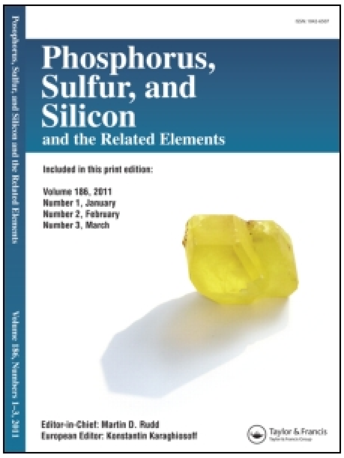

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND PROPERTIES OF THE FIRST DISULFUR AND DISELENIUM COMPLEXES OF PLATINUM

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To cite this Article Tokitoh, Norihiro , Nagata, Kazuto and Takeda, Nobuhiro(2004) 'SYNTHESIS AND PROPERTIES OF THE FIRST DISULFUR AND DISELENIUM COMPLEXES OF PLATINUM', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 915 — 927

To link to this Article: DOI: 10.1080/10426500490428906

URL: http://dx.doi.org/10.1080/10426500490428906

Phosphorus, Sulfur, and Silicon, 179:915–927, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490428906

SYNTHESIS AND PROPERTIES OF THE FIRST DISULFUR AND DISELENIUM COMPLEXES OF PLATINUM

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(Received August 18, 2003; accepted October 3, 2003)

*The reactions of overcrowded platinum(0) complexes $[Pt\{P(Ar)Me_2\}_2]$ (Ar = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt), 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt)) with elemental sulfur and selenium resulted in the formation of the first platinum disulfur and diselenium complexes, $[Pt(S_2)\{P(Ar)Me_2\}_2]$ (**4a** (Ar = Tbt), **4b** (Ar = Bbt) and $[Pt(Se_2)\{P(Ar)Me_2\}_2]$ (**5a** (Ar = Tbt), **5b** (Ar = Bbt)) respectively. The x-ray crystallographic analyses of **4b** and **5b** showed 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 yielded the corresponding disulfur and diselenium monoxide complexes $[Pt(E_2O)\{P(Bbt)Me_2\}_2]$ (**6** (E = S), **7** (E = Se)). The further reactions of **6** and **7** with an excess of oxidants gave the corresponding O,S-coordinated thiosulfato complex $[Pt(S_2O_3)\{P(Bbt)Me_2\}_2]$ (**8**) and the O,O-coordinated selenito complex $[Pt(SeO_3)\{P(Bbt)Me_2\}_2]$ (**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 $CH\cdots E$ (E = O, S, Se) interactions between the methine hydrogens of the o-bis(trimethylsilyl)methyl groups and the Pt-bonded chalcogen atoms.*

Keywords: Bulky phosphine ligand; CH–chalcogen interaction; oxidation; platinum–diselenium complex; platinum–disulfur complex

We thank Ms. Toshiko Hirano and Ms. Tomoko Terada of the Microanalytical Laboratory of the Institute for Chemical Research of Kyoto University for the elemental analysis and HRMS spectra. This work was partially supported by Grants-in-Aid for COE Research on Elements Science (No. 12CE2005), Scientific Research on Priority Area (A) (No. 14078213), 21st Century COE on Kyoto University Alliance for Chemistry, and “Nanotechnology Support Project” from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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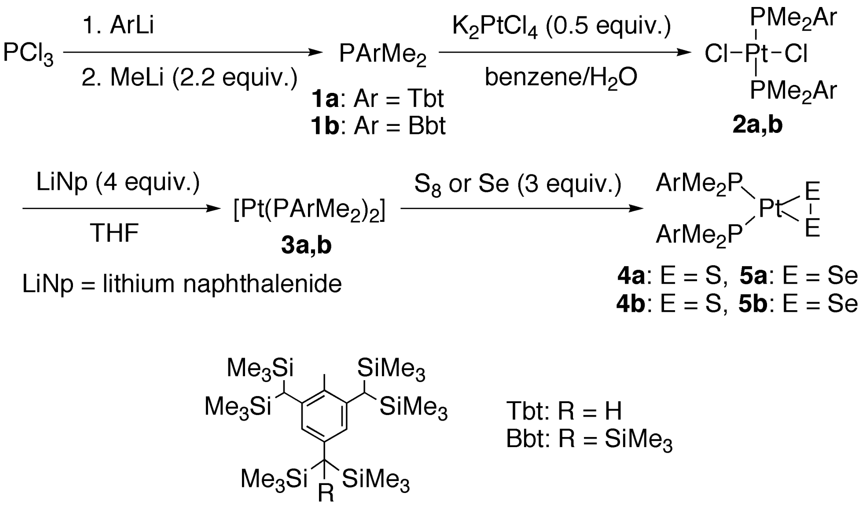
The chemistry of complexes having a diatomic chalcogen ligand has been of much interest from the viewpoints of not only their structure and reactivity but also their synthetic utility.[1] However, there have been few examples of mononuclear metal complexes of diatomic chalcogen, since sulfur and selenium ligands have a strong propensity for bridging metal atoms. To our knowledge, the disulfur and diselenium complexes of platinum remain unknown in contrast to the extensive studies on the dioxygen analogues. In addition, the larger PtE_n (n = 4, 5; E = S, Se) ring systems, e.g., $[Pt(S_5)_3(NH_4)_2]$,[2] $[Pt(S_4)(PPh_3)_2]$,[3] and $[Pt(Se_4)(dppe)]$ (dppe = 1,2-bis(diphenyl-phosphino)ethane),[4] and chalcogenido-bridged bimetallic complexes, e.g., $[Pt_2(\mu\text{-}E)_2(PPh_3)_4]$ (E = S, Se), have been extensively studied.[5]

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),[6] $[Tbt(R)MSe_2]$ (M = Si or Sn),[7] and $[TbtSbS_n]$ (n = 5, 7)[8] having an extremely bulky substituent, Tbt group. These results prompted us to develop a new phosphine ligand bearing a Tbt group, which should be useful 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 $[Pt(E_2)\{P(Ar)Me_2\}_2]$ (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.[9] The dynamic behavior of the novel dichalcogen complexes of platinum and their oxidation products in solution is also described.

RESULTS AND DISCUSSIONS

Bulky phosphine ligands **1** were readily prepared by the treatment of a THF solution of ArLi (Ar = Tbt, Bbt) 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*-$[PtCl_2\{P(Ar)Me_2\}_2]$ (**2a**,**b**), which were practically insoluble in common organic solvents except for halogenated solvent.



SCHEME 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{P(Ar)Me$_2$}$_2$] (**3a**: $\delta_P = 0.9$, $^1J_{PtP} = 3974$ Hz, **3b**: $\delta_P = 3.7$, $^1J_{PtP} = 3869$ Hz). 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$_2$){P(Ar)Me$_2$}$_2$] (**4a**,**b**) as purple crystalline solids together with ArMe$_2$P=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$_2$){P(Ar)Me$_2$}$_2$] (**5a**,**b**), the first platinum diselenium complexes, were also obtained as green crystalline solids when elemental selenium was used instead of elemental sulfur (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 (Figure 1 for **4b**).[1]

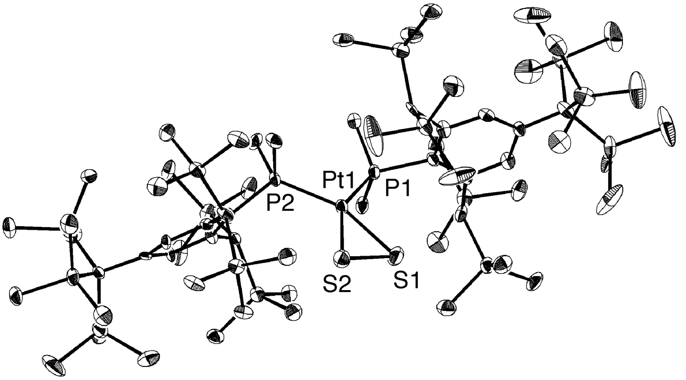
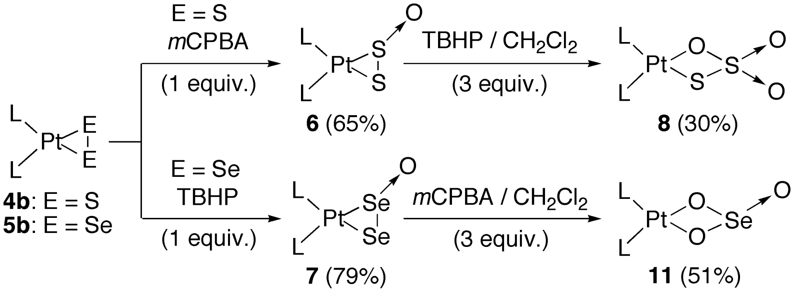


FIGURE 1 ORTEP drawing of [Pt(S_2){P(Bbt)Me_2}$_2$] (**4b**) with thermal ellipsoid plot (50% probability). Selected bond lengths (Å) and angles (°): Pt1–S1 2.348(3), Pt1–S2 2.337(3), S1–S2 2.077(3), Pt1–P1 2.271(2), Pt1–P2 2.265(3); S1–Pt1–S2 52.63(9), Pt1–S1–S2 63.41(11), Pt1–S2–S1 63.96(11), P1–Pt1–S1 102.07(9), P2–Pt1–S2 98.47(9), P1–Pt1–P2 106.87(8).

Crystallographic analysis showed that **4b** and **5b** are isomorphous; their geometries are very similar to each other. The two Bbt groups are situated in opposite positions with regard to the PtP_2 planes to decrease the steric congestion, and the central Pt atoms of **4b** and **5b** have tetracoordinated, planar geometries. 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)(PPh_3)$_2$], 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.

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){P(Bbt)Me_2}$_2$] (**6**) in 65% yield (Scheme 2).[11] The diselenium monoxide complex [Pt(Se_2O){P(Bbt)Me_2}$_2$] (**7**) also was obtained cleanly from **5b** in 79% yield by the use of an equimolar amount of *tert*-butyl hydroperoxide (TBHP).



*m*CPBA = *m*-chloroperbenzoic acid; TBHP = *tert*-butyl hydroperoxide; L = PBbtMe$_2$

SCHEME 2

An attempt at further oxidation of **6** with an excess of TBHP in CH_2Cl_2 yielded the platinum thiosulfato complex [Pt(S_2O_3){P(Bbt)Me$_2$}$_2$] (**8**) in 30% yield together with *trans*-[PtCl(OH){P(Bbt)Me$_2$}$_2$] (**9**) (14%) and phosphine oxide (**10**) (16%). The conversions of the S_2O ligand to the S_2O_3 ligand on platinum is 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_2O_2)(dppe)$_2$]$^+$ via the disulfur monoxide complex [Ir(S_2O)(dppe)$_2$]$^+$.[12] Complexes **8** and **9** showed satisfactory spectral and analytical data, and their molecular structures were finally determined by x-ray crystallographic analyses (Figure 2 for **8**).[10] In the

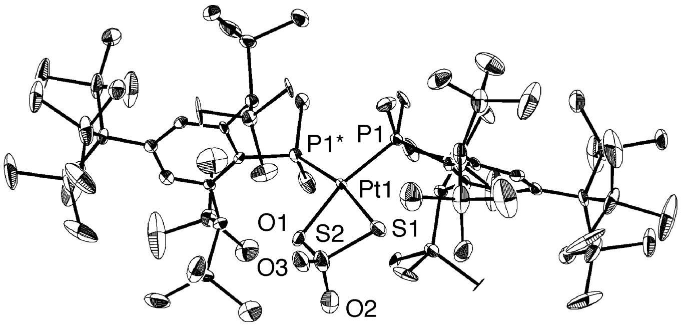


FIGURE 2 ORTEP drawing of [Pt(S_2O_3){P(Bbt)Me$_2$}$_2$] (**8**) with thermal ellipsoid plot (50% probability). Selected bond distances (Å) and angles (°): Pt1–O1 2.21(3), Pt1–P1 2.263(16), Pt1–S1 2.312(16), O1–S2 1.54(3), S1–S2 2.079(13), S2–O2 1.43(2), S2–O3 1.43(2); P1–Pt1–P1* 105.4(2), O1–Pt1–S1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

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.[13] 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 $[Pt(SeO_3)\{P(Bbt)Me_2\}_2]$ (**11**) together with **10** (16%) and a trace amount of **9** (6%). 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. Consequently, the coordination of the SeO_3 ligand can be considered to have the *O*-bound geometry rather than *Se*-bound one, and we describe the geometry of **11** as the chelating structure with *O*,*O* fashion.[14]

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 **4b**, for example, four methine protons of the *o*-bis(trimethylsilyl)methyl (disyl) groups resonate equally at 25°C ($\delta = 3.32$, Figure 3a). On cooling, the resonance was broadened and then separated into two signals below about −50°C. At −60°C, the resonances were observed at a much lower field ($\delta = 4.75$) and at a higher field ($\delta = 1.79$) than that at 25°C (Figure 3). 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 4.75 and 1.79 ppm should be assigned to the methine protons of the *o*-disyl groups. The separation into the two peaks is probably due to the restricted rotation of the P—C and/or P—Pt bonds leading to the non-equivalency of the four methine protons, and the lower shift at 4.75 ppm can be explained in terms of the existence of a considerable interaction (i.e., C—H···S interaction)[15] between the Pt-bonded sulfur and the methine hydrogens of the *o*-disyl group which are directed to the PtS_2 ring. As in the case of the *o*-disyl methine protons, a similar spectral change was observed for the protons of methyl groups bound to the phosphorus atoms, in the variable temperature NMR study. Thus, one broad singlet at 25°C ($\delta = 2.19$) was also separated into two regions below −20°C, and At −60°C, two signals were observed at higher field ($\delta = 1.90$) and at lower field ($\delta = 2.30$) relative to that observed at 25°C.

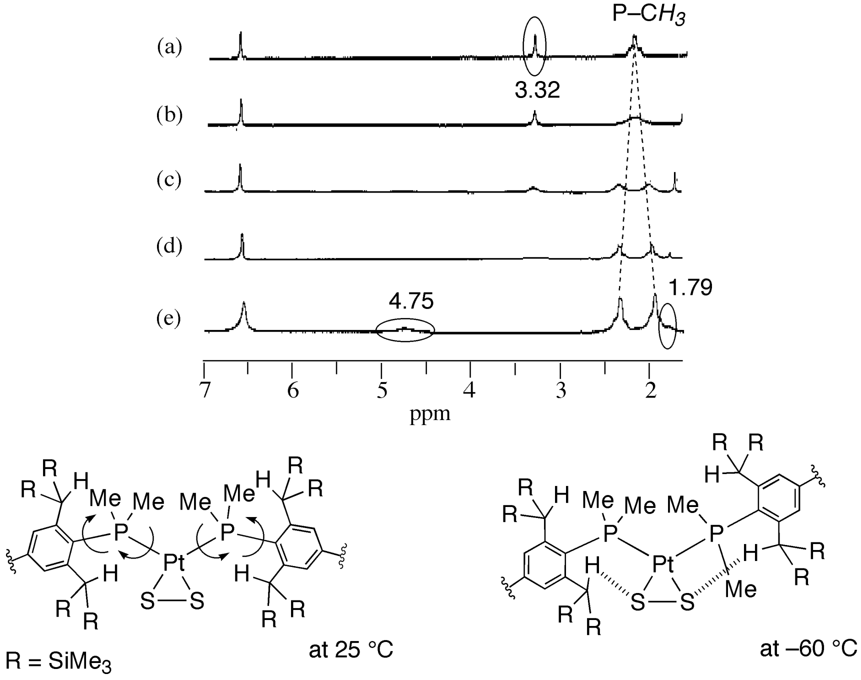


FIGURE 3 ^{1}H NMR spectra of **4b** measured in $CDCl_3$ at (a) 25°C, (b) 0°C, (c) −20°C, (d) −40°C, and (e) −60°C and proposed rotational behavior.

Similarly, **5b**, **8**, and **11** showed the peak separation in the ^{1}H NMR spectra at lowered temperature, which can be explained in terms of the restricted rotation of the P—C and/or P—Pt bonds.

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 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).[16] 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**).

EXPERIMENTAL

All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were dried by standard methods and freshly distilled prior to use. As typical examples, the experimental details for the series of compounds bearing P(Bbt)Me$_2$ ligands are shown below.

Disulfur Complex of Platinum [Pt(S$_2$){P(Bbt)Me$_2$}$_2$] (4b)

A THF suspension (3 mL) of *trans*-[PtCl$_2${P(Bbt)Me$_2$}$_2$] (**2b**; 123 mg, 0.075 mmol) was treated with a THF solution of lithium naphthalenide (0.82 M, 0.37 mL, 0.30 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{P(Bbt)Me$_2$}$_2$] (**3b**) thus obtained was cooled down to −78°C again and treated with S$_8$ (7.2 mg, 0.028 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 (3 mL). After the solution was treated with triphenylphosphine (39 mg, 0.15 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 **4b** as a pale purple crystalline solid (86 mg, 71%) along with BbtMe$_2$P=S (11 mg, 10%). **4b**: m.p. 162.3–163.5°C; ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ 0.16 (s, 72H), 0.21 (s, 54H), 2.19 (br s, 12H), 3.32 (s, 4H), 6.65 (s, 4H); ^{13}C{^{1}H} 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{^{1}H} NMR (120 MHz, CDCl$_3$, 25°C, 85% H$_3$PO$_4$): δ −32.2 ($^1J_{PtP} =$ 3909 Hz); ^{195}Pt{^{1}H} NMR (64 MHz, CDCl$_3$, 25°C, Na$_2$PtCl$_6$): δ −4983 (t, $^1J_{PPt} = 3909$ Hz); UV-vis (CH$_2$Cl$_2$): 366 nm (sh, $\varepsilon = 1100$), 559 nm

($\varepsilon = 110$); 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.

Diselenium Complex of Platinum [Pt(Se$_2$){P(Bbt)Me$_2$}$_2$] (5b)

To a THF solution of [Pt{P(Bbt)Me$_2$}$_2$] (**3b**), which were prepared from *trans*-[PtCl$_2${P(Bbt)Me$_2$}$_2$] (**2b**; 82 mg, 0.050 mmol) and lithium naphthalenide (1.06 M, 0.19 mL, 0.20 mmol) in THF (2 mL) using the above-mentioned method, was added Se powder (11.8 mg, 0.15 mmol) at −78°C. 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 **5b** as a green crystalline solid (60 mg, 70%) along with $TbtMe_2P{=}Se$ (13 mg, 17%). **5b**: m.p. 170.6–171.8°C; ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ 0.17 (s, 72H), 0.22 (s, 54H), 2.23 (br s, 12H), 3.33 (s, 4H), 6.64 (s, 4H);$^{13}C\{^1H\}$ 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, $e = 1700$), 465 nm (sh, $e = 120$), 633 nm ($e = 130$); 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.

Disulfur Monoxide Complex of Platinum [Pt(S$_2$O){P(Bbt)Me$_2$}$_2$] (6)

To a CH_2Cl_2 solution (10 mL) of [Pt(S$_2$){P(Bbt)Me$_2$}$_2$] (**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**: m.p. 175.0–176.5°C; ^1H NMR (300 MHz, $CDCl_3$): δ 0.13 (s, 18H), 0.14 (s, 18H), 0.15 (s, 18H), 0.18 (s, 18H), 0.22 (s, 54H), 1.94 (d,$^2J_{PH}$ = 7.5 Hz, 3H), 2.10 (d, $^2J_{PH}$ = 8.0 Hz, 3H), 2.14 (d, $^2J_{PH}$ = 8.2 Hz, 3H), 2.24 (d, $^2J_{PH}$ = 8.9 Hz, 3H), 3.06 (d, $^4J_{PH}$ = 2.5 Hz, 2H), 3.14 (d, $^4J_{PH}$ = 2.9 Hz, 2H), 6.68 (d, $^4J_{PH}$ = 3.1 Hz, 4H); $^{13}C\{^1H\}$ 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, ε = 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.

Diselenium Monoxide Complex of Platinum $[Pt(Se_2O)\{P(Bbt)Me_2\}_2]$ (7)

To a stirred solution of $[Pt(Se_2)\{P(Bbt)Me_2\}_2]$ (**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**: m.p. 158.2–159.5°C; ^1H NMR (300 MHz, $CDCl_3$): δ 0.12 (s, 36H), 0.13 (s, 18H), 0.17 (s, 18H), 0.20 (s, 54H), 1.99 (d,$^2J_{PH}$ = 7.5 Hz, 3H), 2.10 (d,$^2J_{PH}$ = 8.0 Hz, 3H), 2.14 (d,$^2J_{PH}$ = 8.2 Hz, 3H), 2.24 (d,$^2J_{PH}$ = 8.9 Hz, 3H), 3.06 (s, 2H), 3.18 (s, 2H), 6.66 (s, 4H); $^{13}C\{^1H\}$ 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 (ε = 1700); FAB

MS *m/z*: 1739 $(M)^+$, 1723 $(M\text{-O})^+$; Anal. Calcd for $C_{64}H_{146}OP_2PtSe_2Si_{14}$: C, 44.18; H, 8.46. Found: C, 44.27; H, 8.59.

Thiosulfito Complex of Platinum $[Pt(S_2O_3)\{P(Bbt)Me_2\}_2]$ (8)

To a stirred solution of $[Pt(S_2O)\{P(Bbt)Me_2\}_2]$ (**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 thiosulfito complex **8** as a pale yellow crystalline solid (50 mg, 30%) along with *trans*-$[PtCl(OH)\{P(Bbt)Me_2\}_2]$ (**9**) (23 mg, 14%) and phosphine oxide $BbtMe_2P{=}O$ (**10**) (23 mg, 16%). **8**: m.p. 220.6–221.1°C (decomp.); ^1H NMR (300 MHz, $CDCl_3$): δ 0.17 (s, 36H), 0.19 (s, 36H), 0.22 (s, 54H), 2.05 (d, $^2J_{PH} = 9.1$ Hz, 6H), 2.19 (d, $^2J_{PH} = 9.5$ Hz, 6H), 3.01 (s, 2H), 3.42 (s, 2H), 6.67 (d, $^4J_{PH} = 3.8$ Hz, 2H), 6.70 (d, $^4J_{PH} = 3.6$ Hz, 2H); $^{13}C\{^1H\}$ 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.

Selenito Complex of Platinum $[Pt(SeO_3)\{P(Bbt)Me_2\}_2]$ (11)

To a CH_2Cl_2 solution (10 mL) of $[Pt(Se_2O)\{P(Bbt)Me_2\}_2]$ (**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 selenito complex **11** (103 mg, 51%) as a pale yellow crystalline solid along with **9** (12 mg, 6%) and **10** (27 mg, 16%). **11**: m.p. 222.4–223.8°C (decomp.); ^1H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 72H), 0.20 (s, 54H), 1.98 (t, AA'X spin system, $1/2[{}^2J_{\mathrm{PH}} + {}^4J_{\mathrm{PH}}] = 9.3$ Hz, 12H), 3.49 (s, 4H), 6.66 (s, 4H); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75 MHz, $\mathrm{CDCl_3}$): δ 2.88 ($\underline{\mathrm{C}}\mathrm{H_3}$), 3.03 ($\underline{\mathrm{C}}\mathrm{H_3}$), 5.51 ($\underline{\mathrm{C}}\mathrm{H_3}$), 22.2 (br m, P—$\underline{\mathrm{C}}\mathrm{H_3}$), 22.32, 29.44 ($\underline{\mathrm{C}}\mathrm{H}$), 121.2 (m, AA′X spin system, $1/2[{}^1J_{\mathrm{PC}} + {}^3J_{\mathrm{PC}}] = 29.3$ Hz), 128.67 ($\underline{\mathrm{C}}\mathrm{H}$), 149.12, 151.01 (t, AA′X spin system, $1/2[{}^2J_{\mathrm{PC}} + {}^4J_{\mathrm{PC}}] = 4.5$ Hz); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (120 MHz, $\mathrm{CDCl_3}$): δ −41.7 ($^1J_{\mathrm{PtP}} = 3639$ Hz); $^{77}\mathrm{Se}\{^1\mathrm{H}\}$ NMR (57 MHz, $\mathrm{CDCl_3}$, 25°C): δ 1504; $^{195}\mathrm{Pt}\{^1\mathrm{H}\}$ NMR (64 MHz, $\mathrm{CDCl_3}$): δ −3176 (t, $^1J_{\mathrm{PPt}} = 3639$ Hz); HRMS m/z calcd for $\mathrm{C_{64}H_{146}O_3P_2PtSeSi_{14}}$: 1691.6330, found 1691.6316; Anal. Calcd for $\mathrm{C_{64}H_{146}O_3P_2PtSeSi_{14}}$: C, 45.40; H, 8.69. Found: C, 45.29; H, 8.67.

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[10] 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).

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