prisingly high. The formation of the rotaxanes is good evidence that the CDX includes the α,ω-diaminoalkane and aminoalkyl group in $[CoCl(en)_2(N\text{-}N)]^{2+}$. Table V shows that the yield of rotaxanes containing α-CDX is higher than that containing β-CDX. α-CDX, which has a narrower cavity than β-CDX, appears to be more effective for threading N-N. The yield of the rotaxanes also depends on the methylenic chain length of N-N. The formation of rotaxanes was not observed for N-N = ocn and pxyn. The yield increases with the increase of methylenic chain length of N-N up to don. In N-N = tden, with 14 methylenic chains, however, the yield decreased. A possible explanation for this phenomenon would be as follows: As more than one CDX molecule is threaded by tden, attack of $[CoCl_2(en)_2]^+$ on the free amino group is hindered and/or as the methylenic chain of tden is folded by internal hydrophobic interaction no effective threading can occur.

The rotaxanes prepared in this work are regarded as intermediates to catenanes. That is, for example, the substitution of two Cl^- ions in a rotaxane by an N-N molecule should lead to a catenane. In connection with this, an unsuccessful attempt to prepare a catenane[24] yielded an inclusion compound consisting of α-CDX and 1,10-dodecanedithiol. The attempt failed in the conversion of the dithiol in the compound to a macrocyclic disulfide.

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Registry No. α-CDX, 10016-20-3; β-CDX, 7585-39-9; $[CoCl(Me_2SO)(en)_2](ClO_4)_2$, 15618-10-7; $[Co(Me_2SO)_2(en)_2](ClO_4)_3$, 14781-36-3; $[CoCl(en)_2(ocnH)]Cl_3$, 91686-73-6; $[CoCl(en)_2(denH)]Cl_3$, 91686-74-7; $[CoCl(en)_2(donH)]Cl_3$, 76793-16-3; $[CoCl(en)_2(tdenH)]Cl_3$, 91686-75-8; $[CoCl(en)_2(pxynH)]Cl_3$, 91686-76-9; $[(en)_2ClCo(ocn)CoCl(en)_2]Cl_4$, 91686-77-0; $[(en)_2ClCo(den)CoCl(en)_2]Cl_4$, 91740-99-7; $[(en)_2ClCo(don)CoCl(en)_2]Cl_4$, 91741-00-3; $[(en)_2ClCo(tden)CoCl(en)_2]Cl_4$, 91686-78-1; $[(en)_2ClCo(pxyn)CoCl(en)_2]Cl_4$, 91686-79-2; $[(en)_2ClCo(den)CoCl(en)_2]Br_4$, 91796-34-8; $[(en)_2ClCo(don)CoCl(en)_2]Br_4$, 77069-99-9; $[(en)_2ClCo(den)CoCl(en)_2](ClO_4)_4$, 76748-10-2; $[(en)_2ClCo(don)CoCl(en)_2](ClO_4)_4$, 76748-07-7; $[(en)_2ClCo(tden)CoCl(en)_2](ClO_4)_4$, 91741-02-5; Λ-$[CoCl(en)_2(donH)]^{3+}$, 91741-03-6; $[CoCl_2(en)_2]Cl$, 14040-32-5.

Supplementary Material Available: Table II (molecular rotation data), Table IV (^{13}C NMR spectral data), and Figure 2 (circular dichroism curves) (3 pages). Ordering information is given on any current masthead page.

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A Menschutkin Type Amine Alkylation Involving Methyl Transfer to Benzylamine from Palladium(II) Chelate Complexes of *o*-(Diphenylphosphino)thioanisole

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The reactions between the complexes $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ and $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$ and benzylamine yield the respective thiolato compounds $[PdCl(\mu\text{-}SC_6H_4PPh_2\text{-}o)]_2$ and $Pd(o\text{-}Ph_2PC_6H_4S)_2$. The other product is *N*-methylbenzylamine. Conductivity measurements on acetonitrile solutions of $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ show partial substitution of chloride by benzylamine to give $[PdCl(PhCH_2NH_2)(o\text{-}Ph_2PC_6H_4SMe)]Cl$. Time-dependent intensity measurements on the decrease in the ^1H NMR resonance of the methyl group of the palladium(II) complexes give a rate law: rate = k_2[Pd complex][$PhCH_2NH_2$]. Respective rate constants for $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ and $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$ are in the 10^{-5} and 10^{-3} mol^{-1} s^{-1} range. The complex $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$ has cis stereochemistry ($^4J(PH)$ = 4 Hz), and the partially demethylated intermediate $[Pd(o\text{-}Ph_2PC_6H_4SMe)(o\text{-}Ph_2PC_6H_4S)]BF_4$ also has cis stereochemistry ($^4J(PH)$ = 3.6 Hz). The final complex $Pd(o\text{-}Ph_2PC_6H_4S)_2$ has trans stereochemistry, which is confirmed by X-ray crystallography. The complex $PdS_2P_2C_{36}H_{28}$ has a = 9.735 (3) Å, b = 12.865 (3) Å, and c = 12.732 (4) Å and crystallizes in the monoclinic $P2_1/c$ space group with Z = 2. The activation parameters for the methylation of benzylamine in acetonitrile solvent are ΔH^* = 12 (2) kcal mol^{-1} and ΔS^* = -41 (10) cal K^{-1} mol^{-1}. A mechanism is proposed for these reactions whereby the amine undergoes nucleophilic attack by an S_N2 Menschutkin type reaction at the methyl group of the coordinated thioether. The complex $PtCl_2(o\text{-}Ph_2PC_6H_4SMe)$ has been prepared, and the complex $NiCl_2(o\text{-}Ph_2PC_6H_4SMe)$ also was found to methylate benzylamine.

Introduction

Methyl transfer is a topic of considerable significance in biological chemistry. Two of the most important compounds that have been implicated in such reactions are methylcobalamin and *S*-adenosylmethionine. This latter compound is of interest to use because of its widespread involvement as an in vivo carbonium ion type methylating agent.[2]

In 1966 it was suggested that the dealkylation reaction of dichloro(*o*-(diphenylphosphino)thioanisole)palladium(II) under

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high-temperature reflux conditions in DMF solvent could be relevant to methylation by *S*-adenosylmethionine.[3] This particular example is not unique, and a number of other similar examples have been reported whereby a complexed methyl thioether ligand can be converted to a complexed thiolate by refluxing in solvents such as DMF.[4] Mechanistic considerations lead one to infer that these transition-metal-induced demethylation reactions can be compared to carbonium ion type electrophilic reactivities and that metal coordination to the thioether can lead to two cooperative effects. First, complexation of the methyl thioether group to the transition-metal ion as a σ donor can lead to a reduction of electron density at sulfur and hence carbon; second, the conversion of a weakly bound thioether group to a strongly complexed thiolate moiety will result in a thermodynamic preference for the formation of a (thiolato)metal complex as a leaving group. In support of this mechanistic approach, we have previously shown that the palladium(II)-coordinated methyl thioether group of *o*-(diphenylphosphino)thioanisole has sufficient carbonium ion character to be attcked by thiocyanate or iodide nucleophiles in a Zeisel ether type cleavage reaction[5] and that the reaction is first order in palladium complex and nucleophile, as expected for an S_N2 type pathway.

Of more significance from a biological standpoint is the N-methylation of amines. Carbonium ion alkylation by *S*-adenosylmethionine is an important route for the methylation of ethanolamine and noradrenaline, and methylation of DNA may be of significance to cancer mechanisms.[6] In view of our previous discovery that the energetics of methyl transfer to thiocyanate from bis(thiocyanato)(*o*-(diphenylphosphino)thioanisole)palladium(II) is closely similar to that from methylsulfonium ions,[7] we have now studied the methylation of amines by palladium(II) complexes of *o*-(diphenylphosphino)thioanisole. Since no previous examples exist of amine alkylation by a complexed alkyl thioether group, it is of interest to compare the reactivity of a coordinated methyl thioether group with methyl halides in a Menschutkin type reaction. Kinetic data on these reactions have been obtained by using ^{1}H NMR spectroscopy. Where possible, intermediates have been identified and the rate data used to support a proposed mechanism involving nucleophilic attack of amine at the methyl carbon of the complexed methyl thioether ligand.

Experimental Section

The compound *o*-(diphenylphosphino)thioanisole (*o*-$Ph_2PC_6H_4SMe$) and complexes $PdCl_2$(*o*-$Ph_2PC_6H_4SMe$), $NiCl_2$(*o*-$Ph_2PC_6H_4SMe$), [Pd(*o*-$Ph_2PC_6H_4SMe)_2](BF_4)_2$, and Pd(*o*-$Ph_2PC_6H_4S)_2$ were prepared by published procedures.[4] The compounds phenethylamine, benzylamine, *N*-methylbenzylamine, aniline, *N*-methylaniline, and *N*-methylphenethylamine were commercial samples and were distilled prior to use. Sodium tetrachloropalladate(II) and potassium tetrachloroplatinate(II) were purchased from Johnson Matthey Inc. All ^{13}C and ^{31}P NMR spectra were measured on a Nicolet NT 200 WB Fourier-transform spectrometer operating at 50.31 and 80.98 MHz, respectively. The ^{31}P NMR spectra were obtained in $CDCl_3$ solvent referenced high frequency positive to external 85% H_3PO_4. The ^{13}C NMR spectra used a Me_4Si internal reference in $CDCl_3$ solvent. ^{1}H NMR spectra were measured either at 200 MHz on the Nicolet instrument or at 100 MHz on a Varian EM 390 spectrometer. Conductivity measurements were carried out with use of an Industrial Instruments Conductivity unit incorporating a cell with platinized electrodes. The cell constant was 0.385 cm^{-1}, and measurements were made by using 4.86×10^{-4} M solutions in acetonitrile solvent previously dried by distillation from P_2O_5. Microanalyses were performed by Canadian Microanalytical Services, Vancouver, BC, Canada. Gas chromatographic measurements were made on a Hewlett-Packard Model 5830A instrument using a SP-DB 2250 column purchased from Supelco, Inc. *N*-Methylbenzylamine was purchased from Aldrich. Electronic spectra were recorded on a Cary Model 219 spectrophotometer using 1-cm quartz cells.

Bis(*o*-(diphenylphosphino)thioanisole)palladium(II) Bis(tetrafluoroborate) ([Pd(*o*-$Ph_2PC_6H_4SMe)_2](BF_4)_2$). By the use of a procedure similar to that used for the perchlorate salt,[4d] a solution of *o*-(diphenylphosphino)thioanisole (92.8 mg, 0.3 mmol) in acetone (20 mL) was heated to boiling. To this solution was added a solution of K_2PdCl_4 (45.7 mg, 0.14 mmol) in water (10 mL). The resulting yellow solution was heated for several minutes and filtered into a 50:50 mixture of acetone and water containing KBF_4 (1 g). Cooling to 0 °C yielded an off-white precipitate of the complex, which was filtered, washed with ethanol (95%), and finally washed with diethyl ether; yield 88 mg (70%). Λ_M(3×10^{-4} M in CH_3CN) = 260 Ω^{-1} cm^2 mol^{-1}.

Diiodo(*o*-(diphenylphosphino)thioanisole)platinum(II) (*PtI*$_2$(*o*-$Ph_2PC_6H_4SMe$)). To a 50% aqueous acetone solution of potassium iodide (0.17 g) was added a solution of K_2PtCl_4 (53.9 mg, 0.13 mmol) in water (10 mL). The mixture was refluxed, and a solution of *o*-(diphenylphosphino)thioanisole (40 mg, 0.13 mmol) in acetone (4 mL) was slowly added from a dropping funnel. Refluxing the solution for 12 h yielded an orange-brown precipitate. The complex was recrystallized from dichloromethane by addition of diethyl ether; yield 48 mg (44%). Anal. Calcd for $C_{19}H_{17}I_2PPtS$: C, 30.1; H, 2.26; S, 4.23. Found: C, 29.2; H, 1.75; S, 3.42.

Bis(chloro(μ-*o*-(diphenylphosphino)benzenethiolato)palladium(II)) ([Pd(μ-$SC_6H_4PPh_2$-*o*)Cl]$_2$). Dichloro(*o*-(diphenylphosphino)thioanisole)palladium(II) (43 mg) was dissolved in a mixture of $CHCl_3$ (1.2 mL) and CH_3CN (0.8 mL). Benzylamine (133 μL) was added and the reaction mixture heated at 55 °C for 12 h. After cooling, a solution of HCl (1.6 mL of 0.8 N) was added and the mixture stirred for 1 min. After 15 min a yellow-orange solid precipitated. The solid was filtered, washed with water and methanol, and dried in vacuo; mp >300 °C. Anal. Calcd for $C_{36}H_{28}Cl_2Pd_2P_2S_2$: C, 49.7; H, 3.24; Cl, 8.15. Found: C, 49.6; H, 3.34; Cl, 7.80. The ^{1}H NMR spectrum shows no methyl resonance and the ^{31}P NMR spectrum shows a single resonance at δ 55.9.

Rate Data Collection. Rate data were obtained by measuring the decrease in the intensity of the complexed thiomethyl group as observed by ^{1}H NMR spectroscopy. The integrated areas were referenced to hexamethylcyclotrisiloxane as internal reference. The integrated peak areas of the complexed thiomethyl group and the internal reference sample were measured prior to benzylamine addition, and the logarithm of this value was plotted against time in minutes to establish the zero intercept. All kinetic runs were made under pseudo-first-order conditions where the minimum concentration ratio of benzylamine to complex was 10:1. Solutions were prepared by transferring a standard solution of complex and reference dissolved in CD_3CN to a 5-mm NMR tube via a Pipetman P-200. The amine was then introduced as a measured aliquot by syringe. For measurements using $PdCl_2$(*o*-$Ph_2PC_6H_4SMe$) in CD_3CN solvent, the NMR tube was placed in a constant-temperature bath maintained at 59 ± 1 °C. Time was measured as the intervals between removal of the NMR tube from this constant-temperature bath for measurement of the ^{1}H NMR signal. Since the reaction rate is very slow at ambient temperature, this operation is equivalent to thermally quenching the reaction. The experimental method used for the complex [Pd(*o*-$Ph_2PC_6H_4SMe)_2](BF_4)_2$ was similar, except that now the solution sample remained in the NMR tube in the probe throughout the reaction. This was necessary because of the faster reaction rate. The

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probe was maintained at the 29.5 °C temperature while concentration measurements were being made. Temperature measurements were checked by chemical shift measurements of 1,3-propanediol. Intensity measurements were made at 5-min intervals.

The measurements for $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ in CD_3CN solvent at 59 °C and those for $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$ were made on the Nicolet instrument at 200 MHz. Data were collected over a sweep width of 4000 Hz by using a memory size of 32768. With a 4.00-μs pulse and 1.00-s delay, the acquisition time for data collection was 4.10 s, with a delay time of 1.00 s between pulses. For the sample of $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ and benzylamine, the broadened coverage was integrated between δ 3.11 and δ 3.24 since this range covers the signal area for the shifted methyl signal. From the combined sweep width and memory size and the use of quadrature phase detection, the integrated peak is defined by over 100 data points. For the complex $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$ and benzylamine, the methyl resonance is integrated over the range δ 2.90–2.99. Under the same spectrometer conditions, this integrated peak is defined by 70 data points. For the variable-temperature data collected for a solution of $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ and benzylamine in $CD_3CN/CDCl_3$ (2:3), we used the EM 390 (CW) spectrometer. Area measurements were made by a combination of techniques involving multiple-scan averaging done with the instrument integrator or by using cutting and weighing techniques. Inaccuracies and inconsistencies are inherent in this data set because of the problems of getting consistent and good signal to noise ratios for magnetically dilute samples being measured close to saturation limits. These experimental difficulties are reflected in larger errors in the data collected in Table III.

Treatment of Data[8]

Rate constants k_{obsd} are evaluated from the loss of the respective methyl resonances. For $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ this peak is at δ 3.02, and for $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$ it is at δ 2.92. From conductance data it is apparent that benzylamine partially substitutes chloride ion in $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$. We therefore must consider three rate processes in this reaction with benzylamine:

$$\underset{A}{PdCl_2(o\text{-}Ph_2PC_6H_4SMe)} + \underset{B}{PhCH_2NH_2} \overset{K}{\rightleftharpoons} \underset{C}{[PdCl(PhCH_2NH_2)(o\text{-}Ph_2PC_6H_4SMe)]^+} + \underset{D}{Cl^-}$$

$$\underset{C}{[PdCl(PhCH_2NH_2)(o\text{-}Ph_2PC_6H_4SMe)]^+} + \underset{B}{PhCH_2NH_2} \xrightarrow{k_2} \underset{E}{[PdCl(PhCH_2NH_2)(o\text{-}Ph_2PC_6H_4S)]} + PhCH_2NH_2Me^+$$

$$\underset{A}{PdCl_2(o\text{-}Ph_2PC_6H_4SMe)} + \underset{B}{PhCH_2NH_2} \xrightarrow{k_3} [PdCl_2(o\text{-}Ph_2PC_6H_4S)]^- + PhCH_2NH_2Me^+$$

If C is in equilibrium with A and B, then $K = [C][D]/[A][B]$, and

$$\frac{d[E]}{dt} = \frac{d[A]}{dt} + \frac{d[C]}{dt} = \frac{d[\text{total methyl}]}{dt}$$

$$= k_{obsd}([A] + [C]) = k_2[C][B] + k_3[A][B]$$

$$= \frac{k_2K[A][B]^2}{[D]} + k_3[A][B]$$

Therefore

$$k_{obsd} = \left(\frac{k_2K[A][B]^2}{[D]} + k_3[A][B]\right) \Big/ \left([A] + \frac{K[A][B]}{[D]}\right)$$

$$= \left(\frac{k_2K[B]^2}{[D]} + k_3[B]\right) \Big/ \left(1 + \frac{K[B]}{[D]}\right)$$

Since $K[B]/[D] < 1$, ($K = 10^{-4}$, $[B] = 2 \times 10^{-1}$, $[D] = 7 \times 10^{-5}$)

$$k_{obsd} = \frac{k_2K[B]^2}{[D]} + k_3[B]$$

$$= \left(\frac{k_2K[B]}{[D]} + k_3\right) \Big/ [B]$$

If $k_2K[B]/[D]$ is small, we should observe first-order dependence on [B] since k_3 will be larger. For second-order dependence on [B], it is apparent that $k_2K[B]/[D] > k_3$.

For the case of $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2]^{2+}$, we have again three reactions to consider. The data treatment differs from that for $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ since the initial equilibrium step yields complex H, which has the MeS group uncoordinated and this compound is assumed to be unreactive to demethylation by benzylamine:

$$\underset{F}{Pd(o\text{-}Ph_2PC_6H_4SMe)_2^{2+}} + \underset{G}{2PhCH_2NH_2} \overset{K}{\rightleftharpoons} \underset{H}{Pd(o\text{-}Ph_2PC_6H_4SMe)_2(PhCH_2NH_2)_2^{2+}}$$

$$\underset{F}{Pd(o\text{-}Ph_2PC_6H_4SMe)_2^{2+}} + \underset{G}{PhCH_2NH_2} \xrightarrow{k_2} \underset{J}{Pd(o\text{-}Ph_2PC_6H_4SMe)(o\text{-}Ph_2PC_6H_4S)^+} + PhCH_2NH_2Me^+$$

$$\underset{J}{Pd(o\text{-}Ph_2PC_6H_4SMe)(o\text{-}Ph_2PC_6H_4S)^+} + \underset{G}{PhCH_2NH_2} \xrightarrow{k_3} Pd(o\text{-}Ph_2PC_6H_4S)_2 + PhCH_2NH_2Me^+$$

Since we are measuring initial rates for up to approximately 1 half-life, we can neglect the contribution from the second demethylation step (k_3) without introducing significant errors in the rate constant values k_2. Thus

$$d[J]/dt = k([F] + [H]) = k_2[F][G]$$

Since $K = [H]/[F][G]^2$, then $k([F] + K[F][G]^2) = k_2[F][G]$, $k(1 + K[G]^2) = k_2[G]$, and $k = k_2[G]/(1 + K[G]^2)$.

Crystal Structure Data

Crystals of *trans*-$Pd(o\text{-}Ph_2PC_6H_4S)_2$ suitable for X-ray diffraction were obtained by slow growth from an acetonitrile solution. The orange block-shaped crystals were attached to a glass fiber with epoxy cement. Data were collected on a Nicolet R3 diffractometer using graphite-monochromated Mo Kα (λ = 0.7107 Å) radiation. The reflections were collected by a $2\theta/\theta$ scan technique over a range of 4–50° in 2θ. A summary of pertinent crystallographic parameters is presented in Table I.

An empirical absorption correction was applied to the data by using ψ-scan data from close-to-axial reflections (absorption coeffcient 8.73 cm^{-1}). Data corrected for absorption were refined by a six-parameter procedure to define a pseudoellipsoid used to calculate the corrections (transmission coefficient max/min = 0.736/0.668). A profile fitting procedure was applied to the data to improve the precision of the measurement of weak reflections. No correction for decay was required.

Inspection of the parity group data showed systematic weakness in the general reflection (hkl) when $k + l = 2n + 1$. This weakness coupled with $Z = 2$ indicated that the Pd atom was at the origin (0, 0, 0). The position of the Pd atom was fixed at the origin, and all other non-hydrogen atoms were determined by difference-Fourier techniques. The structure was refined by using the Nicolet SHELXTL (Version 3.0) programs. All non-hydrogen atoms were refined anisotropically with blocked-cascade, least-squares refinement methods. The hydrogen atom positions were calculated in idealized positions on the basis of d(C–H) = 0.96 Å and thermal parameters equal to 1.2 times the isotropic equivalent value for the atom to which it was attached. The final discrepancy indices are $R(F)$ = 3.8% and $R_w(F)$ = 3.3%. The final different map showed a highest peak of 0.30 e $Å^{-3}$ at a distance of 1.22 Å from the Pd atom.

Results and Discussion

Reaction of $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ with Amines. The compound $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ reacts with benzylamine

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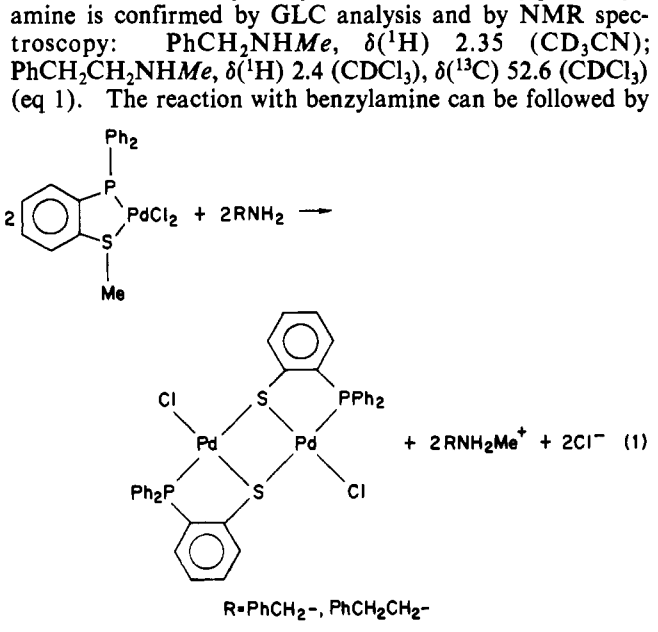
Table I. Crystal and Intensity Data Collection Summary

mol formula	$[PdS_2P_2C_{36}H_{28}]$
fw	346.55
mol wt	693.1
a, Å	9.735 (3)
b, Å	12.865 (3)
c, Å	12.732 (4)
β, deg	110.41 (2)
V, Å^3	1494.5 (7)
cryst system	monoclinic
space group	$P2_1/c$
ρ(calcd), g cm^{-3}	1.541
Z	2
cryst dimens, mm	0.25 × 0.20 × 0.20
radiation	Mo Kα (graphite monochromated)
abs coeff, μ(Mo Kα), cm^{-1}	8.73
temp, °C	25 ± 2
scan speed, deg min^{-1}	variable 2–20
scan type	$2\theta/\theta$
scan range	1.0° below $2\theta(K\alpha_1)$ to 1.0° above $2\theta(K\alpha_2)$
stds monitored	3 stds every 200 reflcns (no decay)
2θ limits, deg	$4 \leq 2\theta \leq 50$
reflcns collected	$\pm h,k,l$
no. of reflcns collected	2941
no. of unique reflcns	1921
no. of unique reflcns used ($F_o > n\sigma(F_o)$)	1330; $n = 2$
weighting factor, g[a]	0.00022
$R(F)$[b]	0.038
$R_w(F)$[c]	0.033
GOF	1.162
highest peak on final diff map, e Å^{-3}	0.300

[a] weight $= 1/[\sigma^2(F) + |g|(F^2)]$. [b] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [c] $R_w = \Sigma w^{1/2}(|F_o| - |F_c|)/\Sigma w^{1/2}(F_o)$.

or phenethylamine in acetonitrile solvent in the temperature range 50–70 °C to give $[PdCl(\mu\text{-}SC_6H_4PPh_2\text{-}o)]_2$[4d] along with *N*-methylbenzylamine or *N*-methylphenethylamine. The formation of *N*-methylbenzylamine and *N*-methylphenethylamine is confirmed by GLC analysis and by NMR spectroscopy: $PhCH_2NH\mathit{Me}$, $\delta(^1H)$ 2.35 (CD_3CN); $PhCH_2CH_2NH\mathit{Me}$, $\delta(^1H)$ 2.4 ($CDCl_3$), $\delta(^{13}C)$ 52.6 ($CDCl_3$) (eq 1). The reaction with benzylamine can be followed by



(1)

^1H NMR spectroscopy from the disappearance of the methyl peak in $PdCl_2(o\text{-}Ph_2PCH_4SMe)$ at δ 3.02 (CD_3CN) and the appearance of the $PhCH_2NHMe$ resonance at δ 2.35. The complex $[PdCl(\mu\text{-}SC_6H_4PPh_2\text{-}o)]$ was isolated from the solution and purified by crystallization. The product shows a single resonance in the ^{31}P NMR spectrum at δ 55.9, and the stoichiometry of the complex is confirmed by combustion analysis. Addition of benzylamine to the complex $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ in acetonitrile solvent at ambient temperature leads to partial chloride ion substitution (eq 2). This reaction

$$PdCl_2(o\text{-}Ph_2PC_6H_4SMe) + PhCH_2NH_2 \rightarrow [PdCl(PhCH_2NH_2)(o\text{-}Ph_2PC_6H_4SMe)]^+ + Cl^- \quad (2)$$

has been followed by measuring changes both in molar conductivity and in the electronic spectrum of the solution on addition of increasing quantities of benzylamine. The solution conductivity data in acetonitrile show that at the higher ratios of benzylamine to palladium thioether complex the molar conductivity increases toward that of a 1:1 electrolyte. From Table II it is apparent that $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ shows negligible ionization in acetonitrile in the absence of benzylamine. Even in the presence of a large excess of $PhCH_2NH_2$, the fraction of ionic complex present (eq 2) is small. This conclusion is based on comparison of the Λ_M value of 45 Ω^{-1} cm^2 mol^{-1} for a 1:200 ratio of $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$:$PhCH_2NH_2$, with the range of 120–160 Ω^{-1} cm^2 mol^{-1} suggested in the literature for 1:1 electrolytes in acetonitrile.[9] The value for Λ_M for 1:40 $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$:$PhCH_2NH_2$ is significant in subsequent sections of this paper because kinetic measurements on the transfer of the methyl group between these two compounds have been carried out under pseudo-first-order conditions using a ratio up to this value. If we assume an approximate linear correlation of conductivity with degree of substitution, we can estimate the value of the degree of dissociation (α) for eq 2. These values calculated for each benzylamine concentration are shown in Table II.[10]

Table II. Changes in Conductivity on Addition of Aliquots of $PhCH_2NH_2$ to an Acetonitrile Solution of $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ (4.86×10^{-4} M)

Λ_M, Ω^{-1} cm^2 mol^{-1}	$[PhCH_2NH_2]$, M	α
1.6	0	
12	2.96×10^{-3}	0.09
21	9.72×10^{-3}	0.15
27	1.94×10^{-2}	0.19
45	9.72×10^{-2}	0.32

Analysis of changes in the electronic spectrum of $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ upon addition of benzylamine agrees with this conclusion. In acetonitrile solution, the complex $PdCl_2(o\text{-}PhPC_6H_4SMe)$ shows an absorption at 359 nm (ϵ = 2700). Addition to benzylamine to this solution causes this absorption band to progressively decrease in intensity and be replaced by a shoulder at 355 nm. This new absorption is due to the solution presence of $[PdCl(PhCH_2NH_2)(o\text{-}Ph_2PC_6H_4SMe)]Cl$, and not a simple adduct, since pentacoordinate palladium(II) complexes have absorptions in the 450–550-nm region.[11] This suggestion is reinforced by the reversal of these spectral changes on addition of chloride ion to the solution and by the independent synthesis of $[PdCl(PhCH_2NH_2)(o\text{-}Ph_2PC_6H_4SMe)]BPh_4$, which shows an absorption band at 350 nm (ϵ = 4000). Using the respective extinction coefficients in conjunction with the absorption changes on addition of benzylamine, we obtain a value of 1.0 (1) × 10^{-4} for the equilibrium constant K in eq 2. This value is somewhat imprecise because the absorption peaks are only partially resolved. The methyl resonance at δ 3.02 is a sharp singlet for acetonitrile solutions of $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$. Addition of the benzylamine causes broadening of this resonance and a slight downfield shift of the center of the resonance. This observation agrees with the broad peak being caused by two unresolved inequivalent methyl resonances from the covalent dichloro and

(9) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.
(10) For $\alpha = \Lambda/\Lambda_0$, we have used Λ_0 = 140 Ω^{-1} cm^2 mol^{-1}.
(11) Hartley, J. G.; Venanzi, L. M.; Goodall, D. C. *J. Chem. Soc.* **1963**, 3930–3936.

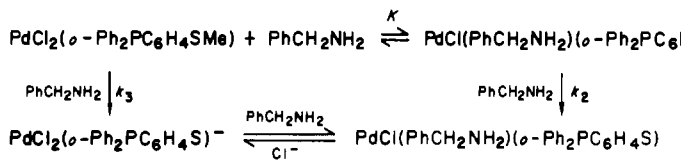
Table III. Rate Constants for the Reaction between *o*-(Diphenylphosphino)thioanisole Complexes of Palladium(II) and Benzylamine in CD_3CN Solvent

[complex], M	[benzylamine], M	k_{obsd}, s^{-1}	k, M^{-1} s^{-1}	temp, °C
		$PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$		
0.014	0.218	1.8×10^{-5}	$8.3\ (2) \times 10^{-5}$	59
0.014	0.317	2.5×10^{-5}	$7.9\ (1) \times 10^{-5}$	59
0.014	0.436	3.2×10^{-5}	$7.3\ (2) \times 10^{-5}$	59
		$[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$		
0.015	0.170	4.1×10^{-4}	$2.4\ (2) \times 10^{-3}$	29.5
0.015	0.220	5.5×10^{-4}	$2.5\ (7) \times 10^{-3}$	29.5
0.015	0.340	8.3×10^{-4}	$2.4\ (5) \times 10^{-3}$	29.5

Table IV. Rate Constants for the Reaction between $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ (0.029 M) and Benzylamine in a Mixed (2:3) Solution of CD_3CN and $CDCl_3$

[benzylamine], M	k_{obsd}, s^{-1}	k, M^{-1} s^{-1}	T, K	10^3T^{-1}, K^{-1}	$\ln k$
0.464	5.6×10^{-5}	$1.2\ (2) \times 10^{-4}$	328.0	3.05	−9.04
0.464	6.7×10^{-5}	$1.4\ (2) \times 10^{-4}$	330.7	3.02	−8.86
0.203	4.0×10^{-5}	$1.9\ (2) \times 10^{-4}$	336.3	2.97	−8.57
0.290	5.2×10^{-5}	$1.8\ (2) \times 10^{-4}$	336.3	2.97	−8.62
0.464	7.8×10^{-5}	$1.7\ (2) \times 10^{-4}$	336.3	2.97	−8.70
0.580	1.2×10^{-4}	$2.1\ (2) \times 10^{-4}$	336.3	2.97	−8.47
0.870	1.8×10^{-4}	$2.1\ (2) \times 10^{-4}$	336.3	2.97	−8.47
0.464	9.8×10^{-5}	$2.1\ (2) \times 10^{-4}$	338.0	2.96	−8.47
0.464	1.2×10^{-4}	$2.5\ (2) \times 10^{-4}$	341.3	2.93	−8.26

Scheme I



the ionic chloro complexes (eq 2). This overlapping may be due simply to the close separation of the resonances, or it may be because the two palladium complexes are in equilibrium. From previous kinetic studies on chloride substitution by amines at palladium(II) centers, it is apparent that second-order rate constants are in the region of 10^{-3} s^{-1}.[12] These rates are comparable to NMR observation rates;[13] hence, the separate resonances due to $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ and $[PdCl(PhCH_2NH_2)(o\text{-}Ph_2PC_6H_4SMe)]Cl$ may be exchange broadened.

Since there have been no previous studies of amine alkylation by transition-metal-complexed methyl thioether groups, we have carried out a kinetic study of the reaction to learn more about the reaction pathway.

Kinetic Measurements on Methyl Transfer from $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ to Benzylamine. Intensity measurements on the decrease in the ^1H NMR methyl resonance at δ 3.02 for $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ with time have been used to obtain the rate law. The reaction is first order in $PdCl_2(o\text{-}Ph_2C_6H_4SMe)$, and the rate of the reaction (eq 3) is dependent

$$PdCl_2(o\text{-}Ph_2PC_6H_4SMe) + PhCH_2NH_2 \rightarrow PdCl_2(o\text{-}Ph_2PC_6H_4S)^- + PhCH_2NH_2Me^+ \quad (3)$$

on benzylamine concentration. Two sets of data have been collected under different experimental conditions. The data in Table III have been measured in acetonitrile, whereas the data in Table IV have been obtained in a mixed $CD_3CN/CDCl_3$ (2:3) solvent system. This mixed solvent has been used since it allows increased concentration of the palladium complex. The quantity of data collected is necessarily limited. In the absence of a useful chromophore change, ^1H NMR methods are the best options for data collection. Because of limited signal-to-noise ratio, it is necessary to collect data on solutions close to saturation in palladium complex, and hence we cannot make wide-ranging concentration changes in this complex. Temperature data have been collected up to the boiling point of the solvent, and the benzylamine concentration has been varied all the way from the minimum required to ensure pseudo-first-order conditions up to the maximum possible without creating the problem of causing substitution of the coordinated thioether ligand by benzylamine.[14] The measured rate constants are summarized in Tables III and IV.

The data for $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ in Table III show that the rate constant k is not completely constant under conditions of changing benzylamine concentration. This observation can be explained on the basis of a dual pathway where demethylation can occur by benzylamine interaction with both the uncharged and cationic complexes as shown in Scheme I. We can ignore a demethylation pathway involving nucleophilic attack by Cl^- since we have independently confirmed that added chloride ions does not react with $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$. From the Experimental Section, it is apparent from the rate law derivation that first-order dependence on benzylamine will occur if $k_2K[PhCH_2NH_2]/[Cl^-] > k_3$ and second-order dependence will be observed if the reverse condition exists. If we assume that $K[PhCH_2NH_2]$ and $[Cl^-]$ are approximately equal,[15] we arrive at the conclusion that an integral order in benzylamine will only be observed if k_2 and k_3 are widely different. The rate constant data (k) in Table III show that the trend in k may show a small decrease with

(12) (a) Palmer, D. A.; Kelm, H. *Inorg. Chim. Acta* **1975**, *14*, L27–L29. (b) Kane-Maguire, L. A. P.; Thomas, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1890–1894.

(13) Louch, W. J.; Eaton, D. R. *Inorg. Chim. Acta* **1978**, *30*, 243–50.

(14) (a) Cattalini, L.; Cusumano, M.; Degetto, S. *J. Chem. Soc., Dalton Trans.* **1978**, 12–14. (b) Cattalini, L.; Marangoni, G.; Coe, J. S.; Vidali, M.; Martelli, M. *J. Chem. Soc. A* **1971**, 593–595.

(15) The $[PhCH_2NH_2]$ is in the range 0.2–0.5 M. We have found K to be 1.0×10^{-4}, and we can calculate $[Cl^-]$ to be in the region of 7×10^{-5} M from $\alpha[PdCl_2(o\text{-}Ph_2PC_6H_4SMe)]$. No measurable rate change is observed with added Cl^- (0.1 M).

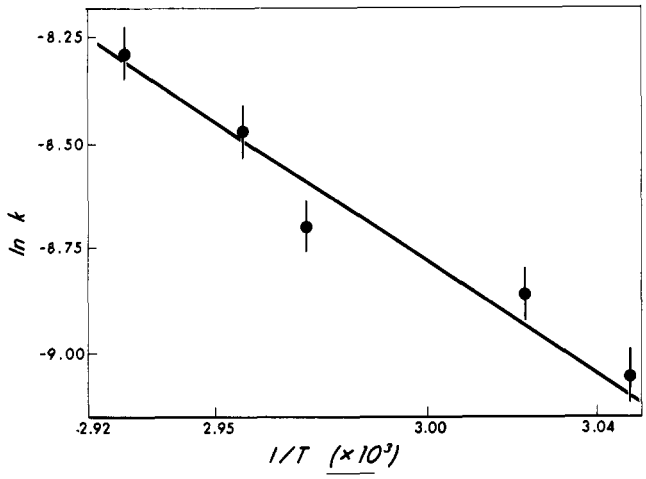


Figure 1. Arrhenius plot for the reaction of $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ with benzylamine.

increasing benzylamine concentration, but the more extensive rate data in Table IV show that k remains constant. Using our rate law derivation, we assume that as we increase $[PhCH_2NH_2]$ we could approach a rate law where the rate is proportional to $[PhCH_2NH_2]^2$. If this occurs, our conversion of k_{obsd} to k should be done by dividing by a benzylamine concentration that is greater than unity. The observed constancy of k shows that the rate is proportional to $[PhCH_2NH_2]$ and that the rate law for our experimental conditions is

$$\text{rate} = k_3[PdCl_2(o\text{-}Ph_2PC_6H_4SMe)][PhCH_2NH_2]$$

The proposed k_3 route by demethylation of the uncharged complex instead of the k_3 route from the ionic complex requires comment. Since the equilibrium constant K is small, k_2 would need to be significantly larger than k_3 for this pathway to be predominant. Intuitively, a cationic complex would be expected to induce greater carbonium ion character to the methyl group, but this effect may be considerably mediated by the coordination of benzylamine, a strong σ donor, in place of the electronegative chloride.

An Arrhenius plot of the temperature-dependent rate data is linear (Figure 1), and an Eyring plot gives $\Delta H^{\ddagger} = 12$ (2) kcal mol^{-1} and $\Delta S^{\ddagger} = -41$ (10) cal K^{-1} mol^{-1}. These values are obtained from the data collected in a mixed $CDCl_3/CDCN$ solvent, but the close similarity of the isothermal k values in Tables III and IV lends credence to the postulate that the kinetics in CD_3CN and $CDCl_3/CD_3CN$ will be closely similar. In the final section of this paper we will discuss these rate constants and activation parameters in relation to a mechanism for the reaction.

Methyl Transfer from $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$ to Benzylamine. In order to assess charge effects, and to possibly enhance the carbonium ion reactivity of the coordinated methyl thioether group, we have measured the methyl transfer rate to benzylamine from a cationic palladium(II) complex of *o*-(diphenylphosphino)thioanisole. This reaction between $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$ and benzylamine in CD_3CN has again been followed by ^1H NMR spectroscopy. The products are $Pd(o\text{-}Ph_2PC_6H_4SMe)_2$ and *N*-methylbenzylamine (eq 4). The known complex $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$[4d]

$$[Pd(o\text{-}Ph_2PC_6H_4SMe)_2]^{2+} + 2PhCH_2NH_2 \rightarrow Pd(o\text{-}Ph_2PC_6H_4S)_2 + 2PhCH_2NH_2Me^+ \quad (4)$$

shows a doublet ^1H NMR resonance at δ 2.92 ($^4J(PH) = 4$ Hz). This downfield-shifted peak verifies thioether coordination, and the large value of $^4J(PH)$ is supportive of a cis stereochemistry with the *S*-methyl groups trans to phosphorus. The methyl $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR resonances are singlets at δ 29.5 and δ 54.2, respectively. This ^{31}P NMR position is close to that of $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ at δ 58.0. The ^{31}P NMR spectrum of the product $Pd(o\text{-}Ph_2PC_6H_4S)_2$ shows a singlet at δ 53.7, which is in the same position as this fully demethylated complex prepared by demethylation in refluxing DMF.[4d] This monomeric red complex shows λ_{max} at 362 nm. Final confirmation of the structure of this complex is by single-crystal X-ray crystallography. The structure (Figure 2) shows the complex to be monomeric and planar about palladium(II).

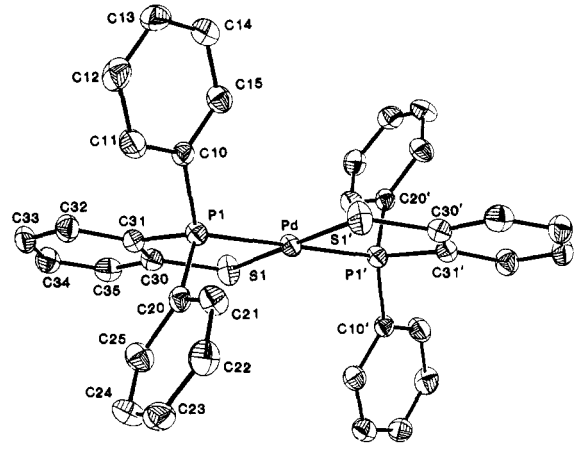


Figure 2. Thermal ellipsoid view of *trans*-$[Pd(o\text{-}(C_6H_5)_2PC_6H_4S)_2]$ at 35% probability. The hydrogens have been removed for clarity.

Table V. Atomic Positional Coordinates ($\times 10^4$) for *trans*-$[(o\text{-}S(C_6H_4)P(C_6H_5)_2)_2Pd]$

atom	*x*	*y*	*z*
Pd	0	0	0
S1	−2413 (2)	152 (1)	−122 (1)
P1	585 (2)	904 (1)	1649 (1)
C10	1755 (6)	2046 (4)	1814 (5)
C11	2499 (6)	2485 (4)	2838 (5)
C12	3257 (7)	3410 (4)	2917 (6)
C13	3242 (7)	3895 (4)	1942 (6)
C14	2542 (7)	3466 (4)	934 (6)
C15	1784 (6)	2535 (4)	845 (5)
C20	1463 (6)	140 (4)	2873 (5)
C21	2966 (7)	108 (4)	3188 (5)
C22	3648 (7)	−727 (4)	4091 (5)
C23	2880 (7)	−1137 (4)	4729 (6)
C24	1394 (8)	−922 (4)	4422 (6)
C25	715 (7)	−314 (4)	3528 (5)
C30	−2392 (6)	946 (4)	1018 (5)
C31	−1134 (6)	1341 (4)	1771 (5)
C32	−1164 (7)	2026 (4)	2643 (5)
C33	−2497 (7)	2268 (4)	2744 (6)
C34	−3772 (7)	1840 (4)	2001 (6)
C35	−3740 (7)	1201 (4)	1146 (5)

The labeling and molecular structure of *trans*-$Pd(o\text{-}Ph_2PC_6H_4S)_2$ are shown in Figure 2. Table V contains a listing of the final atomic positional parameters and estimated standard deviations for all non-hydrogen atoms. Selected bond distances and angles are presented in Table VI; the bond distances and angles of the remaining phenyl moieties are consistent with those expected for phenyl rings.

The molecular *trans*-$Pd(o\text{-}Ph_2PC_6H_4S)_2$ crystallizes in the monoclinic space group $P2_1/c$ with the Pd atom located at the origin. This gives the molecule crystallographic site symmetry $C_i\bar{1}$, in which there is half of a molecule per crystallographically independent unit. This crystallographic symmetry requires that the coordination about the Pd atom be trans and planar. Selected bond lengths and bond angles are given in Table VI and are as anticipated for this type of complex. The *o*-S-(C_6H_4)P group is essentially planar (rmsd (root mean standard deviation) = 0.0439) and forms a dihedral angle with the P1–Pd–S1 plane of 6.6°.

Table VI. Selected Bond Distances and Bond Angles with Estimated Standard Deviation for *trans*-[*o*-S(C_6H_4)P(C_6H_5)$_2$Pd]

(a) Bond Distances (Å)

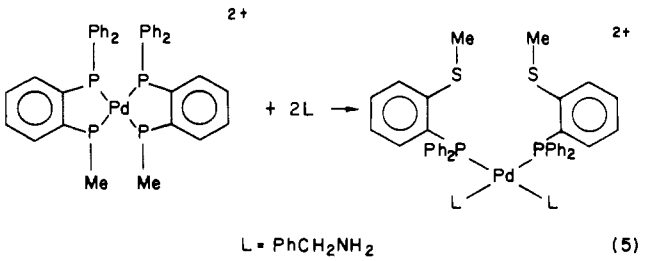
Pd-S1	2.308 (2)	C30-C31	1.363 (7)
Pd-P1	2.291 (1)	C31-C32	1.424 (9)
S-C30	1.769 (6)	C32-C33	1.383 (10)
P1-C0	1.825 (5)	C33-C34	1.386 (8)
P1-C20	1.789 (5)	C34-C35	1.373 (10)
P1-C31	1.823 (7)	C35-C30	1.416 (9)

(b) Bond Angles (deg)

P1-Pd-S1	86.6 (1)	S1-C30-C31	122.9 (5)
P1-Pd-S1′	93.4 (1)	S1-C30-C35	118.8 (4)
Pd-S1-C30	105.9 (2)	C31-C30-C35	118.3 (5)
Pd-P1-C10	117.4 (2)	P1-C31-C30	116.8 (5)
Pd-P1-C20	114.2 (2)	P1-C31-C32	121.7 (4)
Pd-P1-C31	107.0 (2)	C30-C31-C32	121.4 (6)
C31-P1-C10	107.3 (2)	C31-C32-C33	119.1 (5)
C31-P1-C20	105.6 (3)	C32-C33-C34	119.6 (6)
C20-P1-C10	104.6 (2)	C33-C34-C35	121.1 (7)
		C34-C35-C30	120.6 (5)

The Pd–S1 bond length is 2.308 (2) Å, and the Pd–P1 distance is 2.291 (1) Å. The P1–Pd–S1 angle is 86.6 (1)° and the P1–Pd–S1′ angle is 93.4 (1)°. The smaller P1–Pd–S1 angle probably reflects the preferred bite angle of the chelate ligand. The distances and angles are not significantly different from those found in [PdI(μ-$SC_6H_4PPh_2$-*o*)]$_2$,[5b] and the trans stereochemistry is the same as that found for Ni(*o*-$Ph_2PC_6H_4Se)_2$.[16]

At temperatures slightly above ambient, benzylamine causes the methyl resonance in [Pd(*o*-$Ph_2PC_6H_4SMe)_2]^{2+}$ at δ 2.92 to be slowly replaced by the methyl resonance at δ 2.35 in *N*-methylbenzylamine. Data obtained from intensity measurements on the ^{1}H NMR methyl resonance of the complex at δ 2.92 yield respectively values for k_{obsd} of 4.1 (2), 5.5 (7), and 8.3 (5) × 10^{-4} s^{-1} for separate benzylamine concentrations of 0.170, 0.220, and 0.340 M at 29.5 °C. These values translate into a value for k of 2.5 (7) × 10^{-3} mol^{-1} s^{-1}. This rate is significantly faster than that found for the methyl transfer reaction of benzylamine with $PdCl_2$(*o*-$Ph_2PC_6H_4SMe$). Again we have only been able to collect a limited amount of rate data because of side reactions that occur in the presence of too large an excess of benzylamine. Upon initial addition of benzylamine to [Pd(*o*-$Ph_2PC_6H_4SMe)_2]$-$(BF_4)_2$ there is a rapid partial decrease in the methyl resonance at δ 2.92. The kinetic measurements for methyl transfer to benzylamine are made by following the intensity changes in this resonance at δ 2.92, after subtracting this initial intensity drop (Figure 3). This initial loss in intensity correlates to a major extent with the corresponding increase in a ^{1}H NMR resonance at δ 2.26, a position close to that of the methyl group of *o*-$Ph_2PC_6H_4SMe$ itself at δ 2.22 in CD_3CN. These relative intensity changes are proportional to the quantity of added benzylamine and can be reasonably explained by benzylamine substitution of the methyl thioether arm of the chelate ligand (eq 5). Such reactions are fast compared to the methyl-



L = $PhCH_2NH_2$ (5)

transfer reaction,[14] and the calculated rate law in the Ex-

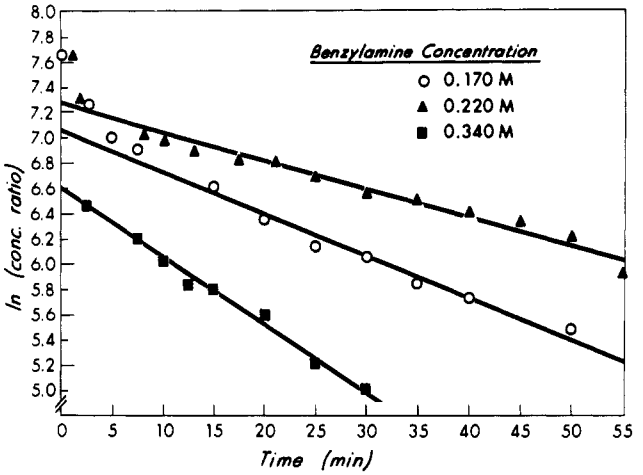


Figure 3. Plot of ln (concentration ratio) against time for the reaction of [Pd(*o*-$Ph_2PC_6H_4SMe)_2](BF_4)_2$ with benzylamine.

perimental Section assumes that in the initial equilibrium step (K) the forward and reverse reactions are rapid. Final support for the premise of thioether substitution by benzylamine comes from the ^{31}P NMR spectrum where the loss in intensity of the ^{31}P NMR resonance at δ 54.7 for [Pd(*o*-$Ph_2PC_6H_4SMe)_2]$-$(BF_4)_2$ corresponds with an increase in a singlet resonance at δ 31.4. This latter peak we assign to [Pd($PhCH_2NH_2)_2$(*o*-$Ph_2PC_6H_4SMe)_2](BF_4)_2$, which has both methyl thioether groups substituted by benzylamine.[17]

The rate constant data in Table III for this reaction show that k is constant over the limited range of benzylamine concentration and that the rate is proportional to the benzylamine concentration. For the sequence of steps

$$[Pd(o\text{-}Ph_2PC_6H_4SMe)_2]^{2+} + 2PhCH_2NH_2 \overset{K}{\rightleftharpoons} [Pd(PhCH_2NH_2)_2(o\text{-}Ph_2PC_6H_4SMe)_2]^{2+}$$

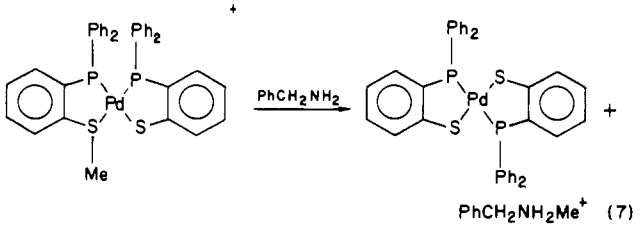
$$[Pd(o\text{-}Ph_2PC_6H_4SMe)_2]^{2+} + PhCH_2NH_2 \xrightarrow{k_2} Pd(o\text{-}Ph_2PC_6H_4SMe)(o\text{-}Ph_2PC_6H_4S)^+ + PhCH_2NH_2Me^+ \quad (6)$$

we derive the expression for the rate constant k:

$$k = \frac{k_2[PhCH_2NH_2]}{1 + K[PhCH_2NH_2]^2}$$

For first-order dependence on [$PhCH_2NH_2$], it is apparent that $K[PhCH_2NH_2]^2 << 1$. Since the uncomplexed compound *o*-$Ph_2PC_6H_4SMe$ does not demethylate with benzylamine, we can reasonably assume that $Pd(PhCH_2NH_2)_2$(*o*-$Ph_2PC_6H_4SMe)_2^{2+}$ is unreactive to demethylation.

The conversion of [Pd(*o*-$Ph_2PC_6H_4SMe)_2]^{2+}$ into Pd(*o*-$Ph_2PC_6H_4S)_2$ occurs in a stepwise manner. This intermediate *cis*-Pd(*o*-$Ph_2PC_6H_4SMe$)(*o*-$Ph_2C_6H_4S)^+$ will also undergo methyl transfer to benzylamine to yield *trans*-Pd(*o*-$Ph_2PC_6H_4S)_2$ (eq 7). In order to simplify our kinetic analysis,



$PhCH_2NH_2Me^+$ (7)

we have only collected rate data over the first half-life of the

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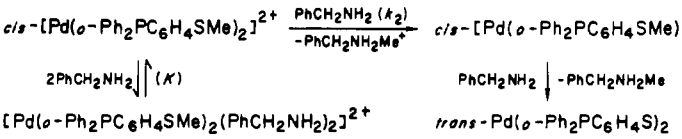
Scheme II



reaction. This intermediate has been identified by NMR spectroscopy since it shows a double doublet methyl (^{1}H) resonance at δ 2.977 (^4J(PH)trans = 3.6 Hz, ^4J(PH)cis = 0.6 Hz). This monomethylated complex [Pd(*o*-$Ph_2PC_6H_4SMe$)(*o*-$Ph_2PC_6H_4S$)]BF_4 can be assigned a cis stereochemistry on the basis of its ^{31}P NMR spectrum. The two inequivalent AB pair phosphorus nuclei show resonances at δ 57.08 (^2J(PP) = 40.5 Hz) and 46.64 (^2J(PP) = 40.5 Hz). This small value of ^2J(PP) correlates with mutually cis-coupled phosphine ligands.[18] Selective proton spin decoupling confirms that the methyl group is bonded to the phosphorus at δ 57.08.

From our experimental data we conclude that the reactions between the cationic complex [Pd(*o*-$Ph_2PC_6H_4SMe)_2$]$^{2+}$ and benzylamine can be summarized by Scheme II. The isomerization in the final step probably occurs via a pentacoordinate benzylamine-complexed intermediate.[19]

Mechanistic Considerations. The reactions of benzylamine with either $PdCl_2$(*o*-$Ph_2PC_6H_4SMe$) or [Pd(*o*-$Ph_2PC_6H_4SMe)_2$]$(BF_4)_2$ can be explained by nucleophilic S_N2 attack of benzylamine at the palladium(II)-induced electrophilic carbon of the thiomethyl ligand. This statement has broad implications, and we use this final section to substantiate the claim.

The rate laws show dependence on both palladium thioether complex and benzylamine. This is to be expected for a Menschutkin type amine alkylation[20] since the strong carbon–sulfur bond in the methyl thioether precludes a S_N1 mechanism where initial heterolytic cleavage of this bond occurs. A second aspect is the rate constants. The observed rate constants for these palladium(II) complexes with benzylamine correlate with those expected for an amine as nucleophile.[7] For reactivity to organic electrophiles, amines and thiocyanate ion are categorized close enough together to be within a single unit in the nucleophilic reactivity order. For alkyl halides the sequence $I^- > SCN^- > PhCH_2NH_2$ is usually observed.[21] Our rate constants for the reaction of the nucleophiles benzylamine, SCN^-, and I^- with PdX_2(*o*-$Ph_2PC_6H_4SMe$) in acetonitrile solvent follow the order $I^- > SCN^- > PhCH_2NH_2$, when we compare these benzylamine data with our previous results on SCN^- and I^-.[5] This parallel in reactivities supports the concept that the methyl-transfer reaction involves nucleophilic attack by amine and the saturated methyl carbon of coordinated *o*-(diphenylphosphino)-thioanisole.

The activation parameters are also supportive of a nucleophilic substitution pathway of the S_N2 type. The $\Delta S^\ddagger$ value of −41 (10) cal $K^{-1}mol^{-1}$ correlates with a transition state having less disorder than the reactants, a situation expected for an associative mechanism. The measured $\Delta H^\ddagger$ is 12 (2) kcal mol^{-1}. This value is significantly smaller than the $\Delta H^\ddagger$ of 22.9 (1.0) kcal mol^{-1} found for the methyl transfer from $Pd(SCN)_2$(*o*-$Ph_2PC_6H_4SMe$) to SCN^-. Nevertheless, there is a charge difference in the transition state between SCN^- and benzylamine as nucleophiles; hence, it is not unexpected that solvation effects will be different in the two transition states.[22] Inspection of the organic literature for the Menschutkin reaction in acetonitrile solvent confirms that an activation enthalpy in the region of 12 kcal mol^{-1} is to be expected.[23] Our data are all reasonably consistent therefore with a Menschutkin type reaction.

For the Menschutkin reaction, the transition state more resembles the reactants than the product pair of dissociation ions.[24] We need therefore to address the question of the role of the palladium (II) substituent on sulfur since *o*-(diphenylphosphino)thioanisole itself does not react with benzylamine. Two roles can be envisaged. Palladium in a divalent oxidation state is an electron-withdrawing substituent; hence, coordination of the thioether group as an electron-pair donor will result in reduced electron density at sulfur and the methyl carbon atoms. A second possible effect driving the methyl transfer reaction is the formation of a (thiolato)palladium(II) complex as product. To a d^8 transition-metal center a thiolato ligand more strongly bonds than a thioether group;[25] hence, from an organic chemistry viewpoint the (thiolato)palladium-(II) complex is a good leaving group.

The effect of palladium(II) coordination on the electrophilicity of the S-bonded methyl group can be discussed in a rational manner. If we presume an S_N2 mechanism and correlate this with the fact that the free ligand does not undergo methyl transfer to benzylamine, it is probable that coordination of the methyl thioether sulfur atom results in at least some withdrawal of electron density from the methyl carbon. This premise is supported by the ^{1}H and ^{13}C NMR spectral data. The NMR chemical shifts of the methyl protons in $PdCl_2$(*o*-$Ph_2PC_6H_4SMe$) and [Pd(*o*-$Ph_2PC_6H_4SMe)_2$]-$(BF_4)_2$ are δ 3.02 and 2.92, respectively, which represent a significant downfield shift from *o*-$Ph_2PC_6H_4SMe$ at δ 2.22. Similarly some support for the claim of some carbonium ion character of the methyl group in these palladium(II) complexes of *o*-(diphenylphosphino)thioanisole comes from comparison between the ^{13}C NMR chemical shift positions of these compounds with those of methyl thioethers and methylsulfonium ions. The methyl group in the complex PdI_2(*o*-$Ph_2PC_6H_4SMe$) shows a resonance at δ 31.1, which is downfield shifted by 13.8 ppm from the resonance at δ 17.3 in *o*-$Ph_2PC_6H_4SMe$.[5] By comparison, the chemical shift difference between the methylsulfonium ion Me_3S^+ ($\delta(^{13}C)$ = 27.5) and dimethyl sulfide ($\delta(^{13}C)$ = 19.8) is only 7.7 ppm.[26,27] This downfield shift for the sulfonium ion from the sulfide is smaller than that found between PdI_2(*o*-$Ph_2PC_6H_4SMe$) and *o*-$Ph_2PC_6H_4SMe$, indicating that there is electrophilic character at the methyl carbon of PdI_2no-$Ph_2PC_6H_4SMe$), insofar at least that chemical shift

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data are a measure of electron density at an atom.

A kinetic comparison between methylsulfonium ion reactivities and those of palladium(II) methyl thioether complexes is possible. The second-order rate constant for methyl transfer from p-$O_2NC_6H_4SMe_2^+$ to benzylamine in acetonitrile solvent at 25 °,c is 4.36×10^{-3} M^{-1} s^{-1}.[7] Comparative respective rate constants for $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$ and $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ are 2.5 (7) $\times 10^{-3}$ M^{-1} s^{-1} at 29.5 °C, and 3.0 (6) $\times 10^{-5}$ M^{-1} s^{-1} at 45 °C. It is apparent that the rate constants for the reaction of benzylamine with p-$O_2NC_6H_4SMe_2^+$ and $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2]^{2+}$ are closely similar but that the reaction with $PdCl_2(Ph_2PC_6H_4SMe)$ is much slower.

The creation of a carbonium ion center at the methyl carbon is not discernible by comparison between methyl carbon–sulfur distances as found by X-ray crystallography. From single-crystal structure data the measured carbon (methyl)–sulfur distances in the carbonium ion of $[PhSMe_2]^+ClO_4^-$ and in the complex $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ are 1.81 (2), 1.83 (2), and 1.815 (11) Å.[28,29] These carbon–sulfur distances are identical with the accepted value (1.82 Å) found in divalent dialkyl sulfides.[30] Structural arguments have, nevertheless, been used to try to propose a direction of attack at an alkyl caron atom of an alkylsulfonium ion compound; nevertheless, the authors conclude that there is no general tendency for nucleophilic centers to approach the α-carbon atoms in any particular direction.[31] The analogous chelate complexes of o-(diphenylphopshino)thioanisole with both nickel and platinum can be prepared. The complex $PtI_2(o\text{-}Ph_2PC_6H_4SMe)$ has been prepared from treating K_2PtCl_4 with excess iodide and 1 mol of o-$Ph_2PC_6H_4SMe$ (eq 8). The ^1H NMR spectrum

$$K_2PtCl_4 + o\text{-}Ph_2PC_6H_4SMe \xrightarrow{2KI} PtI_2(o\text{-}Ph_2PC_6H_4SMe) + 4KCl \quad (8)$$

shows a downfield-shifted methyl resonance at δ 3.62 (^3J(PtH) = 34 Hz) and the ^{31}P NMR spectrum a resonance at δ 43.6 (^1J(PtP) = 1660 Hz). No reactions with this compound have been attempted, but preliminary work on the compound $NiCl_2(o\text{-}Ph_2C_6H_4SMe)$ shows that it will transfer the methyl group to an amine.

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Registry No. $[Pd(o\text{-}Ph_2PC_6H_4SMe)_2](BF_4)_2$, 91741-05-8; $PtI_2(o\text{-}Ph_2PC_6H_4SMe)$, 91686-91-8; $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$, 14876-85-8; $[Pd(\mu\text{-}SC_6H_4PPh_2\text{-}o)Cl]_2$, 91686-92-9; *trans*-$Pd(o\text{-}Ph_2PC_6H_4S)_2$, 91741-06-9; benzylamine, 100-46-9.

Supplementary Material Available: Tables of final atomic positional parameters, bond lengths, bond angles, anisotropic thermal parameters, hydrogen atom coordinates, and structure factors (12 pages). Ordering information is given on any current masthead page.

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Nonadiabatic Effects in Outer-Sphere Electron-Transfer Reactions of Cobalt(III) Complexes: Experimental Probes of Charge-Transfer Perturbations of the Rates of Several Cross-Reactions[1]

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Whereas Franck–Condon models such as the one proposed by Marcus have been successful in treating the electron-transfer reactions of several metal ions, there have been some persistent issues in the reactivity of Co(III) complexes, which are not easily analyzed in terms of Franck–Condon-only models. Herein is presented the evidence for nonadiabatic effects that cause deviations from the Franck–Condon-only models in the reactions of $Co(H_2O)_6^{3+}$–$Fe(phen)_3^{2+}$, $Co((bzo)_3[12]hexaeneN_3)_2^{3+}$–$Co(sep)^{2+}$, and $Co(phen)_3^{3+}$–$Co([9]aneN_3)_2^{2+}$. The presence of an electronic constraint to reactions in the above systems is inferred on the basis that those bimolecular reactions may be perturbed by medium effects when the medium can participate in low-energy charge-transfer interactions. For example, several cross-reactions involving $Co(H_2O)_6^{3+,2+}$ would suggest a self-exchange rate of 10^{-12} M^{-1} s^{-1} for the couple, which differs from the experimentally measured value of 5 M^{-1} s^{-1} as well as that calculated from ground-state structural parameters, on the assumption of Franck–Condon-only models, viz. 7.5×10^{-6} M^{-1} s^{-1}. Such deviations are often the result of "electronic" or nonadiabatic effects. It has been found that those reactions in which an electronic barrier persists are sensitive to both the nature and the concentration of anions in the medium and the observed anion effects are over and above the electrostatic factors. A proposal is made that charge-transfer interactions between the anions and the collision complex may increase the radial parameters within the collision complex to permit better donor–acceptor overlaps, thereby decreasing the electronic constraints. In this work, an experimental means to assess nonadiabatic effects in electron-transfer reactions using three distinctly different sets of reaction partners is presented.

Introduction

Electron-transfer reactions not only are the simplest of oxidation–reduction processes but are also of central importance in many chemical and biological reaction systems.[2-13] At least in limiting cases, these reactions are simple enough that they have attracted a great deal of theoretical atten-

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