

# Searching for molecular arene hydrogenation catalysis in ionic liquids

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## Abstract

Arene hydrogenation by homogeneous catalysts is a highly controversial area of research, with many of the mononuclear complexes shown to catalyse the reaction, being found to be pre-catalysts to nanoparticles, on closer examination. The solvent properties of ionic liquids, i.e., low nucleophilicity and high polarity, make them ideal, at least in principal, for homogeneous arene hydrogenation catalysts. In this paper, we described our attempts to prepare and study such systems, using either simple metal halides or ruthenium complexes including trinuclear ruthenium clusters as catalyst precursors.

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## 1. Introduction

The hydrogenation of benzene and other arenes by molecular catalysts is a fascinating and controversial area of research, in which many highly innovative catalysts have been evaluated. Arene hydrogenation is not just a topic of academic interest, but has industrial application such as the synthesis of cyclohexane (a precursor to adipic acid used to produce nylon) [1], removal of aromatic compounds from fuels [2], and as way to prevent paper from yellowing without addition of bleaches, since the compounds responsible for the yellowing are aromatic macromolecules [3]. All industrial arene hydrogenation catalysts are heterogeneous, including a system that converts benzene to cyclohexene, which is subsequently converted into cyclohexanol [4]. However, there is some interest in finding versatile and selective homogeneous catalysts for the synthesis of fine chemicals, because many substituted arenes are readily available and the most convenient route to a cyclo-

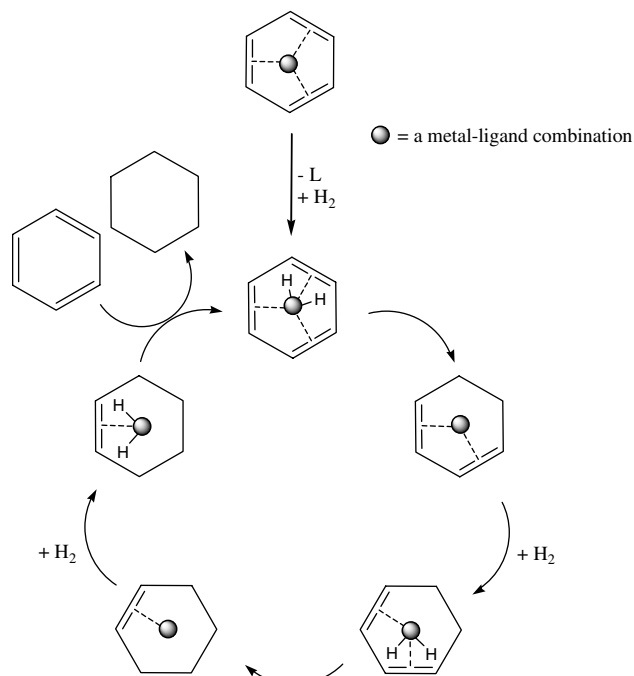
hexyl-analogue would be via hydrogenation at one side of the arene ring [5].

A large number of molecular compounds have been used as pre-catalysts for the hydrogenation of benzene and arenes [6], and some have since been shown to be precursors to heterogeneous catalysts, such as soluble nanoparticles, with many more cases suspected [7]. Most of the catalyst precursors are based on platinum group metals, although not exclusively, and often contain an arene ligand or labile ligands [6]. A mechanism for arene reduction was thus proposed invoking a stepwise hydrogenation-slippage process in which each unsaturated bond of the arene is hydrogenated in turn (see Scheme 1) [8].

What is interesting to note, and contrasts with the usual perception of homogeneous catalysis, is that soluble colloidal (or nanoparticle) arene hydrogenation catalysis tend to operate under milder conditions and exhibit higher activities than molecular catalysts [9]. One explanation for this dichotomy is that the homogeneous arene hydrogenation catalysts are not homogeneous in the first place, as mentioned above. Another possibility is that the arene, when coordinated to the nanoparticle surface, is more highly activated than when

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Scheme 1. The arene-exchange mechanism for the reduction of arenes.

coordinated to a single metal centre. Accordingly, benzene and other arenes have been shown to lie over three metal centres on certain surfaces [10], and such a bonding regime has also been observed in molecular cluster compounds [11]. In this so called  $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$  bonding mode an arene is more highly activated as demonstrated by a Kekulé-like structure combined with indicative spectroscopic data [12]. Thus, clusters where such coordination is possible could prove to be the missing link and might provide definitive proof for homogeneous arene hydrogenation. In addition, since it has recently been shown that catalysis by intact clusters is favoured in polar solvents [13], non-coordinating ionic solvents could facilitate arene hydrogenation [14]. Catalysis by clusters is a well established process [15] and has already been demonstrated in ionic liquids [16]. Nanoparticle catalysis in ionic liquids has also been demonstrated [17] including, remarkably, partial reduction of benzene to cyclohexene [17a].

## 2. Results and discussion

The acidic chloroaluminate ionic liquid [*N*-ethyl-*N*-methyl-imidazolium]Cl–AlCl<sub>3</sub> (*x* = 0.67), combined with electropositive metals such as aluminium, zinc or lithium together with a proton source, have previously been shown to hydrogenate aromatic compounds, and the partial reduction of polyaromatic compounds was also achieved [18]. In addition, the titanium complex Ti( $\eta^6$ -

C<sub>6</sub>H<sub>5</sub>Me)Al<sub>2</sub>Cl<sub>8</sub> is a pre-catalyst for the conversion of benzene to cyclohexane in molecular solvents [19]. Some decomposition of the titanium complex was observed during the reaction and the possibility that metallic particles were responsible for the catalysis cannot be discounted.

Simple metal halides can form arene–metal complexes under reducing conditions [20]. Thus, attempts to generate catalysts from metal chlorides in the Lewis acidic chloroaluminate ionic liquid [*N*-octyl-3-picolinium]Cl–AlCl<sub>3</sub>, were undertaken in the first instance. Essentially, the metal chloride was dissolved in the ionic liquid and benzene added, affording a biphasic mixture. The system was then pressurized with H<sub>2</sub> to 50 bar, stirred at 100 °C for 4 h and the conversion determined by GC. The results from these experiments are summarized in Table 1. A first approximation of the course of the reaction is possible by looking at the two different phases. While cyclohexane is immiscible with the ionic liquid, affording a colourless upper phase, benzene is partially miscible with the chloroaluminate ionic liquid as is visible from a markedly coloured organic phase.

Of the seven salts screened only PdCl<sub>2</sub> and K<sub>2</sub>PtCl<sub>4</sub> showed significant activities, the platinum salt giving almost quantitative conversion to cyclohexane under the conditions employed, with no indication of the formation of either cyclohexene or cyclohexadienes. For this reason, and because under reducing conditions platinum salts are known to form cluster compounds [21], K<sub>2</sub>PtCl<sub>4</sub> was investigated further. Under essentially the same conditions, except with a shorter reaction time to ensure the reaction did not go to completion, the effect of catalyst concentration was studied and the results are listed in Table 2. In all the reactions, with the exception of those employing 1 and 3 mg of K<sub>2</sub>PtCl<sub>4</sub>, deposits of platinum black were present. This observation indicates that the active catalyst could in fact be heterogeneous and not homogeneous. Recycling of the system was attempted and in general slightly lower conversions were observed compared to those obtained in the first cycle.

Next, the effect of temperature was explored and while a reduction in the reaction temperature to 20 °C

Table 1  
Conversion of benzene to cyclohexane using metal chlorides dissolved in [*N*-octyl-3-picolinium]Cl–AlCl<sub>3</sub><sup>a</sup>

Metal chloride	Benzene (%)	Cyclohexane (%)
ZrCl <sub>4</sub>	100	–
NiCl <sub>2</sub>	100	–
PdCl <sub>2</sub>	43	57
CrCl <sub>3</sub>	99.5	0.5
K <sub>2</sub> PtCl <sub>4</sub>	1	99
CoCl <sub>2</sub>	100	–
SmCl <sub>3</sub>	100	–

<sup>a</sup> [*N*-octyl-3-picolinium]Cl–AlCl<sub>3</sub> (1.5 ml), benzene (3 ml), H<sub>2</sub> (50 bar), *t* = 240 min, *T* = 100 °C. Conversion determined by GC.

Table 2

Effect of catalyst concentration and reaction temperature on the activity of  $K_2PtCl_4$  in  $[N\text{-}n\text{-}octyl\text{-}3\text{-}picolinium]Cl\text{-}AlCl_3$ , for the reduction of benzene to cyclohexane<sup>a</sup>

$K_2PtCl_4$	20 °C	50 °C	75 °C
1 mg (0.0071 mol%)	18	63	80
3 mg (0.021 mol%)	51	80	99
5 mg (0.035 mol%)	60	81	99
10 mg (0.071 mol%)	58	83	>99
20 mg (0.14 mol%)	67	84	>99
40 mg (0.28 mol%)	61	>99	>99

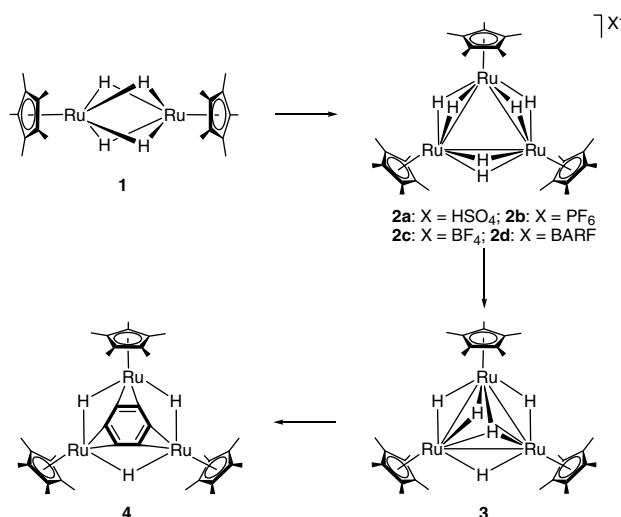
<sup>a</sup>  $[N\text{-}n\text{-}octyl\text{-}3\text{-}picolinium]Cl\text{-}AlCl_3$ , (1.5 ml), benzene (3 ml),  $H_2$  (50 bar),  $t = 180$  min,  $T = 50$  °C.

considerably reduced activity, an increase in temperature by only 25 °C results in a dramatic increase in activity such that near quantitative conversion of benzene to cyclohexane takes place at all catalyst concentrations except the very lowest.

It is worth comparing the use of this simple platinum salt-chloroaluminate ionic liquid system with the widely used and versatile rhodium chloride system derived from  $RhCl_3$ , Aliquat<sup>®</sup> 336 and trioctylamine [22]. Originally, the active catalyst was thought to comprise the solvated ion pair  $[(C_8H_{17})_3NMe]^+[RhCl_4]^-$  [23], but subsequently, the active catalyst was found to be colloidal [7]. Although, the solubility of hydrogen gas in water and ionic liquids is comparable [24], the solubility of benzene is higher in ionic liquids [25], so the  $RhCl_3$ -Aliquat<sup>®</sup> 336-trioctylamine system was evaluated in the hydrophilic ionic liquids  $[C_4C_1im][BF_4]$ ,  $[C_6C_1im][BF_4]$  and  $[C_8C_1im][BF_4]$ , though at significantly higher catalyst loadings, viz. 3.8 mol%. After 190 min at 20 °C, 83–87% conversion was observed. While the platinum salt is clearly more active and does not require any additives, the moisture sensitivity of the employed chloroaluminate ionic liquid certainly represents a drawback.

The nature of the actual platinum catalyst has not been established, but we tend to believe that the active species is not a molecular cluster, but a nanoparticle catalyst. Apart from the presence of black precipitates in the reaction mixture, mercury used as a selective poison for nanoparticle catalysts [26], was found to inhibit activity. In addition, in situ high pressure NMR studies and electrospray ionization mass spectrometry were unable to detect peaks corresponding to molecular species. Both NMR spectroscopy [27] and mass spectrometry [28] have previously been used to determine catalyst species directly in ionic liquids. Therefore, in order to test our hypothesis (see above), we decided to employ a pre-formed molecular cluster as the catalyst in a comparatively inert ionic liquid.

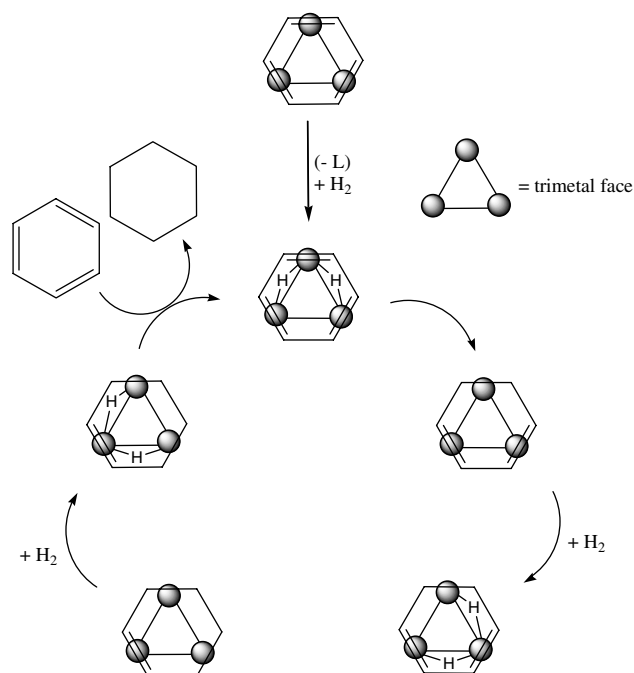
Following a search of potential clusters with (or with the capacity to bind) a face-capping arene ligand the trinuclear ruthenium clusters described by Suzuki and co-workers [29] appeared to be the ideal candidates for evaluation (see Scheme 2). The well characterized arene



Scheme 2.

hydrogenation cluster catalysts  $[H_4Ru_4(\eta^6\text{-arene})_4]^{2+}$ , which operate in water [30], and also ionic liquid [31], were not selected for this study as face-capping coordination is unlikely to occur. In fact, some of the most effective arene hydrogenation catalysts operate in water, but the nature of the true catalyst remains elusive. For example, with the ruthenium catalyst  $[Ru(\eta^6\text{-}p\text{-cymene})(dppe)Cl]^+$  the turnover frequency increases with increasing pH, which is believed to correspond to an increase in nanoparticles [32].

The known cluster **4**, bearing a face-capping benzene ligand, is derived from the dinuclear compound **1** via addition of acid to afford the cationic cluster **2**. Deprotonation and subsequent addition of 1,3-cyclohexadiene leads to the neutral tri-hydrido cluster **4**. The presence of the hydride ligands suggests that the arene hydrogenation mechanism illustrated in Scheme 3 could be feasible. For the purpose of homogeneous hydrogenation studies in benzene, the BARF-analogue of **2a–c** was synthesized by reaction of **1** with  $(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3)_4\text{B}\cdot\text{H}(\text{OEt}_2)_2$ . This cluster is highly soluble in benzene and its structure was established by single crystal X-ray diffraction analysis. Crystals were obtained from slow diffusion of pentane into a diethyl ether solution of **2d** and due to the presence of solvent in the crystal, the asymmetric unit contains two independent molecules. Several of the  $\text{CF}_3$ -groups of the  $\text{BARF}^-$  anions are disordered in the solid state and there is also some disorder in the  $\text{Cp}^*$  rings due to conformational instability. The structure of **2d** is shown in Fig. 1 and key bond parameters are provided in the caption. The ruthenium–ruthenium distances, ranging between 2.6953(7) and 2.7051(7) Å are significantly shorter than those in the benzene-capped cluster **4**, 3.0468(9)–3.0537(8) Å [29]. Comparable lengths are found in trinuclear clusters of the type  $\{(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\}_3(\mu\text{-H})_3\text{-}(\mu_3\text{-BOEt})$  [33] and  $\{(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\}_3(\mu\text{-H})_2\text{-}(\mu_3\text{-S})(\mu_3\text{-CCH}_2\text{C}_6\text{H}_5)$  [34]. The



Scheme 3. The arene-exchange mechanism that could operate at a metal face.

plane of the Cp\*-ring is slightly tilted with respect to the plane spanned by the three ruthenium atoms, resulting in asymmetric bonding between the carbon and ruthenium atoms.

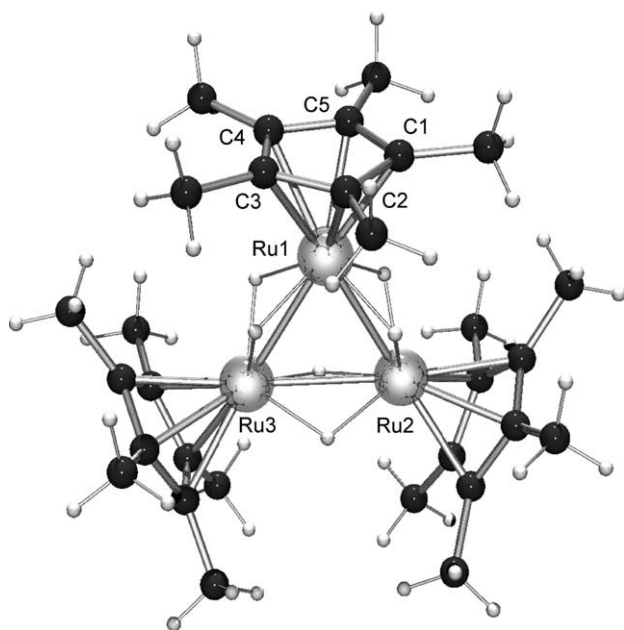


Fig. 1. Ball-and-stick representation of the cationic ruthenium moiety of **2d**. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.6953(7); Ru(1)–Ru(3) 2.7051(7); Ru(2)–Ru(3) 2.7028(8); Ru(1)–C(1) 2.194(6); Ru(1)–C(2) 2.175(6); Ru(1)–C(3) 2.213(6); Ru(1)–C(4) 2.222(6); Ru(1)–C(5) 2.188(6); Ru(1)–Ru(2)–Ru(3) 60.15(2); Ru(2)–Ru(1)–Ru(3) 60.06(2); Ru(2)–Ru(3)–Ru(1) 59.79(2).

Table 3  
Activity of compounds **1–4** for the hydrogenation of benzene in different solvents<sup>a</sup>

Catalyst	Neat cyclohexane (%)	[C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ] (1 ml) cyclohexane (%)	<i>i</i> -PrOH (1.5 ml) cyclohexane (%)
<b>1</b>	0	0	25.0
<b>2a</b>	0	0	0
<b>2b</b>	0	0	4.0
<b>2c</b>	0	0	1.4
<b>2d</b>	0.8	0	0
<b>4</b>	1.5	0	82.2

<sup>a</sup> Catalyst (0.01 mmol), benzene (3 ml), H<sub>2</sub> (50 bar), *t* = 240 min, *T* = 100 °C.

Compounds **1–4** were evaluated as catalysts for the hydrogenation of benzene in neat substrate, in [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] ionic liquid and in 2-propanol and the results from these experiments are compiled in Table 3.

In the [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] ionic liquid none of the compounds show activity in the hydrogenation of benzene, whereas in 2-propanol **4** is quite active. Both [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] and 2-propanol have similar polarity, but while the ionic liquid is essentially non-nucleophilic, the alcohol is a moderate nucleophile. The implication from this comparison is that the active catalyst is not homogeneous, but heterogeneous, such as soluble nanoparticles. The essentially complete inactivity of these hydride complexes in neat benzene and [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] was not anticipated, especially, as it has been demonstrated earlier that these compounds are capable of activating numerous organic substrates such as nitriles, thiols, alkenes and alkynes [35].

The reactivity of **4** was further investigated using high-pressure NMR. A solution of **4** in d<sub>6</sub>-benzene was pressurized with 40 bar of hydrogen and measured at different temperatures. At ambient temperature, no change is observed over a period of several days. Only when the NMR tube was kept at higher temperature were new peaks detected. No measurable amount of semi-deuterated benzene was detected but after 10 h at 80 °C new signals at –7.11 and –13.87 ppm were found which were assigned, by comparison with the literature, to the penta-hydride cluster **3** and the dinuclear species **1**, respectively.

### 3. Concluding remarks

Thus far our attempts to find a molecular cluster system which allows us to demonstrate that the reduction of arenes takes place via a mechanism involving face-capping activation of benzene have not been successful. It is still not possible to rule out the mechanism shown in Scheme 3 which could take place on a metal surface and may account for the superior activity of heterogeneous catalysts in arene hydrogenation. We have, however, identified a very effective and simple ionic liquid

based system for arene hydrogenation based on  $K_2PtCl_4$  and  $[N\text{-octyl-3-picolinium}]Cl-AlCl_3$ . Benzene is partially miscible in the ionic liquid phase whereas the cyclohexane product is immiscible. This gives rise to the ideal situation of high reactions rates, not impeded by phase problems, with the ideal separation properties. It is likely that further optimization of this system will be possible, for example, by using mixtures of different salts which may lead to heteronuclear nanoparticles catalysts with greater activity.

## 4. Experimental

### 4.1. General

All organometallic manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Diethyl ether was distilled from sodium–potassium alloy, hexane and thf from potassium and 2-propanol from  $CaH_2$ . The ruthenium complexes **1** [36], **2a**, **2c**, **3** [35], **2b** [37], **4** [29] and  $(3,5\text{-}(CF_3)_2C_6H_3)_4B \cdot H(OEt)_2$  [38], and the ionic liquids  $[C_4C_{1im}][BF_4]$ ,  $[C_6C_{1im}][BF_4]$  and  $[C_8C_{1im}][BF_4]$  [39], were prepared as described elsewhere. All other chemicals are commercial products and were used as received. Spectra were recorded with Bruker Avance 400. Chemical shifts are given in ppm and coupling constants ( $J$ ) in Hz. Elemental analyses were performed at the EPFL. Electrospray mass spectra were measured on a Thermo Finnigan LCQ Deca XPplus spectrometer using a literature protocol [40].

### 4.2. Catalysis

Catalytic experiments were conducted using a home-built multicell autoclave at specified temperature and hydrogen pressure. To each reaction vessel the catalyst, solvent (1.5 ml) and the substrate (3 ml) were added. After completion of the experiment, the ionic liquid phase was extracted with pentane (5 ml) and conversions determined by GC analysis. When the chloroaluminate ionic liquid was used, all manipulations were carried out in a dry box.

### 4.3. Synthesis

$N$ -octyl-3-picolinium chloride (1 kg) was melted at 70 °C and aluminium chloride (1.1 kg) added at such a rate so that the reaction temperature was maintained between 70 and 80 °C. The resulting solution consisted of >95% of the desired  $N$ -octyl-3-picolinium aluminium chloride ionic liquid.

Synthesis of **2d**: To a solution of  $[Cp^*RuH_2]_2$  (130 mg, 0.27 mmol) in THF (6 ml) was added  $(3,5\text{-}(CF_3)_2C_6H_3)_4B \cdot H(OEt)_2$  (273 mg, 0.27 mmol) in

$Et_2O$  (2.5 ml), resulting in an immediate colour change to dark brown-purple. The solution was stirred at ambient temperature for 2 h, then the solvent removed in vacuo and the remaining product washed thoroughly with hexane to afford **2d** as dark brown solid. Yield: (94%).  $^1H$  NMR ( $CD_2Cl_2$ , 400 MHz):  $\delta$  = 7.21 (br, 8H, *ortho*-BARF), 7.56 (br, 4H, *para*-BARF), 1.96 (s, 45H,  $CH_3$ ), -11.23 (s, 6H).  $^{13}C$  NMR ( $CD_2Cl_2$ , 100 MHz):  $\delta$  = 162.3 (q,  $^1J_{BC}$  = 50, *ipso*-BARF), 135.4 (br, *ortho*-BARF), 129.6 (m, *meta*-BARF), 125.2 (q,  $^1J_{CF}$  = 272,  $CF_3$ ), 118.0 (m, *para*-BARF), 98.2 (Cp\*), 12.4 ( $CH_3$ ). Anal. Calc. for  $C_{62}H_{63}BF_{24}Ru_3$ : C, 47.19; H, 4.02. Found: C, 47.43; H, 3.99%.

### 4.4. Crystallography

Crystals suitable for X-ray diffraction were obtained from slow diffusion of pentane into a diethyl ether solution of **2d**. The unit cell contains two independent cations and anions, together with one molecule of diethyl ether. Data reduction was performed using CrysAlis RED [41]. Structure solution and refinement was performed using the SHELX-97 software package [42], graphical representations of the structures were made with ORTEP32 [43]. The structure was solved by Patterson method and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against  $F^2$ ). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in their geometrically generated positions and refined using a riding model. The hydride hydrogens were located on the Fourier map and restrained using the DFIX command implemented in SHELX. Due to rotation of some  $CF_3$  groups of the counter-anions, several fluorine atoms had to be split over two positions and were refined against each other using one free variable (FVAR)

Table 4  
Crystal structure data of **2d**

Formula	$C_{64}H_{68.50}BF_{24}O_{0.50}Ru_3$
$M$	1615.71
Crystal system	Triclinic
Space group	$P\bar{1}$
$a$ (Å)	19.2066(18)
$b$ (Å)	20.436(2)
$c$ (Å)	20.5901(17)
$\alpha$ (°)	117.369(10)
$\beta$ (°)	103.044(7)
$\gamma$ (°)	93.503(8)
$V$ (Å <sup>3</sup> )	6863.9(11)
$Z$	4
Density (Mg/m <sup>3</sup> )	1.564
$T$ (K)	140(2)
$\theta$ range (°)	$2.91 \leq \theta \leq 25.03$
$\mu$ (mm <sup>-1</sup> )	0.755
Reflections measured	39,957
Unique reflections [ $I > 2\sigma(I)$ ] ( $R_{int}$ )	21,226 (0.0451)
Final $R_1$ , $wR_2$ [ $I > 2\sigma(I)$ ]	0.0605, 0.1537

for each CF<sub>3</sub> group with occupation factors of round about 20–45% for the disordered positions. An adsorption correction (DELABS) [44] was applied. CCDC 262996 contains the supplementary crystallographic data for this paper. 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) (see Table 4).

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