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Phosphite dendrimers and their organometallic derivatives

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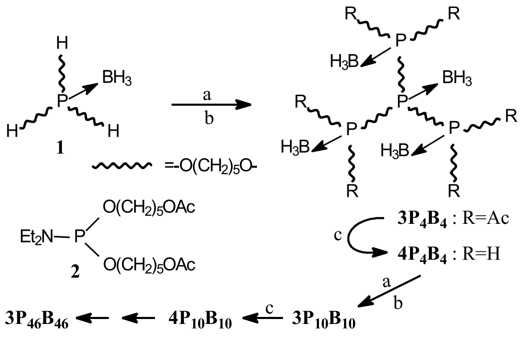
Abstract—The synthesis of new classes of dendrimers, boranophosphate triesters and phosphite-based dendrimers has been accomplished. The latter compounds have been successfully transformed into their palladium(II) and rhodium(I) complexes, possessing metal derivatives attached to the branching points within the dendrimer. © 2003 Elsevier Science Ltd. All rights reserved.

Dendrimers create a new and unique class of unnatural macromolecules exhibiting highly organized, branched structures and well defined molecular weights. During the last decade, enormous progress in the area of dendrimers has been achieved. Excluding the purely synthetic challenge, their potential for applications seems to be the main factor stimulating rapid development.[1] Catalysis appears to be the one of the most promising areas of dendrimer applications, particularly for their metal complexes.[2] Heteroatom-containing dendrimers,[3] especially those based on phosphorus,[4] constitute key precursors for metal complexation.[5] The introduction of a metal derivative to a dendrimer can be effected either by way of its attachment to the surface or via incorporation of a transition metal into the interior, a substantially more difficult task.[6]

Recently, we revealed a divergent strategy for the synthesis of phosphorus-based dendrimers involving a phosphoroamidite approach.[7–9] In this communication, we wish to report on (1) an expedient synthesis of novel, labile phosphite dendrimers via new dendritic boranophosphotriesters and (2) the preparation of transition metal-complexed phosphite dendrimers having a metal derivative within the cascade structure, as candidates for homogenous catalysts.

The start point of our synthesis is the core triol, tris(5-hydroxypentyl)boranophosphate **1**,[10] which can easily be prepared from readily available chemicals in a similar manner to the thio-[7] or selenophosphate[8] cores described previously. The dendrimers **$3P_4B_4$**–**$3P_{46}B_{46}$** were prepared via reiteration of the synthetic strategy as shown in Scheme 1. Phosphitylation of the appropriate polyalcohol **1**, **$4P_4B_4$**, **$4P_{10}B_{10}$**, **$4P_{22}B_{22}$** (generation 3) with phosphoroamidite **2**[8,9] (1.2–1.5 equiv. per OH group) in the presence of an excess of tetrazole (2–2.6 equiv. per OH group) in dichloromethane for 1 h at rt followed by borane–methyl sulfide complex addition [1.1 equiv. per 1 equiv. of the amidophosphite **2**, (0°C, 3 h)] provided cleanly the corresponding dendritic boranophosphotriesters in high isolated (**$3P_4B_4$**, 93%, **$3P_{10}B_{10}$**, 90%, **$3P_{22}B_{22}$**, 82%, **$3P_{46}B_{46}$**, 59%) yields.[11] The phosphite groups, generated during dendrimer synthesis were not very sensitive to oxidation, however we decided to protect them with BH_3 (from the initial step) to avoid any degradation of the dendrimer skeleton during deacetylation. Cleavage of the terminal acetates in **$3P_4B_4$**–**$3P_{22}B_{22}$** using saturated K_2CO_3 in methanol (2.5 h, rt) afforded the corresponding polyols **$4P_4B_4$**–**$4P_{22}B_{22}$** in quantitative yields. The dendritic boranophosphate triesters are colorless liquids whose viscosity increases with increasing generation number.



Scheme 1. *Reagents and conditions*: (a) tetrazole, $Et_2NP[O(CH_2)_5OAc]_2$ **2**, dichloromethane; (b) $(CH_3)_2S{\cdot}BH_3$; (c) K_2CO_3, methanol.

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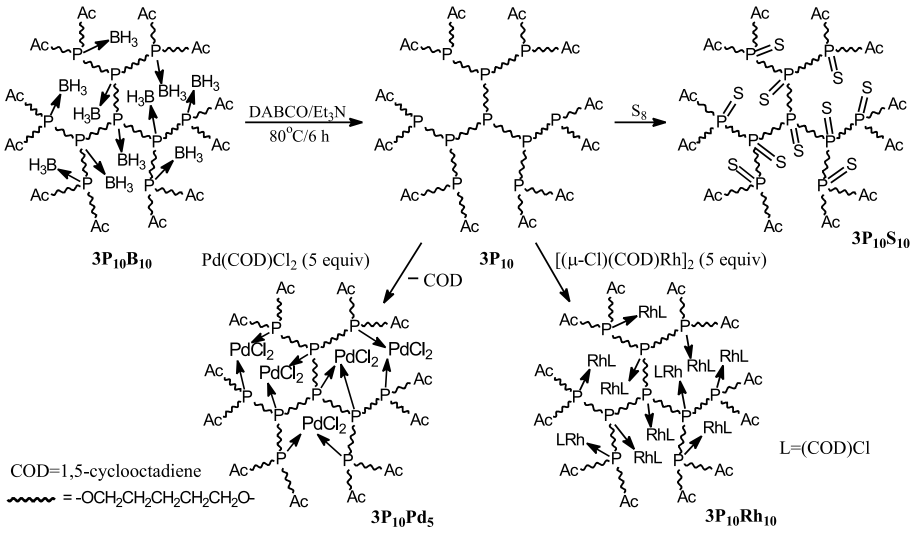
The dendrimers obtained were characterized by ^{1}H, ^{13}C, ^{31}P NMR, FT-IR and MALDI TOF mass spectrometry. Their ^{31}P NMR spectra displayed a characteristic very broad quartet centered at 115 ppm (^1J ^{31}P–^{11}B = ~124 Hz). MALDI TOF mass spectrometry showed only a single peak in the spectrum of $\mathbf{4P_4B_4}$ (calcd for $C_{57}H_{120}O_{24}P_4B_4$: M+Na = 1379.7. Found: *m*/*z* 1380). The mass spectra of larger boranophosphate dendrimers were not conclusive. Removal of the BH_3 groups was carried out by treating compounds $\mathbf{3P_4B_4}$ (6 h), $\mathbf{3P_{10}B_{10}}$ (6 h), $\mathbf{3P_{22}B_{22}}$ (10 h) and $\mathbf{3P_{46}B_{46}}$ (24 h) with DABCO in triethylamine at 80°C (Scheme 2). This reaction was rigorously monitored by ^{31}P NMR (the decline of the signal corresponding to $P\rightarrow BH_3$, together with the appearance of a new signal corresponding to the phosphite groups was observed). The new labile phosphite dendrimers $\mathbf{3P_4}$, $\mathbf{3P_{10}}$, $\mathbf{3P_{22}}$ and $\mathbf{3P_{46}}$ were isolated by simple filtration of the reaction mixture through a short pad of silica gel under an argon atmosphere using dried dichloromethane containing 5% of triethylamine as an eluent.[12] The ^{31}P NMR spectra of the phosphite dendrimers showed only a single resonance line at about 139 ppm due to the coincidence of chemical shifts of the signals from all the phosphorus atoms present in the macromolecule. Moreover, their MALDI-TOF mass spectral analysis was unsuccessful. Therefore, it was necessary to perform an additional experiment to prove that the deboronation reactions did not cause any degradation of the dendrimer framework. For instance, we decided to transform the 2nd generation phosphite dendrimer $\mathbf{3P_{10}}$ into the corresponding thiophosphate dendrimer (Scheme 2). The addition of an excess of elemental sulfur to a solution of $\mathbf{3P_{10}}$ (dichloromethane, 3 h, rt) furnished efficiently the desired dendritic thiophosphate $\mathbf{3P_{10}S_{10}}$. The ^{31}P NMR spectrum of $\mathbf{3P_{10}S_{10}}$ showed three distinct resonances integrating as 6:1:3 (68.50 ppm, 6P), (68.56 ppm, 1P), (68.60 ppm, 3P). Additionally, the MALDI-TOF mass spectrum of $\mathbf{3P_{10}S_{10}}$ verified its molecular weight. Both analyses unambiguously confirmed the proposed structure of $\mathbf{3P_{10}}$.

The phosphite dendrimer possessing 10 trivalent phosphorus atoms throughout the structure provided the possibility of specific complexation with a variety of transition metals. In two series of experiments, the complete loading, forming the metal-containing dendrimers $\mathbf{3P_{10}Pd_5}$ and $\mathbf{3P_{10}Rh_{10}}$ was readily accomplished[13] under standard conditions with 5 equiv. of $[PdCl_2(1,5\text{-}C_8H_{12})]$ and 5 equiv. of rhodium(I) dimer, $[(\mu\text{-}Cl)(1,5\text{-}C_8H_{12})Rh]_2$ (Scheme 2). For the purpose of characterization, ^{31}P NMR spectroscopy was particularly useful. The ^{31}P NMR data of the parent phosphite dendrimer $\mathbf{3P_{10}}$ and of the palladium derivative $\mathbf{3P_{10}Pd_5}$ differ drastically, $\delta = 139.6$ ppm for $\mathbf{3P_{10}}$ and $\delta = 94.6$ ppm for $\mathbf{3P_{10}Pd_5}$. The intramolecular character of the organometallic complex $\mathbf{3P_{10}Pd_5}$ and the presence of five palladium and ten chlorine atoms within the dendrimer was confirmed by MALDI-TOF mass spectrometry [(2,5-dihydroxybenzoic acid) (DHB) calcd for $C_{129}H_{246}O_{54}P_{10}Pd_5Cl_{10} = 3857.5$. Found: *m*/*z* 3859]. However, it is difficult to solve the precise structure of $\mathbf{3P_{10}Pd_5}$.[14] Furthermore, due to the statistical distribution of the metal, the formation of a single defined product $\mathbf{3P_{10}Pd_5}$ appears unlikely. The organophosphite dendrimer $\mathbf{3P_{10}}$ was also smoothly transformed into a rhodium derivative $\mathbf{3P_{10}Rh_{10}}$ by means of a bridge splitting reaction[15] of the rhodium(I) dimer. The ligation of rhodium to phosphite branching points is evidenced by the presence of a doublet [($\delta = 117.9$ ppm, $^1J = 240.8$ Hz) due to P–Rh coupling] in the ^{31}P NMR spectrum, as well as by a downfield shift of the cyclooctadiene proton resonances in its ^{1}H NMR spectrum. No trace of any free phosphite group was detected by ^{31}P NMR, prompting high efficiency in metal loading into the dendrimer.[16] The acquired spectral data, together with literature information[6b] strongly support the structure of $\mathbf{3P_{10}Rh_{10}}$ as drawn in Scheme 2.

The organometallic [Rh(I) and Pd(II)] dendrimers were also prepared starting from the 3rd and 4th generation phosphite dendrimers. Their NMR spectra were virtually identical with the spectra of $\mathbf{3P_{10}Pd_5}$ and $\mathbf{3P_{10}Rh_{10}}$.



Scheme 2.

In all cases, no residual unbound phosphites were observed by ^{31}P NMR. Unfortunately, MALDI-TOF mass spectrometry analysis was not successful for these larger metal complexes. The Rh(I) and Pd(II) metallodendrimers obtained will be tested in organic synthesis as potential homogenous catalysts.

In summary, an efficient synthesis of new dendritic, up to generation 4, boranophosphate triesters was achieved. These compounds were successfully transformed into key labile phosphite dendrimers without any damage to the dendrimer skeleton. The applicability of the phosphite dendrimers was demonstrated by a simple preparation of metal-containing dendrimers.

Acknowledgements

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References

1. New books concerning dendrimers: Newkome, G. R.; Moorefield, C. N.; Vögtle F. *Dendrimers and Dendrons: Concepts, Syntheses, Applications*; Wiley-VCH: Weinheim, 2001; Fréchet, J.; Tomalia, D. *Dendrimers and Other Dendritic Polymers*; John Wiley and Sons, 2001.
2. Recent reviews: Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, *101*, 2991–3024; Kreiter, R.; Kleij, A. W.; Gebbink, R. J. M. K.; van Koten, G. *Top. Curr. Chem.* **2001**, *217*, 163–199; van Manen, H. J.; van Veggel, F. C.; Reinhoudt, D. N. *Top. Curr. Chem.* **2001**, *217*, 121–162; Oostrerom, G. E.; Reek, J. N. H.; Kamer, P. J. C.; van Leeuwen P. W. N. M. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1828–1849.
3. Majoral, J. P.; Caminade, A. M. *Chem. Rev.* **1999**, *99*, 845–880.
4. (a) Majoral, J. P.; Caminade, A. M.; Maraval, V. *Chem. Commun.* **2002**, 2929–2942; (b) Majoral, J. P.; Caminade, A. M. *Top. Curr. Chem.* **2002**, *223*, 111–159.
5. Caminade, A. M.; Maraval, V.; Régis, L.; Majoral, J. P. *Curr. Org. Chem.* **2002**, *6*, 739–774.
6. (a) Miedaner, A.; Curtis, C. J.; Barkley, R. M.; DuBois, D. L. *Inorg. Chem.* **1994**, *33*, 5482–5490; (b) Petrucci-Samija, M.; Guillemette, V.; Dasgupta, M.; Kakkar, A. K. *J. Am. Chem. Soc.* **1999**, *121*, 1968–1969; (c) Reinhoudt, D. N.; Smithers, M. M. A.; Keim, E. G.; Blank, D. H. A.; Kropman, B. L.; van Veggel, F. J. C. M.; Huck, W. T. S. *J. Am. Chem. Soc.* **1995**, *117*, 8293–8294; (d) Seroni, S.; Denti, G.; Compagna, S.; Juris, A.; Ciano, M.; Balzani, V. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1493–1495; (e) Puddephatt, R. J.; Achar, S. *Angew. Chem., Int. Ed. Engl.* **1994**, *331*, 847–849.
7. Salamończyk, G. M.; Kuźnikowski, M.; Skowrońska, A. *Tetrahedron Lett.* **2000**, *41*, 1643–1645.
8. Salamończyk, G. M.; Kuźnikowski, M.; Poniatowska, E. *Chem. Commun.* **2001**, 2202–2203.
9. Salamończyk, G. M.; Kuźnikowski, M.; Poniatowska, E. *Tetrahedron Lett.* **2002**, *43*, 1747–1749.
10. The triacetate derivative of **1** was prepared by the condensation of phosphorus trichloride with pentanediol monoacetate, in the presence of triethylamine, followed by the borane–methyl sulfide complex addition. Yield 95%, after flash chromatography on silica gel (CH_2Cl_2–acetone 50:1). Treatment of the above compound with saturated K_2CO_3 solution in methanol furnished **1**. NMR ($CDCl_3$) $\delta_H = \sim 0.35$ (br s, BH_3, 3H), 1.37–1.73 (m, β,β',γ-CH_2, 18H), 3.59 (t, $J = 6.16$ Hz, α'-CH_2, 6H), 3.95 (dd, $J = 6.29$ Hz, $^3J_{HP} = 13.43$ Hz, α-CH_2, 6H) ppm. $\delta_C = 22.97$, 31.18 (d, $^3J_{C,P} = 5.3$ Hz), 33.02, 62.68, 67.43 (d, $^2J_{C,P} = 3.1$ Hz) ppm. δ_P 113.6–115.2 (br qt, $J = \sim 129$ Hz) ppm.
11. Analytical data for $\mathbf{3P_{46}B_{46}}$: NMR ($CDCl_3$) $\delta_H = \sim 0.40$ (br s, 138H, BH_3), 1.37–1.49 (m, 186H, γ-CH_2), 1.54–1.71 (m, 372H, β,β'-CH_2), 2.02 (s, Ac, 144H), 3.91–4.07 (m, 372H, α,α'-CH_2) ppm. $\delta_C = 20.62$, 21.69, 27.79, 29.56 (dd, $^3J_{C,P(x)} = 5.22$ Hz, $^3J_{C,P(y)} = 4.7$ Hz), 63.97, 66.14, 170.88 ppm. $\delta_P = 114.4$–116.0 (br d, $^1J_{B,P} = \sim 125$ Hz) ppm. MALDI-TOF MS (DHB) (fragmentation) *m*/*z* 874, 905, 977, 1212, 1354, 1567, 1963, 2040, 2143, 2247, 2352, 2457, 2561, 2766, 2871, 3118.
12. Analytical data for $\mathbf{3P_{22}}$: NMR ($CDCl_3$) $\delta_H = 1.26$–1.57 (m, β,β', γ-CH_2, 270H), 1.89 (s, Ac, 72H), 3.77 (dd, $J = 6.26$ Hz, $^3J_{P,H} = 13.6$ Hz, α-CH_2, 90H), 3.96 (t, $J = 6.4$ Hz, α'-CH_2, 90H) ppm. $\delta_C = 20.55$, 22.18, 28.11, 29.84 (d, $^3J_{C,P} = 5.1$ Hz), 64.26, 66.17 ($^2J_{C,P} = 3.0$ Hz), 170.8 ppm. $\delta_P = 139.6$ ppm. MALDI-TOF MS (DHB) (fragmentation) *m*/*z* 392, 448, 536, 640, 741, 783, 850, 939, 963, 1041, 1082, 1147, 1191, 1254, 1360, 1621.
13. Crude complexes $\mathbf{3P_{10}Pd_5}$ and $\mathbf{3P_{10}Rh_{10}}$ were highly pure according to ^{31}P NMR spectroscopy. 1,5-Cyclooctadiene generated in the reaction of palladium(II) complex with $\mathbf{3P_{10}}$ was simply washed out with hexane.
14. NMR data for $\mathbf{3P_{10}Pd_5}$: δ_H (C_6D_6) = 1.22–1.63 (m, β,β', γ-CH_2, 126H), 1.69 (s, Ac, 36H), 3.97 (t, $J = 6.5$ Hz, α'-CH_2, 42H), 4.19–4.27 (m, α-CH_2, 42H) ppm. δ_C ($CDCl_3$) = 20.96, 21.96, 28.16, 29.76, 64.05, 67.63, 172.5 ppm.
15. Examples: Steele, D. F.; Stephenson, T. A. *J. Chem. Soc.* **1972**, 2161–2169; Hartley, F. R.; Murray, S. G.; Potter, D. M. J. *J. Organomet. Chem.* **1983**, *254*, 119–126.
16. ^{1}H NMR data for $\mathbf{3P_{10}Rh_{10}}$: (C_6D_6) $\delta = 1.39$–1.48 (m, CH_2 COD, 40H), 1.61–1.79 (m, β,β', γ-CH_2, 126H), 2.02 (s, Ac, 36H), 2.43–2.54 (m, CH_2 COD, 40H), 3.91–4.05 (m, α,α'-CH_2, 84H), 5.30–5.34 (br s CH=CH COD, 40H) ppm.