Reaction between Dithiirane 1-Oxides and a Platinum(0) Complex

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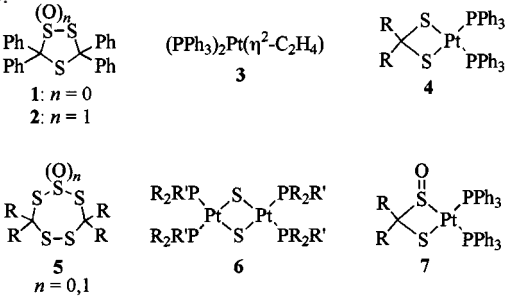
Treatment of dithiirane 1-oxides **9** with $(Ph_3P)_2Pt(\eta^2\text{-}CH_2{=}CH_2)$ (**3**) yielded the corresponding four-membered (sulfenato–thiolato)Pt^{II} complexes **7** in high yields. The structures of **7** were determined by ^{31}P NMR spectroscopy and, for **7e**, X-ray crystallography. Treatment of dithiirane **8** with **3**, on the other hand, gave the (η^2-thiocarbonyl)platinum complex **10** and not the dithiolato Pt^{II} complex **4**.

Introduction

The chemistry of sulfido complexes of platinum has been drawing considerable interest.[1] In recent years, Weigand and Mloston have been extensively studying the reactions of cyclic organosulfur compounds possessing disulfide [−S−S−] and thiosulfinate [−S(O)−S−] linkages with platinum(0) complexes.[2−7] Treatment of 1,2,4-trithiolane **1** and the 1-oxide **2** with $(Ph_3P)_2Pt(\eta^2\text{-}CH_2{=}CH_2)$ (**3**) was reported to give the four-membered dithiolato Pt^{II} complex **4** (R = Ph) and an (η^2-thiocarbonyl)platinum complex.[3,4] Treatment of 1,2,3,5,6-pentathiepanes **5** with **3** yielded both **4** and complex **6**.[3,4] In the case of 1,2,4-trithiolane 4-oxide, the reaction produced (sulfenato−thiolato)Pt^{II} complex **7** and an (η^2-thiocarbonyl)platinum complex.[8] It was also reported that treatment of complex **6** with dichloromethane yielded the corresponding four-membered (dithiolato)Pt^{II} complexes $[(R_2R'P)_2Pt(S_2CH_2)]$.[1,9,10] The complexes **4** and **7** correspond to those derived from dithiirane **8** and dithiirane 1-oxide **9** with **3**, respectively. In connection with our ongoing study on the synthesis and reactivity of isolable, stable dithiiranes,[11−13] the above reports prompted us to examine treatment of dithiiranes **8** and the 1-oxides **9** with **3**.



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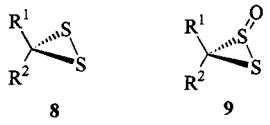
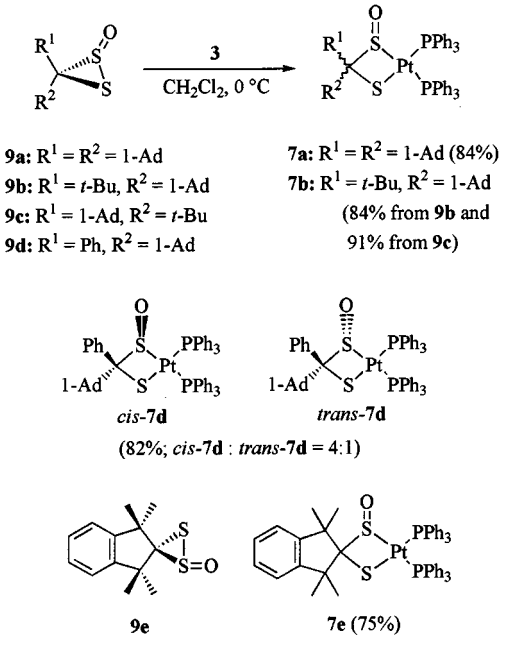


Results and Discussion

Treatment of dithiirane 1-oxides **9a**−**e**[11k] with **3**, carried out in dichloromethane at 0 °C, produced (sulfenato−thiolato)platinum(II) complexes **7a**, **7b**, **7d**, and **7e** in high yields (Scheme 1). The structures of the complexes were supported by their ^{31}P NMR spectroscopic data, summarized in Table 1. The phosphorus atom *trans* to the sulfenato

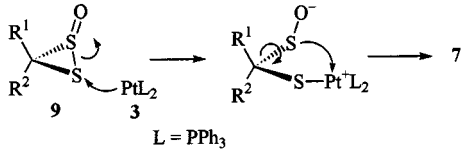


Scheme 1

Table 1. ^{31}P NMR spectroscopic data of (sulfenato−thiolato)Pt^{II} complexes **7a**, **7b**, **7d**, and **7e**, and (η^2-thiocarbonyl)platinum complex **10**

Compound	δ	$^1J(^{195}Pt-^{31}P)$ [Hz]	$^2J(^{31}P-^{31}P)$ [Hz]
7a	16.6	3368	24
	18.0	2371	24
7b (1:1 mixture)	16.3	3358	24
	16.8	3320	25
	17.7	2347	23
	17.9	2354	23
cis-**7d** (major)	16.9	2425	22
	18.6	3449	22
trans-**7d** (minor)	16.2	3326	23
	17.2	2380	23
7e	16.7	2360	23
	17.6	3392	23
10	20.2	2781	9
	23.5	4663	9

(S=O) group had a $^1J(^{195}Pt-^{31}P)$ value smaller than that of the other phosphorus atom, due to the *trans* influence of the S=O group being greater than that of the thiolato group.[2] Dithiirane oxides **9b** and **9c** are epimers. Treatment of both **9b** and **9c** with **3** yielded 1:1 mixtures of diastereomers **7b**, which can be explained by the mechanism proposed by Weigand,[2] involving an attack of the platinum atom on the sulfenyl sulfur atom of **9** to give an open-chain intermediate (Scheme 2). This nonstereospecific reaction was also observed on treatment of **9d** with **3** to give a 4:1 mixture of *cis*-**7d** and *trans*-**7d** in 82% yield. The assignment of the diastereomers was based on the ^1H NMR spectrum of the mixture; one isomer showed signals of characteristically deshielded *ortho*-protons of the phenyl group derived from **9d** (δ = 8.00), owing to the anisotropic effect of the sulfoxide group, and thus was assigned as *cis*-**7d**. Similarly, the signals of the three protons of the 1-adamantyl group of *trans*-**7d** appeared at lower field (δ = 2.07) than those of other 1-adamantyl protons of *cis*- and *trans*-**7d**. These diastereomeric mixtures of **7b** and **7d** could not be separated by chromatography or recrystallization despite much effort. The four-membered cyclic (sulfenato−thiolato)Pt^{II} complexes **7** were thermally fairly stable, but gradually decomposed in solution to give complex mixtures involving triphenylphosphane sulfide.



Scheme 2

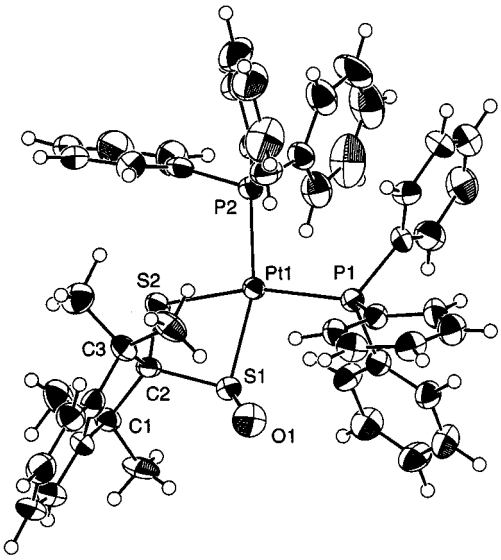
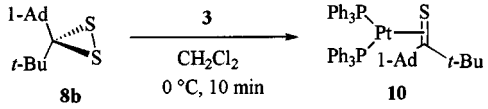


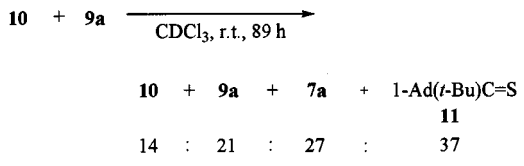
Figure 1. ORTEP drawing of **7e** (50% ellipsoidal probability); relevant bond lengths [Å] and angles [°] data: C1−C2 1.568(9), C2−C3 1.574(9), C2−S1 1.871(7), C2−S2 1.827(6), O1−S1 1.473(6), P1−Pt1, 2.289(2); P2−Pt1 2.314(2), S1−Pt1 2.353(2), S2−Pt1 2.314(2), C1−C2−C3 106.0(5), C1−C2−S1 110.9(5), C1−C2−S2 116.4(5), C3−C2−S1 117.5(5), C3−C2−S2 112.8(5), S1−C2−S2 93.4(3), C2−S1−O1 113.1(4), C2−S1−Pt1 89.6(2), O1−S1−Pt1 120.5(3), C2−S2−Pt1 92.0(3), P1−Pt1−P2 100.7(1), P1−Pt1−S1 95.4(1), P1−Pt1−S2 162.6(1), P2−Pt2−S1 163.9(1), P2−Pt1−S2 93.8, S1−Pt2−S2 70.4(1)

Figure 1 depicts an ORTEP drawing of **7e**. The ligands around the Pt1 atom are not planer, and the torsion angle between the plane S2−Pt1−S1 and the plane P2−Pt1−P1 is 10.4°. The P2−Pt1 bond [2.314(2) Å] is significantly longer than the P1−Pt1 bond [2.289(2) Å], which is attributable to the larger *trans* influence of the sulfenato group in comparison to that of the thiolato group.[2]

We next examined treatment of dithiirane **8b** with **3** in CH_2Cl_2 at 0 °C, which gave the corresponding (η^2-thiocarbonyl)platinum complex **10** in 76% yield, and not the expected bis(thiolato)Pt^{II} complex **4** (Scheme 3). The structure of **10** was determined by comparison of the spectroscopic data with those of an authentic sample prepared by treatment of 1-adamantyl *tert*-butyl thioketone (**11**) with **3**. Similar (η^2-thiocarbonyl)platinum complexes have been synthesized in an analogous way.[4] In this reaction, one sulfur atom of **8b** might be used to produce **6** (R = R′ = Ph), but we did not observe the presence of the complex, probably because of its decomposition in the CH_2Cl_2 used as the solvent in the reaction.[1,9,10] Incidentally, complex **10** reacted slowly with di(1-adamantyl)dithiirane 1-oxide **9a** to give a mixture of **9a**, **10**, **7a**, and **11** in the ratio of 14:21:27:37 after 89 h in $CDCl_3$ (Scheme 4).



Scheme 3



Scheme 4

In conclusion, treatment of dithiirane 1-oxides **9** with a Pt^0 complex **3** yielded the (sulfenato−thiolato)Pt^{II} complexes **7** in high yields, whilst treatment of dithiirane **8b** with **3** gave the (η^2-thiocarbonyl)platinum complex **10**. The former is one of the few reactions of dithiirane derivatives to give a stable product retaining the two sulfur atoms of the starting dithiirane derivative. Thus, the reaction enabled us to trap dithiirane 1-oxides that were not stable enough to be isolable.

Experimental Section

General: Melting points were determined with a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H [400 (or 300 MHz)] and ^{13}C NMR (100.6 MHz) spectra were determined with Bruker AM 400 and ARX 400 (or AC 300 for 300 MHz) spectrometers at 25 °C, with $CDCl_3$ as the solvent unless otherwise noted. IR spectra were taken with a Hitachi 270−50 spectrometer or a Perkin−Elmer System 2000 FT-IR spectrometer. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. Column chromatography was performed with silica gel and the eluent is given in parentheses.

Treatment of 3,3-Di(1-adamantyl)dithiirane 1-Oxide (9a) with $(Ph_3P)_2Pt(C_2H_4)$ (3): Dithiirane 1-oxide **9a** (6.4 mg, 0.018 mmol) and **3** (13.2 mg, 0.018 mmol) were dissolved in CH_2Cl_2 (1 mL) at 0 °C under argon, and the mixture was stirred for 1 h at 0 °C. The solvent was evaporated to dryness, and the residue was subjected to column chromatography (CH_2Cl_2/EtOAc, 5:1) to give [di(1-adamantyl)methanedithiolato(2−)-κ*S*,κ*S*′]bis(triphenylphosphane)platinum *S*-oxide (**7a**) (15.9 mg, 84%): yellow crystals, m.p. 182−183 °C decomp. (CH_2Cl_2/hexane). ^{1}H NMR (400 MHz): δ = 1.50−1.73 (m, 15 H), 1.80−2.01 (m, 9 H), 2.0−3.0 (br. s, 3 H), 2.19−2.27 (m, 3 H), 7.11−7.22 (m, 12 H), 7.22−7.32 (m, 6 H), 7.37−7.49 (m, 12 H). IR (KBr): $\tilde{\nu}$ = 1095 cm^{-1} (S=O). $C_{57}H_{60}OP_2PtS_2$ (1082.25): calcd. C 63.26, H 5.59; found C 63.95, H 6.30.

Treatment of *t*-3-(1-Adamantyl)-*c*-3-*tert*-butyldithiirane *r*-1-Oxide (9b) with $(Ph_3P)_2Pt(C_2H_4)$ (3): In a similar manner, treatment of **9b** (10.0 mg, 0.0357 mmol) with **3** (26.3 mg, 0.0357 mmol) yielded [1-(1-adamantyl)-2,2-dimethylpropane-1,1-dithiolato(2−)-κ*S*,κ*S*′]-bis(triphenylphosphane)platinum *S*-oxide (**7b**) (29.8 mg, 84%): yellow crystals, m.p. 174−176 °C (Et_2O). ^{1}H NMR (300 MHz): δ = 1.17 (s, 6 H), 1.50−1.71 (m, 9 H), 1.83−1.93 (m, 5 H), 2.12−2.17 (m, 2 H), 2.20−2.70 (br. s, 2 H), 7.11−7.22 (m, 12 H), 7.22−7.32 (m, 6 H), 7.37−7.49 (m, 12 H). IR (KBr): $\tilde{\nu}$ = 1096 cm^{-1} (S=O). $C_{51}H_{54}OP_2PtS_2$ (1004.13): calcd. C 61.00, H 5.42; found C 60.69, H 5.67.

Treatment of *c*-3-(1-Adamantyl)-*t*-3-*tert*-butyldithiirane *r*-1-Oxide (9c) with $(Ph_3P)_2Pt(C_2H_4)$ (3): In a similar manner, **9c** (7.3 mg, 0.026 mmol) was allowed to react with **3** (19.2 mg, 0.026 mmol) to give **7b** (20 mg, 77%).

Treatment of *t*-3-(1-Adamantyl)-*c*-3-phenyldithiirane *r*-1-Oxide (9d) with $(Ph_3P)_2Pt(C_2H_4)$ (3): In a similar manner, **9d** (8.2 mg, 0.030 mmol) was treated with **3** (22.5 mg, 0.030 mmol) to give a 4:1 mixture of [*t*-(1-adamantyl)-*c*-phenylmethanedithiolato(2−)-κ*S*,κ*S*′]bis(triphenylphosphane)platinum *r*-*S*-oxide (*cis*-**2d**) and [*c*-(1-adamantyl)-*t*-phenylmethanedithiolato(2−)-κ*S*,κ*S*′]bis-(triphenylphosphane)platinum *r*-*S*-oxide (*trans*-**7d**) (24.6 mg, 82%). IR (KBr): $\tilde{\nu}$ = 1096 cm^{-1} (S=O). ***cis*-7d (Major Isomer):** ^{1}H NMR (400 MHz): δ = 1.48 (br. s, 6 H), 1.60 (br. d, *J* = 11 Hz, 3 H), 1.71 (br. d, *J* = 12 Hz, 3 H), 1.84 (br. s, 3 H), 7.00−7.48 (m, 33 H), 8.00 (dd, *J* = 8, 1.8 Hz, 2 H). ***trans*-7d (Minor Isomer):** ^{1}H NMR (400 MHz): δ = 1.52 (br. s, 6 H), 1.86−1.89 (m, 6 H), 2.07 (br. d, *J* = 10 Hz, 3 H), 7.0−7.48 (m, 35 H).

Treatment of 1,1,3,3-Tetramethylindane-2-spiro-3′-dithiirane 1′-Oxide (9e) with $(Ph_3P)_2Pt(C_2H_4)$ (3): In a similar manner, treatment of **9e** (12.0 mg, 0.0476 mmol) with **3** (35.6 mg, 0.0476 mmol) gave [1,1,3,3-tetramethylindane-2,2-dithiolato(2−)-κ*S*,κ*S*′]bis(triphenylphosphane)platinum *S*-oxide (**7e**) (34.6 mg, 75%): yellow plates, m.p. 187−189 °C decomp. (CH_2Cl_2/hexane). ^{1}H NMR (400 MHz): δ = 1.08 (s, 3 H), 1.40 (s, 3 H), 1.46 (s, 3 H), 1.91 (s, 3 H), 7.02−7.08 (m, 4 H), 7.13−7.30 (m, 18 H), 7.42−7.51 (m, 12 H). IR (KBr): $\tilde{\nu}$ = 1094 cm^{-1} (S=O). $C_{49}H_{46}OP_2PtS_2$ (972.05): calcd. C 60.55, H 4.77; found C 60.29, H 4.71.

Crystal Data for 7e: $C_{49}H_{46}OP_2PtS_2$, M_w = 972.05, yellow plates, 0.20 × 0.18 × 0.06 mm, triclinic, $P\bar{1}$, *a* = 11.3040(4), *b* = 12.2640(5), *c* = 15.2120(7) Å, α = 82.3180(10), β = 81.843(2), γ = 88.816(2)°, *V* = 2068.80(10) Å^3, *Z* = 2, $\rho_{calcd.}$ = 1.561 g cm^{-3}, *F*(000) = 976, μ(Mo-K_α) = 3.61 mm^{-1}. Mac Science DIP3000 diffractometer with a graphite−monochromated Mo-K_α radiation (λ = 0.71073 Å). Data reduction was performed by use of the maXus program system.[14] Absorption correction was performed by SORTAV.[15] Intensity data of 12,835 unique reflections were collected in the range of $-10 \le h \le 12$, $-15 \le k \le 15$, $-19 \le l \le 19$. 10,961 reflections [$I \ge 2\sigma(I)$] were used for refinement (623 parameters). Non-hydrogen atoms were refined anisotropically. The final R_1 = 0.046 (0.057 for all), wR_2 = 0.076, and GOF = 2.366; max/min. residual electron density = 1.84/−1.12 e Å^{-3}. CCDC-172343 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Treatment of 3-(1-Adamantyl)-3-*tert*-butyldithiirane (8b) with 3: Dithiirane **8b**[16] (3.6 mg, 0.013 mmol) was added at 0 °C to a solution of **3** (3.6 mg, 0.013 mmol) in CH_2Cl_2 (1 mL), and the mixture was stirred for 10 min. The color of the solution turned from yellowish orange to colorless. The solvents were evaporated to dryness, and the residue was subjected to column chromatography (hexane/CH_2Cl_2, 1:1) to give [(*S*,1-η)-1-(1-adamantyl)-2,2-dimethylpropane-1-thione]bis(triphenylphosphane)platinum (**10**) (9.6 mg, 76%): colorless crystals, m.p. 163−164 °C decomp. ($CHCl_3$/hexane). ^{1}H NMR (400 MHz): δ = 1.05 (s, 9 H), 1.45−1.52 (m, 6 H), 1.74−1.81 (m, 6 H), 1.81−1.89 (m, 3 H), 7.03−7.11 (m, 12 H), 7.16−7.23 (m, 12 H), 7.52−7.59 (m, 6 H). $C_{51}H_{54}P_2PtS$ (956.08): calcd. C 64.07, H 5.69; found C 64.05, H 5.68.

Treatment of 1-Adamantyl *tert*-Butyl Thioketone (11) with 3: Thioketone **11** (10 mg, 0.042 mmol) was added at 0 °C to a solution of **3** (32 mg, 0.042 mmol) in CH_2Cl_2 (1 mL), and the mixture was stirred for 5 min. The color of the solution turned from purple to colorless. The solvents were evaporated to dryness, and the residue

was subjected to column chromatography (hexane/CH_2Cl_2, 1:1) to give **10** (29 mg, 71%).

Acknowledgments

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[1] S.-W. A. Fong, T. S. A. Hor, *J. Chem. Soc., Dalton Trans.* **1999**, 639−651.
[2] W. Weigand, R. Wünsch, *Chem. Ber.* **1996**, *129*, 1409−1419, and references cited therein.
[3] W. Weigand, R. Wünsch, K. Polborn, G. Mloston, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1518−1522.
[4] W. Weigand, R. Wünsch, C. Robl, G. Mloston, H. Nöth, M. Schmidt, *Z. Naturforsch., Teil B* **2000**, *55*, 453−458.
[5] R. Wünsch, W. Weigand, G. Nuspl, *J. Prakt. Chem.* **1999**, *341*, 768−772.
[6] W. Weigand, R. Wünsch, K. Polborn, *Inorg. Chim. Acta* **1998**, *273*, 106−110.
[7] D. Seebach, A. K. Beck, M. Hayakawa, G. Jaeschke, F. N. M. Kühnle, I. Nägeli, A. B. Pinkerton, P. B. Rheiner, R. O. Duthaler, P. M. Rothe, W. Weigand, R. Wünsch, S. Dick, R. Nesper, M. Wörle, V. Gramlich, *Bull. Soc. Chim. Fr.* **1997**, *134*, 315−331.
[8] S. Bräutigam, R. Wünsch, W. Weigand, A. Majchrzak, G. Mloston, *The Sixth International Conference on Heteroatom Chemistry* (ICHAC-6), Lodz, Poland, **2001**, Book of Abstracts, S4-O-2 (p. 108).
[9] A. Shaver, R. D. Lai, P. H. Bird, W. Wickramasinghe, *Can. J. Chem.* **1985**, *63*, 2555−2558.
[10] V. W.-W. Yam, P. K.-Y. Yeung, K.-K. Cheung, *J. Chem. Soc., Chem. Commun.* **1995**, 267−269.
[11] [11a] A. Ishii, T. Akazawa, M.-X. Ding, T. Honjo, J. Nakayama, M. Hoshino, M. Shiro, *J. Am. Chem. Soc.* **1993**, *115*, 4914−4915. [11b] A. Ishii, T. Akazawa, T. Maruta, J. Nakayama, M. Hoshino, M. Shiro, *Angew. Chem. Int. Ed.* **1994**, *33*, 777−779. [11c] A. Ishii, T. Maruta, K. Teramoto, J. Nakayama, *Sulfur Lett.* **1995**, *18*, 237−242. [11d] A. Ishii, Y.-N. Jin, H. Nagaya, M. Hoshino, J. Nakayama, *Tetrahedron Lett.* **1995**, *36*, 1867−1870. [11e] A. Ishii, K. Umezawa, J. Nakayama, *Tetrahedron Lett.* **1997**, *38*, 1431−1434. [11f] 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. [11g] A. Ishii, *J. Synth. Org. Chem. Jpn.* **1997**, *55*, 897−906. [11h] Y.-N. Jin, A. Ishii, Y. Sugihara, J. Nakayama, *Tetrahedron Lett.* **1998**, *39*, 3525−3528. [11i] A. Ishii, M. Nakabayashi, J. Nakayama, *J. Am. Chem. Soc.* **1999**, *121*, 7959−7960. [11j] A. Ishii, M. Nakabayashi, Y.-N. Jin, J. Nakayama, *J. Organomet. Chem.* **2000**, *611*, 127−135. [11k] A. Ishii, T. Kawai, K. Tekura, H. Oshida, J. Nakayama, *Angew. Chem. Int. Ed.* **2001**, *40*, 1924−1926.
[12] For a review, see: J. Nakayama, A. Ishii, *Adv. Heterocycl. Chem.* **2000**, *77*, 221−284.
[13] See also recent papers on dithiiranes. [13a] K. Shimada, K. Kodaki, S. Aoyagi, Y. Takikawa, C. Kabuto, *Chem. Lett.* **1999**, 695−696. [13b] G. Mloston, J. Romanski, H. P. Reisenauer, G. Maier, *Angew. Chem. Int. Ed.* **2001**, *40*, 393−397.
[14] S. Mackay, C. J. Gilmore, C. Edwards, N. Stewart, K. Shankland, Nonius, The Netherlands, Mac Science, Japan, and The University of Glasgow, **1999**.
[15] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33.
[16] Dithiirane **8b** was prepared by reduction of **9b** with Lawesson's reagent: A. Ishii, M. Saito, J. Nakayama, unpublished results.

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