

Synthesis of 1,3,5-tri- and 1,2,4,5-tetrasubstituted tin and mercury derivatives of benzene. Crystal structure of 1,3,5-tris(chloromercurio)benzene

Nicolette Rot ^a, Frans J.J. de Kanter ^a, Friedrich Bickelhaupt ^{a,*}, Wilberth J.J. Smeets ^b, Anthony L. Spek ^b

^a Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

^b Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, University of Utrecht, Padualaan 8, NL-3584 CH Utrecht, The Netherlands

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Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday.

Abstract

The reaction of 1,3,5-tribromo- or 1,2,4,5-tetrabromobenzene with trimethylstannyl sodium in tetraglyme gave the corresponding polystannylated benzene derivatives **2** and **4**, respectively, in high yield. They were converted with mercuric chloride to the corresponding tris- and tetrakis(chloromercurio)benzenes **5** and **6**, respectively. The structure of **5** was confirmed by X-ray crystallography. Some spectral properties of the new compounds are discussed. The (partial) conversion of **2** to 1,3,5-trilithiobenzene (**8**) was also investigated. © 2000 Elsevier Science S.A. All rights reserved.

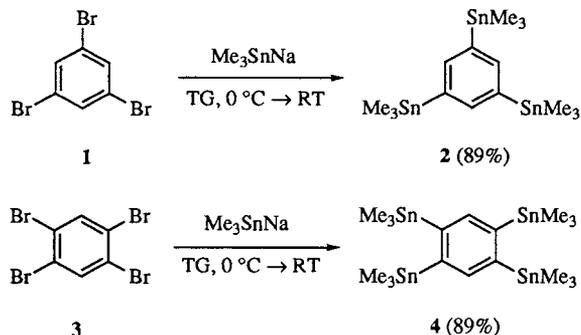
Keywords: Polymetallated benzene; Tin; Mercury

1. Introduction

The field of polymetallated aromatic compounds involving main-group elements comprises areas which have been extensively explored, while others are clearly underdeveloped. This is particularly true for derivatives of Groups 1–3 and 12 with the exception of certain metallocenes; ferrocenes polysubstituted by lithium, sodium, or potassium [1–3] and ruthenocenes polysubstituted by lithium, magnesium, or zinc have been reported [1b,4,5]. In contrast, benzene derivatives carrying three or more of such metals have rarely been prepared [6] or claimed [7]. Recently, we described the synthesis of 1,3,5-trilithiobenzene from 1,3,5-tribromobenzene and lithium 4,4'-di-*tert*-butylbiphenyl (LiDBB) [8].

Polymercurated aromatics have mostly been synthesized by electrophilic aromatic substitution. From the highly reactive $\text{Hg}(\text{O}_2\text{CCF}_3)_2$ and (substituted) benzene

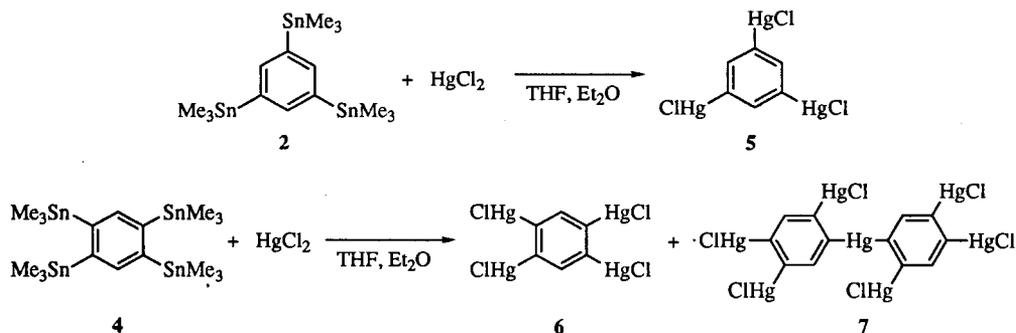
or naphthalene, even permercurated products were obtained [9]. However, severe problems were encountered when partially mercurated products are desired because usually non-separable mixtures were formed [10]¹.



Scheme 1. TG = tetraglyme.

¹ We could not reproduce the reported results; mixtures of polymercurated products were obtained.

* Corresponding author.



Scheme 2.

Among derivatives of Group 14, polysilylated aromatic compounds are rather well known; even several persilylated benzene derivatives have been reported [11]. However, only two compounds of this type involving the heavier Group 14 elements germanium and tin have been prepared: hexakis(trimethylgermyl)benzene [12] and 1-trimethylsilyl-3-trimethylgermyl-5-trimethylstannylbenzene [13]. From 1,3,5-trilithiobenzene and chlorotrimethylstannane, we obtained 1,3,5-tris(trimethylstannyl)benzene which was, however, contaminated by its 1,3-di- and its monosubstituted analog [8].

The formation of product mixtures instead of a single pure product is a general problem in the preparation of polymetallated compounds. In the synthesis of main-group polymetallated compounds, this is often due to the use of (inevitably) impure mercurated starting materials or to drastic synthetic procedures such as halogen-metal exchange or metallation which frequently are not sufficiently specific.

Here, we report the first successful synthesis of pure tri- and tetrametallated benzene derivatives with tin and mercury substituents. Both bear promise as potential precursors for other polymetallated derivatives.

2. Results and discussion

2.1. Polystannylated benzene derivatives

Reaction of 1,3,5-tribromobenzene (**1**) with an excess of freshly prepared trimethylstannyl sodium (Me_3SnNa) in tetraglyme (TG) [14] gave almost pure 1,3,5-tris(trimethylstannyl)benzene (**2**) in an isolated yield of 89% (Scheme 1); GC-MS measurements showed traces of 1,3-bis(trimethylstannyl)benzene. Compound **2** was purified by crystallization from methanol. Unfortunately, the crystals were disordered and unsuitable for X-ray crystal structure determination. However, a gas phase electron diffraction study on **2** has been reported [15].

The tetrasubstituted derivative 1,2,4,5-tetrakis(trimethylstannyl)benzene (**4**) was prepared analogously from 1,2,4,5-tetrabromobenzene (**3**) (89% yield, Scheme 1); it contained traces of the 1,2,4-trisubstituted product. Pure **4** crystallized upon slow evaporation of a hexane-ethanol solution, but an X-ray crystal structure determination showed that it too was disordered, so accurate data could not be obtained.

2.2. Polymercurated benzene derivatives

Addition of the tin compounds **2** or **4** in Et_2O to an excess of HgCl_2 in THF at room temperature gave 1,3,5-tris(chloromercurio)benzene (**5**) (90% isolated yield) or 1,2,4,5-tetrakis(chloromercurio)benzene (**6**) (90% total yield), respectively (Scheme 2). ^{199}Hg -NMR spectroscopy revealed **6** to be accompanied by a minor side-product (about 6%). This species is assumed to be **7** because one low-field shift ($\delta = -871.4$) indicates the presence of a C-Hg-C unit (Ph_2Hg , $\delta = -821.95$ ppm in DMSO), while three signals ($\delta = -1208$, -1301 , and -1315 ppm) suggest three different C-HgCl groups (PhHgCl , $\delta = -1187$ ppm [16]; **6**, $\delta = -1311$ ppm). By washing with DMSO, pentane, and Et_2O , **7** was removed and pure **6** remained as a white powder (84% isolated yield).

Thus, the approach via the tin compounds **2** and **4** is at present the best route to prepare well-defined polymercurated benzene derivatives such as **5** and **6** in pure form and in high yield. Note that the reaction of 1,3,5-trilithiobenzene (**8**) with mercury dibromide gave the tris-bromomercurio analogue of **5** in lower yield and in an inseparable 3:1 mixture with the 1,3-disubstituted derivative [8].

2.3. X-ray crystal structure of **5**·DMSO

Evaporation of a solution of **5** in DMSO over several months gave colorless needles, suitable for X-ray crystal structure determination ($R = 0.0543$). The solid state structure is depicted in Fig. 1. Selected bond distances and angles are summarized in Table 1.

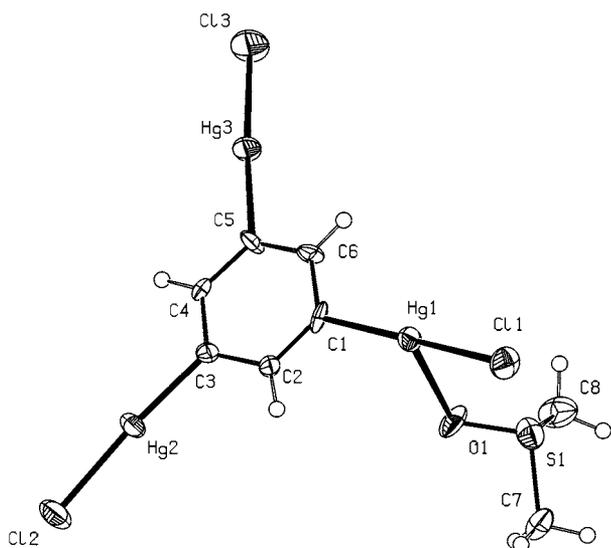


Fig. 1. ORTEP drawing of **5**·DMSO with displacement ellipsoids drawn at the 50% probability level.

One equivalent of DMSO is incorporated in the crystal lattice of **5**. The solvent molecule coordinates directly to one HgCl group via the oxygen atom (--- bond, Fig. 2) as indicated by the distance Hg(1)–O(1) = 2.659(11) Å which is smaller than the sum of their van der Waals radii (2.9–3.13 Å) but longer than a covalent bond (2.01–2.16 Å) [17]. In addition, DMSO coordinates more weakly to a mercury atom of a neighboring molecule (e.g. Hg(2)–O(1a) = 2.958(10) Å, — bond, Fig. 2)). The third HgCl group is not involved in coordination to oxygen. The Hg(1)–O(1) bond is only slightly shorter than that in other DMSO-complexes (C(HgCl)₄·DMSO, 2.777–2.793 Å [18]; 1,8-naphthalenediyl bis-

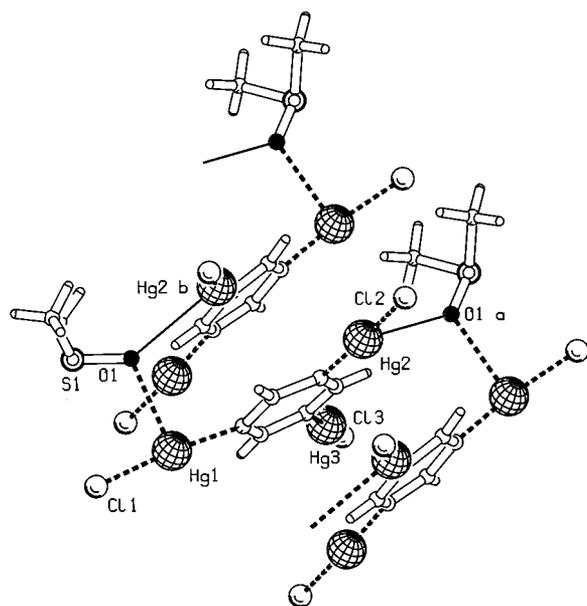


Fig. 2. Intermolecular coordination of oxygen to mercury atoms in **5**·DMSO which bind the title molecule into an infinite chain.

mercury chloride)·DMSO, 2.793–2.804 Å [19a]; 1,2-bis(chloromercurio)benzene·DMF, Hg–O 2.681(13) and 2.777(13) Å [20]; for obvious reasons, it is much shorter in the cationic complex methylmercury tetrafluoroborate: 2.066(8) Å. The different mode of coordination of DMSO to the three HgCl-groups leads to different C–Hg–Cl angles. Although mercury tends to have a linear coordination geometry, the C–Hg–X angle often deviates slightly from 180° depending on the type of secondary interactions [21]. The smallest angle corresponds to the strongest coordination (Hg(1), 173.0(4)°), the largest one to the ‘free’ non-coordinated Hg(3)-atom (175.4(5)°). The C–Hg (2.049(12)–2.061(15) Å) and Hg–Cl bond lengths (2.310(5)–2.324(4) Å) are comparable to those reported [17] (e.g. *p*-tolylmercury chloride [22a] 2.09(2) and 2.331(9) Å, respectively, and 1,2-bis(chloromercurio)benzene: 2.047(16), 2.044(16) and 2.334(5), 2.346(4) Å, respectively) [23].

As expected, the angles at the *ipso*-carbon atoms C(6)–C(1)–C(2) (119.5(12)) and C(2)–C(3)–C(4) (117.2(13)) are smaller than 120° due to the inductive effect of the HgCl substituent which is slightly electron-donating towards the C_{*ipso*}-atom [24]. Unexpectedly, the angle C(4)–C(5)–C(6) (121.1(14)°) is slightly larger than 120°; larger angles were also observed in some 1,2-dimercurated benzene derivatives [25,26]. On average, the intra-annular angles at C_{*ipso*} are slightly larger for mercury (**5**·DMSO, 119.2(13)°) compared to tin (**2**, 117.7(1.7)° [15]), which is in line with tin being slightly more electropositive.

Several intermolecular Hg–Cl distances (3.378(4)–3.600(4) Å) are shorter than the sum of the van der

Table 1
Selected bond lengths (Å) and bond angles (°) of **5**·DMSO

Bond lengths

C(1)–Hg(1)	2.049(12)
C(3)–Hg(2)	2.036(14)
C(5)–Hg(3)	2.061(15)
Hg(1)–Cl(1)	2.324(4)
Hg(2)–Cl(2)	2.310(5)
Hg(3)–Cl(3)	2.322(5)
O(1)–Hg(1)	2.659(11)
O(2)–Hg(2)	2.958(10)

Bond angles

C(6)–C(1)–C(2)	119.5(12)
C(1)–C(2)–C(3)	121.3(13)
C(2)–C(3)–C(4)	117.2(13)
C(3)–C(4)–C(5)	121.3(14)
C(4)–C(5)–C(6)	121.1(14)
C(5)–C(6)–C(1)	119.3(13)
C(1)–Hg(1)–Cl(1)	173.0(4)
C(3)–Hg(2)–Cl(2)	173.7(4)
C(5)–Hg(3)–Cl(3)	175.4(5)

Waals radii (4.25 Å), indicating a tendency towards intermolecular interaction under the formation of a continuous Hg–Cl network as shown in Fig. 3 [18,22].

2.4. NMR spectroscopic studies

Comparison of the chemical shifts (^1H , ^{119}Sn and ^{13}C) and coupling constants of **2** and **4** with those of 1,2-bis(trimethylstannyl)benzene (**9**) and trimethylstannylbenzene (**10**) (Table 2) shows a remarkable analogy between the 1- and 1,3,5-substituted benzene (**10** and **2**, respectively) on the one hand and the *ortho*-substituted systems **9** (1,2-disubstituted) and **4** on the other. The differences are expressed, in particular, by the increased $^1J(\text{Sn}, \text{C}_{\text{ipso}})$ couplings of **4** and **9**; they indicate a change of hybridization around the *ipso*-C atom with more s-character in the Sn–C_{*ipso*} bond. As a consequence, more p-character will remain for the Sn–Me bonds which explains the smaller $^1J(\text{Sn}, \text{C}_{\text{Me}})$ couplings. Similarly, the other NMR data show differences between the crowded (**4**, **9**) and uncrowded (**2**, **10**) compounds.

Analogous effects were observed for the NMR data of **5** and **6** on comparison with those of (chloromercurio)benzene (**11**) and 1,2-bis(chloromercurio)benzene (**12**), respectively (Table 3). Again, the *ortho*-substituted systems **6** and **12** show remarkable similarity. Their ^{199}Hg nuclei are more shielded than those of **11** and **5**, and those of the 1,2,4,5-tetrasubstituted **6** are more

shielded than those of the disubstituted **12**. Also similar to the stannyl analogues, $^{13}\text{C}_{\text{ipso}}$ is more deshielded in the hindered systems **12** and **6** and $^2J(\text{Hg}, ^{13}\text{C})$ is larger.

Undoubtedly, both steric congestion and electronic effects due to the close proximity of the substituents must contribute to these phenomena. Similar observations have been reported for **9** [32,33] and for *ortho*-substituted trimethylsilyl analogues [34] and several explanations have been offered. However, we feel that at present, a satisfactory rationalization is lacking, in particular if one considers that the qualitatively similar trend can be observed for fluorobenzene ($\delta(^{19}\text{F}) = -106.3$ ppm [35], $^1J(\text{F}, \text{C}) = 244.7$ Hz [36]) and 1,2-difluorobenzene ($\delta(^{19}\text{F}) = -138.62$ ppm, $^1J(\text{F}, \text{C}) = 247.1$ Hz [37]), while the fluoro substituent is electronically completely different and steric effects can hardly be of importance.

2.5. Attempted synthesis of 1,3,5-trilithiobenzene (**8**) from **2**

In view of the cumbersome by-product DBB which is inevitable in the synthesis of **8** from **1** [8], it seemed attractive to attempt the preparation of **8** in an alternative fashion by metal–metal exchange from **2** with MeLi. Several experiments were performed (Table 4). The course of the reaction was followed by analysis of the products obtained after quenching with Me_2SO_4 or

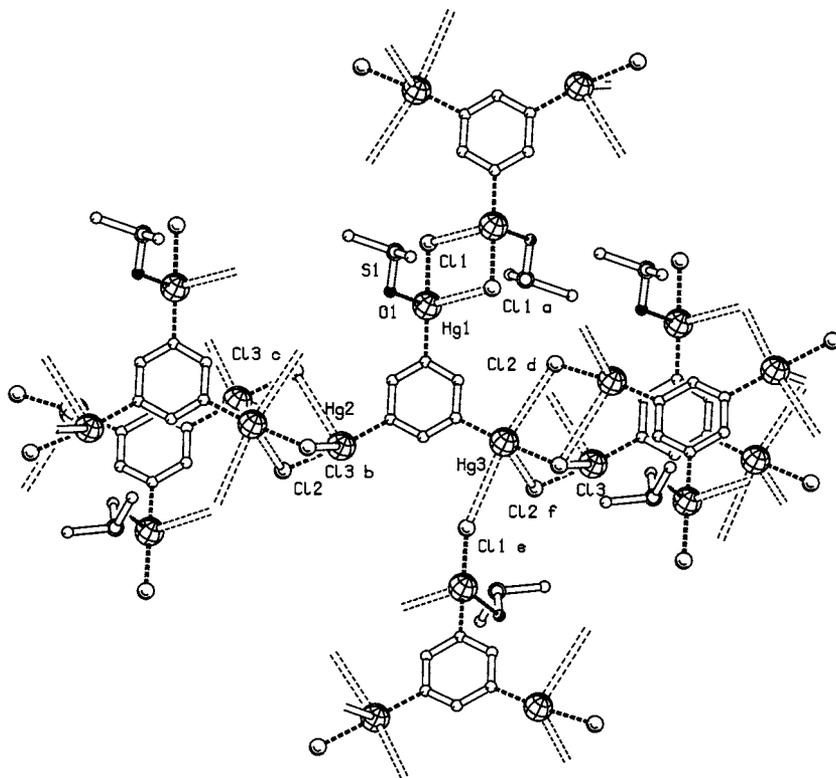


Fig. 3. Illustration of the short intermolecular HgCl contacts in **5**-DMSO.

Table 2
Selected chemical shifts and coupling constants of Me₃Sn-substituted benzene derivatives^a

Compound (substitution pattern)		10 ^b (1)	2 ^c (1,3,5)	9 ^b (1,2)	4 ^c (1,2,4,5)
¹ H	$\delta(\text{CH}_3)$	0.27	0.29	0.31	0.36
¹¹⁹ Sn	$\delta(\text{Sn})$	−30.3	−32.0	−33.8	−34.7
¹³ C	$\delta(\text{C}_{\text{ipso}})$	141.5	142.2	150.7	151.0
	$\delta(\text{CH}_3)$	−9.8	−9.7	−7.2	−7.2
	¹ J(Sn, C _{ipso})	474.4	449.7	528.6	^d
	¹ J(Sn, C _{Me})	347.5	343.4	337.5	334.3

^a Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz.

^b In CCl₄: (¹¹⁹Sn) [27]; (¹H, ¹³C) [28].

^c In C₆D₆.

^d Not determined.

MeSSMe. They were identified by GC–MS analysis; in some cases, absolute yields were determined by GC using hexamethylbenzene as an internal standard.

Depending on the reaction conditions, two to six different products (**18**–**26**) were observed in different amounts (Scheme 3, Table 4), which is taken to indicate the formation of the organolithium compounds **8** and **13**–**17** in the reaction mixture.

In the presence of three equivalents of MeLi (small excess, see Table 4, entry 1), all six products were observed (Me₂SO₄-quench, **18**–**23**). The presence of Me₃Sn-substituents in compounds **21**–**23** indicates incomplete conversion. However, the ‘desired’ product **18**, presumably corresponding to **8**, is also observed, although in low yield (23%). The reduction products **19**, **20** and **22** were presumably formed through hydrogen abstraction from the solvent by intermediates. In order to enforce complete conversion, the amount of the MeLi reagent was increased (entries 3–7), which seemed successful at first sight: the yield of **18** and **24** increased as if more **8** had been formed. In one experiment (entry 6), a yield even higher (84%) than by the LiDBB procedure (70–80%) [8] was found. However, a closer examination shows some inconsistencies: the yields fluctuate under seemingly identical conditions (entry 6 and 7) or the product distribution differs for the same quench reagent depending on the quench procedure (entry 1 and 2).

These observations might be explained by the stepwise formation of products via sequential lithiation-derivatization-lithiation-derivatization etc. which can proceed in the presence of excess MeLi and of less reactive quenching reagents.

In view of these varying quenching results, direct identification of **8** was attempted by NMR spectroscopy. At −50°C, the presence of Me₄Sn ($\delta(^{119}\text{Sn}) = 0$ ppm) in a reaction mixture of **2** and four or six equivalents of MeLi proved that Sn–Li exchange did occur. However, the reaction was obviously incomplete as indicated by resonances at $\delta(^{119}\text{Sn}) = -42.9$

ppm which must be due to benzene derivatives still containing one or two trimethylstannyl substituents. Obviously, the reaction did not go to completion; probably **17** and/or **15** were still present. Additional evidence for the presence of reactive (C–Li) bonds in the product(s) was obtained by quenching the reaction mixture with MeOD upon which the broad ¹¹⁹Sn-NMR signal at $\delta = -42.9$ ppm disappeared and a new sharp line came up at $\delta = -30.7$ ppm.

The difficulty of achieving the third tin–lithium exchange in **15** is probably due to the accumulation of negative charge associated with the first two organolithium functions which counteracts the introduction of a third negative charge; apparently, the energy of the intermediate tin ate-complex [38] will be prohibitive.

3. Conclusions

The successful synthesis of **2**, **4**, **5** and **6** has for the first time given access to well-defined benzene derivatives which are tri- or tetrasubstituted by tin or mercury. Although the attempted conversion of **2** with methyllithium to 1,3,5-trilithiobenzene (**8**) did not go to completion, the four new compounds may prove useful for the preparation of other metallated benzene derivatives with a 1,3,5- or 1,2,4,5-substitution pattern, or in coupling reactions with organic halides catalyzed by palladium(0) complexes such as Stille-type reactions.

4. Experimental

4.1. General

1,3,5-Tribromobenzene (**1**) was recrystallized from methanol and dried under vacuum prior to use. All reactions were carried out under a nitrogen atmosphere unless noted otherwise. Syringes and other glass ware were dried in an oven at 120°C for at least 24 h or

Table 3
Selected chemical shifts and coupling constants in HgCl-substituted benzene derivatives^a

Compound (substitution pattern)		11 (1)	5 (1,3,5)	12 ^b (1,2)	6 (1,2,4,5)
¹⁹⁹ Hg	$\delta(\text{Hg}) - 1192$ ^c	-1191	-1291 ^d / -1299	-1311 ^e	
¹³ C	$\delta(C_{\text{ipso}})$	150.5 ^c / 150.9	152.7	163.1	161.5 ^f
	$^2J(\text{Hg,C})$	117 ^c / 119	110.4	151.8	146.4 ^f

^a Chemical shifts (δ) in ppm, couplings (J) in Hz, in DMSO-*d*₆ unless otherwise noted.

^b Prepared from *ortho*-phenylene mercury and HgCl₂ in acetone [29].

^c In DMF + DMSO-*d*₆ (20%) at 340 K [30].

^d Ref. [31].

^e At 353 K.

^f At 328 K.

flame-dried prior to use. The solvents Et₂O and THF were distilled from LiAlH₄ (predried on NaOH and KOH, respectively) and kept on sodium wire under nitrogen. THF-*d*₈ was dried on molecular sieves and kept under argon. Tetraglyme (tetraethylene glycol dimethylether, Fluka) was distilled from sodium under reduced pressure and kept on sodium wire under nitrogen and protected against light. ¹H- and ¹³C-NMR spectra were measured at 25°C on a Bruker AC 200 or on a Bruker MSL 400 spectrometer. ¹¹⁹Sn-, ¹⁹⁹Hg- and ⁶⁷Li-NMR spectra were measured on a Bruker MSL 400 spectrometer. ¹J(Hg,C) could not be determined due to noise. Sometimes, the coupling between a nucleus (X = H, ¹³C) and tin was discernible, but the signals of ¹¹⁷Sn and ¹¹⁹Sn overlapped; in these cases the Sn nucleus is not specified (i.e. $J(\text{Sn,X})$). GC-MS measurements were performed on a HP 5890 II GC/5971 MS combination (70 eV, Chrompack BP 1 (QSGE) 50 m × 0.25 mm column) or on a HP 5890 GC/5970 MS combination (70 eV, CP-Sil-30 25 m × 0.22 mm column). HRMS measurements were performed on a Finnigan MAT 90 mass spectrometer. GC measurements were performed on an Intersmat gas chromatograph GC 120, equipped with a chrompack column (2 m × 4 mm, 10% OV-101 Chromosorb WHP 80/100) and a thermal conductivity detector. Melting points (uncorrected) were measured in a sealed capillary. Elemental analyses were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany).

4.2. Synthesis of trimethylstannylsodium (Me₃SnNa)

4.2.1. Method I (from Me₃SnCl in tetraglyme)

To a solution of Me₃SnCl (25.03 g, 125.64 mmol) in tetraglyme (230 ml), were added small pieces of sodium (± 0.5 cm³) (8.08 g, 351.41 mmol). After 8 h stirring at r.t., the green reaction mixture was left to stand overnight. After careful decanting through a P4 filter (under Ar or N₂), the molarity of the reagent was determined by acid–base-titration (HCl/NaOH) after quenching an aliquot with water (0.373 M, 68.3% yield).

4.2.2. Method II (from Me₃SnSnMe₃)

To a solution of hexamethyldistannane (1.178 g, 3.595 mmol) in tetraglyme (5 ml), small pieces sodium (± 0.5 cm³) (0.5 g, 21.7 mmol) were added. After 8 h stirring at r.t., the yellow–green reaction mixture was left to stand overnight. After careful decanting through a P4 filter (under Ar or N₂), the reagent was used without further purification (0.615 M, 55.9%, determined by titration, *vide supra*) [14b].

4.3. Synthesis of 1,3,5-tris(trimethylstannyl)benzene (2)

A solution of trimethylstannylsodium in tetraglyme (200 ml, 0.373 M, 74.6 mmol, four equivalents) was added drop-wise over 1.5 h at 0°C to a solution of **1** (5.8241 g, 18.5 mmol) in tetraglyme (100 ml); a cloudy-yellow solution was formed. After stirring for 4 h at 0°C, the reaction mixture was allowed to warm to r.t. overnight to yield a dark-yellow solution. A saturated NH₄Cl solution was added and the reaction mixture was extracted with diethyl ether. After washing the organic layer with water and drying on MgSO₄, the

Table 4

Yields (%) of products from the reaction of **2** and MeLi in THF at -70 → -50°C as derived from quenching reactions

Entry	MeLi (eq.)	8	13	14	15	16	17
1 ^a	3.3	23	29	3	29	3	8
2 ^b	3.3	53	21	3	–	–	–
3 ^{a,c}	4.4	69	5	–	–	–	–
4 ^{a,c}	4.4	62	10	–	–	–	–
5 ^d	4.4	60	–	–	40 - <i>x</i> ^e	–	40 - <i>x</i> ^e
6 ^a	6.6	84	8	–	–	–	–
7 ^a	6.6	65	7	–	–	–	–

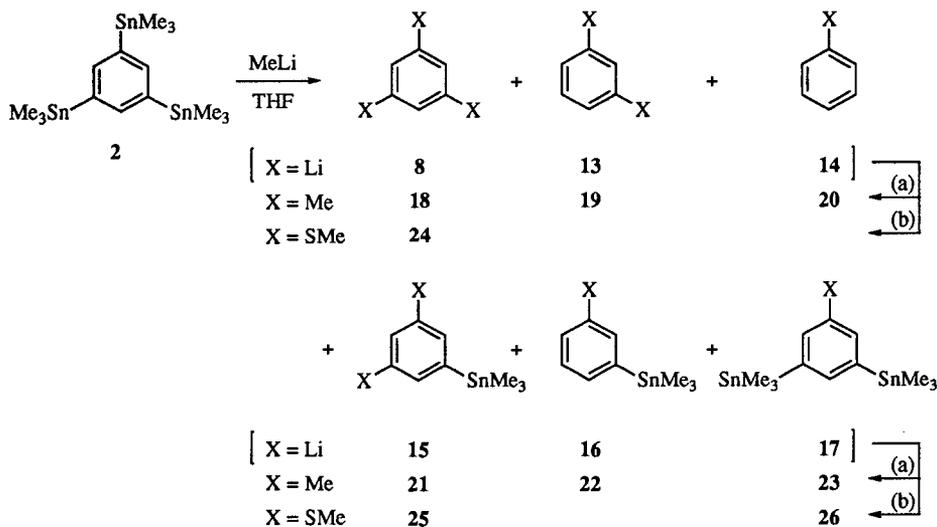
^a Me₂SO₄ quench, yields were determined relative to hexamethylbenzene (internal standard) by GC.

^b Inverse addition of the reaction mixture to Me₂SO₄; yields are relative.

^c Addition of THF to pure MeLi and **2**.

^d MeSSMe quench by inverse addition; yields are relative.

^e As **25** and **26** showed overlapping signals in the GC spectrum, only the total yield of **15** and **17** could be determined.

Scheme 3. (a) Me₂SO₄. (b) MeSSMe, see Table 4.

solvent was evaporated in vacuo to yield a yellow oil of nearly pure **2** (9.34 g, 16.49 mmol, 89%). GC–MS analysis of this product revealed the presence of traces of 1,3-bis(trimethylstannyl)benzene. MS (EI, *m/z*, rel. int.): 404 (1, M⁺, Sn₂-pattern), 387 (100, [M – CH₃]⁺, Sn₂-pattern), 359 (18, [M – 3CH₃]⁺, Sn₂-pattern), 342 (4, [M – 4CH₃]⁺, Sn₂-pattern), 329 (12, [M – 5CH₃]⁺, Sn₂-pattern), 312 (5, [M – 6CH₃]⁺, Sn₂-pattern), 240 (2, Sn-pattern), 223 (2, Sn-pattern), 209 (4, Sn-pattern), 187 (5, Sn-pattern), 165 (5, Sn-pattern), 135 (8, Sn-pattern), 120 (5, Sn-pattern). Pure **2** (NMR) was obtained by recrystallization from MeOH (yellow needles, m.p. 54–55°C). Sublimation gave white needles (95°C, 4 mm Hg). ¹H-NMR (400.1 MHz, THF-*d*₈, –50°C): δ 7.55 (s, ⁴*J*(H,H) = 1.1 Hz, ³*J*(¹¹⁹Sn,H) = 44.1 Hz, ⁵*J*(Sn,H) = 8.9 Hz; *H*_{ar}), 0.27 (s, ²*J*(¹¹⁹Sn,H) = 54.8 Hz; CH₃). ¹H-NMR (400.1 MHz, THF-*d*₈): δ 7.53 (s, ⁴*J*(H,H) = 0.9 Hz, ³*J*(¹¹⁹Sn,H) = 44.4 Hz, ⁵*J*(Sn,H) = 9.6 Hz; *H*_{ar}), 0.28 (s, ¹*J*(C,H) = 128.5 Hz, ³*J*(¹¹⁹Sn,H) = 54.8 Hz; CH₃). ¹H-NMR (200.1 MHz, C₆D₆): δ 7.87 (s, ⁴*J*(H,H) = 1.0 Hz, ³*J*(¹¹⁹Sn,H) = 44.0 Hz, ⁵*J*(¹¹⁹Sn,H) = 9.5 Hz, CH), 0.29 (s, ¹*J*(C,H) = 128.6 Hz, ²*J*(¹¹⁹Sn,H) = 54.3 Hz, CH₃). ¹³C{¹H}-NMR (100.6 MHz, THF-*d*₈, –50°C): δ 143.8 (²*J*(Sn,C) = 33.4 Hz, ⁴*J*(Sn,C) = 9.3 Hz; C(2,4,6)), 142.2 (¹*J*(¹¹⁹Sn,C) = 455.2 Hz, ³*J*(Sn,C) = 33.1 Hz; C_q), –9.6 (¹*J*(¹¹⁹Sn,C) = 344.2 Hz; CH₃). ¹³C{¹H}-NMR (100.6 MHz, THF-*d*₈): δ 143.7 (²*J*(Sn,C) = 33.4 Hz, ⁴*J*(Sn,C) = 9.3 Hz; C(2,4,6)), 142.4 (¹*J*(¹¹⁹Sn,C) = 455.2 Hz, ³*J*(Sn,C) = 33.1 Hz; C_q), –9.5 (¹*J*(¹¹⁹Sn,C) = 344.3 Hz; CH₃). ¹³C{¹H}-NMR (100.6 MHz, C₆D₆): δ 143.4 (²*J*(Sn,C) = 33.2 Hz, ⁴*J*(Sn,C) = 9.4 Hz; C(2,4,6)), 142.2 (³*J*(Sn,C) = 32.8 Hz, ¹*J*(¹¹⁹Sn,C) = 449.7 Hz; C_q), –9.7 (¹*J*(¹¹⁹Sn,C) = 343.4 Hz; CH₃). ¹¹⁹Sn-NMR (149.2 MHz, THF-*d*₈, 30°C): δ = –25.4. ¹¹⁹Sn-NMR (149.2 MHz, THF-*d*₈, –50°C): δ = –30.0. ¹¹⁹Sn-

NMR (149.2 MHz, C₆D₆): δ –32.0 (¹*J*(Sn,C_q) = 449.8 Hz, ¹*J*(Sn,CH₃) = 343.4 Hz, ⁴*J*(¹¹⁹Sn,¹¹⁷Sn) = 38.2 Hz, *J*(Sn,C) = 73.5 Hz, *J*(Sn,C) = 33.5 Hz, *J*(Sn,C) = 9.7 Hz). MS (EI, *m/z*, rel. int.): 566 (1, M⁺, Sn₃ pattern), 551 (100, [M – CH₃]⁺, Sn₃ pattern), 521 (9, [M – 3CH₃]⁺, Sn₃ pattern), 491 (6, [M – 5CH₃]⁺, Sn₃ pattern), 389 (5.5, [C₆H₃Sn₂(CH₃)₅]⁺, Sn₂ pattern) 31. HRMS (EI): Anal. Calc. for C₁₄H₁₇Sn₂¹¹⁸Sn₂¹²⁰Sn ([M – CH₃]⁺): 550.9176. Found 550.918 ± 0.001. Anal. Calc. (%) for C₁₅H₃₀Sn₃: C, 31.80; H, 5.34; Sn, 62.85. Found: C, 31.86; H, 5.30; Sn, 62.5.

4.4. Synthesis of

1,2,4,5-tetrakis(trimethylstannyl)benzene (**4**)

To a suspension of **3** (3.1588 g, 8.023 mmol) in tetraglyme (5 ml), a solution of trimethylstannylsodium in tetraglyme (55 ml, 0.79 M, 43.5 mmol) was added drop-wise at 0°C giving a cloudy-yellow solution. After stirring for 5 h at 0°C, the reaction mixture was allowed to warm to r.t. overnight. A saturated NH₄Cl solution was added and the reaction mixture was extracted with pentane–CH₂Cl₂. After washing the organic layer with water and drying on MgSO₄, the solvent was evaporated in vacuo. The resulting yellow oil consisted of **4** and traces of 1,2,4-tris(trimethylstannyl)benzene (GC–MS): MS (EI, *m/z*, rel. int.): 550 (9, [M – CH₃]⁺, Sn₃ pattern), 402 (10, Sn₃ pattern), 389 (3, [C₆H₃Sn₂(CH₃)₅]⁺, Sn₂ pattern), 371 (14, Sn₂ pattern), 341 (16, Sn₂ pattern), 165 (100 ([CH₃)₃Sn]⁺), 161 (50). Recrystallization by slow evaporation of a solution in hexane–ethanol gave colorless prisms of nearly pure **4** (5.19 g, 7.12 mmol, 89%) which still contained traces of 1,2,4-tris(trimethylstannyl)benzene; for that reason, an elemental analysis was not attempted. M.p. 161°C. ¹H-NMR (400.1 MHz, C₆D₆): δ 7.88 (s, ³*J*(Sn,H) =

46.4 Hz, $^4J(\text{Sn},\text{H}) = 13.4$ Hz; C_{ar},H), 0.36 (s, $^1J(^{13}\text{C},\text{H}) = 128.5$ Hz, $^2J(^{119}\text{Sn},\text{H}) = 53.0$ Hz; CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, C_6D_6): δ 151.0 (C_q), 145.5 ($^2J(^{119}\text{Sn},\text{C}) = 57.4$ Hz; C_{ar}), -7.24 ($^1J(^{119}\text{Sn},\text{C}) = 334.3$ Hz; CH_3). ^{13}C -NMR (50.3 MHz, C_6D_6): δ 151.0 (s, C_q), 145.7 (dd, $^1J(\text{C},\text{H}) = 133.1$ Hz, $^4J(\text{C},\text{H}) = 1.0$ Hz, $J(\text{Sn},\text{C}) = 57.4$ Hz, $J(\text{Sn},\text{C}) = 44.0$ Hz; CH), -7.3 (q, $^1J(\text{C},\text{H}) = 128.5$ Hz; CH_3). ^{119}Sn -NMR (149.2 MHz, C_6D_6): δ -34.7 . MS (EI, m/z , rel. int.): 730 (11, $\text{M}^{+\bullet}$, Sn_4 pattern), 715 (100, $\text{M}^{+\bullet} - \text{CH}_3$, Sn_4 pattern), 565 (13, $[\text{M} - \text{Sn}(\text{CH}_3)_3]^+$, Sn_4 pattern), 550 (12, $[\text{M} - \text{Sn}(\text{CH}_3)_3 - \text{CH}_3]^+$, Sn_3 pattern), 535 (8.2, $[\text{C}_6\text{H}_2\text{Sn}_3 - (\text{CH}_3)_7]^+$, Sn_3 pattern), 387 (20.5, $[\text{C}_6\text{H}_2\text{Sn}_2(\text{CH}_3)_5]^+$, Sn_2 pattern), 357 (20.6, $[\text{C}_6\text{H}_2\text{Sn}_2(\text{CH}_3)_3]^+$, Sn_2 pattern). HRMS (EI): Anal. Calc. for $[\text{C}_{17}\text{H}_{35}^{116}\text{Sn}_2^{120}\text{Sn}]^+$: 710.8824 $[\text{C}_{17}\text{H}_{35}^{116}\text{Sn}^{118}\text{Sn}_2^{120}\text{Sn}]^+$: 710.8817 ($[\text{M}^{+\bullet} - \text{CH}_3]^+$). Found (for m/z : 711 signal): 710.885.

4.5. Synthesis of 1,3,5-tris(chloromercurio)benzene (**5**)

To a solution of HgCl_2 (4.5758 g, 16.85 mmol) in THF (20 ml), **2** (2.3855 g, 4.21 mmol) dissolved in Et_2O (20 ml) was added (under nitrogen) drop-wise at r.t. Almost immediately, a white precipitate formed. After stirring overnight, the solvent was evaporated in vacuo and the resulting powder was boiled three times with water and filtered. The residue was washed with Et_2O and dried in vacuo (2.9805 g, mmol, 90% of pure **5** (NMR)). Slow evaporation of a solution of **5** in $\text{DMSO}-d_6$ gave colorless needles. **5**- DMSO : m.p. $> 330^\circ\text{C}$. ^1H -NMR (200.1 MHz, $\text{DMSO}-d_6$): δ 7.25 ($^3J(\text{Hg},\text{H}) = 197.4$ Hz; CH). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, $\text{DMSO}-d_6$): δ 152.7 ($^3J(\text{Hg},\text{C}) = 216.8$ Hz; C_q), 144.4 ($^2J(\text{Hg},\text{C}) = 110.4$ Hz; CH). ^{13}C -NMR (50.3 MHz, $\text{DMSO}-d_6$): δ 152.5 (C_q), 144.2 (dt, $^1J(\text{C},\text{H}) = 166.6$ Hz, $^3J(\text{C},\text{H}) = 8.3$ Hz; CH). ^{199}Hg -NMR (72 MHz, $\text{DMSO}-d_6$): δ -1190.76 . Anal. Calc. for $\text{C}_6\text{H}_3\text{Hg}_3\text{Cl}_3\text{C}_2\text{D}_6\text{OS}$: C, 11.08; H, 0.35; O, 1.84; S, 3.70. Found: C, 11.15; H, 0.32; O, 1.89; S, 3.27.

4.6. Synthesis of

1,2,4,5-tetrakis(chloromercurio)benzene (**6**)

To a solution of HgCl_2 (0.8905 g, 3.28 mmol) in THF (10 ml), **4** (0.2969 g, 0.41 mmol) dissolved in Et_2O (10 ml) was added (under nitrogen) over 40 min at r.t. A white precipitate was formed. After stirring overnight, the solvent was evaporated in vacuo and the resulting powder was boiled with water and filtered three times. Subsequently, the residue was washed with Et_2O and dried in vacuo to yield a mixture of **6** and **7** (^{199}Hg -NMR). **6**. ^1H -NMR (400.1 MHz, $\text{DMSO}-d_6$, 55°C): δ 7.22 (s, $^3J(\text{Hg},\text{H}) = 195.9$ Hz, $^4J(\text{Hg},\text{H}) = 48.3$ Hz; CH). ^1H -NMR (200.1 MHz, $\text{DMSO}-d_6$): δ 7.17 (s, $^3J(\text{Hg},\text{H}) = 200.4$ Hz, $^4J(\text{Hg},\text{H}) = 50.5$ Hz; CH). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, $\text{DMSO}-d_6$, 80°C): δ 161.5

($^4J(\text{Hg},\text{C}) = 46.4$ Hz; C_q), 145.6 ($^2J(\text{Hg},\text{C}) = 146.4$ Hz, $^3J(\text{C},\text{Hg}) = 239.3$ Hz; CH). ^{13}C -NMR (100.6 MHz, $\text{DMSO}-d_6$): δ 161.5 (d, $^3J(\text{C},\text{H}) = 9.7$ Hz; C_q), 145.6 (d, $^1J(\text{C},\text{H}) = 145.6$ Hz; CH). ^{199}Hg -NMR (72 MHz, $\text{DMSO}-d_6$, 55°C): δ -1310.98 . **7**: ^{199}Hg -NMR (72 MHz, $\text{DMSO}-d_6$): δ -871.4 ($H_{g,\text{symm}}$), -1208.4 (2- H_g), -1301.0 (4/5- H_g), -1315.2 (4/5- H_g).

This mixture was washed consecutively with DMSO (3 ml), Et_2O (100 ml), pentane and Et_2O again to give pure **6** (0.3522 g, 0.346 mmol, 84%). Partial evaporation of the combined washing layers gave a white precipitate consisting of pure **6** (^{199}Hg -NMR), which was washed with water and dried on P_2O_5 in vacuo to give another 0.0251 g of **6** (0.025 mmol, 6%), so that the total isolated yield of **6** was 90%. Addition of water to the supernatant from the precipitate gave a second precipitate which after washing with water and drying on P_2O_5 in vacuo gave 0.097 g of a white powder containing, according to ^{199}Hg -NMR, some **6** and **7** in a ratio of about 2:1. As **6** was difficult to crystallize and could only be obtained as an amorphous powder, an elemental analysis was not performed.

4.7. Reactions of **2** with methylolithium

4.7.1. Reaction of **2** with three equivalents MeLi , Me_2SO_4 quench

Under argon, a solution of MeLi in Et_2O (0.4 ml, 1.69 M, 0.676 mmol) was added drop-wise to **2** (0.1132 g, 0.2 mmol) in THF (10 ml) at -70°C . Subsequently, the yellow reaction mixture was warmed to -50°C and stirred for 30 min. Pure Me_2SO_4 (0.4 ml, 4.23 mmol) was then added drop-wise. The reaction mixture decolorized within a few minutes and was stirred for another 0.5 h. After adding MeOD (0.1 ml), the reaction mixture was allowed to warm to r.t. Water and hexamethylbenzene (0.032 g, 0.2027 mmol) were added and the reaction mixture was extracted with Et_2O , washed with water and brine, and dried (MgSO_4). The products were identified by GC-MS, and the yields were determined by GC relative to the internal standard (see Table 2, entry 1); the responses with regard to the internal standard were assumed to be 1:1, with the exception of **18** and **19**, which are response-corrected. **18**. MS (EI, m/z , rel. int.): 120 (56, $\text{M}^{+\bullet}$), 105 (100, $[\text{M} - \text{CH}_3]^+$), 91 (10, $[\text{C}_7\text{H}_7]^+$), 77 (12, $[\text{C}_7\text{H}_5]^+$). **19**. MS (EI, m/z , rel. int.): 106 (66, $\text{M}^{+\bullet}$), 91 (100, $[\text{M} - \text{CH}_3]^+$), 77 (17, $[\text{C}_7\text{H}_5]^+$), 65 (10, $[\text{C}_5\text{H}_5]^+$), 51 (16), 39 (17). **20**. MS (EI, m/z , rel. int.): 92 (67, $\text{M}^{+\bullet}$), 91 (100, $[\text{M} - \text{H}]^+$), 65 (11, $[\text{C}_5\text{H}_5]^+$), 63 (9), 51 (6). **21**. MS (EI, m/z , rel. int.): 270 (2, $\text{M}^{+\bullet}$, Sn pattern), 255 (100, $[\text{M} - \text{CH}_3]^+$, Sn pattern), 225 (25, Sn pattern), 135 (5, Sn pattern), 120 (6, Sn pattern). **22**. MS (EI, m/z , rel. int.): 256 (1, $\text{M}^{+\bullet}$), 241 (100, $[\text{M} - \text{CH}_3]^+$, Sn pattern), 226 (3, $[\text{M} - 2 \text{CH}_3]^+$, Sn pattern), 211 (27, $[\text{M} - 3$

$\text{CH}_3]^+$, Sn pattern), 135 (6, Sn pattern), 120 (11, Sn pattern). **23**. MS (EI, m/z , rel. int.): 418 (56, $\text{M}^{+\bullet}$, Sn_2 pattern), 403 (100, $[\text{M} - \text{CH}_3]^+$, Sn_2 pattern), 373 (13, $[\text{M} - 3\text{CH}_3]^+$, Sn_2 pattern), 343 (9, $[\text{M} - 5\text{CH}_3]^+$, Sn_2 pattern), 327 (4, Sn_2 pattern), 194 (6, Sn pattern).

4.7.2. Reaction of **2** with three equivalents of MeLi, inverse Me_2SO_4 quench

The reaction was performed in a reaction vessel connected to five other vessels via glass capillaries. During the reaction, all vessels and capillaries were continuously immersed into the cooling liquid (pentane–liquid nitrogen). Under argon, a solution of MeLi in Et_2O (0.7 ml, 1.69 M, 1.183 mmol) was added drop-wise to a solution of **2** (0.2025 g, 0.357 mmol) in THF (19 ml; in the central vessel) at -70°C . Subsequently, the yellow reaction mixture was warmed to -50°C . At different times, samples of about 2 ml were pressed into one of the side vessels containing Me_2SO_4 (0.1 ml). After quenching the last sample, all vessels were allowed to warm to r.t. The work-up and analysis were performed as described above; all aliquots showed the same composition. The results are presented in Table 2.

4.7.3. Reaction of **2** with four equivalents of MeLi, Me_2SO_4 quench

In vacuo, all solvent was evaporated from a solution of MeLi in Et_2O (1.69 M; 0.35 ml (0.5915 mmol) and 0.25 ml (0.4225 mmol), respectively). After addition of **2** (0.0845 g (0.1491 mmol) and 0.0582 g (0.1027 mmol), respectively), the reaction vessel was cooled to -70°C and THF (3 ml) was added drop-wise. The reaction mixture became yellow instantaneously and was stirred for another 0.5 h at -50°C . After adding Me_2SO_4 (0.1 ml) followed after by the addition of MeOD over 30 min (0.1 ml), the mixture was allowed to warm to r.t. After adding water and hexamethylbenzene (0.0246 g (0.1516 mmol) and 0.0162 g (0.0998 mmol), respectively) the reaction mixture was worked-up and analyzed as described above (entry 1). The results are presented in Table 2.

4.7.4. Reaction of **2** with four equivalents MeLi, MeSSMe quench

Under argon, a solution of MeLi in Et_2O (0.142 ml, 1.69 M, 0.2399 mmol) was added drop-wise to **2** (0.0338 g, 0.0597 mmol) in THF (3 ml) at -70°C . Subsequently, the yellow reaction mixture was warmed to -50°C and stirred for 30 min. Then pure MeSSMe was added drop-wise to the solution. The reaction mixture decolorized within a few minutes and was stirred for another 0.5 h. After adding MeOD (0.1 ml), the reaction mixture was allowed to warm to r.t. The work-up was performed as described above (entry 1). The products were identified by GC–MS, and the

Table 5

Crystal data and details of the structure determination for **5**·DMSO

Empirical formula	$\text{C}_8\text{H}_9\text{Cl}_3\text{Hg}_3\text{OS}$
Formula weight	861.34
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	9.0870(9)
b (Å)	20.560(2)
c (Å)	7.8914(9)
β (°)	92.166(6)
V (Å ³)	1473.3(3)
Z	4
D_{calc} (g cm ⁻³)	3.883
$F(000)$	1488
μ (Mo–K α) (mm ⁻¹)	31.8
Crystal size (mm)	0.05 × 0.05 × 0.50
Temperature (K)	250
Radiation (Å)	0.71073
Theta min and max (°)	2.0 and 27.5
Scan (type and range)	0.80 + 0.35 tan(Θ)
Dataset	–11:11; –26:0; –8:10
Total uniq. Data, R_{int}	5182, 3377, 0.046
Observed data [$I > 2\sigma(I)$]	2024
N_{ref} , N_{par}	3377, 147
R , wR , S	0.0543, 0.0831, 0.99
Max. and av. Shift/error	0.00/0.00
Largest difference peak and hole (e Å ⁻³)	–2.00 and 1.50

$$^a w = 1/[\sigma^2(F_o^2) + (0.0213P)^2].$$

relative yields were determined by GC (see Table 2). **24**. MS (EI, m/z , rel. int.): 216 (100, $\text{M}^{+\bullet}$), 200 (5), 183 (49), 171 (8), 168 (9), 154 (24), 139 (13), 125 (12), 121 (10), 108 (8), 95 (10), 82 (6), 69 (12), 63 (16), 45 (22). **25**. MS (EI, m/z , rel. int.): 334 (31, $\text{M}^{+\bullet}$, Sn pattern), 319 (100, $[\text{M} - \text{CH}_3]^+$, Sn pattern), 289 (22, $[\text{M} - 3\text{CH}_3]^+$, Sn pattern), 274 (4, $[\text{M} - 4\text{CH}_3]^+$, Sn pattern), 259 (3, $[\text{M} - 5\text{CH}_3]^+$, Sn pattern). **26**. MS (EI, m/z , rel. int.): 450 (16, $\text{M}^{+\bullet}$, Sn_2 pattern), 435 (100, $[\text{M} - \text{CH}_3]^+$, Sn_2 pattern), 405 (16, $[\text{M} - 3\text{CH}_3]^+$, Sn_2 pattern), 375 (11, $[\text{M} - 5\text{CH}_3]^+$, Sn_2 pattern), 165 (29, $[\text{SnMe}_3]^+$, Sn pattern).

4.7.5. Reaction of **2** with six equivalents of MeLi, Me_2SO_4 quench

The reaction was performed analogous to that of entry 1, using a solution of **2** (0.1133 g (0.2 mmol) and 0.0561 g (0.099 mmol), respectively) in THF (10 ml and 5 ml, respectively) and a MeLi solution in Et_2O (1.69 M; 0.8 ml (1.35 mmol) and 0.385 ml (0.651 mmol), respectively). Yields were determined relative to hexamethylbenzene (GC, 0.0319 g (0.1966 mmol) and 0.0172 g (0.1060 mmol), respectively). The results are presented in Table 2.

4.8. Crystal structure determination of **5**·DMSO

X-ray data were collected at 250 K on an Enraf–Nonius CAD4-T diffractometer (rotating anode) for a

needle-shaped colorless crystal. Unit cell dimensions were derived from the SET4 setting angles of 25 reflections in the range $10.55 < \Theta < 13.85^\circ$. Data were corrected for absorption following the semi-empirical psi-scan correction technique [39] (transmission range 0.674–0.966) using PLATON/ABSP [40].

The structure was solved by automated Patterson techniques using DIRDIF96 [41] and refined on F^2 using SHELXL96 [42]. Hydrogen atoms were taken into account at calculated positions and refined riding on their carrier atoms. A final Fourier difference map showed no significant features other than some residual absorption artifacts near Hg. Numerical details have been collected in Table 5. All geometrical calculations and the illustrations were done with PLATON [40].

Full details of the analysis are available from one of the authors (ALS).

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References

- [1] (a) A.F. Halasa, D.P. Tate, *J. Organomet. Chem.* 24 (1970) 769. (b) A. Bretschneider-Hurley, C.H. Winter, *J. Am. Chem. Soc.* 116 (1994) 6468.
- [2] W.E. Post, T.F. Crimmins, *J. Organomet. Chem.* 161 (1978) C17.
- [3] A.G. Osborne, R.H. Whiteley, *J. Organomet. Chem.* 162 (1978) 79.
- [4] K.N. Seneviratne, A. Bretschneider-Hurley, C.H. Winter, *J. Am. Chem. Soc.* 118 (1996) 5506.
- [5] K.N. Seneviratne, C.H. Winter, *Organometallics* 16 (1997) 2498.
- [6] (a) I. Haiduc, H. Gilman, *J. Organomet. Chem.* 12 (1968) 394. (b) I. Haiduc, H. Gilman, *Rev. Romaine Chim.* 16 (1971) 907. (c) R.D. Howells, H. Gilman, *Tetrahedron Lett.* 14 (1974) 1319. (d) K. Kuroda, N. Ishikawa, *Nippon Kagaku Zasshi* 91(5) (1970) 489; *Chem. Abstr.* 73 (1970) 66669p. (e) P. Buck, G. Köbrich, *Chem. Ber.* 103 (1970) 1420. (f) L.A. Shimp, C. Chung, R.J. Lagow, *Inorg. Chim. Acta* 29 (1978) 77. (g) M.I. of Technology, *Brit. Pat.* 1,444,174 (1976); *Chem. Abstr.* 86 (1977) 106764t.
- [7] J.R. Baran Jr., C. Hendrickson, J.D.A. Laude, R.J. Lagow, *J. Org. Chem.* 57 (1992) 3759.
- [8] N. Rot, F. Bickelhaupt, *Organometallics* 16 (1997) 5027.
- [9] (a) G.B. Deacon, G.J. Farquharson, *J. Organomet. Chem.* 67 (1974) C1–C3. (b) G.B. Deacon, G.J. Farquharson, *Aust. J. Chem.* 29 (1976) 627. (c) G.B. Deacon, G.J. Farquharson, *Aust. J. Chem.* 30 (1977) 1701.
- [10] (a) L. Pesci, *Proc. Nat. Acad. Lincei* [5] 8 I (1899) 130. (b) M. Malaiyandi, H. Sawatzky, G.F. Wright, *Can. J. Chem.* 39 (1961) 1827.
- [11] (a) T. Brennan, H. Gilman, *J. Organomet. Chem.* 11 (1968) 625. (b) I.I. Schuster, W. Weissensteiner, K. Mislow, *J. Am. Chem. Soc.* 108 (1986) 6661. (c) B. Kahr, J.M. Chance, K. Mislow, *Mol. Cryst. Liq. Cryst.* 210 (1992) 195. (d) R.B. King, *J. Organomet. Chem.* 8 (1967) 139. (e) K. Ebata, T. Inada, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.* 116 (1994) 3595. (f) H. Sakurai, K. Ebata, C. Kabuto, A. Sekiguchi, *J. Am. Chem. Soc.* 112 (1990) 1799. (g) W. Weissensteiner, I.I. Schuster, J.F. Blount, K. Mislow, *J. Am. Chem. Soc.* 108 (1986) 6664. (h) A. Sekiguchi, K. Ebata, Y. Terui, H. Sakurai, *Chem. Lett.* (1991) 1417. (i) A. Sekiguchi, K. Ebata, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.* 113 (1991) 1464. (j) P.P. Power, *Chemtracts-Inorg. Chem.* 3 (1991) 153–155. (k) H. Sakurai, *Pure Appl. Chem.* 66 (1994) 1431. (l) K. Ebata, T. Matsuo, T. Inoue, Y. Otsaka, C. Kabuto, A. Sekiguchi, H. Sakurai, *Chem. Lett.* (1996) 1053. (m) K. Ebata, W. Setaka, T. Inoue, C. Kabuto, M. Kira, H. Sakurai, *J. Am. Chem. Soc.* 120 (1998) 1335. (n) C. Rüdinger, P. Bissinger, H. Beruda, H. Schmidbaur, *Organometallics* 11 (1992) 2867. (o) C. Rüdinger, H. Beruda, H. Schmidbaur, *Chem. Ber.* 125 (1992) 1401.
- [12] W. Weissensteiner, I.I. Schuster, J.F. Blount, K. Mislow, *J. Am. Chem. Soc.* 108 (1986) 6664.
- [13] G.J. Chen, C. Tamborski, *J. Organomet. Chem.* 251 (1983) 149.
- [14] (a) H.G. Kuivila, K.R. Wursthorn, *Tetrahedron Lett.* 49 (1975) 4357. (b) H.G. Kuivila, K.R. Wursthorn, *J. Organomet. Chem.* 140 (1977) 29. (c) K.R. Wursthorn, H.G. Kuivila, G.F. Smith, *J. Am. Chem. Soc.* 100 (1978) 2779. (d) G.F. Smith, H.G. Kuivila, R. Simon, L. Sultan, *J. Am. Chem. Soc.* 103 (1981) 833.
- [15] G. Schultz, I. Hargittai, N. Rot, F. Bickelhaupt, *Struct. Chem.* 9 (1998) 209.
- [16] M.A. Sens, N.K. Wilson, P.D. Ellis, J.D. Odom, *J. Magn. Reson.* 19 (1975) 323.
- [17] L. Wardell, *Comprehensive Organometallic Chemistry*, vol. 2, Pergamon, Oxford, 1982, p. 863.
- [18] D.K. Breiting, G. Petrikowski, G. Liehr, R. Sendelbeck, *Z. Naturforsch.* 38b (1983) 357.
- [19] (a) H. Schmidbaur, H.-J. Öller, D.L. Wilkinson, B. Huber, G. Müller, *Chem. Ber.* 122 (1989) 31. (b) H. Schmidbaur, H.-J. Öller, S. Gamper, G. Müller, *J. Organomet. Chem.* 394 (1990) 757.
- [20] A.L. Beauchamp, M.J. Olivier, J.D. Wuest, B. Zacharie, *Organometallics* 6 (1987) 153.
- [21] L.G. Kuz'mina, Y.T. Struchkov, *Croat. Chem. Acta* 57 (1984) 701.
- [22] (a) A.N. Chekhlov, V.K. Brel, I.V. Martynov, *Sov. Phys. Crystallogr.* 31 (1986) 393. (b) M. Tschinkl, A. Schier, J. Riede, F.P. Gabbai, *Inorg. Chem.* 36 (1997) 5706. (c) M. Tschinkl, A. Schier, J. Riede, G. Mehlretter, F.P. Gabbai, *Organometallics* 17 (1998) 2921.
- [23] J.D. Wuest, B. Zacharie, *Organometallics* 4 (1985) 410.
- [24] A. Domenicano, *Stereochemical Applications of Gas-Phase Electron Diffraction Part B*, VCH, New York, 1988, p. 281.
- [25] D.S. Brown, A.G. Massey, D.A. Wickens, *Acta. Crystallogr. B* 34 (1978) 1695.
- [26] E.R.T. Tiekink, *J. Organomet. Chem.* 303 (1986) C53.
- [27] H.J. Kroth, H. Schumann, H.G. Kuivila, C.D. Schaeffer Jr., J.J. Zuckerman, *J. Am. Chem. Soc.* 97 (1975) 1754.
- [28] C.D. Schaeffer Jr., J.J. Zuckerman, *J. Organomet. Chem.* 99 (1975) 407.
- [29] F. Bickelhaupt, *Zur Komplexbildung Metallorganischer Verbindungen in Äther*, Thesis, Eberhard-Karls-Universität, Tübingen, 1957.
- [30] J. Browning, P.L. Goggin, R.J. Goodfellow, N.W. Hurst, L.G. Mallinson, M. Murray, *J. Chem. Soc. Dalton Trans.* (1978) 872.
- [31] J.D. Wuest, B. Zacharie, *Organometallics* 4 (1985) 410.
- [32] H.J. Kroth, H. Schumann, H.G. Kuivila, C.D. Schaeffer Jr., J.J. Zuckerman, *J. Am. Chem. Soc.* 97 (1975) 1754.
- [33] C.D. Schaeffer Jr., J.J. Zuckerman, *J. Organomet. Chem.* 99 (1975) 407.

- [34] J. Schraml, V. Chvalovsky, M. Mägi, E. Lippmaa, R. Calas, J. Dunoguès, P. Bourgeois, *J. Organomet. Chem.* 120 (1976) 41.
- [35] W. Wray, D.N. Lincoln, *J. Magn. Reson.* 18 (1975) 374.
- [36] W. Wray, L. Ernst, E. Lustig, *J. Magn. Reson.* 27 (1977) 1.
- [37] S.L. Manalt, M.A. Cooper, *J. Am. Chem. Soc.* 99 (1977) 4561.
- [38] (a) H.J. Reich, N.H. Phillips, *Pure Appl. Chem.* 59 (1987) 1021. (b) H.J. Reich, J.P. Borst, M.B. Coplien, N.H. Phillips, *J. Am. Chem. Soc.* 114 (1992) 6577.
- [39] A.C.T. North, D.C. Phillips, F.S. Matthews, *Acta Crystallogr. A* 24 (1968) 351.
- [40] A.L. Spek, *Acta Crystallogr. A* 46 (1990) C34.
- [41] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. García-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, *The DIRDIF96 program system*, Technical report of the Crystallographic Laboratory, University of Nijmegen, The Netherlands (1992).
- [42] G.M. Sheldrick, *SHELXL96: Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1996.