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ABSTRACT

Iminopyridine ligands of general formula Gn-*PBE*-**ONN** (Gn-*PBE* = Fréchet-type dendritic wedges of generation G0 (1), G1 (2), G2 (3), and G3 (4); -**ONN** = -O-4-(2,5-Me₂C₆H₂)-N=CH-2-py) have been prepared starting from H-**ONN**. Reaction of these bidentate ligands with [NiBr₂(DME)] results in the nickel(II) complexes [NiBr₂(Gn-*PBE*-**ONN**)] (5–8). The methylaluminoxane (MAO)-activated monometallic complexes have been studied in the transformation of ethylene into mixtures of polyethylene and oily oligomers, and their catalytic performance scrutinized as a function of dendritic size. A comparison with the behavior observed for related polymetallic dendrimers has enabled the dendritic features that affect various catalytic parameters to be determined. Thus, it has been possible to discern whether the dendritic effect detected in the catalysis should be ascribed to the metallic nuclearity rather than the bulkiness of the metallodendrimer.

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1. Introduction

Amongst other attractive applications, dendritic architectures [1] have emerged as promising, well-defined supports for catalytically active metal sites that operate under homogeneous conditions [2], a field in which organocatalysis [3] and dendrimer-encapsulated nanoparticles have also received a great deal of attention [4]. The location of metal complexes, which for catalytic purposes is generally at the periphery or at the core or focal point of the dendritic framework, greatly affects the properties of metallodendrimers [5]. For instance, whilst high local concentrations of metal sites present at the surface of peripheral metallodendrimers are expected to cause crowding or cooperative outcomes, site isolation phenomena can be envisioned for core-functionalized structures, where the metal nanoenvironment is gradually established with increasing dendrimer generation. For either metallodendrimer topology, dendritic effects-distinct features imparted by the dendrimer that would not otherwise be achievable-can come into play and influence numerous properties and applications [6], including catalytic performance [6b].

Following the seminal work published by Brookhart's group in 1995 [7], the renewed widespread research interest in the field of olefin polymerization catalyzed by well-defined late-transition metal complexes has provided a rationale for new catalyst design and reaction control aimed at the synthesis of ethylene derivatives ranging from light oligomers to high molecular weight polymers, with linear to hyperbranched—and dendritic [8]—microstructures, or polyethylenes incorporating polar co-monomers [9]. Among the prevalent pre-catalyst types explored, studies carried out with aryl *N*,*N*-iminopyridyl complexes of late-transition metal halides have shown that variation of the ligand substitution greatly influences the catalytic performance in terms of activity and selectivity (*i.e.*, oligomers vs. polymers, linear vs. branched) [10]. Nickel(II) catalysts of this kind are the most relevant to the present contribution [11].

Although metallodendrimers have also been applied in polymerization processes, apart from a limited number of interesting studies concerning the ROMP [12] or vinyl polymerization [13] of norbornene, most such studies have concentrated on the polymerization of ethylene. A few of these have involved group 4 metallocene-type Ziegler–Natta catalysts embedded at the periphery [14] or core [15] of carbosilane (CS) structures, which generally afford lower catalytic activities and linear polyethylenes with higher polydispersities compared with those of related non-dendritic complexes. Systems based on dendrimers functionalized with late-transition metals have offered greater diversity of outcomes. Thus, Mapolie et al. have found that a first-generation DAB-PPI





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dendrimer with alkyl(imido)pyridylpalladium complexes bound to its periphery is more active than its non-dendritic counterparts for the polymerization of ethylene, whereas the activity and selectivity of related salicylaldimine Ni(II) dendrimers change significantly with the generation (e.g., short oligomers for G1, and polymers for G2) [16]. Li and coworkers have reported peripheral bis(imino)pyridyliron(II) CS dendrimers of up to the second generation (G2), which are able to display much higher activity towards polyethylene formation and produce polymers of much higher molecular weight than the corresponding monometallic reference complex [17]. In contrast, studies published by the Moss group on ethylene oligomerization using bis(imino)pyridyliron or α -diiminepalladium complexes symmetrically substituted with poly(benzvl ether)-also known as Fréchet-type-or CS dendrons concluded that the type and size of the dendrons have little effect on catalytic performance and suggested that this result opens up the possibility to separate the active species from the product stream by means of filtration techniques [18]. Reek, van Leeuwen, and coworkers have described a site-isolation effect in the oligomerization of ethylene promoted by a SHOP-process type complex substituted with CS dendrons, in which the dendritic P,O-ligand suppresses deactivation of the nickel center by avoiding the coordination of a second chelating ligand, thus resulting in much more active catalyst than in the non-dendronized case [19]. Our group has previously described series of CS dendrimers bearing aryl(imido)pyridylnickel(II) complexes at their surface, and found a strong dependence of the ethylene oligomerization/polymerization outcomes on the dendritic generation, which affects the composition of the final insertion product (oligomer/polymer ratios) and other parameters (i.e., activities, polydispersities, and molecular weights). These effects were ascribed to steric interactions of the growing polymer chain and the nanosized catalyst, as well as to the cooperative effects of several metal centers in close proximity [20]. We reached similar conclusions when using the palladium(II) counterparts of these species for the syndiotactic and alternating copolymerization of CO and 4-tert-butylstyrene [21].

Since metallodendritic architectures result in distinctive metal environments, and in light of the fact that the polymerization of ethylene with late-transition metal complexes is influenced by the active site surroundings, we set out to extend our previous studies by exploring the reactivity of monometallic, core-functionalized dendrimers in this type of process. Our studies on the organization of Fréchet-type dendritic arms around metal centers located at the focal point of the dendritic structures, in both solution and the solid state, revealed that the accessibility of the metal center varies with the size of the dendritic ligand [22]. As such, we reasoned that the dendrimer arrangements might modulate the catalytic properties. Herein we report the synthesis and characterization of nickel(II) complexes containing an aryl-N,N'-iminopyridine ligand substituted with Fréchet-type dendrons of up to the third generation. The influence of dendrimer generation on the catalytic behavior of these pre-catalysts is also analyzed, and the results compared to those found for the related peripheral polymetallic dendrimers [20].

2. Results and discussion

2.1. Synthesis of ligands and nickel complexes

Bidentate ligands **1–4** were prepared by treating the hydroxyliminopyridine **HONN** with the corresponding benzyl bromide Gn-*PBE*-Br (Scheme 1), in warm acetone, with K₂CO₃ as the base, and in the presence of 18-crown-6. After appropriate work up, they were isolated in good yields (>74%) as yellow solids that are soluble in acetone and chlorinated solvents, insoluble in alkanes, and scarcely soluble in diethyl ether, with their solubility in this solvent decreasing progressively as the generation number (n) increases.

The ¹H and ¹³C{¹H} NMR spectra of compounds **1–4** show two singlets for the Me¹³ and Me¹⁴ groups (numbering in Scheme 1; δ (¹H/¹³C) 2.2–2.4/16–18), together with another singlet at lower field for the imine group (CH⁷, δ (¹H/¹³C) 8.5/157). The protons of the dendritic moieties give sets of resonances in the three regions characteristic for this type of poly(benzyl ether) dendrons [22a]. The distinctive IR band at 1625–1610 cm⁻¹ for the imine double bond, and that for the pyridine ring at 1565 cm^{-1} , are only observed in the spectra of **1** and **2**, whereas for the compounds with larger dendritic wedges (3 and 4) they are hidden by the very strong absorption due to the aromatic C-C vibrations (ca. 1595 and 1450 cm⁻¹). Similarly, the relative intensity of the asymmetric (ca. 1300 cm^{-1}) and symmetric C–O–C stretching vibrations (ca. 1160 and 1050 $\rm cm^{-1}$) increases significantly on going from **1** to **4**. The positive-ion electrosprav mass spectra (ESI⁺-TOF/MS), carried out in 5 mM ammonium formate solution in CH₂Cl₂/MeOH, exhibit peaks that can be assigned to the protonated molecular ions [M+H]⁺ with the expected isotopic distributions.

Chelates **1–4** reacted with one equivalent of $[NiBr_2(DME)]$ (DME = dimethoxyethane- $\kappa^2 O$,O') in dichloromethane to form complexes $[NiBr_2(Gn-PBE-ONN)]$ **5–8** by displacement of the labile DME ligand (Scheme 1 and Fig. 1). The initial yellow-orange suspensions of the nickel precursor turned red-brown over the course of the reaction. Complexes **5–8** were isolated in good yields (>70%) as orange paramagnetic solids that are stable to air as solids and in solution and are insoluble in alkanes but soluble in acetone and in chlorinated and aromatic solvents.

The paramagnetism of nickel complexes 5-8 precludes their characterization by NMR spectroscopy. However, their identities were established by IR spectroscopy, mass spectrometry, magnetic susceptibility measurements and elemental analysis. Coordination of the iminopyridine ligands to the metal center in 5 and 6 is supported by the collapse of the three intense C=N and C=C bands observed in the range 1626–1565 cm⁻¹ in the free ligand into a single absorption, at around 1590 cm⁻¹, accompanied by two much weaker bands. The shift or disappearance of the C=N_{imine} vibration is attributed to a reduction in the electron density of the double bond upon coordination [20b]. The intense absorption of the dendritic moieties at 1595 cm⁻¹ overlaps the bands of interest in the case of the higher generation complexes 7 (G2) and 8 (G3). The molecular peak was only observed in the ESI⁺-TOF mass spectrum of the G3 complex 8. The protonated free ligand, or fragments thereof arising due to the loss of one or two bromides and the addition of ionizing agents, solvent or a second ligand, were the more characteristic peaks observed in the mass spectra of 5-7 (see Section 4). Magnetic susceptibilities were measured in the solid state and in solution (Table 1) and corrected to take into account the diamagnetic contribution, which varies considerably because of the large differences in molecular magnitude of the complexes under study (from 535 to 2021 g/mol). The resulting solid-phase paramagnetic moments lie in the range 2.70–3.06 $\mu_{\rm B}$ and are therefore close to the spin-only moment expected for two unpaired electrons $(2.82 \ \mu_{\rm B})$ and to reported values for other tetrahedral iminopyridyl Ni(II) complexes [23]. Similar moments were obtained in acetone $(2.84-3.22 \mu_{\rm B})$, thus indicating that the tetrahedral metal environment is maintained in solution.

2.2. Ethylene oligomerization/polymerization

In the presence of ethylene, and upon activation with MAO, nickel complexes **5–8** promote the formation of mixtures of a toluene-soluble fraction of oligomers together with solid polyethylene under mild conditions. Oligomer formation is the consequence of a competitive rate of chain transfer (k_{ct}) relative



Scheme 1.





Table 1							
Magnetic susceptil	oilities and	moments	for	nickel	complexes	[NiBr2(Gn-PH	BE-ONN)]
(5-8).							

Complex $10^6 \chi_D^c$		Solid phase ^a			Solution phase ^b		
	(cm³/ mol)	10 ⁶ χ _M ^d (cm ³ / mol)	10 ⁶ χ _Μ ′ ^e (cm ³ / mol)	${\mu_{\mathrm{eff}}}^{\mathrm{f}}$ (μ_{B})	10 ⁶ χ _M ^d (cm ³ / mol)	10 ⁶ χ _Μ ′ ^e (cm ³ / mol)	$\mu_{ m eff}^{\ \ f}$ ($\mu_{ m B}$)
5	-274	3287	3561	2.91	3111	3385	2.84
6	-414	2638	3052	2.70	3040	3454	2.87
7	-694	3133	3827	3.02	3648	4342	3.22
8	-1254	2675	3929	3.06	2830	4084	3.12

^a At r.t.

 $^{\rm b}\,$ At 20 °C, in acetone-d₆, [Ni] = 1.12 \times 10 $^{-2}$ M.

^c Diamagnetic susceptibility calculated using Pascal's constants.

^d Measured molar magnetic susceptibility. ^e Corrected magnetic susceptibility.

f uB – Bohr Magneter

^f μ B = Bohr Magneton.

to chain propagation (k_p) [24] in a process that is sensitive to the ability of the ligand to sterically block the axial sites of the active center, thus delaying chain transfer and enhancing chain growth [7,24]. The simultaneous formation of oligomers and polymers has been proposed to be caused by hindered rotation of the aryl-N bond, which results in two different propagating faces at the metal [25].

Table 2 lists the catalytic results and data corresponding to the polyolefinic products. The oligomeric oily fractions are composed of even-numbered olefins up to C_{34} that follow Schulz–Flory chain-length distributions with α values ranging from 0.70 to 0.81 ($\alpha = k_p/(k_p + k_{ct}) = \text{mol of } C_{n+2}/\text{mol of } C_n$) [26], with a selectivity of approx. 50 mol% for terminal alkenes. The number average molecular weight (M_n) of these oligomers is in the range 240–265, and their ¹H NMR spectra indicate a relatively low branching (4 branches per 100 C) [27]. The solid polymers have low average molecular weights, relatively wide polydispersities ($M_w = 1000-2500$ and PDI = 2.5–4.0), a low branching (essentially methyl groups in a ratio of 12–16 branches per 1000 main chain carbons) [28], and T_m values (115–118 °C) lower than the regular melting temperatures for HDPE (≥ 135 °C).

The size of the PBE dendron has a limited influence on the oligomerization/polymerization process. Thus, nickel compounds 5-8 exhibit comparable activities in terms of oligomer and polymer production. In studies with Fe bis(imino)pyridyl and Ni and Pd α diimine monometallic complexes, Moss and coworkers also observed that the size (and type) of the dendritic substituent at the para position of the ArN group had a minor effect on the catalytic activity [18]. Amongst the parameters shown in Table 2, only the Schultz-Flory constant α changes regularly with the generation number, although the differences between consecutive values are scarcely significant except for the larger dendrons. Other parameters, as the polymer $M_{\rm w}$, show an irregular and small variation when the generation number increases. A comparison of the catalytic data of the GO-G3 complexes 5-8 with that of the related complexes [NiBr₂(RONN)] where R = H(I) and SiMe₃ (II) (Table 3) suggests that the catalytic outcome is more sensitive to the electronic nature than to the size of the O-substituent at the aryloxy ring of the ligand.

These results are in contrast with the strong influence of the dendrimer generation in ethylene catalysis that we observed in

Table 2

E411	- 11	1	+ - 1	INCD. (C.	DDC ONINI)]	
ernviene	Oligomerization	1/noivmerization	$c_{2}c_{2}c_{3}c_{2}c_{3}c_{3}c_{3}c_{3}c_{3}c_{3}c_{3}c_{3$	1 N B r_{2} $(1.n)$		(5_X)////A() ~
LUIVICIIC	Ungoincinzation		catalyzed by	THIDI / OII	I DL UIIII/	(J)) () ()) ()) ()) ()) ()) () ()) () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () () ()() () () ()() () () ()()()()()()()()(

Precatalyst	Oligomers				Polymer				
	act. ^{b,c}	$\alpha^{d,e}$	α-Olefin (mol%) ^e	M_n^{f}	Yield (g)	act. ^{b,c}	$T_{\rm m} (^{\circ} {\rm C})^{\rm g}$	M_{w}^{h}	PDI ^h
5 (G0)	3.70	0.81	50	266.7	1.58	2.35	116.4	1800	2.69
6 (G1)	2.02	0.79	50	240.1	1.68	2.50	115.4	960	2.53
7 (G2)	3.27	0.76	52	238.3	1.66	2.47	117.1	2320	2.88
8 (G3)	3.13	0.70	50	242.4	2.63	3.91	118.2	2530	3.97

Conditions: 50 mL toluene; $n(Ni) = 14 \mu mol$; Al/Ni = 1000; $t_p = 24$ h; $T_p = 20 \circ C$; $P_{ethylene} = 2$ bar; activities $\pm 7\%$.

^b Activity: $g/(mmol_{Ni} \times h \times bar)$.

Corrected to consider the lower olefin lost during work up.

Schulz-Flory parameter, $\alpha = k_p/(k_p + k_{ct})$ [26].

Determined by GC.

Determined by ¹H NMR spectroscopy [27]. f

^g Determined by DSC (2nd heating run).

Determined by GPC.

Table 3

Ethylene oligomerization/polymerization catalyzed by [NiBr₂(**HONN**)] (I) and carbosilane metallodendrimers Gn-CS-(**ONN**NiBr₂)_m (II-V)/MAO.^{a,b}.

Br



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G0-CS-(ONNNiBr₂)₁ (II) G2-CS-(ONNNiBr₂)₈ (IV) G1-CS-(ONNNiBr₂)₄ (III) G3-CS-(ONNNiBr₂)₁₆ (V)



Me		e 	
/~~.(Mé	$ _{2} _{2} _{4}$	G3- <i>CS</i>

Precatalyst	Oligomers			Polymer			
	Activity	α	M _n	Activity	$M_{ m w}$	PDI	
I	3.70	0.65	341.1	2.09	5880	6.61	
II (G0)	5.21	0.70	265.8	13.21	1640	3.58	
III (G1)	8.32	0.60	284.5	14.88	2160	2.77	
IV (G2)	10.21	0.51	342.5	5.12	10620	11.25	
V (G3)	13.40	0.45	327.6	4.82	17070	14.06	

^a Conditions and considerations as in Table 2.

^b Data from Ref. [20].

our previous studies with CS dendrimers bearing one (G0), four (G1), eight (G2), or sixteen (G3) aryl(imido)pyridylnickel(II) complexes at their periphery (II-V, Table 3) [20]. These polymetallic dendrimers also afforded mixtures of oligomers and polymers with a low degree of branching, similar to that observed for 5-8 (it should be noted that we erroneously described the presence of large branches in the polymer fraction due to a misassignment of some of the ¹³C resonances in the previous report [20]).¹ The comparison of data in Tables 2 and 3 reveals the different evolution of some parameters on going from G0 to G3 for the two series of catalysts, PBE-based monometallic (5-8) and CS-based polymetallic dendrimers (II-V). Thus, a higher generation for II-V results in more oligomers and fewer polymers (from 5.2 to 13.4 and from 13.2 to 4.8 g mmol_{Ni}⁻¹ h^{-1} bar⁻¹, respectively) whereas the productivities for 5-8 are fairly insensitive to the dendrimer generation (2.0-3.5 and $2.5-4.0 \text{ g mmol}_{\text{Ni}}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ for oligomers and polymers, respectively; see Fig. 2). In the case of the Schulz-Flory parameter, a steady and sharp decrease is observed for the polymetallic dendrimers II-V (from 0.70 to 0.45) whereas 5-8 show a more moderate decrease. The polymer molecular weight (also the polydispersity, Fig. 3) increases in one order of magnitude for II-V (from 1600 to 17000) in contrast with the modest increase observed for 5-8 (from 1800 to 2500).

Tomalia pointed out that dendritic effects are related to one or more and perhaps the concurrent interaction of several structure



Fig. 2. Activities by monometallic (5-8) and peripheral (II-V) metallodendrimers of generation G0 to G3.

controlled parameters that include size, shape, surface chemistry, flexibility/rigidity, architecture or elemental composition [6c]. We initially interpreted the dendritic effects observed with the polymetallic CS dendrimers **II-V** as being partly due to the steric interaction between the dendritic structure and the growing polymer chains [20]. From the above comparison between the

¹ We thank one of the referees for comments leading us to correct our previous branching analysis for the polymers.



Fig. 3. Molecular weight and polydispersities of the polymeric fraction obtained by monometallic (**5–8**) and peripheral (**II–V**) metallodendrimers.

monometallic and polymetallic G0–G3 series of catalysts, we can now suggest that the dendritic effects observed with the latter in the polymerization of ethylene are more likely connected with the topology and, more specifically, the metallic nuclearity than with the size (bulkiness) of the dendrimer. Although other features of the CS structures (flexibility, for instance) might influence in the observation of dendritic effects with the polymetallic systems, it is noteworthy that Moss and coworkers observed only a minor impact of the type of dendrimer (CS or PBE) on the catalytic activity of related precursors [18a]. Nevertheless, a steric-based mechanism can yet be considered to explain the observed dendritic effects in **II-V** but considering the interaction between the high local concentration of growing polymer chains in the limited surface of high-generation dendrimers. We also noted previously that another possible contribution to the changes observed with the generation could arise from poor local heat dispersion at the dendritic surface where the active centers are concentrated [21b].

3. Conclusions

Aryliminopyridyl ligands substituted with poly(benzyl ether) dendritic wedges of up to the third generation have been obtained by alkylation of HO-4-(2,5-Me₂Ph)-N=CH-2-py at the phenolic oxygen. Displacement of the labile ligand in [NiBr₂(DME)] by the bidentate N,N'-ligands leads to straightforward formation of the corresponding NiBr₂ chelates. Upon activation with MAO, the nickel derivatives produce ethylene oligomerization and polymerization products under mild conditions. The catalytic properties are much less sensitive to dendrimer generation for these monometallic precursors than those found previously for polymetallic dendrimers with different amounts of the same nickel complex at their periphery. The oligomer/polymer distributions or the polymer molecular weights and polydispersities are likely regulated by the metallic nuclearity of the dendrimer, whereas the Schulz-Flory distribution might also be affected in some extent by the dendrimer bulkiness.

4. Experimental

4.1. Reagents and general techniques

All operations were performed under argon using Schlenk techniques. Unless otherwise stated, reagents were obtained from

commercial sources and used as received. [HO-4-(2,5-Me₂Ph)-N=CH-2-py] (HONN) [20a], [NiBr₂(DME)] [29], and the dendritic benzyl bromides Gn-PBE-Br [30] were prepared according to literature procedures. Solvents were dried prior to use and distilled under argon as described elsewhere [31]. NMR spectra were recorded using Varian Unity 500+, VR-300 or 200 NMR spectrometers. Chemical shifts (δ) are reported in ppm relative to SiMe₄, and were measured relative to the ¹³C and residual ¹H resonances of the deuterated solvents. Assignments for the iminopyridyl fragments are given according to the numbering of the positions depicted in Scheme 1. Coupling constants (J) are given in Hz. The following abbreviations/notations are used: Ph refers to an aromatic ring of the terminal benzyl groups, Ar to the internal rings of benzyl ethers, and ipso refers to the first ring position on going from the bidentate iminopyridyl ligand. IR spectra were recorded using a Perkin-Elmer FT-IR Spectrum-2000 spectrophotometer. The magnetic susceptibilities of the nickel compounds were measured in the solid state at room temperature in an Evans balance (Magway MSB MK1, Sherwood Scientific Ltd.) instrument calibrated using Hg[Co(NCS)₄] as standard, whereas solution $(1.12 \times 10^{-2} \text{ M})$ measurements were determined by the method proposed by Evans [32], using Wilmad coaxial NMR tubes in a Varian VR-300 NMR spectrometer, in acetone-d₆, at 20 °C, and SiMe₄ as a reference. For both methods, corrections for underlying diamagnetism were applied to the data using tabulated Pascal's constants [33]. Elemental analyses were performed by the Microanalytical Laboratories of the University of Alcalá using a LECO CHNS-932 microanalyzer. ESI-TOF mass spectra were recorded by the Research Services at the Universidad Autónoma de Madrid (SIDI) using Applied Biosystems spectrometers. Poly(methyl aluminoxane) improved process (PMAO-IP) in toluene (13 wt% Al) was purchased from Akzo Nobel. Oligomer products were analyzed using a Chrompack CP 9001 gas chromatograph equipped with a CP-Sil 5CB capillary column (10 m, 0.25 mm i.d., 0.12 μ m d.f.) under the following conditions: injector and detector temperature: 250 °C; oven temperature program: 100 °C/5 min, 5 °C/min ramp, 250 °C/15 min. DSC melting endotherms of polymers were recorded using a Perkin-Elmer DSC 6 instrument. Polyethylene molecular weight determinations were performed by the Polymer Technology Laboratory (LTEP) at the Universidad Rey Juan Carlos using a Waters GPCV2000 instrument operating at 145 °C with 1,2,4-trichlorobenzene (TCB) solvent (Number and type of columns: 2 PL Gel 10 micras Mixed B + 1 PL Gel 10 micras 10E6) and polystyrene calibration standards.

4.2. Preparation of dendrons Gn-PBE-ONN (1-4)

Benzyl bromide (n = 0) or the corresponding Fréchet wedge G*n*-*PBE*-Br (n = 1-3), 18-crown-6, K₂CO₃, and **HONN** were stirred in acetone (10–20 mL) at 70 °C for 48 h. The mixture was then filtered through Celite, the solvent removed in vacuo, and the residue treated as described below to give **1–4** as yellow solids.

4.2.1. GO-PBE-ONN (1)

Benzyl bromide (0.18 mL, 1.5 mmol), 18-crown-6 (80 mg, 0.30 mmol), K₂CO₃ (315 mg, 2.28 mmol) and **HONN** (339.4 mg, 1.5 mmol). The oily crude reaction mixture was washed with diethyl ether and hexane. Yield: 376 mg (79.0%). *Anal.* Calc. for C₂₁H₂₀ON₂ (316.40): C, 79.72; H, 6.37; N, 8.85. Found: C, 79.80; H, 6.36; N, 8,86%. ¹H NMR (CDCl₃): δ 2.26 (s, 3 H, Me¹⁴), 2.31 (s, 3 H, Me¹³), 5.08 (s, 2 H, CH₂O), 6.78 (s, 1 H, H³), 6.98 (s, 1 H, H⁶), 7.3–7.5 (m, 6 H, Ph and H¹¹), 7.80 (t, *J*_{H-H} = 7.6 Hz, 1 H, H¹⁰), 8.24 (d, *J*_{H-H} = 7.9 Hz, 1 H, H⁹), 8.56 (s, 1H, H⁷), 8.67 (d, *J*_{H-H} = 4.3 Hz, 1 H, H¹²). ¹³C{¹H} NMR (CDCl₃): δ 16.2 and 17.9 (Me^{13.14}), 70.2 (CH₂O), 113.5 (C³), 119.8 (C⁶), 121.4 (C⁹), 124.6 (C¹¹), 125.7 (C⁵), 127.8 (*p*-Ph), 127.2 and 128.4 (*o*- and *m*-Ph), 131.9 (C²), 136.8 (C¹⁰), 137.4 (*ipso*-Ph), 142.2 (C¹), 149.5 (C¹²), 155.3 (C⁴), 155.7

(C⁸), 157.5 (C⁷). IR (KBr pellet): v 1626 (s, C=N), 1602 and 1454 (s, C=C), 1563 (s, py-ring) 1303 (m, C-O-C_{as}), 1199 and 1023 cm⁻¹ (vs, C-O-C_{sym}). MS (ESI⁺-TOF in CH₂Cl₂/MeOH, NH₄HCOO 5 mM): m/z 317.16 [M + H]⁺.

4.2.2. G1-PBE-ONN (2)

G1-PBE-Br (500 mg, 1.30 mmol), 18-crown-6 (70 mg, 0.262 mmol), K₂CO₃ (271.3 mg, 1.965 mmol) and HONN (296 mg, 1.31 mmol). The crude reaction mixture was washed with diethyl ether and hexane. A second crop of compound 2 was obtained by combining the filtrates and cooling in a freezer overnight (-20 °C). Combined yield: 580 mg (84.0%). Anal. Calc. for C₃₅H₃₂O₃N₂ (528.64): C, 79.52; H, 6.10; N, 5.30. Found: C, 79.67; H, 6.01; N, 5.32%. ¹H NMR (CDCl₃): δ 2.23 (s, 3 H, Me¹⁴), 2.38 (s, 3 H, Me¹³), 5.00 (s, 2 H, ArCH₂O), 5.04 (s, 4 H, PhCH₂O), 6.56 (t, ${}^{4}J_{H-H}$ = 2.1 Hz, 1 H, p-Ar), 6.69 (d, ${}^{4}J_{H-H}$ = 2.1 Hz, 2 H, o-Ar), 6.73 (s, 1 H, H³), 6.96 (s, 1 H, H⁶), 7.3-7.5 (m, 11 H, Ph and H¹¹ overlapping), 7.77 (t, J_{H-H} = 7.9 Hz, 1 H, H¹⁰), 8.22 (d, J_{H-H} = 7.9 Hz, 1 H, H⁹), 8.52 (s, 1 H, H⁷), 8.67 (d, 1 H, J_{H-H} = 4.3 Hz, H¹²). ¹³C{¹H} NMR (CDCl₃): δ 16.1 and 17.9 (Me^{13,14}), 70.1 (ArCH₂O), 70.4 (PhCH₂O), 101.5 (p-Ar), 106.1 (o-Ar), 113.6 (C³), 119.8 (C⁶), 121.4 (C⁹), 124.6 (C¹¹), 125.2 (C⁵), 128.0 (*p*-Ph), 127.5 and 128.6 (*o*- and *m*-Ph), 131.9 (C²), 136.5 (C¹⁰), 136.9 (ipso-Ph), 139.9 (ipso-Ar), 142.3 (C¹), 149.5 (C^{12}), 155.4 (C^{4}), 155.9 (C^{8}), 157.5 (C^{7}), 160.1 (*m*-Ar). IR (KBr pellet): v 1611 (s, C=N), 1593 and 1452 (vs, C=C), 1565 (m, py-ring), 1306 (s, C-O-C_{as}), 1166 cm⁻¹ (vs, C-O-C_{sym}). MS (ESI⁺-TOF in CH₂Cl₂/MeOH,NH₄HCOO 5 mM): *m*/*z* 529.25 [M+H]⁺.

4.2.3. G2-PBE-ONN (3)

G2-PBE-Br (500 mg, 0.62 mmol), 18-crown-6 (33 mg, 0.124 mmol), K₂CO₃ (128 mg, 0.93 mmol) and HONN (140 mg, 0.62 mmol). The crude reaction mixture was washed with diethyl ether, and the resulting oily solid treated with hexane. Yield: 453 mg (76.7%). Anal. Calc. for C₆₃H₅₆O₇N₂ (953.13): C, 79.39; H, 5.92; N, 2.94. Found: C, 78.92; H, 5.84; N, 2.88%. ¹H NMR (CDCl₃): δ 2.23 (s, 3H, Me¹⁴), 2.38 (s, 3H, Me¹³), 4.97 (s, 4 H, G1–ArCH₂O), 5.00 (s, 2 H, G0-ArCH₂O), 5.01 (s, 8 H, PhCH₂O), 6.53 (t, 1 H, ${}^{4}J_{H-H}$ = 1.9 Hz, G0-*p*-Ar), 6.56 (t, ${}^{4}J_{H-H}$ = 1.9 Hz, 2 H, G1-*p*-Ar), 6.67 $(d, {}^{4}J_{H-H} = 1.9 \text{ Hz}, 6 \text{ H}, \text{ GO-o-Ar} \text{ and G1-o-Ar}), 6.74 (s, 1 \text{ H}, \text{H}^{3}),$ 6.95 (s, 1 H, H⁶), 7.3-7.4 (m, 21 H, Ph and H¹¹ overlapping), 7.77 (t, $J_{H-H} = 7.9$ Hz, 1 H, H¹⁰), 8.21 (d, $J_{H-H} = 7.9$ Hz, 1 H, H⁹), 8.52 (s, 1 H, H⁷), 8.67 (d, $J_{H-H} = 4.3$ Hz, 1 H, H¹²). ¹³C{¹H} NMR (CDCl₃): δ 16.1 and 17.9 (Me^{13,14}), 70.0 (G0-CH₂O and G1-CH₂O overlapping), 70.1 (PhCH₂O), 101.4 (G0-p-Ar), 101.6 (G1-p-Ar), 106.1 (G0-o-Ar), 106.3 (G1-o-Ar), 113.5 (C³), 119.8 (C⁶), 121.3 (C⁹), 124.6 (C¹¹), 125.2 (C⁵), 128.0 (p-Ph), 127.5 and 128.6 (o- and m-Ph), 131.9 (C²), 136.5 (C¹⁰), 136.8 (ipso-Ph), 139.3 (G1-ipso-Ar), 139.9 (G0-ipso-Ar), 142.3 (C1), 149.5 (C12), 155.3 (C4), 155.8 (C8), 157.5 (C⁷), 160.0 (G0-*m*-Ar), 160.2 (G1-*m*-Ar). IR (KBr pellet): v 1595 (vs, C=N and C=C overlapping), 1447 (s, C=C), 1296 (s, C-O-C_{as}), 1162 and 1057 cm⁻¹ (vs C–O–C_{sym}). MS (ESI⁺-TOF in $CH_2Cl_2/$ MeOH,NH₄HCOO 5 mM): *m*/*z* 953.42 [M+H]⁺.

4.2.4. G3-PBE-ONN (4)

G3-*PBE*-Br (500 mg, 0.30 mmol), 18-crown-6 (16 mg, 0.06 mmol), K₂CO₃ (63 mg, 0.45 mmol) and **HONN** (68 mg, 0.30 mmol). The crude reaction mixture was washed with diethyl ether, and the resulting oily solid treated with hexane. Yield: 400 g (74.0%). *Anal.* Calc. for C₁₁₉H₁₀₄O₁₅N₂ (1802.10): C, 79.31; H, 5.82; N, 1.55. Found: C, 78.67; H, 5.82; N, 1.38%. ¹H NMR (CDCl₃): δ 2.23 (s, 3 H, Me¹⁴), 2.37 (s, 3 H, Me¹³), 4.94 (s, 8 H, G2-ArCH₂O), 4.96 (s, 4 H, G1-ArCH₂O), 4.97 (s, 2 H, G0-ArCH₂O), 4.99 (s, 16 H, PhCH₂O), 6.5–6.6 (3 × t, 7 H, G0-*p*-Ar, G1-*p*-Ar and G2-*p*-Ar, overlapping), 6.6–6.7 (3 × d, 14 H, G0-*o*-Ar, G1-*o*-Ar and G2-*o*-Ar, overlapping), 6.72 (s, 1 H, H³), 6.94 (s, 1 H, H⁶), 7.2–7.4 (m, 41 H, Ph and H¹¹ overlapping), 7.76 (t, *J*_{H-H} = 7.9 Hz, 1 H,

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 H^{10}), 8.20 (d, J_{H-H} = 7.9 Hz, 1 H, H^9), 8.51 (s, 1 H, H^7), 8.66 (d, J_{H-H} = 4.3 Hz, 1 H, H^{12}). ¹³C{¹H} NMR (CDCl₃): δ 16.2 and 17.9 (Me^{13,14}), 70.0 (G0-CH₂O, G1-CH₂O and G2-CH₂O, overlapping), 70.1 (PhCH₂O), 101.5 (G0-*p*-Ar), 101.6 (G1-*p*-Ar and G2-*p*-Ar, overlapping), 106.0 (G0-o-Ar), 106.4 (G1-o-Ar and G2-o-Ar overlapping), 113.5 (C³), 119.8 (C⁶), 121.3 (C⁹), 124.6 (C¹¹), 125.1 (C⁵), 128.0 (p-Ph), 127.5 and 128.6 (o- and *m*-Ph), 131.9 (C²), 136.5 (C¹⁰), 136.7 (*ipso*-Ph), 139.1 (G2-*ipso*-Ar), 139.2 (G1-*ipso*-Ar), 139.9 (G0-*ipso*-Ar) 142.3 (C¹), 149.5 (C¹²), 155.3 (C⁴), 155.8 (C⁸), 157.5 (C⁷), 160.0 (G0-*m*-Ar) 160.1 (G1-*m*-Ar), 160.2 (G2-*m*-Ar). IR (KBr pellet): *v* 1595 (vs, C=N and C=C overlapping), 1449 (s, C=C), 1297 (s, C-O-C_{*as*}), 1155 and 1047 cm⁻¹ (vs, C-O-C_{*sym*}). MS (ESI⁺-TOF in CH₂Cl₂/MeOH,NH₄HCOO 5 mM): *m*/*z* 1801.76 [M+H]⁺.

4.3. Preparation of [NiBr₂(Gn-PBE-ONN)] (5-8)

A solution of the corresponding ligand Gn-PBE-**ONN** (1–4) in CH₂Cl₂ (15 mL) was slowly added to a stirred suspension of [NiBr₂(DME)] in the same solvent (15 mL) at room temperature. Stirring was continued for 24 h. The initial yellow-orange suspension turned red-brown over the course of the reaction. The mixture was filtered through Celite, the solvent removed in vacuo to dryness, and the residue washed with several portions of hexane and dried in vacuo to give **5–8** as orange paramagnetic solids.

4.3.1. [NiBr₂(GO-PBE-ONN)] (5)

G0-*PBE*-**ONN** (1, 48 mg, 0.15 mmol) and $[NiBr_2(DME)]$ (46 mg, 0.15 mmol). Yield: 61 mg (76.0%). *Anal.* Calc. for $C_{21}H_{20}ON_2NiBr_2$ (534.90): C, 47.15; H, 3.77; N, 5.24. Found: C, 46.80; H, 4.18; N, 4.77%. IR (KBr pellet): v 1600 (m, C=N), 1597 (s, C=C), 1306 (m, C=O-C_{as}), 1201 and 1021 cm⁻¹ (s, C-O-C_{sym}). MS (ESI⁺-TOF in CH₂-Cl₂/MeOH, NH₄HCOO 5 mM): *m/z* 969.46 [(M –Br)₂ + NH₄HCOO]⁺, 735.24 [(1)₂Ni + HCOO]⁺, 313.16 [1+H]⁺.

4.3.2. [NiBr₂(G1-PBE-ONN)] (6)

G1-*PBE*-**ONN** (**2**, 80 mg, 0.15 mmol) and [NiBr₂(DME)] (46 mg, 0.15 mmol). Yield: 80 mg (71.0%). *Anal.* Calc. for $C_{35}H_{32}O_3N_2NiBr_2$ (747.14): C, 56.26; H, 4.32; N, 3.75. Found: C, 56.45; H, 4.84; N, 3.91%. IR (KBr pellet): *v* 1595 (vs, C=N and C=C overlapping), 1305 (m, C–O–C_{as}), 1151 and 1058 cm⁻¹ (vs, C–O–C_{sym}). MS (ESI⁺-TOF in CH₂Cl₂/MeOH, NH₄HCOO 5 mM): *m/z* 1159.41 [(**2**)₂-Ni + HCOO]⁺, 697.16 [M–Br+MeOH]⁺, 529.24 [**2**+H]⁺.

4.3.3. [NiBr(G2-PBE-ONN)] (7)

G2-*PBE*-**ONN** (**3**, 95 mg, 0.10 mmol) and [NiBr₂(DME)] (31 mg, 0.10 mmol). Yield: 84 mg (71.6%). *Anal.* Calc. for $C_{63}H_{56}O_7N_2NiBr_2$ (1171.63): C, 64.58; H, 4.82; N, 2.39. Found: C, 64.14; H, 4.94; N, 2.21%. IR (KBr pellet): v 1595 (vs, C=N and C=C overlapping), 1297 (m, C-O- C_{as}), 1156 and 1054 cm⁻¹ (vs, C-O- C_{sym}). MS (ESI⁺-TOF in CH₂Cl₂/MeOH, NH₄HCOO 5 mM): m/z 2009.76 [(**3**)₂-Ni + HCOO]⁺, 1055.34 [M-2 Br+HCOO]⁺, 953.42 [**3**+H]⁺.

4.3.4. [NiBr(G3-PBE-ONN)] (8)

G3-*PBE*-**ONN** (**4**, 100 mg, 0.055 mmol) and [NiBr₂(DME)] (17 mg, 0.055 mmol). Yield: 86 mg (77.4%). *Anal.* Calc. for $C_{119}H_{104}$ - $O_{15}N_2NiBr_2$ (2020.64): C, 70.73; H, 5.19; N, 1.39. Found: C, 70.15; H, 4.47; N, 1.17%. IR (KBr pellet): v 1595 (vs, C=N and C=C overlapping), 1296 (m, C–O– C_{as}), 1155 and 1053 cm⁻¹ (vs, C–O– C_{sym}). MS (ESI⁺-TOF in CH₂Cl₂/MeOH, NH₄HCOO 5 mM): m/z 2016.5 [M]⁺, 1801.75 [**4**+H]⁺.

4.4. General procedure for ethylene catalytic reactions

The corresponding catalyst precursor was weighed (7.5–28.3 mg) into a 250-mL screw-capped glass pressure reactor equipped with a mechanical stirrer. The reactor was capped and

sealed with a septum, purged with argon, charged with toluene (50 ml), and flushed with ethylene gas fed at constant pressure (2 bar) at 20 °C. PMAO-IP in toluene (Al/Ni = 1000) was added 10 min later with vigorous stirring. After 24 h the ethylene pressure was released, the polymerization reaction quenched with acidified methanol (2% HCl), and the reaction mixture stirred overnight. The polymer was then filtered, washed with methanol, and dried in an oven to constant weight. The reaction filtrate was washed with water, treated with MgSO₄, and the volatiles removed in a rotary evaporator. To minimize experimental error, the polymerization data represent the average of a number of runs disregarding the data from those with yields deviating more than 7%. The mixtures of oligomers were analyzed by GC in pentane as solvent. The integrated areas of heavier oligomers (from C_{12} to C_{32}) were used to calculate the Schulz-Flory α parameter [26], and lower olefins lost during workup were calculated using that α constant. The microstructure of these materials was also determined by ¹H (oligomers, r.t., CDCl₃) or ¹³C{¹H} NMR spectroscopy (polymers, 100 °C, 20% v/v bencene- d_6/TCB).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.07.025.

References

- (a) G.R. Newkome, C.N. Moorefield, F. Vögtle (Eds.), Dendrimers and Dendrons: Concepts, Syntheses, Applications, Wiley-VCH, Weinheim, 2001; (b) J.M.J. Fréchet, D.A. Tomalia (Eds.), Dendrimers and Other Dendritic Polymers, John Wiley & Sons, Chichester, 2002.
- [2] 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.
- [3] A.-M. Caminade, A. Ouali, M. Kellerab, J.P. Majoral, Chem. Soc. Rev. 41 (2012) 4113.
- [4] (a) X.H. Peng, Q.M. Pan, G.L. Rempel, Chem. Soc. Rev. 37 (2008) 1619;
- (b) V.S. Myers, M.G. Weir, E.V. Carino, D.F. Yancey, S. Pande, R.M. Crooks, Chem. Sci. 2 (2011) 1632.
- [5] For some recent reviews on catalysis with metallodendrimers, see: (a) D. Astruc, K. Heuzé, S. Gatard, D. Méry, S. Nlate, L. Plault, Adv. Synth. Catal. 347 (2006) 329;
 - (b) D. Méry, D. Astruc, Coord. Chem. Rev. 250 (2006) 1965;
 - (c) J.N.H. Reek, S. Arévalo, R. van Heerbeek, P.C.J. Kamer, P.W.N.M. van Leeuwen, in: B. Gates, H. Knözinger (Eds.), Advances in Catalysis, vol. 49, Academic Press, San Diego, 2006, pp. 71–151;
 - (d) L.H. Gade (Ed.) Topics in Organometallic Chemistry, vol. 20 (Dendrimer Catalysis), Springer, Berlin, 2006.;
 - (e) R. Andrés, E. de Jesús, J.C. Flores, New J. Chem. 31 (2007) 1161;
 - (f) D. Astruc, C. Ornelas, J. Ruiz, Acc. Chem. Res. 41 (2008) 841;
 - (g) E. de Jesús, J.C. Flores, Ind. Eng. Chem. Res. 47 (2008) 7968;
 - (h) A.-M. Caminade, P. Servin, R. Laurent, J.-P. Majoral, Chem. Soc. Rev. 37 (2008) 56:
 - (i) D. Astruc, E. Boisselier, C. Ornelas, Chem. Rev. 110 (2010) 1857.
- [6] For reviews on dendritic effects, see: (a) H.-F. Chow, C.-F. Leung, G.-X. Wang, Y.-Y. Yang, C. R. Chim. 6 (2003) 735;
 - (b) B. Helms, J.M.J. Fréchet, Adv. Synth. Catal. 348 (2006) 1125;
 - (c) D.A. Tomalia, New J. Chem. 36 (2012) 264.
- [7] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.
- [8] For instance, see: G. Sun, Z. Guan, Macromolecules 43 (2010) 4829.

- [9] For leading reviews in the topic, see: (a) S.D. Ittle, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169;
 (b) S. Mecking, Coord. Chem. Rev. 203 (2000) 325;
 - (c) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 203 (2003) 283;

(d) V.C. Gibson, G.A. Solan in: Z. Guan (Ed.) Topics in Organometallic Chemistry, vol. 26 (Metal Catalysts in Olefin Polymerization), Springer, Berlin, 2009, pp. 107–158.;

- (e) R.H. Camacho, Z. Guan, Chem. Commun. 46 (2010) 7879.
- [10] C. Bianchini, G. Giambastiani, L. Luconi, A. Meli, Coord. Chem. Rev. 254 (2010) 431.
- [11] W.-H. Sun, S. Song, B. Li, C. Redshaw, X. Hao, Y.-S. Li, F. Wang, Dalton Trans. 41 (2012) 11999 (and references therein).
- [12] (a) S. Gatard, S. Nlate, E. Cloutet, G. Bravic, J.-C. Blais, D. Astruc, Angew. Chem., Int. Ed. 42 (2003) 452; (b) S. Catard, S. Kablal, D. Méry, S. Nlate, E. Cloutet, L.V. Saillard, D. Astruc,
 - (b) S. Gatard, S. Kahlal, D. Méry, S. Nlate, E. Cloutet, J.-Y. Saillard, D. Astruc, Organometallics 23 (2004) 1313;
- (c) D. Méry, D. Astruc, J. Mol. Catal. A: Chem. 227 (2005) 1.
 [13] (a) R. Malgas-Enus, S.F. Mapolie, G.S. Smith, J. Organomet. Chem. 693 (2008) 2279;
- (b) R. Malgas-Enus, S.F. Mapolie, Polyhedron 47 (2012) 87.
- [14] (a) D. Seyferth, R. Wryrwa, U.W. Franz, S. Becke, PCT Int. Appl. WO 97/32908, (BAYER), 1997.;
 (b) H.G. Alt, R. Ernst, I. Böhmer, J. Mol. Catal. A: Chem. 191 (2003) 177;
 (c) S. Arévalo, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, M.-M. Rodrigo, S. Vigo, J. Organomet. Chem. 690 (2005) 4620.
- [15] (a) R. Andrés, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, Eur. J. Inorg. Chem. (2002) 2281;

(b) R. Andrés, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, Eur. J. Inorg. Chem. (2005) 3742;

(c) R. Andrés, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, J. Organomet. Chem. 690 (2005) 939.

- [16] (a) G. Smith, R. Chen, S. Mapolie, J. Organomet. Chem. 673 (2003) 111;
 (b) R. Malgas, S.F. Mapolie, S.O. Ojwach, G.S. Smith, J. Darkwa, Catal. Commun. 9 (2008) 1612.
- [17] Z.-J. Zheng, J. Chen, Y.-S. Li, J. Organomet. Chem. 689 (2004) 3040.
- [18] (a) M.J. Overett, R. Meijboom, J.R. Moss, Dalton Trans. (2005) 551;
 (b) B. Blom, M.J. Overett, R. Meijboom, J.R. Moss, Inorg. Chim. Acta 358 (2005) 3491.
- [19] C. Müller, L.J. Ackerman, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Am. Chem. Soc. 126 (2004) 14960.
- [20] (a) J.M. Benito, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, Chem. Commun. (2005) 5217;

(b) J.M. Benito, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, P. Gómez-Sal, Organometallics 25 (2006) 3876.

- [21] (a) J.M. Benito, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, Organometallics 25 (2006) 3045;
 (b) C. Margare, Old J.M. Benite, J.C. Flores, F. de Jarás, Jap. J. Charg. 40 (2000)
 - (b) F. Matínez-Olid, J.M. Benito, J.C. Flores, E. de Jesús, Isr. J. Chem. 49 (2009) 99.
- [22] (a) A. Sánchez-Méndez, J.M. Benito, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, P. Gómez-Sal, Dalton Trans. (2006) 5379;
 (b) A. Sánchez-Méndez, E. de Jesús, J.C. Flores, P. Gómez-Sal, Inorg. Chem. 46 (2007) 4793.
- [23] W.M. Motswainyana, M.O. Onani, S.O. Ojwach, B. Omondi, Inorg. Chim. Acta 391 (2012) 93.
- [24] J. Skupinska, Chem. Rev. 91 (1991) 613.
- [25] (a) C. Bianchini, G. Giambastiani, I.R. Guerrero, A. Meli, E. Passaglia, T. Gragnoli, Organometallics 23 (2004) 6087;
 (b) S. Zai, F. Liu, H. Gao, C. Li, G. Zhou, S. Cheng, L. Guo, L. Zhang, F. Zhu, Q. Wu,
- Chem. Commun. 46 (2010) 4321. [26] (a) G.V. Schulz, Z. Phys. Chem., Abt. B 30 (1935) 379;
- (b) P.J. Flory, J. Am. Chem. Soc. 62 (1940) 1561.
- [27] (a) O. Daugulis, M. Brookhart, Organometallics 21 (2002) 5926;
- (b) O. Daugulis, M. Brookhart, P.S. White, Organometallics 21 (2002) 5926,
- [28] Branching was determined by quantitative 13C NMR analysis according to G.B. Galland, R.F. de Souza, R.S. Mauler, F.F. Nunes, Macromolecules 32 (1999) 1620.
- [29] L.G.L. Ward in: F.A. Cotton (Ed.), Inorganic Syntheses, vol. 13, McGraw-Hill Book Company, New York, 1972, p. 154.
- [30] (a) C.J. Hawker, J.M.J. Fréchet, J. Chem. Soc., Chem. Commun. 22 (1990) 1010;
 (b) C.J. Hawker, J.M.J. Fréchet, J. Am. Chem. Soc. 112 (1990) 7638.
- [31] D.P. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, third ed., Pergamon Press, Oxford, 1988.
- [32] (a) D.F. Evans, J. Chem. Soc. (1959) 2003;
- (b) S.K. Sur, J. Magn. Reson. 82 (1989) 169.
- [33] G.A. Bain, J.F. Berry, J. Chem. Educ. 85 (2008) 532.