corporated in SHELX.[18] Data solution and refinements were performed with the SHELX program system on the University of Adelaide's Cyber (2a) and VAX11/780 (4) computer systems.

Fractional atomic coordinates are listed in Tables V and VI; the numbering schemes used are shown in Figures 1 and 2. Selected interatomic bond distances and angles are given in Table I.

Acknowledgment. We thank the Australian Research Council for support of this work. M.J.L. and A.G.S. were holders of Commonwealth Post-Graduate Research Awards.

Registry No. **2a**, 129571-03-5; **2b**, 129646-59-9; **3**, 124225-89-4; **4**, 129571-05-7; **5**, 129571-06-8; **6**, 129571-07-9; **7**, 129571-08-0; **8**, 129571-09-1; **9**, 129571-10-4; **10a**, 129571-11-5; **10b**, 129646-60-2; **11**, 129571-12-6; **12**, 129571-13-7; **13a**, 129571-14-8; **13b**, 129646-61-3; **13c**, 129571-15-9; **15a**, 129571-16-0; **15b**, 129646-62-4; dcfe, 1113-69-5; TCNE, 670-54-2; $Ru(C_2Ph)(PPh_3)_2(\eta^5\text{-}C_5H_5)$, 58355-23-0; $[Ru[C{\equiv}CPhC(CF_3)_2C(CN)_2](PPh_3)(\eta^5\text{-}C_5H_5)]_2[\mu\text{-}(NC)_2C_6F_4\text{-}p]$, 129571-17-1; MeCN, 75-05-8; acrylonitrile, 107-13-1; 1,2,4,5-tetracyanobenzene, 712-74-3; phthalodinitrile, 91-15-6; tetrafluorophthalodinitrile, 1835-65-0; tetrafluoroterephthalonitrile, 1835-49-0; fumaronitrile, 764-42-1.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom parameters, and bond distances and angles for **2a** and **4** and listings of spectroscopic (UV/visible, FAB MS, and IR) data for organonitrile complexes and electrochemical and UV/visible data for nitrile ligands (19 pages); listings of observed and calculated structure factors for **2a** and **4** (32 pages). Ordering information is given on any current masthead page.

(19) Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

Selective Lithiation of 1-Bromo-2-((trimethylstannyl)methyl)benzene: Synthesis of 1-Bromo-2-(lithiomethyl)benzene, 1-Lithio-2-((trimethylstannyl)methyl)benzene, and α,2-Dilithiotoluene

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Reactions of 1-bromo-2-((trimethylstannyl)methyl)benzene (1) with *n*-butyllithium and *tert*-butyllithium have been investigated. With *n*-butyllithium in tetrahydrofuran (THF) at −70 °C, the only observed process was lithium–tin exchange, yielding 1-bromo-2-(lithiomethyl)benzene (2). In contrast, lithium–halogen exchange occurred when 1 was treated with *tert*-butyllithium in diethyl ether at −80 °C to give 1-lithio-2-((trimethylstannyl)methyl)benzene (3). α,2-Dilithiotoluene could be prepared in high yield from 3 and *tert*-butyllithium in either diethyl ether (room temperature) or THF (−80 °C).

Introduction

Organolithium compounds are generally prepared by traditional methods such as lithium–halogen exchange and metalation.[1] However, when these methods are not selective or mild enough, the lithium–tin exchange reaction often provides a good alternative for the synthesis of the required compound.[2] The mechanism suggested for this transmetalation involves stannate complexes, for which direct evidence was recently provided by ^{119}Sn NMR studies on mixtures of tetramethylstannane and methyllithium or phenyllithium in THF/hexamethylphosphoric triamide (HMPT).[3] When the starting material has both a halogen and a trimethylstannyl group as substituents, lithium–tin exchange can compete effectively with lithium–halogen exchange. This has been demonstrated by the reaction between 1,3-dibromo-5-(trimethylstannyl)benzene and *n*-butyllithium in diethyl ether at −78 °C, which predominantly yielded 1,3-dibromo-5-lithiobenzene.[4] We now report selective lithiation of 1-bromo-2-((trimethylstannyl)methyl)benzene (1) to 1-bromo-2-(lithiomethyl)benzene (2), 1-lithio-2-((trimethylstannyl)methyl)benzene (3), or α,2-dilithiotoluene (4). The last compound had previously been detected in small amounts in metalations of toluene or benzyllithium by *n*-butyllithium/tetramethylethylenediamine (TMEDA).[5]

Results

Reactions of 1 with *n*-BuLi. A series of reactions between 1 and *n*-BuLi was conducted under various conditions (Table I and Scheme I). In a typical experiment, 1 was added to *n*-BuLi in diethyl ether (with some *n*-hexane, see Experimental Section) at the indicated tem-

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(1) (a) Schöllkopf, U. In *Houben Weyl, Methoden der Organischen Chemie*; Müller, E., Ed.; G. Thieme Verlag: Stuttgart, FRG, 1970; Vol. 13/1, p 128. (b) Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 1, p 43. (c) Wakefield, B. J. In *Organolithium Methods*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Academic Press: New York, 1988; p 22.

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(3) (a) Reich, H. J.; Philips, N. H.; Reich, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4101. (b) Reich, H. J.; Philips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102. (c) Reich, H. J.; Philips, N. H. *Pure Appl. Chem.* **1987**, *59*, 1021. See also: Reich, H. J.; Green, D. P.; Philips, N. H. *J. Am. Chem. Soc.* **1989**, *111*, 1344.

(4) Chen, G. J.; Tamborski, C. *J. Organomet. Chem.* **1983**, *251*, 149.

(5) West, R.; Jones, P. C. *J. Am. Chem. Soc.* **1968**, *90*, 2656.

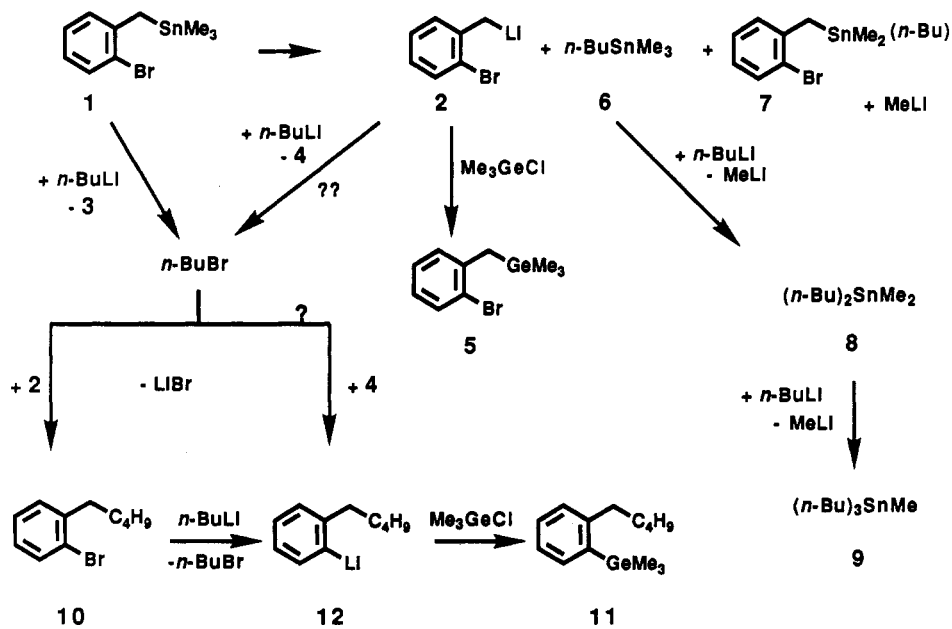
0276-7333/90/2309-2898$02.50/0

Table I. Reactions between 1 and *n*-Butyllithium

				yield[c]							
n-BuLi:1	solvent	temp[a]	time[b]	1	5	6	7	8	9	10	11
1	Et_2O	−70	5	80	16	20					
1	Et_2O	−70	60	72	19	27					
1	Et_2O	−70	60								
		room temp	60	42	25	54	4				
1	Et_2O[d]	−70	60	28	36	30	26	4			
1	Et_2O[e]	−70	30	12	7	53		22	1		
3	Et_2O	−70	60								
		room temp	60		1	20	1	13	10	15	54
3	THF	−70	60		92	14		78	8		

[a] In °C. [b] In min. [c] Yield (%) relative to educt 1. [d] TMEDA (1 equiv) was added. [e] HMPT (1 equiv) was added.

Scheme I



perature, which gave a yellow solution immediately; when the reactions were performed in the presence of TMEDA or HMPT, the mixture turned dark red. After it was stirred for the time and temperature indicated, the reaction mixture was quenched with chlorotrimethylgermane and worked up, whereafter the product ratio was determined by GCMS, ^1H NMR spectroscopy, and isolation of the main products.

Treatment of **1** with *n*-BuLi in equimolar amounts with diethyl ether as the solvent at −70 °C gave rise to lithium–tin exchange only; quenching of the reaction mixture yielded small amounts of 1-bromo-2-((trimethylgermyl)-methyl)benzene (**5**) and *n*-$BuSnMe_3$ (**6**) together with unreacted **1**. The process is apparently not complete, although prolonged reaction times hardly altered the product distribution. When the reaction mixture was warmed to room temperature prior to the quenching reaction, more **2** was formed in addition to nucleophilic substitution of methyl groups at tin, as was shown by the formation of 1-bromo-2-((*n*-butyldimethylstannyl)-methyl)benzene (**7**). The latter reaction became more important when the lithiation was performed in the presence of TMEDA. The addition of HMPT seemed to promote the conversion of **1** to **2**, because butyl-substituted methylstannanes **6**, **8**, and **9** were formed in high yield. However, **2** is apparently not stable in the presence of HMPT, as **5** was isolated in only 7% yield after quenching with Me_3GeCl. Performing the reaction of **1** in diethyl ether at −70 °C with an *excess* of *n*-BuLi increased the yield of **2** to 65%. The need for an excess of *n*-BuLi probably implies reversibility, which has also been observed for the Me_4Sn/*n*-BuLi system.[6] Warming of a mixture containing **1** and *n*-butyllithium (ratio 1:3) in diethyl ether from −70 °C to room temperature resulted in the formation of 1-bromo-2-*n*-pentylbenzene (**10**) and 1-(trimethylgermyl)-2-*n*-pentylbenzene (**11**) along with **6**. The regiochemistry of **11** is based on ^1H NMR chemical shifts of the trimethylgermyl protons (0.47 ppm) and of the benzylic methylene protons (2.71 ppm), which are comparable to those of analogous compounds,[7] and on the $^3J_{HH}$ values (8 Hz) of the benzylic protons. The formation of **10** and **11** requires *n*-butyl bromide as an intermediate, which couples with a benzylic lithium functionality. *n*-Butyl bromide can only be formed in a bromine–lithium exchange reaction at room temperature competing with the tin–lithium exchange, which predominates at −70 °C. Candidates for bromine–lithium exchange are **1** (which is converted to **3**; cf. Scheme II) and **2** (which is converted to **4**); for reasons to be explained in the Discussion, **2** is a less likely possibility. Anyhow, from either **1** or **2**, a minor quantity of *n*-butyl bromide is sufficient to start a catalytic cycle in which **2** couples with *n*-butyllithium to give **10**. The latter is an excellent substrate for bromine–lithium exchange to furnish **12** and *n*-butyl bromide, which reenters the catalytic cycle.

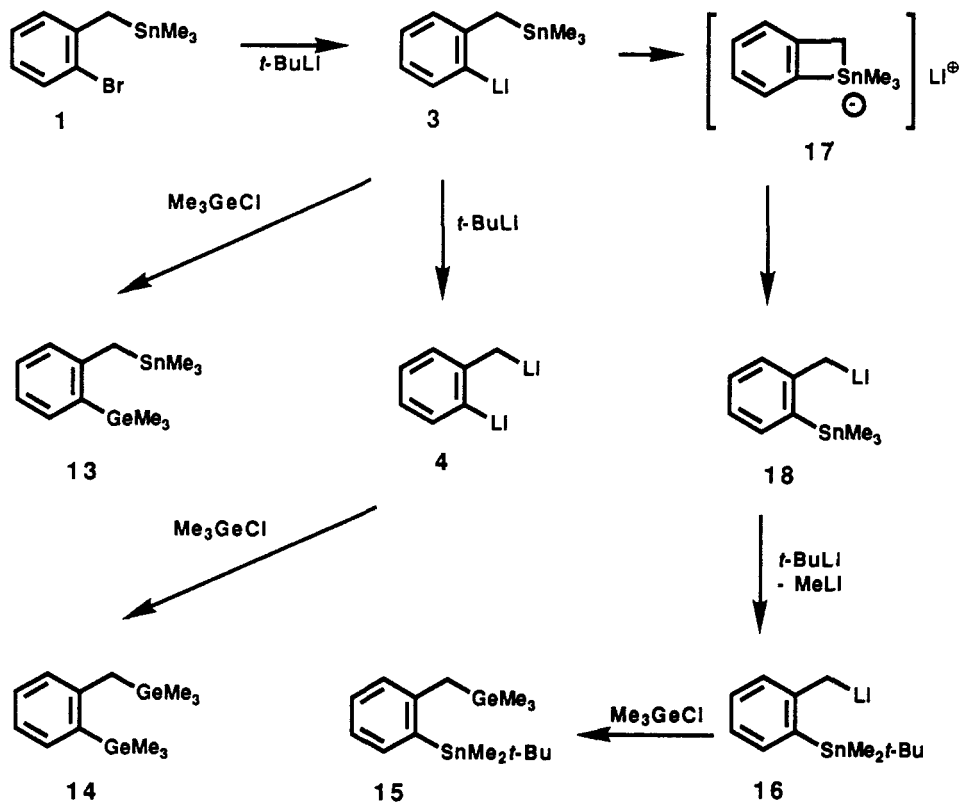
(6) Farah, D.; Karol, T. J.; Kuivila, H. G. *Organometallics* **1985**, *4*, 662.
(7) (a) Trimethyl(2-methylphenyl)germane has been prepared, but NMR data were not reported: Bennett, S. W.; Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Organomet. Chem.* **1971**, *28*, 59. (b) Adcock, W.; Gupta, B. D.; Kitching, W.; Dodrell, D. *J. Organomet. Chem.* **1975**, *102*, 297. (c) Bullpitt, M.; Kitching, W.; Adcock, W.; Dodrell, D. *J. Organomet. Chem.* **1976**, *116*, 161.

Table II. Reactions between 1 and *tert*-Butyllithium[a]

solvent	temp[b]	time[c]	yield[d] 13	14	15	19	20	21
Et_2O	−80	90	89					
Et_2O	−80	90						
	room temp	120		79	17	56	3	11
THF	−80	60		72	15	64	16	1

[a] Ratio *t*-BuLi:1 = 6:1. [b] In °C. [c] In min. [d] Yield (%) relative to 1.

Scheme II



As could be anticipated, THF is more effective than diethyl ether in promoting the tin–lithium exchange reaction. The last entry in Table I shows that after the reaction was quenched, **5** was isolated in 92% yield along with quantitative formation of butylmethylstannanes.

Recently, stannate complexes such as $[Me_5Sn]^-Li^+$ have been detected in solutions of THF/HMPT at −80 °C by ^{119}Sn NMR spectroscopy.[3b,c] The ^{119}Sn NMR spectra, recorded at −80 °C, of equimolar amounts of **1** and *n*-BuLi in diethyl ether, THF, or THF/HMPT did not show high-field signals characteristic of stannate complexes. However, this does not exclude the intermediate formation of stannate complexes, as these species are known to decompose very easily,[3b,c,8] and hence, under our conditions their steady-state concentration may be below the detection level.

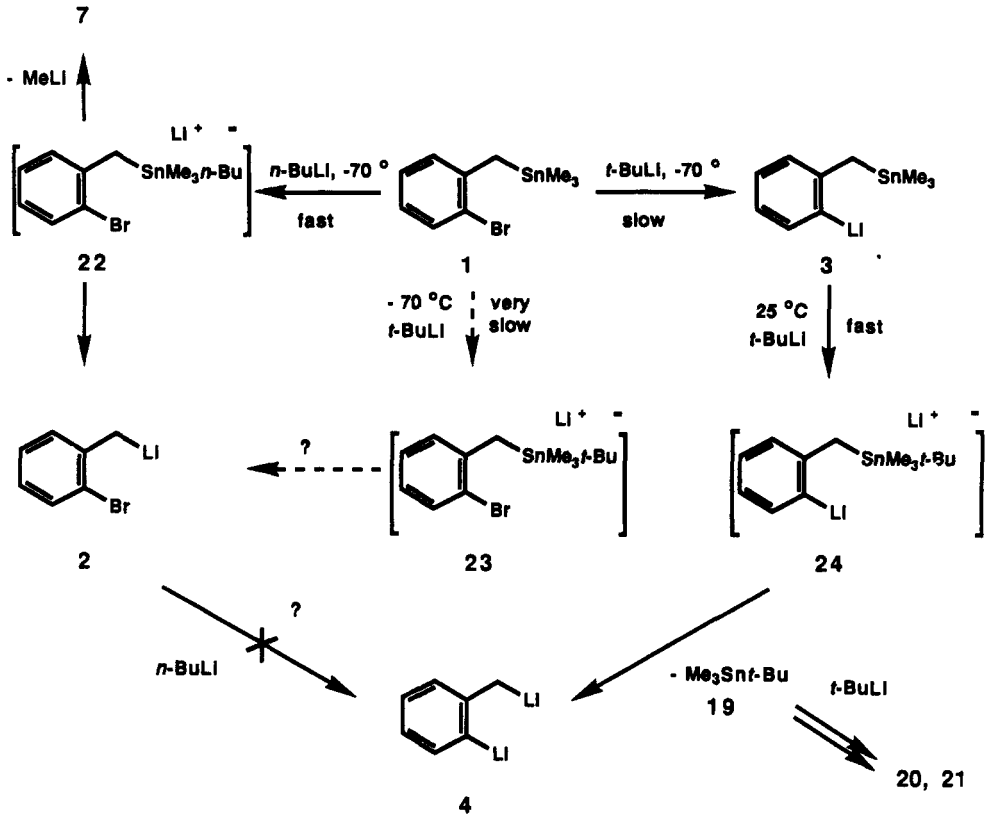
Reactions of 1 with *t*-BuLi. The experiments involving **1** and *n*-BuLi revealed that an excess of the organolithium reagent was required for a quantitative conversion of **1** into **2** for two reasons: first, *n*-BuLi was also consumed by nucleophilic substitution reactions, and second, the lithium–tin exchange is reversible. Therefore, reactions between **1** and *t*-BuLi were conducted with a 6-fold excess of *t*-BuLi (Scheme II). Treatment of **1** with *t*-BuLi in diethyl ether at −80 °C followed by quenching with chlorotrimethylgermane and workup gave 1-(trimethylgermyl)-2-((trimethylstannyl)methyl)benzene (**13**) in 89% isolated yield. Thus, in contrast to the reaction between **1** and *n*-BuLi, lithium–halogen exchange occurs. When prior to the quenching the reaction mixture was warmed to room temperature, **14** and **15** were isolated in 79% and 17% yields, respectively. Compound **15** was identified by ^1H NMR and mass spectroscopy, and the assigned regiochemistry is supported by the benzylic hydrogen–tin coupling constant (5.8 Hz), which has a value characteristic for $^4J_{H\text{-}Sn}$.[7b,c] Similarly, when the reaction was performed in THF at −80 °C, **14** and **15** were formed in 72% and 15% yields, respectively.

The precursors of **14** and **15** are assumed to be **4** and **16**. Their formation may be accounted for as follows: **3** undergoes lithium–tin exchange to yield α,2-dilithiotoluene (**4**) in competition with its rearrangement via stannate complex **17** to **18**. Subsequently, nucleophilic substitution of a methyl group of **18** occurs, affording **16**. Although the sequence of the last two events may have to be reversed, such a reaction mode is supported by analogous rearrangements observed for reactions of **1** with either magnesium or lithium metal,[9] by the interception of 1,2-dihydro-1,1-dimethyl-1-stannabenzocyclobutene by me-

(8) (a) Kaufmann, T.; Kriegesmann, R.; Altepeter, B.; Steinseifer, F. *Chem. Ber.* **1982**, *115*, 1810. (b) Sawyer, J. C.; McDonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 3376. (c) Maercker, A.; Stötzel, R. *Chem. Ber.* **1987**, *120*, 1695.

(9) (a) de Boer, H. J. R.; Akkerman, O. S.; Bickelhaupt, F. *Angew. Chem.* **1988**, *100*, 735. (b) de Boer, H. J. R.; Akkerman, O. S.; Bickelhaupt, F. Submitted for publication.

Scheme III



thylmagnesium bromide,[10] and by reactions of 1,2-dihydro-1,1-diphenyl-1-silabenzocyclobutene and 1,1,2-triphenylsilacyclobut-2-ene with phenyllithium, which showed cleavage of the benzylic or the allylic carbon–silicon bond, respectively.[11]

Discussion

The selectivity that can be achieved in the lithiations of **1** is remarkable: "at will", one can substitute lithium for the benzylic tin substituent (→**2**), for the aromatic bromine (→**3**), or for both (→**4**). This selectivity offers interesting preparative choices, although it should be pointed out that, in certain applications, the presence of the required excess of butyllithium may be inconvenient.

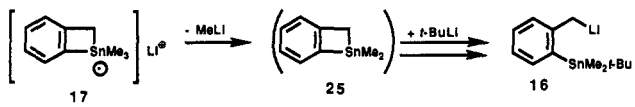
In order to explain this remarkable selectivity, one has to make the following assumptions.

(1) Under identical conditions, lithium–tin exchange is faster than lithium–bromine exchange. As far as we are aware, there is no quantitative information available on this aspect; it deserves further experimental investigation.

(2) Lithium–tin exchange is more sensitive to steric hindrance than lithium–bromine exchange. This assumption is reasonable if one considers that, in the intermediate stannate complex, tin is pentacoordinated (e.g. **22**, Scheme III) while bromine exchanges via either a (loose) radical mechanism or a *di*coordinated ate complex.

(3) Exchange of either tin or bromine by lithium is strongly retarded by electron-donating substituents; this is reasonable in view of the negative charge in the ate complexes, and experimental support is available.[12]

Scheme IV



Scheme III indicates how, on the basis of these assumptions, the observed selectivity can be rationalized. With the sterically undemanding *n*-butyllithium, **1** reacts rapidly according to assumption 1 to form the stannate complex **22**, which can go on to **2**; alternatively, **22** cleaves methyllithium to furnish **7**. At the stage of **2**, the reaction stops, because lithium–bromine exchange is strongly retarded by the benzyllithium function of **2**, which must be considered to be a more or less free, delocalized carbanion; dilithiation to **4** is not observed (assumption 3). For that reason, the formation of **4** from **2** and *n*-butyllithium (Scheme I) must be of minor importance.

The transformation **1** → **22** by *n*-butyllithium would find its counterpart in **1** → **23** by *tert*-butyllithium. However, the latter reaction is extremely slow at −70 °C because of steric hindrance; instead, the normally slower lithium–bromine exchange gets a chance (assumption 2) and leads to **3**. Only when the temperature is raised to 25 °C can the formation of the strongly congested stannate complex **24** occur. Although the presence of the aryllithium function in **3** and **24** will be unfavorable, this may be expected to be less serious because the aryl "anion" is less free and delocalized than the benzyl anion of **2**; moreover, the reaction temperature may be sufficiently high to facilitate

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(11) (a) Gilman, H.; Atwell, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 5589. (b) Gilman, H.; Atwell, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 2678.
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(13) (a) Gilman, H.; Rosenberg, S. D. *J. Org. Chem.* **1959**, *24*, 2063. (b) Seyferth, D.; Suzuki, R.; Murphy, C. J.; Sabet, C. R. *J. Organomet. Chem.* **1964**, *2*, 431.
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(15) West, P.; Waack, R. *J. Am. Chem. Soc.* **1967**, *89*, 4395.
(16) Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371.
(17) Glaze, W. H.; Freeman, C. H. *J. Am. Chem. Soc.* **1969**, *91*, 7198.

this less favorable step. Complex **24** will rapidly go on to **4** and **19**. Incidentally, the rapid exchange of methyl for *tert*-butyl groups in **19**, leading to **20** and **21** (**21** has not been fully identified, see Experimental Section), shows that the formation of congested stannate complexes involving one or more *tert*-butyl groups is possible at room temperature; analogous alkyl-exchange reactions have been reported for the system tetramethylstannane and *tert*-butyllithium.[6] For the same reason, the transformation **18** → **16** (Scheme II) may occur, even though it is in violation of assumption 2. However, in this case, another possibility cannot be fully excluded: extrusion of methyllithium from **17**—in competition with the much more likely cleavage of the benzylic bond (i.e. **17** → **18**)—to give the four-membered **25**, which is attacked and opened by *tert*-butyllithium (Scheme IV); in silicon chemistry, analogous cleavage reactions have been reported.[8c]

Experimental Section

All experiments were performed in glassware that was flame-dried under vacuum (10^{-3} mbar), whereafter it was thrice flushed with argon and again evacuated. The experiments were finally conducted under an atmosphere of argon. Diethyl ether and THF (predried on KOH) were distilled from $LiAlH_4$. Compound **1** was prepared as previously described.[9] Product distributions were determined by GCMS (HP5360 MS/HP5890 GC combination; hexamethylbenzene as internal standard), ^1H NMR analysis, and isolation of the main products. NMR spectra were recorded on a Bruker WH 90 (^1H, 90 MHz) or a Bruker WM 250 instrument (^1H, 250 MHz; ^{13}C, 63 MHz; ^{119}Sn, 93 MHz); the sample temperature was regulated by a Bruker VT-1000 temperature control unit. The products were isolated by preparative-scale GC (Intersmat GC120, 10% OV101 on Chromosorb W, $^1/_4$ in., 1.5 m, TCD). High-resolution mass measurements were performed with a Varian MAT CH5-DF mass spectrometer (EI 70 eV).

Reactions between 1 and 1 Equiv of *n*-Butyllithium. A 25-mL three-necked round-bottomed flask, fitted with a serum cap, was charged via a syringe with 3.0 mL of a 1.13 M solution of *n*-butyllithium (3.4 mmol) in *n*-hexane and 10 mL of diethyl ether, whereafter the resulting solution was cooled to −70 °C. When desired, an equimolar amount of TMEDA or HMPT (Table I) was added. After the addition of **1** (1.04 g, 3.4 mmol), the reaction mixture turned yellow immediately; when the reaction was performed in the presence of TMEDA or HMPT, the mixture turned red. The reaction mixture was stirred for the indicated time at the indicated temperature and subsequently quenched with 0.53 g of chlorotrimethylgermane (3.4 mmol), whereafter—when necessary (Table I)—it was warmed to room temperature. Stirring was continued for 15 min and the mixture hydrolyzed with saturated NH_4Cl solution and diluted with 10 mL of diethyl ether. The organic layer was separated, washed with water, and dried on $MgSO_4$ and the solvents were carefully evaporated. The product distribution was determined as described above.

Reactions between 1 and Excess *n*-Butyllithium. Diethyl ether (10 mL) was added to 2.7 mL of a 1.13 M solution of *n*-butyllithium (3.0 mmol) in *n*-hexane, and the mixture was cooled to −70 °C. After 0.34 g of **1** (1.0 mmol) was added, the reaction mixture turned bright yellow immediately. Stirring was continued for the indicated time at the indicated temperature, whereafter the reaction mixture was quenched with 0.48 g of chlorotrimethylgermane (3.1 mmol). The reaction was continued and worked up as described above.

1-Bromo-2-(lithiomethyl)benzene (2). Compound **2** was prepared by the procedure described above with THF as solvent.

Products Obtained from Reactions between 1 and *n*-Butyllithium. 1-Bromo-2-((trimethylgermyl)methyl)benzene (5): colorless liquid; bp 70 °C at 0.06 mbar; ^1H NMR (250 MHz, $CDCl_3$) δ 0.18 (s, 9 H, $GeCH_3$), 2.44 (s, 2 H, CH_2), 6.92 (td, ^3J = 7.5 Hz, ^4J = 1.9 Hz, 1 H, aryl H), 7.06 (dd, ^3J = 7.9 Hz, ^4J = 1.9 Hz, 1 H, aryl H), 7.17 (td, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 1 H, aryl H), 7.50 (dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1 H, aryl H); ^{13}C NMR ($CDCl_3$) δ −1.7 (q, ^1J = 126 Hz, C_8), 26.8 (t, ^1J = 127 Hz, C_7), 123.3 (s, C_1), 125.4 (dd, ^1J = 163 Hz, ^3J = 8 Hz, C_5), 127.1 (dd, ^1J = 161 Hz, ^3J = 8 Hz, C_4), 129.1 (dd, ^1J = 159 Hz, ^3J = 7 Hz, C_3), 132.6 (dd, ^1J = 164 Hz, ^3J = 7 Hz, C_6), 141.7 (s, C_2); HRMS ($C_{10}H_{15}{}^{79}Br^{74}Ge$) calcd 287.9569, found 287.9592; mass spectrum *m/z* (relative intensity) 288 (7, $M^{\bullet+}$), 273 (34, $M^{\bullet+} - CH_3$), 243 (1, $M^{\bullet+} - 3CH_3$), 169 (12, $C_7H_6Br^+$), 155 (5, $C_6H_4Br^+$), 119 (100, $C_3H_9Ge^+$), 105 (12, $C_2H_5Ge^+$), 90 (28, $C_7H_6^+$), 89 (55, CH_4Ge^+), 75 (6, $C_6H_3^+$). Anal. Calcd for $C_{10}H_{15}BrGe$: C, 41.75; H, 5.26. Found: C, 41.69; H, 5.27.

***n*-Butyltrimethylstannane (6)**:[18] colorless liquid; ^1H NMR (250 MHz, $CDCl_3$) δ 0.05 (s, $^2J_{Sn-H}$ = 50.1, 52.2 Hz, 9 H, $SnCH_3$), 0.84 (t, ^3J = 7.9 Hz, 2 H, $SnCH_2$), 0.90 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.24–1.38 (tq, ^3J = 7.3, 7.4 Hz, ^4J = 0.5 Hz, 2 H, CH_2), 1.43–1.56 (tt, ^3J = 7.4, 7.9 Hz, 2 H, $SnCH_2$);[19] mass spectrum *m/z* (relative intensity) 222 (1, $M^{\bullet+}$), 207 (50, $M^{\bullet+} - CH_3$), 165 (100, $C_3H_9Sn^+$), 151 (65, $C_2H_7Sn^+$), 135 (50, CH_3Sn^+), 121 (15, SnH^+), 120 (16, Sn^+).[20]

1-Bromo-2-((*n*-butyldimethylstannyl)methyl)benzene (7): colorless liquid; ^1H NMR (90 MHz, $CDCl_3$) δ 0.04 (s, $^2J_{Sn-H}$ = 50, 52 Hz, 9 H, $SnCH_3$), 0.86 (m, 5 H, CH_2CH_3), 1.11–1.53 (m, 4 H, CH_2), 2.46 (s, $^2J_{Sn-H}$ = 59 Hz, aryl–CH_2), 6.74–6.93 (m, 1 H, aryl H), 7.03–7.19 (m, 2 H, aryl H), 7.29–7.51 (d, ^3J = 7.3 Hz, aryl H); mass spectrum *m/z* (relative intensity) 376 (1, $M^{\bullet+}$), 361 (7, $M^{\bullet+} - CH_3$), 319 (100, $M^{\bullet+} - CH_3$), 319 (100, $M^{\bullet+} - C_4H_9$), 305 (7, $M^{\bullet+} - C_5H_{11}$), 290 (6), 209 (18), 150 (48), 131 (6), 121 (4), 120 (4).

Di-*n*-butyldimethylstannane (8): colorless liquid; ^1H NMR (90 MHz, $CDCl_3$) δ −0.03 (s, $^2J_{Sn-H}$ = 52 Hz, 6 H, $SnCH_3$), 0.83 (m, 10 H, CH_2CH_3), 1.34 (m, 8 H, CH_2CH_2);[21] mass spectrum *m/z* (relative intensity) 249 (8, $M^{\bullet+} - CH_3$), 207 (62, $M^{\bullet+} - C_4H_9$), 193 (23), 151 (100), 135 (47), 121 (16), 120 (14).[22]

Tri-*n*-butylmethylstannane (9): colorless liquid; mass spectrum *m/z* (relative intensity) 291 (1, $M^{\bullet+} - CH_3$), 249 (35, $M^{\bullet+} - C_4H_9$), 193 (100, $C_5H_{12}Sn^+$), 135 (64), 121 (24), 120 (18).[23]

1-Bromo-2-*n*-pentylbenzene (10): colorless liquid; ^1H NMR (90 MHz, $CDCl_3$) δ 0.98 (t, ^3J = 6 Hz, 3 H, CH_3), 1.25–2.00 (m, 6 H, $CH_2CH_2CH_2$), 2.40 (t, ^3J = 7 Hz, 2 H, CH_2), 7.05–7.50 (m, 4 H, aryl H); mass spectrum *m/z* (relative intensity) 228 (31, $M^{\bullet+}$, 172 (30, $M^{\bullet+} - C_4H_8$), 171 (62), 91 (100).

1-(Trimethylgermyl)-2-*n*-pentylbenzene (11): colorless liquid; ^1H NMR (90 MHz, $CDCl_3$) δ 0.47 (s, 9 H, $GeCH_3$), 0.96 (t, ^3J = 6 Hz, 3 H, CH_3), 1.27–1.84 (m, 6 H, $CH_2CH_2CH_2$), 2.71 (t, ^3J = 6 Hz, 2 H, CH_2), 7.04–7.47 (m, 4 H, aryl H); mass spectrum *m/z* (relative intensite) 266 (2, $M^{\bullet+}$), 251 ($M^{\bullet+} - CH_3$), 209 (8, $M^{\bullet+} - C_4H_9$), 195 (21, $M^{\bullet+} - C_5H_{11}$), 179 (12, $C_3H_9Ge^+$), 165 (8, $C_7H_7Ge^+$), 146 (48), 119 (29), 105 (61), 91 (45), 89 (31).

1-Lithio-2-((trimethylstannyl)methyl)benzene (3). A solution of 3.0 mmol of *t*-BuLi in 2 mL of *n*-pentane was cooled to −80 °C, and 10 mL of diethyl ether was slowly added. This solution was stirred for 15 min, whereafter 167 mg of **1** (0.5 mmol) was added. The reaction mixture became yellow immediately and was stirred for 1.5 h at −80 °C. Addition of 462 mg of chlorotrimethylgermane (3.0 mmol) gave a colorless solution and a white precipitate. The reaction mixture was warmed to room temperature and worked up as described above, whereafter 1-(trimethylgermyl)-2-((trimethylstannyl)methyl)benzene (**13**) was isolated in 89% yield.

α,2-Dilithiotoluene (4). A solution of 3.0 mmol of *t*-BuLi in 2 mL of *n*-pentane was cooled to −80 °C, and 10 mL of diethyl ether was added. Stirring for 15 min was followed by the addition of 167 mg of **1** (0.5 mmol). After 15 min, the yellow reaction mixture became hazy but turned orange-red upon being warmed to room temperature. Stirring was continued for 2 h, whereafter 924 mg of chlorotrimethylgermane (6.0 mmol) was added, giving an almost colorless solution and a white precipitate. After workup, 1-(trimethylgermyl)-2-((trimethylgermyl)methyl)benzene (**14**) was isolated in 70% yield. When the reaction was preformed with THF as the solvent at −80 °C, **14** could be isolated in 72% yield.

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Products Obtained from Reactions between 1 and *t*-BuLi. **1-(Trimethylgermyl)-2-((trimethylstannyl)methyl)benzene (13)**: colorless liquid; ^{1}H NMR (250 MHz, $CDCl_3$) δ −0.03 (s, $^2J_{Sn-H}$ = 50.6, 52.9 Hz, 9 H, $SnCH_3$), 0.33 (s, 9 H, $GeCH_3$), 2.37 (s, $^2J_{Sn-H}$ = 62.5 Hz, 2 H, CH_2), 6.90 (t, ^3J = 7.4 Hz, 2 H, aryl H), 7.09 (td, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1 H, aryl H), 7.23 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1 H, aryl H), 7.32 (m, 1 H, aryl H); ^{13}C NMR (63 MHz, $CDCl_3$) δ −9.3 (q, ^1J = 128 Hz, $SnCH_3$), −0.1 (q, ^1J = 126 Hz, $GeCH_3$), 21.8 (t, ^1J = 125 Hz, CH_2), 122.8 (dd, ^1J = 160 Hz, ^3J = 8 Hz, C_5), 127.3 (d, ^1J = 156 Hz, C_3), 128.8 (dd, ^1J = 159 Hz, ^3J = 8 Hz, C_4), 133.7 (d, ^1J = 170 Hz, C_6), 137.6 (s, C_1), 148.3 (s, C_2); HRMS ($C_{13}H_{24}{}^{74}Ge^{120}Sn$) calcd 374.0127, found 374.0110; mass spectrum *m/z* (relative intensity) 374 (6 $M^{\bullet+}$), 359 (6, $M^{\bullet+} - CH_3$), 240 (3, $C_9H_{12}Sn^+$), 225 (3, $C_8H_9Sn^+$), 209 (3, $C_{10}H_{15}Ge^+$), 194 (15, $C_9H_{12}Ge^+$), 179 (17, $C_8H_9Ge^+$), 165 (100, $C_7H_7Ge^+$), 150 (8, $C_2H_6Sn^+$), 135 (15, CH_3Sn^+), 120 (4, Sn^+), 119 (16, $C_3H_9Ge^+$), 90 (8, CH_3Ge^+). Anal. Calcd for $C_{13}H_{24}GeSn$: C, 42.02; H, 6.51. Found: C, 42.45; H. 6.39.

1-(Trimethylgermyl)-2-((trimethylgermyl)methyl)benzene (14): colorless liquid; properties identical with those reported.[9,10]

1-(Trimethylgermyl)-2-((*tert*-butyldimethylstannyl)methyl)benzene (15): colorless liquid; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.04 (s, 9 H, $GeCH_3$), 0.17 (s, $^2J_{Sn-H}$ = 46.7, 48.9 Hz, 6 H, $SnCH_3$), 1.02 (s, $^3J_{Sn-H}$ = 65.6, 68.2 Hz, 9 H, CCH_3), 2.20 (s, $^4J_{Sn-H}$ = 5.8 Hz, 2 H, CH_2), 6.93–6.96 (m, 2 H, aryl H), 7.09 (td, ^3J = 7.4 Hz, ^4J = 1.6 Hz, 1 H, aryl H), 7.21 (dd, ^3J = 7.8 Hz, ^4J = 2.1 Hz, 1 H, aryl H); mass spectrum *m/z* (relative intensity) 359 (3, $M^{\bullet+} - C_4H_9$), 225 (5, $C_8H_9Sn^+$), 209 (8, $C_{10}H_{15}Ge^+$), 165 (100, $C_7H_7Ge^+$), 149 (10, $C_2H_5Sn^+$), 135 (23, CH_3Sn^+), 121 (12, SnH^+), 120 (10 Sn^+), 91 (10, $C_7H_7^+$), 89 (12, CH_3Ge^+), 57 (22, $C_4H_9^+$).

***tert*-Butyltrimethylstannane (19)**: colorless liquid; ^{1}H NMR (90 MHz, $CDCl_3$) δ −0.05 (s, $^2J_{Sn-H}$ = 48 Hz, 9 H, $SnCH_3$), 1.05 (s, $^3J_{Sn-H}$ = 64 Hz, 9 H, CH_3);[23] mass specrum *m/z* (relative intensity) 222 (2, $M^{\bullet+}$), 207 (7, $M^{\bullet+} - CH_3$), 165 (100, $C_3H_9Sn^+$), 150 (24), 135 (24), 121 (11), 120 (19), 57 (51).[19b]

Di-*tert*-butyldimethylstannane (20): colorless liquid; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.17 (s, $^2J_{Sn-H}$ = 43.5 Hz, 6 H, $SnCH_3$), 1.04 (s, $^3J_{Sn-H}$ = 59.6 Hz, 18 H, CH_3);[24] mass spectrum *m/z* (relative intensity) 264 (1, $M^{\bullet+}$), 249 (2, $M^{\bullet+} - CH_3$), 207 (45, $M^{\bullet+} - C_4H_9$), 193 (3, $C_5H_{12}Sn^+$), 165 (6, $C_3H_9Sn^+$), 151 (88), 135 (47), 121 (12), 120 (15), 57 (100).[25]

Tri-*tert*-butylmethylstannane (21): mass spectrum *m/z* (relative intensity) 235 (17, $M^{\bullet+} - C_5H_{11}$), 207 (8), 151 (100), 135 (31), 121 (9), 120 (9), 57 (35).[26]

^{119}Sn NMR Experiments. A high vacuum dried (10^{-6} mbar) and sealed glass apparatus was equipped with a small reaction flask, two ampules (containing 0.7 mL of a 1.42 M solution of *n*-BuLi in *n*-hexane and a solution of 336 mg of **1** (1.0 mmol) in 2.0 mL of diethyl ether, respectively) and a 10-mm NMR tube. The flask was charged with the solution of *n*-BuLi and cooled to −100 °C. The solution of **1** was cooled to −100 °C, whereafter it was added to the flask. The mixture was transferred to the NMR tube at −100 °C, and the NMR tube was sealed off. The ^{119}Sn NMR spectrum of this mixture, recorded at −80 °C, showed the presence of **1** (7.10 ppm), **6** (0.89 ppm[27]), and **8** (0.35 ppm[25]) in a ratio of 1:9.3:1.3. With THF a similar result was obtained; when 0.5 mL of TMEDA was added before the addition of **1**, only **1** and two unidentified products (22.4 and 67.7 ppm) were observed in a ratio of 3.8:1:7.8.

Registry No. **1**, 54031-00-4; **2**, 129521-10-4; **3**, 129521-11-5; **4**, 129521-12-6; **5**, 129521-13-7; **6**, 1527-99-7; **7**, 129521-14-8; **8**, 1528-00-3; **9**, 1528-01-4; **10**, 13397-96-1; **11**, 129521-15-9; **12**, 129521-16-0; **13**, 114198-52-6; **14**, 113419-98-0; **15**, 129521-17-1; **19**, 3531-47-3; **20**, 35569-11-0; **21**, 35569-12-1; ^{119}Sn, 14314-35-3.

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Cluster Chemistry. 62.[1] Preparation of the Heptanuclear Clusters $Ru_5M_2(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)_2$ (M = Ag, Au): X-ray Structure of $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)_2\{P(OEt)_3\}$

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The heptanuclear title complex was obtained from reactions between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ and a mixture of $[O\{Au(PPh_3)\}_3][BF_4]$ and [ppn][$M(CO)_n$] (M = Co, *n* = 4; M = Mn, *n* = 5) or by reduction (Na/Hg or K[$HBBu^s_3$]) of the Ru_5 complex and treatment with $AuCl(PPh_3)$; the silver analogue was made by the latter route. The structure of a $P(OEt)_3$ derivative of the Au_2Ru_5 cluster was determined. The metal core consists of an $Ru/AuRu_2/Au$ trigonal bipyramid, two edges of which are bridged by Ru atoms. Addition of the $Au_2(PPh_3)_2$ unit has resulted in cleavage of one of the Ru–Ru bonds present in the original Ru_5 cluster. $Au_2Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)_2\{P(OEt)_3\}$ is triclinic, space group $P\bar{1}$, with a = 14.031 (15) Å, b = 16.741 (4) Å, c = 18.721 (6) Å, α = 98.64 (2)°, β = 97.61 (6)°, γ = 98.04 (6)°, and Z = 4; 6848 data were refined to R = 0.0595 and R_w = 0.0617.

Introduction

The reactions of the open pentaruthenium cluster $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**; Scheme I) with H_2 have been discussed in detail previously.[2] There is a stepwise addition of 3 equiv of H_2, so that the first adds to C_β of the μ_5-acetylide–phosphine unit of **1**, converting it into a μ_5-vinylidene–phosphine species with the other H bridging a Ru–Ru bond as in **2**. The second mole of H_2 adds sim-

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