Synthesis of a Novel Organometallic Dendrimer with a Backbone Composed of Platinum-Acetylide Units

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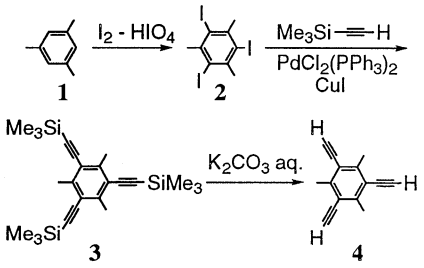
(Received May 22, 1996)

Novel organometallic dendrimers containing platinum-acetylide units in the main chain have been synthesized using 1,3,5-triethynyl-2,4,6-trimethylbenzene (**4**) as a bridging ligand up to a nonanuclear complex (**8**).

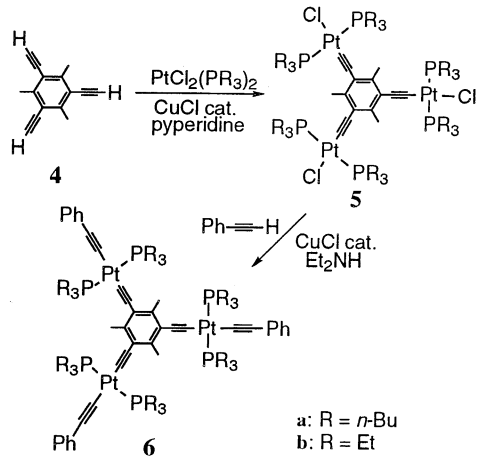
Much attention is currently given to synthesis of highly branched molecules such as dendrimer, because they may have unique physical and chemical properties.[1] Despite extensive studies on organic dendrimers, organometallic dendrimers are still limited.[2] In particular organometallic dendrimers containing metal atoms in the main chain[3] are remarkably rare except for organosilicon dendrimers.[4]

In our laboratory, transition metal poly-yne polymers, in which metal atoms are linked by diyne such as 1,3-butadiyne and *p*-diethynylbenzene, have been studied.[5] Now we anticipate that our system will be extended to the synthesis of organometallic dendrimers by the use of triyne as a bridging ligand. Here we wish to report the synthesis and characterization of novel organometallic dendrimers containing platinum-acetylide units in the main chain.



We have chosen 1,3,5-triethynyl-2,4,6-trimethylbenzene (**4**) as a bridging triyne ligand, and synthesized from mesitylene (**1**) in three steps. Iodination of **1** using iodine and periodic acid dihydrate gave triiodide (**2**) in 90% yield.[6] Treatment of **2** with trimethylsilylacetylene in the presence of a $PdCl_2(PPh_3)_2$–CuI catalyst in diethylamine afforded a trimethylsilylethynyl derivative (**3**) in 79% yield, which was converted to **4** by treatment with aqueous potassium carbonate in 80% yield.[7]

The method used for the synthesis of linear poly-yne polymers has been successively applied for the synthesis of platinum-acetylide dendrimer.[5] Thus, treatment of **4** with dichlorobis(tri-*n*-butylphosphine)platinum in the presence of a CuCl catalyst in piperidine under reflux for 48 h gave trinuclear complex (**5a**) in 67% yield.[8] Observation of the signal attributed to phosphine ligands at δ 6.8 (J_{Pt-P} = 2398 Hz) as a singlet in $^{31}P\{^1H\}$ NMR and the singlet signal of methyl groups bound to aromatic ring at δ 3.08 in ^1H NMR strongly suggests that complex **5a** has a symmetrical structure. Triethylphosphine analog **5b** was also prepared in 36% yield by the reaction of **4** with dichlorobis(triethylphosphine)platinum. Reactions of **5a** and **5b** with phenylacetylene by a CuCl catalyst gave phenylethynyl complexes (**6a**) and (**6b**) in 82% and 83% yields, respectively.



The molecular structure of **5b** was determined by X-ray crystallography,[9] and illustrated in Figure 1. The molecule of **5b** has a 2-fold symmetry axis passing through Cl(2), Pt(2), C(10), C(9), C(8), C(4) and C(5). The Pt–C bond lengths are 1.93(2) and 1.95(2) Å, and the lengths of the C≡C bond are 1.20(2) and 1.19(3) Å. These values are comparable with those of other platinum-acetylide complexes.[10] It is of interest that three coordination planes around Pt atoms are twisted from the aromatic ring by about 60° but the twist directions of three coordination planes are not the same.[11] This phenomenon is likely caused by crystal-packing forces.

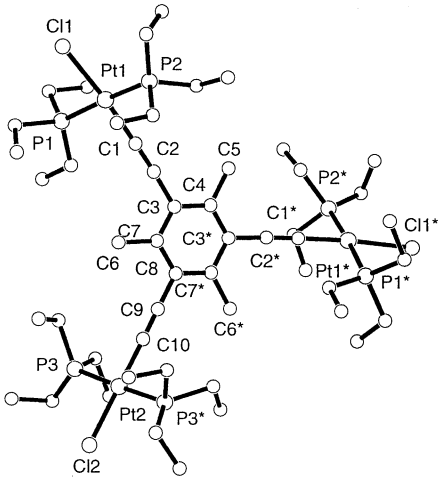
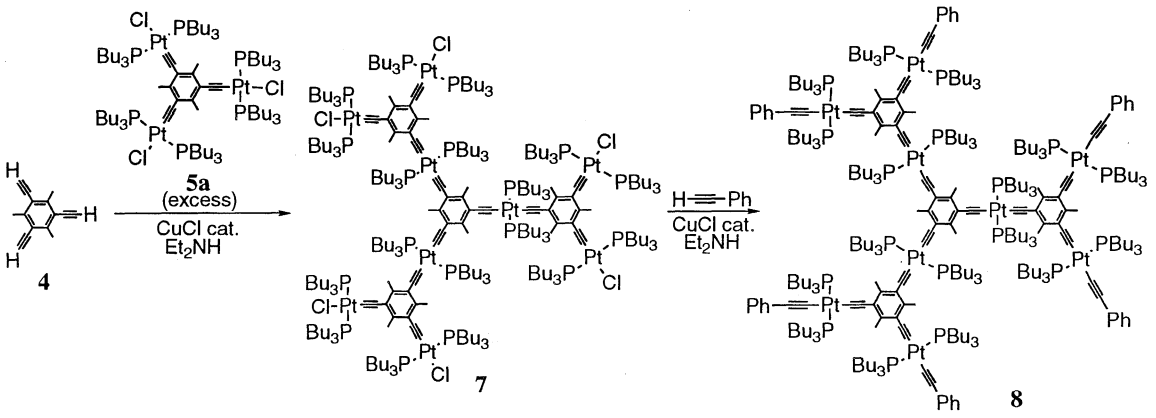


Figure 1. Molecular structure of **5b**. Hydrogen atoms are omitted for clarity.



In order to prepare a dendrimer of next generation, we examined the reaction between **4** and **5a**. When **4** was treated with excess **5a** (molar ratio **4**/**5a** = 1/9) in the presence of a CuCl catalyst in diethylamine, formation of complex (**7**) having a larger molecular weight was confirmed by gel permeation chromatography, but we could not isolate complex **7** in a pure form from the reaction mixture. Introduction of phenylethynyl group as a terminal ligand by treatment of the reaction mixture with phenylacetylene using a CuCl catalyst has enabled isolation of nonanuclear complex (**8**) by column chromatography on alumina followed by recrystallization from ethanol in 11% yield. The $^{31}P\{^{1}H\}$ NMR spectrum of **8** showed two singlet signals at δ 3.9 (J_{Pt-P} = 2388 Hz) and 3.7 (J_{Pt-P} = 2375 Hz) in a 1:2 intensity ratio. The former was assigned to the phosphines bound to three inner platinum atoms and the latter was attributed to those bound to the six external platinum atoms. These data are consistent with the expected structure of **8**, which is also supported by IR, ^{1}H NMR and elemental analysis.

In summary, a successful strategy for the step by step synthesis of a novel platinum-acetylide dendrimer has been developed using 1,3,5-triethynyl-2,4,6-trimethylbenzene (**4**) as a bridging triyne ligand. We are currently investigating the synthesis of platinum-acetylide dendrimers of higher generations as well as their properties.

This work was partially supported by Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236104 from the Ministry of Education, Science, Sports and Culture, Japan. We are grateful to the Materials Analysis Center, ISIR, Osaka University for the support of spectral analysis and X-ray crystallography.

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9 Crystallographic data for **5b**: $C_{51}H_{99}Cl_3P_6Pt_3$, FW = 1589.81, monoclinic, space group *C2/c*, a = 29.590(5) Å, b = 14.679(9) Å, c = 16.77(2) Å, β = 110.15(4)°, V = 6836(6) Å^3, Z = 4, D_{calcd} = 1.54 gcm^{-3}, μ(Mo-Kα) = 63.8 cm^{-1}. Data were measured on a Rigaku AFC5R diffractmeter in the range of 6° < 2θ < 55° with ω-2θ scan technique. The reflections were corrected for Lorentz-polarization effect, decay, and absorption using Ψ scan technique. The structure was solved by Patterson method and refined by full-matrix least-squares method using anisotropic thermal parameters for all non-H atoms except for carbon atoms of triethylphosphine, which are refined isotropically. The hydrogen atoms were located at calculated positions. The final agreement factors are R = 0.069 and R_w = 0.071 for 198 parameters against 3605 reflections with I > 3.0σ(I) out of 8148 unique reflections.

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