1580 *Organometallics* **1999,** *18,* 1580−1582

Dendrimers Containing Zwitterionic [Phosphonium Anionic Zirconocene(IV)] Complexes

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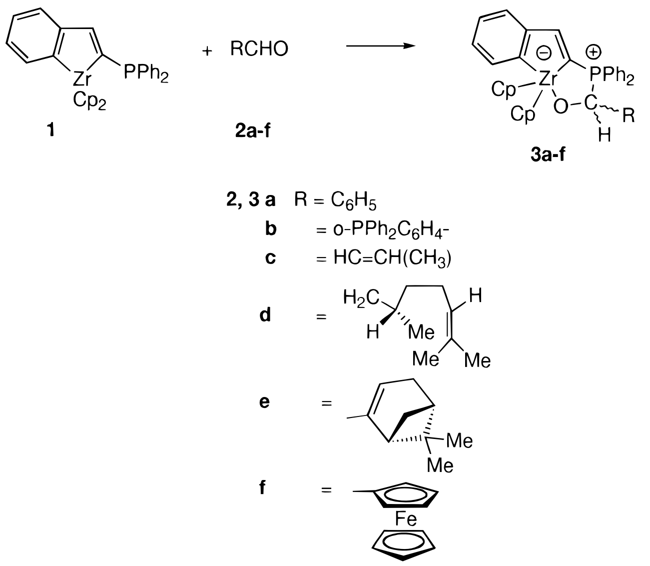
Received October 28, 1998

*Summary: Formal [3+2] cycloaddition reactions between various aldehydes and 2-phosphino-1-zirconaindene (**1**) lead to stable anionic zwitterionic zirconocene complexes. Extension of this method to the reaction of internal or terminated aldehyde containing dendrimers with **1** allows the preparation of the first dendrimers and multidendritic macromolecules containing zwitterionic [phosphonium anionic zirconocene(IV)] complexes.*

The design of monodisperse polyfunctionalized macromolecules is a field of considerable growing interest. Preparation of neutral organic or inorganic dendrimers is well documented,[1] and efficient synthetic routes to the corresponding polycationic[1,2] or polyanionic[1,3] species have also been proposed. Moreover, a variety of metalladendrimers[4] have been obtained, and a few procedures leading to polycationic metalladendrimers are also described.[4,5] In marked contrast, to our knowledge no example of polyzwitterionic metalladendrimers is reported despite the evident potential interest of these new species in organic, organometallic, supramolecular, and polymer chemistry. Indeed these molecules may combine the properties of well-defined spherical nanosize materials and for example properties of anionic transition metal complexes.[6] Since it has already been demonstrated that surface chemistry governs the properties of dendrimers,[1] there is clearly a need to diversify the nature of the outer shell of these highly branched three-dimensional architectures.

Scheme 1



Herein we report the synthesis of a variety of new stable anionic zwitterionic zirconocene complexes containing one oxygen atom directly bonded to zirconium and the extension of this methodology to the high-yield preparation of unprecedented metalladendrimers incorporating, either on the surface or into the internal layers, a large number of 18-electron zirconate complexes.

Unstable anionic group 4 metallocene complexes have been already postulated in mechanistic studies, and their usefulness is demonstrated in a number of reactions.[7] We recently discovered[8] a method of synthesis of stable 18-electron anionic early transition metallocenes. This procedure involves the treatment of 2-phosphino-1-zirconaindene (**1**) and unsaturated species such as alkyne derivatives. Such a formal [3+2] cycloaddition reaction can be performed also with various aldehydes **2** (Scheme 1). Reactions are conducted in toluene for 1 h at either −78 °C or room temperature depending on the aldehyde and afford the desired zwitterionic 18-

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(1) For reviews see: (a) Tomalia, D. A.; Durst, H. D. In *Topics in Current Chemistry*, Vol. 165; *Supramolecular Chemistry I: Directed Synthesis and Molecular Recognition*; Weber, E., Ed.; Springer-Verlag: Berlin, Heidelberg, 1993; pp 193−313. (b) Issberner, J.; Moors, R.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2413. (c) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. In *Dendritic Molecules*; VCH: Weinheim, Germany, 1996. (d) Caminade, A.-M.; Laurent, R.; Majoral J.-P. In *Les Dendrimères*; Ed. Association Ecrin: Paris, 1998.

(2) See for example: (a) Rengan, K.; Engel, R. *J. Chem. Soc., Perkin Trans.* **1991**, 987. (b) Rengan, K.; Engel, R. *J. Chem. Soc., Chem. Commun.* **1992**, 757. (c) Engel, R.; Rengan, K.; Chan, C. S. *Heteroatom. Chem.* **1993**, *4*, 181. (d) Lee, J. J.; Ford, W. T.; Moore, J. A.; Li, Y. *Macromolecules* **1994**, *27*, 4632. (e) Campagna, S.; Dendti, G.; Serroni, S.; Juris, A.; Venturi, M.; Ricevuto, V.; Balzani, V. *Chem. Eur. J.* **1995**, *1*, 211. (f) Ashton, P. R.; Shibata, K.; Shipway, A. N.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2781. (g) Larré, C.; Caminade, A.-M.; Majoral, J.-P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 596. (h) Larré, C.; Donnadieu, B.; Caminade, A.-M., Majoral, J.-P. *J. Am. Chem. Soc.* **1998**, *120*, 4029.

(3) A large number of dendrimers with polyanionic surfaces have been prepared. See for example: (a) Gopidas, K. R.; Leheny, A. R.; Caminati, G.; Turro, N. J.; Tomalia, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 7335. (b) Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1287−1297.

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(5) See for example: (a) Achar, S.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1895. (b) Huck, W. T. S.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *J. Mater. Chem.* **1997**, *7*, 1213. (c) Constable, E. C.; Housecroft, C. E.; Cattalini, M.; Phillips, D. *New J. Chem.* **1998**, 193, and references therein.

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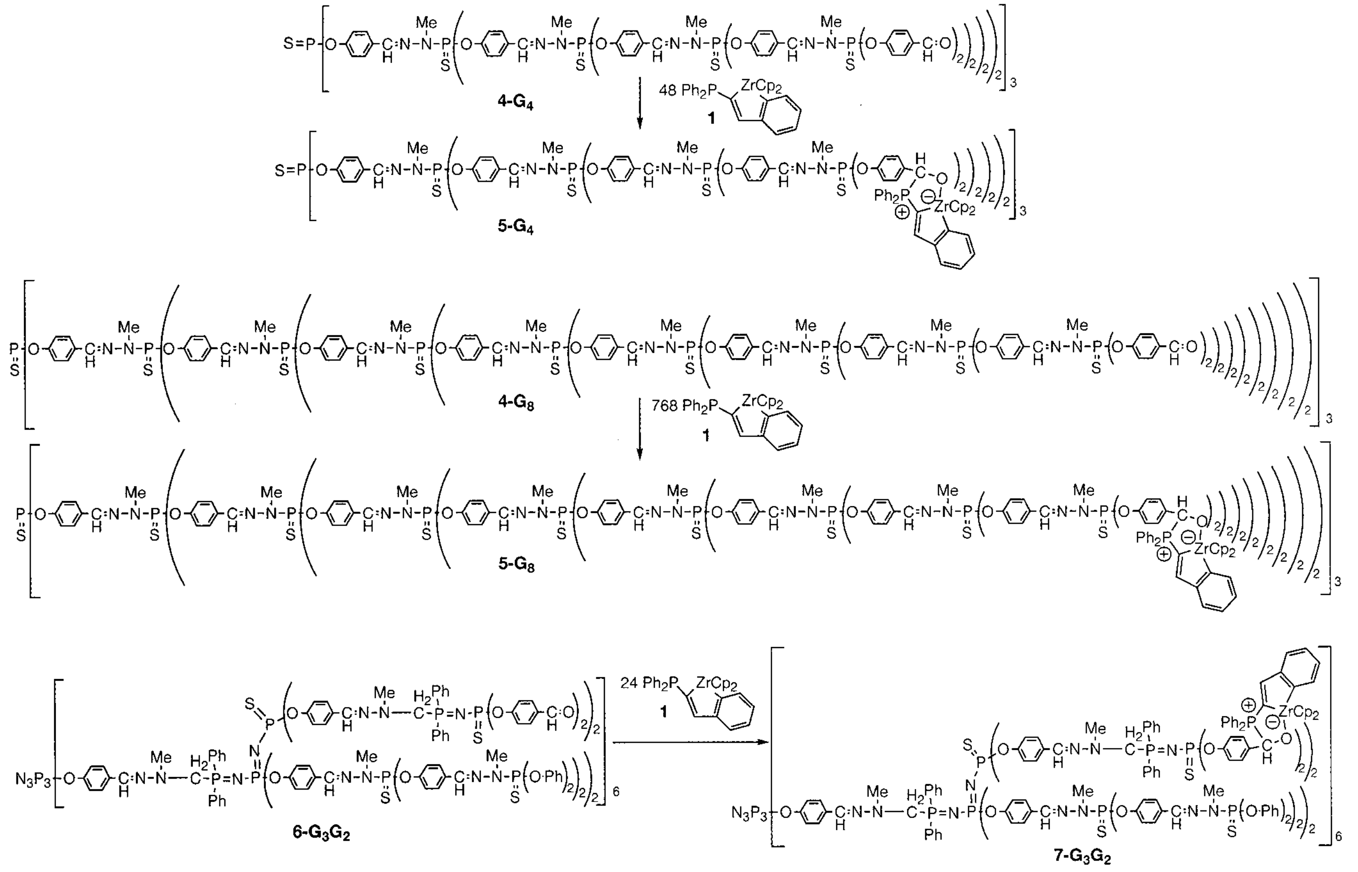
Scheme 2



electron d^0 anionic zirconocenes **3a**–**f** in 53–73% yield after workup.

Characteristic NMR data are detected for these zwitterionic metallocene complexes.[9] In particular in ^{13}C NMR the signal of the sp^2 carbon atom linked to zirconium and phosphorus is significantly shifted to high field ($162.1 < \delta < 164.4$ ppm) with small $^1J_{CP}$ (from 7.4 to 10.8 Hz) (to be compared with $\delta = 184.9$ ppm, $^1J_{CP} = 49.6$ Hz for **1**); moreover a doublet is detected for the carbon atom of the O–C–P linkage at higher field ($82.7 < \delta < 89.9$ ppm; $56.6 < {}^1J_{CP} < 65.8$ Hz).

The structure of one of the two diastereoisomers (3/2 ratio) of complex **3e** obtained from **1** and (1*R*)-(–)-myrtenal was solved by X-ray crystallography studies, which confirm the formation of the suggested cycloadduct (Figure 1).[10]

It can be emphasized that such [3+2] cycloaddition reactions occur selectively on the carbonyl group, al-

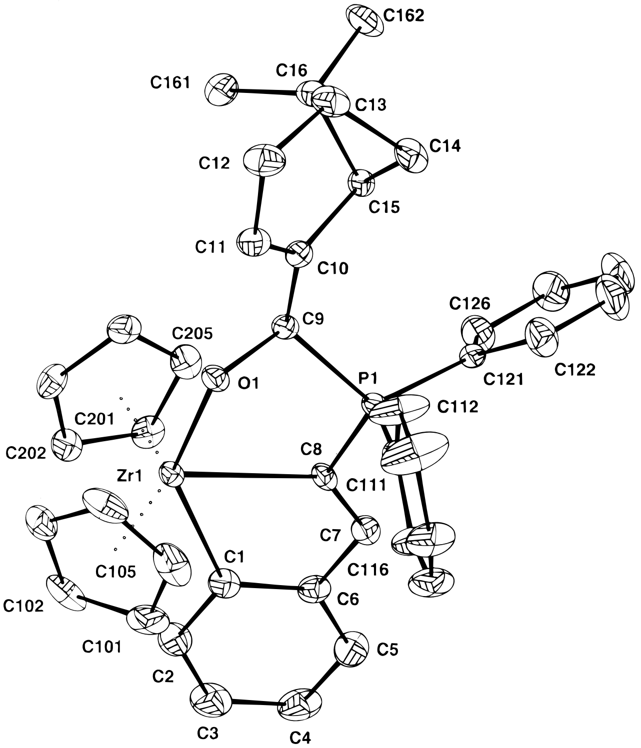


Figure 1. Molecular structure of **3e** (*R* configuration for C(9)) with crystallographic numbering scheme. Selected bond lengths (Å) and bond angles (deg): Zr(1)–C(1) 2.403(3) Zr(1)–C(8) 2.366(3) Zr(1)–O(1) 2.178(2) P(1)–C(121) 1.799(3); P(1)–C(111) 1.807(3); P(1)–C(9) 1.860(3); P(1)–C(8) 1.748(3) C(1)–Zr(1)–C(8) 68.4(1); C(8)–Zr(1)–O(1) 73.8(1) C(8)–P(1)–C(9) 98.9(1).

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lowing therefore the preparation of diversely functionalized zwitterionic zirconocene complexes such as compounds **3b**−**e** possessing either a free phosphino group (**3b**) or free alkenyl groups (**3b**−**e**).

The ability of **1** to react with polyaldehydes was then investigated: the same strategy was used to decorate the surface of the dendrimer **4-G$_4$**[11] (generation 4, 48 terminal aldehyde groups) and the surface of the dendrimer **4-G$_8$**[12] (generation 8, 768 aldehyde chain ends) with respectively 48 and 768 anionic zirconocene moieties. The first zwitterionic metalladendrimers with anionic early transition metal units grafted on the periphery, **5-G$_4$** and **5-G$_8$**, were isolated in 70 and 76% yield, respectively[9,13] (Scheme 2).

Reactions can be easily followed by ^{31}P NMR, which shows the disappearance of the signal due to the phosphino group of **1** ($\delta = 6.9$ ppm) and the appearance of a signal due to the terminal phosphonium groups ($27.2 < \delta < 27.8$ ppm). ^{1}H and ^{13}C NMR spectra show the complete disappearance of singlets due to HC═O groups on behalf of doublets attributed to the O−CH−P fragments.[9,14]

Remarkably a controlled number of anionic zirconocene units can be selectively introduced into the internal layers of a polydendritic macromolecule. Indeed treatment of the multidendritic system **6-G$_3$G$_2$**,[15] constituted by a central dendrimer of generation 3 and by six internal dendrimers of generation 2 possessing 24 internal aldehyde groups, with **1** (excess) cleanly leads to the polyzwitterionic zirconocene polydendritic structure **7-G$_3$G$_2$** (88% yield), in which all the early transition metal anions are located within the cascade structure.[9] NMR data of all the zwitterionic metalladendrimers fit well with that of the dendrimers themselves and with that of the zwitterionic metallocene fragments.[9,14,16]

Study of the properties of these stable new mono- and polyanionic zirconocene containing molecules and macromolecules is under way.

Acknowledgment. Thanks are due to CNRS (France) for financial support. V.C. thanks the Spanish Ministerio de Educacion y Cultura for a postdoctoral fellowship.

Supporting Information Available: General procedures and full data for **3a**−**f**, **5-G$_4$**, **5-G$_8$**, **7-G$_3$G$_2$**; tables of crystal data structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **3e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Most characteristic ^{13}C NMR data for **3a**−**f**, **5-G$_4$**, **5-G$_8$**, **7-G$_3$G$_2$**. ^{13}C{^{1}H} NMR. **3a** (CD$_2$Cl$_2$): $\delta = 86.94$ (d, $^1J_{CP} = 61.1$ Hz PCH), 154.80 (d, $J_{CP} = 32.8$ Hz, ZrC*C*), 162.65 (d, $^1J_{CP} = 9.2$ Hz, ZrCP), 168.29 (s, ZrC*C*H), 194.38 (s, ZrC). **3b** (CDCl$_3$): $\delta = 86.48$ (dd, $^1J_{CP} = 56.6$ Hz, $J_{CP} = 24.6$ Hz, PCH), 155.32 (d, $J_{CP} = 33.1$ Hz, ZrC*C*), 163.89 (d, $^1J_{CP} = 10.2$ Hz, ZrCP), 169.64 (s, ZrC*C*H), 195.23 (s, ZrC). **3c** (CDCl$_3$): $\delta = 86.22$ (d, $^1J_{CP} = 65.8$ Hz PCH), 155.21 (d, $J_{CP} = 32.7$ Hz, ZrC*C*), 162.05 (d, $^1J_{CP} = 7.4$ Hz, ZrCP), 168.14 (s, ZrC*C*H), 195.06 (s, ZrC). **3d** (CDCl$_3$): major diastereoisomer, $\delta = 82.73$ (d, $^1J_{CP} = 63.6$ Hz, PCH), 155.28 (d, $J_{CP} = 32.7$ Hz, ZrC*C*), 163.24 (d, $^1J_{CP} = 10.8$ Hz, ZrCP), 167.50 (s, ZrC*C*H), 194.84 (s, ZrC); minor diastereoisomer, $\delta = 83.29$ (d, $^1J_{CP} = 63.1$ Hz, PCH), 155.28 (d, $J_{CP} = 32.7$ Hz, ZrC*C*), 163.24 (d, $^1J_{CP} = 10.8$ Hz, ZrCP), 167.50 (s, ZrC*C*H), 194.84 (s, ZrC). **3e** (CDCl$_3$): major diastereoisomer, $\delta = 89.91$ (d, $^1J_{CP} = 63.1$ Hz, PCH), 155.05 (d, $J_{CP} = 32.7$ Hz, ZrC*C*), 164.39 (d, $^1J_{CP} = 10.8$ Hz, ZrCP), 166.33 (s, ZrC*C*H), 194.64 (s, ZrC); minor diastereoisomer, $\delta = 89.91$ (d, $^1J_{CP} = 63.1$ Hz, PCH), 155.24 (d, $J_{CP} = 33.2$ Hz, ZrC*C*), 164.17 (d, $^1J_{CP} = 10.7$ Hz, ZrCP), 166.57 (s, ZrC*C*H), 194.74 (s, ZrC). **3f** (CD$_2$Cl$_2$): 85.16 (d, $^1J_{CP} = 60.8$ Hz, PCH), 155.71 (d, $J_{CP} = 32.7$ Hz, ZrC*C*), 163.68 (d, $^1J_{CP} = 8.0$ Hz, ZrCP), 168.42 (s, ZrC*C*H), 195.29 (s, ZrC). **5-G$_4$** (CDCl$_3$): $\delta = 87.07$ (d, $^1J_{CP} = 61.5$ Hz PCH), 155.20 (d, $J_{CP} = 33.0$ Hz, ZrC*C*), 162.62 (s, ZrCP), 169.29 (s, ZrC*C*H), 194.96 (s, ZrC). **5-G$_8$** (CDCl$_3$): $\delta = 87.08$ (d, $^1J_{CP} = 62.7$ Hz PCH), 155.16 (d, $J_{CP} = 33.2$ Hz, ZrC*C*), 162.58 (d, $^1J_{CP} = 9.5$ Hz, ZrCP), 169.25 (s, ZrC*C*H), 194.92 (s, ZrC). **7-G$_3$G$_2$** (CDCl$_3$): $\delta = 87.00$ (d, $^1J_{CP} = 61.5$ Hz, PCH), 155.07 (d, $J_{CP} = 32.6$ Hz, ZrC*C*), 162.81 (d, $^1J_{CP} = 7.6$ Hz, ZrCP), 168.99 (s, ZrC*C*H), 168.99 (s, ZrC).

(10) Crystal data for **3e**: The structure was determined from a monoclinic crystal of dimensions: 0.3 × 0.3 × 0.2 mm^3 (space group $P2_1$), with unit cell dimensions $a = 11.781(1)$ Å, $b = 22.355(2)$ Å, $c = 13.303(2)$ Å, $\beta = 101.12(2)°$, $V = 3444(3)$ Å^3. It has two molecules per unit asymmetric, $\rho_{calcd} = 1.32$ g cm^{-3}, $\mu = 4.28$ cm^{-1}, $F(000) = 1408.87$. A total 23 631 reflections were measured (10 240 independent) with $R_{average} = 0.03$.

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(13) As indicated by ^{31}P NMR and as expected, a mixture of diastereoisomers is obtained for compounds **5-G$_4$**, **5-G$_8$**, and **7-G$_3$G$_2$**.

(14) Attempts to determine mass by several mass spectrometry methods failed until now. Such a problem has already been encountered for the characterization of phosphorus-containing dendrimers and their corresponding complexes.[17] Therefore the monodispersity of the zwitterionic dendrimers reported in this work can be questioned, and it is reasonable to postulate that structure defects cannot be avoided. However ^{31}P NMR indicates that all [3+2] cycloaddition reactions take place on the surface of **4-G$_4$** and **4-G$_8$** and within the cascade structure of **6G$_3$G$_2$** with a precision evaluated to 1%.

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(16) A new stereocenter is established from each aldehyde carbon with formation of diastereoisomers: this can be detected by ^{31}P NMR with the broadening of signals due to terminal P═S and phosphonium groups.

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