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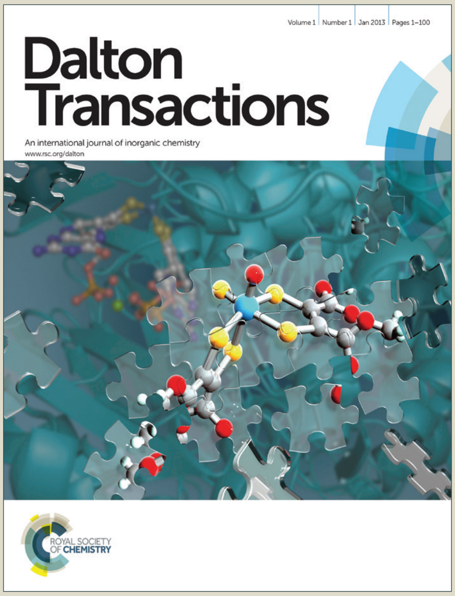

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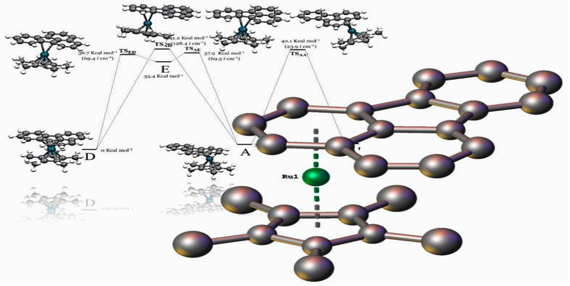


$[(\eta^5\text{-}C_5Me_5)Ru]^+$ fragments ligated to polyaromatic hydrocarbons: an experimental and computational approach of pathways for haptotropic migration[†‡]

Matias Rioja,[a] Paul Hamon,[b] Thierry Roisnel,[b]
Sourisak Sinbandhit,[c] Mauricio Fuentealba,[a,#] Karina Letelier,[a,|]
Jean-Yves Saillard,*[b] Andrés Vega,*[a,d] and Jean-René Hamon,*[b]

[a] *Universidad Andres Bello, Facultad de Ciencias Exactas, Av. República 275, 3er Piso, Santiago, Chile. E-mail: andresvega@unab.cl*
[b] *UMR 6226 «Institut des Sciences Chimiques de Rennes», CNRS-Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France. E-mail : saillard@univ-rennes1.fr, E-mail : jean-rene.hamon@univ-rennes1.fr*
[c] *CRMPO, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France*
[d] *Centro para el Desarrollo de la Nanociencia y la Nanotecnología, CEDENNA, Santiago, Chile*
[#] *Present address: Instituto de Química, Pontificia Universidad Católica de Valparaiso, Chile*
[|] *Present address: Universidad de Santiago, Chile*

[‡] Dedicated to our distinguished colleague and friend professor David Carrillo at the occasion of his 75th birthday

Abstract

Ligand exchange reactions between [Cp*Ru(NCMe)$_3$][PF$_6$] where Cp* stands for η^5-C$_5$Me$_5$ and polycyclic aromatic hydrocarbons (PAHs) pyrene, acenaphthylene and fluoranthene afford the known [Cp*Ru(η^6-pyrene)][PF$_6$] (**1**), and the new mixed sandwiches [Cp*Ru(η^6-acenaphthylene)][PF$_6$] (**2**) and [Cp*Ru(η^6-fluoranthene)][PF$_6$] (**3**), respectively, isolated in quantitative yields (94-100%). Complex **3** is formed as a mixture of two isomers: **3A** as the major product where the [Cp*Ru$^+$] moiety is coordinated to the naphthalene fragment of fluoranthene, and **3B** with coordination of the arenophile to the peripheral benzene ring, in a 90/10 spectroscopic ratio. Composition and identity of the complexes were deduced from elemental analysis, ^{1}H and ^{13}C multidimensional NMR spectroscopy, and mass spectrometry. Compounds **1A**, **3A** and **2A** have been characterized by X-ray structural investigations. That showed that the [Cp*Ru$^+$] unit is η^6-attached to one of the two naphthalene rings in each complex. Heating **1** and **3** at 90 °C in CD$_3$NO$_2$ solutions or **3** at 120 °C in the solid phase did not provide any evidences for thermally induced intramolecular inter-ring haptotropic rearrangement. These rearrangements were modelled by DFT calculations which indicated rather high activation energies.

Introduction

The fused polyaromatic hydrocarbons (PAH) are extended π-conjugated organic systems having rings which share common carbon edges.[1,2] For them, the combination of different factors, such as the different number of rings, the different number of carbons within the rings, the alternance between the different sized rings and finally the different number of electrons in the π system, make them versatile ligands, mostly planar[3] but in some instances curved,[4] forming concave-bound metal complexes.[5] Indeed, these PAH molecules provide the possibility to coordinate one (or more) organometallic fragments, leading to isolable species, which can exhibit, for example, interesting redox behavior.[6-8] In this way, they can provide coordination sites with different geometries and different number of electrons, leading to a large number of advisable species, either mono or polymetallic, which are subject under some circumstances to interconversion through inter-ring haptotropic rearrangements.[9] For instance, the η^6-η^6 inter-ring haptotropic rearrangement in which a 12-electron organometallic moiety migrates along the rim of a polyaromatic system as first proposed by Albright *et al.*,[10] could, indeed, be thermally,[11,12] chemically,[13] photochemically[12,13] or electron driven.[14]

Organometallic complexes of the simplest PAHs like naphthalene,[15] pentalene,[16] azulene,[17] or indacene,[18] are widely known, showing a variety of coordination modes.[19] In contrast to these extensively studied PAH complexes, the corresponding compounds of more extended PAH ligands such as pyrene, acenaphthylene or fluoranthene have been less investigated. However, interesting mononuclear examples including $[(\eta^6\text{-pyrene})Cr(CO)_3]$,[20] $[Cp^*Ir(\eta^6\text{-pyrene})][BF_4]_2$,[21] $[(\eta^6\text{-acenaphthylene})Cr(CO)_3]$,[22] $[Cr(\eta^6\text{-fluoranthene})_2][I]$[23] as well as the two isomers of $[(\eta^6\text{-fluoranthene})Cr(CO)_3]$[24] have been structurally characterized ($Cp^* = \eta^5\text{-}C_5Me_5$). Although scarcer, bimetallic derivatives with an arenophile unit coordinated to each side of the polycyclic aromatic ligand such as $[(\mu\text{-}\eta^6\text{:}\eta^6\text{-benzopyrene})(Cr(CO)_3)_2]$[11] and $[(Cp^*Ru)_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-PAH})][PF_6]_2$ (PAH = chrysene,[7c] corannulene[25]) have also been identified crystallographically. The doubly charged bis-$[Cp^*Ru^+]$ η^6-coordinated phenanthrene, anthracene, pyrene and triphenylene cations were also prepared,[7a,b] but no structural characterization by means of X-ray diffraction is available so far.

If $(\eta^6\text{-PAH})$chromium tricarbonyl derivatives have frequently been employed to study η^6-η^6 inter-ring haptotropic migration,[9,11,12] much fewer η^6-η^6 inter-ring rearrangement have been observed in mixed sandwich compounds. For instance, the arenophiles $[Cp^*Ru^+]$ and its isolobal dicationic $[Cp^*Ir^{2+}]$ counterpart were shown to undergo, likely solvent-assisted, inter-ring haptotropic rearrangement upon reaction of their tris-solvated precursors with acecorannulene,[26] and 1,2,5,6-tetramethylcorannulene,[27] respectively. In contrast, the absence of residual coordinating solvent to facilitate inter-ring rearrangement may explain the very slow, or non-existent, migration of the [Cp*Ru$^+$] moiety generated *in situ* from [Cp*Ru(μ^3-Cl)]$_4$ and a silver salt in deuterated nitromethane, with 1,2,5,6-tetramethylcorannulene.[28] Another example is the rare reversible pH-controlled haptotropic rearrangement in the case of the zwitterionic complex of the 2-naphthoic acid anion, [CpRu(η^6-$C_{10}H_7COO$)], in which the [CpRu$^+$] arenophile moves from the substituted ring to the unsubstituted one upon protonation/deprotonation and subsequent irradiation (Cp = η^5-C_5H_5).[13] Interestingly, haptotropic rearrangement can also be electron-driven. It was, indeed, shown that monoelectronic oxidation of the organo-iron fragment of [Cp*(dppe)Fe-C≡C-1-(η^6-naphthyl)RuCp'][PF_6] in the presence of a coordinating solvent, induces the migration of the [CpRu$^+$] group from the substituted ring to the free one and in the opposite direction for the permethylated arenophile (Cp' = Cp or Cp*, dppe = 1,2-bis(diphenylphosphino)ethane).[14]

In the present work we report on the synthesis, full analytical, spectroscopic and structural characterization of three mononuclear mixed sandwich [Cp*Ru(η^6-PAH)][PF_6] complexes where PAH corresponds to pyrene (**1**), acenaphthylene (**2**), and fluoranthene (**3**). The migratory aptitude of [Cp*Ru$^+$] complexed to pyrene and fluoranthene was tested under thermal conditions in a non-coordinating solvent (CD_3NO_2) and in the solid phase for **3**, but no inter-ring rearrangement could be detected. The experimental results are analyzed in terms of their electronic structure determined by means of density functional theory (DFT) calculations.

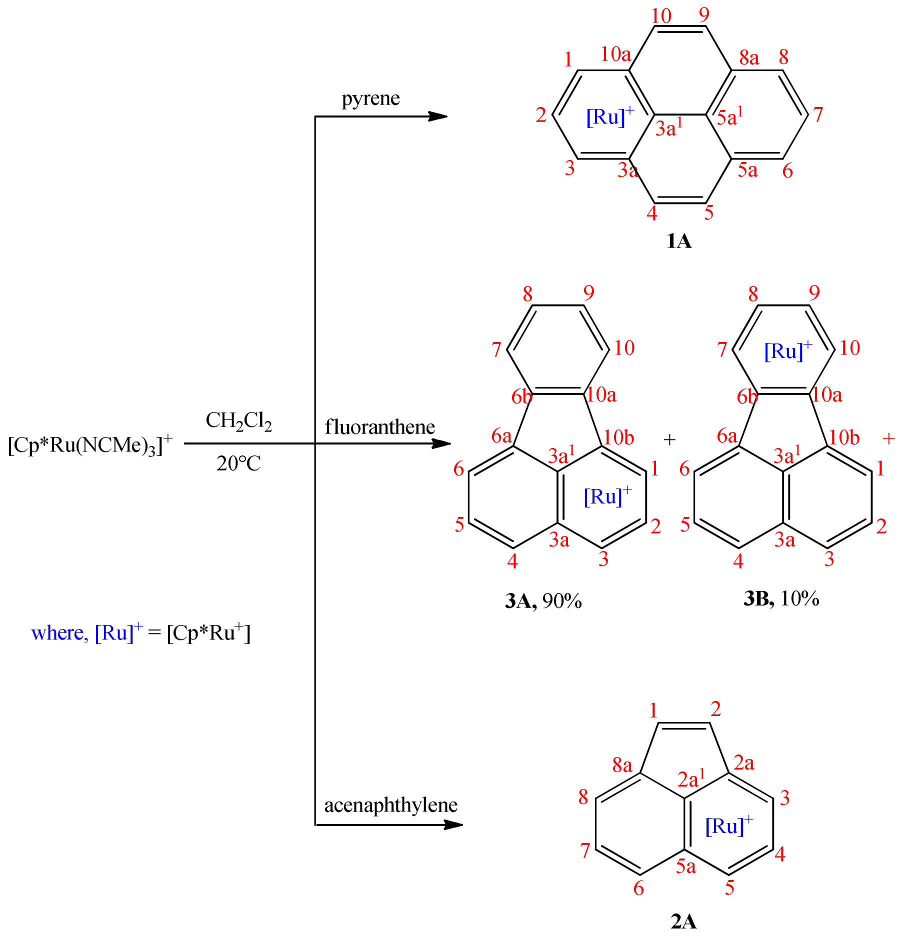
Results and Discussion

Synthesis and characterization of the complexes

The [Cp*Ru(η^6-arene)][PF_6] polyaromatic complexes (arene = pyrene **1**, acenaphthylene **2** and fluoranthene **3**) are prepared by ligand exchange reaction between the arenophile source [Cp*Ru(NCMe)$_3$][PF_6] and the appropriate polyaromatic ligand, in dichloromethane at room temperature (Scheme 1). The two-step procedure (see Experimental section) in which the liberated coordinating acetonitrile solvent is removed after 6h followed by addition of fresh dichloromethane, affords the desired compounds **1-3** in quantitative yields (94-100%). They were isolated as yellow thermally stable crystalline solids. The solid sample of the three compounds **1-3** are stable in dry air for weeks with protection from light.

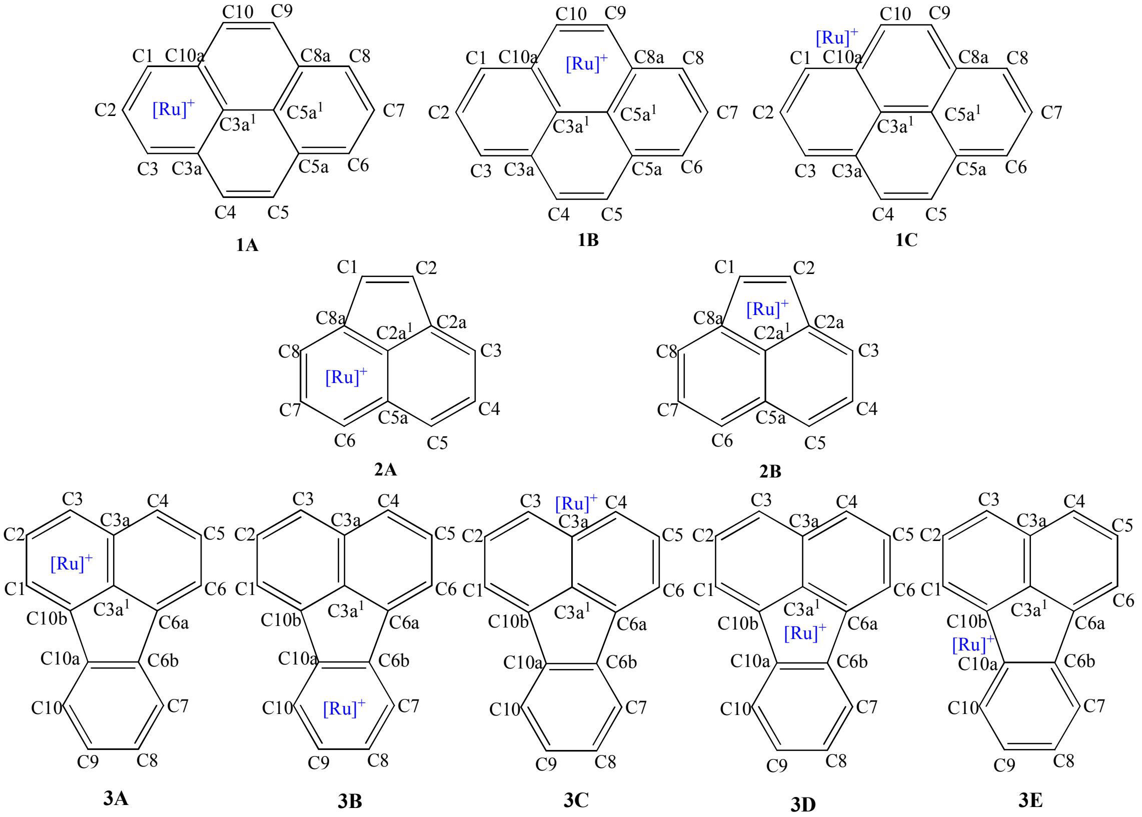
These ionic compounds exhibit a good solubility in common polar organic solvents but are insoluble in diethylether, hydrocarbons and water.

Complex **1** was mentioned earlier in the literature but structural data were not available.[7a,b,29] Complex **3** is isolated as a mixture of two isomers: **3A** as the major product where the [Cp*Ru$^+$] arenophile is coordinated to one ring of the naphthalene core, and **3B** with coordination of the ruthenium center on the peripheral benzene ring (Scheme 1), in a 90/10 spectroscopic ratio. This result is similar to that reported by Oprunenko *et al.* for the reaction of fluoranthene with [$Cr(CO)_3(NC_5H_5)_3$], in the presence of $BF_3{\cdot}OEt_2$ at 25 °C, affording a mixture of two isomeric complexes in a **A**/**B** ratio of 95/5.[24] In this chromium system, the **A** isomer is the kinetically controlled product and the **B** isomer the thermodynamically controlled product.[30]



Scheme 1 Preparation of compounds [Cp*Ru(η^6-polyaromatic)][PF_6] **1-3** with the atom numbering scheme used in this paper. Hexafluorophosphate counter anions have been omitted for clarity.

From all the possible isomers that can be imagined as reaction products or intermediates (Scheme 2), composition and identity of the obtained complexes were deduced from satisfactory elemental analysis, ^{1}H and ^{13}C multidimensional NMR spectroscopic methods, and mass (ESI$^+$) spectrometry. Furthermore, the crystal and molecular structures of **1A**, **2A** and **3A** have been determined by single-crystal X-ray diffraction (*vide infra*). Mass spectra show the isotope clusters of the respective molecular ions at 439 M/z for **1**$^+$, 389 M/z for **2**$^+$ and 439 M/z for **3**$^+$, corresponding to the cationic sandwich species with envelopes of the isotopic patterns in good agreement with the simulated ones.



Scheme 2 Possible isomers for [Cp*Ru(η^6-polyaromatic)]$^+$ (**1**$^+$-**3**$^+$) with their respective names.

Full ^{1}H and ^{13}C{^{1}H} NMR data for **1A**, **2A**, **3A** and **3B** are reported in the Experimental section with assignments related to the atom labeling schemes depicted in Scheme 1. All the signals were unambiguously identified using DEPT analysis and ^{1}H-^{13}C correlation techniques. The spectra were recorded in CD_3NO_2 at 295 K and present the typical trend also observed in other [Cp*Ru(η^6-polyaromatics)]$^+$ compounds,[7,29,30] that is the chemical shifts of the nuclei constituting the rings coordinated to the [Cp*Ru$^+$] moiety show an upfield shift relative to those of non-coordinated ring nuclei, and the coordination induced decrease in scalar $J_{H,H}$ coupling constants. This confirms the hexahapto coordination mode of the ruthenium atom to one of the arene rings in each compound,[19] and at the same time, ascertains the position of the [Cp*Ru$^+$] arenophile on the PAH surface.

For instance, besides the sharp singlet at δ_H = 1.34 ppm attributed to the methyl protons of the Cp* ligand, the ^{1}H NMR spectrum of the pyrene adduct **1A** reveals characteristic upfield shifted triplet and doublet, with ^{1}H,^{1}H coupling of 6.0 Hz, at δ_H = 6.21 (1 H) and 6.52 (2 H) ppm, respectively, whereas the four other types of protons resonate in the 7.61 – 8.21 ppm region with coupling constant of 9.3 Hz. Thus, these data clearly indicate that the pyrene ligand binds in a η^6-mode through an end ring, leaving the two middle- and the other end rings uncomplexed. As expected, the chemical shifts and multiplicity pattern fully agree with those observed previously in both iron[31] and ruthenium[7a,b,29,30] mixed sandwich series, [Cp'M(η^6-pyrene)][PF$_6$].

The ^{1}H NMR spectrum of the acenaphthylene derivative **2A** exhibits also a sharp signal at δ_H = 1.50 ppm assigned to the C_5Me_5 ligand together with resonances at δ_H = 6.36, 6.01 and 6.56 ppm assigned to protons H3, H4 and H5, respectively, that are shifted upfield with respect to the signals of the protons of the uncomplexed ring (7.74 < δ_H <7.99 ppm), thus ascertaining the location of the [Cp*Ru$^+$] moiety onto one of the naphthalene rings. A similar behaviour was also observed for the neutral (η^6-acenaphthylene)tricarbonylchromium derivative.[22] In addition, the protons H1 and H2 on the extra ethene bridge show up as two doublets, at δ_H = 7.12 and 7.44 ppm, assignable to an AB system with a ^{1}H,^{1}H ^3J coupling constant value of 5.4 Hz.

The fluoranthene derivative **3** displays a more complicated ^{1}H NMR spectrum due to the presence of two isomers (**3A** and **3B**, see Scheme 1) identified by two singlets at δ_H = 1.25 and 1.30 ppm, respectively, in a 90/10 ratio, and to the low symmetry of the **3A** aromatic ring system upon ligation to the metal. However, by analyzing the number of signals, the multiplicity pattern and relative intensities of these signals, the major isomer **3A** (90 %) was determined to be the species with the [Cp*Ru$^+$] fragment η^6-bound through one of the two rings of the naphthalene fragment, and the minor isomer **3B** (10 %) with the cationic arenophile unit η^6-coordinated to the outer C_6-ring of the fluoranthene moiety. Despite its small amount in the mixture, the structure of **3B** was conclusively determined by the simplicity of its ^{1}H and ^{13}C resonances owing to a plane of symmetry passing through C3a, C3a^1, and in the middle of C6b-C10a and C8-C9 bonds (see Scheme 1). The major isomer **3A** which is structurally closely related to **2**, exhibits a similar signal pattern with protons H1, H2 and H3 resonating at δ_H = 6.42, 5.99 and 6.52 ppm, respectively, whereas the uncoordinated ring protons including those of the bridging *o*-phenylene ring and integrating for a total number of 7 H, appear downfield shifted in the range δ_H = 7.54 - 8.06 ppm. Conversely, selective upfield shift of the four H7-H10 protons of minor isomer **3B** at δ_H = 5.99 and 6.55 ppm as two multiplets, is diagnostic of the involvement of *o*-phenylene ring in the η^6-complexation to the ruthenium center.

The ^{13}C NMR data are in agreement with the behavior observed with the ^{1}H NMR spectra, exhibiting the expected shielding of the complexed η^6-C_6 ring carbons. The ^{13}C{^{1}H} NMR spectra of compounds **2A** and **3A** show six carbon resonances between δ_C = 83.58 and 99.42 ppm, while compounds **1A** and **3B** having both a symmetry plane, present four and three upfield shifted carbon peaks, respectively, between δ_C = 86.67 and 97.01 ppm, that were assigned to the carbon atoms directly bonded to the ruthenium center. In each case, the three fused-ring carbons, that are also the nuclei of the Ru- coordinated ring the farthest away from the metal (vide infra), are the more deshielded ones (see Experimental Section for details). Nevertheless, all these signals are substantially upfield shifted with respect to those of uncoordinated carbons (123.07 < δ_C < 141.03 ppm), a trend that is now well-established for transition metal arene complexes.[19] In addition, the chemical shifts of the Cp* ligand are found in the narrow regions δ_C = 8.74 - 9.16 ppm and δ_C = 94.35 - 95.16 ppm for the methyl- and C_5-ring carbons, respectively.

Inter-ring rearrangement studies

To test the migratory aptitude of [Cp*Ru$^+$] complexed to pyrene, acenaphthylene and fluoranthene, we first carried out variable-temperature ^{1}H NMR spectroscopic studies, starting from the above isolated compounds **1A**, **2A**, and **3A/3B**. Heating nitromethane-d_3 solutions of either **1A**, **2A** or **3A/3B** to 90 °C for one hour in the NMR spectrometer probe, led to no line broadening nor coalescence of the signal pattern. Even after this experiment, the initial 90/10 ratio of isomers **3A/3B** remained unchanged. This indicates that, for all the three compounds under these conditions, there is no evidence for the migration of [Cp*Ru$^+$] between rings on the NMR time scale. Thus, the ability of the [Cp*Ru$^+$] arenophile to undergo a haptotropic rearrangement was studied under more forcing conditions. Degassed CD_3NO_2

solutions of complexes **1A** and **3A/3B** were warmed under argon in a Schlenk tube to 90 °C, and the progress of the reactions was monitored by ^{1}H NMR spectroscopy.

Heating compound **1A** for two weeks under these conditions did not reveal any experimental evidence for the migration of the [Cp*Ru$^+$] moiety from the terminal ring to the adjacent central rings of the pyrene ligand. After 24 days of heating, the ^{1}H NMR spectrum of the solution indicated the formation of a mixture of three compounds exhibiting Cp* resonances at δ_H = 1.12, 1.68 and 1.85 ppm attributed to the starting material **1A** and two unidentified products, in the ratio 53:29:18, respectively. This ratio changed to 43:34:23 upon heating for ten additional days, But decomposition was also observed with formation of insoluble black solid residue. No attempt to separate and isolate the organometallic derivatives was undertaken.

On the other hand, a solution of [Cp*Ru(η^6-fluoranthene)][PF$_6$] (ratio **3A/3B** = 90/10) in CD_3NO_2 was also heated at 90 °C for three days without any experimental evidence for the migration of the arenophile from one ring to another ; the ratio of isomers remaining unchanged. Addition of up to 10% of CD_3COCD_3, a coordinating solvent expected to assist the migration of 12-electron arenophiles onto π-platform, to this solution and heating for 24 hours has no effect on the proportion of **3A** and **3B**. Even after heating a solid sample of [Cp*Ru(η^6-fluoranthene)][PF$_6$] at 120 °C for a week in a sealed tube under vacuum, the ratio **3A/3B** was not modified.

The behavior of compounds **1A** and **3A/3B** parallels that of η^6-[Cp*Ru$^+$] complex of corannulene ($C_{20}H_{10}$) for which variable-temperature ^{1}HNMR spectroscopy up to 140 °C ($C_2D_2Cl_4$) have ruled out intramolecular migration (DG > 20 kcal/mol) of the [Cp*Ru$^+$] arenophile on the corannulene surface.[32] Neither a mixture of two isomers of [Cp*Ru(η^6-$C_{20}H_6Me_4$)][X] (X = BF$_4$, PF$_6$, SbF$_6$) does interconvert upon heating at 50 °C for two days in CD_3NO_2 solution.[28] Moreover, the behavior of the ionic compound **3** sharply contrasts with that of its neutral isolobal counterpart (η^6-fluoranthene)tricarbonylchromium where the [Cr(CO)$_3$] moiety gradually, fully and irreversibly migrates from the naphthalene unit to the peripheral benzene ring upon heating in decane at 100 °C for 8 hours.[24]

Structural description

Diffraction-quality single crystals for X-ray structure investigation were obtained for compounds **1A**, **2A** and **3A** using the same slow diffusion crystallization method, where diethyl ether was allowed to slowly diffuse into a dichloromethane solution of each compound. All the compounds crystallize in centrosymmetric space groups, as racemates for **2A** and **3A**, even though they display planar chirality upon ligation to the arenophile. The molecular structures of the monocationic entities of compounds **1A**, **2A** and **3A** are presented in Figs. 1, 2 and 3, respectively, with selected bond distances given in the captions. The three crystal structures consist of organometallic ruthenium cations and octahedral hexafluorophosphate anions. Each cation contains a ruthenium center sandwiched between a negatively charged $[C_5Me_5]^-$ ligand and a neutral C_6 arene ring, thus exhibiting the typical η^5-Ru^{II}-η^6 metallocenic coordination mode. This geometry is similar to that observed for several other structurally characterized mononuclear [Cp*Ru(η^6-polyaromatic)]$^+$ complexes.[7a,c,14b,25,28,33,34] Moreover, in their structural features compounds **2A** and **3A** resemble to a large extent those of related ruthenium cationic half-sandwich complexes containing a η^6-bounded naphthalene framework.[14b,34]

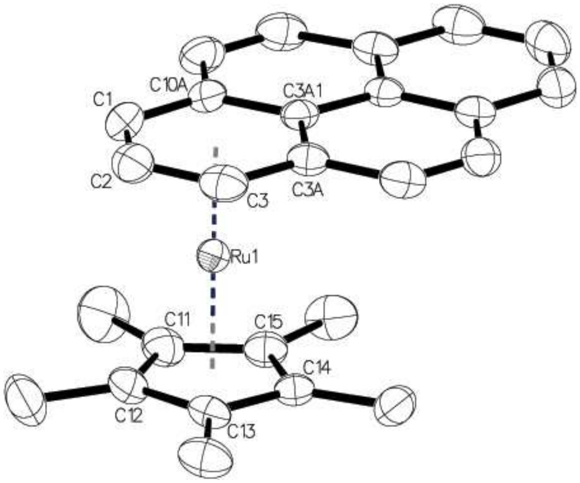


Fig. 1 Molecular structure of the cationic portion of **1A** showing partial atom labelling scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50 % probability. Selected bond distances (Å): Ru1-C1 2.2171(19), Ru1-C2 2.2165(18), Ru1-C3 2.2177(17), Ru1-C3a 2.2587(17), Ru1-C10A 2.2614(17), Ru1-C3a^1 2.2736(17), avg Ru1-C(Cp*) 2.1767(17).

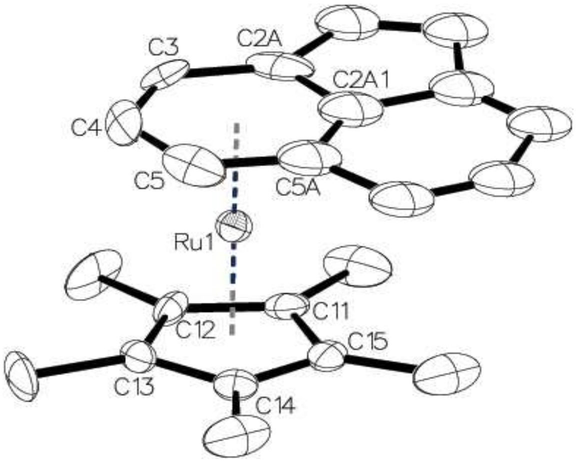


Fig. 2 Molecular structure of the cationic portion of **2A** showing partial the atom labelling scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å): Ru1-C3 2.233(8), Ru1-C4 2.201(8), Ru1-C5 2.211(7), Ru1-C5a 2.255(9), Ru1-C2a^1 2.247(9), Ru1-C2a 2.279(8), avg Ru1-C(Cp*) 2.182(7).

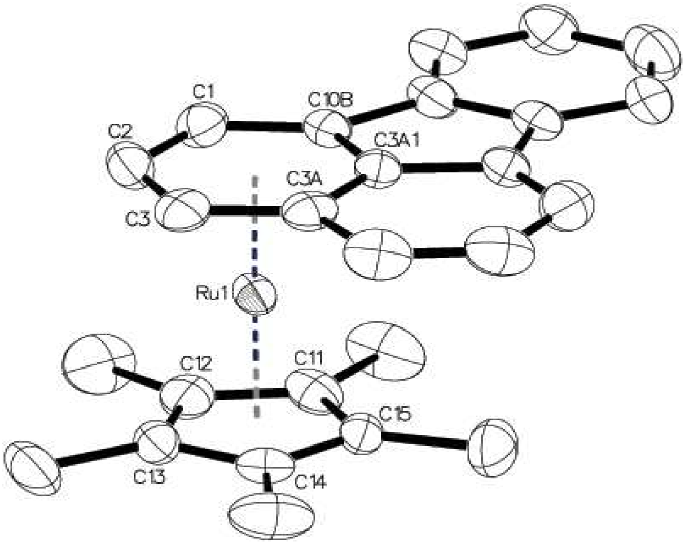


Fig. 3 Molecular structure of the cationic portion of **3A** showing partial atom labelling scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å): Ru1-C1 2.238(10), Ru1-C2 2.201(10), Ru1-C3 2.204(9), Ru1-C10b 2.245(8), Ru1-C3a^1 2.258(8), Ru1-C3a 2.281(9), avg Ru1-C(Cp*) 2.174(9).

In the three mixed sandwich fragments, the polyaromatic skeleton is almost completely flat, with deviations to the least-squares mean plane not higher than 0.02 Å. The

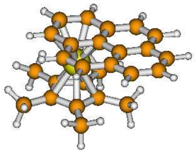
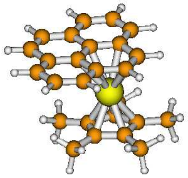
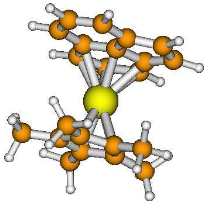
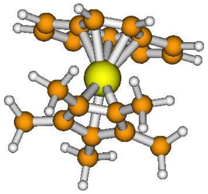
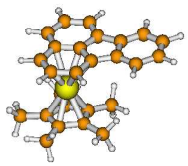
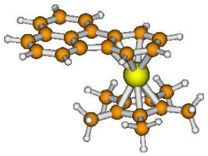
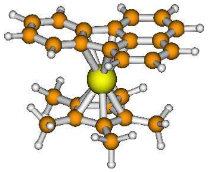
Cp* ring and the C_6-ring of the polycyclic arene system that is bonded to the Ru center are almost coplanar, with the angle formed between the metal ligand centroids and the focal metal atom of 179.1° for **1A**, 178.8° for **2A** and 178.9° for **3A**. The ruthenium atom is coordinated to the C_5Me_5 ligand at a ring centroid-ruthenium distance of 1.820, 1.827 and 1.835 Å, and to one C_6-ring of the polyaromatic ligand at a ring centroid-ruthenium distance of 1.730, 1.732, and 1.732 Å for **1A**, **2A** and **3A**, respectively. Overall, the Ru-C(Cp*) vary between 2.159(7) and 2.193(9)Å whereas the Ru-C(ar) are found between 2.201(8) and 2.281(9) Å. In accordance with the general tendency observed for polyarene metal complexes, the distances between the Ru and carbon atoms at the ring junction are longer than other Ru-coordinated rim carbon bond distances (see Figure captions). Additionally, both in **1A** and **3A** the average C-C distances of 1.424 and 1.417 Å, respectively, of the complexed C_6-ring are slightly longer than that measured (1.399 and 1.391 Å) in the free terminal benzene ring, indicative of the π-back donation from the $[Cp^*Ru^+]$ arenophile that results in a net reduction in C-C bond orders.[19]

Theoretical investigation of the structure and dynamics of complexes 1-3

The major computed values corresponding to the isomers of lower energy are provided in Table 1. It is noteworthy that the DFT data agree with the experimental results. In particular, isomers **1A** and **2A** are found to be the global minima of **1** and **2**, respectively, also in agreement with X-ray structures of related species.[3g, 15j, 21,27,35-38] On the other hand, isomers **3A** and **3B** are found to be nearly isoenergetic (Table 1), in agreement with the fact that both isomers were isolated in the solid-state although only the major isomeric product **3A** produced suitable X-ray quality single crystals. Contrary to what has been observed in the acenaphthylene series,[37,38] no structure of a fluoranthene complex η^5-coordinated through its five-membered ring to a metal center has been reported to date.[39]

Since the first extended Hückel investigation of Albright *et al.*[10] on haptotropic rearrangements in transition-metal complexes of polycyclic polyenes, a substantial number of DFT calculations has been performed on various systems of this type.[14a,40] All these studies agree on the fact that, as pointed out earlier by Albright *et al.*,[10] when an haptotropic shift interconverts two 18-electron isomers, the reaction pathway proceeds through an external (exo) coordination mode of the metal moiety on the periphery of the polycyclic ligand, in such a way that it is η^3- or η^4-bonded to the two neighboring rings involved in the haptotropic shift. Depending on the systems, this external coordination mode is associated either with a high-energy reaction intermediate or a transition state. This external coordination allows the metal to minimize its electron-deficiency (generally down to the 14-electron configuration). We have investigated by DFT calculations the possible isomerization reactions through inter-ring haptotropic rearrangements of the three η^6-polyaromatic complexes **1-3**. The computed energy profiles are displayed in Figs. 4-6. The metrical data of the computed extreme are provided in Tables S1-S3. †

Table 1. Major computed data for the most stable isomers of [(Cp*Ru(η^6-pyrene)]$^+$ (**1**$^+$), [Cp*Ru(η^6-acenaphtylene)]$^+$ (**2**$^+$) and [Cp*Ru(η^6-fluoranthene)]$^+$ (**3**$^+$). Average bond distances are reported, together with their range in brackets. Corresponding experimental X-rays values are also included where available.

		[Cp*Ru(η^6-pyrene)]$^+$ (**1**$^+$)		[Cp*Ru(η^6-acenaphtylene)]$^+$ (**2**$^+$)		[Cp*Ru(η^6-fluoranthene)]$^+$ (**3**$^+$)		
								
Distances/ Å		**1A** (η^5,η^6)	**1B** (η^5,η^6)	**2A** (η^5,η^6)	**2B** (η^5,η^5)	**3A** (η^5,η^6)	**3B** (η^5,η^6)	**3D** (η^5,η^5)
Ru-C(Cp*)	DFT	2.171 [2.160-2.187]	2.183 [2.181-2.189]	2.170 [2.148-2.203]	2.186 [2.174–2.199]	2.185 [2.176-2.196]	2.190 [2.189-2.190]	2.147 [2.140-2.153]
	X-rays	2.178 [2.170-2.182]		2.182 [2.159-2.191]		2.165 [2.149-2.174]		
Ru-C(PAH)	DFT	2.299 [2.315-2.334]	2.269 [2.232-2.317]	2.267 [2.203-2.312]	2.254 [2.215-2.282]	2.264 [2.222-2.329]	2.250 [2.230-2.272]	2.336 [2.312-2.344]
	X-rays	2.241 [2.217-2.274]		2.238 [2.201-2.279]		2.230 [2.182-2.260]		
HOMO-LUMO gap/ eV		4.15	3.41	3.94	2.88	4.22	3.97	2.76
ΔE(ZPE)/ eV		0	0.01	0	0.02	0.01	0	0.04
ΔG/Kcal mol^{-1}		0	9.1	0	10.9	3.8	0	26.4

The free energy profile associated with the interconversion between the pyrene isomers **1A** and 1**B** (Scheme 2). is shown in Fig. 4. It is a two-step process that passes through an exo-coordinated [CpRu(η^3-pyrene)]$^+$ (**1C**) high-energy intermediate in which the metal is bonded to C3, C3a and C4, with an energy barrier of 31.5 kcal/mol.

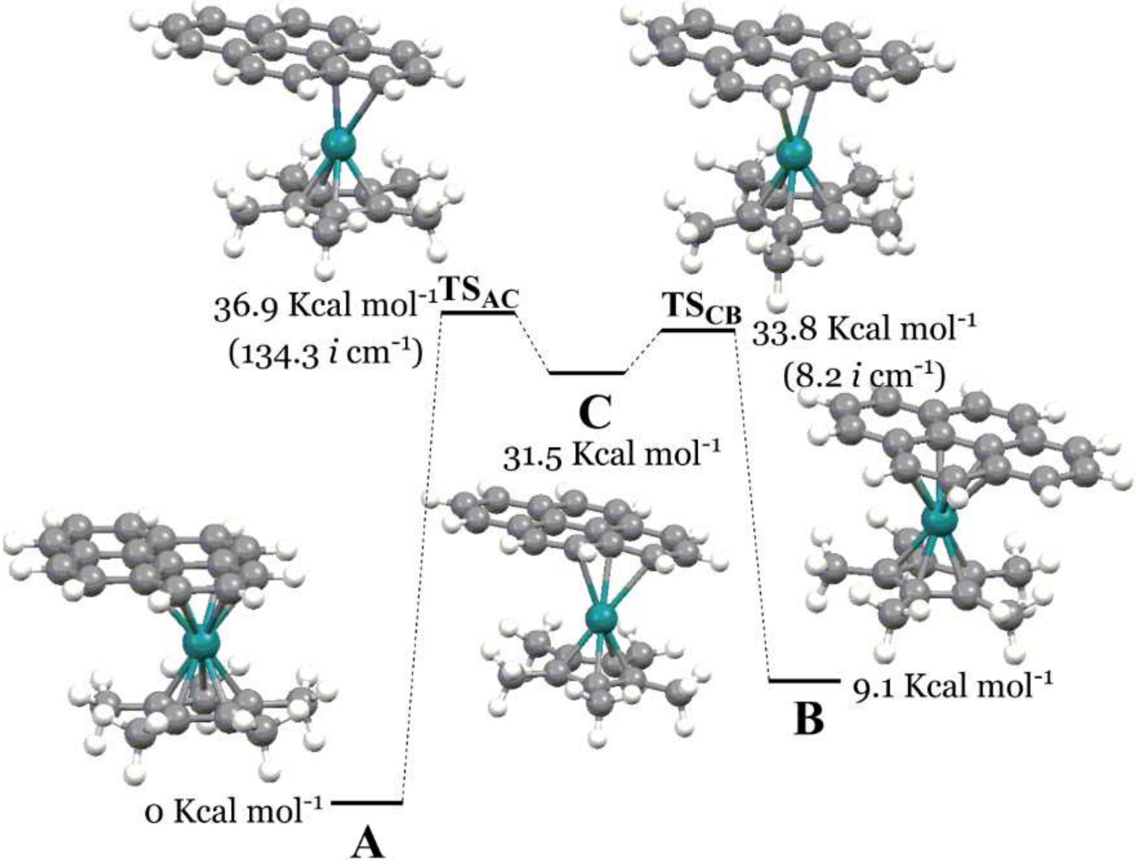


Fig. 4 Schematic free energy (ΔG) profile for the haptotropic shift of the [Cp*Ru$^+$] fragment in [Cp*Ru(η^6-pyrene)]$^+$ (**1**$^+$). The transition state imaginary frequency is given in parentheses.

In the case of the acenaphthylene complex **2**, two different isomerization reactions are found (Fig. 5). One involves the **2A** and **2B** isomers and the other one involves **2A** and its mirror image **2A'** (see Scheme 2). The energy profiles are shown in Fig. 5. Both **2A** ↔ 2**B** and **2A** ↔ 2**A'** interconversions are computed to be one-step process, involving transition states which are in a dissymmetrical trimethylenemethane type coordination mode, with three short Ru-C peripheral bonds (C2, C2a, C3 and C5, C5a, C6, respectively) and one long internal one (C2 and C2a', respectively). One should note that such haptotropic rearrangements involving a transition state rather than a high-energy intermediate may be due to computational level of theory and modelization. Indeed, in this type of haptotropic rearrangements the geometries of the possible intermediate (η^3) and transition state (asymmetrical η^4, distorted towards η^3) are generally not very different and the potential energy surface around the reaction mid-point is very flat. It follows that its shape is subject to subtle changes with respect to the nature of the functional or basis sets used or to the nature of the metal and ligands considered. For example, both one-step and two-step processes were found to compete in the inter-ring haptotropic rearrangement of [CpFe(η^6-naphthalene)]$^+$ (with very similar energy barriers), whereas similar calculations found only the one-step process to exist in the case of the isoelectronic [CpMn(η^6-naphthalene)].[40s] On the other hand, the two pathways have been found for [(η^6-naphthalene)Cr(CO)$_3$] (with similar activation energies),[40j] whereas only the two-step mechanism was found for [CpRu(η^6-naphthalene)]$^+$.[40m] In any cases, the computed energy barriers are in the order of ~ 30-40 kcal/mol.

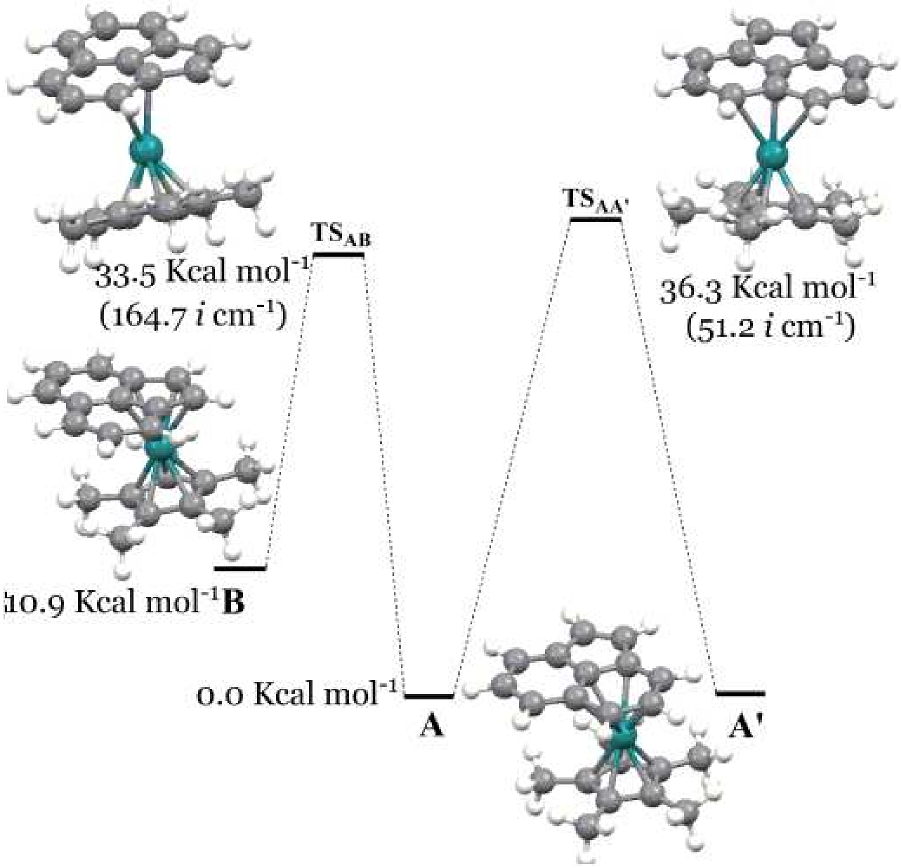


Fig. 5 Schematic free energy (ΔG) profile for the haptotropic shifts of the [Cp*Ru$^+$] fragment in [Cp*Ru(η^6-acenaphtylene)]$^+$ (**2**$^+$). The transition state imaginary frequencies are given in parentheses.

Four pathways were found interconnecting the **A**, **A'**, **B** and **D** isomers of the fluoranthene complex **3** (see Scheme 2). The **3A** ↔ **3A'** interconversion (Figure 6) passes through a transition state having a dissymmetrical methylenemethane coordination mode. The three other isomerization reactions were found to connect through the same η^4-coordinated intermediate **E** in which the Ru atom is bonded to C6, C6a, C6b and C7 (Fig. 6 and Table S3†). The computed energy barriers are close to 40 kcal/mol.

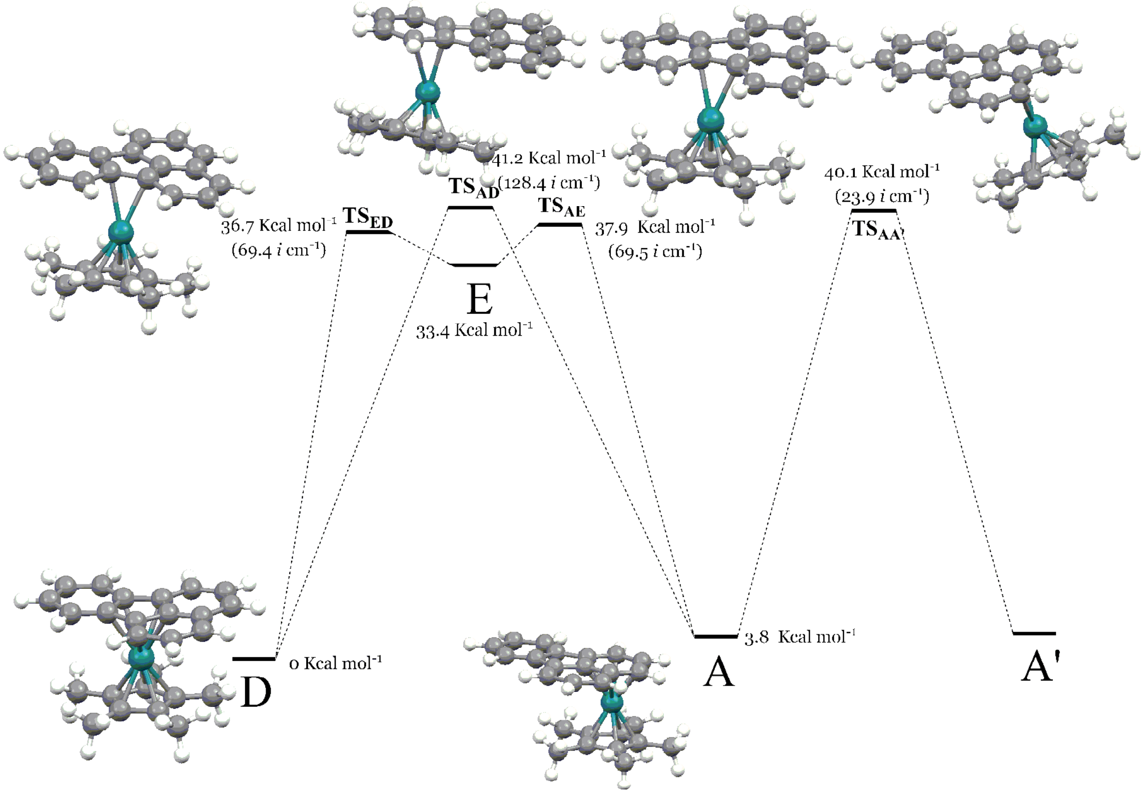


Fig. 6 Schematic free energy (ΔG) profile for the haptotropic shifts of the [Cp*Ru$^+$] fragment in [Cp*Ru(η^6-fluoranthene)]$^{+,}$ (**3**$^+$).). The transition state imaginary frequencies are given in parentheses. The **D** ↔ **E** energy profile is shown in Fig. S1. †

Finally, it should be noted that in any of the three computed complexes, a high-energy intermediate or a transition state in which the metal lies below one or more inner carbon atoms was not found. In any case, the [Cp*Ru$^+$] moiety was found to go through a pathway in which it coordinates to the PAH ligand in an external (exo) mode. This result is at variance with other calculations on $Cr(CO)_3$ complexes of PAH.[40d]

Conclusion

This study presents the complexation of three different polyaromatics by the $[Cp^*Ru^+]$ arenophile, the isolation and full analytical, spectroscopic and structural characterization of the cationic mixed sandwichs $[Cp^*Ru(\eta^6\text{-pyrene})]^+$ ($\mathbf{1}^+$), $[Cp^*Ru(\eta^6\text{-acenaphthylene})]^+$ ($\mathbf{2}^+$) and $[Cp^*Ru(\eta^6\text{-fluoranthene})]^+$ ($\mathbf{3}^+$) as their hexafluorophosphate salts. The fluoranthene derivative **3** is formed as a mixture of two isomers in a 90/10 spectroscopic ratio. The major isomeric product **3A** corresponds to the $[Cp^*Ru^+]$ moiety coordinated to one ring of the naphthalene core and the minor isomer **3B** is that with the organometallic arenophile bounded to the peripheral benzene unit. According to the single- crystal X-ray structure analysis, the organometallic sandwich cations **1A**, **2A** and **3A** exhibit similar metallocene-type geometry and structural features with three long fuzed carbon- and three short rime carbon-ruthenium distances, suggesting potential ability for intramolecular haptotropic shift. However, NMR experiments did not show any evidence for such a process even after heating at 90 °C in CD_3NO_2 solutions or at 120 °C in the solid-state for very long periods of time. DFT modelization of these haptotropic rearrangements found activation energies too high for the process being observed under the considered experimental conditions. We suggest that specific salt effects might render some of these processes observable.[41]

Experimental

General considerations

All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen. Solvents were dried and distilled under dinitrogen by standard methods prior to use.[42] $[Cp^*Ru(NCMe)_3][PF_6]$ was synthesized as reported in the literature.[43] Pyrene, acenaphtylene and fluoranthene were purchased from commercial sources and used without further purification. ^1H and ^{13}C NMR spectra were measured on a Bruker Avance III 400 spectrometer. The chemical shifts (δ_H and δ_C) were referenced relative to tetramethylsilane (TMS), using the residual solvent resonances of the deutero solvent, and expressed in parts per million (ppm). NMR chemical shift assignments are supported by data obtained from ^1H-^1H COSY, ^1H-^{13}C HMQC, and ^1H-^{13}C HMBC experiments, and are given according to the numbering scheme of Scheme 1. High resolution electrospray ionization mass spectra (ESI-MS) were acquired on a MICRO-TOF-Q II spectrometer, at the Centre

Regional de Mesures Physiques de l'Ouest (CRMPO, Rennes). Elemental analyses were carried out on a Thermo-FINNIGAN Flash EA 1112 CHNS/O analyzer by the Microanalytical Service of the CRMPO at the University of Rennes 1, France.

General procedure for the synthesis of [Cp*Ru(η^6-polyaromatic)][PF$_6$] (1-3)

A Schlenk tube was charged with [Cp*Ru(NCMe)$_3$][PF$_6$], a slight excess (10-25%) of the PAH and 5 mL of CH_2Cl_2. The solution was stirred at room temperature (rt) for 6 h. The solvent was removed under reduced pressure and the solid residue dried under vacuum for 2 h. Then, it was redissolved in 5 mL of fresh CH_2Cl_2 and the reaction mixture stirred at rt overnight. The solvent was evaporated under reduced pressure and the solid material washed with 2 x 5 mL portion of diethyl ether, 5 mL of pentane and dried *in vacuo* overnight.

[Cp*Ru(η^6-pyrene)][PF$_6$] (1A). [Cp*Ru(NCMe)$_3$][PF$_6$]: 110 mg (0.22 mmol), pyrene: 60 mg (0.28 mmol), yield: 120 mg (0.21 mmol, 95%) of a pale-yellow powder. Diffraction-quality single crystals were obtained as yellow blocks by slow diffusion of diethyl ether into a dichloromethane solution after one week at 5 °C. Found: C, 54.00; H, 4.35. $C_{26}H_{25}F_6$Pru requires C, 53.52; H, 4.32%. ESI MS (*m/z*), calcd for $C_{26}H_{25}{}^{102}Ru$: 439.09997; found: 439.1007 (2 ppm) (C^+). ^{1}H NMR (400 MHz; CD_3NO_2; 295 K): δ_H 1.34 (15 H, s, $C_5(CH_3)_5$), 6.21 (t, 1 H, $^3J_{HH}$ = 6.0 Hz, H-2), 6.52 (2 H, d, $^3J_{HH}$ = 6.0 Hz, H-1,3), 7.61 (2 H, d, $^3J_{HH}$ = 9.3 Hz, H-4,10), 8.10 (1 H, dd, 2nd order syst., H-7), 8.20 (2 H, d, H-6,8) and 8.21 (2 H, d, $^3J_{HH}$ = 9.3 Hz, H-5,9). $^{13}C\{^1H\}$ NMR (100 MHz; CD_3NO2; 295 K): δ_C 8.94 ($C_5(CH_3)_5$), 86.67 (C-1,3), 88.97 (C-2), 91.41 (C-3a^1), 94.35 ($C_5(CH_3)_5$), 95.15 (C-3a,10a), 124.59 (C-5a^1), 125.75 (C-4,10), 129.83 (C-6,8), 130.54 (C-7), 133.08 (C-5a,8a) and 133.67 (C-5,9).

[Cp*Ru(η^6-acenaphthylene)][PF$_6$] (2A). [Cp*Ru(NCMe)$_3$][PF$_6$]: 160 mg (0.32 mmol), acenaphthylene: 53 mg (0.35 mmol), yield: 160 mg (0.30 mmol, 94%) of a pale-yellow powder. Diffraction-quality single crystals were obtained as yellow plates by slow diffusion of diethyl ether into a dichloromethane solution after one week at 5 °C. Found: C, 49.73; H, 4.20. $C_{22}H_{23}F_6PRu$ requires C, 49.53; H, 4.35%. ESI MS (m/z), calcd for $C_{22}H_{23}{}^{102}Ru$: 389.08377; found: 389.0840 (1 ppm) (C^+). ^{1}H NMR (400 MHz; CD_3NO_2; 295 K): δ_H 1.50 (15 H, s, $C_5(CH_3)_5$), 6.01 (1 H, t, $^3J_{HH}$ = 5.8 Hz, H-4), 6.36 (1 H, d, $^3J_{HH}$ = 5.8 Hz, H-5), 6.56 (1 H, d, $^3J_{HH}$ = 5.8 Hz, H-3), 7.12 (1 H, d, $^3J_{HH}$ = 5.4 Hz, H-2), 7.44 (1 H, d, $^3J_{HH}$ = 5.4 Hz, H-1), 7.74 (1 H, d, $^3J_{HH}$ = 8.7 Hz, H-6),7.85 (1 H, dd, $^3J_{HH}$ = 6.0 and 8.7 Hz, H-7) and 7.99 (1 H, d, $^3J_{HH}$ = 6.0 Hz, H-8). $^{13}C\{^1H\}$ NMR (100 MHz; CD_3NO_2; 295 K): δ_C 9.10 ($C_5(CH_3)_5$), 85.17 (C-3), 89.19 (C-4), 86.90 (C-5), 95.16 ($C_5(CH_3)_5$), 95.51 (C-2a^1), 95.55 (C-

2a), 99.42 (C-5a), 127.05 (C-8), 127.25 (C-6), 131.51 (C-2), 132.78 (C-1), 134.35 (C-7) and 141.03 (C-8a).

[Cp*Ru(η^6-fluoranthene)][PF$_6$] (3A/3B = 90/10). [Cp*Ru(NCMe)$_3$][PF$_6$]: 160 mg (0.31 mmol), fluoranthene: 80 mg (0.39 mmol), yield: 180 mg (0.31 mmol, 100%) of lemon-yellow powder. Diffraction-quality single crystals were obtained as orange blocks by slow diffusion of diethyl ether into a dichloromethane solution after two weeks at 5 °C. Found: C, 53.24; H, 4.27. $C_{26}H_{25}F_6PRu$ requires C, 53.52; H, 4.32%. ESI MS (m/z), calcd for $C_{26}H_{25}{}^{102}Ru$: 439.09997; found: 439.1000 (0 ppm) (C$^+$). ^{1}H NMR (400 MHz; CD_3NO_2; 295 K): isomer **3A**, δ_H 1.25 (15 H, s, $C_5(CH_3)_5$), 5.99 (1 H, t, $^3J_{HH}$ = 5.8 Hz, H-2), 6.42 (1 H, d, $^3J_{HH}$ = 5.8 Hz, H-1), 6.52 (1 H, d, $^3J_{HH}$ = 5.8 Hz, H-3), 7.54 (2 H, m, H-8,9), 7.61 (1 H, d, $^3J_{HH}$ = 8.7 Hz, H-4), 7.80 (1 H, dd, $^3J_{HH}$ = 6.7 and 8.7 Hz, H-5), 7.86 (1 H, m, H-10), 7.94 (1 H, m, H-7) and 8.06 (1 H, d, $^3J_{HH}$ = 6.7 Hz, H-6); Isomer **3B**, δ_H 1.30 (15 H, s, $C_5(CH_3)_5$), 5.99 (2 H, m, H-7,10 or H-8,9), 6.55 (2 h, m, H-8,9 or H-7,10), 7.70 (2 H, dd, $^3J_{HH}$ = 7.0 and 8.2 Hz, H-2,5), 7.99 (2 H, d, $^3J_{HH}$ = 7.0 Hz, H-1,6 or H-3,4) and 8.03 (2 H, d, $^3J_{HH}$ = 8.2 Hz, H-3,4 or H-1,6). $^{13}C\{^1H\}$ NMR (100 MHz; CD_3NO_2; 295 K): isomer **3A**, δ_C 8.74 ($C_5(\mathit{C}H_3)_5$), 83.58 (C-1), 85.19 (C-3), 89.26 (C-2), 95.04 ($\mathit{C}_5(CH_3)_5$), 96.66 (C-10b), 97.04 (C-3a), 97.43 (C-3a^1), 123.07 (C-6), 124.40 (C-7), 124.52 (C-10), 126.29 (C-4), 128.31 (C-6a), 130.88 (C-8), 131.11 (C-9), 134.53 (C-5), 137.29 (C-10a) and 138.46 (C-6b); isomer **3B**, δ_C 9.16 ($C_5(\mathit{C}H_3)_5$), 87.71 (C-7,10), 95.02 ($\mathit{C}_5(CH_3)_5$ and C-8,9), 97.01 (C-6b,10a), 123.23 (C-1,6), 129.29 (C-2,5), 130.32 (C-3,4) and 132.83 (C-6a,10b); C-3a and C-3a^1 not observed.

X-ray Structure Determinations

A crystal of appropriate size of compounds **1A**, **2A** and **3A** was coated in Paratone-N oil and mounted on a cryoloop and transferred to the cold gas stream of the cooling device. Intensity data were collected at T = 150(2) K on a Bruker APEXII AXS diffractometer using Mo-Kα radiation (λ = 0.71073 Å), equipped with a bidimensional CCD detector and were corrected for absorption effects using multiscanned reflections. The structures were solved by direct methods using the *SIR97* program,[44] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-97*)[45] with the aid of the *WINGX* program.[46] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. All the hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. A summary of the details about the data collection and refinement for the X-ray structures of the three compounds are documented in Table 2, and additional crystallographic details are in the CIF files.

The measured crystal of [Cp*Ru(η^6-acenaphthylene)][PF$_6$] (**2A**) was found to be a non-merohedral twin: the final refinement was performed taking into account the presence of such a twinning (HKLF5 SHELXL file, twinning ratio ~35%). A subtle kind of disorder was found, where the position of the five- and six-membered rings could be anyone with respect to the ring where [Cp*Ru$^+$] is coordinated. The two possibilities are observed in the crystal structure, as depicted in Chart 1. The disorder was modelized using two positions whose occupancies were refined and then held constant at 0.50 and 0.50 for the last stages of refinement. These two disordered acenaphthylene groups have been modelized by introducing constraints and restrains in order to make the C_5 and C_6 rings more regular (use of DFIX, SADI and SAME).[45] To stabilize the structural refinement and avoid non-convergence of the least-squares refinement, anisotropic atomic displacements on carbon atoms of these disordered rings have been contrained to be equal. On the other hand, several attempts to improve the structural refinement parameters of **3A** (Table 2) have been made (disorder modelling on PF$_6$ anion, delocalisation of The Ru atom), without significant success. The data set is quite correct (low R$_{int}$, good quality of diffraction frames) but the difference Fourrier map is noisy, with a ratio ABS(delta_rho_max / delta_rho_min) value of 1.45 : this largest peak should normally be interpreted but actually cannot be unless it is due to a non detectable twinning.

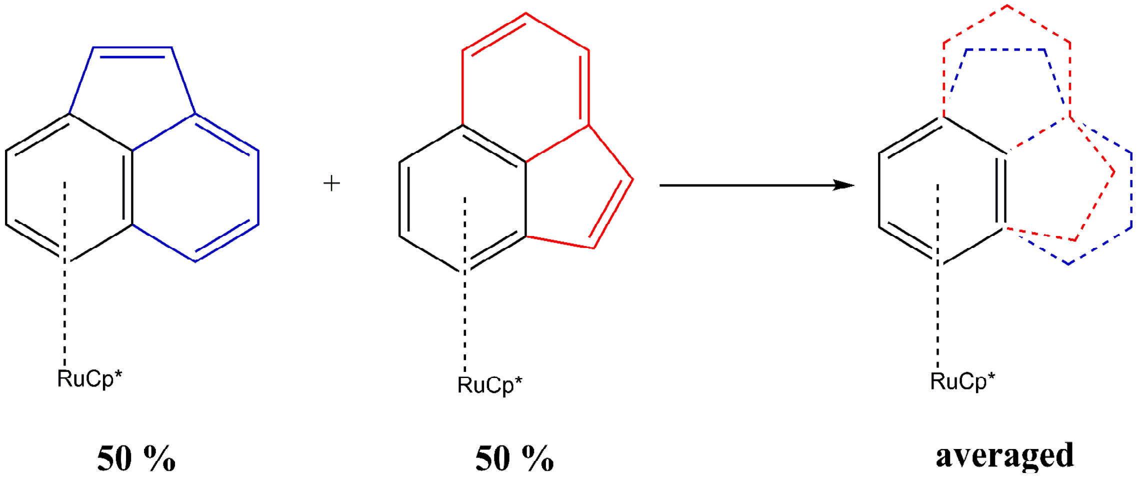


Chart 1 A sketch of the structural disorder exhibited by the acenaphtylene ligand in [Cp*Ru(η^6-acenaphthylene)][PF$_6$] (**2A**)

Table 2 Crystallographic data, details of data collection and structure refinement parameters for compounds **1A**, **2A** and **3A**

	1A	**2A**	**3A**
Empirical Formula	$C_{26}H_{25}F_6PRu$	$C_{22}H_{23}F_6PRu$	$C_{26}H_{25}F_6PRu$
Formula mass, g mol^{-1}	583.50	533.44	583.50
Collection T, K	150(2)	150(2)	150(2)
crystal system	Triclinic	Monoclinic	Triclinic
space group	P -1	P 2_1/n	P -1
a (Å)	7.7855(3)	8.6460(13)	8.4940(4)
b (Å)	8.5249(4)	8.6690(11)	11.0658(6)
c (Å)	17.6313(7)	27.921(3)	12.6900(7)
α (°)	88.2880(10)	90	84.451(3)
β (°)	79.3790(10)	97.352(9)	88.341(3)
γ (°)	87.0630(10)	90	78.305(3)
V (Å^3)	1148.39(8)	2075.5(5)	1162.48(11)
Z	2	4	2
D_{calcd} (g cm^{-3})	1.687	1.707	1.667
Crystal size (mm)	0.29 x 0.27 x 0.13	0.13 x 0.09 x 0.05	0.22 x 0.17 x 0.15
F(000)	588	1072	588
abs coeff (mm^{-1})	0.814	0.892	0.804
θ range (°)	3.10 to 27.47	1.47 to 27.59	2.92 to 27.46
range h,k,l	-10/10, -11/11, -22/20	-11/11, 0/11, 0/36	-10/11, -14/14, -14/16
No. total refl.	15414	7780	14688
No. unique refl.	5246	7780	5205
Max/min transmission	0.900/0.751	0.956/0.882	0.886/0.701
Data/Restraints/Parameters	5246/0/315	7780/0/237	5205/0/312
Final R	$R_1 = 0.0233$	$R_1 = 0.0727$	$R_1 = 0.0953$
[I>2σ(I)]	$wR_2 = 0.0598$	$Wr_2 = 0.1816$	$wR_2 = 0.2347$
R indices (all data)	$R_1 = 0.0242$	$R_1 = 0.1100$	$R_1 = 0.1030$
	$wR_2 = 0.0604$	$wR_2 = 0.1982$	$Wr_2 = 0.2388$
Goodness of fit / F^2	1.105	0.982	1.253
Largest diff. Peak/hole (eÅ^{-3})	1.091 and -0.401	1.071 and -1.002	3.521 and -2.465

Computational details

Density functional theory (DFT) calculations were carried out with the program Gaussian03,[47] using the PBE1PBE[48] functional and a standard double-ξ polarized basis set, namely the LanL2DZ set,[49] augmented with polarization functions on all atoms except H, i.e., a d orbital with exponent 0.8 for C and a f orbital with the same exponent on the transition metals. All stationary points were fully characterized via analytical frequency calculations as either true minima (no imaginary values) or transition states (one imaginary value). In a few cases, small imaginary frequencies associated with a methyl rotational movement have been neglected. The Intrinsic reaction coordinate (IRC)[50] procedure was used to confirm the nature of each transition state connecting two minima. For finding transition states, the STQN[51] method was used with the QST3 option. The representation of the molecular structures was made by using the Molekel4.3 program.[52] It should be noted that several of the calculations reported here have been also carried out considering unsubstituted cyclopentadienyl ligand (C_5H_5) in place of the pentamethylated one (C_5Me_5). The obtained results are fully consistent with those reported here.

Acknowledgments

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Notes and References

[†] **Electronic supplementary information (ESI) available:** Figure S1 showing the D ↔ E energy profile for **3**, computed distances, relative energies and imaginary frequencies for the isomers and transition states for **1**$^+$-**3**$^+$ (Tables S1-S3), crystallographic data for structural analysis (in CIF format), and Cartesian coordinates of all the optimized structures and list of frequencies when computed. CCDC 1002568, 1002569 and 1002570. For ESI and crystallographic data in CIF or other electronic format see DOI:

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