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# Preparation and structural characterization of [CpRu(1,10-phenanthroline)(CH<sub>3</sub>CN)][X] and precursor complexes (X= PF<sub>6</sub>, BAr<sub>F</sub>, TRISPHAT-N)

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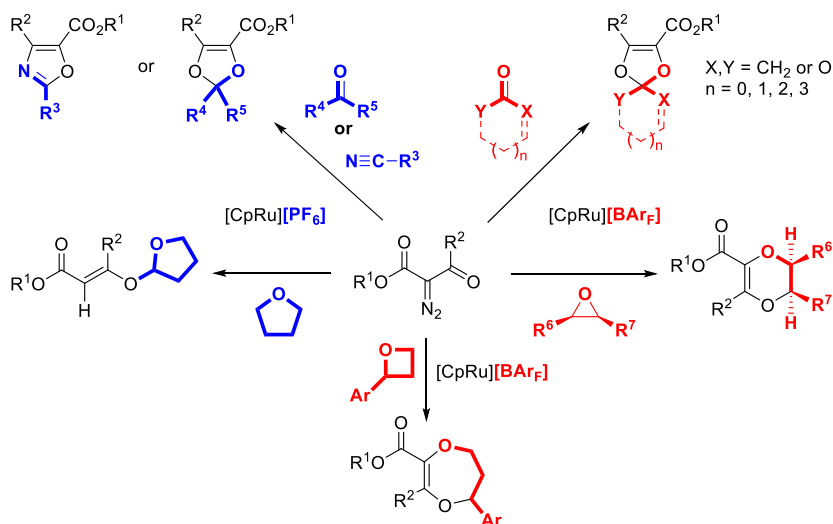
Dedicated to Antonio Togni

Cationic [Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CH<sub>3</sub>CN)<sub>3</sub>]<sup>+</sup> complex, tris(acetonitrile)(cyclopentadienyl)ruthenium(II), gives rise to a very rich organometallic chemistry. Combined with diimine ligands, and 1,10-phenanthroline in particular, this system efficiently catalyzes diazo decomposition processes to generate metal-carbenes which undergo a series of original transformations in the presence of Lewis basic substrates. Herein, syntheses and characterizations of [CpRu(Phen)(L)] complexes with (large) lipophilic non-coordinating (PF<sub>6</sub><sup>-</sup> and BAr<sub>F</sub><sup>-</sup>) and coordinating N-TRISPHAT<sup>-</sup> anions are reported. Complex [CpRu( $\eta^6$ -naphthalene)][BAr<sub>F</sub>] **[1][BAr<sub>F</sub>]** is readily accessible, in high yield, by direct counterion exchange between **[1][PF<sub>6</sub>]** and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAr<sub>F</sub>) salts. Ligand exchange of **[1][BAr<sub>F</sub>]** in acetonitrile generated stable [Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CH<sub>3</sub>CN)<sub>3</sub>][BAr<sub>F</sub>] **[2][BAr<sub>F</sub>]** complex in high yield. Then, the desired [CpRu(Phen)(CH<sub>3</sub>CN)] **[3]** complexes were obtained from either the **[1]** or **[2]** complex in the presence of the 1,10-phenanthroline as ligand. For characterization and comparison purposes, the anionic hemilabile ligand TRISPHAT-N (TTN) was introduced on the ruthenium center, from the complex **[3][PF<sub>6</sub>]**, to quantitatively generate the desired complex [CpRu(Phen)(TTN)] **[4]** by displacement of the remaining acetonitrile ligand and of the PF<sub>6</sub><sup>-</sup> anion. Solid state structures of complexes **[1][BAr<sub>F</sub>]**, **[2][BAr<sub>F</sub>]**, **[3][BAr<sub>F</sub>]**, **[3][PF<sub>6</sub>]** and **[4]** were determined by X-ray diffraction studies and are discussed herein.

**Keywords:** Ruthenium • Cyclopentadienyl • Catalysis • Solid-state

## Introduction

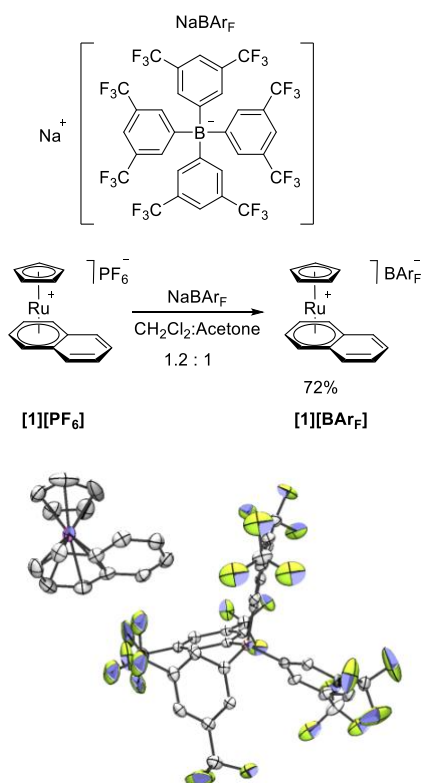
Since its discovery by Gill and Mann in 1982, the cationic [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru(CH<sub>3</sub>CN)<sub>3</sub>]<sup>+</sup> complex, commonly written [CpRu(CH<sub>3</sub>CN)<sub>3</sub>]<sup>+</sup>, has proven to be a powerful building block in organometallic chemistry.<sup>[1-7]</sup> In fact, the CpRu fragment, and its Cp\*Ru analogue, are recognized as effective catalysts for the promotion of many versatile synthetic transformations.<sup>[4, 5, 8-12]</sup> Of importance for the current study, combinations of [CpRu] and nitrogen-based ligands<sup>[1, 3, 13, 14]</sup> such as diimines<sup>[15-26]</sup> were also found to catalyze original processes.<sup>[7, 27, 28]</sup> For example, [CpRu(CH<sub>3</sub>CN)<sub>3</sub>][PF<sub>6</sub>] and pyridine-imine/pyridine-oxazoline ligands are effective catalysts in enantioselective decarboxylative rearrangements of allylic  $\beta$ -ketoesters and carbonates.<sup>[26]</sup> Kitamura successfully applied enantiopure dipyrroloimidazole ligands and [CpRu] in enantioselective dehydrative C-, N-, and O-allylation.<sup>[14, 33, 34]</sup> CpRu(bipyridine) complexes were shown to be active catalysts for both deoxygenation of 1,2-hexanediol and glycerol<sup>[35]</sup> and hydrogenation of ketone in acidic conditions.<sup>[36]</sup> Previously, Herzon *et al.* described the efficient anti-Markovnikov hydration of alkynes catalyzed by [CpRu(N^N)] (N^N = diimine ligand) derivatives.<sup>[37-39]</sup> Of interest in our laboratory, the [CpRu] fragment is also an interesting alternative to transition metal salts and complexes for the decomposition of diazo derivatives providing metal carbene or carbenoid intermediates upon dinitrogen extrusion.<sup>[40-45]</sup> In fact, in the presence of combinations of [CpRu(CH<sub>3</sub>CN)<sub>3</sub>][PF<sub>6</sub>] (as pre-catalysts) and diimine ligands (Phen = 1,10-phenanthroline, in particular),<sup>[8, 46, 47]</sup>  $\alpha$ -diazo- $\beta$ -ketoesters react smoothly and provide selective 1,3-C-H insertions into THF<sup>[48]</sup> and O-H insertions into alcohols. This catalytic system also promotes condensation reactions with nitriles, ketones, aldehydes and more recently with lactones and cyclic carbonates to generate the corresponding heterocycles (**Scheme 1**).<sup>[49, 50]</sup> Finally, in recent studies, regio and *syn*-stereoselective three-atoms insertions into a large variety of epoxides and oxetanes were described leading to the formation of original 1,4-dioxene and 1,4-dioxepine motifs respectively with, as pre-catalyst, the [CpRu(CH<sub>3</sub>CN)<sub>3</sub>][BAr<sub>F</sub>] (BAr<sub>F</sub> = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) specifically.<sup>[51, 52]</sup> In view of the influence played by the BAr<sub>F</sub> or PF<sub>6</sub> anion nature onto the [CpRu] reactivity<sup>[44]</sup> but also, more generally, of the importance of negative counterions in catalysis,<sup>[53-55]</sup> care was then taken to determine the structural impact associated such as seen onto [CpRu(1,10-phenanthroline)(CH<sub>3</sub>CN)][X] and precursor complexes.<sup>[56]</sup>



**Scheme 1.** One-pot reactions of  $\alpha$ -diazoacetates and Lewis bases catalyzed by  $[\text{CpRu}][\text{X}]$  which stands for  $[\text{CpRu}(\text{Phen})\text{CH}_3\text{CN}][\text{X}]$  complexes ( $\text{X} = \text{PF}_6$  (blue),  $\text{BAR}_F$  (red)).

## Results and Discussion

Cationic  $[\text{CpRu}(\eta^6\text{-naphthalene})]^+$  **[1]** (naphthalene = Naph), a practical and general precursor popularized by E. Peter Kündig for the formation of complex  $[\text{CpRu}(\text{CH}_3\text{CN})_3]^+$  **[2]**, is readily accessible with an array of negative counterions, such as  $\text{Cl}^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{SbF}_6^-$ ,  $\text{PF}_6^-$  or  $\text{BF}_4^-$ .<sup>[57]</sup> However and unfortunately, previous attempts to perform anion metathesis of chloride to  $\text{BAR}_F$  by a direct exchange of  $[\text{CpRu}(\eta^6\text{-naphthalene})][\text{Cl}]$  with  $\text{NaBAR}_F$ , were not met with success.<sup>[57]</sup> This problem could be circumvented in our hands starting from the  $[\text{CpRu}(\eta^6\text{-naphthalene})][\text{PF}_6]$  salt instead which was prepared following microwave assisted protocols.<sup>[57, 58]</sup> In practice, a simple mixing for 30 min of  $\text{NaBAR}_F$  and **[1][PF<sub>6</sub>]** in a homogenous dichloromethane/acetone solution (1.2/1) provided, after crystallization from dichloromethane and hexane at 4 °C, the desired  $[\text{CpRu}(\eta^6\text{-naphthalene})][\text{BAR}_F]$  complex namely **[1][BAR<sub>F</sub>]** in good yield (72%, **Scheme 2**). The obtained yellow crystals were furthermore suitable for X-ray diffraction analysis, selected bond lengths and angles are given in **Table 1**.

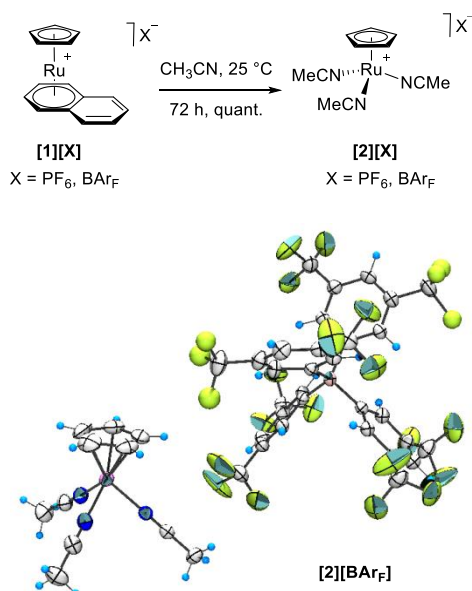


**Scheme 2.** Anion metathesis from  $\text{PF}_6^-$  to  $\text{BAR}_F^-$ ; X-ray structure of **[1][BAR<sub>F</sub>]**. Thermal ellipsoids are drawn at 50 % probability level and hydrogen atoms omitted for clarity.

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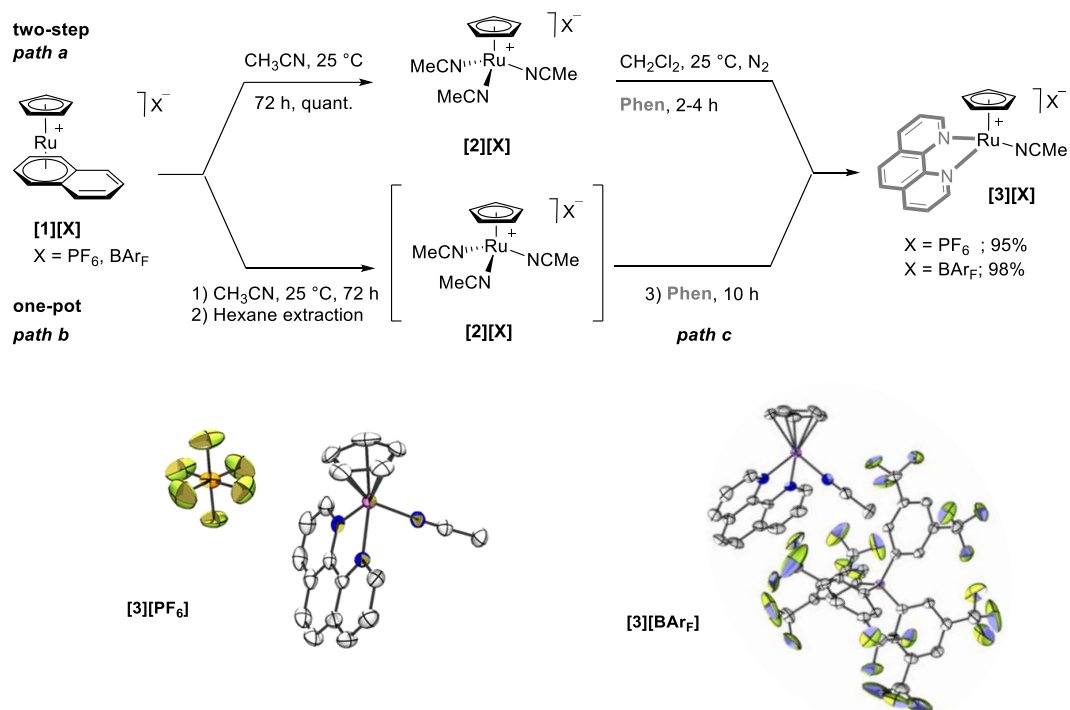
The Ru...Cp distance of 1.811 Å in complex **[1][BAr<sub>F</sub>]** is similar that observed for **[1][PF<sub>6</sub>]** <sup>[59]</sup> and **[1][TRISPHAT]** <sup>[60]</sup> complexes (TRISPHAT = Tris(tetrachlorobenediolato)phosphate) but significantly shorter than the corresponding distance in [CpRu(benzene)][PF<sub>6</sub>] derivative (1.845 Å).<sup>[61, 62]</sup> However, the Ru...Naph distances 1.719, 1.717 and 1.725 for **[1][PF<sub>6</sub>]**, **[1][BAr<sub>F</sub>]** and **[1][TRISPHAT]** respectively, are longer than that reported for the benzene complex highlighting the known higher lability of naphthalene.<sup>[62]</sup> As observed for other **[1][X]** complexes, the bond lengths of the two quaternary carbons of the bicyclic ring were longer (0.05 Å) than other Ru-C<sub>Naphthalene</sub> bonds.<sup>[59],[60]</sup> The Ru-C<sub>Cp</sub> (average 2.166 Å) in **[1][BAr<sub>F</sub>]** is shorter than others reported for [CpRu(η<sup>6</sup>-naphthalene)] complexes.<sup>[59],[60]</sup>

With precursors [CpRu(η<sup>6</sup>-naphthalene)][X] in hand (X = PF<sub>6</sub>, BAr<sub>F</sub>),<sup>[1-3, 57, 63]</sup> targeted derivatives were readily prepared, thanks to the facile haptotropic η<sup>6</sup>→η<sup>4</sup> ring slippage of complexes **[1]** which allowed the straightforward displacement of the naphthalene ligand by acetonitrile molecules (**Scheme 3**).<sup>[57]</sup> At the end of the reaction, the free naphthalene moiety was simply removed by extraction of the acetonitrile solution with dry hexane to afford, after evaporation of the acetonitrile, yellow complexes **[2][PF<sub>6</sub>]** and **[2][BAr<sub>F</sub>]** in quantitative yield.<sup>[64]</sup> Slow diffusion of hexane in a solution of **[2][BAr<sub>F</sub>]** in methylene chloride at 4 °C for 3 days yielded suitable crystals for X-ray diffraction analysis (**Scheme 3**). The Ru...Cp distance of 1.779 Å in complex **[2][BAr<sub>F</sub>]** is found slightly shorter compared to **[1][BAr<sub>F</sub>]**. The three Ru-acetonitrile (AN) bonds are not completely equivalent but their bond distances are in the same range around 2.08-2.09 Å. These differences in the solid state can be explained by the spatial proximity of the acetonitrile moieties to the BAr<sub>F</sub> anion(s) in the crystal unit cell. It was found that the presence of BAr<sub>F</sub><sup>-</sup> as counterion strongly reduces the oxygen and moisture sensitivity of the [CpRu(CH<sub>3</sub>CN)<sub>3</sub>]<sup>+</sup> fragment compared to its PF<sub>6</sub><sup>-</sup> analogue which decomposes under air after a few days only. In addition, the acetonitrile moieties are labile in their own right and this behavior has been strongly exploited to prepare further [CpRu] derivatives under mild conditions.<sup>[1-3, 65-78]</sup>



**Scheme 3.** Synthesis of [CpRu(CH<sub>3</sub>CN)<sub>3</sub>][X]; X-ray structure of **[2][BAr<sub>F</sub>]**. Thermal ellipsoids are drawn at 50 % probability level and hydrogen atoms omitted for clarity.

In our case, care was taken to utilize 1,10-phenanthroline (**Phen**) as a model diimine ligand, and the resulting complexes **[3][X]** were generated either directly from [CpRu(η<sup>6</sup>-naphthalene)][X] or *via* the intermediacy of [CpRu(CH<sub>3</sub>CN)<sub>3</sub>][X] in acetonitrile solutions. Experimentally, 1 equiv of 1,10-phenanthroline was added to a dichloromethane solution of the desired **[2]** complex and the resulting purple mixture was stirred at room temperature under argon. Reaction completion was achieved within 2-4 hours affording the corresponding **[3][X]** moiety (**Scheme 4**, path a).<sup>[79]</sup> Practically, these ligand exchange steps can be combined into a single sequential process using acetonitrile as the single solvent. However, in this case, the coordination of 1,10-phenanthroline to the ruthenium center is slower due to the direct competition with coordinating acetonitrile solvent molecules (**Scheme 4**, paths b and c).<sup>[80]</sup> In each case, the dark purple solution was evaporated to dryness and the crude mixture was allowed to recrystallize in dichloromethane/hexane to afford complex **[3][PF<sub>6</sub>]** in a high yield of 92%. Dark red X-ray quality crystals were further obtained by slow diffusion of hexane in a THF solution of **[3][PF<sub>6</sub>]** at 4 °C for 3 days and a structural analysis was performed (**Scheme 4**). Selected bond lengths and angles are given in **Table 1**. Complex **[3][BAr<sub>F</sub>]** was synthesized using the same ligand exchange procedure giving after recrystallization, in a 1:3 mixture of hexane:dichloromethane, dark red crystals in 98% yield. Selected bond lengths and angles are given in **Table 1** as well.



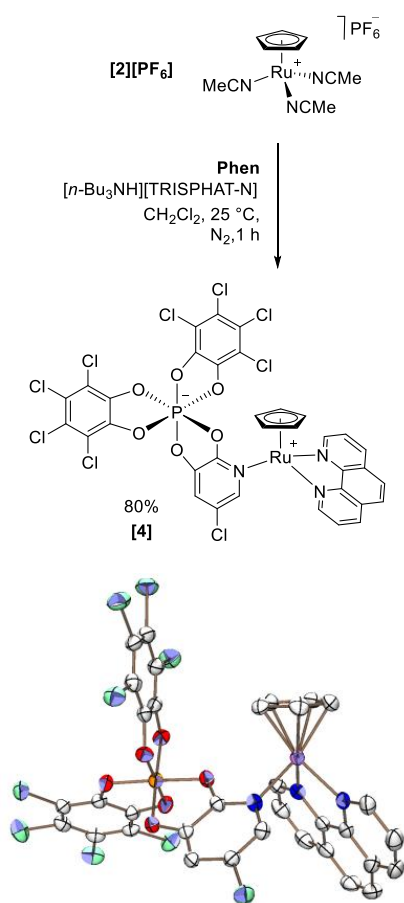
**Scheme 4.** Synthesis of [CpRu(CH<sub>3</sub>CN)<sub>3</sub>][X] and [CpRu(1,10-Phenanthroline)(CH<sub>3</sub>CN)<sub>3</sub>][X] complexes (X = PF<sub>6</sub>, BAR<sub>F</sub>), salts **[2][X]** and **[3][X]** respectively. ORTEP views of **[3][PF<sub>6</sub>]** and **[3][BAR<sub>F</sub>]**. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms are omitted for clarity.

**Table 1.** Selected bond lengths (Å) and angles (deg) for CpRu complexes **1** to **4** with estimated standard deviations in parentheses.<sup>[a]</sup>

Bond lengths /angles	<b>[1][BAR<sub>F</sub>]</b>	<b>[2][BAR<sub>F</sub>]</b>	<b>[3][PF<sub>6</sub>]</b>	<b>[3][BAR<sub>F</sub>]</b>	<b>[4]</b>
Ru-N1 <sub>phen</sub>	-	-	2.105(3)	2.104(3)	2.109(4)
Ru-N2 <sub>phen</sub>	-	-	2.106(3)	2.101(3)	2.088(4)
Ru-N3 <sub>AN</sub>	-	2.081; 2.089; 2.090(3)	2.074(3)	2.074(3)	-
Ru-N <sub>TTN</sub>	-	-	-	-	2.150(4)
Ru-P	-	-	6.281(1)	-	4.872(1)
Ru-B	8.324(4)	9.721(3)	-	7.890(4)	-
Ru-C <sub>Cp</sub>	2.151(6)	2.138(4)	2.152(4)	2.163(4)	2.175(4)
Ru-C <sub>Cp</sub>	2.158(6)	2.143(4)	2.137(4)	2.146(4)	2.155(5)
Ru-C <sub>Cp</sub>	2.167(5)	2.151(4)	2.151(4)	2.141(4)	2.160(5)
Ru-C <sub>Cp</sub>	2.178(6)	2.152(4)	2.156(4)	2.152(4)	2.144(4)
Ru-C <sub>Cp</sub>	2.182(5)	2.152(4)	2.178(4)	2.154(4)	2.133(5)
Ru-C <sub>Naph</sub>	2.198(5)	-	-	-	-
Ru-C <sub>Naph</sub>	2.202(5)	-	-	-	-
Ru-C <sub>Naph</sub>	2.208(5)	-	-	-	-
Ru-C <sub>Naph</sub>	2.213(5)	-	-	-	-
Ru-C <sub>Naph</sub>	2.261(4)	-	-	-	-
Ru-C <sub>Naph</sub>	2.267(4)	-	-	-	-
N1-Ru-N2	-	-	77.2(1)	77.4(1)	77.9(2)
N2-Ru-N3	-	-	85.9(1)	87.2(1)	85.8(1)

<sup>[a]</sup> AN = acetonitrile, Cp = cyclopentadiene; Naph = naphthalene, TTN = Trisphat-N

Previously, our group reported the synthesis and the resolution of hexacoordinated phosphorus(V) TRISPHAT-N anion (TRISPHAT-N = Bis[3,4,5,6-tetrachlorobenzene-1,2-diolato][5-chloropyridine-2,3-diolato]phosphate).<sup>[81]</sup> This chiral anion, owing to the presence of a Lewis basic pyridine moiety in the framework, has the ability to coordinate to metal centers; previous studies demonstrating an allied hemi-lability.<sup>[81, 82]</sup> Furthermore, an important lipophilicity is given by the phosphate skeleton which then allows the ready chromatographic isolation and separation of zwitterionic adducts. In practice, counter ion exchange took place in dichloromethane using the isolated **[3][PF<sub>6</sub>]** complex and racemic [*n*-Bu<sub>3</sub>NH][TRISPHAT-N] salt which generated, in one hour, the desired [CpRu(phen)(TRISPHAT-N)], or [CpRu(phen)(TTN)] **[4]** complex. Alternatively, a complete one-pot reaction could be reached in 3 h only by simply mixing an equimolar amounts of [CpRu(CH<sub>3</sub>CN)<sub>3</sub>][PF<sub>6</sub>], 1,10-phenanthroline and [*n*-Bu<sub>3</sub>NH][TRISPHAT-N] (**Scheme 5**). In each case, the compound was purified by column chromatography (*R<sub>f</sub>* 0.98 in methylene chloride) to give a red solid in good yield (80%). Noteworthy, when attempted, the direct anion exchange metathesis between lipophilic TTN<sup>-</sup> and BAR<sub>F</sub><sup>-</sup> failed, complex **[3][BAR<sub>F</sub>]** being totally recovered at the end of the reaction. Gratifyingly, the desired air and moisture stable **[4]** complex was found to be moderately soluble in dichloromethane/pentane at -20 °C. X-Ray quality crystals were obtained and a structural analysis was performed (**Scheme 5**).



**Scheme 5.** Synthesis and ORTEP view of [CpRu(phen)(TTN)] **[4]** complex. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms are omitted for clarity.

These X-ray structural analyses indicated that the ruthenium atom is  $\pi$ -coordinated to the C<sub>5</sub>H<sub>5</sub> ring and in a  $\sigma$  mode to N donor bidentate phenanthroline and to an acetonitrile fragment in a piano stool mode (**Schemes 3 and 4**). The average Ru-N bond length of 2.104 Å for complexes **[3][PF<sub>6</sub>]** and **[3][BAR<sub>F</sub>]** is in agreement with values for reported piano stool CpRu(N<sup>^</sup>N) complexes with, for example, an average of ~2.095 Å for [CpRu(bipy)(CH<sub>3</sub>CN)][OTf].<sup>[35]</sup> These values highlight the  $\sigma$ -donor character of the 1,10-Phenanthroline ligand. Similarly, the Ru-NC-Me bond length average of 2.074 Å is in line with other Ru-NC-Me complexes (2.071 Å).<sup>[35, 36, 66, 83-85]</sup>

The Ru-C<sub>cp</sub> distances are in the range of 2.137–2.178 Å and their average (2.153 Å) agrees with those reported for [CpRu(bipy)(CH<sub>3</sub>CN)][OTf] cationic complex.<sup>[35]</sup> The Ru-C<sub>p</sub> distance, in which C<sub>p</sub> is the Cp centroid, for complex [PF<sub>6</sub>] is 1.793 Å, and hence comparable to that of 1.791 Å observed for CpRu(bipy) complex. Curiously, both non-coordinating [BAR<sub>F</sub>] and coordinating anion [TTN] showed slightly shorter distances of 1.784 and 1.781 respectively. However, the symmetry breakage in **[4]** caused by the coordination of TRISPHAT-N through the ruthenium center has an effect on the  $\sigma$ -bond lengths as Ru-N1 (2.109 Å) and Ru-N2 (2.088 Å) are not equivalent anymore (**Scheme 5**).

As already mentioned, it has been established that the nature of anionic counterions play a crucial role in catalysis.<sup>[86]</sup> Interactions between cationic and anionic partners can strongly affect the solubility of resulting catalysts, the rate and the selectivity of reactions or even change its course.<sup>[84, 87-97]</sup> For years

it was assumed that anions such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  and  $\text{SbF}_6^-$  were non-coordinating, but now there are better described as “weakly coordinating anion” (WCA).<sup>[98-102]</sup> However, previous investigations have shown that these anions are able to interact with cations either directly or through hydrogen bonds.<sup>[103-107]</sup> To take into account the possible occurrence of such interactions, careful analyses of hydrogen and fluorine contacts were monitored in both solid state (X-ray) and in solution (NMR  $^1\text{H}$ - $^{19}\text{F}$  HOESY experiments). In the X-ray structure packing of **[3][PF<sub>6</sub>]**, hexafluorophosphate anions were showed to interact via  $\text{H} \cdots \text{F}$  interactions not only with the hydrogen atoms of acetonitrile ligands but also with that of the Cp ring ( $\text{H} \cdots \text{F} < 3\text{Å}$ , **Table 2**). The solid state structure of complex **[3][BAr<sub>F</sub>]** was also investigated and once again, relatively short contact between fluorine atoms and both acetonitrile and Cp ligands (2.6-3.0 Å, **Table 2**) could be found. Lastly, the greater distance between the (formally) positively charged ruthenium and negatively charged boron atoms in **[3][BAr<sub>F</sub>]** ( $\text{Ru} \cdots \text{B} : 7.89\text{Å}$ ) advocates *in fine* for a stronger Lewis acidic metal coordination site which, in retrospect, might provide higher catalyst turnover frequency for the  $\text{BAr}_F^-$  salt as compared to complex **[3][PF<sub>6</sub>]** for which the anion/cation pair seems to be tighter ( $\text{Ru} \cdots \text{P} : 6.28\text{Å}$ ). The augmented distance of this anion from the Lewis acid reactive site would have two main possible effects, (i) an increased Lewis acidity which should promote the nucleophilic attack of the diazo reagents and thus favor for the formation of the carbene intermediates, (ii) a possible decrease in coordination competition between anion and substrate, which could also favor an increase in reaction rates as reported for other CpRu catalysts.<sup>[56],[108]</sup>

In solution,  $^1\text{H}$ - $^{19}\text{F}$  HOESY spectra were measured in deuterated dichloromethane for both **[3][PF<sub>6</sub>]** and **[3][BAr<sub>F</sub>]** salts. In both instances, signals corresponding to NOE interactions between the anions and bound acetonitrile and Cp ligands could not be observed. In accordance with other studies in moderately dissociative solvents like  $\text{CD}_2\text{Cl}_2$ ,<sup>[84]</sup> these results suggest that both  $\text{PF}_6^-$  and  $\text{BAr}_F^-$  anions are not strongly paired with [CpRu] fragments in such solutions. The lack of crystallographic literature data for [(Phen)CpRu(CH<sub>3</sub>CN)][X] salts containing more coordinating anions ( $\text{X} = \text{OTf}$  or  $\text{BF}_4$ ) renders difficult to conclude in such cases. However, comparison of the  $\text{Ru} \cdots \text{B}$  distances in complexes **[2][BAr<sub>F</sub>]** and **[CpRu(CH<sub>3</sub>CN)<sub>3</sub>][BF<sub>4</sub>]**,<sup>[109]</sup> with respectively 9.721Å and 5.885Å, shows a large difference ( $\Delta\text{Å} = 3.836\text{Å}$ ) which is expected to impact the reactivity.<sup>[56]</sup>

**Table 2.** Selected bonds lengths [Å] and angles [deg] for complexes **[3]** with estimated standard deviations in parentheses.

C-H...F Hydrogen Bonds interactions (Å)			
C-H...F	H...F	C...F	C-H...F
<b>[3][PF<sub>6</sub>]</b>			
C14-H... F4	3.041(4)	3.884(6)	148.8(2)
C16-H... F1' <sup>[a]</sup>	2.544(5)	3.224(7)	128.6(3)
NC19-H...F3'' <sup>[a]</sup>	2.667(4)	3.642(6)	173.1(2)
NC19-H...F6'' <sup>[a]</sup>	2.588(4)	3.366(6)	136.4(3)
<b>[3][BAr<sub>F</sub>]</b>			
C15-H...F20	2.614(4)	3.266(6)	126.2(3)
C16-H...F20	3.051(5)	3.469(7)	108.3(3)
NC19-H...F7	2.611(5)	3.208(6)	119.4(3)

<sup>[a]</sup> Fluorine atom from a symmetry equivalent molecule of  $\text{PF}_6^-$  in the crystal packing ('') -1+x, y, z and ('') 1-x, -y, 1-z.

## Conclusions

In summary, the synthesis and X-ray structural analyses of [CpRu(Phen)] fragments combined with large lipophilic  $\text{PF}_6^-$ ,  $\text{BAr}_F^-$  and TRISPHAT-N anions were achieved. Starting with the air-stable [CpRu( $\eta^6$ -naphthalene)][PF<sub>6</sub>] precursor, complex [CpRu( $\eta^6$ -naphthalene)][BAr<sub>F</sub>] was prepared on multigram scale through simple ion exchange metathesis from the  $\text{PF}_6^-$  salt. Corresponding [CpRu(CH<sub>3</sub>CN)<sub>3</sub>][X] complexes ( $\text{X} = \text{PF}_6$ ,  $\text{BAr}_F$ ) were generated in acetonitrile, and subsequently used for ligand exchange reaction to afford [CpRu(Phen)CH<sub>3</sub>CN][X] salts in high yield from isolated **[2][X]** precursors. In  $\text{CH}_2\text{Cl}_2$ , hemi-labile TRISPHAT-N anion easily displaced the last acetonitrile ligand of derivatives **[3][X]** to form air stable complex **[4]**, readily purified by chromatography. Care was also taken to study the nature of the solution and solid-state interactions occurring among combinations of CpRu fragments and Phen ligand on one hand, and  $\text{PF}_6^-$ ,  $\text{BAr}_F^-$  and TRISPHAT-N<sup>-</sup> anions on the other. Investigations by  $^1\text{H}$ - $^{19}\text{F}$  HOESY spectroscopy in solution and solid-state X-ray measurements did not indicate any significant ion pairing within both  $\text{PF}_6^-$  and  $\text{BAr}_F^-$  salts. This lack of severe ion pairing constraint is in accordance with the catalytic properties of these derivatives, which allow the facile decomposition of  $\alpha$ -diazo- $\beta$ -ketoesters and subsequent transformations of the derived metal carbenes.

## Experimental Section

The dataset for this article can be found at the following DOI: 10.26037/yareta.rnzapl6k65c7fmyb55l366gope. It will be preserved for 10 years. Synthetic procedures and spectral characterization of new compounds are reported in the electronic supporting information. CCDC-2026525 to 2026529 contain the supplementary crystallographic data for this work. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre* via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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## Author Contribution Statement

T. A., L. E. and C. T. performed the experiments and characterization of all materials and co-wrote the manuscript. L. G. performed the X-ray diffraction studies and co-wrote sections dedicated to solid-state analyses. J. L supervised the work and wrote the manuscript. All authors commented on the manuscript.

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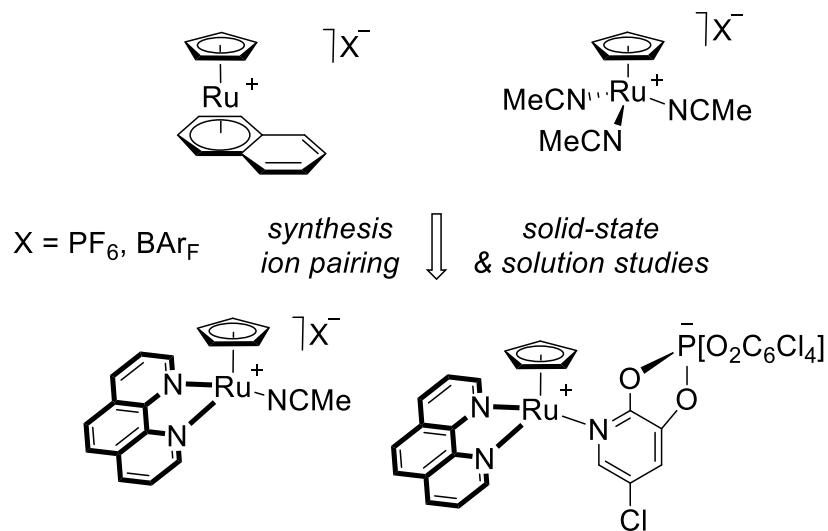
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Combinations of [CpRu(CH<sub>3</sub>CN)<sub>3</sub>] salts and phen ligands are catalysts for diazo decomposition and subsequent carbene reactivity. Ru(II) precursors and phen complexes are characterized in solution and solid-state.