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Macromolecular Architecture of Group 10 Metal-Poly(yne)s: Dendritic, Hyperbranched, and Helical Macromolecules

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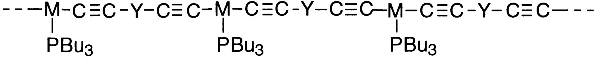
SUMMARY: Novel two- and three-dimensional organometallic polymers of palladium and platinum have been prepared by choice of some acetylene linkages with characteristic structures. When *o*-diethynylbenzene was used for a bridging ligand, a macrocyclic complex was selectively produced. Helical poly(yne) polymers were prepared from the reaction with chiral 1,1'-bi(6-ethynyl-2-naphthol). Platinum acetylide dendrimers, in which platinum atoms are linked by 1,3,5-triethynylbenzene derivatives, have been prepared by a convergent method up to the third generation.

Introduction

The properties of macromolecules depend on the molecular shape, size and rigidity as well as chemical sequence of molecules. Recent progress in the polymer synthesis and organometallic chemistry has provided new and useful methods for the construction of molecular architecture, and many papers showed the precise synthesis of a large number of organic macromolecules having well-controlled molecular shapes such as one-dimensional linear, two-dimensional square and three-dimensional star-shaped, hyper-branched and dendritic macromolecules and so on1–4), whereas there have been a few examples of such organometallic architecture.

About 20 years ago, we reported the synthesis of group 10 metal-poly(yne)polymers having a unique linear rod-like structure in which the *trans* positions of square planar group 10 metals such as platinum and palladium are linked by conjugated diacetylenes like butadiyne5). The molecular shape of these polymers adopts *one-dimensional,* linear rigid structure even in a solution and forms lyotropic liquid crystals which exhibit a response to an external magnetic field.



$$\cdots\underset{\mathrm{PBu_3}}{\overset{\mathrm{PBu_3}}{\mathrm{M}}}-\mathrm{C{\equiv}C-Y-C{\equiv}C}-\underset{\mathrm{PBu_3}}{\overset{\mathrm{PBu_3}}{\mathrm{M}}}-\mathrm{C{\equiv}C-Y-C{\equiv}C}-\underset{\mathrm{PBu_3}}{\overset{\mathrm{PBu_3}}{\mathrm{M}}}-\mathrm{C{\equiv}C-Y-C{\equiv}C}\cdots$$

1

M = Pt, Pd
Y = bond, -C_6H_4-, *etc.*

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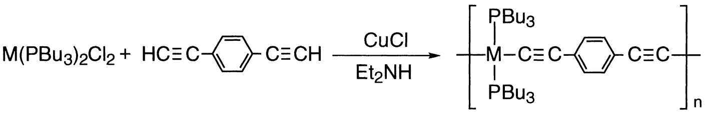
These polymers may be simply prepared by polycondensation between, for example, platinum dichloride and 1,4-diethynylbenzene by the catalysis of a copper halide in amines (eq 1). We are able to obtain soluble poly(yne) polymers with a molecular weight of more than 100,000.



(1)

M = Pt, Pd

One may realize that choice of an appropriate acetylenic linkage in eq 1 lead to a variety of molecular shapes: if we choose 1,2-diethynylbenzene instead of 1,4-diethynylbenzene as the linkage, we may obtain *two-dimensional*, planar poly(yne) macromolecules. Choice of a chiral diethynylbinaphthyl derivative may lead to formation of a *three-dimensional* helical poly(yne) polymer having helical chirality, and 1,3,5-triethynylbenzene derivatives would give *three-dimensional* dendritic macromolecules (Figure 1).

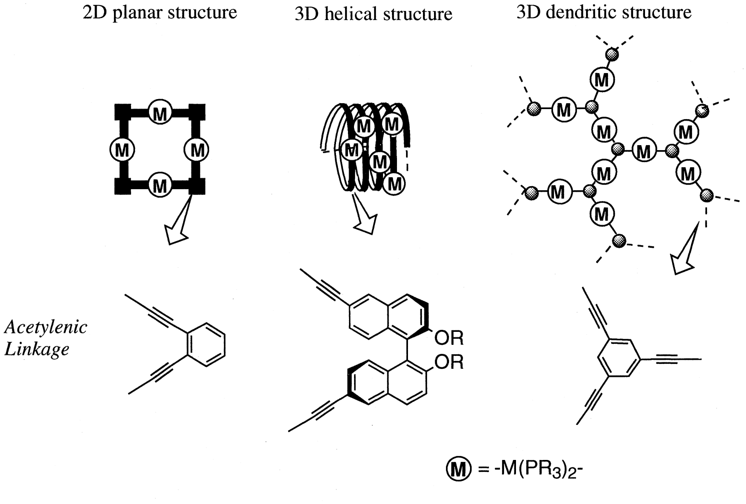
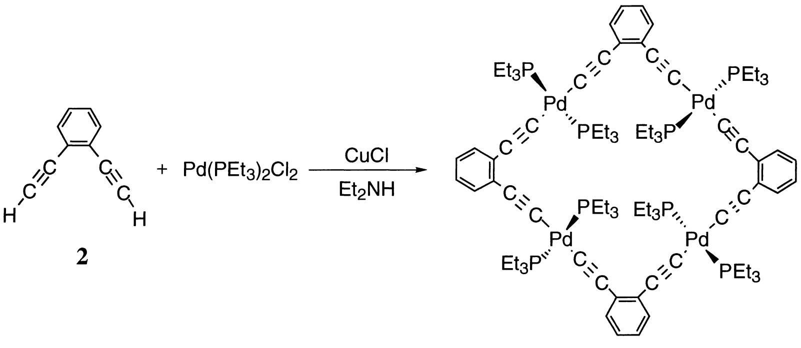


Figure 1. Macromolecular Architectures

The copper-catalyzed dehydrohalogenation (eq 1) between group 10 metal halides and terminal acetylenes proceeds in an amine almost without any side reactions and affords selectively metal acetylide complexes6). Since the acetylides of platinum and palladium are extremely stable in spite of containing a metal-carbon sigma bond and are handled in air, we have challenged to construct two- and three-dimensional architecture of group 10 metal-poly(yne) macromolecules by appropriate choice of acetylenic linkages shown in Figure 1.

Results and Discussion

Macrocyclic Palladium-Acetylide Complexes



2

3

(2)

When *o*-diethynylbenzene (**2**) was treated with an equimolar amount of $Pd(PEt_3)_2Cl_2$ in the presence of a CuCl catalyst in diethylamine at room temperature, a pale yellow complex (**3**) was isolated in 33% yield (eq 2)$^{7)}$. Although gel permeation chromatography exhibited that complex **3** is an oligomeric complex, the NMR spectra showed a simple spectral pattern, suggesting that complex **3** is a macrocyclic complex. Since the angle between two acetylene groups in *o*-diethynylbenzene is 60°, we assumed that complex **3** would be a trinuclear complex. The measurement of the average molecular weight of **3**, however, by vapor pressure osmometry revealed to be ca. 1850, which corresponds to a tetranuclear complex. Finally, the structure of **3**

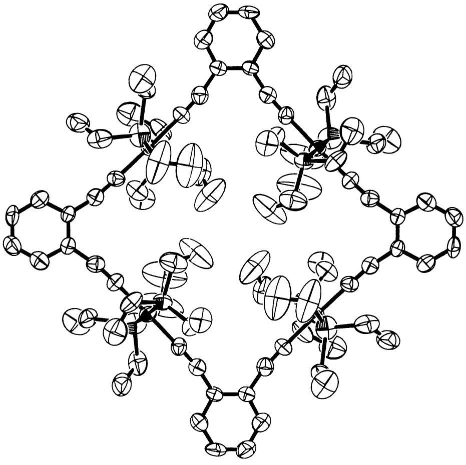
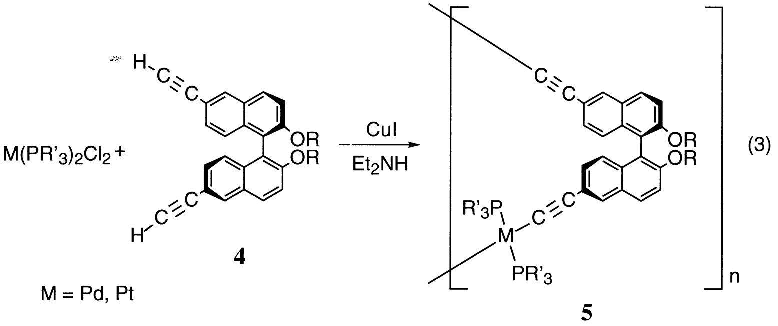


Figure 2 Molecular Structure of Complex 3

was confirmed to be a macrocyclic complex composed of tetranuclear palladium-acetylide by an X-ray analysis (Figure 2). The macrocyclic skeleton involving palladium atoms, acetylenes and aromatic rings lies nearly on the same plane. In order to minimize the steric repulsion between the triethylphosphine ligands, the P–Pd–P axes incline alternatively to opposite direction with respective to the macrocycle, and triethylphosphine ligands on one side of the macrocycle plane are alternatingly situated on the outside and inside of macrocycle. Therefore, tetranuclear complex **3** with minimum strain is selectively produced. On the other hand, treatment of *o*-diethynylbenzene with an equimolar amount of $Pd(PBu_3)_2Cl_2$ did not give a macrocycle but a mixture of linear oligomer complexes due to the larger steric bulk of tributylphosphine than triethylphosphine.

Helical Poly(yne) Polymers



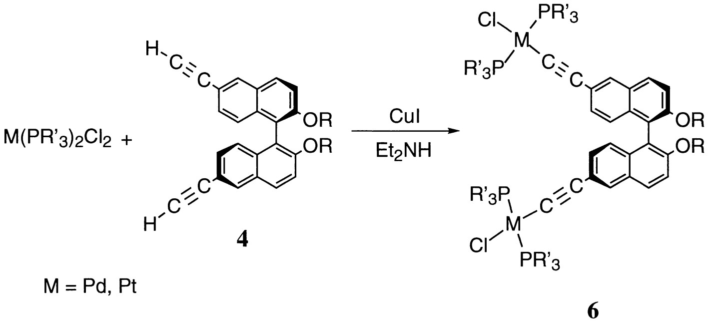
Reactions of chiral acetylene **4**, which was easily prepared from 1,1'-bi-2-naphthol, with an equimolar amount of $M(PR'_3)_2Cl_2$ in the presence of a CuI catalyst in diethylamine resulted in

Table 1. Yields, Molecular Weights and Optical Rotation Powers of Poly(yne) Polymers **5**

	M	R'	R	Yield (%)	$M_w \times 10^{-3}$ [a]	M_w / M_n	$[\alpha]_D$ (deg) [b]
5a	Pd	Et	Me	69	5.4	1.6	–370
5b			Et	71	12	1.9	–227
5c			Pr^i	73	11	1.9	–278
5d		Bu	Me	69	6.1	1.6	–265
5e			Et	63	9.8	1.6	–206
5f			Pr^i	59	7.4	1.6	–182
5g	Pt	Et	Me	73	12	2.7	–364
5h			Et	73	30	2.9	–350
5i		Bu	Me	76	46	3.5	–331
5j			Et	92	100	4.0	–262
5k			Pr^i	71	22	2.2	–288

a: Determined by GPC using poly(styrene) standards.
b: $c = 0.05$ (R = Me, Et), $c = 0.10$ (R = Pr^i), $CHCl_3$ at 25 °C.

the formation of polymers **5** in good yields (eq 3)[8]. The results are surmmarized in Table 1. Polymers **5** are stable and soluble in common organic solvents. The regular structure of **5** was confirmed by the ^1H, ^{13}C and ^{31}P NMR spectra. The average molecular weights of palladium polymers **5a**–**5f** are in the range of 5,400-12,000 regardless of the substituent on acetylene and phosphine ligands. In contrast, the M_ws of platinum polymers **5g**–**5k** were larger than the palladium analogs and were fairly influenced by the substituent on the naphthyl group of acetylene bridges and phosphine ligands. Thus, the M_ws of ethoxy analogs **5h** and **5j** are much higher than those of methoxy and isopropoxy ones. Tributylphosphine analogs **5i** and **5j** have higher M_ws than triethylphosphine analogs **5g** and **5h**.



(4)

As a model compound of the polymer, dinuclear complexes possessing a chiral acetylene-bridge were prepared (eq 4). Treatments of **4** with 2 equivalents of $M(PR'_3)_2Cl_2$ gave dinuclear complexes (**6**). Yields and optical rotation powers are summarized in Table 2. It should be noted that all polymers **5** prepared here showed larger specific optical rotation than both acetylene ligands **4** and model compounds **6**, which may indicate that the main chain of the polymers keeps one-handed helical conformation and induces a helical chirality of the polymers.

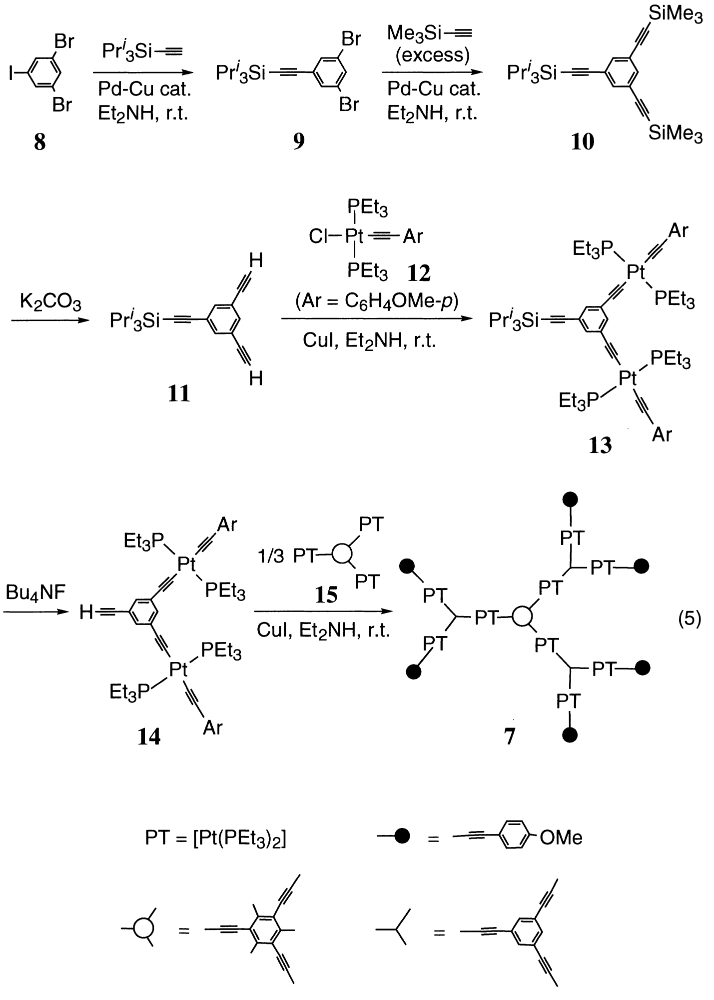
Table 2. Yields and Optical Rotation Powers of Dinuclear Complexes **6**

complex	M	R'	R	Yield (%)	$[\alpha]_D$ (deg)[a]
6a	Pd	Et	Me	82	–142
6b			Et	78	–150
6c	Pt	Et	Me	62	–147
6d			Et	61	–148
6e		Bu	Me	76	–103
6f			Et	57	–87

a: $c = 0.05$, $CHCl_3$ at 25 °C.

Platinum-Acetylide Dendrimer

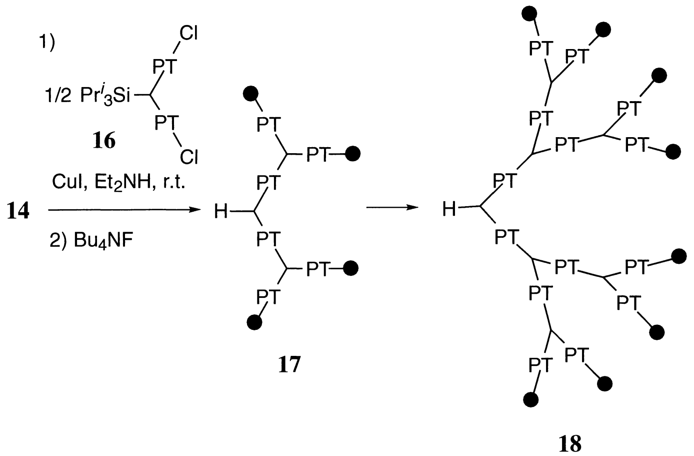
Recently we reported the synthesis of platinum-acetylide dendrimers using triethynylmesitylene as a bridging ligand up to a henicosanuclear complex, which is a dendrimer of second generation[9,10]. However, a large effort was required to isolate the resulting dendrimers from the reaction mixture since no protecting groups were used. Therefore, it would be difficult to extend this method to the preparation of higher generation dendrimers. We have disclosed a novel efficient route for organometallic dendrimer composed of platinum-acetylide units in the main chain by a convergent method[11]. Two kinds of trialkylsilyl groups, trimethylsilyl and tri(*iso*-propyl)silyl, were used for the synthesis of platinum-acetylide dendrimers as a protecting group of terminal acetylene.



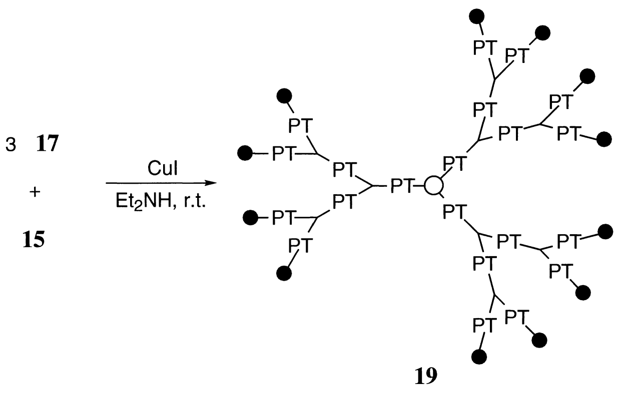
(5)

The synthetic route to G1 dendrimer (**7**) is shown in eq. 5. Treatment of 1,3-dibromo-5-iodobenzene (**8**) with one equivalent of tri(*iso*-propyl)silylacetylene at room temperature in the presence of a $PdCl_2(PPh_3)_2$-CuI catalyst in diethylamine led to the selective formation of the mono(silylethynyl) derivative (**9**), which was quantitatively converted into a tri(silylethynyl) derivative (**10**) by the reaction with excess trimethylsilylacetylene in refluxing triethylamine12). Selective desilylation of the trimethylsilyl group by the reaction with K_2CO_3 gave compound **11** having two terminal acetylenic groups in the molecule. *p*-Methoxyphenylethynylplatinum groups were introduced by the reaction of **11** with two equivalents of platinum complex **12** in the presence of a CuCl catalyst at room temperature to give a dinuclear acetylide complex (**13**). Removal of the tri(*iso*-propyl)silyl group by the treatment with Bu_4NF gave the first generation dendron (**14**). Finally G1 dendron **14** was treated with triplatinum complex **15** in a 3:1 molar ratio to give the first generation dendrimer **7**.

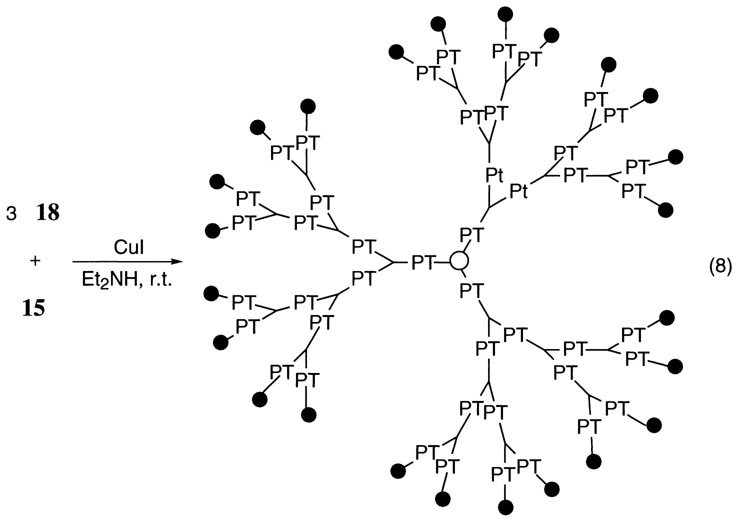
The G1 dendron **14** was successfully grown to the G2 dendron (**17**) by the reaction with a building block (**16**) in a 2:1 molar ratio, followed by desilylation of the tri(*iso*-propyl)silyl group



(6)



(7)



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(eq. 6). The similar reaction of **16** resulted in the formation of the G3 dendron (**18**). Reactions of **17** and **18** with **14** in a 3:1 molar ratio led to the formation of G2 and G3 dendrimers (**19**) and (**20**), respectively (eq. 7 and 8). The G3 dendrimer **20**, which contains forty-five platinum atoms in a molecule, is one of the largest organotransition metal dendrimers and belongs to nanosize materials.

Acknowledgment

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