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sentative of tungsten–carbon double bonds.

Summary. Three aspects of these results deserve mention here. First, the formation of carbene complexes has been achieved by acidification of a bis(alkyne) precursor. Plausible routes to metal carbenes to form active catalysts are sometimes elusive, but from this work it is clear that simple protonation of unsaturated organic ligands can lead to carbene complexes. Second, interconversion of butadienyl, η^2-vinyl, and vinylcarbene ligands has been easily accomplished with only ligand addition reactions and acidification. Third, the ability of these unsaturated carbene ligands to provide additional electron density to the metal from the organic π system as evident in the ground-state properties of these molecules will no doubt be important in stabilizing electron-deficient intermediates along reaction coordinates containing related C_nR_{n+1} ligands.

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Supplementary Material Available: ORTEP drawings showing complete atomic numbering and tables of anisotropic temperature factors, isotropic temperatures factors, complete bond distances and angles, calculated hydrogen positions, and planes and dihedral angles for $(Me_2NCS_2)_3W(\eta^2\text{-}C_4Ph_4H)$ and $(Et_2NCS_2)(\eta^4\text{-}C_4Ph_4H)W{=}S$ (16 pages); listings of observed and calculated structure factors (67 pages). Ordering information is given on any current masthead page.

Kinetics and Mechanism of the Thermal Rearrangement of Some (Chloromethyl)silanes

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Kinetics have been measured for the gas-phase pyrolysis of a series of eight aryl-substituted (chloromethyl)silanes in a stirred flow reactor. These compounds undergo unimolecular rearrangements involving chloro migration to form chlorosilanes with concomitant migration of a group from silicon to carbon; the ease of migration is H > Ar > Me. The kinetic results indicate that the rearrangements are probably concerted in the gas phase.

Introduction

There have been two recent gas-phase kinetic studies of the thermal isomerization of (chloromethyl)dimethylsilane.[1,2] Both studies found that the main reaction was a clean unimolecular isomerization to form trimethylchlorosilane, accompanied by a minor radical chain sequence; the latter could be suppressed by added propene,[1] or by choice of pyrolysis conditions (eq 1).[2]

$$(CH_3)_2Si(CH_2Cl)H \xrightarrow{\Delta} \underset{\text{major}}{(CH_3)_3SiCl} \qquad (1)$$

The unimolecular isomerization, involving migration of chlorine from carbon to silicon and migration of hydrogen from silicon to carbon, is an example of a dyotropic rearrangement. This was originally envisaged by Reetz as a fully concerted process with a doubly bridged transition state,[3] but Bassindale, Brook, et al. concluded from their studies of the thermal rearrangement of a number of α-substituted silanes that α-halo and α-acetoxy silanes followed a stepwise mechanism.[4] They suggested that the first step for α-halo silanes was the formation of a three-center transition state in which the halogen atom bridged between carbon and silicon giving an "inverse ylid" with a $\delta-$ charge on silicon and a $\delta+$ charge on carbon. Subsequently, rapid migration of a group attached to silicon took place. A similar mechanism for α-acetoxy silanes may operate.[4,5] We now report kinetic studies designed to probe both the extent to which rearrangement of (chloromethyl)silanes may be concerted in the gas phase and the charge distribution in the transition state.

Results

We have pyrolyzed and studied the kinetics of eight aryl-substituted (chloromethyl)silanes, $ArMeSi(CH_2Cl)Y$ (Ar equals X–Ph with X = H, *p*-F, *p*-Me, and *m*-CF_3 and Y = H and Me). Kinetic measurements were made in a stirred flow (SFR) apparatus with analysis by gas chromatography; products were identified by pyrolyses in a similar SFR apparatus attached to a GC/mass spectrometer (HP5995C). Both types of apparatus and the procedure for measuring kinetics have been fully described.[6,7]

The main reaction of the four compounds with Y = H was formation of a chlorosilane, with migration of chlorine from carbon to silicon and migration of hydrogen from silicon to carbon, in a manner analogous to the pyrolysis of (chloromethyl)dimethylsilane (eq 2).[1,2] Migration of

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$$\mathrm{ArMeSi(CH_2Cl)H} \xrightarrow{\Delta} \underset{\text{major}}{\mathrm{ArMe_2SiCl}} + \underset{\text{minor}}{\mathrm{Me(H)Si(CH_2Ar)Cl}} \qquad (2)$$

the aryl group to form benzyl-substituted chlorosilanes was a minor reaction with these compounds; however, when Y = Me, this became the major pathway (eq 3). Here, the

$$\mathrm{ArMe_2SiCH_2Cl} \xrightarrow{\Delta} \underset{\text{major}}{\mathrm{Me_2Si(CH_2Ar)Cl}} + \underset{\text{minor}}{\mathrm{ArMeSi(CH_2CH_3)Cl}} \qquad (3)$$

migration of methyl instead of phenyl was observed as a minor process. Rate constants for methyl migration were too slow to be reliably measured but were approximately one-tenth of those for phenyl migration. These rearrangement reactions will be identified subsequently by naming the migrating group. Thus, we will describe the major process in eq 2 as an H-migration.

Kinetic results were obtained by measuring the rates of formation of products. This process was straightforward for the H-migration (Y = H), giving the results in Table I.1. For Ar-migration (Y = Me), there was appreciable scatter at lower temperatures. Accordingly, the results in Table I.2 were obtained by discarding data points taken below 520 °C. It is apparent from Table I that H-migration is about 5 times faster than aryl migration and that substituent effects are minor in both cases. Hammett plots[8] using data collected at several different temperatures were too scattered to be meaningful since substituent effects are so small.

Discussion

Martin, Ring, and O'Neal (MRO) studied the kinetics of pyrolysis of (chloromethyl)dimethylsilane (eq 1) and found a small radical component under their experimental conditions. This could be suppressed fully with added propene.[1] The kinetics of that pyrolysis in our SFR apparatus were unaffected by any of a range of standard trapping agents including propene.[2] The unimolecular rearrangement is favored over bimolecular or surface-induced radical reaction in the SFR because of the high pressure of carrier gas (ca. 3 atm). The Arrhenius parameters and rate constants in Table I.1 for the H-migration are comparable to those obtained for the unimolecular rearrangement of (chloromethyl)dimethylsilane.[1,2] Thus, we conclude that the results in Table I relate to homogenous gas-phase unimolecular rearrangements.

MRO have discussed the H-migration in terms of thermochemical kinetics and transition-state theory.[1] Since both migrating groups H and Cl are atoms with no internal rotations, if one atom bridges between silicon and carbon, there is a loss of one silicon-carbon internal rotation in the bridged transition state. This corresponds to an entropy of activation (ΔS^{*}) of −3.5 eu. At the average temperatures used in this work (see Table I), the Arrhenius A factor would then be expected to be given by $\log A = 12.9 \pm 0.3$. Because bridging the other atom does not freeze any more rotations, $\log A$ would have that value irrespective of whether the rearrangement was stepwise or concerted, and this kinetic argument cannot distinguish between these possibilities.

On the other hand, a distinction may be possible for aryl migration. Aryl migration would freeze an additional rotation giving a total $\Delta S^{*} = -7.0$ eu. At the average temperatures in Table I.2, that value of the entropy of activation corresponds to $\log A = 12.1 \pm 0.3$. Our results in Table I.2 for the aryl migrations all agree well with the prediction of $\log A = 12.1 \pm 0.3$. The H-migration results in Table I.1 are consistent with $\log A = 12.9 \pm 0.3$, with the exception of the result for X = m-$\mathrm{CF_3}$, where $\log A$ is clearly higher. Because of experimental difficulties with compounds of such relatively low volatility (compared with the typical compounds we study by gas phase-kinetic methods), the quality of the kinetic data in Table I was somewhat variable, as indicated by the error limits. However, the H-migration with X = m-$\mathrm{CF_3}$ appeared to be well behaved kinetically, and we have no reason to believe that these Arrhenius parameters are unreliable. Although both H-migration and aryl migration are quite insensitive to substituent effects, it may be significant that in each series the highest A factor, highest activation energy, and lowest rate constant were observed for X = m-$\mathrm{CF_3}$.

Table I. Kinetic Results

X	temp range, K	$\log A$	E_a, kcal·mol^{-1}	$k_{800\mathrm{K}}$, s^{-1}
1. H-Migration (Y = H): $\mathrm{(X\text{-}Ph)SiMe(H)CH_2Cl \rightarrow (X\text{-}Ph)SiMe_2Cl}$				
H	744–828	13.4 ± 0.4	53.3 ± 1.2	0.0706
p-F	754–811	13.2 ± 0.7	52.5 ± 2.6	0.0679
p-Me	753–816	13.2 ± 0.2	52.6 ± 0.7	0.0750
m-$\mathrm{CF_3}$	758–838	14.1 ± 0.3	56.4 ± 0.9	0.0527
2. Aryl Migration (Y = Me): $\mathrm{(X\text{-}Ph)SiMe_2CH_2Cl \rightarrow (X\text{-}PhCH_2)SiMe_2Cl}$				
H	799–849	12.0 ± 0.5	50.7 ± 2.0	0.0135
p-F	798–849	12.1 ± 0.3	51.1 ± 1.2	0.0138
p-Me	794–837	12.4 ± 0.6	52.0 ± 2.1	0.0156
m-$\mathrm{CF_3}$	766–862	12.5 ± 0.5	53.2 ± 1.8	0.0093

Our kinetic results for the aryl migration strongly suggest that this rearrangement is concerted in the gas phase. A simple extension of this result would suggest that the H-migration is also concerted, but we cannot be dogmatic about that for the reasons discussed above. Despite designing this study to probe the electronic nature of the transition state, the nonlinearity of the Hammett plots, and more particularly the very small kinetic differences among widely different aryl substituents, has stymied us. Nevertheless, it is clear that substituent effects are small, suggesting that little charge develops in the transition state.

Although our conclusions differ from those of Bassindale, Brook, et al.,[4] we point out that their experiments differed substantially from ours. They studied 13 compounds; none of those studied was the same as any we studied, and none had a silicon–hydrogen bond. Most of their conclusions were based on relative yields after pyrolyses in sealed tubes at given times and temperatures. Kinetic measurements were carried out on only two compounds. One of these was a highly substituted (bromomethyl)silane undergoing the equivalent of our Me-migration. Reactions under their conditions were very much faster than they would have been under ours; the compound closest to those studied by us was $\mathrm{Ph_3SiCH_2Cl}$, which underwent aryl migration with 16% conversion after 65 min at 330 °C, corresponding to a first-order rate constant of 4.5×10^{-5} s^{-1}. The fastest of our aryl migrations (Table I.2) would have a rate constant of 4×10^{-7} s^{-1} at 330 °C. Likewise, the Arrhenius parameters they measured for Me-migration in a (bromomethyl)silane correspond to a rate constant of 6.2×10^{3} s^{-1} at 800 K, about 4×10^{5} times greater than the rate constants in Table I.2, even though, like us, they found Me-migration to be slower than aryl migration. They also found that (bromomethyl)silanes rearranged more slowly than (chloromethyl)silanes. In sealed tubes, conditions are clearly very

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Table II. ^{1}H NMR Shifts of (Chloromethyl)silanes[a]

$X{-}C_6H_4Si(CH_3)(H)CH_2Cl$

X	CH_3	CH_2	SiH	aryl Hs	*p*-CH_3
H	0.46 d	3.07 d	4.54 m	7.3–7.8 m	
p-CH_3	0.48 d	3.16 d	4.50 m	7.2–7.6 m	2.35 s
p-F	0.52 d	3.19 d	4.53 m	7.1–7.9 m	
m-CF_3	0.58 d	3.27 d	4.59 m	7.5–8.1 m	

$X{-}C_6H_4Si(CH_3)_2CH_2Cl$

X	$(CH_3)_2$	CH_2	aryl Hs	*p*-CH_3
H	0.42 s	3.08 s	7.3–7.7 m	
p-CH_3	0.39 s	3.05 s	7.2–7.6 m	2.33 s
p-F	0.42 s	3.08 s	7.0–7.8 m	
m-CF_3	0.49 s	3.15 s	7.5–8.1 m	

[a] In ppm, relative to tetramethylsilane.

different from those used by MRO[1] and by us, since high pressures of reactants and products may develop, some material may remain in the liquid phase and/or active fresh surfaces may be exposed. Our results, under homogenous gas-phase conditions, indicate that aryl migration and probably also H-migration are concerted processes with little charge separation in the transition state, but it is possible that processes such as the formation of a "reverse ylid"[4] are favored by the conditions in sealed tube experiments with the compounds studied by Brook and co-workers.

Experimental Section

Preparation of Aryl(chloromethyl)methylsilanes. [$X{-}C_6H_4SiMe(H)CH_2Cl$]. A general synthetic scheme was used to prepare the series of compounds with X = H, *p*-CH_3, *p*-F, and *m*-CF_3. It is illustrated by the following preparation of $(C_6H_5)SiMe(H)CH_2Cl$.

Into a three-neck round-bottom flask equipped with magnetic stirring, addition funnel, and a reflux condenser with argon inlet was added magnesium metal (5.1 g, 0.21 mol) and 75 mL of dry diethyl ether. Bromobenzene (31.4 g, 0.20 mol) was added dropwise to form the Grignard reagent. This reagent, after anaerobic and anhydrous transfer by syringe, was added dropwise to a solution of (chloromethyl)methyldichlorosilane (25 g, 0.153 mol). After being stirred for 24 h, the reaction mixture was filtered through a glass fritted tube under argon. The remaining salts were washed with diethyl ether (2 × 200 mL). The volume of solvent was reduced by about half by rotary evaporation, and the resulting solution was added dropwise to a magnetically stirred suspension of lithium aluminum hydride (1.6 g, 0.042 mol) in diethyl ether (100 mL) under an argon atmosphere. After the mixture was stirred for an additional 24 h, aqueous, saturated ammonium chloride (200 mL) workup was carried out. Separation, drying over anhydrous sodium sulfate, and rotary evaporation of the solvent, followed by distillation through a 10-cm Vigreux column, gave $(C_6H_5)SiMe(H)CH_2Cl$: 8.8 g (34%); bp: 54 °C (3.0 Torr). Typical yields for the other aryl derivatives were between 32% and 42%.

Before the pyrolysis studies, each of the compounds prepared was further purified by spinning-band distillation. NMR properties were consistent with the presumed structure for all of the compounds prepared (Table II). Only the compound with X = H was known;[9] the other three gave acceptable carbon, hydrogen combustion analyses. For *p*-CH_3, Calcd for $C_9H_{13}SiCl$: C, 58.51; H, 7.09. Found: C, 58.82; H, 7.30. For *p*-F, Calcd for $C_8H_{10}SiFCl$: C, 50.92; H, 5.34. Found: C, 51.08; H, 5.47. For CF_3, Calcd for $C_9H_{10}SiF_3Cl$: C, 45.28; H, 4.22. Found: C, 45.63; H, 4.46.

Preparation of (Chloromethyl)dimethylsilanes ($X{-}C_6H_4SiMe_2CH_2Cl$). A general synthetic scheme was used to prepare the series of these compounds with X = *p*-Me, *p*-F, and *m*-CF_3 (the compound with X = H is commerically available). The scheme is illustrated by the preparation of $(p{-}Me{-}C_6H_4)SiMe_2CH_2Cl$.

Into a three-neck round-bottom flask equipped with magnetic stirring, addition funnel, and a reflux condenser with nitrogen inlet was added magnesium metal (8.6 g, 0.354 mol) and diethyl ether to just cover the metal. *p*-Bromotoluene (53.7 g, 0.314 mol) was added dropwise to form the Grignard reagent. (Chloromethyl)dimethylchlorosilane (44.9 g, 0.314 mol) was then added dropwise, and the solution was stirred for 24 h. Aqueous workup with saturated aqueous ammonium chloride (400 mL), separation, extraction of the aqueous layer with diethyl ether (2 × 200 mL), drying of the organic layer over anhydrous sodium sulfate, and rotary evaporation of solvent gave 75 mL of a yellow liquid. Distillation through a 30-cm Vigreux column under reduced pressure afforded $(p{-}Me{-}C_6H_4)SiMe_2CH_2Cl$: 37.8 g (61%); bp 78–79 °C (5.5 Torr). Typical yields for the other aryl compounds were between 31% and 42%.

Before the pyrolysis studies, each of the compounds prepared was further purified by spinning-band distillation. NMR properties were consistent with the presumed structure for all of the compounds prepared (Table II). The compound with X = H was obtained from Petrarch Systems, Inc.; the others have been prepared previously, as follows: X = *p*-Me,[10] X = *p*-F,[10] and X = *m*-CF_3.[11]

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Registry No. $(Ph)SiMe_2Cl$, 768-33-2; $(F{-}p{-}C_6H_4)SiMe_2Cl$, 2355-86-4; $(Me{-}p{-}C_6H_4)SiMe_2Cl$, 17881-63-9; $(F_3C{-}m{-}C_6H_4)SiMe_2Cl$, 402-32-4; $(PhCH_2)SiMe_2Cl$, 1833-31-4; $(F{-}p{-}C_6H_4CH_2)SiMe_2Cl$, 121329-74-6; $(Me{-}p{-}C_6H_4CH_2)SiMe_2Cl$, 1833-28-9; $(F_3C{-}m{-}C_6H_4CH_2)SiMe_2Cl$, 121329-75-7; $BrC_6H_4{-}p{-}F$, 460-00-4; $BrC_6H_4{-}p{-}Me$, 106-38-7; $BrC_6H_4{-}m{-}CF_3$, 401-78-5; bromobenzene, 108-86-1; (chloromethyl)methyldichlorosilane, 1558-33-4; (chloromethyl)dimethylchlorosilane, 1719-57-9.

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