Mixed, Neutral–Charged, Platinum–Platinum and Platinum–Palladium Macrocyclic Tetranuclear Complexes

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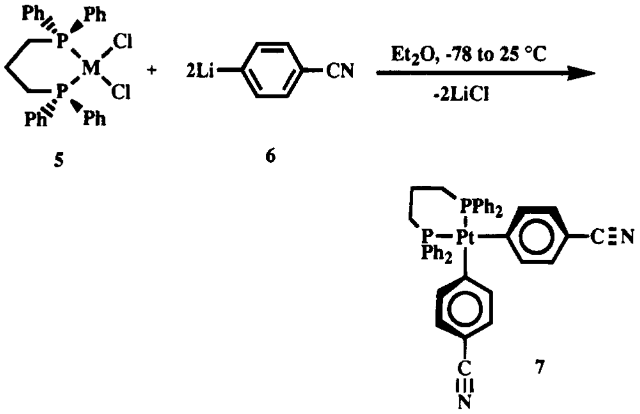
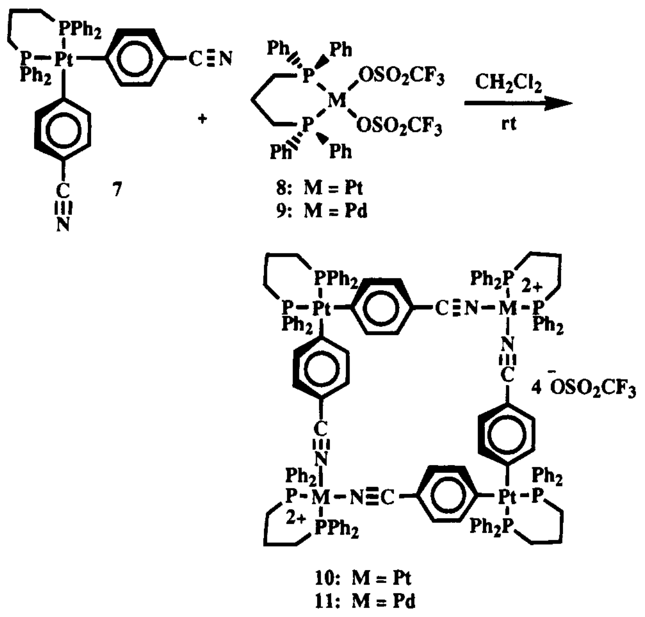
Summary: The interaction of cis-$L_2Pt(-C_6H_4CN\text{-}p)_2$ with cis-$L_2M(OSO_2CF_3)_2$ (L = $Ph_2P(CH_2)_3PPh_2$; M = Pt, Pd) in CH_2Cl_2 at room temperature results in mixed, neutral–charged, tetranuclear Pt–Pt and Pt–Pd macrocyclic complexes in 90% and 96% yields, respectively.

Tetranuclear, macrocyclic ring systems, possessing approximately 90° bond angles and concomitant rigidity, are unique members of the family of the more flexible organic hosts such as cyclodextrins, crown ethers, cyclophanes, calixarines, etc. To our knowledge the few known members of this select group of hosts **1**–**5** (Chart 1) either possess charges at the corners or are neutral.[1-5] Therefore, in this communication we wish to report the first examples of mixed, neutral–charged, homo- and heteronuclear, macrocyclic tetranuclear complexes.

Interaction of the dppp-chelated Pt(II) dichloride **5** with **6** gave after workup the neutral complex **7** in 83% isolated yield. Reaction of **7** with an equimolar amount of triflate complexes **8** and **9**, respectively, in CH_2Cl_2 at room temperature, results in the formation of neutral–charged tetranuclear cyclic complexes **10** and **11** (Scheme 1) in excellent isolated yields, in a matter of minutes via self-assembly. The homonuclear Pt complex **10** is a light pink robust solid, whereas the heteronuclear complex **11** is a stable reddish brown microcrystalline solid; both are soluble in common organic solvents.



Scheme 1



These macrocyclic, tetranuclear triflate complexes have been fully characterized by analytical and spectral (Table 1) means. In particular, the elemental analyses are consistent with the respective compositions of **10** and **11**.[6] The $^{31}P\{^1H\}$ spectra of **10** and **11** each show two singlets with a shift of 0.9 ppm for the P on the neutral Pt and 4.9 ppm for the P attached to the charged Pt for **10** and 1.0 ppm for the P—Pt and 6.4 ppm for the P—Pd in **11**, respectively, relative to the precursors **7**–**9**. Particularly diagnostic for the tetranuclear complexes **10** and **11** are the respective ^1H and $^{13}C\{^1H\}$ NMR spectra. There are two sets of signals, as expected, for the differing methylenes of the chelating dppp units, as well as complex overlapping aromatic resonances for the two sets of phenyl groups of the dppp. Interestingly, the two sets of aromatic resonances for the cyanobenzene unit (α and β to the CN) are virtually identical for **10** and **11**. Integration of the proton signals is in accord with the requirements for **10** and **11**. The ^{19}F spectra display singlets at −79 ppm for **10** and **11**, characteristic for ionic $CF_3SO_3^-$. Finally, the infrared spectra of **11** and **12** show an approximate 40 cm^{-1} upfield shift of CN due to absorption upon complexation in **10** and **11** relative to the free CN stretch of 2212 cm^{-1} for **7**. Such upfield shifts of the CN signal in the infrared region are highly characteristic of complexation to metal ions and are in accord with expectations and literature

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[6] Compound **10**: Anal. Calcd for $Pt_4C_{140}H_{116}P_8S_4N_4O_{12}F_{12}\cdot CH_2Cl_2$: C, 48.12; H, 3.49; N, 1.59; S, 3.64. Found: C, 47.93; H, 3.61; N, 1.55; S, 3.75. Molecular weight: calcd 3387, found 3500 (Galbraith Laboratories, vapor pressure osmometry in CH_2Cl_2). The ^1H NMR in $CDCl_3$ clearly indicates the presence of CH_2Cl_2 solvate for **10**. Compound **11**: Anal. Calcd for $Pt_2Pd_2C_{140}H_{116}P_8S_4N_4O_{12}F_{12}$: C, 51.62; H, 3.71; N, 1.72; S, 3.94. Found: C, 51.33; H, 3.85; N, 1.68; S, 3.94.

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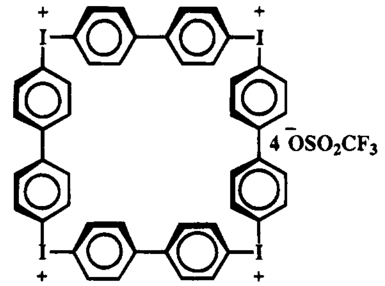
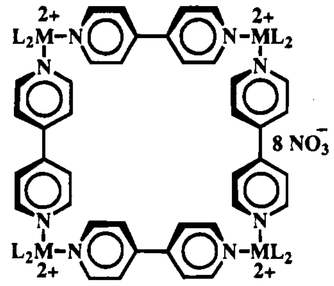
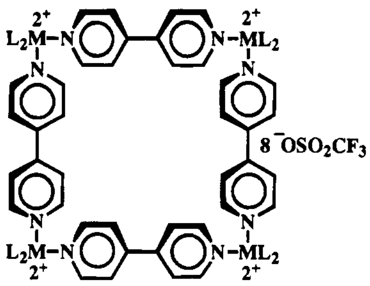
Chart 1



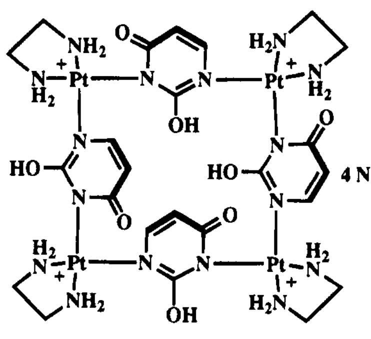
1^1



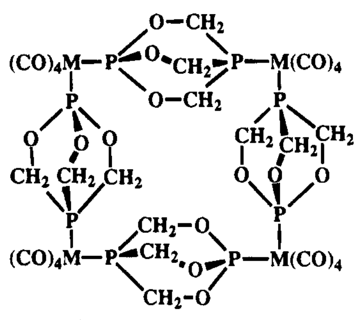
2^2: M = Pt L = $H_2N(CH_2)NH_2$
M = Pd



3^3: M = Pt L = $Ph_2P(CH_2)_2PPh_2$
M = Pd



4^4



5^5: M = Cr, Mo, W

Table 1. Physical and Spectral Data for Compounds 7, 10, and 11

compd	yield (%)	mp (°C)	IR[a]	^1H[b]	$^{13}C\{^1H\}$[b]	$^{31}P\{^1H\}$[b,c]	^{19}F[b,d]
7	83	196−199 dec	3077, 3061 (Ar), 2939 (CH_2), 2212 (CN)	7.5−7.3 (m, 20H), 7.1 (m, 2H), 6.7 (m, 2H), 2.7 (bs, 4H), 1.9 (m, 2H)	133.3 (C_o), 130.5 (C_p), 128.5 (C_m), 131.7 (Pt−P−C_{ipso}), 129.5 (C_α), 136.9 (C_β), 120.8 (C_{ipso}), 172.4 (Pt−$C_{ipso}{}'$, J_{Pt-C} = 96.0 Hz), 104.1 (CN), 26.3 (Pt−P−CH_2), 19.5 (CH_2)	0.69 (s, J_{Pt-P} = 1740 Hz)	
10	90	210−213 dec	3055 (Ar), 2976, 2928, 2865 (CH_2), 2256 (CN), 1274, 1150, 1102, 1029 (OTf)	7.6−7.3 (m, 20H), 7.0 (m, 8H), 6.3 (m, 8H), 3.0 (bs, 8H), 2.6 (bs, 8H), 2.2 (m, 8H), 1.9 (m, 4H)	133.4 (Pt−P−C_o), 131.2 (Pt−P−C_{ipso}), 130.7 (Pt−P−C_p), 128.5 (Pt−P−C_m), 133.2 (Pt′−P−C_o), 133.1 (Pt′−P−C_p), 129.9 (Pt′−P−C_m), 124.5 (Pt′−P−C_{ipso}), 180.4 (Pt−$C_{ipso}{}'$, J_{Pt-C} = 92.7 Hz), 137.3 (Pt−C_β), 129.8 (Pt−C_α), 123.9 (Pt−C_{ipso}), 121.4 (q, OTf, J_{C-F} = 321 Hz), 97.5 (CN), 26.1 (Pt−P−CH_2), 21.7 (Pt′−P−CH_2), 19.6 (CH_2), 18.6 (CH'_2)	−0.21 (s, J_{Pt-P} = 1773 Hz), −12.2 (s, J_{Pt-P} = 3349 Hz)	−79
11	96	169−173 dec	3057 (Ar), 2918 (CH_2), 2249 (CN), 1276, 1152, 1101, 1029 (OTf)	7.6−7.2 (m, 80H), 7.1 (m, 8H), 6.3 (m, 8H), 2.9 (bs, 8H), 2.7 (bs, 8H), 2.3 (m, 4H), 1.9 (m, 4H)	133.3 (Pt−P−C_o), 131.1 (Pt−P−C_{ipso}), 130.6 (Pt−P−C_p), 128.5 (Pt−P−C_m), 133.2 (Pd−P−C_o), 133.1 (Pd−P−C_p), 129.9 (Pd−P−C_m), 125.2 (Pd−P−C_{ipso}), 178.6 (Pt−$C_{ipso}{}'$), 137.2 (Pt−C_β), 129.8 (Pt−C_α), 124.2 (Pt−C_{ipso}, J_{Pt-C} = 99.4 Hz), 121.3 (q, OTf, J_{C-F} = 321 Hz), 98.9 (CN), 26.1 (Pt−P−CH_2), 21.8 (Pd−P−CH_2), 19.5 (CH_2), 18.8 (CH'_2)	13.6 (s), −0.29 (s, J_{Pt-P} = 1765 Hz)	−79

[a] Thin film; CCl_4 cm^{-1}. [b] All measurements in CD_2Cl_2. [c] Referenced to external 85% H_3PO_4 at 0.0 ppm. [d] Referenced to external $CFCl_3$ at 0.0 ppm.

precedents.[7] In conclusion, neutral−charged homonuclear Pt(II)−Pt(II) and heteronuclear Pt(II)−Pd(II) tetranuclear macrocyclic complexes were prepared via self-assembly from easily available precursors in excellent isolated yields. These very stable, highly organic soluble, tetranuclear macrocyclic systems add a new dimension to potential host−guest interactions,[8] and their chemistry is under active investigation.

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Supplementary Material Available: ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra and IR spectra for both **10** and **11** (8 pages). Ordering information is given on any current masthead page.

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