

polarization within the exomethylene bond would make C(1) more negative than C(2). Complex 8 could rearrange as shown to give 9, which is the all σ representation of the η -allylic structure of 4.



Interligand C-C coupling would then occur formally by oxidation of the iron atom when the C(2)-C(3) bond is formed, followed by formation of the Fe-C(1) bond, thus, reducing the Fe atom to its original oxidation state and oxidizing the negatively charged C(1) to a neutral methylene group. By using similar reasoning, it is possible to go directly from 7 to 9. Both mechanisms can be represented as an electrophilic attack by a positively charged acyl carbon atom on the π -electron pair of an adjacent metal-carbon multiple bond with concomitant reduction of the iron atom. Clearly, the η -allylic ligand formation in 4 stabilizes this anion sufficiently to permit its isolation. However, we believe that this interligand coupling reaction is important to both stoichiometric and catalytic reaction chemistry at metal atoms. We propose that interligand C-C coupling may occur between adjacent ligands when (1) the two carbon donor atoms have some degree of unsaturation or acylic character, (2) the two carbon atoms are in close contact (the chelate ring of 1 imposes a C(2)···C(3) contact distance of 2.633 (2) Å, which is considerably shorter than an estimated C···C atomic van der Waals contact distance of 3.2 Å), and (3) the metal atom to which these carbon atoms are bonded can be reduced from an external source (such as C(1) in this example). Other electron sources may be available in metal clusters or other types of mononuclear or polynuclear complexes.

Conversion of 1 to 4 also shows that unsaturated ligands may couple *prior to* a reductive-elimination step. Oxidation or reduction of 4 may cleave the Fe-C allylic bonds to afford acyloin or glycol derivatives. Hydrolysis of the BF₂ group and any further reduction should give a glycol product. It should also be noted that C(2) and O(2) were obtained from CO, while the formal derivation of C(3) and O(3) from CO is possible. From this perspective, this coupling reaction represents a C(1) to C(2)hydrocarbon transformation. We are currently examining the generality of such interligand coupling reactions and the reaction chemistry of 4 and its derivatives, including the potential use of this reaction for stereospecific glycol formation.

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Supplementary Material Available: Details of data collection and data reduction and tables listing the atomic positional and thermal parameters and the observed and calculated structure factors (21 pages). Odering information is given on any current masthead page.

Photolysis of Organopolysilanes. Reaction of Trimethylsilylphenylsilylene with Functional-Group-Substituted Olefins

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Abstract: The photolysis of tris(trimethylsily)phenylsilane (1) in the presence of vinyl chloride or 1-bromo-2-methylpropene afforded, probably via silacyclopropane intermediates, the respective 1-alkenyl-1-halo-1-phenyltrimethyldisilanes in moderate yields. Photolysis of 1 in the presence of *cis*- and *trans*-1-chloropropene proceeded with high stereospecificity to give *cis*- and *trans*-1-(chlorodisilanyl)propene, respectively. Irradiation of 1 in the presence of ethyl vinyl ether afforded 1-methoxy-1-phenyl-1-vinyltrimethyldisilane after methanolysis of the photolysis product. Similar irradiation of 1 in the presence of ethyl vinyl ether, followed by treatment with hydrogen chloride, gave 1-chloro-1-(1'-ethoxyethyl)-1-phenyltrimethyldisilane and 1-chloro-1-(2'-ethoxyethyl)-1-phenyltrimethyldisilane. Irradiation of 1 with *cis*- and *trans*-1-methoxy-1-hexene, followed by ethanolysis, produced the corresponding *cis*- and *trans*-1-(ethoxydisilanyl)-1-hexene with high stereospecificity. Irradiation of 1 with vinyl acetate gave directly 1-acetoxy-1-phenyl-1-vinyltrimethyldisilane.

Introduction

In recent years, considerable attention has been devoted to investigations of silylene intermediates, and many papers that deal with addition of silylenes to carbon–carbon multiple bonds have been reported.¹⁻⁹ We have shown that trimethylsilylphenylsilylene

generated by photolysis of tris(trimethylsilyl)phenylsilane adds readily to many alkenes^{7,10} and alkynes¹¹ to give the silacyclo-

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Scheme I



propanes and silacyclopropenes. We also have reported that 1-trimethylsilyl-1-phenyl-2,2-dimethyl-1-silacyclopropane undergoes photochemical isomerization to give 1-(1'-phenyl-2',2',2'-trimethyldisilanyl)-2-methylpropene via a 1,2-hydrogen shift from the methylene carbon to the silicon atom in the three-membered ring, together with 2-methyl-3-(1'-phenyl-2',2',2'-trimethyldisilanyl)propene arising from a 1,3-hydrogen shift.¹⁰ We thought that the introduction of a functional group



such as alkoxyl or halogen onto the carbon atom of the silacyclopropane ring might facilitate the 1,2-migration, because the formation of a silicon-halogen or silicon-oxygen bond is thermodynamically favorable. To examine this possibility, we have investigated the reaction of trimethylsilylphenylsilylene with olefins bearing a functional substituent. We have also investigated the stereochemistry of these reactions.

Results and Discussion

When a solution of tris(trimethylsilyl)phenylsilane (1) in the presence of a large excess of vinyl chloride in dry hexane was photolyzed by irradiation with a low-pressure mercury lamp bearing a Vycor filter at 0 °C for 2.5 h, a single product which was identified as 1-chloro-1-phenyl-1-vinyltrimethyldisilane (2) was obtained in 33% yield, in addition to 14% of unchanged 1 (Scheme I). Other volatile products detectable by VPC (less than 1% yield) are virtually not observed in the photolysis product. Nonvolatile substances, presumably produced from polymerization of trimethylsilylphenylsilylene, were obtained after distillation of 2.

Similar photolysis of 1 in the presence of 1-bromo-2-methylpropene afforded 1-bromo-1-phenyl-1-(2'-methylpropenyl)trimethyldisilane (3) which could be isolated by preparative VPC in 23% yield as the sole volatile product, in addition to 11% of unchanged 1.

Irradiation of 1 in the presence of chlorobenzene under similar conditions afforded no product to be expected to arise from in-

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Scheme II



sertion of trimethylsilylphenylsilylene into an sp^2 carbon-chlorine bond. This result strongly suggests that compounds 2 and 3 must come from a 1,2-halogen shift of 2-chloro- or 2-bromo-1-silacyclopropane (A) produced transiently, but not from direct insertion of trimethylsilylphenylsilylene into the carbon-chlorine or carbon-bromine bond.

In order to trap the silacyclopropane, we attempted the lowtemperature photolysis of 1 in the presence of vinyl chloride. It is well known that the silacyclopropanes react with oxygen to give nonvolatile substances. Provided that silacyclopropane A was present long enough in the photolysis mixture to react with oxygen, different yields of 2 were to be observed before and after treatment of the mixture with oxygen. Firstly, a hexane solution of 1 in the presence of vinyl chloride was irradiated with a low-pressure mercury lamp at -70 °C for 7 h. VPC analysis of an aliquot which was extracted from the photolysis mixture and warmed to room temperature under nitrogen showed the production of 2 in 22% yield. Secondly, dry oxygen was introduced into the original photolysis mixture at -70 °C to decompose silacyclopropane A which might be present. Analysis of the mixture indicated that no change was observed in the yield of 2. These results suggest that the 1,2-halogen shift occurred rapidly even at low temperature.

Interestingly, photolysis of 1 in the presence of ethyl vinyl ether led to a different result from that described above. Thus, irradiation of 1 with an excess of ethyl vinyl ether in hexane produced an unstable product which was not detected by analytical VPC under various conditions. However, addition of dry methanol to this solution at room temperature immediately afforded 1methoxy-1-phenyl-1-vinyltrimethyldisilane (4) in 17% yield which could be determined by VPC (Scheme II). None of the 1-ethoxy-1-phenyl-1-vinyltrimethyldisilane (5) was observed in this reaction. The fact that the methoxyl/ethoxyl exchange reaction between 5, prepared by an independent route, and methanol under identical conditions proved to be slow enough to be followed by VPC indicates that compound 4 must be produced by the reaction of initially formed 1-trimethylsilyl-1-phenyl-2-ethoxy-1-silacyclopropane (B) with methanol. The ¹H NMR spectrum of the reaction mixture obtained by the photolysis of 1 in the presence of ethyl vinyl ether shows a signal at δ 0.19 ppm, probably due to the methylsilyl protons of the silacyclopropane B. Addition of methanol to the mixture resulted in the disappearance of this signal and the appearance of a new signal at δ 0.22 ppm which is identical with the chemical shift of the methylsilyl resonance of methoxysilane 4. Further evidence for the production of silacyclopropane B was obtained by the reaction of the photolysis product with hydrogen chloride.⁹ Thus, introduction of a dry hydrogen chloride gas admixed with nitrogen into the mixture obtained from the photolysis of 1 in the presence of ethyl vinyl ether produced two products, 1-chloro-1-(1'-ethoxyethyl)-1phenyltrimethyldisilane (6) and 1-chloro-1-(2'-ethoxyethyl)-1-



phenyltrimethyldisilane (7), in 40 and 58% yields, on the basis of silacyclopropane B used.

Interestingly, when a heptane solution of B was heated at 90 °C in the presence of diethylmethylsilane for 40 min, the rearranged isomer 5 was obtained in 12% yield, along with 1,1-di-

identified polymeric substances were also obtained after distillation of the volatile products.

A possible mechanism for the formation of 4 is shown in Scheme II which involves a nucleophilic attack of methanol on the silicon atom in the silacyclopropane ring, followed by elimination of the ethoxyl group from the ring carbon atom.

We have recently reported that the addition of trimethylsilylphenylsilylene to the olefin proceeds with high stereospecificity to give the silacyclopropane.¹⁰ The present reactions make it possible to investigate the stereochemistry of a ring opening of the silacyclopropanes. Thus, irradiation of 1 in the presence of trans-1-chloropropene (97% isomeric purity) gave trans-1-(1'chloro-1'-phenyltrimethyldisilanyl)propene (9a) with 95% isomeric



purity in 39% yield. Similarly, with cis-1-chloropropene (96% isomeric purity), 1 afforded cis-1-(1'-chloro-1'-phenyltrimethyldisilanyl)propene (9b) with 84% isomeric purity in 30% yield, as the sole volatile product. In these photolyses, no change was observed in the isomeric purity of the recovered chloropropenes.

We think that the decrease in the isomeric purity of the products may be ascribed to photochemical isomerization of initially produced chlorosilyl olefins, but not the nonstereospecific ring opening of the silacyclopropanes. Photochemical cis-trans isomerization under similar conditions has been reported.^{12,13} Indeed, irradiation of either 9a or 9b under identical conditions for 32 h afforded an equilibrium mixture consisting of cis and trans isomers in the ratio of 3:7. Furthermore, when compound 1 was photolyzed with cis-1-chloropropene in the presence of 2,4-hexadiene ($E_T = 60$ kcal/mol) as a triplet quencher, cis-chlorodisilanylpropene 9b with 93% isomeric purity was obtained in 19% yield.

We next examined the stereochemistry of the reactions of the silacyclopropane produced by the photolysis of 1 in the presence of cis- and trans-1-methoxy-1-hexene with ethanol. Irradiation of 1 in the presence of *trans*-1-methoxy-1-hexene (99% isomeric purity) in hexane for 1.8 h, followed by treating the mixture with ethanol after irradiation was stopped, afforded trans-1-(1'-ethoxy-1'-phenyltrimethyldisilanyl)-1-hexene (10a) in 17% yield. Its isomeric purity was determined to be higher than 96% by ¹H NMR spectroscopic analysis. Similar photolysis of 1 in the presence of cis-1-methoxy-1-hexene (90% isomeric purity), followed by ethanolysis, produced cis-1-(1'-ethoxy-1'-phenyltrimethyldisilanyl)-1-hexene (10b) with 85% isomeric purity in 22% yield as the sole volatile product (Scheme III).

The photolysis of 1 in the presence of vinyl acetate, however, afforded 1-acetoxy-1-phenyl-1-vinyltrimethyldisilane (11) in 6%



yield, in addition to 17% of the starting 1. Nonvolatile polymeric

Scheme III



substances are obtained after distillation of 11. The fact that no change was observed after addition of acetic acid to the photolysis mixture suggests that the life of a possible intermediate 2-acetoxy-1-silacyclopropane (C), if produced, is exceedingly short.

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of purified nitrogen. Photolysis was carried out using a 10-W low-pressure mercury lamp bearing a Vycor filter. All photolyses were followed by VPC analysis using a 2 m \times 0.5 cm stainless column with 30% Silicone SE-30 on Celite 545. Yields were determined by VPC using an internal standard on the basis of unrecovered tris(trimethylsilyl)phenylsilane.

¹H NMR spectra were determined at ambient temperature with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solution containing cyclohexane as an internal standard. Mass spectra were obtained on a JEOL Model JMS-D 300 equipped with a JMA-2000 data processing system. Ionizing voltage was 24 eV for all compounds. Infrared spectra of thin liquid films were determined using a Hitachi Model EPI-G3 grating infrared spectrophotometer. An Aerograph Model 90-P gas chromatograph with a thermal conductivity detector was used for separating the reaction products. Most of the products were easily separated as colorless liquids by using a 20 ft \times $^{3}/_{8}$ in column containing Silicone SE-30 (30%) on Celite 545.

Materials. Tris(trimethylsilyl)phenylsilane,¹⁰ cis- and trans-1chloropropene,^{14,15} 1-bromo-2-methylpropene,¹⁶ and *cis*- and *trans*-1-methoxy-1-hexene¹⁷ were prepared as reported in the literature.

Photolysis of Tris(trimethylsilyl)phenylsilane (1) in the Presence of Vinyl Chloride. A mixture of 0.9860 g (3.02 mmol) of 1 and ca. 3 g (ca. 56 mmol) of vinyl chloride in 100 mL of dry hexane was placed in a 100-mL reaction vessel, fitted with a low-pressure mercury lamp bearing a Vycor filter. The mixture was irradiated at 0 °C for 2.5 h with a slow stream of nitrogen bubbling through the mixture. Most of the solvent and unchanged vinyl chloride were evaporated away. The residue that remained was distilled under reduced pressure to give a volatile product boiling up to 120 °C (4 mm). The amounts of 1-chloro-1-phenyl-1vinyltrimethyldisilane (2) (0.86 mmol, 33% yield) and unchanged 1 (14%) contained in the distillate were determined by analytical VPC using cetane (0.52 mmol) as an internal standard. Pure 2 was isolated by preparative VPC. IR 1000, 960, 550, 520 cm⁻¹; ¹H NMR δ 0.21 (9 H, s, Me₃Si), 5.7-6.6 (3 H, m, CH₂=CH), 7.3-7.6 (5 H, m, ring protons). Anal. Calcd for C₁₁H₁₇ClSi₂: C, 54.85; H, 7.11; Cl, 14.72. Found: C, 55.04; H, 7.35; Cl, 14.56.

Photolysis of 1 in the Presence of 1-Bromo-2-methylpropene. A mixture of 0.9765 g (3.01 mmol) of 1 and 3.5 g (25.9 mmol) of 1-bromo-2-methylpropene was photolyzed at 0 °C for 2.5 h. The solvent and 1-bromo-2-methylpropene were distilled off, and the residue was then analyzed by VPC as being 3 (0.62 mmol, 23% yield) and unchanged 1 (11% yield) Pure 3 was isolated by VPC. IR 1615 cm⁻¹; ¹H NMR δ 0.18 (9 H, s, Me₃Si), 1.78 (3 H, broad s, MeC=C), 1.99 (3 H, broad s, MeC=C), 5.58 (1 H, broad s, CH=C), 7.3-7.7 (5 H, m, ring protons). Exact mass. Calcd for C₁₃H₂₁BrSi₂: 312.0365, 314.0345. Found: 312.0354, 314.0380.

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the photolysis mixture showed the formation of 9b (0.034 mmol, 19% yield) with 93% isomeric purity.

Photolysis of 1 in the Presence of Vinyl Acetate. A solution of 0.9797 g (3.02 mmol) of 1 and 2.3 g (27.2 mmol) of vinyl acetate in 100 mL of hexane was photolyzed for 2 h with ice cooling. The mixture was analyzed by GLC as being 11 (0.15 mmol, 6% yield) and unchanged 1 (17% yield). After addition of 1 mL of acetic acid to the photolysis mixture, the mixture was again analyzed by VPC. However, no change was observed. Pure 11 was isolated by preparative VPC. IR 1720, 1060 cm⁻¹; ¹H NMR δ 0.17 (9 H, s, Me₃Si), 2.10 (3 H, s, MeCO), 5.7-6.4

(3 H, m, CH2=CH), 7.2-7.6 (5 H, m, ring protons). Exact mass. Calcd for C₁₃H₂₀O₂Si₂: 264.1022. Found: 264.0992.

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Mechanisms of 1,1-Reductive Elimination from Palladium: Coupling of Styrylmethylpalladium Complexes

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Abstract: The complexes (E)- and (Z)-styrylbromobis(triphenylphosphine)palladium(II) [(E)- and (Z)-1a] react with methyllithium in benzene at ambient temperature to give (E)- and (Z)-propenylbenzene, respectively. A similar reaction at -78°C afforded (E)- and (Z)-styrylmethylbis(diphenylmethylphosphine)palladium(II) [(E)- and (Z)-2b] as a cis-trans mixture. On raising the temperature of solutions of (E)- and (Z)-2b, (E)- and (Z)-propenylbenzenes are produced, respectively, and the intermediate olefin complexes (E)- and (Z)-propenylbenzenebis(diphenylmethylphosphine)palladium(0) [(E)- and (Z)-3b] can be observed by NMR. the reductive elimination reaction is intramolecular as determined by a crossover experiment and first order in dialkylpalladium(II) complex when diphenylmethylphosphine is present. The reaction of (E)-2b and trideuteriomethyl iodide gives some 3,3,3-trideuteriopropenylbenzene, again implicating a palladium(IV) intermediate as a possible reductive elimination intermediate in a catalytic coupling cycle.

The coupling of organic halides and organometallic reagents catalyzed by zero-valent nickel and palladium complexes provides a convenient low-energy path for carbon-carbon bond formation.¹⁻⁶ It is generally assumed that oxidative addition of the organic halide to the metal, metathesis of the halide by the organometallic reagent, and reductive elimination of the diorgano species are the key steps in the catalytic generation of a new carbon-carbon σ bond.2-

Although the oxidative addition step has been well studied,¹⁰ the metathesis and reductive elimination steps are less well documented.⁷ Possible modes of carbon-carbon σ bond formation include 1,1-reductive elimination, dinuclear elimination, and radical pathways. Other competing decomposition modes include α - and β -hydrogen elimination.^{9,11-15}

The coupling of methyl to methyl,¹⁶ methyl to fluorophenyl,⁸ and methyl to benzyl¹⁷ by the 1,1-reductive elimination from palladium has been reported. In the first two cases, coupling was

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followed by spectroscopic studies on the isolated diorganobis(phosphine)palladium species. In the 1,1-reductive elimination of methyl and benzyl groups, retention of configuration at the benzyl carbon was observed. 17

For further exploration of the mechanism of 1,1-reductive elimination, particularly the stereochemistry, the coupling of methyl to a vinyl group was undertaken. The palladium-catalyzed coupling of β -bromostyrene and methylmagnesium bromide has been shown to proceed with retention of geometry at the double bond, (Z)- β -bromostyrene yielding (Z)-propenylbenzene.⁶ The suggested mechanism included oxidative addition of (Z)- β bromostyrene to yield (Z)-styrylbromobis(triphenylphosphine)palladium(II), bromide metathesis to give (Z)-styrylmethylbis-(triphenylphosphine)palladium(II), and reductive elimination to produce (Z)-propenylbenzene.

This account reports the isolation of the unstable species (E)and (Z)-styrylmethylbis(diphenylmethylphosphine)palladium(II) and the spectroscopic observation of styryl and methyl coupling.

Results and Discussion

Synthesis of Styrylbromobis(phosphine)palladium(II) Complexes. Styrylbromobis(phosphine)palladium(II) complexes were synthesized by oxidative addition of (E)- or (Z)- β -bromostyrene (or (E)-p-chloro- β -bromostyrene) to tetrakis(phosphine)palladium(0) complexes (Figure 1). As found for similar oxidative addition reactions, the styrylbromopalladium complexes were trans and the reaction proceeded with net retention of the double bond geometry.18-21

Coupling Reactions of Styrylbromobis(phosphine)palladium(II) Complexes and Methyllithium. The coupling of styryl and methyl

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