Journal of Organometallic Chemistry, 469 (1994) 129–133

The reaction of $(Me_3Si)_3CBr$ with Mg in tetrahydrofuran (THF) or diethyl ether. Crystal structure of $(Me_3Si)_3CMg(\mu\text{-}Br)_3Mg(THF)_3$

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(Received August 18, 1993)

Abstract

The only product isolated from the reaction of $(Me_3Si)_3CBr$ with Mg in THF was, as shown by an X-ray diffraction study, $(Me_3Si)_3CMg(\mu\text{-}Br)_3Mg(THF)_3$, which contains one four-coordinate and one six-coordinate Mg atom. A similar product, $(Me_3Si)_3CMg(\mu\text{-}Br)_3Mg(Et_2O)_x$, appears to be formed in the reaction in ether. It is suggested that the high $Br/(Me_3Si)_3C$ ratio in the products may be associated with formation of $(Me_3Si)_3C$ radicals (which go on to give $(Me_3Si)_3CH$) during the reaction with Mg.

Key words: Magnesium; Silicon; Crystal structure; Grignard reagent

1. Introduction

A few years ago we described the preparation and structural characterization of the organomagnesium compounds $[Tsi(THF)Mg(\mu\text{-}Br)_2Li(THF)_2]$ (**1**) [1], and $MgTsi_2$ [2], where Tsi denotes the bulky ligand $(Me_3Si)_3C$. Recently C.L. Smith and his coworkers made the Grignard reagent TsiMgBr from TsiBr and Mg in ether [3*] and we thought it of interest to isolate and characterize the structure of the solid form of the reagent. In the event we were unable to obtain crystals suitable for an X-ray diffraction study from the ethereal solution, but by carrying out the reaction between TsiBr and Mg in THF we were able to isolate the novel complex $TsiMg(\mu\text{-}Br)_3Mg(THF)_3$ (**2**) in a form that allowed structural characterization.

2. Results and discussion

2.1. Reaction in THF; formation of 2

Although the initial studies were concerned with the Grignard reagent formed in diethyl ether it is more convenient to discuss first the product isolated from the reaction in THF.

The reaction between TsiBr and Mg in THF was carried out with Mg that had been activated by exposure to $BrCH_2CH_2Br$ in THF (*cf.* ref. 3) followed by decantation of the solvent and washing of the metal with hot THF to remove $MgBr_2$. The reaction of this magnesium with TsiBr in fresh THF was quite fast. The solvent was subsequently removed under reduced pressure and light petroleum was added. The white solid was filtered off and washed with further light petroleum, and the filtrate and washings were shown by ^1H NMR spectroscopy to contain mainly TsiH along with a little unchanged TsiBr. The white solid was recrystallized from hot toluene to give colourless crystals with a carbon-hydrogen analysis and ^1H NMR spectrum consistent with the formulation $TsiMg_2Br_3(THF)_3 \cdot PhMe$. An X-ray diffraction study showed the product to be $TsiMg(\mu\text{-}Br_3)Mg(THF)_3$ (**2**) (see Fig. 1) with *ca.* 0.5 molecules of toluene of crystallization. The difference between the proportion of toluene revealed by the crystal structure and that indicated by the ^1H NMR spectrum can be attributed to some loss of toluene from the crystal used in the diffraction study (there was considerable decay of the crystal during the data collection). Three moles of TsiBr are required to produce one mole of **2**, and on this basis the amount of the crystalline solid isolated corresponds to a yield in molar terms of 93%; *i.e.* 93% of the bromine in the TsiBr initially taken has ended up in **2**.

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* Reference number with an asterisk indicates a note in the list of references.

0022-328X/94/$7.00
SSDI 0022-328X(93)24146-V

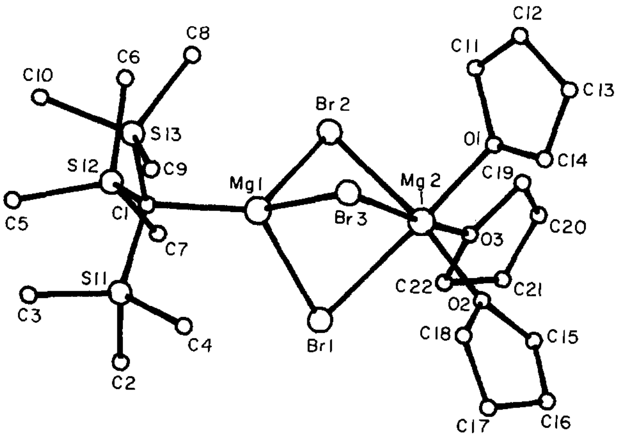

Fig. 1. Molecular structure of $(Me_3Si)_3CMg(\mu\text{-}Br)_3Mg(THF)_3$ (**2**).

It has been known for a long time [4] that fractional crystallization of EtMgCl from THF gives $EtMg_2Cl_3(THF)_3$ (**3**) and Et_2Mg quantitatively. Similar behaviour is observed for EtMgBr in THF [5], but the compound that crystallizes from ether is the mononuclear adduct $[EtMgBr(Et_2O)_2]$ (**4**) [6]. Compound **3** has a dimeric structure in the solid state (Fig. 2) [7], and has been described by Greenwood and Earnshaw as a "curious solvated dimer which features both 5-coordinate trigonal bipyramidal and 6-coordinate octahedral Mg groups" [8], and the structure of **2** is almost equally curious in that it contains both 4-coordinate tetrahedral and 6-coordinate octahedral magnesium centres. However, because the alkyl group in **2** is much larger than that in **3**, 5-coordination at the adjacent Mg is precluded and the halogen atoms are forced together to give a monomeric complex of the original reagent with $MgBr_2$. The resulting structure (Fig. 1) is different from any previously observed.

The bond lengths and angles in **2** are shown in Table 1. The Mg–C bond lengths in **2** (2.16(2) Å), **3** (2.19(3) Å), and **4** (2.15(1) Å) are all within the range commonly found for organomagnesium compounds, but they are somewhat longer than those in Tsi_2Mg (2.116(2) Å). The Mg–Br bond lengths vary with the coordination numbers of Br and Mg in the expected way. Thus the shortest such bond (2.48(1) Å) is that in **4**, in which the Br atom is not involved in bridging. The next longest bonds involve four-coordinate Mg and two-coordinate Br (2.571(9) Å in **2** and 2.533(6) Å in **1**), and the longest bonds involve six-coordinate Mg and two-coordinate Br. The configurations at the respective Mg atoms in **2** are considerably distorted from tetrahedral or octahedral. Thus the mean BrMg(1)Br angle is 91.2(3) and the mean BrMg(2)Br angle 84.1°, suggesting that these angles are compressed by the steric effects of the Tsi group at one end of the molecule and the three THF ligands at the other.

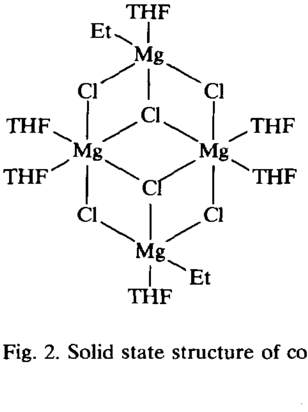

Fig. 2. Solid state structure of compound **3**

It was suggested earlier [7] that the range of structures shown by organomagnesium halides can be rationalized in terms of the steric requirements of the organic groups and donor ligands, and compounds **1–4** nicely illustrate this point. The alkyl-Mg environments are shown in Fig. 3. The decrease in the coordination number of the Mg on going from **3** to **4** is explained by the steric requirement of Et_2O being larger than that of THF. The decrease in the coordination number from 3 to 2 by loss of THF can be attributed to the bulk of Tsi compared with that of Et. We have pointed out elsewhere [1] that in Tsi-metal derivatives coordinated THF may be displaced by formation of μ-halogen bridges with little change in the molecular structure; the progression from **1** to **2** is a further example of this generalization.

In the absence of any external source of $MgBr_2$ the maximum possible yield of $TsiMg(\mu\text{-}Br)_3Mg \cdot 3THF$ in molar terms would be 33%, since 3 molecules of TsiBr are required to provide the 3 atoms of bromine in the product. If TsiMgBr is formed then it evidently decomposes at some stage. In principle this could involve formation of **2** and Tsi_2Mg, but if this had happened we should have expected to observe the Tsi_2Mg, which itself dissolves in hot toluene and crystallizes out on cooling of the solution [2]. The only other product actually detected at any stage was TsiH, present in significant amounts in the light petroleum washings of the residue left after removal of the THF from the original reaction mixture. It seems likely that at some point (probably during the reaction with Mg, since free radicals have frequently been detected during formation of Grignard reagents) the free radical Tsi· is generated, since this is known to be readily formed under some conditions and to abstract a hydrogen atom from C–H bonds [9].

2.2. Reaction in Et_2O; formation of $TsiMgBr \cdot MgBr_2 \cdot xEt_2O$

A reaction carried out as described by Smith *et al.* [3], involving initial activation of the Mg with $BrCH_2CH_2Br$ in ether followed by addition of TsiBr to the mixture (containing some $MgBr_2$) proceeded readily, but no crystalline material could be isolated. From the low organic content of the crude product we formed the impression that it could be $TsiMgBr(EtO_2)_x$ along with $MgBr_2$, and so to minimize the amount of the latter present we repeated the reaction but only after separating and washing the activated Mg carefully to remove the $MgBr_2$ formed from $BrCH_2CH_2Br$. The TsiBr did not react with this Mg even under reflux after addition of a crystal of iodine, but did so readily when some $BrCH_2CH_2Br$ was added. Work-up involving removal of the ether, washing of the residue with cold hexane, extraction with hot toluene, and removal of the toluene from the extract under vacuum left a

TABLE 1. Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

Bonds			
Br(1)–Mg(1)	2.564(9)	Br(1)–Mg(2)	2.728(9)
Br(2)–Mg(1)	2.571(10)	Br(2)–Mg(2)	2.721(10)
Br(3)–Mg(1)	2.578(9)	Br(3)–Mg(2)	2.775(10)
Si(1)–C(1)	1.84(3)	Si(1)–C(2)	2.03(4)
Si(1)–C(3)	1.93(4)	Si(1)–C(4)	1.93(4)
Si(2)–C(1)	1.84(3)	Si(2)–C(5)	1.93(4)
Si(2)–C(6)	2.01(4)	Si(2)–C(7)	1.98(4)
Si(3)–C(1)	1.85(2)	Si(3)–C(8)	1.90(4)
Si(3)–C(9)	2.03(4)	Si(3)–C(10)	1.91(4)
Mg(1)–C(1)	2.16(3)	Mg(2)–O(1)	2.09(2)
Mg(2)–O(2)	2.06(2)	Mg(2)–O(3)	2.04(2)
O(1)–C(11)	1.52(4)	O(1)–C(14)	1.45(4)
O(2)–C(15)	1.49(4)	O(2)–C(18)	1.51(4)
O(3)–C(19)	1.49(5)	O(3)–C(22)	1.51(4)
C(11)–C(12)	1.47(5)	C(12)–C(13)	1.50(6)
C(13)–C(14)	1.42(6)	C(15)–C(16)	1.46(6)
C(16)–C(17)	1.45(6)	C(17)–C(18)	1.51(6)
C(19)–C(20)	1.56(6)	C(20)–C(21)	1.40(6)
C(21)–C(22)	1.52(5)	C(23)–C(24)	1.26(7)
C(24)–C(25)	1.43(8)	C(24)–C(26)	1.32(5)
C(23)–C(25)	1.35(8)		
Angles			
Mg(1)–Br(1)–Mg(2)	74.1(3)	Mg(1)–Br(2)–Mg(2)	74.1(3)
Mg(1)–Br(3)–Mg(2)	73.1(3)	C(1)–Si(1)–C(2)	110(1)
C(1)–Si(1)–C(3)	113(1)	C(1)–Si(1)–C(4)	111(1)
C(2)–Si(1)–C(3)	108(1)	C(2)–Si(1)–C(4)	108(1)
C(3)–Si(1)–C(4)	107(2)	C(1)–Si(2)–C(5)	112(2)
C(1)–Si(2)–C(6)	108(1)	C(1)–Si(2)–C(7)	113(1)
C(5)–Si(2)–C(6)	107(2)	C(5)–Si(2)–C(7)	109(2)
C(6)–Si(2)–C(7)	109(2)	C(1)–Si(3)–C(8)	111(1)
C(1)–Si(3)–C(9)	111(1)	C(1)–Si(3)–C(10)	112(1)
C(8)–Si(3)–C(9)	108(2)	C(8)–Si(3)–C(10)	106(2)
C(9)–Si(3)–C(10)	109(2)	Br(1)–Mg(1)–Br(2)	90.8(3)
Br(1)–Mg(1)–Br(3)	91.5(3)	Br(1)–Mg(1)–C(1)	123.9(7)
Br(2)–Mg(1)–Br(3)	91.2(3)	Br(2)–Mg(1)–C(1)	125.7(8)
Br(3)–Mg(1)–C(1)	123.7(7)	Br(1)–Mg(2)–Br(2)	84.2(3)
Br(1)–Mg(2)–Br(3)	84.1(3)	Br(1)–Mg(2)–O(1)	171.9(7)
Br(1)–Mg(2)–O(2)	87.9(6)	Br(1)–Mg(2)–O(3)	96.6(6)
Br(2)–Mg(2)–Br(3)	84.0(3)	Br(2)–Mg(2)–O(1)	96.3(6)
Br(2)–Mg(2)–O(2)	172.2(7)	Br(2)–Mg(2)–O(3)	89.9(6)
Br(3)–Mg(2)–O(1)	87.9(6)	Br(3)–Mg(2)–O(2)	95.6(6)
Br(3)–Mg(2)–O(3)	173.8(7)	O(1)–Mg(2)–O(2)	91.5(8)
O(1)–Mg(2)–O(3)	91.5(8)	O(2)–Mg(2)–O(3)	90.5(8)
Mg(2)–O(1)–C(11)	118(2)	Mg(2)–O(1)–C(14)	120(2)
C(11)–O(1)–C(14)	118(2)	Mg(2)–O(2)–C(15)	123(2)
Mg(2)–O(2)–C(18)	123(2)	C(15)–O(2)–C(18)	112(2)
Mg(2)–O(3)–C(19)	123(2)	Mg(2)–O(3)–C(22)	124(2)
C(19)–O(3)–C(22)	111(2)	Si(1)–C(1)–Si(2)	113(1)
Si(1)–C(1)–Si(3)	114(1)	Si(1)–C(1)–Mg(1)	105(1)
Si(2)–C(1)–Si(3)	112(1)	Si(2)–C(1)–Mg(1)	105(1)
Si(3)–C(1)–Mg(1)	107(1)	O(1)–C(11)–C(12)	98(3)
C(11)–C(12)–C(13)	108(3)	C(12)–C(13)–C(14)	112(4)
O(1)–C(14)–C(13)	99(3)	O(2)–C(15)–C(16)	103(3)
C(15)–C(16)–C(17)	107(4)	C(16)–C(17)–C(18)	108(4)
O(2)–C(18)–C(17)	98(3)	O(3)–C(19)–C(20)	101(3)
C(19)–C(20)–C(21)	111(4)	C(20)–C(21)–C(22)	108(3)
O(3)–C(22)–C(21)	103(3)	C(23)–C(24)–C(25)	116(5)
C(23)–C(24)–C(26)	132(5)	C(25)–C(24)–C(26)	111(4)
C(24)–C(23)–C(25) ′	124(5)	C(23) ′–C(25)–C(24)	119(5)

′ The symmetry element is: $1-x$, $-y$, $1-z$.

TABLE 2. Fractional atomic coordinates ($\times 10^3$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}
Br(1)	3999(2)	203(2)	794(1)	70(2)
Br(2)	4124(2)	2233(2)	1880(1)	69(2)
Br(3)	4099(2)	−302(2)	2447(1)	71(2)
Si(1)	1099(7)	−328(8)	1278(5)	96(7)
Si(2)	1135(7)	1916(8)	1392(5)	100(8)
Si(3)	1151(7)	655(10)	2548(5)	106(8)
Mg(1)	3032(7)	734(7)	1720(4)	50(6)
Mg(2)	5318(7)	697(7)	1679(4)	54(6)
O(1)	6223(13)	940(13)	2437(8)	70(6)
O(2)	6096(13)	−516(13)	1430(8)	69(6)
O(3)	6142(12)	1566(13)	1144(8)	65(6)
C(1)	1482(17)	739(18)	1737(10)	42(7)
C(2)	1264(24)	−46(25)	377(16)	109(13)
C(3)	−219(25)	−688(26)	1393(16)	109(13)
C(4)	1871(25)	−1459(27)	1484(16)	115(13)
C(5)	−202(27)	1933(30)	1146(17)	136(16)
C(6)	1310(26)	2951(28)	2034(16)	123(14)
C(7)	1921(27)	2260(29)	681(16)	130(14)
C(8)	1965(25)	1452(27)	3048(15)	115(13)
C(9)	1260(26)	−750(27)	2848(15)	114(13)
C(10)	−120(26)	1107(27)	2684(16)	117(14)
C(11)	5966(24)	1767(26)	2867(16)	112(13)
C(12)	6479(26)	1411(29)	3416(16)	127(14)
C(13)	7134(34)	596(37)	3233(21)	194(22)
C(14)	6836(25)	165(26)	2671(16)	111(13)
C(15)	6896(28)	−481(30)	989(18)	137(15)
C(16)	7027(31)	−1509(35)	821(20)	178(20)
C(17)	6146(32)	−2013(34)	970(20)	173(19)
C(18)	5750(27)	−1548(30)	1537(18)	140(15)
C(19)	6889(30)	2241(32)	1399(19)	152(17)
C(20)	7243(30)	2747(33)	806(19)	159(18)
C(21)	6791(29)	2350(31)	283(18)	144(16)
C(22)	5904(26)	1801(27)	486(16)	125(14)
C(23)	4961(36)	347(38)	5561(22)	53(16)
C(24)	4296(36)	623(38)	5205(23)	53(16)
C(25)	4274(44)	178(46)	4616(27)	83(21)
C(26)	3534	1173	5287	49(32)
C(27)	−575(50)	883(51)	4717(31)	110(26)
C(28)	514(39)	276(43)	4821(26)	72(19)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

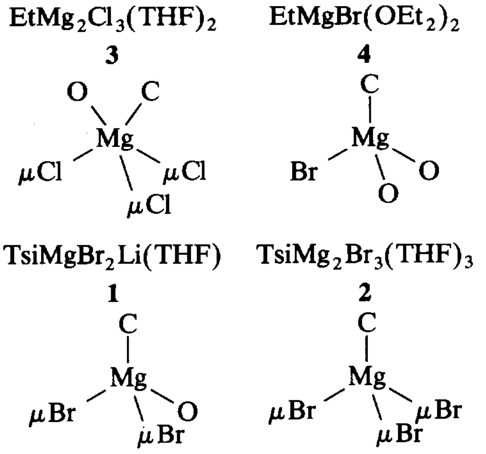

Fig. 3. Coordination to the magnesium atom bearing the organic group in 1–4.

viscous green oil that could not be crystallized. Its ^1H NMR spectrum (which indicated that no Tsi_2Mg was present) was consistent with the formulation $TsiMgBr \cdot 2Et_2O$, but the elemental (C/H) analysis, while not very reliable or reproducible, indicated that the organic content was much too low for that composition. The reason for this became apparent when THF was added and the crystalline material thus formed was crystallized from toluene to give crystals of $TsiMg(\mu\text{-}Br)_3Mg(THF)_3 \cdot 1PhMe$. All of the oil seemed to be converted in this way, implying that it had been wholly or predominantly $TsiMgBr \cdot MgBr_2 \cdot (Et_2O)_x$. If the oil was entirely $TsiMgBr \cdot MgBr_2(Et_2O)_x$ with $x = 2$, as the ^1NMR spectrum implied, then its amount corresponded to incorporation of 46% of the Tsi groups of the initial TsiBr. That this exceeds the 33% incorporation that was shown in the discussion of the reaction in THF to be the maximum possible can be attributed to the formation of additional $MgBr_2$ from the $BrCH_2CH_2Br$ used to promote the reaction.

In the light of the above results it is appropriate to take note now of the fact that from the reaction of TsiBr (0.10 mol) in ether Smith *et al.* obtained a Grignard reagent in 75% yield (0.075 mol) as indicated by titration [10*]. They carried out the reaction in ether containing initially 2 cm^3 (*ca.* 4.3 g, 0.023 mol) of $BrCH_2CH_2Br$, and thus *ca.* 0.023 mol of $MgBr_2$ would be available from that source; hence, of the initial 0.10 mol of TsiBr, at most 0.023 + 0.033, *i.e.* 0.056 mol could have been present as the complex $TsiMgBr \cdot MgBr_2 \cdot x(Et_2O)$.

We confirmed that yields of up to 80% of active TsiMgBr, as indicated by the titration method used by Smith *et al.*, could indeed be obtained when reactions were carried out in solutions containing substantial amounts of $MgBr_2$ produced by reaction of Mg with $BrCH_2CH_2Br$ before addition of TsiBr, but when only small amounts of $MgBr_2$ were present the yields fell below 50% and much TsiH was produced. We also formed the impression that the reaction of the TsiBr was faster the higher the concentration of $MgBr_2$, but more work would be necessary to confirm this. It is possible that the presence of $MgBr_2$ promotes the formation of TsiMgBr at the expense of a competing process involving formation of the Tsi· radical in the reaction with Mg. Further study of this matter is required.

3. Experimental section

3.1. Materials

Solvents were dried by standard methods. Reactions were carried out under dry argon.

3.2. Preparation of $TsiMg(\mu\text{-}Br)_3Mg(THF)_3$ (2)

Magnesium turnings (5 g, excess) were treated with $BrCH_2CH_2Br$ (0.7 cm^3, *ca.* 8 mmol) in hot THF (20 cm^3) with vigorous stirring. After 10 min the solution was decanted from the magnesium, which was then washed with warm THF (5 × 20 cm^3) to remove any traces of $MgBr_2$, and then heated briefly under vacuum. A solution of TsiBr [3] (6.77 g, 21.8 mmol) in THF (20 cm^3) was then added dropwise with stirring, the heat of reaction causing the THF to reflux. When the reaction had subsided the mixture was refluxed for a further 1 h, the solvent then removed under vacuum, and light petroleum (b.p. 60–80°C) added. The white solid was filtered off and washed with further light petroleum (3 × 20 cm^3). The filtrate and washings were combined and the solvent removed to leave an oil, which was shown by ^1H NMR spectroscopy to be mainly TsiH containing a little TsiBr. The white solid was recrystallized from hot (*ca.* 70°C) toluene to give colourless rhombic crystals (5.6 g) of what was shown by an X-ray diffraction study to be $TsiMg(\mu\text{-}Br)_3Mg(THF)_3 \cdot 0.5(PhMe)$. However, the ^1H NMR spectrum of the bulk sample indicated the presence of a *ca.* 1.0 molar proportion of toluene in the bulk product, and the elemental analysis was reasonably consistent with this proportion (Found: C, 42.6; H, 7.4. Calc. for $C_{29}H_{59}Br_3Mg_2O_3Si_3$: 42.0; H, 7.2%). The NMR data were as follows: $\delta(H)$ (THF-d_8) 0.18 (27H, s, Me_3Si), 1.80 (12H, m, $CH_2CH_2CH_2$ of THF), 2.30 (3H, s, PhMe), 3.7 (12H, m, CH_2O of THF), 7.0–7.3 (5H, m, C_6H_5); $\delta(C)$ (THF-d_8,) 7.5 (Me_3Si), 5.0 (C-$SiMe_3$), 21.7 ($PhCH_3$), 26.3 (THF), 66.8 (THF) and 126.0, 128.9, 129.7, and 138.4 (all from C_6H_4).

When heated in a sealed capillary the compound decomposed over the range 100–140°C without melting.

3.3. Reaction of TsiBr with Mg in Et_2O; formation of TsiMgBr · $MgBr_2(Et_2O)_x$

Magnesium (3.0 g, excess) was stirred vigorously with $BrCH_2CH_2Br$ (0.7 cm^3) in Et_2O (8 cm^3). When the reaction had subsided the mixture was stirred for a further 15 min, the ether then decanted off, and the metal washed with dry, degassed THF (2 × 40 cm^3) and then with Et_2O (20 cm^3), and finally heated under vacuum for 20 min and allowed to cool. Ether (60 cm^3) was added, followed (dropwise) by a solution of TsiBr (10.0 g, 0.032 mol) in Et_2O (10 cm^3). The mixture was stirred under reflux for 1 h, but there was no evidence of reaction; upon addition of a crystal of iodine the iodine colour persisted, confirming that no Grignard reagent had been formed. No reaction appeared to take place during a further 0.5 h of reflux, and so a drop (*ca.* 0.1 cm^3) of $BrCH_2CH_2Br$ was added, whereupon reaction began and after 10 min caused gentle refluxing of the ether. When the reaction had subsided the mixture was refluxed for a further 2 h and the ether then removed under vacuum. The residue was washed with cold hexane (4 × 50 cm^3, 0°C) and then extracted with toluene (3 × 90 cm^3). The solvent was evaporated from the extract under vacuum to leave a viscous green oil (9.6 g); δ(H) (toluene-d_8) 0.51 (27H, s, Me_3Si), 1.00 (12H, t, CH_3CH_2 of Et_2O), 3.53 (8H, q, CH_2O). When THF was added the oil was converted into a solid, which was recrystallized from hot toluene to give exclusively **2**.

3.4. Determination of the structure of 2

Crystal data. $C_{22}H_{51}Br_3O_3Mg_2Si_3 \cdot 0.5C_7H_8$. Monoclinic, $P2_1/c$, $M = 782.3$, $a = 13.950(5)$, $b = 13.660(7)$, $c = 21.899(10)$ Å, $\beta = 91.24(3)°$, $U = 4172.0$ Å, $Z = 4$, $D_c = 1.24$ g cm^3, $F(000)$ 1612. Monochromated Mo-K_a radiation, $\lambda = 0.71069$ Å, $\mu = 30$ cm^{-1}.

A crystal of dimensions *ca.* 0.4 × 0.4 × 0.4 mm was sealed in a capillary tube, and data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer. A total of 7960 reflections with $+h$, $+k$, $\pm l$ and $2 < \theta < 25°$ were measured by a $\theta/2\theta$ scan with scan width $\Delta\theta = (0.8 + 0.35\tan\theta)°$ and a maximum scan time of 1 min. A correction was made for Lorentz and polarization effects, for crystal decay of 42% during the data collection, and for absorption using DIFABS (max = 1.27; min = 0.48). After averaging of equivalent reflections ($R_{int} = 0.023$) there were 7817 unique reflections of which 2368 with $|F^2| > 3\sigma(F^2)$ were used in the refinement where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{0.5}/$ Lp. The Br atoms were located by the direct method using the SHELXS-86 program and a difference map was used to find the remaining non-hydrogen atoms. O and C atoms were refined isotropically and the other non-hydrogen atoms anisotropically. The hydrogen atoms of the Me_3Si and THF entities were fixed at calculated positions with $U_{iso} = 1.3$ U_{eq} for the atoms to which they are bonded. There was residual electron density near two inversion centres. In one case this could be clearly attributed to a toluene molecule (disordered about the inversion centre) at half-occupancy, and this was included in the refinement with the coordinates of the C of the Me group (C(26)) fixed. In the other case only two carbon atoms (C(27) and C(28)) could be located and included, but we assume there was part of another toluene again at half-occupancy. The final agreement factors were $R = 0.10$, $R' = 0.13$ with weighting scheme $w = 1/\sigma^2(F)$.

Coordinates of non-hydrogen atoms are listed in Table 2. Lists of thermal parameters and H-atom coordinates have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgments

We thank the SERC for support of the work and the Ministry of Higher Education of the Kingdom of Saudi Arabia for the award of a studentship to S.S.Al-J.

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10 We note in passing that the active content of 0.075 mol could in principle have consisted of Tsi_2Mg and TsiMgBr in 2:1 ratio, since Tsi_2Mg would behave like a 2 molar amount of TsiMgBr in, for example, hydrolysis followed by acid titration. However, it would be unlikely to react with $BrCH_2CH_2Br$ in the double-titration procedure used by Smith *et al.*, and is inert towards $HgCl_2$, which they found to give an 82% yield of Tsi_2Hg on reaction with their TsiMgBr.