



## Communication

Synthesis and structure of penta-platinum  $\sigma$ -bonded derivatives of corannuleneHyunbong Choi<sup>a</sup>, Chulwoo Kim<sup>a</sup>, Ki-Min Park<sup>b</sup>, Jinho Kim<sup>c</sup>, Youngjin Kang<sup>c,\*</sup>, Jaejung Ko<sup>a,\*</sup><sup>a</sup> Department of New Material Chemistry, Korea University, Jochiwon, Chungnam 339-700, Republic of Korea<sup>b</sup> Research Institute of Natural Science Gyeongsang National University, Jinju 660-701, Republic of Korea<sup>c</sup> Division of Science Education, Kangwon National University, Chuncheon 200-701, Republic of Korea

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## ABSTRACT

The synthesis of a new class of Pt(II) complexes with corannulene by way of either oxidative addition or reductive coupling is reported and their crystal structures are investigated. The crystal structure for  $\{trans\text{-Pt}(\text{PEt}_3)_2\text{Cl}\}_4\{cis\text{-Pt}(\text{PEt}_3)_2\text{Cl}\}\text{C}_{20}\text{H}_5$  (**1**) consists of two enantiomers in a unit cell and shows *cis*- and *trans*-configuration around Pt(II) due to bulky  $\text{PEt}_3$  ligands. The pentanuclear Pt(II) complex, **1**, readily reacts with 1-ethynyl-4-nitrobenzene to afford the penta-alkynyl substituted Pt(II) complex (**2**). Although there are still bulky  $\text{PEt}_3$  ligands around the Pt atoms in **2**, all five Pt(II) have *trans*-configurations. The bowl of corannulene in **2** is shallower than that of **1**. Therefore, the bowl depth of corannulene plays a key role in the determination of molecular geometry of  $\sigma$ -bonded pentanuclear complexes bearing corannulene.

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Recently, transition metal complexes with non-planar polycyclic aromatic hydrocarbons, such as fullerene, corannulene, have been attention due to their reactivity, bonding modes and structural diversity [1]. Among polycyclic aromatic hydrocarbons, corannulene ( $\text{C}_{20}\text{H}_{10}$ ) is the minimum fragment of a fullerene retaining the characteristic curvature. Substantial efforts have been directed toward the synthesis of transition metal complexes of corannulene [2], in order to understand the participation of corannulene in the bowl to bowl inversion process [3], and to reveal the reactivity of corannulene [4]. Bowl-to-bowl inversion is a dynamic process in which the convex and concave faces interconvert through a planar transition state [5]. Previous studies [6] indicate that *peri* substituents make the bowl shape of corannulene flatten, leading to decrease the inversion barrier, however bridging the *peri* positions serve to increase the bowl inversion barrier.

Although a number of studies on the structural features and reactivity of sandwiched metal complexes bearing corannulene and corannulene derivatives have been reported, the preparation of metal complexes through a direct sigma-bond between the metal and the corannulene core still remains rare. Sharp group has recently reported Ni(II) and Pt(II) complexes by the reaction of low-valent Ni(0) and Pt(0) metals with corannulene [7]. The relationship between the bowl depth of corannulene derivatives and the substituents at the rim position of corannulene is considered major issue in accordance with reactivity and selectivity of corannulene to the metal [8,9]. Meanwhile, the X-ray structure of 1,3,5,7,9-penta-*tert*-butylcorannulene was reported by the Petrukhina group [9].

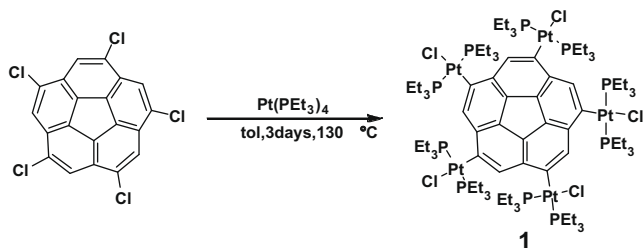
This compound is sterically crowded due to the bulky substituents at the rim positions, leading to a shallow corannulene bowl (bowl depth: 0.72 Å). However, further study on the reactivity of metals using the penta-substituted corannulene and structural characteristics of metal complexes in the solid state have not been reported until now. We are interested in the structural features and reactivity of sterically crowded pentanuclear metal complexes bearing sigma-bonds between the metal and the carbon of corannulene. Herein, we report an X-ray crystal structure of metal-corannulene complex that shows two enantiomers in a unit cell and its reactivity to alkyne functionality.

To synthesize  $\sigma$ -bonded platinum derivatives of corannulene, we adopted a synthetic route involving an oxidative addition reaction between bromocorannulenes and  $\text{Pt}(\text{PEt}_3)_4$ , which was recently reported by the Sharp group [7]. Addition of 10.5 equiv of  $\text{Pt}(\text{PEt}_3)_4$  to 1,3,5,7,9-pentachlorocorannulene in toluene at 130 °C gave yellow solution. Standard work-up and crystallization from methanol gave  $[\text{Pt}_5(\text{PEt}_3)_{10}\text{Cl}_5\text{-}(\text{corannuleny})]$  (**1**) as a spectroscopically pure yellow crystalline solid (Scheme 1) [10]. Yellow crystals of  $[\text{Pt}_5(\text{PEt}_3)_{10}\text{Cl}_5(\text{C}_{20}\text{H}_5)]$  (**1**) suitable for an X-ray structure were grown in methanol at  $-10$  °C.

The X-ray study revealed **1** to be an unusual oxidative addition product of a platinum complex containing two types of phosphine ligands,  $\{trans\text{-Pt}(\text{PEt}_3)_2\text{Cl}\}_4\{cis\text{-Pt}(\text{PEt}_3)_2\text{Cl}\}\text{C}_{20}\text{H}_5$  (Fig. 1), instead of the expected structure of  $\{trans\text{-Pt}_5(\text{PEt}_3)_{10}\text{Cl}_5\}\text{C}_{20}\text{H}_5$  [11]. Interestingly, the asymmetric unit of **1** consists of a racemic mixture of the two enantiomers (A:B = 1:1). Similarly, a sumanene ligand has recently been used to form a trimethyl substituted compound [12] or transition metal Fe(II) complex that displays the enantiomeric isomer of buckybowls [13].

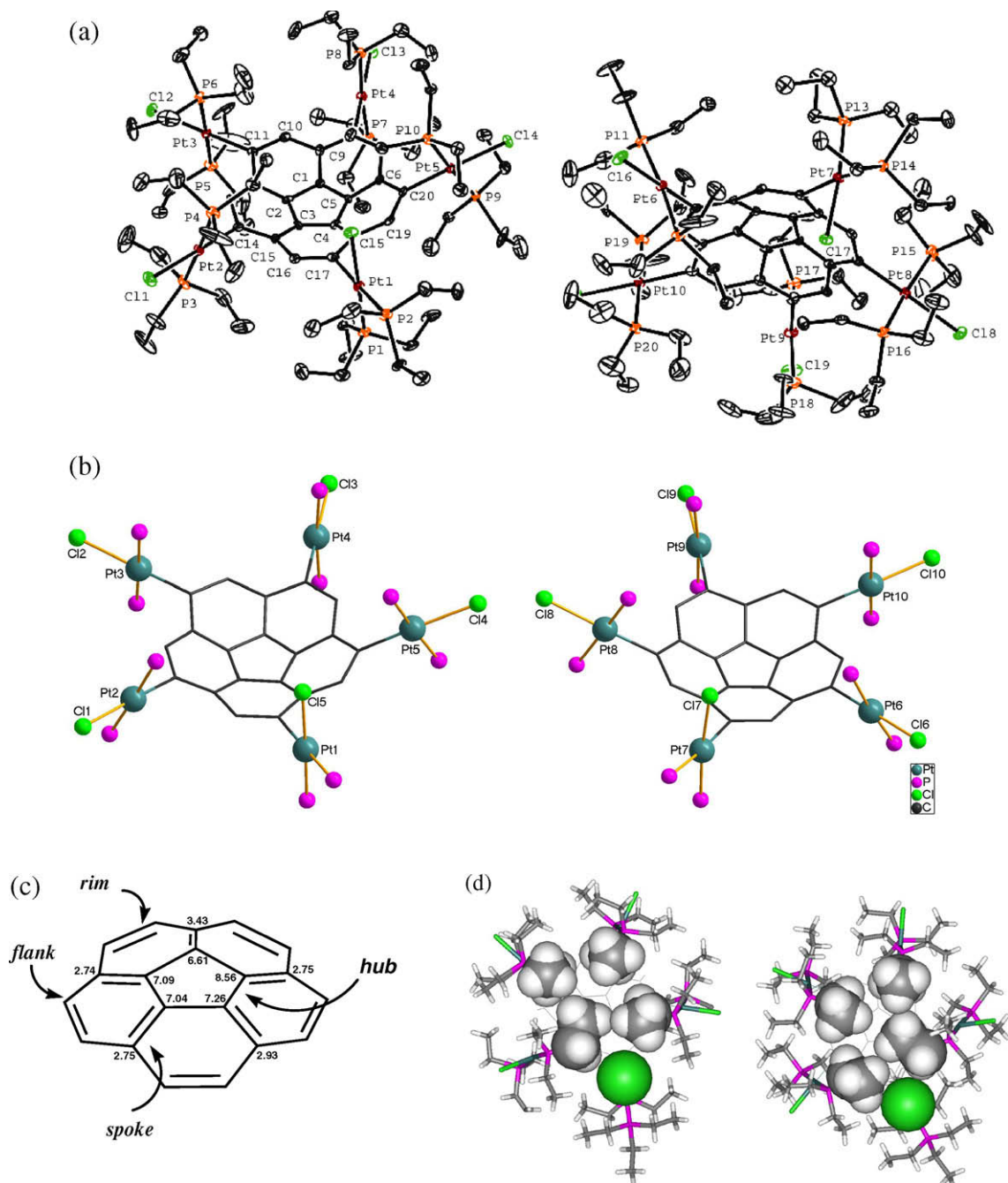
\* Corresponding author.

E-mail addresses: kangy@kangwon.ac.kr (Y. Kang), jko@korea.ac.kr (J. Ko).

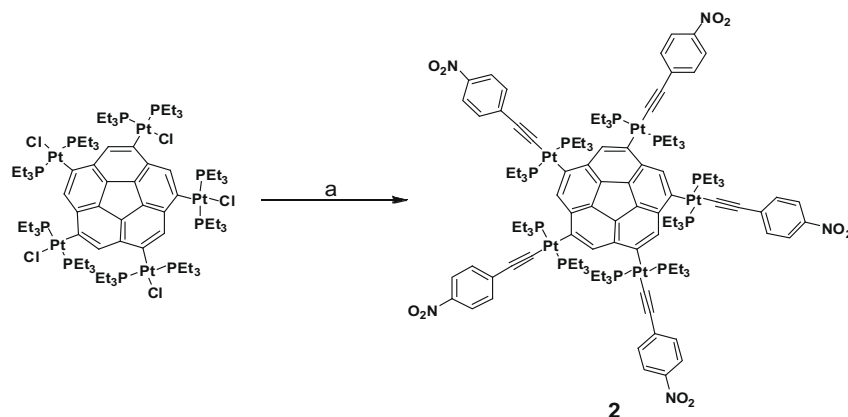


Scheme 1.

The bowl depths for A and B in Fig. 1, which is defined as the separation distances between a centroid of the interior hub plane and the mean plane of the ten atoms on the rim, are 0.77 and 0.80 Å, respectively. While the bowl depths for non-substituted and penta-alkyl substituted corannulene are 0.87 and 0.72 Å, respectively. This fact suggests that there is no room to locate the triethylphosphine ligand of the fifth platinum atom in the *trans* conformation because the bowl depth of **1** is deeper than that of penta-*t*-butyl substituted corannulene. Henceforth, a Cl atom instead of a PEt<sub>3</sub> ligand is located at the endo-position (concave), as shown in Fig. 1.



**Fig. 1.** (a) Ortep drawing of **1** with atom numbering scheme. Hydrogen atoms are omitted for clarity. (b) Perspective view of **1** showing two enantiomeric bowl forms in a unit cell. (c) POAV pyramidalization angles and averaged bond lengths of bowl A form; C–C<sub>hub</sub> = 1.40(2), C–C<sub>rim</sub> = 1.43(2), C–C<sub>flank</sub> = 1.44(2), C–C<sub>spoke</sub> = 1.39(2). (d) Space filling models of **1** showing steric congestion. Left: A, right: B.



**Scheme 2.** Reagents and conditions: (a) 1-ethynyl-4-nitrobenzene,  $\text{Et}_2\text{NH}$ , then toluene,  $\text{CuI}$ .

Such *cis* and *trans*-formation of platinum phosphine complexes has been observed in the oxidative addition product, *cis*- $\text{Pt}(\text{PEt}_3)_2(\text{Br})(1,5,6\text{-tribromo-corannulene-2-yl})$ . This observation for **1** is attributed to both steric hindrance caused by  $\text{PEt}_3$  ligands and those that are attached to them are on average  $7.31^\circ$  and  $2.92^\circ$ , respectively. The analogous values for corannulene are  $8.4^\circ$  and  $3.8^\circ$ , respectively. Thus, the curvature of the corannulene bowl in the hub carbons of **1** is reduced to 87% of that of corannulene; however, curvature for the outer spoke carbons is reduced to 77%. A significant difference in bond lengths is observed in the rim bonds which are elongated to an average of 1.43(2) from 1.402(5) Å in corannulene itself [15]. An elongation of the rim bonds represents an addition of strain to the corannulene unit of **1**. This stretching partially accommodates the steric congestion of the substituents [16]. The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of **1** in solution were consistent with the structure determined by X-ray crystallography. Four singlets ( $\delta$  8.00, 7.88, 7.82, and 7.78) and one doublet at  $\delta$  7.92 ( $J_{\text{PH}} = 8.4$  Hz) in the  $^1\text{H}$  NMR spectrum of **1** indicates that the five corannulene protons are not equivalent. The  $^{31}\text{P}$  NMR spectrum of **1** exhibits four resonances at  $\delta$  9.50, 9.19, 8.37, and 7.86 with a rather large coupling constant of  $^1J_{\text{PTP}}$  (2728–2748 Hz), and two doublets at  $\delta$  4.98 and  $-0.78$  with a small coupling constant of  $^1J_{\text{PTP}}$  (1678 Hz) due to the presence of phosphines with different arrangements around the Pt atom. These results are consistent with the crystal structure, as shown in Fig. 1.

Complex **1** was found to be an efficient reactant for the reductive coupling reaction with an alkyne under mild condition [17]. The reaction of **1** with 1-ethynyl-4-nitrobenzene in the presence of  $\text{CuI}$  and  $\text{Et}_2\text{NH}$  afforded the penta-alkynyl substituted corannulene **2** (Scheme 2). All of the spectral data of **2** were consistent with the expected product. A key feature in the  $^1\text{H}$  NMR spectrum indicates a singlet at  $\delta$  7.73 assigned to the corannulene proton, indicating that five protons on corannulene are now chemically equivalent. One high-field resonance at  $\delta$  6.4 ( $^1J_{\text{PTP}} = 2660$  Hz) in the  $^{31}\text{P}$  NMR spectrum provides evidence that all platinum planes are orthogonal to the corannulene bowl.

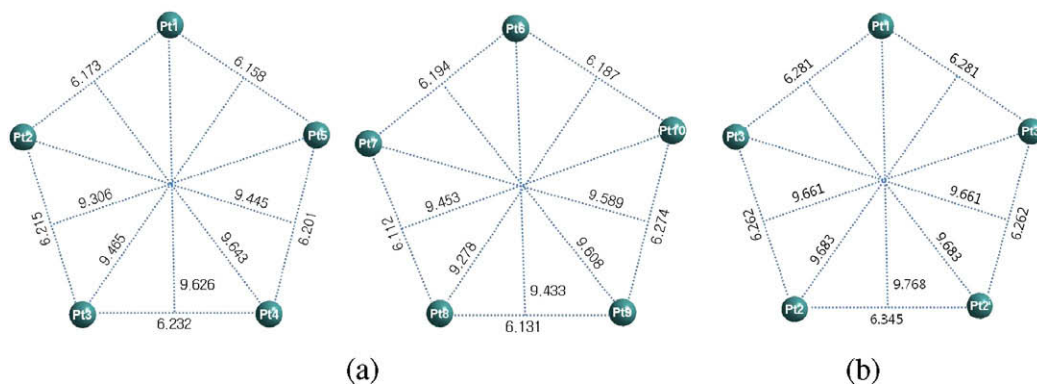
The red single crystals, crystallized from a solution of toluene and hexane slowly decomposed under air. The crystal structure reveals that the corannulene with a regular pentagon conformation is coordinated to a platinum moiety at five carbon sites and five peripheral substituents on the corannulene have a flat configuration. The bond lengths (2.07(3)–2.29(4) Å) of Pt–C(corannulene) observed in **2** are slightly longer than those (1.98(17)–2.08(16) Å) of **1**. These observed elongations imply a stronger *trans* influence of carbon atom attached on triple bond. In order to compare the difference of bowl depth between **1** and **2**, the separation distance, which is defined as the distance of the centroid between two adjacent Pt atoms and Pt atom located in opposite side in the Pt pentagon, was estimated (Fig. 2) [18].

As being anticipated, the average separation distance of **2** (9.68 Å) was measured to be longer than that of **1** (9.48 Å). Moreover, the average separation distance (6.18 Å) between two adjacent Pt atoms in **1** is shorter than that (6.29 Å) of **2**. Both observations imply that the bowl of **2** is shallower than that of **1**, as shown in Fig. 2. Therefore, all of the Pt atoms have a *trans*-con-

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**Fig. 2.** Separation distances (Å) of **1**(a) and **2**(b) in the Pt pentagon. Symmetry code: (i)  $2-x, y, 1.5-z$ .

figuration despite the presence of steric crowding at the endo-position. The structure of **2** in the solid state is consistent with the data of  $^1\text{H}$  and  $^{31}\text{P}$  NMR. Based on our observation and illustration, we believe that the bowl depth of corannulene plays a key role in the determination of molecular geometry in  $\sigma$ -bonded pentanuclear complexes bearing corannulene.

In summary, an oxidative addition reaction of 1,3,5,7,9-pentachlorocorannulene with  $\text{Pt}(\text{PEt}_3)_4$  afforded an interesting platinum  $\sigma$ -bonded derivative of corannulene. The crystal structure for **1** consists of two enantiomers in a unit cell and shows both *cis*- and *trans*-configurations around Pt ions due to the steric congestion of bulky ligands. Compound **1** readily reacts with 1-ethynyl-4-nitrobenzene to afford the penta-alkynyl substituted corannulene with *trans*-configuration around platinum. The bulky peripheral substituents cause a flattening of the bowl.

## Acknowledgment

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## Appendix A. Supplementary material

CCDC 609288 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.07.015.

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- [10] General considerations: All experiments were performed under dry  $\text{N}_2$  atmosphere using standard Schlenk technique. All solvents were freshly distilled over appropriate drying reagents prior to use. All starting materials were purchased from either Aldrich or Strem and used without further purification.  $^1\text{H}$  NMR were recorded on a Varian 300 MHz spectrometer and phosphorus resonance was referenced with respect to external 85%  $\text{H}_3\text{PO}_4$ . Preparation of **1**: To a stirred solution of  $\text{Pt}(\text{PEt}_3)_4$  (0.63 g, 0.94 mmol) in freshly distilled toluene (60 mL) under nitrogen was added, in portions, 1,3,5,7,9-pentachlorocorannulene (40 mg, 0.09 mmol). The resulting bright red solution was then maintained for 3 days in an oil bath at 130 °C. The solvent was removed *in vacuo* at 40 °C, and the residue was suspended in methanol (15 mL) and gently refluxed for 45 min. The suspension was allowed to cool. The product was collected on a frit and washed with cold methanol (5 mL  $\times$  2) to give **1** as a yellow solid. Yield: 0.12 g (52%); mp 283 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.00 (s, 1H), 7.92 (d,  $J_{\text{PH}} = 8.4$  Hz, 1H), 7.88 (s, 1H), 7.82 (s, 1H), 7.78 (s, 1H), 2.02–1.52 (m, 54H), 1.27–0.99 (m, 81H), 0.80 (m, 6H), 0.56 (t,  $J = 8.0$  Hz, 9H);  $^{31}\text{P}\{^1\text{H}\}$ NMR ( $\text{CDCl}_3$ ):  $\delta$  9.50 (s with satellites,  $J_{\text{PP}} = 2742$  Hz), 9.19 (s with satellites,  $J_{\text{PP}} = 2728$  Hz), 8.37 (s with satellites,  $J_{\text{PP}} = 2736$  Hz), 7.86 (s with satellites,  $J_{\text{PP}} = 2748$  Hz), 4.98 (d with satellites,  $J_{\text{PP}} = 1678$ ,  $J_{\text{PP}} = 11.8$  Hz), –0.78 (d with satellites,  $J_{\text{PP}} = 1678$  Hz,  $J_{\text{PP}} = 11.8$  Hz), –0.76 (d with satellites,  $J_{\text{PP}} = 1678$  Hz,  $J_{\text{PP}} = 11.8$  Hz); Elemental analysis Calc. for  $\text{C}_{80}\text{H}_{155}\text{Cl}_5\text{P}_{10}\text{Pt}_5$ : C, 37.25; H, 6.06. Found: C, 36.98; H, 5.96.
- [11] Crystal data for **1**:  $\text{C}_{80}\text{H}_{155}\text{Cl}_5\text{P}_{10}\text{Pt}_5$ ,  $M_r = 5158.88$ , crystal dimensions  $0.18 \times 0.07 \times 0.04$  mm<sup>3</sup>, monoclinic, space group  $P2_1/n$ ,  $a = 38.946(8)$ ,  $b = 14.601(3)$ ,  $c = 39.197(8)$  Å,  $\beta = 109.85(3)^\circ$ ,  $V = 20965(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.634$  g cm<sup>–3</sup>,  $\lambda$  (Mo K $\alpha$ ) = 0.71073 Å,  $T = 233(2)$  K,  $2\theta_{\text{max}} = 51.36^\circ$ , index range:  $-47 \leq h \leq 47$ ,  $-17 \leq k \leq 17$ ,  $-47 \leq l \leq 47$ ,  $\mu = 6.964$  mm<sup>–1</sup>, 39820 measured reflection, 1772 independent reflection,  $R_1 = 0.0692$ ,  $wR_2 = 0.1584$  ( $I > 2\sigma(I)$ ), GOF = 1.007.
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- [17] Preparation of **2**: To a stirred solution of **1** (0.10 g, 0.038 mmol) and 1-ethynyl-4-nitrobenzene (57 mg, 0.387 mmol) in diethylamine (15 mL) was added CuI (1.8 mg) in toluene (15 mL). The reaction was stirred in the dark for 24 h. A white precipitate of diethylammonium iodide was appeared. The solvent was removed on a rotatory evaporator, and the product was purified by column chromatography on silica gel (eluent: ethylacetate/hexane, 1:2). The pure product was obtained by recrystallization from a toluene/hexane solution. Yield: 0.072 g (60%); mp 175 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.10 (d,  $J = 9.0$  Hz, 10H), 7.73 (s, 5H), 7.34 (d,  $J = 9.0$  Hz, 10H), 1.79 (br, 60H), 1.06 (m, 90H);  $^{13}\text{C}\{^1\text{H}\}$ NMR ( $\text{CDCl}_3$ ):  $\delta$  148.6, 148.1, 144.3 (d), 138.8, 137.1, 136.4, 131.7, 130.8, 128.4, 123.8, 110.1, 108.4, 16.2 (d), 8.3;  $^{31}\text{P}\{^1\text{H}\}$ NMR ( $\text{CDCl}_3$ ):  $\delta$  6.4 (s with satellites,  $J_{\text{PP}} = 2660$  Hz); Elemental analysis calc. for  $\text{C}_{120}\text{H}_{175}\text{N}_5\text{O}_{10}\text{P}_{10}\text{Pt}_5$ : C, 46.01; H, 5.63. Found: C, 45.87; H, 5.48.
- [18] In the case of **2**, the bowl depth is hardly obtained by the way of the same method for measuring the depth in **1**, because the carbon atoms of corannulene are disordered.