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Communication

Silane dendrimers containing titanium complexes on their periphery

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Abstract

Hydrosilylation of 4-allyl-2-methoxyphenol (eugenol) with silane dendrimers of first or second generation and $-SiMe_2H$ ending groups affords new dendrimers with $-SiMe_2(CH_2)_3\{C_6H_3(OMe)(OH)\}$ terminating groups. The reaction of the hidroxy functionalities of these dendrimers with $[CpTiCl_3]$ ($Cp = \eta^5-C_5H_5$) provides an effective route for the attachment of cyclopentadienyl titanium complexes to the dendritic periphery. The yields of the prepared dendrimers with $-SiMe_2(CH_2)_3\{C_6H_3(OMe)(OTiCl_2Cp)\}$ terminating groups are near quantitative. All the dendrimers are characterised by ^1H-, $^{13}C\{^1H\}$-, and $^{29}Si\{^1H\}$-NMR spectroscopy, elemental analysis, and (except for Ti dendrimers) MALDI-TOF mass spectroscopy. © 2000 Elsevier Science S.A. All rights reserved.

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The advances achieved on synthetic methodologies since the early 1980s permit the design of functionalised dendrimers providing unusual or novel properties. Dendrimers incorporating transition metals at their core, branches, or periphery may give to new approaches in catalysis as templates for the preparation and stabilisation of monodisperse metal nanoparticles [1], or as spacers in the support of metal complexes to silica [2]. More related to the special structure of dendrimers are (a) the so-called 'dendrizymes,' in which ligands substituted with appropriate dendritic wedges could control the selectivity of the catalytic process [3]; (b) the transition metal-peripheral dendrimers, in which it is expected that the presence of catalytic sites at the surface of the dendrimer will retain the benefits of homogeneous catalysts while facilitating the recovery of the catalyst [4]. Although an increasing number of reports have been published about late transition metal dendrimers [5], titanium and other early transition metals are scarcely represented [6].

Here, we present the synthesis of one of the first examples [6c–d] of dendrimers bearing titanium metals on their periphery. The approach to such compounds comprises generally the use of a supporting dendrimer and an anchoring ligand with appropriate functionalities for selective ligand–dendrimer and ligand–metal attachment. 4–allyl–2–methoxyphenol (eugenol) is an attractive anchoring ligand to link titanium metal complexes to silane dendrimers because its hydroxy and alkene functionalities are reactive towards Ti–Cl and Si–H bonds, respectively. We have recently reported [7] that the reaction of eugenol with $[CpTiCl_3]$ ($Cp = \eta^5-C_5H_5$) under mild conditions affords the aryloxide complex $[CpTi\{OC_6H_3(OMe)(CH_2CH{=}CH_2)\}Cl_2]$ (**1**) in quantitative yields. It has been shown that complexes of the type $[CpTi(OAr)Cl_2]$ are active in olefin hydrogenation and polymerisation catalysis [8].

Eugenol-related dendrimers of first generation **G1OH** and second generation **G2OH** are easily obtained by hydrosilylation of eugenol with the corresponding den-

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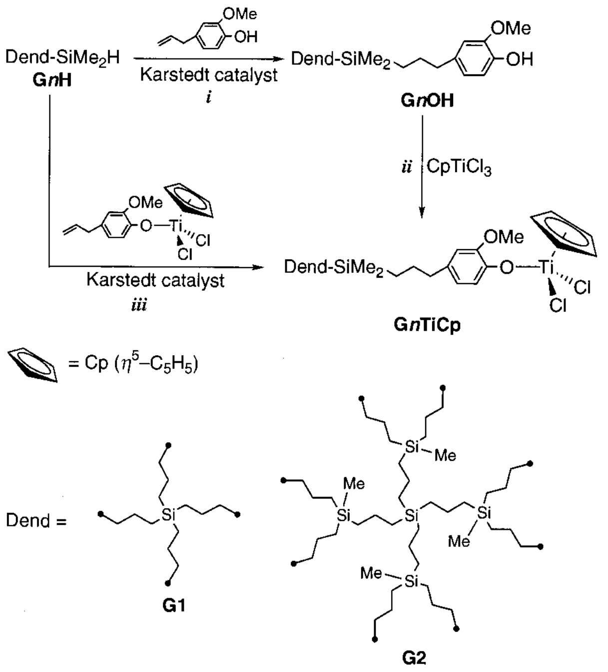
drimers **G*n*H** [9] ($n = 1$ or 2, Scheme 1, reaction (*i*)). The reaction can be monitored by the ^{1}H-NMR resonance of the Si–H proton at ca. 3.8 ppm and is completed after 9 h at 70°C using THF as a solvent and the Karstedt catalyst. These two dendrimers are oils soluble in aromatic solvents and insoluble in saturated hydrocarbons, which helps their purification. The acidity of **G1OH** and **G2OH** dendrimers is enough to allow the alcoholysis of a Ti–Cl bond in [CpTiCl$_3$] (6 h, toluene, 80°C), leading quantitatively to the metallodendrimers **G1TiCp** or **G2TiCp** with 4 or 8 titanium atoms, respectively (Scheme 1, reaction (*ii*)). An alternative route to dendrimers **G*n*TiCp** consists of the reaction of **G*n*H** and complex **1** (Scheme 1, reaction (*iii*)). Preliminary work on Cp* complexes (Cp* = η^5-C$_5$Me$_5$) shows that the first approach is not the most appropriated for the synthesis of **G*n*TiCp*** dendrimers since the pentamethylcyclopentadienyl group makes difficult the alcoholysis reaction of [Cp*TiCl$_3$] as we observed in our previous synthesis of the Cp* analogue of **1** [7].

The novel dendrimers **G*n*OH** and **G*n*TiCp** were spectroscopically characterised by ^{1}H-, ^{13}C{^{1}H}-, and ^{29}Si{^{1}H}-NMR. The chemical shifts of the dendrimeric silicon framework are insensitive to substitutions in the eugenol ligand. For example, the ^{13}C resonances of the Si–Me groups appear in **G*n*OH** and **G*n*TiCp** at the same fields, located at -3.3 ppm for G1, and at -4.9 (innermost) and -3.2 ppm (outermost) for G2 dendrimers. Moreover, the chemical shifts of the Cp proton and carbon atoms observed in titanium dendrimers remain unchanged with generation on going from **1** to **G2TiCp** (6.73 ppm for protons, 121.0 ppm for carbons). This feature suggests that the differences in size and length of the macromolecular systems are not extended to the metal microenvironment. Only three methylene ^{13}C resonances are observed in the second generation dendrimers for the six groups present in the SiCH$_2$CH$_2$CH$_2$Si repeating unity. Overlapping of CH$_2$ peaks, appearing in a narrow range and being somewhat broad, has been often observed in related systems [5g,j]. The MNa$^+$ peak was largely the most intense signal observed at high masses for the **G*n*OH** dendrimers by the MALDI-TOF MS method. Attempts to determine the molecular mass for organometallic dendrimers **G*n*TiCp** have failed until now. We suspect that the titanium periphery reacts with the acid matrices. Other authors have also observed failure in measurements of molecular mass of metallodendrimers by MALDI-TOF techniques [5i–j]. The length of the eugenol ligand, estimated by molecular modelling in 8 Å, provides long external arms to these dendrimers that are characterised by long radii even at the first generation (estimated radius for **G1OH** ca. 13 Å).



where —• correspond to the ending groups shown in equations *i–iii*

Scheme 1. (*i*) 9 h, 70°C, THF; (*ii*) 6 h, 80°C, toluene; (*iii*) 9 h, 70°C, THF.

1. Notes

1.1. Preparation and data for G1OH

A solution of **G1H** (0.37 g, 0.85 mmol), eugenol (0.59 g, 3.6 mmol), and the Karstedt catalyst (1 drop of a solution 3–3.5% Pt in vinyl terminated polydimethylsiloxane) in THF (3 ml) was stirred for 9 h at 70°C and overnight at room temperature (r.t.). Then, the solution was evaporated in vacuo to dryness and the residue washed twice with hexane (20 ml) giving **G1OH** as a pale brown oil (0.60 g, 75%). Anal. Calc. for C$_{60}$H$_{100}$O$_8$Si$_5$: C, 66,1; H, 9.3. Found: C, 65,6; H, 9,4%. ^{1}H-NMR (CDCl$_3$): δ 6.81 (m, 1 H, C$_6$*H*$_3$), 6.65 (m, 2 H, C$_6$*H*$_3$), 5.46 (s, 1 H, O*H*), 3.85 (s, 3 H, O*Me*), 2.53 (m, 2 H, CH$_2$CH$_2$C*H*$_2$Ph), 1.56 (m, 2 H, CH$_2$C*H*$_2$CH$_2$ Ph), 1.29 (m, 2 H, SiCH$_2$C*H*$_2$CH$_2$Si), 0.51 (m br, 6 H, SiC*H*$_2$CH$_2$C*H*$_2$Si and C*H*$_2$CH$_2$CH$_2$Ph overlapping), -0.06 (s, 6 H, Si*Me*$_2$). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 146.3, 143.5, 134.7, 120.9, 114.1, 111.0 (*C*$_6$H$_3$), 55.8 (O*Me*), 39.7, 26.4, 15.3 ((*C*H$_2$)$_3$Ph), 20.3, 18.6, 17.5 (Si(*C*H$_2$)$_3$Si), -3.3 (Si*Me*$_2$). ^{29}Si{^{1}H}-NMR (CDCl$_3$): δ 1.59 (G1-*Si*), 0.77 (G0-*Si*). MS (MALDI-TOF): *m*/*z* 1111.6, Anal. Calc. [MNa$^+$]: 1111.6.

1.2. Preparation and data for G2OH

This dendrimer was prepared by a method similar to that of **G1OH**. Anal. Calc. for C$_{136}$H$_{236}$O$_{16}$Si$_{13}$: C, 65.5; H, 9.5. Found: C, 65.1; H, 9.5%. ^{1}H-NMR (CDCl$_3$): δ 6.79 (m, 2 H, C$_6$*H*$_3$), 6.63 (m, 4 H, C$_6$*H*$_3$), 5.44 (s, 2 H, O*H*), 3.82 (s, 6 H, O*Me*), 2.51 (m, 4 H,

$CH_2CH_2CH_2Ph$), 1.54 (m, 4 H, $CH_2CH_2CH_2Ph$), 1.28 (m, 4 H, $SiCH_2CH_2CH_2Si$), 0.52 (m br, 18 H, $SiCH_2CH_2CH_2Si$ and $CH_2CH_2CH_2Ph$ overlapping), −0.08 (s, 12 H, $SiMe_2$), −0.11 (s, 3 H, SiMe). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 146.3, 143.5, 134.7, 120.9, 114.1, 111.0 (C_6H_3), 55.8 (OMe), 39.7, 26.3, 15.3 ($(CH_2)_3Ph$), 20.1, 18.8, 18.5 ($Si(CH_2)_3Si$), −3.2 ($SiMe_2$), −4.9 (SiMe). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ 1.86 (G2–*Si*), 1.19 (G1–*Si*), not observed (G0–*Si*). MS (MALDI-TOF): *m*/*z* 2512.4, Anal. Calc. [MNa^+]: 2512.5.

1.3. Preparation and data for G1TiCp

A solution of [$CpTiCl_3$] (0.43 g, 2.0 mmol) in toluene (20 ml) was added to a solution of **G1OH** (0.54 g, 0.49 mmol) in toluene (10 ml). The solution was heated at 80°C for 6 h and subsequently stirred overnight at r.t. Then, the solvent was removed in vacuo to obtain **G1TiCp** as a red oil (0.89 g, 100%). Anal. Calc. for $C_{80}H_{116}Cl_8O_8Si_5Ti_4$: C, 52.8; H, 6.4. Found: C, 53.1; H, 6.5%. ^1H-NMR ($CDCl_3$): δ 6.90 (m, 1 H, C_6H_3), 6.73 (s, 5 H, C_5H_5), 6.70 (m, 1 H, C_6H_3), 6.63 (m, 1 H, C_6H_3), 3.86 (s, 3 H, OMe), 2.56 (m, 2 H, $CH_2CH_2CH_2Ph$), 1.57 (m, 2 H, $CH_2CH_2CH_2Ph$), 1.29 (m, 2 H, $SiCH_2CH_2CH_2Si$), 0.52 (m br, 6 H, $SiCH_2CH_2CH_2Si$ and $CH_2CH_2CH_2Ph$ overlapping), −0.06 (s, 6 H, $SiMe_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 157.3, 149.8, 140.0, 120.3, 118.9, 113.1 (C_6H_3), 121.0 (C_5H_5), 56.4 (OMe), 39.9, 26.1, 15.4 ($(CH_2)_3Ph$), 20.3, 18.6, 17.6 ($Si(CH_2)_3Si$), −3.3 ($SiMe_2$). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ 1.62 (G1–*Si*), 0.78 (G0–*Si*).

1.4. Preparation and data for G2TiCp

This dendrimer was prepared by a method similar to that of **G1TiCp**. Anal. Calc. for $C_{176}H_{268}Cl_{16}O_{16}Si_{13}Ti_8$: C, 53.4; H, 6.8. Found: C, 53.3; H, 6.6%. ^1H-NMR ($CDCl_3$): δ 6.89 (m, 2 H, C_6H_3), 6.73 (s, 10 H, C_5H_5), 6.70 (m, 2 H, C_6H_3), 6.60 (m, 2 H, C_6H_3), 3.85 (s, 6 H, OMe), 2.56 (m, 4 H, $CH_2CH_2CH_2Ph$), 1.55 (m, 4 H, $CH_2CH_2CH_2Ph$), 1.30 (m, 4 H, $SiCH_2CH_2CH_2Si$), 0.53 (m br, 18 H, $SiCH_2CH_2CH_2Si$ and $CH_2CH_2CH_2Ph$ overlapping), −0.06 (s, 12 H, $SiMe_2$), −0.09 (s, 3 H, SiMe). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 157.2, 149.8, 139.9, 120.2, 118.9, 113.1 (C_6H_3), 121.0 (C_5H_5), 56.4 (OMe), 39.9, 26.1, 15.4 ($(CH_2)_3Ph$), 20.2, 18.9, 18.5 ($Si(CH_2)_3Si$), −3.2 ($SiMe_2$), −4.9 (SiMe). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ 1.89 (G2–*Si*), 1.20 (G1–*Si*), not observed (G0–Si).

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References

[1] M.Q. Zhao, R.M. Crooks, Angew. Chem. Int. Ed. Engl. 38 (1999) 364.

[2] S.C. Bourque, F. Maltais, W.-J. Xiao, O. Tardif, H. Alper, P. Arya, L.E. Manzer, J. Am. Chem. Soc. 121 (1999) 3035.

[3] H. Brunner, J. Organomet. Chem. 500 (1995) 39.

[4] J.W.J. Knapen, A.W. van der Made, J.C. de Wilde, P.W.N.M. van Leeuwen, P. Wijkens, D.M. Grove, G. van Koten, Nature 372 (1994) 659.

[5] (a) See G.R. Newkome, E. He, C.N. Moorefield, Chem. Rev. 99 (1999) 1689, and references therein. Selected references on the synthesis of periphery-metallated carbosilane dendrimers are: (b) J.L. Hoare, K. Lorentz, N.J. Hovestad, W.J.J. Smeets, A.L. Spek, A.J. Canty, H. Frey, G. van Koten, Organometallics 16 (1997) 4167; (c) A.W. Kleij, H. Kleijn, J.T.B.H. Jastrzebski, W.J.J. Smeets, A.L. Spek, G. van Koten, Organometallics 18 (1999) 268; (d) N.J. Hovestad, J.L. Hoare, J.T.B.H. Jastrzebski, A.J. Canty, W.J.J. Smeets, A.L. Spek, G. van Koten, Organometallics 18 (1999) 2970; (e) B. Alonso, I. Cuadrado, M. Morán, J. Losada J. Chem. Soc., Chem. Commun. (1994) 2575; (f) F. Lobete, I. Cuadrado, C.M. Casado, B. Alonso, M. Morán, J. Losada, J. Organomet. Chem. 509 (1996) 109; (g) C.M. Casado, I. Cuadrado, B. Alonso, M. Morán, J. Losada, J. Electroanal. Chem. 463 (1999) 87; (h) D. Seyferth, T. Kugita, A.L. Rheingold, G.P.A. Yap, Organometallics 14 (1995) 5362; (i) M. Benito, O. Rossell, M. Seco, G. Segalés, Organometallics 18 (1999) 5191; (j) C. Kim, I. Jung, J. Organomet. Chem. 588 (1999) 9.

[6] For example, see (a) V. Cadierno, A. Igau, B. Donnadieu, A.-M. Caminade, J.P. Majoral, Organometallics 18 (1999) 1580; (b) H. Sellner, D. Seebach, Angew. Chem. Int. Ed. Engl. 38 (1999) 1918; P.B. Rheiner, D. Seebach, Chem. Eur. J. 5 (1999) 3221; (c) The preparation of a titanium dendrimer, without preparative or characterisation details, has been reported by K. Brüning, H. Lang, J. Organomet. Chem. 575 (1999) 153; (d) Patents about Group 4 metal-containing dendrimers, their preparation and use as catalysts have been published by D. Seyferth, R. Wryrwa, U.W. Franz, S. Becke, PCT Int. Appl. WO 97/32908, 12 Sep 1997; D. Seyferth, R. Wryrwa, PCT Int. Appl. WO 97/32918, 12 Sep 1997.

[7] S. Arévalo, J.M. Benito, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, J. Organomet. Chem. 592 (1999) 265.

[8] (a) W. Skupinski, A. Wasilewski, J. Organomet. Chem. 282 (1985) 69; (b) K. Nomura, N. Naga, M. Miki, K. Yanagi, A. Imai, Organometallics 17 (1998) 2152 and references therein.

[9] I. Cuadrado, M. Morán, J. Losada, C.M. Casado, C. Pascual, B. Alonso, F. Lobete, Adv. Dendritic Macromol. 3 (1996) 151.