Design and Self-Assembly of Nanoscale Organoplatinum Macrocycles

Joseph Manna, Jeffery A. Whiteford, and Peter J. Stang*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

David C. Muddiman and Richard D. Smith

Environmental Molecular Sciences Laboratory
Pacific Northwest National Laboratory
Richland, Washington 99352

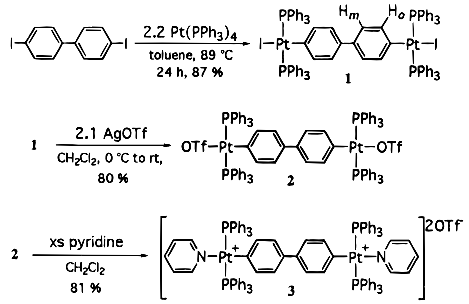
Received June 17, 1996

The design and construction of discrete, functional supramolecular species is an area of expanding development.[1] Nanoscale supramolecular devices that possess microenvironments with unique mechanical, chemical, or optical properties are of significant interest.[2,3] One of the inherent limitations associated with the multicomponent covalent synthesis of nanoscale architectures is the difficulty in predictably generating a single supramolecular moiety in high, extractable yield. The self-assembly, *via* noncovalent interactions (typically hydrogen bonding and metal−ligand dative bonding), of nanoscale complexes provides an attractive alternative to covalent synthesis in that, when employing the proper synthetic strategy, multicomponent units can spontaneously organize into a single supramolecular species.[4]

We recently reported the syntheses, by self-assembly, of rigid cationic tetranuclear organometallic and inorganic macrocycles with approximately 90° linkages at the metal or iodonium center.[5] Herein we describe the synthesis and characterization of two novel organometallic nanodimensional macrocycles. In contrast to our previously reported macrocycles, these new complexes display two *trans*-platinum linear linkages along the sides of the square, as well as platinum or iodonium centers with roughly 90° geometries at the corners of the macrocycle.

The reaction of 4,4′-diiodobiphenyl with 2.2 equiv of $Pt(PPh_3)_4$ provides a simple and effective route, *via* oxidative-addition, to the bisplatinum complex **1** (Scheme 1); this complex displays two oppositely aligned *trans*-platinum centers that will prove useful in the self-assembly process. The utility of zero-valent $Pt(PPh_3)_4$ in the preparation of *trans*-$Pt(PPh_3)_2XR$ complexes (X = halide; R = alkyl, alkenyl, acyl, or aryl) is well documented.[6] Complex **1** is a CH_2Cl_2- and $CHCl_3$-soluble white powder and was characterized by IR, NMR (^1H, ^{31}P, ^{13}C), and mass spectroscopy, as well as physical means. Importantly, the ^1H-NMR spectrum of **1** displays two sets of doublets attributable to the H_o (6.45 ppm) and H_m (5.91 ppm) nuclei of the biphenyl hydrogens magnetically coupled to each other ($^3J_{HH}$ = 8.1 Hz). The $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet for the equivalent *trans*-phosphines at 23.0 ppm, with a $^1J_{PPt}$ of 3095 Hz.[7] Diagnostic of the η^1-aryl carbon−platinum bond is the observed triplet resonance ($^2J_{CP}$ = 8.4 Hz) in the $^{13}C\{^1H\}$ spectrum at 144.1 ppm.[8]

Scheme 1



Reaction of complex **1** with AgOTf yields the desired bistriflate complex **2** in 80% yield. The $^{19}F\{^1H\}$-NMR spectra of **2** displays a singlet at −78 ppm, as is expected for the weakly bound triflate anion. The $^{31}P\{^1H\}$ singlet resonance of **2** is shifted downfield (to 29.3 ppm) relative to **1**. Furthermore, **2** displays a $^1J_{PPt}$ of 3219 Hz, which is significantly larger than **1** and indicative of an increase in the Pt−P bonding interaction and electrophilicity at platinum.[9]

In order to determine the affinity of the bistriflate complex **2** toward nitrogen-based ligands, and therefore its utility in the self-assembly process, excess pyridine was added to a CH_2Cl_2 solution of complex **2**, resulting in the formation of the bispyridine adduct **3**.[10] As confirmed by NMR spectroscopy, this cationic complex proved to be robust and not prone to pyridine loss. The ^1H chemical shifts of the α- and β-pyridine hydrogens of **3** are shifted upfield (presumably due to shielding by PPh_3), relative to free pyridine (H_α = 8.50 ppm; H_β = 6.99 ppm), to 8.04 and 6.72 ppm, respectively. Complex **3** exhibits a clearly distinct $^{31}P\{^1H\}$ chemical shift (21.8 ppm) and $^1J_{PPt}$ (3063 Hz). The formulation of **3** was likewise confirmed by the FAB-MS that displayed a strong isotopic pattern ascribed to $[M-OTf]^+$ centered at 1898 amu.

Modular self-assembly of the novel, hybrid iodonium−organoplatinum nanoscale macrocycle **5** was achieved by addition of a solution of bis[4-(4′-pyridyl)phenyl]iodonium triflate (**4**),[5c] a 90° linkage, to the bistriflate complex, **2** (Scheme 2). The formation of **5** was quantitative by NMR, although workup yielded 81% of product **5**.[11] The $^{31}P\{^1H\}$ NMR of **5** displays a singlet at 22.5 ppm ($^1J_{PPt}$ = 3076 Hz);[12] as expected, these data are similar to those of **3**. Chemical shifts, in acetone-d_6, of the α- and β-pyridine hydrogens (8.52 and 7.18 ppm,

---

[1] Recent reviews: (a) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725−2828. (b) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37−44. (c) Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests*; The Royal Society of Chemistry: Cambridge, England, 1994. (d) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH Publishers: Weinheim, 1995. (e) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537−553.

[2] Drexler, K. E. *Nanosystems: Molecular Machinery, Manufacturing and Computation*; Wiley: New York, 1992.

[3] Recent key references: (a) Fujita, M.; Oguro, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469−471. (b) Bedard, T. C.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 10662−10671. (c) Amabilino, D. B.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1996**, *118*, 3285−3286. (d) van Nostrum, C. F.; Picken, S. J.; Schouten, A.-J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1995**, *117*, 9957−9965. (e) Ashton, P. R.; Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Menzer, S.; Pérez-García, L.; Prodi, L.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 11171−11197. (f) Drain, C. M.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 2313−2315.

[4] Lawrence, D. S.; Jiang, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229−2260.

[5] (a) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1993**, *115*, 9808−9809. (b) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273−6283. (c) Stang, P. J.; Chen, K.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 8793−8797. (d) Stang, P. J.; Whiteford, J. A. *Organometallics* **1994**, *13*, 3776−3777. (e) Stang, P. J.; Olenyuk, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 732−736.

[6] (a) Abel, E. W.; Stone, F. G. A.; Wilkenson, G., Eds. *Comprehensive Organometallic Chemistry II*; Elsevier Science: Tarrytown, New York, 1995; Vol. 9. (b) Stille, J. K. *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: Chichester, England, 1985; Vol. 2, Chapter 9. (c) Sen, A.; Chen, J.-T.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 148−156. (d) Crociani, B.; DiBianci, F.; Giovenco, A.; Berton, A.; Bertani, R. *J. Organomet. Chem.* **1989**, *361*, 255−267.

[7] For comparison, the ^{31}P NMR data for *trans*-$Pt(PPh_3)_2(Ph)I$, synthesized independently, are as follows: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 21.2 (s, $^1J_{PPt}$ = 3081 Hz). See: Anderson, G. K.; Clark, H. C.; Davies, J. A. *Organometallics* **1982**, *1*, 64−70.

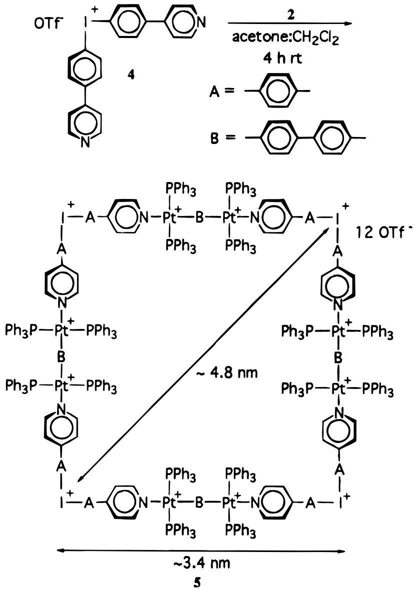
[8] (a) Clark, H. C.; Ward, J. E. H. *J. Am. Chem. Soc.* **1974**, *96*, 1741−1748. (b) Coulson, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 3111−3119.

[9] Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335−422.

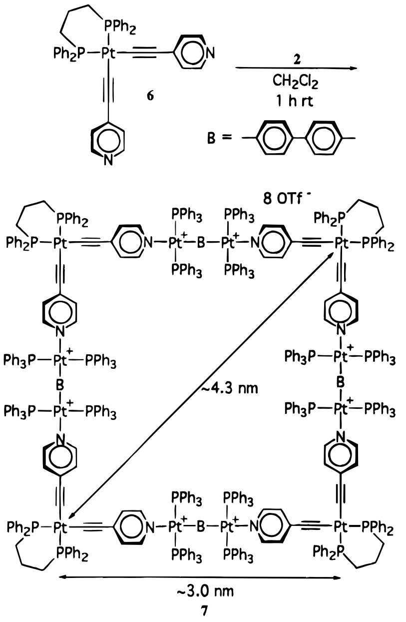
[10] Cationic [*trans*-$Pt(AsMe_3)_2Ph(L)][PF_6]$[8a] and [*trans*-$Pt(PPh_3)_2(\eta^1$-vinyl)(L)][OTf][10a] (L = C_5H_5N and CO) complexes have been reported. (a) Stang, P. J.; Zhong, Z.; Kowalski, M. H. *Organometallics* **1990**, *9*, 833−838.

S0002-7863(96)02041-0 CCC: $12.00

Scheme 2



Scheme 3



respectively) of **5** are translated upfield by 0.26 and 0.53 ppm, respectively, relative to the free ligand **4**. The $^{13}\mathrm{C}\{^1\mathrm{H}\}$ chemical shifts of the 4,4′-bis(*trans*-Pt(PPh$_3$)$_2$)biphenyl portion of **5** is entirely consistent with data for **3**, whereas the resonances of the iodonium corner are akin to those reported for the hybrid *cis*-platinum−iodonium squares.[5c]

The structural formulation of the proposed macrocycle **5** was firmly elucidated by mass spectroscopy. While the matrix-assisted laser desorption ionization (MALDI) spectrum of **5** failed to exhibit a feature attributable to the [M−OTf] 1+ charge state ion (9747 amu), it did, nevertheless, display a distinctive feature at 1500 amu. This peak was tentatively assigned to the [M−6OTf] 6+ charge state. However, due to the limited resolution of the MALDI spectrum, electrospray-ionization Fourier transform ion cyclotron resonance (ESI-FTICR) mass spectrometry was used for analysis of **5**; this technique provides gentle ionization combined with high-resolution capability.[13] The ESI-FTICR MS spectrum of **5** obtained from an acetone solution resolved the peak centered at $m/z = 1500.163$ amu with an m/z peak spacing of $^1/_6$ corresponding to the [M−6OTf] 6+ charge state ion of macrocycle **5**. The observed molecular weight (9000.98 Da) and isotope pattern is in excellent agreement with the theoretical weight (9001.02; error = 4.4 ppm) and pattern.

Modular self-assembly of macrocycle **7** was accomplished by the addition of a CH$_2$Cl$_2$ solution of the 90° corner, **6**,[14] to the linear linkage **2** (Scheme 3). The reaction was quantitative, as determined by NMR spectroscopy.[15] Importantly, the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ spectra of **7** exhibits singlet signals at 21.4 ($^1J_{\mathrm{PPt}} = 3060$ Hz) and −5.5 ($^1J_{\mathrm{PPt}} = 2198$ Hz) ppm with a 2:1 intensity ratio accountable to the *trans*-PPh$_3$ and *cis*-dppp, respectively. The chemical shift of the former phosphorus nuclei parallel the data of complexes **3** and **5**, while the *cis*-dppp phosphorus nuclei of macrocycle **7** are clearly distinct from the monomer **6** (−3.1 ppm, $^1J_{\mathrm{PPt}} = 2185$ Hz). The α- and β-pyridyl hydrogen chemical shifts (7.53 and 5.87 ppm, respectively) of **7** are translated upfield by 0.67 and 0.74 ppm, respectively, relative to the free ligand **6**.

The estimated dimensions of the macrocycle **5** are ~3.4 nm (34 Å) along the edge and ~4.8 nm (48 Å) diagonally.[16] For macrocycle **7** these metrical parameters are ~3.0 and ~4.3 nm, respectively; these values are reasonable since the solid-state structure of hybrid iodonium−metal macrocycle showed it to be generally planar and rigid.[5c] In light of the size of **5** and **7**, experiments aimed at imaging these nanoscale complexes by scanning tunneling microscopy are currently underway. We propose that these new organometallic macrocycles, and other similar complexes currently under investigation, will be potentially useful devices, particularly in the area of organic synthesis and organometallic catalysis.[17] Furthermore, complex **7** is of significant interest in regard to its potential nonlinear optical and electronic properties, given the presence of metal−alkynyl units and possible π-conjugation within the macrocycle frame.[18]

Acknowledgment. Financial support by the NIH (2ROCA16903) and NSF (CHE-9529093) is gratefully acknowledged. Dedicated to Prof. Zvi Rappoport on the occasion of his 60th birthday.

Supporting Information Available: The synthetic procedures for **1**, **2**, **3**, **5**, and **7**; IR, ^{1}H, $^{31}\mathrm{P}\{^1\mathrm{H}\}$, and $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra of **5** and **7**, along with the MALDI and ESI FT-ICR mass spectra of **5** (19 pages). See any current masthead for ordering and Internet access instructions.

JA962041U

---

[11] Selected data for **5**: mp 202−205 °C dec; IR (thin film; acetone-d_6; cm^{-1}) 3058 (C−H), 1393, 1435, 1480 (Ar), 1276, 1260, 1155, 1098 (OTf); ^{1}H NMR (499.8 MHz; acetone-d_6) δ 8.52 (d, 16H, partially obscured, H$_\alpha$−Py), 8.49 (d, 16H, $^3J_{\mathrm{HH}}$ 8.5, H$_\alpha$−PhI), 7.69 (d, 16H, $^3J_{\mathrm{HH}}$ 8.5, H$_\beta$−PhI), 7.18 (d, 16H, $^3J_{\mathrm{HH}}$ 6.5, H$_\beta$−Py), 6.82 (d, 16H, $^3J_{\mathrm{HH}}$ 8.0, H$_o$−Pt), 6.35 (d, 16H, $^3J_{\mathrm{HH}}$ 8.0, H$_m$−Pt); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125.7 MHz; acetone-d_6) δ 153.6 (s, C$_\alpha$−Py), 148.3 (s, C$_\gamma$−Py), 141.3 (s, C$_\gamma$−PhI), 138.6 (s, C$_\alpha$−PhI), 137.7 (s, C$_o$−Pt), 136.8 (s, C$_p$−Pt), 131.6 (s, C$_\beta$−PhI), 128.1 (t, $^2J_{\mathrm{CP}}$ 9, C$_i$−Pt), 126.3 (s, C$_m$−Pt), 124.9 (s, C$_\beta$−Py), 122.4 (q, $^1J_{\mathrm{CF}}$ 322, OTf), 116.4 (s, C$_i$−PhI); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (acetone-d_6) δ 22.5 (s, $^1J_{\mathrm{PPt}}$ 3076); $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (acetone-d_6) δ −77 (s). Anal. Calcd for $\mathrm{C_{436}H_{336}F_{36}I_4N_8O_{36}P_{16}Pt_8S_{12}}$: C, 52.92; H, 3.42; N, 1.13. Found: C, 49.40; H, 3.58; N, 1.03.

[12] Rotation about the I−C or Pt−C(alkyne) bond at both corners of the squares **5** and **7** results in time-averaged equivalency of the PPh$_3$ phosphine nuclei in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR.

[13] Bruce, J. E.; Cheng, X.; Bakhtiar, R.; Wu, Q.; Hofstadler, S. A.; Anderson, G. A.; Smith, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 7839−7847.

[14] Whiteford, J. A.; Stang, P. J. Manuscript in preparation.

[15] Selected data for **7**: mp 215−220 °C dec; IR (thin film; CD$_2$Cl$_2$; cm^{-1}) 3076, 3054 (C−H), 2119 (C≡C), 1605, 1587, 1482, 1435 (Ar), 1265, 1150, 1100, 1030 (OTf); ^{1}H NMR (300 MHz; CD$_2$Cl$_2$) 7.53 (d, $^3J_{\mathrm{HH}}$ 6.5, 16H, H$_\alpha$−Py), 6.67 (d, 16H, $^3J_{\mathrm{HH}}$ 8.1, H$_o$−Pt), 6.30 (d, 16H, $^3J_{\mathrm{HH}}$ 8.1, H$_m$−Pt), 5.87 (d, 16H, $^3J_{\mathrm{HH}}$ 6.4, H$_\beta$−Py); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125.7 MHz; CD$_2$Cl$_2$) δ 150.52 (s, C$_\alpha$−Py), 137.97 (s, C$_o$−Pt), 137.4 (br s, C$_\gamma$−Py), 136.56 (s, C$_p$−Pt), 127.80 (s, C$_\beta$−Py), 126.43 (s, C$_m$−Pt), 121.84 (q, $^1J_{\mathrm{CF}}$ 321, OTf), 122.0 (m, C≡C$_\alpha$−Pt), 107.10 (m, C$_\beta$≡C−Pt); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (CD$_2$Cl$_2$) δ 21.4 (s, 16P, $^1J_{\mathrm{PPt}}$ 3060, PPh$_3$), −5.5 (s, 8P, $^1J_{\mathrm{PPt}}$ 2198, PPh$_2$); $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (CD$_2$Cl$_2$) δ −78 (s). Anal. Calcd for $\mathrm{C_{508}H_{408}F_{24}N_8O_{24}P_{24}Pt_{12}S_8}$: C, 56.47; H, 3.81; N, 1.04. Found: C, 55.32; H, 3.89; N, 1.04.

[16] We can reasonably estimate the dimensions of **5** and **7** employing the following known structural parameters: the I to Pd distance of 11.2 Å for the hybrid iodonium−palladium square,[5c] the Pt to Pd distance for the tetranuclear macrocycle incorporating monomer **6** of 9.6 Å,[14] the 4-C to 4′-C distance of 7.1 Å for biphenyl, and the Pt−C bond length of 2.06 Å for *trans*-Pt(PPh$_3$)$_2$(Ph)Cl.[16a] (a) Conzelmann, W.; Koola, J. D.; Kunze, U.; Strähle, J. *Inorg. Chim. Acta* **1984**, *89*, 147−149.

[17] Reference 1d, Chapter 5.

[18] Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79−154 and references therein.