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Syntheses and Reactivities of 4-Sila- and 8-Phospha-4-silathiophenetriptycenes[1]

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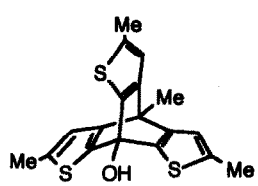
Abstract: The reactions of the trilithium salt **7**, prepared from **5** or **6**, with diethyl carbonate and triphenyl phosphite yield 4-sila and 8-phospha-4-silathiophenetriptycenes, **2** and **3**, respectively. In the UV-Vis spectra of **2** and **3**, the longest absorption maxima appear at 297 and 308 nm, respectively, and, in the ^{31}P NMR, the phosphorus atom of **3** resonates at δ -92.15. Treatment of **3** with *m*-CPBA or cyclohexene sulfide gives the corresponding phosphine oxide (**8**) or phosphine sulfide (**9**), respectively, while the reaction of **3** with S_8/DBU gives disiloxane **10**.

The chemistry of triptycenes, one or two bridgehead carbons of which are replaced by other atoms, is interesting in pursuing the properties of the brigdehead atoms fixed in the rigid skeleton. However, the class of such compounds has been restricted to those having the 15 group elements at the bridgeheads[2] and, until now, only a few reports have appeared on the synthesis of triptycene derivatives having the 14 group elements heavier than carbon at their bridgeheads.[2h, 3] Recently we reported the first synthesis of the thiophene analog of triptycene, **1** (thiophenetriptycene),[4] in which three 2,3-thiophene rings are characteristically oriented in the same direction. It is of interest to investigate the physical and chemical properties of thiophenetriptycenes, which consist of three five-membered thiophene rings and heteroatom-containing bridgeheads, from a viewpoint of the ring strain around the bridgeheads fixed in the rigid ring skeletons with an eye to the comparison with the corresponding triptycene derivatives. Here we report the first synthesis and reactivities of 4-sila- and 8-phospha-4-silathiophenetriptycenes, **2** and **3**.



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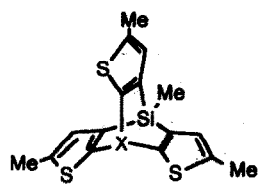
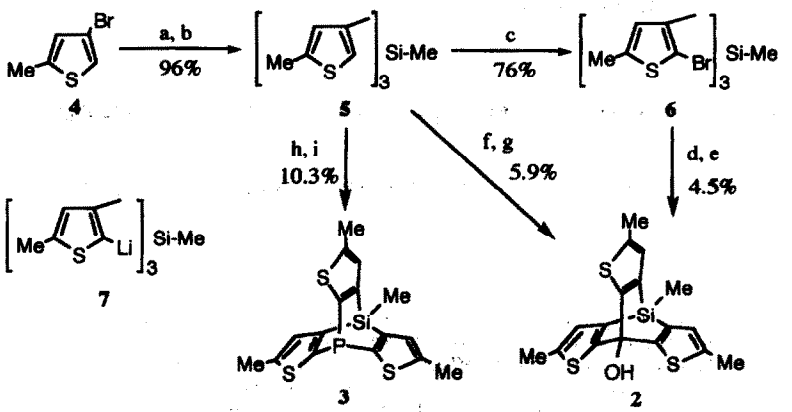


2 : X=C-OH; **3** : X=P

We have prepared two precursors **5** and **6** for **2** and **3** by the method shown in Scheme 1. Lithiation of 4-bromo-2-methylthiophene (**4**) with *sec*-BuLi in Et_2O at -78 °C followed by treatment of $MeSi(OEt)_3$ gave a silane **5** in 96% yield. Bromination of **5** yielding **6** was attained in 76% yield by addition of bromine at -78 °C and then quenching the reaction with aqueous Na_2CO_3 at this temperature to prevent the decomposition of **6** by the HBr. We first attempted the synthesis of **2** by reaction of the trilithium salt **7**, prepared by halogen-metal exchange of **6**, with $(EtO)_2C{=}O$. Thus, lithiation of **6** with *t*-BuLi (6 equiv) followed by treatment of

$(EtO)_2C=O$ gave the desired 4-silathiophenetriptycene **2** though in low yield (4.5%). The trilithium salt **7** was also prepared by direct lithiation of the silane **5** by *n*-BuLi (3 equiv). By opimizing the conditions, **2** was obtained in a slightly improved yield (5.9%) in this way. Similarly, 8-phospha-4-silathiophenetriptycene **3** was synthesized by the reaction of **7** and $P(OPh)_3$ in 10% yield with recovery of **5** (37%).



a: *sec*-BuLi (1 equiv)/Et_2O/-78 °C; b: $MeSi(OEt)_3$ (0.33 equiv)/-78 °C and then r.t., overnight; c: Br_2 (3 equiv)/CH_2Cl_2/-78 °C; d: *t*-BuLi (6 equiv)/THF-Et_2O (1:2)/-78 °C, 1 h; e: $(EtO)_2C=O$/-78 °C, 1 h and then r.t.; f: *n*-BuLi (3 equiv)/THF-Et_2O (1:2)/0 °C, 1 h; g: $(EtO)_2C=O$ (1 equiv)/-78 °C, 1 h and then r.t.; h: *n*-BuLi (3 equiv)/r.t., 3 h; i: $P(OPh)_3$, 2 h.

Scheme 1

Thiophenetriptycenes **2** (mp 226-228 °C) and **3** (mp 235-237 °C) are colorless crystalline compounds and their structures are supported by their spectroscopic data and elemental analyses. Selected spectral data of **2** and **3** are shown below.

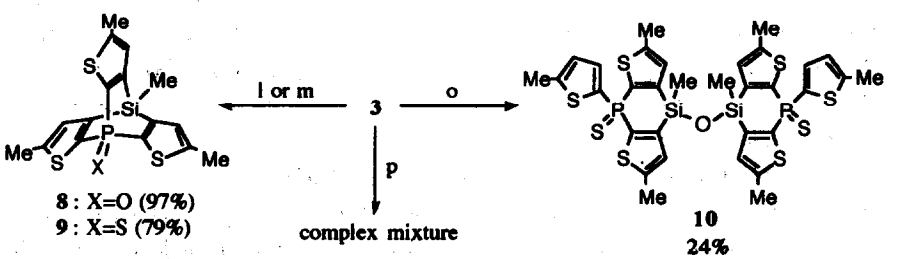
2: ^1H NMR ($CDCl_3$) δ 1.00 (s, 3H), 2.37 (s, 9H), 3.39 (s, 1H), 6.79 (d, 3H).
^{13}C NMR ($CDCl_3$) δ -10.5 (CH_3), 14.7 (CH_3), 82.1 (C), 127.7 (CH), 135.6 (C), 143.1 (C), 162.4 (C).
IR (KBr) 3516 cm^{-1} (OH).
UV-Vis (CH_3CN) λ_{max} (ε) 297 nm (560), 233 (sh, 1420), 217 (3650).

3: ^1H NMR ($CDCl_3$) δ 1.04 (s, 3H), 2.42 (s, 9H), 6.99 (s, 3H).
^{13}C NMR ($CDCl_3$) δ -10.3 (CH_3), 14.7 (CH_3), 129.5 (CH), 142.9 (d, $J_{C\text{-}P}$=4.4 Hz, C), 151.8 (d, $J_{C\text{-}P}$ =13.7 Hz, C), 153.2 (d, $J_{C\text{-}P}$=2.6 Hz, C).
^{31}P NMR ($CDCl_3$) δ -92.15.
UV-Vis (CH_3CN) λ_{max} (ε) 308 nm (1200), 269 (sh, 2030), 264 (2180).

In their ^1H and ^{13}C NMR spectra, three thiophene rings are equivalent due to C_3 symmetry. In the ^{13}C NMR, bridgehead methyls of **2** and **3** are characteristically shielded (δ -10.5 and -10.3, respectively) and the bridgehead carbon of **2** appears at δ 82.1. In the ^{31}P NMR, the bridgehead phosphorus atom of **3** resonates at δ -92.15. This large negative value is characteristic of phosphatriptycenes, which indicates the high s character of the lone pair electrons on the phosphorus atom.[2d] Three important factors influence ^{31}P NMR chemical

shifts of phosphines;[5] (i) the electronegativity of substituents on the phosphorus atom, (ii) the bond angle (∠CPC), and (iii) the effects of π bonding between the substituent and phosphorus atom. Thus, the greater is the electron-withdrawing nature of a substituent, the greater is the shielding. A good correlation is observed between the ^{31}P NMR chemical shifts and C-P-C bond angles of phosphatriptycenes (δ_p and ∠CPC: azaphosphatriptycene: -80 and 93.3°; phosphatriptycene: -65 and 94.5°; diphosphatriptycene: -43 and 97°).[2b] In the present case, the third factor can be neglected because of the orthogonality between the lone pair orbital of the phosphorus atom and π-orbitals of thiophenes. We consider that the greater shielding of the phosphorus atom of **3** compared with other phosphatriptycenes is ascribed to both the greater electron-withdrawing nature of 2-thienyl[5] and the narrower C-P-C bond angle. In the UV-Vis spectra, the longest absorption maxima of **2** and **3** appear at 297 and 308 nm, respectively, which are comparable to that of **1** (λ_{max} 303 nm), indicating that absorption maxima of thiophenetriptycenes are almost independent on the bridgehead atoms.

To investigate the reactivity of 8-phospha-4-silathiophenetriptycene **3**, chalcogenation of the phosphorus atom was examined (Scheme 2). Oxidation of **3** with *m*-CPBA (1 equiv) gave the corresponding phosphine oxide **8** (δ_p 6.41) in 97% yield. Sulfurization and selenation were attempted with elemental sulfur and selenium, respectively, in the presence of a catalytic amount of DBU. However, the expected phosphine sulfide and phosphine selenide were not obtained. In the case of the sulfurization, a disiloxane **10** (δ_p 6.07)[6] was isolated as the only identifiable product. While **3** did not decompose by heating with DBU in refluxing benzene, it gradually decomposed by treating with MeONa in Et_2O at room temperature. Therefore, it seems that a nucleophilic species like DBU^+-M-$(M)_x$-M^- (M=S, Se)[7] attacks the bridgehead silicon atom of **3** to lead to a ring opening. Although it is not clear at the present stage whether the initial nucleophilic substitution is retention or inversion,[8] the easy cleavage of the Si-C(thiophene) bond would be ascribed to the large ring strain of **3**. Disiloxane **10** would be provided by dehydration of two molecules of the corresponding silanol formed by hydrolysis of the ring-opening product having an Si-S bond during aqueous workup. Eventually sulfurization of **3** giving **9** (δ_p 1.59) in 79% yield was performed by the reaction with excess cyclohexene sulfide in refluxing benzene.[9]



l: *m*-CPBA (1 equiv)/CH_2Cl_2/r.t.; m: cyclohexene sulfide (excess)/PhH/refl.;
o: S_8/DBU (cat.)/PhH/r.t.; p: Se/DBU (cat.)/PhH, r.t.

Scheme 2

REFERENCES AND NOTES

1. We call 4,8-dihydro-4,8[3',2']thiophenobenzo[1,2-*b*:5,4-*b*']dithiophene "thiophenetriptycene" for convenience.

2. (X, Y) denotes bridgehead atoms of triptycenes. a) (N, C): Wittig, G.; Steinhoff, G. *Angew. Chem.* **1963**, *75*, 453; Kreil, D. J.; Sandel, V. R. *J. Chem. Eng. Data* **1976**, *21*, 132; Hoefnagel, A. J.; Hoefnagel, M. A.; Wepster, B. M. *J. Org. Chem.* **1981**, *46*, 4209. b) (N, P): Hellwinkel, D.; Schenk, W. *Angew. Chem.* **1969**, *81*, 1049; Schomburg, D.; Sheldrick, W. S. *Acta Cryst.* **1976**, *B32*, 1021; Hellwinkel, D.; Schenk, W.; Blaicher, W. *Chem. Ber.* **1978**, *111*, 1798. c) (N, As): Earley, R. A.; Gallagher, M. J. *J. Chem. Soc. (C)* **1970**, 158. d) (P, C): Jongsma, C.; de Kleijn, J. P.; Bickelhaupt, F. *Tetrahedron* **1974**, *30*, 3465; Vande Griend, L. J.; Verkade, J. G.; Jongsma, C.; Bickelhaupt, F. *Phosphorus* **1976**, *6*, 131; Freijee, F. J. M.; Stam, C. H. *Acta Cryst.* **1980**, *B36*, 1247; van der Putten, N.; Stam, C. H. *ibid.* **1980**, *B36*, 1250. e) (P, P): Weinberg, K. G.; Whipple, E. B. *J. Am. Chem. Soc.* **1971**, *93*, 1801; Weinberg, K. G. *J. Org. Chem.* **1975**, *40*, 3586; Schomburg, D.; Sheldrick, W. S. *Acta Cryst.* **1975**, *B31*, 2427; Sørensen, S.; Jakobsen, H. J. *Org. Magn. Resonance* **1977**, *9*, 101. f) (As, C): Vermeer, H.; Kevenaar, P. C. J.; Bickelhaupt, F. *Liebigs Ann. Chem.* **1972**, *763*, 155; van Rooyen-Reiss, C.; Stam, C. H. *Acta Cryst.* **1980**, *B36*, 1252; Smit, F.; Stam, C. H. *ibid.* **1980**, *B36*, 1254. g) (As, As): McCleland, N. P.; Whitworth, J. B. *J. Chem. Soc.* **1927**, 2753. h) (Sb, C): Jongsma, C.; de Kok, J. J.; Weustink, R. J. M.; van der Ley, M.; Bulthuis, J.; Bickelhaupt, F. *Tetrahedron*, **1977**, *33*, 205. h) (Sb, Sb): Mistry, T. K.; Massey, A. G. *J. Organometal. Chem.* **1981**, *209*, 45; Al-Jabar, N. A. A.; Massey, A. G. *ibid.* **1984**, *276*, 331; Al-Jabar, N. A. A.; Massey, A. G. *ibid.* **1985**, *287*, 57. i) (Bi, Bi): Cullen, W. R.; Wu, A. W. *J. Fluorine Chem.* **1976**, *8*, 183.

3. a) Chernyshev, E. A.; Komalenkova, N. G.; Shashkov, I. A.; Nosova, V. M. *Metalloorg. Khim.* **1990**, *3*, 1187; *Chem. Abstr.* **1991**, *114*, 102174z. b) Recently Dr. M. Takahashi of Ibaraki University has succeeded in the preparation of disila-, phosphasila- and germasilatriptycenes; private communication.

4. Ishii, A.; Kodachi, M.; Nakayama, J.; Hoshino, M. *J. Chem. Soc., Chem. Commun.* **1991**, 751.

5. Allen, D. W.; Taylor, B. F. *J. Chem. Soc., Dalton Trans.* **1982**, 51 and references cited therein.

6. All new compounds gave satisfactory analytical data. Selected spectral data of **10** are as follows: ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6H), 2.38 (s, 6H), 2.53 (s, 12H), 6.63 (m, 2H), 6.72 (m, 4H), 7.15 (dd, J=3.6 (H-H), 9.7 (H-P) Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 0.33 (CH_3), 15.2 (CH_3), 15.5 (CH_3), 126.6 (d, $J_{C\text{-}P}$=13.9 Hz, CH), 130.5 (d, $J_{C\text{-}P}$=13.4 Hz, CH), 135.0 (d, $J_{C\text{-}P}$=11.8 Hz, CH), 138. 0 (d, $J_{C\text{-}P}$=105.3 Hz, C), 143.1 (d, $J_{C\text{-}P}$=105.7 Hz, C), 144.5 (d, $J_{C\text{-}P}$=12.0 Hz, C), 149.3 (d, $J_{C\text{-}P}$=4.8 Hz, C), 149.6 (d, $J_{C\text{-}P}$=6.0 Hz, C); MS *m/z* 806 (M^+).

7. Bartlett, P. D.; Meguerian, G. *J. Am. Chem. Soc.* **1956**, *78*, 3710.

8. Bassindale, A. R.; Taylor, P. G.: Reaction Mechanisms of Nucleophilic Attack at Silicon. In *The Chemistry of Organic Silicon Compounds*; Patai, S; Rappoport, Z. Eds.; John Wiley & Sons, Inc.: New York, 1989; Chap. 13, pp. 839-892.

9. Neureiter, N. P.; Bordwell, F. G. *J. Am. Chem. Soc.* **1959**, *81*, 578.

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