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Articles in the issue include:

PERSPECTIVES:

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Dalton Trans., 2010, DOI: 10.1039/C003097J

Kinetic studies of reactions of organosilylenes: what have they taught us?
Rosa Becerra and Robin Walsh
Dalton Trans., 2010, DOI: 10.1039/C0DT00198H

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Tsukasa Matsuo, Megumi Kobayashi and Kohei Tamao
Dalton Trans., 2010, DOI: 10.1039/C0DT00287A

Organosilicon compounds meet subatomic physics: Muon spin resonance
Robert West and Paul W. Percival
Dalton Trans., 2010, DOI: 10.1039/C0DT00188K

HOT ARTICLE:

Novel neutral hexacoordinate silicon(IV) complexes with two bidentate monoanionic benzamidinato ligands
Konstantin Junold, Christian Burschka, Rüdiger Bertermann and Reinhold Tacke
Dalton Trans., 2010, DOI: 10.1039/C0DT00391C

Chiral cyclotrisiloxanes†

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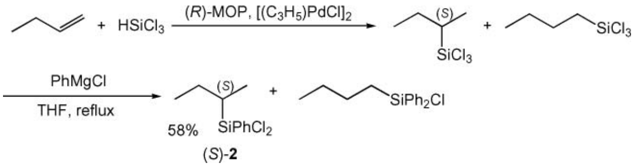
We have synthesized and separated the enantiomer pair of chiral cyclotrisiloxanes for the first time. Three-blade propeller-like alignment of three phenyl groups in tri(2-butyl)triphenylcyclotrisiloxane induced a positive Cotton effect with (*R*)-2-butyl group, and a negative effect with (*S*)-2-butyl substituent.

Since the first isolation of chiral silicon compounds by Sommer,[1] chiral silanes have been widely utilized as Lewis acids,[2] chiral auxiliaries,[3] and chiral transfer units.[4] Although silicon-stereogenic silanes[5] and polymeric compounds[6] are relatively well investigated, chiral silsesquioxanes or siloxanes are almost unexplored.[7,8] Cyclic siloxanes are easily accessible from chlorosilanes, and are stable compounds. Therefore the preparation of chiral siloxanes is promising in various applications like starting compounds of chiral siloxanes or chiral templates. Here we will report the first synthesis and isolation of an enantiomer pair of chiral cyclotrisiloxanes.

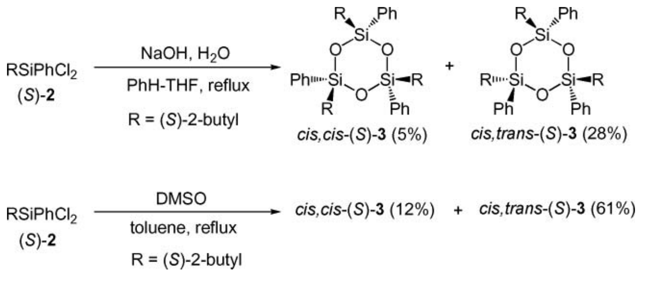
In 2003, we reported the synthesis of hexakis(2,4,6-triisopropylphenylsilsesquioxane) **1**, and the X-ray crystal analysis revealed that the enantiomer pair originating from the restricted rotation of the bulky Tip (2,4,6-triisopropylphenyl) groups was included in the single lattice.[8] This result prompted us to prepare a chiral cyclotrisiloxane, which is half part hexasilsesquioxane. Regarding chiral cyclotrisiloxanes, Moller's group reported the synthesis of hexa((*S*)-2-methylbutyl)cyclotrisiloxane.[9] Unfortunately in their case, only slight optical rotation was observed and no other information regarding stereostructure was obtained. We devised to introduce chiral secondary alkyl groups and aryl groups on the silicon atom in cyclotrisiloxane. In this compound, controlling chirality by propeller-like orientation of aryl groups can be expected.

Our synthesis began with hydrosilylation using a chiral template reported by Uozumi and Hayashi.[10] As shown in Scheme 1, 1-butene was treated with trichlorosilane in the presence of (*R*)-2-diphenylphosphino-2-methoxy-1,1′-binaphtyl and $[(C_3H_5)PdCl]_2$. Hydrosilylation occurred at positions 1 and 2 of 1-butene, and two trichlorosilanes were obtained. As the boiling points of the two compounds are close, we could not separate by distillation. By measuring NMR spectra of the mixture, we calculated the yields of both compounds to be 67% ((*S*)-2-butyldichlorophenylsilane) and 15% (butyltrichlorosilane). We then treated the mixture with PhMgBr, and obtained products that could be successfully separated. The yield of pure (*S*)-2-butyldichlorophenylsilane (*S*)-**2** was 58%. Because we could not determine the optical purity of chlorosilane **2**, (*S*)-**2** was transferred to 1,2-dibutyl-1,1,2,2-tetraphenyldisilane, and optical purity was measured to be 94% ee after purification. A similar experiment using (*S*)-2-diphenylphosphino-2-methoxy-1,1′-binaphtyl gave (*R*)-2-butyldichlorophenylsilane (*R*)-**2**.



Scheme 1 Synthesis of (*S*)-2-butyldichlorophenylsilane **2**.

Dichlorosilane (*S*)-**2** was hydrolyzed under basic conditions, and 2,4,6-tri((*S*)-2-butyl)-2,4,6-triphenylcyclotrisiloxane **3** was obtained. The isomeric mixture was separated with recycle-type HPLC, and (*S*)-*cis*,*cis*-**3** and (*S*)-*cis*,*trans*-**3** were obtained in 5% and 28% yield, respectively (Scheme 2). The yields were further improved by the reaction of (*S*)-**2** with DMSO in toluene; (*S*)-*cis*,*cis*-**3** was obtained in 12% yield, and (*S*)-*cis*,*trans*-**2** was given in 61% yield (Scheme 2).[11] A similar procedure could be applied to (*R*)-**2**, and (*R*)-*cis*,*cis*-**3** and (*R*)-*cis*,*trans*-**3** were obtained. In all cases, a single enantiomer was obtained by stereospecific manner.



Scheme 2 Synthesis of tri((*S*)-2-butyl)triphenylcyclotrisiloxane **3**.

The CD spectra of *cis*,*cis*-**3** and *cis*,*trans*-**3** showed Cotton band of phenyl groups in the region of 250–280 nm, and (*R*)-*cis*,*cis*-**3** and (*R*)-*cis*,*trans*-**3** indicated positive Cotton effect and (*S*)-*cis*,*cis*-**3** and (*S*)-*cis*,*trans*-**3** showed negative Cotton effect (Fig. 1 and 2). These results clearly indicate that the phenyl groups in **3** locate in chiral alignment, and that is the origin of the Cotton effect. Noticeably, molar ellipticities of *cis*,*cis*-**3** was more than twice as large than that of *cis*,*trans*-**3**, indicating that the diastereotopic structure of *cis*,*cis*-**3** effectively leads to the three-blade propeller form. Although cyclotrisiloxane rings are flexible,

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† Electronic supplementary information (ESI) available: Detailed experimental procedure of all compounds and X-ray crystal analysis report of *P*-**4** and *M*-**4**. CCDC reference numbers 769810 and 769811. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00135j

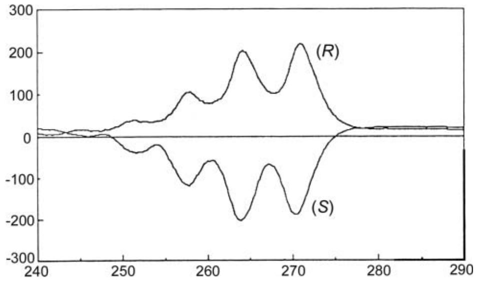

Fig. 1 Circular dichroism spectra of *cis*,*cis*-(*S*)-**3** and *cis*,*cis*-(*R*)-**3** in hexane.

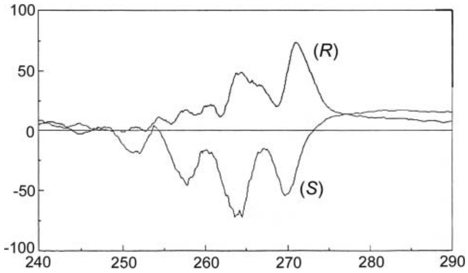

Fig. 2 Circular dichroism spectra of *cis*,*trans*-(*S*)-**3** and *cis*,*trans*-(*R*)-**3** in hexane.

steric interaction of two *cis*-aligned phenyl groups are significant and the chiral structure was maintained.

Unfortunately, the obtained *cis*,*cis*-**3** and *cis*,*trans*-**3** did not give satisfactory single crystals for X-ray analysis. In order to examine the conformation of chiral **3**, we calculated the molecular dynamics, however we could not determine the stable conformation. Therefore, we investigated the crystal structures of hexaphenylcyclotrisiloxane **4**, as similar propeller-like structures have been reported. Several crystal structures for **4** were reported and for those that crystallized in the monoclinic crystal system, $P2_12_12_1$ showed chirality.[12] As in the case of **1**, the phenyl groups of **4** formed a three-blade propeller structure with either *P* or *M* chirality (Fig. 3). We determined the absolute structure of **4**, and measured the CD spectra in solid phase. The molecular crystal in the *M*-conformation indicated negative Cotton effect, and the molecular crystal in *P*-conformation showed positive effect (Fig. 4). From this result, it is plausible that phenyl groups in (*R*)-*cis*,*cis*-**3** and (*R*)-*cis*,*trans*-**3** form *M*-chiral propeller, and *P*-chiral propeller was formed with (*S*)-*cis*,*cis*-**3** and (*S*)-*cis*,*trans*-**3**.

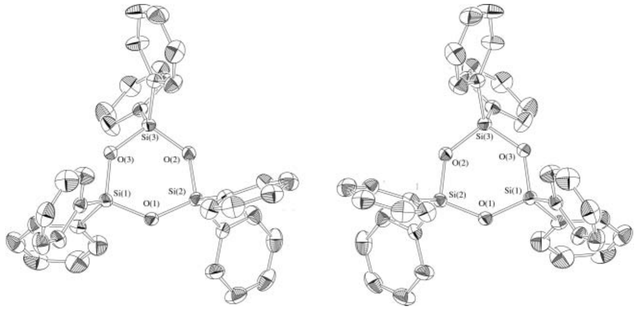

Fig. 3 Molecular structures of *P*-**4** (left) and *M*-**4** (right) with 30% probability level.

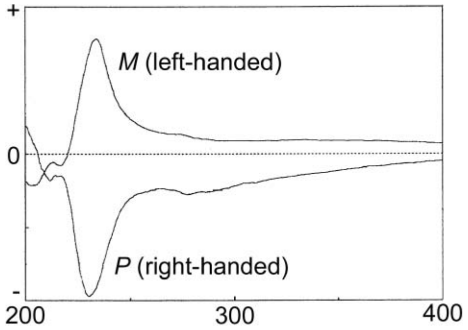

Fig. 4 Circular dichroism spectra of *P*-**4** and *M*-**4** (solid state).

Conclusions

We have prepared and separated the first enantiomer pair of cyclotrisiloxanes by introducing chiral secondary alkyl groups and phenyl groups. The three-blade propeller alignment of phenyl groups was successfully induced by chiral alkyl groups, and an enantiomer pair of *cis*,*cis*- and *cis*,*trans*-isomers were separated.

Notes and references

1 L. H. Sommer, in *Stereochemistry, Mechanisim and Silicon*, McGraw-Hill, New York, 1965.
2 B. Mathieu, L. de Fays and L. Ghosez, *Tetrahedron Lett.*, 2000, **41**, 9561; S. Shirakawa, R. Berger and J. L. Leighton, *J. Am. Chem. Soc.*, 2005, **127**, 2858; S. Shirakawa, P. Lombardi and J. L. Leighton, *J. Am. Chem. Soc.*, 2005, **127**, 9974; K. Tran and J. L. Leighton, *Adv. Synth. Catal.*, 2006, **348**, 2431; G. Notte and J. L. Leighton, *J. Am. Chem. Soc.*, 2008, **130**, 6676; S. C. Valdez and J. L. Leighton, *J. Am. Chem. Soc.*, 2009, **131**, 14638.
3 P. J. Stang and A. E. Learned, *J. Org. Chem.*, 1989, **54**, 1779; P. Huber, S. Bratovanov, S. Bienz, C. Syldatk and M. Pietzsch, *Tetrahedron: Asymmetry*, 1996, **7**, 69; K. Kobayashi, T. Kato, M. Unno and S. Masuda, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1393; M. Trzoss, J. Shao and S. Bienz, *Tetrahedron*, 2002, **58**, 5885; M. Trzoss, J. Shao and S. Bienz, *Tetrahedron: Asymmetry*, 2004, **15**, 1501; K. Tran, P. J. Lombardi and J. L. Leighton, *Org. Lett.*, 2008, **10**, 3165.
4 A. G. Brook, T. J. D. Vandersar and W. Limburg, *Can. J. Chem.*, 1978, **56**, 2758; D. Wang and T. H. Chan, *Tetrahedron Lett.*, 1983, **24**, 1573; K. Tamao, R. Kanatani and M. Kumada, *Tetrahedron Lett.*, 1984, **25**, 1913; J. S. Panek and J. V. Schaus, *Tetrahedron*, 1997, **53**, 10971; H. Ito, T. Ishizuka, T. Okumura, H. Yamanaka, J. Tateiwa, M. Sonoda and A. Hosomi, *J. Organomet. Chem.*, 1999, **574**, 102; B. Zhu and J. S. Panek, *Org. Lett.*, 2000, **2**, 2575; J. S. Panek and P. Liu, *J. Am. Chem. Soc.*, 2000, **122**, 11090; J. V. Schaus, N. Jain and J. S. Panek, *Tetrahedron*, 2000, **56**, 10263; B. Zhu and J. S. Panek, *Eur. J. Org. Chem.*, 2001, 1701; T. Hu, N. Takenaka and J. S. Panek, *J. Am. Chem. Soc.*, 2002, **124**, 12806; Q. Su and J. S. Panek, *Angew. Chem., Int. Ed.*, 2005, **44**, 1223; M. Oestreich and S. Rendler, *Angew. Chem., Int. Ed.*, 2005, **44**, 1661; M. Oestreich, *Chem.–Eur. J.*, 2006, **12**, 30; S. Rendler, M. Oestreich, P. Craig and G. C. Lloyd-Jones, *J. Am. Chem. Soc.*, 2007, **129**, 502; S. Rendler, R. Froehlich, M. Keller and M. Oestreich, *Eur. J. Org. Chem.*, 2008, 2582; D. T. Hog and M. Oestreich, *Eur. J. Org. Chem.*, 2009, 5047.
5 R. J. P. Corriu, G. F. Lanneau and M. Leard, *J. Organomet. Chem.*, 1974, **64**, 79; R. J. P. Corriu, G. F. Lanneau and G. Guiraud, *J. Organomet. Chem.*, 1974, **64**, 63; C. L. Smith and R. Gooden, *J. Organomet. Chem.*, 1974, **81**, 33; G. Cerveau, E. Colomer and R. J. P. Corriu, *Organometallics*, 1982, **1**, 867; G. L. Larson and E. Torres, *J. Organomet. Chem.*, 1985, **293**, 19; B. F. Bonini, G. Maccagnani, S. Masiero, G. Mazzanti and P. Zani, *Tetrahedron Lett.*, 1989, **30**, 2677; B. F. Bonini, S. Masiero, G. Mazzanti and P. Zani, *Tetrahedron Lett.*, 1991, **32**, 6801; R. Tacke, F. Wuttke and H. Henke, *J. Organomet. Chem.*, 1992, **424**, 273; M. Unno, H. Masuda and H. Matsumoto, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 2749; P. J. Coelho and L. Blanco, *Synlett*, 2001, 1455; P. J. Coelho and L. Blanco, *Tetrahedron*, 2003, **59**, 2451;

H.-S. Oh, L.-S. Park and Y. Kawakami, *Chirality*, 2003, **15**, 646; O. Girshberg, I. Kalikhman, D. Stalke, B. Walfort and D. Kost, *J. Mol. Struct.*, 2003, **661–662**, 259; K. Suzuki, Y. Kawakami, D. Velmurugan and T. Yamane, *J. Org. Chem.*, 2004, **69**, 5383; M. Campagna, M. Trzoss and S. Bienz, *Org. Lett.*, 2007, **9**, 3793; K. Igawa, J. Takada, T. Shimono and K. Tomooka, *J. Am. Chem. Soc.*, 2008, **130**, 16132; N. Oka, M. Nakamura, N. Soeda and T. Wada, *J. Organomet. Chem.*, 2009, **694**, 2171; K. Igawa, N. Kokan and K. Tomooka, *Angew. Chem., Int. Ed.*, 2010, **49**, 728.

6 X. Wan, H. S. Kwok and B. Z. Tang, *Polym. Mater. Sci. Eng.*, 1997, **77**, 513; B. Z. Tang, X. Wan and H. S. Kwok, *Eur. Polym. J.*, 1998, **34**, 341; M. Oishi, J.-Y. Moon, W. Janvikul and Y. Kawakami, *Polym. Int.*, 2001, **50**, 135; H.-S. Oh, I. Imae, Y. Kawakami, S. S. S. Raj and T. Yamane, *J. Organomet. Chem.*, 2003, **685**, 35; S. Y. Park, K. Uenishi and Y. Kawakami, *Macromol. Chem. Phys.*, 2005, **206**, 1199.

7 I. M. Saez, J. W. Goodby and W. John, *J. Mater. Chem.*, 2001, **11**, 2845; A. Brethon, J. J. E. Moreau and M. W. C. Man, *Tetrahedron: Asymmetry*, 2004, **15**, 495; S. Shinke, T. Tsuchimoto and Y. Kawakami, *Silicon Chem.*, 2007, **3**, 243; J. Miyake and Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6035; Y. Kaneko and N. Iyi, *J. Mater. Chem.*, 2009, **19**, 7106.

8 M. Unno, Y. Imai and H. Matsumoto, *Silicon Chem.*, 2003, **2**, 175.

9 L. A. Schwegler, A. Molenberg and M. Moller, *Acta Polym.*, 1997, **48**, 438.

10 Y. Uozumi and T. Hayashi, *J. Am. Chem. Soc.*, 1991, **113**, 9887.

11 Spectral data of *cis*,*cis*-(*S*)-**3** and *cis*,*trans*-(*S*)-**3**: *cis*,*cis*-(*S*)-**3**: colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (t, 9H, J = 7.5 Hz), 1.03–1.07 (m, 3H), 1.11 (d, 9H, J = 7.5 Hz), 1.24–1.30 (m, 3H), 1.69–1.74 (m, 3H), 7.13 (t, 6H, J = 7.9 Hz). ^{13}C NMR (128 MHz, CDCl3) δ 12.9, 13.4, 22.7, 23.8, 127.2, 129.5, 133.8, 134.4. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −26.17. MS (EI, 70 eV) m/z (%) 534 (M^+, 4), 477 (100). IR (neat, cm^{-1}) 3071, 2959, 2930, 2870, 2856, 1958, 1884, 1591, 1460, 1429, 1379, 1215, 1123, 1033, 1013, 993, 854, 733, 696, 598, 513. *cis*,*trans*-(S)-**3**: colorless waxy semisolid. ^{1}H NMR (500 MHz, $CDCl_3$), δ 0.69–0.78 (m, 7H), 0.88 (t, 8H, J = 6.9 Hz), 0.91–0.99 (m, 7H), 1.12–1.17 (m, 3H), 1.37–1.50 (m, 1H), 1.57–1.62 (m, 3H), 7.29–7.43 (m, 10H), 7.59–7.63 (m, 3H), 7.71–7.74 (m, 2H). ^{13}C NMR (128 MHz, $CDCl_3$) δ 12.55, 12.76, 12.82, 13.09, 13.26, 13.29, 22.45, 22.61, 22.70, 23.45, 23.67, 23.83, 127.4, 127.6, 129.7, 129.8, 133.8, 133.9, 134.8, 135.1. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −23.28, −23.27, −23.05. MS (EI, 70 eV) m/z (%) 534 (M^+, 1), 477 (98), 421 (70), 365 (100). IR (neat, cm^{-1}) 3071, 2959, 2870, 1958, 1884, 1460, 1429, 1122, 1034, 993, 733, 696.

12 P. E. Tomlins, J. E. Lydon, D. Akrigg and B. Sheldrick, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1985, **41**, 292.