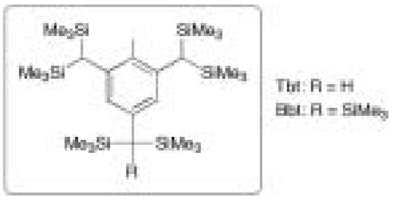
VII-G Synthesis of Compounds Having a Novel Bonding Containing Heavier Main Group Elements

Double-bond compounds of main group elements of the second row such as olefins, carbonyl compounds, aromatic compounds, and azo compounds play very important roles in organic chemistry. However, the chemistry of their heavier element homologues has been undeveloped most probably due to their high reactivity and instability under ambient conditions. Since the first isolation of stable diphosphene (P=P), silene (Si=C), and disilene (Si=Si) in 1981 by taking advantage of steric protection, various double-bond compounds containing heavier main group elements have been synthesized and characterized.

On the other hand, we have developed an extremely bulky aromatic substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (denoted as Bbt hereafter). These substituents were found to be very effective steric protection groups for a variety of reactive species containing a heavier main group element. We have synthesized a variety of unprecedented low-coordinate compounds of heavier main group elements as stable compounds by taking advantage of kinetic stabilization using a new type of steric protection groups, Tbt and Bbt, and elucidated their properties.



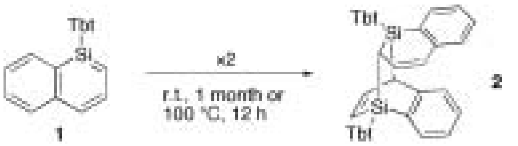
VII-G-1 Synthesis and Properties of the First Stable 1-Silanaphthalene

TAKEDA, Nobuhiro[1]**; SHINOHARA, Akihiro**[1]**; TOKITOH, Norihiro**[2]
([1]Kyoto Univ.; [2]IMS and Kyoto Univ.)

[*Organometallics* **21**, 4024–4026 (2002)]

Since aromatic compounds play very important roles in organic chemistry, much attention has been also paid to the chemistry of silaaromatic compounds. However, there are few reports on the synthesis and isolation of silaaromatic compounds stable at room temperature because of their high reactivity. Very recently, we have successfully synthesized the first stable silabenzene, 2-silanaphthalene, and 9-silaanthracene by taking advantage of an extremely bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). On the other hand, there is no report for the synthesis of 1-silanaphthalene, which is a structural isomer of 2-silanaphthalene, although much attention has been focused on the similarities and differences between 1- and 2-silanaphthalenes.

The first 1-silanaphthalene **1** was successfully synthesized as moisture-sensitive, pale yellow crystals by taking advantage of Tbt group. The structure of **1** was determined based on its ^{1}H, ^{13}C, and ^{29}Si NMR, Raman, and UV/vis spectra together with theoretical calculations. These data clearly indicated that **1** has aromaticity comparable with naphthalene as well as Tbt-substituted 2-silanaphthalene. In contrast to the thermal stability of 2-Tbt-2-silanaphthalene, 1-Tbt-1-silanaphthalene (**1**) readily dimerizes in solution even at room temperature to give the corresponding [2+4] dimmer **2**.



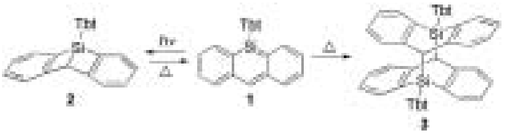
VII-G-2 Photochemical and Thermal Reactions of a Kinetically Stabilized 9-Silaanthracene: The First Spectroscopic Observation of a 9,10-Dewar-9-Silaanthracene Isomer

SHINOHARA, Akihiro[1]**; TAKEDA, Nobuhiro**[1]**; TOKITOH, Norihiro**[2]
([1]Kyoto Univ.; [2]IMS and Kyoto Univ.)

[*J. Am. Chem. Soc.* **125**, 10804–10805 (2003)]

In recent decades, much attention has been paid to the chemistry of silaaromatic compounds. Recently we have succeeded in the synthesis of novel silaaromatic species such as silabenzene, 1-silanaphthalene, 2-silanaphthalene, and 9-silaanthracene by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group. In this paper we present the photochemical and thermal reaction of the stable 9-silaanthracene **1**.

Irradiation of **1** with the light of λ = 300–500 nm afforded the corresponding 9,10-Dewar-9-silaanthracene **2**, the formation of which was experimentally demonstrated by the ^{1}H, ^{13}C, and ^{29}Si NMR spectra. It should be noted that **2** is the first example of spectroscopically identified 9,10-Dewar-9-silaanthracene. Dewar isomer **2** was found to be a marginally stable species in solution and to undergo gradual thermal tautomerization into **1** even at –80 °C in hexane. On the other hand, thermal reactions of 9-silaanthracene **1** afforded the head-to-tail [4+4] dimer **3** either in solution or in the solid state. The dimer **3** was thermally very stable and its molecular structure was definitively determined by X-ray crystallographic analysis. The isolation and characterization of **3** are of particular note as the first unambiguous experimental evidence for the [4+4] dimer of 9-silaanthracene derivatives.



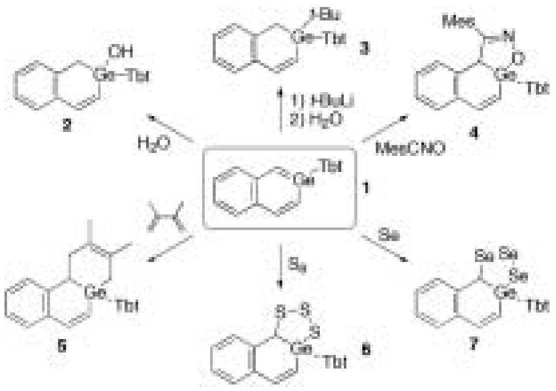
VII-G-3 Synthesis and Properties of the First Stable Neutral Germaaromatic Compound, 2-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-2-Germanaphthalene

NAKATA, Norio[1]**; TAKEDA, Nobuhiro**[1]**;**
TOKITOH, Norihiro[2]
([1]Kyoto Univ.; [2]IMS and Kyoto Univ.)

[*Organometallics* **22**, 481–489 (2003)]

While there have been relatively many informations on silaaromatic compounds, the studies on germaaromatic compounds are very few. In this paper, we present the synthesis and properties of the first stable 2-germanaphthalene.

The first stable neutral germaaromatic compound, 2-germanaphthalene **1** was synthesized by taking advantage of an extremely bulky and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). The molecular structure and aromaticity of **1** were discussed on the basis of its NMR, UV-vis and Raman spectra, X-ray crystallographic analysis, and theoretical calculations, which indicate the delocalization of π-electrons in the 2-germanaphthalene ring of **1**. 2-Germanaphthalene **1** reacted with water, *t*-BuLi, mesitonitrile oxide, 2,3-dimethyl-1,3-butadiene, elemental sulfur, and elemental selenium to give the corresponding adducts **2**–**7** across the Ge–C double bond.



VII-G-4 η^6-Germabenzene Complexes of Chromium and Molybdenum

NAKATA, Norio[1]**; TAKEDA, Nobuhiro**[1]**;**
TOKITOH, Norihiro[2]
([1]Kyoto Univ.; [2]IMS and Kyoto Univ.)

[*Angew. Chem., Int. Ed.* **42**, 115–117 (2003)]

Germabenzenes are the most fundamental germaaromatic compounds having a simple 6π-electron ring system. However, very little has been known about the synthesis and characterization of germaaromatic compounds due to their extremely high reactivity. Very recently, we have succeeded in the synthesis and properties of the first stable germabenzene **1** bearing an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). Meanwhile, in recent decades there has been considerable interest in the transition metal complexes containing sila- and germaaromatic compounds as ligands from the viewpoints of their coordination fashion and unique structure. However, the molecular structure and reactivity of η^6-sila- and germabenzene complexes have never been known.

The first η^6-germabenzene complexes, [M(η^6-C_5H_5GeTbt)$(CO)_3$] [M = Cr (**2**), Mo (**3**)], were synthesized by the ligand exchange reaction of the corresponding acetonitrile complexes, [M$(CH_3CN)_3(CO)_3$] (M = Cr, Mo) with **1**. These reactions are interesting also as the first examples showing the aromatic character of the germabenzene **1** from the standpoint of its reactivity. The low-temperature X-ray crystallographic analysis of Cr complex **2** revealed that the germabenzene ring was almost planar and η^6-coordinated to the $Cr(CO)_3$ group.

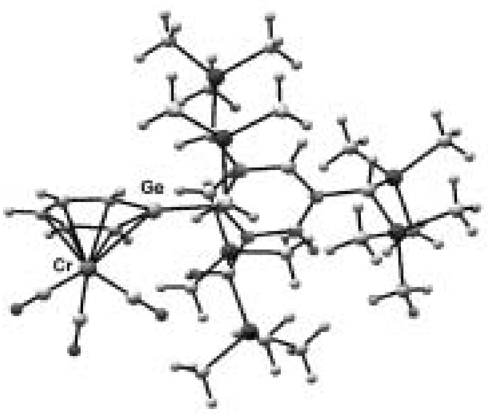


Figure 1. Molecular Structure of Germabenzene Complex of Chromium **1**.

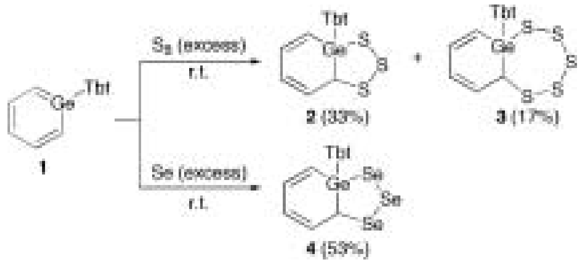
VII-G-5 Reaction of Stable Germabenzene with Chalcogens: Synthesis and Structure of a Novel Germanium Analog of Pentathiepane, 1,2,3,4,5,6-Pentathiagermepane

NAKATA, Norio[1]**; TAKEDA, Nobuhiro**[1]**;**
TOKITOH, Norihiro[2]
([1]Kyoto Univ.; [2]IMS and Kyoto Univ.)

[*J. Organomet. Chem.* **672**, 66–71 (2003)]

Much attention has been paid to the chemistry of cyclic polychalcogenides from the standpoints of chemical and physical properties as well as from that of biological activities. In contrast to the widely explored chemistry of transition metal polychalcogenido complexes, very little has been known for cyclic polychalcogenides containing a heavier group 14 element. We examined the synthesis of cyclic polychalcogenides containing germanium by the reactions of a stable germabenzene **1** bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group with elemental sulfur and selenium.

Treatment of a germabenzene **1** with elemental sulfur gave a 1,2,3,4-trithiagermolane **2** together with a novel 1,2,3,4,5,6-pentathiagermepane **3**, which is the germanium analog of pentathiepane. On the other hand, the reaction of **1** with elemental selenium gave only 1,2,3,4-triselenagermolane **4**. All the newly obtained polychalcogenides containing a germanium atom were characterized by NMR spectroscopy and elemental analysis. The molecular structures of **2** and **3** were determined by X-ray crystallographic analysis. In addition, the thermal interconversion between pentasulfide **3** and trisulfide **2** plus 1/4 S_8 was confirmed.



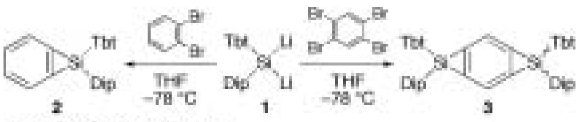
VII-G-6 Syntheses and Structures of Silicon Analogues of Cyclopropabenzenes

TAJIMA, Tomoyuki[1]**; HATANO, Ken**[2]**; SASAKI, Takayo**[1]**; SASAMORI, Takahiro**[1]**; TAKEDA, Nobuhiro**[1]**; TOKITOH, Norihiro**[3]**; TAKAGI, Nozomi; NAGASE, Shigeru**
([1]Kyoto Univ.; [2]Kyushu Univ.; [3]IMS and Kyoto Univ.)

[*Chem. Lett.* **32**, 220–221 (2003); *J. Organomet. Chem.* **686**, 118–126 (2003)]

Since the finding of significant deformation for the fused aromatic rings in the series of benzocycloalkanes, it has been one of the important subjects assigned to organic chemists to solve a riddle for such deformation. Cyclopropabenzene has attracted special attention because of the most severely enforced deformation in this series. However, there is no example for the synthesis of its heteroatom analogs, heteracyclopropabenzenes, as stable compounds until our project started. In this paper, we present the synthesis of the first stable silacyclopropazenzene and bis(silacyclopropa)benzenes, which are the first stable heteracyclopropabenzenes, by taking advantage of 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl (Tbt) group.

The reactions of an very crowded diaryldilithiosilane **1** with *o*-dibromobenzene and 1,2,4,5-tetrabromobenzene resulted in the formation of the first stable silacyclopropabenzene **2** and bis(silacyclopropa)-benzenes **3**, respectively. The crystallographic analyses and theoretical calculations revealed that the deformation in benzene rings of **2** ans **3** is less than that of cyclopropabenzenes, which show severe deformation of the benzene rings caused by the fused cyclopropane rings. The successful isolation of **2** is noteworthy because no carbon analogues, bis(cyclopropa)benzenes, have been synthesized yet.



Dip = 2,6-diisopropylphenyl

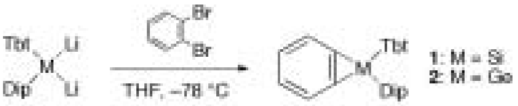
VII-G-7 Synthesis and Isolation of the First Germacyclopropabenzene: A Study to Elucidate the Intrinsic Factor for the Ring Deformation of Cyclopropabenzene Skeletons

TOKITOH, Norihiro[1]**; HATANO, Ken**[2]**; SASAKI, Takayo**[3]**; SASAMORI, Takahiro**[3]**; TAKEDA, Nobuhiro**[3]**; TAKAGI, Nozomi; NAGASE, Shigeru**
([1]IMS and Kyoto Uniiv.; [2]Kyushu Univ.; [3]Kyoto Univ.)

[*Organometallics* **21**, 4309–4311 (2002)]

Cyclopropabenzenes have attracted much attention because it is expected that the fused cyclopropane rings result in the severe deformation of the benzene rings. Recently, we have synthesized silacyclopropabenzene **1** as the first example of a stable heteracyclopropabenzene by the reaction of a sterically hindered dilithiosilane, Tbt(Dip)$SiLi_2$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl, Dip = 2,6-diisopropylphenyl), with 1,2-dibromobenzene. This successful synthesis of **1** naturally prompted us to examine the synthesis of germacyclopropabenzenes.

The treatment of an overcrowded diaryldilithiogermane, Tbt(Dip)$GeLi_2$, generated by exhaustive reduction of Tbt(Dip)$GeBr_2$, with 1,2-dibromobenzene resulted in the formation of the first stable germacyclopropabenzene **2**, which was fully characterized by ^1H and ^{13}C NMR spectra, FAB-MS, and X-ray structural analysis. As well as the case of silacyclopropabenzene **1**, the structural parameters of **2** indicated that the germacyclopropane ring can enjoy annelation with much less perturbation, in contrast to the severe distortion in cyclopropabenzene rings.



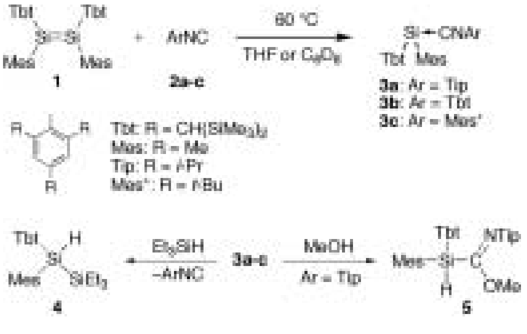
VII-G-8 Synthesis and Properties of the First Stable Silylene-Isocyanide Complexes

TAKEDA, Nobuhiro[1]**; KAJIWARA, Takashi**[1]**; SUZUKI, Hiroyuki**[2]**; OKAZAKI, Renji**[2]**; TOKITOH, Norihiro**[3]
([1]Kyoto Univ.; [2]Univ. Tokyo; [3]IMS and Kyoto Univ.)

[*Chem. Eur. J.* **9**, 3530–3543 (2003)]

Recently, various types of compounds containing a stable double bond to silicon have been synthesized by taking advantage of steric protection due to bulky substituents. On the other hand, the chemistry of compounds containing silicon as part of a cumulated double-bond system has been less explored. As for heavier analogues of ketenimines (>C=C=N–), it has been reported that a stannaketenimine (>SnCN–) is rather stannylene-isocyanide complex (>Sn←CN–) than cumulative compound (>Sn=C=N–), while 1-phospha-3-silaallene (>SiCP–) and 1-phospha-3-germaallene (>GeCP–) represent allenic character (>M=C=P–). However, there is no report for stable silicon analogues (>SiCN–) and their properties have not been revealed, although their properties have attracted much interest.

We successfully synthesized Tbt(Mes)SiCNAr (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = mesityl) (**3a-c**), by the reactions of a kinetically stabilized disilene **1**, with bulky isocyanides **2a-c**. The spectroscopic data of **3a-c** and theoretical calculations indicated that the **3a-c** are not classical cumulative compounds but the first stable silylene-Lewis base complexes. The reaction with triethylsilane giving silylene adduct **4** indicated the dissociation of the complexes **3a-c** to the corresponding silylene [Tbt(Mes)Si:] and isocyanides **2a-c** at room temperature. In additrion, **3a** reacted with methanol to give methanol adduct **5** *via* electrophilic attack on the silicon atom, which is most likely resulted from the contribution of the zwitterionic resonance structures [Tbt(Mes)Si$^-$–C$^+$=N–Ar] and [Tbt(Mes)Si$^-$–C≡N$^+$–Ar].



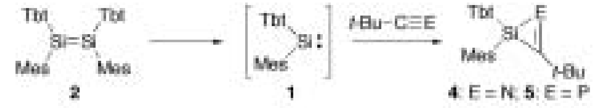
VII-G-9 Stable 2*H*-Azasilirene and 2*H*-Phosphasilirene: Addition Reaction of an Overcrowded Silylene to a Nitrile and a Phosphaalkyne

TOKITOH, Norihiro[1]; SUZUKI, Hiroyuki[2]; TAKEDA, Nobuhiro[3]; KAJIWARA, Takashi[3]; SASAMORI, Takahiro[3]; OKAZAKI, Renji[2];
([1]IMS and Kyoto Univ.; [2]Univ. Tokyo; [3]Kyoto Univ.)

[*Silicon Chem.* in press]

In recent decades, there has been much interest in the chemistry of divalent silicon species, silylenes, from the viewpoint of not only fundamental chemistry but also applied chemistry such as material science and organic syntheses. Much attention has been paid to their reactivities such as addition to olefins, alkynes, isocyanides, and so on in comparison with the reactivities of carbenes. On the other hand, we have succeeded in the formation of very crowded silylene **1** bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group by thermolysis of the corresponding disilene **2** at 60 °C or that of silylene–isocyanide complex **3** at room temperature.

In this paper, we present the reaction of an overcrowded silylene **1** with pivalonitrile and *t*-butylphosphaalkyne to give the corresponding [1+2]cycloadducts, 2*H*-azasilirene and 2*H*-phosphasilirene derivatives, **4** and **5**, respectively. This is the first example of the isolation of a stable 2*H*-azasilirene derivative, and the X-ray crystallographic analysis of **4** unambiguously revealed its three-membered ring structure in the solid state. In addition, DFT calculations supported three-membered ring character in the structures of the 2*H*-azasilirene **4** and 2*H*-phosphasilirene **5**.



VII-G-10 Synthesis and Reactions of New Diphosphenes Bearing Extremely Bulky Substituents

SASAMORI, Takahiro[1]; TAKEDA, Nobuhiro[1]; TOKITOH, Norihiro[2]
([1]Kyoto Univ.; [2]IMS and Kyoto Univ.)

[*J. Phys. Org. Chem.* **16**, 450–462 (2003)]

Multiple-bond compounds between heavier group 15 elements have fascinated chemists for a long time. Since the first isolation of the diphosphene Mes*P=PMes* (Mes* = 2,4,6-tri-*t*-butylphenyl), intensive studies have been performed using several steric protection groups on the chemistry of a variety of diphosphenes.

In this paper, we present the synthesis of new diphosphenes, Tbt–P=P–Tbt (**1**) and Bbt–P=P–Bbt (**2**), having extremely bulky substituents, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl groups (Bbt), which are effective to the stabilization of distibenes (Ar–Sb=Sb–Ar) and dibismuthenes (Ar–Bi=Bi–Ar). The X-ray crystallographic analysis revealed their unique structures in the solid state. Furthermore, the conformations of these extremely overcrowded diphosphenes, **1** and **2**, are twisted in different ways in spite of the close structural similarity between Tbt and Bbt groups. DFT calculations were performed to estimate the energy difference between the two conformations of diphosphenes. In addition, their structures and physical properties were compared with those of their heavier congeners, distibenes (Ar–Sb=Sb–Ar, Ar = Tbt and Bbt) and dibismuthenes (Ar–Bi=Bi–Ar, Ar = Tbt and Bbt) having the same substituents. Although the reactivities of the extremely hindered diphosphenes might be considerably suppressed owing to the severe steric congestion, it was found that they can react with elemental sulfur and selenium to give the corresponding thia- and selenadiphosphirane derivatives, respectively.

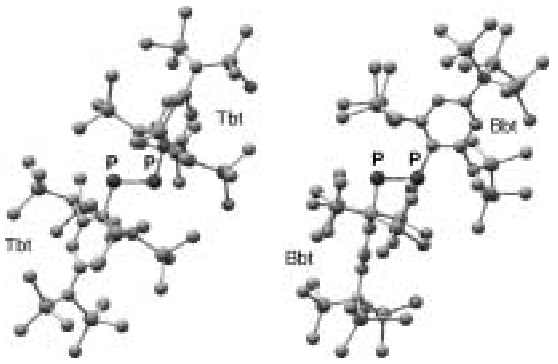


Figure 1. Molecular Structures of **1** (left) and **2** (right).

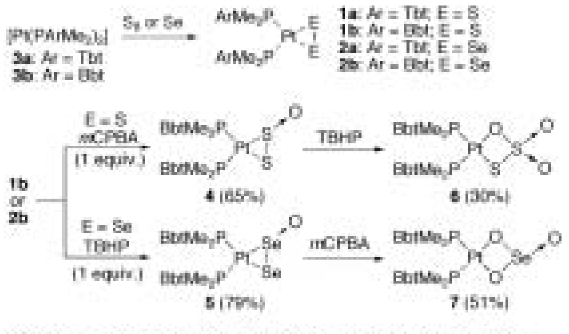
VII-G-11 Synthesis, Structure, and Properties of the First Disulfur and Diselenium Complexes of Platinum

NAGATA, Kazuto[1]**; TAKEDA, Nobuhiro**[1]**;**
TOKITOH, Norihiro[2]
([1]Kyoto Univ.; [2]IMS and Kyoto Univ.)

[*Chem. Lett.* **32**, 170–171 (2003), *Bull. Chem. Soc. Jpn.* **76**, 1577–1587 (2003)]

Much attention has been focused on the chemistry of transition metal complexes having O_2, S_2, and Se_2 ligands from the viewpoints of not only fundamental chemistry but also catalysis and biochemistry. However, the disulfur and diselenium complexes of platinum remain unknown probably due to the strong propensity of sulfur and selenium ligands for bridging metal atoms.

We succeeded in the synthesis of the first disulfur and diselenium complexes of platinum, **1** and **2**, by taking advantage of bulky phosphine ligands bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) or 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)-methyl]phenyl (Bbt) group, which sterically protect the mononuclear complexes from the oligomerization. Complexes **1** and **2** were synthesized by the reaction of zerovalent platinum complexes **3** with elemental sulfur and selenium, respectively. Crystallographic analysis of **1b** and **2b** showed that their central Pt atoms have tetracoordinated, planar geometries, and their PtE_2 (E = S, Se) parts have three-membered-ring structures. The oxidation of **1b** and **2b** with an equimolar amount of *m*-chloroperbenzoic acid or *t*-butyl hydroperoxide in dichloromethane afforded the corresponding disulfur and diselenium monoxide complexes, **4** and **5**, respectively. An interesting difference in reactivity between **4** and **5** was shown in the further reactions with an excess of oxidants, which produced the corresponding *O,S*-coordinated thiosulfate complex **6** and the *O,O*-coordinated selenite complex **7**, respectively. The dynamic behavior in solution was revealed by the variable-temperature NMR spectroscopy for **1b**, **2b**, **6**, and **7**, which indicates the existence of the intramolecular CH···E (E = O, S, Se) interactions between the methine hydrogens of the *o*-bis(trimethylsilyl)-methyl groups and the Pt-bonded heteroatoms.



*m*CPBA = *m*-chloroperbenzoic acid; TBHP = *tert*-butyl hydroperoxide