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Synthesis of organometallic dendrimers by ligand exchange reactions: reversible bonding of dendrons to a core in transition metal acetylide dendrimers

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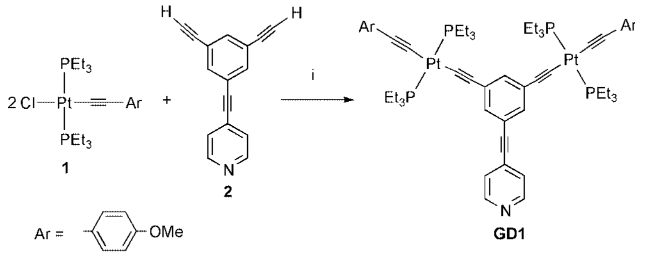
Ligand exchange reactions of chloride ligands on a trinuclear palladium acetylide core with platinum acetylide dendrons having a 4-pyridyl group at a focal point result in the quantitative formation of novel organometallic dendrimers, which easily revert to the core and the dendrons by treatment with Bu_4NCl.

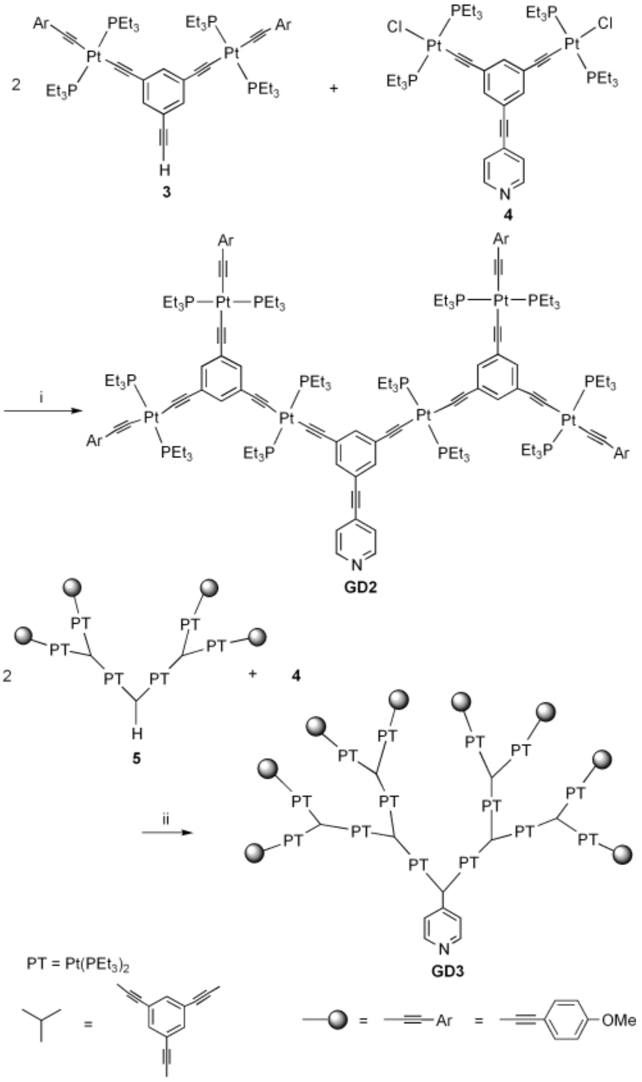
Dendrimers are three-dimensional macromolecules with regularly hyperbranched structures, and have a wide range of potential applicable to the development of new materials.[1] In recent years, attention has shifted towards dendritic molecules containing metal centers since they exhibit characteristic properties such as redox behavior and catalysis.[2] Previously we have synthesized novel organometallic dendrimers composed of platinum acetylide units.[3,4] On the other hand, configurational and constitutional changes in a dendritic molecule responding to simple external stimuli are of interest for the practical application of dendrimers.[5,6] Thus, we engaged in the construction of organometallic dendrimers containing switchable metal components by adopting coordination bonds. Herein we report the syntheses of novel organometallic dendrimers in which platinum–acetylide dendrons are reversibly bonded to a palladium acetylide core.

It is well known that halide ligands on transition metal atoms are reversibly substituted for neutral ligands such as phosphine and pyridine. We have therefore designed platinum–acetylide dendrons having a 4-pyridyl group at a focal point and have achieved successful preparation by a convergent method as shown in Scheme 1. Reaction of the platinum acetylide complex **1** with 1,3,5-triethynylbenzene derivative **2**, which has two terminal acetylenes and one pyridylethynyl group, in the presence of a Cu(I) catalyst gave the first generation dendron **GD1** in 74% yield. Similar reactions of diplatinum **3** and hexaplatinum complexes **5**, which were prepared as reported previously,[4] with **4** gave second and third generation dendrons **GD2** and **GD3** in 60 and 44% yield, respectively (Scheme 2). Trace analysis on these reactions by GPC showed that sharp peaks due to **GD2** with a higher molecular weight relative to those of **3** and **4** grew with consumption of the substrates. Purification by column chromatography on alumina followed by reprecipitation from CH_2Cl_2–hexane gave a single product which was confirmed by GPC analysis. Although no molecular ion peaks of these dendrons except for **GD1** were detected in the mass spectrum, full characterization was performed by means of NMR spectral analyses. For example, the ^{31}P NMR spectrum of **GD3** exhibited two singlet signals at δ 11.0 and 10.8 in a 4 : 3 integral ratio. The former was assignable to the phosphine on the platinum atoms bound to the *p*-methoxyphenylethynyl groups on the surface of the dendron, whereas the latter was due to the phosphines on inner platinum atoms. In the ^1H NMR spectrum, a sharp signal due to methoxy protons appeared at δ 3.78 with twelve-fold intensity of those of the signals due to α- and β-protons of pyridyl groups at the focal point.

We then examined the synthesis of dendrimers by the ligand exchange reaction of the trinuclear platinum–acetylide complex



Scheme 1 *Reagents and conditions*: i, Cu(I) cat., Et_2NH, room temp., 1 d, 74%.



Scheme 2 *Reagents and conditions*: i, Cu(I) cat., Et_2NH, room temp., 3 h, 60%; ii, Cu(I) cat., Et_2NH, room temp., 3 h, 44%.

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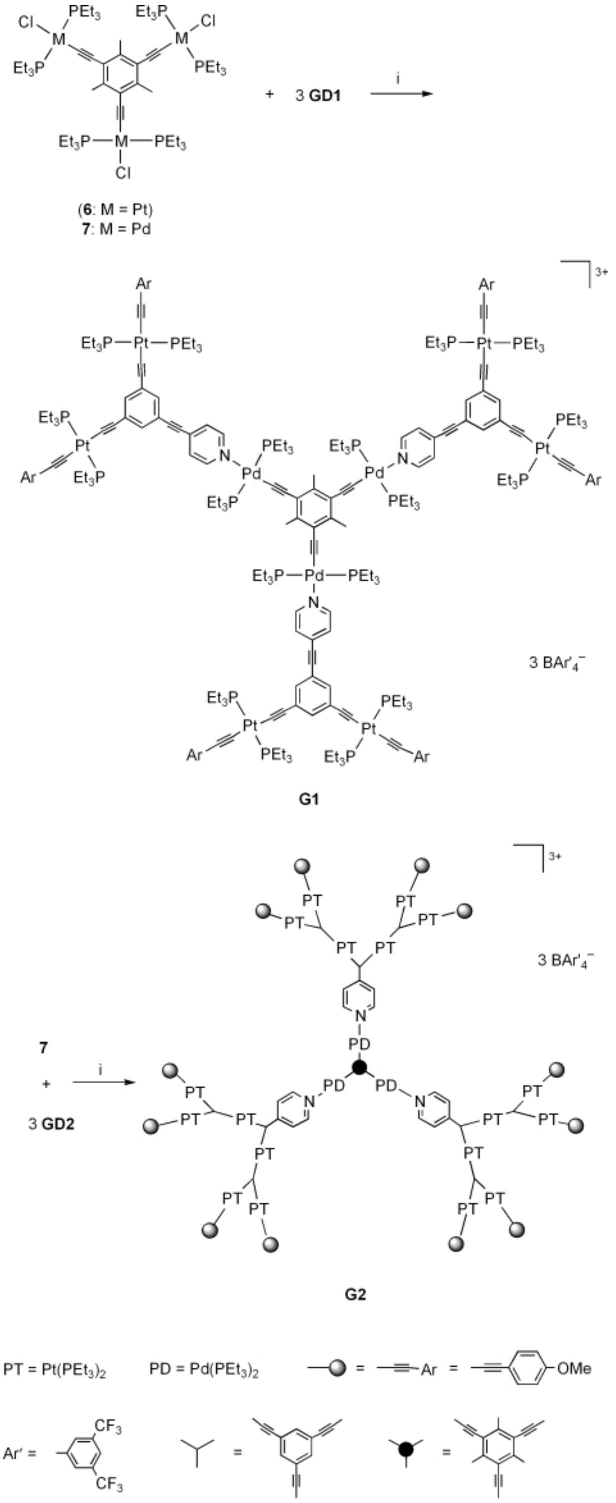

Scheme 3 *Reagents and conditions*: i, 3.3 NaBAr′$_4$, benzene, room temp., 30 min, quantitative yields.

6 with dendrons.[7] Although chloride ligands on complex **6** are easily replaced with pyridine in the presence of KPF$_6$, the reaction of complex **6** with **GD1** allowed only partial ligand exchange to give a mixture of the desired dendrimer and other complexes having one or two **GD1** in the molecule. Therefore, the core was changed to a palladium–acetylide complex **7** and it was found that the treatment with **GD1** in the presence of NaBAr′$_4$ (Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) resulted in complete ligand exchange and produced the first generation dendrimer **G1** in a quantitative yield (Scheme 3). Similarly, the second generation dendrimer **G2** was also prepared by the reaction of **7** with **GD2** in quantitative yield. However, no exchange of chloride ligand with **GD3** took place and third generation dendrimer **G3** did not form at all. The difference in reactivity between **GD2** and **GD3** may arise from the steric effect of **GD3**.

The absence of structural defects in dendrimers **G1** and **G2** was confirmed by spectral analysis. A singlet signal assignable to PEt$_3$ on palladium was observed at δ 32.2 in the ^{31}P NMR spectrum of **G2** while the spectrum of **7** showed a signal at δ 32.7. The ^{1}H NMR spectrum of **G2** exhibited a sharp singlet at δ 2.87 due to the methyl protons of the central mesitylene moiety while the methyl signal of **7** was observed at δ 3.14. In the ^{1}H NMR spectrum of **G2** the integral ratio of the central methyl signal relative to that of the methoxy protons situated at the surface was 1 : 4. These data clearly suggest that all chloride ligands on palladium were replaced with the pyridyl groups of **GD2**, and are consistent with the structure of **G2**.

Treatment of dendrimer **G1** with excess Bu$_4$NCl in benzene led to the quantitative formation of core **7** and dendron **GD1** (Scheme 4). Similar treatment of dendrimer **G2** regenerated **7** and **GD2** in quantitative yield. These results suggest that the bonding of dendrons **GD1** and **GD2** to core **7** can be reversibly controlled by the ligand exchange reaction. Quantitative formation of **G1** and dissociation into **7** and **GD1** were repeated up to three times by successive treatment of NaBAr′$_4$ and Bu$_4$NCl, respectively. These results show the first examples of morphology control in dendrimers by chemical stimuli other than light.[6]

$$\textbf{G1}\text{ or }\textbf{G2}\xrightarrow{\text{i}}\textbf{7}+3\,\textbf{GD1}\text{ or }3\,\textbf{GD2}$$

Scheme 4 *Reagents and conditions*: i, 9 Bu$_4$NCl, benzene, room temp., 30 min, quantitative yields.

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