hydridocarbyne **3b** and the "dimers" **5a** and **5b** are underway.

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Supplementary Material Available: Details of syntheses and full analytical and spectral data for compounds **2b**, **3b**, **4a,b** and **5a,b**, complete tables of crystal data, positional and thermal parameters, bond distances and bond angles, a drawing of **5b** with the complete numbering scheme, and an expansion of the gated-decoupled ^{13}C NMR methylidyne signal of **3b** (23 pages); listing of calculated and observed structure factors for **5b** (20 pages). Ordering information is given on any current masthead page.

(Thiepine)iron Tricarbonyl: Stabilization of Thermally Labile Parent Thiepine by Transition-Metal Complexation†

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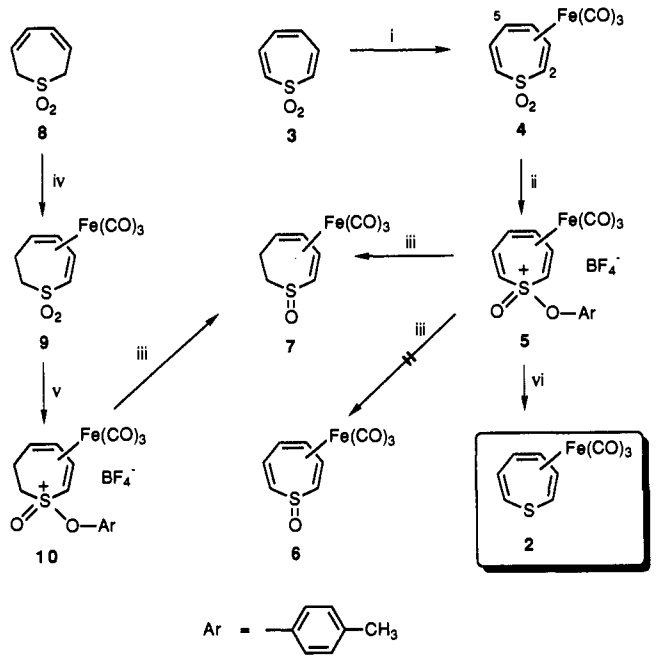
Despite the successful synthesis of several monocyclic thiepine derivatives stabilized by bulky groups at both the 2- and 7-positions,[1] the parent thiepine (**1**) has eluded synthesis.[2] This is mainly due to the pronounced thermal instability of **1**. Ready loss of sulfur from **1** presumably occurs by valence isomerization of **1** to the corresponding thianorcaradiene followed by irreversible cheletropic loss of sulfur.[3] On the other hand, the ability of transition metals to stabilize labile species by complexation[4] has allowed isolation of kinetically unstable conjugated molecules such as cyclobutadiene,[5] pentalene,[6] and norcaradiene.[7] Actually, in the field of thiepines, a transition-metal complexation strategy has recently been utilized to synthesize and isolate thermally unstable 1-benzothiepine 1-oxide by us.[8] Herein we disclose the first synthesis and characterization of (thiepine)iron tricarbonyl (**2**), which demonstrates the possibility of detection of thiepine **1**.

Scheme I[a]



[a] Synthesis of **2**. Reagents and conditions: (i) 1.5 equiv of $Fe_2(CO)_9$, THF, 50 °C, 12 h, 99%; (ii) 1.5 equiv of p-$CH_3C_6H_4N_2^+$ BF_4^-, 95 °C, 5 min under sonication, 21%; (iii) 4.0 equiv of LAH, 1:2:1 DME-THF-ether, −100 °C, 1 h, 24%; (iv) 4.0 equiv of $Fe_2(CO)_9$, benzene, 75 °C, 48 h, 67%; (v) 2.0 equiv of p-$CH_3C_6H_4N_2^+$ BF_4^-, 95 °C, 10 min under sonication, 10%; (vi) 15.0 equiv of SmI_2, THF, 0 °C, 38%.

1 **2**

Our synthetic route to (thiepine)iron tricarbonyl (**2**) involves unique methodology for the reduction of sulfone to sulfide. The reaction of stable thiepine 1,1-dioxide (**3**)[9] with 1.5 equiv of $Fe_2(CO)_9$ in THF at 50 °C for 12 h furnished the iron tricarbonyl complex **4**,[10] yellow needles, mp 169-170 °C dec, in 99% yield. The η^4-complexation in **4** was confirmed on the basis of its ^1H and ^{13}C NMR spectra which exhibited substantially high field chemical shifts for 2- (δ_H = 3.73, δ_C = 67.4) and 5-positions (δ_H = 3.13, δ_C = 50.8).

Recently, the conversion of sulfones into sulfoxides has been reported by a two-stage procedure involving initial reaction of a sulfone with an arenediazonium tetrafluoroborate to form an aryloxysulfoxonium salt[11] and subsequent reaction of this either with $NaBH_4$-Al_2O_3[12] or with phenylmethanethiol.[13] Reaction of finely pulverized **4** with p-toluenediazonium tetrafluoroborate without solvent at 95 °C for 5 min under sonication afforded a 1:1 mixture of stereoisomers of the p-tolyloxysulfoxonium salts **5a**[10] and **5b**[10] which could, though tedious, be separated[14] by

† Dedicated to Professor Ronald Breslow on the occasion of his 60th birthday.

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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 (δ_H = 7.73 and 7.58, δ_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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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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(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, β = 101.82 (3)°, V = 4334 (3) Å^3, ρ_{calc} = 1.870 g/cm^3; μ = 11.42 cm^{-1}; Nicolet $P3$ diffractometer, Mo Kα radiation (λ = 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.

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