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Degradation of silicone grease by Grignard reagents: bis(μ-dimethylphenylsilanolato-κ^2O:O)bis[bromido(diethyl ether)magnesium(II)]

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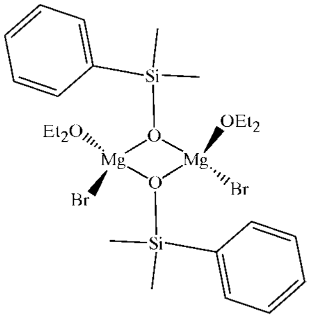
The title compound, [$Mg_2Br_2(C_8H_{11}OSi)_2(C_4H_{10}O)_2$], was obtained by slow dissolution of silicone grease in a diethyl ether solution of phenylmagnesium bromide. The molecules lie about inversion centres and do not display any short intermolecular interactions. There are only a handful of crystal structures of triorganosiloxomagnesium complexes reported previously, and the structure also illustrates the type of species that may be present in solution after accidental contact of Grignard reagents with silicon grease.

Comment

Silicone greases are degraded by strong bases, such as alkali metal hydroxides or main-group organometallic reagents. This is a well known method for cleaning silicone grease from glassware; a solution of potassium hydroxide in, for example, methanol effectively dissolves the grease (Shriver & Drezdzon, 1986). On using silicon grease as a lubricant for stoppers and stopcocks in the Schlenk technique, knowledge of the reactivity towards different reagents is of importance, since accidental contact may lead to undesired species in solution. Apblett & Barron (1990) published a study on the action of trimethylaluminium on polytriorganosiloxanes and isolated four different products of the type [{$Me_2Al(OSiMe_2R)$}$_2$]. In the case of R = Ph (Dow Corning silicon grease), they were able to determine the crystal structure of the product. We now report the structure of the corresponding degradation product obtained by the action of a Grignard reagent, phenylmagnesium bromide, upon Dow Corning high-vacuum silicone grease.

It was found that Dow Corning high-vacuum silicone grease dissolved slowly in an excess of phenylmagnesium bromide in diethyl ether solution at 277 K, and colourless air-sensitive crystals were obtained. The crystals were found to be the title compound, (I).

Molecules of (I) are dinuclear and the molecules are situated at crystallographic inversion centres (Fig. 1), the coordination geometry around atom Mg1 being best described as distorted tetrahedral. Molecules of (I) do not appear to be involved in any directed intermolecular interactions in the crystalline state, although there are possibilities, for example, for C—H$\cdots\pi$ interactions (Nishio, 2004). Geometry calculations show that there are no significant intermolecular interactions between molecules of (I) in the solid state. The structural knowledge of magnesium siloxide complexes is scarce; there are only nine crystal structures of triorganosiloxomagnesium complexes in the Cambridge Structural Database (CSD; Version 5.28 of November 2006; Allen, 2002). There are no structures of siloxo magnesium halides, and the structure most similar to (I) is probably bis(diethyl ether)bis(tetrahydroborato)bis(μ_2-trimethylsiloxo)dimagnesium (Bremer *et al.*, 2005). In addition, a number of calcium, barium and strontium complexes have been structurally characterized, showing a wide variety of aggregation states. Magnesium alkoxides (and siloxides) tend to form insoluble oligomers in the absence of Lewis bases. This tendency is lower for sterically bulky alkoxides, such as in (I). In the case of magnesium triphenylsiloxide (Zechmann *et al.*, 2001), a trinuclear complex, tetrakis(μ_2-triphenylsiloxo)bis(triphenylsiloxy)trimagnesium toluene solvate, was crystallized from toluene, while a dinuclear complex, bis(μ_2-triphenylsiloxo)bis(triphenylsiloxy)bis(tetrahydrofuran)dimagnesium, was crystallized from tetrahydrofuran. This latter complex is slightly similar to (I). A rather different behaviour is observed for three Ca, Sr and Ba complexes with monodentate ligands. In these cases, the metal centres are bridged by three siloxo ligands, *viz.* tris(μ_2-*tert*-butylsiloxo)(*tert*-butylsiloxy)tetrahydrofurandibarium (Drake *et al.*, 1992), tetraamminetriphenylsiloxytris(μ_2-triphenylsiloxo)dicalcium toluene solvate (Darr *et al.*, 1993) and tris(μ_2-triphenylsiloxo)pentaamminetriphenylsiloxydistrontium toluene solvate (Baxter *et al.*, 1998). In a few cases, when employing crown-ether ligands, monomers may be obtained, such as the two isomomorphous complexes (15-crown-5)tetrahydrofuranbis(triphenylsiloxy)strontium tetrahydrofuran solvate and (15-crown-5)tetrahydrofuranbis(triphenylsiloxy)barium tetrahydrofuran solvate (Wojtczak *et al.*, 1996).



(I)

A comparison with zinc siloxides could also be made. A complex similar to (I) is diiodobis(tetrahydrofurane)bis(μ_2-triethylsiloxo)dizinc (Driess *et al.*, 2000). This complex was prepared by oxidation of a tetranuclear cubane-type methyl zinc triethylsiloxide complex by iodine, followed by solvatization with tetrahydrofuran. In addition, a trinuclear complex, dimethyltetrakis(μ_2-triphenylsiloxy)trizinc toluene solvate (Merz *et al.*, 2003), is similar to the magnesium triphenylsiloxide crystallized from toluene, indicating the close similarities between the magnesium and zinc siloxides. As expected, the structure of (I) also shows similarities with the structures of dinuclear alkoxymagnesium halides crystallized from ethers, for example dibromobis(diethyl ether)bis(μ_2-phenolato)dimagnesium (Bocelli *et al.*, 1997) and bis(μ_2-1,1-diphenylethyoxo)bis(1,1-diphenylethoxy)bis(tetrahydrofuran)-dimagnesium (Zechmann *et al.*, 2001).

There are two other structures of dimethylphenylsiloxo metal derivatives in the CSD, apart from [{$Me_2Al(OSiMe_2Ph)$}$_2$], *viz.* tetrakis[(η^6-benzene)(μ_3-dimethylphenylsiloxo)potassium] (Fuentes *et al.*, 1991) and a rhenium complex (Tetrick *et al.*, 1998). Of these three complexes, only [{$Me_2Al(OSiMe_2Ph)$}$_2$] shows some similarities with (I).

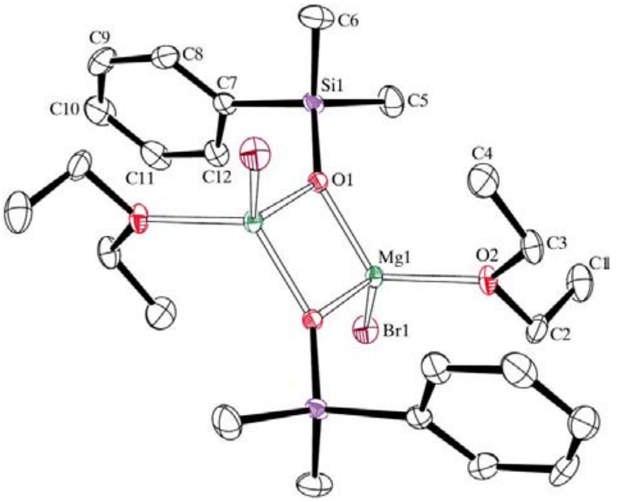


Figure 1
The molecular structure of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and all H atoms have been omitted.

Experimental

Bromobenzene (1 ml, 10 mmol) was added dropwise to a stirred mixture of magnesium (0.3 g, 12.5 mmol) and diethyl ether (5 ml). The mixture was stirred overnight and allowed to settle. A 2.5 ml portion of the clear solution was transferred to a new Schlenk tube containing a small amount (10^{-2} g) of Dow Corning high-vacuum silicone grease. The mixture was layered carefully with hexane and left at 277 K. After five months, it was found that colourless air-sensitive crystals of (I) had formed.

Crystal data

$[Mg_2Br_2(C_8H_{11}OSi)_2(C_4H_{10}O)_2]$
$M_r = 659.18$
Monoclinic, $P2_1/n$
$a = 10.5525\ (18)$ Å
$b = 11.4674\ (17)$ Å
$c = 13.412\ (2)$ Å
$\beta = 91.77\ (5)°$
$V = 1622.3\ (4)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.64$ mm^{-1}
$T = 100\ (2)$ K
$0.3 \times 0.2 \times 0.1$ mm

Data collection

Rigaku R-AXIS-IIC image-plate system diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000) $T_{min} = 0.440$, $T_{max} = 0.767$
10801 measured reflections
2891 independent reflections
2652 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.061$
$S = 1.06$
2891 reflections
158 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

All H atoms were included in calculated positions (C—H = 0.93–0.97 Å) and refined using a riding model, with U_{iso}(H) values of 1.2 or 1.5 times U_{eq}(C).

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3070). Services for accessing these data are described at the back of the journal.

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