Mixed Phosphinine-Ether Macrocycles

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Introduction

It is now well established that the replacement of nitrogen by phosphorus atoms in aromatic structures causes dramatic changes in the resulting electronic properties.[1] Thus, molecules such as phosphinines show a poorer σ-donating ability but an enhanced electron π-accepting power not only with respect to their nitrogen counterparts, pyridines, but also with respect to phosphines. The combination of these two effects proved to be particularly efficient for the stabilization of reduced transition metal centers. Though some advances have been recently achieved in this direction with ligands such as 2,2′-biphosphinines,[2] there is still a lack of phosphinine-based structures able to encapsulate transition metals with various geometries. Two years ago, we developed a successful synthetic approach toward the first sp^2-hybridized phosphorus macrocycles, the silacalix[*n*]phosphinines ($n = 3$ or 4, *n* meaning the number of phosphinine subunits).[3,4]

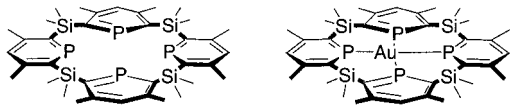
As part of a program aimed at devising access to more flexible structures having different cavity sizes, we explored the synthesis of a new class of macrocycles including two phosphinines subunits and two or four ether functions.[5,6] Herein, we report on these results.

Results and Discussion

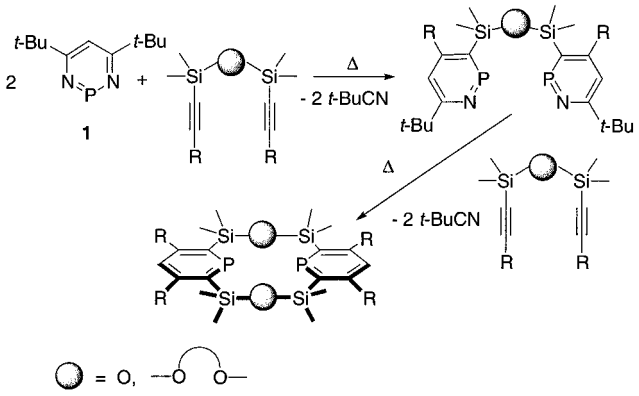
Following a strategy similar to the one devised for the synthesis of silacalix[*n*]phosphinines,[3] we investigated the reactivity of 1,3,2-diazaphosphinines toward silyl-substituted diynes incorporating one or two ether functions. As previously noted, the presence of silyl groups at the alkyne moieties is necessary to ensure a complete regioselectivity in the cycloaddition processes.[7] The general route of this "one-pot" synthesis is presented in Scheme 1. In a first step, 1 equiv of the selected diyne is reacted with 2 equiv of 1,3,2-diazaphosphinine to afford a bis(1,2-azaphosphinine) intermediate which did not need to be isolated. In the second step, which has to be performed under dilute conditions to minimize the formation of linear oligomers, the cavity is closed by reacting a second equivalent of diyne.

All of our experiments were conducted with the readily available 4,6-bis(*tert*-butyl)-1,3,2-diazaphosphinine **1**.[8] The three diynes **2**, **3**, and **4** were synthesized in excellent yields by reacting (phenylethynyl)chlorodimethylsilane[9] with water or with the corresponding 1,2- or 1,3-diols in THF, respectively (Scheme 2). Whereas diynes **3** and **4** were previously unknown, compound **2** had already been

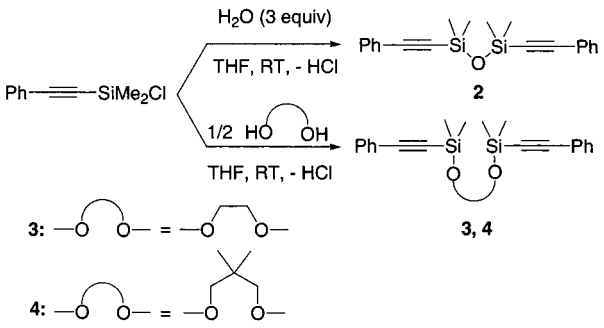
Chart 1



Scheme 1



Scheme 2



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(2) (a) Le Floch, P.; Mathey, F. *Coord. Chem. Rev.* **1999**, *179*−*180*, 771. (b) Rosa, P.; Mézailles, N.; Ricard, L.; Mathey, F.; Le Floch, P. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 1823.

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(4) Mézailles, N.; Avarvari, N.; Maigrot, N.; Ricard, L.; Mathey, F.; Le Floch, P.; Cataldo, L.; Berclaz, T.; Geoffroy, M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3194.

(5) For references concerning the synthesis of macrocycles including phosphorus, see: (a) Pabel, M.; Wild, S. B. In *Comprehensive Heterocyclic Chemistry II*; Katritsky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: New York, 1996; Vol. 9, p 947. (b) Caminade, A.-M.; Majoral, J. P. *Chem. Rev.* **1994**, *94*, 1183.

(6) For references concerning the synthesis of macrocycles including oxygen atoms (ethers), see: (a) Dietrich, B. In *Comprehensive Heterocyclic Chemistry II*; Katritsky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: New York, 1996; Vol. 9, p 809. (b) Gokel, G. W.; Fedders, M. F. In *Comprehensive Heterocyclic Chemistry II*; Katritsky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: New York, 1996; Vol. 9, p 863.

(7) For a theoretical discussion concerning the mechanism of Diels−Alder reactions between 1,2-aza and 1,3,2-diazaphosphinines with alkynes, see: Frison, G.; Sevin, A.; Avarvari, N.; Mathey, F.; Le Floch, P. *J. Org. Chem.* **1999**, *5*, 2109.

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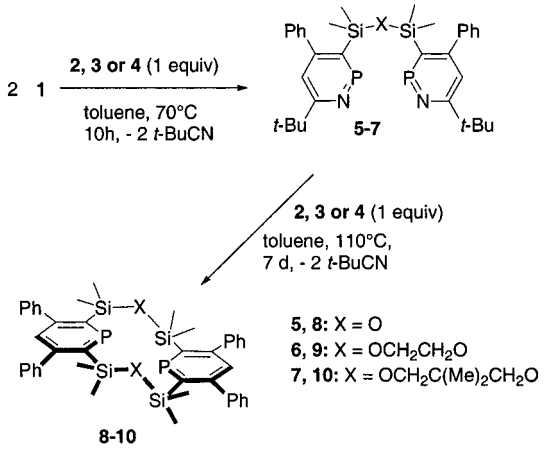
Scheme 3



synthesized through the reaction of copper(I) phenylethynilide with 1,3-dichlorotetramethyldisiloxane with a lower yield (34%).[10] New diynes **3** and **4** proved to be difficult to obtain in pure form either by distillation or classical solvent extraction. Attempts to purify them by chromatographic separation resulted in loss of large amounts of compound (more than 40%). Therefore, the crude products were used in subsequent steps, their purity being estimated to 97% by ^{1}H and ^{13}C NMR spectroscopy.

Reaction of diazaphosphinine **1** with diynes proceeded cleanly in toluene at 70 °C to afford bis-azaphosphinines **5**−**7**, which were only identified by ^{31}P NMR spectroscopy. As previously mentioned, these intermediates were not isolated because of the high reactivity of the P=N double bond toward moisture. Each compound appears as a singlet at very similar chemical shifts (δ = 305.6 ppm for **5**, 306.2 ppm for **6** and 306.8 ppm for **7**). The ring-closing step requires high dilution conditions to minimize the formation of oligomers, and a series of experiments showed the ideal concentration to be 7×10^{-3} mol/L. We also found that reduction of the volume to maintain a steady concentration of reagents is essential for the success of these cyclizations. In each case, at least 7 days were necessary to achieve a total conversion (Scheme 3).

Due to the presence of siloxy groups, macrocycles **8**−**10** were found to be moisture sensitive and their purification by chromatography proved to be difficult (loss of about 30%). Fortunately, they were found to be poorly soluble in acetone and methanol and thus were easily separated from oligomers. Macrocycle **8** was recovered with a yield of 50% and **9** and **10** with yields of 25%. Interestingly, we noted that formation of **8** is favored with regards to that of oligomers. Though no mechanistic studies have been performed yet, we believe that this result is partially explained by the reduced flexibility of intermediate **5** compared to **6** and **7**. Formulations of these new macrocycles were confirmed by NMR techniques, mass spectroscopy, elemental analysis and X-ray diffraction studies in all cases. As expected, the ^{1}H and ^{13}C NMR data of compound **8** show a AXX′ spin-system pattern due to the proximity of the two phosphinine nucleus (^6J(P−P) ≠ 0 Hz). On the contrary in spectra of **9** and **10** no coupling is observed because of the remoteness of the two subunits. X-ray diffraction study reveal that, in each case, the molecule presents a center of symmetry and the two phosphinine rings are located in two parallel planes. However this particular conformation is not maintained in solution and **9** as well as **8** and **10** are totally fluxional (all $SiMe_2$ and CH_2 groups of the spacer group being magnetically equivalent in ^{1}H and ^{13}C NMR).

In summary, we report a one-pot synthesis of a new class of phosphinine-based macrocycles incorporating ether-containing linkers of variable length. Future work will focus on their use in coordination chemistry and catalysis either as chelate (in the case **8**) or as encapsulating ligand (**9** and **10**).

Experimental Section

Starting Materials and General Procedures. All reactions were routinely performed under an inert atmosphere of nitrogen by using Schlenk techniques and dry deoxygenated solvents. Dry THF, hexanes, and toluene were obtained by distillation from Na/benzophenone. Dry Celite was used for filtration. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants are given in hertz. Mass spectra were obtained at 70 eV with a HP 5989 B spectrometer coupled a with HP 5890 chromatograph by the direct inlet method. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. Elemental analyses were performed by the "Service d'analyze du CNRS", at Gif sur Yvette, France.

Synthesis of 1,3-Bis(phenylethynyl)tetramethyldisiloxane 2. Water (1 mL, 55.6 mmol) was added dropwise to a solution of phenylethynyldimethylchlorosilane (5.75 g, 29 mmol) in THF (50 mL) at room temperature. After 2 h, magnesium sulfate was added, and the reaction was stirred for 1 h. After filtration and evaporation of the solvent, diyne **2** was recovered as a colorless oil that was used without any further purification. Yield: 3.7 g (78%). For characterizations see ref 10.

General Procedure for the Synthesis of Diynes 3 and 4. Glycol or 2,2-dimethyl-1,3-propanediol (5.1 mmol) was added dropwise to a solution of phenylethynyldimethylchlorosilane (2.0 g, 10.30 mmol) in THF at room temperature. After the complete evaporation of HCl gas, the solvent was evaporated and diynes **3** and **4** were recovered as a colorless oils and used without any further purification.

1,2-Bis(phenylethynyldimethylsiloxy)ethane 3. Yield: 3.70 g (95%). ^{1}H NMR ($CDCl_3$): δ 0.35 (s, 12H, 2 $SiMe_2$), 3.90 (s, 4H, CH_2−O), 7.28−7.50 (m, 10H, CH of C_6H_5). ^{13}C NMR ($CDCl_3$): δ 0.7 (2 $SiMe_2$), 65.0 (CH_2−O), 92.1 (≡CPh), 105.8 (s, ≡CSi), 123.1−132.6 (C_6H_5). MS: *m*/*z* 378 (M, 100).

1,3-Bis(phenylethynyldimethylsiloxy)-2,2-dimethylpropane 4. Yield: 4.11 g (95%). ^{1}H NMR ($CDCl_3$): δ 0.32 (s, 12H, 2 $SiMe_2$), 0.91 (s, 6H, 2 Me), 3.50 (s, 4H, CH_2O), 7.28−7.50 (m, 10H, CH of C_6H_5). ^{13}C NMR ($CDCl_3$): δ 0.7 (2 $SiMe_2$), 38.0 (s, Me), 69.6 (CH_2O), 92.8 (≡CPh), 105.6 (s, ≡CSi), 123.5−132.7 (C_6H_5). MS: *m*/*z* 420 (M, 100).

General Procedure for Syntheses of Macrocycles 8−10. Diyne **2**, **3**, or **4** (1 mmol) was added at room temperature to a solution of diazaphosphinine **1** (2 mmol) in toluene (10 mL). The resulting solution was then heated at 70 °C, and the formation of intermediates **5**, **7**, or **8** was monitored by ^{31}P NMR spectroscopy. After 10 h, the reactions were complete, and a second equivalent of diyne (1 mmol) was added. The volume of the solution was made up to 120 mL by adding toluene, and the mixture was heated at reflux. The formation of macrocycles was monitored by ^{31}P NMR spectroscopy. To maintain a steady concentration of the intermediate and diyne, small volumes (approximately 20 mL) of solvent were evaporated each day. After 7 days, the intermediates had disappeared indicating the end of the reaction. The resulting mixture was then quickly filtered through silica gel with toluene as eluent. After evaporation of toluene, addition of acetone (20 mL) to the brown residues caused precipitation of macrocycles. After filtration and wash-

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ings with acetone (2 × 5 mL) and methanol (2 × 5 mL), macrocycles **8**−**10** were recovered as white powders.

8. Yield: 0.38 g (50%). Mp: 220 °C dec. ^{31}P NMR ($CDCl_3$): δ 281.5 (s). ^{1}H NMR ($CDCl_3$): δ 0.08 (s, 24H, $SiMe_2$), 7.40−7.50 (m, 21H, C_6H_5 and H_4 of phosphinines). ^{13}C NMR ($CDCl_3$): δ 2.9 (s, $SiMe_2$), 128.2−131.0 (m, CH of C_6H_5), 131.6 (virtual t, AXX′, ΣJ(C−P) = 23.4, C_4 of phosphinines), 146.5 (s, C_{ipso} of C_6H_5), 153.3 (virtual t, AXX′, ΣJ(C−P) = 12.3, $C_{3,5}$ of phosphinines), 161.2 (AXX′, ΣJ(C−P) = 195.5, $C_{2,6}$ of phosphinines). MS: *m*/*z* 757 (M, 100). Anal. Calcd for $C_{42}H_{46}O_2P_2Si_4$: C, 66.63; H, 6.12. Found: C, 66.48; H, 6.21.

9. Yield: 0.21 g (25%). Mp: 220 °C dec. ^{31}P NMR ($CDCl_3$): δ 279.7 (s). ^{1}H NMR ($CDCl_3$): δ 0.07 (s, 24H, 4 × $SiMe_2$), 3.90 (s, 8H, 4 × OCH_2), 7.31−7.37 (m, 22H, 4 × C_6H_5 and H_4 of phosphinines). ^{13}C NMR ($CDCl_3$): δ 1.5 (s, $SiMe_2$), 64.7 (s, OCH_2), 128.2−129.6 (m, CH of C_6H_5), 133.5 (d, ^3J(C−P) = 20.6, C_4 of phosphinine), 145.4 (s, C_{ipso} of C_6H_5), 154.5 (d, ^2J(C−P) = 10.9, $C_{3,5}$ of phosphinines), 163.6 (d, ^1J(C−P) = 89.5, $C_{2,6}$ of phosphinines). MS: *m*/*z* 846 (M, 100). Anal. Calcd for $C_{46}H_{54}O_4P_2Si_4$: C, 63.57; H, 6.44. Found: C, 63.46; H, 6.38.

10. Yield: 0.23 g (25%). Mp: 220 °C dec. ^{31}P NMR ($CDCl_3$): δ 279.7 (s). ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 24H, 4 × $SiMe_2$), 0.90 (s, 12H, Me), 3.60 (s, 8H, 4 × OCH_2), 7.30 (s, 2H, H_4 of phosphinines), 7.40−7.50 ((m, 20H, 4 × C_6H_5). ^{13}C NMR ($CDCl_3$): δ 1.1 ($SiMe_2$), 22.3 (s, Me), 38.4 (s, *C*Me_2), 69.0 (s, OCH_2), 128.1−129.8 (m, CH of C_6H_5), 133.1 (d, ^3J(C−P) = 20.1, C_4 of phosphinine), 146.1 (s, C_{ipso} of C_6H_5), 154.3 (d, ^2J(C−P) = 10.6, $C_{3,5}$ of phosphinines), 163.9 (d, ^1J(C−P) = 89.9, $C_{2,6}$ of phosphinines). MS: *m*/*z* 930 (M, 100). Anal. Calcd for $C_{52}H_{66}O_4P_2Si_4$: C, 67.20; H, 7.16. Found: C, 67.12; H, 7.09.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra of compounds **3** and **4**, X-ray data, and an ORTEP view of macrocycle **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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