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Synthesis, Structure, and Properties of the First Disulfur and Diselenium Complexes of Platinum

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The first platinum disulfur and diselenium complexes, [Pt(S_2)($ArMe_2P$)$_2$] (Ar = Tbt (**4a**), Bbt (**4b**)) and [Pt(Se_2)($ArMe_2P$)$_2$] (Ar = Tbt (**5a**), Bbt (**5b**)), have been synthesized by the reactions of the corresponding overcrowded platinum(0) complexes [Pt($ArMe_2P$)$_2$] with elemental sulfur and selenium. Molecular structures of **4b** and **5b** were established by X-ray crystallographic analyses, which show a novel three-membered PtE_2 (E = S, Se) ring structure with a square planar geometry around the platinum center. The oxidation of **4b** and **5b** with an equimolar amount of *m*-chloroperbenzoic acid or *tert*-butyl hydroperoxide in dichloromethane afforded the corresponding disulfur and diselenium monoxide complexes [Pt(E_2O)($BbtMe_2P$)$_2$] (E = S (**6**), Se (**7**)), respectively. An interesting difference in reactivity between **6** and **7** was shown in the further reactions with an excess of oxidants, which produced the corresponding *O*,*S*-coordinated thiosulfate complex [Pt(S_2O_3)($BbtMe_2P$)$_2$] (**8**) and the *O*,*O*-coordinated selenite complex [Pt(SeO_3)($BbtMe_2P$)$_2$] (**11**), respectively. The dynamic behavior in solution was revealed by the variable-temperature NMR spectroscopy for **4b**, **5b**, **8**, and **11**, 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.

The study of transition metal complexes having small fragments which would be highly reactive as free species (e.g. CO, NO, S_2, Se_2 etc.) is one of the most effective methods to explore the properties and reactivities of these small molecules. In particular, the chemistry of dichalcogen complexes has attracted much attention due to their unique structure,[1] biological interest,[2] potential and synthetic utility.[3] The disulfur and diselenium ligands can bind to metals in a variety of bridging geometries and also in the side-on manner as a terminal ligand.[1] Since the first mononuclear side-on bonded disulfur complexes, [Nb(Cp)$_2$(S_2)X] (X = Cl, Br, I, SCN), were synthesized by Werber et al. in 1968,[4] there has been gradually increasing activity in the synthesis and structure determination of analogous disulfur and diselenium complexes for various transition metals. However, it is often difficult to prepare the mononuclear complexes because sulfur and selenium ligands have a strong propensity for bridging metal atoms.[5] Although examples of mononuclear complexes containing the side-on bonded dioxygen ligand are known for most transition metals, the analogous disulfur and diselenium complexes previously reported are those of limited metal atoms having a high coordination number.[1] As for platinum complexes, the PtE_2 (E = S, Se) ring systems remain unknown, although the larger PtE_n (n = 4, 5; E = S, Se) ring systems, e.g., [Pt(S_5)$_3$(NH_4)$_2$],[6] [Pt(S_4)(PPh_3)$_2$],[7] and [Pt(Se_4)(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane),[8] and chalcogenido-bridged bimetallic complexes, e.g., [Pt_2(μ-E)$_2$(PPh_3)$_4$] (E = S, Se), have been extensively studied.[9] Morris and Walker et al. have postulated that a disulfur complex [Pt(S_2)(PPh_3)$_2$] might form in the reaction of the zero valent platinum [Pt(PPh_3)$_4$] with elemental sulfur, but it would undergo further reaction immediately to give a bimetallic complex [Pt_2(μ-S)$_2$(PPh_3)$_4$].[10] On the other hand, Lorenz et al. have reported that the reaction of [Pt(C_2H_4)(PPh_3)$_2$] with thiirane *S*-oxide affords the corresponding disulfur dioxide complex [Pt(S_2O_2)(PPh_3)$_2$].[11] They failed, however, in the synthesis of a disulfur complex [Pt(S_2)(PPh_3)$_2$] by the analogous reaction with thiirane. These two reports imply that the PtS_2 ring systems might be highly reactive and/or unstable species, and that some stabilization should be necessary to isolate the PtS_2 system as a stable complex.

We have previously reported the synthesis of cyclic polychalcogenides containing a heavier main group element such as [Tbt(R)ME_4] (M = Si, Ge, Sn, or Pb; E = S or Se; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl),[12] [Tbt(R)MSe_2] (M = Si or Sn),[13] and [TbtSbS_n] (n = 5, 7)[14] having an extremely bulky substituent, Tbt group. These results prompted us to introduce the Tbt substituent to the phosphorus atom and to take advantage of the new bulky phosphine ligand for the synthesis of novel classes of transition metal polychalcogenides. The Tbt group would be expected to protect the metal center to avoid the formation of polynuclear complexes or cluster compounds. In this paper, we describe the synthesis and characterization of the first disulfur and diselenium complexes of platinum [Pt(E_2)($ArMe_2P$)$_2$] (Ar = Tbt, Bbt; E = S, Se) by utilizing the new bulky phosphine ligands bearing a Tbt or 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) group and their oxidation reaction.[15] The dynamic behavior of the novel dichalcogen complexes of platinum and their oxidation products in solution is also described.

Results and Discussion

Synthesis of Disulfur and Diselenium Complexes of Platinum. Bulky phosphine ligands **1** were readily prepared by the treatment of a THF solution of ArLi (Ar = Tbt, Bbt)

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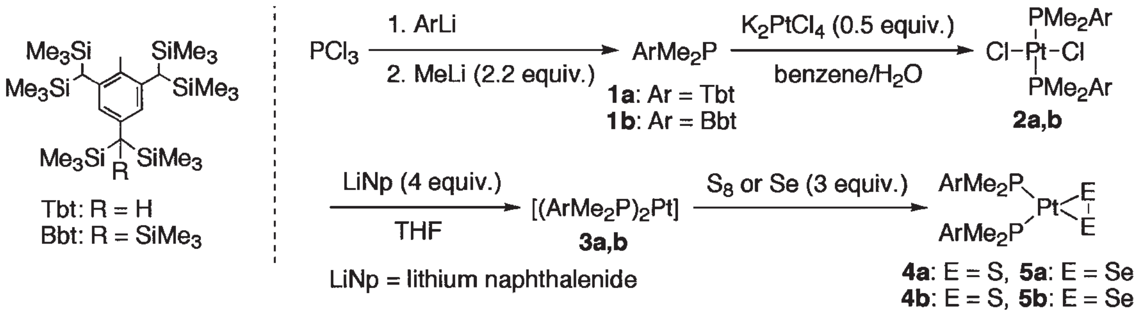


Scheme 1.

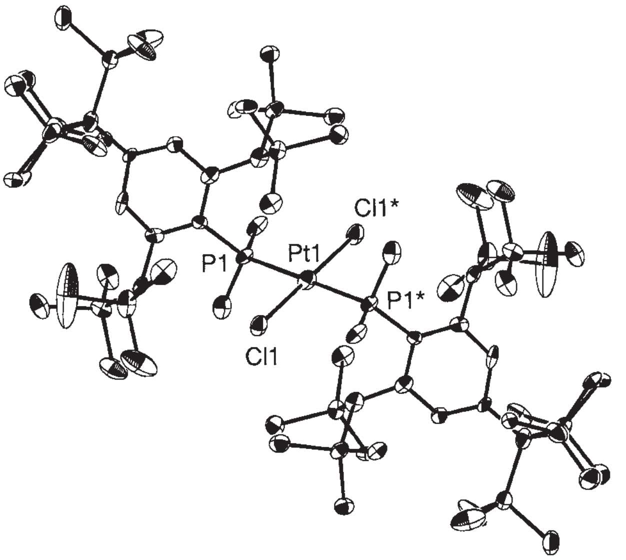


Fig. 1. ORTEP drawing of [$PtCl_2(BbtMe_2P)_2$] (**2b**) with thermal ellipsoid plots (50% probability). Selected bond lengths (Å) and angles (°): Pt1–Cl1 2.306(3), Pt1–P1 2.313(3); Cl1–Pt1–P1 87.15(9), Cl1–Pt1–P1* 92.85(9).

with an equimolar amount of phosphorous trichloride, followed by the addition of a solution of MeLi (2.2 equiv) in diethyl ether (Scheme 1). The ligand exchange reaction of **1a**,**b** with K_2PtCl_4 in benzene/H_2O at room temperature was very sluggish to afford gray precipitates of *trans*-[$PtCl_2(ArMe_2P)_2$] (**2a**,**b**), which were practically insoluble in common organic solvents except for halogenated solvent. The ^{31}P resonance of **2b** was observed at −14.7 ppm with $^1J_{PPt}$ value of 2351 Hz. There is a tendency for the complexes [$PtCl_2(PPh_3)$] to occupy the *trans* geometry when their $^1J_{PPt}$ values are less than 2500 Hz, while the *cis* geometry is expected when their $^1J_{PPt}$ values are more than 3000 Hz.[16] Therefore, the $^1J_{PPt}$ value of **2b** indicated the *trans* geometry of this Pt complex. The molecular structure of **2b** was finally determined by X-ray crystallographic analysis (Fig. 1).

When platinum dichlorides **2a**,**b** were reduced with an excess amount of lithium naphthalenide in THF, the ^{31}P NMR spectra of the mixtures showed signals with ^{195}Pt satellites, which are assigned to those of [$Pt(ArMe_2P)_2$] (**3a**: $\delta_P = 0.9$, $^1J_{PtP} = 3974$ Hz, **3b**: $\delta_P = 3.7$, $^1J_{PtP} = 3869$ Hz).[17] The successive treatment of the mixtures with elemental sulfur (3 equiv. as S) resulted in the formation of the first platinum disulfur complexes [$Pt(S_2)(ArMe_2P)_2$] (**4a**,**b**) as purple crystal-

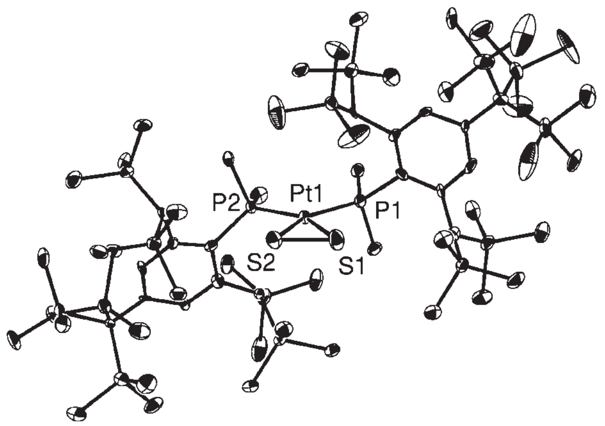


Fig. 2. ORTEP drawing of [$Pt(S_2)(BbtMe_2P)_2$] (**4b**) with thermal ellipsoid plots (50% probability). Selected bond lengths (Å) and angles (°): Pt1–S1 2.348(3), Pt1–S2 2.337(3), S1–S2 2.077(3), Pt1–P1 2.271(2), Pt1–P2 2.265(3); S1–Pt1–S2 52.63(9), Pt1–S1–S2 63.41(11), Pt1–S2–S1 63.96(11), P1–Pt1–S1 102.07(9), P2–Pt1–S2 98.47(9), P1–Pt1–P2 106.87(8).

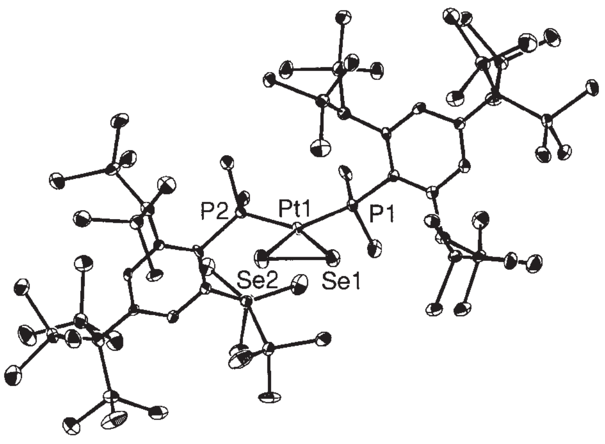


Fig. 3. ORTEP drawing of [$Pt(Se_2)(BbtMe_2P)_2$] (**5b**) with thermal ellipsoid plots (50% probability). Selected bond lengths (Å) and angles (°): Pt1–Se1 2.4491(10), Pt1–Se2 2.4658(10), Se1–Se2 2.3363(11), Pt1–P1 2.271(2), Pt1–P2 2.261(2); Se1–Pt1–Se2 56.76(3), Pt1–Se1–Se2 61.98(3), Pt1–Se2–Se1 61.26(3), P1–Pt1–Se1 95.44(6), P2–Pt1–Se2 99.94(6), P1–Pt1–P2 107.85(7).

Table 1. Comparison of Bond Lengths (Å) and Angles (°) in Polychalcogenido Complexes of Platinum and Related Systems

Complex	Pt–E	Pt–P	E–Pt–E	P–Pt–P	Ref
$[Pt(O_2)(PPh_3)_2]\cdot C_6H_5CH_3$	1.90, 1.99	2.22, 2.28	38	100	20a
$\cdot 1.5C_6H_6$	2.01(3), 2.01(2)	2.282(11), 2.253(12)	43(1)	101.2(4)	20b
$\cdot 2CHCl_3$	2.006(7)	2.233(3)	44.05(40)	101.23(12)	20c
$[Pt(S_2)(BbtMe_2P)_2]$ (**4b**)	2.348(3), 2.337(3)	2.271(2), 2.265(3)	52.63(9)	106.87(8)	this work
$[Pt(Se_2)(BbtMe_2P)_2]$ (**5b**)	2.4656(10), 2.4489(9)	2.261(2), 2.273(2)	56.76(3)	107.77(7)	this work
$[Pt(S_3O)(Ph_3P)_2]$	2.341(3), 2.318(2)	2.271(2), 2.299(2)	80.73(9)	98.47(8)	21
$[Pt(S_4)(Ph_3P)_2]$	2.360(6), 2.366(5)	2.300(5), 2.283(5)	92.0(3)	99.3(2)	7b
$[Pt(S_4)(dppe)]$[a]	2.327(3), 2.344(3)	2.250(2), 2.250(2)	95.3(1)	86.8(1)	22
$[Pt(Se_4)(dppe)]$[a]	2.445(3), 2.448(2)	2.246(5), 2.242(5)	98.09(8)	86.31(20)	8a
$[Pt_2(\mu\text{-}S)_2(dppy)_4]$[b]	2.333(1)	2.275(2), 2.279(1)	80.42(6)	102.98(6)	23
$[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$	2.433(1), 2.465(1)	2.278(2), 2.275(2)	79.61(6)	99.6(1)	9b

a) dppe = 1,2-bis(diphenylphosphino)ethane. b) dppy = 2-diphenylphosphinopyridine.

line solids together with $ArMe_2P{=}S$ and a trace amount of unidentified platinum polysulfido complexes, which could be converted into **4a**,**b** by further reaction with triphenylphosphine. The use of 6 molar amounts of elemental sulfur (as S) in the reaction of **3a** also gave the disulfur complex **4a** as a main product (54%) despite the slight decrease in the yield. The diselenium analogues $[Pt(Se_2)(ArMe_2P)_2]$ (**5a**,**b**), the first platinum diselenium complexes, were also obtained as green crystalline solids when elemental selenium was used instead of elemental sulfur, as shown in Scheme 1. These dichalcogen complexes, **4** and **5**, are both air-stable in the solid state, while they decomposed to the corresponding phosphine chalcogenides and metallic platinum on standing in solution at room temperature for several days. Complexes **4** and **5** showed satisfactory spectral and analytical data, and the molecular structures of **4b** and **5b** were finally determined by X-ray crystallographic analysis (Figs. 2 and 3).

Table 2. ^{195}Pt NMR Spectroscopic Data[a)]

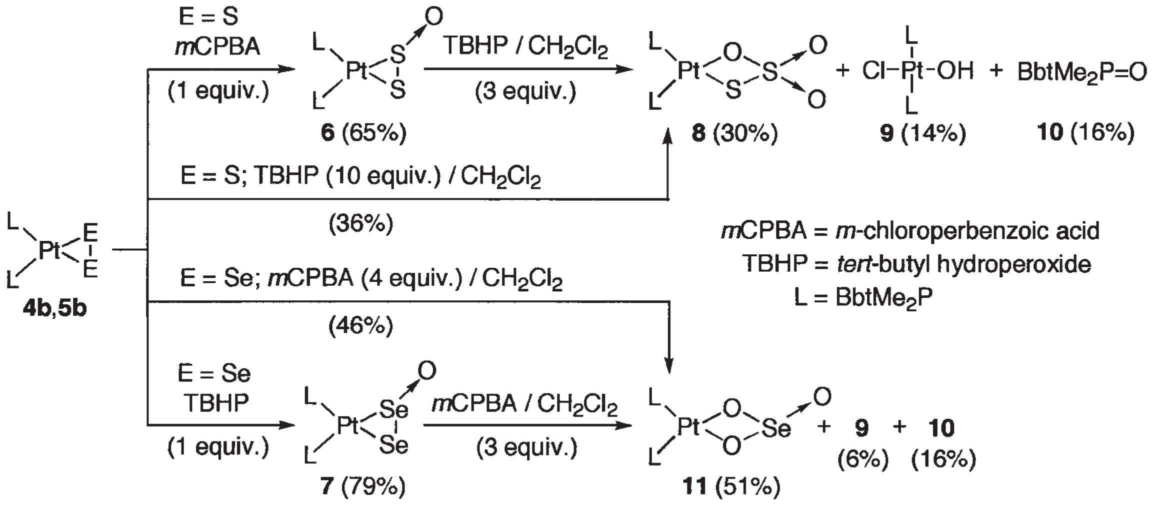
Complex	^{195}Pt NMR/δ	$^{1}J_{PtP}$/Hz
$[Pt(O_2)(TbtMe_2P)_2]$	−4191	4014
$[Pt(O_2)(BbtMe_2P)_2]$	−4218	3998
$[Pt(S_2)(TbtMe_2P)_2]$ (**4a**)	−4977	3869
$[Pt(S_2)(BbtMe_2P)_2]$ (**4b**)	−4983	3909
$[Pt(Se_2)(TbtMe_2P)_2]$ (**5a**)	−5024	3821
$[Pt(Se_2)(BbtMe_2P)_2]$ (**5b**)	−5030	3865

a) Measured in $CDCl_3$.

Crystal Structures of the Disulfur and Diselenium Complexes of Platinum. Crystallographic analysis showed that **4b** and **5b** are isomorphous; their geometries are very similar to each other. The dihedral angles between the E–Pt–E plane (**4b**: E = S, **5b**: E = Se) and the P–Pt–P plane are 4.8° and 2.9°, and the sums of the bond angles around the central Pt atom are 360.07(5)° and 360.01(2)°, respectively, which indicates the planar geometries around the central Pt atoms of **4b** and **5b**. The two Bbt groups are situated in opposite positions with regard to the PtP_2 planes to decrease the steric congestion. The S–S bond length of 2.077(3) Å and Se–Se bond length of 2.3363(11) Å are close to those reported for other side-on bonded disulfur and diselenium complexes; these bond lengths are longer than those of the S=S bond (1.887 Å)[18] and the Se=Se bond (2.19(3) Å)[19] in the gas phase, respectively. The Pt–E (E = S, Se) and Pt–P bond lengths are very similar to the values found for the related platinum complexes shown in Table 1.[7b,8a,9b,19,20–23] Therefore, these dichalcogen complexes, **4b** and **5b**, have three-membered structures containing Pt(II) rather than Pt(0) dichalcogen resonance forms which would have higher double bond character between both chalcogen atoms. It is noteworthy that the P–Pt–P bond angles (106.87(8)° in **4b** and 107.85(7)° in **5b**) are larger than those for other related platinum polychalcogenido complexes and an analogous dioxygen complex $[Pt(O_2)(Ph_3P)_2]$, as shown in Table 1, reflecting the severe steric repulsion between two Bbt groups. We suppose the steric repulsion enlarges the bond angles of P–Pt–P and hence narrows the angles of E–Pt–E, thus favoring the selective formation of the three-membered ring.

Comparison of the NMR Spectra for Dichalcogen Complexes of Platinum. Dioxygen complexes, $[Pt(O_2)(ArMe_2P)_2]$ (Ar = Tbt, Bbt), were easily formed by exposing a mixture including $[Pt(ArMe_2P)_2]$, which was prepared by the reduction of *trans*-$[PtCl_2(ArMe_2P)_2]$ with lithium naphthalenide, to air or O_2 atmosphere. However, the identification of their structure was made by only NMR spectroscopy because they decompose in solution to give complicated mixtures. The multinuclear NMR spectroscopic data for the dichalcogen complexes of platinum are summarized in Table 2. As for the PtE_2 (E = O, S, Se) complexes, Table 2 shows the lower-field shift of the ^{195}Pt resonances and the increase of the $^{1}J_{PtP}$ values in the order of the $O_2 > S_2 > Se_2$ complexes. The former tendency is consistent with that reported for the platinum complexes having Group 16 elements as the coordinated atoms of the ligands.[24] The latter indicates that the NMR *trans*-influence is higher in the order of $O_2 > S_2 > Se_2$ ligand.

Oxidation Reactions of the Disulfur and Diselenium Complexes of Platinum. The monooxidation of **4b** with an equimolar amount of *m*-chloroperbenzoic acid (*m*CPBA) in dichloromethane (CH_2Cl_2) was completed within 2 h at −20 °C and gave the corresponding disulfur monoxide complex $[Pt(S_2O)(BbtMe_2P)_2]$ (**6**) in 65% yield (Scheme 2).[25] On the other hand, the diselenium monoxide complex $[Pt(Se_2O)(BbtMe_2P)_2]$ (**7**) was obtained cleanly from **5b** in 79% yield by the use of an equimolar amount of *tert*-butyl hydroperoxide (TBHP). In the ^{31}P NMR spectra, two doublets having different coupling constants with ^{195}Pt appeared at $\delta =$ -29.7 ($^{1}J_{PtP} = 4263$ Hz, $^{2}J_{PP} = 8$ Hz) and -32.8



Scheme 2.

($^1J_{\rm PtP} = 3254$ Hz, $^2J_{\rm PP} = 8$ Hz) for **6** and $\delta = -34.8$ ($^1J_{\rm PtP} = 3431$ Hz, $^2J_{\rm PP} = 12$ Hz) and -38.7 ($^1J_{\rm PtP} = 3974$ Hz, $^2J_{\rm PP} = 12$ Hz) for **7**, respectively, which are consistent with the two non-equivalent phosphorus atoms in both complexes. The infrared spectrum of **6** showed a strong band at 1042 $\rm cm^{-1}$, approximately 40 $\rm cm^{-1}$ higher than ν(SO) value in [Mo(Cp)$_2$(S$_2$O)] (1003 $\rm cm^{-1}$)[26] but very similar to that observed for [Ir(S$_2$O)(dppe)$_2$]PF$_6$ (1049 $\rm cm^{-1}$).[27]

Figure 4 shows the electronic absorption spectra of the monoxide complexes, **6** and **7**, and the dichalcogen complexes, **4b** and **5b**. The spectral pattern of **4b** is similar to that of **5b**, but each absorption band of **5b** is red-shifted compared to the corresponding band of **4b** (Fig. 4a). Similar red shifts on going from S$_2$ to Se$_2$ complexes have been reported for Ir and Rh complexes.[28] In the spectra of **6** and **7**, one broad absorption was observed as a shoulder peak around 380 nm (ε = ca. 2640 $\rm M^{-1}\,cm^{-1}$) and at 392 nm ($\varepsilon = 1780\ \rm M^{-1}\,cm^{-1}$), respectively, while the characteristic lowest energy absorptions of the side-on bonded ME$_2$ complexes at 559 nm ($\varepsilon = 110\ \rm M^{-1}\,cm^{-1}$) for **4b** and 633 nm ($\varepsilon = 130\ \rm M^{-1}\,cm^{-1}$) for **5b** have disappeared (Fig. 4b). These PtE$_2$O complexes are less stable than the corresponding PtE$_2$ complexes and undergo slow decomposition both in the solid state and in solution. In particular, slow reversion of **7** to the complex **5b** was observed in CH$_2$Cl$_2$ solution.

An attempt at further oxidation of **6** with an excess of TBHP in CH$_2$Cl$_2$ yielded the platinum thiosulfate complex [Pt(S$_2$O$_3$)(BbtMe$_2$P)$_2$] (**8**) together with *trans*-[PtCl(OH)-(BbtMe$_2$P)$_2$] (**9**) and phosphine oxide (**10**). Complex **8** could also be obtained from the disulfur complex **4b** under the similar reaction conditions with an excess of TBHP, and **8** is considered to be formed via **6** in this reaction. On the other hand, the reaction of **6** with an excess of *m*CPBA resulted in the formation of a complex mixture including the complex **8**. These conversions of the S$_2$ or S$_2$O ligand to the S$_2$O$_3$ ligand on platinum are in sharp contrast to the reported exhaustive oxidation of a disulfur complex of iridium [Ir(S$_2$)(dppe)$_2$]$^+$ to the corresponding disulfur dioxide complex [Ir(S$_2$O$_2$)(dppe)$_2$]$^+$ via the disulfur monoxide complex [Ir(S$_2$O)(dppe)$_2$]$^+$.[29] Similarly to these systems, the disulfur dioxide complex such as [Pt(S$_2$O$_2$)(BbtMe$_2$P)$_2$] may be initially formed in the oxidation of **6**. When **6** was treated with an equimolar amount of TBHP below -10 °C, **6** did not change even after a prolonged reaction time. On warming up to 10 °C, the reaction proceeded immediately to form a complicated mixture with **8** being the

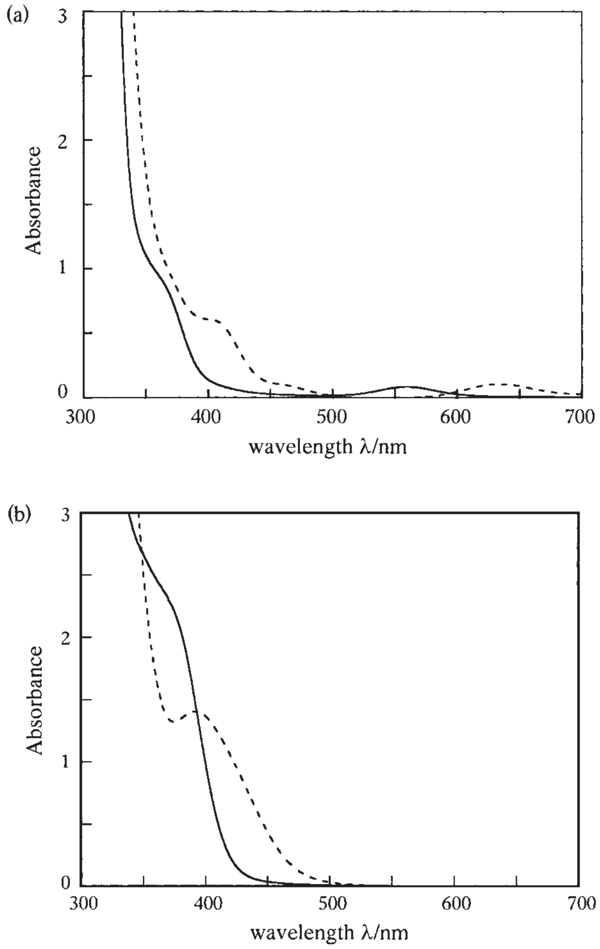


Fig. 4. Electronic spectra in CH$_2$Cl$_2$ solution of (a) **4b** (—) and **5b** (- - -), (b) **6** (—) and **7** (- - -).

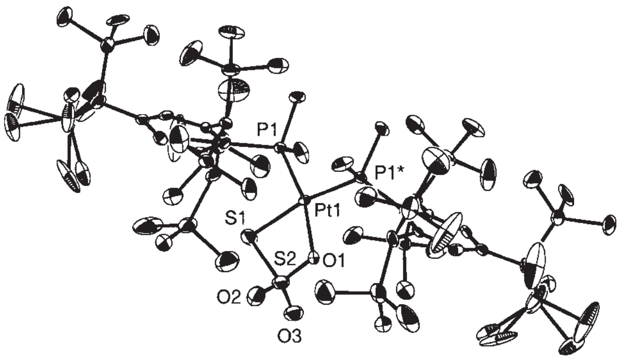


Fig. 5. ORTEP drawing of $[Pt(S_2O_3)(BbtMe_2P)_2]$ (**8**) with thermal ellipsoid plots (50% probability). Selected bond lengths (Å) and angles (°): Pt1–O1 2.21(3), Pt1–P1 2.263(16), P1–S1 2.312(16), O1–S2 1.54(3), S1–S2 2.079(13), S2–O2 1.43(2), S2–O3 1.43(2); P1–Pt1–P1* 105.4(2), O1–Pt1–S1 77.3(6), Pt1–O1–S2 98.1(15), Pt1–S1–S2 81.3(5), O1–S2–S1 101.4(10).

major component (20% isolated yield). However, the intermediates were too complex to be isolated, and the mechanism for this transformation is unclear at present. As for the formation of complex **9**, it may be explained in terms of the reaction of some intermediates with CH_2Cl_2 used as solvent, since the reaction in THF did not give **9**. Complexes **8** and **9** showed satisfactory spectral and analytical data, and their molecular structures were finally determined by X-ray crystallographic analyses (Fig. 5 for **8**). In the molecular structure of **8**, the platinum atom has essentially square-planar geometry and the S_2O_3 ligand coordinates to the platinum with *O*,*S* fashion.[30] The sum of the bond angles around the central Pt atom is 359.9(6)°, which supports the planar geometry around the central Pt atom. The PtSSO ring is slightly bent, and the dihedral angle between S1–Pt1–O1 and S1–S2–O1 planes is 15.2°.

Interestingly, further reaction of **7** with an excess of *m*CPBA in CH_2Cl_2 yielded not the Se_2O_3 complex but the selenite complex $[Pt(SeO_3)(BbtMe_2P)_2]$ (**11**) together with **10** and a trace amount of **9**. Complex **11** could also be obtained from the diselenium complex **5b**, as well as in the case of analogous sulfur system, by the reaction with an excess of *m*CPBA. On the other hand, the reaction of **7** with an excess of TBHP did not afford **11** but only resulted in the partial conversion into **9**. The composition and structure of **11** were determined by HRMS, elemental analysis, and multinuclear NMR spectroscopy. In the NMR spectra of **11**, the ^{31}P resonance was observed as a singlet having a coupling with ^{195}Pt nuclei at $\delta = -41.7$ ($^1J_{PtP} = 3639$ Hz) and the ^{195}Pt resonance appeared as a triplet at $\delta = -3176$ resulting from coupling to two equivalent phosphorus atoms. In the ^{77}Se NMR spectrum, only one sharp signal was observed at $\delta = 1504$ in contrast to the broadened signals of **5b** ($\delta = 689$, 1135) and **7** ($\delta = 582$); no satellite peaks due to the ^{77}Se–^{195}Pt couplings could be found. On the basis of these results, the coordination of the SeO_3 ligand should be considered to have the *O*-bound geometry rather than *Se*-bound one, and we can describe the geometry of **11** as the chelating structure with *O*,*O* fashion.[31] This structure of **11** was also supported by the fluxional behavior mentioned below.

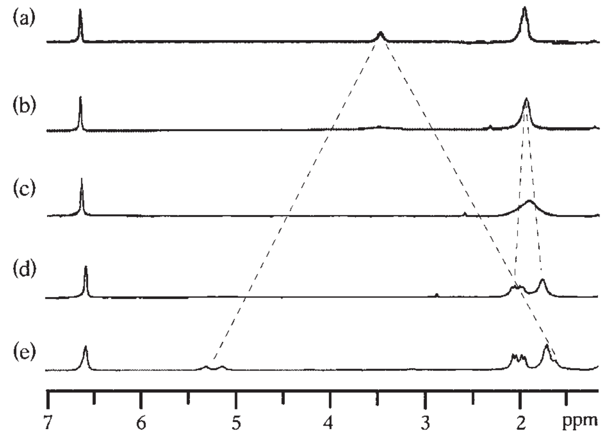


Fig. 6. ^1H NMR spectra of $[Pt(SeO_3)(BbtMe_2P)_2]$ (**11**) measured in $CDCl_3$ at (a) 25 °C, (b) 0 °C, (c) −20 °C, (d) −40 °C, and (e) −60 °C.

Structural Implication of Intramolecular C–H···E (E = O, S, Se) Interactions. Of particular note among the structural features of the novel platinum complexes obtained here is a dynamic process in solution, as revealed by the variable-temperature NMR spectroscopy. In the ^1H NMR spectra of **11**, for example, four methine protons of the *o*-bis(trimethylsilyl)-methyl (disyl) groups resonate equally at 25 °C ($\delta = 3.49$, Fig. 6a). On cooling, the resonance was broadened and then separated into two regions below about −50 °C. At −60 °C, the resonances were observed at a much lower field ($\delta = 5.15$, 5.33) and at a higher field ($\delta = 1.67$) than that at 25 °C (Fig. 6e). Although the latter peak is almost overlapped to the neighboring peak, it could be confirmed by decoupling experiments in ^1H NMR spectroscopy indicating that these signals at 5.15, 5.33 and 1.67 ppm should be assigned to the methine protons of the *o*-disyl groups.[32]

The separation into the three peaks is probably due to the restricted rotation of the P–C and/or P–Pt bonds leading to the inequality of the four methine protons, and the lower shifts of the two resonances can be explained in terms of the existence of a considerable interaction (i.e., C–H···O interaction)[33] between the Pt-bonded oxygens and the methine hydrogens of the *o*-disyl group which are directed to the $PtSeO_3$ ring. A spectral change, which can be interpreted in terms of the same restricted rotation, was observed for the protons of methyl groups bound to the phosphorus atoms, and one broad singlet at 25 °C ($\delta = 1.98$, Fig. 6a) was also separated into two regions below −40 °C. At −60 °C, one broad signal was observed at higher field ($\delta = 1.75$) and the other one like an AB quartet appeared at lower field ($\delta = 2.03$) relative to that observed at 25 °C (Fig. 6e). In addition, the ^{31}P NMR resonance at 25 °C (Fig. 7a) was split into an AB quartet ($^2J_{PP} = 23$ Hz) while keeping the $^1J_{PtP}$ coupling at −60 °C (Fig. 7b), probably due to two nonequivalent phosphorus atoms being in a fixed conformation at −60 °C. Similarly, **4b**, **5b**, and **8** showed the peak separation in the ^1H NMR spectra at lowered temperature (Table 3).[34]

The large differences of the chemical shift ($\Delta\delta$) between separated peaks in **4b** and **5b** indicate the existence of the C–H···S and C–H···Se interactions, respectively.[35] As for the

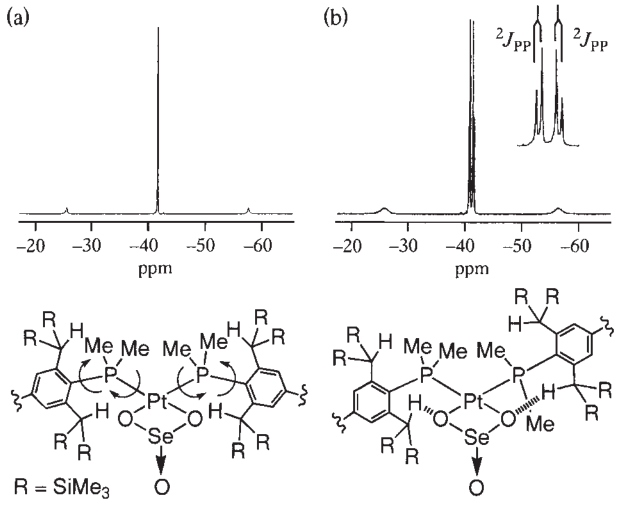


Fig. 7. ^{31}P NMR spectra of [Pt(SeO$_3$)(BbtMe$_2$P)$_2$] (**11**) measured in CDCl$_3$ and proposed rotational behavior at (a) 25 °C and (b) −60 °C.

Table 3. ^{1}H NMR Chemical Shifts (δ, ppm) of Methine Protons of *o*-Disyl Groups in Platinum Complexes

Complex	δ/ppm 25 °C	δ/ppm −60 °C	$\Delta\delta$
4b	3.32	4.75, 1.79	2.96
5b	3.32	4.73, 1.75	2.98
8	3.01	4.18, 1.71	2.47
	3.41	5.11, 1.65	3.46
11	3.50	5.14, 1.66	3.48
		5.31, 1.66	3.65

thiosulfate complex **8**, the two peaks due to nonequivalent methine protons at 25 °C were split into two regions with different degrees of the peak separation at low temperature. Two values of $\Delta\delta$ are 3.46 and 2.47 ppm, and the larger $\Delta\delta$ is comparable to those of **11**. Therefore, the signal at lower field observed for **8** can be attributed to that of a C–H···O interaction, while the other signal should be attributed to that of a C–H···S interaction. In all fluxional processes, the spin-spin coupling between the ^{31}P and ^{195}Pt nuclei was almost totally retained, which indicated that the bond characters between the P and Pt atoms are intramolecularly conserved. Within the time scale of the NMR experiments, a dissociative displacement involving Pt–P or Pt–E bond cleavage can be excluded. In addition, the low-temperature ^{1}H NMR measurements on **6** and **7** resulted in the observation of the broadening of the methine signals, which suggests the occurrence of a similar dynamic process. However, no clear separation of the signals was observed even at −60 °C. In contrast to the above NMR experiments on the platinum complexes containing chalcogen atoms, the methine protons of the *o*-disyl groups in **1b** and **2b** did not change in the ^{1}H NMR measurements at 25 °C to −60 °C. These results indicate that the occurrence of the above-mentioned fluxional process should not be attributed only to the restricted rotation concerned with the bulky phosphine ligand.

In the crystalline states, the C···S distances of 4.114–5.132 Å in **4b** and C···Se distances of 4.115–5.172 Å in **5b** are somewhat longer than the corresponding sums of van der Waals radii (3.70 Å and 3.85 Å).[36] On the basis of these findings, we suppose that the observed C–H···E (E = O, S, Se) interaction might be weak, and the restricted rotation in solution should be attributed not only to the C–H···E interaction but also to the steric effects of the bulky substituents. It is interesting that the existence of specific C–H···E interactions, which have been rare in transition metal complexes, was indicated by the variable-temperature NMR experiments for these novel platinum complexes.

In addition, the *o*-benzyl proton signal coalesced at 227 ± 2 K for **4b** and at 241 ± 2 K for **5b**, and the activation parameters could be estimated: $\Delta G^{\ddagger} = 10.4 \pm 0.1$ kcal mol^{-1} (**4b**), 11.0 ± 0.1 kcal mol^{-1} (**5b**).

Conclusion

Since the late 1960s, when the first mononuclear side-on bonded disulfur complexes were reported, it has taken nearly three decades for this chemistry to mature, except for Group 10 metals. We successfully synthesized the first disulfur and diselenium complexes of platinum, [Pt(S$_2$)(ArMe$_2$P)$_2$] (**4**; Ar = Tbt, Bbt) and [Pt(Se$_2$)(ArMe$_2$P)$_2$] (**5**; Ar = Tbt, Bbt) by the reaction of overcrowded platinum(0) complexes coordinated by new bulky phosphine ligands bearing a Tbt or Bbt group with elemental sulfur and selenium, respectively, and their molecular structures were definitively determined. Results revealed that the platinum atom of each complex has a square planar geometry and the E$_2$ (E = S, Se) ligand is bound to the platinum center in a side-on orientation with a three-membered PtE$_2$ ring structure.

The comparison of the reactivities of the Pt-bonded S$_2$ and Se$_2$ fragment toward the oxidants such as *m*CPBA and TBHP showed some interesting results. The behaviors of [Pt(S$_2$)(BbtMe$_2$P)$_2$] (**4b**) and [Pt(Se$_2$)(BbtMe$_2$P)$_2$] (**5b**) toward the monooxidation are similar to each other, and the corresponding S$_2$O and Se$_2$O complexes are obtained, respectively, although the appropriate oxidants for **4b** and **5b** are not identical. Interestingly, further oxidation of the S$_2$O and Se$_2$O complexes with an excess of oxidants afforded the *O*,*S*-coordinated thiosulfate (S$_2$O$_3$) complex and the *O*,*O*-coordinated selenite (SeO$_3$) complex, respectively.

It is noteworthy that the variable temperature NMR studies indicated the existence of the specific CH···E (E = O, S, and Se) interactions in solution for some novel platinum complexes. At low temperature, the observation of considerably lower shift of the methine protons of the *o*-disyl groups is probably caused by a large isotropic deshielding effect of the Pt-bonded heteroatoms (such as O, S, and Se). As shown in Figs. 2 and 3, all the methine hydrogens of the *o*-disyl groups are directed toward the PtE$_2$ (E = S, Se) ring, avoiding steric repulsion of the two trimethylsilyl groups of the *o*-disyl group with the PtE$_2$ ring. However, the existence of such interactions is ambiguous in the crystalline states. This result indicates that the CH···E interactions might not be strong probably due to weakly polarized CH groups. The PtE$_2$ complexes synthesized in the present work are considered to be useful precursors for novel low-coordinated platinum species such as Pt=S, which is of much interest, and further investigation is currently in progress.

Experimental

General Procedure. All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were dried by standard methods and freshly distilled prior to use. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), ^{31}P NMR (120 MHz), ^{77}Se NMR (57 MHz), and ^{195}Pt NMR (64 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL JNM AL-300 spectrometer. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. Wet column chromatography (WCC) was performed on Wakogel C-200. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 or LC-918 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: chloroform). Electronic spectra were recorded on a JASCO V-570 UV/vis spectrometer. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. 3-Chloroperbenzoic acid (*m*CPBA) and *tert*-butyl hydroperoxide were purchased commercially. Iodometric titrations of the oxidants were conducted to determine the amount of active oxygen present, with the weights and molar amounts listed in the preparative section. 1-Bromo-2,4,6-tris[bis(trimethylsilyl)methyl]benzene (TbtBr) was prepared according to the reported procedure.[37]

Preparation of Phosphines TbtMe$_2$P (1a) and BbtMe$_2$P (1b). To a solution of TbtBr (3.16 g, 5 mmol) in THF (50 mL) was added *tert*-butyllithium (2.36 M pentane solution, 4.9 mL, 11.5 mmol) at −78 °C. After 30 min, phosphorous trichloride (0.48 mL, 5.5 mmol) was added. The reaction mixture was warmed to room temperature and then stirred for 15 h. The solvents and remaining phosphorous trichloride were evaporated under reduced pressure; next, 50 mL of THF was added again to the residue. After the flask was cooled to −78 °C, methyllithium (1.14 M diethyl ether solution, 11.0 mL, 12.5 mmol) was added dropwise. The reaction mixture was warmed to room temperature and then stirred for 3 h. After the solvents were evaporated under reduced pressure, 50 mL of *n*-hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. After removal of the solvent from the filtrate, the residue was reprecipitated from CH_2Cl_2/ethanol to afford TbtMe$_2$P (**1a**, 1.88 g, 61%) as a white powder. Phosphine **1b** was obtained as a white powder (1.04 g, 75%) from BbtBr (1.40 g, 2 mmol) according to the procedure described for the preparation of **1a**.

1a: mp 159.8–161.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.04 (s, 36 H), 0.06 (s, 18 H), 1.29 (s, 1 H), 1.40 (d, $^2J_{PH} = 5.4$ Hz, 6 H), 3.08 (s, 1 H), 3.11 (s, 1 H), 6.27 (s, 1 H), 6.38 (s, 1 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 0.77 ($\underline{C}H_3$), 0.85 ($\underline{C}H_3$), 1.18 ($\underline{C}H_3$), 13.84 (d, $^1J_{PC} = 14.8$ Hz, P–$\underline{C}H_3$), 26.19 ($\underline{C}H$), 26.47 ($\underline{C}H$), 30.25 ($\underline{C}H$), 122.53 ($\underline{C}H$), 126.87 (d, $^1J_{PC} = 14.2$ Hz), 127.54 ($\underline{C}H$), 144.08, 151.64 (d, $^2J_{PC} = 16.6$ Hz), 151.85(d, $^2J_{PC} = 13.6$ Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): δ −61.3; HRMS *m/z* calcd for $C_{29}H_{65}PSi_6$ 612.3439, Found 612.3460.

1b: mp 168.4–170.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.07 (s, 36 H), 0.25 (s, 27 H), 1.43 (d, $^2J_{PH} = 5.6$ Hz, 6 H), 3.34 (d, $^4J_{PH} = 12.2$ Hz, 2 H), 6.71 (d, $^4J_{PH} = 2.7$ Hz, 2 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 1.60 ($\underline{C}H_3$), 5.47 ($\underline{C}H_3$), 13.95 (d, $^1J_{PC} = 16.6$ Hz, P–$\underline{C}H_3$), 21.91, 26.84 (d, $^3J_{PC} = 21.6$ Hz, $\underline{C}H$), 127.28 (d, $^3J_{PC} = 1.8$ Hz, $\underline{C}H$), 129.56 (d, $^1J_{PC} = 14.8$ Hz), 145.69, 151.52 (d, $^2J_{PC} = 16.0$ Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): δ −59.7; HRMS *m/z* calcd for $C_{32}H_{73}PSi_7$ 684.3835, Found 684.3837.

Preparation of *trans*-[PtCl$_2$(TbtMe$_2$P)$_2$] (2a) and *trans*-[PtCl$_2$(BbtMe$_2$P)$_2$] (2b). A solution of a mixture of BbtMe$_2$P including a trace of oxidized BbtMe$_2$P=O (1.15 g, ca. 1.51 mmol as **1b**; ca. 90% of total content estimated by ^{1}H NMR) in degassed benzene (15 mL) was transferred to an aqueous solution (4 mL) of K_2PtCl_4 (285 mg, 0.69 mmol) via cannula at room temperature, and the mixture was stirred for 7 days. The gray precipitates were collected and washed with water, ethanol, and *n*-hexane to afford complex **2b** (655 mg, 58%) as a gray powder. Complex **2a** was obtained as a gray powder (1.43 g, 69%) from a mixture of TbtMe$_2$P and TbtMe$_2$P=O (2.50 g, ca. 3.06 mmol as **1b**; ca. 75% of total content estimated by ^{1}H NMR) and K_2PtCl_4 (577 mg, 1.39 mmol) according to the procedure described for the preparation of **2b**. Since **2a** was almost insoluble in common organic solvents, no spectral and analytical data could be obtained. **2b**: mp 210.0–210.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.20 (s, 72 H), 0.25 (s, 54 H), 1.84 (br s, 12 H), 2.76 (s, 4 H), 6.68 (s, 4 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 2.63 ($\underline{C}H_3$), 5.67 ($\underline{C}H_3$), 20.00 (t, AA′X spin system, $1/2[^1J_{PC} + {}^3J_{PC}] = 26.8$ Hz, P–$\underline{C}H_3$), 21.89, 27.40 ($\underline{C}H$), 126.90 (t, AA′X spin system, $1/2[^1J_{PC} + {}^3J_{PC}] = 19.1$ Hz), 128.05 ($\underline{C}H$), 146.90, 149.59 (t, AA′X spin system, $1/2[^2J_{PC} + {}^4J_{PC}] = 5.5$ Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): δ −14.7 ($^1J_{PPt} = 2350$ Hz); $^{195}Pt\{^1H\}$ NMR (64 MHz, $CDCl_3$, 25 °C, Na_2PtCl_6): δ −3921 (t, $^1J_{PtP} = 2350$ Hz); Anal. Calcd for $C_{64}H_{146}Cl_2P_2PtSi_{14}$: C, 46.96; H, 8.99. Found: C, 46.85; H, 9.02.

Preparation of Disulfur Complexes [Pt(S$_2$)(TbtMe$_2$P)$_2$] (4a) and [Pt(S$_2$)(BbtMe$_2$P)$_2$] (4b). A THF suspension (2 mL) of *trans*-[PtCl$_2$(TbtMe$_2$P)$_2$] (**2a**; 75 mg, 0.050 mmol) was treated with a THF solution of lithium naphthalenide (1.02 M, 0.20 mL, 0.20 mmol) at −78 °C. The reaction mixture was stirred for 1 h while being warmed up to room temperature. After stirring for 1 h, the solution of [Pt(TbtMe$_2$P)$_2$] (**3a**) thus obtained was cooled down to −78 °C again and treated with S_8 (4.8 mg, 0.019 mmol, 3eq. as S). The reaction mixture was stirred for 4 h while being warmed up to room temperature. After removal of the solvent, chloroform was added to the residue and the mixture was filtered through Celite®. The filtrate was evaporated; then the crude product was dissolved again in chloroform (2 mL). After the solution was treated with triphenylphosphine (26 mg, 0.10 mmol) at 50 °C for 1.5 h, the solvent was evaporated. The residue was purified by preparative gel permeation liquid chromatography (eluent; $CHCl_3$) to afford **4a** as a pale purple crystalline solid (44 mg, 59%) along with TbtMe$_2$P=S (17 mg, 26%). Complex **4b** was obtained as a pale purple crystalline solid (86 mg, 71%) from *trans*-[PtCl$_2$(BbtMe$_2$P)$_2$] (**2b**; 123 mg, 0.075 mmol) according to the procedure described for the preparation of **4a**.

4a: mp 178.8–181.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.04 (s, 36 H), 0.11 (s, 36 H), 0.14 (s, 36 H), 1.31 (s, 2 H), 2.16 (d, $^2J_{PH} = 7.8$ Hz, 12 H), 3.02 (s, 2 H), 3.34 (s, 2 H), 6.23 (s, 2 H), 6.40 (s, 2 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 1.01 ($\underline{C}H_3$), 1.99 ($\underline{C}H_3$), 2.20 ($\underline{C}H_3$), 27.4 (br m, P–$\underline{C}H_3$), 27.63 ($\underline{C}H$), 27.82 ($\underline{C}H$), 30.47 ($\underline{C}H$), 122.2 (m, AA′X spin system, $1/2[^1J_{PC} + {}^3J_{PC}] = 24.4$ Hz), 124.53 ($\underline{C}H$), 129.89 ($\underline{C}H$), 145.26, 150.35 (t, AA′X spin system, $1/2[^2J_{PC} + {}^4J_{PC}] = 4.9$ Hz), 150.92 (t, AA′X spin system, $1/2[^2J_{PC} + {}^4J_{PC}] = 5.3$ Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): δ −30.7 ($^1J_{PtP} = 3869$ Hz); $^{195}Pt\{^1H\}$ NMR (64 MHz, $CDCl_3$, 25 °C, Na_2PtCl_6): δ −4977 (t, $^1J_{PPt} = 3869$ Hz); FAB MS *m/z*: 1484 $(M)^+$; Anal. Calcd for $C_{58}H_{130}P_2PtS_2Si_{12}$: C, 46.88; H, 8.82. Found: C, 46.56; H, 8.90.

4b: mp 162.3–163.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.16 (s, 72 H), 0.21 (s, 54 H), 2.19 (br s, 12 H), 3.32 (s, 4 H), 6.65 (s, 4 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 2.85 ($\underline{C}H_3$), 5.57 ($\underline{C}H_3$), 22.05, 27.6 (br m, P–$\underline{C}H_3$), 28.08 ($\underline{C}H$), 125.1 (m, AA′X spin system, $1/2[^1J_{PC} + {}^3J_{PC}] = 24.0$ Hz), 128.59 ($\underline{C}H$), 148.26, 151.10 (t, AA′X spin system, $1/2[^2J_{PC} + {}^4J_{PC}] = 4.9$ Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): δ −32.2 ($^1J_{PtP} = 3909$ Hz); $^{195}Pt\{^1H\}$ NMR (64 MHz, $CDCl_3$, 25 °C, Na_2PtCl_6): δ −4983 (t, $^1J_{PPt} = 3909$ Hz); UV-vis (CH_2Cl_2): 366 nm (sh, $\mathcal{E} = 1100$), 559 nm ($\mathcal{E} = 110$); FAB MS *m/z*: 1628 $(M)^+$; Anal. Calcd for $C_{64}H_{146}P_2PtS_2Si_{14}$: C, 47.15; H, 9.03. Found: C, 47.09; H, 9.28.

Preparation of Diselenium Complexes [Pt(Se$_2$)(TbtMe$_2$P)$_2$] (5a) and [Pt(Se$_2$)(BbtMe$_2$P)$_2$] (5b). A THF suspension (4 mL) of *trans*-[PtCl$_2$(TbtMe$_2$P)$_2$] (**2a**; 149 mg, 0.10 mmol) was treated with a THF solution of lithium naphthalenide (0.90 M, 0.44 mL, 0.40 mmol) at −78 °C. The reaction mixture was stirred for 1 h while being warmed up to room temperature. After stirring for 1 h, the solution of [Pt(TbtMe$_2$P)$_2$] (**3a**) thus obtained was cooled down to −78 °C again and then treated with Se (23.7 mg, 0.30 mmol). The reaction mixture was stirred for 4 h while being warmed up to room temperature. After removal of the solvent, chloroform was added to the residue; the mixture was next filtered through Celite®. After the filtrate was evaporated, the residue was purified by preparative gel permeation liquid chromatography (eluent; $CHCl_3$) to afford **5a** as a green crystalline solid (110 mg, 70%) along with TbtMe$_2$P=Se (24 mg, 17%). Complex **5b** was obtained as a green crystalline solid (60 mg, 70%) from *trans*-[PtCl$_2$(BbtMe$_2$P)$_2$] (**2b**; 82 mg, 0.050 mmol) according to the procedure described for the preparation of **5a**.

5a: mp 187.1–188.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.04 (s, 36 H), 0.12 (s, 36 H), 0.15 (s, 36 H), 1.31 (s, 2 H), 2.18 (d, $^2J_{PH} = 7.1$ Hz, 12 H), 3.01 (s, 2 H), 3.28 (s, 2 H), 6.21 (s, 2 H), 6.39 (s, 2 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 1.05 ($\underline{C}H_3$), 2.17 ($\underline{C}H_3$), 2.38 ($\underline{C}H_3$), 27.72 ($\underline{C}H$), 27.87 ($\underline{C}H$), 28.4 (m, P–$\underline{C}H_3$), 30.44 ($\underline{C}H$), 122.5 (m, AA′X spin system, $1/2[^1J_{PC} + {}^3J_{PC}] = 24.4$ Hz), 124.58 ($\underline{C}H$), 129.98 ($\underline{C}H$), 145.11, 149.91 (t, AA′X spin system, $1/2[^2J_{PC} + {}^4J_{PC}] = 4.9$ Hz), 150.42 (t, AA′X spin system, $1/2[^2J_{PC} + {}^4J_{PC}] = 4.9$ Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): δ −42.1 ($^1J_{PtP} = 3821$ Hz); $^{77}Se\{^1H\}$ NMR (57 MHz, $CDCl_3$, 25 °C): δ 556; $^{195}Pt\{^1H\}$ NMR (64 MHz, $CDCl_3$, 25 °C, Na_2PtCl_6): δ −5024 (t, $^1J_{PPt} = 3821$ Hz); FAB MS *m/z*: 1579 $(M)^+$; Anal. Calcd for $C_{58}H_{130}P_2PtSe_2Si_{12}$: C, 44.10; H, 8.30. Found: C, 43.71; H, 8.30.

5b: mp 170.6–171.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.17 (s, 72 H), 0.22 (s, 54 H), 2.23 (br s, 12 H), 3.33 (s, 4 H), 6.64 (s, 4 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 2.99 ($\underline{C}H_3$), 5.60 ($\underline{C}H_3$), 22.03, 28.11 ($\underline{C}H$), 29.7 (br m, P–$\underline{C}H_3$), 125.0 (m, AA′X spin system, $1/2[^1J_{PC} + {}^3J_{PC}] = 23.8$ Hz), 128.67 ($\underline{C}H$), 148.20, 150.80 (t, AA′X spin system, $1/2[^2J_{PC} + {}^4J_{PC}] = 4.9$ Hz); ^{31}P NMR (120 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): δ −44.1 ($^1J_{PtP} = 3865$ Hz); ^{77}Se NMR (57 MHz, $CDCl_3$, 25 °C): δ 582; ^{195}Pt NMR (64 MHz, $CDCl_3$, 25 °C, Na_2PtCl_6): δ −5030 (t, $^1J_{PPt} = 3865$ Hz, $^1J_{SePt} = 262$ Hz); UV-vis (CH_2Cl_2): 407 nm (sh, $\mathcal{E} = 1700$), 465 nm (sh, $\mathcal{E} = 120$), 633 nm ($\mathcal{E} = 130$); FAB MS *m/z*: 1723 $(M)^+$; Anal. Calcd for $C_{64}H_{146}P_2PtSe_2Si_{14}$: C, 44.59; H, 8.54. Found: C, 44.32; H, 8.59.

Monooxidation of Disulfur Complex [Pt(S$_2$)(BbtMe$_2$P)$_2$] (4b). To a CH_2Cl_2 solution (10 mL) of [Pt(S$_2$)(BbtMe$_2$P)$_2$] (**4b**; 195 mg, 0.12 mmol) was added a CH_2Cl_2 solution (2.5 mL) of *m*CPBA (purity: 73%; 31.2 mg, 0.13 mmol) at −20 °C. After the mixture was stirred for 2 h at the same temperature, the reaction was quenched by aqueous $NaHCO_3$. The organic layer was separated, and then the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was reprecipitated from CH_2Cl_2/*n*-hexane to afford the corresponding disulfur monoxide complex **6** (128 mg, 65%) as a yellow crystalline solid. **6**: mp 175.0–176.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.13 (s, 18 H), 0.14 (s, 18 H), 0.15 (s, 18 H), 0.18 (s, 18 H), 0.22 (s, 54H), 1.94 (d, $^2J_{PH} = 7.5$ Hz, 3 H), 2.10 (d, $^2J_{PH} = 8.0$ Hz, 3 H), 2.14 (d, $^2J_{PH} = 8.2$ Hz, 3 H), 2.24 (d, $^2J_{PH} = 8.9$ Hz, 3 H), 3.06 (d, $^4J_{PH} = 2.5$ Hz, 2 H), 3.14 (d, $^4J_{PH} = 2.9$ Hz, 2 H), 6.68 (d, $^4J_{PH} = 3.1$ Hz, 4 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 2.84 ($\underline{C}H_3$), 2.93 ($\underline{C}H_3$), 3.03 ($\underline{C}H_3$), 5.61 ($\underline{C}H_3$), 21.5 (m, P–$\underline{C}H_3$), 22.09, 25.91 (dd, $^1J_{PC} = 32.4$ Hz, $^3J_{PC} = 2.5$ Hz, P–$\underline{C}H_3$), 28.47 (d, $^3J_{PC} = 6.2$ Hz, $\underline{C}H$), 28.9 (m, P–$\underline{C}H_3$), 29.9 (m, P–$\underline{C}H_3$), 28.69 (d, $^3J_{PC} = 7.5$ Hz, $\underline{C}H$), 126.64 (d, $^1J_{PC} = 43.6$ Hz), 126.68 (d, $^1J_{PC} = 44.8$ Hz) 128.56 ($\underline{C}H$), 128.61 ($\underline{C}H$), 148.29, 148.40, 150.47 (d, $^2J_{PC} = 3.7$ Hz), 150.61 (d, $^2J_{PC} = 3.8$ Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$): δ −29.7 (d, $^1J_{PtP} = 4263$ Hz, $^2J_{PP} = 8$ Hz), −32.8 (d, $^1J_{PtP} = 3254$ Hz, $^2J_{PP} = 8$ Hz); $^{195}Pt\{^1H\}$ NMR (64 MHz, $CDCl_3$): δ −4708 (dd, $^1J_{PPt} = 3254$, 4263 Hz); IR (KBr): ν (SO) = 1042 cm^{-1}; UV-vis (CH_2Cl_2): 379 nm (sh, $\mathcal{E} = 2640$). FAB MS *m/z*: 1645 $(M + H)^+$, 1629 $(M - O + H)^+$; Anal. Calcd for $C_{64}H_{146}OP_2PtS_2Si_{14}$: C, 46.69; H, 8.94. Found: C, 46.53; H, 9.11.

Monooxidation of Diselenium Complex [Pt(Se$_2$)(BbtMe$_2$P)$_2$] (5b). To a stirred solution of [Pt(Se$_2$)(BbtMe$_2$P)$_2$] (**5b**; 207 mg, 0.12 mmol) in CH_2Cl_2 (10 mL) was added dropwise a 5.6 M *n*-decane solution of TBHP (26 µL, 0.14 mmol) at 0 °C. After 1 hour, the reaction mixture was stirred for 2 h while being warmed up to room temperature. After removal of the solvent, the residue was separated by silica gel column chromatography ($CHCl_3$) and subsequent preparative gel permeation liquid chromatography (eluent; $CHCl_3$) to afford the corresponding diselenium monoxide complex **7** as a yellow crystalline solid (165 mg, 79%). **7**: mp 158.2–159.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.12 (s, 36 H), 0.13 (s, 18 H), 0.17 (s, 18 H), 0.20 (s, 54H), 1.99 (d, $^2J_{PH} = 7.5$ Hz, 3 H), 2.10 (d, $^2J_{PH} = 8.0$ Hz, 3 H), 2.14 (d, $^2J_{PH} = 8.2$ Hz, 3 H), 2.24 (d, $^2J_{PH} = 8.9$ Hz, 3 H), 3.06 (s, 2 H), 3.18 (s, 2 H), 6.66 (s, 4 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 2.97 ($\underline{C}H_3$), 3.09 ($\underline{C}H_3$), 5.60 ($\underline{C}H_3$), 22.16 (d, $^1J_{PC} = 35.8$ Hz, P–$\underline{C}H_3$), 22.17, 28.03 (d, $^1J_{PC} = 33.3$ Hz, P–$\underline{C}H_3$), 28.59 (d, $^3J_{PC} = 6.8$ Hz, $\underline{C}H$), 28.82 (d, $^3J_{PC} = 6.8$ Hz, $\underline{C}H$), 29.86 (dd, $^1J_{PC} = 28.4$ Hz, $^3J_{PC} = 6.2$ Hz, P–$\underline{C}H_3$), 30.13 (dd, $^1J_{PC} = 36.4$ Hz, $^3J_{PC} = 8.6$ Hz, P–$\underline{C}H_3$), 125.68 (d, $^1J_{PC} = 43.2$ Hz), 126.21 (d, $^1J_{PC} = 49.3$ Hz), 128.68 ($\underline{C}H$), 128.73 ($\underline{C}H$) 148.50 (d, $^4J_{PC} = 2.5$ Hz), 148.68 (d, $^4J_{PC} = 2.5$ Hz), 150.40 (d, $^2J_{PC} = 9.9$ Hz), 150.58 (d, $^2J_{PC} = 9.9$ Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$): δ −34.8 (d, $^1J_{PtP} = 3431$ Hz, $^2J_{PP} = 12$ Hz), −38.7 (d, $^1J_{PPt} = 3974$ Hz, $^2J_{PP} = 12$ Hz); $^{77}Se\{^1H\}$ NMR (57 MHz, $CDCl_3$, 25 °C): δ 689, 1135 ($^1J_{PtSe} = 416$ Hz); $^{195}Pt\{^1H\}$ NMR (64 MHz, $CDCl_3$): δ −4768 (dd, $^1J_{PPt} = 3431$, 3974 Hz); UV-vis (CH_2Cl_2): 392 nm ($\mathcal{E} = 1700$); FAB MS *m/z*: 1739 $(M)^+$, 1723 $(M - O)^+$; Anal. Calcd for $C_{64}H_{146}OP_2PtSe_2Si_{14}$: C, 44.18; H, 8.46. Found: C, 44.27; H, 8.59.

Reaction of Disulfur Monoxide Complex 6 with an Excess Amount of TBHP. To a stirred solution of [Pt(S$_2$O)(BbtMe$_2$P)$_2$] (**6**; 164 mg, 0.10 mmol) in CH_2Cl_2 (5 mL) was added dropwise a 5.6 M *n*-decane solution of TBHP (53 µL, 0.30 mmol) at −20 °C. The reaction mixture was stirred for 20 h while being warmed up to room temperature. After removal of the solvents, the residue was separated by preparative gel permeation liquid chromatography (eluent; $CHCl_3$) and subsequent silica gel column chromatography ($CHCl_3$) to afford *O,S*-coordinated thiosulfite complex **8** as a pale yellow crystalline solid (50 mg, 30%) along with *trans*-[PtCl(OH)($BbtMe_2P$)$_2$] (**9**) (23 mg, 14%) and phosphine oxide $BbtMe_2P{=}O$ (**10**) (23 mg, 16%). **8**: mp 220.6–221.1 °C (decomp.); ^1H NMR (300 MHz, $CDCl_3$): δ 0.17 (s, 36 H), 0.19 (s, 36 H), 0.22 (s, 54H), 2.05 (d, $^2J_{PH} = 9.1$ Hz, 6 H), 2.19 (d, $^2J_{PH} = 9.5$ Hz, 6 H), 3.01 (s, 2 H), 3.42 (s, 2 H), 6.67 (d, $^4J_{PH} = 3.8$ Hz, 2 H), 6.70 (d, $^4J_{PH} = 3.6$ Hz, 2 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 2.92 ($\underline{C}H_3$), 3.06 ($\underline{C}H_3$), 5.61 ($\underline{C}H_3$), 5.65 ($\underline{C}H_3$), 22.48, 22.59, 26.6 (br m, P–$\underline{C}H_3$), 29.47 (d, $^3J_{PC} = 5.5$ Hz, $\underline{C}H$), 29.59 (d, $^3J_{PC} = 5.5$ Hz, $\underline{C}H$), 120.05 (d, $^1J_{PC} = 64.7$ Hz), 122.75 (d, $^1J_{PC} = 54.9$ Hz), 128.77 (d, $^3J_{PC} = 8.0$ Hz, $\underline{C}H$), 129.11 (d, $^3J_{PC} = 8.6$ Hz, $\underline{C}H$), 149.47 (d, $^4J_{PC} = 2.5$ Hz), 150.05 (d, $^4J_{PC} = 3.1$ Hz), 151.06 (d, $^2J_{PC} = 10.5$ Hz), 151.38 (d, $^2J_{PC} = 9.9$ Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$): δ −31.5 (d, $^1J_{PtP} = 3240$ Hz, $^2J_{PP} = 21$ Hz), −48.1 (d, $^1J_{PtP} = 4137$ Hz, $^2J_{PP} = 21$ Hz); $^{195}Pt\{^1H\}$ NMR (64 MHz, $CDCl_3$): δ −3995 (dd, $^1J_{PPt} = 3240$, 4137 Hz). FAB MS *m/z*: 1677 $(M + H)^+$; Anal. Calcd for $C_{64}H_{146}O_3P_2PtS_2Si_{14}$: C, 45.80; H, 8.77. Found: C, 45.74; H, 8.80.

9: mp 178.8–180.4 °C (decomp.); ^1H NMR (300 MHz, $CDCl_3$): δ 0.12 (s, 18 H), 0.16 (s, 18 H), 0.18 (s, 18 H), 0.19 (s, 18 H), 0.25 (s, 27 H), 0.26 (s, 27 H), 1.78–1.96 (m, 12 H), 2.48 (s, 1 H), 2.73 (s, 2 H), 3.16 (s, 1 H), 4.00 (s, 1 H), 6.65–6.74 (m, 4H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 2.18 ($\underline{C}H_3$), 2.34 ($\underline{C}H_3$), 2.58 ($\underline{C}H_3$), 2.70 ($\underline{C}H_3$), 5.53 ($\underline{C}H_3$), 5.68 ($\underline{C}H_3$), 19.08 (t, AA′X spin system, $1/2[^1J_{PC} + {}^3J_{PC}] = 19.7$ Hz, P–$\underline{C}H_3$), 19.68 (t, AA′X spin system, $1/2[^1J_{PC} + {}^3J_{PC}] = 19.7$ Hz, P–$\underline{C}H_3$), 21.27 (t, AA′X spin system, $1/2[^1J_{PC} + {}^3J_{PC}] = 16.9$ Hz, P–$\underline{C}H_3$), 21.77, 21.86, 26.74 ($\underline{C}H$), 27.26 ($\underline{C}H$), 30.91 ($\underline{C}H$), 127.2 (m), 128.02 ($\underline{C}H$), 128.24 ($\underline{C}H$), 146.75, 148.39 (t, AA′X spin system, $1/2[^2J_{PC} + {}^4J_{PC}] = 3.7$ Hz), 148.62 (t, AA′X spin system, $1/2[^2J_{PC} + {}^4J_{PC}] = 6.8$ Hz), 149.38 (t, AA′X spin system, $1/2[^2J_{PC} + {}^4J_{PC}] = 5.2$ Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$): δ −9.97 ($^1J_{PtP} = 2683$ Hz); $^{195}Pt\{^1H\}$ NMR (64 MHz, $CDCl_3$): δ −4263 (t, $^1J_{PPt} = 2683$ Hz); Anal. Calcd for $C_{64}H_{147}ClOP_2PtSi_{14}$: C, 47.49; H, 9.15. Found: C, 47.63; H, 9.25.

10: mp 169.4–170.7 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 0.08 (s, 36 H), 0.25 (s, 27 H), 1.84 (d, $^2J_{PH} = 12.5$ Hz, 6 H), 3.29 (s, 2 H), 6.71 (d, $^4J_{PH} = 3.6$ Hz, 2 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 1.73 ($\underline{C}H_3$), 5.43 ($\underline{C}H_3$), 22.26, 23.39 (d, $^1J_{PC} = 69.7$ Hz, P–$\underline{C}H_3$), 25.54 (d, $^3J_{PC} = 3.7$ Hz, $\underline{C}H$), 124.40 (d, $^1J_{PC} = 98.6$ Hz), 128.69 (d, $^3J_{PC} = 9.9$ Hz, $\underline{C}H$), 148.36 (d, $^4J_{PC} = 2.5$ Hz), 149.89 (d, $^2J_{PC} = 11.1$ Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$): δ 37.67; FAB MS *m/z*: 701 $(M)^+$; Anal. Calcd for $C_{32}H_{73}OPSi_7$: C, 54.79; H, 10.49. Found: C, 54.78; H, 10.65.

Reaction of Diselenium Monoxide Complex 7 with an Excess Amount of *m*CPBA. To a CH_2Cl_2 solution (10 mL) of [Pt(Se_2O)($BbtMe_2P$)$_2$] (**7**; 209 mg, 0.12 mmol) was added a CH_2Cl_2 solution (2.5 mL) of *m*CPBA (purity: 73%; 85.1 mg, 0.36 mmol) at −50 °C. The reaction mixture was stirred for 4 h while being warmed up to room temperature. After removal of the solvent, the residue was separated by silica gel column chromatography ($CHCl_3$:Et_2O = 5:1) and subsequent preparative gel permeation liquid chromatography (eluent; $CHCl_3$) to afford *O,O*-coordinated selenite complex **11** (103 mg, 51%) as a pale yellow crystalline solid along with **9** (12 mg, 6%) and **10** (27 mg, 16%). **11**: mp 222.4–223.8 °C (decomp.); ^1H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 72 H), 0.20 (s, 54 H), 1.98 (t, AA′X spin system, $1/2[^2J_{PH} + {}^4J_{PH}] = 9.3$ Hz, 12 H), 3.49 (s, 4 H), 6.66 (s, 4 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 2.88 ($\underline{C}H_3$), 3.03 ($\underline{C}H_3$), 5.51 ($\underline{C}H_3$), 22.2 (br m, P–$\underline{C}H_3$), 22.32, 29.44 ($\underline{C}H$), 121.2 (m, AA′X spin system, $1/2[^1J_{PC} + {}^3J_{PC}] = 29.3$ Hz), 128.67 ($\underline{C}H$), 149.12, 151.01 (t, AA′X spin system, $1/2[^2J_{PC} + {}^4J_{PC}] = 4.5$ Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$): δ −41.7 ($^1J_{PtP} = 3639$ Hz); $^{77}Se\{^1H\}$ NMR (57 MHz, $CDCl_3$, 25 °C): δ 1504; $^{195}Pt\{^1H\}$ NMR (64 MHz, $CDCl_3$): δ −3176 (t, $^1J_{PPt} = 3639$ Hz); HRMS *m/z* calcd for $C_{64}H_{146}O_3P_2PtSeSi_{14}$: 1691.6330, Found 1691.6316; Anal. Calcd for $C_{64}H_{146}O_3P_2PtSeSi_{14}$: C, 45.40; H, 8.69. Found: C, 45.29; H, 8.67.

Crystallographic Data for 2b, 4b, 5b, and 8. The intensity data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å). The structures were solved by direct method with SIR-97.[38] Two sets of the three methyl carbons of the trimethylsilyl group on the Bbt group and solvated hexane are disordered in **2b**. In Fig. 1, the minor part of the disordered carbons and a fragment of solvated hexane are omitted for clarity. The three methyl carbons of the one trimethylsilyl group on the Bbt group are disordered in **4b**. In Fig. 2, the minor part of the disordered carbons is omitted for clarity. The P_2PtSe_2 plane and the four methyl carbons bound to each phosphorus atom are disordered in **5b**. In Fig. 3, the major orientation (96%) is represented. Since there is the disorder of two sets of PtS_2O_3 units, which overlap with each other by the C_2 symmetry operation, with occupancies of 0.5 and 0.5, the structure of **8** was best solved as a molecule having pseudo 2-fold symmetry in space group $C2/c$ with $Z = 4$. The attempts to solve the structure in space group Cc with $Z = 4$ did not give better results compared to the above one. Two sets of the three methyl carbons of the two trimethylsilyl group on the Bbt group are also disordered. In Fig. 5, another part of the disordered carbons and one PtS_2O_3 core are omitted to avoid confusion. All non-hydrogen atoms (except for the minor ones or another part of the disordered moieties in the cases of **2b**, **4b**, **5b**, and **8**) were refined anisotropically. The final cycles of full-matrix least-squares refinement were based on 10897 (**2b**), 16756 (**4b**), 14928 (**5b**), and 7753 (**8**) observed reflections (all data) and 478 (**2b**), 761 (**4b**), 821 (**5b**), and 477 (**8**) variable parameters. Crystal data for all molecules are summarized in Table 4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-197753 (**2b**), no. CCDC-169659 (**4b**), no. CCDC-169660 (**5b**), and no. CCDC-194234 (**8**), respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Variable-Temperature NMR Experiment. In a typical experiment, approximately 10 mg of the complex was dissolved in 0.6 mL of $CDCl_3$ which was filtered through an alumina column. The ^1H NMR spectrum was recorded over a temperature range from 213 to 298 K, and the four methine protons of the *o*-bis(trimethylsilyl)methyl groups were monitored for complexes **4b**, **5b**, **8**, and **11**. The ^{31}P NMR spectrum was also recorded over a temperature range from 213 K to 298 K, and the two phosphorous atoms of phosphine ligands were monitored for complexes **11**.

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Table 4. Crystal Data for Complexes **2b**, **4b**, **5b**, and **8**

	2b	**4b**	**5b**	**8**
Formula	$C_{64}H_{146}Cl_2P_2PtSi_{14}\cdot n\text{-}C_6H_{14}$	$C_{64}H_{146}P_2PtS_2Si_{14}$	$C_{64}H_{146}P_2PtSe_2Si_{14}$	$C_{64}H_{146}P_2PtO_3S_2Si_{14}$
F_w	1637.00	1630.22	1724.02	1678.22
Cryst syst	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	Cc	Cc	$C2/c$
a/Å	9.0300(15)	40.121(8)	40.213(2)	39.77(2)
b/Å	16.7900(18)	9.130(3)	9.1551(15)	9.320(5)
c/Å	17.630(2)	23.740(6)	23.860(2)	23.870(13)
α/°	68.930(5)			
β/°	89.250(6)	91.2201(19)	89.0303(7)	90.921(11)
γ/°	86.470(3)			
V/Å^3	2489.4(6)	8694(4)	8782.8(17)	8847(8)
Z	1	4	4	4
T/K	93(2)	93(2)	93(2)	93(2)
D_{calcd}/g cm^{-3}	1.092	1.245	1.304	1.260
μ/cm^{-1}	16.9	19.3	26.9	19.0
goodness-of-fit on F^2	0.75	1.00	1.08	1.28
R_1	0.075	0.062	0.047	0.108
wR_2	0.188	0.146	0.127	0.216

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