

Syntheses and Structures of Platinum Siloxides Bridged by a Sulfur or Selenium Atom and a Unique 1,3-Aryl Migration from Silicon to Platinum through the Si–O–Pt Linkages

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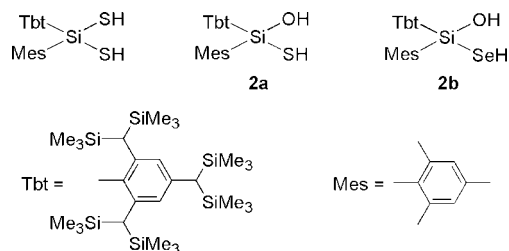
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Summary: Platinum siloxides bridged by a sulfur or selenium atom, [Tbt(Mes)Si(μ -O)(μ -E)Pt(PPh₃)₂] (**1a**: E = S, **1b**: E = Se), were synthesized by utilizing hydroxysilanechalcogenols, Tbt(Mes)Si(OH)(EH) (**2a**: E = S, **2b**: E = Se), which were kinetically stabilized by an effective combination of steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and mesityl (Mes), as key building blocks. Platinum siloxide **1** underwent a unique 1,3-migration of the Mes group from the silicon atom to the platinum center on treatment with chloride ion in the presence of a Brønsted acid, affording the corresponding chloro(hydroxysilane)chalcogenoloplatinums, [TbtSi(OH)(Cl)(μ -E)Pt(Mes)(PPh₃)₂] (**3a**: E = S, **3b**: E = Se), in moderate yields.

The chemistry of late transition metal alkoxides has been extensively studied by organic and inorganic chemists, and their wide application to various organometallic reactions has been reported.¹ In particular, 1,3-migration reaction of a carbon substituent in late transition metal alkoxides through their C–O–M linkages is involved as an important step in various catalytic processes.^{2,3} Hartwig and his co-workers have reported the stoichiometric 1,3-aryl migration reaction of an isolated Rh(I) alkoxide, that is, the intramolecular transmetalation from carbon to rhodium through the C–O–Rh linkage.^{4a} They have also reported similar intramolecular transmetalation of a Rh(I) boronate with 1,3-aryl migration from boron to rhodium through the B–O–Rh linkage.^{4b} Both of these systems afforded the corresponding C=O or B=O double-bond products or their oligomerization products. By contrast, there have been very few

Chart 1. Overcrowded Silanedichalcogenols



reports on similar 1,3-migration reactions of metal siloxides, i.e., silicon analogues of metal alkoxides, though several catalytic processes are known to involve a 1,3-migration reaction of a metal siloxide as a transmetalation step in their plausible mechanisms, such as palladium(0)-catalyzed cross-coupling reactions of organosilanols with aryl halides.^{5,6} On the other hand, recently, we have succeeded in the synthesis and the first structural characterization of overcrowded silanedichalcogenols, such as silanedithiol [Tbt(Mes)Si(SH)₂], hydroxysilanethiol [**2a**: Tbt(Mes)Si(OH)(SH)], and hydroxysilaneselenol [**2b**: Tbt(Mes)Si(OH)(SeH)], bearing an effective combination of steric protection groups on the silicon atom, i.e., 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt^{7,8}) and mesityl (Mes) (Chart 1).⁹ Furthermore, we have reported the application of the silanedithiol in the synthesis of novel silanedithiolato complexes of palladium and platinum.^{9b} This finding prompted us to investigate the utility of **2a** and **2b** in the synthesis of metal

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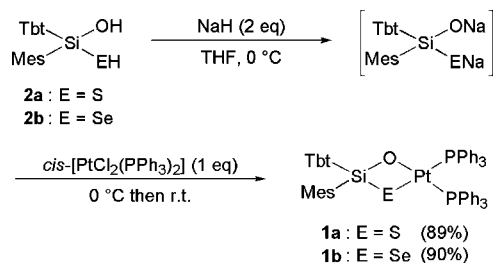
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Scheme 1. Synthesis of Platinum Siloxides Bridged by a Sulfur (1a) or Selenium (1b) Atom


siloxides bridged by a sulfur or selenium atom with a view to elucidate their reactivities as metal siloxides. We describe here the syntheses and structural characterization of the novel platinacycles [Tbt(Mes)Si(μ -O)(μ -E)Pt(PPh₃)₂] (**1a**: E = S, **1b**: E = Se), in which we utilized stable hydroxysilanechalcogenols, Tbt(Mes)Si(OH)(EH) (**2a**: E = S, **2b**: E = Se),^{9b} as key reagents. In addition, we have found a unique 1,3-migration reaction of the Mes group from the silicon to the platinum atoms in the reactions of **1** with chloride ion in the presence of a Brønsted acid.

The reactions of **2a** or **2b** with 2 molar equiv of sodium hydride followed by the addition of a THF solution of *cis*-[PtCl₂(PPh₃)₂] afforded the corresponding platinum siloxides bridged by a sulfur or selenium atom, **1a** (89%) or **1b** (90%), respectively, as air- and moisture-stable pale yellow crystals (Scheme 1). When the reactions were performed by utilizing *n*-BuLi instead of sodium hydride, the same products were obtained in similar yields.

The structures of platinacycles **1a** and **1b** were determined by NMR spectroscopic data, elemental analyses, and X-ray crystallographic analyses (Figure 1). The core four-membered rings of **1a** and **1b** were found to have a puckered geometry, and their central platinum atoms deviated slightly from tetragonal planar geometry, which is typical for neutral, four-coordinated Pt(II) complexes¹⁰ [sum of the interior bond angles of the central four-membered rings: for **1a**, 356.20°; for **1b**, 355.98°; sum of the bond angles around the platinum atoms: for **1a**, 351.68°; for **1b**, 361.01°; dihedral angles between the E(1)–Pt(1)–O(1) and P(1)–Pt(1)–P(2) planes: for **1a** (E = S), 9.99(11)°; for **1b** (E = Se), 10.97(12)°]. The lengths of the Pt–P bonds [**1a**: 2.2327(9) Å; **1b**: 2.2324(12) Å] situated opposite the Pt–O bonds are slightly shorter than those situated opposite the Pt–S [for **1a**: 2.2758(10) Å] or Pt–Se [for **1b**: 2.2835(12) Å] bonds, resulting from the *trans* influence of chalcogen atoms. Therefore, their ³¹P{¹H} NMR spectrum showed the two signals with apparently different ¹J_{Pt} values [**1a**: 6.9 (¹J_{Pt} = 3532 Hz), 25.1 (¹J_{Pt} = 3209 Hz) ppm; **1b**: 6.2 (¹J_{Pt} = 3537 Hz), 24.7 (¹J_{Pt} = 3206 Hz)]. In both cases, the signals at higher field have larger ¹J_{Pt} coupling constants than those at lower field, and the former are assigned to the phosphorus atoms situated in *trans* position to the oxygen atom and the latter to those in *trans* position to the sulfur or selenium atom. In this system, the *trans* influence of the sulfur and selenium atoms on the silicon atom was similar, but larger than that of the oxygen atom. This tendency is essentially consistent with that reported for some related platinum chalcogenides.¹¹

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When **1a** or **1b** was treated with 1 molar equiv of acetic acid, the protonation of their oxo units was confirmed by NMR spectroscopy, but the resulting oxonium salts remained unchanged. Tatsumi et al. have recently reported a similar reactivity of germanium analogues, where they have isolated the corresponding oxonium salts.¹² The addition of LiCl to the THF solutions of the reaction mixtures of **1a** or **1b** with acetic acid resulted in the formation of the corresponding chloro(hydroxy)silanechalcogenoltoplatinum complexes **3a,b**, in which the mesityl group had migrated from the silicon to the platinum metal center. The resulting products were formed in moderate yield (Scheme 2). Similarly, the reaction of **1b** with 1 molar equiv of anhydrous HCl (Et₂O solution) followed by the addition of an excess of water produced directly the corresponding dihydroxysilaneselenoltoplatinum complex **4b**, the formation of which is most likely rationalized in terms of the hydrolysis of the initially generated **3b**.¹³ The structures of **3a,b** and **4b** were confirmed by NMR and mass spectroscopy together with elemental analysis, and that of **4b** was determined by X-ray crystallographic analysis (Figure 2).¹⁴

Although the formation of **3a,b** from **1a,b** can be explained as the result of 1,3-migration of the mesityl group from the silicon to platinum atom through the Si–O–Pt linkages,¹⁵ it was found that treatment of **1** with a Brønsted acid and chloride ion is indispensable for the transformation of **1a,b** to **3a,b**. In general, the 1,3-migration reaction of a hydrogen atom or carbon substituent in late transition metal alkoxides is known to produce the corresponding carbonyl compounds as the elimination products.^{2–4} However, **1a,b** were found to be thermally and photochemically stable, and they did not undergo any transmetalation or hydrolysis under the conditions used even after the workup procedure with water. Therefore, this result ruled out the reaction pathway via the initial 1,3-migration (thermal or photochemical) of the mesityl group giving the corresponding silicon–oxygen double-bond species, [TbtSi(=O)–EPt(Mes)(PPh₃)₂] (**5**), followed by hydrolysis. On the other hand, the prerequisite activation of a silicon atom for the transmetalation of organosilanes is known to generate a five-coordinate silicate by the addition of some activator such as fluoride ion.¹⁶ Taking this information into account, the transformation of **1** to **3** should be interpreted in terms of the intermediacy of five-coordinate silicates generated by the nucleophilic attack of chloride ion on the silicon atom of the initially formed oxonium complex. Then, the Mes group on the silicon atom should migrate to the electron-deficient platinum center to afford the stable, neutral platinum complexes **3**. Since the significant breakthrough of the palladium-catalyzed organosilicon cross-coupling reactions that takes advantage of the addition of a nucleophilic promoters developed by Hiyama and

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(13) Isolated **3b** was converted into **4b** in 90% yield by reaction with an excess of H₂O in diethyl ether.

(14) In contrast to the highly strained geometry around the platinum atom in the structures of **1a,b**, the platinum atom of **4b** has an almost planar geometry due to the release of the ring strain and steric repulsion, which naturally resulted in the increase of the Si–Se–Pt angle of **4b** [111.96(10)°] as compared with that of **1b** [75.32(10)°].

(15) Although there have been some reports on the catalytic reactions involving 1,3-migration of carbon substituents, such as an alkenyl group, from a silicon atom to a transition metal center in metal siloxides, stoichiometric reactions with such a migration have not been reported so far. See ref 5.

(16) Pioneering studies by Kumada and Hiyama have shown that the addition of an activator such as fluoride ion activates organosilicon compounds to afford the corresponding five-coordinate silicate species, which promote the transition-metal-catalyzed cross-coupling reactions with various organic halides. See ref 6.

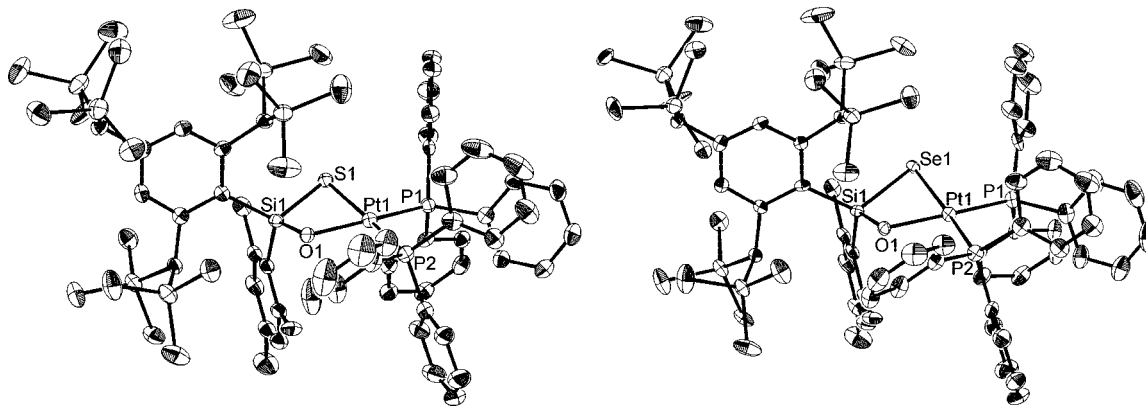


Figure 1. ORTEP drawings of **[1a·hexane]** (left) and **[1b·2(benzene)]** (right) (50% probability). The hydrogen atoms and solvents were omitted for clarity. Selected bond lengths [Å] and angles [deg]: for **1a**, Si(1)–S(1) 2.1708(13), Si(1)–O(1) 1.636(3), Pt(1)–S(1) 2.3495(9), Pt(1)–O(1) 2.076(2), Pt(1)–P(1) 2.2397(9), Pt(1)–P(2) 2.2758(10), S(1)–Si(1)–O(1) 97.07(10), Si(1)–O(1)–Pt(1) 100.02(12), Si(1)–S(1)–Pt(1) 78.34(4), S(1)–Pt(1)–O(1) 80.77(7), S(1)–Pt(1)–P(1) 87.48(3), P(1)–Pt(1)–P(2) 99.30(4), P(2)–Pt(1)–O(1) 93.27(7); for **1b**, Si(1)–Se(1) 2.3152(12), Si(1)–O(1) 1.635(3), Pt(1)–Se(1) 2.4565(5), Pt(1)–O(1) 2.067(3), Pt(1)–P(1) 2.2324(12), Pt(1)–P(2) 2.2835(12), Se(1)–Si(1)–O(1) 95.82(11), Si(1)–O(1)–Pt(1) 103.37(14), Si(1)–Se(1)–Pt(1) 75.32(3), Se(1)–Pt(1)–O(1) 81.47(8), Se(1)–Pt(1)–P(1) 87.00(3), P(1)–Pt(1)–P(2) 99.71(4), P(2)–Pt(1)–O(1) 92.83(8).

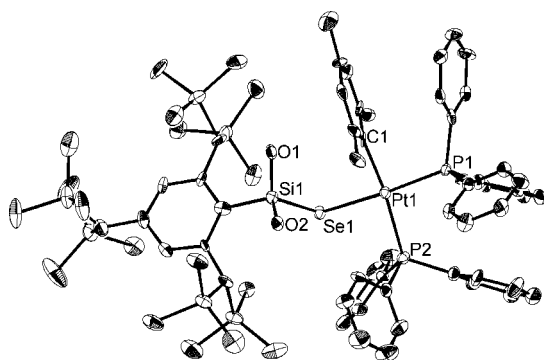
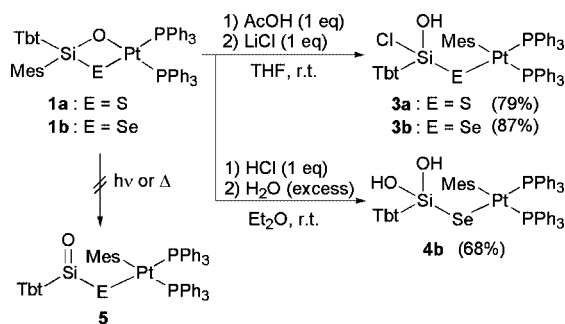


Figure 2. ORTEP drawing of **4b** (30% probability). The hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si(1)–O(1) 1.637(9), Si(1)–O(2) 1.653(8), Si(1)–Se(1) 2.236(4), Pt(1)–Se(1) 2.5009(13), Pt(1)–C(1) 2.043(12), Pt(1)–P(1) 2.259(3), Pt(1)–P(2) 2.352(3), Si(1)–Se(1)–Pt(1) 111.96(10), Se(1)–Pt(1)–C(1) 89.7(3), C(1)–Pt(1)–P(1) 89.0(3), P(1)–Pt(1)–P(2) 97.11(11), P(2)–Pt(1)–Se(1) 169.41(9).

Scheme 2. 1,3-Migration Reactions of the Mes Group from **1a,b**



his co-workers, wide ranging investigations of various functionalized organosilicon compounds have been described.⁶ It should be noted that the 1,3-migration reactions described here

are very important, as they provide the first experimental demonstration of the transmetalation of a carbon substituent from a silicon atom to a transition metal center in a metal siloxide, a process that is postulated as a plausible mechanism for some silicon-containing catalytic systems, such as the palladium(0) catalyzed cross-coupling reaction of aryl- or alkenylsilanols with aryl or vinyl iodides in the presence of tetrabutylammonium fluoride, reported by Denmark and his co-workers.⁵ The key to isolate the 1,3-migration products as silicon-containing platinum complexes is the use of chalcogen-bridged platinum siloxides as starting materials.

In summary, we have succeeded in the syntheses of novel platinacycles **1a,b**, by taking advantage of hydroxysilanechalcogenols **2a,b** as key building blocks. The structures of these complexes were characterized by NMR spectroscopic data and X-ray crystal structural analysis. Furthermore, unique 1,3-aryl migration reactions of the metal siloxides through their Si–O–Pt linkages giving chloro(hydroxy)silanechalcogenolato platinum **3a,b** were experimentally demonstrated and achieved for the first time. Further investigation on the reaction mechanism and applications toward the catalytic systems are currently under way.

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Supporting Information Available: X-ray crystallographic data of **1a,b** and **4b** in CIF format, experimental procedures, and spectral data. These materials are available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data for **1a**, **1b**, and **4b** have also been deposited with the Cambridge Crystallographic Data Centre, as CCDC Nos. 673348, 673349, and 673347, respectively.

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