

Synthesis and Structural Characterization of a Tetranuclear Platinum(II) Metallamacrocycle Containing 1,3-Diisocyanoarene Ligands

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A new tetranuclear platinum(II) metallamacrocycle, including four 1,3-diisocyanoarene ligands, was synthesized and characterized. The reaction of PtI_2(cod) with an equimolar amount of the 1,3-diisocyanoarene ligand in dichloromethane under diluted conditions gave the metallamacrocycle [$(PtI_2)_4$(1,3-diisocyanoarene)$_4$]. X-ray crystallographic analysis showed that the complex adopted a square ring structure with *trans* arrangement of coordinated isocyanides around the Pt atoms. GPC, ESI-MS, IR, and NMR analysis of the metallamacrocycle showed that the tetranuclear macrocyclic scaffold was maintained in solution.

Synthesis of metallamacrocycles through coordination of rigid bridging ligands to transition metals is an active research field in coordination and supramolecular chemistry.[1] This coordination-driven approach provides a new method for the construction of nano-sized architectures, which cannot be created through conventional synthetic methods based on making covalent bonds between precursor molecules. One intriguing target is metallamacrocycles that have a nano-sized cavity and metal sites at the inner wall of the cavity. These compounds are expected to be useful as molecular sensors or catalysts that show unique selectivities.[2]

In order to construct such metallamacrocycles, we have focused our attention on multidentate isocyanide ligands. The high affinity of isocyanides for transition metals and ease of synthesis make them versatile ligands for preparation of various transition-metal complexes, such as metallamacrocycles, liquid crystals, and catalysts.[3–9] We have reported recently that a monodentate aryl isocyanide ligand, which has two bulky groups at the ortho positions of the isocyano group, shows high activity in Rh-catalyzed hydrosilylation (Fig. 1).[9] The bulkiness of the ligand has a large influence on their coordination properties by inhibiting overcoordination, which leads to deactivation of the catalyst. Inspired by these results, we have designed bidentate 1,3-diisocyanoarene ligands bearing bulky substituents at 4- and 6-positions (Fig. 2).[4] We think that macrocyclization through *trans*-coordination to metal units should result in the creation of the central cavity bearing multiple metal sites. The bulky groups would act as an outer shell to shield the external surface of the macrocycles (Fig. 2).

We report here the synthesis and structural characterization of a tetranuclear Pt^{II} metallamacrocycle, consisting of four bulky 1,3-diisocyanoarene ligands and four *trans*-PtI_2 units. A flat square shape of the metallamacrocycle was established by X-ray crystallographic analysis. Although 1,4- and 1,2-diisocyanoarenes have previously been utilized for the synthesis of metallamacrocycles, to the best of our knowledge, this is the first example of metallamacrocycles involving 1,3-diisocyanoarene as a coordinating unit.[4–6]

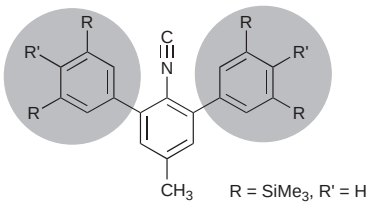

Fig. 1. Bulky monodentate isocyanide.

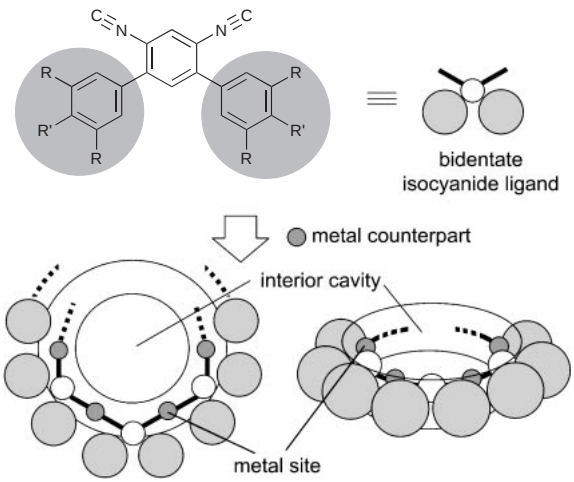

Fig. 2. Expected formation of a metallamacrocycle through metal-complexation of bidentate bulky 1,3-diisocyanoarenes.

Results and Discussion

Synthesis of the 1,3-diisocyanoarenes started from 4,6-diiodo-1,3-phenylenediamine (**1**),[10] which was easily prepared through iodination of 1,3-phenylenediamine according to the literature procedure (Scheme 1). Twofold Suzuki–Miyaura

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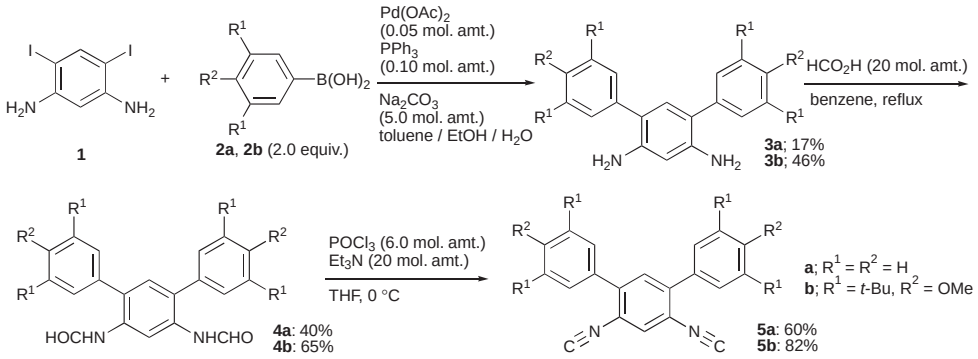
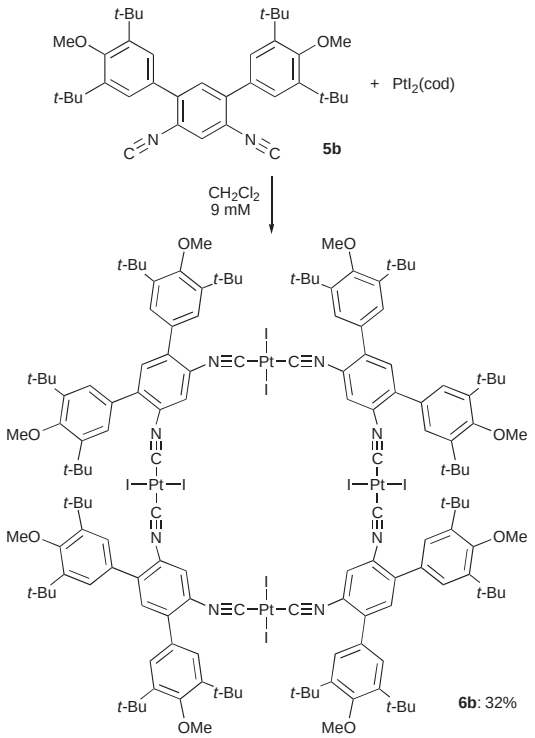


Scheme 1.



Scheme 2.

coupling of **1** with boronic acids **2a** and **2b**[11] afforded **3a** (17%) and **3b** (46%), respectively. Formylation through condensation with formic acid (**4a**, 40%; **4b**, 65%), followed by dehydration of the formamides with $POCl_3/Et_3N$ (**5a**, 60%; **5b**, 82%), afforded diisocyanoarenes **5a** and **5b** in total yields of 3.0 and 25%, respectively.

Mixing PtI_2(cod) with an equimolar amount of 1,3-diisocyanoarene **5a** in CH_2Cl_2 resulted in the formation of an insoluble material even under the high dilution conditions (9 mM) (1 M = 1 mol dm^{-3}). Reaction of PtI_2(cod) with **5b**, which is more soluble than **5a** owing to the 3,5-di-*tert*-butyl-4-methoxyphenyl (DTBM) substituent, gave a clear solution of crude mixture in CH_2Cl_2 (Scheme 2). The major product **6b** was isolated in 32% yield by silica gel chromatography followed by preparative GPC (gel permeation chromatography). While GPC analysis indicated that the crude product contained some oligomeric and polymeric products of molecular weights higher and lower than **6b**, only **6b** could successfully be purified and characterized. Reaction at higher substrate concentrations resulted in a decrease in the product yield. Changing the solvent to toluene caused a significant decrease in the yield of **6b**.

^{1}H, ^{13}C NMR, IR, FAB mass measurements, and X-ray crystal structure analysis showed that **6b** had a tetranuclear macrocyclic structure, consisting of four Pt atoms and four 1,3-diisocyanoarenes as shown in Scheme 2. ^{1}H NMR signals at 7.50 and 7.60 corresponding to the two aromatic protons on the central benzene ring of the free isocyanide ligand shifted downfield to δ 7.58 and 8.03 upon coordination to the Pt^{II} atom, respectively, whereas the other ^{1}H NMR signals of the ligand scarcely shifted upon coordination. The ^{13}C NMR resonances for the isocyano carbons were not observed due to their low intensity. ^{1}H and ^{13}C NMR spectra displayed a single set of signals for the four coordinated ligands, indicating the formation of a highly symmetrical complex. The IR spectra of **6b** in the solid state showed a single stretching absorption (2166 cm^{-1}) for the coordinated isocyano groups at a higher wavenumber (52 cm^{-1}) than that for the free isocyanide (2114 cm^{-1}). The observation of only one absorption indicates that the complex has *trans* configuration around the Pt^{II} atoms rather than *cis*.[12] Direct evidence for the formation of the tetranuclear complex was provided by using high-resolution FAB mass spectrometry. Isotropically resolved peaks attributable to the loss of each iodide ($[\mathbf{6b} - I]^+$, m/z = 3925.7, 3926.7, 3927.7, 3928.7) were observed.

Single-crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from Bu_2O/CH_2Cl_2. From crystal structure analysis (*R*, 9.8%; *wR*2, 13.4%),[13] **6b** had a slightly distorted, square planar, tetranuclear ring structure, in which the four Pt atoms were at the center of each side of the square and the four coordinating 1,3-diisocyanoarenes were at the apexes (Fig. 3). There was an inversion center located at the center of the square. Selected bond lengths and angles are listed in Table 1. There were no solvent molecules in the cavity of the square, and two Bu_2O molecules per one metallamacrocycle were present between the squares. The dimensions of the distorted square were 12.6 and 13.4 Å, determined from the atom distances of Pt(1)···Pt(1′) and Pt(2)···Pt(2′), respectively. The Pt atoms and the central rings of the 1,3-diisocyanoarene ligands were almost in the same plane, whereas the aromatic rings of DTBM substituents were twisted from the central rings of the ligands with dihedral angles of 36–55°. The coordination geometry around the Pt atoms was a slightly distorted square planar with two *trans*

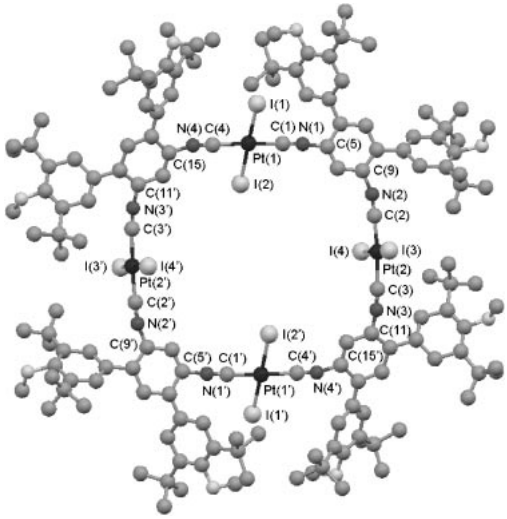


Fig. 3. Molecular structure of tetranuclear complex **6b**. The disordered oxygen and carbon atoms of the DTBM substituents are omitted for clarity.

Table 1. Selected Bond Distances, and Angles with esd's for **6b**

Bond distances/Å			
Pt(1)–C(1)	1.94(2)	Pt(1)–C(4)	2.00(2)
Pt(2)–C(2)	1.95(2)	Pt(2)–C(3)	2.00(2)
Pt(1)–I(1)	2.584(2)	Pt(1)–I(2)	2.578(2)
Pt(2)–I(3)	2.575(3)	Pt(2)–I(4)	2.574(2)
Pt(1)···Pt(1′)	12.6	Pt(2)···Pt(2′)	13.4
Bond angles/deg			
C(1)–N(1)–C(5)	175(1)	C(2)–N(2)–C(9)	163(1)
C(3)–N(3)–C(11)	169(1)	C(4)–N(4)–C(15)	163(1)
Pt(1)–C(1)–N(1)	177(2)	Pt(1)–C(4)–N(4)	177(1)
Pt(2)–C(2)–N(2)	178(2)	Pt(2)–C(3)–N(3)	170(1)

isocyanides and two *trans* iodine atoms. All coordination bond lengths centered at the Pt atoms are normal as compared with the values for mononuclear *trans*-$PtI_2(CNAr)_2$ complexes.[12]

Although the natural bonding angle determined by the two isocyano groups of the 1,3-diisocyanoarene (**5b**) was 120°, the four 1,3-diisocyanoarenes were located at the right-angled corners. Whereas most isocyanide–Pt^{II} complexes adopt a linear arrangement of a C–N–C–Pt tetrad, considerable bent distortions of the tetrads, in which the C–N–C and N–C–Pt angles were 163–175 and 170–178°, respectively, were observed. This result shows the bridging isocyanide ligand is rigid enough to allow the construction of discrete metallamacrocyclic structures, and flexible enough to form constrained ring structures.

The tetranuclear macrocyclic scaffold of **6b** was maintained in solution. Mass spectral measurements (ESI-MS) of the complex in acetone–methanol exhibited isotropically resolved peaks ($[\mathbf{6b} - I]^+$, $m/z = 3926.7$, 3927.6, 3928.7) corresponding to the tetranuclear complex. GPC analysis (JAIGEL-1H and 2H) of **6b** in $CHCl_3$ displayed a single peak, suggesting that neither higher nor lower molecular weight complexes form through isomerization of **6b**. The IR spectrum of a

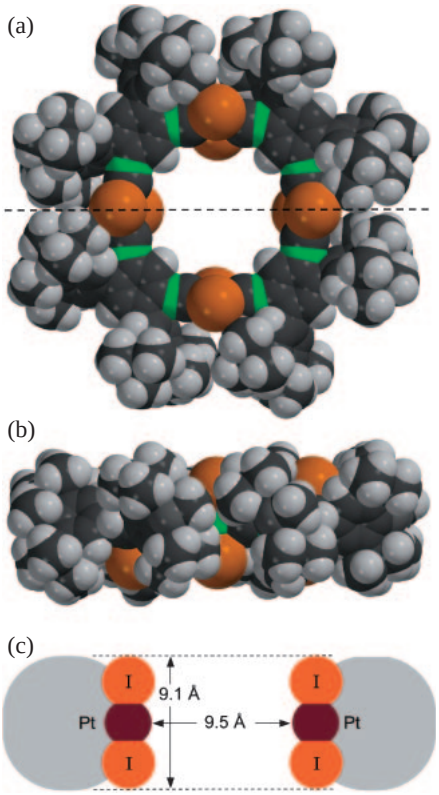


Fig. 4. A space-filling model optimized with the force field simulation. (a) Top view. (b) Side view. (c) Illustration of a cross-section created by slicing **6b** by a plane shown in Fig. 4a as a dotted line.

chloroform solution of the complex showed a single absorption (2181 cm^{-1}), which indicates that the complex maintains its *trans*-configuration in solution. The high stability of the complex in solution is also supported by the fact that the ^1H and ^{13}C NMR spectra of **6b** in $CDCl_3$ remained unchanged even after several days. This stability would be due to the inertness of the coordination bond between the isocyano carbon and the Pt^{II} center.

In order to estimate the shape and dimensions of the interior cavity of the square, force field simulations (MMFF94, MacSpartan Pro 1.0.4.) were conducted. The initial structure for optimization was generated by adding valence hydrogens to the molecular structure derived form the X-ray crystallographic analysis. A space-filling model of the optimized structure is shown in Figs. 4a and 4b. From these models, metallamacrocycle **6b** had a boxy cavity surrounded by the square ring with a thickness defined by the I–Pt–I unit (ca. 9.1 Å)[14] (Fig. 4c). The dimensions of the basal plane were ca. 9.5 × 9.5 Å.[15] Figure 4 visualizes that the external surface of the Pt atoms is effectively shielded by the DTBM substituents.

Conclusion

We synthesized and characterized a metallamacrocycle consisting of the four Pt atoms and four 1,3-diisocyanoarene ligands. The 1,3-diisocyanoarene ligand is both rigid enough to allow the formation of discrete metallamacrocyclic structures and flexible enough to form constrained ring structures. This ligand should be a versatile building block for the

construction of transition metal-containing metallamacrocycles having a nano-sized cavity.

Experimental

General. NMR spectra were recorded on a Varian Gemini 2000 (^{1}H: 300 MHz; ^{13}C: 75.4 MHz) spectrometer. Tetramethylsilane (^{1}H), $CDCl_3$ (^{13}C) were employed as internal and external standards, respectively. Infrared spectra were recorded on a Perkin-Elmer Spectrum One. Elemental analyses were performed at the Center for Instrumental Analysis, Hokkaido University. Low- and high-resolution mass spectra were recorded on a JEOL JMS-T50LC and JMS-700TZ mass spectrometers. Melting points were measured with a Yanaco MP500D apparatus. All reactions were carried out under an argon atmosphere. Materials were obtained from commercial suppliers and were purified using the standard procedures, unless otherwise noted. Compounds **1**, **2b**, and PtI_2(cod) were prepared according to literature procedures.[10,11,16] GPC (gel permeation chromatography) analysis and purification were performed on a LC-908 recycle GPC system (Japan Analytical Industry Co., Ltd.), using JAIGEL-1H and 2H columns.

Synthesis of Ligands. **3b**: The mixture of **1**[10] (0.756 g, 2.10 mmol), **2b**[11] (1.664 g, 6.30 mmol), $Pd(OAc)_2$ (24 mg, 0.11 mmol), PPh_3 (55 mg, 0.21 mmol), Na_2CO_3 (1.114 g, 10.5 mmol) in toluene (10 mL), ethanol (10 mL) and H_2O (6 mL) was stirred at reflux under argon overnight. The reaction mixture was extracted with CH_2Cl_2 and washed with aqueous NaOH (6 M), brine and water. The organic layer was dried over Na_2SO_4, and filtered, and the solvent was evaporated. The residue was subjected to silica-gel chromatography (ethyl acetate:hexane = 5:95–30:70) to give **3b** as a colorless solid (0.526 g, 46%); ν_{max}(neat)/cm^{-1} 3440, 3370, 3361, 2963, 1620, 1607, 1219; mp 270 °C (dec.); ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.45 (36H, s, –C(C*H*$_3$)$_3$), 3.74 (6H, s, –OC*H*$_3$), 3.76 (4H, br, –N*H*$_2$), 6.22 (1H, s, Ar–*H*), 6.98 (1H, s, Ar–*H*), 7.34 (4H, s, Ar–*H*); ^{13}C NMR (75.4 MHz; $CDCl_3$): δ 32.1, 35.8, 64.1, 102.1, 119.8, 127.6, 132.3, 133.6, 143.71, 143.80, 158.2; Anal. Calcd for $C_{36}H_{52}N_2O_2$: C, 79.36; H, 9.62; N, 5.14%. Found: C, 79.09; H, 9.78; N, 5.06%.

3a: Prepared from **1** (2.30 g) and **2a** (1.95 g) according to a procedure similar to that for the synthesis of **3b**. The crude product was purified by silica-gel chromatography (MeOH:CH_2Cl_2 = 5:95 and ethyl acetate:CH_2Cl_2 = 0:100–5:95) to afford **3a** (0.29 g, 17%) as a pale yellow solid; mp 101 °C; ^{1}H NMR (300 MHz; $CDCl_3$): δ 3.73 (4H, br, –N*H*$_2$), 6.21 (1H, s, Ar–*H*), 6.98 (1H, s, Ar–*H*), 7.26–7.50 (10H, m, Ar–*H*); ^{13}C NMR (75.4 MHz; $CDCl_3$): δ 102.2, 119.3, 126.7, 128.8, 129.3, 132.7, 139.6, 144.0.

4b: The mixture of **3b** (1.60 g, 2.94 mmol) and formic acid (2.4 mL) in benzene (40 mL) was heated at reflux under nitrogen for 3 h, using a Dean–Stalk apparatus. After formic acid was added to the reaction mixture (10 mL at 3 h and 20 mL at 7 h), the mixture was heated at reflux overnight. The reaction mixture was neutralized with aqueous Na_2CO_3 and extracted with CH_2Cl_2. The organic layer was washed with brine and water, dried over Na_2SO_4, and filtered, and the solvent was evaporated. The remaining crude solid was recrystallized from hot Bu_2O and CH_2Cl_2, giving **4b** as a colorless crystalline solid (1.06 g, 65%) as a mixture of the isomers due to *cis–trans* isomerism of the *N*-formylamino groups. Four different sets of ^{1}H NMR resonances for the formyl groups were observed; ν_{max}(neat)/cm^{-1}: 3290, 2961, 2865, 1693, 1665, 1607, 1220; mp 274 °C; ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.44–1.46 (36H, m, –C(C*H*$_3$)$_3$), 3.76–3.77 (3H, m, –OC*H*$_3$), 7.10–7.45 (2H, m, –N*H*CHO), 8.38 (0.8H, br s, –NHC*H*O), 8.54 (0.5H, s, –NHC*H*O), 8.78 (0.2H, d, J = 11.5 Hz, –NHC*H*O), 8.86 (0.5H, d, J = 11.5 Hz, –NHC*H*O); ^{13}C NMR (75.4 MHz; $CDCl_3$): δ 31.97, 35.83, 35.89, 35.92, 64.3, 106.9, 109.8, 115.8, 127.5, 127.57, 127.63, 127.7, 128.9, 129.0, 129.9, 130.5, 130.8, 130.9, 131.3, 131.5, 132.4, 133.1, 133.5, 133.9, 134.0, 144.7, 144.8, 145.0, 145.1, 158.9, 159.0, 159.5, 159.6, 159.7, 161.6, 162.1; Anal. Calcd for $C_{38}H_{52}N_2O_4$: C, 75.96; H, 8.72; N, 4.66%. Found: C, 75.83; H, 8.90; N, 4.66%.

4a: Prepared from **3a** (62 mg, 0.24 mmol) according to a procedure similar to that for the synthesis of **4b**. The crude product was purified by recrystallization from CH_2Cl_2/hexane to afford **4a** (30 mg, 0.095 mmol, 40%) as a mixture of the isomers due to *cis–trans* isomerism of the *N*-formylamino groups. Four different sets of ^{1}H NMR resonances for the formyl groups were observed; ν_{max}(neat)/cm^{-1} 3226, 3060, 2883, 1650, 1639; mp 221 °C; ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.22–7.55 (14H, m, Ar–*H* and –N*H*CHO), 8.30–8.40 (0.9H, m, –NHC*H*O), 8.57 (0.5H, s, –NHC*H*O), 8.85 (0.6 H, d, J = 11.1 Hz, –NHC*H*O); ^{13}C NMR (75.4 MHz; $CDCl_3$): δ 107.6, 110.2, 115.7, 128.29, 128.34, 128.4, 128.5, 128.6, 129.2, 129.36, 129.4, 129.5, 129.8, 131.7, 132.6, 133.5, 133.8, 136.2, 136.6, 136.7, 137.2, 143.3, 159.0, 159.2, 161.6, 162.1; Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86%. Found: C, 75.91; H, 5.19; N, 8.81%.

5b: To a stirred suspension of **4b** (500 mg, 0.83 mmol) in THF (25 mL) and triethylamine (2.3 mL), $POCl_3$ (465 µL, 5.0 mmol) was added dropwise at 0 °C. The mixture was stirred over night at 0 °C, quenched with aqueous Na_2CO_3 and extracted with CH_2Cl_2. The organic layer was washed with brine and water, dried over Na_2SO_4, and filtered, and the solvent was evaporated. The crude mixture was subjected to silica gel chromatography (ethyl acetate:hexane = 0:100–5:95) to give **5b** as a white solid (387 mg, 82%); ν_{max}(neat)/cm^{-1} 2114 (NC); mp 172 °C (dec.); ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.48 (36H, s, –C(C*H*$_3$)$_3$), 3.77 (6H, s, –OC*H*$_3$), 7.42 (4H, s, Ar–*H*), 7.50 (1H, s, Ar–*H*), 7.60 (1H, s, Ar–*H*); ^{13}C NMR (75.4 MHz; $CDCl_3$): δ 31.9, 36.0, 64.3, 123.4, 127.2, 127.5, 129.7, 132.4, 140.6, 144.4, 160.5, 168.9; Anal. Calcd for $C_{38}H_{48}N_2O_2$: C, 80.81; H, 8.57; N, 4.96%. Found: C, 80.79; H, 8.79; N, 4.99%.

5a: Prepared from **4a** (0.385 g, 1.21 mmol) according to a procedure similar to that for the synthesis of **5b** (202 mg, 0.721 mmol, 60%); mp 113 °C; ν_{max}(neat)/cm^{-1} 2124, 2113 (NC); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.45–7.56 (11H, m, Ar–*H*), 7.64 (1H, s, Ar–*H*); ^{13}C NMR (75.4 MHz; $CDCl_3$): δ 123.8(br), 126.9, 128.83, 128.85, 129.3, 132.8, 135.3, 140.0, 169.5; HR-EIMS: m/z 280.0997, calculated for $C_{20}H_{12}N_2$ $[M]^+$: 280.1000.

Synthesis of the Metallamacrocycle 6b. To a stirred solution of PtI_2(cod)[16] (99 mg, 0.177 mmol) in CH_2Cl_2 (19.7 mL), a solution of **5b** (100 mg, 0.177 mmol) in CH_2Cl_2 (19.7 mL) was added dropwise. After the reaction mixture was stirred for 1 h, the solvent was evaporated, and the crude mixture was subjected to silica gel chromatography (ethyl acetate:hexane = 5:95) and preparative GPC (JAIGEL-1H and -2H, $CHCl_3$) to give **6b** (57 mg, 32%); ν_{max}(neat)/cm^{-1} 2166 (NC); ν_{max}($CHCl_3$)/cm^{-1} 2181 (NC); ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.48 (144H, s, –C(C*H*$_3$)$_3$), 3.77 (24H, s, –OC*H*$_3$), 7.35 (16H, s, Ar–*H*), 7.58 (4H, s, Ar–*H*), 8.03 (4H, s, Ar–*H*); ^{13}C NMR (75.4 MHz; $CDCl_3$): δ 32.0, 36.0, 64.6, 123.2, 127.2, 128.8, 131.3, 132.8, 142.3, 144.9, 161.3; HRMS (FAB$^+$): m/z 3925.6769 (80%), 3926.6787 (97%), 3927.6804 (100%), 3928.6821 (89%); ESI-MS (acetone/MeOH): m/z 3926.70, 3927.60, 3928.71, calculated for $C_{152}H_{192}I_7N_8O_8Pt_4$ $[M-I]^+$: 3925.6767 (81.7%), 3926.6785 (98.4%), 3927.6802 (100%), 3928.6819 (88.5%); Anal. Calcd for $C_{152}H_{192}I_8N_8O_8Pt_4$:

Table 2. Summary of Crystal Data and Details of Data Collection and Refinement Parameters for $[(PtI_2)_4(1,3\text{-diisocyanoarene})_4]_{0.5}\cdot(n\text{-}C_4H_9)_2O$ ($\mathbf{6b}_{0.5}\cdot(n\text{-}C_4H_9)_2O$)

Formula	$Pt_2I_4O_5N_4C_{84}H_{94}$
MW	2137.49
Crystal system	triclinic
Space group	$P\bar{1}$ (#2)
a/Å	16.079(2)
b/Å	16.413(2)
c/Å	23.296(5)
α/deg	78.81(2)
β/deg	81.45(2)
γ/deg	60.68(1)
V/Å^3	5248.0(1)
Z	2
D_{calcd}/g cm^{-3}	1.353
Crystal size/mm^3	0.40 × 0.20 × 0.01
μ(Mo Kα)/cm^{-1}	38.69
$2\theta_{max}$/deg	55.0
No. of measured reflns	43424
Unique reflns	23039 ($R_{int} = 0.027$)
Observed reflns	9982 ($I > 3.00\sigma(I)$)
No. of variables	535
R	0.098
Rw	0.134
GOF	2.62
Max Shift/error in final cycle	0.316
Max peak in diff Fourier map/eÅ^{-3}	9.40
Min peak in diff Fourier map/eÅ^{-3}	−4.66

C, 45.02; H, 4.77; N, 2.76%. Found: C, 44.88; H, 4.58; N, 2.71%. A single crystal of $\mathbf{6b}\cdot(n\text{-}Bu_2O)$ was obtained by recrystallization from dichloromethane and dibutyl ether, mounted on a glass capillary and transferred to the diffractometer in a cold gas stream.

X-ray Crystal Structure Analysis of $\mathbf{6b}\cdot(n\text{-}Bu_2O)$. The data were collected at 123 K on a Rigaku/MSC Mercury CCD diffractometer. Cell constants and an orientation matrix for data collection were obtained. All of the data were corrected for Lorentz and polarization effects. A summary of the cell parameters, data collection conditions, and refinement results is given in Table 2. The structures were solved by direct methods[17] and expanded using Fourier techniques.[18] Hydrogen atoms were not included in the calculations. All calculations were performed using the teXsan crystallographic software package.[19] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-633577 for **6b**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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