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I.P. Beletskaya on Her Jubilee

Template-Directed Synthesis of Macroheterocycles by Ring-Closing Metathesis of Olefin-Substituted Pyridines in the Coordination Sphere of a Triplatinum Complex*

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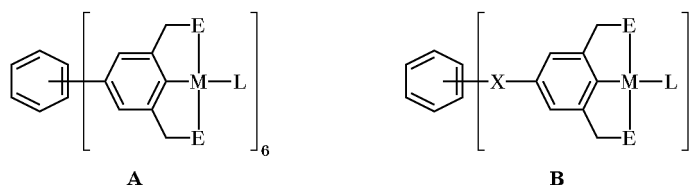
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Abstract—Mono- and tris-3,5- and 2,6-pyridinediyl-containing macroheterocycles were synthesized by metathesis of olefin-substituted pyridines in the coordination sphere of mono- and tris-platinum complexes, respectively. Tris(2,6-pyridinediyl)-containing macroheterocycles were hydrogenated over palladium catalyst. The hydrogenated macrocycle was used as ligand for the triplatinum template. The structure of the resulting complex was established by X-ray analysis.

Macrocyclic compounds are widely used as ligands for complex formation with metal cations and some small polar organic molecules, e.g., urea [1]. However, only a few examples of the use of macrocycles as ligands for rigid polymetallic complexes have been reported [2]. Some complexes (**A** and **B**) were synthesized by us previously [3–5]. They seemed to be ideal scaffolds for both synthesis and complexation of macrocyclic ligands [3, 4]. A few reports in the literature describe synthesis of macrocycles by metathesis of olefin-substituted ligands in the coordination sphere of organometallic complexes whereby mono-metallic complexes were mainly used [6]. In a number

of recent reports, the synthesis of catenanes [7], molecular knots [8], and molecular wires insulated with a double helix of alkene chains [9] were described.

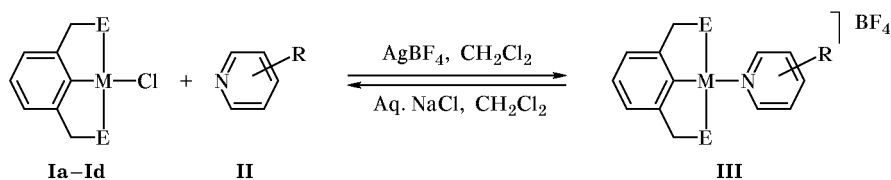
We recently published the results of a model study aimed at selecting an appropriate pincer complex **I** and bis-olefin-containing ligand **II** for ring-closing metathesis (RCM) [10]. In the course of this study, pincer platinum and palladium complexes **I** were tested as protecting groups for bis-olefin-substituted pyridines in RCM. Coordination of the bis-olefin-substituted pyridines to the pincer complexes was achieved in the presence of AgBF₄. As a result, cationic complex **III** was formed (Scheme 1). Here,



A, M = Pd, E = SPh; M = Pd, E = SPh₂; M = Pt, E = PPh₂; M = Pd, E = 1-pyrazolyl; **B**, M = Pd, E = NMe₂, X = bond; M = Pt, E = NMe₂, X = bond; M = Pd, E = NMe₂, X = *p*-phenylene; M = Pt, E = NMe₂, X = *p*-phenylene; M = Pd, E = PPh₂, X = C≡C.

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Scheme 1.



I, M = Pt, E = NMe₂ (a); M = Pd, E = SPh (b), PPh₂ (c), NMe₂ (d).

pincer metal complexes **III** act as a kind of protected pyridine ligands which can be subjected to RCM. Normally, competitive coordination of free pyridine in solution to the active site of metathesis catalyst leads to fast deactivation of the latter, so that unprotected substituted pyridines cannot be used in RCM.

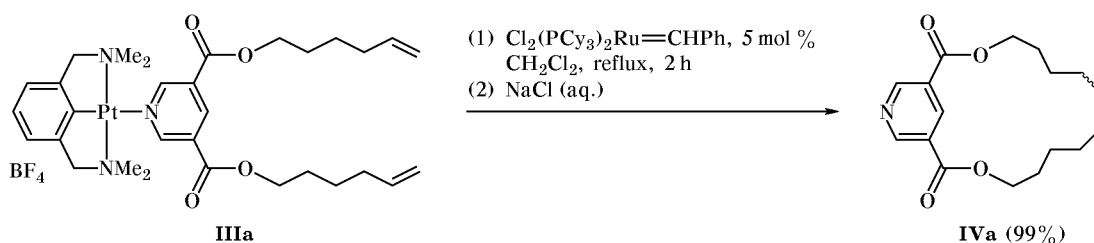
Bis(5-hexenyl) pyridine-3,5-dicarboxylate coordinated to NCN-Pt complex **IIIa** readily reacts under RCM conditions. The reaction is complete in 2 h, and, after deprotection (by treatment with aqueous NaCl), the corresponding macrocycle **IVa** was isolated in quantitative yield (Scheme 2). However, palladium complexes **Ib–Id** cannot be used as protecting groups for bis-olefin-substituted pyridines. Under RCM conditions, isomerization of pincer palladium complexes **IIIb** and **IIIc** occurred to give the corresponding internal olefins (Scheme 3). The latter are less reactive in further RCM in the presence of the first-generation Grubbs catalyst, Cl₂(PCy₃)₂Ru=CHPh.

Complex **IIIc** is stable in solution in the absence of a metathesis catalyst, but the rate of metathesis with **IIIc** is much lower than with the corresponding

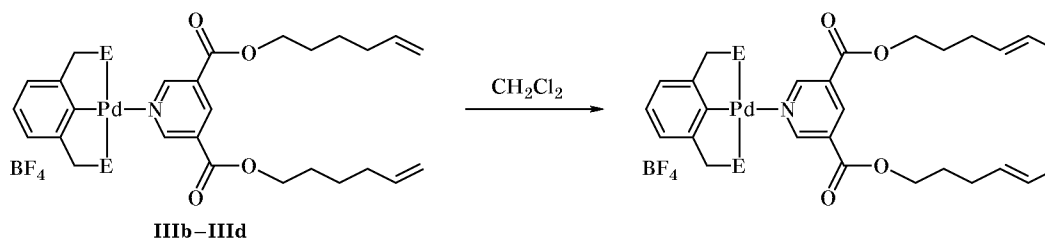
platinum complex **IIIa**, and the yield of the ring-closed product is only 50%. The remaining part of the starting complex undergoes isomerization to the internal olefin complex.

2,6-Bis-olefin-substituted pyridines protected by NCN-Pt complex **IIIe** or **III f** react at a much lower rate than their 3,5-substituted analog **IIIa**, and metathesis products **IVb** and **IVc**, respectively, are formed in lower yields (Scheme 4). In this case, the slow reaction may be explained by unfavorable position of the olefin-containing substituents. The alkene chains in 2,6-bis-olefin-substituted pyridines are affected by increased steric hindrance created by the pincer moiety and the pyridine ring; so that the RCM process is forced to take place via a back-flip conformation. This slows the reaction down and shifts the selectivity toward the competing isomerization process. Therefore, the best option for the synthesis of oligopyridine-diyl-containing macrocycles on an oligometallic template is the use of NCN-Pt complexes in combination with 2,6-bis-olefin-substituted pyridines; analogous palladium complexes promote side reactions,

Scheme 2.

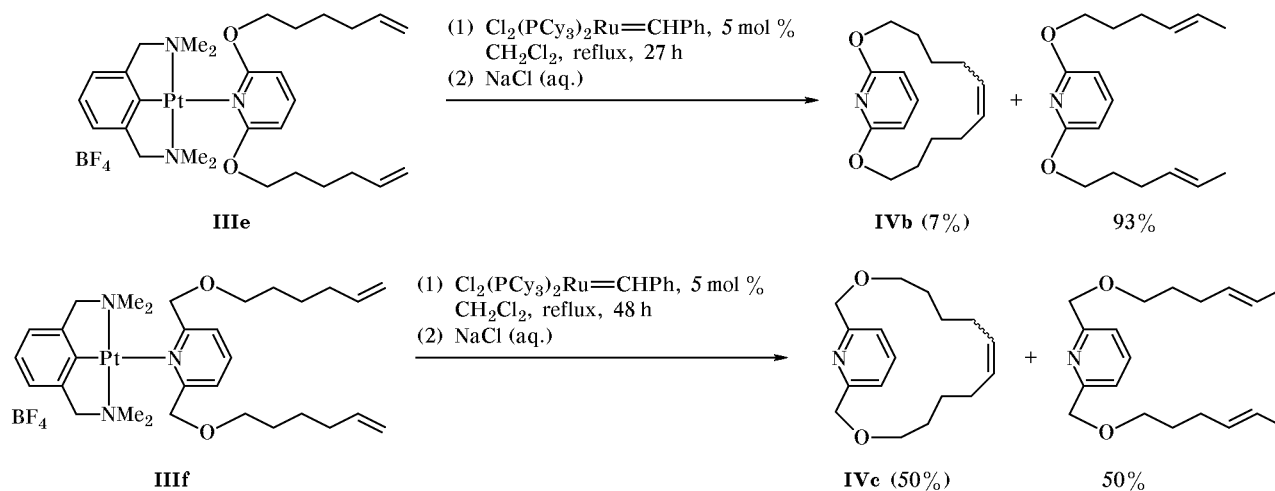


Scheme 3.



III, E = SPh (b), PPh₂ (c), NMe₂ (d).

Scheme 4.



namely double bond migration in the substrate, while 3,5-bis-olefin-substituted pyridines give rise to mono-pyridine-containing macrocycles as the major products (e.g., **IVa**) due to the absence of ring strain in the closed product. For these reasons, our first attempts to synthesize a hexapyridinediyl-containing macrocycle from a hexa-SCS-Pd complex as template and bis-(5-hexenyl)pyridine-3,5-dicarboxylate as substrate failed [10]. However, we succeeded in obtaining 69- and 75-membered macrocyclic compounds **VIIIa** and **VIIIb** from triplatinum complex **V** [3] and 2,6-bis-olefin-substituted pyridines **IIa** and **IIb** (Scheme 5).

Substituted pyridines **IIa** and **IIb** were obtained from 9-decen-1-ol and 2,6-dibromopyridine or 2,6-bis-(chloromethyl)pyridine, respectively. The reaction of triplatinum complex **V** with 3 equiv of **IIa** or **IIb** in the presence of AgBF_4 resulted in formation of cationic complexes **VIa** and **VIb**, respectively, in quantitative yield. Prolonged reaction time (16 h) was necessary since AgBF_4 is poorly soluble in methylene chloride, though its solubility increases in the presence of pyridines **IIa** and **IIb**. Ring-closing metathesis of **VIa** and **VIb** in the presence of the first-generation Grubbs catalyst $\text{Cl}_2(\text{Cy}_3\text{P})\text{Ru}=\text{CHPh}$ (5 mol % per mole of pyridine) gave cationic macrocyclic complexes **VIIa** and **VIIb**. The reaction was carried out in a dilute solution (10^{-3} M) to favor intramolecular process. Macrocycles **VIIIa** and **VIIIb** were detached from the template by treatment of the concentrated reaction mixture with an aqueous solution of sodium chloride in a two-phase system. This process was accompanied by quantitative recovery of the neutral template precursor **V**, so that it could be used in further experiments. Macrocyclic compounds **VIIIa** and **VIIIb** were isolated by preparative thin-layer

chromatography in 67 and 44% yield, respectively. By-products were monopyridine-containing macrocycles and noncyclic oligomers. Our attempt to increase the reaction rate and reduce the amount of catalyst by using more efficient second-generation Grubbs catalyst, $\text{Cl}_2(\text{Cy}_3\text{P})(\text{IMes})\text{Ru}=\text{C}_5\text{H}_8$ (**XI**) [11], resulted in a dramatic decrease of the yield of **VIIIb** (20%). In addition, considerable amounts of polymers were formed. These findings indicate the occurrence of a secondary ring-opening polymerization in which complex **XI** is known to be more active than the first-generation Grubbs catalyst [12].

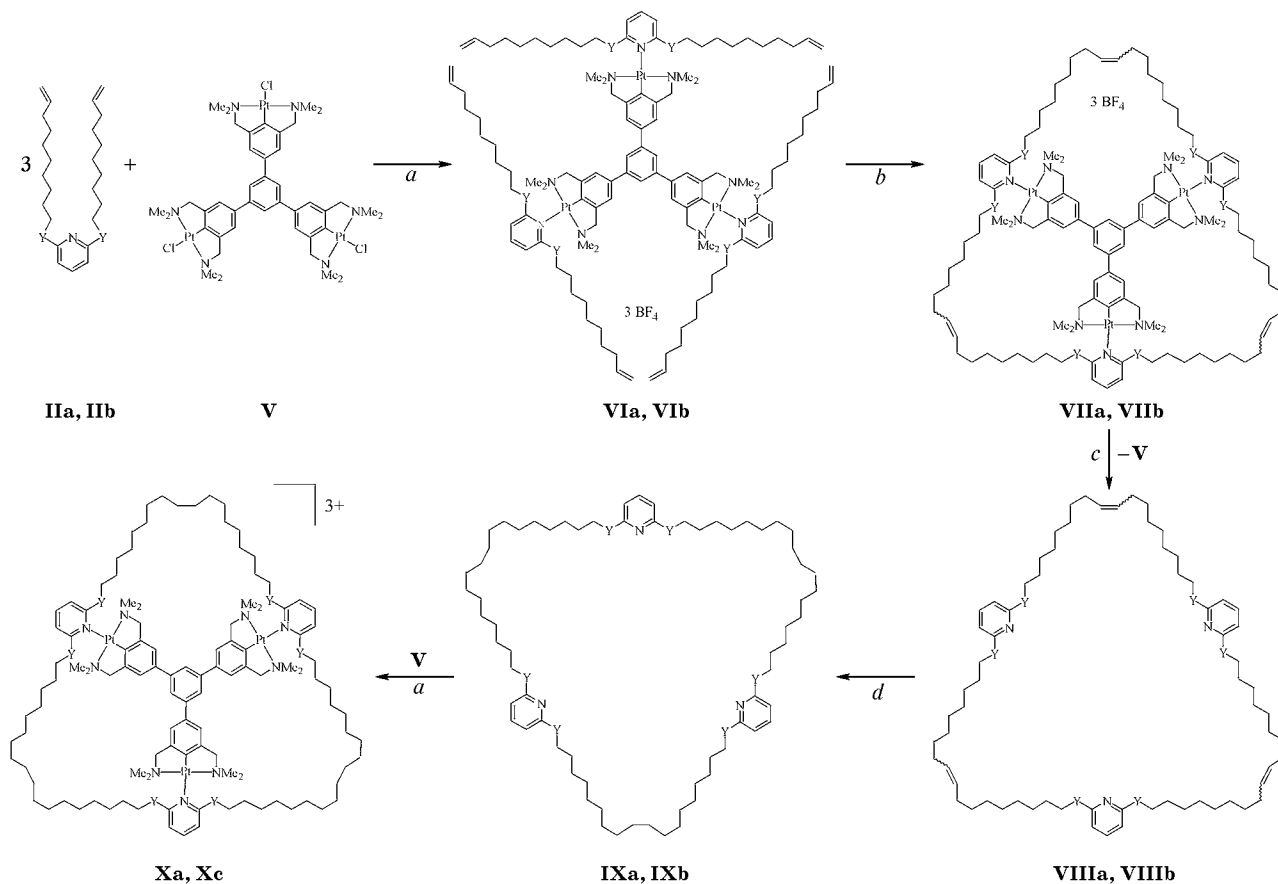
Insofar as macrocycles **VIIIa** and **VIIIb** were formed as mixtures of *cis*- and *trans*-trisolefines, for analytical purposes, they were hydrogenated to the corresponding saturated derivatives **IXa** and **IXb**. The hydrogenation of **IXb** was accompanied by side splitting of the benzyl ether moieties.**

According to the mass-spectral data, compounds **IXa** and **IXb** contained small impurities of macrocycles having one CH_2 group less than the major product. These impurities are likely to be formed by cross-metathesis of the α -olefin with β -olefin, the latter arising from double bond migration. Unfortunately, it was impossible to separate the impurities by thin-layer chromatography.

The molecules of macrocycles **IXa** and **IXb** are conformationally flexible; therefore, they were studied as ligands for conformationally rigid template **V**. For this purpose, complex **V** was mixed with **IXa** and AgBF_4 in methylene chloride. Removal of the solvent,

** Probably, the use of PtO_2 as hydrogenation catalyst [13] or a nitrogen-containing base as inhibitor of the side reaction [14] could increase the yield of **IXb**.

Scheme 5.



a: AgBF₄, CH₂Cl₂; *b*: Cl₂(Cy₃P)₂Ru=CHPh, 5 mol %, CH₂Cl₂; *c*: NaCl, H₂O/CH₂Cl₂; *d*: H₂, Pd/C; **II**, **VI–X**, Y = O (*a*), CH₂O (*b*); **X**, X = BF₄ (*a*), BPh₄ (*c*).

followed by extraction with acetone, gave cationic complex **Xa** in nearly quantitative yield (96%). Crystals suitable for X-ray crystal structure determination were obtained for salt **Xc** which was prepared by exchange reaction of **Xa** with NaBPh₄ in acetone. The structure of the cationic fragment of **Xc** is shown in figure, and some bond lengths and bond angles are given in table. The central benzene ring of the template is substituted at the 1-, 3-, and 5-positions with aryldiamine pincer moieties, each at a different twist angle [the dihedral angles between the central and NCN-pincer aryl ring planes range from 25.6(3) to 85.1(5)°]. The NCN-pincer groups are cycloplatinated at the position between the two CH₂NMe₂ substituents, yielding two five-membered PtC₃N chelate rings per group. The macrocyclic tris-pyridinediyl ligand is coordinated through the pyridine nitrogen atoms to the three peripheral metal atoms of the framework, in the *trans* position with respect to C^{*ipso*}. Thus the coordination geometry at each Pt(II) center in the complex is square-planar. The three pyridine

rings of the ligand are oriented almost orthogonally to the corresponding PtCN₃ coordination planes, the dihedral angles range from 84.3(4) to 89.8(3)°. The pyridine rings are linked at the 2- and 6-positions by saturated O(CH₂)₁₈O bridges to form a 69-membered macrocycle.

EXPERIMENTAL

All reactions were carried using standard Schlenk techniques under dry oxygen-free nitrogen unless otherwise stated. The solvents were carefully dried and distilled over appropriate drying agents prior to use. All standard reagents were purchased from Acros or Aldrich. The ¹H (200 or 300 MHz) and ¹³C NMR spectra (50 or 75 MHz) were recorded on Varian Mercury 200 and Varian Inova 300 spectrometers at 25°C using TMS as internal reference. Gas chromatographic–mass spectrometric analysis was performed on a Perkin–Elmer Autosystem XL chromatograph coupled with a Perkin–Elmer Turbo-

Some bond lengths d and bond angles ω in the cation of salt **Xc**

Bond	d , Å	Angle	ω , deg
Pt ¹ –C ¹	1.910(5)	C ¹ Pt ¹ N ¹	81.72(18)
Pt ¹ –N ¹	2.104(4)	C ¹ Pt ¹ N ²	81.19(18)
Pt ¹ –N ²	2.087(4)	N ¹ Pt ¹ N ⁷	94.71(15)
Pt ¹ –N ⁷	2.191(4)	N ² Pt ¹ N ⁷	102.39(15)
Pt ² –C ^{13A}	1.916(5)	C ¹ Pt ¹ N ⁷	176.32(17)
Pt ² –N ^{3A}	2.094(6)	N ¹ Pt ¹ N ²	162.86(16)
Pt ² –N ^{4A}	2.071(5)	C ^{13A} Pt ² N ^{3A}	80.4(2)
Pt ² –N ⁸	2.192(4)	C ^{13A} Pt ² N ^{4A}	81.8(2)
Pt ³ –C ²⁵	1.929(5)	N ^{3A} Pt ² N ⁸	98.4(2)
Pt ³ –N ⁵	2.090(4)	N ^{4A} Pt ² N ⁸	99.5(2)
Pt ³ –N ⁶	2.093(4)	C ^{13A} Pt ² N ⁸	176.87(19)
Pt ³ –N ⁹	2.183(5)	N ^{3A} Pt ² N ^{4A}	161.8(3)
		C ²⁵ Pt ³ N ⁵	82.24(19)
		C ²⁵ Pt ³ N ⁶	81.33(19)
		N ⁵ Pt ³ N ⁹	96.92(17)
		N ⁶ Pt ³ N ⁹	99.55(17)
		C ²⁵ Pt ³ N ⁹	178.3(2)
		N ⁵ Pt ³ N ⁶	163.49(18)

mass mass spectrometer (PE-17 capillary column, 30 m × 0.32 mm, film thickness 50 μm). The electro-spray ionization mass spectra were measured on a Micromass Quattro Ultima spectrometer. Preparative thin-layer chromatography was performed on Merck 1.13895 plates coated with a 1-mm layer of silica gel 60 F₂₅₄.

2,6-Bis(9-decenyloxy)pyridine (IIa). Sodium foil, 0.74 g (32 mmol), was added to a solution of 5.0 g (32 mmol) of 9-decen-1-ol in 50 ml of THF. The mixture was stirred under reflux until the metal dissolved completely, and the solvent was distilled off under reduced pressure. Dry dimethylformamide, 50 ml, and 2,6-dibromopyridine, 3.79 g (16 mmol), were added to the residue, and the mixture was stirred at 95°C overnight. The solvent was evaporated, the residue was dissolved in 15 ml of water and extracted with ether (3 × 50 ml). The extracts were combined, dried over magnesium sulfate, filtered, and evaporated. The residue was distilled under reduced pressure. Yield 6.0 g (97%), colorless oil. ¹H NMR spectrum (200 MHz, CDCl₃), δ , ppm: 1.33 m (20H, 10CH₂), 1.76 m (4H, 2CH₂, $J = 7.0$ Hz), 2.05 m (4H, 2CH₂, $J = 7.0$ Hz), 4.23 t (4H, 2CH₂, $J = 7.0$ Hz), 4.97 m (4H, 2CH₂), 5.82 m (2H, 2CH), 6.25 d (2H, 2CH, $J = 7.7$ Hz), 7.45 t (1H, CH, $J = 7.7$ Hz). ¹³C NMR spectrum (75 MHz, CDCl₃), δ_C , ppm: 26.25, 29.05, 29.22, 29.27, 29.53, 29.57, 33.93, 66.12, 101.12, 114.27,

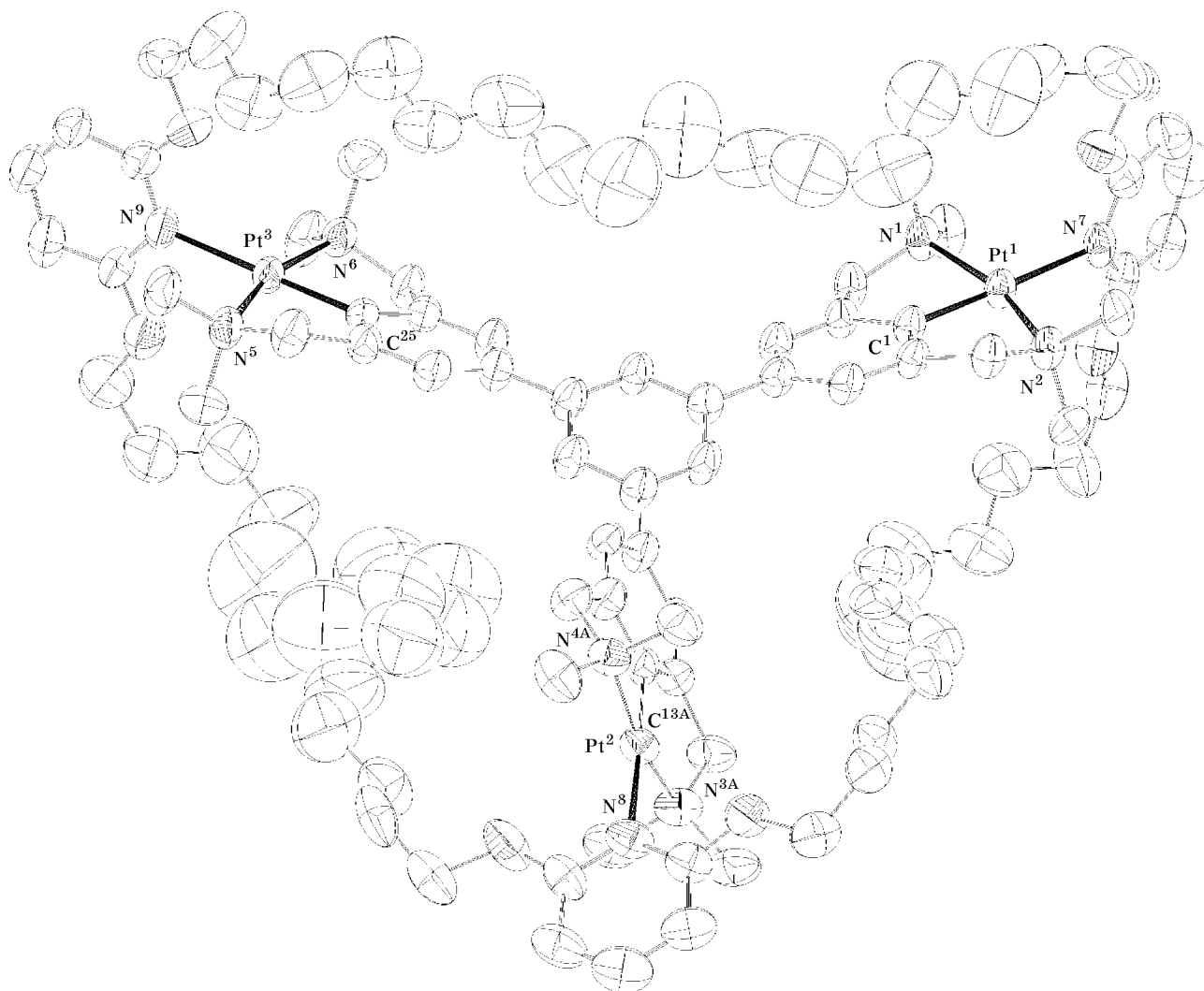
139.28, 140.85, 163.04. GC–MS data: m/z 388; calculated for C₂₅H₄₁NO₂: 387.6. Found, %: C 77.39; H 10.60; N 3.54. C₂₅H₄₁NO₂. Calculated, %: C 77.47; H 10.66; N 3.61.

2,6-Bis(9-decenyloxymethyl)pyridine (IIb).

Metallic sodium, 0.74 g (32 mmol), was added to a solution of 5.0 g (32 mmol) of 9-decen-1-ol in 50 ml of THF, and the mixture was stirred under reflux until the metal dissolved completely. 2,6-Bis-(chloromethyl)pyridine hydrochloride [10], 2.26 g (10.7 mmol), was added, and the mixture was stirred under reflux overnight and evaporated under reduced pressure. The residue was dissolved in 15 ml of water and extracted with ether (3 × 50 ml). The extracts were combined, dried over magnesium sulfate, and filtered. The solvent and unreacted 9-decen-1-ol were removed under reduced pressure, and the residue was distilled in a vacuum. Yield 4.3 g (97%), white solid. ¹H NMR spectrum (200 MHz, CDCl₃), δ , ppm: 1.30 m (20H, 10CH₂), 1.64 m (4H, 2CH₂, $J = 7.0$ Hz), 2.04 m (4H, 2CH₂, $J = 7.0$ Hz), 3.54 t (4H, 2CH₂, $J = 6.6$ Hz), 4.60 s (4H, 2CH₂), 4.97 m (4H, 2CH₂), 5.82 m (2H, 2CH), 7.34 d (2H, 2CH, $J = 7.7$ Hz), 7.70 t (1H, CH, $J = 7.7$ Hz). ¹³C NMR spectrum (75 MHz, CDCl₃), δ_C , ppm: 26.27, 29.02, 29.17, 29.53, 29.85, 33.90, 71.33, 73.85, 114.23, 119.77, 137.24, 139.27, 158.42. GC–MS data: m/z 416; calculated for C₂₇H₄₅NO₂: 415.7. Found, %: C 78.02; H 10.91; N 3.62. C₂₇H₄₅NO₂. Calculated, %: C 78.02; H 10.91; N 3.47.

Cationic complex VIa. A mixture of 1.36 g (1.02 mmol) of template precursor **V**, 0.6 g (3.07 mmol) of AgBF₄, and 1.19 g (3.07 mmol) of 2,6-bis(9-decenyloxy)pyridine (**IIa**) in 70 ml of methylene chloride was stirred overnight with protection from light. The mixture was filtered, and the filtrate was evaporated under reduced pressure. Yield 2.67 g (99%), glassy solid. ¹H NMR spectrum (200 MHz, acetone-*d*₆), δ , ppm: 1.27 m (60H, 30CH₂), 1.76 m (12H, 6CH₂, $J = 7.2$ Hz), 1.97 q (12H, 6CH₂, $J = 7.2$ Hz), 2.99 s (36H, 3NMe₂), 4.33 s (12H, 6CH₂), 4.42 t (12H, 6CH₂, $J = 6.6$ Hz), 4.90 m (12H, 6CH₂), 5.75 m (6H, 6CH), 6.98 d (6H, 6CH, $J = 8.4$ Hz), 7.42 s (6H, 6CH), 7.82 s (3H, 3CH), 8.15 t (3H, 3CH, $J = 8.0$ Hz). ¹³C NMR spectrum (50 MHz, acetone-*d*₆), δ_C , ppm: 26.80, 29.52, 29.78, 29.95, 30.02, 34.28, 54.32, 70.23, 77.62, 101.24, 114.18, 119.53, 124.10, 138.40, 139.58, 144.12, 144.67, 145.43, 145.84, 163.87. Found, %: C 53.10; H 6.76; N 4.70. C₁₁₇H₁₈₀B₃F₁₂N₉O₆Pt₃. Calculated, %: C 52.94; H 6.84; N 4.75.

Cationic complex VIb. A mixture of 1.64 g (1.22 mmol) of template precursor **V**, 0.72 g



ORTEP representation of cationic complex **Xc**. Only the major conformation of each of the disordered groups is shown. Tetraphenylborate ions and hydrogen atoms are omitted for clarity.

(3.67 mmol) of AgBF_4 , and 1.53 g (3.68 mmol) of 2,6-bis(9-decenyloxymethyl)pyridine (**IIb**) in 70 ml of methylene chloride was stirred overnight with protection from light. The mixture was filtered, and the filtrate was evaporated under reduced pressure. Yield 3.30 g (98.6%), glassy solid. ^1H NMR spectrum (200 MHz, acetone- d_6), δ , ppm: 1.33 m (60H, 30CH_2), 1.71 m (12H, 6CH_2 , $J = 6.4$ Hz), 2.03 q (12H, 6CH_2 , $J = 6.6$ Hz), 2.96 s (36H, 6NMe_2), 3.82 t (12H, 6CH_2 , $J = 6.4$ Hz), 4.46 s (12H, 6CH_2), 4.96 m (12H, 6CH_2), 5.84 m (18H, 6CH , 6CH_2), 7.51 s (6H, 6CH), 7.88 s (3H, 3CH), 7.94 d (6H, 6CH , $J = 7.7$ Hz), 8.30 t (3H, 3CH , $J = 7.7$ Hz). ^{13}C NMR spectrum (50 MHz, acetone- d_6), δ_{C} , ppm: 26.87, 29.56, 29.70, 30.06, 30.39, 34.36, 54.50, 72.33, 73.64, 77.87, 114.53, 119.76, 124.37, 126.56, 139.09,

139.65, 140.62, 143.91, 145.70, 158.68, 160.08. Found, %: C 53.86; H 6.94; N 4.48. $\text{C}_{123}\text{H}_{192}\text{B}_3\text{F}_{12}\text{N}_9\text{O}_6\text{Pt}_3$. Calculated, %: C 53.95; H 7.07; N 4.60.

Macrocyclic VIIIa. Cationic complex **VIa**, 2.6 g (0.98 mmol), and $\text{Cl}_2(\text{Cy}_3\text{P})_2\text{Ru}=\text{CHPh}$ (Grubbs' catalyst), 120 mg (0.147 mmol), were dissolved in succession in 1000 ml of methylene chloride. The mixture was stirred under reflux overnight, cooled to room temperature, and concentrated to a volume of 200 ml under reduced pressure. A saturated aqueous solution of sodium chloride, 50 ml, was added, and the mixture was stirred overnight. The organic layer was separated and dried over MgSO_4 , and the solvent was evaporated. The residue was extracted with hexane, and the product was isolated by preparative TLC on silica gel using hexane–methylene chloride

(2:1) as eluent. Yield 0.71 g (67%), colorless oil which solidified at room temperature. ^1H NMR spectrum (200 MHz, CDCl_3), δ , ppm: 1.30 m (60H, 30 CH_2), 1.75 m (12H, 6 CH_2 , $J = 6.8$ Hz), 1.97 m (12H, 6 CH_2), 4.23 t (12H, 6 CH_2 , $J = 6.8$ Hz), 5.37 m (6H, 6CH), 6.24 d (6H, 6CH, $J = 8.0$ Hz), 7.44 t (3H, 3CH, $J = 7.9$ Hz). ^{13}C NMR spectrum (75 MHz, CDCl_3), δ_{C} , ppm: 26.18, 29.15, 29.26, 29.49, 29.56, 29.72, 32.69, 66.09, 101.18, 130.49, 140.88, 163.02. ES-MS data: m/z : 1079.0; calculated for $\text{C}_{69}\text{H}_{111}\text{N}_3\text{O}_6$: 1078.64. Found, %: C 76.68; H 10.47; N 3.83. $\text{C}_{69}\text{H}_{111}\text{N}_3\text{O}_6$. Calculated, %: C 76.83; H 10.37; N 3.90.

Macrocycle VIIIb. Cationic complex **VIIb**, 2.0 g (0.73 mmol), and $\text{Cl}_2(\text{Cy}_3\text{P})_2\text{Ru}=\text{CHPh}$, 90 mg (0.109 mmol), were dissolved in succession in 750 ml of methylene chloride. The mixture was stirred under reflux overnight, cooled to room temperature, and concentrated to a volume of 150 ml under reduced pressure. A saturated aqueous solution of sodium chloride, 40 ml, was added, and the mixture was stirred overnight. The organic layer was separated, dried over MgSO_4 , and evaporated. The residue was extracted with hexane, and the product was isolated by preparative TLC on silica gel using methylene chloride-acetone (15:1) as eluent. Yield 0.37 g (44%), colorless oil which solidified at room temperature. ^1H NMR spectrum (200 MHz, CDCl_3), δ , ppm: 1.28 m (60H, 30 CH_2), 1.64 m (12H, 6 CH_2 , $J = 6.8$ Hz), 1.97 m (12H, 6 CH_2), 3.54 t (12H, 6 CH_2 , $J = 6.4$ Hz), 4.60 s (12H, 6 CH_2), 5.37 m (6H, 6CH), 7.33 d (6H, 6CH, $J = 7.7$ Hz), 7.69 t (3H, 3CH, $J = 7.7$ Hz). ^{13}C NMR spectrum (75 MHz, CDCl_3), δ_{C} , ppm: 26.24, 29.08, 29.47, 29.50, 29.66, 29.81, 32.64, 71.26, 73.84, 119.82, 130.45, 137.21, 158.43. ES-MS data: m/z 1163.0; calculated for $\text{C}_{75}\text{H}_{123}\text{N}_3\text{O}_6$: 1162.8. Found, %: C 77.42; H 10.73; N 3.54. $\text{C}_{75}\text{H}_{123}\text{N}_3\text{O}_6$. Calculated, %: C 77.47; H 10.66; N 3.61.

For recyclization of template precursor **V**, the residue undissolved in hexane was washed with ethanol (3 \times 30 ml) and dissolved in 200 ml of chloroform. The solution was filtered through a layer of silica gel, and the solvent was evaporated under reduced pressure. Yield 0.93 g (95%), white solid.

Macrocycle IXa. Compound **VIIIa**, 500 mg (0.463 mmol), was dissolved in 15 ml of methylene chloride, and 50 mg of palladium catalyst (10% of Pd on charcoal) was added. The mixture was stirred for 4 h at room temperature under hydrogen and was then filtered. The filtrate was evaporated under reduced pressure. Yield 500 mg (99%), white solid. ^1H NMR spectrum (200 MHz, CDCl_3), δ , ppm: 1.25 m (84H, 42 CH_2), 1.75 m (12H, 6 CH_2 , $J = 6.8$ Hz), 4.24 t

(12H, 6 CH_2 , $J = 6.8$ Hz), 6.24 d (6H, 6CH, $J = 7.7$ Hz), 7.44 t (3H, 3CH, $J = 7.7$ Hz). ^{13}C NMR spectrum (75 MHz, CDCl_3), δ_{C} , ppm: 26.16, 29.25, 29.51, 29.69, 29.76, 66.07, 101.19, 140.86, 163.00. ES-MS data: m/z : 1084.9; calculated for $\text{C}_{69}\text{H}_{111}\text{N}_3\text{O}_6$: 1084.7. Found, %: C 76.30; H 10.81; N 3.79. $\text{C}_{69}\text{H}_{111}\text{N}_3\text{O}_6$. Calculated, %: C 76.40; H 10.87; N 3.87.

Macrocycle IXb. Compound **VIIIb**, 340 mg (0.292 mmol), was dissolved in 15 ml of methylene chloride, and 34 mg of palladium catalyst (10% of Pd on charcoal) was added. The mixture was stirred for 4 h at room temperature under hydrogen and was then filtered. The product was isolated by preparative TLC using methylene chloride-acetone (15:1) as eluent. Yield 266 mg (78%), white solid. ^1H NMR spectrum (200 MHz, CDCl_3), δ , ppm: 1.27 m (84H, 42 CH_2), 1.63 m (12H, 6 CH_2 , $J = 6.8$ Hz), 3.53 t (12H, 6 CH_2 , $J = 6.4$ Hz), 4.60 s (12H, 6 CH_2), 7.33 d (6H, CH, $J = 7.7$ Hz), 7.69 t (3H, CH, $J = 7.7$ Hz). ^{13}C NMR spectrum (75 MHz, CDCl_3), δ_{C} , ppm: 26.24, 29.51, 29.64, 29.70, 29.83, 71.27, 73.85, 119.86, 137.23, 158.44. ES-MS data: m/z 1169.2; calculated for $\text{C}_{75}\text{H}_{129}\text{N}_3\text{O}_6$: 1168.8. Found, %: C 77.05; H 11.21; N 3.49. $\text{C}_{75}\text{H}_{129}\text{N}_3\text{O}_6$. Calculated, %: C 77.07; H 11.12; N 3.60.

Cationic complex Xa. A mixture of 122 mg (0.092 mmol) of template precursor **V**, 54 mg (0.276 mmol) of AgBF_4 , and 100 mg (0.092 mmol) of compound **IXa** in 20 ml of methylene chloride was stirred overnight with protection from light. The mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was dissolved in 10 ml of acetone, the solution was filtered, and the filtrate was evaporated under reduced pressure. Yield 226 mg (95%), white solid. ^1H NMR spectrum (200 MHz, acetone- d_6), δ , ppm: 1.04 m (60H, 30 CH_2), 1.45 m (12H, 6 CH_2), 1.92 m (24H, 12 CH_2), 2.98 s (36H, 6 NMe_2), 4.31 s (12H, 6 CH_2), 4.41 m (12H, 6 CH_2), 6.95 d (6H, 6CH, $J = 8.0$ Hz), 7.39 s (6H, 6CH), 7.82 s (3H, 3CH), 8.14 t (3H, 3CH, $J = 8.2$ Hz). ^{13}C NMR spectrum (50 MHz, acetone- d_6), δ_{C} , ppm: 27.09, 29.60, 29.92, 30.03, 30.12, 30.23, 30.46, 54.39, 70.47, 77.78, 98.03, 101.25, 119.54, 124.15, 138.43, 144.19, 144.78, 145.37, 145.91, 163.98. ES-MS data: m/z 771.77; calculated for $[\text{C}_{111}\text{H}_{174}\text{N}_9\text{O}_6\text{Pt}_3]^{3+}$: 771.75. Found, %: C 51.60; H 6.74; N 4.82. $\text{C}_{111}\text{H}_{174}\text{B}_3\text{F}_{12}\text{N}_9\text{O}_6\text{Pt}_3$. Calculated, %: C 51.75; H 6.81; N 4.89.

X-Ray analysis of salt Xc. Salt **Xc** was prepared from salt **Xa** by exchange reaction with NaBPh_4 in acetone. Colorless plates of **Xc** were obtained by

recrystallization from acetone–ether. The intensity data were collected for a single crystal ($0.27 \times 0.15 \times 0.06 \text{ mm}^3$) on a Nonius KappaCCD diffractometer with a rotating anode ($\text{MoK}\alpha$, λ 0.71073 Å) at 150 K, to a maximum resolution of $2\theta_{\text{max}}$ 55°. Total of 109149 reflections were measured, 38222 of which were unique, and 24201 were with $I > 2\sigma(I)$ ($R_{\text{int}} = 0.058$). An absorption correction was applied using the multi-scan technique with PLATON/MULABS ($\mu = 2.548 \text{ mm}^{-1}$, 0.705–0.856 transmission range) [15]. The structure was solved by automated Patterson methods using DIRDIF99 software [16] and was refined on F^2 by the least-squares procedure using SHELXL97 program [17]. Structure validation and preparation of molecular graphics were performed using PLATON software package [12]. Triclinic system, $\text{C}_{111}\text{H}_{174}\text{N}_9\text{O}_6\text{Pt}_3 \cdot 3(\text{C}_{24}\text{H}_{20}\text{B})$, $M_r = 3273.49$, space group $P\bar{1}$ (no. 2); $a = 18.9296(1)$, $b = 20.6363(1)$, $c = 22.4100(2)$ Å; $\alpha = 80.4058(3)$, $\beta = 86.3821(3)$, $\gamma = 76.7954(3)^\circ$; $V = 8400.66(10) \text{ \AA}^3$; $Z = 2$, $\rho_{\text{calc}} = 1.294 \text{ g/cm}^{-3}$; 2219 refined parameters, 3563 restraints, $R(F)$ [$I > 2\sigma(I)$] = 0.0517, $wR(F^2)$ = 0.1357, $S = 1.04$, $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 1.92/-1.49 \text{ e \AA}^{-3}$. CCDC 185367 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

The asymmetric unit of **Xc** contains one independent cationic complex and three independent tetraphenylborate anions, as well as disordered solvent molecules (acetone/ether) which could not be resolved in the difference Fourier map. The solvent contribution was treated using PLATON/SQUEEZE (58 *e* per unit) [15]. Each of the three macrocycle bridges in the cation is disordered over two conformations at different twist angles relative to the central benzene ring [with refined occupancies of 0.655(6):0.345]. All non-hydrogen atoms were refined with anisotropic displacement parameters, but the displacement parameters of disordered atoms were restrained to be approximately isotropic. Hydrogen atoms were constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of the corresponding carrier atom.

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