$1.50\ (2) \times 10^{-2}$
7.65	31.0	58	1.11×10^{-4}	$1.45\ (2) \times 10^{-2}$
		cis-$Pt(o\text{-}Ph_2PC_6H_4S)(o\text{-}Ph_2PC_6H_4SEt)^+$		
21.1	0	42.2	5.36×10^{-5}	$2.54\ (6) \times 10^{-3}$
21.1	0	51.2	1.52×10^{-4}	$7.20\ (4) \times 10^{-3}$
21.1	0	60.1	4.04×10^{-4}	$1.91\ (6) \times 10^{-2}$
21.1	0	67.7	9.45×10^{-4}	$4.48\ (4) \times 10^{-2}$

Table VI that the complex *cis*-$Pt(o\text{-}Ph_2PC_6H_4SEt)_2^{2+}$ is a better ethylating agent than is *cis*-$Pt(o\text{-}Ph_2PC_6H_4S)(o\text{-}Ph_2PC_6H_4SEt)^+$ but that neither complex reacts as rapidly as ethyl iodide. These complexes also show a lower selectivity toward differences in amine structure than does ethyl iodide. For ethyl iodide the rate decreases by a factor of 23 on changing from butylamine to tributylamine, but for the platinum complexes the difference factor is only 5.

The data in Table V plotted in Figure 3 show that the reaction rates for primary and secondary amines are dependent on electronic effects. For the four amines used, the plot is linear with a slope β of 0.28. By comparison, the analogous slope β for the methylsulfonium ions is 0.36.[11] This small value of β indicates a low sensitivity of the rate to changes in pK_a of the attacking nucleophile. This insensitivity to added nucleophile, along with the finding of a second slope for tertiary amines, is suggestive of a transition state that more clearly resembles reactants rather than products.

We make two conclusions from these kinetic data. The first conclusion, which derives from data in Tables I and VI, is that, under the same temperature and solvent conditions, the electrophilicities of the methylenic groups of EtI and *cis*-$Pt(o\text{-}Ph_2PC_6H_4SEt)_2^{2+}$ are equal when their reactivities are compared by using butylamine, an amine of small steric bulk, as nucleophile. The second conclusion is that the low selectivity to electronic and steric effects is due to the transition state being early along the reaction path, where the long bond-forming nitrogen–carbon interaction attenuates the substituent effects. This factor will likely be most evidenced in the steric selectivity.

The deethylation of *cis*-$Pt(o\text{-}Ph_2PC_6H_4SEt)_2^{2+}$ and *cis*-$Pt(o\text{-}Ph_2PC_6H_4S)(o\text{-}Ph_2PC_6H_4SEt)^+$ can be accomplished with bromide ion (eq 9). The rate data for these reactions are collected in Table

$$cis\text{-}Pt(o\text{-}Ph_2PC_6H_4SEt)_2^{2+} \xrightarrow[-EtBr]{Br^-} cis\text{-}Pt(o\text{-}Ph_2PC_6H_4S)(o\text{-}Ph_2PC_6H_4SEt)^+ \xrightarrow[-EtBr]{Br^-} Pt(o\text{-}Ph_2PC_6H_4S)_2 \quad (9)$$

VII. The second-order rate constants in DMF solvent are greater than those found with amine nucleophiles. Under conditions of constant ionic strength the values of k_1 with changing bromide ion concentration are constant until high bromide ion concentrations are reached, when k_1 decreases. The lowering in k_1 is suggestive of competition from a second reaction pathway; two likely side reactions are complexation of Br^- to the axial ligand positions at platinum(II) or substitution of a coordinated thiophenetole moiety by bromide ion. Both of these pathways will decrease the electrophilicity of the ethyl group bonded to sulfur.

The faster rate for bromide ion over amine nucleophiles is not predicted by the Swain–Scott nucleophilic constants for the two reagents.[12] The higher reactivity of bromide ion in our case is best explained by charge effects. We anticipate that the overall dipositive charge on the electrophile will lead to accelerated rates in the reactions with anionic nucleophiles such as Br^-.

Registry No. *cis*-$[Pt(o\text{-}Ph_2PC_6H_4SEt)_2](BF_4)_2$, 104130-67-8; *cis*-$[Pt(o\text{-}Ph_2PC_6H_4S)(o\text{-}Ph_2PC_6H_4SEt)]BF_4$, 104130-69-0; $[Pd(o\text{-}Ph_2PC_6H_4SEt)_2](BF_4)_2$, 104155-44-4; K_2PtCl_4, 10025-99-7; Na_2PtCl_4, 13820-53-6; $o\text{-}Ph_2PC_6H_4SEt$, 104130-70-3; Et_4NBr, 71-91-0; ethyl iodide, 75-03-6; sodium, 7440-23-5; hydrogen bromide, 10035-10-6; *n*-butyllithium, 109-72-8; chlorodiphenylphosphine, 1079-66-9; benzylamine, 100-46-9; dibenzylamine, 103-49-1; butylamine, 109-73-9; dibutylamine, 111-92-2; trimethylamine, 75-50-3; diethylamine, 109-89-7; tributylamine, 102-82-9; *o*-aminobenzenethiol, 137-07-5.

(11) Coward, J. K.; Sweet, W. D. *J. Org. Chem.* **1971**, *36*, 2337–2346.
(12) Swain, C. G.; Scott, C. B. *J. Am. Chem. Soc.* **1953**, *75*, 141–147.
(13) Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45–92.
(14) Korolev, B. A.; Mal'tseva, M. A.; Tarasov, A. I.; Vasnev, V. A. *Zh. Obshch. Khim.* **1974**, *44*, 833–837.