

Note

Stepwise formation of metallo-prisms of iridium and rhodium complexes bearing pentamethylcyclopentadienyl ligands

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Abstract

Reactions of $[M(\text{Cp}^*)\text{Cl}(\mu\text{-Cl})_2]$ ($M = \text{Ir}(\mathbf{1a})$; $M = \text{Rh}(\mathbf{1b})$) with tridentate ligands *tpt* (*tpt* = 2,4,6-tripyridyl-1,3,5-triazine) gave the corresponding trinuclear complexes $[M_3(\text{Cp}^*)_3(\mu_3\text{-4-}tpt\text{-}\kappa\text{N})\text{Cl}_6]$ ($M = \text{Ir}(\mathbf{2a})$; $M = \text{Rh}(\mathbf{2b})$), which can be converted into hexanuclear complexes $[M_6(\text{Cp}^*)_6(\mu_3\text{-4-}tpt\text{-}\kappa\text{N})_2(\mu\text{-Cl})_6](\text{O}_3\text{SCF}_3)_6$ ($M = \text{Ir}(\mathbf{3a})$; $M = \text{Rh}(\mathbf{3b})$) by treatment with AgO_3SCF_3 , respectively. X-ray of $\mathbf{3b}$ revealed that each of six pentamethylcyclopentadienyl metal moieties was connected by two $\mu\text{-Cl}$ -bridged atoms and a tridentate ligand to construct a cation triangular metallo-prism cavity with the volume of about 273 \AA^3 based on the distance of the two triazine moieties is 3.62 \AA .

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1. Introduction

Organometallic half-sandwich complexes have become very interesting building blocks for supramolecular chemistry. Many half-sandwich complexes of iridium, rhodium and ruthenium occupy the corner positions are of the most promising building blocks for two- and three-dimensional supramolecular constructions [1]. In particular, metallo-prisms complexes of platinum and palladium bearing diphosphine and diamine derivatives have been used extensively by many groups [2]. Hupp and co-workers have employed two hexa-rhenium molecular prisms [3]. Recently, some (Arene)ruthenium metallo-prisms have been reported by Therrien et al. [4]. In contrast, to our knowledge, organo-iridium and organo-rhodium complexes containing chloro ligands have not been extensively studied [5].

In previous work, we [6] and others [7] have designed and synthesized tetranuclear rhodium and iridium supra-

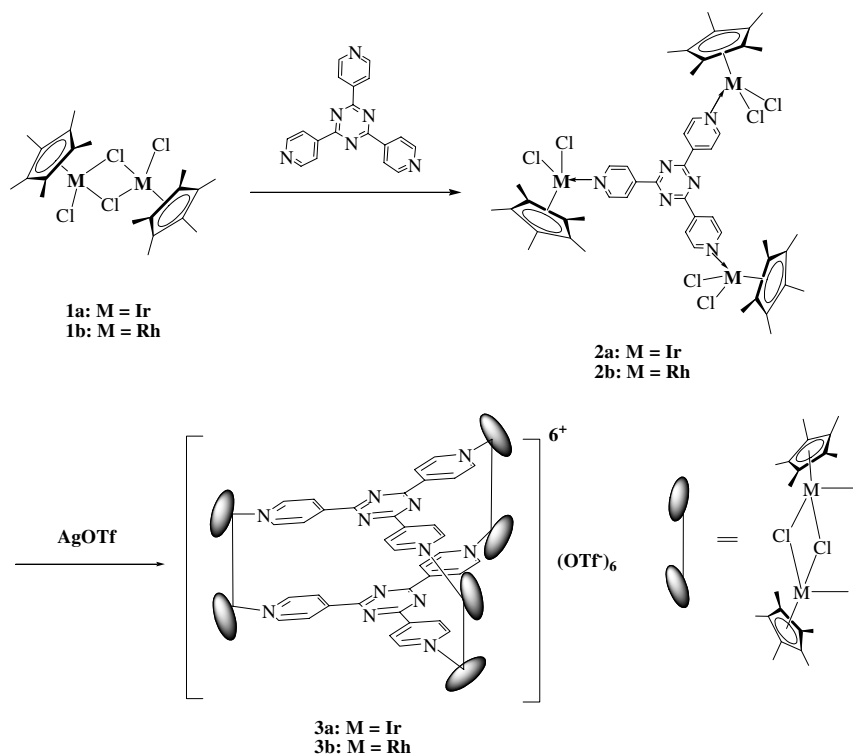
molecules bearing cyclopentadienyl derivatives and two different types of ligands. Using the similar approach, we report the stepwise formation of iridium and rhodium metallo-prisms bearing pentamethylcyclopentadienyl and bridging chloro ligands, connected by two 2,4,6-tripyridyl-1,3,5-triazine (*tpt*) subunits (Scheme 1).

2. Results and discussion

In our previous report [8], the trinuclear complex $\mathbf{2a}$ can be obtained in high yield by stirring a mixture of $[\text{Cp}^*\text{IrCl}(\mu\text{-Cl})_2]$ ($\mathbf{1a}$) and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (*tpt*) in CH_2Cl_2 at room temperature for 18 h. The molecular consists of three (Cp^*Ir) fragments linked by one *tpt* ligand in a star-shape trimer.

Similarly, the red solids of trinuclear complex $\mathbf{2b}$ can be prepared in 92% yield through stirring a CH_2Cl_2 solution of a mixture of $[\text{Cp}^*\text{RhCl}(\mu\text{-Cl})_2]$ ($\mathbf{1b}$) and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (*tpt*) at room temperature for 18 h. In the ^1H NMR spectra, the Cp^* methyl protons appear at 1.63 ppm as a singlet and the resonances for the pyridyl are around 8.93 and 8.63 ppm.

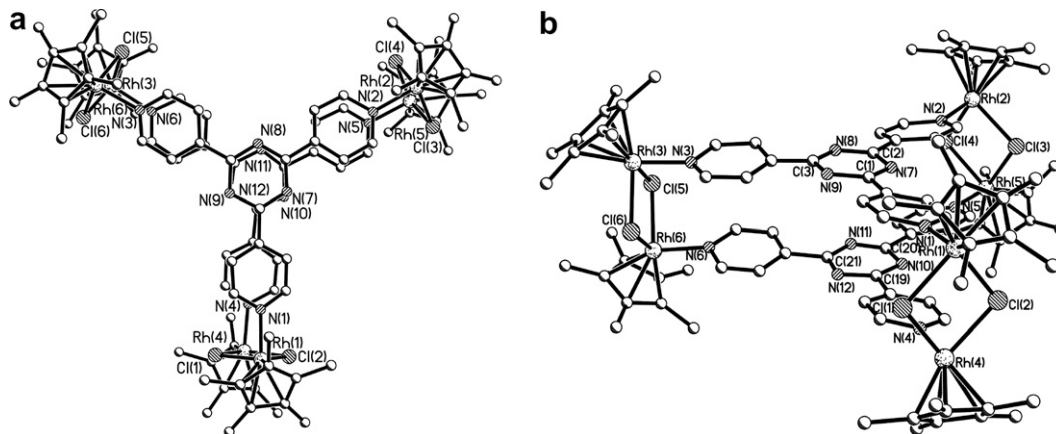
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Scheme 1. Synthesis of complexes **3a** and **3b**.

When the trinuclear complexes **2a** or **2b** were treated with AgOTf in a 1:3 molar ratio in CH₂Cl₂ solution at room temperature, yellow crystals, formulated as [M₆(Cp*)₆(μ₃-4-tpt-κN)₂(μ-Cl)₆](O₃SCF₃)₆ (M = Ir(**3a**); M = Rh(**3b**)) were formed in high yields followed by separation of AgCl, respectively, which bridged by chloro ligands, and connected by two 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt) subunits. In IR spectra, the absorptions of the coordinated 2,4,6-tris(pyridin-4-yl)-1,3,5-triazine ligand of **3a** and **3b** appear at about 1520, 1380, 810 cm⁻¹ and the strong absorptions at about 1261, 1030, 639 cm⁻¹ which can be assigned to the triflate anions stretching. The ¹H NMR spectra of **3a** and **3b** displayed similar signal patterns for the pyridyl protons with two singlets at δ = 8.95 and 8.65 for **3a** and at δ = 9.00 and

8.66 for **3b**. In addition, the structure of [Rh₆(Cp*)₆(μ₃-4-tpt-κN)₂(μ-Cl)₆](O₃SCF₃)₆ (**3b**) was determined by single crystal X-ray analysis (Fig. 1).

The molecular structure of **3b** contains six octahedral rhodium centers, which are bridged by six chloro ligands and two tpt units with an average Rh···Rh separation of 3.66 Å, these Rh···Rh distances are comparable to those found in the chloro-bridged tetranuclear complexes [6a]. All of the rhodium clips are nearly 90° and the triazine moieties are paralleled from each other. Interestingly, the pyridines are slight twisted from the normal to the corresponding triazine moieties range of 7.8–11.7°, respectively. The centroid···centroid distance between the two triazine moieties is 3.62 Å, which show strong parallel π-stacking

Fig. 1. Crystal structure of the cationic part of **3b**; (a) viewed down the *b* axis and (b) viewed along the *a* axis (hydrogen atoms are omitted for clarity).

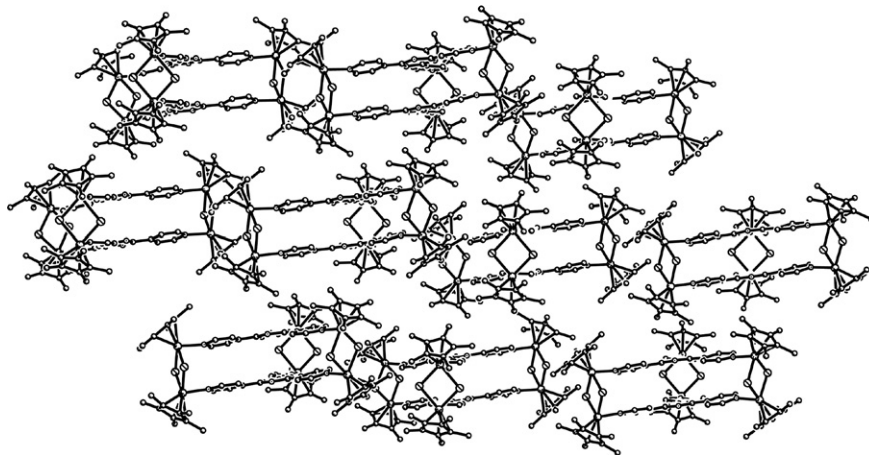


Fig. 2. Crystal packing of the cationic part of **3b**.

Table 1
Selected bond distances (Å) and angles (°) for **3b**

Bond distance (Å) in 3b			
Rh(1)–N(1)	2.0985(5)	Rh(1)–Cl(1)	2.4450(5)
Rh(2)–N(2)	2.1047(5)	Rh(2)–Cl(3)	2.4333(6)
Rh(3)–N(3)	2.0764(4)	Rh(3)–Cl(5)	2.4343(5)
Rh(3)–Cl(6)	2.4412(5)	Rh(4)–N(4)	2.1092(5)
Rh(4)–Cl(1)	2.4466(5)	Rh(5)–N(5)	2.1145(5)
Rh(6)–N(6)	2.1026(4)	Rh(6)–Cl(6)	2.4431(5)
Bond angle (°) in 3b			
N(1)–Rh(1)–C(40')	95.021(18)	N(1)–Rh(1)–C(39)	107.780(14)
N(1)–Rh(1)–C(38)	146.103(10)	N(1)–Rh(1)–C(40)	92.320(17)
N(1)–Rh(1)–C(37)	151.638(11)	N(1)–Rh(1)–C(41)	113.390(18)
N(1)–Rh(1)–Cl(1)	87.950(11)	C(39)–Rh(1)–Cl(1)	162.027(4)
C(38)–Rh(1)–Cl(1)	125.946(5)	C(40)–Rh(1)–Cl(1)	134.890(3)
C(47)–Rh(2)–N(2)	93.019(9)	C(51)–Rh(2)–N(2)	109.764(8)
N(2)–Rh(2)–Cl(3)	88.396(8)	N(3)–Rh(3)–Cl(5)	86.535(16)
N(4)–Rh(4)–Cl(1)	89.893(17)	N(5)–Rh(5)–Cl(4)	88.641(7)

interactions between the aromatic rings of 4-tpt subunits and the distance is similar to that found in related $[\text{Ru}_6(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})_6(\mu_3\text{-}4\text{-tpt-}\kappa\text{N})_2(\mu\text{-Cl})_6](\text{O}_3\text{SCF}_3)_6$ and $[\text{Ru}_6(\eta^6\text{-C}_6\text{Me})_6(\mu_3\text{-}4\text{-tpt-}\kappa\text{N})_2(\mu\text{-Cl})_6](\text{O}_3\text{SCF}_3)_6$ complexes [4b]. The average Rh–N and Rh–Cl bond lengths are 2.10 and 2.44 Å, which similar to that found in related the Ir–N and Ir–Cl bond lengths are 2.090(17) Å and 2.400(5) Å in **2a**. Viewed down the *b* axis, the complex has a perfect trinuclear triangular structure with Rh···Rh lengths of 13.2 Å. The volume of the metallo-prism is about 273 Å³ based on the distance of the two triazine moieties.

In the crystal packing of **3b**, no π – π stacking interacting systems are observed between the independent molecules (Fig. 2). Selected bond lengths and angles are presented in Table 1.

3. Conclusion

In summary, we have successfully developed the step-wise formation of hexanuclear iridium and rhodium metal-

lo-prisms. Similar procedures have the potential to lead to many new and interesting forms of molecular architecture and the use of molecular materials are now in progress in our group.

4. Experimental

4.1. General procedures

All manipulations were performed under an atmosphere of argon using standard Schlenk techniques. All solvents were dried and deoxygenated before use. The solvents diethyl ether, hexane were refluxed and distilled over sodium/benzophenone ketyl and CH_2Cl_2 were dried over CaH_2 under nitrogen prior to use. 2,4,6-Tris(4-pyridyl)-1,3,5-triazine (tpt) [9], $[\text{Cp}^*\text{IrCl}_2]_2$ [10], $[\text{Cp}^*\text{RhCl}_2]_2$ [10], were prepared according to the reported procedures.

Elemental analyses were performed on Elementar III Vario EI Analyzer. IR spectra were recorded on a Nicolet AVATAR-360IR spectrometer and ¹H NMR (500 MHz) spectra were obtained on a Bruker DMX-500 spectrometer.

4.2. Synthesis of $[\text{Cp}_3^*\text{Ir}_3(\mu_3\text{-}4\text{-tpt-}\kappa\text{N})\text{Cl}_6]$ (**2a**)

To a solution of **1a** (120 mg, 0.15 mmol) in CH_2Cl_2 (20 mL) was added tpt (32 mg, 0.1 mmol) at room temperature. After stirring for 18 h, the solvent was filtrated and reduced to about 3 mL under vacuum. Hexane was added slowly into the red solution, giving orange solids of **2a** (146 mg, 96%). Anal. Calcd for $\text{C}_{48}\text{H}_{57}\text{Cl}_6\text{Ir}_3\text{N}_6$: C, 38.25; H, 3.81. Found: C, 37.97; H, 3.69%. IR (KBr, cm^{-1}): 1516(s), 1371(s), 810(s). ¹H NMR (500 MHz, CDCl_3): δ = 1.63 (s, 45H, C_5Me_5), 8.66 (br, 6H, pyridyl), 8.97 (br, 6H, pyridyl).

4.3. Synthesis of $[\text{Cp}_3^*\text{Rh}_3(\mu_3\text{-}4\text{-tpt-}\kappa\text{N})\text{Cl}_6]$ (**2b**)

To a solution of **1b** (93 mg, 0.15 mmol) in CH_2Cl_2 (20 mL) was added tpt (32 mg, 0.1 mmol) at room

temperature. After stirring for 18 h, the solvent was filtered and reduced to about 3 mL under vacuum. Hexane was added slowly into the red solution, giving orange solids of **2b** (115 mg, 92%). Anal. Calcd for $C_{48}H_{57}Cl_6Rh_3N_6$: C, 46.51; H, 4.64. Found: C, 46.32; H, 4.29%. IR (KBr, cm^{-1}): 1515(s), 1370(s), 811(s). 1H NMR (500 MHz, $CDCl_3$): $\delta = 1.63$ (s, 45H, C_5Me_5), 8.63 (br, 6H, pyridyl), 8.93 (br, 6H, pyridyl).

4.4. Synthesis of $[Cp^*_6Ir_6(\mu_3-4-tpt-\kappa N)_2(\mu-Cl)_6](O_3SCF_3)_6$ (**3a**)

$AgSO_3CF_3$ (77 mg, 0.3 mmol) was added to a solution of **2a** (151 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) at room temperature and stirred for 3 h. The solution was filtered to remove the undissolved compound. The filtrate was concentrated and diethyl ether was added slowly into the yellow solution, giving yellow solids of **3a** (135 mg, 72%). Anal. Calcd for $C_{102}H_{114}Cl_6F_{18}Ir_6N_{12}O_{18}S_6$: C, 33.14; H, 3.11. Found: C, 32.48; H, 2.89%. IR (KBr, cm^{-1}): 1521(s), 1377(s), 1262(s), 1031(s), 811(s), 639(s). 1H NMR (500 MHz, $CDCl_3$): $\delta = 1.59$ (s, 90H, C_5Me_5), 8.65 (br, 12H, pyridyl), 8.95 (br, 12H, pyridyl).

4.5. Synthesis of $[Cp^*_6Rh_6(\mu_3-4-tpt-\kappa N)_2(\mu-Cl)_6](O_3SCF_3)_6$ (**3b**)

$AgSO_3CF_3$ (77 mg, 0.3 mmol) was added to a solution of **2b** (123 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) at room temperature and stirred for 3 h. The solution was filtered to remove the undissolved compound. The filtrate was concentrated and diethyl ether was added slowly into the yellow solution, giving yellow solids of **3b** (102 mg, 65%). Anal. Calcd for $C_{102}H_{114}Cl_6F_{18}Rh_6N_{12}O_{18}S_6$: C, 38.76; H, 3.64. Found: C, 38.32; H, 3.25%. IR (KBr, cm^{-1}): 1518(s), 1381(s), 1260(s), 1032(s), 808(s), 639(s). 1H NMR (500 MHz, $CDCl_3$): $\delta = 1.63$ (s, 90H, C_5Me_5), 8.63 (br, 12H, pyridyl), 8.93 (br, 12H, pyridyl).

5. Crystallography

Diffraction data of **3b** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All the data were collected at room temperature and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL) [11], SADABS [12] absorption corrections were applied to the data. There is strong disorder in all the anions and solvents and some of the triflate anions were never found. Therefore, new data sets corresponding to omission of the missing anions were generated with the SQUEEZE algorithm and the structures were refined to convergence. Four of the six pentamethylcyclopentadienyl ligands are also disordered, which were refined with 60/40 site occupancy and fixed structures. Non-hydrogen atoms, except some carbon atoms in the disordered pentamethylcyclopentadienyl fragments, were

Table 2
Crystallographic data for complex **3b**

	3b
Formula	$C_{102}H_{114}Cl_6F_{18}Rh_6N_{12}O_{18}S_6$
<i>M</i>	3160.57
Crystal system	Monoclinic
Space group	$P2(1)/c$
<i>a</i> (Å)	12.267(3)
<i>b</i> (Å)	37.165(9)
<i>c</i> (Å)	31.422(8)
β (°)	90.47
<i>V</i> (Å ³)	14,325(6)
<i>Z</i>	4
<i>D</i> _{calc} (g/cm ³)	1.466
<i>F</i> (000)	6336
Crystal size/mm	0.24 × 0.18 × 0.12
Collected reflections	60,190
Unique	25,239
Parameters	988
Goodness-of-fit on F^2	0.606
Final <i>R</i> indices ($I > 2\sigma(I)$) ^a	$R_1 = 0.0619$ $wR_2 = 0.1347$
<i>R</i> indices (for all data)	$R_1 = 0.1968$ $wR_2 = 0.1521$
Largest difference in peak/hole (e/Å ³)	0.630, −0.572

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}.$$

refined anisotropically, and hydrogen atoms were located at calculated positions. A summary of the crystallographic data and selected experimental information are given in Table 2.

Acknowledgements

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Appendix A. Supplementary data

CCDC 660961 contains the supplementary crystallographic data for this **3b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.11.008](https://doi.org/10.1016/j.jorganchem.2007.11.008).

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