Isolation and Reaction of 1,2-Dithietan-3-one: Formation of Thiolato Thiocarboxylato Metal Complexes

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The reaction of 4,4-di-*tert*-butyl-1,2-dithietan-3-one with triphenylphosphine afforded 1,1-di-*tert*-butylthiiran-2-one (86%). The reaction of 4,4-di-*tert*-butyl-1,2-dithietan-3-one with phenylmagnesium bromide gave *S*-phenyl 2-*tert*-butyl-2-mercapto-3,3-dimethylbutanethioate in 83% yield. The reaction of 4,4-di-*tert*-butyl-1,2-dithietan-3-one with tetrakis(triphenylphosphine)palladium(0) gave square-planar complex in 84% yield, whose structure was determined by X-ray crystallographic analysis.

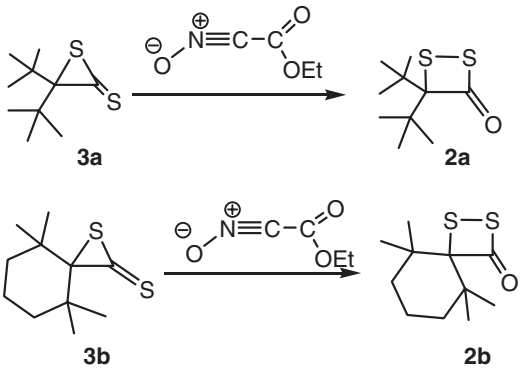
Three- and four-membered cyclic compounds containing two heteroatoms have been studied extensively.[1] Because of their unique structures and chemical reactivities, three- and four-membered rings containing an S–S bond have also received great attention from both experimental and theoretical perspectives.[2] 1,2-Dithietanes **1**, in particular, have stimulated fundamental theoretical and chemical interests.[1] Isolated examples of compounds bearing the 1,2-dithietane ring system are dithiatopazine **1a**, 3,4-diethyl-1,2-dithietane 1,1-dioxide **1b**, and sulfurane **1c**.[3–5] On the other hand, five-membered ring compounds containing an S–S bond, such as 1,2-dithiolan-3-ones and 1,2-dithiolan-3-one 1-oxides[6,7] are well known, which are of interest because of their chemical behavior and biological activities. We have also reported the synthesis of five-membered disulfide, 1,2-dithiolan-3-thione, which reacted with benzyne to afford spirocyclic 1,3-benzodithiol.[8] In a previous paper, we have communicated the isolation of 1,2-dithietan-3-ones **2**, which are four-membered analogs of **1a** and **1b**. (Chart 1).[9] In this paper, we would like to show full details of the isolation and reaction of **2**.

Results and Discussion

As shown in a preliminary communication,[10] 1,2-dithietan-3-one **2a** was synthesized by cycloaddition and cycloreversion of 3,3-di-*tert*-butylthiiran-2-thione (**3a**) with nitrile oxide generated from ethyl chlorooxyimidoacetate and triethylamine in 82% yield (Scheme 1). 5,5,9,9-Tetramethyl-1,2-dithiaspiro-[3,5]non-3-one (**2b**) was also synthesized in 80% yield.

Synthesis of α-Thiolactone 5. According to Schaumann and Behrens, α-thiolactones **4** were synthesized by oxidation of di-*tert*-butyl thioketene with nitrones such as 5,5-dimethyl-1-pyrroline *N*-oxide.[11] However, the scope and limitation were not described. Nicolaou et al. reported that the reaction of dithiatopazine **1a** with triphenylphosphine gave an episulfide and triphenylphosphine sulfide.[4] Thus, we attempted the synthesis of α-thiolactone **4a** from 1,2-dithietan-3-one **2a** and triphenylphosphine. One sulfur atom in **2a** was eliminated by treatment with triphenylphosphine in $CDCl_3$ at room temperature for 4 days to give 3,3-di-*tert*-butylthiiran-2-one (**4a**) in 82% yield along with triphenylphosphine sulfide (Scheme 2). Thus, a completely different method for the synthesis of α-thiolactone was achieved.

Thermal Behavior of 1,2-Dithietan-3-one. Nicolaou et al. reported that dithiatopazine **1a** was thermally decomposed when heated in xylene at 140 °C for 1 h to give an olefinic compound and diatomic sulfur.[4] To compare the stability of



Scheme 1.

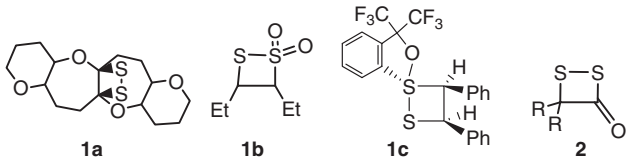
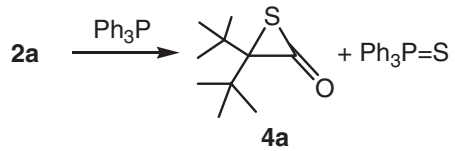


Chart 1.



Scheme 2.

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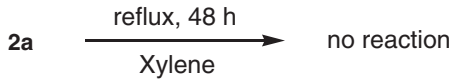
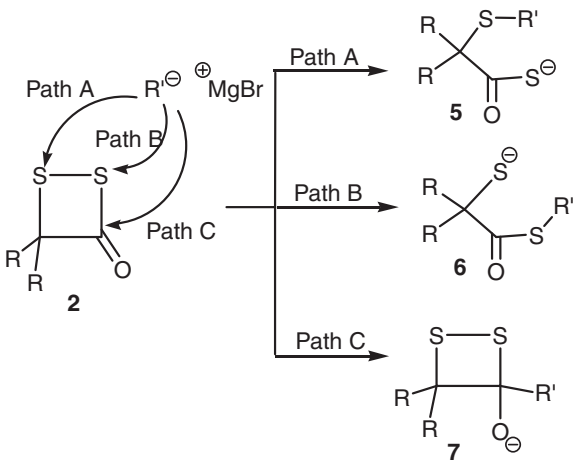


Scheme 3.



Scheme 4.

dithiatopazine with that of **2a**, **2a** was refluxed in xylene-d_{10} at 140 °C for 2 days. Surprisingly, **2a** was recovered unchanged, suggesting that **2a** was more stable than **1a** (Scheme 3). Since sublimation of **2a** was observed at 160 °C, the thermal stability of dithiatopazine and **2a** was quite different.

Reaction of 1,2-Dithietan-3-one 2 with Grignard Reagents. Unusual thermal stability of **2** prompted us to investigate reactivity of **2a** toward a nucleophile. To confirm the reactivity of **2** toward nucleophiles, the reaction of **2a** with Grignard reagents was carried out. Three pathways are plausible in the reaction of 1,2-dithietan-3-one **2** with Grignard reagents (Scheme 4).

When **2a** was reacted with phenylmagnesium bromide, only one isomer was obtained. In the ^{1}H NMR spectrum, signals of methyl and aromatic protons resonated at δ 1.32 (18H) and 7.43 (5H), respectively. In the ^{13}C NMR spectrum, signals of C=O and quaternary ring carbon resonated at δ 203.27 and 80.53, respectively. In the IR spectrum, a band assignable to C=O was observed at 1677 cm^{-1}. The above results indicate that the product is not isomer **7** but isomers **5** or **6**. Finally, the structure of the product was determined by X-ray crystallographic analysis (Figure 1). The obtained product was *S*-phenyl 2-*tert*-butyl-2-mercapto-3,3-dimethylbutanethioate (**6a**). *S*-Methyl 2-*tert*-butyl-2-mercapto-3,3-dimethylbutanethioate (**6b**) and *S*-propyl 2-*tert*-butyl-2-mercapto-3,3-dimethylbutanethioate (**6c**) were also synthesized in a similar manner (Scheme 5). In addition, the reaction of **2a** with methyllithium also afforded butanethioate **6b** in 77% yield.

In order to elucidate the electronic structure and reactivity of compound **2**, we carried out theoretical calculations for 4,4-di-*tert*-butyl-1,2-dithietan-3-one (**2a**). In the structural optimization of the model molecule using the B3LYP method,[12] one local minimum of **2a** was found with geometries similar to the crystalline structure of **2b**. The composition of the LUMO orbitals of **2a** is depicted in Figure 2. It was found that the LUMO is located on σ^*-orbitals of the sulfur–sulfur bond of

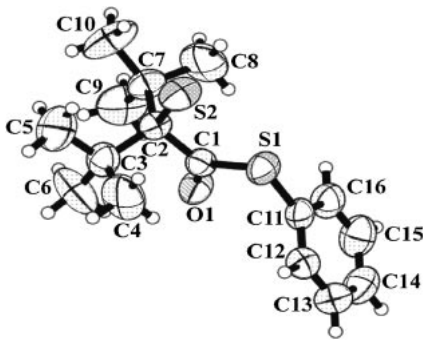
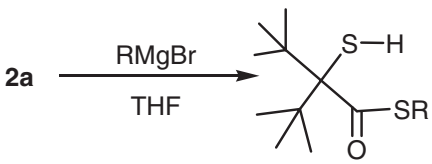


Figure 1. ORTEP drawing of compound **6a**. Selected bond lengths [Å] and angles [°] of **6a**. S1–C11 1.776(2), S1–C1 1.8003(17), S2–C2 1.8506(17), O1–C1 1.200(2), C1–C2 1.549(2); C11–S1–C1 98.90(8), O1–C1–C2 122.46(15), O1–C1–S1 120.63(13), C2–C1–S1 116.91(11), C1–C2–S2 109.03(11).



Scheme 5.

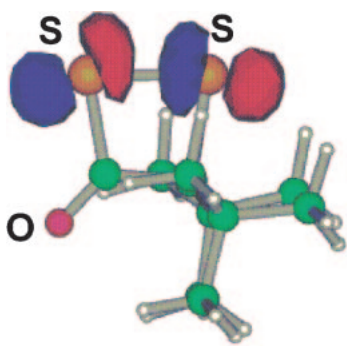
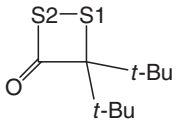


Figure 2. Plot of the LUMO orbitals of **2a** at the B3LYP/6-311+G(d,p) level.

2a, indicating the disulfide moiety of **2a** is very highly reactive toward nucleophiles. Mulliken atomic charges of **2a** showed the sulfur atom at the 2-position is more positive than the 1-position (Table 1). Additionally, the sulfur atom at the 2-position is less bulky than that at the 3-position.

To compare thermal stability of **5** and **6**, total energies (corrected with zero-point energies) of 2-methyl-2-(methylthio)propanethioic acid (**5d**) and *S*-methyl 2-mercapto-2-methylpropanethioate (**6d**) were calculated at the B3LYP/6-31G(d) level (Chart 2).[12] The result showed that **6d** was found to be 8.90 kJ mol^{-1} more stable than **5d** at the ground-state S_0. Thus, the regioselective formation of compounds **6a–6c** in the reactions of **2a** with Grignard reagents can be supported by the theoretical calculations of **2a** together with a consideration for bulkiness of the *tert*-butyl groups of **2a** (Scheme 6).

Table 1. Mulliken Atomic Charges of **2a**



Basis set	S1	S2
6-31G(d)	−0.015	+0.082
6-311+G(d,p)	−0.654	+0.037

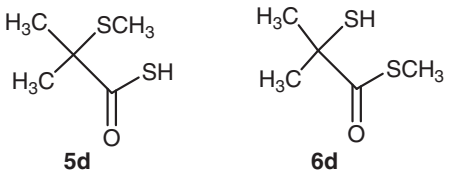
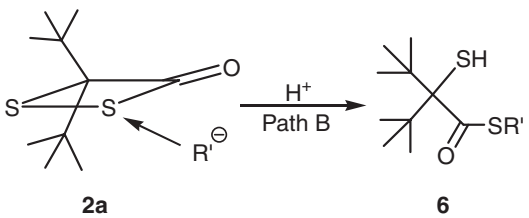
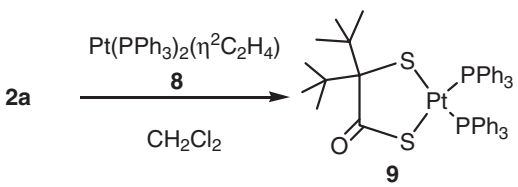


Chart 2.



Scheme 6.



Scheme 7.

Synthesis of Platinum and Palladium Complexes from 1,2-Dithietan-3-one. In recent years, several sulfur–platinum complexes have been synthesized.[13] Previously, we have reported the reaction of α-dithiolactone **3a** with (η^2-ethylene)bis(triphenylphosphine)platinum(0) (**8**) afforded the corresponding dithiolato–platinum complex.[14] Although isolated examples of dithiooxalato–platinum complexes and their analogs are well known,[15] to the best of our knowledge, there are no reports on the isolation of thiolato thiocarboxylato–platinum complex. Thus, we attempted the synthesis of thiolato thiocarboxylato–platinum complex by reacting 1,2-dithietan-3-one **2a** with **8**. Treatment of **2a** with **8** at room temperature resulted in the formation of thiolato thiocarboxylato–platinum complex **9** in 94% yield (Scheme 7).

Signals of methyl and aromatic protons appeared at δ 1.15 (s, 18H), 7.10–7.52 (m, 30H) in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum, signals of C=O and quaternary ring carbon of **9** resonated at δ 221.9 ($J_{C-P} = 20.7$ Hz) and 71.4 ($J_{C-P} = 4.2$ Hz), respectively. The ^{31}P NMR spectrum of **9** showed two signals that resonated at δ 19.3 ($J_{Pt-P} = 2846$ Hz, $J_{P-P} = 27$ Hz) and 26.0 ($J_{Pt-P} = 3013$ Hz, $J_{P-P} = 27$ Hz). In the ^{195}Pt NMR spectrum, the signal representative of **9** was observed at δ −4745 ($J_{Pt-P} = 2846$ and 3013 Hz). Generally,

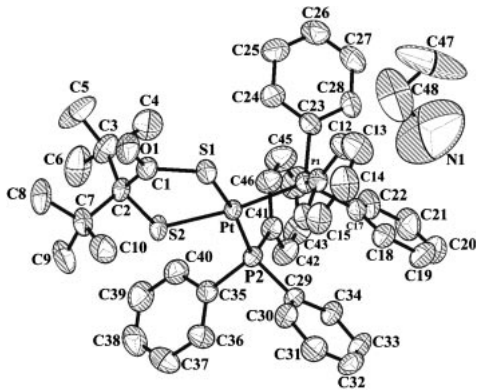
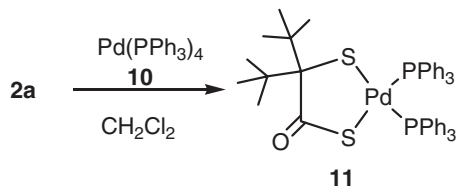


Figure 3. ORTEP drawing of complex **9**. Selected bond lengths [Å] and angles [°] of **9**. Pt1–P2 2.2870(9), Pt1–S2 2.3028(9), Pt1–S1 2.3058(9), Pt1–P1 2.3110(9), S1–C1 1.764(4), S2–C2 1.852(4), O1–C1 1.212(4), C1–C2 1.535(5); P2–Pt1–S2 88.31(3), S2–Pt1–S1 85.95(3), P2–Pt1–P1 97.08(3), S1–Pt1–P1, 89.23(3), C1–S1–Pt1 108.43(12), C2–S2–Pt1 109.52(12), O1–C1–C2 122.5(3), O1–C1–S1 116.3(3), C2–C1–S1 121.2(2), C1–C2–S2 111.0(2).



Scheme 8.

^{195}Pt NMR signals of dithiolato–platinum complexes and their analogs were observed in the range of δ −4400– −5060.[15] The chemical shifts of the above complexes are similar to that of **9**, indicating that **9** is a Pt^{II} complex. X-ray crystallographic analysis of **9** was carried out. In the ORTEP drawing of **9** shown in Figure 3, the crystal contained one molecule of acetonitrile (recrystallization solvent) per one molecule of **9**. The sum of bond angles of P2–Pt1–S2, S2–Pt1–S1, P2–Pt1–P1, and S1–Pt1–P1 is ca. 360°, suggesting that complex **9** has planar structure (also see Supporting Information; Table S14).

To compare the reactivity of palladium with that of platinum toward 1,2-dithietan-3-one **2a**, the reaction of **2a** with tetrakis(triphenylphosphine)palladium(0) (**10**) was carried out. Treatment of **2a** with **10** at room temperature resulted in the formation of thiolato thiocarboxylato–palladium complex **11** in 84% yield (Scheme 8).

Signals of methyl and aromatic protons appeared at δ 1.15 (s, 18H), and 7.12–7.47 (m, 30H) in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum, signals of C=O and the quaternary ring carbon of **11** resonated at δ 220.27 ($J_{C-P} = 25.1$ Hz) and 75.8 ($J_{C-P} = 6.7$ Hz), respectively. The ^{1}H and ^{13}C NMR data of **11** are similar to those of platinum complex **9**. The ^{31}P NMR spectrum of **11** showed two signals that resonated at δ 24.5 ($J_{P-P} = 52$ Hz) and 32.6 ($J_{P-P} = 52$ Hz). Finally, the structure of **11** was determined by X-ray crystallographic analysis. In the ORTEP drawing of **11** shown in Figure 4, the crystal contained one molecule of acetonitrile (recrystallization solvent) per one molecule of **11**. The sum of bond angles of S2–Pd1–P2, S1–

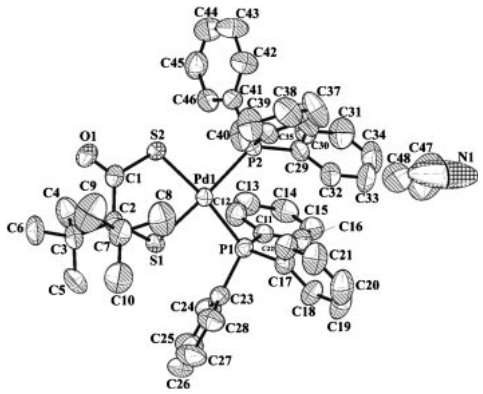


Figure 4. ORTEP drawing of complex **11**. Selected bond lengths [Å] and angles [°] of **11**. Pd1–S1 2.2888(11), Pd1–S2 2.2970(11), Pd1–P1 2.3170(10), Pd1–P2 2.3547(11), S1–C2 1.858(4), S2–C1 1.766(4), C1–O1 1.212(5), C1–C2 1.531(6); S1–Pd1–S2 85.43(4), S1–Pd1–P1 87.88(4), S2–Pd1–P2 89.79(4), P1–Pd1–P2 97.56(4), C2–S1–Pd1 110.29(14), C1–S2–Pd1 109.00(15), O1–C1–C2 122.5(4), O1–C1–S2 116.6(4), C2–C1–S2 121.0(3), C1–C2–S1 110.2(3). $R = 0.0497$, $wR = 0.1465$.

Pd1–S2, P1–Pd1–P2, and S1–Pd1–P1 is ca. 360°, suggesting that complex **11** has planar structure (also see Supporting Information; Table S14).

The bond lengths and angles of the five-membered ring of **9** are similar to those of **11**. The bond lengths of Pt–P (2.2870 and 2.3110 Å) in **9** are shorter than those of Pd–P (2.3170 and 2.3547 Å) in **11**.

In summary, synthesis of α-thiolactone **4a** by reacting 1,2-dithietan-3-one **2a** with triphenylphosphine was achieved. The reaction of **2a** with Grignard reagents gave 2-mercapto-2-methylpropanethioates **6**. Reaction of **2a** with (η^2-ethylene)-bis(triphenylphosphine)platinum(0) (**8**) gave a novel thiolato thiocarboxylato–platinum complex **9** in high yield. Thiolato thiocarboxylato–palladium complex **11** was obtained in a similar manner.

Experimental

General. All chemicals were obtained from commercial suppliers and were used without further purification. Analytical TLC was carried out on precoated plates (Merck silica gel 60, F254) and flash column chromatography was performed on silica (Merck, 70–230 mesh). NMR spectra (^{1}H at 400 MHz, ^{13}C at 100 MHz, ^{31}P at 162 MHz, and ^{195}Pt at 86 MHz) were recorded in $CDCl_3$, and chemical shifts are expressed in ppm relative to internal TMS for ^{1}H and ^{13}C, and external Na_2PtCl_6 (D_2O) for ^{195}Pt NMR. Melting points were uncorrected. Synthesis of 1,2-dithietan-3-one **2a** and α-thiolactone **4a** was shown in a previous communication.

Synthesis of 1,2-Dithietan-3-one 2b. 1,2-Dithietan-3-one **2b** was synthesized in a similar manner according to the previous communication.[10] To a solution of **3b** (0.086 g, 0.40 mmol) and ethyl chlorooxyimidoacetate (0.066 g, 0.43 mmol) in THF (1.0 mL) was added a solution of triethylamine (0.048 g, 0.48 mmol) in THF (1.0 mL) in one portion at room temperature. After being stirred for 2 h, the reaction mixture was filtered and evaporated to give yellow oily crystals, which were chromatographed over silica gel by elution with hexane to give pure **2b** (0.078 g, 0.32 mmol). **2b**: yellow crystals: mp 100–105 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.10 (s, 6H), 1.31 (s, 6H), 1.47–1.61 (m, 4H), 1.73–1.79 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.20, 26.10, 29.25, 37.86, 38.90, 114.14, 193.94. IR $\nu = 1724\,cm^{-1}$ (C=O). UV–vis (hexane): λ_{max} (ε) 292.5 (711), 398.0 (106). Anal. Calcd for $C_{11}H_{18}OS_2$: C, 57.35; H, 7.87%. Found: C, 57.04; H, 7.80%. HRMS Calcd for $C_{11}H_{18}OS_2$ (M^+), 230.0799; Found 230.0822.

Reaction of 2a with Phenylmagnesium Bromide. To a solution of **2a** (0.055 g, 0.25 mmol) in benzene was added phenylmagnesium bromide in THF complex (1.0 M) (0.29 mL, 0.29 mmol) and stirred for 1 h. After being washed with water, the reaction mixture was evaporated to give a pale yellow oil, which was chromatographed over silica gel by elution with hexane to give pure **6a** (0.061 g, 0.20 mmol). **6a**; colorless crystals; mp 52–58 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.32 (s, 18H), 2.34 (s, 1H), 7.35–7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 30.91, 42.38, 80.53, 129.40, 129.40, 132.33, 134.84, 203.27; IR $\nu = 1676\,cm^{-1}$ (C=O); Anal. Calcd for $C_{16}H_{24}OS_2$: C, 64.82; H, 8.16%. Found: C, 64.80; H, 7.89%.

X-ray crystal data and structure refinement for **6a**. Crystal data for $C_{16}H_{24}OS_2$. FW 296.47, Monoclinic, space group: $P2_1/c$, $a = 6.8289(17)$ Å, $b = 15.395(4)$ Å, $c = 16.041(4)$ Å, $\alpha = 90°$, $\beta = 94.953(3)°$, $\gamma = 90°$, $V = 1680.2(7)$ Å^3, $Z = 4$, $D_{calcd} = 1.172\,Mg\,m^{-3}$, μ (Mo Kα) $= 0.414\,mm^{-1}$, the final R and wR were 0.0474 and 0.1354, respectively, using 9657 reflections.

6b; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.25 (s, 18H), 2.17 (s, 4H, Me + SH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.07, 30.71, 41.91, 79.87, 205.04; IR $\nu = 1667\,cm^{-1}$ (C=O); Anal. Calcd for $C_{11}H_{22}OS_2$: C, 56.36; H, 9.46%. Found: C, 56.64; H, 9.24%.

6c; colorless crystals; mp $\leq$30 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.26 (s, 18H), 1.27 (s, 3H), 1.29 (s, 3H), 2.14 (s, 1H), 3.33–3.40 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.58, 30.87, 36.96, 42.10, 79.64, 204.41; IR $\nu = 1661\,cm^{-1}$ (C=O); Anal. Calcd for $C_{13}H_{26}OS_2$: C, 59.49; H, 9.98%. Found: C, 59.15; H, 9.95%.

Synthesis of Platinum Complex 9. To a solution of **2a** (0.011 g, 0.050 mmol) in dichloromethane (2 mL) was added (η^2-ethylene)bis(triphenylphosphine)platinum(0) (**8**) (0.037 g, 0.050 mmol). After stirring for 10 min, the reaction mixture was evaporated to give a black-yellow solid. The residue was recrystallized from acetonitrile–chloroform (2:1) to give **9** (0.044 g, 0.047 mmol). Compound **9**; yellow crystals; mp 266–272 °C (dec.); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.15 (s, 18H), 7.10–7.52 (m, 30H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 30.51, 43.25 ($J_{P-C} = 18.3$ Hz), 71.40 ($J_{P-C} = 4.2$ Hz), 127.66 (*meta*-Ph, $J_{P-C} = 10.4$ Hz), 127.97 (*meta*-Ph, $J_{P-C} = 10.4$ Hz), 129.84 (*ipso*-Ph, $J_{P-C} = 54.9$ Hz), 130.44–130.46 (br, *para*-Ph), 131.02 (*ipso*-Ph, $J_{P-C} = 54.6$ Hz), 134.78–135.52 (m, *ortho*-Ph), 221.90 ($J_{Pt-C} = 20.7$ Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 19.3 ($J_{Pt-P} = 2846$ Hz, $J_{P-P} = 27$ Hz), 26.0 ($J_{Pt-P} = 3013$ Hz, $J_{P-P} = 27$ Hz); ^{195}Pt NMR ($CDCl_3$, 86 MHz, Na_2PtCl_6): δ −4745 ($J_{Pt-P} = 2846$, 3011 Hz); IR $\nu = 1090$ (S=O), 1607 (C=O), and 424 (Pt–S) cm^{-1}; Anal. Calcd for $C_{46}H_{48}OP_2PtS_2 \cdot H_2O$: C, 57.79; H, 5.27%. Found: C, 57.65, H, 4.98%. Single crystals of **9** were recrystallized from its acetonitrile solution.

X-ray crystallographic data for **9**: crystal data for $C_{48}H_{51}NOP_2S_2Pt$. FW 979.05, Triclinic, space group: $P\bar{1}$, $a = 10.9455(4)$, $b = 12.8134(5)$, $c = 18.0138(7)$ Å, $\alpha = 91.4058(4)°$, $\beta = 107.0700(4)°$, $\gamma = 114.2731(4)°$, $V = 2170.84(14)$ Å^3, $Z = 2$, $D_{calcd} = 1.498\,Mg\,m^{-3}$, μ (Mo Kα) $= 0.414\,mm^{-1}$, the final R and wR were 0.0243 and 0.0738, respectively, using 25867 reflections.

Synthesis of Palladium Complex 11. To a solution of **2a** (0.022 g, 0.10 mmol) in dichloromethane (2 mL) was added tetrakis(triphenylphosphine)palladium(0) (**10**) (0.037 g, 0.050 mmol). After stirring for 10 min, the reaction mixture was evaporated to give a black-yellow solid. The residue was recrystallized from acetonitrile–chloroform (2:1) to give **11** (0.044 g, 0.047 mmol). **11**; reddish yellow crystals; mp 211.0–222.2 °C (dec.); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.16 (s, 18H), 7.16–7.47 (m, 30H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 30.63, 42.84, 75.84 (J_{P-C} = 6.7 Hz), 127.89 (*meta*-Ph, J_{P-C} = 10.4 Hz), 128.24 (*meta*-Ph, J_{P-C} = 10.4 Hz), 130.31 (*ipso*-Ph, J_{P-C} = 43.9 Hz), 130.36–130.39 (br, *para*-Ph), 131.46 (*ipso*-Ph, J_{P-C} = 40.9 Hz), 134.76 (*ortho*-Ph, J_{P-C} = 12.3 Hz), 135.07 (*ortho*-Ph, J_{P-C} = 12.3 Hz), 220.27; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.5 (J_{P-P} = 52.2 Hz), 32.6 (J_{P-P} = 52.2 Hz); IR ν = 1607 (C=O). Anal. Calcd for $C_{46}H_{48}OP_2PdS_2 \cdot H_2O$: C, 63.70; H, 5.81%. Found: C, 63.40, H, 5.63%. Single crystals of **11** were obtained from its acetonitrile solution.

X-ray crystallographic data for **11**: crystal data for $C_{48}H_{51}NOP_2PdS_2$. FW 890.36, Triclinic, space group: $P\bar{1}$, a = 10.9854(10) Å, b = 12.8425(11) Å, c = 18.0120(16) Å, α = 91.4570(10)°, β = 107.0700(10)°, γ = 114.2710(10)°, V = 2183.1(3) Å^3, Z = 2, D_{calcd} = 1.354 Mg m^{-3}, μ (Mo Kα) = 0.414 mm^{-1}, the final R and wR were 0.0497 and 0.1465, respectively, using 26182 reflections.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre. Deposition numbers CCDC-726799 for compound **6a**, and CCDC-726800 for Pt complex **9**, and CCDC-726801 for Pd complex **11**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information

Bond lengths and bond angles of **2b**, **6a**, **9**, and **11**. Theoretically optimized coordinate of **2a**. Observed and calculated structural parameters of **2a** and **2b**. Distance from a least-squares plane of complex **9** and **11**. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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