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Reaction of 3,3-di-*tert*-butylthiirane-2-thione *S*-oxide (α-dithiolactone *S*-oxide): synthesis of thiolato sulfinato-platinum and palladium complexes

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Abstract—Thermolysis of 3,3-di-*tert*-butylthiirane-2-thione *S*-oxide **4** gave di-*tert*-butyl ketone **5** and carbon disulfide (CS_2). Treatment of α-dithiolactone *S*-oxide **4** with excess *m*-CPBA or triphenylphosphine gave di-*tert*-butylthioketene *S*-oxide **3** almost quantitatively. Treatment of **4** with (η^2-ethylene)bis(triphenylphosphine)platinum(0) **13** or tetrakis(triphenylphosphine) palladium **17** resulted in the formation of thiolato sulfinato–platinum complex **15** or palladium complex **18**, respectively. The structure of complex **15** was determined by X-ray crystallographic analysis.

1. Introduction

Sulfines (**1**) (thioketone *S*-oxide) belong to a class of heterocumulenes, and are synthesized by oxidizing thioketone with peracid,[1] ozone,[1d,2] or singlet oxygen.[3] The reactions of sulfines **1** with thioketones,[4] alkenes,[5] acetylenes,[6] dienes,[7] nucleophiles,[8] metal complexes,[9] or thiation reagent[10] are well known. Recently, we have reported the synthesis of 3,3-di-*tert*-butylthiirane-2-thione (**2**) from di-*tert*-butylthioketene *S*-oxide (**3**)[11] with Lawesson reagent (LR).[12] Oxidation of **2** with *m*-chloroperoxybenzoic acid (*m*-CPBA) gave 3,3-di-*tert*-butylthiirane-2-thione *S*-oxide (**4**), another type of sulfine, the structure of which was determined by X-ray crystallographic analysis (Chart 1).[12a] It is interesting to compare the reactivity of **4** with that of normal sulfines. Herein, we describe the reaction of **4** and the isolation of platinum and palladium complexes from **4**.

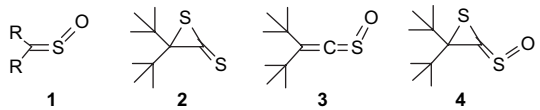
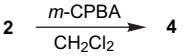


Chart 1.

2. Results and discussion

2.1. Thermolysis of 4

α-Dithiolactone *S*-oxide **4** was synthesized by reacting **2** with *m*-CPBA (1.2 equiv) (Scheme 1).[12] Compound **4** left in $CDCl_3$ at room temperature for 1 day was recovered unchanged. To confirm its thermal stability, **4** was refluxed in $CDCl_3$, which resulted in the formation of di-*tert*-butyl ketone (**5**) and carbon disulfide (CS_2) in almost quantitative yield. When refluxed in toluene-d_8, **4** was decomposed within 30 min. Pushkara Rao and Ramamurthy described that the thermolysis or photolysis of sulfines **1** gave the corresponding ketones and elemental sulfur.[13] Although they stated that the phototransformation might proceed through oxathiirane intermediates, no explanation was given for the thermolysis of **1**, suggesting that the reaction mechanism for the thermolysis of **1** is unclear. Thus, we attempted to elucidate the reaction mechanism for the thermolysis of sulfine **1**. The rate of thermolysis of **4** was monitored by ^{1}H NMR spectroscopy, and a first-order reaction with a rate constant of 4.82×10^{-2} min^{-1} at 353 K in toluene-d_8 was observed. Variable temperature NMR spectroscopy over the range of 333–363 K with toluene-d_8 as solvent was used to obtain activation parameters $\Delta H^{\ddagger}$=82.6 kJ mol^{-1} and



Scheme 1.

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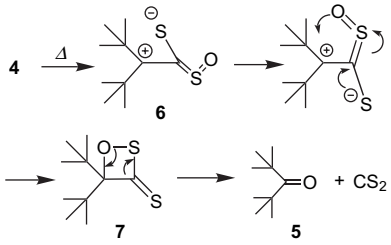
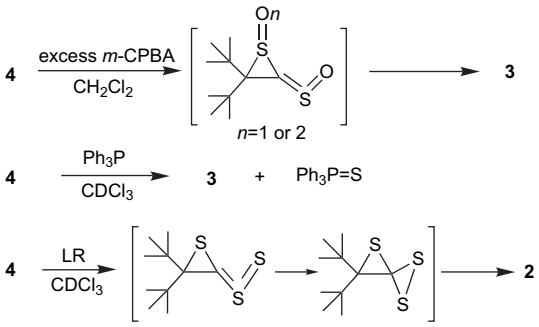
$\Delta S^{\ddagger}=-71.6\ \mathrm{J\,K^{-1}\,mol^{-1}}$. The rate of thermolysis of **4** in CD_3CN was lower than that in toluene-d_8. The above result and the negative entropy of activation might be an indication of the presence of a rigid cyclic intermediate **7** that was responsible for the decomposition of **4**. Presumably, the initially formed **7** via ionic intermediate **6** was further decomposed to give di-*tert*-butyl ketone **5** and CS_2 (Scheme 2).



Scheme 2.

2.2. Reaction of 4

The oxidation of **4** with excess *m*-CPBA gave **3** almost quantitatively (Scheme 3). Presumably, SO or SO_2 was further extruded from the initially formed episulfide *S*-oxide or *S*,*S*-dioxide to give **3**. Schaumann and Behrens reported that the oxidation of α-thiolactone afforded the corresponding ketene, the intermediate of which might be episulfide *S*-oxide.[14] The present result is similar to that of Schaumann and Behrens. Desulfurization of **4** by triphenylphosphine in refluxing $CDCl_3$ gave **3** in almost quantitative yield along with triphenylphosphine sulfide. The ring strain of the episulfide led to the elimination of the sulfur of **4**. The reaction of **4** with LR at room temperature afforded corresponding **2**, suggesting that the initially formed thiosulfine was further isomerized to give dithiirane, the sulfur atom of which was extruded to give **2**.



Scheme 3.

We have previously described that the reactions of **2** with dimethyl acetylenedicarboxylate (DMAD) (**8**) or benzyne (**9**) afforded 1,3-dithioles (**10a**) or (**10b**) in good yields, respectively (Chart 2).[12] To compare the reactivity of **2** with that of **4**, we reacted **4** with DMAD **8** (Scheme 4). When **4** and **8** in $CDCl_3$ were refluxed for 1 day, di-*tert*-butyl ketone **5** was obtained, and no cycloadduct (**11**) was detected by ^1H NMR spectroscopy of the crude mixture. Similarly, cycloaddition did not take place on treatment of **4** with benzyne **9**, which was generated by reacting *o*-trimethylsilylphenyl trifluoromethanesulfonate (**12**) with tetrabutylammonium

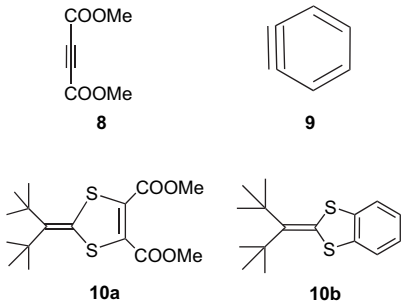
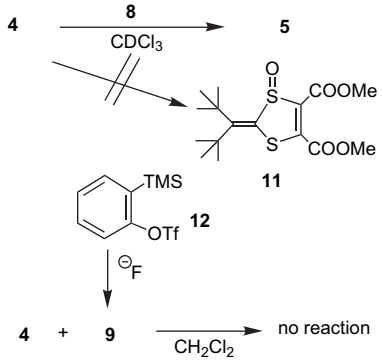


Chart 2.

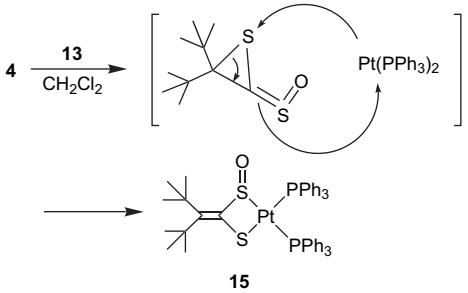
fluoride. Apparently, **4** is not reactive enough to intercept DMAD **8** and benzyne **9**.



Scheme 4.

2.3. Synthesis of platinum and palladium complexes

Gosselink et al. have described the synthesis of sulfine–platinum complexes.[9a–c] Several sulfur–platinum complexes synthesized from (η^2-ethylene)bis(triphenylphosphine)platinum(0) (**13**)[15] are also well known, including thioketone–platinum complexes,[15e] dithiolato–platinum complexes,[15e] and thiolato sulfinato–platinum complexes.[15f] We have already reported that the reaction of **2** with **13** afforded dithiolato–platinum complex (**14**).[12b] Thus, we tried to synthesize the platinum complex by reacting **4** with **13**. Treatment of **4** with **13** at room temperature resulted in the formation of thiolato sulfinato–platinum complex (**15**) in 91% yield. Weigand and Wusch assumed that the addition of soft platinum(0) atom takes place probably at the soft thiolate sulfur atom rather than at the hard sulfenate sulfur.[15a] Based on the report by Weigand and Wusch, we propose the mechanism that the platinum atom in **13** attacks the episulfide sulfur atom in **4** to give complex **15** (Scheme 5).



Scheme 5.

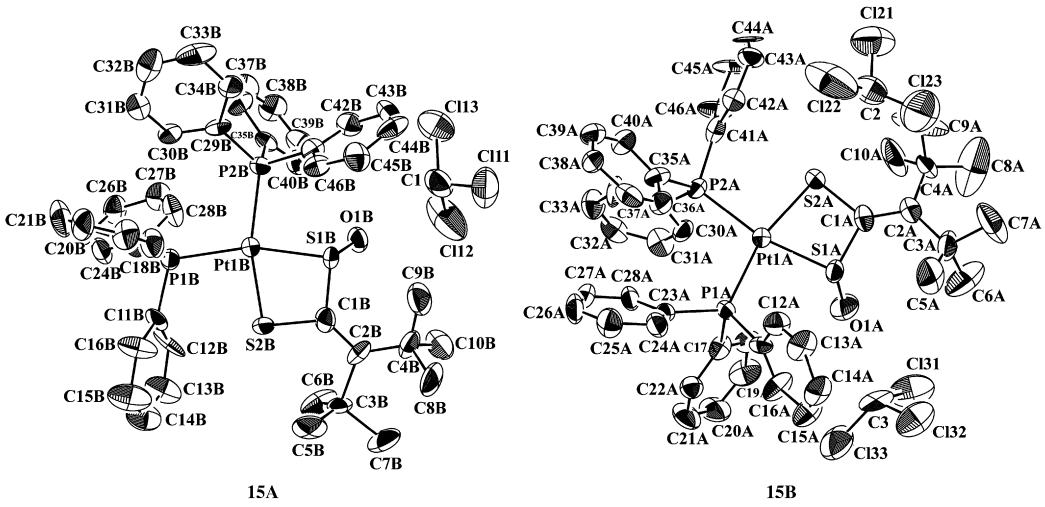


Figure 1. ORTEP drawing of complex **15**.

Since the recrystallization of complex **15** from chloroform gave single crystals, X-ray crystallographic analysis was carried out. In the ORTEP drawing of **15** shown in Figure 1, the crystal contained three molecules of chloroform per two molecules of **15**. Complex **15** has two molecular structures (**15A** and **15B**). The bond lengths of the four-membered ring of **15A** are similar to those of **15B**. The bond lengths of Pt–P and C═C of **15A** are also similar to those of **15B**. However, the bond length of S═O of **15A** is shorter than that of **15B**. The bond angles of the four-membered ring of **15A** are similar to those of **15B**. Comparison with the X-ray crystallographic data of thiolato sulfinato–platinum complex (**16**) (bond lengths: C–S: 1.871 and 1.827, S–O: 1.473, Pt–S: 2.353, and Pt–S: 2.314 Å. Bond angles: S–Pt–S: 70.4, C–S–Pt: 89.6, C–S–Pt: 92.0, and S–C–S: 93.4)[15f] demonstrated that the C–S bond lengths of the four-membered ring of **15** are shorter than those of **16** (Chart 3). The S–C–S bond angles of **15** are larger than those of **16**. In **15**, the sum of the bond angles of S2–Pt1–S1, P1–Pt1–P2, S1–Pt1–P1, and S2–Pt1–P2 is ca. 360°, and the sum of the interior angles of the quadrangle C1–S1–Pt1–S2 is also ca. 360°, suggesting that **15** is planar.

Selected bond lengths: C1A–C2A: 1.360(3), Pt1A–S2A: 2.303(4), Pt1A–S1A: 2.312(4), S1A–O1A: 1.457(19), S1A–C1A: 1.800(2), S2A–C1A: 1.790(2), Pt1A–P1A: 2.325(4), Pt1A–P2A: 2.336(4), C1B–C2B: 1.340(2), Pt1B–S2B: 2.273(4), Pt1B–S1B: 2.331(4), S1B–O1B: 1.530(14), S1B–C1B: 1.790(2), S2B–C1B: 1.773(18), Pt1B–P2B: 2.333(4), Pt1B–P1B: 2.334(4) Å. Selected bond angles: S2A–Pt1A–S1A: 73.97(16), P1A–Pt1A–P2A: 102.70(15), S1A–Pt1A–P1A: 90.21(15), S2A–Pt1A–P2A: 93.16(16), C1A–S1A–Pt1A: 92.0(6), C1A–S2A–Pt1A: 92.4(7), S2A–C1A–S1A: 101.2(9), O1A–S1A–C1A: 107.8(11), O1A–S1A–Pt1A: 111.8(8), S2B–Pt1B–S1B: 73.42(16), P1B–Pt1B–P2B: 105.51(16), S1B–Pt1B–P2B: 90.65(16), S2B–Pt1B–P1B: 90.42(16), C1B–S1B–Pt1B: 91.3(6), C1B–S2B–Pt1B: 93.8(7), S2B–C1B–S1B: 101.0(9), O1B–S1B–C1B: 106.3(9), O1B–S1B–Pt1B: 109.0(5)°.

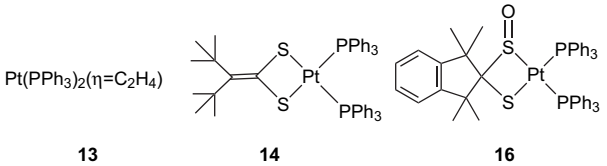


Chart 3.

The ^{31}P NMR spectrum of **15** showed two signals that resonated at δ 16.6 (J_{Pt-P}=2390 Hz, J_{P-P}=26 Hz) and 17.6 (J_{Pt-P}=3278 Hz, J_{P-P}=26 Hz). The chemical shifts and the J_{Pt-P} values of the signals of **15** are similar to those of the reported thiolato sulfinato–platinum complexes.[15f,h] In the ^{195}Pt NMR spectrum, the signal representative of **15** was observed at δ −4307 (Chart 4). The J_{Pt-P} values of **15** are 2367 and 3303 Hz, which are the same as the data obtained by ^{31}P NMR measurement. The values of the platinum signal of **15** indicate that **15** is a Pt(II) complex. Complex **14** showed a signal that resonated at δ −4399 (J_{Pt-P}=2948 Hz) in the ^{195}Pt NMR spectrum, and the chemical shift and the J_{Pt-P} value of that signal are similar to those of general dithiolato–platinum complexes.[16] The values of the signal of **15** are similar to those of **14**.

Gosselink et al. reported that the reactions of sulfines **1** with tetrakis(triphenylphosphine) palladium (**17**) gave sulfine–palladium complex.[9d] To compare the reactivity of palladium with that of platinum, we reacted **4** with **17**. The reaction gave thiolato sulfinato−palladium complex (**18**) in 85% yield (Scheme 6). In the ^{31}P NMR spectrum, complex **18** demonstrated signals that resonated at δ=22.4 (J_{P-P}=64.5 Hz) and 25.8 (J_{P-P}=64.5 Hz). A band assignable to the S═O bond in **18** was also observed at 1093 cm^{-1} in the IR spectrum. To confirm the difference in stability between **15** and **18**, these two compounds were left in dichloromethane at −20 °C. After 1 day, **15** was recovered unchanged, whereas **18** was decomposed, suggesting that **15** was more stable than **18** in the solvent.

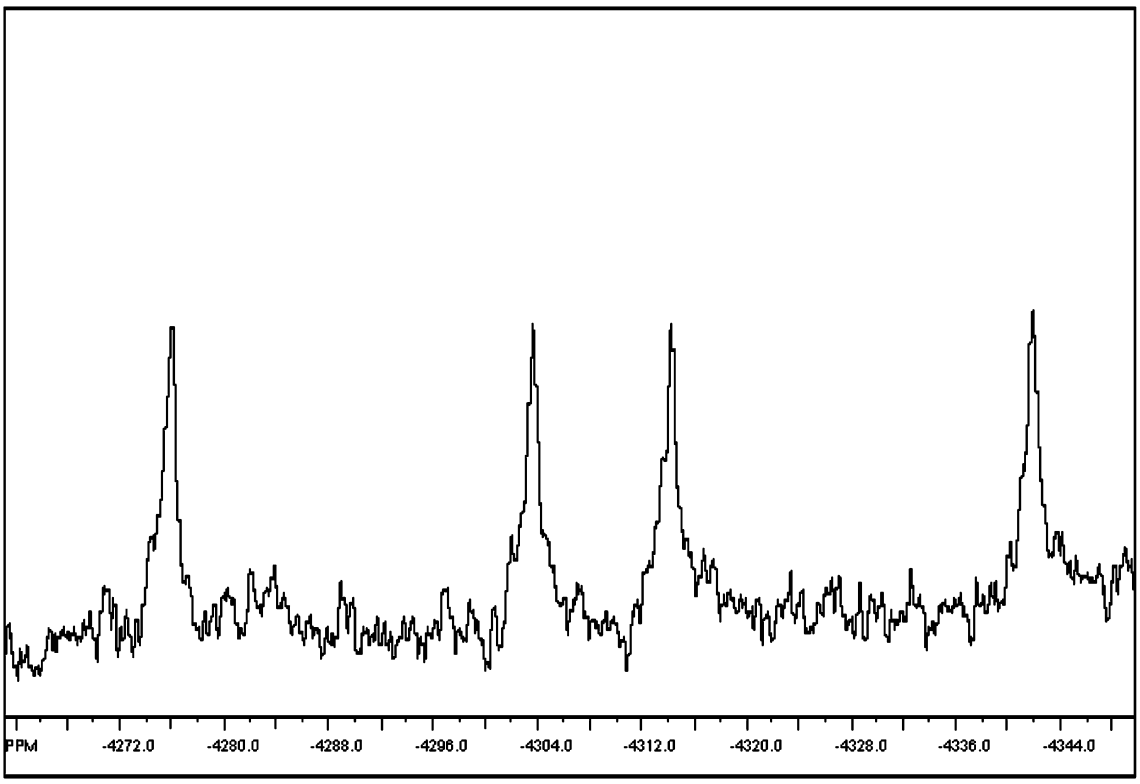
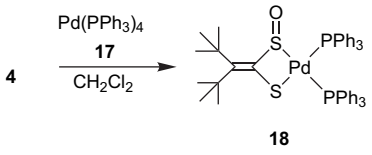


Chart 4. ^{195}Pt NMR spectrum of **15**.



Scheme 6.

3. Conclusion

Thermolysis of α-dithiolactone *S*-oxide **4** gave di-*tert*-butyl ketone **5** and CS_2. Moreover, variable temperature NMR spectroscopy over the range of 333–363 K in toluene-d_8 resulted in activation parameters $\Delta H^{\ddagger}$=82.6 kJ mol^{-1} and $\Delta S^{\ddagger}$=−71.6 J K^{-1} mol^{-1}. The reaction of **4** with excess *m*-CPBA or triphenylphosphine gave di-*tert*-butylthioketene *S*-oxide **3** almost quantitatively. The reaction of **4** with LR at room temperature afforded the corresponding α-dithiolactone **2**. Treatment of **4** with (η^2-ethylene)-bis(triphenylphosphine)platinum(0) **13** or tetrakis(triphenylphosphine) palladium **17** resulted in the formation of thiolato sulfinato–platinum complex **15** or palladium complex **18** in good yields, respectively. The structure of complex **15** was determined by X-ray crystallographic analysis.

CCDC 642214 contains the supplementary crystallographic data for complex **15**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4. Experimental

4.1. 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 with 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 parts per million 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.

4.1.1. Thermolysis of 4. Compound **4** (0.011 g, 0.05 mmol) was heated for 1 day in chloroform-*d* at 60 °C. Decomposition of **4** and formation of di-*tert*-butyl ketone **5** and CS_2 was observed by NMR spectroscopy. The reaction mixture was evaporated to give a colorless oil, which was chromatographed over silica gel by elution with hexane–dichloromethane (1:1) to give pure **5** (0.0057 g, 0.04 mmol).

4.1.2. Oxidation of 4. To a solution of **4** (0.011 g, 0.05 mmol) in dichloromethane (2 mL) was added a solution of *m*-chloroperbenzoic acid (0.043 g, 0.25 mmol) in one portion. After being stirred for 1 h, 10 mL of hexane was added to the reaction mixture, which was filtered and evaporated to give a deep-yellow solid, which was chromatographed over silica gel by elution with hexane–dichloromethane (1:1) to give pure **3** (0.009 g, 0.048 mmol).

4.1.3. Reaction of 4 with triphenylphosphine. Triphenylphosphine (0.053 g, 0.20 mmol) was added to a solution of **4** (0.022 g, 0.10 mmol) in $CDCl_3$. A solution was heated for 2 h in 60 °C. The formation of **3** was monitored by NMR spectroscopy. The reaction mixture was evaporated to give a colorless solid, which was chromatographed over silica gel by elution with hexane–dichloromethane (1:1) to give pure **3** (0.018 g, 0.0968 mmol).

4.1.4. Thiation of 4. Lawesson reagent (0.61 g, 0.15 mmol) was added in one portion to a solution of 3,3-di-*tert*-butylthiirane-2-thione *S*-oxide **4** (0.022 g, 0.10 mmol) in chloroform (4 mL). After being stirred for 3 h, the reaction mixture was evaporated to give yellow oily crystals, which were chromatographed over silica gel by elution with hexane to give pure **2** (0.0186 g, 0.092 mmol).

4.1.5. Reaction of 4 with dimethyl acetylenedicarboxylate 8. To a solution of **4** (0.026 g, 0.12 mmol) in $CDCl_3$ was added dimethyl acetylenedicarboxylate **8** (0.018 g, 0.20 mmol). The solution was heated for 1 day in 60 °C and the reaction was monitored by ^{1}H NMR spectroscopy. The reaction mixture was evaporated to give a colorless oil, which was chromatographed over silica gel by elution with hexane–dichloromethane (1:1) to give pure **5** (0.0142 g, 0.10 mmol).

4.1.6. Reaction of 4 with benzyne 9. Tetrabutylammonium fluoride in THF complex (1.0 M) (0.12 mL, 0.12 mmol) was added to a solution of **4** (0.022 g, 0.1 mmol) and *o*-trimethylsilylphenyl trifluoromethanesulfonate (0.030 g, 0.1 mmol) in dichloromethane (5 mL). After the reaction mixture had been stirred for 0.5 h, it was evaporated to give a red-yellow oil, which was washed with water and extracted with hexane. The combined extracts were dried over magnesium sulfate, filtered, and evaporated to give orange oily crystals, which were chromatographed over silica gel by elution with hexane–dichloromethane (1:1) to recover **4**.

4.1.7. Synthesis of platinum complex 15. (η^2Ethylene)bis-(triphenylphosphine)-platinum(0) **13** (0.037 g, 0.05 mmol) was added to a solution of **4** (0.011 g, 0.05 mmol) in dichloromethane (2 mL). After the reaction mixture had been stirred for 10 min, it was evaporated to give black-yellow solid. The residue was recrystallized from chloroform to give yellow crystals **15** (0.0427 g, 0.0455 mmol). Compound **15**; yellow crystals; mp 223.3–227.0 °C (dec); ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.36 (s, 9H), 1.40 (s, 9H), 7.16–7.46 (m, 30H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ=32.17, 33.27, 39.93, 42.29, 128.17, 128.27, 128.35, 128.45, 129.99, 130.46, 130.69, 130.75, 134.81, 134.84, 134.93, 134.96; ^{31}P NMR ($CDCl_3$, 162 MHz) δ=16.6 (J_{Pt-P}=2390 Hz, J_{P-P}=26 Hz), 17.6 (J_{Pt-P}=3278 Hz, J_{P-P}=26 Hz); ^{195}Pt NMR ($CDCl_3$, 86 MHz, Na_2PtCl_6) δ=−4307 (J_{Pt-P}=2367, 3303 Hz); IR ν=1093 cm^{-1} (S═O); Anal calcd for $C_{46}H_{48}P_2S_2Pt\cdot H_2O$: C, 59.92; H, 5.25. Found: C, 59.82; H, 5.33.

4.1.8. X-ray crystallographic analysis of complex 15. Single crystals of **15** were obtained by recrystallization from chloroform. The diffraction data were collected with a DIP Image Plate diffractometer with Cu Kα radiation (λ=1.54184) to a maximum 2θ value of 140.16° at 293 K. The structure was solved by SIR92 and refined SHELXL-97. Complex **15**; formula $C_{46}H_{48}OP_2PtS_2$, FW 938.055, monoclinic, space group=$P2_1$, a=12.7160(3), b=15.4370 (4), c=24.6670 (6) Å, α=90.00, β=93.9130(10), γ=90.00°, V=4830.8(2) Å^3, Z=4, D_x=1.290 Mg m^{-3}, μ(Mo Kα)=8.636 mm^{-1}, the final R and wR were 0.0851 and 0.2200, respectively, using 16,533 reflections.

4.1.9. Synthesis of palladium complex 18. Tetrakis(triphenylphosphine) palladium **17** (0.058 g, 0.05 mmol) was added to a solution of **4** (0.011 g, 0.05 mmol) in dichloromethane (2 mL). After the reaction mixture had been stirred for 30 min, it was evaporated to give black-yellow solid. The residue was recrystallized from hexane–dichloromethane (1:1) to give yellow crystals **18** (0.0361 g, 0.0425 mmol). Compound **18**; yellow crystals; mp 125.1–128.8 °C (dec); ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.35 (s, 9H), 1.43 (s, 9H), 7.14–7.42 (m, 30H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ=31.66, 33.08, 40.26, 42.45, 128.06, 128.16, 128.27, 128.37, 130.07, 130.84, 130.90, 131.18, 131.27, 134.36, 134.46, 134.48, 134.58, 145.49, 150.17; ^{31}P NMR ($CDCl_3$, 162 MHz) δ=22.4 (J_{P-P}=64.5 Hz), 25.8 (J_{P-P}=64.5 Hz); IR ν=1093 cm^{-1} (S═O); Anal. Calcd for $C_{46}H_{48}OP_2S_2Pd$: C, 65.05; H, 5.70. Found: C, 65.44; H, 5.94.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.04.004.

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