Heteroatom Chemistry
Volume 7, Number 2, 1996

Hexamethylhydrazinocyclotriphosphazene $N_3P_3(NMeNH_2)_6$: Starting Reagent for the Synthesis of Multifunctionalized Species, Macrocycles, and Small Dendrimers

Raymond Kraemer, Christophe Galliot, Joëlle Mitjaville, Anne-Marie Caminade, and Jean Pierre Majoral*

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

Received 19 October 1995; Revised 27 November 1995.

ABSTRACT

Hexamethylhydrazinocyclotriphosphazene $N_3P_3(NMe–NH_2)_6$ **1** *is a useful precursor for the synthesis of functionalized hexahydrazones (***3a–f***), multicyclic (***5***) and multimacrocyclic (***7***) species, and small dendrimers (***8*** and* **10***). © 1996 John Wiley & Sons, Inc.*

INTRODUCTION

The synthesis of complex molecular architectures is an area of current research in organic chemistry and always remains a challenge in heteroatom chemistry. Highly sophisticated pathways have been designed, but few methods combine simple reactions, high yields, and easily prepared starting reagents. In this perspective, we have already demonstrated that phospho mono-, di-, and tri-hydrazides are high-performance reagents for the synthesis of macrocycles [1], cryptands or multimacrocyclic species [2], and even dendrimers [3]. We show in this article that the hexahydrazide $N_3P_3(NMe–NH_2)_6$ is also a useful starting reagent for the synthesis of a large variety of functionalized species, from simple hydrazones to multimacrocycles and dendrimers.

RESULTS AND DISCUSSION

The reaction of $N_3P_3(NMe–NH_2)_6$ **1** with aldehydes **2a–f** in tetrahydrofuran (THF) leads, in near quantitative yield, to the synthesis of the corresponding hexafunctionalized hydrazones **3a–f** (Scheme 1). The formation of **3a–f** is characterized by ^{31}P NMR spectroscopy, which shows the expected shielding for the signal of the cyclotriphosphazene ring ($\Delta\delta \approx 12$). Furthermore, ^1H and ^{13}C NMR and IR spectroscopy indicate the disappearance of aldehyde functions on behalf of imine functions, and mass spectrometry confirms in all cases the formation of the hydrazones.

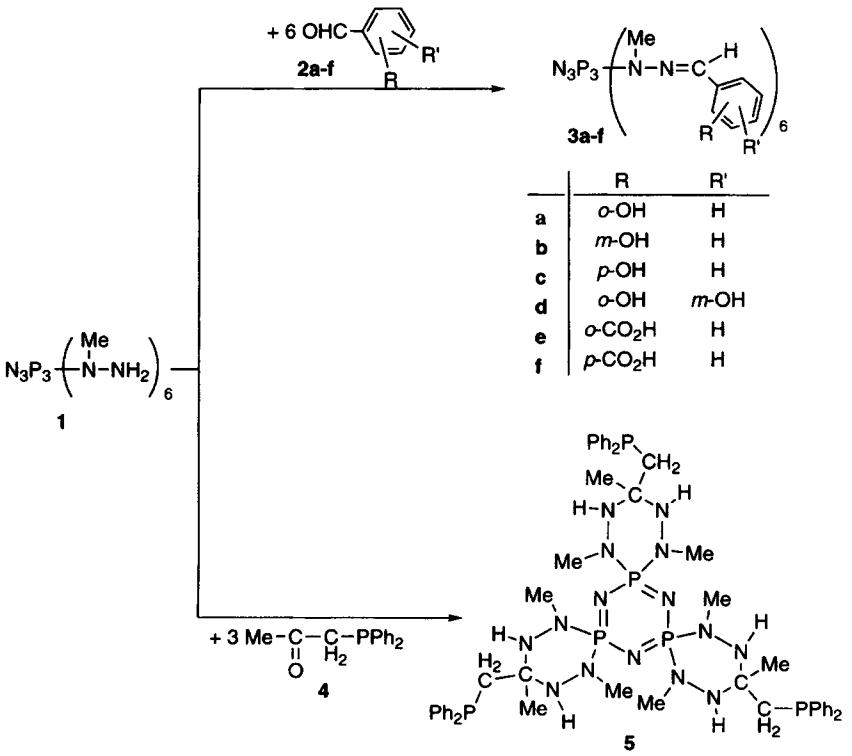
A different behavior is observed with the ketone **4**. Only 3 equivalents of **4** react with the hexahydrazide **1**, even when an excess of **4** is used (Scheme 1). H–C=N functions are not detected, either in the ^1H NMR spectra, which show N–H functions at δ = 4.36, or in the ^{13}C NMR spectra, where a new signal at δ = 77.3 corresponding to N–C–N groups has appeared. Furthermore, mass spectrometry confirms the formation of **5** and not of a hexahydrazone species. In fact, this result is not surprising, since it is well known that only 1 equivalent of ketone reacts with phosphodihydrazides, to give heterocycles [4].

Two structures could be anticipated for **5**: a

*To whom correspondence should be addressed.

© 1996 John Wiley & Sons, Inc.
CCC 1042-7163/96/020149-06

SCHEME 1



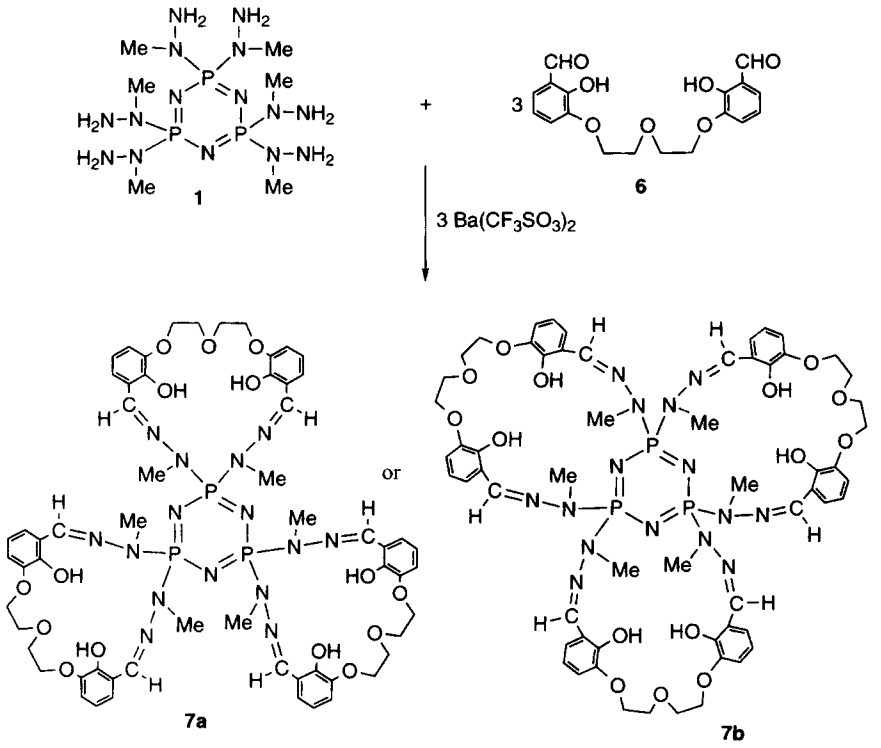
triansa structure, with 3 eight-membered rings based on the connection of two N–NH_2 branches linked to two different phosphorus atoms, and a trispiro structure, with 3 six-membered rings based on the connection of two N–NH_2 branches linked to the same phosphorus. No example of the former structure has ever been described, whereas several trispiro structures, with 3 six-membered rings borne by the cyclotriphosphazene core, are known [5]. Thus, one may presume that **5** is best represented by the trispiro structure depicted on Scheme 1.

The easy and quantitative formation of the multicyclic compound **5** prompted us to investigate the reactivity of long-chain dialdehydes with the cyclotriphosphazene **1**, in order to obtain a new multimacrocyclic compound, with three macrocyclic rings directly grafted on the cyclotriphosphazene ring. In this perspective, we chose the dialdehyde **6** [6], which allowed us to isolate monophosphorus macrocycles when reacted with phosphodihydrazides R–P(S)[NMe–NH_2]$_2$ [2c], in order to try to minimize oligomeric products. However, the treatment of hexamethylhydrazinocyclotriphosphazene **1** (1 equivalent) with the dialdehyde **6** (3 equivalents) in THF at room temperature gives only insoluble oligomers. To overcome this difficulty, the same reaction was performed in the presence of barium triflate (3 equivalents) (Scheme 2). ^{31}P NMR spectroscopy of the resulting mixture revealed the presence of a very broad signal at δ = 12.5 and a sharp singlet at δ = 11.5. The compound corresponding to the sharp singlet **7** was isolated after several extractions with methanol. Spectral data confirmed that this derivative **7** comes from a (1 + 3) cyclocondensation reaction; in particular, mass spectrometry gives a signal at m/z = 1337 corresponding to $[7 + 1]^+$. Elemental analysis shows that barium triflate only helped in the construction of the polymacrocycle **7** but was not trapped in the cavities. This is not surprising since we have already demonstrated that an analogous cavity obtained for a monomacrocycle was not large enough to permit such a complexation [2c].

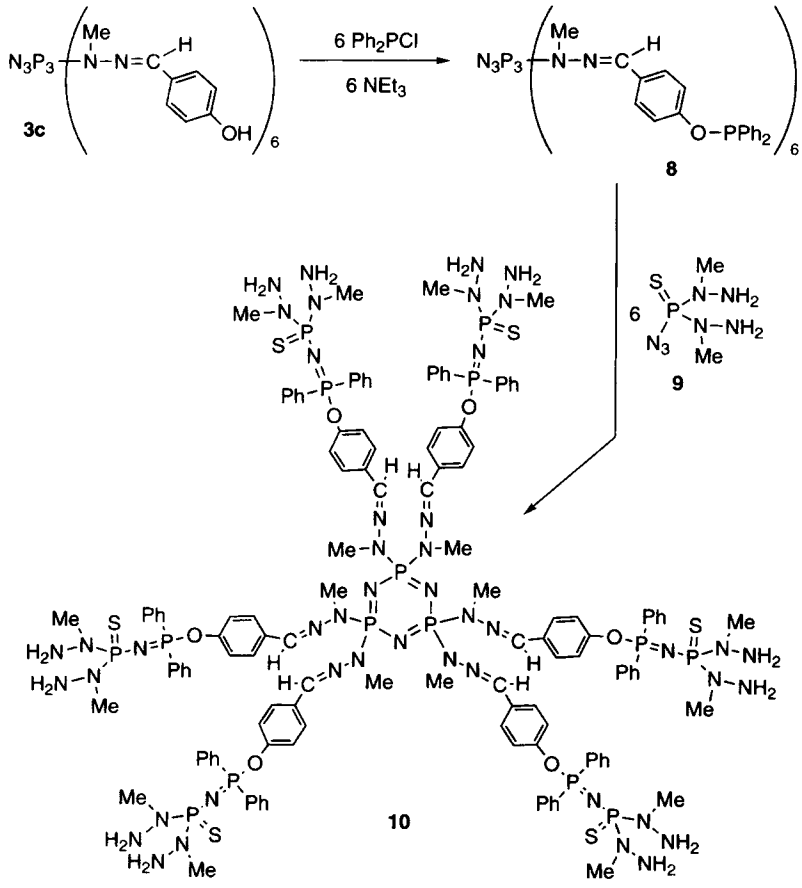
Two structures could be proposed for **7**, as for the tetracyclic compound **5**: the trispiroform **7a** and the triansa **7b**. Attempts to grow crystals suitable for X-ray studies have failed to date; therefore, the choice of the structure must be speculative at present. However, we have already seen that trispirocyclotriphosphazenes bearing six-membered rings are known, and bispirocyclotriphosphazenes possessing two macrocycles grafted on the cyclotriphosphazene core have been described [7]. On the other hand, no triansa macrocyclic cyclotriphosphazenes have ever been isolated. Therefore, compound **7** might be better represented as the trispiro macrocyclic cyclotriphosphazene **7a** rather than the corresponding triansa species **7b**.

The formation of **7** is interesting from two points of view. First, this is a unique example in phosphorus

SCHEME 2



SCHEME 3



macrocyclic chemistry of a reaction involving the condensation between 1 equivalent of a reagent and 3 equivalents of another, a process requiring six bond-forming reactions in one pot! Second, derivative **7** is the first phosphorus species possessing three macrocycles directly grafted to a six-membered ring core.

In order to obtain other multimacrocyclic compounds, we tried to react the phenoxyhexahydrazones **3a–c** with phenyldichlorophosphine oxide or sulfide, in the presence of triethylamine, but we obtained only oligomers from which it was impossible to isolate any multimacrocyclic species of defined structure.

However, these phenoxyhexahydrazones could be interesting starting reagents for the synthesis of a new class of macromolecules: dendrimers [3,8]. We [3c] and others [9] have recently described the construction of these highly branched multifunctionalized macromolecules, starting from cyclotriphosphazene cores. We report here new attempts to synthesize dendrimers, using a three-step procedure, the first step being the obtention of **3c** (Scheme 3). The grafting of diphenylchlorophosphine on each phenoxy group, in the presence of triethylamine allowed us to isolate the hexaphosphine **8** in the second step. In order to obtain the first generation of the dendrimer, we needed to again graft methylhydrazino groups at the periphery of the molecule. This was achieved, using a Staudinger reaction between the azidophosphodihydrazide **9** [1t] and the hexaphosphine **8**. However, this reaction proceeded very slowly, even when heated, and it was impossible to avoid partial oxidation of **8**. Therefore, the dodecahydrazide **10** has not been isolated in the pure state and was only characterized by NMR spectroscopy. In particular, the ^{31}P NMR spectrum consists of one singlet (δ = 16.4, N_3P_3 core) and two doublets at δ = 19.8 and 69.6 (J_{PP} = 16.8 Hz) corresponding to both phosphorus atoms of the P=N–P(S) linkage. These data are in perfect agreement with those obtained for analogous linkages in cryptands [2].

Work is in progress to extend the scope of the reactivity and uses of hexamethylhydrazinocyclotriphosphazene and related compounds.

EXPERIMENTAL SECTION

All manipulations were carried out with standard high vacuum or dry argon atmosphere techniques. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC 200 spectrometer. ^{31}P NMR chemical shifts (δ) were reported relative to 85% H_3PO_4. Mass spectra were recorded on a Finniganmat TSQ 700 or 95 spectrometer (FAB).

Synthesis of Hexamethylhydrazinocyclotriphosphazene **1**

To a solution of methylhydrazine (25.53 mL, 480 mmol) in 200 mL of chloroform was added dropwise a solution of hexachlorocyclotriphosphazene (13.90 g, 40 mmol) in 60 mL of chloroform at 0°C. The mixture was stirred for 10 hours at room temperature, then filtered through celite. The solvent was evaporated, and the residue was washed several times with a light petroleum ether/chloroform (3/1) solution.

1: White powder. Melting point: 170°C, 88% yield. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 29.5; ^1H NMR ($CDCl_3$): δ 2.6 (brs, 18H, CH_3), 3.7 (brs, 12H, NH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 39.5 (m, CH_3); IR (KBr) 3080 and 3180 (V_{NH_2}); mass spectra: *m/z* 405 $[M]^+$. Anal. calcd for $C_6H_{30}N_{15}P_3$: C, 17.78; H, 7.45; N, 51.82. Found: C, 17.85; H, 7.70; N, 51.09.

General Procedure for the Synthesis of Hexahydrazones **3a–d**

To a solution of hexahydrazine **1** (1.621 g, 4 mmol) in 60 mL of THF was added a solution of 1,2-, 1,3-, or 1,4-hydroxybenzaldehyde (2.930 g, 24 mmol) or 1,2,3-dihydroxybenzaldehyde (3.312 g, 24 mmol) in 60 mL of THF. The mixture was stirred for 4 hours at room temperature, then concentrated, and pentane was added to precipitate the hexahydrazones **3a–d**.

3a: Pale yellow powder. 85% yield. Melting point: 150°C (decomp.). $^{31}P\{^1H\}$ NMR (THF): δ 16.1; ^1H NMR ($DMSOd_6$): δ 3.32 (brs, 18H, CH_3), 6.91 (m, 12H, C_6H_4), 7.23 (m, 6H, C_6H_4), 7.51 (m, 6H, C_6H_4), 8.08 (s, 6H, HC=N), 11.0 (brs, 6H, OH); $^{13}C\{^1H\}$ NMR ($DMSOd_6$): δ 31.0 (m, CH_3), 116.0–140.2 (m, C_6H_4), 139.8 (m, HC=N), 156.4 (s, C–OH); mass spectra: *m/z* 1030 $[M + 1]^+$. Anal. calcd for $C_{48}H_{54}N_{15}O_6P_3$: C, 55.98; H, 5.28; N, 20.40. Found: C, 55.99; H, 5.42; N, 20.15.

3b: Pale yellow powder. 87% yield. Melting point: 180°C (decomp.). $^{31}P\{^1H\}$ NMR (THF): δ 16.4; ^1H NMR ($DMSOd_6$): δ 3.33 (brs, 18H, CH_3), 6.83 (m, 6H, C_6H_4), 7.21 (m, 18H, C_6H_4), 7.73 (s, 6H, HC=N), 9.60 (brs, 6H, OH); $^{13}C\{^1H\}$ NMR (CD_3OD): δ 32.9 (m, CH_3), 114.2–139.1 (m, C_6H_4), 139.4 (m, HC=N), 158.8 (s, C-OH); mass spectra: *m/z* 1030 $[M + 1]^+$. Anal. calcd for $C_{48}H_{54}N_{15}O_6P_3$: C, 55.98; H, 5.28; N, 20.40. Found: C, 56.03; H, 5.43; N, 20.23.

3c: White powder. 90% yield. Melting point: 173°C (decomp.). $^{31}P\{^1H\}$ NMR (THF): δ 17.0; ^1H NMR ($DMSOd_6$): δ 3.31 (brs, 18H, CH_3), 6.83 (d, $^3J_{HH}$ = 8.6 Hz, 12H, C_6H_4), 7.5 (d, $^3J_{HH}$ = 8.6 Hz, 12H, C_6H_4), 7.7 (s, 6H, HC=N), 9.7 (brs, 6H, OH); $^{13}C\{^1H\}$ NMR (CD_3OD): δ 32.8 (m, CH_3), 116.5–129.6 (m, C_6H_4), 139.2 (m, HC=N), 159.3 (s, C–OH); IR (KBr):

1670 ($V_{C=N}$), 3080 (V_{OH}); mass spectra: *m/z* 1030 $[M+1]^+$. Anal. calcd for $C_{48}H_{54}N_{15}O_6P_3$: C, 55.98; H, 5.28; N, 20.40. Found: C, 56.01; H, 5.38; N, 20.18.

3d: Beige powder. 93% yield. Melting point: 140°C (decomp.).$^{31}P\{^1H\}$ NMR (THF): δ 15.7; ^1H NMR ($DMSOd_6$): δ 3.34 (brs, 18H, CH_3), 6.7–7.0 (m, 18H, C_6H_3), 8.10 (s, 6H, HC=N), 9.06 (brs, 6H, OH), 10.80 (brs, 6H, OH); $^{13}C\{^1H\}$ NMR ($DMSOd_6$): δ 31.1 (m, CH_3), 116.2–119.8 (m, C_6H_3), 140.9 (m, HC=N), 144.9 (s, C–OH), 145.3 (s, C–OH); IR (KBr): 3100 (V_{OH}); mass spectra: *m/z* 1126 $[M+1]^+$. Anal. calcd for $C_{48}H_{54}N_{15}O_{12}P_3$: C, 51.20; H, 4.83; N, 18.65. Found: C, 51.22; H, 4.97; N, 18.45.

General Procedure for the Synthesis of Hexahydrazones 3e–f

To a solution of hexahydrazine **1** (1.621 g, 4 mmol) in 60 mL of THF was added a solution of 2- or 4-carboxybenzaldehyde (3.603 g, 24 mmol) in 60 mL of THF. The mixture was stirred for 3 hours at room temperature and a white precipitate appeared. This mixture was filtered, and the precipitate was washed several times with pentane, to give **3e–f**.

3e: White powder. 97% yield. Melting point: 180°C. $^{31}P\{^1H\}$ NMR ($DMSOd_6$): δ 16.9; ^1H NMR ($DMSOd_6$): δ 3.36 (brd, $^3J_{HP}$ = 9 Hz, 18H, CH_3), 7.48–8.63 (m, 30H, C_6H_4, HC=N), 13.1 (brs, 6H, CO_2H); $^{13}C\{^1H\}$ NMR ($DMSOd_6$): δ 31.7 (m, CH_3), 128.1–133.1 (m, C_6H_4), 137.6 (s, C–CO_2H), 139.3 (m, HC=N), 170.3 (s, CO_2H); mass spectra: *m/z* 1198 $[M+1]^+$. Anal. calcd for $C_{54}H_{54}N_{15}O_{12}P_3$: C, 54.14; H, 4.54; N, 17.53. Found: C, 54.02; H, 4.39; N, 17.41.

3f: White powder. 98% yield. $^{31}P\{^1H\}$ NMR (MeOH): δ 18.4; ^1H NMR ($DMSOd_6$): δ 3.41 (brs, 18H, CH_3), 7.89–7.97 (m, 30H, C_6H_4, HC=N), 12.8 (brs, 6H, CO_2H); $^{13}C\{^1H\}$ NMR ($DMSOd_6$): δ 31.5 (m, CH_3), 126.0–130.3 (m, C_6H_4), 137.1 (m, HC=N), 139.6 (s, C–CO_2H), 170.5 (s, CO_2H); mass spectra: *m/z* 1198 $[M+1]^+$. Anal. calcd for $C_{54}H_{54}N_{15}O_{12}P_3$: C, 54.14; H, 4.54; N, 17.53. Found: C, 53.97; H, 4.41; N, 17.45.

Synthesis of the Triphosphine 5

To a solution of $Ph_2PCH_2C(O)CH_3$ **4** (0.250 g, 1.03 mmol) in 5 mL of THF was added a solution of hexahydrazine **1** (0.070 g, 0.17 mmol) in 2.5 mL of THF, and in the presence of molecular sieves (4 Å). The mixture was stirred for 24 hours at room temperature, then filtered, and the solvent was evaporated. The resulting residue was washed several times with pentane to eliminate excess of **4** (white powder).

5: White powder. 82% yield. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −24.6 (s, PPh_2), 30.2 (s, N_3P_3); ^1H NMR (C_6D_6): δ 1.25 (s, 9H, C–CH_3), 2.33 (brs, 6H, CH_2), 2.59 (d, $^3J_{HP}$ = 4.7 Hz, 18H, N–CH_3), 4.36 (brs, 6H, NH), 6.9–7.5 (m, 30H, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 24.4 (d, $^3J_{CP}$ = 11.8 Hz, C–CH_3), 36.4 (brs, N–CH_3), 38.6 (d, $^1J_{CP}$ = 17 Hz, P–CH_2), 77.3 (d, $^2J_{CP}$ = 14.5 Hz, N–C–N), 127.0–141.0 (m, C_6H_5); IR (KBr): 3253 (V_{NH}); mass spectra: *m/z* 1078 $[M+1]^+$. Anal. calcd for $C_{51}H_{69}N_{15}P_6$: C, 56.82; H, 6.45; N, 19.49. Found: C, 56.43; H, 6.31; N, 19.36.

Synthesis of Compound 7

A solution of dialdehyde **6** (0.519 g, 1.5 mmol) in 25 mL of THF and a solution of hexahydrazine **1** (0.202 g, 0.5 mmol) in 25 mL of methanol were added dropwise and simultaneously to a solution of barium triflate (0.654 g, 1.5 mmol) in 50 mL of THF. The mixture was stirred for 24 hours at room temperature, and then the solvent was evaporated. The powder thus obtained was extracted twice with methanol (20 mL). The resulting combined solutions were evaporated to dryness, then extracted twice with methanol (10 mL). Evaporation of the combined solutions gave **7**.

7: Yellow powder. 10% yield. $^{31}P\{^1H\}$ NMR (CD_3OD): δ 11.5; ^1H NMR (CD_3OD): δ 3.32 (m, 18H, CH_3), 3.9–4.3 (m, 24H, CH_2O), 6.7–7.0 (m, 18H, C_6H_3), 7.83 (s, 6H, HC=N); $^{13}C\{^1H\}$ NMR (CD_3OD): δ 33.3 (brs, CH_3), 68.0 (brs, O–CH_2), 70.7 (brs, O–CH_2), 113.7 (s, C_6H_3), 118.8 (s, C_6H_3), 120.8 (s, C–CH=N), 121.7 (s, C_6H_3), 144.5 (brs, H–C=N), 146.7 (s, C–OH or C–O–CH_2), 147.7 (s, C–OH or C–O–CH_2); mass spectra: *m/z* 1337 $[M+1]^+$. Anal. calcd for $C_{60}H_{72}N_{15}O_{15}P_3$: C, 53.93; H, 5.43; N, 15.72. Found: C, 53.80; H, 5.31; N, 15.59.

Synthesis of Compound 8

To a solution of hexahydrazone **3c** (0.51 g, 0.50 mmol) in 30 mL of THF was added triethylamine (418 μL, 3 mmol). The solution was stirred for 30 minutes. Then chlorodiphenylphosphine (540 μL, 3 mmol) was added. The mixture was stirred again for 1 hour, then filtered, and the solvent was evaporated to give **8** as a white powder, extremely sensitive to air and moisture.

8: White powder. 94% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.2 (s, N–P=N), 110.5 (s, Ph_2P); ^1H NMR ($CDCl_3$): δ 3.23 (brs, 18H, CH_3), 7.0–7.9 (m, 90H, C_6H_4, C_6H_5, HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 32.1 (m, CH_3), 118.4–135.4 (m, C_6H_4, C_6H_5), 140.5 (d, $^3J_{CP}$ = 18.0 Hz, HC=N), 157.1 (d, $^2J_{CP}$ = 9.5 Hz, C–OP).

REFERENCES

[1] (a) J. P. Majoral, M. Badri, A. M. Caminade, M. Delmas A. Gaset, *Inorg. Chem., 27,* 1988, **3873**; (b) M. Badri,

J. P. Majoral, A. M. Caminade, M. Delmas, A. Gaset, A. Gorgues, J. Jaud, *J. Am. Chem. Soc., 112,* 1990, **5618;** (c) J. P. Majoral, M. Badri, A. M. Caminade, A. Gorgues, M. Delmas, A. Gaset, *Phosphorus, Sulfur and Silicon, 49–50,* 1990, **413;** (d) M. Badri, J. P. Majoral, F. Gonce, A. M. Caminade, M. Sallé, A. Gorgues, *Tetrahedron Lett., 31,* 1990, **6343;** (e) F. Gonce, A. M. Caminade, J. P. Majoral, *Tetrahedron Lett., 32,* 1991, **203;** (f) J. P. Majoral, M. Badri, A. M. Caminade, M. Delmas, A. Gaset, *Inorg. Chem., 30,* 1991, **344;** (g) J. P. Majoral, M. Badri, A. M. Caminade, *Heteroatom Chem., 2,* 1991, **45;** (h) D. Colombo, A. M. Caminade, J. P. Majoral, *Inorg. Chem., 30,* 1991, **3365;** (i) J. P. Majoral, A. M. Caminade: in The Chemistry of Inorganic Ring Systems, R. Steudel (ed): *Studies in Inorganic Chemistry,* Elsevier Science Publ. B. V., Amsterdam, Vol. 14, chap. 12, p. 209 (1992); (j) F. Gonce, A. M. Caminade, J. Jaud, P. Vignaux, J. P. Majoral, *Bull. Soc. Chim. Fr., 129,* 1992, **237;** (k) B. Oussaid, B. Garrigues, A. M. Caminade, J. P. Majoral, *Phosphorus, Sulfur and Silicon, 73,* 1992, **41;** (l) F. Gonce, A. M. Caminade, F. Boutonnet, J. P. Majoral, *J. Org. Chem., 57,* 1992, **970;** (m) A. M. Caminade, D. Colombo-Khater, J. Mitjaville, C. Galliot, P. Mas, J. P. Majoral, *Phosphorus, Sulfur and Silicon, 75,* 1993, **67;** (n) D. Colombo-Khater, A. M. Caminade, B. Delavaux-Nicot, J. P. Majoral, *Organometallics, 12,* 1993, **2861;** (o) B. Oussaid, B. Garrigues, J. Jaud, A. M. Caminade, J. P. Majoral, *J. Org. Chem., 58,* 1993, **4500;** (p) A. M. Caminade, J. P. Majoral, *Chem. Rev., 94,* 1994, **1183;** (q) N. Launay, F. Denat, A. M. Caminade, J. P. Majoral, J. Dubac, *Bull. Soc. Chim. Fr., 131,* 1994, **758;** (r) J. P. Majoral, A. M. Caminade, A. Igau; in L. D. Quin, J. G. Verkade (eds): *Phosphorus-31 NMR Spectral Properties in Compounds Characterization and Structural Analysis,* VCH Publishers, Inc., Deerfield Beach, FL, chap. 5, p. 57 (1994); (s) C. Galliot, A. M. Caminade, J. P. Majoral, M. Kuznikowski, M. Zablocka, K. M. Pietrusiewicz, *Chem. Ber., 128,* 1995, **443;** (t) J. Mitjaville, A. M. Caminade, J. C. Daran, B. Donnadieu, J. P. Majoral, *J. Am. Chem. Soc., 117,* 1995, **1712;** (u) D. Prévoté, C. Galliot, A. M. Caminade, J. P. Majoral, *Heteroatom. Chem., 6,* 1995, **313;** (v) J. Mitjaville, A. M. Caminade, J. P. Majoral, *Synthesis,* 1995, **952.**

[2] (a) J. Mitjaville, A. M. Caminade, R. Mathieu, J. P. Majoral, *J. Am. Chem. Soc., 116,* 1994, **5007;** (b) J. Mitjaville, A. M. Caminade, J. P. Majoral, *J. Chem. Soc. Chem. Commun.,* 1994, **2161;** (c) J. Mitjaville, A. M. Caminade, J. P. Majoral, *Tetrahedron Lett.* 1994, **6865;** (d) J. Mitjaville, A. M. Caminade, J. C. Daran, B. Donnadieu, J. P. Majoral, *J. Am. Chem. Soc., 117,* 1995, **1712.**

[3] (a) N. Launay, A. M. Caminade, R. Lahana, J. P. Majoral, *Angew. Chem. Int. Ed. Engl. 33,* 1994, **1589;** (b) N. Launay, A. M. Caminade, J. P. Majoral, *J. Am. Chem. Soc., 117,* 1995, **3282;** (c) C. Galliot, D. Prévoté, A. M. Caminade, J. P. Majoral, *J. Am. Chem. Soc., 117,* 1995, **5470;** (d) M. Slany, M. Bardaji, M. J. Casanove, A. M. Caminade, J. P. Majoral, B. Chaudret, *J. Am. Chem. Soc., 117,* 1995, **9764.**

[4] (a) J. P. Majoral, R. Kraemer, J. Navech, F. Mathis, *Tetrahedron Lett.,* 1975, **1481;** (b) J. P. Majoral, R. Kraemer, J. Navech, F. Mathis, *Tetrahedron, 32,* 1976, **2633;** (c) J. P. Majoral, M. Revel, J. Navech, *Phosphorus and Sulfur, 4,* 1978, **317.**

[5] (a) J. F. Labarre, *Top. Curr. Chem., 129,* 1985, **173;** (b) R. A. Shaw, *Phosphorus, Sulfur and Silicon, 45,* 1989, **103.**

[6] C. J. van Staveren, J. van Eerden, F. C. J. M. van Veggel, S. Harkema, D. N. Reinhoudt, *J. Am. Chem. Soc., 110,* 1988, **4994.**

[7] J.-F. Labarre, F. Sournies, *Adv. Supramol. Chem., 4,* 1993, **555.**

[8] For reviews concerning dendrimers see: (a) D. A. Tomalia, A. M. Naylor, W. A. Goddard III, *Angew. Chem. Int. Ed. Engl., 29,* 1990, **138;** (b) J. Issberner, R. Moors, F. Vögtle, *Angew. Chem. Int. Ed. Engl., 33,* 1994, **2413;** (c) A. M. Caminade, J. P. Majoral, *Main Group Chemistry News, 3,* 1995, **14.**

[9] F. Sournies, F. Crasnier, M. Graffeuil, J. P. Faucher, R. Lahana, M. C. Labarre, J. F. Labarre, *Angew. Chem. Int. Ed. Engl., 34,* 1995, **578.**