Heteroatom Chemistry
Volume 6, Number 4, 1995

Synthesis of Onio-, Dionio-, and Trionio-Substituted Phosphines; the Nucleophilic Behavior of DBN and DBU toward Main Group Electrophiles

Ghenwa Bouhadir, Robert W. Reed, Régis Réau, and Guy Bertrand*

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse, Cédex, France

Received 27 December 1994

ABSTRACT

1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) react with chloro- and dichloro-phosphines leading to onio- and dionio-substituted phosphines. Similarly, onio-substituted silicon and tin derivatives are prepared; they are used as onio-substituent transfer reagents in the synthesis of a trionio-substituted phosphine.

INTRODUCTION

Strong nonionic bases [1] play a key role in organic and inorganic synthesis because of the simplicity of handling and mildness of reaction conditions [2]. Before the discovery in the late 1980s that phosphazenes and phosphatranes are extremely strong bases [**1c–h**], amidines such as 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were the strongest neutral bases available [**1a–b**]. DBN and DBU have found many useful applications because of their non-nucleophilic behavior; as examples, they have proved to be superior reagents for dehydrohalogenation reactions and important catalysts in the synthesis of macromolecules [**1a–b**, **2e–g**]. However, several authors have reported unexplained phenomena connected with their use [3], and recently, it has been shown that these so-called "non-nucleophilic strong bases" can indeed exhibit nucleophilic behavior [4,5].

In this article, we wish to report that DBN and DBU react with a variety of main group electrophiles, including low reactive ones, giving a direct entry to onio-substituted phosphorus, tin, and silicon derivatives; the synthesis of di- and trionio-substituted phosphines is also presented.

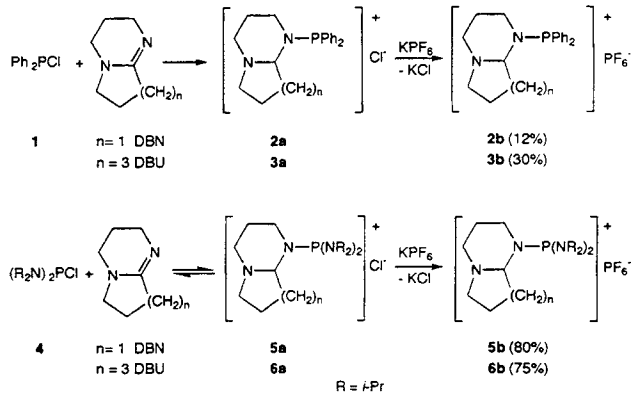
RESULTS AND DISCUSSION

Chlorodiphenylphosphine **1** readily reacts with DBN in dichloromethane solution, affording the cationic phosphine **2a** in 90% yield, as determined spectroscopically (Scheme 1). The presence in the ^{13}C NMR spectrum of a doublet at δ 169.88 (J_{PC} = 33.3 Hz) for the NCN moiety clearly indicates that the bicyclic amidine is bound to the phosphorus atom; furthermore, the ionic structure is proved by an anion exchange reaction with potassium hexafluorophosphate giving derivative **2b** (mp: 193–195°C) in 12% overall isolated yield. Note that the spectroscopic data for **2b** are essentially identical to those of **2a**. Surprisingly, DBN also acts as a nucleophile toward bis(diisopropylamino)chlorophosphine **4**, a bulky and low reactive electrophile. In dichloromethane solution, **4** and DBN are in equilibrium with the corresponding cationic phosphine **5a**. This equilibrium is shifted toward the

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

*To whom correspondence should be addressed.

1042-7163/95/$5.00 + .25

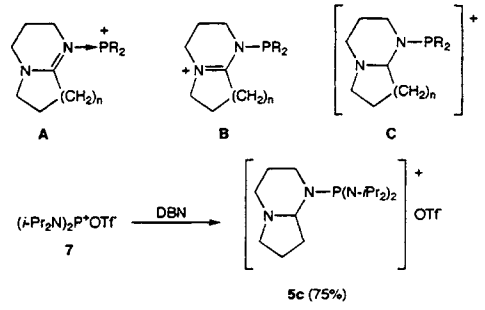


SCHEME 1

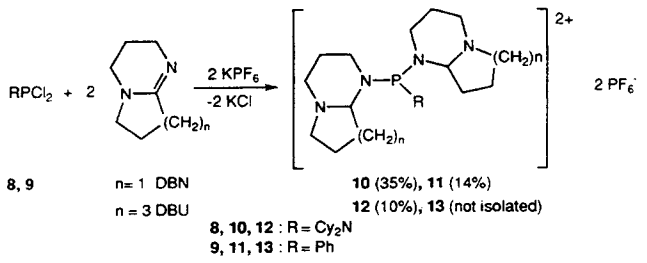
product in acetonitrile, while, by exchanging the chloride for hexafluorophosphate, derivative **5b** (mp: 128–130°C) is obtained in 80% yield (Scheme 1).

The same pattern of reactivity is found with DBU, the adducts being more sensitive than those obtained with DBN. However, onio-substituted phosphines **3b** and **6b** can be isolated and fully characterized. It is important to note that, under the same experimental conditions, 4-dimethylaminopyridine, which is known to react with chlorophosphites or trichlorophosphine to give onio-substituted compounds [6], is inert toward aminochlorophosphine **4**, demonstrating that DBN and DBU are indeed strong nucleophiles.

An X-ray diffraction study performed on **5b** [4] revealed that the structure of these salts is intermediate between those of phosphenium-base adducts **A** [7] and onio-substituted phosphines **B**. The positive charge is delocalized on the cluster (structure **C**), a situation comparable to that of borylium ions in which a divalent boron atom is stabilized by an electron pair donor [8] (Scheme 2). Therefore, it is not surprising that bis(diisopropylamino)-phosphenium trifluoromethanesulfonate **7** [9] reacts with one equivalent of DBN at 0°C in dichloromethane solution affording derivative **5c** (75% yield) (Scheme 2).



SCHEME 2



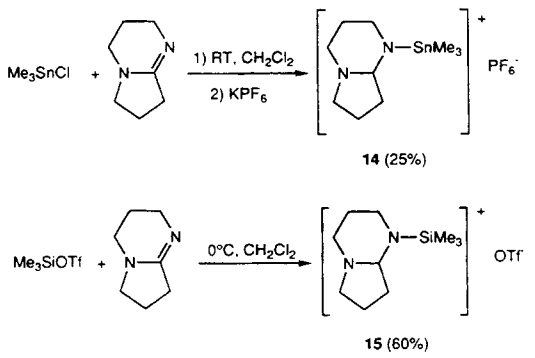
SCHEME 3

The next step was to prepare polycationic species (Weiss-type compounds [6]). Dionio-substituted phosphines **10** and **11** were prepared in 35 and 14% yields, respectively, by treatment of dichlorophosphines **8** and **9** with DBN, followed by an exchange reaction with KPF_6 (Scheme 3). The spectroscopic data for the bicyclic amidine substituents of compounds **10** and **11** are essentially identical, and an X-ray diffraction study performed on **10** [4] revealed that here also the positive charges are strongly delocalized. These derivatives formally result from the interaction of two DBN molecules with monocoordinated phosphorus dications (RP^{2+}) [10]. The DBU adducts **12** and **13** were prepared according to the same procedure. As already observed in the monocationic series, they are less stable than their DBN analogs; as an example, derivative **13** could not be isolated in pure form (Scheme 3).

The addition of three equivalents of DBN to a dichloromethane solution of trichlorophosphine led to a complicated mixture, and despite an exchange reaction with KPF_6, all attempts to isolate the desired trionio phosphine failed. Thus, in order to overcome this problem, we searched for "onio-substituent transfer agents," and, taking into account the high reactivity of tin- and silicon-nitrogen bonds, tin and silicon onio-substituted derivatives **14** and **15** seemed to be good candidates. Successive addition of one equivalent of DBN and KPF_6 to a dichloromethane solution of trimethylchlorostannane afforded derivative **14**, isolated in 25% yield after crystallization (mp = 77–79°C), while trimethylsilyltrifluoromethanesulfonate reacted with DBN at 0°C giving salt **15** (mp = 56–57°C) in 60% yield (Scheme 4). These two compounds are extremely moisture sensitive, the silyl salt **15** being more stable than its stannyl analog **14**.

In order to check the ability of compounds **14** and **15** to transfer their onio-substituent, they were added to chloro- and dichloro-phosphines **4** and **8**. Indeed, the corresponding onio-substituted phosphines were formed in quantitative yields according to NMR spectroscopy.

More interestingly, and in contrast with the reaction of PCl_3 with DBN, trionio-substituted phosphine **16** was cleanly obtained by treating PCl_3 with



SCHEME 4

three equivalents of the silyl derivative **15** at 0°C. After crystallization from a CH_3CN/Et_2O mixture, the tricationic salt **16** was isolated in 40% yield (mp: 110–113°C). The elemental analysis confirms that three molecules of DBN are present in the molecule. The amidine substituents are magnetically equivalent and the NCN carbons appear as a doublet at δ 169.05 (J_{PC} = 42.1 Hz) in the ^{13}C spectrum (Scheme 5).

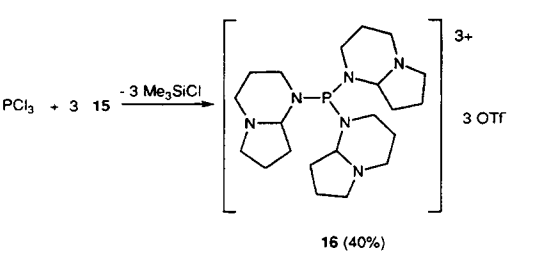
The reactivity of the onio-substituted silane **15** toward chlorophosphines opens new perspectives in the synthesis of polyonio-substituted derivatives of main group elements and transition metals.

EXPERIMENTAL

All experiments were performed in an atmosphere of dry argon. Melting points are uncorrected. ^1H, ^{13}C, ^{31}P, ^{119}Sn, and ^{29}Si spectra were recorded on a Brucker AC80, AC200, or WM250 spectrometer. ^1H, ^{13}C, and ^{29}Si NMR chemical shifts are reported in parts per million relative to Me_4Si as external standard. ^{31}P and ^{119}Sn NMR downfield chemical shifts are expressed with a positive sign, in parts per million, relative to external 85% H_3PO_4 and Me_4Sn, respectively. Conventional glassware was used.

Representative Procedure for the Synthesis of Derivatives **2–6** *and* **10–12**

An acetonitrile solution (20 mL) of DBN (5.6 mL; 45 mmol) was added dropwise at room temperature to an acetonitrile solution (20 mL) of phosphane **4** (12.0 g; 45 mmol) to afford **5a**. This solution was added slowly at 0°C to an acetonitrile solution (20 mL) of KPF_6 (8.3 g; 45 mmol) and stirred for 24 hours. The precipitated KCl was filtered off, and the solvent removed under vacuum. The products were purified as indicated in the following section.



SCHEME 5

2a: Characterized in solution. ^1H NMR ($CDCl_3$) δ 1.95 (m, 4H), 3.10 (m, 6H), 3.80 (m, 2H), 7.25 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 17.85 (d, J = 5.0 Hz), 19.30 (s), 33.65 (d, J = 25.2 Hz), 42.79 (d, J = 7.4 Hz), 42.29, 55.50, 128.92, 130.62 (s), 132.00 (d, J = 21.4), 169.88 (d, J = 33.3 Hz), the C_{ipso} are not observed. ^{31}P NMR ($CDCl_3$) δ +70.77.

2b: 12% yield. Colorless solid, mp 193–195°C precipitated at room temperature from CH_2Cl_2. ^1H NMR ($CDCl_3$) δ 2.04 (quint, J = 5.7 Hz, 2H), 2.28 (quint, J = 7.1 Hz, 2H), 3.15 (t, J = 5.7 Hz, 2H), 3.43 (m, 4H), 3.93 (t, J = 7.1 Hz, 2H), 7.53 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 17.31 (d, J = 5.7 Hz), 18.76 (s), 33.12 (d, J = 25.2 Hz), 42.46 (d, J = 6.5 Hz), 42.63, 54.99 (s), 128.80 (d, J = 5.8 Hz), 130.50 (s), 130.90 (d, J = 13.0 Hz), 131.82 (d, J = 21.8 Hz), 169.85 (d, J = 33.2 Hz). ^{31}P NMR ($CDCl_3$) δ −144.61 (sept, J = 710.9 Hz), +71.23. Anal. calcd for $C_{19}H_{22}N_2F_6P_2$: C, 50.22; H, 4.88; N, 6.17. Found: C, 50.18; H, 4.89; N, 6.11.

3a: ^{31}P NMR (CH_2Cl_2) δ +71.00.

3b: 30% yield. Colorless crystals, mp 140–143°C crystallized at −40°C from CH_3CN/Et_2O. ^1H NMR ($CDCl_3$) δ 1.80 (m, 8H), 3.21 (m, 2H), 3.54 (m, 4H), 3.74 (m, 2H), 7.57 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 20.46, 22.75, 25.13, 28.26 (s), 31.27 (d, J = 36.2 Hz), 44.04 (d, J = 6.1 Hz), 49.87, 58.08 (s), 129.34 (d, J = 6.6 Hz), 130.83 (s), 131.16 (d, J = 16.1 Hz), 131.99 (d, J = 21.8 Hz), 173.07 (d, J = 26.3 Hz). ^{31}P NMR ($CDCl_3$) δ −144.12 (sept, J = 710.9 Hz) +71.56. Anal. calcd for $C_{21}H_{26}N_2F_6P_2$: C, 52.29; H, 5.43; N, 5.81. Found: C, 52.19; H, 5.50; N, 5.83.

5a: 90% yield, viscous oil, washed three times with Et_2O (3 × 10 mL): ^1H NMR ($CDCl_3$) δ 1.10 (d, J = 6.7 Hz, 12H), 1.73 (d, J = 6.7 Hz, 12H), 2.21 (m, 4H), 3.08 (m, 2H), 3.54 (m, 8H), 3.87 (t, J = 7.3 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 18.75 (d, J = 5.7 Hz), 19.51 (s), 23.76 (d, J = 7.9 Hz), 23.91 (d, J = 7.3 Hz), 31.15 (d, J = 27.6 Hz), 42.52 (d, J = 3.4 Hz), 43.64 (s), 47.71 (d, J = 14.4 Hz), 53.83 (s), 164.94 (d, J = 30.9 Hz). ^{31}P NMR ($CDCl_3$) δ +108.56.

5b: 80% yield. Colorless crystals, mp 128–130°C crystallized at −40°C from CH_2Cl_2/Et_2O. ^1H NMR ($CDCl_3$) δ 1.16 (d, J = 7.0 Hz, 12H), 1.22 (d, J = 7.0 Hz, 12H), 2.01 (m, 2H), 2.15 (m, 2H), 3.11 (t, J = 7.0 Hz, 2H), 3.46 (sept d, J = 7.0 and 13.1 Hz, 4H), 3.53 (m, 2H), 3.72 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 18.60 (d, J = 6.1 Hz), 19.31 (s), 23.79 (d, J = 7.2 Hz), 24.01 (d, J = 7.2 Hz), 31.55 (d, J = 27.2 Hz), 42.52 (d, J = 3.2 Hz), 43.14 (s), 47.81 (d, J = 14.2 Hz), 53.53 (s), 165.04 (d, J = 31.1 Hz). ^{31}P NMR ($CDCl_3$) δ −144.5 (sept, J = 711.2 Hz), +108.90. Anal. calcd

for $C_{19}H_{40}N_4F_6P_2$: C, 45.56; H, 8.05; N, 11.19. Found: C, 45.59; H, 8.10; N, 11.13.

6a: ^{31}P NMR (CH_2Cl_2) δ +108.71.

6b: 75% yield. Colorless crystals, mp 100°C crystallized at −40°C from CH_2Cl_2/Et_2O. ^1H NMR ($CDCl_3$) δ 1.24 (d, J = 7.0 Hz, 12H), 1.30 (d, J = 7.0 Hz, 12H), 1.71 (m, 6H), 2.10 (m, 2H), 2.78 (m, 2H), 3.41 (sept d, J = 7.0 and 14.1 Hz, 4H), 3.20 (m, 2H), 3.72 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 20.32, 23.33 (s), 23.50 (d, J = 7.2 Hz), 23.95 (d, J = 7.2 Hz), 25.63, 28.21 (s), 29.23 (d, J = 26.2 Hz), 42.49 (d, J = 3.2 Hz), 47.80 (d, J = 14.3 Hz), 49.12, 54.54 (s), 168.15 (d, J = 21.6 Hz). ^{31}P NMR ($CDCl_3$) δ −144.51 (sept, J = 711.8 Hz), +109.63. Anal. calcd for $C_{21}H_{44}N_4F_6P_2$: C, 47.72; H, 8.39; N, 10.61. Found: C, 47.69; H, 8.46; N, 10.73.

5c: 75% yield. Colorless crystals, mp 125°C crystallized at −40°C from CH_2Cl_2/Et_2O. ^1H NMR ($CDCl_3$) δ 1.19 (d, J = 7.0 Hz, 12H), 1.22 (d, J = 7.0 Hz, 12H), 2.04 (m, 2H), 2.10 (m, 2H), 3.14 (t, J = 7.0 Hz, 2H), 3.50 (sept d, J = 7.0 and 13.1 Hz, 4H), 3.57 (m, 2H), 3.72 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 18.61 (d, J = 6.1 Hz), 19.21 (s), 23.77 (d, J = 7.2 Hz), 23.81 (d, J = 7.2 Hz), 31.05 (d, J = 27.3 Hz), 42.42 (d, J = 3.2 Hz), 43.21 (s), 47.77 (d, J = 14.2 Hz), 53.04 (s), 120.02 (q, J = 320.2 Hz), 165.21 (d, J = 31.1 Hz). ^{31}P NMR ($CDCl_3$) δ +108.93. Anal. calcd for $C_{20}H_{40}N_4F_3O_3PS$: C, 47.61; H, 7.99; N, 11.10. Found: C, 47.59; H, 8.03; N, 11.13.

10: 35% yield. Colorless crystals, mp 180–183°C crystallized at −40°C from THF/Et_2O. ^1H NMR (CD_3CN) δ 1.15–1.88 (m, 20H), 2.08 (m, 4H), 2.20 (m, 4H), 3.01 (m, 2H), 3.15 (m, 4H), 3.46 (m, 8H), 3.69 (m, 4H). ^{13}C NMR (CD_3CN) δ 18.30 (d, J = 5.9 Hz), 19.23, 25.20, 26.35 (s), 32.13 (d, J = 26.2 Hz), 34.63 (d, J = 7.4 Hz), 42.59 (s), 43.31 (d, J = 3.7 Hz), 55.14 (s), 58.15 (d, J = 11.6 Hz), 167.75 (d, J = 35.1 Hz). ^{31}P NMR (CD_3CN) δ −145.06 (sept, J = 706.8 Hz), +108.82. Anal. calcd for $C_{26}H_{46}N_5F_{12}P_3$: C, 41.66; H, 6.18; N, 9.34. Found: C, 41.69; H, 6.23; N, 9.37.

11: 14% yield. Pale yellow solid, mp 214–217°C precipitated at −40°C from CH_2Cl_2/Et_2O. ^1H NMR (CD_3CN) δ 2.12 (m, 8H), 3.18 (m, 4H), 3.50 (m, 8H), 3.72 (m, 4H), 7.37 (m, 5H). ^{13}C NMR (CD_3CN) δ 18.13 (d, J = 5.7 Hz), 19.08 (s), 34.20 (d, J = 25.1 Hz), 44.05 (s), 44.93 (d, J = 5.9 Hz), 56.38, 130.07 (s), 130.48 (J = 22.0 Hz), 132.07 (s), 171.49 (d, J = 38.3 Hz), the C_{ipso} are not observed. ^{31}P NMR (CD_3CN) δ −143.79 (sept, J = 708.6 Hz), +102.28. Anal. calcd for $C_{20}H_{29}N_4F_{12}P_3$: C, 37.16; H, 4.52; N, 8.67. Found: C, 37.23; H, 4.57; N, 8.71.

12: 10% yield. Colorless crystals, mp 212–216°C crystallized at −40°C from CH_2Cl_2/Et_2O. ^1H NMR (CD_3CN) δ 1.00–2.25 (m, 36H), 3.25–3.75 (m, 18H). ^{13}C NMR (CD_3CN) δ 20.14 (d, J = 0.9 Hz), 25.49, 26.23, 26.42, 28.53 (s), 28.71 (d, J = 15.2 Hz), 35.13 (d, J = 8.6 Hz), 40.09 (d, J = 3.5 Hz), 47.46 (s), 48.89 (d, J = 5.4 Hz), 54.67 (d, J = 3.1 Hz), 55.45 (d, J = 6.3 Hz), 164.85 (d, J = 9.4 Hz). ^{31}P NMR (CD_3CN) δ −139.21 (sept, J = 706.8 Hz), +99.86. Anal. calcd for $C_{30}H_{54}N_5F_{12}P_3$: C, 44.72; H, 6.75; N, 8.69. Found: C, 44.67; H, 6.70; N, 8.64.

13: ^{31}P NMR (CD_3CN) δ −143.79 (sept, J = 709.6 Hz), +98.28.

Synthesis of Onio-Substituted Stannane and Silane

14: A mixture of dichloromethane solution (20 mL) of DBN (2.9 mL; 23.5 mmol), KPF_6 (4.4 g; 23.9 mmol) and Me_3SnCl (4.7 g; 23.6 mmol) was stirred at −20°C for 2 hours. The solution was allowed to warm to room temperature. After filtration, the solvent was removed under vacuum. Dichloromethane (10 mL) was added, and the solution was filtered and cooled to −40°C. **14** was obtained as white crystals: 25% yield, mp 77–79°C. ^1H NMR (CD_3CN, $CDCl_3$) δ −0.51 (s, J_{117Sn} = 59.1 Hz, J_{119Sn} = 61.3 Hz, 9H), 1.82 (quintlike, J = 6.0 Hz, 2H), 2.12 (quintlike, J = 8.1 Hz, 2H), 2.51 (t, J = 8.1 Hz, 2H), 3.21 (m, 4H), 3.41 (t, J = 8.1 Hz, 2H). ^{13}C NMR (CD_3CN, $CDCl_3$) δ −3.11 (J_{117Sn} = 408.7 Hz, J_{119Sn} = 427.2 Hz), 18.21, 19.14, 31.92, 41.15, 43.02, 52.87, 166.15 (s). ^{119}Sn NMR (CD_3CN, $CDCl_3$) δ +107.12. Anal. calcd for $C_{10}H_{21}N_2F_6Sn$: C, 27.74; H, 4.89; N, 6.47. Found: C, 27.70; H, 4.91; N, 6.42.

15: A dichloromethane solution (10 mL) of Me_3SiOTf (2.2 mL; 12.0 mmol) was added dropwise at room temperature to a dichloromethane solution (10 mL) of DBN (1.5 mL; 12.0 mmol). The solvent was removed under vacuum. **15** was crystallized at −40°C as white needles from CH_2Cl_2/Et_2O: 60% yield, mp 56–57°C. ^1H NMR (CD_3CN, C_6D_6) δ 0.31 (s, 9H), 1.92 (quintlike, J = 6.1 Hz, 2H), 2.02 (quintlike, J = 8.1 Hz, 2H), 2.81 (t, J = 8.1 Hz, 2H), 3.31 (m, 4H), 3.62 (t, J = 8.1 Hz, 2H). ^{13}C NMR (CD_3CN, C_6D_6) δ −0.61, 17.60, 18.23, 31.10, 41.65, 42.32, 53.23 (s), 119.55 (q, J = 321.1 Hz), 167.2. ^{29}Si NMR (CD_3CN, C_6D_6) δ +22.62. Anal. calcd for $C_{11}H_{21}N_2F_3O_3SSi$: C, 38.14; H, 6.11; N, 8.08. Found: C, 38.10; H, 6.11; N, 8.07.

Synthesis of Trionio-Substituted Phosphine **16**

A dichloromethane solution (10 mL) of **15** (2.4 g; 6.9 mmol) was added dropwise at 0°C to a dichloromethane solution (10 mL) of PCl_3 (0.3 mL; 2.3 mmol). The solution was allowed to warm to room temperature, and the solvent was removed under vacuum. **16** was crystallized at room temperature from CH_3CN/Et_2O as white crystals: 40% yield, mp 110–113°C. ^1H NMR (CD_3CN) δ 2.20 (m, 12H), 3.25 (t-like, J = 8.1 Hz, 6H), 3.62 (m, 12H), 3.92 (m, 6H). ^{13}C NMR (CD_3CN) δ 16.20 (d, J = 6.1 Hz), 18.53 (s), 33.23 (d, J = 27.2 Hz), 43.57 (s), 44.12 (d, J = 4.2 Hz), 56.11 (s), 120.21 (q, J = 320.1 Hz), 169.05 (d, J = 42.1 Hz). ^{31}P NMR (CD_3CN) δ +108.92. Anal. calcd for $C_{24}H_{36}N_6F_9O_9PS_3$: C, 33.88; H, 4.27; N, 9.88. Found: C, 33.90; H, 4.21; N, 9.81.

ACKNOWLEDGMENTS

Thanks are due to the Centre Culturel Hariri and the Canada/France Exchange Program for grants to G. Bouhadir and R. W. Reed, respectively, and to Expansia and the CNRS for financial support of this work.

REFERENCES

[1] (a) I. Hermecz, *Adv. Heterocyclic Chem., 42,* 1987, 83; (b) H. Oediger, F. Möller, K. Eiter, *Synthesis,* 1972, 591; (c) R. Schwesinger, C. Hasenfratz, H. Schlemper, L. Walz, E. M. Peters, K. Peters, H. G. von Schnering, *Angew. Chem. Int. Ed. Engl., 32,* 1993, 1361; (d) R. Schwesinger, *Angew, Chem. Int. Ed. Engl., 26,* 1987, 1164; (e) R. Schwesinger, M. Misfeldt, K. Peters, H. G. von Schnering, *Angew. Chem. Int. Ed. Engl., 26,* 1987, 1165; (f) R. Schwesinger, H. Schlemper, *Angew. Chem. Int. Ed. Engl., 26,* 1987, 1167; (g) J. Tang, J. Dopke, J. G. Verkade, *J. Am. Chem. Soc., 115,* 1993, 5015; (h) J. S. Tang, J. G. Verkade, *Tetrahedron Lett., 34,* 1993, 2903.

[2] (a) R. Schwesinger, *Chimia, 39,* 1985, 269; (b) T. Pietzonka, D. Seebach, *Chem. Ber., 39,* 1991, 1837; (c) T. Pietzonka, D. Seebach, *Angew. Chem. Int. Ed. Engl., 31,* 1992, 1481; (d) T. Pietzonka, D. Seebach, *Angew. Chem. Int. Ed. Engl., 32,* 1993, 716; (e) A. H. Cowley, *Acc. Chem. Res., 17,* 1984, 386; (f) D. A. Evans, S. J. Miller, M. D. Ennis, *J. Org. Chem., 58,* 1993, 471; (g) M. L. Morinfox, M. A. Lipton, *Tetrahedron Lett., 34,* 1993, 7899; (h) T. Shimokawa, T. Suzuki, T. Nishikubo, *Polymer J., 26,* 1994, 967.

[3] (a) Th. C. Klebach, R. Lourens, F. Bickelhaupt, *J. Am. Chem. Soc., 100,* 1978, 100; (b) A. H. Cowley, J. E. Kilduff, J. G. Lasch, S. K. Mehrotra, N. C. Norman, M. Pakulski, B. R. Whittlesey, J. L. Atwood, W. E. Hunter, *Inorg. Chem., 23,* 1984, 2582; (c) J. Escudié, C. Couret, H. Ranaivonjatovo, J. Satgé, *J. Chem. Soc. Chem. Commun.,* 1984, 1621; (d) T. R. Juneja, D. K. Garg, W. Schäfer, *Tetrahedron, 38,* 1982, 551; (e) H. O. House, M. B. de Tar, D. Von Derveer, *J. Org. Chem., 22,* 1979, 3793; (f) T. A. Van Der Knapp, F. Bickelhaupt, *Phosphorus Sulfur, 21,* 1984, 227; (g) S. Kim, H. Chang, *Bull. Chem. Soc. Jpn, 58,* 1985, 3669.

[4] For a preliminary account of this work, see R. Reed, R. Réau, F. Dahan, G. Bertrand, *Angew. Chem. Int. Ed. Engl., 32,* 1993, 399.

[5] (a) L. L. McCoy, D. Mal, *J. Org. Chem., 46,* 1981, 1016; (b) R. D. Chambers, A. J. Roche, A. S. Batsanov, J. A. K. Howard, *J. Chem. Soc. Chem. Commun.,* 1994, 2055; (c) W. A. Schenk, P. Urban, E. Dombrowski, *Chem. Ber., 126,* 1993, 679; (d) H. Lammers, P. Cohen-Fernandez, C. Habraken, *Tetrahedron, 50,* 1994, 865.

[6] (a) R. Weiss, S. Engel, *Synthesis,* 1991, 1077; (b) R. Weiss, S. Engel, *Angew. Chem. Int. Ed. Engl., 31,* 1992, 216.

[7] (a) M. Sanchez, M. R. Mazière, L. Lamandé, R. Wolf: in M. Regitz, O. J. Scherer (eds): *Multiple Bonds and Low Coordination in Phosphorus Chemistry,* Thieme, Stuttgart p. 129 (1990); (b) N. Burford, P. Losier, S. V. Sereda, T. S. Cameron, G. Wu, *J. Am. Chem. Soc., 116,* 1994, 6474.

[8] P. Kölle, H. Nöth, *Chem. Rev., 85,* 1985, 399.

[9] (a) A. H. Cowley, M. C. Cushner, J. S. Szobota, *J. Am. Chem. Soc., 100,* 1978, 7784; (b) C. Roques, M. R. Mazière, J. P. Majoral, M. Sanchez, *Tetrahedron Lett., 29,* 1988, 4547.

[10] A. Mehdi: Ph.D. Thesis, University of Montpellier, Montpellier, France, 1994.