column chromatography on silica gel with a mixture of chloroform and acetonitrile (3:1). Attempts to reduce **5** with a hydride reagent proved unsatisfactory. Thus, $LiAlH_4$ reduction of the mixture of **5a** and **5b** at −100 °C for 30 min yielded, instead of the expected thiepine 1-oxide complex (**6**), the 6,7-dihydrothiepine 1-oxide complex (**7**).[10] The structure of **7** followed from its NMR spectra together with its independent synthesis starting from 2,7-dihydrothiepine 1,1-dioxide (**8**)[9] as shown in Scheme I. The formation of **7** can reasonably be rationalized on the basis that a positive charge in **5a** and **5b** mainly resides in the 6-position as exemplified by the low-field ^1H and ^{13}C NMR chemical shifts of this position ($\delta_H = 7.73$ and 7.58, $\delta_C = 161.0$ and 160.4, respectively). A likely mechanism, therefore, involves initial hydride attack at the 6-position of **5** with elimination of the *p*-tolyloxy group followed by a second hydride attack at the 7-position.

At this stage, we focused our attention on a lanthanide reagent for the reduction. The main oxidation state of lanthanides is +3, hence divalent lanthanides are one-electron donors. Furthermore, another characteristic feature of lanthanides is their strong oxophilicity which can be helpful for the activation of oxygenated organic functions.[15] In view of these characteristics of lanthanides, samarium diiodide[16] may be a versatile reagent to reduce an aryloxysulfoxonium salt to sulfide.

On reaction with the SmI_2–THF complex, either in the presence or in the absence of HMPA,[17] **5** was reduced quite easily, without saturation of the 6,7-double bond, to the desired (thiepine)iron tricarbonyl (**2**),[10] which could be isolated and purified by chromatography on silica gel as stable yellow needles (38% yield, mp 54.5–55 °C after recrystallization from hexane). The structural assignment is fully supported by the spectral properties of this complex. The mass spectrum shows the parent ion peak at m/z 250 (exact mass, calcd for $C_9H_6O_3SFe$ 249.9387, found 249.9374). The infrared carbonyl absorptions (Nujol) occur at 2055, 1998, and 1981 cm^{-1}. The ^1H NMR (400 MHz, $CDCl_3$)[18] spectrum exhibits six ring protons at δ 3.92 (H-5, $J_{5,6} = 8.6$, $J_{5,4} = 8.2$, $J_{5,7} = J_{5,3} = 1.0$ Hz), 4.09 (H-2, $J_{2,3} = 7.3$, $J_{2,7} = 2.6$, $J_{2,4} = 1.6$ Hz), 4.77 (H-4, $J_{4,5} = 8.2$, $J_{4,3} = 4.6$, $J_{4,2} = 1.6$ Hz), 4.94 (H-3, $J_{3,2} = 7.3$, $J_{3,4} = 4.6$, $J_{3,5} = 1.0$ Hz), 5.94 (H-7, $J_{7,6} = 10.2$, $J_{7,2} = 2.6$, $J_{7,5} = 1.0$ Hz), and 6.04 (H-6, $J_{6,7} = 10.2$, $J_{6,5} = 8.6$ Hz). The ^{13}C NMR (100 MHz, $CDCl_3$)[18] spectrum indicates ring carbons at δ 57.9 (C-2), 62.7 (C-5), 83.9 (C-3), 93.3 (C-4), 120.5 (C-6), and 121.1 (C-7), along with the carbonyl carbon at 210.9 ppm. The complex **2** absorbs in the ultraviolet in cyclohexane: λ_{max} (log ϵ) 262 (4.04) and 335 nm (sh 3.54) with tailing up to 470 nm. An X-ray structural analysis, which to date has been unsuccessful due to its sensitivity upon X-ray irradiation, is to be carried out on the complex **2** in order to obtain detailed structural information.

These results demonstrate that thiepine is highly stabilized as a ligand in the complex **2**. Attempts to free the thiepine ligand from the iron tricarbonyl complex by low-temperature oxidation and/or irradiation are now underway. Furthermore, the general utilization of SmI_2 in reduction of sulfones to sulfides will be the topic of future reports from these laboratories.

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Supplementary Material Available: Spectral data for **2**, **4**, **5**, **7**, **9**, and **10** (8 pages). Ordering information is given on any current masthead page.

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(14) The available NMR data (see supplementary material) did not allow differentiation between the two stereoisomers.

(15) For reviews, see: (a) Kagan, H. B.; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573–6614. (b) Imamoto, T.; Tawarayama, Y.; Kusumoto, T.; Yokoyama, M. *Yuki Gosei Kagaku Kyokai Shi* **1984**, *42*, 143–152. (c) Imamoto, T. *Yuki Gosei Kagaku Kyokai Shi* **1988**, *46*, 540–552. (d) Inanaga, J. *Yuki Gosei Kagaku Kyokai Shi* **1989**, *47*, 200–211.

(16) The reduction of some sulfones to sulfides on treatment with SmI_2–THF complex in the presence of HMPA was recently described (Handa, Y.; Inanaga, J.; Yamaguchi, M. *J. Chem. Soc., Chem. Commun.* **1989**, 298–299); however direct reduction of **4** with this reducing system was unsuccessful.

(17) Inanaga, J.; Ishikawa, M.; Yamaguchi, M. *Chem. Lett.* **1987**, 1485–1486.

(18) Assignments were made with use of the NOESY, NOEDS, H-H COSY, and C-H COSY techniques.

Ring-Opening and Insertion of a Cyclic Thioether into a Palladium–Chlorine Bond

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Recently, a number of metal complexes[1,2] and surfaces[3] have been shown to mediate the ring-opening of cyclic thioethers. These studies have provided insight into the hydrodesulfurization of fossil fuels and revealed new patterns of reactivity such as the ring-opening, oligomerization of 3,3-dimethylthietane.[2] In the course of our studies of the reactivity of $Pd_2(\mu\text{-}Cl)_2Cl_2(PMe_3)_2$ (**1**) with sulfur ligands,[4-6] we have examined the reactivity of the dipalladium complex with thietane and have found a novel ring-opening, migratory insertion reaction to occur.

Reaction of **1** (0.200 g, 390 μmol) with 60 μL (830 μmol) of thiethane in 30 mL of refluxing ethanol gives rise to *cis*-$Pd_2Cl_2(\mu\text{-}SCH_2CH_2CH_2Cl)(\mu\text{-}Cl)(PMe_3)_2$ (**3**), as seen in Scheme I. After 48 h of reaction time, purified **3**[7] is isolated in 56% yield by allowing the filtered reaction mixture to stand at −10 °C and recrystallizing the resulting precipitate from chloroform. The molecular structure of **3** was determined through a single-crystal X-ray diffraction study.[8] An ORTEP diagram of the obtained structure is seen in Figure 1. The heavy atom framework is similar to that which has been previously[6,9] found for dipalladium

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(1) (a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387–394. (b) Hachgenei, J. W.; Angelici, R. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 909–910. (c) Ogilvy, A. E.; Draganjac, M.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1988**, *7*, 1171–1177. (d) Ogilvy, A. E.; Skaugset, A. E.; Rauchfuss *Organometallics* **1989**, *8*, 2739–2741. (e) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199–204. (f) Adams, R. D.; Pompeo, M. P. *Organometallics* **1990**, *9*, 1718–1720. (g) Adams, R. D.; Pompeo, M. P. *Organometallics* **1990**, *9*, 2651–2653. (h) Adams, R. D.; Chen, G.; Sun, S.; Wilfe, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 868–869. (i) Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1990**, *9*, 2875–2876. (j) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559–564.

(2) Adams, R. D.; Pompeo, M. P. *J. Am. Chem. Soc.* **1991**, *113*, 1619–1626.

(3) (a) Friend, C. M.; Roberts, J. *Acc. Chem. Res.* **1988**, *21*, 394–400 and references therein. (b) Calhorda, M. J.; Hoffmann, R.; Friend, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 50–61.

(4) Padilla, E. M.; Yamamoto, J. H.; Jensen, C. M. *Inorg. Chim. Acta* **1990**, *174*, 209–215.

(5) (a) Padilla, E. M.; Jensen, C. M. *Polyhedron* **1991**, *10*, 89–93. (b) Yamamoto, J. H.; Yoshida, W.; Jensen, C. M. *Inorg. Chem.* **1991**, *30*, 1353–1357.

(6) Padilla, E. M.; Golen, J. A.; Richmann, P. R.; Jensen, C. M. *Polyhedron*. In press.

(7) Spectroscopic data for **3**: ^1H NMR (500 MHz, CD_2Cl_2) δ 3.76 (t, $J_{H\text{-}H} = 6.3$ Hz, 2 H, SCH_2), 3.00 (t, $J_{H\text{-}H} = 7.5$ Hz, 2 H, $ClCH_2$), 2.34 (q, $J_{H\text{-}H} = 6.5$ Hz, 2 H, $CH_2CH_2CH_2$), 1.66 (d, $J_{P\text{-}H} = 12.0$ Hz, 18 H, $P(CH_3)_3$); $^{31}P\{^1H\}$ NMR (122 MHz CD_2Cl_2) δ 7.1 (s); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 43.8 ($ClCH_2$), 36.6 (SCH_2), 34.4 ($CH_2CH_2CH_2$), 16.4 ($J_{P\text{-}C} = 40.8$ Hz, $P(CH_3)_3$). Anal. Calcd: C, 18.61; H, 4.16. Found: C, 18.62; H, 4.07.

(8) Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetone solution of **3**. Crystallographic data for **3**·acetone$_{0.5}$: monoclinic $P2_1/c$, $Z = 4$ (2 symmetry independent molecules of **3** and one acetone solvate per asymmetric unit), $a = 13.445$ (8) Å, $b = 28.47$ (1) Å, $c = 11.566$ (2) Å, $\beta = 101.82$ (3)°, $V = 4334$ (3) Å^3, $\rho_{calc} = 1.870$ g/cm^3; $\mu = 11.42$ cm^{-1}; Nicolet *P*3 diffractometer, Mo Kα radiation ($\lambda = 0.71073$ Å); 7468 independent reflections with $4° < 2\theta < 50°$ collected, 4498 reflections used in refinement with $I > 3\sigma(I)$; $R = 0.044$, $R_w = 0.055$, GOF = 1.57. The β carbon of one of the symmetry independent molecules of **3** and the acetone solvate were found to be thermally disordered.

(9) Jain, V. K.; Patel, R. P.; Muralidharan, K. V.; Bohra, R. *Polyhedron* **1989**, *8*, 2151–2155.

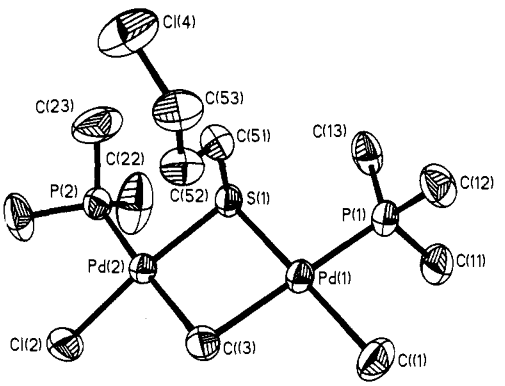
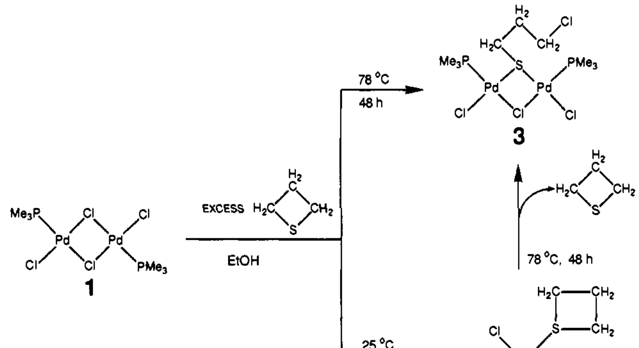


Figure 1. ORTEP projection of *cis*-$Pd_2Cl_2(\mu\text{-}SCH_2CH_2CH_2Cl)(\mu\text{-}Cl)(PMe_3)_2$ (**3**) thermal ellipsoids at 50% probability. Selected bond lengths (Å): Pd(1)–S(1), 2.279 (4); Pd(2)–S(1), 2.289 (3); C(53)–Cl(4) 1.76 (1). The hydrogen atoms have been omitted for clarity.

Scheme I

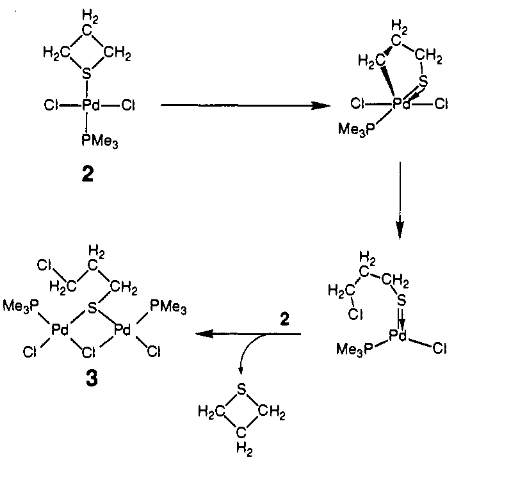


μ-thiolato complexes. The presence of the chloride atom at the end of the μ-alkylthiolate hydrocarbon chain is consistent with the ^1H and $^{13}C\{^1H\}$ NMR spectra observed for **3**.

To probe the mechanism of the formation of **3**, a solution of **1** (0.200 g, 390 μmol) in 30 mL of ethanol was treated with 60 μL (830 μmol) of thietane at 25 °C. As seen in Scheme I, within 0.5 h **1** was converted to the thietane adduct, *trans*-$PdCl_2(PMe_3)(\overline{SCH_2CH_2CH_2})$ (**2**), which was isolated[10] in 86% yield. The formation of $PdCl_2(\overline{SCH_2CH_2CH_2})_2$ from the reaction of thietane with $K_2[PdCl_4]$[11] and the general dimer cleavage reaction which results upon the addition of neutral Lewis bases to solutions of **1**[4,12] provide precedents for this reaction. The intermediacy of **2** in the formation of **3** is demonstrated by refluxing a solution of **2** (0.075 g, 230 μmol) in 30 mL of ethanol for 48 h whereupon **3** is produced in 60% yield.

The ring-opening of coordinated thiethane in other organometallic systems has been found[1f] to be promoted by photolysis. Such a process does not seem to play a major role in our system as **3** was obtained in 52% yield when the reaction of **1** with thietane was carried out with rigorous exclusion of light. Another mechanistic possibility involves the ring-opening of coordinated thietane upon nucleophilic attack on **2** by dissociated chloride.

Scheme II



Cleavage of S–C bonds upon reaction of palladium thioether complexes with SCN^-, I^-, and Br^- has been observed.[13,14] However, $PdCl_2(o\text{-}Ph_2PC_6H_4SMe)$ was found[14] to be unreactive with Cl^- under conditions similar to ours. A mechanism involving external nucleophilic attack by Cl^- seems unlikely to be operating in our system as reflux of an ethanolic solution of **2** (0.075 g, 230 μmol in 30 mL) containing 1 equiv (0.025 g, 230 μmol) of $[NMe_4][Cl]$ gave rise to a complex product mixture which was seen by ^1H NMR and far-infrared spectroscopic analysis to contain largely $PdCl_2(PMe_3)_2$ and $PdCl_4^{2-}$ with **3** present as only a minor, <10%, component. Apparently, as has been found for $[PdCl(PhCH_2NH_2)(o\text{-}Ph_2PC_6H_4SMe)][BPh_4]$[14] and $[Pd(o\text{-}Ph_2AsC_6H_4SMe)_2][ClO_4]_2$,[15] nucleophilic attack by Cl^- is regioselective for the palladium center rather than the α-carbon of the coordinated thietane of **2**. In view of these observations, we suggest this conversion involves a S–C oxidative addition[16] of coordinated theitane followed by a C–Cl reductive elimination as seen in Scheme II although a radical mechanism cannot be ruled out at this point.

This work adds to the growing recognition of the novel reactivity of cyclic thioethers upon coordination to metal complexes. The ring-opening, migratory insertion reaction we have observed is equivalent to the ring-opening of thietane resulting from nucleophilic attack at its 3-position. With very few exceptions, attempts at such nucleophilic additions to thietanes by standard organic methodology results instead in thietane polymerization.[17] The unusual metal-mediated reaction we have observed might be incorporated into new chemical processes which could be carried out in conjunction with desulfurization of fossil fuels.

Acknowledgment. We thank Dr. Karl Harrison for his assistance in the X-ray diffraction studies. This work was supported by the University of Hawaii Research Council.

Supplementary Material Available: Tables of thermal parameters, bond distances, bond angles, and atom coordinates for *cis*-$Pd_2Cl_2(\mu\text{-}SCH_2CH_2CH_2Cl)(\mu\text{-}Cl)(PMe_3)_2Cl_2\cdot acetone_{0.5}$ (7 pages); listing of structure factor parameters (13 pages). Ordering information is given on any current masthead page.

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(10) Purified **2** is obtained removing the ethanol solvent and recrystallizing the crude product first from benzene and then from chloroform–hexane. Spectroscopic data for **2**: ^1H NMR (500 MHz, CD_2Cl_2) δ 3.53 (t, $J_{H\text{-}H}$ = 7.6 Hz, 4 H, SCH_2), 2.91 (q, $J_{H\text{-}H}$ = 7.6 Hz, 2 H, $CH_2CH_2CH_2$), 1.60 (d, $J_{P\text{-}H}$ = 12.9 Hz, 18 H, $P(CH_3)_3$); $^{31}P\{^1H\}$ NMR (122 MHz CD_2Cl_2) δ 4.6 (s). Anal. Calcd: C, 22.00; H, 4.62; Cl, 21.65. Found: C, 21.86; H, 4.38; Cl, 21.57. IR (CsI ν_{Pd-Cl}) 359 cm^{-1}.

(11) Abel, E. W.; Booth, M.; Orrell, K. G. *J. Chem. Soc., Dalton Trans.* **1979**, 1994–2002.

(12) (a) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 2445–2450. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 952.

(13) (a) Roundhill, D. M.; Roundhill, S. G. N.; Beaulieu, W. B.; Bagghi, U. *Inorg. Chem.* **1980**, *19*, 3365–3373. (b) Benefiel, A.; Roundhill, S. G. N. *Inorg. Chem.* **1986**, *25*, 4027–4031.

(14) Benefiel, A.; Roundhill, S. G. N.: Fultz, W. C.; Rheingold, A. L. *Inorg. Chem.* **1984**, *23*, 3316–3324.

(15) Lockyer, T. N. *Aust. J. Chem.* **1974**, *27*, 259–267.

(16) Generation of Pd(IV) species upon oxidative addition to Pd(II) compounds is precedented by reactions such as $PdCl_4^{2-} + Cl_2 \rightarrow PdCl_6^{2-}$ and $Pd(py)_2Cl_2 + Cl_2 \rightarrow Pd(py)_2Cl_4$ (ref 12, p 958). Additionally, there is strong evidence for oxidative addition of less powerful oxidants to Pd(II) species to generate Pd(IV) reaction intermediates (for example see: Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933–4941).

(17) Dittmer, D. C.; Sedergran, T. C. In *The Chemistry of Heterocyclic Compounds*; Weissberger, A., Taylor, E. C., Eds.; Wiley: New York, 1985; Vol. 42, Part 3, pp 466–468.