Organometallics **1998,** *17,* 1241−1244 1241

Double Insertion of Carbon Disulfide into Pb−S Bonds of Lead(II) Bis(arenethiolate): Synthesis and Crystal Structure of Lead(II) Bis(aryl trithiocarbonate)

Naokazu Kano, Norihiro Tokitoh,* and Renji Okazaki*

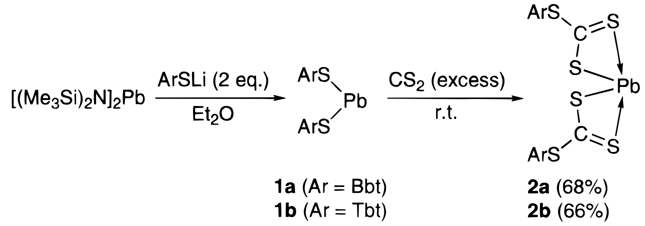
Department of Chemistry, Graduate School of Science, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Received October 3, 1997

*Summary: The first lead(II) bis(aryl trithiocarbonate) compounds, $(ArSCS_2)_2Pb$ (**2a**, Ar = Bbt (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl); **2b**, Ar = Tbt (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl)), were obtained by reaction of the corresponding lead(II) bis(arenethiolate) species, $(ArS)_2Pb$: (**1**) with carbon disulfide. The crystal structure of **2a**·CH_2Cl_2 was established by X-ray crystallographic analysis. The formation of **2** can be rationalized in terms of double insertion of carbon disulfide into two lead−sulfur bonds of **1**.*

Introduction

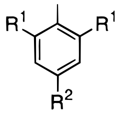
Scheme 1



1a (Ar = Bbt)
1b (Ar = Tbt)

2a (68%)
2b (66%)

The chemistry of divalent group 14 element compounds has stimulated wide interest.[1] In contrast to divalent silicon, germanium, and tin species, which have been extensively studied, the corresponding lead species (plumbylenes) have been much less explored. Among plumbylenes, lead(II) dithiolates, $(RS)_2Pb$, have received attention,[2] but only a few of their reactions have been reported to date.[2a] In the course of our work on the heavier congeners of carbenes, in which we have been taking advantage of kinetic stabilization afforded by an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt),[3] we recently reported that the reactions of Tbt(R)M: (M = Si, Ge, Sn) with carbon disulfide give different types of adducts depending on M.[4] Jutzi and co-workers also reported an interesting reaction of decamethylsilicocene, $(Me_5C_5)_2Si$, with carbon disulfide to form an unexpected dithiadisiletane derivative.[5]



Bbt: $R^1 = CH(SiMe_3)_2$, $R^2 = C(SiMe_3)_3$
Tbt: $R^1 = R^2 = CH(SiMe_3)_2$

We are interested in the difference in reactivity among the group 14 elements and have carried out reactions of lead(II) bis(arenethiolate) compounds, $(ArS)_2Pb$ (**1**), with carbon disulfide and have discovered that the double-insertion reaction of carbon disulfide into Pb−S bonds occurs, giving the first lead(II) bis(aryl trithiocarbonate) compounds, **2a** and **2b** (Scheme 1). We also describe the X-ray crystallographic analysis of **2a**. In connection with our previous work,[3] extremely bulky groups, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (denoted as Bbt) and Tbt, were employed as aryl groups.[6]

Results and Discussion

Lead(II) bis(arenethiolate) **1** (**1a**, Ar = Bbt; **1b**, Ar = Tbt) was prepared in situ as a dark red solution by the nucleophilic substitution of a lead(II) diamide, $[(Me_3Si)_2N]_2Pb$,[8] with 2 equiv of ArSLi in ether at −40 °C.

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S0276-7333(97)00861-3 CCC: $15.00
Publication on Web 02/05/1998

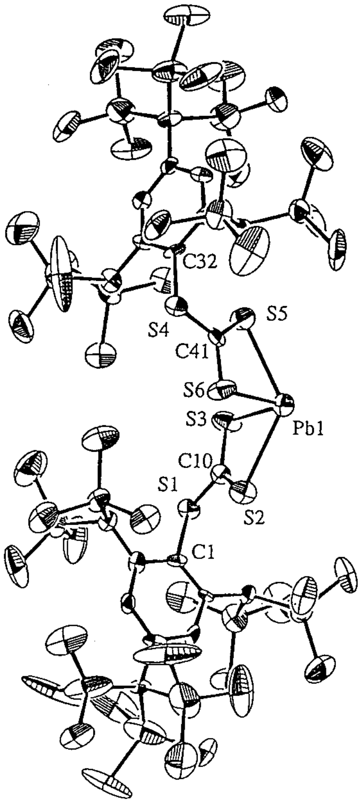

Figure 1. ORTEP drawing of **2a**·CH_2Cl_2 with thermal ellipsoid plot (30% probability). The dichloromethane molecule was omitted for clarity.

Although **1** was not isolated, its characteristic absorption for **1b** (λ_{max} 538 nm in hexane) was observed in the electronic spectrum as in the cases of other plumbylenes.[9] After the reaction mixture was warmed to room temperature, an excess of carbon disulfide was added to give the lead(II) bis(aryl trithiocarbonate) (**2a**, 68%; **2b**, 66%) as stable yellow crystals (Scheme 1). Complexes **2a** and **2b** were found to be stable to air and moisture at room temperature.

The structures of **2a** and **2b** were determined by ^{1}H, ^{13}C, and ^{207}Pb NMR, elemental analysis, and FAB mass spectroscopy. Since their ^{1}H and ^{13}C NMR spectra showed one set of signals due to Bbt or Tbt groups, the two sets of trithiocarbonate ligands are considered to be equivalent in solution at room temperature. The structure of **2a** was established by X-ray crystallography for a crystal of modest quality obtained from a dichloromethane−ethanol solution. The ORTEP drawing of **2a**·CH_2Cl_2 is shown in Figure 1. Selected bond distances and bond angles are given in Table 1. Lead(II) bis(aryl trithiocarbonate) **2a** exists as a monomer, and there is no intermolecular interaction between lead and sulfur atoms. The lead atom is surrounded by four intramolecular sulfur atoms of two bidentate trithiocarbonate ligands. The configuration around the lead atom is best described as a distorted-pyramidal structure. The two carbon atoms of the bidentate ligands are trigonal planar, and the C−S bond lengths (1.631(19)−1.695(19) Å) in each trithiocarbonate ligand are between the sums of covalent bond radii of single (1.81 Å) and double bonds (1.62 Å), even when the large standard deviations are taken into account.[10] On the other hand, one Pb−S bond (2.669(6) or 2.673(7) Å) is significantly shorter than the other one (2.850(6) or 2.883(7) Å) in each ligand, although both Pb−S bond lengths are longer than the sum of the covalent bond radii of Pb and S (2.50 Å).[10] Two sulfur atoms of the thiocarbonyl units, S(2) and S(5), are located on different sides of the plane that contains the central lead atom and the other two sulfur atoms S(1) and S(4). These configurations are most reasonably interpreted in terms of one strong and one weak coordination bond between the S atoms of the trithiocarbonate ligand and Pb. Although there are some $Pb^{II}S_4$ complexes chelated by two sets of sulfur ligands, such as lead(II) bis(dithiocarbonate),[11] lead(II) bis(dithiocarbamate),[12] and lead(II) bis(dithiophosphate),[13] complex **2a** is, to our knowledge, the first example of crystallographically analyzed lead(II) bis(trithiocarbonate). Moreover, its unique synthetic method is worthy of note; the above-mentioned $Pb^{II}S_4$ compounds usually were synthesized by nucleophilic attack of the corresponding alkali-metal salts on lead(II) compounds.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $(BbtSCS_2)_2Pb·CH_2Cl_2$

(a) Bond Distances			
Pb(1)−S(2)	2.883(7)	C(10)−S(3)	1.693(18)
Pb(1)−S(3)	2.673(7)	C(41)−S(4)	1.756(18)
Pb(1)−S(5)	2.850(6)	C(41)−S(5)	1.631(19)
Pb(1)−S(6)	2.669(6)	C(41)−S(6)	1.695(19)
C(10)−S(1)	1.783(20)	C(1)−S(1)	1.810(18)
C(10)−S(2)	1.647(18)	C(32)−S(4)	1.812(17)
(b) Bond Angles			
S(3)−Pb(1)-S(6)	95.8(2)	S(1)−C(10)-S(2)	123.2(11)
S(3)−Pb(1)-S(5)	82.2(2)	S(2)−C(10)-S(3)	124.8(13)
S(5)−Pb(1)-S(6)	64.2(2)	S(4)−C(41)-S(5)	123.7(12)
S(2)−Pb(1)-S(6)	81.5(2)	S(4)−C(41)-S(6)	112.1(11)
S(2)−Pb(1)-S(5)	129.1(2)	S(5)−C(41)-S(6)	124.0(11)
S(2)−Pb(1)-S(3)	64.2(2)	C(1)−S(1)-C(10)	106.0(8)
S(1)−C(10)-S(3)	111.9(11)	C(32)−S(4)-C(41)	106.0(9)

The fact that **2** bears two trithiocarbonate ligands on the lead atom indicates the presence of some insertion process of carbon disulfide in its formation from **1**. We propose the mechanism shown in Scheme 2 for the formation of **2**. Complex **1** first interacts with carbon disulfide to form the ylide **3**, as we suggested previously in the reaction of germylene and stannylene.[4] An arylthio group subsequently migrates from lead to the ylidic carbon atom to give the intermediary lead(II)

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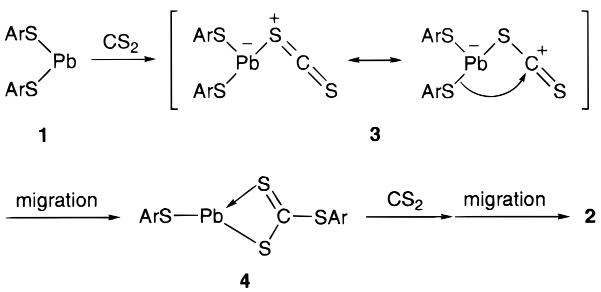
Scheme 2



compound **4**, which further reacts with another carbon disulfide molecule to give the final product **2** by repeating a similar insertion process.

Although the migratory insertion of carbon disulfide into a metal−sulfur bond is known for some transition-metal complexes,[14] such double insertion of carbon disulfide as suggested above for **2** has not been observed in the case of other heavier group 14 element divalent compounds, $R^1(R^2)M$: (M = Si, Ge, Sn).[4,5] Interestingly, the reaction of the aryl(arylthio)plumbylene Tbt(TbtS)-Pb: (**5**)[15] with carbon disulfide also gave **2b** in 20% yield together with TbtSH (16%) and TbtH (18%).[16] Although the reaction mechanism is unclear at present, the reaction must involve not only the insertion of carbon disulfide into the Pb−S bond but also the formal insertion of a sulfur atom into the Pb−C(Tbt) bond followed by reaction with carbon disulfide. Further work is in progress to elucidate a detailed mechanism for this interesting reaction.

Experimental Section

All experiments were performed under an argon atmosphere unless otherwise noted. Solvents and carbon disulfide were dried by standard methods and freshly distilled prior to use. ^{1}H (500 MHz), ^{13}C (125 MHz), and ^{207}Pb (105 MHz) NMR spectra were recorded on a JEOL α-500 MHz spectrometer at 27 °C. Chemical shifts were measured with tetramethylsilane as an internal standard for ^{1}H and ^{13}C NMR and with tetramethylplumbane for ^{207}Pb NMR as an external standard. High-resolution mass spectral data were obtained on a JEOL SX-102 mass spectrometer. Preparative HPLC was performed on an LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAI-gel 1H and 2H columns (eluent: toluene). All melting points were determined on a Yanaco micro melting point apparataus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo. 1-Bromo-2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]benzene (BbtBr),[6] 2,4,6-tris[bis(trimethylsilyl)methyl]-1-mercaptobenzene (TbtSH),[15] bis[bis(trimethylsilyl)amino]lead(II) ($[(Me_3Si)_2N]_2Pb$),[8] and {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}{[2,4,6-tris[bis(trimethylsilyl)methyl]phenyl]thio}plumbylene (Tbt(TbtS)Pb)[15] were prepared according to the procedures reported in the literature.

Synthesis of 2,6-Bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl Tetrasulfide, $BbtS_4Bbt$. To an ether solution (5 mL) of BbtLi, which was prepared from BbtBr (1.41 g, 2.00 mmol) and a hexane solution of *t*-BuLi (1.60 M, 2.80 mL) at −72 °C, was added elemental sulfur (641 mg, 2.50 mmol) at −72 °C. After the mixture was gradually warmed to the room temperature, a 10% aqueous NaOH solution of pottasium ferricyanide was added to the reaction mixture at room temperature. After it was stirred for 5 h, the reaction mixture was separated. The aqueous phase was extracted with ether, and the extract was then combined with the organic phase. The combined solution was dried with anhydrous $MgSO_4$ and evaporated to give a yellow solid. Separation of the crude solid with preparative HPLC afforded $BbtS_4Bbt$ (897 mg, 65%) as a pale yellow solid. $BbtS_4Bbt$: yellow crystals, mp 276−281 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.09 (s, 72H), 0.26 (s, 54H), 3.22 (s, 4H), 6.87 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.26 (q), 5.27 (q), 22.77 (s), 28.74 (d), 126.75 (d), 130.65 (s), 147.12 (s), 150.19 (s); HRMS (FAB) found *m/z* 1375.6138, calcd for $C_{60}H_{135}S_4Si_{14}$ ($[M + H]^+$) 1375.6217. Anal. Calcd for $C_{60}H_{134}S_4Si_{14}$: C, 52.32; H, 9.81; S, 9.31. Found: C, 52.21; H, 9.49; S, 9.49.

Synthesis of 2,6-Bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]-1-mercaptobenzene, BbtSH. To a THF solution (30 mL) of $BbtS_4Bbt$ (860 mg, 0.625 mmol) was added $LiAlH_4$ (100 mg, 2.65 mmol) at 0 °C. After it was stirred at room temperature for 1 h, the reaction mixture was further refluxed for 8 h. After being poured into ice-cooled dilute aqueous HCl, the organic phase was separated, and the aqueous phase was extracted with hexane. The combined solution was dried with anhydrous $MgSO_4$ and evaporated to give a white solid. Separation of the crude solid with preparative HPLC afforded BbtSH (657 mg, 80%) as a colorless solid. BbtSH: colorless crystals, mp 158−161 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.03 (s, 36H), 0.24 (s, 27H), 2.47 (s, 1H), 3.04 (s, 2H), 6.82 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.95 (q), 5.23 (q), 21.68(s), 28.86 (d), 123.33 (s), 126.52 (d), 142.88 (s), 146.65 (s); HRMS (FAB) found *m/z* 656.3427, calcd for $C_{30}H_{68}SSi_7$ ($[M]^+$) 656.3494. Anal. Calcd for $C_{30}H_{68}SSi_7$: C, 54.80; H, 10.42; S, 4.88. Found: C, 54.91; H, 10.21; S, 4.70.

Synthesis of Lead(II) Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl trithiocarbonate} (2a). An ether solution (5 mL) of BbtSLi, which was prepared from BbtSH (329 mg, 0.501 mmol) and a pentane solution of *n*-BuLi (1.64 M, 0.32 mL) at −72 °C, was added to an ether solution (5 mL) of $[(Me_3Si)_2N]_2Pb$ (130 mg, 0.246 mmol) at −60 °C. After the reaction mixture was gradually warmed to room temperature, carbon disulfide (0.30 mL, 4.99 mmol) was added to it. After it was stirred for 30 min, the reaction mixture was filtered to remove insoluble materials with Celite. The filtrate was evaporated to give a reddish oil. Separation of the crude oil with silica gel chromatography afforded **2a** (281 mg, 68%) as a yellow solid. **2a**: yellow crystals, mp 230−239 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.03 (s, 36H), 0.13 (s, 36H), 0.26 (s, 54H), 2.56 (s, 4H), 6.85 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.24 (q), 2.11 (q), 5.27 (q), 22.57 (s), 27.82 (d), 127.04 (s), 127.28 (d), 147.69 (s), 149.52 (s), 242.18 (s); ^{207}Pb NMR (105 MHz, $CDCl_3$) δ 1087 (br s); HRMS (FAB) found *m/z* 1671.5502, calcd for $C_{62}H_{135}S_6Si_{14}Pb$ ($[M + H]^+$) 1671.5424. Anal. Calcd for $C_{62}H_{134}S_6Si_{14}Pb$: C, 44.52; H, 8.08; S, 11.50. Found: C, 44.22; H, 7.85; S, 11.65.

Synthesis of Lead(II) Bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl trithiocarbonate} (2b). An ether solution (4 mL) of TbtSLi, which was prepared from TbtSH (227 mg, 0.388 mmol) and an ether solution of MeLi (1.09 M, 0.37 mL) at −72 °C, was added to an ether solution (4 mL) of $[(Me_3Si)_2N]_2Pb$ (100 mg, 0.189 mmol) at −40 °C. After the reaction mixture was gradually warmed to room temperature, carbon disulfide (0.23 mL, 3.8 mmol) was added to it. After it was stirred for 30 min, the reaction mixture was filtered to remove insoluble materials with Celite. The filtrate was evaporated to give a yellow solid. Separation of the crude solid with silica gel chromatography afforded **2b** (196 mg, 66%) as a yellow solid. **2b**: pale yellow crystals, mp 216−224 °C dec; ^{1}H NMR

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[16] Reaction of the diarylplumbylene Tbt_2Pb: with excess carbon disulfide gave a complex mixture. No product bearing both Tbt groups and a lead atom has been identified so far.

(500 MHz, $CDCl_3$) δ 0.00 (s, 36H), 0.05 (s, 36H), 0.11 (s, 36H), 1.37 (s, 2H), 2.37 (br s, 4H), 6.36 (br s, 2H), 6.52 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.21 (q), 0.75 (q), 1.71 (q), 26.93 (d), 30.96 (d), 122.58 (d), 124.87 (s), 127.46 (d), 146.21 (s), 149.55 (s), 242.95 (s); ^{207}Pb NMR (105 MHz, $CDCl_3$) δ 1115 (br s); HRMS (FAB) found *m/z* 1526.4343, calcd for $C_{56}H_{118}S_6Si_{12}Pb$ ($[M]^+$) 1526.4556. Anal. Calcd for $C_{56}H_{118}S_6Si_{12}Pb$: C, 44.01; H, 7.78; S, 12.59. Found: C, 44.14; H, 7.58; S, 12.32.

Crystal Structure Data for 2a·CH$_2$Cl$_2$. Yellow prismatic crystals of **2a**·CH_2Cl_2 were grown by the slow evaporation of its saturated solution in ethanol and dichloromethane at room temperature. **2a**·CH_2Cl_2: $C_{63}H_{136}Cl_2PbS_6Si_{14}$, FW = 1757.43, triclinic, space group $P\bar{1}$ (No. 2), $a = 18.764(5)$ Å, $b = 21.375(5)$ Å, $c = 12.292(2)$ Å, $\alpha = 91.59(2)°$, $\beta = 95.85(2)°$, $\gamma = 79.23(2)°$, $V = 4817(1)$ Å^3, $Z = 2$, $D_{calcd} = 1.211$ g cm^{-3}, μ(Mo Kα) = 21.45 cm^{-1}, $F(000) = 1844$. A yellow prismatic crystal of **2a**·CH_2Cl_2 having dimensions of 0.65 × 0.15 × 0.15 mm was mounted on a glass fiber. The data set was collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) at 296 K and a rotating anode generator. The structure was solved by heavy-atom Patterson methods (SAPI).[17] The intensities were corrected for Lorentz and polarization effects. The final cycle of full-matrix least-squares refinement was based on 3961 observed reflections ($I > 3.00\sigma(I)$) and 760 variable parameters and converged (largest parameter shift was 1.38 times its esd) at R (R_w) = 0.082 (0.065) with GOF = 2.23. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp.

Reaction of 5 with Carbon Disulfide. To a THF solution (2 mL) of Tbt(TbtS)Pb (21.6 mg, 0.0161 mmol) was added carbon sulfide (30 mL, 0.50 mmol) at room temperature. After degassing and sealing, the reaction mixture was stirred at room temperature for 8 h and further refluxed for 2 h. The reaction mixture was filtered with Celite to remove insoluble materials, giving a yellow solid after evaporation. Separation of the crude solid with silica gel chromatography afforded **2b** (4.9 mg, 20%), TbtSH (3.0 mg, 16%), and TbtH (3.2 mg, 18%).

Acknowledgment. This work was partially supported by Grants-in-Aid for Scientific Research Nos. 05236102 and 07454193 from the Ministry of Education, Science, Sports and Culture of Japan. We are also grateful to Shin-etsu Chemical Co., Ltd., and Tosoh Akzo Co., Ltd., for the generous gifts of chlorosilanes and alkyllithiums, respectively.

Supporting Information Available: Tables of all bond lengths and angles, atomic coordinates, and positional and thermal parameters for **2a**·CH_2Cl_2 (44 pages). Ordering information is given on any current masthead page.

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[17] Fan, H.-F. SAPI91, Structure Analysis Programs with Intelligent Control; RIGAKU Corp., Tokyo, Japan, 1991.