Unusual Oxidation of Dichalcogenido Complexes of Platinum

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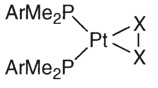
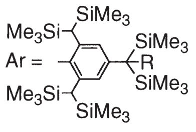
Novel platinum complexes having an oxochalcogenido ligand such as S_2O, Se_2O, S_2O_3, and SeO_3 were synthesized by the oxidation reactions of the overcrowded dichalcogenido platinum complexes $[(BbtMe_2P)_2PtX_2]$ (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl; X = S, Se).

Over the past few decades, the complexes having oxopolychalcogenido ligands, as well as polychalcogenido complexes, have attracted much interest not only in coordination chemistry but also in the biological and catalytic fields.[1] For example, the mononuclear S_2O complexes including two types, $L_nMSS(O)R$ and $L_n\overline{MSS}O$, have great possibility for the synthesis of thiosulfinate esters, which have exhibited important biological activities.[2] To our knowledge, the reported examples of the latter S_2O complexes are limited only to the metallacycles coordinated with the S_2O ligand in η^2-S,S fasion, and those complexes and analogous Se_2O complexes have been prepared via the oxidation of the corresponding disulfur and diselenium complexes.[3]

Meanwhile, we have recently succeeded in the synthesis of the first disulfur and diselenium complexes of platinum $[(ArMe_2P)_2PtX_2]$ (Ar = Tbt, Bbt; X = S, Se) by taking advantage of bulky phosphine ligands bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) or Bbt group.[4] Here, we report the investigation on the oxidation of the dichalcogenido platinum complexes $[(BbtMe_2P)_2PtX_2]$ (**1a**; X = S, **1b**; X = Se) leading to the formation of novel disulfur and diselenium monoxide complexes of platinum, and the further reactions of these monoxide complexes with an excess of oxidants giving unexpected thiosulfate (S_2O_3) and selenite (SeO_3) complexes.

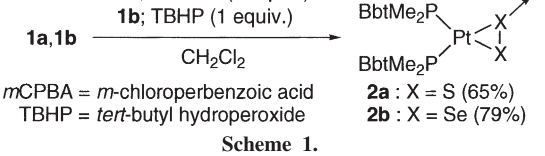


1a : Ar = Bbt, X = S
1b : Ar = Bbt, X = Se



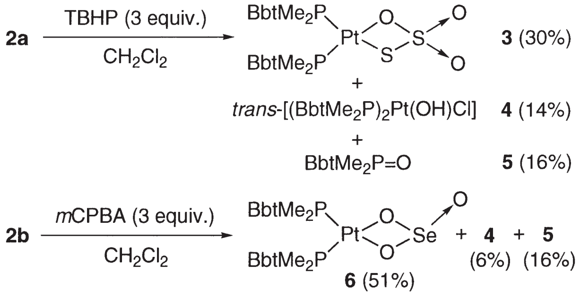
Tbt : R = H, Bbt : R = $SiMe_3$

The monooxidation of **1a** with an equimolar amount of *m*-chloroperbenzoic acid (*m*CPBA) in dichloromethane (CH_2Cl_2) completed at −20 °C within 2 h and gave $[(BbtMe_2P)_2PtS_2O]$ (**2a**) in 65% yield (Scheme 1). In the case of **1b**, however, the reaction with *m*CPBA was so complicated that the products could not be sufficiently purified and isolated. We found that *tert*-butyl hydroperoxide (TBHP) was a more appropriate oxidant than *m*CPBA for the monooxidation of **1b**, and $[(BbtMe_2P)_2PtSe_2O]$ (**2b**) was obtained cleanly from **1b** in 79% yield by the use of an equimolar amount of TBHP. The molecular structures of the novel S_2O[5] and Se_2O complexes of platinum (**2a**,**b**) were confirmed by mass spectrometry, elemental analysis, and NMR spectroscopy.[6]



Scheme 1.

Interestingly, an attempt at further oxidation of **2a** with an excess of TBHP in CH_2Cl_2 yielded not the expected S_2O_2 complex[7] but the platinum thiosulfate complex $[(BbtMe_2P)_2PtS_2O_3]$ (**3**) together with *trans*-$[(BbtMe_2P)_2Pt(OH)Cl]$ (**4**) and phosphine oxide (**5**) (Scheme 2).



Scheme 2.

This conversion of the S_2O ligand to the S_2O_3 ligand is in sharp contrast to the reported exhaustive oxidation of a disulfur complex of iridium $[(dppe)_2IrS_2]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) to the corresponding disulfur dioxide complex $[(dppe)_2IrS_2O_2]^+$ via the disulfur monoxide complex $[(dppe)_2IrS_2O]^+$.[8] Complexes **3** and **4** showed satisfactory spectral and analytical data,[9] and the molecular structure of **3** was finally determined by X-ray crystallographic analysis (Figure 1).[10] The platinum atom has essentially square-planar geometry and the S_2O_3 ligand is coordinated to the platinum with chelating in η^2-O,S fasion.[11] Formation of **3** is significantly dependent on the temperature rather than the quantity of oxidants. When **2a** was treated with an equimolar amount of TBHP below −10 °C, **2a** did not change even after a prolonged reaction time. On warming up to 10 °C, the reaction proceeded immediately to form a complex mixture with **3** being the major component (20% isolated yield). However, attempts to characterize and isolate the intermediates have been unsuccessful. The formation of complex **4** may be explained in terms of the reaction of some intermediate with CH_2Cl_2 used as solvent, since the reaction of **2a** with TBHP (3 equiv) in THF did not give **4**.

Surprisingly, further reaction of **2b** with an excess of *m*CPBA in CH_2Cl_2 yielded neither Se_2O_2 nor Se_2O_3 complex but the selenite complex $[(BbtMe_2P)_2PtSeO_3]$ (**6**)[12] together with **5** and a trace amount of **4**. The composition and structure of **6** were determined by HRMS, elemental analysis, and multinuclear NMR spectroscopy. The ^{31}P NMR spectrum of **6** shows one signal with the expected ^{195}Pt satellites ($\delta = -41.7$, $^1J_{PtP} = 3639$ Hz),

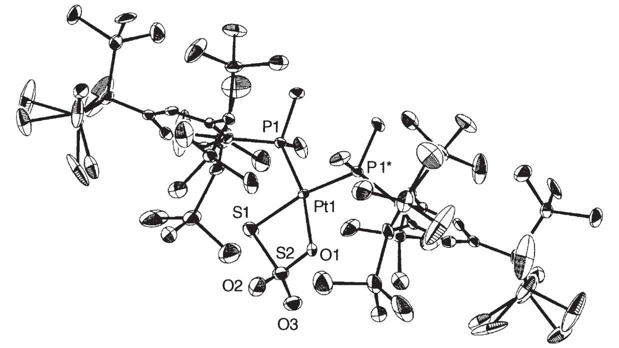


Figure 1. ORTEP drawing of **3** with thermal ellipsoid plot (50% probability). Selected bond distances (Å) and angles (°): Pt1–O1 2.21(3), Pt1–P1 2.263(16), Pt1–S1 2.312(16), O1–S2 1.54(3), S1–S2 2.079(13), S2–O2 1.43(2), S2–O3 1.43(2); P1–Pt1–P1* 105.4(2), O1–Pt1–S1 77.3(6), Pt1–O1–S2 98.1(15), Pt1–S1–S2 81.3(5), O1–S2–S1 101.4(10).

which are comparable with those of **1b** ($\delta = -44.1$, $^1J_{PtP} = 3865$ Hz), therefore, the $PtSeO_3$ moiety in **6** has presumably a mirror plane vertical to the PtP_2 plane as the $PtSe_2$ ring in the complex **1b**. In the ^{77}Se NMR spectrum, only one resonance was observed at lower field ($\delta = 1504$) than those of **2b** ($\delta = 689$, 1135) and **1b** ($\delta = 582$), although the satellite peaks due to the ^{77}Se–^{195}Pt couplings could not be found. The ^{195}Pt NMR signal was observed at $\delta = -3176$, but such a large low field shift in comparison to those of **2b** ($\delta = -4768$) is not observed for the conversion of **1b** ($\delta = -5030$) to **2b**. Since the ^{195}Pt resonance usually moves to lower field in the order of O > S > Se > Te for some platinum complexes having Group 16 elements as the coordinated atoms of the ligands,[13] coordination of the SeO_3 ligand in **6** should be considered to have the O-bound geometry rather than Se-bound one. On the basis of these results, we can describe the geometry of **6** as the structure with the chelating O,O-bound geometry.[14]

Thus, the S_2O and Se_2O complexes **2a**,**b** here obtained have shown different reactivities toward an excess of oxidant. Although the mechanism of both unusual reactions has been unclear at present, attempts to characterize and isolate the intermediates are currently in progress.

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References and Notes

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5 Very recently, Nakayama and Ishii et al. have synthesized the disulfur monoxide complex $[(PPh_3)_2PtS_2O]$ through the reaction of cyclic polysulfides *S*-oxide(s) with $[(PPh_3)_2Pt(C_2H_4)]$; M. Murata, A. Ishii, and J. Nakayama, at the 81st Annual Meeting of the Chemical Society of Japan, March 2002, Abst., No. 4B334.

6 **2a**: mp 175.0–176.5 °C; ^{1}H 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); $^{31}P\{^1H\}$ 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. **2b**: mp 158.2–159.5 °C; ^{1}H 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); $^{31}P\{^1H\}$ 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.

7 I.-P. Lorenz and J. Kull, *Angew. Chem., Int. Ed. Engl.*, **25**, 261 (1986).

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9 **3**: mp 220.6–221.1 °C (decomp.); ^{1}H 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); $^{31}P\{^1H\}$ 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. **4**: mp 178.8–180.4 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.12 (s, 18H), 0.16 (s, 18H), 0.18 (s, 18H), 0.19 (s, 18H), 0.25 (s, 27H), 0.26 (s, 27H), 1.78–1.96 (m, 12H), 2.48 (s, 1H), 2.73 (s, 2H), 3.16 (s, 1H), 4.00 (s, 1H), 6.65–6.74 (m, 4H); $^{31}P\{^1H\}$ 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. The existence of the chlorine atom in **4** was confirmed by X-ray fluorescence spectroscopy.

10 Crystallographic data for **3**: $C_{64}H_{146}O_3P_2PtS_2Si_{14}$, $M = 1678.22$, monoclinic, space group $C2/c$, $a = 39.77(2)$, $b = 9.320(5)$, $c = 23.870(13)$ Å; $\beta = 90.921(11)°$; $V = 8847(8)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.260$ g cm^{-3}, $\mu = 19.0$ cm^{-1}, $R_1 = 0.108$ ($I > 2\sigma(I)$), $wR_2 = 0.216$ (all data) for 7753 observed reflections and 477 variable parameters, $T = 93(2)$ K, GOF = 1.28. Since there is the disorder of two sets of PtS_2O_3 units, which are overlapped each other by the C_2 symmetry operation, with occupancies of 0.5 and 0.5, the structure of **3** was best solved as a molecular 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 three methyl carbons of the two trimethylsilyl group on the Bbt group are also disordered. In Figure 1, another part of the disoredered carbons and one PtS_2O_3 core are omitted to avoid confusion. All non-hydrogen atoms were refined anisotropically.

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12 **6**: mp 222.4–223.8 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 72H), 0.20 (s, 54H), 1.98 (t, AA'X spin system, $1/2[^2J_{PH} + {}^4J_{PH}] = 9.3$ Hz, 12H), 3.49 (s, 4H), 6.66 (s, 4H); $^{31}P\{^1H\}$ 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.

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