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Hybrid, Iodonium–Transition Metal, Cationic Tetranuclear Macrocyclic Squares†

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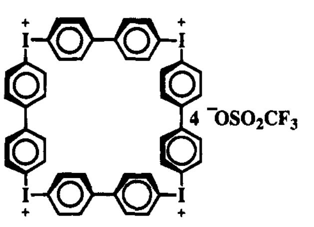
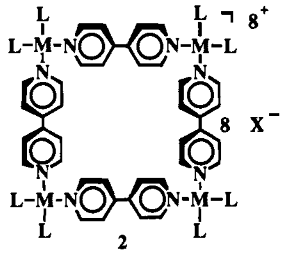
There is considerable current interest in conformationally rigid, tetranuclear, macrocyclic ring systems with approximately 90° bond angles.[1–7] To date, two different types of macrocyclics have been reported: one type with covalent bonds and a main group element, iodine,[6] at the corners, **1**, and the other type with transition metals[1–5] at the corners held by chelating ligands as illustrated by **2**. In this communication, we report the first example of hybrid main group iodonium–transition metal macrocyclic squares.



1

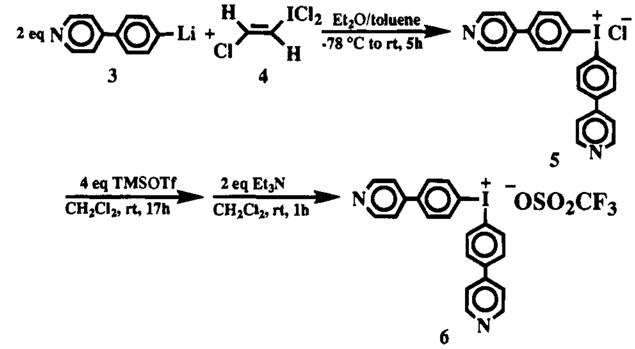


2

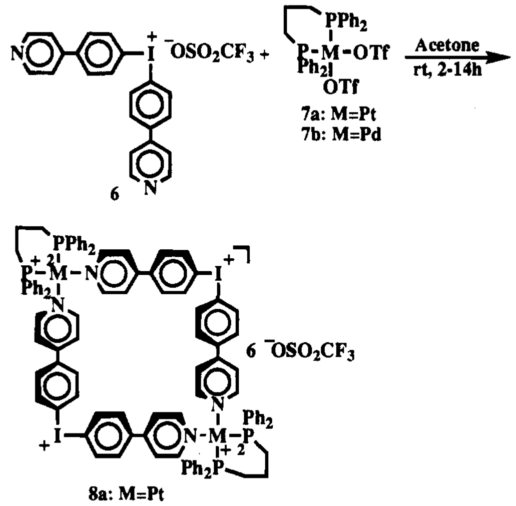
As more conventional recent methods[8,9] of preparing the nitrogen-containing heteroaryl iodonium precursor **6** failed, we employed the procedures outlined in Scheme 1 for the formation of **6**. Reaction of the bromophenylpyridine-derived anion **3** with vinyliodonium dichloride[10] **4** gave bis(aryl)iodonium chloride **5** in 30–35% isolated yield. Conversion of **5** to the desired bis(aryl)iodonium triflate **6** proceeded smoothly in 95–98% isolated yield. Compound **6** is a stable, albeit somewhat hygroscopic, off-white microcrystalline solid.

Interaction of **6** with 1 equiv of the square planar chelated bis(triflates)[3] **7** in acetone at room temperature gave the hybrid tetranuclear cationic macrocyclic squares **8**, via self-assembly as shown in Scheme 2. Macrocyclic compounds **8** are remarkably stable, white, microcrystalline solids, soluble in organic solvents, and are fully characterized by analytical and spectral means as summarized in Table 1. In particular, the elemental analyses are consistent with the respective composition of **8**. The $^{31}P\{^1H\}$ signals for **8** are sharp singlets shifted by 7.1 and 11.1 ppm, respectively, relative to the precursor[3] metal triflates **7**. Especially diagnostic for the macrocyclic tetranuclear squares are the respective ^1H NMR signals. The phenylpyridine units show four multiplets, respectively, as expected for these symmetrical systems. Moreover, the signals α to the pyridyl nitrogen and α to the iodonium moiety are shifted downfield upon complexing, relative to the precursor iodonium salt **6**. For **8a** and **8b**, the α-Py hydrogens are shifted by ~0.4 ppm and the α-iodonium units by ~0.05 ppm, relative to **6**. In contrast the β-Py hydrogens are shifted upfield by approximately 0.2 ppm in both **8a** and **8b** relative to **6**, presumably due to the shielding provided by the dppp phenyl rings of the chelating phosphine ligand on the metal. Integration of the proton signals is consistent with the relative intensities demanded by the macrocyclics, **8a** and **8b**. Also, as one would expect for such closely related congeners, the ^1H as well as ^{13}C NMR spectra for **8a** and **8b** are very similar, whereas their ^{31}P signals are significantly different. Furthermore, the spectral data of these novel hybrid macrocyclic squares closely track the respective NMR signals of the related pure iodonium bond macrocycle[6] **1** as well as the pure transition metal bond macrocycles[3] **2**.

Scheme 1



Scheme 2



8a: M=Pt
8b: M=Pd

In summary, novel hybrid main group iodonium–transition metal, cationic, macrocyclic squares can be prepared in high yields via self-assembly from readily available precursors. These unique macrocycles add a new dimension to supramolecular[12] as well as potential host–guest[13] chemistry.

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† Dedicated to Professor Frank Albert Cotton on the occasion of his 65th birthday.

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(11) Anal. Calcd for **8a** ($C_{104}H_{84}F_{18}I_2N_4P_4Pt_2O_{18}S_6{\cdot}3H_2O$): C, 41.17; H, 2.99; I, 8.37; N, 1.85; S, 6.34. Found: C, 41.38; H, 2.99; I, 8.33; N, 1.83; S, 6.32. Calcd for **8b** ($C_{104}H_{84}F_{18}I_2N_4P_4Pd_2O_{18}S_6{\cdot}6H_2O$): C, 42.91; H, 3.32; I, 8.72; N, 1.93; S, 6.61. Found: C, 42.72; H, 3.05; I, 9.02; N, 1.99; S, 6.62.

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Table 1. Physical and Spectral Data for Compounds **6** and **8**

compd	yield (%)	mp (°C)	IR (cm^{-1})[a]	^1H NMR, δ (mult; J (Hz))[b]	$^{13}C\{^1H\}$ NMR, δ (mult; J (Hz))[b]	$^{31}P\{^1H\}$ NMR, δ (mult; J (Hz))[b,c]	^{19}F NMR, δ[b,d]
6	95−98	176−178 dec	3103, 3019, 1600, 1478 (Ar) 1263, 1160, 1030 (OTf)	8.63 (d, 6.1; 4H, H_α-Py), 8.37 (d, 8.4; 4H, H_α-PhI), 7.92 (d, 8.4; 4H, H_β-PhI), 7.73 (d, 6.3; 4H, H_β-Py)	151.02 (d, 9.0; C_α-Py), 148.36 (s, C_γ-Py), 143.38 (s; C_γ-PhI), 137.43 (d, 11.2; C_α-PhI), 131.81 (d, 11.6; C_β-PhI), 123.48 (d, 11.0; C_β-Py), 121.86 (q, 318.4; CF_3), 116.92 (s; C−I)		−79.6 (s)
8a	73	253−256 dec	3089, 3052, 1617, 1437 (Ar), 1278, 1257, 1162, 1029 (OTf)	9.06 (bd, 5.0; 8H, H_α-Py), 8.42 (d, 8.7; 8H, H_α-PhI), 7.88−7.70 (m; 24H, H_β-PhI and H_o-PhP), 7.53 (d, 6.7; 8H, H_β-Py), 7.48−7.34 (m; 24H, H_m- and H_p-PHP), 3.49 (bs; 8H, PCH_2), 2.34 (m; 4H, PCH_2CH_2)	151.76 (s; C_α-Py), 149.48 (s; $C\gamma$-Py), 139.80 (s; C_γ-PhI), 137.88 (d, 4.1; C_α-PhI), 134.13 (bs; C_o-PhP), 133.03 (s; C_p-PhP), 131.59 (d, 4.1; C_β-PhI), 130.19 (t, 5.6; C_m-PhP), 126.07 (m; C_{ipso}-PhP), 125.30 (s; C_β-Py), 122.23 (q, 320.7; CF_3), 117.59 (s; C-I), 21.76 (m; PCH_2), 18.52 (bs; PCH_2CH_2)	−13.0 (s; $J_{Pt-P} = 3040$)	−78.0 (s)
8b	64	228−230 dec	3057, 1613, 1437 (Ar), 1277, 1256, 1156, 1028 (OTf)	9.03 (d, 6.4; 8H, H_α-Py), 8.41 (d, 8.8; 8H, H_α-PhI), 7.87−7.72 (m; 24H, H_β-PhI and H_o-PhP), 7.47 (d, 6.6; 8H, H_β-Py), 7.44−7.32 (m; 24H, H_m- and H_p-PhP), 3.38 (bs; 8H, PCH_2) 2.37 (m; 4H, PCH_2CH_2)	151.73 (s; C_α-Py), 148.93 (s; C_γ-Py), 140.18 (s; C_γ-PhI), 137.35 (s; C_α-PhI), 134.09 (t, 5.0; C_o-PhP), 133.00 (s; C_p-PhP), 131.55 (s; C_β-PhI), 130.30 (t, 5.6; C_m-PhP), 126.63 (m; C_{ipso}-PhP), 124.77 (s; C_β-Py), 122.20 (q, 321.2; CF_3), 117.34 (C−I), 21.78 (m; PCH_2); 18.50 (bs; PCH_2CH_2)	8.9 (s)	−78.0 (s)

[a] Thin film, acetone. [b] NMR solvents: **6**, CD_3OD; **8a** and **8b**, acetone-d_6. [c] Referenced to external 85% H_3PO_4 in a sealed capillary at 0.0 ppm. [d] Referenced to external $CFCl_3$ in a sealed capillary at 0.0 ppm.

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

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