that the reaction suggested in Scheme VII is consistent with all experimental findings, and we note that the process of M^+-mediated formation of C_4H_8 from 2 can be accounted for in terms of C–C bond activation without C–H activation.[24]

C. Co^+-Mediated Formation of C_2H_4 and C_2H_6 from 2. These two reactions are, again, remarkably specific. Ethylene formation involves the $\omega/(\omega - 1)$ positions of an ethyl chain, as is the case for the production of molecular hydrogen (see above). We suggest that the two reactions which are subject to large primary kinetic isotope effects favoring the elmination of H_2 versus HD and D_2 and of C_2H_4 versus $C_2H_2D_2$ and C_2D_4, respectively, proceed in the same way as the analogous reactions of the isomeric complex 1-Co^+ (Scheme III).

High specificity is also the hallmark for the generation of ethane from 2-Co^+, in that the reaction is not preceded by any exchange processes. The neutral species is built up by an intact ethyl group and a hydrogen atom that is provided by the methylene part of the second ethyl group. All other positions are inert. From the ratio of $C_2H_4D_2$ versus C_2H_5D (for **2d**-Co^+) and of C_2HD_5 versus $C_2H_3D_3$ (for **2h**-Co^+) one can estimate the isotope effect k_H/k_D = 1.3. The data given in Table III for the formation of ethane from 2-Co^+ are in line with the mechanism postulated in Scheme VIII.

Acknowledgment. The financial support of this work by the Volkswagen-Stiftung, the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, the Graduiertenkolleg Chemie (Berlin), and the Gesellschaft von Freunden der Technischen Universität Berlin is gratefully acknowledged. We are indebted to Dr. Thomas Weiske for technical assistance, Dipl.-Chem. Detlef Schröder, and Prof. Peter Armentrout for enlightening discussions, and the reviewers for helpful comments.

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[24] Prof. P. Armentrout (private communication to H.S., Nov 1989) has suggested an alternative mechanism that proceeds through an initial C–H bond activation step. While this variant cannot be ruled out with certainty, in contrast to the simplicity of Scheme VII it is extremely complex and introduces several assumptions, none of which have to be made by postulating direct C–C bond activation.

Silylative Decarbonylation. 3. Transfer Selectivity and Substituent Rate Effects[1]

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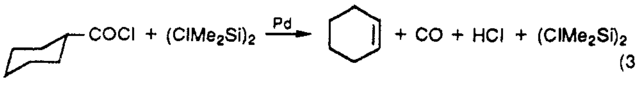
This report describes investigations into those variables that affect the rate of the silylative decarbonylation reaction of aromatic acid chlorides and chloromethyldisilanes. Electron-withdrawing substituents on the aromatic acyl halide enhanced the rate of product formation, and a Hammett analysis of a series of competitive reactions gave a ρ value of +2.4. Sequential replacement of chloride for methyl on the disilane did not result in a similar rate enhancement. The reactions were first order in disilane reagent as shown by continuous carbon monoxide monitoring. The use of unsymmetrical disilanes in reactions with acid chlorides resulted in the preferential transfer of the lesser chlorinated silicon to the aromatic ring and chlorination of the more halogenated silicon. Introduction of as few as one chlorine, e.g., chloropentamethyldisilane, led to the exclusive formation of decarbonylated products in stark contrast to hexamethyldisilane reactions. Mechanistic implications of these observations are discussed.

Introduction

The palladium-catalyzed reaction of aromatic acid chlorides with methylchlorodisilanes yields predominately arylchlorosilane products (eq 1).[2] This process, which we have termed silylative decarbonylation, provides a convenient and general route to many previously unavailable substituted arylchlorosilanes and siloxanes from which a variety of novel high-temperature silicone polymers and copolymers can be prepared.[3] In contrast, the metal-catalyzed reaction of hexamethyldisilane with analogous aromatic acid chlorides gives primarily acyltrimethylsilanes (eq 2), except in the case of aromatic acid chlorides bearing

$$\mathrm{ArCOCl} + (\mathrm{Cl}_{3-n}\mathrm{Me}_n\mathrm{Si})_2 \xrightarrow{\mathrm{Pd}} \mathrm{ArSiMe}_n\mathrm{Cl}_{3-n} + \mathrm{CO} + \mathrm{Me}_n\mathrm{SiCl}_{4-n} \quad (1)$$

$$\mathrm{ArCOCl} + (\mathrm{Me}_3\mathrm{Si})_2 \xrightarrow{\mathrm{Pd}} \mathrm{ArCOSiMe}_3 + \mathrm{Me}_3\mathrm{SiCl} \quad (2)$$



(3)

very strong electron-withdrawing substituents.[2a,4] Aliphatic acid chlorides are not silylated by methylchlorodisilanes when subjected to analogous reaction conditions but instead undergo decarbonylation and β-hydrogen elimination to yield olefins, HCl, and CO (eq 3).[2a,5]

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[1] (a) Part 2: Rich, J. D. *Organometallics* **1989**, *8*, 2606. (b) Preliminary results of this work were presented at the VIII International Symposium on Organosilicon Chemistry, June 7–12, 1987, St. Louis, MO.

[2] (a) Rich, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5886. (b) Rich, J. D. U.S. Patent 4,709,054, 1987, to General Electric Co. (c) Rich, J. D. U.S. Patent 4,604,477, 1986, to General Electric Co.

[3] (a) Rich, J. D.; Liu, W. L. U.S. Patent 4,563,154, 1985. (b) Rich, J. D. U.S. Patent 4,604,442, 1986; U.S. Patent 4,678,610, 1987. (c) Policastro, P. P.; Rich, J. D. U.S. Patent 4,668,754, 1987. (d) Rich, J. D.; Policastro, P. P.; Hernandez, P. K. U.S. Patent 4,794,153, 1988; 4,780,501 (1989, all to General Electric Co.

[4] (a) Yamamoto, Y.; Suzuki, S.; Tsuji, J. *Tetrahedron Lett.* **1980**, 1653. (b) Eaborn, C.; Griffiths, R.; Pidcock, A. *J. Organomet. Chem.* **1982**, *225*, 331.

[5] See: Tsuji, J.; Piro, P.; Wender, I. In *Organic Synthesis via Metal Carbonyls*, Wiley-Interscience: New York, 1977; Vol. 2, pp 631–636 and references therein.

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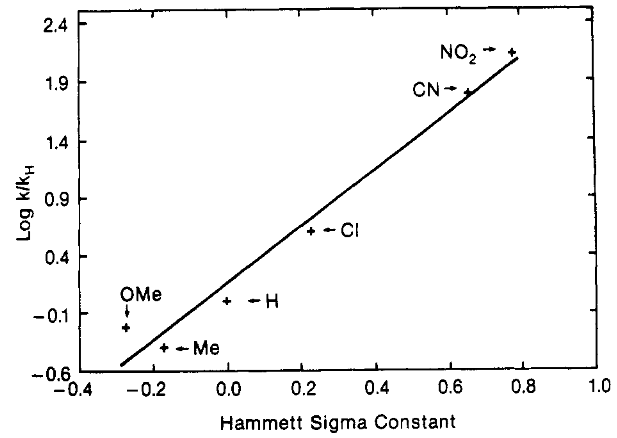


Figure 1. Hammett σ–ρ analysis of the reaction of para-substituted aromatic acid chlorides with 1,2-dichlorotetramethyldisilane. All reactions carried out in refluxing *o*-xylene, $\rho = +2.4$.

In addition to the effect of acid chloride and silicon substituents on the nature of the reaction products, it was qualitatively observed that the rate of reaction was controlled by the electronic influence of the aromatic substituents. To further understand the complex parameters that govern this intriguing reaction, a study was undertaken to examine the effect of substituents on the reaction rate and to investigate the transfer selectivity of unsymmetrical disilanes in reactions with aromatic acid chlorides.

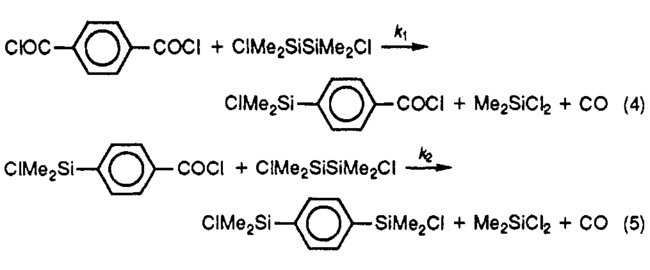
Results and Discussion

Aromatic Substituent Rate Effect. A competitive rate study of the palladium-catalyzed reaction of various aromatic acid chlorides with 1,2-dichlorotetramethyldisilane was carried out in the following manner. Equimolar amounts of para-substituted aryl acid chloride and benzoyl chloride were dissolved in xylene to which was added 1 mol % of bis(benzonitrile)palladium dichloride and 2 mol % of triphenylphosphine. The reactions were carried out at 140 °C, and the relative reactant and product compositions determined by gas chromatography. Relative reaction rates as determined by GC are as follows:

$$\begin{array}{lcccccc} & p\text{-NO}_2 > & p\text{-CN} > & p\text{-Cl} > & \text{H} > & \text{Me} \approx & \text{OMe} \\ k/k_{\text{H}} & 130 & 60 & 4 & 1 & 0.4 & 0.6 \end{array}$$

A Hammett analysis of the log of the relative rates, k/k_{H}, versus para substituent σ constants showed a reasonably good correlation (0.988) with a ρ value of +2.4 (see Figure 1).[6]

In addition to the mechanistic implications of the large positive ρ value, the rate effects were also of synthetic importance, particularly with regard to the silylation of industrially important poly(acid chlorides) (e.g., iso- and terephthaloyl chloride). The palladium-catalyzed reaction of equimolar amounts of 1,2-dichlorotetramethyldisilane with terephthaloyl chloride (neat, 130 °C), gave a 99:1 ratio of *p*-(chlorodimethylsilyl)benzoyl chloride to 1,4-bis(chlorodimethylsilyl)benzene (eq 4). This fortunate phenomenon eliminated the need of a tedious separation of reaction products, and the silylated acid chloride was obtained by simple vacuum distillation (90% isolated yield).[2c] Similar results were obtained when isophthaloyl chloride was used or when other chlorinated methyldisilanes such as *sym*-tetrachlorodimethyldisilane were reacted with either tere- or isophthaloyl chloride. The silylated aromatic acid chlorides provided entry to a number of valuable silicone polymer and copolymer applications.[3] Synthesis of bis(chlorodimethylsilyl)benzene, an important precursor to the silphenylene class of silicone rubber, was prepared either stepwise from *p*-(chlorodimethylsilyl)benzoyl chloride (eq 5) or by direct reaction of 2 equiv of disilane with the diacid chloride (64% yield).



The stepwise silylation of terephthaloyl chloride can be explained by a simple rate phenomenon, taking into account the substituent effects shown in Figure 1. In the first silylation of terephthaloyl chloride the unreacted *p*-acyl chloride influences the reacting site as an electron-withdrawing substituent. Assuming that reaction of terephthaloyl chloride with excess 1,2-dichlorotetramethyldisilane occurs in two discrete steps, the second step involves silylation of *p*-(chlorodimethylsilyl)benzoyl chloride with the silyl group being a weaker withdrawing substituent than acyl chloride.

Calculation of the rate difference between acyl chloride and chlorodimethylsilyl substituents should be given by $\log (k_{\text{COCl}}/k_{\text{SiMe}_2\text{Cl}}) = \rho(\sigma_{\text{COCl}} - \sigma_{\text{SiMe}_2\text{Cl}})$. When the 2:1 statistical factor is taken into account, the observed rate differences for the first and second silylations of terephthaloyl chloride is given by $k_{\text{COCl}}/k_{\text{SiMe}_2\text{Cl}}$. Difficulty arises in defining reliable values for $\sigma_{\text{SiMe}_2\text{Cl}}$ and σ_{COCl}. The substituent constant σ for chlorodimethylsilyl has been determined from dipole moment (+0.30),[7] from NMR studies (+0.15),[7,8] and from kinetics of bromination of silyl-substituted phenyldimethylsilanes (+0.02).[9] If the substituent constant for COCl is estimated to be +0.5, then the calculated rate difference for the first and second silylations, using the three values for $\sigma_{\text{SiMe}_2\text{Cl}}$ is 5.8, 12.8, or 25.4. The large differences in σ for $-\text{SiMe}_2\text{Cl}$, which have been attributed to solvent effects, preclude any meaningful comparison between calculated and observed rate differences.

Kinetics were also investigated by measuring the volume of carbon monoxide gas evolved during the reaction by using a microprecessor-controlled self-leveling buret. The experiments were carried out at 145 °C under pseudo-first-order conditions in acid chloride (1.2 M in *o*-xylene) with 1,2-dichlorotetramethyldisilane (0.05 M). Bis(methyldiphenylphosphine)palladium dibromide was employed as catalyst because it gave continuously homogeneous solutions, whereas the standard synthetic catalyst (bis(benzonitrile)palladium dichloride and triphenylphosphine) gave less reproducibly homogeneous reactions. IR analysis of the gas collected in the buret confirmed carbon monoxide as the only product isolated. The pseudo-first-order plots for the reactions of 1,2-dichlorotetramethyldisilane with excess terephthaloyl chloride, trimellitic anhydride acid chloride, and *p*-nitrobenzoyl chloride are shown in Figure 2. The observed rate con-

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(6) Hammett σ constants were obtained from: Ritchie, C. D.; Segar, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323. Deviation of those groups that are electron donating, *p*-Me, and especially *p*-OMe, was not surprising since donor acid chlorides undergo several side reactions, such as benzil formation and decarbonylation without silylation to give substituted chlorobenzenes.[2a]

(7) Yen, V. K.; Papouskova, Z.; Schraml, J.; Chvalovsky, V. *Coll. Czech. Chem. Commun.* **1973**, *38*, 3167.

(8) Lipowitz, J. *J. Am. Chem. Soc.* **1972**, *94*, 1582.

(9) Mares, F.; Plzak, Z.; Hetflejs, J.; Chvalovsky, V. *Coll. Czech. Chem. Commun.* **1971**, *36*, 2957.

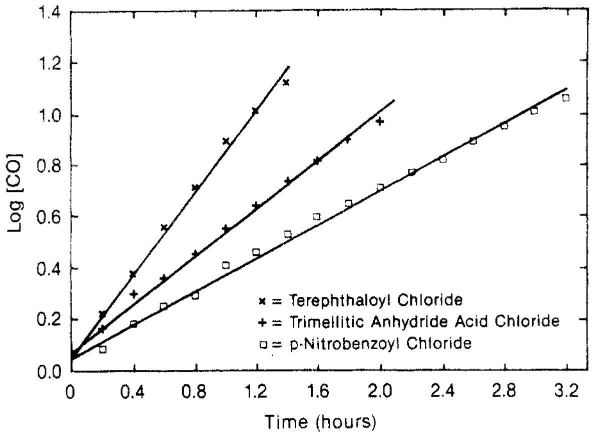


Figure 2. Pseudo-first-order kinetic plots for the reactions of terephthaloyl chloride, trimellitic anhydride acid chloride and *p*-nitrobenzoyl chloride with 1,2-dichlorotetramethyldisilane. First-order rate constant found: terephthaloyl, $k = 5.1 \times 10^{-4}$ s^{-1}; trimellitic, $k = 3.0 \times 10^{-4}$ s^{-1}; *p*-nitro, $k = 2.1 \times 10^{-4}$ s^{-1}. Reaction temperature 145 °C.

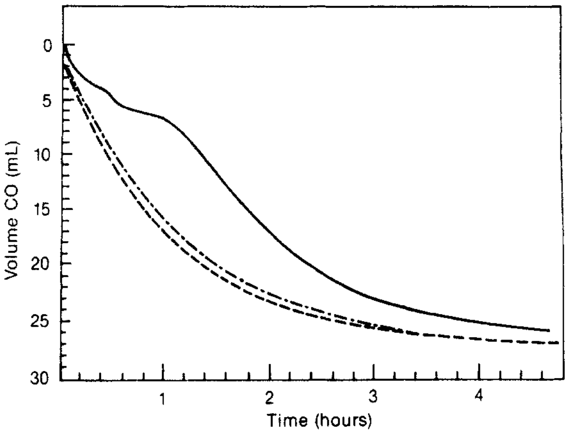


Figure 3. Volume change vs time plot for the reaction of terephthaloyl chloride and 1,2-dichlorotetramethyldisilane: —, first aliquot of disilane; ---, second aliquot of disilane; -·-, third addition of disilane. Reaction temperature 145 °C, $(MePh_2P)_2Pd$ Br_2 employed as catalyst.

stants were 5.1×10^{-4} s^{-1} for terephthaloyl chloride, 3.0×10^{-4} s^{-1} for trimellitic anhydride acid chloride, and 2.1×10^{-4} s^{-1} for *p*-nitrobenzoyl chloride.

The order of reactivity terephthaloyl > trimellitic > *p*-nitrobenzoyl was predicted on the basis of relative electron-withdrawing ability of the substituent and taking into account the concentration effect on two reacting sites in terephthaloyl chloride. However, if the observed rate for terephthaloyl chloride is corrected for the inherent concentration factor, it is still greater than for *p*-nitrobenzoyl chloride, 1.1×10^{-4} s^{-1} vs 0.97×10^{-4} s^{-1}. This would appear to be in contradiction to the results obtained from competitive reactions as described in Figure 1, since the para σ value for nitro must be greater than $-COCl$. This may be due to the high effective concentration of acid chloride (1.22 M for terephthaloyl chloride), which could change solvation characteristics of the medium. Alternatively, since the observed rate constant is described by $k_{obs} = k[\text{cat.}][\text{ArCOCl}]$, the rate is a function of the active catalyst concentration, which may vary from reaction to reaction or by substituent effects. Under competitive conditions, the active catalyst is presumed to be the same for different substituted acid chlorides and as such is held in equal concentration for both substrates.

Attempts to carry out kinetic studies under conditions of excess disilane were unsuccessful and led to formation of precipitated palladium black. Efforts to determine the reaction order of acid chloride and catalyst in dilute *o*-xylene solutions (<0.5 M) by either gas volumetric or NMR analysis gave inconsistent results. This led to the discovery of a pronounced solvent effect on the silylative decarbonylation reaction. Polar aprotic solvents such as anisole, veratrole, and especially nitrobenzene accelerated the rate of the silylation process, while high-boiling nonpolar solvents such as decane and mesitylene retarded the usual reaction. For synthetic applications, running the process in a neat mixture of chlorodisilane and acid chloride melt generally gave the best results.

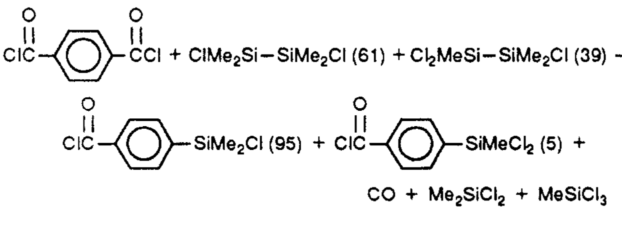
While determining the synthetic scope of the silylative decarbonylation process we often noted an induction period to CO gas evolution after addition of the catalyst. Figure 3 shows a typical plot of carbon monoxide volume change versus time for the reaction of terephthaloyl chloride and 1,2-dichlorotetramethyldisilane. After addition of the first aliquot of disilane, a pronounced induction period was observed. Following addition of the second and subsequent aliquots of disilane, no induction period was observed and a smooth pseudo-first-order reaction was seen. These results indicate that conversion of the palladium dibromide complex to some active form occurs, which then carries out the desired aromatic silylation reaction.

Unlike the aromatic acid chloride substituent, which had a major effect on the rate of the silylation reaction, the groups attached to the silicon atoms of the disilane had only a small effect on the observed reaction rate. For example, the relative rate of reaction of hexamethyldisilane with benzoyl chloride was about half that of 1,2-dichlorotetramethyldisilane and 1,1,2,2-tetrachlorodimethyldisilane. This result is somewhat surprising in light of the large effect the silyl substituents play in determining the final product distribution (see the Introduction).

Transfer Selectivity of Unsymmetrical Disilanes. A study of transfer selectivity of unsymmetrical disilanes was undertaken to gain insight into the mechanism of the silylative decarbonylation reaction. Reaction of chloropentamethyldisilane with benzoyl chloride in the presence of bis(benzonitrile)palladium dichloride and triphenylphosphine at 145 °C for 20 h yielded a 4.3:1 mixture of phenyltrimethylsilane and phenyldimethylchlorosilane (eq 6). Neither benzoyltrimethylsilane nor benzoyldimethylchlorosilane was formed. Dimethyldichlorosilane and trimethylchlorosilane were also obtained in a 4:1 ratio.

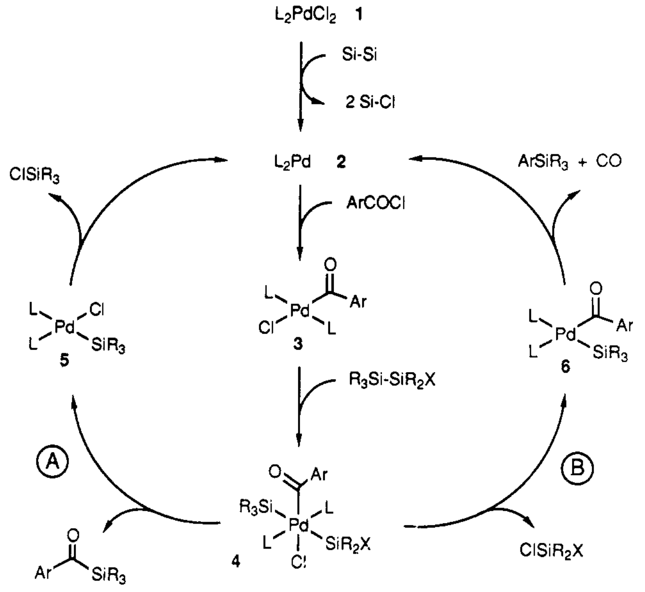
$$\begin{aligned} &ClMe_2SiSiMe_3 + PhCOCl \rightarrow \\ &\qquad \underset{4.3}{Ph\text{-}SiMe_3} \ \ \overset{}{:}\ \ \underset{1}{+ PhSiMe_2Cl} + \\ &\qquad\qquad CO + Me_2SiCl_2 + Me_3SiCl \quad (6) \end{aligned}$$

In a similar study terephthaloyl chloride was reacted with a mixture containing 39% 1,1,2-trichlorotrimethyldisilane and 61% 1,2-dichlorotetramethyldisilane (130 °C, N_2, 10 h). The product mixture contained 4-(chlorodimethylsilyl)benzoyl chloride and 4-(dichloromethylsilyl)benzoyl chloride in a 95:5 ratio (eq 7). Based on a purely random statistical transfer of silicon to the aromatic ring one would expect a distribution of 80:20 for chlorodi-



(7)

Scheme I



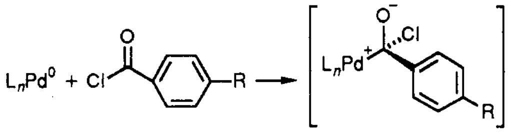
methylsilyl and dichloromethylsilyl, respectively. The net result is a 6.7:1 preference for transfer of the least chlorinated silicon group.

The reaction of chloropentamethyldisilane with benzoyl chloride (eq 6) dramatically points out the influence of even as few as one chlorine substituent on the course of the silylative decarbonylation process. As long as one or more of the substituents on the disilane is chlorine, the products obtained are decarbonylated arylsilanes. By comparison, hexamethyldisilane reacts with benzoyl chloride under similar conditions to give 93% benzoyltrimethylsilane and only 7% phenyltrimethylsilane.

Mechanistic Considerations. Any proposed mechanism for the silylative decarbonylation process must be consistent with the observations that (1) introduction of as few as one chlorine on the disilane leads to complete decarbonylation of the aromatic product, even when the group transferred does not contain a chlorine substituent as in the case of chloropentamethyldisilane; (2) electron-withdrawing aromatic groups and donor phosphine ligands increase the rate of reaction, and the large positive ρ, +2.4, suggests substantial negative charge buildup in a rate-determining step of the reaction; (3) the least halogenated silicon of the disilane is transferred preferentially to the aromatic ring.

The reaction can be described in terms of a series of addition–elimination processes as shown in Scheme I. Initial reduction of the palladium dichloride complex, 1, by disilane leads to a coordinatively unsaturated Pd(0) complex, 2. Although precedented by similar reactions of platinum and nickel systems,[10] even this initial step is not well understood and could be the subject of an independent investigation. Alternatives include stepwise addition–elimination involving palladium in the +2 and +4 oxidation states, a four-center mechanism, or an intermediate involving a σ-bound Si–Si bond. Addition of disilane to the initial catalyst in the absence of acid chloride leads to rapid formation of palladium black above 100 °C. This is presumably the decomposition fate of intermediate 2.

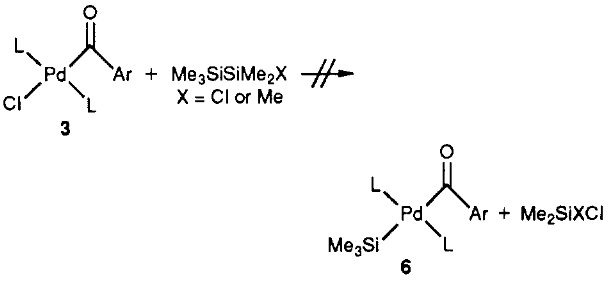
Attack of the palladium complex 2 on the acid chloride to give 3 can best be described in terms of a nucleophilic addition reaction (eq 8). A charge-separated intermediate



(8)

would be consistent with the +2.4 ρ value and with the observation that the reaction of benzoyl chloride with 1,2-dichlorotetramethyldisilane is 4 times faster in anisole than in o-xylene. Further evidence is derived from the fact that the reaction rate is increased with more strongly donating phosphines, which enhance the nucleophilicity of the metal. The magnitude and sign of the ρ value are consistent with studies involving reaction of low-valent palladium with aryl halides. These have also been described in terms of nucleophilic attack by the metal.[11] The rate of the palladium-catalyzed reaction of disilanes with aryl halides is also faster with electron-withdrawing substituents.[12]

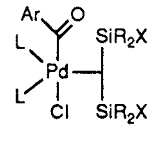
Reaction of complex 3 with disilane could follow several pathways. However, benzoyl chloride reacts with chloropentamethyldisilane to give predominantly phenyltrimethylsilane while reaction with hexamethyldisilane gives benzoyltrimethylsilane. Trimethylsilyl is transferred to the aromatic product in both cases. Therefore, one cannot invoke a simple transmetalation of 3 with disilane (eq 9)



(9)

since the intermediate, 6, and the subsequent organic products would be the same for both disilanes (X = Cl and X = Me). Rather, the intermediate that determines product distribution must contain both silicon groups from the disilane.

Addition of disilane to 3 would yield a bissilylpalladium(IV) complex, 4 (Scheme I). Several examples of addition–elimination reactions that involve Pd(IV) complexes have been documented.[13] In this context conversion of 3 to the Pd(IV) complex 4 would not be unusual. However, one can alternatively describe 4 as a Pd(II) complex with σ-bonded disilane as shown here:



Similar σ complexes of dihydrogen are well-known[14] and

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(10) (a) Urata, H.; Suzuki, H.; Moroka, Y.; Ikawa, T. *J. Organomet. Chem.* **1982**, *234*, 367. (b) Lefort, M.; Simmonet, C.; Birot, M.; Delevis, G.; Dunogues, J.; Calas, R. *Tetrahedron Lett.* **1980**, 1857.

(11) (a) Fauvarque, J. F.; Pfluger, F.; Troupel, M. *J. Organomet. Chem.* **1981**, *208*, 419. (b) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287.

(12) (a) Matsumoto, H.; Shono, K.; Nagai, Y. *J. Organomet. Chem.* **1981**, *208*, 145. (b) Matsumoto, H.; Yoshihiro, K.; Nagashima, S.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1977**, *128*, 409.

(13) (a) Aye, K.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D.; Watson, A. A. *Organometallics* **1989**, *8*, 1518. (b) Byers, P. K.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D. *Organometallics* **1988**, *7*, 1363. (c) Byers, P. K.; Canty, A. J. *J. Chem. Soc., Chem. Commun.* **1988**, 639. (d) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1093. (e) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1722. (f) Uson, R.; Fornies, J.; Navarro, R. *J. Organomet. Chem.* **1975**, *96*, 307.

σ-bound Si–H compounds have been described in the literature.[15] Considering that silicon–silicon compounds are known to have low-lying σ and σ^* orbitals available, σ-bound complexes of these species would seem reasonable.[16]

Partitioning of **4** between two reductive elimination pathways, A and B, would then determine the product distribution. Electronic effects of substituents and stereochemistry at the metal would be expected to influence the relative rates for these two parallel reactions. Curtis and Epstein point out that subtle differences in ligands can dramatically change product distributions in metal-catlayzed redistribution reactions of silicon that involve successive addition–elimination steps.[17] The importance of both substituent effects and stereochemistry in reductive elimination from Pd(IV) silyl species has been demonstrated.[18] Finally, with chlorodisilanes the highly oxidized palladium complex **4** might be expected to reductively eliminate the most electronegative silyl substituent to give $ClSiR_2X$. This could explain the preferential transfer selectivity of the least halogenated silicon to the aromatic ring.

Scheme I provides a useful framework for discussing the observed product distributions and transfer selectivity, but the kinetic data require some additional analysis. The observed aromatic substituent effects, large positive ρ value, catalyst ligand effects, and solvent dependence all indicate that conversion of **2** to **3** is the slow step in the reaction, but dependence of reaction rate on disilane concentration suggests that the step **3** → **4** is the rate-limiting step. One possible explanation, offered by a reviewer, is that a preequilibrium exists between **2** and **3**:

$$\underset{\mathbf{2}}{L_2Pd} + ArCOCl \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{\mathbf{3}}{L_2Pd(COAr)Cl} \xrightarrow[k_{34}]{\text{disilane}} \mathbf{4}$$

If one assumes a steady-state condition for **3**, the overall rate = $k_{34}[\text{disilane}][\mathbf{3}] = k_{34}[\text{disilane}]k_{23}[\mathbf{2}][ArCOCl]/(k_{32} + k_{34}[\text{disilane}])$. If no rapid equilibrium exists ($k_{32} = 0$ or $k_{32} \ll k_{34}[\text{disilane}]$) the rate = $k_{23}[\mathbf{2}][ArCOCl]$ and disilane dependence is absent. If the preequilibrium is rapid ($k_{32} \gg k_{34}[\text{disilane}]$) the rate = $k_{obs}[\mathbf{2}][\text{disilane}][ArCOCl]$, but this model offers no clear explanation for the observed aromatic substituent effects.

An alternative explanation is that oxidative addition of disilane preceeds that of acid chloride:

$$\underset{\mathbf{2}}{L_2Pd} + \text{disilane} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{\mathbf{3}}{L_2Pd(SiR_3)_2} \xrightarrow[k_{34}]{ArCOCl} \mathbf{4}$$

If the same pre-equilibrium analysis is applied here the overall rate = $k_{obs}[\mathbf{2}][\text{disilane}][ArCOCl]$ when $k_{32} \gg k_{34}[ArCOCl]$. This could account for both disilane rate dependence and the substituent effects.

A third possibility, which includes no preequilibrium, is that steps **2** → **3** and **3** → **4** (Scheme I) are of comparable rates. If the other steps are fast, then a steady state will be reached in which the active catalyst is partitioned between **2** and **3**. Any factors that increase the rate for **2** → **3** will also increase [**3**] and the rate for **3** → **4**. In the same way, factors that change the rate for **3** → **4** will effect [**2**] and the rate for **2** → **3**. Under these circumstances both disilane concentration and aromatic substituents would affect the rate.

Conclusions

The rate of the silylative decarbonylation reaction of aryl acid chlorides and disilanes was found to be controlled by the electron-withdrawing ability of the aromatic acid chloride. The reaction was determined to be first order in disilane. Replacement of chloro for methyl on the disilane had only a small effect on the overall rate of the reaction but dramatically controls the ultimate product distribution of either aryl or acyl silane. When unsymmetrical disilanes were employed in the silylative decarbonylation process, preferential transfer of the least halogenated silicon atom to the aromatic ring was found.

A mechanism consistent with these observations is described as a series of addition–elimination steps. Although further evaluation of this mechanism and possible alternatives awaits a more detailed study, the rate studies and transfer selectivity experiments described here have practical application in the synthesis of polysiloxane monomers from aromatic acid chlorides.

Experimental Section

Materials. The aromatic acid chlorides used were obtained from Aldrich Chemical Co. and were utilized as received or redistilled if analysis showed the purity to be <98%. 1,2-Dichlorotetramethyldisilane was obtained by distillation from the product stream of the direct reaction between methyl chloride and silicon. *sym*-Tetrachlorodimethyldisilane and pentamethylchlorodisilane were prepared by known procedures.[19,20] *o*-Xylene solvent was dried from sodium/benzophenone prior to use. All reactions were carried out under an inert atmosphere of nitrogen unless otherwise specified. No special precautions were taken to ensure complete removal of oxygen or water. Gas chromatography analyses were performed on a Shimadzu GC-9A in conjunction with a Shimadzu R1B data integrator.

Determinations of the Relative Reaction Rates of Substituted Aromatic Acid Chlorides with 1,2-Dichlorotetramethyldisilane. A series of competitive reactions between substituted aromatic acid chlorides and benzoyl chloride with 1,2-dichlorotetramethyldisilane were carried out. As a typical example the competitive reaction between *p*-chlorobenzoyl chloride and benzoyl chloride is described. A reaction mixture containing 0.52 g (3.56 mmol) of benzoyl chloride, 0.63 g (3.61 mmol) of *p*-chlorobenzoyl chloride, 1.54 g (7.82 mmol) of 1,2-dichlorotetramethyldisilane, and 0.24 g (1.18 mmol) of tetradecane were dissolved in 10.0 mL of volumetric *o*-xylene. TCD response factors for the starting materials were then determined. The reaction mixture was then heated to 139 ± 0.5 °C, and a catalyst mixture containing 27 mg (1 mol %) of bis(benzonitrile)palladium dichloride and 37 mg (2 mol %) of triphenylphosphine was introduced. The progess of the reaction was monitored periodically by gas chromatography.

The relative rate constant k_x/k_H was determined by using procedures similar to those previously described.[21] A brief analysis is given below. Assume that two competing reactions occur:

$$A + B \xrightarrow{k_1} C$$

$$A + D \xrightarrow{k_2} E$$

where A = 1,2-dichlorotetramethyldisilane, B = benzoyl chloride, C = (chlorodimethylsilyl)benzene, D = *p*-chlorobenzoyl chloride,

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and E = *p*-(chlorodimethylsilyl)phenyl chloride. Solving for the rate of reaction dB and dD

$$dB/k_1[B] = dD/k_2[D]$$

integrating, and solving for time $t = 0$ to t give

$$k_2/k_1 = \ln (D/D_0)/\ln (B/B_0)$$

where D = [D] at time = t and D_0 = [D] at $t = 0$.

With this analysis, for example, at $t = 1440$ s, 30% of the benzoyl chloride and 73% of the *p*-chlorobenzoyl chloride had reacted, giving $k_{Cl}/k_H = 3.63$. The validity of the method can be checked by using a procedure described assuming that at any time, t, the sum of reactants and products of interest equals the initial concentration, for example, at time t, for the reaction of benzoyl chloride[22]

$$[B] + [C] = [B_0]$$

With this analogy, the relative reaction rate k_x/k_H at time t can be derived:

$$k_x/k_H = k(E/D + 1)/k(C/B + 1)$$

The relative response factors for C and E were subsequently determined, and the rate k_{Cl}/k_H was determined at $t = 1440$ s to be 3.59, in good agreement with the previously described value.

Determination of Reaction Order and Pseudo-First-Order Rates Using Continuous Monitoring of Carbon Monoxide Formation. A continuously recording self-leveling buret was used to determine the change in reaction volume with time due to carbon monoxide formation.[23] In a typical procedure, 4.16 g (1.98 × 10^{-2} mol) of trimellitic anhdride acid chloride and 16 mg (2.39 × 10^{-5} mol) of bis(methyldiphenylphosphine)palladium dibromide were dissolved in 25 mL volumetric amount of *o*-xylene and heated to reflux temperature (bath temperature 145 ± 1 °C). A 0.250-g (1.34 × 10^{-3} mol) aliquot of 1,2-dichlorotetramethyldisilane was introduced, and the volume change versus time continuously recorded (see Figure 3). When no further change in volume occurred, the procedure was repeated with a fresh 0.25-g aliquot of 1,2-dichlorotetramethyldisilane. Pseudo-first-order rate constants with readily determined, and good linearity was observed for at least 2 half-lives.

Reaction of Chloropentamethyldisilane with Benzoyl Chloride. A reaction mixture containing 2.0 g (1.24 × 10^{-2} mol) of chloropentamethyldisilane, 1.6 g (1.15 × 10^{-2} mol) of benzoyl chloride, 50 mg (1 mol %) of bis(benzonitrile)palladium dichloride, and 69 mg (2 mol %) of triphenylphosphine were heated neat to 135 °C for 14 h. The product mixture, analyzed by gas chromatography, contained 73% phenyltrimethylsilane, 17% phenyldimethylchlorosilane, 2% chlorobenzene, 0.3% benzil, and two smaller products of <1%. All products and response factors were determined by comparison with authentic samples.

Reaction of a Standard Mixture of Chlorinated Disilanes, As Obtained from the Direct Reaction of Methyl Chloride and Silicon, with Trimellitic Anhydride Acid Chloride. A sample of methylchlorosilane direct process residue was obtained and distilled, with the boiling fraction 140–55 °C collected. Analysis of the fraction by proton NMR showed it to contain 72% *sym*-tetrachlorodisilane, 19% 1,1,2-trichlorotrimethylsilane, and 9% 1,2-dichlorotetramethyldisilane. A reaction mixture containing 3.5 g of the above-described mixture and 3 g of trimellitic anhydride acid chloride was heated to 145 °C, to which was added 21 mg (0.4 mol %) of bis(benzonitrile)palladium dichloride and 30 mg of triphenylphosphine. After 3 h the progress of the reaction was monitored by gas chromatography and after correction for response factors showed relative yields of 54% 4-(chlorodimethylsilyl)phthalic anhydride and 46% 4-(dichloromethyl)phthalic anhydride. Purely random statistical transfer of silyl groups would predict 18% 4-(chlorodimethyl)silylphthalic anhydride and 82% 4-(dichloromethylsilyl)phthalic anhydride.

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Registry No. Benzoyl chloride, 100-44-7; *p*-chlorobenzoyl chloride, 122-01-0; 1,2-dichlorotetramethyldisilane, 4342-61-4; chloropentamethyldisilane, 1560-28-7; phenyltrimethylsilane, 768-32-1; phenyldimethylchlorosilane, 768-33-2; *sym*-tetrachlorodisilane, 814-98-2; 1,1,2-trichlorotrimethyldisilane, 13528-88-6; 4-(chlorodimethylsilyl)phthalic anhydride, 116088-82-5; 4-(dichloromethylsilyl)phthalic anhydride, 104209-26-9; terephthaloyl chloride, 100-20-9; trimellitic anhydride acid chloride, 1204-28-0; *p*-nitrobenzoyl chloride, 122-04-3.

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