

## Synthesis and Structural Characterisation of the Cyclosiloxymagesium Compound $[(\text{py})_2\text{Li}]_2-\mu\text{-Mg}\{[\text{Ph}_2\text{SiO}]_2\text{O}\}[\{\text{Ph}_2\text{SiO}\}_3\text{O}]$ having Both Six- and Eight-membered Magnesiasiloxane Rings

Majid Motevalli, Dipti Shah, Syed A. A. Shah and Alice C. Sullivan\*

Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London, UK E1 4NS

The dilithium salt,  $[(\text{Ph}_2\text{SiOLi}\cdot\text{THF})_2\text{O}]$ , reacts with  $\text{MgCl}_2\cdot 2\text{THF}$  to give, on addition of pyridine, the unexpected lithium bridged spirocyclic magnesiasiloxane compound  $[(\text{py})_2\text{Li}]_2-\mu\text{-Mg}\{[\text{Ph}_2\text{SiO}]_2\text{O}\}[\{\text{Ph}_2\text{SiO}\}_3\text{O}]$  which is the first example of a molecular magnesium siloxide compound to be characterised and also the first example of a spirocyclic metallasiloxane having rings with different degrees of oligomerisation.

Among the group 2 metals, siloxide derivatives for barium only, notably  $[\text{Ba}(\text{OSiPh}_3)_2]_3\cdot\text{THF}$ ,<sup>1</sup> and  $[\text{Ba}\{(\text{OSiPh}_2)_2\text{O}\}]_3\cdot 2\text{-tetraglyme}$ <sup>2</sup> have been reported. We report here on the first example of a magnesiasiloxane<sup>3</sup> isolated from the reaction between  $\text{MgCl}_2\cdot 2\text{THF}$  and the dilithium salt  $[(\text{Ph}_2\text{SiOLi}\cdot\text{THF})_2\text{O}]$ .<sup>†</sup>

We have reported reactions of this type for a range of divalent metal chlorides of the first transition metal series.<sup>4</sup> The products isolated had a structure of type A bearing two six-membered metallasiloxane rings, indicative of a simple metathesis reaction. The isolation of compound **1**, which incorporates both six- and eight-membered magnesiasiloxane rings was unexpected. The reaction leading to **1** is thus more

complex than related reactions with transition metal dichlorides. In this case a chain expansion of one of the siloxane units from tetraphenyldisiloxanediolate to octaphenyltrisiloxanediolate has occurred. We have previously reported<sup>5</sup> a similar chain expansion in 2:1 and 3:1 reactions between  $[(\text{Ph}_2\text{SiOLi}\cdot\text{THF})_2\text{O}]$  and  $\text{TiCl}_4$  giving a product with two eight-membered titanasiloxane rings and have since observed<sup>6</sup> similar transformations for tetravalent zirconium, hafnium and tin. In addition both thermal- and base-promoted ring enlargement of the compound  $\text{PhB}\{(\text{OSiPh}_2)_2\text{O}\}$  has been reported.<sup>7</sup>

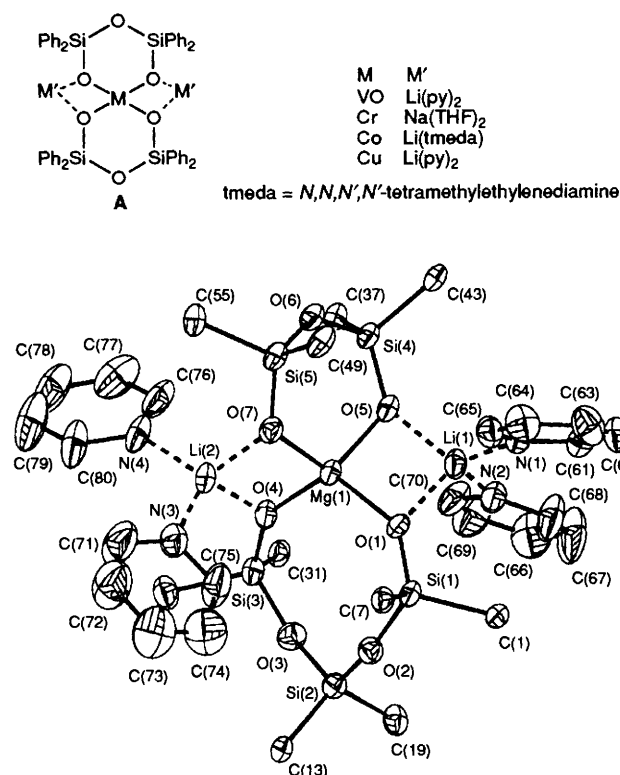
The isolation of **1** with both six- and eight-membered rings represents the first example of a spirocyclic metallasiloxane having metallasiloxane rings with different degrees of oligomerisation. Spirocyclic siloxanes showing structural features of this type are well known.<sup>8</sup>

The molecular structure of **1** is shown in Fig. 1 along with selected bond lengths and angles.‡ The geometry at the four-coordinate magnesium centre is distorted tetrahedral and the six- and eight-membered relatively planar rings (maximum deviations from the mean planes are 0.24 and 0.34 Å respectively) are twisted some 84.8° with respect to each other. The Mg–O distances in the two rings are similar and close to those in  $\text{Mg}(\text{acac})_2(\text{H}_2\text{O})_2$  [ $\text{Mg}-\text{O}(\text{C})$  2.03 Å]<sup>9</sup> but the geometrical constraints of the six-membered ring generally results in smaller angles at magnesium and oxygen compared to those in the eight membered-ring; for example (Si)O–Mg–O(Si) bite angles are 104.6(3) and 114.7(3)°, the average Si–O–Mg angles are 123.6(3) and 142.9(3)° while the Si–O–Si angles are 133.2(2) and 157.2(2), 160.5(2)° which are close to those reported for  $[\text{Ph}_2\text{SiO}]_3$ ,<sup>10</sup> and  $[\text{Ph}_2\text{SiO}]_4$ <sup>11</sup> [131.8(8) and 152.3(2), 167.4(2)°]. The indications are that ring strain is greater in the six-membered ring as expected, and in each case is similar to that of the related cyclic siloxanes.

While the <sup>29</sup>Si NMR spectrum of **1** in [<sup>2</sup>H<sub>8</sub>]toluene shows the expected number of resonances for structure **1**, the <sup>7</sup>Li NMR spectrum recorded at 300 K shows three resonances indicating the presence of a number of species in solution. We are currently investigating the variable-temperature solution behaviour of this and related calcium, strontium and barium derivatives.

We thank the SERC for a studentships to D. S. and S. A. A. S., and Mr Peter Haycock of the University of London Intercollegiate Research Services, for <sup>29</sup>Si NMR spectra.

Received, 5th July 1994; Com. 4/04805F



**Fig. 1** Molecular structure of compound **1** (phenyl ring carbons omitted) with selected bond lengths (Å) and angles (°): Mg(1)–O(1) 1.926(3), Mg(1)–O(5) 1.954(3), Mg(1)–O(4) 1.923(3), Mg(1)–O(7) 1.942(3), Si(1)–O(1) 1.586(3), Si(1)–O(2) 1.638(3), Si(2)–O(2) 1.612(3), Si(2)–O(3) 1.600(3), Si(3)–O(3) 1.641(3), Si(3)–O(4) 1.587(3), Si(4)–O(5) 1.600(3), Si(4)–O(6) 1.643(3), Si(5)–O(6) 1.641(3), Si(5)–O(7) 1.596(3), Li(1)–O(1) 1.991(8), Li(1)–O(5) 1.937(5), Li(2)–O(4) 2.000(9), Li(2)–O(7) 1.925(8), Li(1)–N(1) 2.066(8), Li(1)–N(2) 2.053(9), Li(2)–N(3) 1.998(9), Li(2)–N(4) 2.011(9), O(1)–Mg–O(4) 114.85(14), O(7)–Mg–O(5) 104.53(14), O(1)–Mg–O(5) 94.14(14), O(4)–Mg–O(7) 93.86(14), O(7)–Mg–O(1) 125.6(2), O(4)–Mg–O(5) 126.62(14), Si(5)LO(6)–Si(4) 133.2(2), Si–O–Si(av)(8-ring) 158.8(2), Si–O–Mg(av)(6-ring) 123.5(2), Si–O–Mg(av)(8-ring) 142.2(2), O–Si–O(av)(6-ring) 111.9(2), O–Si–O(av)(8-ring) 112.8(2)

### Footnotes

† The reagents  $\text{MgCl}_2\cdot 2\text{THF}$  (4.34 mmol) and  $[(\text{Ph}_2\text{SiOLi})_2\text{O}]$  (8.68 mmol) were stirred in THF (40 cm<sup>3</sup>) for 12 h. The THF was removed and the residue treated with toluene (50 cm<sup>3</sup>), and filtered. The insoluble residue gave positive lithium and chloride tests. Pyridine (2 cm<sup>3</sup>) was added to the toluene filtrate and compound **1** was deposited as colourless moisture-sensitive crystals (4.32 g, 72% based on

available magnesium, 90% based on available silicon); mp 238–242 °C;  $^{29}\text{Si}$  NMR ( $\text{C}_7\text{D}_8$ , 300 K)  $\delta$  -40.75(s), -43.68(s), -44.98(s).  $\ddagger$  Crystal data for compound 1:  $\text{C}_{80}\text{H}_{70}\text{Li}_2\text{MgN}_4\text{O}_7\text{Si}_5$ ,  $M = 1378.07$ , monoclinic, space group  $P2_1/n$ ,  $a = 21.614(8)$ ,  $b = 15.458(5)$ ,  $c = 22.152(2)$  Å,  $\beta = 99.51(1)^\circ$ ,  $U = 7299.47(69)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.254$  g cm<sup>-3</sup>;  $\lambda(\text{Mo-K}\alpha) = 0.71069$  Å,  $\mu = 1.574$  cm<sup>-1</sup>,  $F(000) = 2888$ .

Data were recorded with a CAD4 diffractometer operating in the  $\omega$ -2 $\theta$  scan mode. A total of 23501 reflections were collected of which 11487 were independent. The structure was solved by standard heavy-atom techniques and refined by least squares on  $F^2$ ,<sup>12</sup> with phenyl groups treated as rigid hexagons, (C–C 1.395 Å, C–C–C 120°), and with inclusion of hydrogen atoms, at fixed positions, (C–H 0.96 Å), except those attached to pyridine which were allowed to refine freely. The final  $R$  indices were  $R_1 = 0.0461$ ,  $wR_2 = 0.0343$  for [ $I > 2\sigma(I)$ ] and  $R_1 = 0.1193$ ,  $wR_2 = 0.0593$  (all data) for 862 parameters.  $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ,  $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]\}^{1/2}$ . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

## References

- 1 J. A. Darr, S. R. Drake, D. J. Williams and A. M. Z. Slawin, *J. Chem. Soc., Chem. Commun.*, 1993, 866.
- 2 K. G. Caulton, M. H. Chisholm, S. R. Drake and J. C. Huffman, *J. Chem. Soc., Chem. Commun.*, 1990, 1345.
- 3 For a recent review of magnesium compounds, see R. Holloway and M. Melnik, *J. Organomet. Chem.*, 1994, **465**, 1.
- 4 M. B. Hursthouse, M. A. Mazid, M. Motevalli, M. Sanganee and A. C. Sullivan, *J. Organomet. Chem.*, 1990, **381**, C43; M. B. Hursthouse, M. Motevalli, M. Sanganee and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1991, 1790; M. Motevalli, M. Sanganee, P. D. Savage, S. A. A. Shah and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1993, 1312; I. Abrahams, M. Motevalli, M. Sanganee, D. Shah and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1993, 1514.
- 5 M. A. Hossain, M. B. Hursthouse, A. A. Ibrahim, M. Mazid and A. C. Sullivan, *J. Chem. Soc., Dalton Trans.*, 1989, 2347.
- 6 M. Motevalli, S. A. A. Shah and A. C. Sullivan manuscript in preparation.
- 7 D. A. Foucher, A. J. Lough and I. Manners, *Inorg. Chem.*, 1992, **31**, 3034.
- 8 For examples see E. Lukevics, O. Pudova and R. Sturkovich, *Molecular Structure of Organosilicon Compounds*, Ellis Horwood, Chichester, 1989.
- 9 B. Morosin, *Acta Crystallogr., Sect. B.*, 1967, **22**, 316.
- 10 N. G. Bokii, G. N. Zakharova and Y. T. Struchkov, *Zh. Strukt. Khim.*, 1972, **13**, 291; P. E. Tomlins, J. E. Lydon, D. Akrigg and B. Sheldrick, *Acta Crystallogr., Sect. C.*, 1985, **41**, 292.
- 11 M. A. Hossain, M. B. Hursthouse and M. A. Malik, *Acta Crystallogr., Sect. B.*, 1979, **35**, 522.
- 12 G. M. Sheldrick, SHELXL 93, program for crystal structure determination, University of Göttingen, 1993.