Design, Synthesis, and Electrochemical Behavior of New Electronic Systems Involving *σ,σ*- and *σ,π*-Interaction

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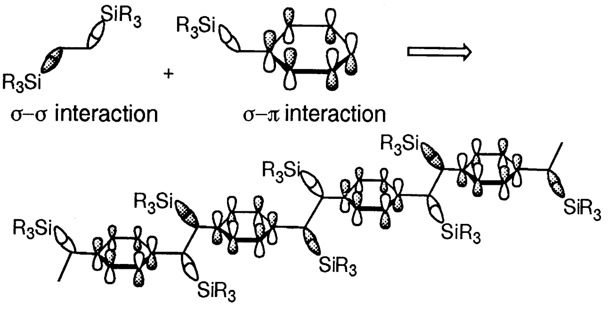
1,2-Bis(trimethylsilyl)-1,2-diphenylethane and its homologues were synthesized and the studies on their electrochemical behavior revealed that there is definite interaction between the σ,π-interaction system (the C-Si bonds and the benzene rings) and the σ,σ-interaction system (the neighboring C-Si bonds) which causes significant decrease of the oxidation potentials.

The interaction of a C-Si σ orbital with a neighboring π-system such as an aromatic ring is known as σ,π-interaction and such interaction causes significant increase of the HOMO level.[1] The interaction of two neighboring C-Si σ orbitals is also known to cause significant increase of the HOMO level.[2] In the study directed toward new materials based on the unique properties of silicon, we have been interested in new electronic systems which involve both σ,σ-interaction systems and σ,π-interaction systems. In this paper we wish to describe the synthesis and electrochemical properties of the molecules in which the σ,σ-interaction systems and the σ,π-interaction systems are conjugated with each other as shown in Scheme 1.



Scheme 1.

As a key methodology for the construction of such systems, we chose the reductive coupling of the benzyl halide bearing a silyl group at the benzylic carbon. First, we examined the most simple case, i.e. the reductive coupling of α-(trimethylsilyl)benzyl bromide (**1**) (eq 1) using various reducing agents including low valent vanadium,[3] magnesium metal,[4] low valent titanium,[5,6] cathodic reduction with a Mg sacrificial anode,[7] and Ni-complex mediated cathodic reduction.[8] As shown in Table 1, low valent titanium gave the best results.

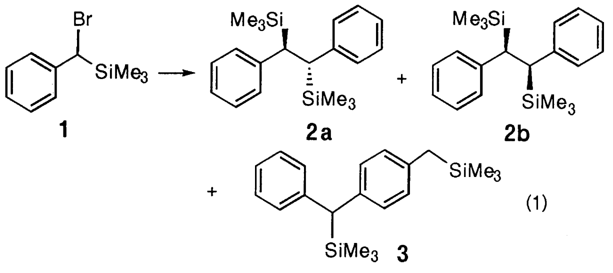
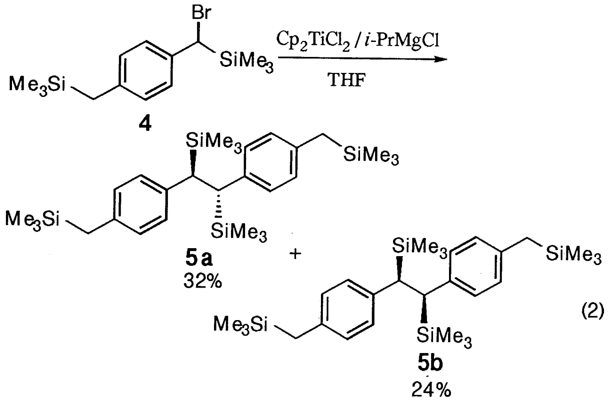


Table 1. Reductive Coupling of α-(trimethylsilyl)benzyl bromide

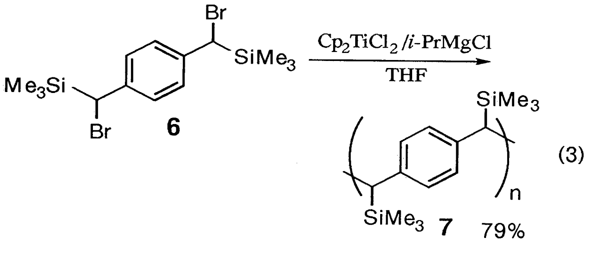
reagent	2 Yield/%	2a/2b	3 Yield/%
VCl_3/LAH	25	48 : 52	-
Mg	13	54 : 46	-
$TiCl_4$/LAH	46	54 : 46	29
Cp_2TiCl_2/*i*-PrMgCl	54	52 : 48	3
+e/Mg(-)-Mg(+)	39	54 : 46	-
+e/Ni(+)-Cu(-), $Ni(acac)_2$, PPh_3	40	53 : 47	5

The coupling of α-(trimethylsilyl)benzyl bromide using Cp_2TiCl_2/*i*-PrMgCl gave a mixture of two diastereomers of the head-to-head coupling product (**2a** and **2b**) together with a small amount of the head-to-tail coupling product (**3**). Stereochemistry of the one of the head-to-head coupling product was assigned as *meso* by the comparison with its ^{1}H NMR spectrum with that of an authentic sample prepared by the reaction of *E*-1,2-diphenylethyelene with Me_3SiCl/Mg.[9]

The next homologue, compound **5**, was also synthesized by the reductive coupling of α-trimethylsilyl-*p*-(trimethylsilylmethyl)benzyl bromide (**4**) with Cp_2TiCl_2/*i*-PrMgCl (eq 2).



The reductive coupling of α,α'-bis(trimethylsilyl)-*p*-xylene dibromide (**6**) with Cp_2TiCl_2 /*i*-PrMgCl gave rise to the formation of the polymeric product (**7**) (M_n = 3700, M_w/M_n = 1.72, determined by GPC with reference to polystyrene standards) as shown in eq 3. ^{1}H NMR analysis indicated that the polymer was atactic.



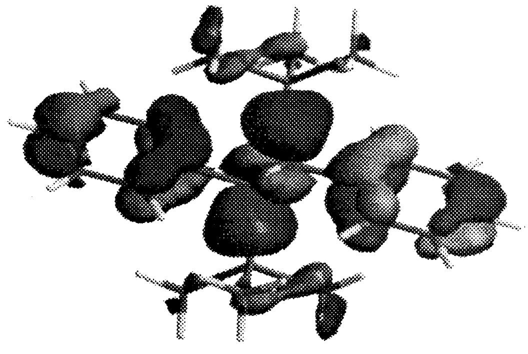


Figure 1. HOMO of **2a** obtained by PM3 calculation (Spartan Ver. 4.0).

The oxidation potentials of the synthesized compounds were determined by rotating disk electrode voltammetry. Table 2 summarizes the results. The oxidation potentials of two isomers of 1,2-bis(trimethylsilyl)-1,2-diphenylethane (**2a** and **2b**) were found to be less positive than those of benzyltrimethylsilane (**8**) (a σ,π-interaction system) and 1,2-bis(trimethylsilyl)ethane (**9**) (a σ,σ-interaction system). These results suggests that there is an interaction between the σ,π-interaction system and the σ,σ-interaction system in **2** to decrease the oxidation potential, if we assume that the kinetic parameters of the electron transfer reactions of these compounds are similar. Therefore, it seems to be reasonable to mention that there is some conjugation between the σ,π-interaction system and the σ,σ-interaction system.

This is consistent with the results of molecular orbital calculations which indicates that the HOMO (highest occupied molecular orbital) is delocalized through two C-Si bonds and two benzene rings as shown in Figure 1.

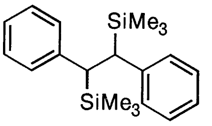
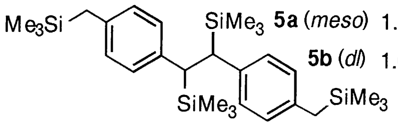
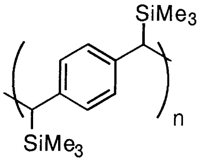
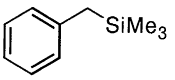
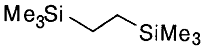
The oxidation potentials of **5a** and **5b** were less positive than those of **2a** and **2b**, indicating that the additional σ,π-interaction caused further decrease of the oxidation potential. Although it was difficult to determine the oxidation potential of the polymeric compound **7** in CH_3CN because of its low solubility, the oxidation potential determined in CH_2Cl_2 was found to be similar to those of **5a** and **5b** determined in CH_2Cl_2. Probably, the polymer chain is not straight in solution, and therefore the extension of the conjugation of the σ,σ-interaction systems and σ,π-interaction systems is not effective throughout the polymer chain.

The absorption spectra of the synthesized compounds were also studied. Compounds **7**, **5a**, and **5b** showed the absorptions at wavelengths longer than those of **8**, **9**, **2a**, and **2b**.

The present study demonstrates the potentiality of the conjugation between the σ,σ-interaction systems and the σ,π-interaction systems. Further studies concerning the extension of this new conjugate system and its applications in material science are underway.

We thank Prof. Yoshiki Chujo, Department of Polymer Chemistry, Kyoto University for the determination of the molecular weight of the polymer.

Table 2. Oxidation potentials of 1,2-bis(trialkylsilyl)-1,2-diphenylethane derivatives and related compounds[a]

compound	oxidation potential Ed(V)[b]	Ed(V)[c]	absorption spectrum λ max (logε)[d]
 **2a** (*meso*)	1.23		234 (4.31)
2b (*dl*)	1.32		233 (4.35)
 **5a** (*meso*)	1.08	1.16	244 (4.45)
5b (*dl*)	1.09	1.19	240 (4.35)
 **7**		1.16	250 (4.41)[e]
 **8**	1.39		230 (3.64)
 **9**	1.74		< 200

[a] The decomposition potentials were determined with rotating disk voltammetry using a glassy carbon working electrode and a Ag/AgCl reference electrode. [b] Determined in $LiClO_4/CH_3CN$. [c] Determined in Bu_4NClO_4/CH_2Cl_2 [d] Determined in CH_2Cl_2. [e] Based on the average molecular weight.

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