

International Research Center for Elements Science - Organic Main Group Chemistry -

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Visitor

BESSION, Eric Univeriste de Montpellier II, France, 2 July 2003 - 20 August 2003

Scope of Research

Our research is concerned with some new aspects in the elemento-organic chemistry, including (1) the design and synthesis of novel π -conjugated systems containing main group elements such as boron and silicon for electronic and photonic applications, (2) the synthesis, structural studies, and synthetic applications of organosilicon compounds, such as pentacoordinate silicon compounds and functionalized silyl anions, (3) the elucidation of the σ -conjugation in the polysilane framework using the configuration-constrained oligosilane model systems, (4) the old but new chemistry of the disilapropellane and related compounds, and (5) the development of new efficient reactions using main group element reagents and transition metal complex catalysts.

Research Activities (Year 2003)

Presentations

Elements Science: Elemento-Organic Chemistry directed toward Materials Science (Plenary lecture), Tamao K, The International Symposium on Dynamic Complexes, 4 August, Tokyo, Japan.

Silole-Containing π - and σ -Conjugated Polymers, Tamao K, The Third International Workshop on Silicon-Containing Polymers, 23 - 24 June, Troy, New York, USA.

Organosilicon Chemistry, Cross-Coupling Reaction, and Fruitful Blend with Each Other, Tamao K, The Noyori Forum, 20 - 21 September, Kanagawa, Japan.

Elements Science: Organo Main Group Chemistry directed toward Materials Science, Tamao K, Synthetic Organic Chemistry Workshop, Society of Synthetic Organic Chemistry, Japan, 5 - 6 November, Tokyo, Japan.

Relationship between Structure and Photophysical Properties of Disilanes, Tsuji H, Casher DL, Kubota M, Kobayashi T, Toshimitsu A, Michl J, Tamao K, 50th Symposium on Organometallic Chemistry, 30 September, Osaka, Japan.

Grants

Tamao K, Elements Science towards Construction of Organic and Inorganic Frameworks Focusing on Quality of Elements, Grant-in-Aid for Scientific Research on COE, April 2000 - March 2005.

Tsuji H, Development of new method of controlling silicon chain conformation aiming at controlling photo-physical properties of oligosilanes, Grant-in-Aid for Young Scientists (B), 1 April 2003 - 31 March 2005.

Tsuji H, Construction of new conjugation system containing polysilane and porphyrin, Grant-in-Aid on Priority Areas, 1 April 2003 - 31 March 2004.

Awards

Tamao K, The Asahi Prize, Development of Innovative Organometallic Reactions, Asahi Culture Foundation, 31 January.

Tamao K, The 14th Mukai Prize, Discovery of Cross-Coupling Reaction and Its Application, Tokyo Ohka Foundation for Promotion of Science and Technology, 5 June.

σ * Transition in anti,cisoid-Alternating Oligosilanes up to Docosasilane (Si₂₂)

The photophysical properties of polysilane σ -conjugated system are sensitive to the silicon backbone conformation. So far, we have demonstrated the conformation dependence on the basis of UV absorption spectra of conformationally constrained tetra- and hexasilanes, which claims that an *anti* link (SiSiSiSi dihedral angle $\omega \sim 180^\circ$) effectively extends the σ -conjugated system while a *syn* turn ($\omega < \text{ca. } 30^\circ$) at the termini does not [1]. For a better understanding of the electronic states and photophysical properties in polysilanes, we have extended the investigation to longer silicon chain compounds.

As shown in Figure 1a, on the basis of the UV absorption spectra of the *anti,cisoid*-alternating oligosilanes 2-4, experimental clear-cut evidence is presented for the generally accepted idea that the σ conjugation in polysilanes does not effectively extend through a tetrasilane fragment with a small dihedral angle such as a *cisoid* turn ($\omega \sim 30^\circ$) [2], which was confirmed to be the case with longer *anti,cisoid*-alternating oligosilanes up to Si₂₂ [3].

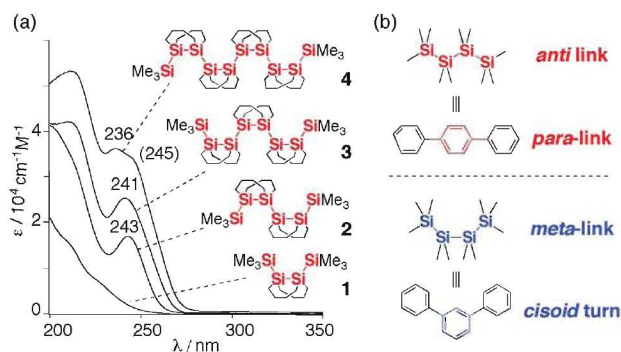


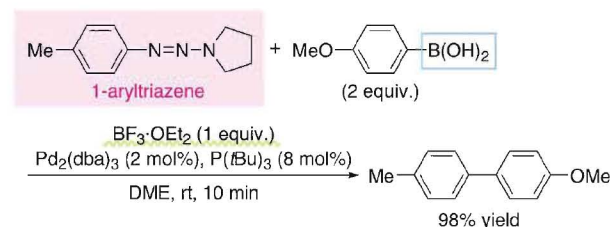
Figure 1. (a) UV absorption spectra of the *anti,cisoid*-alternating oligosilanes 1-4; (b) comparison between σ - and π -conjugation systems.

The UV absorption of all-*transoid* permethylated oligosilanes and the *anti,cisoid*-alternating oligosilanes is similar to that of π -conjugated poly(*p*-phenylene)s and poly(*m*-phenylene)s, respectively (Figure 1b). Thus, the effect of the conformation isomerism on the photophysical properties in the σ -conjugation systems corresponds to that of the position isomerism in the π -conjugated systems.

1. Tsuji H, Michl J, Tamao K. *J. Organomet. Chem.*, **685**, 9-14 (2003).
2. Tsuji H, Terada M, Toshimitsu A, Tamao K. *J. Am. Chem. Soc.*, **125**, 7486-7487 (2003).
3. Honnaiah M, Tsuji H, Tamao K, submitted for publication.

Lewis Acid Induced Palladium Catalyzed Cross-Coupling Reaction of 1-Aryltriazene with Areneboronic Acids

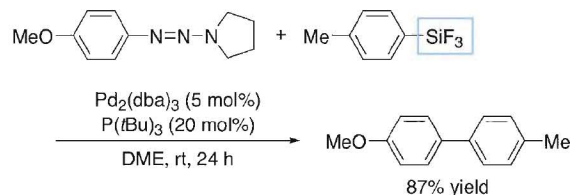
Nickel or palladium-catalyzed cross-coupling reaction utilizing organic halides and a variety of organometallic reagents has become one of the most powerful synthetic tool for the formation of carbon-carbon and carbon-heteroatom bond. We have recently developed the cross-coupling reaction of 1-aryltriazenes, instead of organic halides, as an electrophile with organometallic reagents such as areneboronic acids and aryltrifluorosilanes. The cross-coupling reaction of 1-(*p*-tolyl)triazene with *p*-anisylboronic acid proceeds smoothly in the presence of a catalytic amount of palladium catalyst and phosphine ligand together with 1 equiv. of boron trifluoride (Scheme 1). The addition



Scheme 1. Cross-coupling reaction of 1-aryltriazene with areneboronic acid.

of boron trifluoride is essential for the formation of biaryl product; no reaction occurs at all without Lewis acid. The reaction proceeds quickly even at room temperature to afford the desired product in high yield.

While the reaction mechanism is not clear at the present time, it is supposed that the boron trifluoride plays two roles in the reaction process; (1) the boron trifluoride first serves as a Lewis acid toward the 1-aryltriazene to enhance the reactivity of *sp*²-carbon-nitrogen bond and (2) the resulting borate moiety serves as a fluoride base to promote a transmetalation of the areneboronic acid.



Scheme 2. Cross-coupling reaction of 1-aryltriazene with aryltrifluorosilane.

A similar cross-coupling reaction of 1-aryltriazene with aryltrifluorosilanes has also been achieved without a Lewis acid, although the increased amount of catalyst and prolonged reaction time are necessary (Scheme 2). It is supposed that the Lewis acidic trifluorosilane itself serves as a Lewis acid to enhance the reactivity of the triazene component.