

Self-assembled chloro-bridged metallo-prismatic cations of the general formula $[M_6(\eta^5-C_5Me_5)_6(\mu_3-tpt)_2(\mu-Cl)_6]^{6+}$ (M = Rh, Ir; tpt = 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine)

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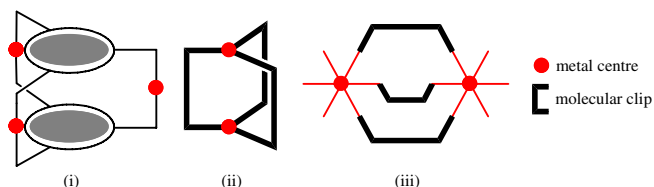
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Abstract

Two cationic pentamethylcyclopentadienyl metal-based hexanuclear complexes with trigonal prismatic architecture have been synthesised through a two-step strategy. The dinuclear complexes $[M(\eta^5-C_5Me_5)(\mu-Cl)Cl]_2$ (M = rhodium and iridium) react with 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine (tpt) in dichloromethane to give the trinuclear complexes $[Rh_3(\eta^5-C_5Me_5)_3(\mu_3-tpt)Cl_6]$ (**1**) and $[Ir_3(\eta^5-C_5Me_5)_3(\mu_3-tpt)Cl_6]$ (**2**), respectively. Addition of silver triflate to **1** and **2** in dichloromethane connects two identical triangular panels to form the hexanuclear metallo-prismatic cations $[Rh_6(\eta^5-C_5Me_5)_6(\mu_3-tpt)_2(\mu-Cl)_6]^{6+}$ (**3**) and $[Ir_6(\eta^5-C_5Me_5)_6(\mu_3-tpt)_2(\mu-Cl)_6]^{6+}$ (**4**), respectively. Cations **3** and **4** have been isolated as their triflate salts and characterised by 1H NMR, IR and UV/visible spectroscopy.

Keywords: Bridging ligands; Pentamethylcyclopentadienyl ligands; N ligands; Iridium; Rhodium; Supramolecular chemistry

The simplest three-dimensional construction that involves the fewest components is the triangular prism. The strategy to self-assemble metal-based triangular prisms can be divided in three major routes [1]: (i) assemblies of tripodal ligands with metal centres of C_2 symmetry [2], (ii) assemblies of three molecular clips with metal centres of C_3 symmetry [3], (iii) assemblies of three molecular clips with metal centres of restrained symmetry [4].



Recently, we introduced arene ruthenium and pentamethylcyclopentadienyl rhodium and iridium complexes as versatile building blocks in supramolecular chemistry. The use of these η^5 - or η^6 -ligands, which occupy three of the six coordination sites at the metal centre, generates a pre-organised arrangement before the formation of the supramolecular assembly. A series of cationic triangular metallo-prisms containing bridging chloro [5] and oxalato [6] ligands connected by 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine (tpt) subunits have been synthesised using this approach. Herein we report the synthesis and characterisation of two new triangular metallo-prismatic cations incorporating pentamethylcyclopentadienyl rhodium and iridium building blocks, bridged by chloride atoms, and connected by 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine (tpt) tripodal ligands.

The dinuclear pentamethylcyclopentadienyl complexes $[M(\eta^5-C_5Me_5)(\mu-Cl)Cl]_2$ (M = rhodium and iridium) react in dichloromethane with 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine (tpt) to form in good yield (>65%) the trinuclear

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complexes $[\text{Rh}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-tpt})\text{Cl}_6]$ (**1**) [7] and $[\text{Ir}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-tpt})\text{Cl}_6]$ (**2**) [8], respectively, see Scheme 1.

Addition of silver triflate to **1** and **2** in dichloromethane connects two identical triangular panels to afford the hexanuclear metallo-prismatic cations $[\text{Rh}_6(\eta^5\text{-C}_5\text{Me}_5)_6(\mu_3\text{-tpt})_2(\mu\text{-Cl})_6]^{6+}$ (**3**) [9] and $[\text{Ir}_6(\eta^5\text{-C}_5\text{Me}_5)_6(\mu_3\text{-tpt})_2(\mu\text{-Cl})_6]^{6+}$ (**4**) [10] in acceptable yield (>40%), see Scheme 2. Cations **3** and **4** are isolated as their trifluoromethanesulfonate salt.

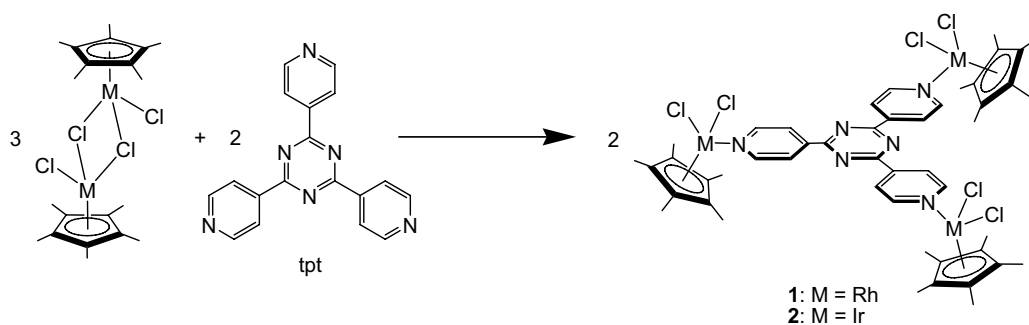
The ^1H NMR spectra of **1–4** display a similar signal pattern of the pyridyl protons, see Fig. 1. Unlike **1** and **2**, where the H_α and H_β are found at expected positions ($\delta = 9.25$ and 8.6 ppm), in **3** and **4** the signals of H_α and H_β are almost superimposed at $\delta \approx 8.75$ ppm. Upon formation of the triangular prisms **3** and **4**, the H_α signal is shifted upfield, whereas the H_β signal remains almost the same. In all complexes, the signals of the methyl protons of the pentamethylcyclopentadienyl ligand are observed at about 1.55 ppm. This chemical shift is characteristic of the formation of a trigonal prismatic structure as observed in the η^6 -arene ruthenium analogues $[\text{Ru}_6(\eta^6\text{-C}_6\text{Me}_6)_6(\mu_3\text{-tpt})_2(\mu\text{-Cl})_6]^{6+}$ and $[\text{Ru}_6(\eta^6\text{-}i\text{-Pr}^1\text{C}_6\text{H}_4\text{Me})_6(\mu_3\text{-tpt})_2(\mu\text{-Cl})_6]^{6+}$ [5].

The infrared spectra of **1–4** are dominated by absorptions of the coordinated 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine ligand, which are only slightly shifted as compared

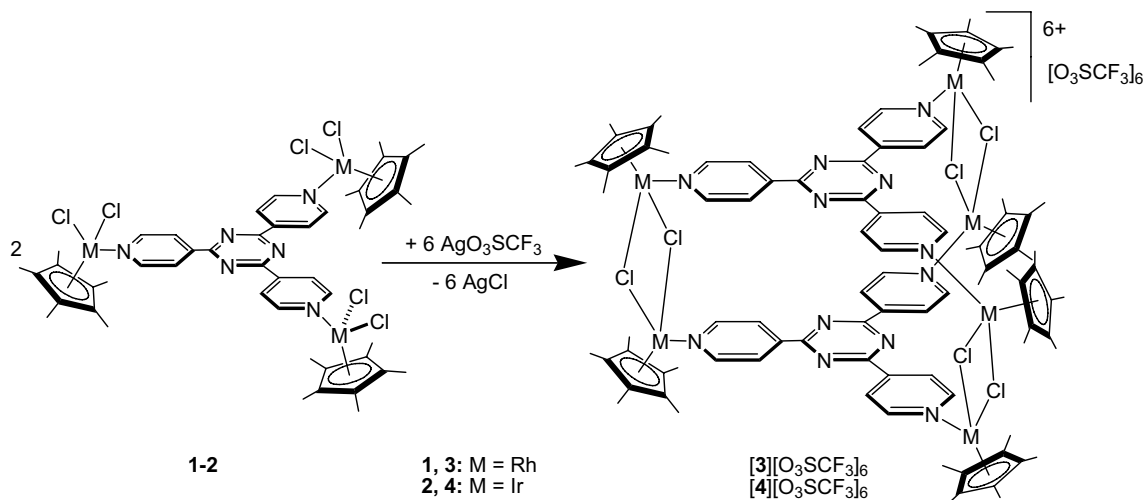
to the free ligand [1515 (s), 1374 (s), 794 (s), 641 (s) cm^{-1}] [11]. In addition to the tpt signals, strong absorptions attributed to the triflate anions are observed in the infrared spectra of **3** and **4** [1260 (s), 1031 (s), 638 (s) cm^{-1}] [12]. Despite a molecular weight of 3160.7 g mol^{-1} for **3** $[\text{O}_3\text{SCF}_3]_6$ and 3696.5 g mol^{-1} for **4** $[\text{O}_3\text{SCF}_3]_6$, the two compounds are quite soluble in chloroform, dichloromethane and acetone.

It is well known that coordinating solvents can cleave chloro-bridged dinuclear arene ruthenium complexes [5,13]. In order to examine the stability of the chloro-bridged prisms **3** and **4** in solution, we recorded the ^1H NMR spectra in various deuterated solvents (CD_2Cl_2 , $(\text{CD}_3)_2\text{CO}$, CD_3CN) with different coordinating ability. At room temperature and even elevated temperature, ^1H NMR experiments for **3** and **4** in dichloromethane- d_2 and acetone- d_6 showed no signal changes indicating the cleavage of the chloro-bridges or the presence of free tpt units. However, in acetonitrile- d_3 , all complexes show additional signals attributed to species generated by the coordination of CD_3CN ligands in line with cleavage of the chloro-bridges.

The UV/visible spectra of the neutral triangular panels **1** and **2** in CH_2Cl_2 show a broad low energy band at 430 nm, in agreement with a metal-to-ligand charge transfer



Scheme 1.



Scheme 2.

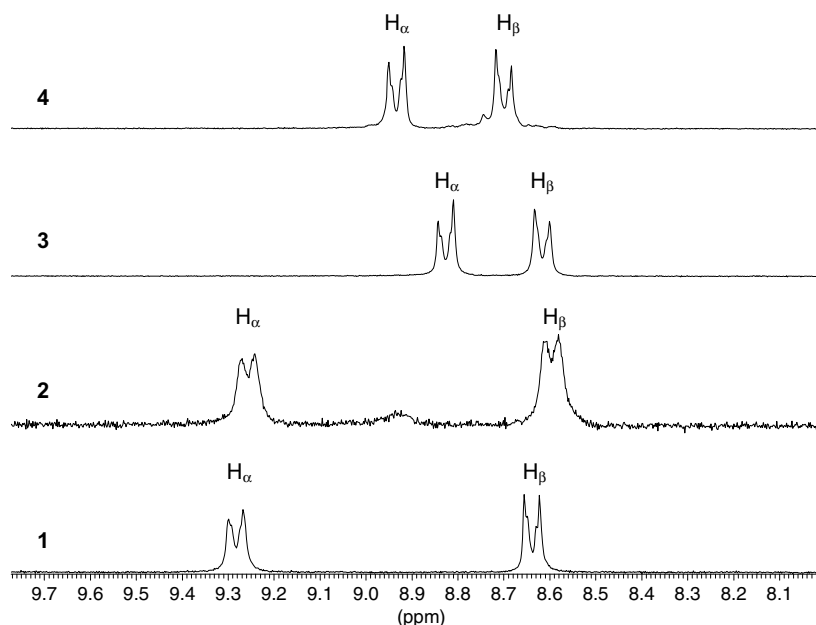


Fig. 1. ^1H NMR spectra of cations 1–4 in CD_2Cl_2 , showing the pyridyl region of the 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine ligand.

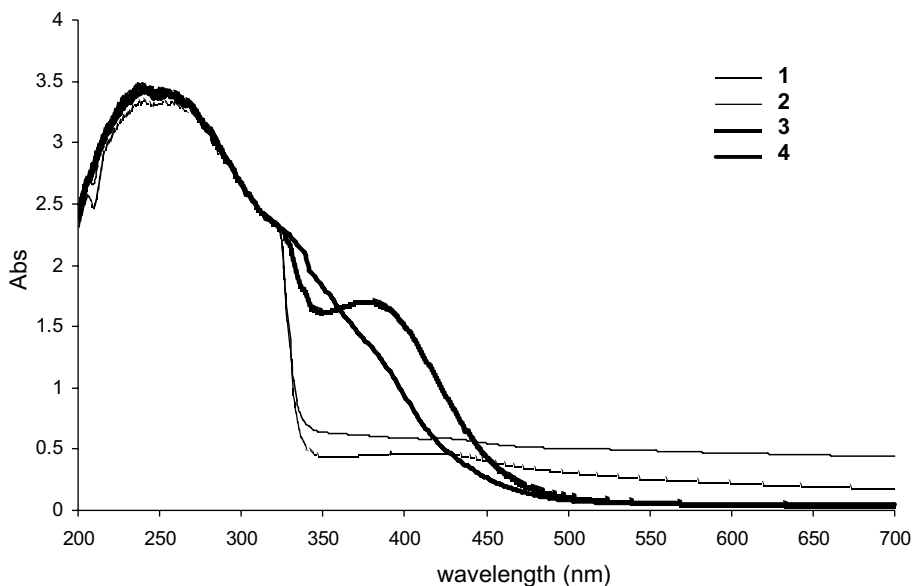


Fig. 2. UV/visible spectra of 1–4 in CH_2Cl_2 .

(MLCT) transition [13,14]. The triangular metallo-prisms **3** and **4** display in addition an intense high energy bands at 390 nm. This absorption is assigned to the interligand π -stacking interactions due to the face-to-face orientation of the aromatic panels, as previously reported for related systems [15] (see Fig. 2).

In conclusion, we have shown a simple and straightforward synthesis of chloro-bridged pentamethylcyclopentadienyl rhodium and iridium metallo-prisms. Metallo-prisms **3** and **4** show strong π -stacking interactions between the tpt units as demonstrated by NMR and UV/visible spectroscopy. All spectroscopic data are similar to those observed

for the analogous complexes $[\text{Ru}_6(\eta^6\text{-C}_6\text{Me}_6)_6(\mu_3\text{-tpt})_2(\mu\text{-Cl})_6]^{6+}$ and $[\text{Ru}_6(\eta^6\text{-}i\text{-Pr}^1\text{C}_6\text{H}_4\text{Me})_6(\mu_3\text{-tpt})_2(\mu\text{-Cl})_6]^{6+}$ for which the prismatic structure was confirmed by single crystal X-ray structure analysis [5].

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- [7] $[Rh_3(\eta^5-C_5Me_5)_3(\mu_3-tpt)Cl_6]$ (**1**): A mixture of $[Rh(\eta^5-C_5Me_5)(\mu-Cl)Cl]_2$ (154 mg, 0.25 mmol) and *tpt* (52 mg, 0.17 mmol) is suspended in dichloromethane (20 mL) and stirred for 3 h at 40 °C. The volume is reduced to 5 mL, and the orange–yellow solid is precipitated by the addition of diethyl ether and filtered. Yield of 140 mg (68 %). 1H NMR (200 MHz, CD_2Cl_2): δ (ppm) = 9.29 (d, 6H, $^3J_{H-H}$ = 6.60 Hz, H_α), 8.61 (d, 6H, H_β), 1.58 (s, 45H, C_5Me_5); ^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ (ppm) = 167.56, 152.24, 134.37, 126.42, 94.91, 9.39; IR (cm^{-1}): 1517 (s), 1373 (s), 814 (s). Anal. Calcd. for $C_{48}H_{57}N_6Cl_6Rh_3$: C, 46.51; H, 4.63; N, 6.78. Found: C, 46.57; H, 4.32; N, 6.85.
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- [9] $[Rh_6(\eta^5-C_5Me_5)_6(\mu_3-tpt)_2(\mu-Cl)_6]^{6+}$ (**3**): A mixture of **1** (70 mg, 0.056 mmol) and AgO_3SCF_3 (44 mg, 0.17 mmol) in dichloromethane (20 mL) is stirred at 50 °C for 3 h and then filtered. The filtrate is concentrated (3 mL), and diethyl ether is slowly added to precipitate an orange solid. Yield of 65 mg (73 %). 1H NMR (200 MHz, CD_2Cl_2): δ (ppm) = 8.82 (d, 12H, $^3J_{H-H}$ = 6.60 Hz, H_α), 8.61 (d, 12H, H_β), 1.59 (s, 90H, C_5Me_5); ^{13}C { 1H } NMR (100.62 MHz, acetone- d_6): δ (ppm) = 170.42, 154.70, 144.15, 126.40, 98.53, 8.72; IR (cm^{-1}): 1521 (s), 1383 (s), 1261 (m), 1160 (m), 1031 (m), 809 (s), 639 (s). Anal. Calcd. for $C_{102}H_{114}Cl_6N_{12}O_{18}S_6F_{18}Rh_6$: C, 38.76; H, 3.63; N, 5.32. Found: C, 38.38; H, 3.85; N, 5.06.
- [10] $[Ir_6(\eta^5-C_5Me_5)_6(\mu_3-tpt)_2(\mu-Cl)_6]^{6+}$ (**4**): This compound is prepared by the same procedure as described above for **3** using AgO_3SCF_3 (53 mg, 0.21 mmol) and **2** (90 mg, 0.078 mmol). Yield of 50 mg (40 %). 1H NMR (200 MHz, CD_2Cl_2): δ (ppm) = 8.93 (d, 12H, $^3J_{H-H}$ = 6.96 Hz, H_α), 8.69 (d, 12H, H_β), 1.52 (s, 90H, C_5Me_5); ^{13}C { 1H } NMR (100.62 MHz, acetone- d_6): δ (ppm) = 169.75, 154.53, 144.03, 126.59, 90.45, 8.09; IR (cm^{-1}): 1638 (s), 1617 (s), 1501 (s), 1373 (m), 1258 (m), 1031 (m), 811 (s), 638 (s). Anal. Calcd. for $C_{102}H_{114}Cl_6N_{12}O_{18}S_6F_{18}Ir_6$: C, 33.14; H, 3.11; N, 4.55. Found: C, 33.46; H, 3.31; N, 4.39.
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