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Template Synthesis of a Huge Macrocycle by Olefin Metathesis Using Easily Accessible $[Pt(PEt_3)_2]$ Templates

Kyu Ho Song, Sang Ook Kang,* and Jaejung Ko*[a]

Abstract: We have reported the template synthesis of a 90-membered macrocycle by olefin metathesis. The macrocycle **7** was prepared by an initial six-oxidative-addition reaction of **2** by $[Pt(PEt_3)_4]$. The definite structure of a six-oxidative product was confirmed by the crystal structure. The coordination of 2,6-bis(hex-5-enyloxy)pyridine to **3** led to the hexacationic aryl complex of type **4**. The metathesis of olefin-substituted pyridine with Grubbs catalyst ($[PhCH{=}RuCl_2(Cy_3P)_2]$) formed the expected macrocycle **5**. The olefin metathesis reaction was formed under high dilution to suppress intermolecular olefin metathesis polymerization. The detachment of the newly formed macrocycle **6**, followed by reduction to alkane macrocycle **7** by using palladium on charcoal and hydrogen led to a huge macrocycle. The mild and easy access of the template protocol opens a host of potential subsequent transformations toward the construction of a variety of macrocycles.

Keywords: hexaphenylbenzene · macrocycles · olefin metathesis · template synthesis

Introduction

Olefin metathesis has emerged as one of the most important synthetic methods for the preparation of macrocycles.[1] For productive metathesis to occur, the olefins should be approximately organized in a way favoring the desired connection of adjacent residues. A suitable preorganization of the reacting alkenyl groups by a template can be achieved by metal–ligand coordination,[2] covalent attachment to a suitable template molecule,[3] and hydrogen bonding.[4] Several groups reported olefin metathesis in the metal coordination sphere by using phenanthroline-containing olefins[5] and olefin-substituted phosphines.[6] In these cases, the metal ion serves as the template to prepare the ligands, prior to metathesis in order to construct macrocycles. Recently, Koten et al.[7] has explored the application of metalated pincer complexes for use as supramolecular scaffolds for the controlled synthesis of macrocycles. They[8] have successfully demonstrated that the tris-NCN-Pt (tris-NCN-Pt = C_6H_3[Cl-Pt-4-$C_6H_3(CH_2$-$NMe_2)_2$-3,5]$_3$-1,3,5; see ref. [8]) pincer complex is a suitable template for the construction of macroheterocycles. However, the templated synthesis of macrocycles by using the hexacationic aryl (YCY-M-pyridine)$_6$ (Y = NMe_2, SPh; M = Pt, Pd; see ref. [9]) complex of the type **1** was not successful, probably as a result of steric factors or pyridine dissociation.[9] We envisioned that if we could introduce the more efficient metal moieties which are able to alleviate any steric issues, a system like **4** would offer an ideal template for the formation of a variety of macrocycles. Here we report the facile interconnecting of a 2,6-bis(hex-5-enlyoxy)pyridine substituent by alkene metathesis using a $[Pt(PEt_3)_2]$ hexatemplate of type **5** to form a 90-membered hexa(pyridyl)macrocycle. Such a platinum moiety can be achieved through a simple oxidative addition reaction.

Results and Discussion

Our strategy for the synthesis of a selective supramolecule utilizes the metal-based templation with hexacationic platinum moieties. The synthesis of **5** is conveniently prepared in three steps from the hexakis(4-iodophenyl)hexaphenylbenzene **2**.[10] The template precursor **3** was easily synthesized by an oxidative addition reaction. An oxidative addition reaction of $[Pt(PEt_3)_4]$ (7.0 equiv) with **2** gave the hexaplatinum species **3** (Scheme 1).

The ^{31}P NMR spectrum of **3** in $CDCl_3$ displays a single resonance at $\delta = 3.31$ ppm with ^{195}Pt satellites. The J(P,Pt)

[a] Dr. K. H. Song, Prof. Dr. S. O. Kang, Prof. Dr. J. Ko
Department of Chemistry, Korea University
Jochiwon, Chungnam 339–700 (Korea)
Fax: (+82) 41-867-5396
E-mail: jko@korea.ac.kr

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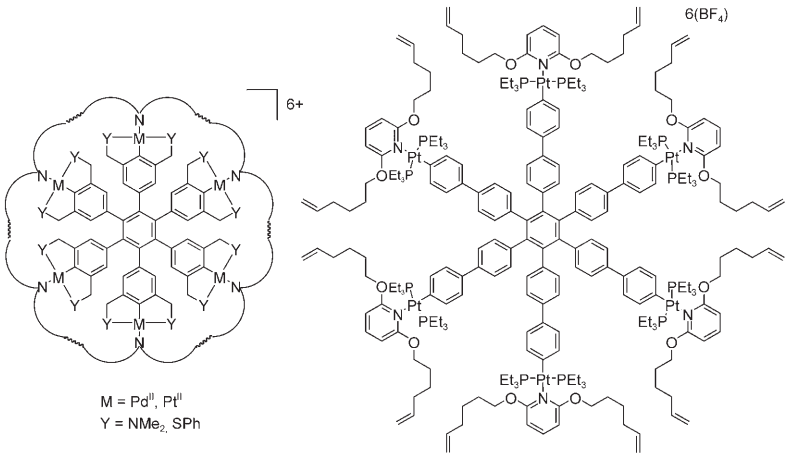


1 4

coupling constant of 2724 Hz is typical for a *trans* geometry about the platinum atom.[11] To help visualize the spacial relationships in **3**, the crystal structure of the solvate **3**[12] was determined (Figure 1). Each of the hexaplatinum moieties in **3** is tilted at a different angle with respect to the central benzene ring, the twist angles between the central benzene ring, and the second peripheral aryl rings ranging from 44.19(1.01) to 81.53(0.56)°. Treatment of **3** with 2,6-bis(hex-5-enyloxy)pyridine (10.0 equiv) in the presence of $AgBF_4$ resulted in the hexacationic complex **4**. A prolonged reaction time (eight hours) is required due to the poor solubility of $AgBF_4$ in CH_2Cl_2. Complex **4** was obtained pure after removal of insoluble silver iodide, followed by recrystallization from CH_2Cl_2/Et_2O. The ^{1}H NMR spectrum of **4** showed a large downfield shift of $\delta =$ 0.5 and 0.1 ppm for the 2,6-disubstituted pyridine and terminal olefin upon coordination of the pyridine moiety to the platinum complex (Figure 2b). Complex **4** was then treated with Grubbs catalyst ([PhCH=$RuCl_2(Cy_3P)_2$]). The olefin metathesis reaction was performed under high dilution (0.0001 M) to suppress intermolecular olefin metathesis polymerization. As expected, the macrocycle formed around template **5** could be isolated by preparative thin-layer chromatography in 80% yield. The reaction progress was monitored by ^{1}H NMR spectroscopy. The time needed for conversion of **5** to 80% yield was found to be considerably longer (three days). After three days, the ^{1}H NMR spectrum of **5** indicated that all terminal olefins had been replaced by disubstituted olefins (Figure 2c). The ^{1}H NMR spectrum of **5** was broadened relative to **4**, due to restricted internal motion or *cis*/*trans*-hexaolefinic macrocycles. Despite the broad peaks, the ^{1}H NMR spectrum shows clear evidence of a high degree of metathesis. The methine resonance assigned to the terminal alkene of **5** at $\delta = 5.93$ ppm had completely disappeared, and a new resonance at $\delta = 5.53$ ppm due to the presence of disubstituted alkenes had been developed. The detachment of the newly formed macrocycle of **6** from the hexacationic template occured by reacting **5** with an aqueous NaI solution, generating the neutral macrocycle **6**. The macrocycle product was completely purified by silica-gel chromatography. The MALDI-TOF mass spectrum of the product exhibited one intense signal, corresponding to the calculated mass of **6**. The peak $[M+2Na]^+$ found in **6** as the base peak confirms the size of macrocycle. A comparison of the measured and the calculated isotopic distribution of **6** shows a good agreement.[13] The ^{1}H NMR spectrum of **6** became much sharper and more simplified due to the free internal motion (Figure 2d). A key feature in the ^{1}H NMR spectrum of **6** occurs at $\delta = 5.46$ ppm, about $\delta = 0.1$ ppm upfield of the resonance from that of **5** for the olefin peak. As compound **6** was formed as mixture of *cis*/*trans*-hexaolefinic macrocycles, the alkene units have been reduced to alkanes for analytical purposes. Thus, the alkane macrocycle **7** was formed from **6** in 99% yield by using palladium on charcoal and hydrogen at an ambient temperature and pressure. The disappearance of the resonance at $\delta = 5.46$ ppm in **6** demonstrated the formation of saturated macrocycle **7** (Figure 2e). All new compounds described above were characterized by microanalysis and NMR spectroscopy (^{1}H, ^{13}C, and ^{31}P NMR).

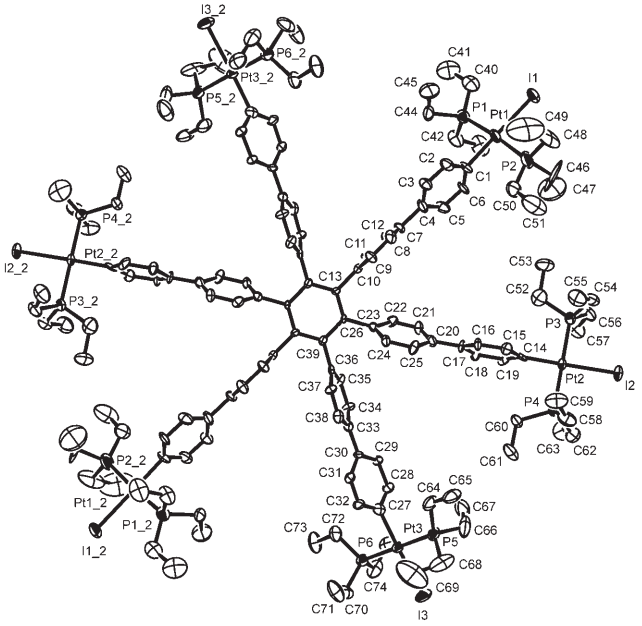
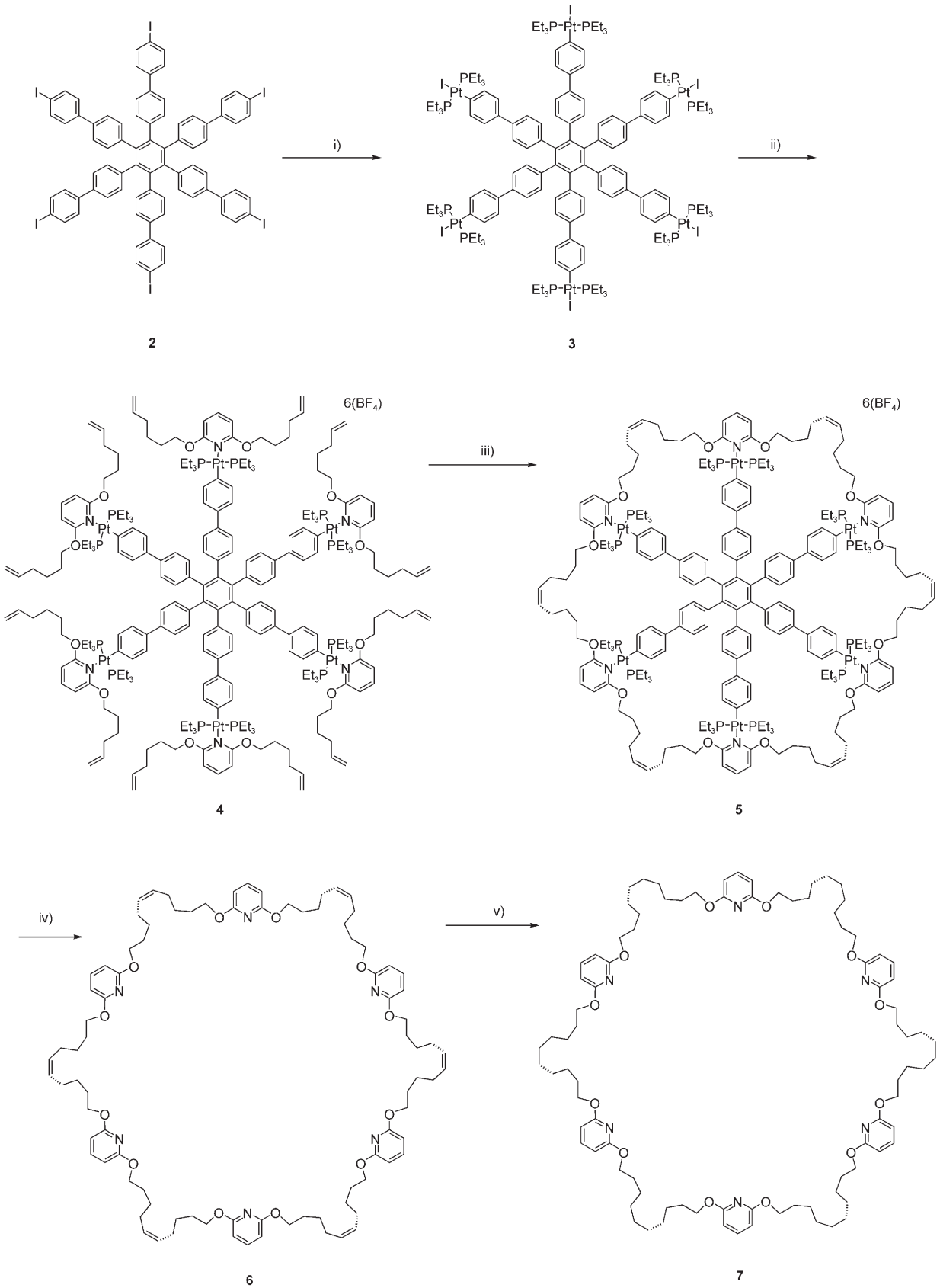


Figure 1. ORTEP drawing of hexaplatinum complex **3** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and solvent (toluene) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–P1 2.320(5), Pt1–P2 2.319(5), Pt1–I1 2.7078(16); P1-Pt1-P2 174.85(17), C1-Pt1-I1 178.7(4), C1-Pt1-P1 85.5(4), C1-Pt1-P2 90.4(4).



2 3 4 5 6 7

Scheme 1. i) $[Pt(PEt_3)_4]$, toluene, 50 °C; ii) $AgBF_4$, 2,6-bis(hex-5-enlyoxy)pyridine, CH_2Cl_2; iii) $[PhCH{=}RuCl_2(Cy_3P)_2]$, CH_2Cl_2; iv) aq NaI, CH_2Cl_2; v) H_2 (g), Pd/C 10 wt.%, CH_2Cl_2.

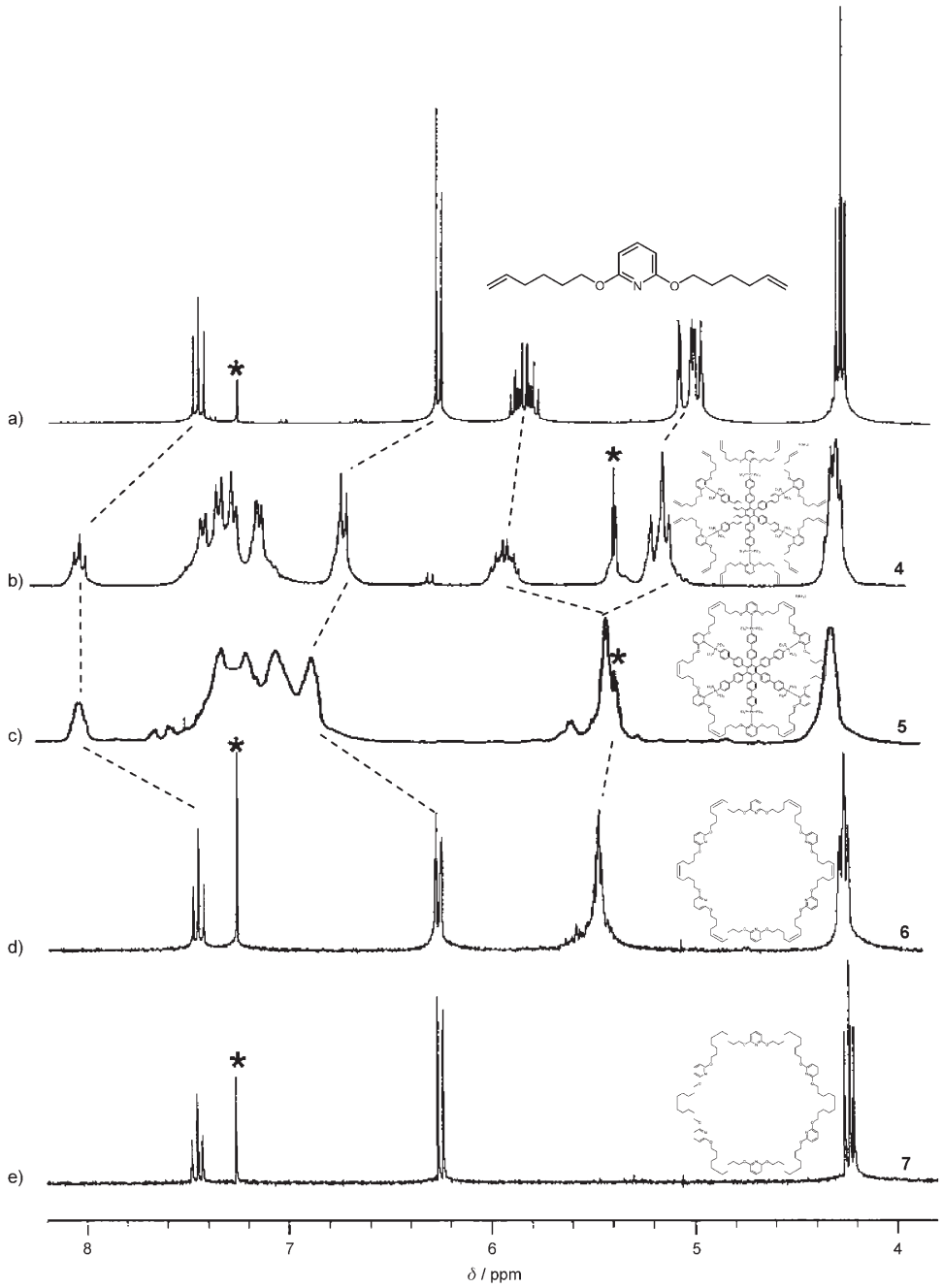


Figure 2. Selected ^{1}H NMR spectra in the region of $\delta = 4 \approx 8$ ppm: a) compound of 2,6-bis(hex-5-enyloxy)pyridine, b) complex **4**, c) complex **5**, d) macrocycle **6**, and e) saturated macrocycle **7**. The asterisk (*) indicates the deuterated solvents (CD_2Cl_2, $CDCl_3$).

Conclusion

We have disclosed the synthesis of a large macrocycle by metathesis of olefin-substituted pyridine on $[Pt(PEt_3)_2]$ hexatemplate. The hexaplatinum template **3** was easily synthesized by a six-oxidative-addition reaction. The mild and easy access of the distinct template protocol opens a host of potential subsequent transformations toward the construction of a variety of macrocycles. Additional investigations into the novel synthesis of a large number of macrocycles by using corannulene and porphyrin are now being undertaken in this laboratory.

Experimental Section

All manipulations were performed in a dry and oxygen-free atmosphere (N_2) by using Schlenk-line and glovebox techniques. Solvents were purified prior to use by distillation over appropriate drying agents under nitrogen. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.00, 75.44, and 121.44 MHz, respectively. Elemental analyses were performed with a Carlo Elba Instruments CHNS-O EA 1108 analyzer. 2,6-Bis(hex-5-enyloxy)pyridine,[7a] hexakis(4-iodo-phenyl)hexaphenylbenzene,[10] and $[Pt(PEt_3)_4]$[12] were prepared according to methods in the literature and the others were purchased from Aldrich.

Compound 3: $[Pt(PEt_3)_4]$ (0.95 g, 1.4 mmol, 7 equiv) dissolved in toluene (5 mL) was added to a stirred solution of hexakis(4-iodo-phenyl)hexaphenylbenzene **2** (0.35 g, 0.2 mmol) in freshly distilled toluene (45 mL) under nitrogen. The resulting solution was stirred at 50 °C for 48 h until the reaction mixture was completely dissolved. The solvent was removed in vacuum. Pure **3** was isolated by silica-gel chromatography ($R_f = 0.35$; CH_2Cl_2/hexane 3:1) as a white crystalline solid in 92% yield. M.p. 270 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.22$ (d, $^3J(H,H) = 6.9$ Hz, 12H), 7.20 (d, $^3J(H,H) = 7.5$ Hz, 12H), 7.06 (d, $^3J(H,H) = 7.5$ Hz, 12H), 6.94 (d, $^3J(H,H) = 6.9$ Hz, 12H), 1.75 (m, 72H), 1.00 ppm (m, 108H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 140.4$, 139.1, 137.9, 136.7, 134.3, 132.0, 125.9, 124.6, 121.6, 15.2, 7.9 ppm; ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): $\delta = 3.31$ (s with satellites, $J(Pt,P) = 2724$ Hz); elemental analysis calcd (%) for $C_{150}H_{228}P_{12}I_6Pt_6$ (4335.0): C 41.56, H 5.30; found: C 41.28, H 5.19.

Compound 4: 2,6-Bis(hex-5-enyloxy)pyridine (0.057 g, 0.23 mmol, 10 equiv) was added to a stirred suspension of **3** (0.1 g, 0.023 mmol) and $AgBF_4$ (0.035 g, 0.184 mmol) in dichloromethane (70 mL) under exclusion of light. The reaction was continued for 8 h in the dark. The resulting mixture was filtered over Celite and evaporated in vacuum. The product was washed with ether and toluene several times. The pure product was obtained by recrytallization from dichloromethane/ether in 91% yield. M.p. 280 °C (decomp); ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): $\delta = 7.96$ (t, $^3J(H,H) = 8.1$ Hz, 6H), 7.34 (d, $^3J(H,H) = 7.8$ Hz, 12H), 7.26 (d, $^3J(H,H) = 8.1$ Hz, 12H), 7.19 (d, $^3J(H,H) = 8.1$ Hz, 12H), 7.06 (d,

^3J(H,H) = 7.8 Hz, 12H), 6.64 (d, ^3J(H,H) = 8.1 Hz, 6H), 5.93 (m, 12H; vinyl), 5.16 (m, 24H; vinyl), 4.19 (t, ^3J(H,H) = 7.9 Hz, 24H; OCH_2), 2.23 (m, 24H), 1.99 (m, 24H), 1.68 (m, 24H), 1.17 (m, 72H), 0.92 ppm (m, 108H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 25°C): δ = 163.7, 146.2, 141.2, 137.8, 136.3, 134.7, 132.8, 130.5, 129.5, 126.5, 125.5, 124.7, 124.1, 101.6, 70.6, 29.0, 26.2, 18.0, 13.4, 7.9 ppm; $^{31}P\{^1H\}$ NMR (121 MHz, [D$_6$]acetone, 25°C): δ = 4.87 (s with satellites, J(Pt,P) = 2813 Hz); elemental analysis calcd (%) for $C_{252}H_{378}B_6F_{24}N_6O_{12}P_{12}Pt_6$ (5746.7): C 52.67, H 6.63; found: C 52.38, H 6.52.

Compound 5: Compound **4** (0.1 g, 0.018 mmol) and Grubbs catalyst (5.4 mg, 0.009 mmol, 30 mol%) were dissolved in dichloromethane (180 mL). The resulting solution was stirred until the terminal vinyl protons had disappeared in the ^{1}H NMR spectrum (about 3 d). The resulting mixture was filtered over Celite and evaporated in vacuum. The product was washed with toluene several times. The pure product was obtained by preparative thin-layer chromatography from dichloromethane/ether in 80% yield. M.p. 284°C (decomp); ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C): δ = 8.13 (t, ^3J(H,H) = 8.4 Hz, 6H), 7.48 (d, ^3J(H,H) = 7.5 Hz, 12H), 7.38 (d, ^3J(H,H) = 8.1 Hz, 12H), 7.28 (d, ^3J(H,H) = 7.5 Hz, 12H),7.20 (d, ^3J(H,H) = 8.1 Hz, 12H), 6.95 (d, ^3J(H,H) = 8.4 Hz, 12H; py), 5.53 (m, 12H; vinyl), 4.40 (t, ^3J(H,H) = 8.1 Hz, 24H; OCH_2), 2.23 (m, 24H), 2.05 (m, 24H), 1.65 (m, 24H), 1.35 (m, 72H), 1.07 ppm (m, 108H); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone, 25°C): δ = 163.7, 146.2, 140.2, 137.7, 136.3, 134.8, 132.8, 130.6, 126.5, 126.1, 125.7, 124.2, 101.6, 70.6, 32.7, 26.2, 23.5, 13.4, 7.9 ppm; $^{31}P\{^1H\}$ NMR (121 MHz, [D$_6$]acetone, 25°C): δ = 4.88 (s with satellites, J(Pt,P) = 2809 Hz); elemental analysis calcd (%) for $C_{240}H_{354}B_6F_{24}N_6O_{12}P_{12}Pt_6$ (5578.3): C 51.67, H 6.40; found: C 51.59, H 6.36.

Compound 6: Saturated aqueous NaI (20 mL) was added to a stirred solution of **5** in dichloromethane (20 mL). After 8 h, the organic layer was separated, dried with $MgSO_4$, and filtered. The resulting ring-closing metathesis product was isolated by silica-gel chromatography (R_f = 0.2 CH_2Cl_2/hexane 1:5) as a light-yellow oil in 74% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 7.45 (t, ^3J(H,H) = 8.1 Hz, 1H), 6.25 (d, ^3J(H,H) = 8.1 Hz, 2H), 5.46 (m, 2H; vinyl), 4.24 (t, 4H; OCH_2), 2.12 (m, 4H), 1.84 (m, 4H), 1.64 ppm (m, 4H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25°C): δ = 162.9, 140.8, 134.7, 101.2, 65.4, 32.5, 25.7, 23.4 ppm.

Compound 7: Pd/C 10 wt.% (0.5 g) was added to a stirred solution of **6** in dichloromethane (30 mL). The reaction was continued for 24 h under a H_2 atmosphere. The resulting mixture was filtered and evaporated in vacuum. The pure product was isolated by flash chromatography (CH_2Cl_2/hexane 1:5) as an oil in 84% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 7.45 (t, ^3J(H,H) = 8.0 Hz, 1H), 6.25 (d, ^3J(H,H) = 8.0 Hz, 2H), 4.23 (t, 4H; OCH_2), 1.78 (m, 4H), 1.40 (m, 4H), 1.31 (m, 4H), 0.89 (m, 4H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25°C): δ = 163.0, 140.8, 101.1, 66.1, 31.7, 25.9, 22.7, 14.1 ppm.

X-ray crystallography for complex 3: Formula = $C_{157}H_{236}P_{12}I_6Pt_6$; M_r = 4334.90; triclinic; space group = $P\bar{1}$; a = 14.214(3), b = 19.191(4), c = 22.312(5) Å; α = 92.09(3), β = 103.29(3), γ = 103.69(3)°; V = 5728(2) Å^3; Z = 1 (half of complex **3** is unique in the unit cell); ρ_{calcd} = 1.310 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 4.576 mm^{-1}; T = 233 K, $F(000)$ = 2194; 71082 reflections collected of which 27477 were unique; R_1 = 0.0774, wR_2 = 0.1722; 848 parameters and 0 restraints. A suitable crystal was grown by using toluene. X-ray crystallographic data were collected by using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.7173 Å) with a Bruker AXS SMART CCD area-detector diffractometer. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of the range 1.88° < 2θ < 57.20° with 71082 reflections. These reflections were measured every 100 reflections throughout data collection and showed no significant variation in intensity. Intensity data were collected with φ-scan data. All calculations were carried out with the SHELXL-97 program. The structure was solved by the direct method. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were included in the calculated positions. The SQUEEZE procedure in the PLATON takes care of the contribution of a disordered solvent to the calculated structure factors by back-Fourier transformation of the continuous density found in a masked region of the difference map. The masked region is defined as the solvent accessible void left by the ordered part of the structure.[14] CCDC-632214 for complex **3** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

MALDI-TOF mass spectrometry: The measurement was performed by using an Voyager DE-STR-TOF mass spectrometer equipped with a reflector, and controlled by the Voyager Instrument Contrl Panel 5.1 software (Applied Biosystems, CA, USA). In MALDI-TOF MS reflector mode, ions generated by a pulsed UV laser beam (nitrogen laser, λ = 337 nm, 20.0 Hz) were accelerated to a kinetic energy of 20 kV; extraction mode = delayed, polarity = positive, accelerating voltage = 20,000 V, grid voltage = 68%, mirror voltage ratio = 1.12, extraction delay time = 150 nanoseconds, acquisition mass range = 700–2,500 Da, number of laser shots = 200/spectrum, laser intensity = 2700, laser repetition rate = 20.0 Hz, matrix = CHCA (α-cyano-4-hydroxycinnamic acid), and low mass gate = 600 Da. External calibration of MALDI mass spectra was carried out by using singly charged monoisotopic peaks of a mixture of des-Arg1-bradykinin (m/z: 904.4681), angiotensin I (m/z: 1296.6853), Glu1-fibrinopeptide B (m/z: 1570.6774), and neurotensin (m/z: 1673.96). Calibration of these mass spectra was performed automatically by utilizing a customized macro command of the Data Explorer 4.0 software. The macro command was used for the calibration of the monoisotopic singly charged peaks of the above mentioned peptides.

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[13] [Macrocycle **6**+2 Na] = [$C_{90}H_{126}N_6O_{12}Na_2$] = 1528.92.

[14] See the SQUEEZE instruction at http://www.cryst.chem.uu.nl/platon/.

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