Inorg. Chem. **2007**, *46*, 4793–4795

Inorganic Chemistry

Communication

Crystal Structures of Poly(aryl ether) Dendrons with Palladium Scorpionate Complexes at Their Focal Point[†]

Alberto Sánchez-Méndez, Ernesto de Jesús,* Juan C. Flores,* and Pilar Gómez-Sal[‡]

Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, 28871 Alcalá de Henares, Madrid, Spain

Received March 26, 2007

Novel palladium(II) complexes with bis(pyrazol-1-yl)methane ligands at the focal point of G0–G3 poly(aryl ether) Fréchet-type dendrons are reported. The molecular structures of the metallodendrimer series G0, G1, and G2 [(dend)CH(3,5-Me_2pz)$_2$($PdCl_2$)] have been determined by X-ray diffraction methods. The three structures show a similar three-dimensional organization of the metal complex, which is progressively engulfed by the branches with increasing dendrimer generation.

Most dendrimers are flexible molecules, and therefore their structures have been largely debated.[1] de Gennes and Hervet, for example, have postulated a model with the end groups at the surface of the dendrimer,[2a] while Lescanec and Muthukumar have predicted an inward folding of the chain ends.[2b] Several computational and experimental techniques have been used to gain structural information regarding dendrimers in solution and the solid state,[3] but only X-ray diffraction techniques allow the acquisition of highly precise data regarding the internal molecular conformations. Unfortunately, the growth of single crystals of suitable quality has been restricted mainly to small dendrimers because of a variety of problems, in part due to the conformational flexibility of these molecules.[4−6]

Poly(aryl ether) dendrons based on 3,5-dihydroxybenzyl alcohol, developed by Fréchet, are among the most popular dendritic structures[7] and have been widely used in organometallic catalysis,[8] usually after metal functionalization at the core or focal point. The conformation adopted by the dendritic arms of these catalysts in solution is important because it determines the nanoenvironment and accessibility of the metal centers. The few X-ray structures obtained for Fréchet-type dendrons (G1 and G2, Scheme 1) show dendron arrangements that are extended and essentially planar (see below).[4] However, several studies have proposed different degrees of back-folding both in the solid state and in solution.[3,9,10] We have recently suggested that bis(pyrazol-1-yl)methanenickel(II) complexes are partially enclosed by the dendritic arms of poly(aryl ether) dendrons to which they were linked.[11] These studies were carried out in a chloroform-d_1 solution, and our conclusions were based on the significant

---

[†] Dedicated to the late Prof. Trofimenko.

* To whom correspondence should be addressed. E-mail: ernesto.dejesus@uah.es (E.deJ.), juanc.flores@uah.es (J.C.F.).

[‡] Crystal structure determinations: pilar.gomez@uah.es (P.G.-S.).

(1) (a) *Dendrimers and Other Dendritic Polymers*; Fréchet, J. M. J., Tomalia, D. A., Eds.; Wiley-VCH: New York, 2002. (b) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Syntheses, Applications*; Wiley-VCH: Weinheim, Germany, 2001.

(2) (a) de Gennes, P.-G.; Hervet, H. *J. Phys., Lett.* **1983**, *44*, L351−L352. (b) Lescanec, R. L.; Muthukumar, M. *Macromolecules* **1990**, *23*, 2280−2288.

(3) (a) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665−1688. (b) Bauer, B. J.; Amis, E. J. work in Chapter 11 of ref 1b.

(4) Structures of G2 dendrimers based on 3,5-dihydroxybenzyl alcohol: (a) Karakaya, B.; Claussen, W.; Gessler, K.; Saenger, W.; Schlüter, A.-D. *J. Am. Chem. Soc.* **1997**, *119*, 3296−3301. March, R. E. *Acta Crystallogr., Sect. B* **1999**, *55*, 931−936. (b) Brevis, M.; Clarkson, G. J.; Goddard, V.; Helliwell, M.; Holder, A. M.; McKeown, N. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 1092−1094. Brevis, M.; Clarkson, G. J.; Helliwell, M.; Holder, A. M.; McKeown, N. B. *Chem.*−*Eur. J.* **2000**, *6*, 4630−4636. (c) Vögtle, F.; Plevoets, M.; Nieger, M.; Azzellini, G. C.; Credi, A.; De Cola, L.; De Marchis, V.; Venturi, M.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 6290−6298.

(5) Other G2 structures: (a) Seyferth, D.; Son, D. Y.; Rheingold, A. L.; Ostrander, R. L. *Organometallics* **1994**, *13*, 2682−2690. (b) de Groot, D.; Eggeling, E. B.; de Wilde, J. C.; Kooijman, H.; van Haaren, R. J.; van der Made, A. W.; Spek, A. L.; Vogt, D.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Chem. Commun.* **1999**, 1623−1624. (c) Huang, B.; Paquette, J. R. *Org. Lett.* **2000**, *2*, 239−242. (d) Wang, R.; Yang, J.; Zheng, Z.; Carducci, M. D.; Jiao, J.; Seraphin, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 549−552.

(6) Structures of transition-metal dendrimers (G1): (a) Seyferth, D.; Kugita, T.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1995**, *14*, 5362−5366. (b) Kriesel, J. W.; König, S.; Freitas, M. A.; Marshall, A. G.; Leary, J. A.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 12207−12215. (c) Leininger, S.; Stang, P. J.; Huang, S. *Organometallics* **1998**, *17*, 3981−3987. (d) Coupar, P. I.; Jaffrès, P.-A.; Morris, R. E. *J. Chem. Soc., Dalton Trans.* **1999**, 2183−2187. (e) Kleij, A. W.; Klein Gebbink, R. J. M.; van den Nieuwenhuijzen, P. A. J.; Kooijman, H.; Lutz, M.; Spek, A. L.; van Koten, G. *Organometallics* **2001**, *20*, 634−647. (f) Fujihara, T.; Obora, Y.; Tokunaga, M.; Sato, H.; Tsuji, Y. *Chem. Commun.* **2005**, 4526−4528. (g) Sato, H.; Fujihara, T.; Obora, Y.; Tokunaga, M.; Kiyosu, J.; Tsuji, Y. *Chem. Commun.* **2007**, 269−271.

(7) Hawker, C.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010−1013. Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638−7647.

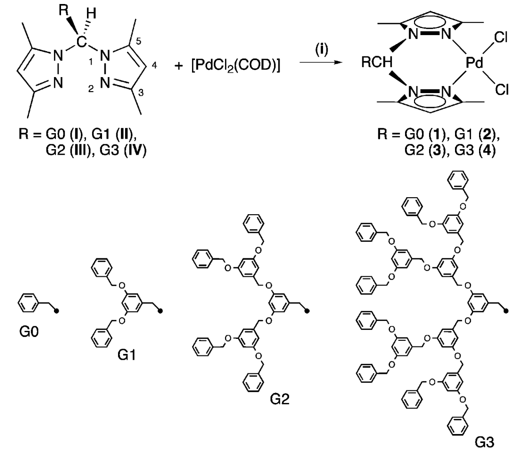
(8) For recent reviews about dendrimers, see: (a) Reek, J. N. H.; Arévalo, S.; van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Adv. Catal.* **2006**, *49*, 71−151. (b) Méry, D.; Astruc, D. *Coord. Chem. Rev.* **2006**, *250*, 1965−1979. (c) Gade, L. H., Ed. *Dendrimer Catalysis*; Springer: Berlin, 2006. (d) Andrés, R.; de Jesús, E.; Flores, J. C. *New J. Chem.* **2007**, doi:10.1039/b615761k.

(9) (a) Wooley, K. L.; Klug, C. A.; Tasaki, K.; Schaefer, J. *J. Am. Chem. Soc.* **1997**, *119*, 53−58 and references cited therein. (b) Riley, J. M.; Alkan, S.; Chen, A.; Shapiro, M.; Khan, W. A.; Murphy, W. R., Jr.; Hanson, J. E. *Macromolecules* **2001**, *34*, 1797−1809 and references cited therein.

(10) Naidoo, K. J.; Hughes, S. J.; Moss, J. R. *Macromolecules* **1999**, *32*, 331−341.

10.1021/ic7005748 CCC: $37.00

Scheme 1. Synthesis of the Palladium Complexes[a]



[a] (i) toluene, 80 °C, 3 h, 83−92% yield.

attenuation observed for the NMR longitudinal relaxation times (T_1) of protons situated in all of the dendritic layers due to the effect of the paramagnetic nickel(II) center. Here we report the preparation of diamagnetic palladium(II) analogues and the elucidation of their single-crystal structures up to the second generation.

The coordination chemistry of poly(pyrazoly-1-yl)alkane ligands has made significant progress during the past few years[12,13] because of advances in their synthesis[14] and because of their wide range of attractive applications, particularly in catalysis.[15] We have combined scorpionate ligands with metallodendrimers by taking advantage of the facile functionalization of the bridging methine carbon atom in poly(pyrazol-1-yl)methane,[16] first described by Reger et al.,[17] which permits the easy preparation of the dendritic ligands RCH(3,5-Me$_2$pz)$_2$ (**I**−**IV**, Scheme 1).[11] The new complexes **1**−**4** were synthesized in warm toluene by displacement of the diene ligand of [PdCl$_2$(COD)] (COD = η^4-1,5-cyclooctadiene) with **I**−**IV** (see the Supporting Information for experimental details and characterization data). Coordination of the ligands to the metal center causes a significant downfield shift of the ^{1}H NMR resonances due to the methyl substituents at the 3 position of the pyrazolyl ring (see Scheme 1) and to the methylene and ortho protons of the benzyl group directly bonded to the palladacycle ($\Delta\delta \approx +0.5, +1.7$, and $+0.5$ ppm, respectively). The C, H, and N elemental analyses and the IR and mass spectrometry (MS) spectra are all consistent with the proposed structures.

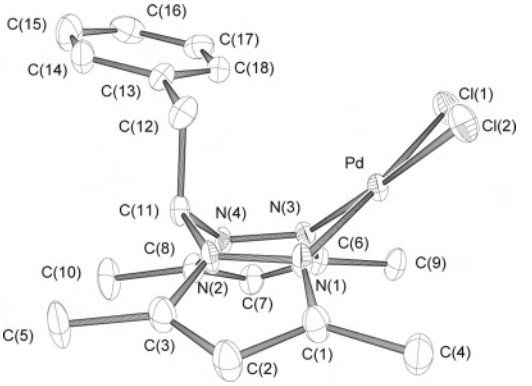


Figure 1. Molecular structure and numbering scheme for **1**. Selected bond lengths (Å): Pd−Cl(1) 2.2797(16), Pd−Cl(2) 2.2883(16), Pd−N(1) 2.031(5), Pd−N(3) 2.027(5), C(11)−N(2) 1.458(7), C(11)−N(4) 1.457(7). Selected bond angles (deg): Cl(1)−Pd−Cl(2) 89.10(6), N(1)−Pd−N(3) 85.69(19), Cl(1)−Pd−N(3) 91.87(15), Cl(2)−Pd(1)−N(1) 93.16(14), N(2)−C(11)−N(4) 109.6(4). Dihedral angle (deg): Pd⋯C(11)−C(12)−C(13) 112.0.

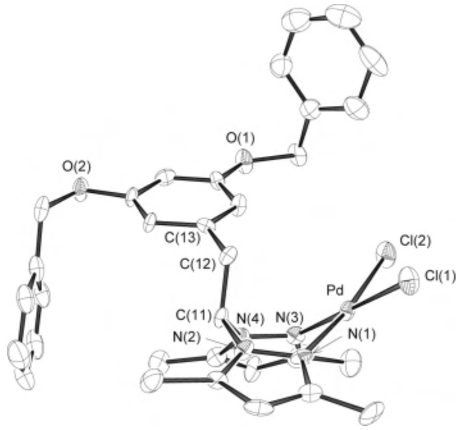


Figure 2. Molecular structure and numbering scheme for **2** (molecule A). Selected bond lengths (Å): Pd−Cl(1) 2.281(2), Pd−Cl(2) 2.292(2), Pd−N(1) 2.046(7), Pd−N(3) 2.012(6), C(11)−N(2) 1.451(9), C(11)−N(4) 1.463(10). Selected bond angles (deg): Cl(1)−Pd−Cl(2) 90.29(8), N(1)−Pd−N(3) 86.3(3), Cl(1)−Pd−N(1) 92.2(2), Cl(2)−Pd−N(3) 91.05(19), N(2)−C(11)−N(4) 110.3(6). Dihedral angle (deg): Pd⋯C(11)−C(12)−C(13) 115.6.

The X-ray molecular structures of **1** (G0), **2** (G1), and **3** (G2) consist of discrete monometallic molecules (Figures 1−3, respectively). The structural parameters defining the $-$CH(3,5-Me$_2$pz)$_2$PdCl$_2$ moieties are almost identical for the three complexes, with the palladium atoms exhibiting rather square-planar geometries. The Pd(NN)$_2$C palladacycles adopt pronounced boat conformations in which the benzyl groups attached to the methine carbons (C11) occupy axial positions, thereby avoiding the steric hindrance that would arise in the equatorial positions with the adjacent methyl groups at the 5 position of the pyrazolyl ring. This steric repulsion confers rigidity on the metallacycle because no boat-to-boat conformational exchange is observed in solution. The dendritic substituents are oriented asymmetrically in relation to the

---

[11] Sánchez-Méndez, A.; Benito, J. M.; de Jesús, E.; de la Mata, F. J.; Flores, J. C.; Gómez, R.; Gómez-Sal, P. *Dalton Trans.* **2006**, 5379−5389.

[12] Trofimenko, S. *Scorpionates. The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

[13] (a) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejada, J.; Lara-Sánchez, A. *Dalton Trans.* **2004**, 1499−1510. (b) Pettinari, C.; Pettinari, R. *Coord. Chem. Rev.* **2005**, *249*, 525−543. (c) Pettinari, C.; Pettinari, R. *Coord. Chem. Rev.* **2005**, *249*, 663−691. (d) Bigmore, H. R.; Lawrence, S. C.; Mountford, P.; Tredget, C. S. *Dalton Trans.* **2005**, 635−651.

[14] (a) Reger, D. L.; Grattan, T. C.; Brown, K. J.; Little, C. A.; Lamba, J. J. S.; Rheingold, A. L.; Sommer, R. D. *J. Organomet. Chem.* **2000**, *607*, 120−128. (b) Juliá, S.; Sala, P.; del Mazo, J.; Sancho, M.; Ochoa, C.; Elguero, J.; Fayet, J.-P.; Vertut, M.-C. *J. Heterocycl. Chem.* **1982**, *19*, 1141−1145. (c) Julia, S.; del Mazo, J. M.; Avila, L.; Elguero, J. *Org. Prep. Proced. Int.* **1984**, *16*, 299−307.

[15] (a) Bigmore, H. R.; Dubberley, S. R.; Kranenburg, M.; Lawrence, S. C.; Sealey, A. J.; Selby, J. D.; Zuideveld, M. A.; Cowley, A. R.; Mountford, P. *Chem. Commun.* **2006**, 436−438. (b) Lawrence, S. C.; Ward, B. D.; Dubberley, S. R.; Kozak, C. M.; Mountford, P. *Chem. Commun.* **2003**, 2880−2881. (c) Milione, S.; Montefusco, C.; Cuenca, T.; Grassi, A. *Chem. Commun.* **2003**, 1176−1177.

[16] Sánchez-Méndez, A.; Silvestri, G. F.; de Jesús, E.; de la Mata, F. J.; Flores, J. C.; Gómez, R.; Gómez-Sal, P. *Eur. J. Inorg. Chem.* **2004**, 3287−3296.

[17] (a) Reger, D. L.; Semeniuc, R. F.; Smith, M. D. *J. Organomet. Chem.* **2003**, *666*, 87−101. (b) Reger, D. L.; Semeniuc, R. F.; Smith, M. D. *J. Chem. Soc., Dalton Trans.* **2002**, 476−477.

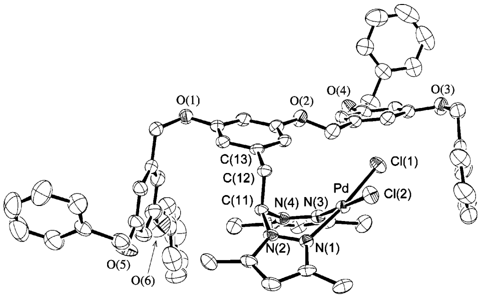
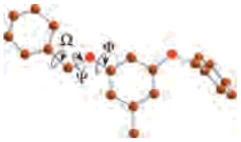


Figure 3. Molecular structure and numbering scheme for **3**. Selected bond lengths (Å): Pd−Cl(1) 2.2852(15), Pd−Cl(2) 2.2826(12), Pd−N(1) 2.038(3), Pd−N(3) 2.018(3), C(11)−N(2) 1.451(5), C(11)−N(4) 1.454(5). Selected bond angles (deg): Cl(1)−Pd−Cl(2) 89.43(5), N(1)−Pd−N(3) 85.92(14), Cl(1)−Pd−N(3) 92.34(10), Cl(2)−Pd−N(1) 92.10(10), N(2)−C(11)−N(4) 108.9(3). Dihedral angle (deg): Pd···C(11)−C(12)−C(13) 114.5.

Table 1. Structural Parameters Determined by Single-Crystal X-ray Diffraction for G2 Fréchet-Type Poly(aryl ether) Dendrons



	percentage of dihedral angles that fall in the specified range (%)			
	Φ (0 or 180 ± 15°)	Ψ (180 ± 15°)	Ω (0 ± 15°)	mean Ψ (deg)
ref 4a	100	100	67	177
ref 4b	100	67	33	144
ref 4c	100	100	33	174
complex **3**	100	33	17	110

palladacycle, with dihedral angles defined by the Pd···C(11) molecular axes and the C(12)−C(13) bonds in the range of 112.0−115.6°.

Several features can be highlighted regarding the conformational arrangement of the dendritic substituents. First, it looks as if there has been an onionlike growth on going from **1** to **3** in which the layer of a new generation is essentially built on top of the preexisting structure of the preceding generation. Second, the dendritic arms in **2** and **3** adopt a disposition that is clearly nonplanar, with adjacent aromatic rings mainly almost orthogonally. Finally, the dendritic moiety in **3** tends to wrap up the palladium complex at the core. The topology of the entire dendritic moiety is determined by the arrangements of the benzyl branches around each ramification unit, which are defined by the three dihedral angles involved in the ether linkage (Table 1).[10] The relative orientation of the aromatic rings is determined by the values of Φ and Ω (which are 0 or 180° for a planar structure), whereas the central dihedral angle Ψ is the most important when considering the overall structure. The branch is fully extended if this dihedral angle is 180° and completely back-folded to the dendritic core when it is 0°. The percentage of branches adopting a planar and extended disposition (±15°) are summarized in Table 1 for all of the structures of Fréchet-type poly(aryl ether) G2 dendrimers reported to date.[4] The compounds referenced in Table 1 are identical with **3** except in the function located at their focal points. The dihedral angle Φ is almost 0 or 180° in all cases, which means that the $-CC_6H_3(OC-)_2$ core is virtually planar (as is commonly observed, for example, in derivatives of anisole).[18] The singularity of the crystal structure of **3** arises from the fact that this is the first case in which significant back-folding is observed in a poly(aryl ether), with four of their six branch units having Ψ between 71° and 86°.[19] A dependence of the structure and shape of dendrons on the functional group at the focal point (or periphery) has been observed previously and has been used to control the size of supramolecular assemblies in bulk.[20]

Because crystallization is a kinetically controlled process, crystal structures do not necessarily represent energy minima. Moreover, both crystal-packing forces and intramolecular interactions determine their energies. In spite of this, solid-state studies are valuable as a guide to conformations that are easily reachable in solution. In fact, the picture obtained here in the solid state, according to which the dendritic wedge does not spread but tends to enfold the palladium center, essentially matches the conclusion of our previous report, where related nickel complexes were studied in a CDCl$_3$ solution by T_1 measurements of their ^{1}H NMR resonances.[11] In other words, it is very likely that the accessibility of the metal center in complexes **1**−**3** in a CDCl$_3$ solution at any given moment must be very close to those depicted in Figures 1−3. It should be noted, however, that the arrangement of the poly(benzylphenyl ether) dendritic arms can be affected by the nature of the solvent.[3,9,10]

In summary, we have presented the single-crystal structures of a series of scorpionate dendrimers of palladium that includes, to the best of our knowledge, the first higher generation (G2) transition-metal dendrimer to be crystallographically characterized so far. The solid-state structure of this G2 metallodendrimer shows that the dendritic wedges tend to wrap up the palladium center rather than spreading. Further synthetic, catalytic, and structural work with these types of dendronized ligands is currently underway in the context of palladium chemistry.

Acknowledgment. We are grateful for financial support from the Ministerio de Educación y Ciencia (Project CTQ2005-00795/BQU), the Comunidad de Madrid (Project S-0505/PPQ/0328-03), and the Universidad de Alcalá (FPI grant to A.S.-M.). P. G.-S. is also indebted to “Factoria de Cristalización” (Consolider-Ingenio 2010).

Supporting Information Available: Preparative details and characterization data (NMR, IR, and MS) for the new compounds and X-ray crystallographic information for complexes **1**−**3** in CIF format. This material is available free of charge via the Internet at http://pub.acs.org.

IC7005748

---

(18) Bellard, S.; Elliot, R.; McDonald, E. *Acta Crystallogr., Sect. B* **1982**, *38*, 669−671.

(19) Several crystal structures of dendrimers built of other motifs also showed a tendency to back-folding. For example, see: Larré, C.; Donnadieu, B.; Caminade, A.-M.; Majoral, J.-P. *Chem.*−*Eur. J.* **1998**, *4*, 2031−2036. Larré, C.; Bressolles, D.; Turrin, C.; Donnadieu, B.; Caminade, A.-M.; Majoral, J.-P. *J. Am. Chem. Soc.* **1998**, *120*, 13070−13082.

(20) Percec, V.; Cho, W.-D.; Ungar, G. *J. Am. Chem. Soc.* **2000**, *122*, 10273−10281 and references cited therein.