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18-Atom-Ringed Macrocyclic Tetra-imidazoliums for Preparation of Monomeric Tetra-carbene Complexes

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Summary: 18-Atom-ringed macrocyclic tetra-imidazolium ligands have been synthesized by a two-step procedure and are the smallest free tetra-imidazoliums to date. The structures of the tetra-imidazoliums were characterized by multinuclear NMR and high-resolution ESI/MS to distinguish them from the potential di-imidazolium species. These tetra-imidazolium ligands form monomeric tetra-carbene complexes of platinum through in situ deprotonation.

The stabilization of complexes that contain metal−ligand multiple bonds, such as oxo and nitride ligands, is dependent on the symmetry and donor strength of the auxiliary ligands bound to the transition metal.[1] Recent advancements in the preparation of iron oxos and nitrides for bioinorganic models of O_2 and N_2 activation have employed neutral tetra-dentate weak σ-donors, such as cyclam, as the auxiliary macrocyclic ligand.[2] Current research on 3-fold symmetry complexes of iron[3] and cobalt[4] has demonstrated that increasing the σ-donor strength of the auxiliary ligands stabilizes novel imido and nitride complexes. To our knowledge, few neutral tetra-dentate strong σ-donor ligands have been synthesized. In fact, few macrocyclic tetra-dentate phosphines have been prepared and isolated, due to their difficult syntheses, instability, and sensitivity to O_2.[5] Lately, N-heterocyclic carbenes (NHCs) have become a more attractive alternative to phosphines for many catalytic applications.[6] In addition to strong σ-donation, NHCs exhibit other beneficial properties, in particular their resistance to degradation in the presence of O_2.[7] This communication presents easy-to-synthesize, strong σ-donor macrocyclic tetra-NHCs that exclusively produce monomeric transition metal complexes.

Recently synthesized tetra-N-heterocyclic carbene complexes include the classes of tetra-monodentate carbenes, bis-bidentate carbenes, and macrocyclic tetra-dentate carbenes.[8] These tetra-carbene complexes have found potential applications as near-UV-phosphorescent emitters,[9] radiopharmaceuticals,[10] and catalyst precursors.[11] Yet, of these tetra-NHCs, only three examples of monomeric macrocyclic tetra-carbene complexes have been prepared, and both synthetic approaches are somewhat limited in scope. Hahn's synthesis of the first macrocyclic tetra-carbene complex requires a templating reaction on platinum.[12] In addition to requiring a tetra-isocyanide complex as a precursor to the monodentate carbene ligands, the synthesis also requires harsh reagents such as phosgene. The other two examples have been prepared from a macrocyclic tetra-imidazolium ligand, and although a few macrocyclic tetra-imidazoliums have been synthesized,[13] only one of these species has been employed as a ligand for synthesizing tetra-carbene complexes. Murphy's group was able to prepare a 24-atom-ringed tetra-imidazolium using 1,3-diiodopropane as the key dielectrophile for ring formation.[14] This tetra-carbene ligand is so large and flexible that some metal complexes are monomeric, such as palladium[14] and cobalt,[15] but others are dimeric, such as silver[14] and copper.[14] Since most NHC complexes are prepared from imidazoliums, this approach provides a wider ranging scope than templating.

Results and Discussion

We have synthesized 18-atom-ringed tetra-imidazolium macrocycles that should exclusively favor monomeric complexation. These imidazoliums were synthesized in multigram

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(1) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds: The Chemistry of Transition Metal Complexes Containing Oxo, Nitrido, Imido, Alkylidene, Or Alkylidyne Ligands*; Wiley: New York, 1988. (b) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1993**, *123*, 149.

(2) (a) Rohde, J.-U.; In, J.-H.; Lim, M. H.; Brennessel, W. W.; Bukowski, M. R.; Stubna, A.; Muenck, E.; Nam, W.; Que, L. *Science* **2003**, *299*, 1037. (b) Li, F.; England, J.; Que, L. *J. Am. Chem. Soc.* **2010**, *132*, 2134. (c) Meyer, K.; Bill, E.; Mienert, B.; Weyhermueller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **1999**, *121*, 4859. (d) Berry, J. F.; Bill, E.; Bothe, E.; DeBeer George, S.; Mienert, B.; Neese, F.; Wieghardt, K. *Science* **2006**, *312*, 1937.

(3) (a) Scepaniak, J. J.; Fulton, M. D.; Bontchev, R. P.; Duesler, E. N.; Kirk, M. L.; Smith, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 10515. (b) Vogel, C.; Heinemann, F. W.; Sutter, J.; Anthon, C.; Meyer, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 2681. (c) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 6252. (d) Brown, S. D.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 322.

(4) (a) Jenkins, D. M.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 11238. (b) Hu, X.; Meyer, K. *J. Am. Chem. Soc.* **2004**, *126*, 16322. (c) Shay, D. T.; Yap, G. P. A.; Zakharov, L. N.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1508.

(5) (a) Kyba, E. P.; Davis, R. E.; Hudson, C. W.; John, A. M.; Brown, S. B.; McPhaul, M. J.; Liu, L.-K.; Glover, A. C. *J. Am. Chem. Soc.* **1981**, *103*, 3868. (b) Kyba, E. P.; Hudson, C. W.; McPhaul, M. J.; John, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 8053. (c) Mizuta, T.; Okano, A.; Sasaki, T.; Nakazawa, H.; Miyoshi, K. *Inorg. Chem.* **1997**, *36*, 200.

(6) (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (b) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612.

(7) Strassner, T. *Top. Organomet. Chem.* **2007**, *22*, 125.

(8) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677.

(9) (a) Unger, Y.; Zeller, A.; Taige, M. A.; Strassner, T. *Dalton Trans.* **2009**, 4786. (b) Unger, Y.; Zeller, A.; Ahrens, S.; Strassner, T. *Chem. Commun.* **2008**, 3263.

(10) Quezada, C. A.; Garrison, J. C.; Tessier, C. A.; Youngs, W. J. *J. Organomet. Chem.* **2003**, *671*, 183.

(11) Lee, C.-S.; Pal, S.; Yang, W.-S.; Hwang, W.-S.; Lin, I. J. B. *J. Mol. Catal. A Chem.* **2008**, *280*, 115.

(12) Hahn, F. E.; Langenhahn, V.; Luegger, T.; Pape, T.; Le Van, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 3759.

(13) (a) Sato, K.; Onitake, T.; Arai, S.; Yamagishi, T. *Heterocycles* **2003**, *60*, 779. (b) Shi, Z.; Thummel, R. P. *J. Org. Chem.* **1995**, *60*, 5935. (c) Wong, W. W. H.; Vickers, M. S.; Cowley, A. R.; Paul, R. L.; Beer, P. D. *Org. Biomol. Chem.* **2005**, *3*, 4201.

(14) McKie, R.; Murphy, J. A.; Park, S. R.; Spicer, M. D.; Zhou, S.-Z. *Angew. Chem., Int. Ed.* **2007**, *46*, 6525.

(15) Park, S. R.; Findlay, N. J.; Garnier, J.; Zhou, S.; Spicer, M. D.; Murphy, J. A. *Tetrahedron* **2009**, *65*, 10756.

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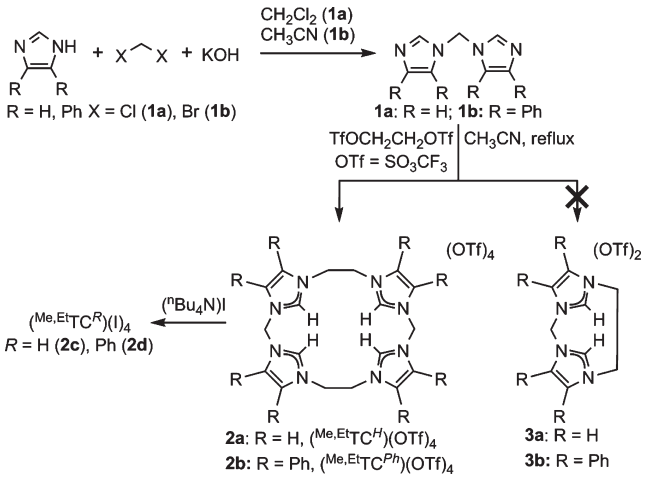
Scheme 1



quantities using a simple two-step process starting from commercially available imidazoles and without the use of dilute solvent conditions (Scheme 1). We prepared 1,1′-methylene(bis-imidazole) (**1a**) using the methods of Diez-Barra[16] and Claramunt.[17] We synthesized 1,1′-methylenebis(4,5-diphenylimidazole) (**1b**) in high yield by adding dibromomethane to a basic solution of 4,5-diphenylimidazole in acetonitrile (Scheme 1). Although previous syntheses of macrocyclic tetra-imidazolium species have employed dihaloalkanes or dihaloxylenes as the key dielectrophile for ring formation,[13,14] we were unsuccessful in our attempts at similar reactions to produce smaller sized macrocycles with reagents such as diiodomethane and 1,2-diiodoethane. However, utilizing the stronger dielectrophile 1,2-bis(trifoxy)ethane[18] allowed us to prepare the 18-atom-ringed macrocyclic tetra-imidazoliums, $(^{Me,Et}TC^{H})(OTf)_4$ (**2a**) and $(^{Me,Et}TC^{Ph})(OTf)_4$ (**2b**), shown in Scheme 1, each in greater than 15% yield and within 3 days. We were then able to exchange the counteranions from triflates to iodides by mixing **2a** and **2b** with excess $(^{n}Bu_4N)I$ in an acetonitrile solution to yield $(^{Me,Et}TC^{H})(I)_4$ (**2c**) and $(^{Me,Et}TC^{Ph})(I)_4$ (**2d**), respectively.

One challenge in these syntheses is distinguishing between the di-imidazolium species (**3**) shown in Scheme 1 and the desired macrocyclic species (**2**) since they are often synthesized concurrently.[13b,14] ^1H and ^{13}C NMR for the white solids formed were consistent with imidazolium formation, and although this evidence was not sufficient to distinguish between **2** and **3**,[19] high-resolution ESI/MS conclusively confirmed the formation of **2**, as opposed to **3**. The ESI/MS spectrum exhibited peaks at *m*/*z* 167.1 and 799.1 (Figure 1), which are associated with $\{(^{Me,Et}TC^{H})(OTf)\}^{3+}$ and $\{(^{Me,Et}TC^{H})(OTf)_3\}^{+}$, respectively, and are unique to **2a**. In addition, the peak at *m*/*z* 325.1 exhibited isotopomers that were 1/2 of a mass unit apart, which is consistent with $\{(^{Me,Et}TC^{H})(OTf)_2\}^{2+}$ from **2a** and not with the 1+ ion of **3a**-OTf. The ratio of the isotopomers at *m*/*z* 325.1 is consistent with only **2a** and not a mixture of **2a** and **3a**. Furthermore, no peak was found at *m*/*z* 88.1, which would match the 2+ ion of **3a**-2OTf. Combined, these data demonstrate that only the macrocyclic 18-atom ring, **2a**, was isolated from the reaction. Similar data were obtained from the ESI/MS for **2b**.

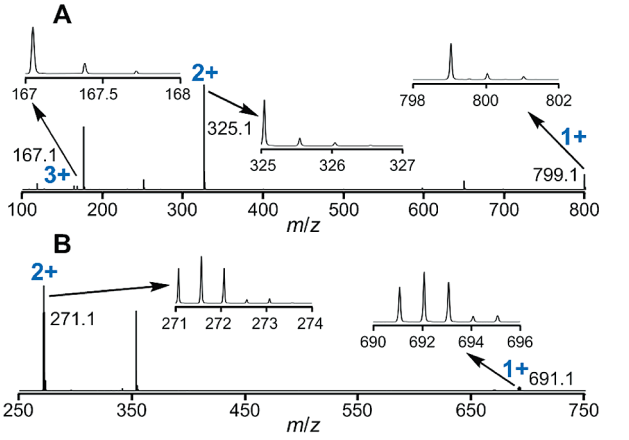
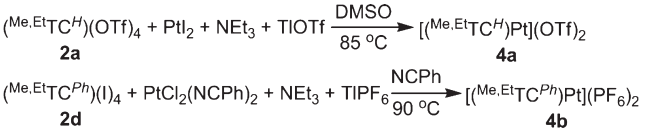


Figure 1. Example electrospray ionization mass spectrum measured for an acetonitrile solution of **2a** (A) and **4a** (B). (A) The insets show highlights for the $\{(^{Me,Et}TC^{H})(OTf)\}^{3+}$, $\{(^{Me,Et}TC^{H})(OTf)_2\}^{2+}$, and $\{(^{Me,Et}TC^{H})(OTf)_3\}^{+}$ ions, which are denoted as "3+", "2+", and "1+", respectively. (B) The insets show highlights for the $[(^{Me,Et}TC^{H})Pt]^{2+}$ and $\{[(^{Me,Et}TC^{H})Pt](OTf)\}^{+}$ ions, which are denoted as "2+" and "1+", respectively.

Scheme 2



To test the ability of **2** to form monomeric metal complexes, we synthesized platinum complexes (Scheme 2). Bis-bidentate platinum[9,10] and palladium[20] carbene complexes that are similar in size to **4** have been prepared previously via in situ deprotonation with a weak base from the free imidazolium ligands. Thallium salts were employed in the reaction to remove any iodide ions and prevent anion confusion during purification. Spectroscopic characterization of **4** was consistent with a tetracarbene complex. The ESI/MS of **4a** (Figure 1) shows peaks at *m*/*z* 271.1 and 691.1 that are associated with $[(^{Me,Et}TC^{H})Pt]^{2+}$ and $\{[(^{Me,Et}TC^{H})Pt](OTf)\}^{+}$, respectively. The geminal AB splitting pattern in the ^1H NMR of the protons on the methylene position on **4a** demonstrates the rigidity of the ligand in solution,[9,20b] which is in direct contrast to Murphy's complex.[14] The ^{13}C NMR of **4a** is consistent with NHC formation with the carbene peak at 158 ppm, for which platinum satellites could be observed with a $^{195}Pt-C$ coupling constant of 942 Hz.[12] Similar NMR and ESI/MS data were obtained for **4b**, although the platinum satellites on the carbene carbon in the ^{13}C NMR could not be resolved. To confirm the conformation of **4**, a single crystal of **4b** was examined and a structure demonstrating connectivity of the macrocyclic ligand was obtained (Figure 2). The X-ray structure corroborates the high-resolution ESI/MS evidence for **2** that demonstrates that these species are indeed macrocycles.

In conclusion, we have demonstrated a facile, two-step synthesis of 18-atom-ringed tetra-imidazolium ligands that employed 1,2-bis(trifoxy)ethane as the key dielectrophile. The ligands can be prepared on a multigram scale quickly

(16) Diez-Barra, E.; De la Hoz, A.; Sanchez-Migallon, A.; Tejeda, J. *Heterocycles* **1992**, *34*, 1365.
(17) Claramunt, R. M.; Elguero, J.; Meco, T. *J. Heterocycl. Chem.* **1983**, *20*, 1245.
(18) Lindner, E.; Von Au, G.; Eberle, H. J. *Chem. Ber.* **1981**, *114*, 810.
(19) Tapu, D.; Dixon, D. A.; Roe, C. *Chem. Rev.* **2009**, *109*, 3385.
(20) (a) Fehlhammer, W. P.; Bliss, T.; Kernbach, U.; Bruedgam, I. *J. Organomet. Chem.* **1995**, *490*, 149. (b) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G.; Spiegler, M. *J. Organomet. Chem.* **1999**, *575*, 80.

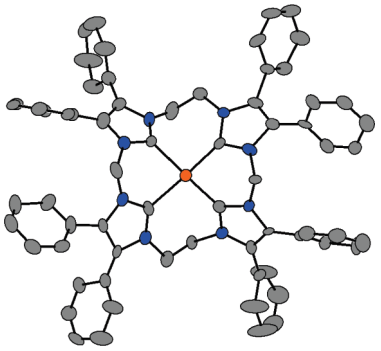


Figure 2. Crystal structure of [($^{Me,Et}TC^{Ph}$)Pt](PF_6)$_2$ (**4b**). Orange, blue, and gray ellipsoids (50% probability) represent Pt, N, and C, respectively. Counteranions, solvent molecules, and hydrogens have been omitted for clarity.

and cleanly without the use of dilute solvent conditions. These 18-atom-ringed tetra-imidazoliums (**2**) ligate to form monomeric transition metal complexes such as **4**. Future research will evaluate the catalytic properties of complexes supported by **2**.

Experimental Section

Syntheses of organic compounds were performed under normal atmospheric conditions. Syntheses of platinum complexes were performed under a dry nitrogen atmosphere with the use of either a drybox or standard Schlenk techniques. Solvents were dried on an Innovative Technologies (Newburgport, MA) Pure Solv MD-7 solvent purification system and degassed by three freeze−pump−thaw cycles on a Schlenk line to remove O_2 prior to use. DMSO-d_6, acetonitrile-d_3, and chloroform-d were degassed by three freeze−pump−thaw cycles prior to drying over activated molecular sieves. These NMR solvents were then stored under N_2 in a glovebox. The compounds 1,1′-methylene(bis-imidazole) (**1a**)[16,17] and 1,2-diylbis(trifluoromethanesulfonate)ethane (also called 1,2-bis(trifoxy)ethane)[18] were prepared as described previously. All other reagents were purchased from commercial vendors and used without purification. ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra were recorded at ambient temperature on a Varian Mercury 300 MHz or a Varian INOVA 600 MHz narrow-bore broadband system. ^{1}H and ^{13}C NMR chemical shifts were referenced to the residual solvent. ^{19}F NMR chemical shifts are reported relative to an external standard of neat $CFCl_3$. All mass spectrometry analyses were conducted at the Mass Spectrometry Center located in the Department of Chemistry at the University of Tennessee. The DART analyses were performed using a JEOL AccuTOF-D time-of-flight (TOF) mass spectrometer with a DART (direct analysis in real time) ionization source from JEOL USA, Inc. (Peabody, MA). The ESI/MS analyses were performed using a QSTAR Elite quadrupole time-of-flight (QTOF) mass spectrometer with an electrospray ionization source from AB Sciex (Concord, Ontario, Canada). All mass spectrometry sample solutions were prepared in acetonitrile. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance. Carbon, hydrogen, and nitrogen analyses were obtained from Atlantic Microlab, Norcross, GA.

Synthesis of 1,1′-Methylenebis(4,5-diphenylimidazole), 1b. 4,5-Diphenylimidazole (13.2 g, 0.0610 mol) and potassium hydroxide powder (5.0 g, 0.089 mol) were added to a 240 mL glass jar with a Teflon lid and dissolved with 100 mL of acetonitrile and stirred for 15 min. Dibromomethane (5.2 g, 0.030 mol) was then diluted with 3 mL of acetonitrile, and this solution was slowly added to the glass jar. The reaction was then stirred for 72 h. After the reaction was complete, 16 mL of ice cold water was added to the mixture and stirred for an additional 15 min, which precipitated a white solid. The white solid was collected over a 150 mL medium sintered-glass frit and dried under reduced pressure to give the product (12 g, 89% yield). ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 7.51 (m, 6H), 7.40 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 4H), 7.19 (m, 10H), 6.77 (s, 2H), 5.73 (s, 2H). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 139.1, 136.7, 133.8, 131.1, 129.8, 129.7, 129.6, 128.3, 127.4, 126.9, 126.6, 53.1. IR (neat): 3059, 1600, 1500, 1442, 1357, 1304, 1231, 1193, 1072, 1017, 950, 922, 790, 774 cm^{-1}. DART MS (m/z): [M − H]$^+$ 453.3. Anal. Calcd for $C_{31}H_{24}N_4$: C, 82.27; H, 5.35; N, 12.38. Found: C, 82.11; H, 5.21; N, 12.19.

Synthesis of 3,9,14,20-Tetraaza-1,6,12,17-tetraazoniapentacyclohexacosane-1(23),4,6(26),10,12(25),15,17(24),21-octaene Tetra-trifluoromethanesulfonate ($^{Me,Et}TC^{H}$)(OTf)$_4$), 2a. 1,1′-Methylene(bisimidazole) (**1a**) (7.39 g, 0.0499 mol) was dissolved in acetonitrile (220 mL) in a 500 mL round-bottom flask, and 1,2-diylbis(trifluoromethanesulfonate)ethane (16.3 g, 0.0499 mol) was then slowly added into the stirring solution. The solution was heated to reflux and stirred for 2 days. The solution was then filtered hot through a 60 mL fine sintered-glass frit, and a white solid was collected. The white solid was then dried under reduced pressure to give the product (3.73 g, 15.8% yield). ^{1}H NMR (DMSO-d_6, 300.1 MHz): δ 8.99 (s, 4H), 8.07 (s, 4H), 7.87 (s, 4H), 6.52 (s, 4H), 4.80 (s, 8H). ^{13}C NMR (DMSO-d_6, 75.46 MHz): δ 137.7, 123.6, 123.1, 120.7 (q, J_{FC} = 322 Hz), 58.5, 48.9. ^{19}F NMR (DMSO-d_6, 282.3 MHz): δ −77.1. IR (neat): 3110, 1578, 1553, 1369, 1273, 1247, 1226, 1150, 1075, 1028, 886, 858, 774, 724 cm^{-1}. ESI/MS (m/z): [M − OTf]$^+$ 799.1, [M − 2OTf]$^{2+}$ 325.0, [M − 3OTf]$^{3+}$ 167.1. Anal. Calcd for $C_{22}H_{24}F_{12}N_8O_{12}S_4$: C, 27.85; H, 2.55; N, 11.81. Found: C, 27.92; H, 2.47; N, 11.74.

Synthesis of 4,5,10,11,15,16,21,22-Octaphenyl-3,9,14,20-tetraaza-1,6,12,17-tetraazoniapentacyclohexacosane-1(23),4,6(26),10,12(25),15,17(24),21-octaene Tetra-trifluoromethanesulfonate ($^{Me,Et}TC^{Ph}$)(OTf)$_4$), 2b. 1,1′-Methylenebis(4,5-diphenylimidazole) (**1b**) (10.0 g, 0.0222 mol) was added to a 500 mL round-bottom flask, dissolved with acetonitrile (175 mL), and stirred for 20 min. 1,2-Diylbis(trifluoromethanesulfonate)ethane (7.23 g, 0.0222 mol) was diluted with acetonitrile (5 mL) and pipetted into the round-bottom flask. The reaction mixture was heated to reflux for 72 h. After cooling to room temperature, a white solid was collected by slowly pouring the solution over a 150 mL medium sintered-glass frit a few milliliters at a time. Each aliquot was filtered through before adding the next one. This slow filtration yielded the product, which was dried under reduced pressure (3.25 g, 18.9% yield). ^{1}H NMR (DMSO-d_6, 300.1 MHz): δ 10.02 (s, 4H), 7.46 (m, 16H), 7.29 (t, J = 7.2 Hz, 8H), 7.18 (d, J = 6.0 Hz, 8H), 7.00 (d, J = 6.9 Hz, 8H), 6.61 (s, 4H), 4.68 (s, 8H). ^{13}C NMR (DMSO-d_6, 75.46 MHz): δ 136.8, 132.7, 132.3, 131.0, 130.7, 130.2, 129.4, 129.3, 123.2, 122.4, 120.6 (q, J_{F-C} = 322 Hz), 56.0, 46.8. ^{19}F NMR (DMSO-d_6, 282.3 MHz): δ −77.8. IR (neat): 3145, 3067, 1560, 1445, 1372, 1336, 1278, 1254, 1241, 1226, 1177, 1027, 765 cm^{-1}. ESI/MS (m/z): [M − OTf]$^+$ 1407.2, [M − 2OTf]$^{2+}$ 629.2, [M − 3OTf]$^{3+}$ 369.8. Anal. Calcd for $C_{70}H_{56}F_{12}N_8O_{12}S_4$: C, 53.98; H, 3.62; N, 7.19. Found: C, 53.84; H, 3.47; N, 7.37.

Synthesis of 3,9,14,20-Tetraaza-1,6,12,17-tetraazoniapentacyclohexacosane-1(23),4,6(26),10,12(25),15,17(24),21-octaene Tetraiodide ($^{Me,Et}TC^{H}$)(I)$_4$), 2c. In a 120 mL jar with a Teflon lid, acetonitrile (70 mL) and ($^{Me,Et}TC^{H}$)(OTf)$_4$ (**2a**) (3.12 g, 0.00329 mol) were added and stirred. DMSO (14 mL) was added dropwise until all of the solids dissolved. Tetrabutylammonium iodide (12.2 g, 0.0329 mol) was then dissolved in acetonitrile (25 mL) in a 100 mL beaker. The tetrabutylammonium iodide solution was poured into the 120 mL jar, immediately forming a white precipitate. The acetonitrile mixture stirred overnight, and the white solid was collected on a 60 mL fine sintered-glass frit. The white solid was subsequently washed with THF (2 × 30 mL) and acetonitrile (1 × 30 mL) on the 60 mL fine sintered-glass frit. The white solid was then dried under reduced pressure to yield the product (2.28 g, 80.5% yield). ^{1}H NMR (DMSO-d_6, 300.1 MHz): δ 9.11 (s, 4H), 8.11 (s, 4H), 7.91 (s, 4H), 6.58 (s, 4H), 4.84 (s, 8H). ^{13}C NMR (DMSO-d_6, 75.46 MHz): δ 137.6, 123.5,

123.0, 58.4, 48.7. IR (neat): 3094, 3023, 1563, 1550, 1441, 1327, 1170, 1153, 1022, 824, 764, 750, 728 cm^{-1}. Anal. Calcd for $C_{18}H_{24}I_4N_8$: C, 25.14; H, 2.81; N, 13.03. Found: C, 25.09; H, 3.07; N, 12.39.

Synthesis of 4,5,10,11,15,16,21,22-Octaphenyl-3,9,14,20-tetraaza-1,6,12,17-tetraazoniapentacyclohexacosane-1(23),4,6(26),10,12(25),15,17(24),21-octaene Tetraiodide ($(^{Me,Et}TC^{Ph})(I)_4$), 2d. $(^{Me,Et}TC^{Ph})(OTf)_4$ (**2b**) (9.36 g, 0.00602 mol) was added as a solid to an acetonitrile (300 mL) solution of tetrabutylammonium iodide (8.89 g, 0.0241 mol) in a 500 mL Erlenmeyer flask. This mixture was stirred overnight, and the white solid was collected on a 150 mL medium sintered-glass frit and dried under reduced pressure to yield the pure product (8.84 g, 93.7% yield). ^{1}H NMR (DMSO-d_6, 300.1 MHz): δ 10.65 (s, 4H), 7.59 (d, J = 6.6 Hz, 8H), 7.47 (m, 24 H), 7.21 (d, J = 7.5 Hz, 8H), 6.97 (s, 4H), 4.75 (s, 8H). ^{13}C NMR (DMSO-d_6, 75.46 MHz): δ 136.0, 133.2, 132.2, 131.7, 131.5, 131.2, 131.1, 129.6, 129.5, 123.8, 123.4, 57.7, 46.5. IR (neat): 2964, 1561, 1488, 1446, 1373, 1252, 1215, 1030, 759 cm^{-1}. Anal. Calcd for $C_{66}H_{56}I_4N_8$: C, 53.97; H, 3.84; N, 7.63. Found: C, 52.33; H, 3.89; N, 7.26.

Synthesis of $[(^{Me,Et}TC^{H})Pt](OTf)_2$, 4a. $(^{Me,Et}TC^{H})(OTf)_4$ (**2a**) (0.174 g, 0.184 mmol) was dissolved in DMSO (1 mL) in a 20 mL vial. Platinum(II) iodide (0.0824 g, 0.184 mmol) was dissolved in 1 mL of DMSO and was added to the $(^{Me,Et}TC^{H})(OTf)_4$ solution. Triethylamine (0.0762 g, 0.753 mmol) was then added to the reaction mixture. This solution was heated to 85 °C and stirred for 48 h. After the reaction mixture was removed from the heat and allowed to cool to room temperature, thallium(I) trifluoromethanesulfonate (0.130 g, 0.367 mmol) was dissolved in DMSO (1 mL) and was added to the reaction mixture. This mixture was stirred for 15 min and then filtered over Celite to remove thallium(I) iodide. DMSO was then removed under reduced pressure to leave the crude solid. The crude solid was washed with THF (3 × 10 mL) and dried under reduced pressure, leaving a white solid. To further purify the white solid, it was dissolved in acetonitrile (2 mL), and the resulting solution was then filtered over Celite and crystallized via vapor diffusion of ether into the acetonitrile solution. White crystals were collected and dried under reduced pressure to give the pure product (0.0715 g, 46.3% yield). ^{1}H NMR (DMSO-d_6, 300.1 MHz): δ 7.68 (d, J = 1.8 Hz, 4H), 7.57 (d, J = 2.1 Hz, 4H), 6.40 (d, J = 12.9 Hz, 2H), 5.95 (d, J = 13.5 Hz, 2H), 4.86 (m, 4H), 4.61 (m, 4H). ^{13}C NMR (DMSO-d_6, 150.9 MHz): δ 157.8 (s and Pt satellites, J_{Pt-C} = 942 Hz for ^{195}Pt (^{195}Pt = 33.8% abundance)), 123.3, 121.6, 120.6 (q, J_{F-C} = 322 Hz), 62.5, 48.7. ^{19}F NMR (DMSO-d_6, 282.3 MHz): δ −77.0. IR (neat): 3131, 1574, 1428, 1244, 1224, 1152, 1026, 857, 812, 757, 707 cm^{-1}. ESI/MS (m/z): $[M - OTf]^+$ 692.1, $[M - 2OTf]^{2+}$ 271.6. Anal. Calcd for $C_{20}H_{20}F_6N_8O_6PtS_2$: C, 28.54; H, 2.40; N, 13.31. Found: C, 28.67; H, 2.21; N, 13.16.

Synthesis of $[(^{Me,Et}TC^{Ph})Pt](PF_6)_2$, 4b. $(^{Me,Et}TC^{Ph})(I)_4$ (**2d**) (0.153 g, 0.104 mmol) was dissolved in benzonitrile (10 mL) in a 20 mL vial. Dichlorobis(benzonitrile)platinum(II) (0.0492 g, 0.104 mmol) was dissolved in 2 mL of benzonitrile and was added to the $(^{Me,Et}TC^{Ph})(I)_4$ solution. Triethylamine (0.0528 g, 0.521 mmol) was then added to the reaction mixture. This solution was heated to 90 °C and stirred for 24 h. After the reaction mixture was removed from the heat and allowed to cool to room temperature, thallium(I) hexafluorophosphate (0.219 g, 0.626 mmol) was dissolved in benzonitrile (2 mL), added to the reaction mixture, and stirred for 24 h. The reaction mixture was then filtered over Celite to remove thallium(I) iodide. Benzonitrile was then removed under reduced pressure to leave the crude solid. The crude solid was dissolved in acetone (5 mL) and filtered over Celite. The product was crystallized via vapor diffusion of ether into the acetone solution. The collected crystals were washed with methylene chloride (2 mL) and diethyl ether (3 × 10 mL) (0.010 g, 6.6% yield). ^{1}H NMR (DMSO-d_6, 300.1 MHz): δ 7.45 (m, 16H), 7.39 (t, J = 7.9 Hz, 8H), 7.25 (t, J = 7.7 Hz, 8H), 7.13 (d, J = 7.1 Hz, 8H), 6.14 (d, J = 14.1 Hz, 2H), 5.72 (d, J = 14.2 Hz, 2H), 4.79 (m, 4H), 4.5 (m, 4H). ^{13}C NMR (DMSO-d_6, 150.9 MHz): δ 158.8, 132.2, 131.1, 130.9, 130.2, 129.8, 129.7, 128.9, 128.8, 126.0, 125.3, 58.1, 46.8. ^{19}F NMR (DMSO-d_6, 282.3 MHz): δ −70.1 (d, J = 711 Hz). IR (neat): 1489, 1467, 1404, 1369, 1235, 828, 786, 766, 735 cm^{-1}. ESI/MS (m/z): $[M - PF_6]^+$ 1297.34, $[M - 2PF_6]^{2+}$ 576.19. Anal. Calcd for $C_{66}H_{52}F_{12}N_8P_2Pt$: C, 54.97; H, 3.63; N, 7.77. Found: C, 54.69; H, 3.54; N, 7.79.

X-ray Structure Determinations. X-ray diffraction measurements were performed on single crystals coated with Paratone oil and mounted on Kaptan loops. Each crystal was frozen under a stream of N_2 while data were collected on a Bruker APEX diffractometer. A matrix scan using at least 20 centered reflections was used to determine initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT 4.05. Absorption corrections, including odd and even ordered spherical harmonics, were performed using SADABS. Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structure. The structure was solved by Patterson maps with the aid of successive difference Fourier maps and was refined against all data using the SHELXTL 5.0 software package. The structure of **4b** was solved in the space group *Cc*. The crystal suffered from twinning, which led to a lower quality structure. Despite repeated attempts with different solvent combinations, we were unable to grow crystals that did not exhibit twinning. The carbon, nitrogen, platinum, and phosphorus atoms were refined anisotropically, while the disordered fluorine atoms were refined isotropically. Three of the fluorine atoms (F4, F7, and F11) were split equally over two positions to improve the electron density model of the PF_6's. The solvent molecules in the unit cell were modeled as ethers. They are disordered and were refined isotropically.

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Supporting Information Available: X-ray crystallographic files (CIF). These materials are available free of charge via the Internet at http://pubs.acs.org.