Organotellurium Compounds. 6. Synthesis and Reactions of Some Heterocyclic Lithium Tellurolates

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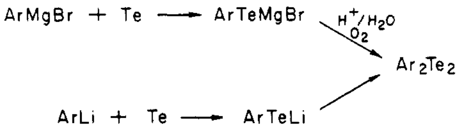
α-Lithio derivatives of furan, thiophene, benzo[*b*]thiophene, pyridine, *N*-tosylpyrrole, and *N*-tosylindole as well a 4-lithiodibenzothiophene react readily with tellurium in THF. Representative conversions of the resulting heterocyclic lithium tellurolates to ditellurides, alkyl tellurides, and telluroacetals are described.

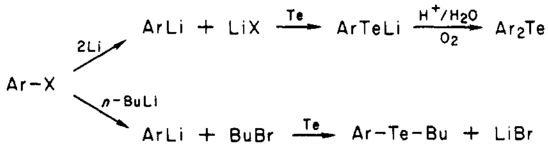
Elemental tellurium has long been known to insert into the carbon–metal bonds of metal acetylides,[1-7] Grignard reagents,[8-13] and various organolithium compounds.[14-24] The two latter classes of compounds have been used extensively for the preparation of aromatic ditellurides by hydrolysis and air oxidation according to eq 1.



(1)

In the Grignard reactions the presence of limited amounts of oxygen during the reaction with elemental tellurium seems to be essential. The formation of ditellurides during the course of the reaction, however, results in secondary reactions. Early studies using ethyl ether as solvent[10] gave mixtures of ditellurides and tellurides, a complication later eliminated by the use of THF as solvent.[12] Although convenient for some special cases, the Grignard reaction shows a poor generality and the reaction mechanism is not well understood.[12]

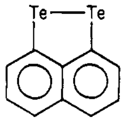
The organolithium compounds used for reactions with elemental tellurium have been synthesized from aromatic halides either by direct halogen–metal exchange or by exchange via *n*-butyllithium. Aromatic ditellurides are easily accessible by the former route via oxidative workup[14,18] (eq 2). The latter reaction, however, produces *n*-butyl aryl tellurides as the main products due to the rapid alkylation of the nucleophilic lithium arenetellurolates by the exchange product *n*-butyl bromide[14,15] (eq 2).



(2)

X = Br, I

The exchange reaction with *n*-butyllithium has, nevertheless, been used for the synthesis of 1,2-ditelluraacenaphthene (1) and related compounds from 1,8-dibromonaphthalene, although the yields of the desired products are low.[22,23]

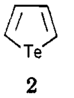


1

Heteroatom-facilitated lithiations constitute a well-recognized avenue for the synthesis of a variety of organolithium compounds. This subject has recently been extensively reviewed,[25] and the last 10 years have seen intensive explorations into this area, especially concerning new functional groups that promote metalation. This approach seemed especially promising for the syntheses of heteroaromatic ditellurides and related compounds, since the lithiation step using *n*-butyllithium produces the inert butane as the only byproduct (eq 3).

$$\text{Ar–H} \xrightarrow{\text{BuLi}} + \text{BuH} \xrightarrow{\text{Te}} \text{ArTeLi} \xrightarrow[\text{O}_2]{\text{H}^+/\text{H}_2\text{O}} \text{Ar}_2\text{Te}_2 \qquad (3)$$

Ar = heteroaromatic



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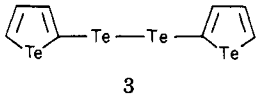

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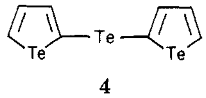

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The lithiation of tellurophene (2) with *n*-butyllithium in diethyl ether, followed by reaction with elemental tellurium, is, to the best of our knowledge, the only example in the literature using this methodology for the synthesis of a heterocyclic organotellurium compound. After oxi-

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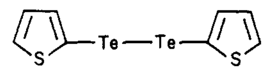
dative workup, the monotelluride (4) was isolated in low yield rather than the expected ditelluride (3).[26]

In this paper we report the reaction of elemental tellurium with a variety of heterocyclic organolithium compounds generated via heteroatom-facilitated lithiations and some reactions of the resulting lithium tellurolates. All of our reactions were carried out in THF rather than diethyl ether, since this solvent has been recommended in the reaction of tellurium with some benzenoid organometallic species.[12,20]

Results and Discussion

2-Lithiothiophene and 2-lithiofuran are easily obtained by treatment of thiophene and furan, respectively, with *n*-butyllithium in THF. When finely ground elemental tellurium was added to these solutions under N_2, the metal was completely consumed at room temperature within 30 min to give yellowish solutions of the corresponding lithium arenetellurolates. By contrast, the analogous reaction of tellurium with phenyllithium in THF was reported[20] to require 2 h of stirring followed by 1 h of reflux without going to completion.

The resulting heterocyclic lithium tellurolates are extremely air-sensitive and are easily converted to the corresponding ditellurides when submitted to aqueous oxidative workup. Di-2-thienyl ditelluride (5) and di-2-furyl ditelluride (6) were synthesized and isolated in this way in 74% and 60% yields, respectively. The latter compound has to our knowledge not been reported in the literature, while the former one was synthesized in an unspecified yield only by a lengthy procedure from 2-thienylmercuric chloride.[27]



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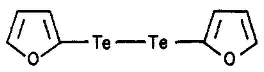
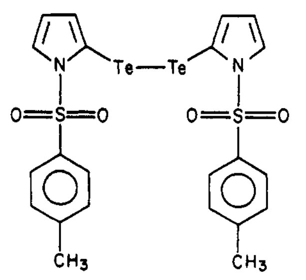


6

Pyrrole and indole can be regiospecifically lithiated in the 2-position when bearing a suitable nitrogen protecting group. In this respect, the benzenesulfonyl group has proven to be very useful, allowing lithiation with *tert*-butyllithium in THF at temperatures slightly below 0 °C.[28,29] When finely ground elemental tellurium was introduced into solutions of 2-lithio-*N*-tosylpyrrole or 2-lithio-*N*-tosylindole, it was completely consumed within 1 hour, producing orange-yellow solutions of the corresponding lithium tellurolates. Oxidative aqueous workup afforded the new crystalline ditellurides 7 and 8 in 63% and 37% yields, respectively. Rapid oxidations using aqueous potassium ferricyanide gave cleaner reactions with higher isolated yields of the desired products as compared to the slower air oxidations.

N-Lithioindole, generated from indole and 1 equiv of *n*-butyllithium, did not react with elemental tellurium under the usual reaction conditions.

n-Butyllithium cannot be used to lithiate pyridine in the 2-position since ring alkylation occurs rather than proton abstraction even at low temperatures. 2-Lithiopyridine could, however, be generated by treatment of 2-bromopyridine in THF with *tert*-butyllithium at −78 °C. Addition of elemental tellurium to this solution, followed by aqueous potassium ferricyanide workup, afforded di-2-pyridyl ditelluride (9) in 56% yield as a red viscous oil.



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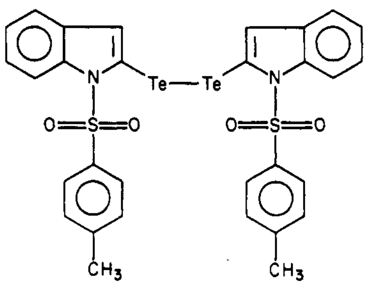

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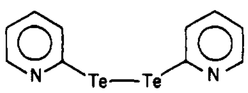
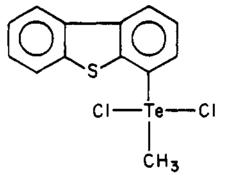


9

Lithium or sodium arenetellurolates are very nucleophilic species, which are easily alkylated[20] or acylated[30] by alkyl halides and acyl halides, respectively.

As a heterocyclic example of the latter reaction, dibenzothiophene was lithiated, the lithio reagent was reacted with elemental tellurium, and the resulting tellurolate was alkylated with methyl iodide. The oily methyltelluro compound was characterized by reaction with SO_2Cl_2 to give the solid white dichloride 10, obtained in 74% overall yield.



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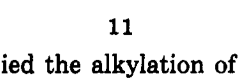
The lithium tellurolate obtained from benzo[*b*]thiophene, butyllithium, and finely ground elemental tellurium also could be alkylated by addition of 1 equiv of methyl iodide to give 2-methyltellurobenzo[*b*]thiophene (11), in 82% yield. The compound is a low melting but highly crystalline solid.



11

Seebach[20] studied the alkylation of lithium benzenetellurolate with diiodomethane as a synthesis of bis(phenyltelluro)methane (12), a telluroacetal of formaldehyde.

$$\text{Ph-Te-CH}_2\text{-Te-Ph}$$

12

However, the yield in this process was very low (6%) as compared with the earlier telluroacetal synthesis involving

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the addition of diazomethane to a diaryl ditelluride.[31]

We have now found that several representative heterocyclic lithium tellurolates react with dichloromethane in THF to give good yields of telluroacetals. Compounds **13a** and **13b** were thus obtained in 68% and 67% yields, respectively, starting from benzo[*b*]thiophene and *N*-tosylindole. In both cases, a large excess of dichloromethane was rapidly syringed into a solution of the lithium tellurolate at room temperature. The reaction mechanism seems to involve two consecutive nucleophilic substitutions, the former slow and rate-determining and the latter fast, since the intermediate chloromethyl tellurides (**14**) could never be isolated.

Ar–Te–CH$_2$–Te–Ar
13a, Ar = benzo[*b*]thien-2-yl
13b, Ar = *N*-tosyl-2-indolyl

Ar–Te–CH$_2$–Cl
14

Experimental Section

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Mass spectra were recorded by using a Hitachi Perkin-Elmer RHM-2 machine and a Perkin-Elmer 270B instrument. All tellurium containing mass peaks are reported for ^{130}Te. NMR spectra were obtained by using a Bruker WM 250 instrument. They were recorded in $CDCl_3$ solutions containing Me_4Si as internal standard and are reported in δ units. Infrared spectra were recorded with a Perkin-Elmer 137 instrument.

All preparations of lithium arenetellurolates were performed under nitrogen in a three-necked 250-mL flask fitted with a septum, a glass stopper, and a reflux condenser connected to a nitrogen tank via a Firestone valve. Commercial solutions of *n*-butyllithium and *tert*-butyllithium were syringed into solutions of the appropriate heteroaromatic compound to freshly distilled THF (sodium/benzophenone). Elemental tellurium was finely ground in a mortar and added rapidly to the reaction flask. A brisk stream of nitrogen was passed through the open system during the addition to prevent any introduction of air.

N-Tosylindole[32] and *N*-tosylpyrrole[33] were synthesized according to literature methods.

Di-2-thienyl Ditelluride (5). *n*-Butyllithium (11.0 mL, 2.2 M, 24.2 mmol) was added to an ice-cooled stirred solution of thiophene (2.0 g, 23.8 mmol) in dry THF (50 mL). After 10 min at 0 °C and 50 min at room temperature, elemental tellurium (2.9 g, 22.7 mmol) was rapidly added. All tellurium had completely dissolved after 30 min when the yellowish solution was poured into a beaker containing water (300 mL).

Dichloromethane (200 mL) was then added and air passed through the two-phase system for 1 h. To effect complete oxidation, we left the beaker overnight in the open air. The organic phase was separated and the aqueous phase extracted several times with dichloromethane. The combined organic extracts were dried ($CaCl_2$) and evaporated to give a red solid. Recrystallization from ethanol afforded 3.54 g (74%) of di-2-thienyl ditelluride (**5**): mp 89–90 °C (lit.[27] 88 °C); MS, *m*/*e* (relative intensity) 426 (21), 296 (14), 213 (84), 166 (100); NMR δ 6.93–6.97 (m, 1 H), 7.39–7.41 (m, 1 H), 7.45–7.47 (m, 1 H).

Di-2-furyl Ditelluride (6). This compound was prepared analogously to the preparation of di-2-thienyl ditelluride from *n*-butyllithium (25 mL, 1.85 M, 46.2 mmol), furan (3.0 g, 44.2 mmol), and elemental tellurium (5.7 g, 44.6 mmol) in dry THF (100 mL). Recrystallization of the red crude material from ethanol afforded 5.2 g (60%) of di-2-furyl ditelluride (**6**): mp 81–83 °C; MS, *m*/*e* (relative intensity) 394 (2), 264 (7), 260 (10), 134 (100); NMR δ 6.37–6.39 (m, 1 H), 6.80–6.82 (m, 1 H), 7.56–7.57 (m, 1 H). Anal. Calcd for $C_8H_6O_2Te_2$: C, 24.68; H, 1.55. Found: C, 24.45; H, 1.62.

Bis(*N*-tosyl-2-pyrryl) Ditelluride (7). *tert*-Butyllithium (4.3 mL, 2.0 M, 8.6 mmol) was added at −23 °C to a stirred solution of *N*-tosylpyrrole (1.9 g, 8.6 mmol) in dry THF (50 mL). After 15 min elemental tellurium (1.0 g, 7.8 mmol) was added and the cooling bath removed. All tellurium was consumed after 1 h at room temperature when the yellowish red solution was poured into water (200 mL) containing $K_3Fe(CN)_6$ (2.7 g, 8.2 mmol) and the mixture extracted several times with dichloromethane. Drying ($CaCl_2$) and evaporation of the organic phase afforded a semisolid that was recrystallized twice from acetonitrile to give 1.72 g (63%) bis(*N*-tosyl-2-pyrryl) ditelluride (**7**). The compound crystallized in a yellow microcrystalline form, mp 149–150 °C, from concentrated solutions and in a red, highly crystalline form, from more dilute solutions: mp 160–162 °C; MS, *m*/*e* (relative intensity) $(M - Te)^+$ 570 (29), 260 (29), 155 (64), 91 (100); NMR δ 2.42 (s, 3 H), 6.21–6.24 (m, 1 H), 6.51–6.53 (m, 1 H), 7.28 (d, 2 H), 7.44–7.46 (m, 1 H), 7.77 (d, 2 H). Anal. Calcd for $C_{22}H_{20}N_2O_4S_2Te_2$: C, 37.98; H, 2.90. Found: C, 37.72; H, 3.04.

Bis(*N*-tosyl-2-indolyl) Ditelluride (8). This compound was prepared analogously to the preparation of bis(*N*-tosyl-2-pyrryl) ditelluride from *tert*-butyllithium (4.6 mL, 2.0 M, 9.2 mmol), *N*-tosylindole (2.5 g, 9.2 mmol), and elemental tellurium (1.15 g, 9.0 mmol) in dry THF (50 mL). The yellowish red THF solution was poured into water (200 mL) containing $K_3Fe(CN)_6$ (3.0 g, 9.1 mmol). Extractions with dichloromethane, drying ($CaCl_2$), and evaporation afforded a semisolid that was crystallized from acetonitrile to give 1.34 g (37%) of bis(*N*-tosyl-2-indolyl) ditelluride as a yellow microcrystalline powder: mp 197–199 °C; MS, *m*/*e* (relative intensity) 800 (1), 670 (9), 231 (100), 91 (78); NMR δ 2.35 (s, 3 H), 7.06 (s, 1 H), 7.14–7.20 (several peaks, 2 H), 7.23 (d, 2 H), 7.27–7.29 (m, 1 H), 7.85 (d, 2 H), 8.00–8.03 (m, 1 H); IR (KBr) 1165, 1355 cm^{-1} (SO_2–N stretching). Anal. Calcd for $C_{30}H_{24}N_2O_4S_2Te_2$: C, 45.28; H, 3.04; N, 3.52; S, 8.06; Te, 32.06. Found: C, 45.36; H, 3.10; N, 3.48; S, 8.26; Te, 31.84.

Di-2-pyridyl Ditelluride (9). *tert*-Butyllithium (6.4 mL, 2.0 M, 12.8 mmol) was added at −78 °C to a stirred solution of 2-bromopyridine (2.0 g, 12.7 mmol). After 1 h elemental tellurium (1.55 g, 12.1 mmol) was added and the cooling bath removed. Most of the tellurium was consumed after 1 h at room temperature when the reaction mixture was poured into water (300 mL) containing $K_3Fe(CN)_6$ (4.0 g, 12.2 mmol). Extraction with dichloromethane, drying ($CaCl_2$), and evaporation afforded a red oil that was submitted to chromatographic purification (SiO_2, CH_2Cl_2 containing 5% MeOH). Di-2-pyridyl ditelluride (**9**), 1.39 g (56%), was obtained as a viscous red oil that solidified after several months of refrigeration: mp 50–51 °C (lit.[34] 50–51.5 °C); MS, *m*/*e* (relative intensity) 416 (7), 286 (22), 156 (100); NMR δ 7.00–7.05 (m, 1 H), 7.35–7.42 (m, 1 H), 8.02–8.06 (m, 1 H), 8.44–8.47 (m, 1 H). Anal. Calcd for $C_{10}H_8N_2Te_2$: C, 29.20; H, 1.96. Found: C, 29.26; H, 2.05.

4-Methyltellurodibenzothiophene *Te*,*Te*-Dichloride (10). *n*-Butyllithium (8.5 mL, 1.60 M, 13.6 mmol) was added at room temperature to a stirred solution of dibenzothiophene (2.5 g, 13.6 mmol) in THF (50 mL). After 2 h elemental tellurium (1.7 g, 13.3 mmol) was added and the stirring continued for another 3 h when almost all tellurium was consumed. Addition of methyl iodide (1.95 g, 13.7 mmol) in THF (5 mL) caused a color change from reddish brown to pale yellow. The reaction mixture was poured into water (200 mL) and extracted with ethyl ether. Drying ($CaCl_2$) and evaporation gave a yellow oil that was dissolved in a mixture of CCl_4 (40 mL) and hexane (10 mL). Addition of excess sulfuryl chloride, SO_2Cl_2, caused precipitation of 4-methyltellurodibenzothiophene *Te*,*Te*-dichloride (**10**): yield 3.91 g (74%); mp 209–211 °C ($CHCl_3$/hexane); MS, *m*/*e* (relative intensity) (M − 2 Cl) 328 (66), 313 (62), 183 (68), 139 (100); NMR δ 3.58 (s, 3 H), 7.50–7.58 (several peaks, 2 H), 7.65–7.71 (t, 1 H), 7.89–7.92 (m, 1 H), 8.02–8.05 (d, 1 H), 8.17–8.21 (m, 1 H), 8.31–8.35 (d, 1 H). Anal. Calcd for $C_{13}H_{10}Cl_2STe$: C, 39.35; H, 2.54. Found: C, 39.07; H, 2.65.

2-Methyltellurobenzo[*b*]thiophene (11). *n*-Butyllithium (6.5 mL, 2.3 M, 15 mmol) was added at room temperature to a stirred solution of benzo[*b*]thiophene (2.1 g, 15.7 mmol) in THF (50 mL). After 1 h elemental tellurium (1.9 g, 14.9 mmol) was added, and the stirring continued until all tellurium was consumed (1 h). Addition of methyl iodide (2.2 g, 15.0 mmol) in THF (7 mL) caused a color change from orange-red to pale yellow. The

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reaction mixture was then poured into water (200 mL) and extracted with ethyl ether. Drying ($CaCl_2$) and evaporation yielded an oil that solidified upon standing. Recrystallization from hexane gave 3.37 g (82%) of 2-methyltellurobenzo[*b*]thiophene (**11**): mp 39 °C; MS, *m/e* (relative intensity) 278 (84), 263 (100), 133 (72); NMR δ 2.26 (s, 3 H), 7.24–7.32 (several peaks, 2 H), 7.56 (s, 1 H), 7.71–7.83 (several peaks, 2 H). Anal. Calcd for C_9H_8STe: C, 39.19; H, 2.92. Found: C, 39.30; H, 3.02.

Bis(benzo[*b*]thien-2-yltelluro)methane (13a). A solution of lithium 2-benzo[*b*]thiophenetellurolate was prepared in THF as described above for the preparation of 2-methyltellurobenzo[*b*]thiophene (**11**). Dry dichloromethane (40 mL) was added to this solution and stirring continued overnight at room temperature. The reaction mixture was then poured into water (200 mL) and extracted with more dichloromethane. Drying ($CaCl_2$) and evaporation afforded a solid that was recrystallized from CH_3CN to give 2.70 g (68%) of bis(benzo[*b*]thien-2-yltelluro)methane (**13a**): mp 125–127 °C; MS, *m/e* (relative intensity) 540 (2), 266 (18), 263 (8), 148 (18), 147 (100), 133 (24); NMR δ 3.93 (s, 1 H), 7.28–7.36 (several peaks, 2 H), 7.59 (s, 1 H), 7.72–7.83 (several peaks, 2 H). Anal. Calcd for $C_{17}H_{12}S_2Te_2$: C, 38.12; H, 2.26. Found: C, 38.12; H, 2.44.

Bis((*N*-tosyl-2-indolyl)telluro)methane (13b). A solution of lithium *N*-tosyl-2-indoletellurolate was prepared in THF as described above for the synthesis of bis(*N*-tosyl-2-indolyl) ditelluride (**8**). Dry dichloromethane (20 mL) was added to this solution and stirring continued overnight at room temperature. The reaction mixture was then poured into water (200 mL) and the solution extracted with more dichloromethane. Drying ($CaCl_2$) and evaporation afforded a semisolid that was submitted to chromatographic purification (SiO_2, CH_2Cl_2/hexane (2:3)). The yield of bis((*N*-tosyl-2-indolyl)telluro)methane (**13b**) was 2.43 g (67%): mp 182–183 °C (ether/hexane); NMR δ 2.33 (s, 3 H), 3.91 (s, 1 H), 6.68 (s, 1 H), 7.16–7.23 (several peaks, 4 H), 7.34–7.38 (m, 1 H), 7.84 (d, 2 H), 8.02–8.06 (m, 1 H). Anal. Calcd for $C_{31}H_{26}N_2O_4S_2Te_2$: C, 45.97; H, 3.24. Found: C, 45.85; H, 3.28.

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Registry No. 5, 66697-24-3; **6**, 79045-78-8; **7**, 79991-46-1; **8**, 79991-47-2; **9**, 78301-14-1; **10**, 79991-48-3; **11**, 79991-49-4; **13a**, 79991-50-7; **13b**, 79991-51-8; thiopene, 110-02-1; furan, 110-00-9; *N*-tosylpyrrole, 17639-64-4; *N*-tosylindole, 31271-90-6; 2-bromopyridine, 109-04-6; dibenzothiophene, 132-65-0; benzo[*b*]thiophene, 95-15-8; lithium 2-benzo[*b*]thiophenetellurolate, 79991-52-9; lithium *N*-tosyl-2-indoletellurolate, 79991-53-0; tellurium, 13494-80-9.

Structures of Two μ-(Alkylthio)-μ-(alkylmercurithio)-bis(tricarbonyliron) Complexes, (μ-RS)(μ-RHgS)$Fe_2(CO)_6$ (R = CH_3 and C_2H_5)

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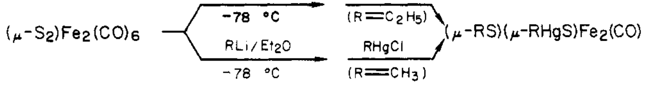
The structures of (μ-RS)(μ-RHgS)$Fe_2(CO)_6$ with R = CH_3 and C_2H_5 have been determined by X-ray diffraction. Crystals of both compounds are triclinic, belonging to space group $P\bar{1}$, and the cell constants are as follows: for R = CH_3, a = 7.841 (4) Å, b = 7.819 (3) Å, c = 13.197 (4) Å, α = 100.70 (3)°, β = 74.59 (3)°, γ = 107.13 (3)°; R = C_2H_5, a = 8.041 (5) Å, b = 8.463 (4) Å, c = 13.346 (6) Å, α = 101.35 (3)°, β = 79.94 (4)°, γ = 107.51 (4)°. The molecular structures consist of a dimeric unit, $[Fe(CO)_3]_2$, with short Fe–Fe distances of 2.512 (5) and 2.508 (4) Å, respectively, for R = CH_3 and C_2H_5. In addition, the Fe atoms are bridged by the two sulfur atoms of the alkylthio and alkylmercurithio groups. The angles between the three bonds, two Fe–S and one S–C or S–Hg, around the S atoms have the following average values for the complex with R = CH_3: FeSFe = 67.4 (2)°; FeSC = 115 (1)°; FeSHg = 110 (1)°. For the complex with R = C_2H_5 these angles are 66.9 (8), 116 (1), and 110 (1)°, respectively. Thus the four atoms Fe_2SC or Fe_2SHg are not coplanar, and in both compounds the S–C and S–Hg bonds of a molecule bend toward the same direction with respect to the Fe–S–Fe skeleton. This configuration is in agreement with that of (μ-C_2H_5S)$_2Fe_2(CO)_6$.

Introduction

The complexes (μ-RS)(μ-RHgS)$Fe_2(CO)_6$ were obtained by the reactions shown in Scheme I.[2] The formation of the complex with R = CH_3 was straightforward, but the isolation of the compound with R = C_2H_5 was unexpected and involved an unusual ethyl group transfer from boron to sulfur. Although the structures could with confidence be assigned on the basis of their IR, NMR, and mass spectra, their stereoconfigurations also were of interest, in particular, the relative positions of the RS and RHgS groups in the molecules. This paper reports the crystal-

Scheme I



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