ORGANOMETALLICS

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pubs.acs.org/Organometallics

Divergent Route to the Preparation of Hybrid Pt–Fe 2,4,6-Tris(4-ethynyl)phenyl-1,3,5-triazine Metallodendrimers for Nonlinear Optics

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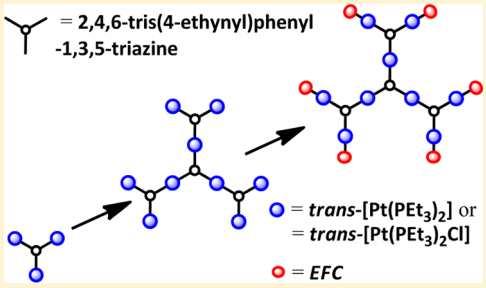
Supporting Information

ABSTRACT: The synthesis strategy for the preparation of novel platinum acetylide homometallic and heterobimetallic dendrimers (containing Fe as the other metal fragment) based on a 2,4,6-tris(4-ethynyl)phenyl-1,3,5-triazine core (**3**) is reported. All the dendrimer generations (G0–G2) were synthesized under copper-free conditions following a divergent route. The G0-Pt dendrimer (**4**) was synthesized using the 1,3,5-triazine core (**3**) and *cis*-$[Pt(PEt_3)_2Cl_2]$ with a molar ratio of 1/4. The advantage of the current method is that different dendrimers can be prepared by following the same procedure with only changes in the molar ratios of the reactants involved. For instance, when **3** reacts with **4** in a 4/1 molar ratio, the G1 dendrimer **7** is afforded without the peripheral Pt moiety, but the G1 dendrimer with the peripheral Pt moiety (**8**) is formed when **3** reacts with **4** in a 1/3 molar ratio. On the other hand, the G2 dendrimer with a peripheral Pt moiety (**9**) is synthesized when **7** reacts with **4** in a 1/6 molar ratio. The heterobimetallic dendrimers were synthesized up to generation 1 by capping the corresponding Pt dendrimers with the ethynylferrocenyl group (EFC). The respective G0 (**6**)- and G1-capped (**10**) dendrimers were synthesized when EFC reacted with **4** and **8** in molar ratios of 9/1 and 18/1, respectively. Nonlinear optical (NLO) polarizabilities measured by hyper-Rayleigh scattering (HRS) have been evaluated for the core **3**, for the G0 dendrimer **4**, and for the G0 dendrimer capped with EFC (**6**). In spite of the fact that the stability of the higher generations in chloroform is too low to allow HRS measurements, the reported NLO results show a remarkable enhancement (plus 50%) upon capping the zero dendrimer generation (**6**), reflecting the importance of the introduction of electron donor organometallic capping groups in the hyperpolarizabilities of the resulting dendrimers.



INTRODUCTION

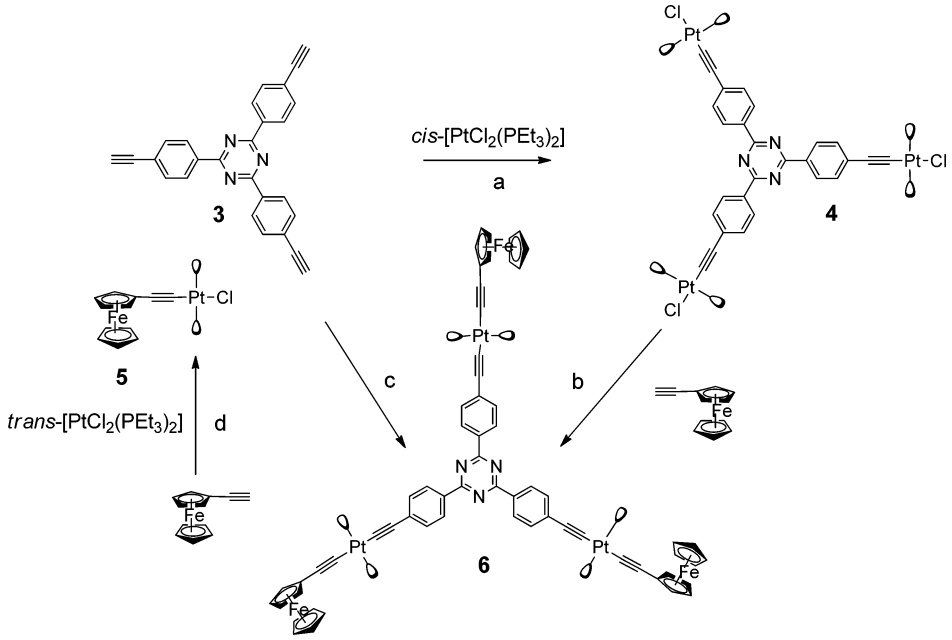
Recently, there has been tremendous interest in the synthesis and development of well-defined functionalized nanoscopic dendritic macromolecules with specific functions. The incorporation of transition metals into simple organic dendrimers provides them with desirable functionalities. These new materials[1] offer an attractive strategy for enhancement and modulation of material properties such as nonlinear optical (NLO),[2] liquid crystalline,[3] luminescent,[4] light-harvesting,[5] and electronic[6] properties. Although many organometallic dendrimers have been prepared so far, most of them contain metallic species either only at the core[7] or at the surface,[8] owing to their low stabilities and limited synthetic availability. Dendrimers with transition-metal ions in every branching point have so far been prepared[9] less and therefore still remain a topical challenge.

Organometallic conjugated compounds are particularly interesting for NLO applications, such as electro-optic modulators or frequency converters, because they combine the highly polarizable π-electron system of a conjugated ligand with the electron-donating or -accepting character of the metal center(s). This allows for the formation of noncentrosymmetric push–pull systems with high nonlinear polarizabilities (hyperpolarizability β).[2a−e] Instead of the traditional dipolar design, such an NLO-active complex can also have an octupolar symmetry (e.g., an electron-accepting core symmetrically surrounded by three conjugated arms with electron donors), resulting in a vanishing dipole moment. This is more likely to yield a favorable macroscopic arrangement and a better transparency/hyperpolarizability trade-off.[10] Suitably designed dendrimers also offer the prospect of further enhanced NLO responses by assembling multiple octupolar units in well-defined orientations and by extending the conjugated system.[2e−i]

Received: August 3, 2012

   dx.doi.org/10.1021/om300745v | *Organometallics* XXXX, XXX, XXX–XXX

Scheme 1. Synthesis of Compounds 4–6[a]



[a]Legend: (a) **3** and *cis*-$[PtCl_2(PEt_3)_2]$ (1/4 molar ratio), toluene/piperidine (2/1, v/v), 111 °C, 48 h; (b) $CHCl_3/Et_2NH$, CuI, 60 °C, 20 h; (c) toluene/diethylamine (1/1, v/v), CuI, 48 °C, 18 h; (d) $CHCl_3/Et_2NH$, CuI, 60 °C, 20 h. The shaded "teardrop" denotes PEt_3.

Apart from the specific metal, the core group or building block in an organometallic dendrimer plays a pivotal role in regulating its characteristic properties. In terms of NLO properties, octupolar organic compounds with a 1,3,5-triazine core are expected to have larger first hyperpolarizabilities than the analogous organic compounds with a 1,3,5-benzene core,[2h] since the triazine core is more electron withdrawing and possesses a larger nucleophilic susceptibility than the benzene core.[11] Thus, organometallic dendrimers with a 2,4,6-trisubstituted 1,3,5-triazine core might also have interesting physical properties: in particular, nonlinear optical properties. Over the past decade, much attention has been focused on the synthesis and characterization of purely organic dendrimers containing a 1,3,5-triazine core.[12] The symmetry and electronic properties of the triazine core have made it a valued molecular skeleton for exploring a wide range of interesting applications such as antitumor agents,[12a,13a] molecular recognition,[12c,e] gene therapy,[13b] OLEDs,[13c] and catalytic supports.[13d] However, organometallic dendrimers with the 2,4,6-trisubstituted-1,3,5-triazine core are extremely rare, to the best of our knowledge; so far, only one example of a zero-generation dendrimer based on the 2,4,6-tris(4-ethynyl)phenyl-1,3,5-triazine core (**3**) with Ru and Au has appeared in the literature[14] and a few others with additional N and S donors have been used to construct supramolecular and luminescent coordination complexes.[15,16] However, higher generation truly organometallic dendrimers based on the 2,4,6-trisubstituted 1,3,5-triazine core are uncommon,[17,18] and to date they have never been prepared with the 2,4,6-tris(4-ethynyl)phenyl-1,3,5-triazine core at a generation greater than 0. This could be due to the low stability/solubility of the products or to severe obstacles in the synthetic chemistry.[18] Platinum–acetylide complexes have attracted our attention, as they are not only thermally robust and stable[19] but also have the potential to provide new nanoscopic organometallic materials with unique properties.[20] The capping group plays an important role in the electronic communication throughout the organometallic dendrimer as well as in the NLO properties.[2i] Ethynylferrocene (EFC) is a good choice, because it is a good electron reservoir and a redox-active group.[21]

On the basis of our continued interest in the field of synthesis and characterization of organometallic dendrimers,[22] we present here the synthesis of novel platinum–acetylide dendrimers up to the second generation (G2) with a 2,4,6-tris(4-ethynyl)phenyl-1,3,5-triazine core using the divergent strategy. Also, the zero (G0)- and first-generation (G1) dendrimers were successfully capped with ethynylferrocene, the so-called hybrid Pt–Fe 2,4,6-tris(4-ethynyl)phenyl-1,3,5-triazine metallodendrimers. The second-order NLO properties of the zero-generation dendrimers (capped and uncapped with EFC) are reported.

RESULTS AND DISCUSSION

1. Synthesis. The G0 dendrimer **4** was prepared by treating 2,4,6-tris(4-ethynyl)phenyl-1,3,5-triazine (**3**) with *cis*-$[PtCl_2(PEt_3)_2]$ in a 1/4 molar ratio using toluene and piperidine as solvents (2/1, v/v) (Scheme 1). The reaction was carried out at 111 °C for 48 h without using any Cu(I) salt as a cocatalyst. The use of Cu salt leads to the formation of a gelatinous precipitate, which is difficult to characterize due to its utter insolubility.

The G1 dendrimer **7** without the peripheral metal moiety was prepared using the triazine core (**3**) and the G0 dendrimer **4** at a molar ratio of 4/1. By a reaction protocol similar to that used for the G0 dendrimer **4**, when **3** and **4** were used at a molar ratio of 1/3, another G1 dendrimer (**8**) with a peripheral metal Pt moiety was generated. A similar reaction of G1 dendrimer **7** with G0 dendrimer **4** at a molar ratio of 1/6 led to the successful formation of the G2 dendrimer **9** with a peripheral metal Pt moiety (Scheme 2). Surprisingly, our attempts to prepare **8** in significant yield starting from **7** using *cis*-$[PtCl_2(PEt_3)_2]$ were less successful.

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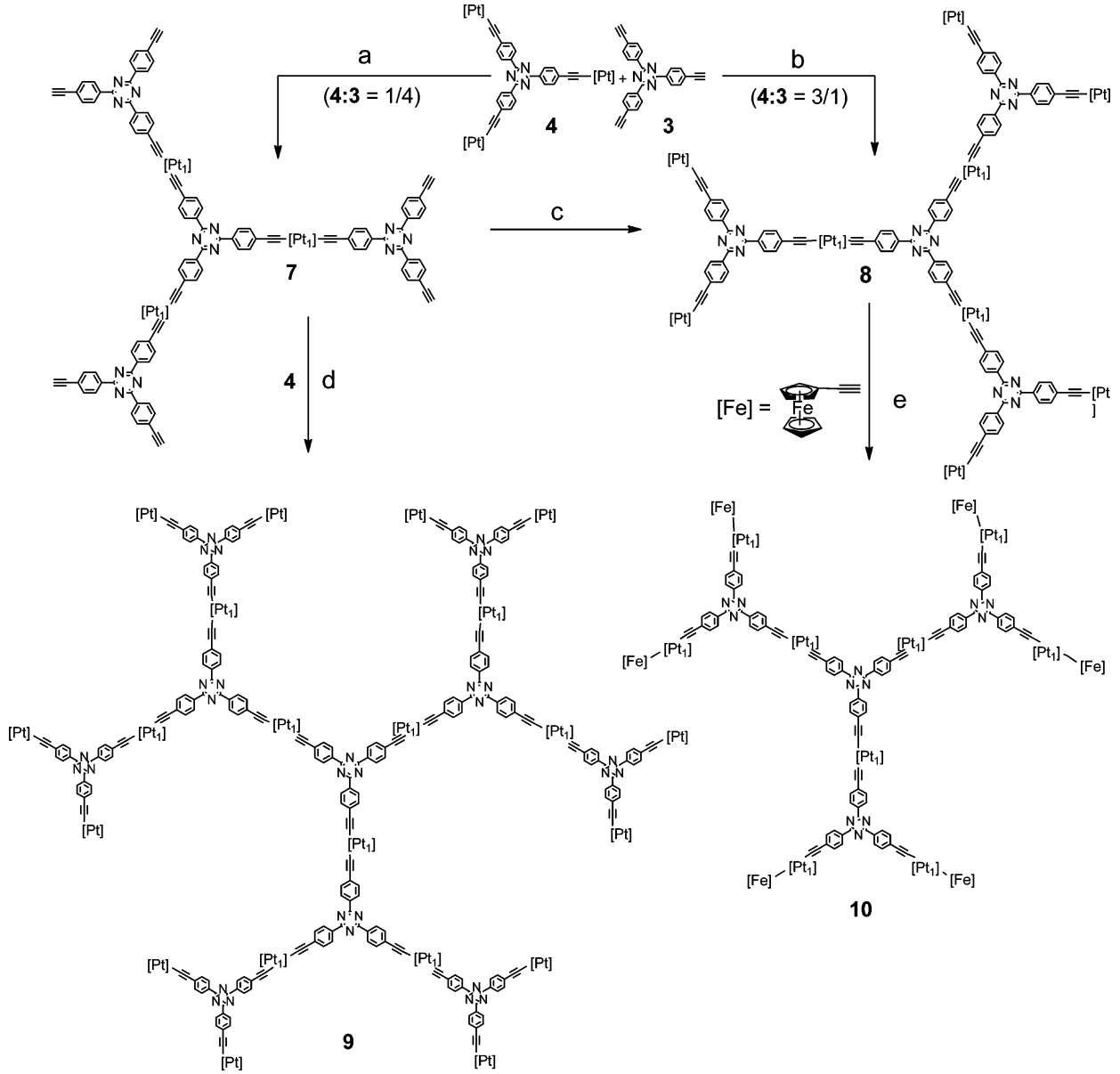
Scheme 2. Synthesis of Compounds 7−10[a]



[a]Legend for **7**−**9** (toluene/piperidine (2/1, v/v), 111 °C, 48 h): (a) **3** and **4** (4/1 molar ratio); (b) **3** and **4** (1/3 molar ratio); (c) **7** and *cis*-$[PtCl_2(PEt_3)_2]$ (1/9 molar ratio); (d) **7** and **4** (1/6 molar ratio). Legend for **10**: (e) **8** and EFC (ethynylferrocene) (1/18 molar ratio), $CHCl_3$/Et_2NH, CuI, 60 °C, 20 h. [Pt] = Pt_1Cl; [Pt_1] = *trans*-$[Pt(PEt_3)_2]$.

The successful synthesis of G0−G2 generation dendrimers following the divergent synthetic route tempted us to extend this protocol toward the capping of the G0 dendrimer in an effort to increase its NLO response. Therefore, the capping of the G0 dendrimer was carried out with ethynylferrocene and the successful preparation of the desired compound **6** was accomplished by either (I) coupling the G0 dendrimer directly with the capping group EFC or (II) coupling the platinated EFC group[23] (**5**) with compound **3** (Scheme 1). Method II was cumbersome and gave lower yield after purification in comparison to method I. Our successful results in capping the G0 dendrimer encouraged us to extend the capping reaction to the G1 dendrimer as well, in this case following method I. The ^{1}H NMR spectrum, though not well resolved, proves that at least five or even six out of six positions of **10** were capped by EFC (for further details see the Experimental Section and the Supporting Information).

2. Characterization. *2.1. ^{1}H and ^{31}P NMR.* The ^{1}H NMR spectrum of building block **3** showed two doublets at δ 8.72 and 7.69; the former signal is assignable to the ortho protons (with respect to the triazine core) in the aryl groups and the latter to the meta protons. In the zero-generation metallodendrimer **4**, the corresponding proton signals in the aromatic region showed a slight upfield shift, arising at δ 8.60 and 7.40, respectively. The drifting of electrons from d_{z^2} orbitals on the Pt atom to the triazine core make the aromatic protons more shielded in **4** in comparison to the triazine core **3**. The first (**7** and **8**)- and second-generation (**9**) dendrimers showed a similar pattern for the aromatic protons in their ^{1}H NMR spectra. The capped zero (**6**)- and first-generation (**10**) dendrimers also showed a similar trend in their ^{1}H NMR

dx.doi.org/10.1021/om300745v | *Organometallics* XXXX, XXX, XXX−XXX

spectra. In compound **7**, as the chemical and magnetic surroundings around the internal and external aryl groups are not identical, four different aromatic proton environments were obtained instead of six because of coincidences; two distinct doublets appeared for each corresponding ortho and meta proton of the internal and external aryl groups, respectively. Due to the influence of the two triazine cores, the ^{1}H NMR signals for the $P(CH_2CH_3)_3$ protons appeared at higher δ values (δ 2.24 and 1.30) in comparison with the corresponding ethyl protons (δ 2.09 and 1.25) in **4**. The presence of the electronegative chloro group coordinated to the Pt atom in **4** made the P nucleus (in PEt_3) more deshielded (δ 14.9) in comparison to the P nucleus in **7** (δ 11.2) without the chloro group. The six acetylenic protons in **7** were not observed due to the presence of piperidine, which functioned as a base to abstract these acidic protons. As a result, six piperidinium salt molecules are visible in the form of two singlets at δ 3.14 (24H) and 1.63 (36H) in the ^{1}H NMR spectrum (for further details see the Supporting Information).

As for **7**, the ^{1}H NMR spectrum of **8** showed four doublets at the aromatic region for aryl protons. The proton signals for the ethyl group were observed at δ 2.14 (m, 36H), 2.09 (m, 72H), and 1.29 (m, 162H); the first signal is assignable to the $-CH_2CH_3$ protons (italics) of the inner phosphane group, whereas the second signal is attributed to the same protons but of the corresponding ethyl groups linked to the outer phosphane atoms, and the last signal corresponds to the overall $-CH_2CH_3$ protons. These data are consistent with the ^{31}P NMR spectrum of **8**, which exhibited two singlets at δ 14.9 ($J_{Pt,\,P}$ = 2380 Hz) and 11.2 ($J_{Pt,\,P}$ = 2358 Hz) in a 2/1 integral ratio, which correspond to the phosphane groups bound to the six outer and three inner platinum atoms, respectively. Due to the presence of electronegative chloro groups attached to the terminal "Pt" atom, the terminal phosphorus atoms are more deshielded in comparison to the inner phosphorus atoms. Although the inner and outer phosphane groups have different shielding effects, this difference is only visible on the adjacent $-CH_2CH_3$ protons.

Compound **9** exhibited a pattern similar to that of **8** in its ^{1}H and ^{31}P NMR spectra. The number and position of aryl and ethyl protons observed in the ^{1}H NMR spectrum are in agreement with the proposed structure of **9**. Only a slight deviation of integral value from that expected was observed for $-CH_2CH_3$ protons (italics); signals for 90 protons at δ 2.33 and 162 protons at δ 2.09 were seen instead of 108 and 144 protons, respectively. The ^{1}H NMR spectrum of first (**8**)- and second-generation (**9**) metallodendrimers, in spite of being large molecules with high molecular weights, indicates the presence of a highly symmetric structure. The ^{31}P NMR spectrum of **9** showed two singlets with satellites at δ 14.9 ($J_{Pt,\,P}$ = 2378 Hz) and 11.2 ($J_{Pt,\,P}$ = 2356 Hz) with an integral ratio of about 16/9 instead of the expected 4/3. Apart from showing the expected proton signals and ratios for the proposed structure, compounds **7**–**9** also showed the presence of the conjugated acid of piperidine, a byproduct of the reaction which is extremely difficult to remove completely.

The ^{1}H NMR spectra of **6** and **9** showed the expected number of proton signals and shifts. In the case of **10**, the integral value tallies with 48 EFC proton signals (although the spectrum is not well resolved) instead of 54, indicating that at least 5 or even 6 EFC groups are bound to the external Pt atoms. The ^{31}P NMR spectrum of **6** showed one signal at δ 11.2 ($J_{Pt,\,P}$ = 2349 Hz), and that of **10** showed two signals at δ 11.7 ($J_{Pt,\,P}$ = 2351 Hz) and 11.4 ($J_{Pt,\,P}$ = 2354 Hz) in about a 1/1 integral ratio. The latter and former signals are assigned to the internal and the external phosphanes, respectively. The results show that the EFC group has a relatively lower deshielding effect than the −Cl group on the phosphane atoms. The magnitude of the $J_{Pt,\,P}$ value (~2350–2375 ppm) in ^{31}P NMR spectra strongly supports a trans arrangement[24] of the PEt_3 group around the corresponding "Pt" atom.

2.2. ^{13}C NMR. The ^{13}C NMR spectra are in good agreement with the corresponding ^{1}H NMR spectra for each compound. It is noteworthy that upon metalation the acetylenic carbon atom bearing the Pt moiety in compound **4** showed an 18 ppm downfield shift. In compound **6**, three responses appeared in the region 111.2–102.0 ppm for three chemically and magnetically different acetylenic "C" atoms, whereas four distinct ^{13}C responses in the region 70.2–67.0 ppm are obtained for Cp *C* atoms. In compound **7**, four ^{13}C responses for aromatic carbons bearing chemically different protons are obtained in the region 144.2–130.9 ppm. This result well supports the corresponding proton NMR spectrum of the aryl protons. Compounds **8** and **9** both showed two distinct ^{13}C responses at around 16.6 and 14.6 ppm for the $-CH_2CH_3$ group (italics); the former is assignable to the inner and the latter to the outer $-CH_2-$ carbon, respectively. Compound **10** showed three distinct responses at 70.1, 69.3, and 67.06 ppm for the *C*H carbons of the Cp ring.

2.3. UV–Vis Spectroscopy. The UV–vis spectrum of **3** in dichloromethane showed an intense band with λ_{max} at 304 nm, which can be attributed to the $\pi \rightarrow \pi^*$ transition occurring from the pheripheral aryl group to the central triazine core (Figure 1). The Pt metallodendrimers **4**, **8**, and **9** each showed

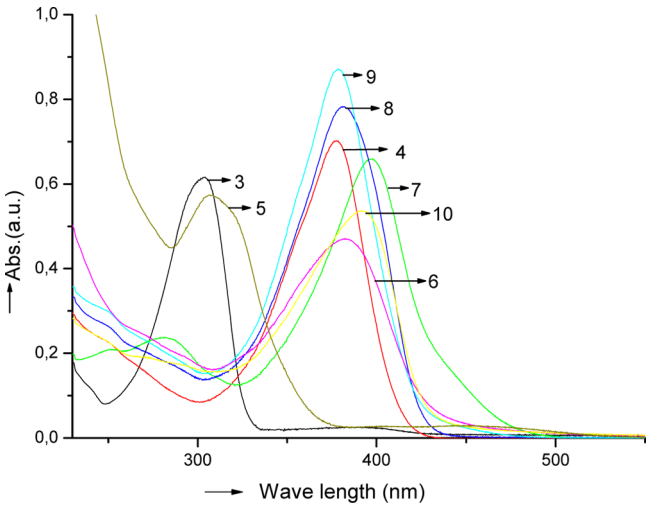


Figure 1. UV–vis spectra of compounds **3**–**10**.

an intense band with λ_{max} at 378, 382, and 378 nm, respectively, which are longer than that of **3**. The replacement of the acetylenic protons of the triazine core by $[Pt(PEt_3)_2Cl]$ originates a bathochromic shift. The more ionic Pt–C bonds in compounds **4**, **8**, and **9** (in comparison to the C–H bonds in compound **3**) make the π conjugation system more electron rich and, thereby, stabilizes the excited state (LUMO) relative to the ground state (HOMO), resulting in a smaller energy gap (HOMO to LUMO) for electronic transition; as a result, absorption occurs at a longer wavelength. It is noteworthy that the increase of π conjugation on going from the zero- to the

dx.doi.org/10.1021/om300745v | *Organometallics* XXXX, XXX, XXX–XXX

second-generation metallodendrimers does not have a significant effect on the λ_{max} value other than the gradual increase of molar absorptivity (ε (M^{-1} cm^{-1}) = 3485 × 10^2 (**4**), 1168 × 10^3 (**8**), 1303 × 10^3 (**9**)). Compound **7** showed two absorption bands with λ_{max} at 284 and 398 nm which can be attributed to the intraligand $\pi \rightarrow \pi^*$ transition occurring in the external and internal triazine cores, respectively. The Pt EFC compound **5** and the Pt metallodendrimers capped with EFC (**6** and **10**) present an intense absorption band with λ_{max} at 306, 384, and 392 nm, respectively; these results show a gradual increase in the bathochromic shift upon replacement of the chloro group in compounds **4** and **8** by ethynylferrocene (capped Pt metallodendrimers **6** and **10**).

2.4. Infrared Spectroscopy. The *trans*-chloroalkynylplatinum metallodendrimers **4**, **8**, and **9** exhibit a C≡C stretching frequency at relatively higher wavenumbers (i.e., 2113, 2095, and 2111 cm^{-1}, respectively) in comparison to compound **7**, where the chloro group is replaced by the acetylide group of the triazine core. This evidence can be explained by suggesting that the chloro group has relatively more electron withdrawing capacity from the C≡C bond in comparison to the triazine core, resulting in the higher wavenumber. Compounds **5**, **6**, and **10** showed similar trends. The C≡C stretching frequency in compound **5** having a chloro group appeared at ν 2115 cm^{-1}, whereas the same group in **6** and **10**, upon substitution of the chloro group by ethynylferrocene, appeared at ν 2096 and 2093 cm^{-1}, respectively.

3. NLO Studies. The NLO results obtained by hyper-Raleigh scattering[25] (HRS, with full correction for any spurious multiphoton-induced fluorescence contributions[26]) for the triazine core **3**, the G0 dendrimer **4**, and the G0 dendrimer capped with EFC (**6**) show an increase of the NLO response, from the core **3** to compound **6**, yielding hyperpolarizabilities (β_{xxx} component, measured at 1550 nm) of 41 × 10^{-30} esu for **3**, 59 × 10^{-30} esu for **4**, and 91 × 10^{-30} esu for **6** (corresponding to static values of 33 × 10^{-30}, 42 × 10^{-30}, and 65 × 10^{-30} esu, respectively), reflecting the importance of the introduced electron-donating organometallic moieties. Despite the use of the electron-accepting triazine core, the Pt donor complex **4** still only yields relatively modest hyperpolarizability (yet ∼50% higher than the free triazine core, which itself performs comparably or even better than other 1,3,5-triazine derivatives[27]). However, the additional capping with ferrocene units results in a further enhancement of β by another ∼50% (while maintaining an excellent transparency throughout the visible range: λ_{max} 384 nm for **6**), showing that the two metals cooperatively result in a larger effective donor strength at the periphery of the octupolar complex. Unfortunately, under experimental conditions, higher generation dendrimers present limited stability in chloroform, preventing the NLO measurements; therefore, we restricted our NLO studies to the smaller dendrimer generation, G0 dendrimer **4**, and the G0 dendrimer capped with EFC (**6**).

CONCLUSIONS

In summary, we have prepared, by using a reaction strategy under copper-free conditions coupled to a divergent synthetic protocol, Pt metallodendrimers up to the second generation using 2,4,6-tris(4-ethynyl)phenyl-1,3,5-triazine as a core. In addition, the synthesized metallodendrimers were capped up to the first generation with the ethynylferrocenyl fragment, giving the hybrid Pt−Fe 2,4,6-tris(4-ethynyl)phenyl-1,3,5-triazine metallodendrimers **6** and **10**. The first hyperpolarizabilities (β) for the triazine core **3**, the zero-generation dendrimer **4**, and the heterometallodendrimer **6** were also reported. We found that it is possible to increase significantly the hyperpolarizability by capping Pt metallodendrimers with ferrocene units. This work not only introduces a novel approach to reach target metallodendrimers by a short-cut route but also provides a new pathway in the direction of more efficient NLO systems based on hybrid metallodendrimers. Current work is underway to extend the new reaction route to other metal fragments[28] and to prepare more soluble and higher (hetero) metallodendrimer generations.

EXPERIMENTAL SECTION

General Information. All the experiments were carried out under dry nitrogen atmosphere by using standard vacuum line Schlenk techniques. All solvents used for the reactions were distilled under a nitrogen atmosphere and collected prior to use. Acetone was dried over $CaSO_4$ and distilled. Toluene and tetrahydrofuran were distilled from sodium/benzophenone, whereas methylene chloride and chloroform were distilled from calcium hydride. Diethylamine and triethylamine were distilled from potassium hydroxide. Usually, in most of the cases, solvents were degassed using dry nitrogen immediately prior to the reaction. Chemicals were purchased from Sigma−Aldrich or Acros. The starting materials, compounds 2,4,6-[4-$BrC_6H_4]_3$-1,3,5-C_3N_3 (**1**),[28] 2,4,6-[4-$(Me_3SiC{\equiv}C)C_6H_4]_3$1,3,5-$C_3N_3$ (**2**),[29] and 2,4,6-[4-$(HC{\equiv}C)C_6H_4]_3$-1,3,5-C_3N_3 (**3**),[28] were prepared by literature methods, and their purity was confirmed by NMR and MS. The complex *trans*-$[PtCl(C{\equiv}CC_5H_4FeC_5H_5)(PEt_3)_2]$ (**5**), which structural characterization was not published, was prepared by modifying a procedure reported by Vives et al.[30] All of the new compounds were characterized by ^1H, ^{13}C, and ^{31}P NMR, UV−vis, FTIR, and when possible, by EA and MS (in the case of compounds **7**, **9** and **10**, despite the variety of conditions tested, we have not succeeded in locating the molecular ions in the mass spectra of these metallodendrimers).

Physical Measurements. FTIR spectra were recorded with a Nicolet Avatar 360 FTIR spectrometer, calibrated with polystyrene, in KBr pellets; only specific bands are cited in the text. The UV−vis spectra were recorded with a GBC-Cintra 40 UV−vis spectrometer using a 1 cm optical path quartz cell with freshly prepared solutions (ca. 2 × 10^{-4} M) in distilled methylene chloride. Elemental analyses were carried out with a VariolEL instrument from Elementar Analysensysteme. The mass spectra (TOF-MS) were recorded with a Micromass LCT spectrometer. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were performed with a Bruker Avance II+ 400 at 299 K (probe temperature). The chemical shifts (δ) are reported in ppm and referenced to residual solvent peaks for ^1H and $^{13}C\{^1H\}$ NMR. The $^{31}P\{^1H\}$ NMR is referenced to external 85% H_3PO_4 aqueous solution.

NLO Measurements. The molecular first hyperpolarizabilities β of compounds **3**, **4**, and **6** were determined in dilute chloroform solution by means of the hyper-Rayleigh scattering (HRS) technique,[25] at the fundamental wavelength of 1550 nm, far from resonance. Briefly, our highly sensitive HRS setup (described in detail in ref 25) consists of a Ti:sapphire regenerative amplifier (Spectra-Physics Spitfire), pumping an optical parametric amplifier (Spectra-Physics OPA-800CP) tuned to 1550 nm (pulse duration ∼2 ps, repetition rate 1 kHz, pulse energy at the sample ∼20 μJ). A narrow spectral range around the second harmonic wavelength is detected in parallel by means of an intensified charge-coupled device (I-CCD) with red-sensitive photocathode, coupled to a spectrograph, enabling fast and complete correction for any multiphoton fluorescence background. Such a fluorescence background was observed for compounds **3** and **4** (respectively ∼2.5 and 1.2 times the solution HRS signal after integration over the 12 nm wide central region), underlining the necessity of this spectral analysis of the scattered light, even for these weakly fluorescent compounds.

For both complexes **4** and **6** and the organic core **3**, octupolar (D_{3h}) symmetry is assumed, so that the only non-zero components of the $\boldsymbol{\beta}$ tensor are $\beta_{xxx} = -\beta_{xyy} = -\beta_{yxy} = -\beta_{yyx}$ (with the x axis oriented along

dx.doi.org/10.1021/om300745v | *Organometallics* XXXX, XXX, XXX−XXX

one of the three molecular arms).[31,32] Chloroform itself was used as an internal calibration standard (as described before),[2c,26,33] adopting the effective $|\beta_{xxx}|$ value of 0.49×10^{-30} esu as determined in ref 34. In this way, the β_{xxx} component is obtained from the equation

$$|\beta_{xxx}^{\text{complex}}| = \sqrt{\frac{N_{\text{chloroform}}}{N_{\text{complex}}} \frac{S_{\text{solution}}^{(2\omega)} - S_{\text{chloroform}}^{(2\omega)}}{S_{\text{chloroform}}^{(2\omega)}}} \sqrt{\frac{9}{20}} |\beta_{xxx}^{\text{eff,chloroform}}| \quad (1)$$

The reported results for β are expressed in the B* convention.[35] As all of the investigated compounds absorb only at very short wavelength (λ_{max} 304, 378, and 384 nm for **3**, **4**, and **6**, respectively), they were all measured far from resonance, and the obtained hyperpolarizabilities can be reliably extrapolated to the static limit simply using the undamped two-level model.[36]

With the exception of higher dendrimer generations, all compounds were found to be stable in solution, i.e. no decomposition was observed in the linear absorption spectra; to limit effects of local photodecomposition in the laser focus, the solutions were stirred during the measurement to continuously refresh the exposed molecules. No correction for reabsorption of the HRS light at 775 nm was necessary (as this reabsorption was completely negligible; see Figure 1). The experimental error on β, excluding the systematic error on the calibration value of chloroform, is estimated to be ±5%.

Characterization of Compounds 1−3. *2,4,6-[4-BrC$_6$H$_4$]$_3$-1,3,5-C$_3$N$_3$ (**1**).*[29] Yield: 1.9 g (90%). δ_H (400 MHz; $CDCl_3$; Me_4Si): 8.60 (6H, d, J = 8.1 Hz, C_6H_4), 7.71 (6H, d, J = 8.1 Hz, C_6H_4). m/z (EI^+): 545.00 ([M^+], calcd for $C_{21}H_{12}N_3Br_3$ 544.86).

*2,4,6-[4-(Me$_3$SiC≡C)C$_6$H$_4$]$_3$-1,3,5-C$_3$N$_3$ (**2**).*[29] Yield: 2.2 g (66%). δ_H (400 MHz; $CDCl_3$): 8.67 (6H, d, J = 8.4 Hz, C_6H_4), 7.64 (6H, d, J = 8.4, C_6H_4), 0.31 (27H, s, $Si(CH_3)_3$). m/z (EI^+): 597.24 ([M^+], calcd for $C_{36}H_{39}N_3Si_3$ 597.25).

*2,4,6-[4-(HC≡C)C$_6$H$_4$]$_3$-1,3,5-C$_3$N$_3$ (**3**).*[28] Yield: 0.21 g (94%). δ_H (400 MHz; $CDCl_3$): 8.72 (6H, d, J = 8.8 Hz, C_6H_4), 7.69 (6H, d, J = 8.4 Hz, C_6H_4), 3.28 (3H, s, C≡C*H*). δ_C (100.6 MHz; $CDCl_3$): 172.2 (s, C_3N_3), 136.0 (s, C of C_6H_4), 132.4 (s, CH of C_6H_4), 128.8 (s, CH of C_6H_4), 127.0 (s, C of C_6H_4), 84.0 (s, *C*≡CH), 80.0 (s, C≡*C*H). ν_{max} (KBr)/cm^{-1}: 3290.20 (m (medium)), 3239.46 (m, C≡C), 1575.39 (s (strong), in-plane vibration of triazine ring), 1409.71 (w (weak)), 1372.85 (s), 1359.10 (s), 869.25 (w), 816.23 (C−H wagging) {658.98 (m) and 645.93 (m), out of plane ring vibration}. λ_{max} (CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}): 304 (30650); m/z (EI^+): 381.00 ([M^+], calcd for $C_{27}H_{15}N_3$ 381.13).

Preparation and Analytical Data of Compounds 4−10. *Synthesis of 2,4,6-[4-(Cl(PEt$_3$)$_2$PtC≡C)C$_6$H$_4$]$_3$-1,3,5-C$_3$N$_3$, Pt-G0 Dendrimer (**4**).* In a well-dried Schlenk tube, 0.046 g (0.12 mmol) of **3** and 0.271 g (0.54 mmol) of *cis*-[$PtCl_2(PEt_3)_2$] were dissolved in 45 mL of degassed toluene/piperidine (2/1, v/v), and the solution was refluxed (111 °C) for 48 h. The reaction solution was then vacuum-dried. The crude compound was washed with acetone followed by diethyl ether several times and filtered. After filtering, the title compound was obtained as a light yellow solid. It was then further purified through column chromatography on silica gel using benzene/chloroform as eluents. After crystallization from a dichloromethane/hexane solvent system, the title compound was obtained as light yellow crystals. Yield: 0.119 g (56%). δ_H (400 MHz; $CDCl_3$): 8.60 (6H, d, J = 8.4 Hz, C_6H_4), 7.40 (6H, d, J = 8.4 Hz, C_6H_4), 2.09 (36H, m, CH_2CH_3) and 1.25 (54H, m, CH_2CH_3). δ_C (100.6 MHz; $CDCl_3$): 171.1 (s, C_3N_3), 133.1 (s, C of C_6H_4), 130.9 (s, CH of C_6H_4), 128.6 (s, CH of C_6H_4), 102.5 (s, C≡C−Pt), 88.2 (s, C≡C−Pt), 14.5 (s, CH_2CH_3) and 8.1 (s, CH_2CH_3). δ_P (161.9 MHz, $CDCl_3$) 14.9 (s, $J_{Pt,P}$ = 2378 Hz). ν_{max} (KBr)/cm^{-1}: 2964.45 (m), 2876.10 (w), 2113.37 (s, C≡C), 1598.57 (s), 1562.48 (s), 1507.27 (s), 1454.71 (w), 1405.03 (m), 1359.35 (s), 1257.8 (w), 1173.75 (m), 1144.89 (w), 1034.94 (m), 818.95 (s), 766.73 (s), 734.29 (m). λ_{max} (CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}): 378 (34850). m/z (EI^+): 1779.59 ([$M + H]^+$, calcd for $C_{63}H_{103}Cl_3N_3P_6Pt_3$ 1779.46). Anal. Calcd for $C_{63}H_{103}Cl_3N_3P_6Pt_3$: C, 42.53; H, 5.78; N, 2.36. Found: C, 43.02; H, 6.03; N, 3.24.

*Synthesis of trans-[PtCl(C≡CC$_5$H$_4$FeC$_5$H$_5$)(PEt$_3$)$_2$] (**5**).*[30] In a well-dried Schlenk tube, 0.302 g (0.6 mmol) of *trans*-[$PtCl_2(PEt_3)_2$] was dissolved in degassed $CHCl_3$ (50 mL). Then 0.130 g (0.6 mmol) of ethynylferrocene complex (EFC) and 0.006 g of CuI (5 mol %), as catalyst were added along with 0.5 mL of $NHEt_2$. The solution was heated to 60 °C for 20 h. Thereafter the solution was dried under vacuum and chromatographed through silica gel using chloroform and methanol (98/2−96/4) as eluents. The title compound was obtained as a orange-red solid. Yield: 0.149 g (42%). δ_H (400 MHz; $CDCl_3$): 4.21 (2H, s, C_5H_4−C≡C), 4.13 (5H, s, C_5H_5), 4.06 (2H, s, C_5H_4−C≡C), 2.05 (12H, m, CH_2CH_3), 1.21 (18H, m, CH_2CH_3). δ_P (161.9 MHz, $CDCl_3$) 14.46 (s, $J_{Pt,P}$ = 2407 Hz)). δ_C (100.6 MHz; $CDCl_3$): 96.0 (s, Cp−*C*≡*C*−Pt), 72.7 (s, C of Cp), 70.2, 69.6, and 67.1 (s, *C*H of Cp and C_5H_4(Cp)), 14.7 (s, CH_2CH_3), 9.1 (s, CH_2CH_3). ν_{max} (KBr)/cm^{-1}: 3093.20 (w), 2932.41 (w), 2875.87 (w), 2115.70 (m, C≡C), 1451.68 (s), 1411.05 (m), 1252.04 (w), 1230.15 (w), 1104.82 (m), 1035.27 (s), 1003.85 (w), 922.88 (w), 813.15 (m), 768.81 (s), 733.38 (m), 522.58 (m), 486.81 (m). λ_{max} (CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}): 306 (28550) m/z (EI^+): 676.10 ([$M]^+$, calcd for $C_{24}H_{40}ClFeP_2Pt$ 676.12), 699.11 ([$M + Na]^+$, calcd for $C_{24}H_{39}ClFeP_2PtNa$ 699.11).

*Synthesis of Pt-G0 Dendrimer Capped with EFC (**6**). Method I.* In a well-dried Schlenk tube, **4** (0.089 g, 0.05 mmol) and ethynylferrocene (0.098g, 0.45 mmol) were dissolved in degassed CH_3Cl (30 mL) and diethylamine (4.5 mL). After 10 min, CuI (0.002g, 0.01 mmol, 20 mol %) was added and the mixture was heated to 60 °C with stirring for 20 h. The solvent was removed on a rotavap, and the crude compound was chromatographed on silica gel using $CHCl_3$ and MeOH (98/2−95/5) as eluents. After drying, the title compound was obtained as an orange-red semisolid. Yield: 0.048 g (42%).

Method II. In a well-dried Schlenk tube, **3** (0.038 g, 0.1 mmol) and **5** (0.236 g, 0.4 mmol) were dissolved in degassed toluene (4 mL) and diethylamine (4 mL). After 10 min, CuI (0.004 g, 0.02 mmol, 20 mol %) was added and the mixture was heated to 48 °C with stirring for 18 h. The solvent was removed on a rotavap, and the crude compound was chromatographed on silica gel using $CHCl_3$ and MeOH (98/2−95/5) as eluents. After drying, the title compound was obtained as an orange-red semisolid. Yield: 0.076 g (36%). δ_H (400 MHz; $CDCl_3$): 8.61 (6H, d, J = 8 Hz, C_6H_4), 7.40 (6H, d, J = 8 Hz, C_6H_4), 4.23 (6H, s, C_5H_4−C≡C), 4.14 (15H, s, C_5H_5), 4.06 (6H, s, C_5H_4−C≡C), 2.21 (36H, m, CH_2CH_3), 1.26 (54H, m, CH_2CH_3). δ_C (100.6 MHz; $CDCl_3$): 171.1 (s, C_3N_3), 132.2 (s, C of C_6H_4), 130.9 (s, *C*H of C_6H_4), 128.8 (s, CH of C_6H_4), 128.6 (s, C of C_6H_4), 111.2 (s, C≡C−Pt), 104.0 (s, Cp−C≡*C*−Pt), 102.0 (s, (triazine)C≡C−Pt), 70.2 (s, *C*H of C_5H_4(Cp)), 69.4 (s, C of Cp), 68.1 (s, *C*H of C_5H_4(Cp)), 67.0 (s, C of C_5H_4(Cp)), 16.5 (s, CH_2CH_3), 8.4 (s, CH_2CH_3). δ_P (161.9 MHz, $CDCl_3$): 11.2 (s, $J_{Pt,P}$ = 2349 Hz). ν_{max} (KBr)/cm^{-1}: 3093.11 (w), 2962.24 (w), 2929.03 (w), 2874.16 (w), 2096.39 (m, C≡C), 1724.64 (w), 1597.66 (m), 1561.46 (m), 1501.2 (s), 1452.34 (w), 1356.60 (m), 1261.19 (w), 1173.45 (w), 1143.35 (w), 1103.89 (m), 1034.15 (m), 817.89 (m), 766.17 (m), 732.28 (w). λ_{max} (CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}): 384 (23250). m/z (EI^+): 2299.77 ([$M + H]^+$, calcd for $C_{99}H_{130}N_3P_6Pt_3Fe_3$ 2300.57), 2321.75 ([$M + Na]^+$, calcd for $C_{99}H_{129}N_3P_6Pt_3Fe_3Na$ 2322.55). Anal. Calcd for $C_{99}H_{129}N_3P_6Pt_3Fe_3$: C, 51.70; H, 5.65; N, 1.83. Found: C, 51.94; H, 5.71; N, 1.52.

*Preparation of Pt-G1 (without Metal End (**7**) and with Metal End (**8**)) and Pt-G2 (with Metal End (**9**)) Metallodendrimer.* To prepare these compounds, the same procedure as for the preparation of compound **4** was followed. Only the stoichiometric ratios were varied, depending on the specific reactions, along with an additional purification treatment.

Additional Purification Treatment. Each dry compound was stirred in a round-bottom flask in an acetone and methanol mixture for about 12 h. Most of the piperidinium salt mixed with the desired compound passes to the methanolic solution. The solid part was filtered off on a gouche filter and washed thoroughly with acetone and diethyl ether and then vacuum-dried. These compounds are very difficult to purify through column chromatography, as they get stuck near the baseline unless a solvent with very high polarity is used for elution. As a result, other undesired compounds also come out along with the desired one. Therefore, precipitation is the only tool to purify the desired

dx.doi.org/10.1021/om300745v | *Organometallics* XXXX, XXX, XXX−XXX

compounds. Initially these compounds were purified by the precipitation method using dichloromethane and hexane as solvents. Finally, several reprecipitations of each compound from the dichloromethane/hexane solvent system afforded an almost pure compound (for further information regarding the purification process, see the Supporting Information).

*Synthesis of Pt-G1 without Metal End (**7**).* Starting from **3** (0.091 g, 0.24 mmol) and **4** (0.091 g, 0.06 mmol), the compound was obtained as a light orange-yellow solid. Yield: 0.101 g (60%). δ_H (400 MHz; $CDCl_3$): 8.62 (12H, d, J = 6 Hz, C_6H_4), 8.58 (12H, d, J = 8 Hz, C_6H_4), 7.44 (12H, d, J = 5.2 Hz, C_6H_4), 7.31 (12H, d, J = 8.4 Hz, C_6H_4), 2.24 (36H, m, CH_2CH_3), 1.30 (54H, m, CH_2CH_3). δ_C (100.6 MHz; $CDCl_3$): 171.1 (s, C_3N_3), 171.0 (s, C_3N_3), 133.4 (s, C of C_6H_4), 133.0 (s, C of C_6H_4), 131.4 (s, CH of C_6H_4), 130.9 (s, CH of C_6H_4), 128.6 (s, C of C_6H_4), 111.2 (s, C≡C−Pt), 98.2 (s, C≡C, C≡C−Pt), 16.5 (s, CH_2CH_3), 8.4 (s, CH_2CH_3). δ_P (161.9 MHz, $CDCl_3$): 11.2 (s, $J_{Pt,P}$ = 2358 Hz). ν_{max} (KBr)/cm^{-1}: 2948.26 (w), 2808.81 (w), 2513.00 (w), 2413.53 (w), 2092.27 (s, C≡C), 1632.33 (m), 1596.62 (m), 1563.64 (m), 1501.00 (s), 1359.47 (s), 1211.75 (m), 1143.84 (w), 1115.39 (m), 1032.12 (w), 933.58 (w), 818.23 (m), 766.82 (w). λ_{max} (CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}): 398 (49690). Anal. Calcd for $C_{144}H_{144}N_{12}P_6Pt_3$: C, 61.47; H, 5.16; N, 5.97. Found: C, 58.43; H, 5.97; N, 6.75 (although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date).

*Synthesis of Pt-G1 Dendrimer with Metal End (**8**).* Starting from **3** (0.015 g, 0.039 mmol) and **4** (0.210 g, 0.117 mmol), the compound was obtained as a light yellow solid. Yield: 0.144 g (66%). δ_H (400 MHz; $CDCl_3$): 8.62 (12H, m, C_6H_4), 8.60 (12H, m, C_6H_4), 7.44 (12H, d, J = 7.6 Hz, C_6H_4), 7.40 (12H, d, J = 7.4 Hz, C_6H_4), 2.24 (36H, m, inner CH_2CH_3), 2.09 (72H, m, outer CH_2CH_3), 1.29 (162H, m, CH_2CH_3). δ_C (100.6 MHz; $CDCl_3$; Me_4Si): 171.1 (s, C_3N_3), 133.1 (s, C of C_6H_4), 130.9 (s, CH of C_6H_4), 128.6 (s, C and CH of C_6H_4), 111.2 (s, C≡C−Pt), 98.2 (s, C≡C−Pt), 16.6 (s, inner CH_2CH_3), 14.6 (s, outer CH_2CH_3), 8.2 (s, CH_2CH_3). δ_P (161.9 MHz, $CDCl_3$): 14.9 (s, $J_{Pt,P}$ = 2380 Hz, outer P), 11.2 (s, $J_{Pt,P}$ = 2358 Hz, inner P). ν_{max} (KBr)/cm^{-1}: 2964.23 (w), 2932.79 (w), 2875.87 (w), 2095.02 (s, C≡C), 1633.08 (s), 1588.05 (s), 1563.06 (s), 1509.72 (s), 1404.21 (m), 1366.87 (s), 1240.83 (w), 1173.72 (m), 1144.38 (m), 1034.00 (s), 864.20 (w), 849.49 (w), 817.98 (s), 766.78 (m), 733.60 (m). λ_{max} (CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}): 382 (116800). m/z (EI^+): 5466.07 ($[M - 4Cl]^+$, calcd for $C_{216}H_{318}Cl_2N_{12}P_{18}Pt_9$ 5466.68). Anal. Calcd for $C_{216}H_{318}Cl_6N_{12}P_{18}Pt_9$: C, 46.25; H, 5.71; N, 3.0. Found: C, 46.65; H, 5.68; N, 3.35. Our attempts to prepare **8** from **7** using *cis*-$[PtCl_2(PEt_3)_2]$ in a molar ratio of 1/9 gave compound **8** but with decreased yield.

*Synthesis of Pt-G2 Dendrimer with Metal End (**9**).* Starting from **7** (0.04 g, 0.014 mmol) and **4** (0.151 g, 0.0852 mmol), the compound was obtained as a yellow solid. Yield: 0.103 g (54%). δ_H (400 MHz; $CDCl_3$): 8.60 (60H, d, J = 8.4 Hz, C_6H_4), 7.44 (24H, d, J = 6.8 Hz, C_6H_4), 7.39 (d, J = 8.0 Hz, 24H, C_6H_4), 7.30 (12H, d, J = 8.4 Hz, C_6H_4), 2.23 (90H, m, inner CH_2CH_3), 2.09 (162H, m, outer CH_2CH_3), 1.23 (378H, m, CH_2CH_3). δ_C (100.6 MHz; $CDCl_3$): 171.1 (s, C_3N_3), 133.1 (s, C of C_6H_4), 130.9 (s, CH of C_6H_4), 128.6 (s, CH of C_6H_4), 123.3 (s, C of C_6H_4), 111.1 (s, C≡C−Pt), 102.5 (s, C≡C−Pt), 88.1 (s, C≡C), 16.5 (s, inner CH_2CH_3), 14.6 (s, outer CH_2CH_3), 8.2 (s, CH_2CH_3). δ_P (161.9 MHz, $CDCl_3$): 14.9 (s, $J_{Pt,P}$ = 2378 Hz, outer P), 11.2 (s, $J_{Pt,P}$ = 2356 Hz, inner P). ν_{max} (KBr)/cm^{-1}: 2933.24 (w), 2963.98 (w), 2875.85 (w), 2111.41 (m, C≡C), 1632.32 (w), 1603.41 (s), 1597.65 (s), 1508.49 (s), 1453.25 (w), 1404.34 (m), 1363.87 (s), 1293.33 (w), 1242.85 (w), 1174.19 (m), 1144.61 (w), 1115.99 (w), 1034.72 (m), 850.86 (w), 818.47 (s), 766.85 (s), 733.79 (m). λ_{max} (CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}): 378 (130300).

*Synthesis of Pt-G1 Dendrimer with Capping by EFC (**10**).* In a Schlenk tube, compound **8** (0.06 g, 0.01 mmol) and ethynylferrocene (0.040 g, 0.18 mmol, 18 equiv with respect to Pt-G1 dendrimer (**8**)) were dissolved in a mixture of degassed chloroform (20 mL) and diethylamine (3 mL). After 10 min, CuI (0.001 g, 0.005 mmol, 50 mol %) was added and the mixture heated to 60 °C with stirring for 20 h. The compound was dried after removing the solvent on a rotavap and washed with acetone followed by diethyl ether several times. Afterward, the compound was stirred in a round-bottom flask in an acetone and methanol mixture for about 12 h. The solid part was filtered off on a gouche filter and washed thoroughly with acetone and diethyl ether and then vacuum-dried. The title compound was a brown-red solid. Yield: 0.026 g (38%). δ_H (400 MHz; $CDCl_3$): 8.59 (24H, m, C_6H_4), 7.41 (24H, m, C_6H_4), 4.23, 4.14, and 4.06 (appeared as a broad band, 48H, Cp ring), 2.18 (108H, m, CH_2CH_3), 1.23 (162H, m, CH_2CH_3). δ_C (100.6 MHz; $CDCl_3$): 171.1 (s, C_3N_3), 133.1 (s, C of C_6H_4), 130.9 (s, CH of C_6H_4), 128.6 (s, CH of C_6H_4), 111.2 (s, C≡C), 104.0 (s, C≡C), 70.1 (s, CH of C_5H_4(Cp)), 69.3 (s, C of Cp), 67.1 (s, CH of C_5H_4(Cp)), 16.5 (s, CH_2CH_3), 8.2 (s, CH_2CH_3). δ_P (161.9 MHz, $CDCl_3$) 11.7 (s, $J_{Pt,P}$ = 2351 Hz), 11.4 (s, $J_{Pt,P}$ = 2354 Hz). ν_{max} (KBr)/cm^{-1}: 2950−2875 (3 weak peaks), 2093.63 (m, C≡C), 1598.02 (m), 1562.14 (m), 1501.19 (s), 1404.65 (w), 1358.63 (m), 1175.00 (w), 1135.0 (w), 818.18 (m), 865.00 (w). λ_{max} (CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}): 392 (52600). Anal. Calcd for $C_{288}H_{372}Fe_6N_{12}P_{18}Pt_9$: C, 52.01; H, 5.64; N, 2.53. Found: C, 49.68; H, 5.37; N, 3.06 (although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date).

■ ASSOCIATED CONTENT

Supporting Information

Text regarding the purification process of higher dendrimer generations and figures giving ^1H, ^{13}C, and ^{31}P NMR and MS spectra of the compounds prepared in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We greatly appreciated the financial support of Fundação para a Ciência e a Tecnologia (FCT) for the purchase of NMR and mass spectrometers with funds from POCI 2010 (FEDER) and the Portuguese Government (Contracts PTNMR-REDE/1517/RMN/2005 and RNEM-REDE/1508/REM/2005), as well as for the research project PTDC/QUI/64202/2006 and the pluriannual base funding of CQM (PEst-OE/QUI/UI0674/2011). M.G.J. also thanks the FCT for a Ph.D. grant (SFRH/BD/65036/2009). K.R. acknowledges support from the Academy of Finland (project nos. 130629, 122350, 140718). Financial support from the Fund for Scientific Research−Flanders (FWO; projects G.0129.07 and G.0206.12) is gratefully acknowledged. J.C. is a postdoctoral fellow of the FWO.

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