being further investigated, as is the extension of the present work to other organic silylenes.

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Kinetics and Mechanism of the Reaction of Palladium(II) Complexes of *o*-Diphenylphosphinothioanisole and *o*-Diphenylphosphinoselenoanisole with the Nucleophiles Thiocyanate and Iodide

Sir:

The conversion of methyl thioether complexes into thiolato metal compounds by the loss of a methyl group has been reported for a range of compounds.[1] The reaction with nonfluorinated ligands is commonly found to occur under high temperature conditions, and in only a few cases has an attempt been made to determine the fate of the alkyl group. The reaction has received attention because of its possible similarity to the demethylation of *S*-adenosylmethionine.[2] Mechanistically there has been a suggestion that an ionic pathway is involved with the reaction resembling the Zeisel ether cleavage.[1f] More recently, however, Shaw has found that the addition of halide ion had minimal effect on the dealkylation of $PtCl_2[PPh_2(o\text{-}MeOC_6H_4)]_2$ to *cis*-$Pt[PPh_2(o\text{-}OC_6H_4)]_2$.[3] There has hitherto been no kinetic investigations published on these demethylation reactions, and, in view of current interest in methylsulfonium and similar complexes,[4] we have decided to investigate more fully one of these reactions.

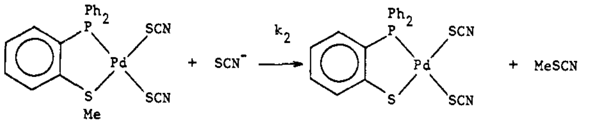
The first aim was to try to effect the reaction under more controlled conditions in order to compare the data obtained with that from the demethylation of *S*-adenosylmethionine and methylsulfonium compounds.[5] Previously the conversion of methyl thioether into thiolato complexes of palladium(II) has been carried out in refluxing DMF. We have now found that the reaction proceeds readily at temperatures above 55 °C in the presence of a nucleophile such as thiocyanate or iodide.[6] We have therefore made a kinetic study of the reaction between $(o\text{-}Ph_2PC_6H_4SMe)Pd(SCN)_2$ and $(o\text{-}Ph_2PC_6H_4SMe)PdI_2$ with their respective nucleophiles SCN^- and I^-.

Table I. Rate Data for the Reaction of $(o\text{-}Ph_2PC_6H_4SMe)Pd(SCN)_2$ (0.020 M) with SCN^- in CD_3CN Solvent

temp, °C	$[NaSCN]_0$, M	k_2(obsd), s^{-1}
75	0.213	3.25×10^{-4}
75	0.420	4.15×10^{-4}
75	0.635	5.79×10^{-4}
65	0.222	1.21×10^{-4}
55	0.222	0.38×10^{-4}

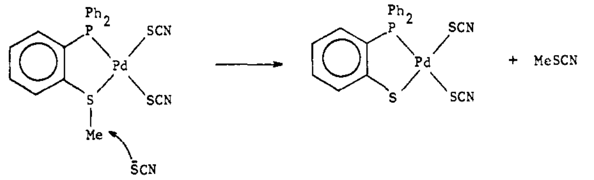
Table II. Rate Data for the Demethylation of $(o\text{-}Ph_2PC_6H_4SeMe)Pd(SCN)_2$ (0.023 M) with SCN^- in $CD_3CN\text{-}CH_2Cl_2$ (3:1) Solvent

temp, °C	$[NaSCN]_0$, M	k_2(obsd), s^{-1}
55	0.225	2.51×10^{-3}
45	0.225	1.05×10^{-3}
35	0.231	0.353×10^{-3}



(1)

The reaction between $(o\text{-}Ph_2PC_6H_4SMe)Pd(SCN)_2$ and SCN^- follows the rate law rate = k_2[complex]$[SCN^-]$[(eq 1). The rate has been measured by following the decrease in size of the ^1H NMR methyl peak in the complex.[7] The compound MeSCN is formed during the reaction. This was identified by comparison of its ^1H NMR chemical shift and its gas chromatographic retention time against those authentic samples. The kinetics has also been followed by measuring the increase in MeSCN concentration, and the same rate constant found. This isomer MeSCN appears to be the one formed directly in the reaction since initially added MeNCS is recovered unchanged at the end. These data are in agreement with a mechanism involving direct nucleophilic attack by the thiocyanate sulfur at the methyl carbon of the coordinated ligand (eq 2). The data are shown in Table I. It is apparent that a plot



(2)

of k_2(obsd) against [NaSCN] is not linear. This deviation for ionic reactions in nonaqueous solvents has been observed before and arises because effects such as ion pairing cause the activity of the thiocyanate ion to be less than that obtained simply by using the value for [NaSCN].[8] The degree of dissociation has previously been related to both the dielectric constant and donor number of the particular solvent, and is roughly proportional to both these quantities. From these data it is apparent that there will be considerable ion pairing of NaSCN in this solvent. For the solvent Me_2SO, however, dissociation should be more complete, and this is borne out by the ^{23}Na chemical-shift data for NaSCN in this solvent.[9] At 77.6 ± 0.2 °C the respective rate constants k_2(obsd) in $Me_2SO\text{-}d_6\text{-}CH_2Cl_2$ (3:1) solvent are 2.26×10^{-4} and 4.06×10^{-4} for NaSCN concentrations of 0.222 and 0.387 M. Using the approximation that $[SCN^-]$ = [NaSCN], the rate constants k_2 are 1.02×10^{-3} and 1.05×10^{-3} M^{-1} s^{-1}, showing the ion pairing effect to be negligible in this solvent. From an Eyring plot of the data in Table I the values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 22.9 ± 1.0 kcal/mol and −9.2 ± 2.1 cal/mol, respectively.

We have measured the rate of the reaction of the selenium analogue $(o\text{-}Ph_2PC_6H_4SeMe)Pd(SCN)_2$ with SCN^- (Table II). These data confirm the previous suggestion that the rate

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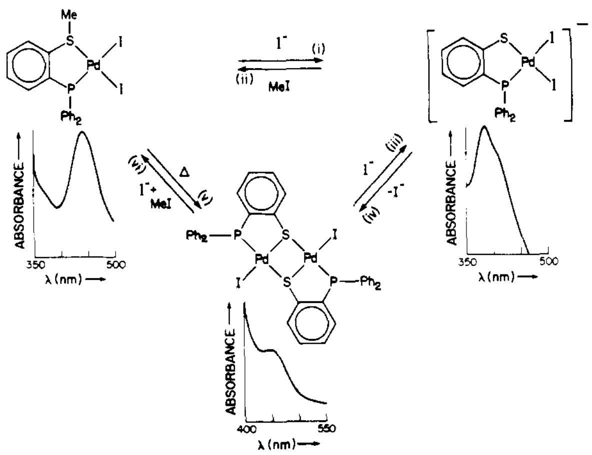
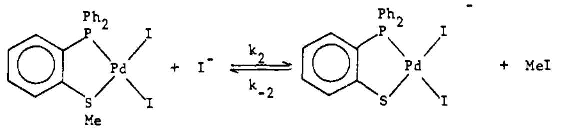


Figure 1. Interconversion reactions and electronic spectra of reactants and products.

is faster,[1g] the enhancement being 66-fold at 55 °C. The respective activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 18.9 ± 1.3 kcal/mol and −12.9 ± 2.3 cal/mol, considerably lower than the corresponding values for the thioether complex.

For reaction with the nucleophile iodide (eq 3), the situation is more complicated. This reaction does not go to completion



(3)

because the competing back-reaction leads to the establishment of an equilibrium condition. Because of the lower solubility of the starting iodo complex in CD_3CN, these kinetics were run in a $CDCl_3$-CD_3CN (1:2.5) mixed solvent. The data were obtained at 80 °C, and, because of the nonlinearity of the log[concentration] against time plots, they were analyzed by an initial rate method. From tangents of the plots of concentration against time for the four NaI concentrations 0.10, 0.21, 0.30, and 0.42 M, the rates −d[concentration]/d*t* can be found for both 20 and 30% demethylation. This gives seven values (the reaction with [NaI] = 0.10 M reaches equilibrium before 30% demethylation) which can be solved for simultaneously. The respective values of k_2 and k_{-2} are 3.4×10^{-3} and 2.5×10^{-1} M^{-1} s^{-1}.[10] This leads to an equilibrium constant K of 1.4×10^{-2} at 80 °C.[11,12] As a check we have separately measured the equilibrium constant K. Using a concentration of 0.01 M (o-$Ph_2PC_6H_4SMe$)PdI_2, we have allowed equilibrium to be established over 75 min with sodium iodide concentrations of 0.10, 0.30, and 0.42 M. After attainment of equilibrium, the final concentrations of initial complex are 6.7×10^{-3}, 5.8×10^{-3}, and 4.8×10^{-3} M, leading to an average K of $1.8 \pm 0.35 \times 10^{-2}$. These results are obviously less accurate than those obtained in the thiocyanate case; nevertheless the data show sufficient internal consistency to be useful.

The final product in these iodide reactions is the complex anion [(o-$Ph_2PC_6H_4S$)PdI_2]$^-$. This differs from the dimer product [(o-$Ph_2PC_6H_4S$)PdI]$_2$ obtained by heating (o-$Ph_2PC_6H_4SMe$)PdI_2 in DMF. Under our experimental conditions an excess of anion is present in the reaction mixture and this causes the difference. The electronic spectrum (Figure 1) of this anion [(o-$Ph_2PC_6H_4S$)PdI_2]$^-$ shows a band at 390 nm with a shoulder at 410 nm.[13] This contrasts with the spectra of both (o-$Ph_2PC_6H_4SMe$)PdI_2 and [(o-$Ph_2PC_6H_4S$)PdI]$_2$ which show absorptions at 450 and 460 nm, respectively. If we assign these electronic bands to M ← I (LMCT) transitions, the higher energy band is to be expected in the anion where electrons are being transferred to a negatively charged metal center. As shown in Figure 1, these three complexes are interconvertible. We have separately observed all these reactions and spectral changes, with the exception of the conversion of [(o-$Ph_2PC_6H_4S$)PdI_2]$^-$ into [(o-$Ph_2PC_6H_4S$)PdI]$_2$, where we were unable to *completely* remove iodide to yield pure dimer. Interestingly, a pure sample of dimer prepared by thermolysis in DMF will not react with methyl iodide without prior addition of iodide ion to the solution.

Our data are thus in agreement with the earlier suggestion that *demethylation from methyl thioether-palladium(II) complexes occurs in a manner similar to the Zeisel ether cleavage.* Quantitative comparison with the energetics of demethylation from S-adenosylmethionine is somewhat imprecise because of differences in reaction conditions for the separate studies, but our value of 23.6 kcal/mol for E_a compares very favorably with the value of 23.8 kcal/mol found by Coward in S-adenosylmethionine analogue compounds.[5b] Each reaction appears to involve nucleophilic attack at a saturated carbon, and *the close similarity of the activation parameters shows that coordination of thioether in an uncharged palladium(II) complex can create a methyl group of comparable electrophilicity with one on a sulfonium ion.*

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(6) We have confirmed that the free ligand o-$Ph_2PC_6H_4SMe$ demethylates insignificantly under these conditions. In a series of related experiments, we find that the complex (o-$Ph_2PC_6H_4SMe$)$Pd(SCN)_2$ demethylates within 20 min in refluxing Me_2SO and within 2 h under reflux with DMF and benzonitrile. The complex does not demethylate significantly after 90 min in refluxing acetonitrile, and there is no demethylation with the electrophile mercuric chloride, or under UV irradiation. Interestingly we have prepared the new compound $RuCl_2$(o-$Ph_2PC_6H_4SMe$)$_2$ and find that it will not readily demethylate.

(7) The initial size of the peak was measured in the NMR spectrometer and the capped tube transferred to the thermostated bath. The time to achieve the reaction temperature after immersion is 15 s. The recorded times are the interval at which the reaction mixture is at the bath temperature. Removal and cooling quenches the reaction. The concentration of the complex was calculated from peak height ratios referred to the initial value, and checks were made that for the sharp peak height measurement could be substituted for integrated area. The rate constant was found from plots of log[concentration] against time which was linear for ~2 half-lives.

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(10) These values have been calculated using the following approximations for the iodide ion concentrations: [NaI] = 0.1, [I^-] = 0.088; [NaI] = 0.21, [I^-] = 0.15; [NaI] = 0.3, [I^-] = 0.21; [NaI] = 0.42, [I^-] = 0.27. These data are measured for sodium iodide in anhydrous acetone and we have made the assumption that our mixed solvent system will approximate this solvent in dielectric constant and donor number.

(11) We have added sodium perchlorate to these solutions in view of ionic strength effects but find little change in the observed reaction rates.

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(13) This spectrum was obtained by allowing the reaction to proceed to completion under conditions where the methyl iodide distills from an open tube.

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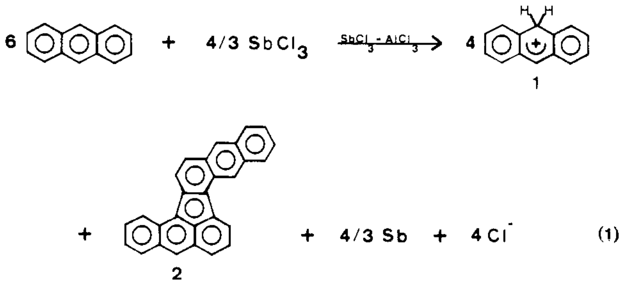
Protonation of Some Arenes in an Aprotic Medium

Sir:

We have found that the dissolution of anthracene (up to 5 mol %) in an aprotic liquid, anhydrous $SbCl_3$–10 mol % $AlCl_3$, at 80–130 °C, results in the prompt formation of stable solutions of the 9-anthracenium ion (**1**) in 50–60% yields. The proton source for this novel reaction is the condensation-dehydrogenation of a part of the anthracene combined with the reduction of $SbCl_3$ to amorphous metal. The principal condensed product is anthra[2,1-*a*]aceanthrylene (**2**) and in terms of this product the overall reaction is as shown in eq 1. Under similar conditions 9,10-dimethylanthracene (**3**) formed the 9*H*-9,10-dimethylanthracenium cation (**4**) and naphthacene (**5**) formed the 5-naphthacenium cation (**6**), while naphthalene (**7**) was not protonated.



Previously, the protonation of anthracene and similar arenes had only been achieved by providing strong proton donors such as in superacid media[1] or with $AlCl_3$–HCl.[2] In contrast, we deliberately suppressed such proton donors by working with carefully purified materials under clean argon atmospheres in glove boxes and vacuum-tight reaction vessels. Commercial 99.99% anhydrous $SbCl_3$ from three vendors was further purified by refluxing over Sb metal (to remove $SbCl_5$) followed by vacuum sublimation at 40 °C and then distillation under Ar in a sealed system to yield a colorless solid that melted at 73 °C to a colorless liquid. Aluminum chloride was made according to a published procedure[3] from zone-refined 99.9999% Al and semiconductor-grade anhydrous HCl to yield a colorless solid.

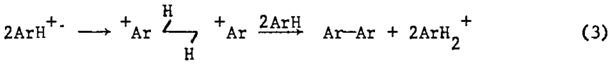
In our experiments, the formation of arenium ions was studied by ^{1}H NMR measurements on the melt both with and without a $(CH_3)_4N^+$ internal standard. The identity of **1** was confirmed from a comparison of its integrated ^{1}H NMR spectrum with that obtained from an authentic sample of 9-anthracenium heptachlorodialuminate,[2] $C_{14}H_{11}Al_2Cl_7$, in $SbCl_3$ without extra $AlCl_3$. Cation **4** was identified by comparison with the published spectrum,[4] and **6** was identified by comparison with the spectrum of **1**. These cations formed rapidly, in <10 min at 80–130 °C, and remained unchanged for some hours. The NMR spectra of other products, such as **2**, were not resolved but appeared as a broad, nondescript envelope in the aromatic region.

In the case of anthracene the reaction products from the NMR studies and from larger scale reactions performed in sealed glass ampules or Schlenk glassware were determined following hydrolysis of the melt in 6 M HCl and dissolution of the organics in CH_2Cl_2. The organic products were isolated by LC and identified by UV, NMR, and mass spectroscopy. Elemental Sb was analyzed by atomic absorption spectroscopy and X-ray diffraction. The identity and amounts of the products remained the same for all reaction conditions studied, 10–60 min at 80–130 °C. The mole ratio of **1**:**2**:Sb was found to follow the stoichiometry required by reaction 1.

In an earlier study[5] we showed that anthracene and **5** in $SbCl_3$ without excess $AlCl_3$ undergo hydrogen redistribution reactions to form hydroaromatics (not found in the presence of excess $AlCl_3$) and condensed aromatics including three bianthracenes and **2**.[6] Furthermore, no reduction of the $SbCl_3$ solvent was observed. Under the same conditions we found **7** to be unreactive.

The presence of excess $AlCl_3$ is necessary for reaction 1 to occur, and in our experiments the $AlCl_3$/arene mole ratio was 2 or more. A consideration of published electrochemical data[7] obtained in molten $SbCl_3$ implicates the arene radical cation as an intermediate in these self-protonation reactions. The results show that the role of the $AlCl_3$ is that of enhancing the oxidizing power of $SbCl_3$. These facts can be accounted for by reactions 2 and 3.

$$ArH + 1/3\ SbCl_3 \longrightarrow ArH^{+\cdot} + 1/3\ Sb + Cl^- \qquad (2)$$



$$2ArH^{+\cdot} \longrightarrow {}^{+}Ar\overset{H}{\underset{H}{\diagup}}{}^{+}Ar \xrightarrow{2ArH} Ar{-}Ar + 2ArH_2^{+} \qquad (3)$$

On the basis of the electrochemical data,[7] it can be shown that the presence or absence of excess $AlCl_3$ in $SbCl_3$ should affect reaction 2 in a way that parallels the influence of $AlCl_3$ on the protonation–solvent reduction reactions presented here. That is, for anthracene, **3**, and **5** at moderate concentration levels in $SbCl_3$, reaction 2 is thermodynamically favorable with excess $AlCl_3$ present but unfavorable with $AlCl_3$ absent,[8] whereas for **7** reaction 2 is not favorable whether $AlCl_3$ is present or absent.[9] Enhancement of the oxidizing strength of $SbCl_3$ by added $AlCl_3$ arises from the reaction of $AlCl_3$ (or substances derived from it)[10] with Cl^- released through the reduction of $SbCl_3$.

We have recently obtained intense, well-resolved ESR spectra for the radical cations of anthracene, **3**, and **5** (but not **7**) formed from dilute solutions of the parent hydrocarbons in $SbCl_3$–$AlCl_3$ melts without the addition of other oxidants. These and other data[11] indicate that reaction 2 occurs and is influenced by added $AlCl_3$ in at least qualitative agreement with what would be expected from the electrochemical measurements.

We have presented a novel arene self-protonation reaction in an aprotic $SbCl_3$–$AlCl_3$ melt for which there is considerable evidence that the reaction proceeds through an oxidation of the arene to a radical cation by the $SbCl_3$. The function of the $AlCl_3$ appears to be that of enhancing the oxidizing power of the $SbCl_3$ solvent. Our investigations of this chemistry continue, and a full report will soon be prepared.

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