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Transition Metal Based Cationic Molecular Boxes. Self-Assembly of Macrocyclic Platinum(II) and Palladium(II) Tetranuclear Complexes†

Peter J. Stang* and Danh H. Cao

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

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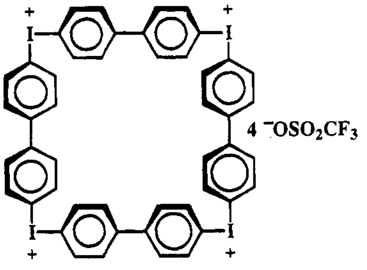
Host–guest chemistry,[1] inclusion phenomena,[2] and noncovalent molecular interactions[3] are fundamental problems at the frontiers of both organic and inorganic chemistry.[4] The vast majority of currently known hosts are reasonably flexible organic molecules such as calixarenes, crown ethers, cyclophanes, cyclodextrins, and related species that preferentially bind cationic guests.[1,2] Considerably less is known about both more rigid inorganic or organometallic hosts and anion selective hosts and inclusion phenomena.[5-7]

We recently reported[8] the preparation of the macrocyclic tetraaryl tetraiodonium species, **1**, a novel cationic molecular box. This prompted us to examine the possible formation of other related macrocyclic, cationic, rigid box-like structures with unique, approximately 90°, bond angles. In this communication we report the preparation and characterization, via self-assembly, of platinum- and palladium-based cationic, tetranuclear, macrocyclic complexes.



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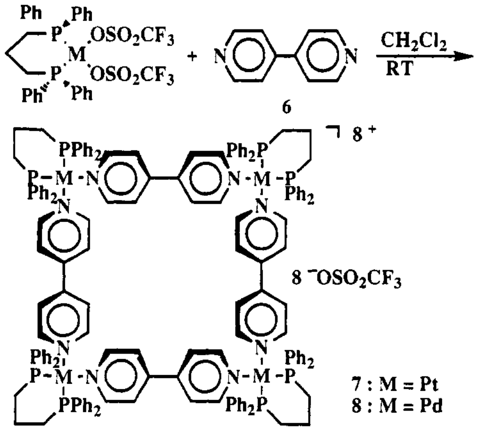
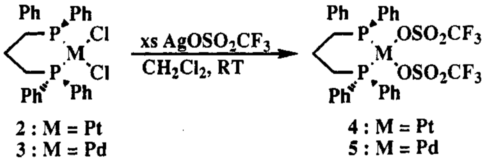
Chelation of $PtCl_2$ or $PdCl_2$ with 1,3-bis(diphenylphosphino)propane (dppp) by standard procedures results in complexes **2** and **3**, respectively. Interaction of these metal(II) dichlorides with AgOTf gives, after workup, the related triflate complexes, **4** and **5**. Reaction of triflate complexes **4** and **5** with an equimolar amount of 4,4′-bipyridine, **6**, in CH_2Cl_2 at room temperature results in the formation of molecular boxes **7** and **8** (Scheme 1), via self-assembly in a matter of minutes, in excellent isolated yields.

Scheme 1





The Pt complex **7** is a clear, colorless solid, and the Pd complex **8** is an off-white solid. Both compounds are air-stable, robust, microcrystalline solids highly soluble in such organic solvents as CH_2Cl_2, $CHCl_3$, CH_3NO_2, EtOH, MeOH, and acetone, but insoluble in ether, hexane, pentane, benzene, toluene, CH_3CN, and H_2O.

These cationic, macrocyclic, tetranuclear, triflate complexes are characterized by analytical, spectral (Table 1), and chemical means. Specifically, the elemental analyses are consistent with the respective compositions of **7** and **8**.[9] Both the $^{31}P\{^1H\}$ and ^{19}F spectra display sharp singlets as expected for the highly symmetrical boxes, **7** and **8**. The $^{31}P\{^1H\}$ signals for **7** and **8** are shifted about 6 and 11 ppm, respectively, relative to the precursor metal(II) triflates **4** and **5**. Particularly diagnostic for the macrocyclic tetranuclear complexes **7** and **8** are the respective ^1H and $^{13}C\{^1H\}$ NMR spectra. The methylene signals of the chelating dppp unit are downfield, as expected for the cationic species, **7** and **8**, relative to the neutral precursors, **4** and **5**. Most importantly, the coordinated 4,4′-bipyridine ligands in **7** and **8** display only two signals in the proton NMR, as predicted for these symmetrical systems, at 9.0 and 6.9 ppm, compared to 8.7 and 7.5 ppm for the uncoordinated 4,4′-bipyridine starting material. The unusual upfield shift of H_β of the bipyridyl units is likely due to the shielding provided by the dppp phenyl rings in the macroring as seen in Figure 1 for **12**. Integration of the proton signals is consistent with the requirements for **7** and **8**.

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† Dedicated to Professor Donald J. Cram on the occasion of his 75th birthday.

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(9) Compound **7**. Anal. Calcd for $Pt_4C_{156}H_{136}P_8S_8N_8O_{24}F_{24}\cdot 2CH_2Cl_2$: C, 42.96; H, 3.19; N, 2.54; S, 5.81. Found: C, 42.90; H, 3.34; N, 2.59; S, 5.83. Compound **8**. Anal. Calcd for $Pd_4Cl_{156}H_{136}P_8S_8N_8O_{24}F_{24}\cdot 2CH_2Cl_2$: C, 46.71; H, 3.74; N, 2.76; S, 6.31. Found: C, 46.53; H, 3.56; N, 2.79; S, 6.48.

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Table 1. Physical and Spectral Data for Compounds **4**, **5**, **7**, and **8**

compd	yield, %	mp, °C	IR[a]	^{1}H[b]	^{13}C{^{1}H}[b]	^{31}P{^{1}H}[b,c]	^{19}F[b,d]
4	98	148–150 dec	3043, 2962, 1290, 1170, 1102, 1031 (all OTf)	7.6–7.4 (m, 20H), 2.7 (m, 4H), 2.2 (m, 2H)	133.3 (C_o), 133.2 (C_p), 129.8 (C_m), 123.6 (C_{ipso}), 120.0 (q, OTf, J_{C-F} = 317 Hz), 23.5 (P(CH$_2$)), 18.7 (CH$_2$)	–6.9 (s, J_{Pt-P} = 3726 Hz)	–77
5	92	189–190 dec	3062, 2920, 1274, 1168, 1098, 1019 (all OTf)	7.6–7.4 (m, 20H), 2.7 (m, 4H), 2.3 (m, 2H)	133.6 (C_o), 133.3 (C_p), 129.7 (C_m), 123.9 (C_{ipso}), 120.2 (q, OTf, J_{C-F} = 317 Hz), 23.3 (P(CH$_2$)), 18.6 (CH$_2$)	20.0 (s)	–76
7	87	288–290 dec	3053, 2966, 1262, 1156, 1102, 1028 (all OTf)	9.0 (m, H_α, 16H), 7.7 (bs, 36H), 7.4 (bs, 44H), 6.9 (m, H_β, 16H), 3.3 (bs, 16H), 2.3 (m, 8H)	151.8 (C_α), 146.0 (C_γ), 133.5 (C_o), 132.4 (C_p), 129.6 (C_m), 124.6 (C_{ipso}), 125.0 (C_β), 121.3 (q, OTf, J_{C-F} = 319 Hz), 21.5 (P(CH$_2$)), 18.0 (CH$_2$)	–12.9 (s, J_{Pt-P} = 3041 Hz)	–76
8	96	208–210 dec	3096, 3059, 1249, 1156, 1099, 1028 (all OTf)	9.0 (m, H_α, 16H), 7.6 (bs, 36H), 7.3 (m, 44H), 6.9 (m, H_β, 16H), 3.2 (m, 16H), 2.3 (m, 8H)	151.6 (C_α), 145.8 (C_γ), 133.4 (C_o), 132.3 (C_p), 129.7 (C_m), 125.3 (C_{ipso}), 124.0 (C_β), 121.3 (q, OTf, J_{C-F} = 319 Hz), 21.6 (P(CH$_2$)), 18.0 (CH$_2$)	9.4 (s)	–78

[a] Thin film CCl$_4$, cm^{-1}. [b] All chemical shifts in CD$_2$Cl$_2$. [c] Referenced to external 85% H$_3$PO$_4$ at 0.0 ppm. [d] Referenced to external CFCl$_3$ at 0.0 ppm.

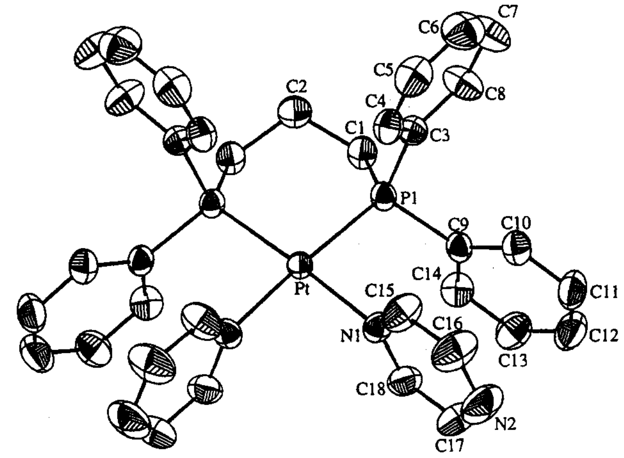
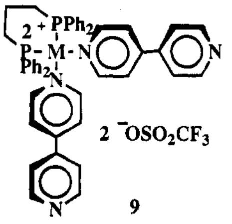


Figure 1. ORTEP diagram of **12**.

Interestingly, attempts to isolate possible precursors, such as **9** or **10**, or to observe them by NMR spectroscopy have to date been unsuccessful. This implies that the second and subsequent steps of this interesting self-assembly process are kinetically faster than the first step. In contrast, reaction of pyrazine, **11**, with either **4** or **5** gives exclusively the respective monomers, **12** and **13**. Attempts to force the reaction (by longer reaction time or higher temperature) of **4** or **5** with **11** still results only in the formation of **12** and **13** with no detectable amount (by NMR) of any macrocyclic, tetranuclear species analogous to **7** and **8**. Likewise, the reaction of equimolar amounts of **12** or **13** with **4** and **5**, even under forcing conditions, results in only reisolated starting materials or decomposition products (under extreme conditions). The structures of **12** and **13** are established by spectral means and confirmed by single-crystal X-ray structure[10] determinations. We attribute the inability of pyrazine to form macrocyclic, tetranuclear boxes, in contrast to 4,4′-bipyridine, to both electronic and steric factors. Because of direct charge delocalization of **12** and **13**, the nucleophilicity of the second nitrogen is diminished in these species as compared to the second nitrogen in 4,4′-bipyridine. More plausible is the steric interaction of the phenyl groups on the chelating dppp ligand, which in the case of the much smaller pyrazine moiety impede the approach of a second dppp-chelated metal center, therefore preventing the formation of the tetranuclear complex. This conjecture is clearly evident from the X-ray structure of **12** (Figure 1).



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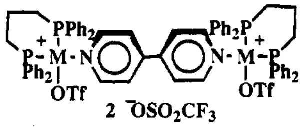

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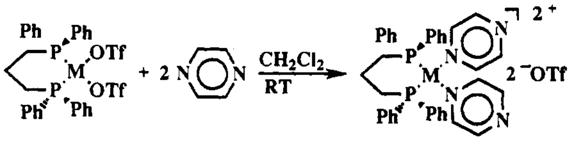

4 : M = Pt
5 : M = Pd

11

12 : M = Pt
13 : M = Pd

Finally, very preliminary data indicate that both the methyl and aromatic protons as well as the carbons of 1,3,5-trimethoxybenzene experience some concentration dependent upfield shifts in the ^{1}H and ^{13}C{^{1}H} NMR, respectively, in the presence of either **7** or **8**. These results suggest noncovalent host–guest type interactions with the 1,3,5-trimethoxybenzene presumably inside the macrocyclic boxes of **7** and **8**.

In summary, charged, macrocyclic, tetranuclear Pt(II) and Pd(II) molecular boxes were prepared in high isolated yields, via self-assembly of readily available precursors. These stable, highly organic soluble species nicely compliment the somewhat related water soluble systems of Fujita and Ogura[6] and the very recently reported metal analogue of calix[4]arene.[11] Molecular boxes of type **1** as well as **7** and **8** are under active investigation and will be the subject of future reports.

Acknowledgment. Financial support by the NSF (CHE-9101767) is gratefully acknowledged.

Supplementary Material Available: ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra of both **7** and **8** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) Crystal data for **12**: PtC$_{38}$H$_{36}$P$_2$S$_2$Cl$_2$N$_4$F$_6$S$_6$; M = 1150.80, monoclinic, space group $P2_1/m$ (No. 11); a = 11.116(2) Å, b = 14.563(2) Å, c = 13.921(2) Å, β = 98.67(2)°; V = 2227.59 Å^3; D_{calcd} = 1.716 g cm^{-3}; Z = 2. $R(F)$ = 0.0289, $R_w(F)$ = 0.0332. Complete structural data have been deposited at Cambridge Crystallographic Data Centre.

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