

Invention of Synthetic Reactions Based on σ -Bond Activation

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RDI Professor

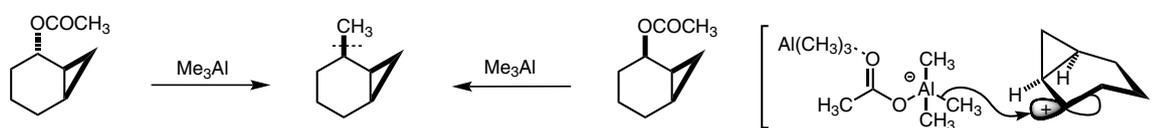
Research and Development Initiative, Chuo University

1. Introduction

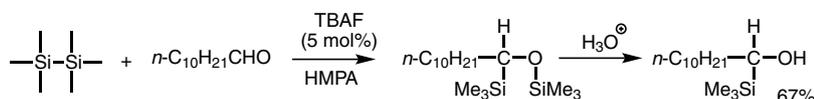
During my studies with Professor Hitosi Nozaki, we had weekly discussions about the present and future of our chemistry. It may have been in the summer of 1980 that Professor Nozaki said one day "When I gave a lecture in Europe, I asked the audience 'Do you know a reaction system that involves both carbanionic and carbocationic species?' No one gave me the correct answer." He then suggested the reaction of allylic acetate with trialkylaluminum, R_3Al , whereby an allylic cation and alanate are produced and the alanate delivers an alkyl anion to the allylic cationic center. The audience then understood his meaning. The reaction of organoaluminums is well-documented, but Professor Nozaki's view is quite unique and straightforward. I am convinced this new point of view, or philosophy, is essential for devising and developing novel synthetic reactions. We have observed that the reaction of trimethylaluminum with diastereometric cyclopropylmethyl-type acetates provides the same product, *endo*-methylated norcarane, and have shown that the reaction¹ proceeds via a common cyclopropylmethyl-type carbocationic intermediate (Scheme 1).

2. Organosilicon Reagent/Fluoride Ion

It would be fascinating if both the cationic and anionic species were generated by the cleavage of element–element bonds. I pictured a reaction scheme in which disilane and a fluoride ion produce a silyl anion and fluorosilane, with the fluorosilane behaving similar to an electrophilic silyl cation. I found that when hexamethyldisilane and tetrabutylammonium fluoride (TBAF) are mixed in hexamethylphosphoric triamide (HMPA) in the presence of an aldehyde, carbonyl attack of the trimethylsilyl anion occurs, followed by *O*-trimethylsilylation. After aqueous workup, we obtained an α -silyl alcohol, demonstrating that the designed reaction² works well. Heterolysis of an element–element bond is conceptually rewarding and is closely related to the recently established activation of molecular hydrogen by a frustrated base pair (Scheme 2).



Scheme 1.



Scheme 2.

During this research, Dr. Kiyosi Kondo, who later became the president of the Sagami Chemical Research Center (SCRC), often visited Kyoto. Dr. Kondo repeatedly and earnestly invited me to move to Kyoto. I finally agreed, and in 1981 started my own research group at SCRC at the age of 34. Dr. Michio Obayashi, one of my first PhD coworkers, soon discovered that hexamethyldisilane/TBAF reductively disilylates butadienes. For example, 2,3-dimethyl-1,3-butadiene is converted to (*E*)-1,4-bis(trimethylsilyl)-2,3-dimethyl-2-butene.² Product formation is believed to involve a trimethylsilyl anion which undergoes single electron transfer (SET) to butadiene to give a trimethylsilyl radical and a butadiene radical anion. Coupling of these at the terminal carbon should give a TMSCH₂-substituted allylic anion, which attacks hexamethyldisilane to give the product and a silyl anion. In HMPA, SET should readily occur from a naked (i.e., in the absence of a metal counter-ion) hard silyl anion. Regardless, you may consider the net transformation as an insertion of butadiene between the Si-Si σ -bond of hexamethyldisilanes (Scheme 3).

We set about generalizing the basic concept of organosilicon compound/fluoride ion-based reaction to generate metal-free (naked) anionic species, and found that halomethyl(trimethyl)silanes and trifluorovinyl(trimethyl)silane undergo an addition reaction³ with aldehydes, even at room temperature, upon treatment with tris(dimethylamino)sulfur difluoro(trimethyl)silicate (TASF) in HMPA or THF. This finding is remarkable given that halomethylolithiums

and trifluorovinylolithium are both unstable organometallic species and were thought only to be generated at extremely low temperatures. Thus, the idea that removal of a metal counter-ion from carbenoids (i.e., organometals with a leaving group on the α -carbon) to generate naked carbanionic species with a leaving group on the α -carbon led to the discovery of useful synthetic reactions that can be conducted at ambient temperature. We further extended the concept of organosilicon reagents/fluoride ion-based reaction to hydrosilane/fluoride ion in the hope of generating a naked hydride. Dr. Makoto Fujita, currently a professor at the University of Tokyo, carried out reactions of α -chiral ketones with dimethylphenylsilane/fluoride ion and observed *threo*-selective reduction.³ We expected that a pentacoordinate hydrosilicate should be sufficiently bulky to stereoselectively reduce ketone carbonyls according to the Felkin-Ahn model transition state.

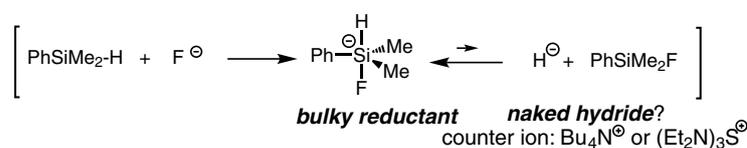
It is reasonable to assume that hydrido and electronegative fluoro groups in trigonal bipyramidal pentacoordinate silicate should be both apical, and organic substituents locating at equatorial positions. Since the bond angles of H-Si-organic groups in the trigonal bipyramide are 90°, the pentacoordinate hydride is likely bulkier than tetrahedral (109.5°) borohydrides. Consequently, carbonyl groups are reduced with a high level of stereoselectivity. In any event, we failed to produce a naked hydride (Scheme 4, 5).⁴



Scheme 3.



Scheme 4.



Scheme 5.

3. Cross-Coupling Reaction with Organosilicon Compounds

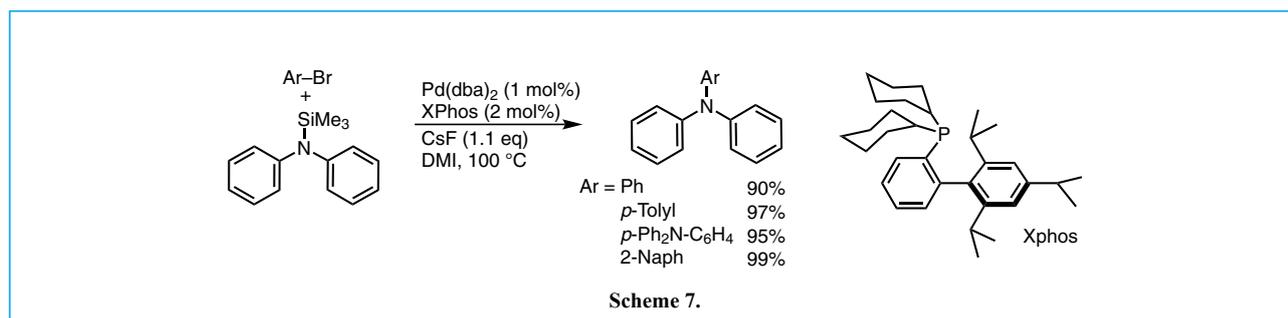
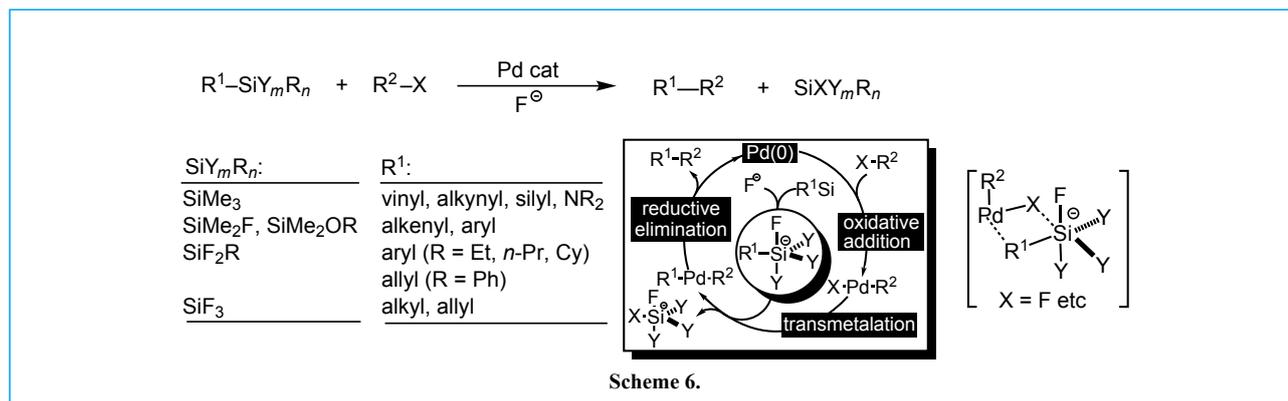
We next envisaged what would happen if a transition metal catalyst was present in the organosilicon/fluoride ion system. Is the organic group on silicon successfully transferred to the transition metal, or does the fluoride ion simply attack the transition metal center to give metal fluoride and lose catalytic activity? To find out, Dr. Yasuo Hatanaka, who is currently a professor at Osaka City University, mixed Pd(II) complex, TASF as a fluoride source, trimethylvinylsilane and 1-iodonaphthalene in HMPA, and isolated 1-vinylnaphthalene in a nearly quantitative yield.⁵ His findings demonstrate that our working hypothesis was correct; this new silicon-based cross-coupling reaction was later named *Hiyama Coupling*. The TASF fluoride source may be replaced with TBAF or KF. To our surprise, KOH could also activate the C–Si bond. However, attempts to extend this approach to substituted vinylsilanes were unsuccessful. This limitation was overcome by introducing a fluorine or alkoxy group on silicon: this effectively extended the scope of the cross-coupling reaction and demonstrated that a heteroatom on silicon assists formation of pentacoordinate silicates, an essential species for successful reaction. A theoretical study⁶ and our intuition both suggested a four-membered cyclic transition state for the transmetalation from Si to Pd. Fluoride is believed to play a key role in the transmetalation. The following scheme summarizes the silicon-based cross-coupling reaction (Scheme 6).

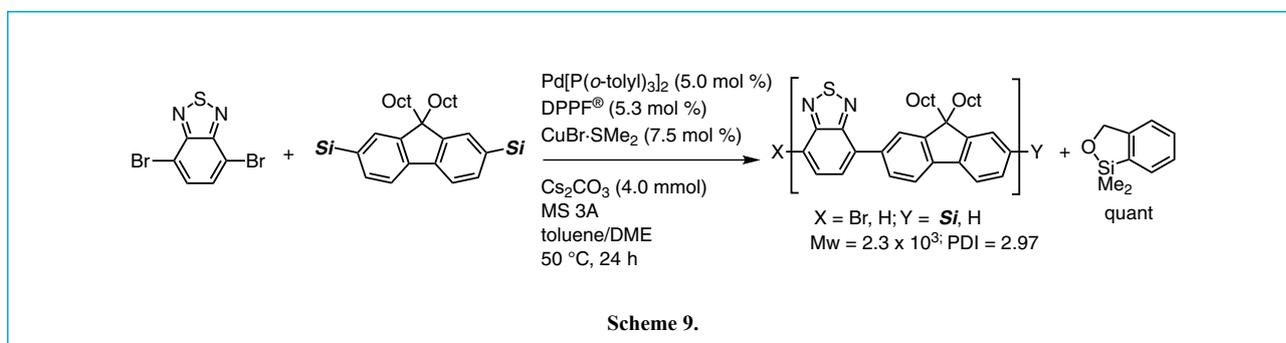
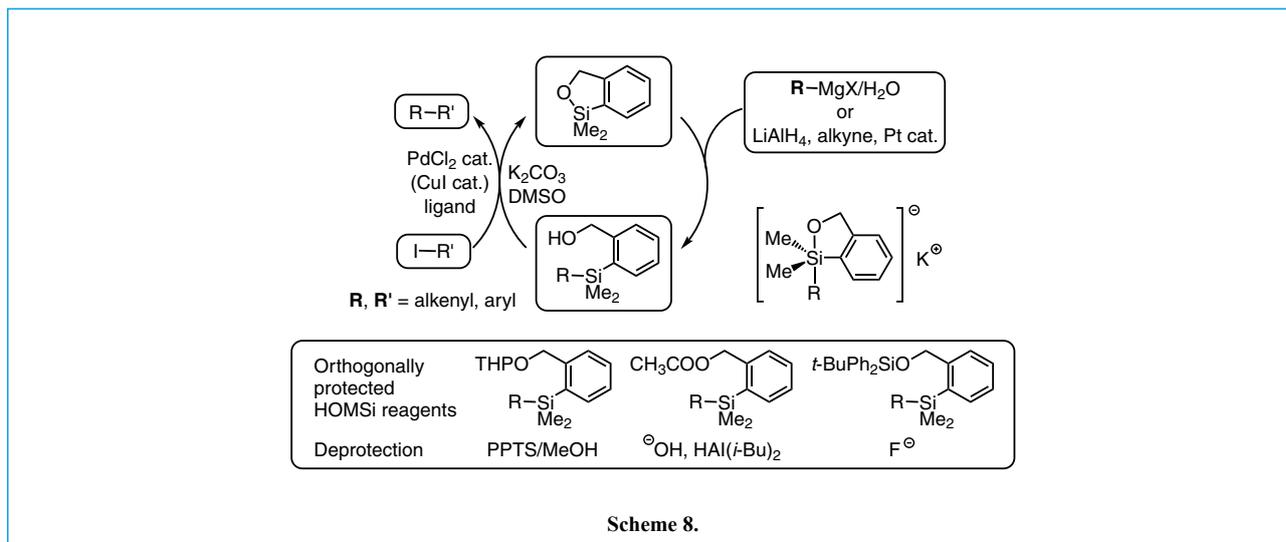
Halosilanes and alkoxy silanes are sensitive to moisture and are thus incompatible with chromatographic purification, so cross-coupling with these organosilicon reagents is less

accessible compared to Suzuki-Miyaura coupling. Accordingly, while Professor Kyoko Nozaki was working with me in Kyoto, she showed that one organic group on tetraorganosilanes can be in situ converted to a halo- or alkoxy group by the action of a fluoride ion. We recently found that C–N coupling⁷ is conveniently achieved with trimethylsilylamines and allows easy synthesis of triaryl amines which display a characteristic reactivity profile different from that obtained using Hartwig–Buchwald coupling (Scheme 7).

In 2004, Dr. Yoshiaki Nakao, who is currently a professor at Kyoto University, suggested using HOMSi (dimethyl(*o*-hydroxymethylphenyl)silane) tetraorganosilane reagents⁸, predicting that they would be converted to a pentacoordinate structure by intramolecular nucleophilic attack of the hydroxyl group. Protection of the hydroxyl group with a common protecting group significantly stabilizes the silicon reagents under chromatographic separation and common reaction conditions; upon deprotection, the reagents become coupling-active. After the reaction, the silicon residue is recovered as a cyclic silyl ether, which is reconverted back to the HOMSi reagent by reaction with organolithium or –magnesium reagents. Recently, direct C–H silylation of (hetero)aromatics and terminal alkenes has been demonstrated starting with a THP-protected HOMSi hydride reagent and an iridium catalyst (Scheme 8).

Cross-coupling reaction with HOMSi reagents has recently been applied to polymer synthesis under mild conditions. The resulting π -conjugated polymers find important applications as light-emitting and solar-cell materials (Scheme 9).⁹



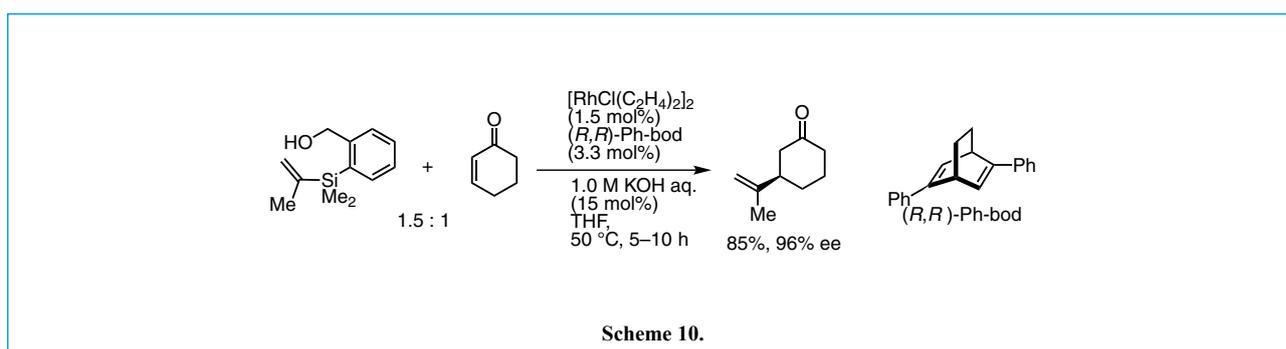


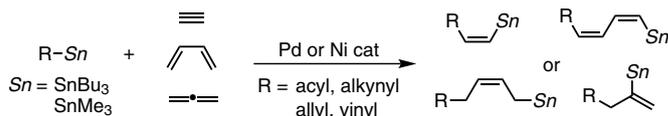
4. Conjugate addition of HOMSi Reagents

Once we discovered that transmetalation from Si to Pd is possible, we assumed that the same transformation from Si to Rh could be achieved. Indeed, Rh-catalyzed conjugate addition of organosilicon reagents had some precedents. We collaborated with Professor Tamio Hayashi, then at Kyoto University and currently a professor at Singapore National University, and with Dr. Ryo Shintani, currently a professor at the University of Tokyo. Together, we showed that HOMSi reagents undergo conjugate addition to enones, α,β -unsaturated esters, and amides with high enantioselection using a chiral diene ligand.¹⁰ Here again, the cogenerated cyclic silyl ether is readily recovered and converted back to the corresponding HOMSi reagent (Scheme 10).

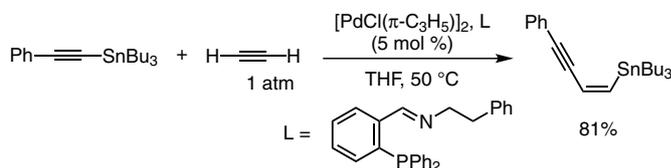
5. Carbostannylation Reaction of Alkynes and Dienes

In 1997, I was invited back to Kyoto University to head the research group of the late Professor Hidemasa Takaya, and to begin research with Dr. Eiji Shirakawa, currently a professor at Kwansai Gakuin University. Dr. Shirakawa had been examining the Migita-Kosugi-Stille coupling reaction mechanism and had evidence for a novel catalytic cycle involving oxidative addition of Pd(0) to the C–Sn bond, followed by transmetalation with organic halides. I was surprised at his proposed mechanism, and suggested that involvement of the oxidative adduct C–Pd(II)–Sn may lead to the insertion of an unsaturated C–C bond between the C–Pd or Pd–Sn bond; if this was indeed the case, then a new synthetic reaction might be realized, leading to insertion of an





Scheme 11.



Scheme 12.

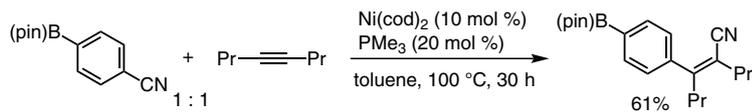
alkyne between the C–Sn bond. This reaction proceeded well and was named ‘transition metal-catalyzed *carbostannylation*’.¹¹ Various organostannane reagents, and alkynes or dienes are applicable to the transformation. A typical example, shown below, is the addition of alkynylstannane to ethyne to give (*Z*)-but-3-yn-1-enyl(tributyl)stannane. This carbostannylation reaction has made various π -conjugated organostannanes accessible (Scheme 11, 12).

addition of Ni(0) to C–CN bonds. I immediately suggested examining the reaction in the presence of unsaturated substrates, as we did for the carbostannylation reaction. To our delight, a couple of weeks later Dr. Nakao twittered that this approach would be feasible. However, the initial protocol needed 10 mol% of Ni(0) catalyst and required a 1 or 2 days to achieve synthetically meaningful yields. Although the catalyst was lazy (the turn over number was roughly 6~7), we called the new reaction *carbocyanation* (Scheme 13).¹¹

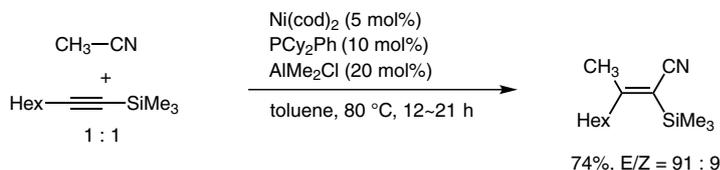
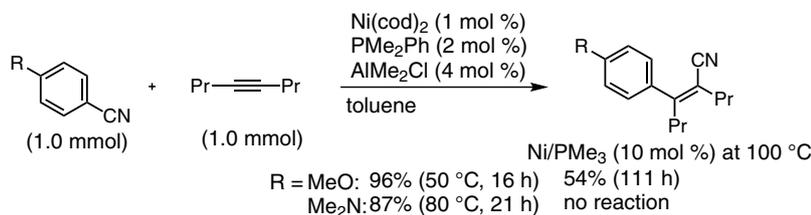
6. Carbocyanation Reaction of Alkynes and Alkenes

In 2002, Professor Kyoto Nozaki moved to the University of Tokyo as a full professor and Dr. Yoshiaki Nakao, currently a professor at Kyoto University, joined my research group. One day he visited me to discuss the work of Professor W. D. Jones at Rochester University on the synthetic potential of oxidative

After we published the first paper on the new reaction, we improved the catalytic efficiency by adding a mild Lewis acid such as organoaluminum, -borane, or -zinc to make the reaction truly catalytic.¹² Under these new conditions, not only aryl cyanides, but allyl and alkenyl cyanides were also applicable, as were acetonitriles: CH₃–CN was cleaved into CH₃ and CN fragments and added to internal alkynes in a *syn* manner (Scheme 14).



Scheme 13.



Scheme 14.

7. Hydro(hetero)arylation of Alkynes and Alkenes

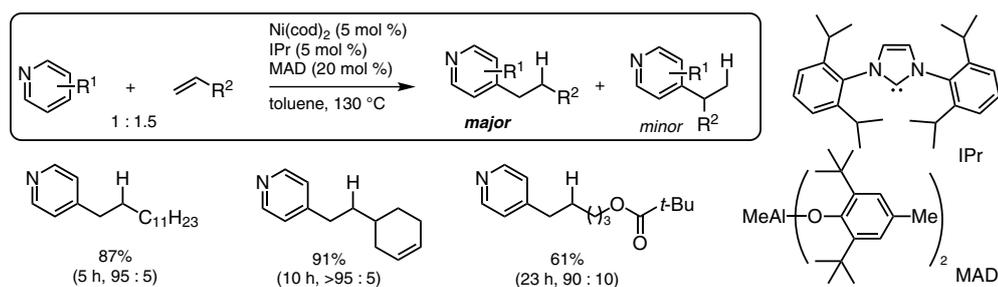
While studying the carbocyanation of *N*-protected 3-cyanoindoles under the original conditions, we observed the formation of a small amount of byproduct and attributed it to C(2)–H activation followed by alkyne insertion. Tuning the protecting group and ligand resulted in C–H activation occurring uniformly with heteroaromatics and polyfluoroaromatic compounds.¹³ The most synthetically significant discovery was C(4)-selective normal alkylation¹⁴ of pyridines with terminal olefins using Ni(cod)₂/iPr ligand and an aluminum Lewis acid MAD. Given that pyridine and its homologs are inert towards Friedel-Crafts reaction, site-selective heteroarylation with terminal olefins provides a new route to the *n*-alkylation of pyridines (Scheme 15).

The observed regioselectivity is understood insofar as (1) the bulky MAD is coordinated by the pyridine nitrogen, (2) Ni-Ipr interacts with the pyridine ring π -electrons, (3) steric repulsion between the metal centers causes Ni to locate far from the nitrogen and interact at C(4), (4) Ni(0) is oxidatively added

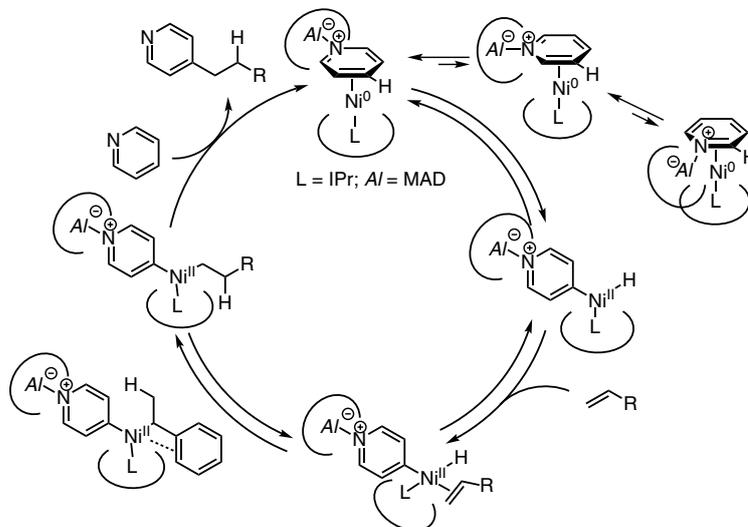
to C(4)–H, (5) hydronickeleation of the terminal olefins occurs, and (6) quick reductive elimination is caused by the two bulky ligands. Accordingly, the bulkiness of the Ni ligands and the aluminum metal are key to selective alkylation (Scheme 16).

The concept of Ni(0)/Lewis acid is applicable to *N,N*-dimethylformamide (DMF), whose formyl C–H bond oxidatively adds to Ni(0). The resulting Ni–H bond undergoes regioselective addition to terminal olefins, then subsequent reductive elimination to produce alkanamide under one-carbon homologation of olefin (Scheme 17).¹⁵

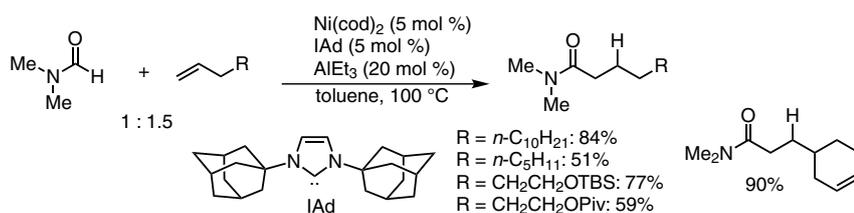
Polyfluorobenzenes undergo C–H activation by Ni(0) in the absence of a Lewis acid; it is possible that the most electrophilic position is activated to effect hydroarylation.¹⁶ Accordingly, polyfluorobenzonitriles first undergo carbocyanation and then hydroarylation of the internal alkynes to give extensively π -conjugated polyfluorobenzenes.¹⁷ The structure of the oxidative adduct of the C–CN bond to Ni(0) can be unambiguously determined by X-ray crystallography (Scheme 18).



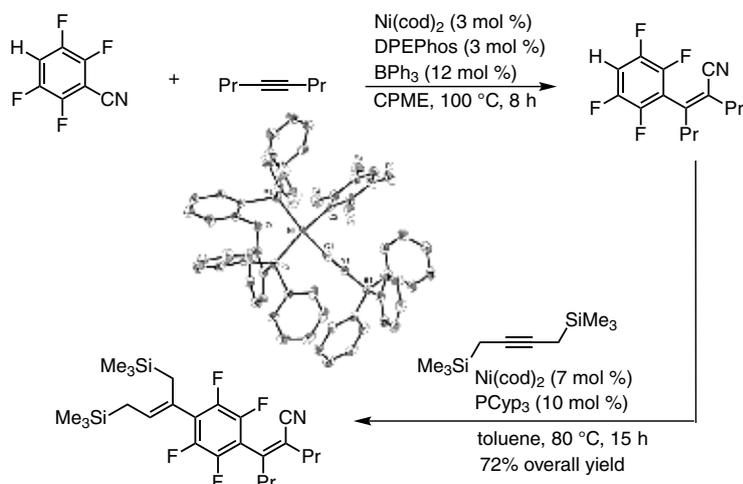
Scheme 15.



Scheme 16.



Scheme 17.

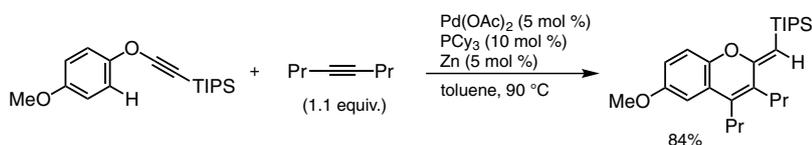


Scheme 18.

8. *ortho*-C–H Activation of Phenyl Silylethynyl Ethers and Cromane Ring Formation with Alkynes

I retired from Kyoto University in 2010 and immediately moved to my present position at the Research and Development Initiative (RDI), Chuo University. Dr. Yasunori Minami joined me soon after receiving his PhD from Osaka University. We started studying the interaction of transition metal complexes with *p*-methoxyphenyl TIPS-ethynyl ether in the presence of 4-octyne, with the intention of cleaving either of the

etheral C–O bonds. However, to our surprise, the *ortho*-C–H bond was found to be selectively activated by Pd(0), allowing incorporation of 4-octyne to give 2-(TIPS-methylene) benzochromene. This reaction is attributed to nucleophilic attack of Pd(0) on the α -carbon of the ethynoxy group to give a Pd(II) intermediate, which then oxidatively adds to the *ortho*-C–H bond to mediate chromene annulation.¹⁸ Worthy of note is the silylethynoxy group behaved as an acceptor of Pd(0) to produce Pd(II) temporarily before oxidative addition to an *ortho*-C–H bond. This is a new type of directing group of *ortho*-C–H activation (Scheme 19).



Scheme 19.

Conducting the reaction using an allene in lieu of an internal alkyne produced 2,3-bismethylenechromane.^{19a} This readily underwent Diels–Alder reaction to stereoselectively provide the tetracyclic ring structure. Isocyanates also react with the same alkynyl ether to give solid benzoxazine^{19b} which emits light upon UV irradiation, even in the solid state (Scheme 20).

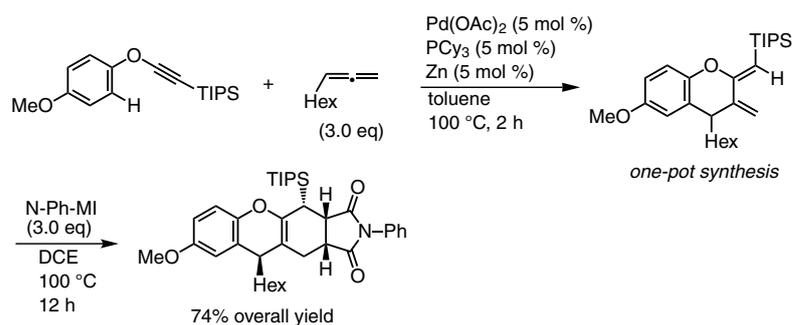
The Pd(II)/Zn catalyst promotes cyclization of 2,6-dimethylphenyl TIPS-ethynyl ether to give 2-(TIPS-methylene)dihydrobenzofuran. Thus, γ -C–H bond activation is made feasible (Scheme 21).²⁰

Under similar conditions, 2-(TIPS-ethynyloxy)-2-biphenyl underwent δ -C–H activation to form an oxatricyclic product **21** which was readily converted to the 10,10-disubstituted 9-oxaphenanthrene framework, often used as potent electron carrier materials (Scheme 22).

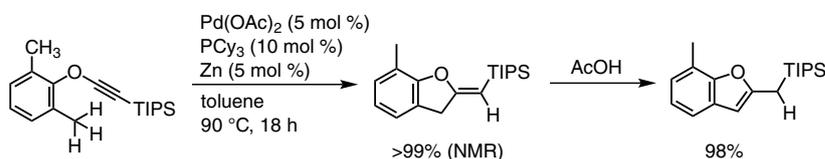
In summary, this is the story to date of how I have invented synthetic reactions for C–C formation. I, of course, encountered problems during my research; now readers know how I analyzed the problems, how I constructed working hypotheses, and how I solved the problems. Invention of reactions described herein would suggest how it is essential to understand reaction mechanism and pay attention to relating science and technology.

Acknowledgments

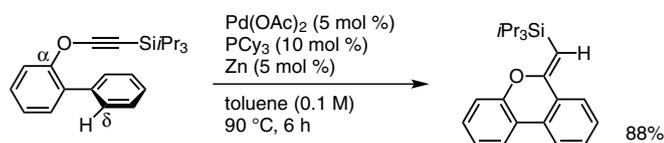
The author is deeply indebted to Kyoto University, Sagami Chemical Research Center, Tokyo Institute of Technology, and Chuo University: all kindly provided research laboratories and financial support. In addition, the Ministry of Education, Culture, Science, Sports, and Technology, the Japan Society for the Promotion of Science, the Japan Science and Technology Agency, and Sumitomo Chemicals Ltd. are gratefully acknowledged for financial support. I sincerely thank all my collaborators, whose names are listed in the literature cited below, for their dedication to helping me discover and confirm the chemistry I described above.



Scheme 20.



Scheme 21.



Scheme 22.

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Introduction of the author:

Tamejiro Hiyama

RDI Professor

Research and Development Initiative, Chuo University

[Education]

- 1965 - 1969: Bachelor of Engineering at Kyoto University
 1969 - 1972: Master (& 1 year for PhD) of Engineering at Kyoto University
 1975.9.23: PhD of Engineering at Kyoto University (Prof. Hitosi Nozaki, mentor)
 1975 - 1976: Postdoctoral Fellow at Harvard University (Prof. Yoshito Kishi)

[Academic Career]

- 1972 - 1981: Assistant Professor at Fac. Engineering, Kyoto University
 1981 - 1983: Research Fellow & Group Leader at Sagami Chemical Research Center
 1983 - 1988: Senior Research Fellow & GL at SCRC
 1988 - 1992: Executive Research Fellow & GL at SCRC
 1992 - 1997: Professor at Res. Lab. Resources Utilization, Tokyo Institute of Technology
 1997 - 2010: Professor at Graduate School of Eng., Kyoto University
 2010 - present: RDI Professor at Chuo University

[Honors]

- 1980 The Chemical Society of Japan Award for Young Chemists
- 2004 The Japanese Liquid Crystal Society (JLCS) Award
- 2007 The Synthetic Organic Chemistry Award, Japan
- 2008 The Chemical Society of Japan (CSJ) Award
- 2012 The Humboldt Research Award

[Research Interests]

Novel Organometallic Reagents and Reactions for Selective Organic Synthesis, Organofluorine and Organosilicon Chemistry, Synthesis of Biologically Active Substances, Design and Synthesis of Novel Functionality Molecules and Materials.

[Achievements]

Synthetic Reactions with Carbenoid Reagents, Carbon-Carbon Bond Forming Reactions with Cr(II) reagents (Nozaki-Hiyama-Kishi Reaction or NHK Reaction), Condensation of Ester Magnesium Enolates with Nitriles (Hiyama Reaction), Silicon-Based Cross-Coupling Reaction (Hiyama Coupling), Polysilacage Compounds for s-Conjugation Materials, Oxidative-Desulfurization-Fluorination Reactions, Carbostannylation Reaction of Alkynes and Dienes, Carbocyanation Reaction of Alkynes and Alkenes, Hydro(hetero)arylation Reaction of Alkynes and Alkenes, Design and Synthesis of Liquid Crystal and Light-Emitting Materials, Synthesis of Biologically Active Compounds.

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TCI Related Products

Chapter 2

H0638	Hexamethyldisilane		10mL	100mL
T1125	TBAF (ca. 1mol/L in Tetrahydrofuran)		25mL	100mL
T1037	TBAF Hydrate		25g	100g
U0009	Undecanaldehyde		25mL	250mL
D1148	2,3-Dimethyl-1,3-butadiene		10mL	25mL
D2196	Dimethylphenylsilane			25mL

Chapter 3

B1374	Pd(dba) ₂		1g	5g
C2204	Cesium Fluoride		25g	100g
D1477	DMI	25mL	100mL	500mL
D4243	1,1-Dimethyl-1,3-dihydrobenzo[c][1,2]oxasilole		1g	5g
D3842	4,7-Dibromo-2,1,3-benzothiadiazole	1g	5g	25g
B2027	1,1'-Bis(diphenylphosphino)ferrocene	1g	5g	25g
C2160	Cesium Carbonate		25g	100g

Chapter 4

C2461	[RhCl(C ₂ H ₄) ₂] ₂			200mg
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Chapter 5

A1479	[PdCl(π-C ₃ H ₅) ₂]		500mg	1g
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Chapter 7

M1211	MAD (= Methylaluminum Bis(2,6-di- <i>tert</i> -butyl-4-methylphenoxide) (0.4mol/L in Toluene)			50mL
B3465	IPr (= 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene)		1g	5g
T0925	Triethylaluminum (15% in Toluene, ca. 1.1mol/L)			100mL
B2867	DPEphos		5g	25g
T2248	Tricyclohexylphosphine		1g	5g

Chapter 8

A1424	Palladium(II) Acetate		1g	5g
P2161	Palladium(II) Acetate (Purified)			1g
T1165	Tricyclohexylphosphine (ca. 18% in Toluene, ca. 0.60mol/L)			25mL