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Synthesis of New Chiral $\sigma^2\lambda^2$-Phosphenium Cations

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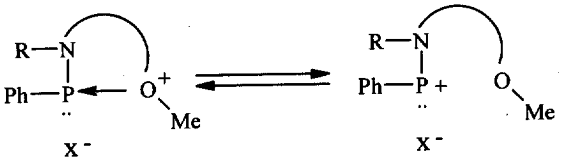
Abstract : The synthesis of two new chiral $\sigma^2\lambda^2$-phosphenium cations **3** and **9** bearing proximal methoxy groups and their corresponding phosphine-borane adducts is reported . Phosphenium **9** has been successfully used in a chelotropic cycloaddition reaction with 2,3-dimethyl butadiene leading to the formation of a new $\sigma^4\lambda^4$-adduct.

Keywords : Chiral $\sigma^2\lambda^2$-Phosphenium Cations ; Organophosphorus chemistry ; Cycloaddition reaction

In the last few years, there was an increasing attention for the synthesis of a new class of cationic species and principally those coming from Si[1], Ge[2], Sn[3], As[4] and P[5] compounds. Thus, the phosphorus analogues $\sigma^2\lambda^2$-phosphenium cations have been well studied. The presence of a vacant orbital and a lone electron pair confers to these amphoteric cationic derivatives a great diversity in reactivity in organic and in coordination chemistry[6]. In this area, Kee *et al.* have recently reported the synthesis of the first phosphenium compounds from chiral C_2 symmetry (1*R*,2*R*)-1,2-diaminocyclohexane[7].

This work prompt us to report our results dealing with the synthesis of two new chiral phosphenium compounds and their application in organic synthesis[8]. These chiral phosphenium compounds have the distinctive feature to involve a Lewis acid base interaction between the electrophilic phosphorus atom and a proximal methoxy group. Such an interaction can play a determining role on the stability of these super-reactive species and their use as chiral Lewis acid catalysts (Scheme 1)[9].



Scheme 1

Phosphenium cation **3** derived from (*S*)-methoxy methyl pyrrolidine **1** has been synthesized according to a classical procedure as outlined below (Scheme 2)[10].

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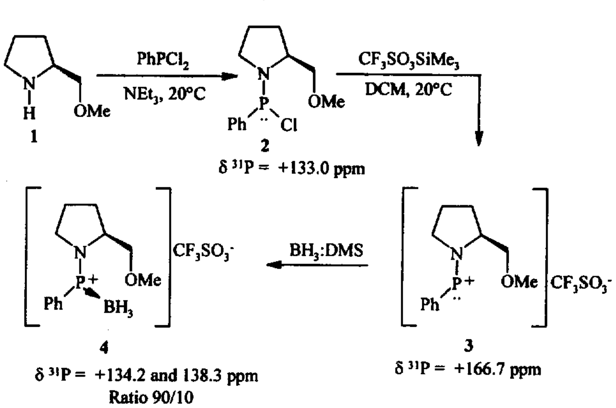
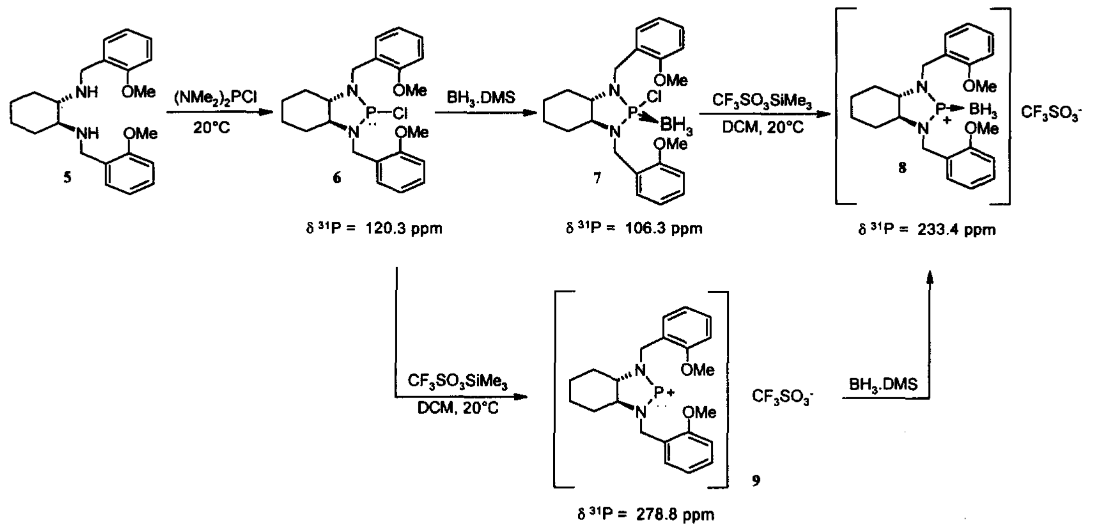


Scheme 2

An equimolar mixture of dichlorophenylphosphine (3.3g, 18 mmole), (*S*)-methoxy methyl pyrrolidine (2.1g, 18 mmole) in THF (15 mL) is stirred at room temperature in presence of 2 equiv. of NEt_3 during 4h. Subsequent treatment of the corresponding chlorophosphine **2** by $CF_3SO_3SiMe_3$ led to the corresponding phosphenium compound **3** clearly characterized by ^{31}P NMR spectroscopy[10]. A single resonance signal is observed at δ +166.7 ppm in the range expected for two-coordinate phosphenium cations[6]. The corresponding more stable phosphenium-borane cation has been also isolated by column chromatography in 80% chemical yield as a mixture of the two diastereomers in a ratio 90/10. This diastereoselectivity probably results from a tetracoordinated chiral phosphorus center due to the interaction described above. This mixture has been successfully storred under nitrogen atmosphere for one month, but it has not be able to determine the absolute configuration at the phosphorus atom of the major diastereomer formed. This compound has been used as catalyst (3 mol%) in the enantioselective reduction of acetophenone by $BH_3{:}SMe_2$. Thus, due to its electrophilic properties **4** has appeared to be an efficient catalyst leading in few minutes at -10°C in toluene to 1-phenyl ethanol in 90% yield and in *20% ee*. It is noteworthy that it was the first time to our knowledge that such an organophosphorus compound has been used as an asymmetric catalyst.

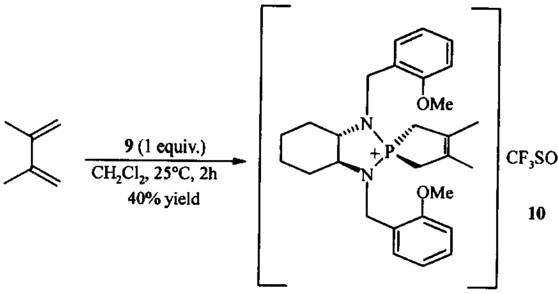
An other phosphenium cation **9** has been synthesized from chiral diamine **5** possessing a C_2 symmetry[11] (Scheme 3).



Scheme 3

Generally obtained by treatment of PCl_3 by 1 equiv. of the desired chiral diamine, this reaction presents the disadvantage to led to the formation of various inseparable phosphorus compounds. Thus, upon work up the reaction mixture gave a mediocre yield (20 %) in **9**. This contrast with the rapid and excellent conversion of diamine **5** in the presence of $ClP(NMe_2)_2$. Indeed, the reaction was over within an hour at room temperature but to our surprise, the chlorodiazaphospholidine compound **6** was formed in virtually quantitative yield. This reaction occurs quantitatively in CH_2Cl_2 at 0°C in the absence of NEt_3. The rapid formation of **6** suggests that this exchange reaction probably proceeds by oxidation of –NH- function of **5** on $ClP(NMe_2)_2$ and reductive elimination of Me_2NH. According to the procedure applied above, the phosphenium **9** and the corresponding borane complex **8** have been easily prepared in good chemical yield (88 and 83% respectively)[11]. Phosphenium cation **9** is relatively stable to air and moisture due to the presence of the methoxy group stabilizing the phosphorus atom. It is noteworthy that the corresponding phosphenium borane adduct **8** has been prepared following two possible pathways in 60% yield.

Due to its high reactivity, phosphenium **9** has been successfully applied in a chelotropic cycloaddition reaction with 2,3-dimethyl butadiene in dichloromethane at room temperature[12]. The expected $\sigma^4\lambda^4$-adduct **10** has been obtained in 40% yield and clearly characterized by NMR spectroscopy[13].



10

δ ^{31}P = 33.6 ppm

Scheme 4

In summary, we have reported the synthesis of two new phosphenium compounds and the first application of such compounds in a cycloaddition reaction. Further studies are underway to promote this methodology and examine the potential of chiral phosphenium salts in various asymmetric synthesis, coordination chemistry and catalysis.

References and Notes

(1) (a) Johannsen, M.; Jorgensen, K. A.; Helmchen, G. *J. Am. Chem. Soc.* **1998**, *120*, 7637-7638. (b) Heinicke, J. ; Oprea, A. ; Kindermann, M. K. ; Karpati, T. ; Nyulaszi, L. ; Veszpremi, T. *Chem. Eur. J.* **1998**, *4*, 541-545. (c) West, R. ; Buffy, J. J. ; Haaf, M. ; Müller, T. ; Gehrhus, B. ; Lappert, M. F. ; Apeloig, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1639-1640.

(2) Suzuki, H. ; Okabe, K. ; Uchida, S. ; Watanabe, H. ; Goto, M. *J. Organomet. Chem.* **1996**, *509*, 177-183.

(3) Nakazawa, H. ; Yamaguchi, Y. ; Miyoshi, K. *Organometallics* **1996**, *15*, 1337-1339.

(4) Burford, N. ; Clyburne, J. A. C. ; Losier, P. ; Parks, T. M. ; Cameron, T. S. *Phosphorus, Sulfur, Silicon* **1994**, *93*, 301-305.

(5) (a) Dyer, P. ; Baceiredo, A. ; Bertrand, G. *Inorg. Chem.* **1996**, *35*, 46. (b) Guerret, O.; Bertrand, G. *Acc. Chem. Res.* **1997**, *30*, 486.

(6) Cowley, A. H. ; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367.

(7) Jones, V. A. ; Thornton-Pett, M. ; Kee, T. P. *J. Chem. Soc., Chem. Commun.* **1997**, 1317-1318.

(8) Brunel, J. M. *Thesis*, Aix-Marseille, **1994**.

(9) Santelli, M.; Pons, J. M. *Lewis Acids and Selectivity in Organic Synthesis*, CRC Press : Boca Raton, **1995**. (b) Corey has reported the synthesis of new cationic oxazaborinane with an interaction $[R'_2B \leftarrow N^+R_3]$. This new class of super-reactive chiral Lewis acid catalysts were used in the asymmetric Diels-Alder reaction. Hayashi, Y.; Rohde, J. J.; Corey, E. J. *J. Am. Chem. Soc.* **1996**, *118*, 5502-5503.

(10) **3** : Viscous oil ; $[\alpha]^{20}_D = -45$ ($c = 1$, CH_2Cl_2) ; ^1H NMR δ (ppm, $CDCl_3$) 1.75-2.97 (m, 4H), 3.13-3.82 (m, 7H), 4.02-4.25 (m, 1H), 7.71-7.88 (m, 5H) ; ^{13}C δ (ppm, $CDCl_3$) 25.0, 29.4, 49.2, 58.2, 59.1, 59.4, 127.8, 128.5(d, J = 13 Hz), 128.8, 129.1, 130.1, 132.4 ; ^{31}P δ (ppm, $CDCl_3$) 166.7. **4** : solid ; mixture of two diastereomers (90/10) ^1H NMR δ (ppm, $CDCl_3$) 1.68-2.97 (m, 4H), 3.10-3.95 (m, 9H), 4.02 (m, 1H), 4.1-4.25 (m, 1H), 7.71-7.96 (m, 5H) ; ^{13}C δ (ppm, $CDCl_3$) 25.2, 26.3, 29.4, 48.9, 49.1, 58.2, 59.3, 59.4, 126.8, 128.5, 128.7, 128.8, 129.1, 130.1, 132.4 ; ^{31}P δ (ppm, $CDCl_3$) 134.2 and 138.3 (q, J = 76.1 Hz); ^{11}B δ (ppm, $CDCl_3$) –41.3 (d, J = 77.8 Hz).

(11) **7** : Oil ; b.p. = 152°C (0.1 mbar) ; $[\alpha]^{20}_D = -39$ ($c = 1$, CH_2Cl_2) ; ^1H NMR δ (ppm, $CDCl_3$) 0.60-2.82 (m, 13H), 3.40-4.32 (m, 10H), 6.36-7.01 (m, 6H), 7.36-7.60 (dd, J = 9 Hz, 2H) ; ^{13}C δ (ppm, $CDCl_3$) 23.7, 24.2, 29.4, 36.2, 36.3, 55.0, 65.8, 66.1, 109.7, 110.3, 120.1, 120.7, 127.1, 128.1, 129.2, 131.3, 156.3 (d, J = 24 Hz) ; ^{31}P δ (ppm, $CDCl_3$) 106.3 (q, 74.5 Hz); ^{11}B δ (ppm, $CDCl_3$) –36.2 (d, J = 75.1 Hz). **8** Viscous oil ; ^1H NMR δ (ppm, $CDCl_3$) 1.36-2.68 (m, 10H), 3.58 (s,6H), 4.20-4.53 (m, 7H), 6.81-7.85 (m, 8H) ; ^{13}C δ (ppm, $CDCl_3$) 25.7, 32.5, 44.7, 52.4 (d, J = 12 Hz), 61.0, 110.8, 119.2 (d, J = 12 Hz), 127.1, 127.4, 125.6, 128.6, 129.2, 155.5 ; ^{31}P δ (ppm, $CDCl_3$) 233.4 (q, 70.3 Hz); ^{11}B δ (ppm, $CDCl_3$) –38.2 (d, J = 69.9 Hz). **9** White solid ; $[\alpha]^{20}_D = -39$ ($c = 1$, CH_2Cl_2) ; ^1H NMR δ (ppm, $CDCl_3$) 1.37-2.60 (m, 10H), 3.69 (s,6H), 4.11-4.46 (ddd, J = 10 Hz, 4H), 6.89-7.8 (m, 8H) ; ^{13}C δ (ppm, $CDCl_3$) 25.7, 31.5, 45.7, 54.4 (d, J = 13 Hz), 61.0, 109.8, 120.2 (d, J = 14 Hz), 127.1, 127.3, 127.6, 128.1, 129.2, 157.5 ; ^{31}P δ (ppm, $CDCl_3$) 278.8.

(12) (a) Regitz, M.; Scherer, O. J. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Georg Thieme Verlag, New-York, **1990**, pp 129-148. (b) Soo Hoo, C. K. ; Baxter, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 7443-7444. (c) Cowley, A. H ; Kemp, R. A. ; Lasch, J. G. ; Norman, N. C. ; Stewart, C. A. *J. Am. Chem. Soc.* **1983**, *105*, 7444-7445.

(13) **10** : Pale yellow solid ; $[\alpha]^{20}_D = -35$ ($c = 1$, CH_2Cl_2) ; ^1H NMR δ (ppm, $CDCl_3$) 1.04-2.80 (m, 20H), 3.91 (s, 3H), 3.93 (s, 3H), 4.90-5.23 (m, 4H), 6.96-7.71 (m, 8H) ; ^{13}C δ (ppm, $CDCl_3$) 23.5, 26.6, 29.8, 30.4, 32.3, 39.2, 47.2, 55.3, 61.0, 100.3, 109.8, 119.2, 121.7, 127.5, 128.2, 129.4, 143.2, 151.3 ; ^{31}P δ (ppm, $CDCl_3$) 33.6.