Pergamon

Tetrahedron Letters, Vol. 35, No. 37, pp. 6865-6866, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01441-8

Facile Syntheses of Phosphorus Containing Multisite Receptors

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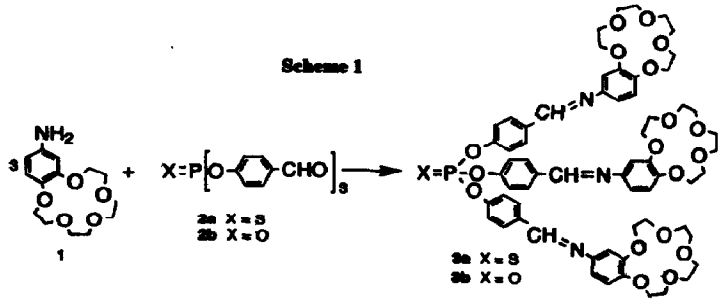
Abstract: 4-aminobenzo-15-crown-5 quantitatively reacts with phosphorus containing tri or hexaaldehydes to give the multisite receptors **3a,b**, **5**.

It has been demonstrated that cation or anion binding properties of bis macrocyclic species in which the two macrocycles are interconnected by short chains, markedly differ from those observed with monomacrocycles.[1] Complexation by a bis(crown ether) became more specific for certain alkali metal cations whose sizes slightly exceed the size of the cavity, the cation being sandwiched intramolecularly by the two adjacent crown ether rings. Similarly multisite receptors possessing more than two macrocyclic cavities linked to a central core were also found to enhance cation or anion encapsulating abilities and to act as ion and electron carriers.[2]

We currently pay attention to the design of new systems incorporating heteroatom donors such as phosphorus, sulfur and allowing the grafting of a number of macrocycles.[3] We report an easy and quantitative preparation of new phosphorus containing polymacrocycles in which three or six crown ethers are bounded either to an acyclic phosphorus core or to rigid cyclotriphosphazene moieties.

Treatment of 4-aminobenzo-15-crown-5 **1** (3 equiv) with the triarylphosphane **2a** or **2b** (1 equiv) in THF solution, at room temperature, and in the presence of molecular sieve (4Å) leads quantitatively after 24 h to derivatives **3a** or **3b** respectively in which three crown ethers are linked to a $X{=}PO_3$ core (X = S or O) (Scheme 1). ^{31}P NMR spectra of **3a** and **3b** exhibit one singlet (**3a** δ 51.3 ppm ; **3b** δ -18.9 ppm). ^{1}H NMR, IR spectroscopy show the disappearance of signals and absorption frequencies of aldehyde and amino groups and the appearance of the characteristic signals of imine functions.[4] Mass spectrometry (**3a** m/z: 1222 $[M+1]^+$; **3b** m/z: 1206 $[M+1]^+$) corroborates the proposed structures.

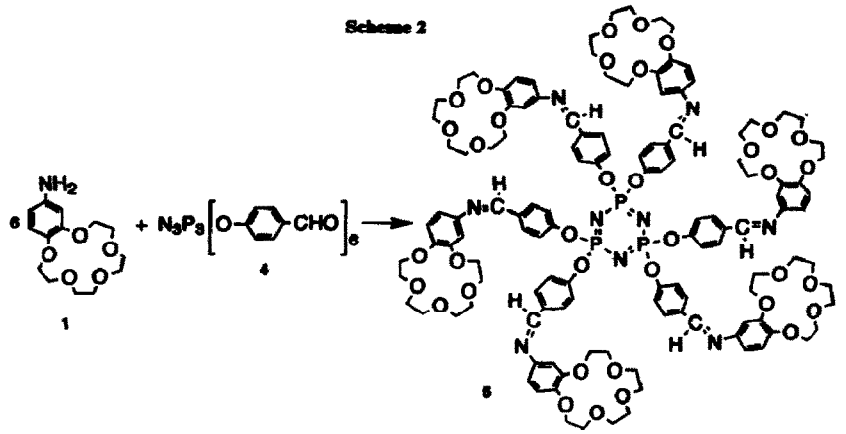
Scheme 1



Similarly, the reaction of **1** (6 equiv) with the hexa(phenoxy-4-carboxaldehyde)cyclotriphosphazene **4** (1 equiv) in refluxing THF affords, after 24 h, the hexa (crown ether) substituted cyclotriphosphazene **5**[4] as a yellow powder (Scheme 2). ^{31}P NMR spectrum shows one sharp singlet at 8.3 ppm (**4** δ = 7.1 ppm) indicating the equivalence of the three phosphorus atoms. Structure of **5** is confirmed by all the other spectral data including mass spectrometry (m/z: 2453 $[M+1]^+$).

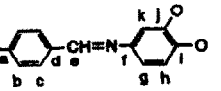
Preliminary complexation reactions have been performed either with **3a** or **5**. Sodium tetraphenyl borate (3 equiv) readily reacts with **3a** giving rise to the corresponding sodium complex **6**, (**3a**-$3Na^+$, $3BPh_4^-$). Complexation is followed mainly by ^{13}C NMR which shows a characteristic shielding of about 2 ppm for methylene carbon atoms and ipso carbon (O-Cipso) of the crown.[4] Addition of sodium tetraphenylborate (6 equiv) to **5** leads cleanly to the expected complex **7**, (**5**-$6Na^+$, $6BPh_4^-$) for which it is possible to detect the same shielding phenomena than the one observed in ^{13}C NMR for **3a**.

Scheme 2



Investigation of the complexing properties of these hosts as well as other related species is in progress.

References and notes:

1. See for example: Izatt, R. M.; Pawlak, K.; Bradshaw, J. S. *Chem. Rev.* **1991**, *91*, 1721-2085.
2. See for example: a. Helgeson, R. C.; Tarnowski, T. C.; Timko, J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6411-6418; b. Hendriks, R. ; Sielcken, O. E.; Drenth, W. ; Nolte, R. J. M. *J. Chem. Soc. Chem. Commun.* **1986**, 1464-1465; c. Sielcken, O. E.; van Tilborg, M. M. ; Roks, M. F. F.; Hendriks, R. ; Drenth, W.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1987**, *109*, 4261-4265; d. Sielcken, O. E.; van de Kuil, L. A. ; Drenth, W.; Schoonman, J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1990**, *112*, 3086-3093.
3. Mitjaville, J. ; Caminade, A. M.; Majoral J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 5007-5008.
4. Selected spectroscopic data. Assignments made as follows:  **3a:** $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 51.3 (s) ppm. ^1H NMR ($CDCl_3$): δ = 3.7-4.2 (m, 48H, CH_2), 6.7-6.9 (m, 9H, C_6H_3), 7.3 (d, $^3J_{HH}$ = 8.6 Hz, 6H, C_6H_4), 7.9 (d, $^3J_{HH}$ = 8.6 Hz, 6H, C_6H_4), 8.4 (s, 3H, CH=N) ppm. ^{13}C $\{^1H\}$ NMR (CD_3CN): δ = 69.2-71.6 (m, CH_2), 108.3 (s, Ck, C_6H_3), 114.7 (s, Ch, C_6H_3), 115.3 (s, Cg, C_6H_3), 122.6 (d, $^3J_{CP}$ = 5 Hz, Cb, C_6H_4), 131.1 (d, $^4J_{CP}$ = 1 Hz, Cc, C_6H_4), 135.7 (d, $^5J_{CP}$ = 2 Hz, Cd, C_6H_4), 146.1 (s, Cf, C_6H_3), 148.9 (s, Ci or Cj, C_6H_3), 150.6 (s, Cj or Ci, C_6H_3), 153.2 (d, $^2J_{CP}$ = 8 Hz, C-O-P), 158.0 (s, CH=N) ppm. MS: m/z 1222 $[M+1]^+$. Anal. Calcd for $C_{63}H_{72}N_3O_{18}PS$: C, 61.90; H, 5.94; N, 3.44. Found: C, 61.66; H, 6.09; N, 3.34; **3b:** ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ = -18.9 (s) ppm. ^1H NMR ($CDCl_3$): δ = 3.4-4.2 (m, 48H, CH_2), 6.5-6.9 (m, 9H, C_6H_3), 7.2 (d, $^3J_{HH}$ = 8 Hz, 6H, C_6H_4), 7.8 (d, $^3J_{HH}$ = 8 Hz, 6H, C_6H_4), 8.3 (s, 3H, CH=N) ppm. ^{13}C $\{^1H\}$ NMR ($CDCl_3$): δ = 68.2-70.1 (m, CH_2), 106.8 (s, Ck, C_6H_3), 111.9 (s, Ch, C_6H_3), 113.8 (s, Cg, C_6H_3), 119.7 (d, $^3J_{CP}$ = 5.3 Hz, Cb, C_6H_4), 129.0 (d, $^4J_{CP}$ = 1 Hz, Cc, C_6H_4), 133.5 (d, $^5J_{CP}$ = 2.2 Hz, Cd, C_6H_4), 144.3 (s, Cf, C_6H_3), 147.1 (s, Ci or Cj, C_6H_3), 149.1 (s, Cj or Ci, C_6H_3), 151.5 (d, $^2J_{CP}$ = 8.2 Hz, C-O-P), 155.9 (s, CH=N) ppm. MS: m/z 1206 $[M+1]^+$. Anal. Calcd for $C_{63}H_{72}N_3O_{19}P$: C, 62.72; H, 6.01; N, 3.48. Found: C, 62.63; H, 5.95; N, 3.46; **5:** ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ = 8.3 (s) ppm. ^1H NMR ($CDCl_3$): δ = 3.5-4.1 (m, 96H, CH_2), 6.5-6.7 (m, 18H, C_6H_3), 6.9 (d, $^3J_{HH}$ = 7 Hz, 12H, C_6H_4), 7.6 (d, $^3J_{HH}$ = 7 Hz, 12H, C_6H_4), 8.3 (s, 6H, CH=N) ppm. ^{13}C $\{^1H\}$ NMR (CD_3CN): δ = 69.3-71.7 (m, CH_2), 108.2 (s, Ck, C_6H_3), 114.3 (s, Ch, C_6H_3), 115.1 (s, Cg, C_6H_3), 122.1 (br .s, Cb, C_6H_4), 130.9 (s, Cc, C_6H_4), 135.5 (s, Cd, C_6H_4), 145.9 (s, Cf, C_6H_3), 148.6 (s, Ci or Cj, C_6H_3), 150.4 (s, Cj or Ci, C_6H_3), 153.0 (br .s, C-O-P), 157.9 (s, CH=N) ppm. MS: m/z 2453 $[M+1]^+$. Anal. Calcd for $C_{126}H_{144}N_9O_{36}P_3$: C, 61.68; H, 5.92; N, 5.14. Found: C, 61.63; H, 5.89; N, 5.13; **6:** ^{31}P $\{^1H\}$ NMR (CD_3CN): δ = 51.8 (s) ppm. ^1H NMR (CD_3CN): δ = 3.6-4.3 (m, 48H, CH_2), 6.9-8.2 (m, 81H, C_6H_3, C_6H_4 and C_6H_5), 8.7 (s, 3H, CH=N) ppm. ^{13}C $\{^1H\}$ NMR (CD_3CN): δ = 68.4-69.6 (m, CH_2), 108.1 (s, Ck, C_6H_3), 115.3 (s, Ch, C_6H_3), 115.8 (s, Cg, C_6H_3), 122.8 (d, $^3J_{CP}$ = 7.0 Hz, Cb, C_6H_4), 122.9 (s, C_4, C_6H_5), 126.8 (d, $^2J_{CB}$ = 2.6 Hz, C_6H_5), 131.5 (s, Cc, C_6H_4), 135.6 (d, $^5J_{CP}$ = 2.0 Hz, Cd, C_6H_4), 136.9 (s, C_3, C_6H_5), 146.9 (s, Ci or Cj, C_6H_3), 147.2 (s, Cj or Ci, C_6H_3), 148.8 (s, Cf, C_6H_3), 153.5 (d, $^2J_{CP}$ = 8.0 Hz, C-O-P), 159.1 (s, CH=N), 165.0 (q, $^1J_{CB}$ = 49.0 Hz, C_6H_5) ppm. Anal. Calcd for $C_{135}H_{132}B_3N_3Na_3O_{18}PS$: C, 72.10; H, 5.87; N, 1.87. Found: C, 72.01; H, 5.79; N, 1.84; **7:** ^{31}P $\{^1H\}$ NMR (CD_3CN): δ = 14 (s) ppm. ^1H NMR (CD_3CN): δ = 3.7-4.2 (m, 96H, O-CH_2), 6.9-7.9 (m, 162H, C_6H_3, C_6H_4 and C_6H_5), 8.5 (s, 6H, CH=N) ppm. ^{13}C $\{^1H\}$NMR (CD_3CN): δ = 68.1-69.5 (m, CH_2), 107.9 (s, Ck, C_6H_3), 115.1 (s, Ch, C_6H_3), 115.6 (s, Cg, C_6H_3), 122.2 (s, Cb, C_6H_4), 122.8 (s, C_4, C_6H_5), 126.7 (d, $^2J_{CB}$ = 2.1 Hz, C_6H_5), 131.2 (s, Cc, C_6H_4), 134.9 (s, Cd, C_6H_4), 136.8 (s, C_3, C_6H_5), 146.6 (s, Ci or Cj, C_6H_3), 147.1 (s, Cj or Ci, C_6H_3), 148.6 (s, Cf, C_6H_3), 153.4 (br .s, C-O-P), 159.2 (s, CH=N), 164.8 (q, $^1J_{CB}$ = 49.4 Hz, C_6H_5) ppm. Anal. Calcd for $C_{270}H_{264}B_6N_9Na_6O_{36}P_3$: C, 71.94; H, 5.90; N, 2.80. Found: C, 71.74; H, 5.81; N, 2.76.

(*Received in France* 16 *June* 1994; *accepted* 22 *July* 1994)