Synthesis and characterization of a trigonal bipyramidal supramolecular cage based upon rhodium and platinum metal centers†

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The reaction of 4-ethynyl-pyridine with *tert*-butyl lithium followed by its addition to (Me$_3$tacn)RhCl$_3$ affords the facial octahedral complex (Me$_3$tacn)Rh(CCPy)$_3$, condensation of which with the square planar complex cis-(DCPE)Pt(NO$_3$)$_2$ results in a self-assembled trigonal bipyramidal cage with Rh(III) and Pt(II) atoms occupying the vertices.

The synthesis and study of self-assembling supramolecular complexes has become an area of great interest in recent years.[1–7] The geometry of each species involved in the assembly plays a significant role in determining the overall shape of the molecule.[8–14] The square planar geometries of platinum(II) and palladium(II) are particularly common for directing the formation of supra-molecules in which square or near orthogonal angles are important,[15–17] however, a variety of other metals have also been used.[18–21] The ability of *N*-donating ligands to coordinate to platinum and form such structures has been well studied, and is well suited for the self-assembly mechanisms of supramolecular complexes.

For some time, our group has studied the self-assembly of platinum–alkyne based molecular squares.[15] We have also recently reported the formation of an octahedral rhodium(III) acetylide complex having a facial conformation.[22] By tailoring the alkynes on the rhodium to feature σ-donating pyridines, guest units now contain a transition metal directing a three dimensional geometry. These units would be suitable for the formation of edge-directed supramolecular structures, such as cubes, with transition metals occupying the vertices.[3]

(Me$_3$tacn)RhCl$_3$ (Me$_3$tacn = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane), **1**, was prepared according to literature procedures.[23] The generation of the pyridylacetylide by reaction of the 4-ethynylpyridine with *tert*-butyl lithium followed by its addition to **1** gave (Me$_3$tacn)Rh(CCPy)$_3$, **2**, as a light brown solid in moderate yield (56%). The structure of **2** was determined by single crystal X-ray diffraction studies (Fig. 1).‡ The ^{1}H and ^{13}C NMR spectra of **2** are consistent with the given structure. In the ^{13}C NMR spectrum the acetylide resonances are 102.2 ($^1J_{\mathrm{Rh-C}}$ = 48.0 Hz) and 100.2 ($^2J_{\mathrm{Rh-C}}$ = 9.2 Hz) ppm for C$_\alpha$ and C$_\beta$, respectively. The IR spectrum shows an alkyne stretching frequency of 2103 cm^{-1}. This is consistent with alkyne stretching frequency for the phenyl derivative (Me$_3$tacn)Rh(CCPh)$_3$ which we have recently reported.[22]

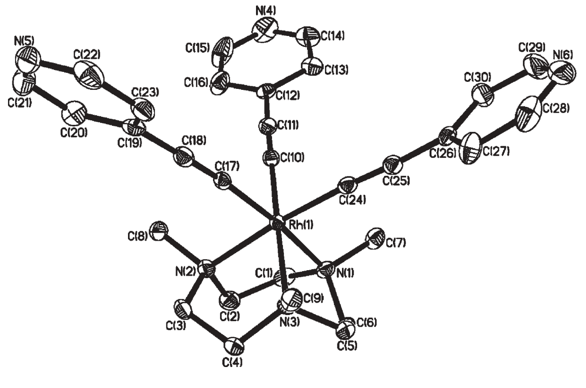
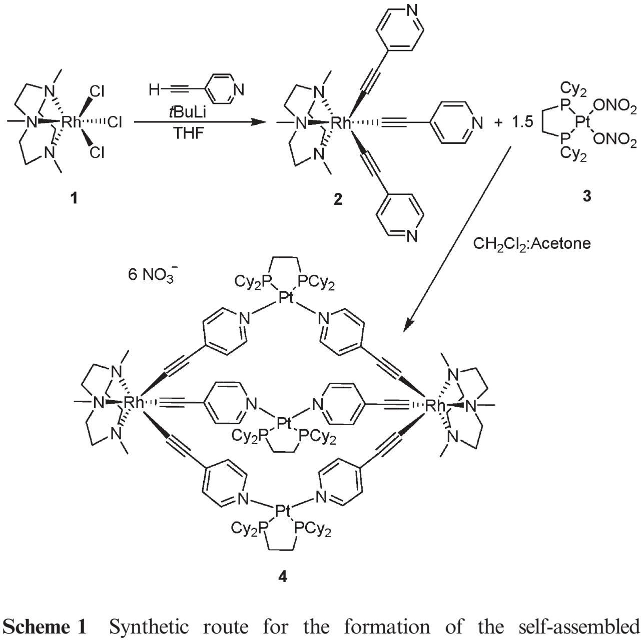


Fig. 1 Crystal structure of **2** with thermal ellipsoids shown at 50% probability. Only one of the two independent molecules is shown. Hydrogen atoms removed for clarity.

(DCPE)Pt(NO$_3$)$_2$ (1,2-Bis(dicyclohexylphosphino)ethane = DCPE), **3**, was synthesized by the reaction of (DCPE)PtCl$_2$ with two equivalents of AgNO$_3$ to yield **3** as a colorless crystalline solid (93%). Complex **3** was characterized by ^{1}H, ^{13}C and ^{31}P NMR



Scheme 1 Synthetic route for the formation of the self-assembled trigonal bipyramidal cage.

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analysis. The alkyl region of the ^{1}H and ^{13}C NMR spectra of **3** were complex and difficult to interpret due to the cyclohexyl rings, but are consistent with other compounds containing the 1,2-bis(dicyclohexylphosphino)ethane ligand.[15] The ^{31}P NMR spectrum of complex **3** gives a resonance at 58.3 ppm with a P–Pt coupling of 3839 Hz.

The hexacationic trigonal bipyramidal cage, **4**, was synthesized by the condensation of **2** and **3** in a 2 : 3 ratio, respectively, in CH_2Cl_2 (Scheme 1). The resulting orange oil was taken up into methanol and allowed to slowly crystallize. This gave the novel complex **4** as a yellow crystalline solid in excellent yield (85%).

Multinuclear (^{1}H, ^{13}C, ^{31}P and ^{195}Pt) NMR analysis of **4** is consistent with the proposed structure. In the ^{1}H NMR spectrum, the resonances for the hydrogen atoms *ortho* to the nitrogen atom of the pyridine ring are seen as a doublet of doublets with couplings of 7.0 and 2.4 Hz. The larger coupling (7.0 Hz) is attributed to the expected coupling with the adjacent hydrogen of the pyridine ring. The smaller coupling (2.4 Hz) is attributed to a coupling with the ^{195}Pt nuclei. The ^{31}P and ^{195}Pt spectra show magnetically equivalent nuclei for both the phosphorus and platinum nuclei, respectively. The ^{31}P NMR spectrum gave a resonance of 59.0 ppm with a P–Pt coupling of 3113 Hz. The ^{195}Pt NMR spectrum shows a resonance at −1674.28 ppm with a Pt–P coupling of 3134 Hz. The IR spectrum shows an alkyne stretching frequency of 2103 cm^{-1} which is consistent with the proposed structure.

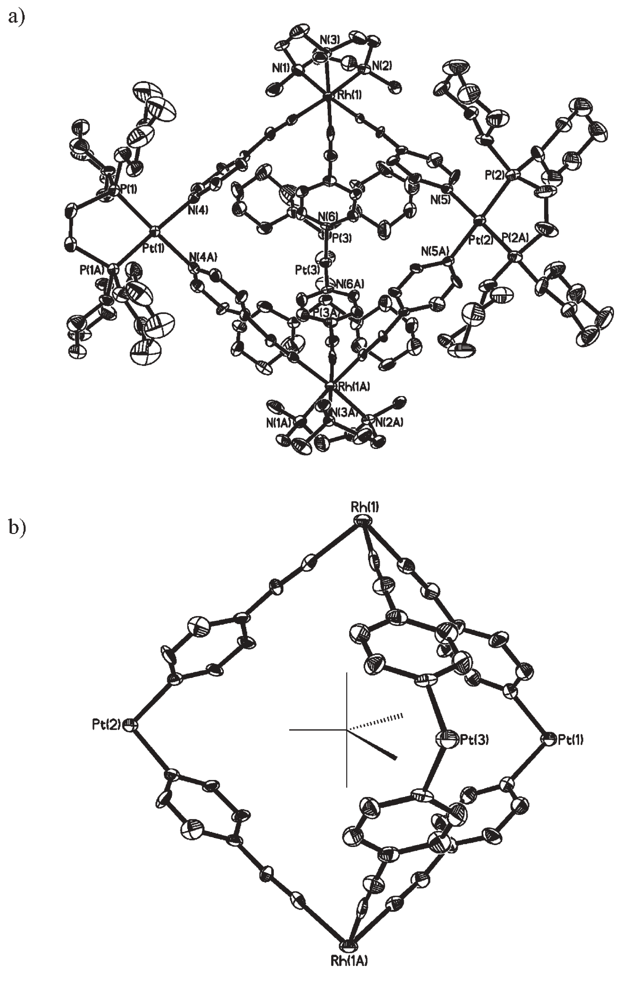

Fig. 2 (a) Crystal structure of the cage portion of **4** with hydrogen atoms removed for clarity and thermal ellipsoids shown at 20% probability. (b) View of the trigonal bipyramidal geometry of **4** with organic ligands removed. There is crystallographically imposed mirror symmetry with the three independent Pt atoms on the mirror plane. Similarly, the letter "A" of Rh(1A) indicates that this atom is at equivalent position (x, 3/2 − y, z).

The crystals of **4**, grown by slow evaporation of methanol, were found to be poorly diffracting and also fairly solvent sensitive. Recrystallization from a mixture of acetonitrile and toluene afforded large yellow crystals from which a solution of the cage portion of **4** could be achieved by single crystal X-ray diffraction (Fig. 2).

Both the N–Pt–N and C–Rh–C bond angles of the cage deviate significantly from 90° with averages of 84.9° and 87.9° (C–Rh–C averages 90.7 for **2**) respectively. The strain of the N–Pt–N bonds is most likely due to the sterically bulky cyclohexyl substituents of the chelating phosphine. The low resolution of the data prevented determination of more than the connectivity of the hexacationic cage. Along with the counter anions, we believe the void spaces are filled with solvent molecules such as water, which is consistent with the ^{1}H NMR spectra. Attempts to grow better quality crystals of **4** from other solvents and by anion exchange are currently under way.

In conclusion, we have synthesized and structurally characterized a novel hexacationic trigonal bipyramidal cage, **4**, with rhodium and platinum atoms occupying the vertices. The formation of **4** was based upon the coordination chemistry of the tripodal pyridylacetylide complex, **2**, and the platinum nitrate complex, **3**. Complex **4** was characterized by multinuclear NMR studies examining the ^{1}H, ^{13}C, ^{31}P and ^{195}Pt nuclei. All data are consistent with the proposed structure and confirmed by X-ray crystallography. Efforts are already under way to synthesize larger supramolecular compounds based upon the coordination chemistry of complex **4** using a variety of transition metals.

Notes and references

‡ Crystal data: for **2**: $C_{30}H_{33}N_6Rh$, M_w = 580.53, colorless crystal 0.42 × 0.07 × 0.06 mm, a = 20.996(2) Å, b = 11.6667(11) Å, c = 24.063(2) Å, α = 90°, β = 114.499(2)°, γ = 90°, V = 5363.8(9) Å^3, D_c = 1.438 Mg cm^{-3}, μ = 0.667 mm^{-1}, Z = 8, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 100 K, ω and φ scans, 46820 reflections collected, 12862 independent (R_{int}) 0.0448, 673 refined parameters, $R1/wR2$ ($I \geqslant 2\sigma(I)$) = 0.0668/0.1297 and $R1/wR2$ (all data) = 0.0753/0.1333, maximum (minimum) residual electron density 1.293 (−1.402) e Å^{-3}, hydrogen atom positions were calculated and U_{iso}(H) values were fixed according to a riding model. For cage portion of **4**: $C_{138}H_{210}N_{12}P_6Pt_3Rh_2$, M_w = 3014.09, colorless crystal 0.39 × 0.30 × 0.12 mm, a = 19.541(3) Å, b = 22.799(3) Å, c = 23.890(3) Å, α = 90°, β = 103.095(2)°, γ = 90°, V = 10366(2) Å^3, D_c = 0.966 Mg cm^{-3}, μ = 2.253 mm−1, Z = 2, monoclinic, space group $P21/m$ (No. 11), λ = 0.71073 Å, T = 100 K, ω and φ scans, 65598 reflections collected, 15784 independent (R_{int}) 0.1246, 673 refined parameters, $R1/wR2$ ($I \geqslant 2\sigma(I)$) = 0.0760/0.1775 and $R1/wR2$ (all data) = 0.1375/0.1978, maximum (minimum) residual electron density 3.181 (−2.098) e Å^{-3}, hydrogen atom positions were calculated and U_{iso}(H) values were fixed according to a riding model. CCDC 602644–602645. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608991g

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