

Self-assembled hexanuclear arene ruthenium metallo-prisms with unexpected double helical chirality†

Padavattan Govindaswamy,^a David Linder,^b Jérôme Lacour,^b Georg Süss-Fink^a and Bruno Therrien*^a

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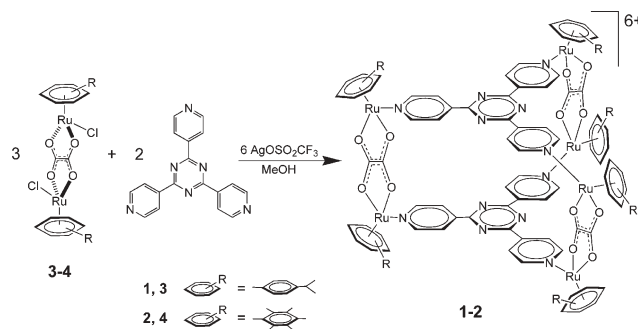
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Self-assembly of 2,4,6-tripyridyl-1,3,5-triazine (tpt) subunits with arene ruthenium building blocks and oxalato bridges affords cationic triangular metallo-prisms of the type $[\text{Ru}_6(\text{arene})_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$ (arene = C_6Me_6 and $p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me}$); the unexpected double helical chirality of the metallo-prisms observed in the solid state persists in solution giving rise to two different stereodynamic processes as demonstrated by NMR enantiodifferentiation experiments.

The self-assembly of transition metal complexes to give discrete supramolecular architectures has been studied by several groups and is the subject of some extensive reviews.¹ Both, two- and three-dimensional architectures are known, in which the metal centres or the branched ligands or a combination of both control the shape of the resulting assemblies. The simplest three-dimensional construction which involves the fewest components is the triangular prism: only five building blocks are necessary to obtain a triangular prism; two trigonal subunits, and three linear connecting units.² However, metal-based triangular prisms including more components³ are known as well. If no stereogenic elements are introduced within the components of the prism and the two planar triangular subunits perfectly eclipsed, the triangular prism possesses a D_{3h} symmetry, and is therefore achiral. However, a slight deviation from the eclipsed conformation reduces the achiral point group D_{3h} to the chiral D_3 symmetry group and therefore generates “double-rosette” type helicity with P or M configuration.⁴ Moreover, concerted rotation of some aromatic rings of the tritopic subunits creates three-bladed propeller chirality with Δ (clockwise) or Λ (counterclockwise) configuration. Whereas either or both of these stereogenic elements can easily be detected in the solid state, so far, it has been hardly observed in solution,⁵ the complexes being too configurationally labile or the system being achiral in solution.

Herein we report the synthesis and characterisation of two cationic triangular metallo-prisms incorporating arene ruthenium building blocks, bridged by oxalato ligands, and connected by two 2,4,6-tripyridyl-1,3,5-triazine (tpt) subunits (Scheme 1). The single-crystal structure analyses of $[\text{Ru}_6(p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3][\text{OSO}_2\text{CF}_3]_6$ (**1**)⁶ and $[\text{Ru}_6(\text{C}_6\text{Me}_6)_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3][\text{OSO}_2\text{CF}_3]_6$ (**2**)⁷ are presented. The behaviour of **1** and **2** in solution was studied by NMR spectroscopy in the



Scheme 1

presence of chiral solvating agents demonstrating for both the presence of chiral conformations.

Compounds **1** and **2** were prepared following a two-step strategy in which the known dinuclear oxalato complex $[\text{Ru}_2(p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})_2(\text{C}_2\text{O}_4)\text{Cl}_2]$ (**3**)⁸ and the new oxalato dinuclear complex $[\text{Ru}_2(\text{C}_6\text{Me}_6)_2(\text{C}_2\text{O}_4)\text{Cl}_2]$ (**4**) are used as metal “clips” (Scheme 1). The coordinatively unsaturated intermediate formed upon addition of $\text{AgOSO}_2\text{CF}_3$ presumably allows the $\text{Ru}_2(\text{arene})_2(\text{C}_2\text{O}_4)^{2+}$ moieties to adopt a syn geometry upon coordination to the tpt unit. The complexes were isolated and characterised as their triflate salts, $[\text{Ru}_6(p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$ (**1**) and $[\text{Ru}_6(\text{C}_6\text{Me}_6)_6(\text{tpt})_2(\text{C}_2\text{O}_4)_3]^{6+}$ (**2**), which turned out to be quite soluble in $(\text{CH}_3)_2\text{CO}$, CH_3CN and MeOH , and only sparingly soluble in CH_2Cl_2 and CHCl_3 .

The molecular structures of **1** and **2** have been solved by single-crystal X-ray analysis of the triflate salts, for the IR and NMR data see supporting information.† From a structural point of view, the two tpt subunits are expected to be around 5.5 Å apart, based on the Ru–Ru separation observed in **3** (mean 5.503(6) Å).⁸ Indeed, the single-crystal X-ray structure analyses of **1** and **2** reveal an average Ru–Ru separation of 5.49 Å. Surprisingly, the two central triazine units in **2** are very close. The centroid⋯centroid distance between the two triazine moieties is only 3.42 Å as compared to 3.83 Å in **1**, where the tpt ligands adopt an almost perfect eclipsed conformation (negligible “double-rosette” chirality) with moderate three-bladed propeller helicity (Fig. 1). Indeed, the twist angle between the two tpt subunits is only 4.0° whereas the pyridyl rings of the two tpt units are tilted by 16.6° out of the plane of the triazine ring. Unlike $[\mathbf{1}][\text{OSO}_2\text{CF}_3]_6$, in which the complex has a crystallographically imposed threefold symmetry, $[\mathbf{2}][\text{OSO}_2\text{CF}_3]_6$ possesses a twofold symmetry.

Interestingly, the ruthenium oxalato clips are tilted by 20.5° out of the plane of the tpt subunits in **2**, in order to improve the π -stacking interaction between the two tpt ligands (Fig. 2).

^aInstitut de Chimie, Université de Neuchâtel, Case postale 158, CH-2009, Neuchâtel, Switzerland. E-mail: bruno.therrien@unine.ch

^bDepartment of Organic Chemistry, University of Geneva, Quai E. Ansermet 30, CH-1211, Geneva 4, Switzerland

† Electronic supplementary information (ESI) available: Preparation and characterisation of complexes **1–4**, full NMR experiments, and X-ray crystal data for **1–2**. See DOI: 10.1039/b610155k

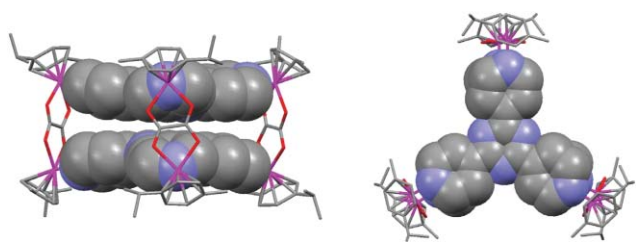


Fig. 1 Van der Waals representation of **1**, view along the C_2 axis (left) and the C_3 axis (right).

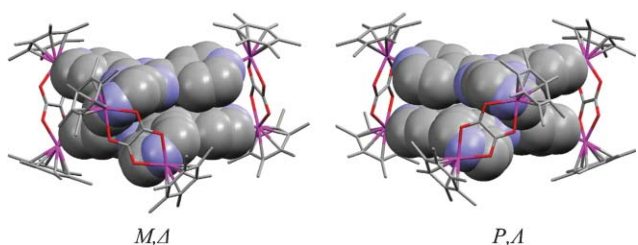


Fig. 2 Van der Waals representations of the two (M,A) and (P,A) enantiomers of **2**.

Therefore, the two tpt subunits are “staggered”, thus generating a “double-rosette” like chirality. The Bailar twist angles,⁹ that indicate the degree of deviation from trigonal prism, are 15.5, 15.5 and 18.1°, respectively (Fig. 3). Moreover, the pyridyl rings of the two tpt units are tilted by as much as 36° out of the plane of the triazine ring. It creates a Δ/A propeller isomerism which is, in this case, probably enforced by the strong M/P double-rosette helicity. As a consequence, **2** adopts only two enantiomeric configurations (M,A) and (P,A) (as viewed along the C_3 axis); both being present in the racemic crystal (Fig. 2). It is noteworthy that in the chloro-bridged analogous compounds $[\text{Ru}_6(p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})_6(\text{tpt})_2\text{Cl}_6]^{6+}$ and $[\text{Ru}_6(\text{C}_6\text{Me}_6)_6(\text{tpt})_2\text{Cl}_6]^{6+}$ the two tpt units are perfectly eclipsed and no chirality was observed.¹⁰

Given these observations in the solid state, the question arises whether the “double” helical chirality of **2** persists in solution and, if so, whether the exchange between the (M,A) and (P,A) enantiomers is slow enough on the NMR time-scale to be observed.

At room or low-temperature, $^1\text{H-NMR}$ experiments for **1** and **2** in acetone- d_6 showed no signals indicating the presence of

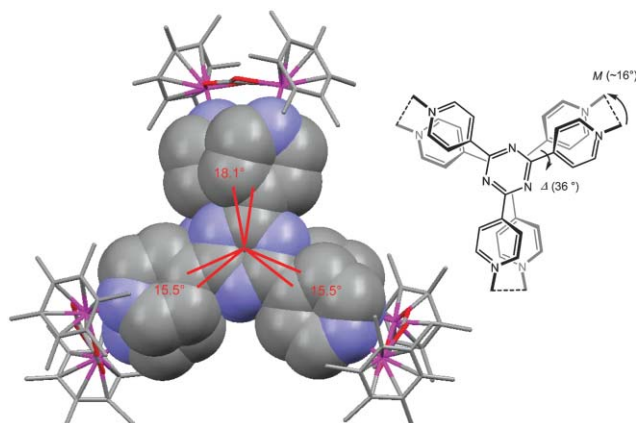
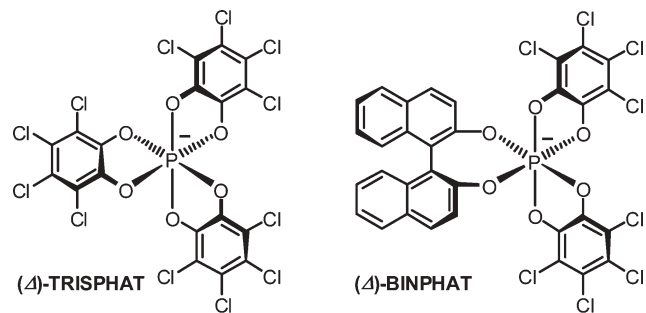


Fig. 3 Bailar twist angles and schematic representation of the double M (double rosette) and A (propeller) helicity of **2**.

diastereotopic atoms or groups, suggesting, as just mentioned, either fast enantiomerisation on the NMR time-scale or an absence of helical chirality in solution. To shed some light on this issue, complexes **1** and **2** were studied in the presence of anionic NMR chiral solvating agents,¹¹ namely TRISPHAT¹² and BINPHAT.¹³

Whereas an immediate and complete precipitation occurred upon addition of salt $[\text{Bu}_4\text{N}][(\Delta)\text{-TRISPHAT}]$ (1.0 equiv.) to acetone- d_6 solutions of **1** and **2**, no such behaviour was observed upon the incremental addition of $[\text{Bu}_4\text{N}][(\Delta)\text{-BINPHAT}]$, which induced a decent enantiodifferentiation of all aromatic signals of **1** and **2**.¹⁴



In the case of **2**, at 298 K, an effective split of NMR signals was observed in the presence of (Δ)-BINPHAT anion (1 : 1 ratio) with one set of signals for each enantiomer of the racemic cationic complex (Fig. 4). Not too surprisingly, the difference in chemical shifts ($\Delta\delta$) between the split signals increases upon the addition of larger amounts of the NMR chiral solvating agent (1.0 to 6.0 equiv.). The most shifted signals are those of the tpt ligand ($\Delta\delta_{\text{max}}$ 0.75 ppm). All in all, it is the typical behaviour of a chiral racemic entity in the presence of an effective NMR chiral solvating agent indicating, most probably, that the (M,A) and (P,A) configurations of compound **2** remains in solution at 298 K.

With this result in hand, the study of the solution behaviour of **1** was initiated. At 298 K and in the presence of (Δ)-BINPHAT, $^1\text{H-NMR}$ analyses of $[\mathbf{1}][\text{OSO}_2\text{CF}_3]_6$ revealed, to our surprise, both (i) a clean enantiodifferentiation of the arene protons and of the methyl groups of the isopropyl substituent of the *para*-cymenes and (ii) broad resonances for the pyridyl protons of the tpt subunits (Fig. 5, spectrum b).

This NMR behaviour is in sharp contrast to that of **2**. Considering that the broad resonances at 298 K are the result of stereodynamics, a variable-temperature NMR experiment was performed (233–298 K, acetone- d_6) which revealed, as expected, a

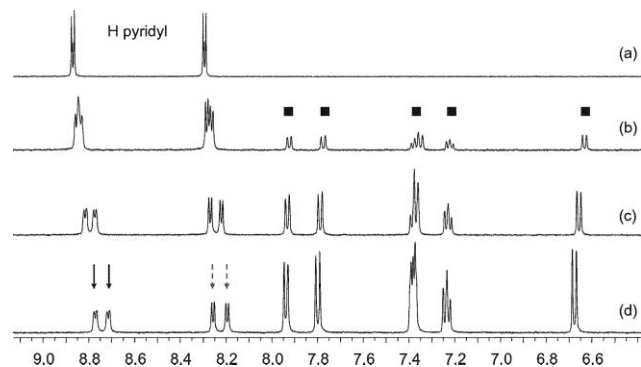


Fig. 4 $^1\text{H-NMR}$ spectra (parts, 500 MHz, acetone- d_6) of $[\mathbf{2}][\text{OSO}_2\text{CF}_3]_6$ in the presence of (a) 0, (b) 1.0, (c) 3.0 and (d) 6.0 equiv. of $[\text{Bu}_4\text{N}][(\Delta)\text{-BINPHAT}]$ (signals indicated by ■).

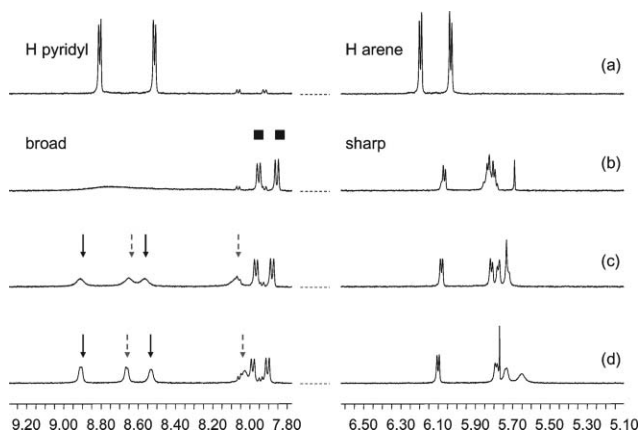


Fig. 5 $^1\text{H-NMR}$ spectra (parts, 500 MHz, acetone- d_6) of $[\mathbf{1}][\text{OSO}_2\text{CF}_3]_6$: (a) 298 K, (b) 298 K, (c) 273 K, (d) 253 K; spectra (b), (c), and (d) being measured in the presence of 3.0 equiv. of $[\text{Bu}_4\text{N}][(-)\text{-BINPHAT}]$ (signals indicated by ■).

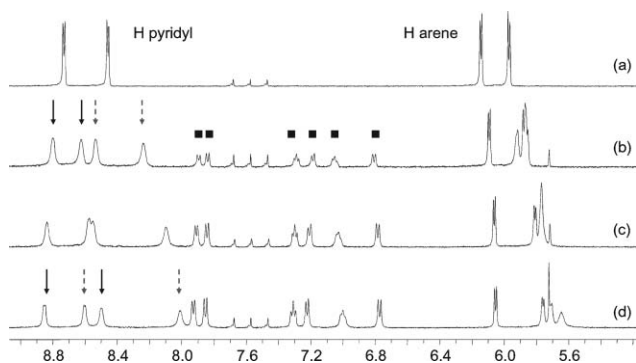


Fig. 6 $^1\text{H-NMR}$ spectra (parts, 500 MHz, acetone- d_6) of $[\mathbf{1}][\text{OSO}_2\text{CF}_3]_6$ at 253 K in the presence of (a) 0, (b) 1.0, (c) 2.0, (d) 3.0 equiv. of $[\text{Bu}_4\text{N}][(-)\text{-BINPHAT}]$ (signals indicated by ■).

sharpening and a splitting of the pyridyl signals at low temperature.

At 253 K, in the presence of $(-)\text{-BINPHAT}$ anion (1.0–3.0 equiv.), salt $[\mathbf{1}][\text{OSO}_2\text{CF}_3]_6$ behaves essentially as compound $[\mathbf{2}][\text{OSO}_2\text{CF}_3]_6$ (Fig. 6). The better split signals are those of the aromatic protons and those of the tpt subunits in particular ($\Delta\delta_{\text{max}}$ 0.45 ppm, H tpt).

At this point, these results can be rationalised by considering that two decoupled stereodynamic phenomena are at play in complex **1**: (i) a slow-on-the-NMR-time-scale double-rosette interconversion ($P \rightleftharpoons M$, indicated by the enantiodifferentiation of the signals of the *para*-cymene moieties at 298 K) and (ii) a faster propeller isomerism ($\Delta \rightleftharpoons \Delta$) involving the pyridine moieties of the tpt subunits. This uncoupling of the two interconversion pathways probably indicates that, in accordance with the solid state structure, the *M* or *P* “double rosette” conformations of **1** are not as strongly “staggered” as in **2** (*i.e.*, a poor tilt of oxalato dimetallic clips) allowing an independent propeller isomerism of the pyridyl moieties.

In conclusion, we have shown a simple and straightforward synthesis of arene ruthenium metallo-prisms. The oxalato derivatives **1** and **2** possess a double helical chirality induced by a twist of the tpt units and a concerted tilt of pyridyl moieties,

which persists in solution as shown by the NMR spectrometric measurements in the presence of $(\Delta)\text{-BINPHAT}$ anion.

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- Crystal data for **1**: $\text{C}_{108}\text{H}_{108}\text{F}_{18}\text{N}_{12}\text{O}_{30}\text{Ru}_6\text{S}_6$, $M = 3194.84$, Trigonal, space group $P3c1$ (No. 158), cell parameters $a = 18.100(3)$, $c = 25.705(5)$ Å, $V = 7293(2)$ Å³, $T = 173(2)$ K, $Z = 2$, $D_c = 1.455$ g cm⁻³, λ (Mo K α) = 0.71073 Å, 12150 reflections measured, 6305 unique ($R_{\text{int}} = 0.0709$) which were used in all calculations. The structure was solved by direct method (SHELXL-97) and refined by full-matrix least-squares methods on F^2 with 439 parameters. $R_1 = 0.0647$ ($I > 2\sigma(I)$) and $wR_2 = 0.1713$, GOF = 0.831; max./min. residual density 0.503/–0.449 eÅ⁻³. CCDC 614959. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610155k.
- Crystal data for **2**: $\text{C}_{120}\text{H}_{132}\text{F}_{18}\text{N}_{12}\text{O}_{30}\text{Ru}_6\text{S}_6$, $M = 3363.16$, Monoclinic, space group $C2/c$ (No. 15), cell parameters $a = 27.333(5)$, $b = 19.941(4)$, $c = 28.163(6)$ Å, $\beta = 99.68(3)^\circ$, $V = 15132(5)$ Å³, $T = 173(2)$ K, $Z = 4$, $D_c = 1.476$ g cm⁻³, λ (Mo K α) = 0.71073 Å, 55313 reflections measured, 13447 unique ($R_{\text{int}} = 0.0389$) which were used in all calculations. The structure was solved by direct method (SHELXL-97) and refined by full-matrix least-squares methods on F^2 with 667 parameters. $R_1 = 0.0525$ ($I > 2\sigma(I)$) and $wR_2 = 0.1568$, GOF = 1.038; max./min. residual density 1.212/–1.381 eÅ⁻³. CCDC 614960. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610155k.
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