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Novel formation of 1,2-dithiolane-3-thione from β-dithiolactone. Isolation of dithiolato-palladium and -platinum complexes

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Abstract—Sulfurization of β-dithiolactone (**4**) gave corresponding 1,2-dithiolane-3-thione (**2a**) via an ionic intermediate. Oxidation of β-dithiolactone **4** by *m*-CPBA afforded corresponding *S*-oxide (**11**), while dioxide (**12**) was obtained when 3 equiv of *m*-CPBA was used. Dithiolane-3-thione **2a** reacted with ethylenebis(triphenylphosphine)platinum or tetrakis(triphenylphosphine)palladium to afford the corresponding dithiolato-platinum (**20**) and dithiolato-palladium (**21**) complexes in good yields.

1. Introduction

In recent years, considerable attention has been devoted to cyclic polysulfides because of their unique structures and biological activities.[1] Compounds containing the 3*H*-1,2-dithiole-3-thione ring system (**1**) have continued to attract attention as cancer preventing agents. Oltipraz (4-methyl-5-pyrazinyl-3*H*-1,2-dithiole-3-thione) has undergone large-scale clinical trials in this respect, and simpler derivatives were found to be as effective.[2] These five-membered dithiole derivatives were synthesized using sulfurization reagents such as P_4S_{10},[3] Lawesson's reagent (LR), and elemental sulfur.[4] However, to our knowledge, there is no report on the synthesis of 1,2-dithiolane-3-thiones (**2**) except for our recent communication.[5] Four-membered dithiolato-platinum complexes were synthesized by reacting ethylenebis(triphenylphosphine)platinum with 1,2,4-trithiolanes or dithiiranes.[6] We have also reported the synthesis of α-dithiolactones (**3**), which on reaction with ethylenebis(triphenylphosphine)platinum, afforded dithiolato-platinum complex in almost quantitative yields.[7] These results prompted us to investigate the reactivity of 3-mercapto-2,2,4-trimethyldithio-3-pentenoic acid β-dithiolactone (**4**), which was easily synthesized from 2,2,4,4-tetramethyl-1,3-cyclobutanedione (**5**),[8] because its reactivity was relatively unknown (Chart 1).[9] We report herein the synthesis and reaction of 1,2-dithiolane-3-thione (**2**) by sulfurization of β-dithiolactone **4** and the isolation of dithiolato-platinum and -palladium complexes from **2**.

Chart 1.

2. Results and discussion

2.1. Synthesis of 5-isopropylidene-4,4-dimethyl-1,2-dithiolane-3-thione 2a

β-Dithiolactone **4** was synthesized by reacting dione **5** with P_4S_{10} according to the method reported by Elam and Davis.[8] When the reaction of **4** with P_4S_{10} was carried out in pyridine for 3 h, compound **4** was recovered in 68% yield along with small amount of a by-product whose spectroscopic nature was similar to that of **4**. Its ^{1}H NMR spectrum showed methyl signals at 1.65 (6H), 1.95 (3H), and 1.99 (3H) ppm; its ^{13}C NMR spectrum showed signals at 248 ppm for thione and at 128 and 137 ppm for olefin; and its MS spectrum showed M^+ at 204. Together, the results indicate that the by-product is a novel five-membered polysulfide, 5-isopropylidene-4,4-dimethyl-1,2-dithiolane-3-thione (**2a**) (7%). To improve the yield of **2a**, the reaction conditions, namely, thionation reagent, solvent, temperature, and reaction time, were varied. The results are shown in Table 1. When elemental sulfur was used in the place of P_4S_{10}, dithiolane **2a** was obtained in 52% yield along with starting **4** (42%) (entry 3). When the reaction of dione **5** with elemental sulfur instead of P_4S_{10} was carried out, starting dione **5** was recovered unchanged (entry 6). These results suggest that the formation of **2a** from **5** requires not only a thionation reagent but also a thiation reagent. Thus, the one-pot synthesis of novel dithiolane-3-thione **2a** was achieved from commercially available dione **5** (entry 7) (Scheme 1).

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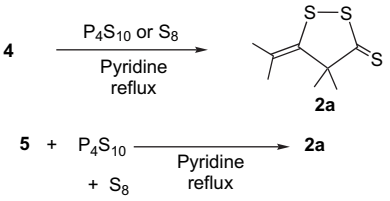
Table 1. Reaction of **4** or **5** with sulfurization reagents

Entry	Substrate	Sulfurization reagent	Solvent	Condition/temp	Time	Recovered **4**	Product **2a**
						Yield (%)	
1	**4**	P_4S_{10}	Pyridine	Reflux	3	68	7
2	**4**	P_4S_{10}	Toluene	Reflux	14	74	8
3	**4**	S_8	Pyridine	Reflux	3	42	52
4	**4**	S_8	Pyridine	rt	3	43	47
5	**4**	LR	Toluene	Reflux	24	76	3
6	**5**	S_8	Pyridine	Reflux	14	0	0
7	**5**	P_4S_{10}+S_8	Pyridine	Reflux	14	40	51

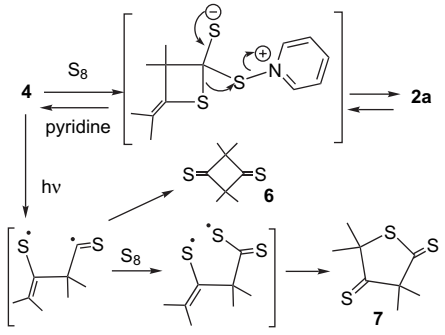
Previously, 1,2-dithiole-3-thiones **1** were synthesized by reacting β-ketoesters with P_4S_{10} (or LR) and elemental sulfur.[3,4] Recently, Curphey reported that the yields of **1** were improved by adding hexamethyldisiloxane.[10] However, there is no report on the synthesis of 1,2-dithiolane-3-thione **2** using sulfurization reagents.



Scheme 1.

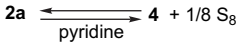
2.2. Reaction mechanism

How do we account for the formation of **2a**? If a radical mechanism was plausible, 2,2,4,4-tetramethyl-1,3-cyclobutanedithione (**6**) and 3,3,5,5-tetramethyl-4-thioxothiolane-2-thione (**7**) would be formed, as Muthuramu et al. suggested in the photolysis of **4**.[9a,11] The following observation that the thermolysis of **4** in refluxing toluene gave small amount of **2a** (entry 2) and **2a** was obtained even at rt in pyridine (entry 4) suggested that the concerted or radical process was not operative. Additionally, when the reaction of **4** with elemental sulfur in pyridine was carried out in dark at rt, **2a** was obtained in 50% yield. Thus, the ionic mechanism shown in Scheme 2 might be plausible.



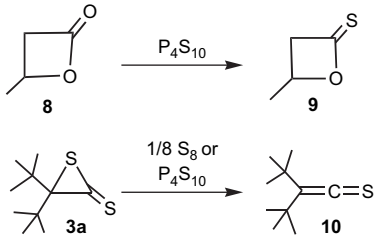
Scheme 2. Radical mechanism.[9a,11]

Since the yield of **2a** was in the range of 7–52% along with starting **4** under several conditions, we assumed that the reaction could be equilibrated with **2a** and **4**. To confirm this assumption, we carried out the thermolysis of **2a** under basic conditions. When **2a** was left to stand for 1 h in deuterated pyridine at 100 °C, dithiolactone **4** was produced in 25% yield. After 4 h, compound **4** was formed in 40% yield based on NMR analysis. Additionally, when **4** was treated with elemental sulfur (1 atom equiv) in deuterated pyridine at rt for 24 h, dithiolane-2-thione **2a** was obtained in 50% yield based on NMR analysis, suggesting that equilibration was observed under these conditions (Scheme 3).



Scheme 3.

Other four-membered cyclic lactones such as γ-butyrolactone (**8**) afforded not the corresponding 1,2-dithiolane-3-thione but γ-butyrothiolactone (**9**) in a similar manner, as reported by Filippi et al.[12] The reaction of α-dithiolactone **3a** with elemental sulfur or tetraphosphorus decasulfide gave di-*tert*-butyl thioketene (**10**) in 85% yield, suggesting that methyl and *exo*-methylene groups play an important role in the stabilization of 1,2-dithiolane-3-thione (Scheme 4).



Scheme 4.

2.3. Oxidation of 1,2-dithiolane-3-thione 2a

In general, the oxidation of dithioesters affords corresponding thiocarbonyl *S*-oxides (sulfines).[13] Since 1,2-dithiolane-3-thione **2a** has three sulfur atoms, there are three possibilities for the initial oxidation step and two options for additional oxidation. In the case of 1,2-dithiole-3-thiones **1**, initial oxidation by *m*-CPBA or peracetic acid occurred at thiocarbonyl sulfur, while further oxidation gave not the corresponding dioxides but 1,2-dithiolium salts.[14] Thus, we were interested in the oxidation behavior toward **2a**. Treatment of **2a** with *m*-CPBA (1.2 equiv) at rt in dichloromethane resulted in the formation of monoxide in 44% yield along with dioxide (21%). Comparing their ^{13}C NMR spectra, we found that the thiocarbonyl carbon signal (243 ppm) of **2a** was shifted to 213 and 208 ppm (monoxide and dioxide, respectively), clearly showing that the monoxide should be

5-isopropylidene-4,4-dimethyl-1,2-dithiolane-3-thione *S*-oxide (**11**). When 3 equiv of *m*-CPBA was used, 5-isopropylidene-4,4-dimethyl-1,2-dithiolane-3-thione 1,*S*-dioxide (**12**) was obtained in 74% yield, and its structure was confirmed by ^{1}H NMR and ^{13}C NMR analyses. Finally, the structure of dioxide **12** was confirmed by X-ray crystallographic analysis (Fig. 1). Since dioxide **12** has the *Z*-form, the regiochemistry of sulfine **11** should also have the *Z*-form (Scheme 5).

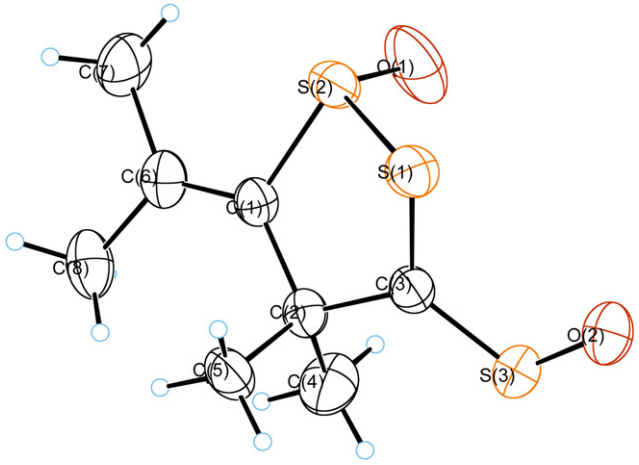
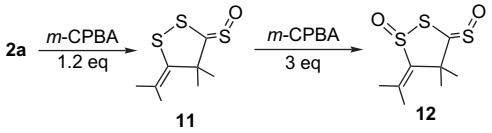


Figure 1. ORTEP drawing of 5-isopropylidene-4,4-dimethyl-1,2-dithiolane-3-thione 1,*S*-dioxide (**12**). *Selected bond lengths*: S(1)–S(2) 2.1195 (9) Å, S(1)–C(3) 1.733 (2) Å, S(2)–O(1) 1.473 (3) Å, S(2)–C(1) 1.796 (2) Å, S(3)–O(2) 1.476 (2) Å, S(3)–C(3) 1.628 (2) Å. *Selected bond angles*: S(2)–S(1)–C(3) 90.36 (8)°, S(1)–S(2)–O(1) 108.28 (9)°, S(1)–S(2)–C(1) 92.64 (7)°, O(1)–S(2)–C(1) 107.01 (12)°, O(2)–S(3)–C(3) 112.07 (13)°, S(2)–C(1)–C(2) 115.61 (15)°, S(2)–C(1)–C(6) 115.1 (2)°, C(2)–C(1)–C(6) 129.2 (2)°, C(1)–C(2)–C(3) 106.5°.



Scheme 5.

2.4. Synthesis of dithiolato-platinum and -palladium complexes

Weigand et al. studied the reactions of disulfides and thiosulfinates with platinum(0) complexes, and reported that the reaction of 1,2,4,5-tetrathiane and 1,2,4-trithiolane with ethylenebis(triphenylphosphine)platinum (**13**) gave dithiolato-platinum complex (**14**) and thiocarbonyl-platinum complex (**15**) as a 1:1 mixture.[15] Although Ishii et al. were able to isolate dithiolato complex (**16**) by reacting tetrathiolane with **13**, the yield was low.[16,17] We have recently reported the synthesis of dithiolato-platinum complex (**17**) by reacting α-dithiolactone **3a** with **13**.[7b] The reaction of 1,2-dithiole-3-thione **1** with palladium dichloride gave 2:1 complex (**18**),[18] whereas the reaction with **13** gave dithiocarboxylato-thiolato-platinum complex (**19**) (Chart 2).[19] These results prompted us to investigate the reaction of **2a** with **13**. We were interested in whether the product would be a 2:1 complex, a dithiocarboxylato-thiolato-platinum complex, or a dithiolato-platinum complex.

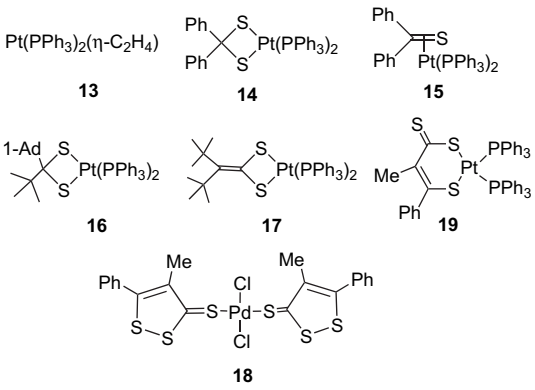
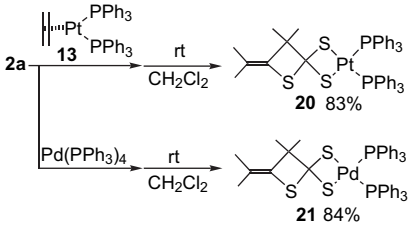


Chart 2.

The reaction of **2a** with **13** (1 equiv) at rt was completed in 10 min to give yellow crystals. Its ^{1}H NMR spectrum showed three methyl signals at 1.33 (3H), 1.37 (3H), and 1.61 (6H) ppm. Its ^{13}C NMR spectrum showed five aliphatic carbon signals at 20.03 (CH_3), 21.52 (CH_3), 26.84 (2×CH_3), 61.79 (q), and 79.53 (q) ppm, and two olefin signals at 115.47 and 130.69 ppm. No thiocarbonyl carbon signal was observed. Thus, the structure should be bis(triphenylphosphine)-1,3-dithiolato-platinum complex (**20**). Similarly, dithiolato-palladium complex (**21**) was obtained by reacting **2a** with tetrakis(triphenylphosphine)palladium (Scheme 6), and the structure was confirmed by ^{1}H, ^{13}C, and ^{31}P NMR measurements and elemental analysis. Its ^{1}H NMR spectrum showed two methyl signals at 1.34 (9H) and 1.61 (3H) ppm, and its ^{13}C NMR spectrum showed five aliphatic carbon signals at 19.85 (CH_3), 21.26 (CH_3), 26.32 (2×CH_3), 61.33 (q), and 81.52 (q) ppm, and two olefin signals at 115.15 and 133.46 ppm. The ^{31}P NMR spectrum of **20** showed a signal at 21.65 ppm (J_{Pt-P}=3012 Hz), whereas only one singlet was observed at 30.37 ppm in the ^{31}P NMR spectrum of **21**. The ^{195}Pt NMR spectrum of **20** showed a signal at −4349.28 (J_{Pt-P}=3012 Hz), suggesting that this compound should be a Pt(II) complex. This is the first example of successful synthesis of a dithiolato-palladium complex.



Scheme 6.

On recrystallization from dichloromethane–acetonitrile, palladium complex **21** afforded relatively unstable single crystals, whereas platinum complex **20** gave stable single crystals that can be determined by X-ray crystallographic analysis. The ORTEP drawing is shown in Figure 2.[20]

The bond lengths of the four-membered ring of **20** are C–S: 1.815, 1.810 Å and S–Pt: 2.314, 2.321 Å. The bond lengths of the four-membered ring of dithiolato-platinum complex

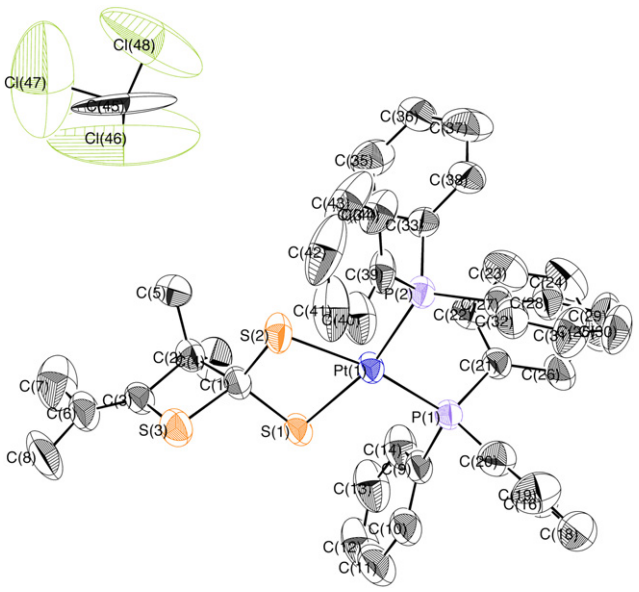


Figure 2. ORTEP drawing of complex **20**. *Selected bond lengths*: Pt1–P1 2.2850 (19) Å, Pt1–P2 2.2925 (18) Å, Pt1–S1 2.3136 (17) Å, Pt1–S2 2.321 (2) Å, S1–C1 1.815 (7) Å, S2–C1 1.810 (7) Å, S3–C3 1.733 (8) Å, S3–C1 1.850 (7) Å, C1–C2 1.600 (10) Å, C2–C3 1.527 (10) Å. *Selected bond angles*: P1–Pt1–P2 101.24 (6)°, P1–Pt1–S1 92.61 (6)°, P2–Pt1–S1 165.65 (7)°, P1–Pt1–S2 91.18 (7)°, S1–Pt1–S2 74.84 (7)°, C1–S1–Pt1 91.1 (2)°, C1–S2–Pt1 90.9 (2)°, C3–S3–C1 78.5 (3)°, C2–C1–S2 120.3 (5)°, C2–C1–S1 117.0 (5)°, S2–C1–S1 102.0 (3)°, C2–C1–S3 90.1 (4)°, S2–C1–S3 114.9 (4)°, S1–C1–S3 113.1 (4)°, C3–C2–C1 93.0 (6)°, C2–C3–S3 97.2 (5)°.

17 are C–S: 1.790, 1.780 Å and S–Pt: 2.290, 2.283 Å,[7b] and are quite similar to those of **20**.

In summary, we have synthesized a novel type of five-membered cyclic dithiolactone, 1,2-dithiolane-3-thione **2a**, by reacting dithiolactone **4** with elemental sulfur via an ionic intermediate. Oxidation of **2a** gave the corresponding monoxide **11** and dioxide **12**, whose structures were determined by X-ray crystallographic analysis. The reaction of **2a** with **13** gave a new type of dithiolato-platinum complex **20**, whose structure was confirmed by X-ray crystallographic analysis.

3. Experimental

3.1. 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 NMR, and external Na_2PtCl_6 (D_2O) for ^{195}Pt NMR. Melting points were uncorrected.

3.2. Reaction of 4 with P_4S_{10}

To a refluxing solution of **4** (344 mg, 2.0 mmol) in pyridine (22 mL) was added P_4S_{10} (222 mg, 0.50 mmol) in one portion. After refluxing for 3 h, the reaction mixture was poured into water and extracted with hexane (10 mL×3). The combined extracts were dried over magnesium sulfate, filtered, and evaporated to give reddish orange oil, which was chromatographed over silica gel by elution with hexane to afford a mixture of **2a** and **4**. The mixture was subjected to gel permeation chromatography to afford **2a** (29 mg, 0.14 mmol) and **4** (234 mg, 1.36 mmol). *Compound **2a***: yellow oil; ^{1}H NMR ($CDCl_3$) δ=1.65 (s, 6H, CH_3), 1.95 (s, 3H, CH_3), 1.99 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ=21.63 (CH_3), 26.60 (CH_3), 29.13 (2×CH_3), 64.43, 128.43 (=C), 137.37 (=C), 248.05 (C=S); MS: M^+ 204. Calcd for $C_8H_{12}S_3$: 204. Anal. Found: C, 46.66; H, 5.81%. Calcd for $C_8H_{12}S_3$: C, 47.01; H, 5.92%.

3.3. Synthesis of 2a from 4 and elemental sulfur

To a solution of **4** (344 mg, 2.0 mmol) in pyridine (10 mL) was added elemental sulfur (64 mg, 1 atom equiv) in one portion. After refluxing for 3 h, the reaction mixture was poured into water and extracted with hexane (10 mL×3). The combined extracts were dried over magnesium sulfate, filtered, and evaporated to give reddish orange oil, which was chromatographed over silica gel by elution with hexane to afford a mixture of **4** and **2a**. Separation was accomplished by gel permeation chromatography to afford pure **4** (145 mg, 0.84 mmol) and **2a** (206 mg, 1.01 mmol).

3.4. One-pot synthesis of 2a from cyclobutanedione 5

To a solution of **5** (280 mg, 2.0 mmol) in pyridine (10 mL) was added elemental sulfur (64 mg, 1 atom equiv) and P_4S_{10} (222 mg, 0.5 mmol) was added in one portion. After refluxing for 14 h, the reaction mixture was poured into water (20 mL) and extracted with hexane (10 mL×3). The combined extracts were dried over magnesium sulfate, filtered, and evaporated to give reddish orange oil, which was chromatographed over silica gel by elution with hexane to afford a mixture of **2a** and **4**. Separation was subjected to gel permeation chromatography to afford pure **2a** (205 mg, 1.0 mmol) and **4** (140 mg, 0.80 mmol).

3.5. Oxidation of 2a

To a solution of **2a** (204 mg, 1.0 mmol) in chloroform (5 mL) was added *m*-CPBA (208 mg, 1.2 mmol) in one portion. After stirring for 1 h, the reaction mixture was poured into aq Na_2CO_3 (10%), separated, dried over magnesium sulfate, filtered, and evaporated to afford yellow oil of monoxide **11**. The crude product was chromatographed over silica gel by elution with hexane–ethyl acetate (5:1) to afford pure **11** (97 mg, 0.44 mmol) and dioxide **12** (50 mg, 0.21 mmol). *5-Isopropylidene-4,4-dimethyl-1,2-dithiolane-3-thione S-oxide **11***: pale orange oil; ^{1}H NMR ($CDCl_3$) δ=1.77 (s, 6H, CH_3), 1.95 (s, 3H, CH_3), 1.98 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ=21.39 (CH_3), 27.77 (CH_3), 29.95 (2×CH_3), 56.33, 128.84 (=C), 136.86 (=C), 213.05 (C=S=O). Anal. Found: C, 43.21; H, 5.36%. Calcd for $C_8H_{12}OS_3$: C, 43.60; H, 5.49%. *5-Isopropylidene-4,4-dimethyl-1,2-dithiolane-3-thione 1,S-dioxide **12***: yellow prisms (hexane); mp 105–106 °C; ^{1}H NMR ($CDCl_3$) δ=1.82 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.32 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ=22.31 (CH_3),

26.12 (CH_3), 30.91 (CH_3), 32.83 (CH_3), 55.83, 143.81 (=C), 152.36 (=C), 207.91 (C=S=O). Anal. Found: C, 40.36; H, 5.03%. Calcd for $C_8H_{12}O_2S_3$: C, 40.65; H, 5.12%.

3.6. Oxidation of 2a; synthesis of dioxide 12

To a solution of **2a** (204 mg, 1.0 mmol) in chloroform (5 mL) was added *m*-CPBA (516 mg, 3.0 mmol) in one portion. After stirring for 1 h, the reaction mixture was poured into aq Na_2CO_3 (10%), separated, dried over magnesium sulfate, filtered, and evaporated to afford pale orange oil of dioxide **12** (221 mg, 0.94 mmol). The crude product was chromatographed over silica gel by elution with hexane–ethyl acetate (4:1) to afford pure **12** (175 mg, 0.74 mmol).

X-ray crystallographic data for ***12***: crystal data for $C_8H_{12}O_2S_3$. Yellow plates. Crystallized from hexane–dichloromethane (5:1). Cu Kα radiation. M=236.37, a=9.3630 (2) Å, b=14.0200 (4) Å, c=16.0220 (4) Å, V=2103.20 (9) Å^3, T=298 K, orthorhombic, space group=*Pbca*, S=1.067, Z=8, 1976 independent reflections, R=0.0459 for 1724 reflections ($I>2\sigma$ (I)), wR=0.1187, S=1.067.

3.7. Synthesis of dithiolato-platinum complex 20

To a solution of **2a** (8.3 mg, 0.040 mmol) in dichloromethane (1 mL) was added a solution of ethylenebis(triphenylphosphine)platinum **13** (30 mg, 0.040 mmol) in dichloromethane (0.5 mL) at rt. After standing for 10 min, the reaction mixture was filtered and recrystallized from chloroform–acetonitrile (1:2) to afford yellow plates of **20** (30 mg, 0.033 mmol). mp 266 °C (dec); ^{1}H NMR ($CDCl_3$) δ=1.33 (s, 3H, CH_3), 1.36 (s, 3H, 2×CH_3), 1.61 (s, 3H, CH_3), 7.10–7.18 (m, 12H, Ph), 7.22–7.27 (m, 6H, Ph), 7.36–7.46 (m, 12H, Ph); ^{13}C NMR ($CDCl_3$) δ=20.03 (CH_3), 21.52 (CH_3), 26.84 (2×CH_3), 62.79 (q-C), 79.53 (S–C–S), 115.47 (=C), 127.87 (d, J_{PC}=5.2 Hz, *o*-Ph), 127.92 (d, J_{PC}=5.2 Hz, *o*-Ph), 130.44 (*p*-Ph), 133.69 (=C), 134.80 (d, J_{PC}=5.4 Hz, *m*-Ph), 134.85 (d, J_{PC}=5.4 Hz, *m*-Ph). Aromatic *ipso*-carbons were too complicated to assign; ^{31}P NMR ($CDCl_3$) δ=21.65 (J_{Pt-P}=3012 Hz); ^{195}P NMR ($CDCl_3$) δ=−4349.3 (J_{Pt-P}=3012 Hz). Anal. Found: C, 55.70; H, 4.59%. Calcd for $C_{44}H_{42}P_2S_3Pt$+H_2O 56.10; H, 4.71%.

X-ray crystallographic data for ***20***: crystal data for $C_{44}H_{42}P_2PtS_3\cdot CHCl_3$. Yellow plates. Crystallized from chloroform–acetonitrile. Cu Kα radiation. M=990.15, a=11.2600 (2) Å, b=20.5590 (4) Å, c=20.0910 (4) Å, β=102.99 (1)°, V=4531.77 (15) Å^3, T=293 K, monoclinic, space group=$P2_1/c$, Z=4. 8322 independent reflections, R=0.0763 for 6522 reflections ($I>2\sigma$ (I)), wR=0.1894, S=1.339.

3.8. Synthesis of dithiolato-palladium complex 21

To a solution of **2a** (21 mg, 0.10 mmol) in dichloromethane (1 mL) was added a solution of tetrakis(triphenylphosphine)palladium (115 mg, 0.10 mmol) at rt. After stirring for 10 min, the reaction mixture was filtered and recrystallized from dichloromethane–acetonitorile (1:2) to afford yellow needles of **21** (70 mg, 0.84 mmol, 84%); mp 205 °C (dec); ^{1}H NMR ($CDCl_3$) δ=1.34 (s, 9H, CH_3), 1.62 (s, 3H, CH_3), 7.10–7.19 (m, 12H, Ph), 7.14–7.41 (m, 18H, Ph); ^{13}C NMR ($CDCl_3$) δ=19.85 (CH_3), 21.26 (CH_3), 26.20 (2×CH_3), 61.33 (q-C), 81.53 (S–C–S), 115.15 (=C), 127.88 (d, J_{PC}=5.2 Hz, *o*-Ph), 127.94 (d, J_{PC}=5.2 Hz, *o*-Ph), 130.06 (*p*-Ph), 130.76 (d, J_{PC}=20.2 Hz, *ipso*-Ph), 130.97 (d, J_{PC}=20.2 Hz, *ipso*-Ph), 133.46 (=C), 134.48 (d, J_{PC}=6.3 Hz, *m*-Ph), 134.53 (d, J_{PC}=6.3 Hz, *m*-Ph); ^{31}P NMR ($CDCl_3$) δ=30.37. Anal. Found: C, 62.33; H, 5.21%. Calcd for $C_{44}H_{42}P_2S_3Pd$+H_2O 61.93; H, 5.20%.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.08.097.

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20. Crystallographic data of **12** and **20** were deposited with Cambridge Crystallographic Centre. Deposition numbers: CCDC-657892 for dioxide **12** and CCDC-657893 for dithiolate-platinum complex **20**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.