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# Design of bis(acylamino)triazine containing ruthenium-acetylides as self-complementary supramolecular units

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# 1. Introduction

Self-assembly is an area of vigorous research activity that has strongly impacted several facets of Materials Science. It is motivated by the anticipation that careful design of functional molecular systems that self-assemble through the concerted action of multiple non-covalent interactions will direct the tailoring of materials with specific physical and chemical properties [1-3]. Being able to design and construct large and complex architectures from small molecular modules requires a precise knowledge of the basic structural units that are formed by intermolecular interactions in a reversible and predictable manner [4]. The structural and functional properties of the final supramolecular assemblies result from the assembling information stored in the molecular components, which are dictated by the interplay of both geometrical and conformational constraints, and by the presence of complementary recognition end-groups. Hydrogen bonds are the ideal non-covalent interactions to be used in molecular organization because they combine directionality with strength, along with a reversible character, providing access to a vast variety of predictable functional assemblies [5-7].

# ABSTRACT

A series of systematically varied 'rigid-rod' octahedral ruthenium-acetylide complexes, bearing conjugated bis(acylamino)triazine (DAT) substituents capable of ADAD-DADA pairing, of general formula  $trans-[(dppe)_2Ru(Cl)(C \equiv C - C_6H_4 - DAT(R)_2)]$  (R = Et, *i*-Pr, *t*-Bu, *n*-C<sub>5</sub>H<sub>11</sub>) have been synthesized and thoroughly characterized in solution by <sup>1</sup>H NMR and in the solid state. trans- $[Ru(-C \equiv C - C_6H_4 - DAT(R)_2)2]$  $(dppe)_2$  (R = n-C5H11) has also been designed to form discrete oligomeric chains in solution. © 2010 Elsevier B.V. All rights reserved.

The combination of transition metals and hydrogen bonding interactions has recently become increasingly important in several areas of chemistry because of the specific optical, magnetic and electronic properties of coordination and organometallic compounds, and their potential applications in many fields such as materials, biomedicine, engineering, communications, microelectronics and sensors [8]. One challenging problem in this area is then learning how to combine hydrogen bonding modules with functional systems to drive molecular organization in predetermined patterns [9]. An interesting strategy has focused on the design of pendant ligands which contain specific hydrogen bonding modules to be involved in intermolecular interactions; the crucial feature of this strategy is that the metal should preferentially coordinate to the active site in the pendant ligand, rather than to heteroatoms in the hydrogen bonding modules. Indeed, many metal carbon bonds are reactive toward the types of functional groups, such as the protic groups used as hydrogen bond donors, which are commonly used in self-assembly and crystal engineering [8]. Very few suitable synthons have been identified to date but recent approaches by our group and others show that alkynes are interesting building motifs for this purpose [10–14]. In particular, alkynes substituted by nucleobases and by urea-pyrimidinedione constitute valid candidates that allow for the synthesis of transition metal species capable of acting as supramolecular synthons, both in solution and



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in the solid state [11,13]. We also illustrated that  $trans-[(dppe)_2Ru$  (Cl)(C $\equiv$ C-R)] bearing terminal hydrogen bonding receptors can be used as efficient sensors exhibiting large guest-induced colour changes due to interactions of anions with these receptors [12].

Our current approach consists on the introduction of diaminotriazine units as hydrogen bonding modules at the remote end of *trans*-[(dppe)<sub>2</sub>Ru(Cl)(C $\equiv$ C–R)] alkynyl–ruthenium derivatives. Metal–acetylide complexes constitute valid candidates in this context to generate well-defined supramolecular architectures. The linear and rigid arrangement of atoms in M–C $\equiv$ C–R structure makes them particularly attractive building blocks for a wide range of complex architectures and applications in materials chemistry (electron transfer, nonlinear optics, sensing, etc) due to the efficient electronic coupling between the metal and the remote groups through the  $\pi$ -conjugated path [15,16].

1,3,5-Triazines constitute a family of heterocycles that have been widely investigated in chemical molecular-recognition studies [17–22]. For instance, Asadi et al. designed Janus-bases in which diaminotriazine—uracil self-complementary units are capable of ADA—DAD pairing [23]. On the other hand, Rotello and coworkers investigated the modulation of recognition in conjugated bis(acy-lamino)triazine moieties and flavin via triple hydrogen bonding formation, demonstrating an efficient electronic communication in the bis(acylamino)triazine based receptors [24]. Rotello and coworkers also established that the dimerisation of substituted bis(acylamino)triazine are determined by the nature of the substituents [25].

We present herein the synthesis and characterization of organoruthenium complexes bearing conjugated bis(acylamino) triazine moieties for their ability to form ADAD-DADA pairing. A structure determination unambiguously demonstrates the formation of homodimer pairs via quadruple hydrogen bonding formation. These assemblies have also been thoroughly characterized in solution by <sup>1</sup>H NMR. We thus provide evidence that the accurate design of the multivalent molecular building blocks allows the versatile generation of complex and discrete assemblies of rigidrod ruthenium  $\sigma$ -acetylides, such as dimers, featuring a controlled geometry.

## 2. Experimental

### 2.1. Crystallography

Single crystal of 7a was mounted on a Nonius four-circle diffractometer equipped with a CCD camera and a graphite monochromated Mo K $\alpha$  radiation source ( $\lambda = 0.71073$  Å) from the Centre de Diffractométrie (CDFIX), Université de Rennes 1, France. Data collection was performed at 293(2) K. Compound 7a (C<sub>69</sub>H<sub>64</sub>ClN<sub>5</sub>O<sub>2</sub>P<sub>4</sub>Ru) crystallizes in the monoclinic centrosymmetric  $P2_1/c$  space group, a = 12.6702(3), b = 24.7937(9), c = 20.9616(7) Å,  $\beta = 112.228(9)^{\circ}$ , V = 6095.5(3) Å<sup>3</sup>, Z = 4,  $\rho = 1.368 \text{ g cm}^{-3}, \mu = 4.56 \text{ cm}^{-1}, F(000) = 2600. \text{ Structure was}$ solved with SHELXS-97 [26] and refined with SHELXL-97 programs by full-matrix least squares methods on  $F^2$ . The refinement of 739 parameters of 13846 unique reflections [7727 observed intensities  $I \ge 2\sigma(I)$ ] was performed with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model on calculated positions. Final residues  $R_1 | I \ge 2\sigma$ (I)] = 0.0556;  $wR_2$  = 0.1142. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-784980.

Single crystal of **7c** ( $0.18 \times 0.15 \times 0.15$  mm) was mounted on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatized Mo K $\alpha$  radiation source ( $\lambda = 0.71073$  Å). RuP<sub>4</sub>Cl<sub>3</sub>C<sub>74</sub>H<sub>76</sub>N<sub>15</sub>O<sub>3</sub>, Mr = 1414.70, triclinic, *P* – 1, *a* = 12.8727(7),



**Scheme 1.** (i) Dicyandiamide (1.3 equiv.), KOH (0.21 equiv.), 2-ethoxyethanol (60 ml), reflux, 24 h. (ii) acyl chloride (3.8 equiv.), pyridine, reflux, 72 h. (iii)  $PdCl_2(PPh_3)_2$  (0.05 equiv.), Cul (0.1 equiv.), TMSA (3 equiv.), THF (40–60 ml),  $iPr_2NH$  (25–40 ml), 50 °C, 72 h. (iv)  $Bu_4NF$  (solution 1 M, 1.5 equiv.), THF (25 ml),  $H_2O$  (1 ml), r.t, 2 h.

b = 16.2361(9), c = 18.2229(9) Å,  $\alpha = 108.311(6), \beta = 98.442(4),$  $\gamma = 105.193(6)^{\circ}$ , V = 3378.5(3) Å<sup>3</sup>, Z = 4,  $\rho = 1.391$  g cm<sup>-3</sup>,  $\mu = 4.98 \text{ cm}^{-1}$ , F(000) = 1468, T = 110(1) K. The data collection [27]  $(2\theta_{\rm max}=54^\circ,{
m omega~scan}$  frames via 0.7° omega rotation and 15 s per frame, range HKL:H -18,17 K -24,23 L -20,26) gives 31855 reflections. The data leads to 14249 independent reflections from which 7878 with  $I > 2.0\sigma(I)$ . The structure was solved with SIR-97 [28] which reveals the non-hydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms are found with a Fourier Difference. The whole structure was refined with SHELXL-97 [26] by the full-matrix least square techniques use of  $F^2$ magnitude; x, y, z,  $\beta_{ii}$  for Ru, P, Cl, N, C and O atoms, x, y, z in riding mode for H atoms; 811 variables and 9147 observations with  $I > 2.0\sigma(I)$ ; calc  $w = 1/[\sigma^2(F_0^2) + (0.038P)^2]$  where  $P = (F_0^2 + 2F_c^2)/3$ with the resulting R = 0.045,  $R_w = 0.095$  and  $S_w = 0.864$ ,  $\Delta 
ho < 1.31$  e Å<sup>-3</sup>. Atomic scattering factors were taken from International Tables for X-ray crystallography (1992) [29]. The ORTEP view was realised with PLATON98 [30]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-646840.

# 3. Results and discussion

#### 3.1. Synthesis of ruthenium-acetylide complexes

The synthetic methodologies employed for the preparation of the new ruthenium derivatives have been adapted from previously reported procedures [31]. Substituted alkynes  $H-C\equiv C-C_6H_4-DAT$ (R)<sub>2</sub> (R = Et, *i*-Pr, *t*-Bu, *n*- $C_5H_{11}$ ) required for the syntheses of the alkynyl complexes **6a–d** were prepared by well-established organic synthetic procedures from their bromoaromatic precursors (Scheme 1) [25]. 6-(4-Bromophenyl)-1,3,5-triazine-2,4-diamine **1** was prepared by reaction of commercially available dicyandiamide in excess with 4-bromobenzonitrile in 2-ethoxyethanol in the presence of KOH, at reflux for 24 h. The presence of bromine allows the introduction of an acetylenic unit in a further step. After purification, the product was isolated as a brown powder (89%) the solubility of which is limited to highly polar solvents (DMSO). Attempts to perform Sonogashira coupling at this stage resulted in low yields. It readily appeared that the 2,4-diaminotriazine



 $\begin{array}{l} \textbf{Scheme 2. (i) } [cis-(Cl)(PPh_2CH_2CH_2PPh_2)_2Ru] [TfO] \textbf{5} (1.2 equiv.), CH_2Cl_2 (30-50 ml), r.t., 20 h.; (ii) K_2CO_3 (6 equiv.), CH_2Cl_2 (30-50 ml), r.t., 16 h. (iii) \textbf{4d} (1.0 equiv.), NEt_3 (3 equiv.), KPF_6 (3 equiv.), CH_2Cl_2 (30 ml), 35 °C, 3 days. \end{array}$ 

derivatives were scarcely soluble in solvents of low polarity. Taking into consideration the solubility of these components in low polar solvent such as CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub> as a crucial factor when designing self-assembled structures, acylation of **1** was achieved by treating with an excess of corresponding carboxylic acid chloride in dry pyridine at reflux for 72 h. Purification by silica column afforded **2a**–**d** as white crystalline solids (77–79%). As expected the solubility of these compounds is good, even in low polar solvent such as chloroform (Scheme 1).

**3a–d** were prepared by the Sonogashira coupling of **2a–d** with (trimethylsilyl)acetylene in the presence of  $PdCl_2(PPh_3)_2$  and Cul. The reaction was carried out in a 1:1mixture of THF and diisopropylamine at 50 °C for 72 h. Further purification by column chromatography on silica afforded **3a–d** as white powders in 80–85%

yield. The (DAT)-substituted alkynes 4a-d were obtained using a slight excess of tetrabutylammonium fluoride in THF at ambient temperature, as white crystalline products after purification on silica column (84–87%). These new acetylenes were characterized by NMR spectroscopy and mass spectrometry.

The reaction of a slight excess (1.2 equiv.) of alkynes  $H-C \equiv C-C_6H_4-DAT(R)_2$  (R = Et, *i*-Pr, *t*-Bu, *n*-C<sub>5</sub>H<sub>11</sub>) **4a**-**d** and [*cis*-(Cl)(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>Ru][TfO] 5 in dichloromethane at room temperature for 20 h resulted in the formation of intermediate vinylidene species 6 (Scheme 2) [31]. These reactions were monitored by <sup>31</sup>P NMR in order to ensure their completion. Solvent was removed and the resulting residue was washed with diethyl ether, affording purple vinylidene species **6a**–**d**. Further purification can be achieved by diphasic recrystallisation from dichloromethane/ pentane (1:2) to give crystals of vinylidene complexes, but **6a-d** were generally clean enough to be used in the next step. These vinylidenes were then dissolved in CH<sub>2</sub>Cl<sub>2</sub> before being deprotonated using dry potassium carbonate (methylene chloride, room temperature, 16 h). The resulting alkynyl compounds were washed with water before being purified by diphasic recrystallisation from dichloromethane/pentane (1:2) as crystalline orange powders in approximately 58-65% yields (based on 5). All the spectroscopic data of compounds **7a-d** are consistent with their proposed structures.

Several attempts to synthesize the bis alkynyl compounds 8a and **b** from the parent vinylidene species **6a** and **b** were unsuccessful, even in the presence of large excess of alkynes 4a and b. Monitoring of the reaction by <sup>31</sup>P NMR indicated that the complexes **8a** and **b** formed in small amounts but precipitated during the course of the procedure. Completion of the formation was never observed and separation from complexes 7a and b, also formed during this step by deprotonation of the parent complexes 6a and b revealed not possible. We thus decided to synthesize 8d bearing longer alkyl chains. The reaction of an excess ( $\sim 2.1$  equiv.) of  $H-C \equiv C-C_6H_4-DAT(R)_2$  (R =  $n-C_5H_{11}$ ) **4d** and [*cis*-(Cl) (PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>Ru][TfO] **5** in dichloromethane at room temperature for 5 h resulted in the formation of intermediate vinylidene species **6d** (Scheme 2) as depicted by <sup>31</sup>P NMR. To this solution were successively added KPF<sub>6</sub> (3 equiv.) and NEt<sub>3</sub> (3 equiv.), under inert atmosphere. The mixture was allowed to stir for 72 h at 35 °C to ensure the completion of the reaction as



Fig. 1. Variable-concentration (mmol L<sup>-1</sup>) <sup>1</sup>H NMR study of 7a (left) and 7c (right) in CDCl<sub>3</sub> at 233 K.

Table 1

Bond lengths [Å] and angles [°] for **7c**.



**Fig. 2.** Chemical shifts of <sup>1</sup>H resonances of the amido NH groups for **7a**–**d** and **8d** at various concentrations in CDCl<sub>3</sub> at 233 K.

depicted by <sup>31</sup>P NMR ( $\delta$ CDCl<sub>3</sub> = 54.44 ppm). This compound was tentatively purified by crystallisation from dichloromethane/ pentane, giving rise to amorphous powders of **8d**. All the spectroscopic data of compound **8d** are consistent with the proposed structure.

# 3.2. Solution-state <sup>1</sup>H NMR titrations

<sup>1</sup>H NMR dilution experiments in CDCl<sub>3</sub> were carried out for the (DAT)-substituted ruthenium—acetylide complexes **7a**–**d** and **8d**. The intermolecular hydrogen bonding is evidenced by the fact that the signals of both amide protons appear in the downfield area. **7a,b** and **d** revealed important downfield shifting of the protons of the two amido NH groups, when concentration was increased (Fig. 1 left: **7a**). Conversely, shifting of the protons of the two amido NH groups, when concentration of **7c** increased was much smaller (Fig. 1 right). Using these <sup>1</sup>H NMR dilution experiments, we

Ru(1)-C(53)	1.996(4)	Ru(1)-P(3)	2.3425(10)
Ru(1)-P(4)	2.3446(10)	Ru(1)-P(1)	2.3746(10)
Ru(1)-P(2)	2.3872(10)	Ru(1)-Cl(1)	2.4832(9)
O(1)-C(64)	1.216(4)	O(2)-C(69)	1.231(5)
N(1)-C(62)	1.339(4)	N(1)-C(61)	1.339(4)
N(2)-C(62)	1.314(4)	N(2)-C(63)	1.344(5)
N(3)-C(63)	1.323(4)	N(3)-C(61)	1.347(4)
N(4) - C(62)	1.390(4)	N(4)-C(64)	1.388(5)
N(4)-H(4)	0.8800	N(5)-C(63)	1.372(4)
N(5)-C(69)	1.382(5)	N(5)-H(5)	0.8800
C(53)-C(54)	1.204(5)	C(54)-C(55)	1.442(5)
C(55)-C(56)	1.411(5)	C(55)-C(60)	1.415(4)
C(56)-C(57)	1.371(5)	C(57)-C(58)	1.398(5)
C(58)-C(59)	1.399(5)	C(58)-C(61)	1.476(5)
C(59)-C(60)	1.373(5)	C(64) - C(65)	1.531(5)
C(65)-C(68)	1.513(5)	C(65)-C(67)	1.527(6)
C(65)-C(66)	1.551(5)	-	-
C(53)-Ru(1)-P(3)	84.63(10)	C(53) - Ru(1) - P(4)	85.56(10)
C(53) - Ru(1) - P(1)	98.20(10)	C(53) - Ru(1) - P(2)	97.65(10)
C(53) - Ru(1) - Cl(1)	175.41(10)	C(54) - C(53) - Ru(1)	176.1(3)
C(53)-C(54)-C(55)	171.4(4)	C(62)-N(1)-C(61)	113.9(3)
C(62)-N(2)-C(63)	113.6(3)	C(63)-N(3)-C(61)	114.1(3)
C(62)-N(4)-C(64)	128.5(3)	C(62) - N(4) - H(4)	115.7
C(64) - N(4) - H(4)	115.7	C(63)-N(5)-C(69)	130.2(3)
C(63)-N(5)-H(5)	114.9	C(69) - N(5) - H(5)	114.9
N(3) - C(61) - N(1)	125.1(3)	N(3)-C(61)-C(58)	116.9(3)
N(1)-C(61)-C(58)	118.0(3)	N(2)-C(62)-N(1)	126.9(3)
N(2)-C(62)-N(4)	118.9(3)	N(1)-C(62)-N(4)	114.1(3)
N(3)-C(63)-N(2)	126.4(3)	N(3)-C(63)-N(5)	121.3(3)
N(2)-C(63)-N(5)	112.3(3)	O(1)-C(64)-N(4)	123.2(3)
O(1)-C(64)-C(65)	120.7(4)	N(4)-C(64)-C(65)	116.0(3)
O(2)-C(69)-N(5)	122.3(4)	O(2)-C(69)-C(70)	123.5(4)

determined the K<sub>ass</sub> of the corresponding homodimer pairs [25]. The K<sub>ass</sub> of the homodimer **7a**–**7a** in CDCl<sub>3</sub> was calculated to be approximately  $65 \pm 5$  M<sup>-1</sup>. This value is larger than that of the homodimer pair **7b**–**7b** (ca.  $50 \pm 5$  M<sup>-1</sup>) and notably larger than that of **7c**–**7c** (ca.  $15 \pm 5$  M<sup>-1</sup>). Similar tendencies can be observed for the organic analogues **2a**–**c**, but the electron withdrawing effect of the bromo substituant results in a lowering of the shifting of the protons of the amido NH groups. The K<sub>ass</sub> of the **2**–**2** homodimers ( $30 \pm 5$  M<sup>-1</sup> for **2a**). At a first glance, the presence of the strong electron donating *trans*-[(dppe)<sub>2</sub>Ru(Cl)(C=C–)] moiety would enhance the hydrogen bond accepting capability of the triazine ring nitrogen.



**Fig. 3.** Variable-concentration <sup>1</sup>H NMR study of **8d** in CDCl<sub>3</sub> at 233 K.



Fig. 4. Packing of compound 7c at 110 K, showing the H-bonds, selected bond lengths and angles are given in Table 1.



**Fig. 5.** Packing of compound **7a** at 293 K, showing the H-bond *i*: 2 - x, -y, 2 - z; Table 2 gives selected bond lengths and angles.

Steric effects also strongly affect the relative stability of the homodimers in solution: the calculated  $K_{ass}$  for **7c** is the smallest value for all the series. A rationale for this behavior may be traced back to the greater hindrance between the pivaloyl group and the triazine ring that would result in a less planar arrangement of donor (D) and acceptor (A) in this complex.

Similarly, the chemical shift of the amido NH hydrogens in **7d** and **8d** moved downfield with higher concentrations, suggesting that these hydrogens are involved in strong hydrogen bonding (see Figs. 2 and 3). The K<sub>ass</sub> of the **7d**–**7d** and **8d**–**8d** were calculated to be approximately 70 and 75  $\pm$  5 M<sup>-1</sup>, in the same range as **7a**. The differences in the shifts in **7a** and **7d** or **8d** may be attributed to differences in the aggregation capacity of these derivatives. These data suggest that the complex **8d** is capable of forming discrete oligomeric chains in solution, due to the hydrogen bond supported dimerisation of the diamidotriazine units.

### 3.3. Solid state structure of complexes 7a and 7c

To obtain unambiguous information about the hydrogen bonding in these systems, crystal structures of crystals of **7a** and **7c** were determined by X-ray diffraction. Single crystals suitable for Xray structure determination could only be obtained by very slow evaporation of a pentane—dichloromethane solution mixture (ca. 1/2) of **7c**, into the air, at room temperature.

Details of the X-ray analysis are given in Experimental section (Table S2). Selected bond lengths and angles are listed in Table 1. A plot of the complex is shown in Fig. 4. The solid state structure revealed a monomeric structure, in which the triazine unit of the monomer was hydrogen bonded to a water molecule. One of the amido groups in **7c** is rotated in the direction of the metal centre which presumably results in better stabilisation due to interaction between the NH group and the ring nitrogen atom. We attribute this result to the large size of the butyl group connected to the diacyl diaminotriazine unit, which disfavours the linear self-associating mode and facilitates the organization of the receptor for foreign molecules. Most bond lengths and angles about the Cl-Ru-C(53)-C(2)-C(3) units in this structure are classical. For instance, the Cl–Ru (2.4832(9) Å), Ru–C(53) (1.996(4) Å), C(53)–C (54) (1.204(5) Å) and C(54)–C(55) (1.442(5) Å) data for this complex fall within the range of those previously reported for related trans-bis(bidentate octahedral phosphine)ruthenium-alkynyl complexes [12,32-35]. The dihedral angle formed by the planes of the phenyl and triazine rings is close to coplanarity  $(10.0 \pm 0.1^{\circ})$  confirming the conjugated pathway from one part of this model to the other (see also Table 1). Bond lengths and angles in this heterocyclic ring fall within the range of those previously reported for comparable fragments [36,37].

Orange crystals of 7a were obtained upon slow diffusion of a dichloromethane-pentane solution and investigated by X-ray crystallography. A plot of the complex is shown in Fig. 5 while significant bond parameters are given in Table 2. Most bond lengths and angles about the Cl-Ru-C(53)-C(54)-C(55) units in this structure are close to bond lengths and angles in 7c. Meanwhile, comparing the structures in 7a and 7c, the Ru–C(53) bond length of 1.988(4) Å is short with respect to that observed in 7c (1.997(3) Å) while the C(53)-C(54) bond of 1.221(5) Å is longer than a typical CC triple bond (average value 1.189 Å) and slightly longer than that in 7c (1.205(4) Å. Finally, the C(54)–C(55) distance of 1.424(5) Å shows some character of a double bond. Similarly, the C(58)-C(61) distance of 1.456(5) Å in **7a** is short with respect to the C(58)-C(61) distance of 1.478(4) Å in 7c. These differences between adjacent CC bonds could arise from a stronger push-pull character in 7a, compared to 7c, due to the formation of hydrogen bonds that enhances the electron withdrawing character of the triazine ring. Indeed, an

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Tab

|--|--|

Ru-P(1)	2.3460(11)	Ru-P(2)	2.3551(11)
Ru-P(3)	2.3994(11)	Ru-P(4)	2.3870(11)
Ru-Cl	2.4811(10)	Ru-C(53)	1.988(4)
O(1) - C(64)	1.218(5)	O(2)-C(67)	1.191(5)
N(1)-C(63)	1.332(5)	N(1)-C(61)	1.342(5)
N(2)-C(62)	1.347(5)	N(2)-C(63)	1.334(5)
N(3)-C(62)	1.327(5)	N(3)-C(61)	1.339(5)
N(4) - C(62)	1.377(5)	N(4)-C(67)	1.382(5)
N(4)-H(4)	0.860	N(5)-C(63)	1.386(4)
N(5)-C(63)	1.386(5)	N(5)-C(64)	1.378(5)
N(5)-H(5)	0.860	C(53)-C(54)	1.221(5)
C(54)-C(55)	1.424(5)	C(55)-C(60)	1.399(6)
C(55)-C(56)	1.379(5)	C(56)-C(57)	1.383(6)
C(57)-C(58)	1.384(6)	C(58)-C(59)	1.395(5)
C(58)-C(61)	1.456(5)	C(59)-C(60)	1.372(5)
C(64)-C(65)	1.491(5)	-	-
C(53)-Ru-P(1)	83.74 (11)	C(53)-Ru-P(2)	84.36(11)
C(53)-Ru-P(3)	97.22 (11)	C(53)-Ru-P(4)	100.44 (11)
C(53)-Ru-Cl(1)	174.83(11)	C(54) - C(53) - Ru(1)	175.2(4)
C(53)-C(54)-C(55)	174.6(5)	C(61)-N(1)-C(63)	114.5(3)
C(62)-N(2)-C(63)	112.7(3)	C(61)-N(3)-C(62)	115.0(4)
C(62) - N(4) - C(67)	127.7(4)	C(63)-N(5)-C(64)	131.2(3)
N(1)-C(61)-N(3)	124.5(4)	N(1)-C(61)-C(58)	118.2(3)
N(3)-C(61)-C(58)	117.3(4)	N(1)-C(63)-N(2)	127.0(4)
N(2)-C(62)-N(4)	115.7(3)	N(1)-C(63)-N(5)	118.4(3)
N(3)-C(62)-N(2)	126.4(4)	N(3)-C(62)-N(4)	117.9(4)
N(2)-C(63)-N(5)	114.6(3)	O(1)-C(64)-N(5)	117.3(4)
O(1)-C(64)-C(65)	120.3(4)	N(4)-C(67)-C(68)	114.1(4)
O(2)-C(67)-N(4)	123.1(4)	O(2)-C(67)-C(68)	122.9(4)

inspection of the crystal packing reveals that each molecule of **7a** is involved in a homodimer pair formation due to four hydrogen bonds established by the amide hydrogen atoms with both the triazine N (2) atom and one carbonyl group (Fig. 5). These dimers connect two diacyl diaminotriazine acetylide ligands together in a co-planar manner such that the ruthenium—acetylide units are orientated in opposing directions. The first type of H-bonds involves an N(5)—H amide unit with the triazine nitrogen N(2) of one neighbour molecule [N(5)…N(2): 3.225(5) Å], whereas the second amide hydrogen atom interacts with the oxygen atom of one carbonyl group of the same neighbour [N(4)…O(1): 2.818(5) Å].

#### 4. Conclusion

New ruthenium–acetylide compounds containing conjugated bis(acylamino)triazine moieties have been synthesized and fully characterized. The data provide unambiguous evidence that the accurate design of the bis(acylamino)triazine building blocks allows the versatile generation of complex and discrete assemblies, such as homodimer pairs via quadruple hydrogen bonding formation, featuring a controlled geometry. These assemblies have been thoroughly characterized in solution by <sup>1</sup>H NMR, in the solid state by X-ray structure determinations, evidencing the importance of sterically demanding groups in the formation of the expected hydrogen bonding array. Extensions of these molecules to the preparation of various metallopolymers for nonlinear optics are currently being carried out in our lab.

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### **Appendix A. Supplementary material**

CCDC-784980 and CCDC-646840 contain the supplementary crystallographic data for complexes **7a** and **7c** respectively. 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 (Synthesis of alkynes and related complexes; procedures for calculations of K<sub>ass</sub>.) associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010. 09.047.

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