New and Efficient Syntheses of Symmetrical Phosphorus-containing Cryptands

Joëlle Mitjaville, Anne-Marie Caminade and Jean-Pierre Majoral*

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

Phosphorus cryptands **3–5** are obtained *via* [2 + 3] cyclocondensations between phosphodihydrazides **1a, b** and phosphorus-*p,p*-dialdehydes **2a, b** while another phosphorus cryptand **10** is prepared by treatment of the sodium salt of a phosphodihydrazone **8** with a dihalogenated phosphorus-containing macrocycle **9**.

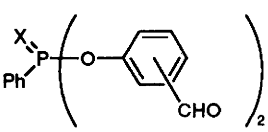
In view of the widespread use of phosphorus-containing macrocycles[1]—specifically for complexation of cations, transition metals, neutral organic species, *etc.*—it is somewhat surprising only a few reports deal with the synthetic approach to phosphorus-containing cryptands.[2] Moreover, most of the reactions suffer from numerous drawbacks. Therefore, there is a need to find strategies which allow the formation of species which might present useful complexation properties.

We recently proposed a general route to unsymmetrical cryptands.[2r] We now report novel access to phosphorus cryptands possessing identical links between phosphorus atoms. The strategies used have the potential for ready modification to the preparation of a wide range of such new derivatives.

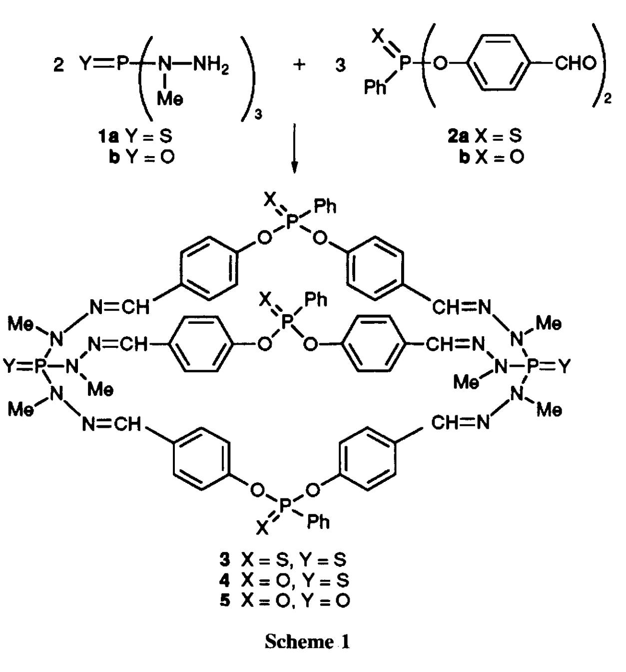
The appropriate first method consists of the treatment of phosphotrihydrazides $(Y)(PNMeNH_2)_3$ **1a** (Y = S) or **1b** (Y = O), (2 equiv.), with the phosphorus dialdehydes $PhP(X)\text{-}O\text{-}p\text{-}C_6H_4\text{-}CHO)_2$ **2a** (X = S) or **2b** (X = O), (3 equiv.) in THF, at room temperature and in the presence of molecular sieve (4Å) (Scheme 1). Reactions are monitored by ^{31}P NMR. After stirring for 24 h, compounds **3–5**[†] are obtained in good yield (**3**: 60; **4**: 60; **5**: 50%). ^{31}P NMR spectra exhibit two signals for each derivative {**3** δ 73.2 [N–P(S)–N] and 82.5 [O–P(S)–O); **4** δ 73.3 [N–P(S)–N] and 11.8 [O–P(O)–O]; **5** δ 12.1 [N–P(O)–N] and 11.1 [O–P(O)–O]}. ^1H NMR spectra show the disappearance of resonances attributed to aldehyde groups (δ 9.8) and NH_2 groups (δ 3.5). ^{13}C NMR and IR spectroscopy confirm the proposed structures, which are also corroborated by mass spectrometries (FAB$^+$) (**3** *m/z* 1435 $[M + 1]^+$; **4** *m/z*: 1387 $[M + 1]^+$; **5** *m/z*: 1355 $[M + 1]^+$). All these results are in agreement with [2 + 3] cyclocondensation reactions leading to symmetrical cryptands possessing five phosphorus atoms and two different environments around phosphorus.

The use of phosphorus *o,o*-dialdehyde **6** or phosphorus *m,m*-dialdehyde **7** instead of **2a** or **2b** leads to a mixture of the expected cryptands and oligomeric species. Attempts to isolate the cryptands have so far been unsuccessful.

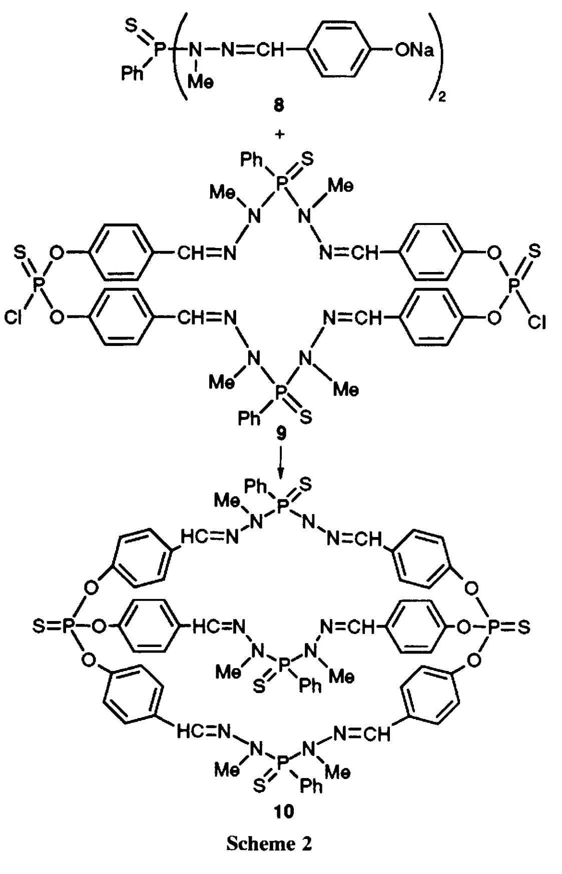
The observation that a number of phosphorus-containing macrocycles, obtained *via* [2 + 2] cyclocondensations between phosphodihydrazides **1a** or **1b** and various dialdehydes, present an unusual butterfly-like structure[3] is at the origin of the second approach to the synthesis of another symmetrical cryptand. It was expected that the bridging of the two wings of such a structure—provided one is able to functionalize these wings—would offer an alternative to the synthesis of such a cryptand. Indeed, the slow addition of the disodium salt **8** to the dihalogenated phosphorus macrocycle **9** in THF at room temperature leads to the new symmetrical cryptand **10**[†] (90% yield) possessing five phosphorus atoms and the same linkages than **3** but with three N–P(S)–N links and two O–P(=S)–O links instead of two N–P(S)–N and three O–P(=S)–O moieties (Scheme 2). All the spectroscopic data for **10** are fully consistent with the proposed structure which displays two signals at δ 78.5 and 57.8 in ^{31}P NMR and a molecular ion at *m/z*: 1435 $[M + 1]^+$.



6 X = O or S *o*-CHO
7 X = O or S *m*-CHO



Scheme 1



Scheme 2

Extension of these efficient methods to the preparation of other cryptands as well as studies concerning complexation properties of these new systems are underway.

Received, 15th June 1994; Com. 4/03634D

Footnote

† *Selected spectral data for* **3**–**5**, **10**. **3**: mp 170 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ 2.7–3.7 (m, 18H, P-N-Me), 6.6–8.2 (m, 45H, C_6H_4, C_6H_5 and HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.8 (br s, P-N-Me), 121.1–132.3 (m, C_6H_5 and C_6H_4), 135.4 (br s, HC=N), 149.9 (d, $^2J_{CP}$ = 9 Hz, C-O-P). Anal. Cald for $C_{66}H_{63}N_{12}O_6P_5S_5$: C, 55.24; H, 4.42; N, 11.71. Found: C, 54.99; H, 4.27; N, 11.62%. **4**: mp 210 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ 2.8–3.5 (m, 18H, P-N-Me), 6.5–8.1 (m, 45H, C_6H_4, C_6H_5 and HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.6 (br s, P-N-Me), 120.7–131.9 (m, C_6H_5 and C_6H_4), 134.3 (br s, HC=N), 151.2 (d, $^2J_{CP}$ = 8.7 Hz, C-O-P). Anal. Calcd for $C_{66}H_{63}N_{12}O_9P_5S_2$: C, 57.14; H, 4.57; N, 12.11. Found: C, 57.26; H, 4.69; N, 12.15%. **5**: ^{1}H NMR ($CDCl_3$) δ 3.1 (d, $^3J_{HP}$ = 6 Hz, 18H, P-N-Me), 6.8–8.9 (m, 45H, C_6H_4, C_6H_5 and HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 32.2 (d, $^2J_{CP}$ = 7.6 Hz, P-N-Me), 121.3–130.7 (m, C_6H_5 and C_6H_4), 134.7 (br s, HC=N), 149.7 (d, $^2J_{CP}$ = 9.1 Hz, C-O-P). Anal. Calcd for $C_{66}H_{63}N_{12}O_{11}P_5$; C, 58.48; H, 4.69; N, 12.40. Found: C, 58.57; H, 4.75; N, 12.49%. **10**: ^{1}H NMR ([^{2}H]$_8$ THF) δ 2.8–3.6 (m, 18H, P-N-Me), 7.0–8.5 (m, 45H, C_6H_4, C_6H_5 and HC=N); $^{13}C\{^1H\}$ NMR [^{2}H]$_8$ THF) δ 31.8 (br s, P-N-Me), 122.6–135.4 (m, C_6H_5 and C_6H_4), 137.4 (br s, HC=N), 152.1 (d, $^2J_{CP}$ = 7 Hz, C-O-P). Anal. Calcd for $C_{66}H_{63}N_{12}O_6P_5S_5$: C, 55.24; H, 4.42; N, 11.71. Found: C, 55.36; H, 4.49; N, 11.76%.

References

1 (*a*) E. N. Tsvetkov, A. N. Bovin and V. K. Syundyukova, *Russ. Chem. Rev.*, 1988, **57**, 776; (*b*) E. I. Sinyavskaya, *Koord. Khim.*, 1986, **12**, 1155; (*c*) M. I. Kabachnik and Y. M. Polikarpov, *Zh. Obsch. Khim.*, 1988, **58**, 1937 (*J. Gen. Chem. SSSR*, 1988, **58**, 1729); (*d*) R. M. Izatt, K. Pawlak, J. S. Bradsjaw and R. L. Bruening, *Chem. Rev.*, 1991, **91**, 1721; (*e*) A. M. Caminade and J.-P. Majoral, *Chem. Rev.*, 1994, **94**, 1183.

2 (*a*) J. E. Parks, B. E. Wagner and R. H. Holm, *J. Am. Chem. Soc.*, 1970, **92**, 3500; (*b*) M. R. Churchill and A. H. Reis, *J. Chem Soc., Chem. Commun.*, 1970, 879; (*c*) V. P. Rudavskii, D. M. Zagnibeda and M. N. Kucherova, *Farm. Zh. (Kiev)*, 1975, **30**, 47; (*d*) E. E. Nifant'ev, A. I. Zavalishina, E. I. Smirnova and V. F. Filimonov, *Zh. Obshch. Khim.*, 1985, **55**, 2806; (*e*) C. Bolm, and K. B. Sharpless, *Tetrahedron Lett.*, 1988, **29**, 5101; (*f*) A. A. Chaikovskaya, T. N. Kudrya, R. I. Yurchenko, O. M. Voitsekhovskaya and A. M. Pinchuk, *Zh. Obshch. Khim.*, 1988, **58**, 1925; (*g*) A. Höhn, R. J. Geue, A. M. Sargeson and A. C. Willis, *J. Chem. Soc., Chem. Commun.*, 1989, 1644; (*h*) B. P. Friedrichsen and H. W. Whitlock, *J. Am. Chem. Soc.*, 1989, **111**, 9132; (*i*) R. A. Pascal Jr., A. P. West Jr. and D. Van Engen, *J. Am. Chem. Soc.*, 1990, **112**, 6406; (*j*) B. P. Friedrichsen, D. R. Powell and H. W. Whitlock, *J. Am. Chem. Soc.*, 1990, **112**, 8931; (*k*) S. B. Wild, *Pure Appl. Chem.*, 1990, **62**, 1139; (*l*) T. N. Koodrja, A. S. Stepanek, R. I. Yurchenko, A. A. Tchaikovskaja and S. E. Lavrova, *Phosphorus, Sulfur and Silicon*, 1990, **51**, 384; (*m*) A. H. Van Oijen, H. B. A. De Bont, J. H. Van Boom and R. M. J.Liskamp, *Tetrahedron Lett.*, 1991, **32**, 7723; (*n*) R. P. L'Esperance, A. P. West Jr., D. Van Engen and R. A. Pascal Jr., *J. Am. Chem. Soc.*, 1991, **113**, 2672; (*o*) A. P. West, N. Smyth, C. M. Kraml, D. M. Ho and R. A. Pascal, *J. Org. Chem.*, 1993, **58**, 3502; (*p*) R. W. Alder, C. Ganter, C. J. Harris, and A. G. Orpen, *Phosphorus, Sulfur and Silicon*, 1993, **77**, 234; (*q*) K. M. Pietrusiewicz and M. Kuznikowski, *Phosphorus, Sulfur and Silicon*, 1993, **77**, 57; (*r*) J. Mitjaville, A.-M. Caminade, R. Mathieu and J.-P. Majoral, *J. Am. Chem. Soc.*, 1994, **116**, 5007.

3 See for example: (*a*) M. Badri, J.-P. Majoral, A.-M. Caminade, M. Delmas, A. Gaset, A. Gorgues and J. Jaud, *J. Am. Chem. Soc.*, 1990, **112**, 5618; (*b*) B. Oussaid, B. Garrigues, J. Jaud, A.-M. Caminade and J.-P. Majoral, *J. Org. Chem.*, 1993, **58**, 4500.