Contribution

Photocontrol of the Coordination Numbers of the Main Group Elements: Properties of Azobenzenes Bearing a Main-Group-Element Substituent and Their Application

Naokazu Kano
Takayuki Kawashima

Department of Chemistry, Graduate School of Science, The University of Tokyo

1. Introduction

Each main group element in main group compounds usually takes its own specific coordination number, oxidation number and bonding state. An unusual valence can be achieved by appropriate molecular design and synthetic methods, and such an unusual valence results in characteristic, unique structures and properties. The reactivity of the main group compounds markedly depends on the coordination number. For instance, silicon, which belongs to group 14 and is located just under carbon in the periodic table, generally shows the tetracoordination state like an sp^3 carbon. Silicon can also take a high coordination state, such as penta- or hexa-coordination states, when the appropriate ligands are used under suitable conditions. In highly coordinated silicon compounds, the electrophilicity of the central silicon increases compared to that of the tetracoordinated silicon compounds, and the nucleophilicity of the substituents on the silicon also increases (Figure 1). Thus, some synthetic reactions have been developed by using these properties of highly coordinated silicon compounds as their intermediates or transition states, as seen in the Tamao oxidation reaction.1) In other examples, organophosphorus compounds, whose phosphorus center takes a trivalent and tricoordination state, have widely been used as ligands for transition metals. When the phosphorus takes pentavalent and tetracoordination or pentavalent and pentacoordination states, the usefulness of these phosphorus compounds is dramatically reduced.

Considering elemental properties and their relationship with the coordination numbers, control of the oxidation state and the coordination number of the main group elements by using some external stimuli is quite interesting. This will lead to new methods for control of organic reactions, based on the control of physical properties and reactivity of main group compounds. For example, if the coordination state could be easily switched so that an element could take an activated coordination state at a certain period but an inactivated state at another, this would be useful for the regulation of copolymerization reactions. Moreover, if this could be used as a substrate, it could possibly provide a new method for protection or deprotection of the ligands.

However, main group compounds taking unusual coordination states are unstable in general, and some stabilization modification is required for actual use. For example, steric protection methods are often used for stabilization of low-coordinated main group compounds, by introducing a bulky substituent onto the main group element in order to prevent oligomerization or polymerization. In addition, elimination reactions are considered to proceed easily in the highly coordinated compounds because the highly coordinated compounds often behave as intermediates in organic reactions. Therefore, it is required that an electron-withdrawing group should be introduced to reduce the electron density of the central element and to stabilize the polarized bonds, and that multidentate ligands should be used to take advantage of the favorable entropy contribution. There are limitations in molecular design for the stabilization of

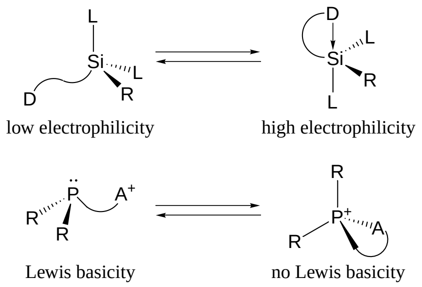


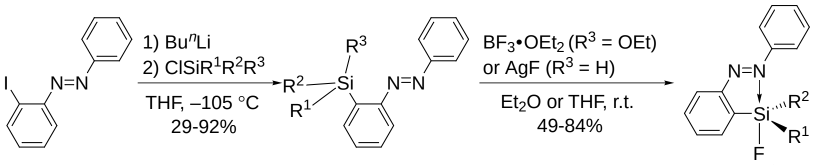
Figure 1. Changes in physical properties of silicon and phosphorus compounds induced through changes in their coordination numbers.

unusual coordination states of main group elements. In order to reversibly control a coordination number, it is essential to regulate the positional relationship between a central element and its ligands. For this purpose, the substituent as a ligand needs to meet these demands and limitations. Because of these limitations, it was previously impossible to develop main group compounds with specific groups that met the following two points, 1) stabilization of the unusual coordination state and 2) structural control by an external stimulus.

One possible method of control by an external stimulus is offered by photoirradiation. There are several compounds that have been known to change their structures in response to photoirradiation. Among them, azobenzene has widely been reported as a photoresponsive molecule, which can be photoisomerized, in various types of photoswitching reactions.2) We have directed our attention on this property of azobenzene, namely, that azobenzene has a structure with a proper rigidity and can undergo photoisomerism, as well as the fact that its azo group can work both as a Lewis base or an electrophile depending on the reagents used. We expected that control of the coordination number of the main group element could be achieved by reversible photoisomerization between (*E*)- and (*Z*)-isomers when azobenzene was used as an intramolecular ligand. First, we introduced a main-group-element substituent to the 2-position of the azobenzene, and thus, we made use of the azo group as a photoresponsive and coordination site or as an electrophilic site. As a result, we have demonstrated that the coordination numbers of main group compounds of silicon, boron and phosphorus could be controlled by photoirradiation, and that their structures, physical properties and reactivity could also be well photocontrolled in several systems. In this report, we focused on development of these methods and introduced methods to control the coordination number of main group elements as well as their applications. We also discuss the characteristics of azobenzene itself as a main group element substituent.

2. Photocontrol of the Structures of the Silanes and Silicates Based on the Changes of the Coordination Numbers of Silicon

A 2-(phenylazo)phenyl group was introduced onto the silicon via a lithio derivative prepared by reaction of 2-iodoazobenzene (*E*)-**1** with butyllithium at –105 °C (Figure 2).3,4) The coordination state of the silicon can be easily confirmed by the ^{29}Si NMR spectroscopy. The differences in chemical shift between the synthesized 2-(phenylazo)phenyl derivatives and the corresponding phenyl derivatives was found to be only within ±2 ppm, indicating that the silicon takes a tetracoordination state, in which its azo group had almost no perturbation on its coordination state. Since it was expected that the electrophilicity of the silicon would be increased by fluorination, monofluorosilanes (*E*)-**3e** and (*E*)-**3f** were synthesized by reaction of monohydrosilanes (*E*)-**2e** and (*E*)-**2f**, respectively, with silver fluoride. Difluorosilane (*E*)-**3g** and trifluorosilane (*E*)-**3d** were also synthesized by reaction of diethoxysilane (*E*)-**2g** and triethoxysilane (*E*)-**2d**, respectively, with BF_3•OEt_2. When the coordination state of the silicon of the (*E*)-**3d-g** was compared to a corresponding phenyl derivative by ^{29}Si NMR, (*E*)-**3d-g** were found to show upfield shifts more than 11 ppm. It was found that pentacoordination state of the silicon atom, which was coordinated by the azo group, in the fluorosilane derivatives markedly contributed to its spectral property in solution. The presence or absence of this coordination was confirmed by X-ray crystallography. In the compound without fluorine atoms, the bulky silicon substituent was found to be located opposite to the nitrogen atom. In contrast, it was shown that in the presence of at least one fluoro group on the silicon atom, the pentacoordinated silicon atom can interact with a lone pair of the nitrogen atom, resulting in a distorted trigonal bipyramidal structure around the silicon atom. Formation of an N-Si dative bond induced by substitution of the fluorine atom is ascribed to increased electrophilicity of the silicon atom with the electronegative fluorine atom, as seen in the previously reported organosilanes with ligands other than the azo group.



(*E*)-**1**

(*E*)-**2a**: $R^1 = R^2 = R^3$ = Me
(*E*)-**2b**: $R^1 = R^2$ = Me, R^3 = Ph
(*E*)-**2c**: R^1 = Me, $R^2 = R^3$ = Ph
(*E*)-**2d**: $R^1 = R^2 = R^3$ = OEt
(*E*)-**2e**: $R^1 = R^2$ = Me, R^3 = H
(*E*)-**2f**: $R^1 = R^2$ = Ph, R^3 = H
(*E*)-**2g**: R^1 = Ph, $R^2 = R^3$ = OEt

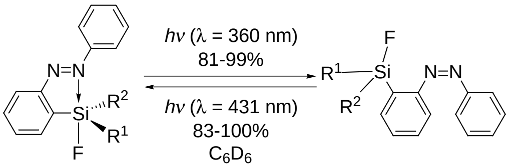
(*E*)-**3d**: $R^1 = R^2$ = F
(*E*)-**3e**: $R^1 = R^2$ = Me
(*E*)-**3f**: $R^1 = R^2$ = Ph
(*E*)-**3g**: R^1 = Ph, R^2 = F

Figure 2. Synthesis of pentacoordinated fluorosilanes bearing an azo group.

Difference in the coordination state of the silicon atom can easily be distinguished as difference in the colors of crystals of the compounds. Tetracoordinated silicon-substituted azobenzenes, which has no fluorine atoms, display a red or orange color, while pentacoordinated silicon-substituted azobenzenes (*E*)-**3d-g** exhibit yellow. In the UV/visible spectra of the tetracoordinated (*E*)-**2a-g** compounds in the dichloromethane solution, their absorption maxima ascribed to the π–π^* and n–π^* transitions were observed at 325-327 nm and 441-456 nm, respectively. Compared to the azobenzene without a substituent (π–π^* 318 nm and n–π^* transition 441 nm), tetracoordinated (*E*)-**2a-g** were slightly red-shifted, and the red-shifts demonstrated raise of the energy levels of both n- and π-orbitals by an inductive effect of the electron-donating organosilicon group. In contrast, in azobenzenes (*E*)-**3d-g** with the pentacoordinated silicon substituent, the absorption maximum ascribed to the π–π^* transition was observed red-shifted at approximately 336-349 nm, while the absorption maximum ascribed to the n–π^* transition was observed oppositely blue-shifted. As a result, the absorption spectrum ascribed to the n–π^* transition was not clearly detected in the compounds (*E*)-**3d** or (*E*)-**3g**, probably because it was hidden beneath the π–π^* transition. These results showed that formation of a dative bond from the nitrogen to the silicon atom profoundly stabilized the n-orbital, and the π-orbital became relatively unstable as compared to the π^*-orbital.

When (*E*)-**3d-g** were irradiated with light with a wavelength ascribed to the π–π^* transition (λ = 360 nm) using a super-high pressure mercury lamp and a colored glass filter, they isomerized to the corresponding compounds (*Z*)-**3d-g** in high yields of 81~99% (Figure 3). The compounds produced after isomerization showed orange-color. The absorption maximum around 340 nm decreased, while an absorption maximum around 440 nm, which was ascribed to the π–π^* transition, increased. Furthermore, when the (*Z*)-isomer was irradiated with a light around this wavelength (λ = 431 nm), the (*Z*)-isomer could be reversibly changed back to the (*E*)-isomer.

The coordination state of the (*Z*)-isomers after photoisomerization was examined by ^{29}Si NMR. The (*Z*)-isomers were downfield shifted as compared to the corresponding (*E*)-isomers, and their chemical shifts were similar to the phenyl derivatives, demonstrating that the (*Z*)-isomers take a tetracoordination state. In particular, both (*E*)-**3f** and (*Z*)-**3f** isomers of the fluorodiphenylsilyl derivative could be isolated, suggesting that the silicon atom takes both penta- and tetra-coordination states in (*E*)-**3f** and (*Z*)-**3f** isomers, respectively. Both structures were further confirmed by X-ray crystallography, demonstrating structural change around the silicon atom by the photoisomerization.



(*E*)-**3** (*Z*)-**3**

Figure 3. Photoswitching between tetracoordination and pentacoordination states in the fluorosilanes bearing an azo group.

Since we successfully photoswitched the tetra- and penta-coordination states of the fluorosilanes, we next attempted to develop various photoswitching systems with different coordination numbers of the silicon atom using a similar method. Following pentacoordination, hexacoordination was investigated. Since a silicate with intramolecular coordination is known to form a hexacoordination state, we attempted to produce further higher coordination states of the silicon atom by transformation of (*E*)-**3d** to a silicate. We conducted fluorination of trifluorosilane (*E*)-**3d** by addition of potassium fluoride and 18-crown-6 and obtained silicate (*E*)-**4d** (Figure 4).5) When the yellow silicate (*E*)-**4d** was irradiated with light with a wavelength similar to that of the π–π^* transition of the azo group, isomerization proceeded almost quantitatively, resulting in the formation of the reddish orange silicate (*Z*)-**4d**. Isomerization of the (*Z*)-**4d** isomer to the (*E*)-**4d** isomer also proceeded quantitatively, suggesting that quantitative photoisomerization could be done reversibly between (*E*)- and (*Z*)-isomers. Both low-temperature ^{19}F and ^{29}Si NMR spectroscopy and X-ray crystallography revealed that (*E*)-**4d** had a distorted octahedral structure with a hexacoordinated silicon atom, while (*Z*)-**4d** showed a trigonal bipyramidal structure with a pentacoordinated silicon atom (Figure 5). The most dramatic change in structure was found in the C–Si–F angle, which was 99.47(5)° and 163.73(6)° in the (*E*)-**4d** isomer, whilst it was 117.77(19)° and 126.67(19)°, respectively, in the (*Z*)-**4d** isomer. Moreover, the F–Si–F angle, which had been 95.76(5)° in the (*E*)-**4d**, changed to 115.53(6)°. It is noteworthy that photoirradiation alone induced such a great structural change around the silicon atom without any addition of chemical reagents. Thus, we have succeeded in controlling the coordination-number change between the penta- and hexa-coordinated silicate **4d** by photoirradiation and this has been accompanied by control of the conformation around the silicon atom.

There have been many reports in which the physical properties of compounds were photoswitched by using the photoisomerization of azobenzene. In these previous studies, the substituent was located at the *para*- or *meta*-positions of the azo group in most cases,2) and photocontrol of physical properties was achieved by regulating the positional relationships or directions of the substituents in each of (*E*)- and (*Z*)-isomers. Unlike these previous photoswitching systems, however, the photoswitching system that we introduce here is unique in that the structure around the silicon atom can be switched by using the changes in their positional relationships between the silicon and the lone pair of the nitrogen atom. Even in the compound bearing organic substituents on the silicon atom, if the direction of the substituent could be switched using this method and the resultant is further combined with directional regulation of the *para*-substitutent of the azo group, this system may surely be applied to various types of photocontrol of physical properties.

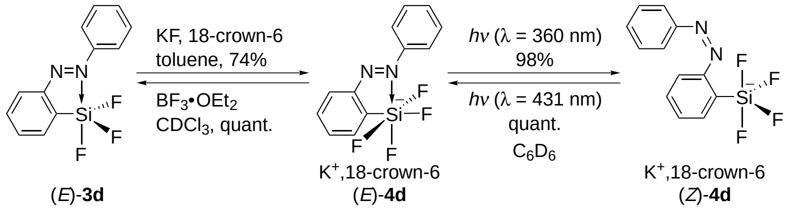


Figure 4. Photoswitching between the pentacoordination and hexacoordination states in the tetrafluorosilicates bearing the azo group.

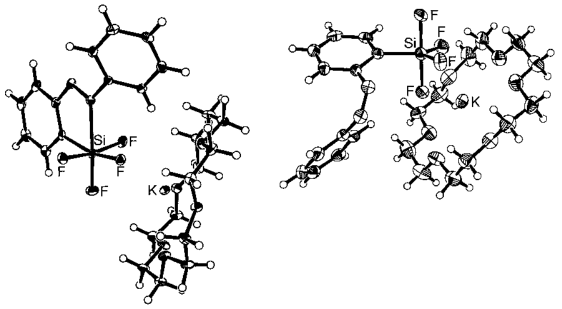


Figure 5. ORTEP drawings of the tetrafluorosilicate (*E*)-**4d** and (*Z*)-**4d** isomers bearing the azo group.

3. Photoswitching of Reactivity of the Disiloxane Based on the Change of the Coordination Number of the Silicon

In the previous two sections, we have shown that photoirradiation could control the resultant structures of the silicon compounds. Then, the next question arises, “Can we also regulate their reactivity?” When the stability of the trifluorosilane (*E*)-**3d** was examined, it was found that the trifluorosilane (*E*)-**3d** was gradually hydrolyzed in solution to yield 1,1,3,3-tetrafluorodisiloxane (*E,E*)-**5** (Figure 6).6) Compound (*E,E*)-**5** possesses two azobenzene units within its own molecule. Reflecting the fact that the azobenzene could easily be stacked in the crystalline state, two azobenzenes were found to stack in almost parallel with a distance of 3.4 - 3.6 Å between two sets of benzene rings, by using the Si–O–Si site as a spacer. In the absence of light, disiloxane (*E,E*)-**5** further slowly degraded at room temperature for another 2 days and formed into a mixture of (*E*)-**3d** and oligosiloxane (*E*)-**6**$_n$ (n = 2, 3). The degradation reaction of (*E,E*)-**5** was facilitated by photoirradiation, and all (*E,E*)-**5** completely disappeared after a 2 hr photoirradiation. As a result of this reaction, tetracoordinated disiloxane (*Z,Z*)-**5**, whose two azo groups were isomerized, was produced in addition to (*Z*)-**3d**. When (*Z,Z*)-**5** was left alone in the dark at room temperature, it gave (*E*)-**3d**, and its formation rate from (*Z,Z*)-**5** was markedly faster than that from (*E,E*)-**5**.

In the compound (*E,E*)-**7**, which corresponds to the tetrahydro-derivative of (*E,E*)-**5**, reactivity was further significantly changed between prior to and after photoirradiation. In the presence of a catalytic amount of tetrabutylammonium fluoride, (*E,E*)-**7** was hydrolyzed to give diphenylhydrazine **8** accompanying cleavage of the C–Si bonds (Figure 7).7) On the other hand, when a similar reaction was attempted using tetracoordinated silicon compound (*Z,Z*)-**7** that quantitatively formed by photoirradiation of (*E,E*)-**7**, silsesquioxane **9** was obtained without cleavage of the C–Si bonds although the azo groups were reduced. Thus, it was demonstrated that the reactivity accompanied by a cleavage of the carbon–silicon bond could be successfully controlled by photoirradiation.

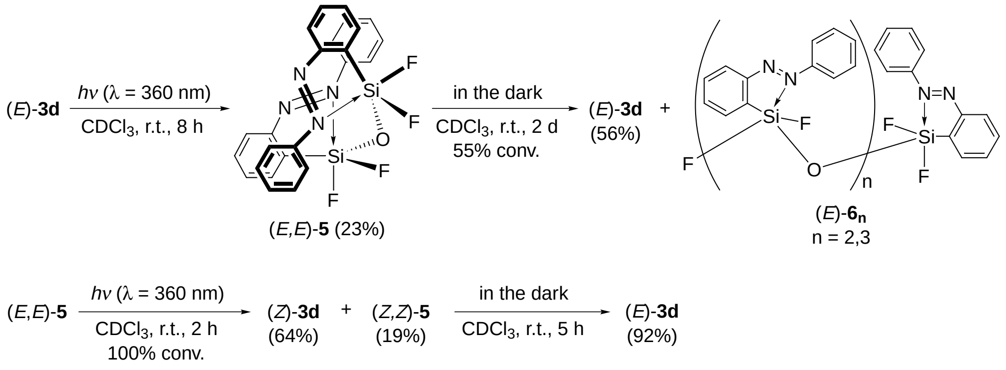


Figure 6. Change of reactivity induced by photoirradiation of tetrafluorodisiloxane bearing the azo groups.

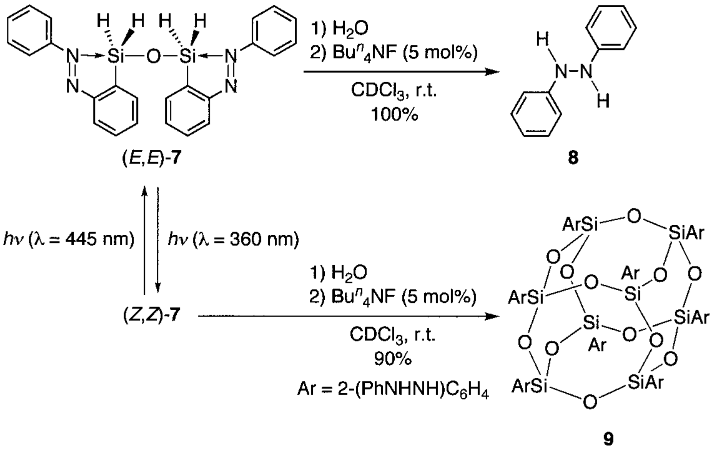


Figure 7. Change in the reactivity of a tetrahydrodisiloxane bearing the azo groups induced by photoirradiation.

4. Photoswitching of the Reactivity of the Allylsilane by Change of the Coordination Number of Silicon

As shown in the previous sections, it is well-known that the reactivity of organosilicon compounds significantly differs according to their silicon coordination numbers. Although we do not discuss their reaction mechanisms in detail here, the different reactivity in the compounds with different coordination numbers is explained by the following reasons. In contrast to the formal charge distribution, the bond between silicon and the substituent becomes a polarized, 3-center-4-electron bond in the penta- and hexa-coordination states. This leads to the increased electrophilicity of the substituents, and its substituents are more activated than the tetracoordination state. In general, the coordination number of silicon can be modified from tetracoordination to higher penta- or hexa-coordination states by addition of reagents into the system to prepare a reactive highly coordinated species. However, as described above, control of the coordination number can easily be achieved by photoirradiation of the azo group alone without addition of any specific chemical reagents. Next, we attempted to control the Hosomi-Sakurai Reaction,[8] a well-known reaction using silicon reagents, and investigated photocontrol of the reactivity of the allylsilane bearing azo groups.

Allyldifluorosilane with the azo groups, (*E*)-**10**, was synthesized, and its coordination state was investigated by using multi-nuclear NMR spectroscopy and X-ray crystallographic analysis. As expected, it was demonstrated that the silicon atom was pentacoordinated in (*E*)-**10** while (*Z*)-**10**, which was obtained by photoisomerization, showed tetracoordination state of the silicon atom.[9,10) Benzaldehyde was added as an electrophilic, but no reaction proceeded. Therefore, potassium fluoride was treated with (*E*)-**10** in the presence of 18-crown-6 in order to activate (*E*)-**10**, resulting in production of *N*-allylated silicate **11** (Figure 8). On the other hand, after (*E*)-**10** was photoisomerized to (*Z*)-**10**, followed by the reaction with KF in the presence of 18-crown-6 in the dark, no reaction proceeded at all. Interestingly, photoirradiation induced the reaction to proceed and produced the compound **11**, similar to the case of (*E*)-**10**. Since the pentacoordinated (*E*)-**10** and tetracoordinated (*Z*)-**10** could be mutually converted by photoirradiation; these results showed that photoirradiation could switch the reactivity of the allylsilane. The results from several control experiments revealed that formation of compound **11** from (*E*)-**10** was an intramolecular reaction, in which the allyl group was transferred from the silicon atom to the nitrogen atom at the γ-position. It was also clarified that not only the nitrogen coordination-induced increase in nucleophilicity of the allyl group but also increased electrophilicity of the silicon atom, enhanced polarization of the azo groups and a six-membered ring transition state all play important roles in the process of these reactions.

When the azo group is considered to be a substrate of the reaction, (*Z*)- and (*E*)-isomers can be thought to correspond to the protected and deprotected states, respectively, in the multi-step reactions including the allylation reaction described above. In other words, protection and deprotection of the reaction groups were done by photoirradiation using different wavelengths.

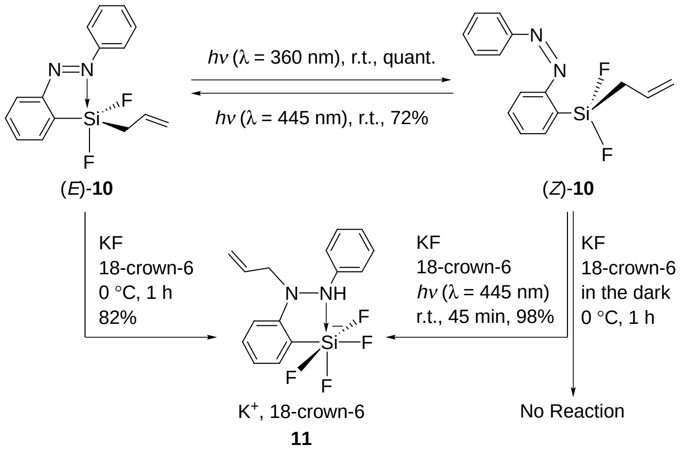


Figure 8. Photoswitching of reactivity of the allylsilane bearing the azo group.

5. Photoswitching of Lewis Acidity of the Boron Compounds Bearing the Azo Group

As a practical application of the main group elements, there are some methods that can modify the properties of the main group elements themselves, in addition to the increased nucleophilicity of the substituent as seen in cases of the silicon compounds. For example, organic boron compounds possess Lewis acidity and this property has been widely used in various organic synthesis reactions. As a fundamental study to control the reactivity of reactions with boron compounds as a Lewis acid catalyst, we investigated whether light regulated the coordination number of catecholborane bearing the azobenzene moiety as well as its Lewis acidity, and evaluated the change in Lewis acidity using complex formation with pyridine as its reaction index.

Boronic acid with the azobenzene sites was subjected to a dehydration condensation reaction, and the catecholborane (*E*)-**12** was prepared. Photoisomerization of (*E*)-**12** proceeded reversibly in benzene solution under photoirradiation, although its isomerization efficiency was not high (Figure 9).11) When an equimolar amount of pyridine was treated with catecholborane (*Z*)-**12**, the ^{11}B NMR results showed a marked upfield shift, and it was demonstrated that a complex was formed with pyridine as a Lewis base in this isomer. By contrast, there was no significant change in the chemical shift when the (*E*)-**12** isomer was treated with pyridine, suggesting that the intramolecular coordination of the (*E*)-**12** might disturb intermolecular coordination of pyridine, resulting in failure of complex formation of (*E*)-**12** with pyridine. Moreover, the photoisomerization reaction reversibly proceeded even after pyridine was added. That is, when (*Z*)-**12**•py was irradiated with light, the equilibrium between (*E*)-**12**•py and (*E*)-**12** was markedly shifted towards (*E*)-**12**. These results suggest that most pyridine molecules forming complexes with catecholborane may have been released from the boron atom and become free. When a complex formation constant was estimated from the chemical shift value measured by ^{11}B NMR after changing the molar equivalent of pyridine, it was found that the complex formation constant increased by approximately 300-fold after photoisomerization from (*E*)-**12** to (*Z*)-**12**. Thus, judging by the results from the complex formation reaction with pyridine molecules, the photocontrol of Lewis acidity in boron compounds was successfully performed.

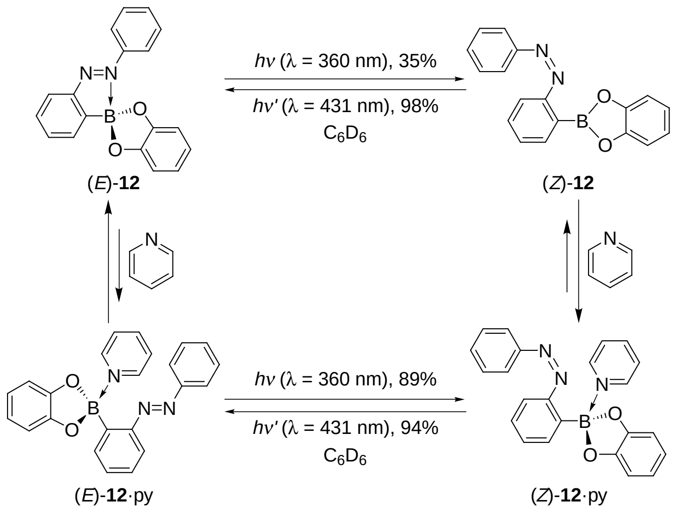


Figure 9. Photoswitching of Lewis acidity of the catecholborane bearing the azo group.

6. Control of the Equilibrium Between Phosphinoazobenzene and the Intramolecular Phosphonium Salt

In the silicon or boron compounds described above, the azo group in these compounds worked as a nucleophilic site. Then we considered whether it would be possible to control the coordination number of the main group elements when the azo group functions as an electrophilic site as well. Organic phosphorus compounds are one of the main group compounds that behave as a nucleophilic reagent or a Lewis base in a normal coordination state. For example, phosphine has been widely used as a ligand to transition metals. If we could show that we can control the coordination number of organic phosphorus compounds, it could be expected that we might be able to control the coordination ability of compounds with transition metals and their resultant catalytic activities.

2-Lithioazobenzene was treated with chlorodiphenylphosphine and the synthesis of the corresponding phosphines was attempted similarly to the reactions using silicon and boron. However, no corresponding phosphines were obtained. After a process of trial and error, we found that 2-iodoazobenzene (*E*)-**1** was converted to phosphine sulfide (*E*)-**14** via diphenylhydrazine (*E*)-**13**. Desulfurization of (*E*)-**14** with tributylphosphine resulted in the synthesis of 2-diphenylphosphinoazobenzene (*E*)-**15** (Figure 10).12) Compound (*E*)-**14** can also be obtained by the reaction of 2-lithioazobenzene with diphenylthiophosphinic chloride (**13**). Since the phosphino group generally behaves as a nucleophile but not an electrophile, it is expected that the azo group may behave as an electron acceptor. However, compound (*E*)-**15** displayed a phosphine structure in which there was no interaction between the nitrogen and phosphorus atoms of the azo groups in the crystal state. Compound (*E*)-**15** in toluene solution showed thermochromism and displayed a red color at 100 °C but became black at low temperature such as –78 °C, and such a behavior was quite different from that of a usual azobenzene. In addition, the ^{31}P NMR chemical shift of (*E*)-**15** showed a significant temperature-dependence. At temperatures above 60 °C, it showed one singlet at –9.2 ppm while it showed a broad signal between 20 and –60 °C and showed singlets at each of 30.1 ppm and –10.3 ppm below –60 °C. The signals in the high field belong to the phosphine structure, whereas the signals in the low field belong to the intramolecular phosphonium salt **16** based on the comparison of the observed chemical shifts to those estimated by GIAO calculation. It was suggested that intramolecular phosphonium salt **16** should be a product of intramolecular attack of the phosphine site onto the azo groups. The black color at low temperatures corresponds to the transition of the intramolecular charge transfer of the zwitter-ion **16**, while the red color at a high temperature is ascribed to the π–π* transition of the azo group.

Taking consideration of all these results, it was found that the phosphine (*E*)-**15** and the intramolecular phosphonium salt **16** form an equilibrium at room temperature. When the temperature was raised, the equilibrium was shifted towards (*E*)-**15**, while low - temperature leads to a shift towards **16**. It was demonstrated that we could successfully control the equilibrium between phosphine (*E*)-**15** and phosphonium salt **16** by changing the temperature. When the reaction solution at an equilibrium was reacted with selenium and BH_3•SMe_2, phosphine selenide (*E*)-**17a** and phosphine-borane (*E*)-**17b** were formed, respectively, showing that this phosphine had a general reactivity as the phosphine. It can easily react with water unlike usual phosphines. For example, in the similar derivative (*E*)-**15'**, which had a methyl group at the 4' position, the presence of a very slight amount of water facilitated the formation of phosphine oxide **18** with diphenylhydrazino groups. The intramolecular phosphonium salt derived from the 2-phosphinoazobenzene showed properties similar to those of an intermediate of the Mitsunobu Reaction.14) Their reactivity also supported the existence of the equilibrium between the phosphines and intramolecular phosphonium salt.

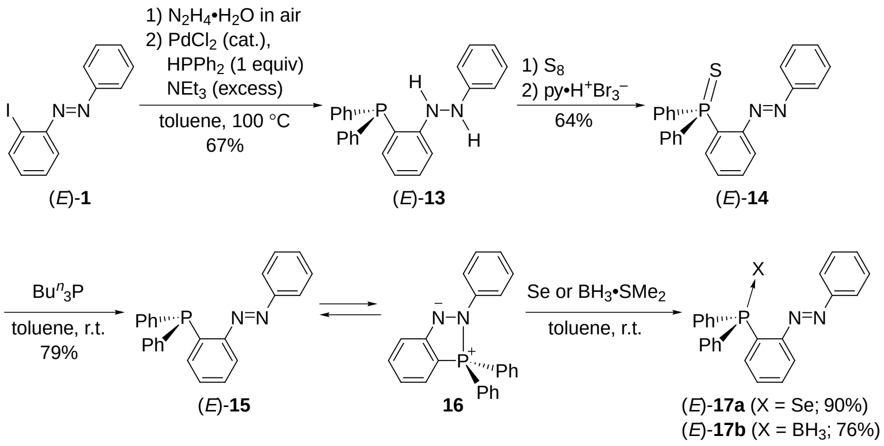


Figure 10. Synthesis of phosphine with the azo group and an equilibrium between the azo-substituted phosphine and its intramolecular phosphonium salt.

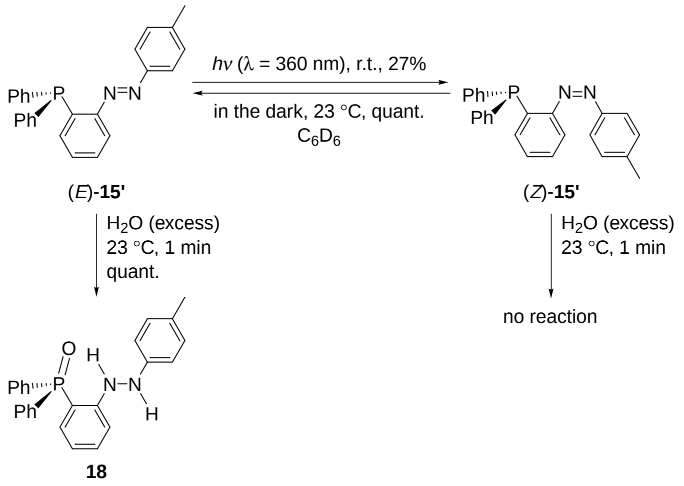


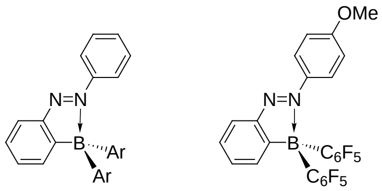
Figure 11. Photoswitching of the reactivity of the phosphine with the azo group.

Then, we wondered whether the coordination number of these phosphine compounds could be regulated by photoirradiation, and found that no isomerization occurred after photoirradiation onto the (*E*)-**15**. However, when (*E*)-**15'**, which had a methyl group, was photoirradiated, photoisomerization proceeded to yield (*Z*)-**15'**, (Figure 11).[13) We then monitored the reactions between (*E*)-**15'** or (*Z*)-**15'** and water. (*E*)-**15'** quickly reacted with water and completely disappeared a minute later while there was no change observed in the (*Z*)-**15'**. Finally, (*Z*)-**15'** also yielded **18** after a long time reaction because of its thermal isomerization. Thus, the reactivity of the phosphine which equilibrated with the intramolecular phosphonium salt toward water could be controlled by photoirradiation within a limited time.

7. Development of Fluorescent Azobenzene with the Boron Substituent

As discussed in the previous sections, the azobenzenes with main group substituents at the 2-position display various colors such as yellow, orange, red and black. Practically, the azobenzenes further display a variety of different colors by modifying the substituents, and this property of azobenzene has been used as a fundamental structure of azo dyes. The azo dyes account for almost half of the worldwide industrial dyes production, and occupy an important position in the dyeing industry. Some pigments, which are termed fluorescent dyes, not only absorb a specific spectrum of light but also emit the light as fluorescence. However, azobenzenes generally do not emit any significant fluorescence at room temperature by photoirradiation because photoisomerization usually proceeds in azobenzenes. It has been reported that some palladium complexes15) with the azobenzene as a ligand and some aggregates16) bearing an azobenzene as a component can exceptionally emit weak fluorescence. In such palladium complexes with azobenzene as a ligand, however, fluorescence quantum yields were only 10^{-5} to 10^{-3}.

We have been synthesizing azobenzene compounds that can undergo photoisomerization without disturbing the interaction between the nitrogen atom of the azo group and the main group elements. In the case of the azobenzene with the boron substituent at the 2-position, the isomerization yield was very low compared to the case of the silicon. It was required to find a boron-substituted azobenzene that could more effectively isomerize under photoirradiation. In the continuation of this search, we have investigated various substituents on the aromatic rings of the azobenzenes or on the boron atom, and examined the relationship between the types of substituents and their optical properties. As a result, it was found that an equilibrium between tri- and tetra-coordination states tended to shift towards the tetracoordination state and this led to increased red-shift in the absorption spectrum when the compound had an electron donor at the 4'-position of the azobenzene group or an electron-withdrawing groups on the boron atom. Moreover, it was also shown that the stronger their dative bond became the lower their isomerization rate became, and that there were some compounds that failed to proceed to isomerization. These results suggest that the boron-substituted azobenzene compounds are not suitable for the control of coordination number, which had been our first goal. Further detailed analyses, however, showed that among various boron-substituted azobenzenes that could not photoisomerize, bis(pentafluorophenyl)boryl-substituted azobenzene (*E*)-**19** emitted green fluorescence in solution under room light (Figure 12).17) It was found that the fluorescence quantum yield was 0.23 in hexane solution at room temperature, which was relatively high for an azobenzene. However the compound (*E*)-**20**, in which pentafluorophenyl groups were replaced with *p*-fluorophenyl groups, did not emit any fluorescence at all. These results indicated that there might be a relationship between the strength of the N–B covalent bond and fluorescence intensity. Therefore, we next investigated various substituent groups on the aromatic rings, and found that the compound (*E*)-**21** that had a methoxy group at 4'-position of the azobenzene had an even stronger fluorescence intensity and its fluorescence quantum yield was 0.76 in hexane solution at room temperature. This value is the highest fluorescence quantum yield that has ever been reported among the azobenzene derivatives. It showed that (*E*)-**21** emitted fluorescence 30,000-fold more effectively than unsubstituted azobenzene.



(*E*)-**19** (Ar = C_6F_5)
(*E*)-**20** (Ar = *p*-FC_6H_4)

(*E*)-**21**

Figure 12. The boron-substituted, fluorescent azobenzenes.

Therefore, we next attempted to determine the reasons for emission of fluorescence in the boron-substituted azobenzene compounds both theoretically and experimentally. It was speculated that the N–B dative bond may not only suppress structural changes in the azobenzenes but also relatively raise the energy level of the π orbital by lowering the energy level of the n-orbital. This inverted order of the energy levels will make the π–π^* transition as a transition from the ground state to the lowest excited singlet state. As a result, a transition from the lowest excited singlet state to the ground state will be allowed, and this further results in an efficient yield of the absorbed photoexcitation energy as fluorescence.

We had not envisaged that introduction of the boron substituents to the azobenzenes would induce fluorescence emission at the beginning of this study. However, we have demonstrated here that the boron-substituted azobenzenes emit significantly more intense fluorescence than the reported palladium complexes. The unique properties of main group elements have provided azobenzenes with more intense fluorescence, without using expensive palladium.

8. Summary

We introduced a model system, which can switch the physical properties and structures of the main group compounds by using photoirradiation-induced isomerization of the azobenzenes as a key reaction. This method is considered to be applicable to other main group elements as well, and it is highly expected to dynamically control specific physical properties of elements other than those described here. If we can further develop new methods that can practically control the coordination number of the main group compounds based on the concepts discussed here, we believe that application of this method will open a new way to the control of organic reactions using the activation/deactivation methods corresponding to the coordination states of the main group elements. It is recently reported that a new effective synthetic method has been developed using masking and unmasking on the boron element,18) and it would be desirable if the method introduced here can be applied for such a purpose. The results in the current study are fundamental and experimental, and do not directly lead to actual use and application in a practical level. We think, however, our concept here is different from conventional ones. Therefore, we will be pleased if this unique concept may be used for control of organic reactions or chemical processes such as protection and deprotection. It is noteworthy that we found an unexpected, surprising product, fluorescent azobenzenes, during the research of the main group compounds. We are sure that there must exist a big goldmine hidden in the world of the main group compounds, waiting for us to find and exploit.

Finally, we are deeply grateful to all the students who contributed and dedicated themselves to this work.

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Introduction of authors

Naokazu Kano

Associate Professor, Graduate School of Science, The University of Tokyo.

[Brief career history] 1993, B.S. from Department of Chemistry, School of Science, The University of Tokyo. 1998, Ph.D. from Graduate School of Science, The University of Tokyo (Mentor: Renji Okazaki, Ph.D.). 1998~2006, Research Associate of Department of Electro-Communications, The University of Electro-Communication, and Graduate School of Science, The University of Tokyo. 2006~2007, Postdoctoral Fellow of Massachusetts Institute of Technology (Boston, MA), since 2007, Present post. 2004, Research Planning Association Award, The Society of Synthetic Organic Chemistry, Japan. 2005, The Society of Silicon Chemistry Award for Young Chemists.
[Specialty] Main Group Chemistry

Takayuki Kawashima

Professor, Graduate School of Science, The University of Tokyo.

[Brief career history] 1969, B.S. from Department of Chemistry, School of Science, The University of Tokyo. 1974, Ph.D. from Graduate School of Science, The University of Tokyo (Mentor: Professor Naoki Inamoto). 1974~1976, Research Associate of Graduate School of Science, The University of Tokyo. 1976, Postdoctoral Fellow of Iowa State University. 1977, Postdoctoral Fellow of University of Utah. 1990, Lecturer of Department of Chemistry, School of Science,The University of Tokyo. 1992, Associate Professor. since 1998, Present post.
[Specialty] Organic Reaction Chemistry.