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Synthesis and Reaction of α-Dithiolactone

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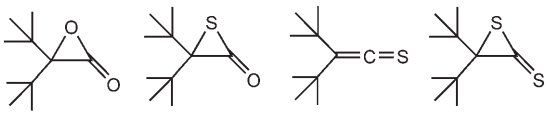
Abstract: Treatment of di-*tert*-butylthioketene *S*-oxide (**5a**) with Lawesson reagent at room temperature resulted in the formation of 3,3-di-*tert*-butylthiirane-2-thione (**4a**) in high yield. The oxidation of **4a** with *m*CPBA (*m*CPBA = *m*-chloroperbenzioc acid) gave 3,3-di-*tert*-butylthiirane-2-thione *S*-oxide (**6**) almost quantitatively. The reactions of **4a** with dimethyl acetylenedicarboxylate (DMAD) and benzyne afforded dimethyl 2-(2,2,4,4-tetramethylpentan-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**13**) and 2-(2,2,4,4-tetramethylpentan-3-ylidene)benzo[*d*][1,3]-dithiole (**15**), respectively, in high yields, suggesting that **4a** is an excellent 1,3-dipole. The reaction of **4a** with ethylenebis(triphenylphosphine)platinum (**16**) gave dithiolato-platinum complex (**22**) in high yield. The structure of **22** was determined by X-ray crystallographic analysis.

Keywords: alpha-thiolactone · benzo-1,3-dithiole · benzyne · platinum · synthetic methods

Introduction

Three-membered cyclic compounds containing two heteroatoms have been studied extensively.[1–5] The isolation of a series of stable dithiiranes was reported by Ishii and Nakayama.[1a–c] Methods for the synthesis of α-lactams include the reaction of *N*-*tert*-butyl-2-bromo-2-phenylacetamide with potassium *tert*-butoxide,[2a] the reaction of 2-bromo-3,3-dimethyl-*N*-*tert*-butylbutyramide with potassium *tert*-butoxide,[2b] and the reaction of α-chloro-α-phenylacetanilide with sodium hydride.[2c] Although α-lactones **1**[3] have been proposed as intermediates, there is only one example reported to date of an α-lactone isolable by electronic stabilization, namely, 3,3-bis(trifluoromethyl)oxirane-2-one,[3a] which is relatively stable at 25 °C with a half-life of 8 h. The sterically congested α-lactone, 3,3-di-*tert*-butyloxirane-2-one (**1a**), is stable at −60 °C but polymerizes at −20 °C.[3b] Schaumann and Behrens reported the synthesis and characterization of 3,3-di-*tert*-butylthiirane-2-one (**2a**), a thio analogue of α-lactone, which was synthesized by reacting di-*tert*-butylthioketene (**3a**) with nitrones.[4] Compound **2a** is stable at room temperature but decomposes at 65 °C. Although α-dithiolactone (**4**) has been proposed as an intermediate for the synthesis of 1,2,4,5-tetrathianes, 1,2,4-trithiolanes, and disulfides,[5] there has been no report of the isolation of **4**. As **2a** is more stable than **1a**, we hypothesized that 3,3-di-*tert*-butylthiirane-2-thione (**4a**) would be the most isolable α-dithiolactone. We recently communicated the synthesis of **4a**[6] and herein report the full details of the synthesis and reaction of **4**.



1a **2a** **3a** **4a**

Results and Discussion

Synthesis of α-dithiolactone: As Schaumann and Behrens reported the synthesis of α-thiolactone (**2**) by the oxidation of thioketene, the thiation of **3a** is expected to be one of the simplest ways to obtaining α-dithiolactone. Di-*tert*-butylthioketene (**3a**) was synthesized from di-*tert*-butylketene according to a reported method.[7] When the reaction of **3a** with Lawesson reagent (LR) was carried out at room temperature for 20 h, the target compound was not isolated. Thus,

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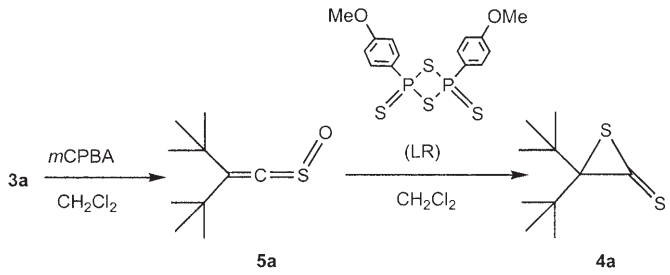
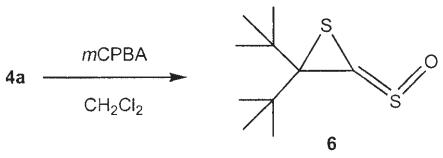
another synthetic method was required. Based on the report by Shimada and Takikawa of the LR-mediated synthesis of dithiirane from thioketone *S*-oxides under mild conditions,[1d] we attempted the synthesis of **4a** by reacting di-*tert*-butylthioketene *S*-oxide (**5a**) with LR. Compound **3a** was oxidized with *m*CPBA to give **5a** in 92% yield.[7,8] Treatment of **5a** with LR at room temperature for 12 h resulted in the formation of **4a** in 88% yield (Scheme 1).



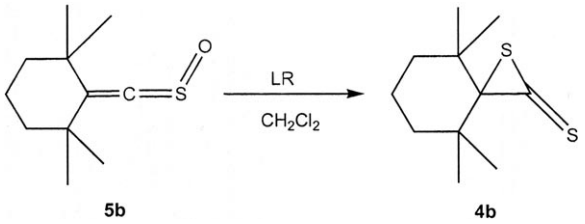
Scheme 1.

The structure of **4a** was confirmed by NMR spectroscopy, IR spectrometry, elemental analysis, and MS analysis. The oxidation of **4a** with *m*CPBA (1 equiv) gave 3,3-di-*tert*-butylthiirane-2-thione *S*-oxide (**6**) almost quantitatively (Scheme 2). Structural proof of **6** was provided by NMR



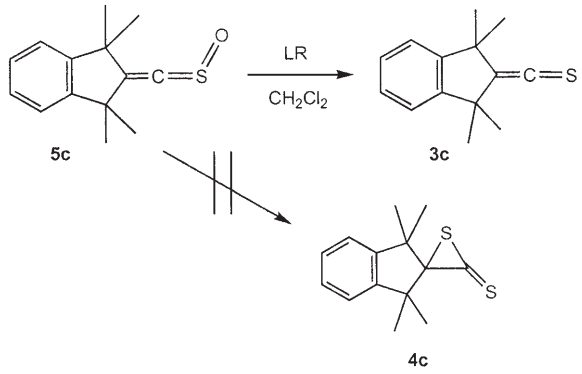
Scheme 2.

spectroscopy, IR spectrometry, elemental analysis, and X-ray crystallographic analysis.[6] Similarly, treatment of (2,2,6,6-tetramethylcyclohexylidene)methanethione *S*-oxide (**5b**) with LR at room temperature resulted in the formation of 3,3-(2′,2,′6′,6′-tetramethylcyclohexyl)thiirane-2-thione (**4b**) in 64% yield (Scheme 3). However, the reaction of



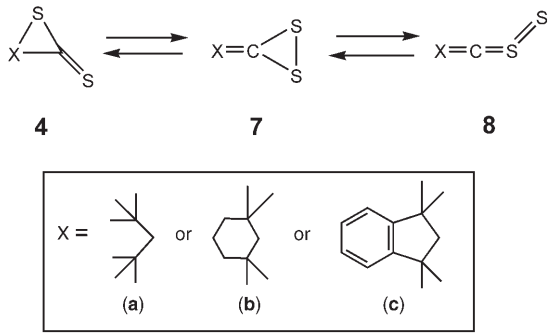
Scheme 3.

(1,1,3,3-tetramethyl-1*H*-inden-2(3*H*)-ylidene)methanethione *S*-oxide (**5c**) with LR at room temperature gave not 3,3-(1′,1′,3′,3′-tetramethyl-2′-indan)thiirane-2-thione (**4c**), but (1,1,3,3-tetramethyl-1*H*-inden-2(3*H*)-ylidene)methanethione (**3c**), suggesting that the steric effect of **4c** is smaller than that of **4a** and **b** (Scheme 4).



Scheme 4.

As α-dithiolactone is an isomer of dithiirane (**7**) and thioketene *S*-sulfide (**8**), the stabilities of α-dithiolactone **4**, dithiirane **7**, and thioketene *S*-sulfide **8** were compared (Scheme 5).[9]



Scheme 5.

By means of geometry optimization and frequency calculation at the B3LYP/6-31G(d,p) level, **4a** was calculated to be 56.5 and 79.9 kJ mol^{-1} more stable than 3-(2,2,4,4-tetramethylpentan-3-ylidene)dithiirane (**7a**) and di-*tert*-butylthioketene *S*-sulfide (**8a**), respectively, at the ground state S_0 (Figure 1). The difference in zero vibration energy between **4a** and **7a** is similar to that between **4b** and 3-(2,2,6,6-tetramethylcyclohexylidene)dithiirane (**7b**), whereas the difference in zero vibration energy between **4c** and **7c** is smaller than the above, suggesting that **4c** easily isomerizes to **7c**, which might explain the difficulty of isolating **4c**.

To confirm the stability of **4**, thermolysis of **4** was carried out. When α-dithiolactones **4a** and **4b** were refluxed in [D_8]toluene, thioketenes **3a** and **3b** were obtained. The rate of thermolysis of **4a** could be conveniently and accurately monitored by ^{1}H NMR spectroscopy. First-order reaction was observed by this technique. A rate constant of 1.14×

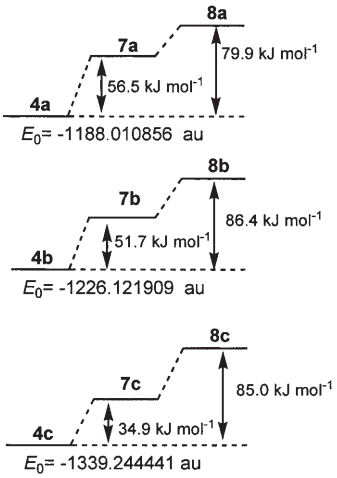
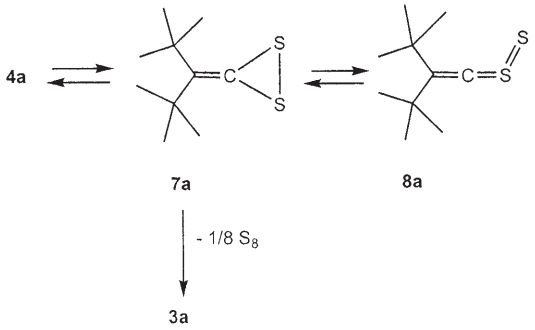


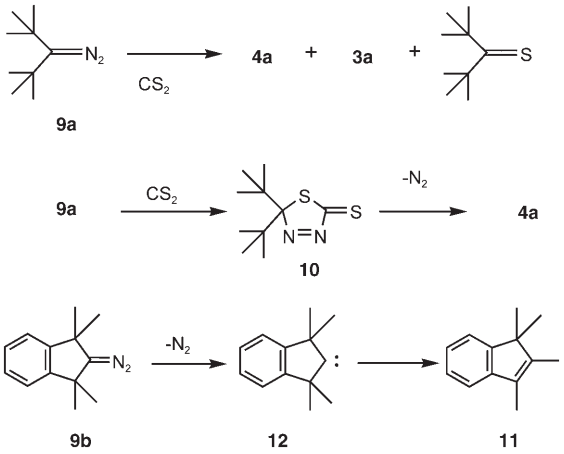
Figure 1. Calculated zero vibration energies of **4**, **7**, and **8**.

$10^{-2}\,h^{-1}$ at 393 K in [D_{10}]xylene was observed. Addition of sulfur did not affect the rate constant of this reaction, suggesting that direct sulfur extrusion of **4a** or **7a** might be operative. By comparison with the calculated zero vibration energy of **4a** and **7a**, **4a** was speculated to isomerize to **7a**, which extruded sulfur to give **3a** (Scheme 6).



Scheme 6.

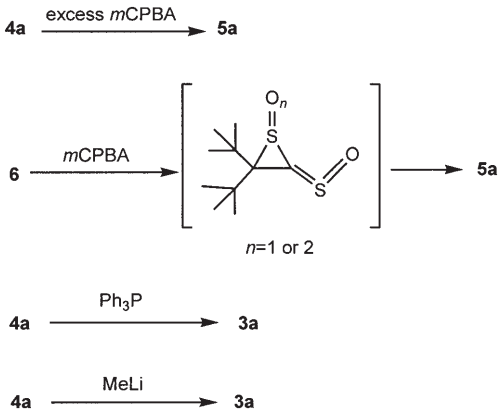
As the synthesis of thioketene *S*-oxide **5a** requires eight steps, starting from commercially available pivalonitrile,[7] a much shorter synthetic method of **4** is preferable. Schönberg reported the synthesis of 3,3,6,6-tetraphenyl-1,2,4,5-tetrathiane by reacting diphenyldiazomethane with carbon disulfide,[5d] the intermediate of which was surmised to be α-dithiolactone. Therefore, we attempted the synthesis of **4a** by reacting di-*tert*-butyl diazomethane (**9a**) with carbon disulfide (Scheme 7). When **9a** was heated in refluxing carbon disulfide for two days, **4a** was obtained in 17% yield along with **3a** in 34% yield and di-*tert*-butyl thioketone in 27% yield. We speculated that the extrusion of nitrogen from intermediate **10** would give **4a**. This is another method for the synthesis of **4a**. Refluxing a solution of diazo-1,1,3,3-tetramethylindane (**9b**) in carbon disulfide for one day afforded not **4c** but 1,1,2,3-tetramethyl-1*H*-indene (**11**)[10] in 58% yield, suggesting that **9b** did not react with carbon disulfide,



Scheme 7.

and carbene intermediate (**12**),[11] thus formed by nitrogen extrusion, rearranged to give **11**.

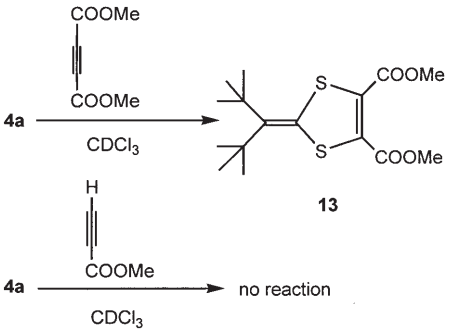
Reaction of α-dithiolactone: The oxidation of **4a** with excess *m*CPBA gave **5a** almost quantitatively (Scheme 8).



Scheme 8.

Reaction of **6** with *m*CPBA gave the same results. Presumably, initially formed *S*-oxide **6** was further oxidized to give episulfide *S*-oxide or *S,S*-dioxide, which extruded SO or SO_2 to give **5a**. Schaumann and Behrens reported that the oxidation of α-thiolactone afforded the corresponding ketene, the intermediate of which might be episulfide *S*-oxide.[4] The present result is similar to that of Schaumann and Behrens. The desulfurization of **4a** with triphenylphosphine in refluxing chloroform gave **3a** in almost quantitative yield along with triphenylphosphine sulfide. The reaction of **4a** with methyllithium in benzene at room temperature afforded **3a** almost quantitatively. The ring strain of episulfide eliminated the sulfur of **4a**.

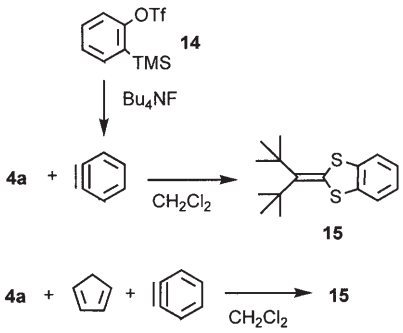
To confirm 1,3-dipolarophilic reactivity, the reaction of **4a** with different acetylenes was carried out (Scheme 9). The



Scheme 9.

reaction of **4a** with DMAD in [D]chloroform afforded dimethyl 2-(2,2,4,4-tetramethylpentan-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**13**) in almost quantitative yield, whereas the reaction of **4a** with methyl propiolate in [D]chloroform led to the recovery of starting **4a** . Huisgen et al. reported that DMAD is 337 times more reactive as a 1,3-dipolarophile than methyl propiolate.[12] The difference in reactivity between DMAD and methyl propiolate in the present study is similar to that reported by Huisgen et al.

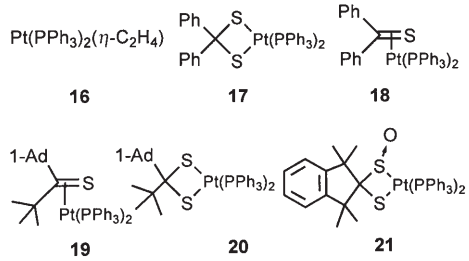
Treatment of **4a** with benzyne from *o*-trimethylsilylphenyl trifluoromethanesulfonate (**14**) and tetrabutylammonium fluoride (Scheme 10) resulted in the formation of 2-(2,2,4,4-



Scheme 10.

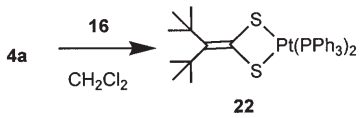
tetramethylpentan-3-ylidene)benzo[*d*][1,3]dithiole (**15**) in 90% yield. When a 1:1 mixture of **4a** and furan was reacted with benzyne, only **15** was obtained in 85% yield , suggesting that **4a** is more reactive than furan. Thus, α-dithiolactone is an excellent 1,3-dipole.

Synthesis of platinum complex: Weigand and Mloston studied the reactions of disulfides and thiosulfinates with platinum(0) complexes[13] and reported that the reaction of 1,2,4,5-tetrathiane and 1,2,4-trithiolane with ethylene (bistriphenylphosphine)platinum (**16**) gave dithiolato complex **17** and thiocarbonyl-platinum complex **18**, respectively.[14] They stated that the X-ray crystallographic analysis of **17** was unsuccessful due to the formation of **17** and **18** as a 1:1 mixture. Ishii and Nakayama reported that the reaction of dithiirane with **16** gave thiocarbonyl-platinum complex **19** and not dithiolato complex **20** and the reaction of dithiirane



oxide with **16** afforded (sulfenato-thilato)-platinum complex **21**.[15] Although Ishii and Nakayama isolated dithiolato complex **20** by reacting tetrathiolane with **16**, no X-ray crystallographic analysis of complex **20** was reported due to its low yield.[16] Thus, we attempted the formation of the dithiolato complex by reacting **4a** with **16**, and conducted X-ray crystallographic analysis of the resultant compound.

Treatment of **4a** with **16** gave (bistriphenylphosphine)-2-(2,2,4,4-tetramethylpentan-3-ylidene)-1,3-dithiolato-platinum (**22**) in 90% yield (Scheme 11). The reaction was completed within 3 min. As the recrystallization of **22** from hexane-dichloromethane (3:1) gave single crystals, its X-ray crystallographic analysis was carried out. Figure 2 shows an ORTEP drawing of **22**.



Scheme 11.

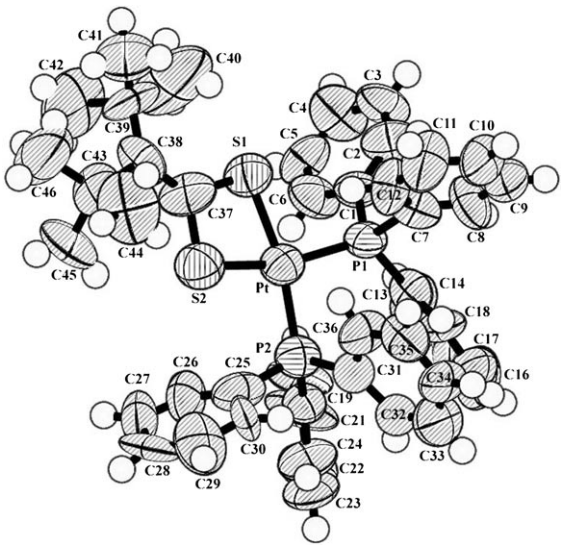


Figure 2. ORTEP drawing of complex **22**. Bond lengths: C37–S1: 1.790(3), C37–S2: 1.780(3), Pt–S1: 2.290(7), and Pt–S2: 2.283(8) Å. Bond angles: S2-C37-S1: 103.4(14), S2-Pt-S1: 75.6(3), C37-S1-Pt: 90.2(9), and C37-S2-Pt: 90.7(10)°.

The bond lengths of the four-membered ring of **22** are C–S: 1.790, 1.780 Å and S–Pt: 2.290, 2.283 Å. The bond lengths of the four-membered ring of (sulfenato-thiolato)platinum complex **21** are C–S: 1.871 or 1.827 Å and S–Pt: 2.353 or 2.314 Å.[15] The bond lengths of the four-membered ring of **22** are shorter than those of the four-membered ring of **21**. Thus, complex **22** might be more stable than **21**. In the ^{31}P NMR spectrum, the phosphorus signal of **22** resonated at $\delta = 22.7$ ppm (J(Pt,P) = 2961 Hz). Weigand and Mloston reported that the phosphorus signal of **17** resonated at $\delta =$ 22.1 ppm (J(Pt,P) = 2970 Hz).[14] Ishii and Nakayama reported that the phosphorus signal of the **20** resonated at $\delta =$ 22.9 ppm (J(Pt,P) = 2925 Hz).[16] The phosphorus signal of **22** is similar to those of **17** and **20**.

Conclusions

Treatment of **5a–b** with LR at room temperature resulted in the formation of **4a–b** in high yields. This is the first example of the isolation of α-dithiolactones. The oxidation of **4a** with *m*CPBA (1 equiv) gave **6** almost quantitatively. Structural proof of **6** was provided by X-ray crystallographic analysis. Thermolysis of **4a** gave thioketene **3a** quantitatively. The reactions of **4a** with DMAD and benzyne afforded **13** and **15**, respectively, in high yields, suggesting that α-dithiolactone is an excellent 1,3-dipolarophile. The reaction of **4a** with **16** gave **22** in high yield. The structure of **22** was determined by X-ray crystallographic analysis.

Experimental Section

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) were recorded in $CDCl_3$ solvent, and chemical shifts are expressed in ppm relative to internal TMS. Melting points were uncorrected.

CCDC-605410 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of (1,1,3,3-tetramethyl-1*H*-inden-2(3*H*)-ylidene)methanethione (3c): 1,1,3,3-Tetramethyl-indan-2-carboxylic acid (0.218 g, 1.0 mmol) was refluxed in thionyl chloride (10 mL). After the reaction mixture had been stirred for 2 h, it was evaporated to give a yellow oil (1,1,3,3-tetramethyl-indan-2-carbonyl chloride). The mixture of 1,1,3,3-tetramethyl-indan-2-carbonyl chloride and P_4S_{10} (0.189 g, 0.85 mmol) was refluxed in pyridine (5 mL) for 9 h. The reaction mixture was evaporated to give a reddish-yellow oil, which was chromatographed over silica gel by elution with hexane to give pure **3c** (0.024 g, 0.11 mmol). Purple oil; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 1.22$ (s, 6H; CH_3), 1.24 (s, 6H; CH_3), 7.31 (t, 1H, $J = 8.0$ Hz), 7.42 (d, 1H, $J = 8.0$ Hz), 7.61 (t, 1H, $J = 8.0$ Hz), 7.91 ppm (d, 1H, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 25.9$ (CH_3), 26.1 (CH_3), 47.5, 48.8, 65.0, 123.3, 124.4, 127.6, 134.5, 143.2, 160.5, 254.9 ppm; elemental analysis calcd for $C_{14}H_{16}S$: C 77.72, H 7.45; found: C 77.39, H 7.72.

Synthesis of (1,1,3,3-tetramethyl-1*H*-inden-2(3*H*)-ylidene)methanethione *S*-oxide (5c): A solution of *m*CPBA (0.052 g, 0.30 mmol) in dichloromethane (2 mL) was added to a solution of (1,1,3,3-tetramethyl-1*H*-inden-2(3*H*)-ylidene)methanethione (**3c**) (0.054 g, 0.25 mmol) in dichloromethane (3 mL). After the reaction mixture had been stirred for 0.5 h, the reaction mixture was evaporated to give white-yellow crystals, which were chromatographed over silica gel by elution with hexane to give pure **5c** (0.049 g, 0.21 mmol). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 1.17$ (s, 6H), 1.28 (s, 6H), 7.28–7.34 (m, 2H), 7.47 (t, 1H, $J = 7.6$ Hz), 7.91 (d, 1H, $J = 8.0$ Hz) 8.63 ppm (d, 1H, $J = 7.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 25.2$, 26.1, 50.2, 53.6, 123.0, 127.8, 128.6, 132.8, 136.3, 153.7, 199.7 ppm; elemental analysis calcd for $C_{14}H_{16}OS \cdot 1/2\,H_2O$: C 69.67, H 7.10; found: C 69.80, H 7.25.

Synthesis of 3,3-di-*tert*-butylthiirane-2-thione (4a): A solution of Lawesson reagent (0.606 g, 1.5 mmol) was added in one portion to a solution of di-*tert*-butylthioketene *S*-oxide (**5a**) (0.186 g, 1.0 mmol) in dichloromethane (15 mL). After the reaction mixture had been stirred for 12 h, it was evaporated to give yellow oily crystals, which were chromatographed over silica gel by elution with hexane to give pure **4a** (0.137 g, 0.64 mmol). Sublimation of this compound gave the analytically pure sample. Yellow crystals; m.p. 98–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 1.28$ ppm (s, 18H; *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 30.4$, 39.5, 76.3, 226.7 ppm (C=S); IR (KBr): $\tilde{\nu} =$ 1367 cm^{-1} (C=S); EIMS *m*/*z* (%): found: 202 $[M]^+$ (4.1), 170 $[M-S]^+$ (2.5), 146 (11.7), 145 $[M-t\mathrm{Bu}]^+$ (16.5), 126 (15.7), 113 (15.1), 111 (26.8), 99 (8.1), 69 (15.2), 57 [*t*Bu] (100); elemental analysis calcd for $C_{10}H_{18}S_2$: C 59.35, H 8.96; found: C 59.05, H 8.65; UV/Vis: λ_{max} (ε) = 317.5 nm (4780), 269.0 (3974 mol^{-1} dm^3 cm^{-1}).

Synthesis of 3,3-(2,2,6,6-tetramethylcyclohexyl)thiirane-2-thione (4b): A solution of Lawesson reagent (0.606 g, 1.5 mmol) was added in one portion to a solution of (2,2,6,6-tetramethylcyclohexylidene)methanethione *S*-oxide (**5b**) (0.198 g, 1.0 mmol) in dichloromethane (15 mL). After the reaction mixture had been stirred for 12 h, it was evaporated to give yellow oily crystals, which were chromatographed over silica gel by elution with hexane to give pure **4b** (0.137 g, 0.64 mmol). Sublimation of this compound gave the analytically pure sample. Yellow crystals; m.p. 59–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 0.97$ (s, 6H), 1.24 (s, 6H), 1.75 (s, 4H), 1.75 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 18.8$, 27.8, 28.6, 38.5, 40.7, 75.4, 226.7 ppm. IR (KBr): $\tilde{\nu} = 1379$ cm^{-1} (C=S); elemental analysis calcd for $C_{11}H_{18}S_2$: C 61.62; H 8.46; found: C 61.16; H 8.07.

Thiation of (1,1,3,3-tetramethyl-1*H*-inden-2(3*H*)-ylidene)methanethione *S*-oxide (5c): Lawesson reagent (31 mg, 0.06 mmol) was added to a solution of (1,1,3,3-tetramethyl-1*H*-inden-2(3*H*)-ylidene)methanethione *S*-oxide (**5c**) (0.010 mg, 0.04 mmol) in [D]chloroform. After the reaction mixture had been stirred for 3 h, it was monitored by NMR spectroscopy. The presence of (1,1,3,3-tetramethyl-1*H*-inden-2(3*H*)-ylidene)methanethione (**3c**) was observed by ^{1}H NMR spectroscopic analysis. The reaction mixture was then evaporated to give a purple oil, which was chromatographed over silica gel by elution with hexane to give pure **3c** (0.008 g, 0.04 mmol).

Synthesis of 3,3-di-*tert*-butylthiirane-2-thione *S*-oxide (6): A solution of *m*-chloroperbenzoic acid (0.204 g, 1.2 mmol) in dichloromethane (3 mL) was added in one portion to a solution of 3,3-di-*tert*-butylthiirane-2-thione (**4a**) (0.161 g, 0.8 mmol) in dichloromethane (10 mL). After the reaction mixture had been stirred for 0.5 h, hexane (10 mL) was added to the reaction mixture, which was subsequently filtered and evaporated to give a deep-yellow oil. This oil was chromatographed over silica gel by elution with hexane/dichloromethane 1:1 to give pure **6** (0.164 g, 0.75 mmol). Yellow crystals; m.p. 97–99 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C,TMS): $\delta = 1.25$ ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 31.5$, 40.9, 83.4, 181.0 ppm; IR (KBr): 1095 cm^{-1} (C=S=0); elemental analysis calcd for $C_{10}H_{18}S_2O$: C 55.00, H 8.31; found: C 55.18, H 8.36; UV/Vis: λ_{max} (ε) = 321.5 nm (4580 mol^{-1} dm^3 cm^{-1}).

Reaction of di-*tert*-butyldiazomethane (9a) with carbon disulfide: A solution of di-*tert*-butyldiazomethane (**9a**) (0.77 g, 5.0 mmol) in carbon disulfide (30 mL) was stirred and refluxed for two days. After this time, the reaction mixture was evaporated to give a yellow oil, which was chromatographed over silica gel by elution with hexane to give **4a** (0.172 g, 0.85 mmol), **3a** (0.289 g, 1.70 mmol), and di-*tert*-butyl thioketone (0.213 g,

1.35 mmol). Purple oil; b.p. 70–75 °C (25 mmHg) (lit.[17] b.p. 61 °C (14 mmHg)).

Reaction of diazo-1,1,3,3-tetramethylindane (9b) with carbon disulfide: A mixture of 1,1,3,3-tetramethyl-2-indanone hydrazone (220 mg, 1.1 mmol), barium manganate (700 mg, 13.5 mmol), and calcium oxide (700 mg, 12.5 mmol) was refluxed in dichloromethane (5 mL). After the reaction mixture had been stirred for 1 h, it was filtered through celite. The reaction mixture was then evaporated to give diazo-1,1,3,3-tetramethyl indane (**9b**). A solution of **9b** in carbon disulfide (15 mL) was stirred and heated at 45 °C for a day. After this time, the reaction mixture was evaporated to give a red-yellow oil, which was chromatographed over silica gel by elution with hexane to give colorless oil **11** (0.110 g, 0.64 mmol).

Thermolysis of 4a: Compound **4a** (0.020 g, 0.10 mmol) was heated for four days in [D_8]toluene at 100 °C. Decomposition of **4a** and the formation of **3a** was observed by NMR spectroscopy. The reaction mixture was evaporated to give a purple oil, which was chromatographed over silica gel by elution with hexane to give **3a** (0.014 g, 0.088 mmol).

Reaction of 4a with triphenylphosphine: Triphenylphosphine (0.026 g, 0.10 mmol) was added to a solution of **4a** (0.020 g, 0.10 mmol) in [D]chloroform. The resulting reaction mixture was then heated for four days at 60 °C. The formation of **3a** was monitored by NMR spectroscopy. The reaction mixture was evaporated to give a purple oil, which was chromatographed over silica gel by elution with hexane to give **3a** (0.015 g, 0.092 mmol) and triphenylphosphine sulfide (0.027 g, 0.092 mmol).

Reaction of 4a with methyllithium: Methyllithium in diethyl ether (1.0 M, 0.25 mL, 0.25 mmol) was added to a solution of **4a** (0.050 g, 0.25 mmol) in benzene and the resulting mixture was stirred for 1 h. After the reaction mixture had been washed with water, it was evaporated to give a purple oil **3a** (0.040 g, 0.24 mmol).

Reaction of 4a with dimethyl acetylenedicarboxylate: Dimethyl acetylenedicarboxylate (0.036 g, 0.25 mmol) was added to a solution of **4a** (0.025 g, 0.12 mmol) in chloroform. After the reaction mixture had been refluxed for 2 h, it was evaporated to give yellow crystals. The mixture was purified on silica gel with hexane/dichloromethane 1:1 to give dimethyl 2-(2,2,4,4-tetramethylpentan-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**13**) (0.038 g, 0.11 mmol). Yellow crystals; m.p. 87.1–89.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 1.43$ (s, 18H; CH_3), 3.82 ppm (s, 6H; OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C, TMS): $\delta =$ 32.5 (*t*Bu), 41.5, 53.5 (OCH_3), 123.4, 130.4, 142.6, 160.8 ppm; elemental analysis calcd for $C_{16}H_{24}O_4S_2$: C 55.78, H 7.02; found: C 55.68, H 7.24.

Reaction of 4a with methyl propiolate: To a solution of **4a** (0.020 g, 0.10 mmol) in [D]chloroform was added methyl propiolate (0.018 g, 0.20 mmol). The solution was heated for two days at 60 °C and the reaction was monitored by NMR spectroscopy. After 24 h, **4a** was recovered unchanged.

Synthesis of 2-(2,2,4,4-tetramethylpentan-3-ylidene)benzo[*d*][1,3]dithiole (15): Tetrabutylammonium fluoride in THF complex (1.0 M, 1.0 mL, 1.0 mmol) was added to a solution of **4a** (0.101 g, 0.5 mmol) and *o*-trimethylsilylphenyl trifluoromethanesulfonate (0.149 g, 0.5 mmol) in dichloromethane (10 mL). After the reaction mixture had been stirred for 0.5 h, it was evaporated to give a red-yellow oil. The reddish-yellow oil washed with water and extracted with hexane. The combined extract was dried over magnesium sulfate, filtered, and then evaporated to give orange crystals, which were recrystallized from hexane to give yellow crystals **15** (0.125 g, 0.45 mmol). Yellow crystals; m.p. 46.2–52.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 1.51$ (s, 18H, *t*Bu), 6.99–7.02 (m, 2H), 7.19–7.21 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 32.9$ (*t*Bu), 41.5, 119.9, 124.9, 125.4, 136.9, 142.3 ppm; elemental analysis calcd for $C_{16}H_{22}S_2$: C 69.01, H 7.96; found: C 68.98, H 7.99.

Reaction of 4a and furan with benzyne: Tetrabutylammonium fluoride in THF complex (1.0 M, 0.606 g, 1.5 mmol) was added to a solution of **4a** (0.051 g, 0.25 mmol), furan (0.017 g, 0.025 mmol), and *o*-trimethylsilylphenyl trifluoromethanesulfonate (0.075 g, 0.025 mmol) in dichloromethane (5 mL). After the reaction mixture had been stirred for 0.5 h, it was evaporated to give a reddish-yellow oil, which was washed with water and extracted with hexane. The combined solution was dried over magnesium sulfate, filtered, and evaporated to give orange crystals. The orange crystals were recrystallized from hexane to give yellow crystals **15** (0.059 g, 0.21 mmol).

Synthesis of platinum complex (22): Ethylene (bistriphenylphosphine)-platinum (**16**) (0.075 g, 0.10 mmol) was added to a solution of **4a** (0.020 g, 0.10 mmol) in dichloromethane (2 mL). After the reaction mixture had been stirred for 0.5 h, it was evaporated to give a black-yellow solid. The residue was recrystallized from hexane/dichloromethane 3:1 to give yellow crystals **22** (0.083 g, 0.09 mmol). Yellow crystals; m.p. 253.0–255.1 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 1.38$ (s, 18H; *t*Bu), 7.12–7.46 ppm (m, 45H; PPh_3); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C, TMS): $\delta = 34.0$ (*t*Bu), 40.9, 127.8, 130.3, 130.9, 134.9, 137.2. 142.1 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 27 °C, H_3PO_4) $\delta = 22.7$ ppm (*J*-(Pt,P) = 2961 Hz); elemental analysis calcd for $C_{46}H_{48}P_2S_2Pt$: C 59.92, H 5.25; found: C 59.82, H 5.33.

Crystallographic data for 22: $C_{46}H_{48}P_2PtS_2$, monoclinic, $P2_1/n(14)$, $a =$ 13.572(2), $b = 19.845(2)$, and $c = 16.1360(17)$ Å, $\alpha = 90°$, $\beta = 107.374(6)°$, $\gamma = 90°$, $V = 4147.7(8)$ Å^3, $Z = 4$, Density (calcd) = 1.476 Mg m^{-3}, Crystal size $0.40 \times 0.40 \times 0.05$ mm^3. The final cycle of full-matrix least-squares refinement was based on 3994 observed reflections and variable parameters 456 with $R1 = 0.0890$ and $Rw = 0.2301$. *S* (goodness-of-fit) = 1.095. Reflection data were obtained at 293 K on a DIP-3200 X-ray diffractometer (Bruker AXS Co. LTD) with an imaging plate, $Cu_{K\alpha}$ radiation, and Ni filter.

[1] a) A. Ishii, T. Akazawa, T. Maruta, J. Nakayama, M. Hoshino, M. Shiro, *Angew. Chem.* **1994**, 106, 829–830; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 777–778; b) A. Ishii, T. Akazawa, M. -X. Ding, T. Honjo, T. Maruta, S. Nakamura, H. Nagaya, M. Ogura, K. Teramoto, M. Shiro, M. Hoshino, J. Nakayama, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 509–523; c) A. Ishii, R. Yamashita, M. Saito, J. Nakayama, *J. Org. Chem.* **2003**, *68*, 1555–1558; d) K. Shimada, K. Kodaki, S. Aoyagi, Y. Takikawa, C. Kabuto, *Chem. Lett.* **1999**, 695–696.

[2] a) R. V. Hoffmann, Z. Zhao, A. Costales, D. Clarke, *J. Org. Chem.* **2002**, *67*, 5284–5294; b) J. C. Sheehan, J. H. Beeson, *J. Am. Chem. Soc.* **1967**, *89*, 362–366; c) S. Sarel, H. Leader, *J. Am. Chem. Soc.* **1960**, *82*, 4752–4753.

[3] a) W. Adam, J. -C. Liu, O. Rodriquez, *J. Org. Chem.* **1973**, *38*, 2269–2270; b) R. Wheland, P. D. Bartlett, *J. Am. Chem. Soc.* **1970**, *92*, 6057–6058; c) W. Adam, R. Rucktaschel, *J. Am. Chem. Soc.* **1971**, *93*, 557–559; d) O. L. Chapman, P. W. Wojkowski, W. Adam, O, Rodriquez, R. Rucktaschel, *J. Am. Chem. Soc.* **1972**, *94*, 1365–1367.

[4] E. Schaumann, U. Behrens, *Angew. Chem.* **1977**, *89*, 750–775; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 722–723.

[5] a) K. Masaki, K. Akimoto, A. Ishii, S. Kumakura, J. Nakayama, *Sulfur Lett.* **1995**, *19*, 73–83; b) U. Kunze, R. Merkel, W. Winter, *Chem. Ber.* **1982**, *115*, 3653–3662; c) W. Winter, B. Hanspeter, H. Meier, *Z. Naturforsch. B* **1980**, *35*, 1015–1018; d) A. Schönberg, E. Frese, K. -H. Brosowski, *Chem. Ber.* **1962**, *95*, 3077–3083.

[6] K. Okuma, T. Shigetomi, Y. Nibu, K. Shioji, M. Yoshida, Y. Yokomori, *J. Am. Chem. Soc.* **2004**, *126*, 9508–9509.

[7] a) E. U. Elam, F. H. Rash, J. T. Dougherty, V. W. Gootlett, K. C. Brannock, *J. Org. Chem.* **1968**, *33*, 2738–2741; b) E. Schaumann, *Chem. Ber.* **1982**, *115*, 2755–2765.

[8] V. J. Rao, V. Ramamurthy, *J. Chem. Soc. Chem. Commun.* **1981**, 638–639.

[9] Ab initio MO calculations were carried out by using Gaussian 98 program at the B3LYP/6-31G(d,p) level. One au = 2624.6 kJ mol^{-1}. Calculated vibration frequencies of **1a**, **4**, and **5** were not imaginary. Gaussian 98 (Revision A.9) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Jr. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. A. Millam, D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari,

J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

[10] a) L. Skattebol, B. Boulette, *J. Org. Chem.* **1966**, *31*, 81–85; b) J. Buddrus, *Chem. Ber.* **1968**, *101*, 4152–4162; c) R. Knorr, J. Freudenreich, T. Roman, J. Mehlstaubl, P. Bohrer, *Tetrahedron* **1993**, *49*, 8837–8854.

[11] a) A. Ishii, R. Okazaki, N. Inamoto, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 861–867; b) R. Okazaki, A. Ishii, N. Inamoto, *Tetrahedron Lett.* **1984**, *25*, 5147–5150.

[12] R. Huisgen, X. Li, H. Giera, E. Langhals, *Helv. Chim. Acta*, **2001**, *84*, 981–999.

[13] a) W. Weigand, R. Wusch, *Chem. Ber.* **1996**, *129*, 1409–1419; b) W. Weigand, R. Wusch, K. Polborn, G. Mloston, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1518–1522; c) R. Wusch, W. Weigand, G. Nuspl, *J. Prakt. Chem.* **1999**, *341*, 768–772; d) W. Weigand, R. Wusch, K. Polborn, *Inorg. Chim. Acta* **1998**, *273*, 106–110.

[14] W. Weigand, R. Wusch, C. Robl, G. Mloston, H. Noth, M. Schmidt, *Z. Naturforsch. B* **2000**, *55*, 453–458.

[15] A. Ishii, M. Saito, M. Murata, J. Nakayama, *Eur. J. Org. Chem.* **2002**, 979–982.

[16] A. Ishii, M. Murata, H. Oshida, K. Matsumoto, J. Nakayama, *Eur. J. Inorg. Chem.* **2003**, 3716–3721. See also M. Green, R. B. L. Osborn, F. G. A. Stone, *J. Chem. Soc. A* **1970**, 944–946.

[17] D. H. R. Barton, F. S. Guziec, Jr., I. Shahak, *J. Chem. Soc. Perkin Trans. 1* **1974**, 1794–1799.

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