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Synthesis and X-ray structural analysis of platinum and ethynyl-platinum corannulenes: supramolecular tectons†

Roman Maag^a, Brian H. Northrop^b, Anna Butterfield^a, Anthony Linden^a, Oliver Zerbe^a, Young Min Lee^c, Ki-Whan Chi^c, Peter J. Stang^b, and Jay S. Siegel^a

Roman Maag: ; Brian H. Northrop: ; Anna Butterfield: ; Anthony Linden: ; Oliver Zerbe: ; Young Min Lee: ; Ki-Whan Chi: ; Peter J. Stang: stang@chem.utah.edu; Jay S. Siegel: jss@oci.uzh.ch

^a Organic Chemistry Institute, University of Zurich, Winterthurerstrasse 190, 8057 Switzerland; Fax: +41 44 635 4281; Tel: +41 44 635 6888

^b Department of Chemistry, University of Utah, Salt Lake City, Utah 84107, USA

^c Department of Chemistry, University of Ulsan, Ulsan, 680-749, Republic of Korea

Abstract

The synthesis and characterization of two direct platinum (**1** and **6a/b**) and three ethynyl-platinum corannulene derivatives (**2**, **8** and **9**), bearing 2, 4, or 5 square planar platinum centers, are presented. The structure of the bowl bearing substituents remains comparable to corannulene and the dynamic behavior of the bowl inversion as assessed by VT NMR supports a persistent bowl structure in solution. These platinum-corannulenes are well-structured tectons for the future assembly of coordination Platonic polyhedra.

Introduction

Platonic solids have served as targets for total chemical synthesis in covalent¹ as well as supramolecular variants.^{2,3} Their designs come from replacement of Platonic graph vertices by an appropriate molecular fragment, for example by CH in the case of cubane⁴ and dodecahedrane,⁵ or a 4-spoke Holliday junction in cubic DNA *nano*-constructs.⁶ Supramolecular targets often include symmetry and geometry-tailored organic tectons and metal–ligand junctions.^{2,3} Among Platonic symmetries, examples of 5-fold symmetric derivatives capable of participating in such assemblies do not yet appear. Such 5-fold symmetric tectons could provide direct access to icosahedrally symmetric supramolecular structures.⁷

Direct metallation **1** and metalloalkynyl **2** targets (Scheme 1), based on corannulene,⁸ readily spring to mind when 5-fold symmetry is the goal. Given the success with metal mediated 5-fold coupling chemistry^{9,10} starting from pentachlorocorannulene **3**,¹¹ accessing metallated derivatives seemed promising.

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Correspondence to: Peter J. Stang, stang@chem.utah.edu; Jay S. Siegel, jss@oci.uzh.ch.

Note added in proof

During the typesetting of this manuscript we were able to obtain ³¹P, ¹H-HSQC data (*cf.* page 6 of the supplementary information), which confirms a small additional peak in the ¹H NMR (δ 7.77 ppm) and ³¹P (δ 14.89 ppm) NMR of **1** belongs to the all *trans* isomer. Crude integration of the peaks indicates that the all *trans* component constitutes *ca.* 10% of the solution structure under these conditions.

Previous work on the tetrabromide **4,8e-g** provided additional precedence for dimetallation of corannulene when the halogen is bromine (Scheme 2). Even if somewhat hampered by isomeric product formation and limited to disubstitution, this initial platinum insertion work proved the principal.¹² Direct metallation of 1,6-dibromo-2,7-dimethylcorannulene **5**¹⁰ with Pt(PEt₃)₄ addresses the isomer issue and provides a clean dimetallated tecton **6a** with essentially diametrically opposed binding sites on corannulene.

Pentakis-Pt(PEt₃)₂Cl corannulene **1** was obtained from a reaction mixture of Pt(PEt₃)₄ and **3** in toluene heated to 95 °C over 5 days. The product was recrystallized twice from hot MeOH (48% overall yield). An analogous procedure yielded compound **6a** in 79% yield after trituration of the crude product with *n*-pentane. For better crystallization and leaving group properties for the future construction of supramolecular assemblies, the bromine atoms in compound **6a** were exchanged with MeCN using a silver(I) salt with the weakly coordinating hexabromocarborane anion.¹³ Thus, the corresponding metathesis product **6b** was synthesized.

Hypothetical compound **7** seems too sterically crowded to form; however, extending the site of metallation with alkyne spacers could alleviate steric problems associated with metallation of vicinal sites. Methods to convert the halide family **3–5** into their respective TMS-alkyne derivatives are established.^{10,11b} A one-pot method for converting TMS-alkyne to Pt-alkyne derivatives was found using CsF, CuI and Pt(PEt₃)₂I₂ in a solvent mixture of DMF/CH₂Cl₂/H₂O (Scheme 3). DMF seems to be an important solvent in this reaction, it is believed to be crucial for the stabilization of the intermediate copper acetylenes. Without DMF, the reaction mixture does not exhibit the red color, which is indicative for the formation of the cuprates. Pentakis-ethynyl, tetrakis-ethynyl, and bis-ethynyl platinum derivatives **2**, **8** and **9**, were prepared in 35%, 89%, and 85% yield, respectively, from halides **3–5**. The *in situ* platination of the corresponding TMSA-corannulenes proceeds in high yields and is especially attractive for derivatives with adjacent TMSA substituents because the isolation of the free alkynes, which may undergo *Bergman* cyclizations,¹⁴ can be avoided. Furthermore, subsequent alkylation reactions on the platinum center do not occur.

X-Ray quality single crystals were obtained for compounds **1**, **6b**, and **9** (Fig. 1).[‡] The bowl depth from hub centroid to rim plane is 0.764(12) Å in **1**, slightly shallower than the 0.87 Å¹⁵ of the parent corannulene. The flattening could occur through a relief of steric crowding either around the rim or transannularly. Notable is the stereochemistry at the five platina in **1**, four of which bear phosphines in a *trans* stereochemistry and one *cis*. This novel relationship could support the idea that transannular strain causes the bowl to flatten, but in any case raises the question of whether this stereochemistry persists in solution.

High-resolution 700 MHz ¹H spectra of **1** display five distinct rim proton resonances. Four appear as singlets consistent with only *cis* aryl-Pt-Cl relationships; one is a doublet (8.2 Hz), consistent with coupling to a *trans* phosphine. The ³¹P NMR reveals a cluster of eight PEt₃

[‡]**X-Ray crystal data for compound 1:** C₈₀H₁₅₅Cl₅P₁₀Pt₅, *M_r* = 2579.11, monoclinic, space group *P2₁/n*, *a* = 38.9473(4), *b* = 14.4159(1), *c* = 39.1396(4) Å, β = 110.8408(3)°, *V* = 20537.5(3) Å³, *Z* = 8, *D_x* = 1.668 g cm⁻³, *T* = -113 °C, *Nonius KappaCCD* area-detector diffractometer, Mo Kα radiation, λ = 0.71073 Å, μ = 7.079 mm⁻¹, θ_{max} = 25.0°, 238902 measured reflections, 35803 symmetry-independent reflections (*R_{int}* = 0.104), 26731 reflections with *I* > 2σ(*I*), refinement on *F*², 2361 parameters, 6428 restraints, *R*(*F*) [*I* > 2σ(*I*) reflections] = 0.0658, *wR*(*F*²) [all reflections] = 0.1334, *S*(*F*²) = 1.138. **X-Ray crystal data for compound 6b:** C₅₀H₇₈N₂P₄Pt₂·2CH₆B₁₁Br, *M_r* = 2453.86, orthorhombic, space group *P2₁2₁2*, *a* = 31.0338(2), *b* = 33.4144(2), *c* = 8.0692(1) Å, *V* = 8367.57(13) Å³, *Z* = 4, *D_x* = 1.948 g cm⁻³, *T* = -113 °C, *Nonius KappaCCD* area-detector diffractometer, Mo Kα radiation, λ = 0.71073 Å, μ = 9.184 mm⁻¹, θ_{max} = 25.0°, 65724 measured reflections, 14693 symmetry-independent reflections (*R_{int}* = 0.090), 12856 reflections with *I* > 2σ(*I*), refinement on *F*², 959 parameters, 396 restraints, *R*(*F*) [*I* > 2σ(*I*) reflections] = 0.0683, *wR*(*F*²) [all reflections] = 0.1864, *S*(*F*²) = 1.025. **X-Ray crystal data for compound 9:** C₅₀H₇₂I₂P₄Pt₂·1.5(CHCl₃), *M_r* = 1619.89, monoclinic, space group *P2₁/n*, *a* = 20.7278(2), *b* = 14.8192(1), *c* = 22.0662(2) Å, β = 115.2373(6)°, *V* = 6131.09(9) Å³, *Z* = 4, *D_x* = 1.755 g cm⁻³, *T* = -113 °C, *Nonius KappaCCD* area-detector diffractometer, Mo Kα radiation, λ = 0.71073 Å, μ = 5.877 mm⁻¹, θ_{max} = 27.5°, 141083 measured reflections, 14009 symmetry-independent reflections (*R_{int}* = 0.077), 11811 reflections with *I* > 2σ(*I*), refinement on *F*², 557 parameters, 126 restraints, *R*(*F*) [*I* > 2σ(*I*) reflections] = 0.0782, *wR*(*F*²) [all reflections] = 0.2250, *S*(*F*²) = 1.059.

groups oriented *trans* about Pt between 13–16 ppm and two PET_3 groups oriented *cis* about Pt at 11 and 5 ppm. A ^{31}P EXSY experiment displays fast exchange among all eight P signals from the *trans* oriented Pt complexes, which accounts for the loss in the $^2\text{J } ^{31}\text{P}, ^{31}\text{P}$ coupling for these signals. In contrast, the EXSY shows no exchange between the ^{31}P signals of the *cis*-Pt complex, and ^{31}P COSY confirms the 14.7 Hz $^2\text{J } ^{31}\text{P}, ^{31}\text{P}$ coupling. Satellite signals due to the $^1\text{J } ^{31}\text{P}, ^{195}\text{Pt}$ coupling are also evident in the spectrum. Interestingly, increased CSA-mediated relaxation of ^{195}Pt leads to considerable broadening of these signals on the 400 MHz spectrometer. The satellites have the appropriate integral according to the 33% abundance of ^{195}Pt and the direct $^{31}\text{P}, ^{195}\text{Pt}$ coupling constant of 2834 Hz corresponds well to P-Pt bond length of 2.296 Å found in the X-ray diffraction analysis as well as a *cis* P-Pt-Cl geometry.¹⁶ Satellite signals are additionally observed for the signals corresponding to the *cis* aryl-Pt-Cl geometry displaying coupling constants of 4200 and 2800 Hz, reflecting one *trans* and one *cis* P-Pt-Cl relation. All together this makes a compelling case for equivalence of the solution and solid structure of **1**. The single *cis* stereochemistry likely results from steric crowding on the endo side of the bowl.

The structure of **6b** was crystallized as the acetonitrile adduct with two non bound carborane anions. It is not anticipated that this will cause any great structural distortions, but such complexes may have a benefit in complexation chemistry as the nitriles should be very labile ligands.¹⁷

The bowl depth of **6b** is 0.893(13) Å, slightly shallower than its reaction precursor **5** (0.92 Å),¹⁰ but slightly deeper than the parent corannulene (0.87 Å).¹⁵ The proximity of the ethyl groups on the endo phosphine, reminds one of the attractive van der Waals interactions seen in *sym*-pentamaneisylcorannulene. Variable temperature ^{31}P NMR experiments on **6a** revealed an inversion barrier of 10.7 ± 0.2 kcal/mol,^{9c} on a par with the *ca.* 11 kcal/mol expected for corannulene.

The structure of **9** revealed a bowl depth of 0.872(9) Å, essentially that of corannulene. Both Pt centers have a *trans* orientation of the PET_3 ligands and all bond lengths are within normal parameters. The angle between the vectors emanating from roughly diametrically opposing positions on the rim is 140–150° with substantial flexibility due to the low-energy mode of bowl inversion.

In conclusion, the efficient synthesis and structure determination of platinum corannulene derivatives bodes well for the assembly of these supramolecular tectons into higher-order coordination Platonic polyhedra.^{2,3,6,19}

Experimental

Materials and Methods: compounds **3–5** were prepared according to literature procedures^{8e–g,10,11b} Reactions were conducted under nitrogen atmospheres unless noted. Dry toluene was used from an MBraun solvent purification system. CH_2Cl_2 and *n*-hex. were used after simple distillation. K_2PtCl_4 and PET_3 (10% in hexanes) (Pressure Chemical Co., Strem Chemicals) were used as purchased, $^{18}\text{Pt}(\text{PET}_3)_4$ and $\text{Pt}(\text{PET}_3)_2\text{I}_2$ were prepared by known procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). NMR spectra were recorded on a Varian Unity 300 and on Bruker 300, 400, 500, 600 and 700 MHz spectrometers. The ^1H NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P NMR resonances are referenced to an external sample of 85% H_3PO_4 (δ 0.0). Infrared spectra were recorded on a JASCO FT/IR–4100 spectrophotometer.

1,3,5,7,9-Pentakis[chlorobis(triethylphosphine)platinum]-corannulene (1)

In a 100 mL Schlenk flask was placed 1.1 g (19.3 mmol) of KOH under inert atmosphere, followed by 10 mL of degassed EtOH and 1 mL degassed H₂O. The flask was stirred at room temperature until homogeneous. Upon homogeneity, 2.5 g (21.2 mmol) of PET₃ was added *via* syringe. In a separate 50 mL Schlenk flask was placed 1.6 g (3.85 mmol) of K₂[PtCl₄] under inert atmosphere, followed by 5 mL of degassed H₂O. The aqueous K₂[PtCl₄] was then transferred to the KOH/PET₃ flask *via* cannula. The reaction mixture was allowed to stir at room temperature for 1 h and then at 60 °C for 3 h. The reaction was then allowed to cool and the solvent was evaporated under high vacuum. The crude Pt(PET₃)₄ product was taken up in freshly distilled toluene (10 mL) and transferred *via* cannula through a syringe containing glass wool (to filter particulates) into a Schlenk flask containing 110 mg (0.25 mmol) of **3** under inert atmosphere. The reaction mixture was then closed and allowed to stir at 90–95 °C for 5 days. After 5 days the solvent was evaporated under reduced pressure and the product was recrystallized twice from MeOH. Yield: 318 mg (48%). ¹H{³¹P} NMR (700 MHz, CD₂Cl₂): 7.91 (s, 1H); 7.82 (s, 1H); 7.79 (s, 1H); 7.71 (s, 1H); 7.68 (s, 1H); 2.1–1.3 (m, 60H, CH₂); 1.25–0.85 (m, 72H, *trans*-CH₃); 0.71 (t, 9H, *cis*-CH₃); 0.45 (t, 9H, *cis*-CH₃). ¹³C{¹H} NMR (150.9 MHz, CDCl₃): 138–128 (Ar-C) 16.5 - 12.7 (CH₂); 7.7–6.6 (CH₃). ³¹P{¹H} NMR (175 MHz): 15.51, 15.23, 15.10, 14.98, 14.92, 14.72, 14.15, 13.62 (8 *trans* P); 10.89 (d, ²J_{P-P} = 14.7 Hz, *cis* P); 5.11 (d, ²J_{P-P} = 14.7 Hz, *cis* P). For ¹J_{P-P} see spectrum in the supplementary information. HR-ESI (TOF, *m/z*): Calcd. for C₈₀H₁₅₅Cl₅P₁₀Pt₅: 2578.61448; found: 2578.61485 (M⁺). Calcd. for C₈₀H₁₅₅Cl₄P₁₀Pt₅: 2543.64686; found: 2543.64588 ([M–Cl]⁺, main intensity).

2,5-Dimethyl-1,6-bis[*trans*-bromobis(triethylphosphine)platinum]-corannulene (6a)

Schlenk conditions: To a degassed solution of 1,6-dibromo-2,5-dimethylcorannulene (50 mg, 0.115 mmol) in toluene (20 mL) was added *via* syringe a solution of Pt(PET)₄ (176 mg, 0.264 mmol) in toluene (20 mL). The reaction mixture turned red and stirring was continued at room temperature for 24 hrs. The now yellow solution was heated to reflux another 24 hrs. After cooling to room temperature, the solution was filtered through a pad of celite (open to air) and the filtrate was evaporated to give a reddish, oily residue. The residue was covered with *n*-pentane and cooled to –78 °C. After supersonication, the supernatant was removed and the procedure is repeated until a yellow powder was obtained. (117 mg, 79%). FT/IR: 2964 (m), 2932 (m), 2906 (m), 2876 (m), 2360 (w), 2334 (w), 1610 (w), 1455 (m), 1411 (m), 1375 (w), 1331 (w), 1287 (w), 1256 (w), 1144 (w), 1034 (s), 1009 (w), 986 (w), 926 (w), 828 (w), 793 (w), 764 (s), 729 (m), 688 (m). ¹H NMR (400 MHz, C₆D₆): 8.45 (d, ³J_{H-H} = 8.7 Hz, 2H); 7.90 (s, 2H); 7.72 (d, ³J_{H-H} = 8.7 Hz, 2H); 3.17 (s, CH₃, 3H); 1.70–1.40 (m, CH₂, 24H); 0.72 (dt, ³J_{H-H} = 7.7 Hz, ³J_{H-P} = 15.9 Hz, CH₃, 36H). ¹³C{¹H} NMR (150.9 MHz, CDCl₃): 139.59 (t, ¹J_{C-Pt} = 490 Hz, ²J_{C-P} = 9 Hz), 138.08, 135.37, 133.79, 133.54, 133.08, 131.45, 130.93, 128.63, 124.68, 123.90, 24.25 (Ar-CH₃), 15.31 (virtual quint. ¹J_{C-P} = 16.8 Hz), 8.13 (virtual t, ²J_{C-P} = 2.7 Hz). ³¹P NMR (162 MHz, C₆D₆): 10.92 (s, ¹J_{P-P} = 2725 Hz). HR-ESI (TOF, *m/z*): Calcd. for C₄₆H₇₂Br₂P₄Pt₂: 1299.22970; found: 1299.22965 (M⁺). Calcd. for C₄₆H₇₂BrP₄Pt₂: 1219.30250; found: 1219.30579 ([M – Br]⁺).

2,5-Dimethyl-1,6-bis[*trans*-acetonitrilobis(triethylphosphine)-platinum]corannulene hexabromocarboranate (6b)

Glovebox: 2,5-dimethyl-1,6-bis[Pt(PET₃)₂Br]corannulene (**6**, 7.1 mg, 5.47 mmol) and silver(I) hexabromocarboranate (8 mg, 11 mmol) were placed in a 2 mL-vial and suspended in D₃CCN (1 mL). The yellow suspension became clearer, prior to the precipitation of AgBr. The vial was covered in aluminium foil and the reaction mixture was stirred for 20 hrs. at room temperature. The clear supernatant solution was analyzed by NMR spectroscopy; single crystals were grown by slow diffusion of *n*-hexane into a solution of **6b** in acetone.

1,6-Bis{[*trans*-iodobis(triethylphosphine)platinum]ethynyl}-2,5-dimethylcorannulene (9)

A solution of 1,6-bis[2-(trimethylsilyl)ethynyl]-2,5-dimethylcorannulene (50.7 mg, 0.108 mmol) in DMF (5 ml) and CH₂Cl₂ (7.5 ml) was prepared in a 50 ml Schlenk flask, equipped with stir bar. CsF (35 mg, 0.226 mmol) in H₂O (0.5 ml) was added and the mixture gets slightly darker and turbid. After 5 min. CuI (43 mg, 0.226 mmol) was added in one step and the mixture was stirred for 10 min. at room temperature, resulting in a red suspension. A solution of Pt(PEt₃)₂I₂ (156 mg, 0.228 mmol) in CH₂Cl₂ (2 ml) was added, followed by another 2 ml of DMF. The mixture was stirred for 2 days and became a clear yellow solution (except insoluble copper salts). The solvents were removed under reduced pressure and the residue was taken up with CH₂Cl₂ and filtered through a pad of celite. EtOH was added, and the solvents were removed giving a yellow solid. Column chromatography on silica gel with *n*-hex/CH₂Cl₂ gave **9** as a yellow solid (132 mg, 85%): ¹H NMR (600 MHz, CDCl₃): 8.01 (d, ³J_{H-H} = 8.7 Hz, 2H); 7.85 (s, 2H); 7.75 (d, ³J_{H-H} = 8.8 Hz, 2H); 2.89 (s, 6H); 2.29–2.12 (m, 24H); 1.19 (dt, ³J_{H-H} = 7.7 Hz, ³J_{H-P} = 16.6 Hz, 36H). ¹³C{¹H} NMR (150.9 MHz, CDCl₃): 135.98, 135.79, 134.26, 133.20, 132.42, 130.72, 130.22, 127.02, 126.64, 124.98, 124.54, 100.54 (t, ²J_{C-P} = 14.6 Hz, ¹J_{C-Pt} = 1452 Hz), 98.25 (t, ³J_{C-P} = 2.7 Hz, ²J_{C-Pt} = 400 Hz), 16.90 (virtual t, ¹J_{C-P} = 17.6 Hz), 16.88, 8.54 (t, ²J_{C-P} = 10.7 Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃): 6.77 (s, ¹J_{Pt-P} = 2326 Hz); FT/IR: 2963 (m), 2932 (m), 2908 (w), 2875 (w), 2364 (w), 2098 (m), 1454 (m), 1411 (m), 1378 (m), 1348 (w), 1324 (w), 1254 (w), 1034 (s), 1007 (w), 822 (w), 797 (w), 766 (s), 731 (s), 702 (m). HR-ESI (TOF, *m/z*): Calcd. for C₅₀H₇₂I₂P₄Pt₂: 1441.20352; found: 1441.20491 ([M + H]⁺). Calcd. for C₅₀H₇₂IP₄Pt₂(MeCN): 1354.31803; found: 1354.31780 ([M – I + MeCN]⁺, main intensity).

1,2,5,6-Tetrakis{[*trans*-iodobis(triethylphosphine)platinum]-ethynyl}corannulene (8)

A solution of 1,2,5,7-tetrakis(2-[trimethylsilyl]ethynyl)-corannulene (100 mg, 0.158 mmol) in DMF (5 ml) and CH₂Cl₂ (4 ml) was prepared in a 50 ml Schlenk flask, equipped with stir bar, and cooled in an ice-bath. CsF (106 mg, 0.698 mmol) in H₂O (2 ml) was added and the mixture gets slightly darker and turbid. After 5 min. CuI (132 mg, 0.693 mmol) was added in one step and the mixture was stirred for 10 min. at room temperature, resulting in a red suspension. A solution of Pt(PEt₃)₂I₂ (475 mg) in CH₂Cl₂ (4 ml) was added, followed by another 5 ml of DMF. The mixture was stirred for 2 days and became a clear yellow solution (except insoluble copper salts). CH₂Cl₂ was removed under reduced pressure and a mixture of MeOH/H₂O was added, resulting in a bright yellow precipitate. The precipitate was washed with H₂O and MeOH and dissolved in CH₂Cl₂ and filtered through a pad of celite. EtOH was added; CH₂Cl₂ was removed giving **2** as a bright yellow precipitate, which was filtered again and washed with EtOH and Et₂O (362 mg, 89%): ¹H NMR (500 MHz, CDCl₃): 7.94 (d, ³J_{H-H} = 8.8 Hz, 2H); 7.93 (s); 7.83 (d, ³J_{H-H} = 8.8 Hz, 2H); 2.39–2.18 (m, CH₂, 48H); 1.28–1.13 (m, CH₃, 72H). ¹³C{¹H} NMR (150.9 MHz, CDCl₃): 135.42, 134.25, 133.73, 131.39, 130.74, 130.19, 128.07, 127.92, 127.43, 126.12, 125.61, 108.00 (t, ²J_{C-P} = 12.5 Hz; ¹J_{C-Pt} = 1481 Hz), 106.87 (t, ²J_{C-P} = 12.5 Hz), 97.99 (t, ³J_{C-P} = 2.6 Hz), 97.66 (t, ³J_{C-P} = 2.6 Hz; ²J_{C-Pt} = 405 Hz), 16.67 (t, ¹J_{C-P} = 16.6 Hz, CH₂), 16.59 (t, ¹J_{C-P} = 16.6 Hz, CH₂), 8.66 (s, CH₃), 8.64 (s, CH₃). ³¹P{¹H} NMR (107.2 MHz, CDCl₃): 1.93 (s, ¹J_{Pt-P} = 2354 Hz); 1.81 (s, ¹J_{Pt-P} = 2359 Hz); FT/IR: 2962 (m), 2930 (m), 2911 (m), 2875 (m), 2362 (w), 2088 (w), 1989 (s, C≡C), 1608 (w), 1452 (m), 1413 (m), 1379 (m), 1344 (m), 1322 (w), 1254 (m), 1033 (s), 1006 (m), 763 (s), 730 (s), 712 (s). HR-ESI (TOF, *m/z*): Calcd. for C₇₆H₁₂₆I₃P₈Pt₄(MeCN): 2489.37316; found: 2489.37573 ([M – I + MeCN]⁺). Calcd. for C₇₆H₁₂₆I₂P₈Pt₄(MeCN)₂: 1201.74851; found: 1201.74765 ([M – 2I + 2MeCN]²⁺, main intensity).

1,3,5,7,9-Pentakis{[*trans*-iodobis(triethylphosphine)platinum]-ethynyl}corannulene (2)

A suspension of 1,3,5,7,9-pentakis(2-[trimethylsilyl]ethynyl)-corannulene (100 mg, 0.137 mmol) in DMF (15 ml) and CH₂Cl₂ (15 ml) and THF (10 ml) was prepared in a 50 ml Schlenk

flask, equipped with stir bar. CsF (108 mg, 0.711 mmol) in H₂O (2 ml) was added and the mixture gets slightly darker. After 5 min. CuI (136 mg, 0.711 mmol) was added in one step and the mixture was stirred for 20 min. at room temperature, resulting in a red suspension. A solution of Pt(PEt₃)₂I₂ (488 mg, 0.711 mmol) in CH₂Cl₂ (5 ml) was added, followed by another 5 ml of DMF. The mixture was stirred for 2 days and became a clear yellow solution (except insoluble copper salts). The solvents were removed under reduced pressure and the residue was taken up in CH₂Cl₂ and filtered through a pad of celite. EtOH was added, CH₂Cl₂ was removed and the brownish yellow precipitate was filtered and washed with EtOH (crude yield: 397 mg). Column chromatography on silica gel with *n*-hex./EtOAc gave **3** as a yellow solid (139 mg, 35%): ¹H NMR (500 MHz, CDCl₃): 7.88 (s, 5H); 2.35–2.12 (m, CH₂, 60H); 1.19 (dt, ³J_{H-H} = 7.7 Hz, ³J_{H-P} = 16.6 Hz, CH₃, 90H). ¹³C{¹H} NMR (150.9 MHz, CDCl₃): 133.31, 131.45, 126.74, 126.36, 99.37 (t, ³J_{C-P} = 2.7 Hz; ²J_{C-Pt} = 400 Hz), 95.1 (t, ²J_{C-P} = 14.5 Hz; ¹J_{C-Pt} = 1450 Hz), 16.76 (t, ¹J_{C-P} = 17.5 Hz), 8.35 (t, ²J_{C-P} = 7.6 Hz). ³¹P{¹H} NMR (202.5 MHz, CDCl₃): 7.23 (s, ¹J_{Pt-P} = 2329 Hz); FT/IR: 2963 (m), 2931 (m), 2911 (m), 2875 (m), 2098 (m, C≡C), 1605 (w), 1453 (m), 1421 (s), 1377 (m), 1350 (w), 1302 (w), 1253 (m), 1195 (m), 1076 (w), 1033 (s), 1005 (m), 878 (w), 764 (s), 730 (s), 702 (m), 633 (m); HR-ESI (TOF, *m/z*): Calcd. for C₉₀H₁₅₅I₄P₁₀Pt₅(MeCN): 3070.41867; found: 3070.41640 ([M – I + MeCN]⁺). Calcd. for C₉₀H₁₅₅I₃P₁₀Pt₅(MeCN)₂: 1492.27005; found: 1492.26967 ([M – 2I + 2MeCN]²⁺, main intensity).

Supplementary Material

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Fig. 1. Asymmetric unit of the X-ray structure of **1** (top) – hydrogens omitted, **6b** (middle) and **9** (bottom).

Scheme 1.

Retrosynthetic strategy for the formation of pentakis platinum (1) and ethynyl-platinum (2) corannulene derivatives from 1,3,5,7,9-pentachloro corannulene 3.

Scheme 2.

Synthetic protocols for the direct metallation of various halo corannulenes.

Scheme 3.

The two-step conversion of halo corannulenes 3–5 to ethynyl–platinum corannulenes 2, 8–9.

a, See ref. 12, 13. b, (i) CsF/H₂O, (ii) CuI/DMF (iii) Pt(PEt₃)₂I₂/CH₂Cl₂.