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Synthesis and Characterization of Organoplatinum Dendrimers with 1,3,5-Triethynylbenzene Building Blocks

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The multinuclear complexes 1,3,5-[*trans*-I$(Et_3P)_2PtC{\equiv}C]_3C_6H_3$ (**1**) and 1,2,4,5-[*trans*-I$(Et_3P)_2PtC{\equiv}C]_4C_6H_2$ (**2**) were prepared via σ-acetylide synthetic methodologies by reaction of tri- and tetraethynylbenzene with diiodobis(triethylphosphine)platinum. The combination of this synthetic coupling strategy with the divergent synthetic principle for the formation of dendrimers led to organometallic first- and second-generation dendrimers with ethynylplatinum units in the main chain. The outer spheres of the dendrimers consist of either terminal acetylenic groups or bis(triethylphosphine)platinum iodide groups. All compounds were fully characterized by elemental analysis, mass spectrometry, NMR, and vibrational spectroscopy. The single-crystal structure of a first generation dendrimer **3** with terminal acetylene groups was determined by X-ray analysis. It shows an out-of-plane twisting of all three terminal 1,3,5-triethynylbenzene groups as well as a twisting of one of the coordination planes around a platinum atom, relative to the central aromatic ring.

Introduction

In recent years there has been a growing interest in the design of oligomeric and polymeric transition metal complexes containing σ-bonded acetylene units because of their significantly altered physical properties compared to conjugated organic oligomers and polymers.[1] The ability of the transition metal d orbitals to interact with p orbitals of conjugated alkynyl ligands is one major factor in stabilizing vinylidene intermediates[2] as well as catalyzing cross coupling reactions.[3]

Moreover, the electronic delocalization across the transition metal center[4] influences the magnetic and the nonlinear optical properties and behavior.[5] Although the classical nonlinear optical (NLO) materials have donor−bridge−acceptor character, it has recently been shown that nonpolar molecules with a 3-fold rotation symmetry can have nonzero β values and are therefore under investigation for potential NLO applications.[6]

Highly branched systems with metal centers on the surface or within the dendrimers encompassing all these characteristics are of considerable current interest.[1c,5a,7] Furthermore, the attractive advantage of organometallic dendrimers over their polymeric counterparts lies additionally in their precise molecular architecture as well as in their predetermined chemical composition.[8] Although many studies have been done on surface-modified dendrimers,[8,9] only a few organometallic dendrimers with interior metal centers are known due to a lack of appropriately designed building blocks.[8,10] Recent results show that numerous bimetallic and polymetallic complexes linked by rigid alkynyl and alkynyl−aryl backbones with a large extent of π-delocalization

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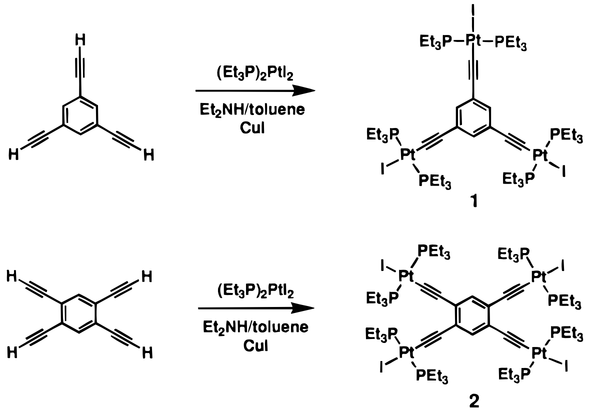
Scheme 1



constitute the most efficient link between organometallic building blocks.[11]

Herein we report the molecular assemblies of a variety of neutral multinuclear platinum complexes with a backbone of σ-bonded tri- and tetraethynylbenzene units. In a stepwise divergent synthetic approach[12] the synthesis of a first- and a second-generation dendrimer is facilitated where the *trans*-bis(triethylphosphine)platinum units serve as functionalities and are covalently connected through conjugated organic building blocks. The structure of the first-generation dendrimer was established by an X-ray determination.

Results and Discussion

Preparation of the Precursors 1,3,5-[*trans*-I(Et$_3$P)$_2$PtC≡C]$_3$C$_6$H$_3$ (1) and 1,2,4,5-[*trans*-I(Et$_3$P)$_2$PtC≡C]$_4$C$_6$H$_2$ (2). The polycondensation between metal halides and acetylenic compounds has been shown to proceed smoothly in the presence of a cuprous halide catalyst and an amine base.[13a] This method developed for the synthesis of polyyne polymers could successfully be transferred to the formation of two-dimensional systems.[5a,11b,13b,14]

Reaction of the tri- and tetraethynylbenzene with 9 and 12 equiv, respectively, of diiodobis(triethylphosphine)platinum in a mixture of toluene and diethylamine generates, in the presence of cuprous(I) iodide, the 1,3,5-tris- and 1,2,4,5-tetrakis-substituted complexes **1** and **2** in good yields (Scheme 1). The use of the diiodoplatinum compound was shown to be more reactive and to give higher yields than the corresponding dichloroplatinum compound due to a more labile halogen−metal bond.[15−17] Purification of the complexes **1** and **2** was achieved by column chromatography on silica gel and afforded the products as slightly yellow crystals. In addition, all of the excess diiodobis(triethylphosphine)platinum was quantitatively recovered in analytically pure form and was therefore used in further reactions.

Both platinum compounds were characterized by NMR (^{1}H, ^{31}P{1H}, ^{13}C{^{1}H}), vibrational spectroscopy (IR), and mass spectrometry (FAB-MS), as well as elemental analysis and physical means (vide infra). These multinuclear complexes are air- and moisture-stable solids and are highly soluble in benzene, chloroform, and methylene chloride, insoluble in hexanes, and partly soluble in diethyl ether. They can be stored over a long period of time without decomposition.

Although, we never observed a partly substituted product,[5a] the yield of the final complexes dropped with smaller excesses of diiodobis(triethylphosphine)platinum. A plausible explanation for this can be found in the high reactivity of the remaining iodoplatinum bond, which is still activated by the triethylphosphine ligands and not sterically hindered. Therefore, competing oligomerization reactions, which are well-known in this field of chemistry,[13,16,17] can occur and lower the overall yield.

The ^{31}P{^{1}H} NMR spectra of **1** and **2** are very similar in that each compound shows one singlet resonance for the triethylphosphine ligands at $\delta = 11.3$ (**1**) and 11.1 ppm (**2**), respectively. Compared to the resonance of the starting material, the substitution of one iodo ligand with an acetylenic unit results in a downfield shift of almost 8 ppm. The phosphorus−platinum single-bond spin−spin couplings of 2327 (**1**) and 2333 Hz (**2**) are in the expected range for a *trans*-PtP$_2$ system. The ^{1}H NMR spectra show only one single resonance in the aromatic region, beside the signals for the triethylphosphine ligands, at $\delta = 7.02$ (**1**) and 7.10 (**2**), respectively, strongly suggesting that the complexes **1** and **2** have a symmetrical structure. No signals in the range for terminal acetylenes were detected, excluding the existence of partly substituted products within the detection limits of NMR.

Formation of a First-Generation Dendrimer via a Divergent Strategy. The concept of the divergent iterative strategy, defined by Moorefield and Newkome,[12] involves an initial monomer (core or zeroth-generation) which possesses one or more reactive site(s), and then a new generation of building blocks is added to form the first-generation dendrimer. Continuing to use this building block after transformation of the terminal groups into functionalized groups will result in the formation of the next generation dendrimer. The number of terminal groups depends on the number of reactive sites provided by the building blocks (Scheme 2).

Applying this strategy to our systems, we were able to form the first-generation dendrimer **3** by reacting the trinuclear complex **1** with an excess of 1,3,5-triethynylbenzene under the same reaction conditions already described for the formation of complexes **1** and **2** (Scheme 3).

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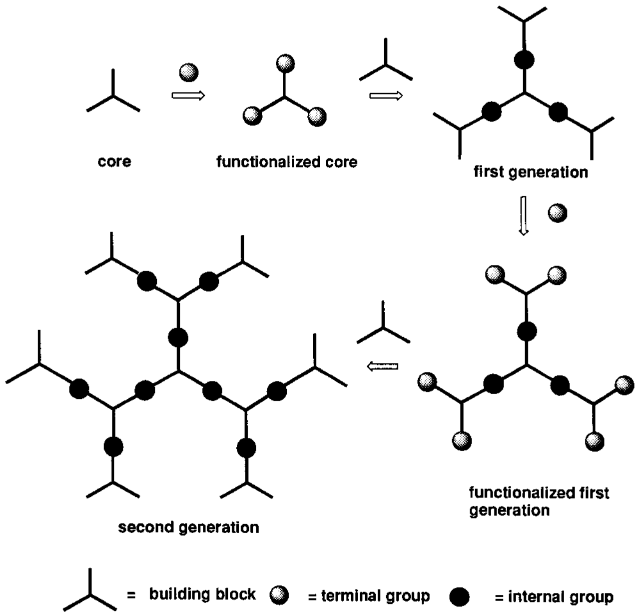
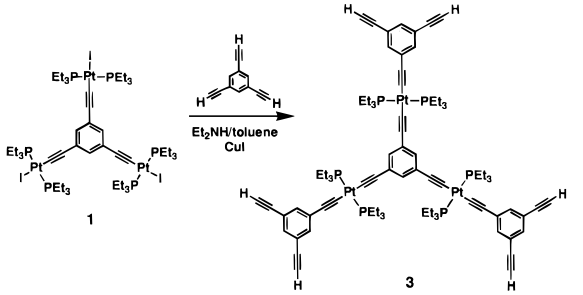
Scheme 2



Scheme 3



Again, a 9-fold excess of the building block triethynylbenzene is necessary to avoid side reactions and a concomitant decrease in overall yield. Separation of dendrimer **3** from the crude reaction mixture was achieved by standard column chromatography on silica gel. The bis-ethynyl substitution of the bis(triethylphosphine)platinum function results in a downfield shift of the $^{31}P\{^1H\}$ NMR resonance for **3** from $\delta = 11.3$ to 14.3 ppm compared to the monosubstituted complex **1**. The P–Pt coupling constant increases slightly from 2327 to 2357 Hz but is still consistent with a trans configuration at the transition metal.

An analogous downfield shift was observed in the ^{13}C NMR spectra for the resonances of the core acetylene nuclei. The signal for the carbon atom σ-bonded to the platinum shifted from $\delta = 100.1$ to 109.8 ppm, and the signal for the other acetylenic carbon shifted from $\delta = 90.2$ to 107.3 ppm on conversion of **1** to **3**. The corresponding acetylenic resonances for the newly formed ethynyl platinum unit were found at $\delta = 107.8$ and 122.3 ppm, whereas the signals at $\delta = 83.0$ and 78.0 ppm were assigned to the terminal acetylenic units.

In the ^1H NMR spectra the characteristic signal for the terminal acetylene protons was found at $\delta = 3.14$ ppm, whereas for the magnetically and chemically different aromatic protons of the inner and outer benzene rings, three distinguishable resonances were found with an integration ratio of 3:6:3. Based upon complex **1** the signal at $\delta = 6.98$ ppm was assigned to the three core protons. The signal at $\delta = 7.35$ ppm was assigned to the six protons in the ortho position and the resonance at $\delta = 7.37$ to the three protons in the para position of the outer aromatic rings.

Fast atom bombardment mass spectrometric (FAB-MS) analysis of **3** gave the molecular peak at 1888 amu as well as an isotopic distribution pattern which was consistent with the calculated composition.[18]

All attempts to prepare the corresponding dendrimer from the 1,2,4,5-tetrasubstituted complex **2** and 1,3,5-triethynylbenzene have failed so far. Only a mixture of partly substituted products was observed. A reasonable explanation for this fact can be seen in the higher steric demand of the hypothetical ortho-substituted system compared to the meta-substituted system of **3**.

Single-Crystal X-ray Structure Analysis of Dendrimer 3. The geometrical features of dendrimers are of considerable interest since they influence the chemical and physical properties of these compounds. Bond angles and twisting affect the overlapping of orbitals, the size and accessibility of cavities are important features for potential guests, and the shape and accessibility of the outer sphere may influence catalytic reactivities. Therefore we attempted to grow crystals of all dendrimers. To date, we were only successful in obtaining X-ray quality crystals for the smallest dendrimer, **3**. Crystallographic data for this crystal structure are summarized in Table 1, and important geometric parameters are shown in Table 2. An ORTEP plot of the first-generation dendrimer **3** is shown in Figure 1.

Because of the marginal precision of this crystal structure, we will only discuss the reliable features that are apparent. As a result of the monoclinic cell and the determined space group ($C2/c$), the molecule shows a 2-fold symmetry axis passing through C(16), C(15), C(19), C(20), Pt(2), C(26), C(25), C(22), C(21), and C(24).

All three platinum atoms show the expected square planar coordination geometry with cis bond angles close to 90°. The Pt(2)–P(3) bond distance of 2.39(1) Å is longer than the Pt(1)–P(1) and Pt(1)–P(2) bond distances of 2.25(2) and 2.26(1) Å. On the other hand the Pt(1)–C(8) as well as the Pt(1)–C(18) bond distances of 2.28(6) and 2.31(4) Å are much longer than the corresponding Pt(2)–C(20) and Pt(2)–C(26) bonds length of 1.83(5) and 2.09(4) Å. Due to the size of the estimated standard deviations any detailed discussion of a possible alkyne–metal π-bonding is not reasonable.

The most interesting structural feature of this structure analysis is an out-of-plane twisting of all three terminal 1,3,5-triethynylbenzene groups as well as a twisting of the coordination plane around the platinum atom Pt(1) relative to the central aromatic ring. The coordination plane around Pt(2) is almost parallel to the inner aromatic ring, whereas the adjacent outer triethynylbenzene ring is located almost perpendicular to the inner aromatic ring. These findings for the respective orientation of the aromatic ring systems in the solid state suggest a three-dimensional rather than a two-dimensional polyhexagonal graphite-like structure for the polyyne polymers postulated by Lewis.[13b]

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Table 1. Crystallographic Data for the X-ray Diffraction Analysis of 3

empirical formula	$C_{84}H_{108}P_6Pt_3$	fw	1888.89
crystal color, habit	yellow, needle	cryst syst	monoclinic
a (Å)	28.595(1)	b (Å)	20.978(1)
c (Å)	15.0764(9)	β (deg)	97.511(2)
V (Å^3)	8966.5(8)	space group	$C2/c$ (No. 15)
Z value	4	density (g/cm^3)	1.399
F(000)	3744.00	$2\theta_{\max}$	54.50
no. of reflections	total: 20 954 unique: 8744	p-factor	0.0300
structure solution	Patterson methods	no. of variables	210
no. of observations ($1 > 3.00\sigma$(I))	1918	R	0.089
reflection/parameter ratio	9.13	R_w	0.064
GOF	2.63	minimum peak in final diff map (e/Å^3)	−2.28
maximum peak in final diff map (e/Å^3)	0.61		

Table 2. Selected Bond Distances and Bond Angles for 3

Bond Lengths (Å)			
Pt(1)−P(1)	2.25(2)	Pt(1)−P(2)	2.26(1)
Pt(1)−C(8)	2.28(6)	Pt(1)−C(18)	2.31(4)
Pt(2)−P(3)	2.39(1)	Pt(2)−P(3)	2.39(1)
Pt(2)−C(20)	1.83(5)	Pt(2)−C(26)	2.09(4)
P(1)−C(29)	1.96(5)	P(1)−C(31)	1.68(6)
P(1)−C(33)	2.00(8)	P(2)−C(35)	1.98(4)
P(2)−C(37)	1.94(5)	P(2)−C(39)	1.77(5)
P(3)−C(41)	1.80(6)	P(3)−C(43)	2.09(8)
P(3)−C(45)	1.94(5)	C(21)−C(25)	1.42(6)
C(17)−C(18)	1.17(5)	C(1)−C(7)	1.47(6)
C(7)−C(8)	1.16(7)	C(25)−C(26)	1.27(6)
C(19)−C(20)	1.31(6)	C(13)−C(14)	1.36(5)
C(13)−C(16)	1.36(4)	C(13)−C(17)	1.33(5)
C(14)−C(15)	1.39(4)	C(15)−C(19)	1.34(7)
Bond Angles (deg)			
P(1)−Pt(1)−P(2)	178.1(6)	P(1)−Pt(1)−C(8)	93(2)
P(1)−Pt(1)−C(18)	89(1)	P(2)−Pt(1)−C(8)	88(2)
P(2)−Pt(1)−C(18)	90(1)	C(8)−Pt(1)−C(18)	177(2)
P(3)−Pt(2)−P(3)	177.0(8)	P(3)−Pt(2)−C(20)	91.5(4)
P(3)−Pt(2)−C(26)	88.5(4)	P(3)−Pt(2)−C(20)	91.5(4)
P(3)−Pt(2)−C(26)	88.5(4)	C(20)−Pt(2)−C(26)	180.0(2)
C(1)−C(7)−C(8)	169(7)	Pt(1)−C(8)−C(7)	158(6)
C(14)−C(13)−C(16)	133(4)	C(14)−C(13)−C(17)	114(4)

Divergent Approach to the Formation of a Second-Generation Dendrimer. In the divergent construction of dendrimers, functionalization of the outer sphere is a key step. One of the prime considerations is the complete conversion of all the terminal sites of the growing cascade.[12] Incomplete conversion generally results in branching defects that can affect topology and physical properties.

The step-by-step construction of the second-generation dendrimer **5** first affords a functionalization of the terminal acetylenic groups of the first-generation dendrimer **3**. By reacting compound **3** with an excess of diiodobis(triethylphosphine)platinum, all terminal acetylene groups of **3** were converted into the corresponding [*trans*-iodobis(triethylphosphine)ethynyl]platinum units, giving rise to the formation of compound **4**, which provides the reactive site for further substitution reactions (Scheme 4).

Purification of complex **4** was done by column chromatography on aluminum oxide, as attempts to use silica gel resulted in a loss of most of the product. The complex was obtained in 44% yield as an air- and moisture-stable pale yellow powder. Compound **4** was fully characterized by NMR (^{1}H, ^{31}P{1H}, ^{13}C{^{1}H}), vibrational spectroscopy (IR), and mass spectrometry (FAB-MS), as well as elemental analysis.

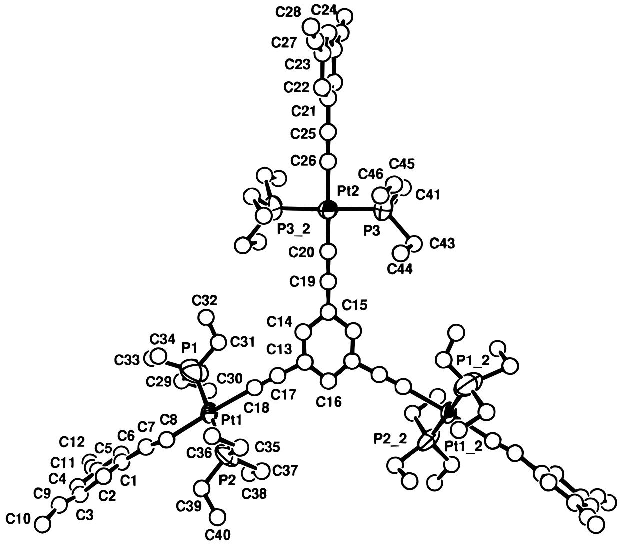
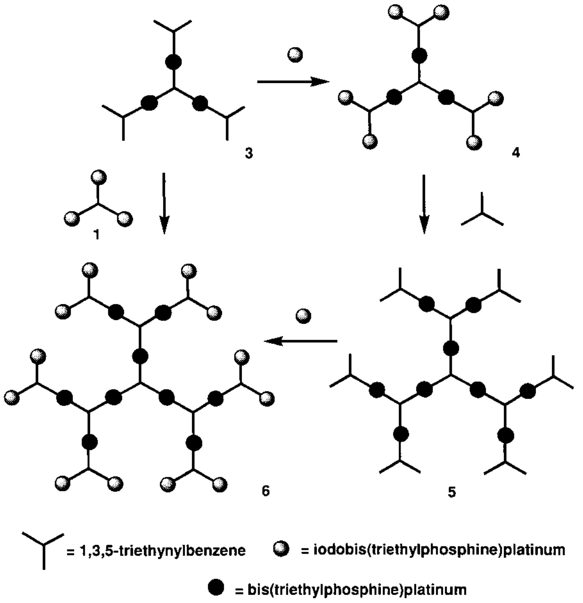


Figure 1. ORTEP plot of the first-generation dendrimer **3**. Hydrogen atoms omitted for clarity.

Two different phosphorus resonances were observed in the ^{31}P{^{1}H} NMR spectrum for the inner and outer diethylphosphineplatinum units of the dendrimer **4**. The signal at $\delta = 14.1$ ppm was assigned to the phosphine ligands of the bis-ethynyl-substituted bis(triethylphosphine)platinum units, and the resonance at $\delta = 11.4$ ppm was assigned to the phosphine ligands of the [*trans*-iodobis(triethylphosphine)ethynyl]platinum units in the outer sphere. The phosphorus−platinum spin−spin coupling constants of 2365 Hz for the inner and 2321 Hz for the outer platinum units are similar to those observed for the complexes **1** and **3** and are characteristic for trans-substituted PtP_2 systems.

In addition, the two chemically different triethylphosphine ligands show inseparable resonances in the ^{1}H NMR spectrum for the methylene as well as the methyl groups. For the three sets of different aromatic protons three distinguishable signals were detected with an integration ratio of 3:6:3. The singlet at $\delta = 6.94$ ppm was assigned to the protons of the core ring, whereas the AB^2 spin system at $\delta = 6.99$ and 6.97 ppm with a $^4J_{HH} = 2.8$ Hz was assigned to the ortho and para

Scheme 4



protons of the outer aromatic rings. Fast atom bombardment mass spectrometric (FAB-MS) analysis gave the molecular peak at 5231 amu as well as an isotopic distribution pattern that was consistent with the calculated composition for compound **4**.[18]

To generate the second-generation dendrimer **5**, the functionalized first-generation dendrimer **4** was reacted with an 18-fold excess of 1,3,5-triethynylbenzene. Although we were able to confirm the product by $^{31}P\{^1H\}$ NMR spectroscopy, so far we could not isolate the dendrimer in a pure form from the reaction mixture via this procedure.

However, a functionalized second-generation dendrimer **6** was prepared by reaction of the first-generation dendrimer **3** with the trinuclear platinum compound **1** (Scheme 4). The reaction was performed in a mixture of diethylamine and toluene in the presence of cuprous iodide, and the product isolated in 43% yield by column chromatography on aluminum oxide.

Only two different phosphorus resonances were observed in the $^{31}P\{^1H\}$ NMR spectrum for the two inner and one outer diethylphosphineplatinum units of the dendrimer **6**. The signal at $\delta = 14.2$ ppm was assigned to the phosphine ligands of the bis-ethynyl-substituted bis(triethylphosphine)platinum units of the inner core sphere as well as to the bis(triethylphosphine)platinum units of the inner first sphere. No splitting of the signal was observed, which maybe explained by the nearly magnetical equivalence of the chemically different phosphine ligands. The resonance at $\delta = 11.5$ ppm was assigned to the phosphine ligands of the [*trans*-iodobis-(triethylphosphine)ethynyl]platinum units in the outer sphere. The phosphorus−platinum spin−spin coupling constants of 2357 Hz for all inner and 2319 Hz for the outer platinum units are similar to those observed for the first-generation dendrimer **4**.

In contrast to complex **4**, separate signals in the aromatic region of the ^1H NMR spectrum could not be assigned to the five different sets of aromatic protons, as only one broad signal for the 30 aromatic protons was observed. These data are consistent with the expected structure for the functionalized second-generation dendrimer **6**, which is also supported by vibrational spectroscopy as well as elemental analysis as given in the Experimental Section.

Conclusions

We have established that 1,3,5-triethynylbenzene and diiodobis(triethylphosphine)platinum are effective building blocks for the synthesis of several dendrimers. The step-by-step divergent strategy is an effective methodology for the formation of transition metal dendrimers with an alkynyl−aryl backbone. Considering that, compared to the all-carbon analogue dendrimeres, the transition metal fragments serve as a spacer that effectively prevents proximal groups from interfering, higher generation dendrimers can be generated. By intermolecularly connecting the branches of the dendrimers, we are currently investigating transition metal linked polycondensated systems with honeycomb-like structures.

Experimental Section

General Methods. All experiments were performed under an inert atmosphere of nitrogen utilizing standard Schlenk techniques. Solvents used were of reagent or HPLC grade and purified in the following manner: benzene was distilled over sodium/potassium (2:1) alloy, toluene was distilled over sodium metal, diethyl ether was distilled over sodium/benzophenone, triethylamine was distilled over potassium hydroxide, and hexanes and methylene chloride were distilled over calcium hydride.[19] All NMR solvents (CD_2Cl_2 and $CDCl_3$) were stored over 4 Å molecular sieves prior to use.

Triethylphosphine, 1,3,5-tribromobenzene, 1,2,4,5-tetrabromobenzene, and tetrakis(triphenylphosphine)palladium were purchased from the Aldrich Chemical Co. and used without further purification. Trimethylsilylacetylene was purchased from Lancaster Synthesis Inc. *trans*-Diiodobis(triethylphosphine)platinum was prepared by standard literature procedure.[20]

All NMR spectra were obtained at room temperature with a Varian XL-300 or VXR-500 spectrometer employing a deuterium sample as an internal lock unless noted otherwise. The operating frequencies of the former spectrometer for the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were 300.0, 75.4, and 121.4 MHz, respectively. For the latter spectrometer, the operating frequencies of the ^1H and $^{13}C\{^1H\}$ NMR spectra were 499.8 and 125.7 MHz, respectively. The ^1H chemical shifts are reported relative to the residual nondeuterated solvent of CD_2Cl_2 (5.32 ppm) or $CDCl_3$ (7.27 ppm). The $^{13}C\{^1H\}$ chemical shifts are reported relative to $CDCl_3$ (77.0 ppm) or CD_2Cl_2 (54.0 ppm). The $^{31}P\{^1H\}$ NMR spectra were referenced to sealed external standards of 85% phosphoric acid.

Mass spectra were obtained with a Finnigan MAT 95 mass spectrometer with a Finnigan MAT ICIS II operating system under positive ion fast atom bombardment (FAB) conditions at 8 keV. 3-Nitrobenzyl alcohol was used as a matrix in CH_2Cl_2; polypropylene glycol and cesium iodide were used as a reference for peak matching.

Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. IR spectra were obtained with a Mattson Polaris FT-IR spectrometer at 2 cm^{-1} resolution. Reported melting points were obtained with a Mel-Temp capillary apparatus and are uncorrected.

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(19) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*: Pergamon Press: Tarrytown, NY, 1988.

(20) Jensen, K. A. *Z. Anorg. Allg. Chem*. **1936**, *229*, 225−232.

1,3,5-Triethynylbenzene.[21] In a 100 mL round-bottom Schlenk flask 1,3,5-tribromobenzene (2.66 g, 8.4 mmol) and trimethylsilylacetylene (11.7 mL, 80 mmol) were dissolved in 60 mL of freshly distilled THF and 15 mL of dry triethylamine. A mixture of tetrakis(triphenylphosphine)palladium (1.470 g, 1.26 mmol) and copper(I) iodide (193 mg, 1.01 mmol) was added, and the suspension stirred for 36 h at room temperature in the absence of light. After removal of the solvents the residue was suspended in 100 mL of diethyl ether and washed twice with 100 mL of water, and the organic phase was dried over magnesium sulfate. Removing the solvent and separation by column chromatography on silica gel afforded 2.26 g (74%) of the 1,3,5-tris(trimethylsilylethynyl)benzene eluting as the second fraction with hexanes. Desilylation of 1,3,5-tris(trimethylsilylethynyl)benzene (2.276 g, 6.22 mmol) was achieved by stirring the compound in a saturated KOH solution of methanol for 4 h. Hydrolysis and extraction of the organic product with diethyl ether and subsequent column chromatography on silica gel with hexanes/diethylether (1:1) yielded 912 mg (98%) of the 1,3,5-triethynylbenzene as a white powder (overall yield: 72%).

1,2,4,5-Tetraethynylbenzene.[22] 1,2,4,5-Tetrabromobenzene (3.17 g, 8.05 mmol) and trimethylsilylacetylene (15.5 mL, 100.3 mmol) were reacted with a mixture of tetrakis(triphenylphosphine)palladium (1.950 g, 1.68 mmol) and copper(I) iodide (260 mg, 1.73 mmol) in 50 mL of freshly distilled THF and 15 mL of triethylamine. After stirring the mixture for 4 h at room temperature in the dark, the solvents were removed under reduced pressure. Workup was performed analogous to the procedure for the 1,3,5-tris(trimethylsilylethynyl)benzene and afforded 2.715 g (73%) of 1,2,4,5-tetrakis(trimethylsilylethynyl)benzene. Desilylation of the product and separation by column chromatography finally yielded 987 mg (97%) of 1,2,4,5-tetraethynylbenzene as plates possessing a metallic luster (overall yield: 71%).

1,3,5-Tris[[*trans*-iodobis(triethylphosphine)platinum]ethynyl]benzene (1). To a 100 mL round-bottom Schlenk flask were added *trans*-diiodobis(triethylphosphine)platinum (2.060 g, 3.01 mmol) and 1,3,5-triethynylbenzene (75 mg, 0.50 mmol). Then, 30 mL of toluene and 20 mL of dry diethylamine were added under nitrogen. The solution was stirred for 10 min at room temperature, and 20 mg (0.11 mmol) of cuprous(I) iodide was added in one portion. After 3 h at room temperature, a small amount of diethylammonium iodide started precipitating out of solution. The solvent was then removed in vacuo, and the remaining yellow residue was separated by column chromatography on silica gel. The first fraction containing excess diiodobis(triethylphosphine)platinum was recovered almost quantitatively (1.050 g, 1.60 mmol) by elution with hexanes/benzene (3:1). The second fraction with benzene as eluent gave the product **1** as slightly yellow crystals after recrystallization from dichloromethane. Yield: 0.510 g (56%); mp 302 °C dec; IR (thin film; CD_2Cl_2; cm^{-1}) 2964, 2931, 2908 ($C{-}H$), 2112 ($C{\equiv}C$), 1567, 1454, 1410 (Ar); ^1H NMR (CD_2Cl_2) 7.02 (s, 3 H, aromatic-H), 2.22 (m, 36 H, CH_2), 1.18 (m, 54 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 130.5 (s, C_{ortho}), 128.8 (s, C_{ipso}), 100.1 (s, $^1J_{CPt} = 415$ Hz, $C{-}Pt$), 90.2 (s, $^3J_{CP} = 28$ Hz, $C{\equiv}C$), 17.1 (pseudo quin, $J_{CP} = 13$ Hz, PCH_2), 8.6 (pseudo t, $J_{CP} = 13$ Hz, PCH_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 11.3 (s, $^1J_{PPt} = 2327$ Hz); FAB-MS *m*/*z* (relative intensity) 1821 (M^+, 5), 119 (Et_3P, 100). Anal. Calc for $C_{48}H_{93}I_3P_6Pt_3$: C, 31.60; H, 5.14. Found: C, 31.63; H, 5.14.

1,2,4,5-Tetrakis[[*trans*-iodobis(triethylphosphine)platinum]ethynyl]benzene (2). In a 100 mL round-bottom Schlenk, *trans*-diiodobis(triethylphosphine)platinum (1.602 mg, 2.34 mmol) and 1,2,4,5-tetraethynylbenzene (33.9 mg, 0.195 mmol) were dissolved in 30 mL of toluene and 20 mL of dry diethylamine. A 20 mg (0.11 mmol) portion of copper(I) iodide was added, and the reaction mixture stirred for 4 h at room temperature. The solvent was then removed in vacuo, and the remaining yellow residue was separated by column chromatography on silica gel. The excess diiodobis(triethylphosphine)platinum was nearly quantitatively recovered (1.050 g) with hexanes/benzene (3:1), whereas the product was isolated with hexanes/benzene (1:4). Yellow crystals of the complex **2** were obtained after crystallization from dichloromethane. Yield: 205 mg (43.8%); mp 312 °C dec; IR (thin film; CD_2Cl_2; cm^{-1}) 2963, 2933, 2914 ($C{-}H$), 2113 ($C{\equiv}C$), 1471, 1456, 1410 (Ar); ^1H NMR (CD_2Cl_2) 7.10 (s, 2 H, aromatic-H), 2.21 (m, 48 H, CH_2), 1.18 (m, 72 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 136.5 (s, aromatic-CH), 125.8 (s, $^3J_{CPt} = 33$ Hz, ipso-C), 104.2 (s, $^1J_{CPt} = 422$ Hz, $C{\equiv}C{-}Pt$), 93.4 (s, $^3J_{CP} = 29$ Hz, $C{\equiv}C$), 17.2 (pseudo quin, $J_{CP} = 17$Hz, PCH_2), 8.8 (pseudo t, $J_{CP} = 14$ Hz, PCH_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 11.1 (s, $^1J_{PPt} = 2333$ Hz); FAB-MS *m*/*z* (relative intensity) 2403 (M^+, 1), 119 (Et_3P, 100). Anal. Calc for $C_{62}H_{122}I_4P_8Pt_4$: C, 30.98; H, 5.12. Found: C, 31.24; H, 4.98.

First-Generation Dendrimer: 1,3,5-Tris[[*trans*-(1′,3′,5′-triethynylbenzene)bis(triethylphosphine)platinum]ethynyl]benzene (3). In a 25 mL round-bottom Schlenk flask 1,3,5-tris[[*trans*-iodobis(triethylphosphine)platinum]ethynyl]benzene (**1**) (400 mg, 0.22 mmol) and 1,3,5-triethynylbenzene (295 mg, 2.00 mmol) were dissolved in 10 mL of toluene and 10 mL of diethylamine. After 5 min 10 mg (0.05 mmol) of cuprous(I) iodide was added, and the mixture was stirred at room temperature for 3 h. The solvent was then removed in vacuo, and the remaining pale yellow residue was separated by column chromatography on silica gel. The excess 1,3,5-triethynylbenzene was isolated as the first fraction with hexanes as eluent, whereas subsequent elution with benzene yielded the pure product **3**. After crystallization from dichloromethane the dendrimer **3** was obtained as bright yellow colored crystals. Yield: 0.315 g (76%); mp 156−158 °C; IR (thin film; CD_2Cl_2; cm^{-1}) 3301, 3226 ($C{-}H$), 2964, 2932, 2906 ($C{-}H$), 2093 (CC), 1567, 1452, 1410 (Ar); ^1H NMR (CD_2Cl_2) 7.37 (m, 3 H, aromatic-H), 7.35 (m, 6 H, aromatic-H), 6.98 (s, 3 H, aromatic-H), 3.14 (s, 6 H, $C{\equiv}C{-}H$), 2.18 (m, 36 H, CH_2), 1.22 (m, 54 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 135.1 (s, C_{ortho}), 132.0 (s, C_{ortho}), 130.7 (s, C_{meta}), 130.1 (s, C_{ipso}), 128.7 (s, C_{ipso}), 122.7 (s, C_{para}), 122.3 (s, $^3J_{CP} = 29$ Hz, $C{\equiv}C$), 109.8 (s, $C{-}Pt$), 107.8 (s, $C{-}Pt$), 107.3 (s, $^3J_{CP} = 29$ Hz, $C{\equiv}C$), 83.0 (s, $C{\equiv}C{-}H$), 78.0 (s, $C{-}H$), 16.6 (pseudo quin, $J_{CP} = 13$ Hz, PCH_2), 8.6 (pseudo t, $J_{CP} = 13$ Hz, PCH_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 14.3 (s, $^1J_{PPt} = 2357$ Hz); FAB-MS *m*/*z* (relative intensity) 1888 (M^+, 6), 119 (Et_3P, 100). Anal. Calc for $C_{84}H_{108}P_6Pt_3$: C, 53.36; H, 5.71. Found: C, 53.18; H, 5.71.

Functionalized First-Generation Dendrimer (4). To a 25 mL round-bottom Schlenk flask were added *trans*-diiodobis(triethylphosphine)platinum (760 mg, 1.112 mmol), 1,3,5-tris[[*trans*-(1′,3′,5′-triethynylbenzene)bis(triethylphosphine)platinum]ethynyl]benzene (**3**) (116 mg, 0.061 mmol), 7 mL of toluene, and 5 mL of dry diethylamine under nitrogen. Next, 10 mg (0.05 mmol) of cuprous(I) iodide was added, and the solution was stirred at room temperature for 4 h. The solvent was then removed in vacuo, and the remaining yellow residue was separated by column chromatography on aluminum oxide. The excess diiodobis(triethylphosphine)platinum was recovered nearly quantitatively (450 mg) as the first fraction with hexanes/benzene (3:1) as eluent, whereas the product was eluted with benzene. Recrystallization from dichloromethane afforded the functionalized first-generation dendrimer **4** as a pale yellow powder. Yield: 132 mg (41%); mp 290−294 °C dec; IR (thin film; CD_2Cl_2; cm^{-1}) 2968, 2945 ($C{-}H$), 2109, 2095 ($C{\equiv}C$) 1566, 1459, 1410 (Ar); ^1H NMR (CD_2Cl_2) δ 6.99 (d, 6 H, $^4J_{HH} = 2.8$ Hz, aromatic-H), 6.97 (t, 3 H, $^4J_{HH} = 2.8$ Hz, aromatic-H), 6.94 (s, 3 H, aromatic-H), 2.21 (m, 108 H, CH_2), 1.21 (m, 162 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 17.3 (m, PCH_2),

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[21] (a) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627−630. (b) Trumbo D. L.; Marvel C. S. *J. Polym. Sci. Part A, Poly. Chem.* **1986**, *24*, 2311−2326.

[22] Berris, B. C.; Hovakeemian, G. H.; Vollhardt, P. C. *J. Chem. Soc., Chem. Commun.* **1983**, *9*, 502−503.

8.7 (m, PCH_2CH_3): $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 14.1 (s, $^1J_{PPt} = 2365$ Hz, P_{inner}), 11.4 (s, $^1J_{PPt} = 2321$ Hz, P_{outer}); FAB-MS *m*/*z* (relative intensity) 5231 (M^+, 2), 119 (Et_3P, 100). Anal. Calc for $C_{156}H_{282}I_6P_{18}Pt_9$: C, 35.81; H, 5.43. Found: C, 36.16; H, 5.49.

Second-Generation Dendrimer (6). 1,3,5-Tris[[*trans*-(1′,3′,5′-triethynylbenzene)bis(triethylphosphine)platinum]-ethynyl]benzene (**3**) (506 mg, 0.277 mmol) and 1,3,5-tris[[*trans*-iodobis(triethylphosphine)platinum]ethynyl]benzene (**1**) (29.1 mg, 0.015 mmol) were dissolved in 5 mL of toluene and 4 mL of dry diethylamine under nitrogen. Next 4 mg (0.02 mmol) of copper(I) iodide was added in one portion, and the solution was stirred for 4 h at room temperature followed by removal of the solvents under reduced pressure. The remaining yellow residue was separated by column chromatography on aluminum oxide. With hexanes/benzene (1:1) the excess 1,3,5-tris-[[*trans*-iodobis(triethylphosphine)platinum]ethynyl]benzene was nearly quantitatively recovered (412 mg), whereas the product was eluted with hexanes/benzene (1:3). Recrystallization from dichloromethane/hexanes (2:1) afforded 79 mg of an almost white powder. Yield: 79 mg (43%); mp 284−285 °C dec; IR (thin film; CD_2Cl_2; cm^{-1}) 2967, 2940 (C−H), 2109 (C≡C) 1562, 1455, 1410 (Ar); ^1H NMR (CD_2Cl_2) δ 7.03−6.91 (bs, 30 H, aromatic-H), 2.31−2.12 (m, 252 H, CH_2), 1.32−1.11 (m, 378 H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 14.2 (s, $^1J_{PPt} = 2357$ Hz, P_{inner}), 11.5 (s, $^1J_{PPt} = 2319$ Hz, P_{outer}). Anal. Calc for $C_{372}H_{660}I_{12}P_{42}Pt_{21}$: C, 37.06; H, 5.51. Found: C, 36.86; H, 5.38.

X-ray Analysis of 3. A yellow needle crystal having approximate dimensions of 0.11 × 0.03 × 0.02 mm was mounted on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated Mo Kα radiation. The space group *C*2/*c* (No. 15) was unambiguously determined from the systematic absence in the data as well as a statistical analysis of intensity distribution and the successful solution and refinement of the structure. The data were collected at a temperature of 23 °C to a maximum 2θ value of 54.5°. Data were collected in 0.00° oscillations with 25.0 s exposures. The crystal-to-detector distance was 5.04 mm with the detector at the zero swing position. Of the 20 954 reflections that were collected, 8744 were unique. The linear absorption for Mo Kα radiation was 47.9 cm^{-1}. The data were corrected for Lorentz and polarization effects; however due to the small size of the crystal, no further absorption corrections were done. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in F_{calc}: the values for f' and f'' were those of Creagh and McAuley. The values for the mass attenuation coefficients are those of Creagh and Hubbel. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[23] The structure was refined to values of 0.089 (R) and 0.064 (R_w) based on full-matrix least-squares refinement on F^2 of 1918 reflections ($I > 3.00\sigma(I)$) and 210 variable parameters.

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Supporting Information Available: Crystal structure data for **3** including tables of calculated positional parameters and *U* for the hydrogen atoms, non-hydrogen positional parameters and anisotropic thermal parameters, complete bond lengths, angles, and torsional angles are provided (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS. See any current masthead page for ordering information.

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[23] TeXscan: Single Crystal Structure Analysis Software, Version 4.2; Molecular Structure Corporation: The Woodlands, TX, 1995.