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Unprecedented oxidation of half-sandwiched ruthenium(II) in the excess of ammonium hexafluorophosphate and formation of nanosized Ru–RuS₂

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ABSTRACT

The [{(η^6 -*p*-cymene)RuCl(μ -Cl)}₂] reacts with *N*-{2-(phenylthio)ethyl}morpholine (**L**) and excess NH₄PF₆ in CH₃OH at room temperature (24 h), resulting in [(η^6 -*p*-cymene)RuCl₂(**L**)][PF₆] (**1**) and [(η^6 -*p*-cymene) RuCl(NH₃)₂][PF₆] (**2**) unexpectedly. The complex **1** is first example of a 17e⁻ half-sandwich complex of η^6 -arene with Ru(III) formed due to unexpected oxidation of Ru(II) in the presence of excess NH₄PF₆. The **1** is authenticated by EPR and on the basis of DFT calculations. The single crystal structures authenticate both **1** and **2**. The Ru—S bond length in **1** is 2.413(3) Å whereas in **2** Ru—N bond distances are 2.141(3) and 2.149(3) Å. Attempt to catalyze transfer hydrogenation of ketones with 2-propanol with **1** has given spherical and block shaped Ru–RuS₂ (70:30 w/w%) nano-particles of average size 5–8 nm.

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1. Introduction

Half-sandwich compounds of ruthenium(II) having η^6 -arene are important in organometallic chemistry [1,2] and generally stable. An extensive chemistry of such compounds is known [3]. Numerous half-sandwich complexes of $(\eta^6$ -arene)Ru(II) unit with hybrid organochalcogen ligands (having N and/or O as other donor atoms) behaving as monodentate [4,5], bidentate [6–9] and tridentate [10–13], have been reported in last decade. Half-sandwich complexes of Ru(III) are generally formed by $(\eta^5-Cp/Cp^*)Ru(III)$ unit and most of them are binuclear. However, monomeric species are also known. The reaction of $[{\eta^5-Cp^*RuCl(\mu-Cl)}_2]$ with 3thiapentane-1,5-dithiolate (tpdt = $S(CH_2CH_2S^{-})_2$) results in a monomeric complex $[\eta^5-Cp^*Ru(III)(tpdt)]$ [14]. Becker et al. have reported oxidative addition of alkyl or aryl di-sulfides/selenides, REER (R = t-Bu, Ph, p-tolyl; E = S, Se) with labile cationic complex [η⁵-CpRu(CH₃CN)₃][PF₆], resulting in binuclear species $[\eta^{5}-CpRu(CH_{3}CN)(\mu-ER)_{2}(CH_{3}CN)Ru(\eta^{5}-Cp)][PF_{6}]_{2}$ [15]. The reaction of $[{(\eta^6-p-cymene)RuCl(\mu-Cl)}_2]$ with $Li_2[S_2C_2(B_{10}H_{10})]$ gives $[(\eta^6-p-cymene)Ru(S_2C_2(B_{10}H_{10}))]$ a mononuclear (16e⁻) complex first, which in the presence of an excess of sulfur formed binuclear complex $[(\eta^6 - p - cymene)Ru(I)(\mu - S_2)Ru(III)(S_2C_2(B_{10}H_{10}))_2]$ [16]. Half-sandwich complexes of Ru(IV) are also known and have received considerable attention, particularly from the point of view of catalysis [17]. Zhang et al. reported that the treatment of $[\eta^5-Cp^*Ru(CH_3CN)_3][PF_6]$ with HN[SeP(*i*-Pr)_2]₂ afforded a Ru(IV) complex, $[\eta^5-Cp^*Ru(\eta^2-Se_2P(i-Pr)_2)\{\eta^2-SeP(i-Pr)_2\}][PF_6]$ [18]. Electrochemically synthesized complexes of η^5 -Cp*Ru(IV) with dithiocarbamate and carbonodithiolate ligands are also known [19].

Apart from academic curiosity the current interest in halfsandwich species of Ru(II) has stemmed from their various applications e.g. catalytic transfer hydrogenation of ketones [20–23] in aqueous as well as non-aqueous media. The use of 2-propanol as hydrogen source in this process is interesting as it avoids inflammable H₂ gas [24–29]. The species found suitable for catalyzing transfer hydrogenation [30–51] in last one decade include halfsandwich species [(η^6 -arene)Ru(bipy)(OH₂)]²⁺, [(η^6 -arene)Ru(N,N) CI]⁺ and [RuCl(η^6 -benzene/*p*-cymene)(N,N)][BPh₄] ((N,N) = 2hydroxyphenyl bis(pyrazol-1-yl)methane or 2-hydroxyphenyl bis(3,5-dimethylpyrazol-1-yl)methane). Transfer hydrogenation of ketones with 2-propanol catalyzed by ruthenium(III) species has also been reported [52–57].

The first monomeric $17e^{-}$ species having half-sandwich unit (η^{6} -arene)Ru(III), [(η^{6} -*p*-cymene)RuCl2(L)][PF6] (1) is **formed unexpectedly** by reaction of [{(η^{6} -*p*-cymene)RuCl(μ -Cl)}₂] with *N*-{2-(phenylthio)ethyl}morpholine (L) and NH₄PF₆ (excess) in methanol at room temperature for 24 h (Scheme 1). In an attempt to catalyze hydrogenation of ketones with 2-propanol with 1 spherical and block shaped Ru–RuS₂ (70:30 w/w%) nano-particles of average size 5–8 nm were formed. In this paper these results are reported.





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Scheme 1. Synthesis of L and complexes 1-2.

2. Experimental

2.1. Physical measurement

Perkin-Elmer 2400 Series II C, H, N analyzer was used for elemental analysis. The ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13 and 75.47 MHz respectively. IR spectra in the range 4000-400 cm⁻¹ were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. The UV-visible spectra were recorded on Shimadzu UV-vis-NIR-1601 spectrometer. The EPR spectrum was recorded on JEOL JES-FE3XG operated at 1 mV and 9.43 GHz (University of Delhi, New Delhi, India). The conductivity measurements were carried out in CH₃CN (concentration ca. 1 mM) using ORION conductivity meter model 162. The cyclic voltammetric studies were performed on BAS CV 50 W instrument at the University of Delhi (Department of Chemistry). A three-electrode configuration composed of a Pt disk working electrode (3.1 mm² area), a Pt wire counter electrode, and an Ag/AgCl reference electrode was used for the measurements. Ferrocene was used as an internal standard $(E_{1/2} = 0.500 \text{ V versus Ag/AgCl})$ and all the potentials are expressed with reference to Ag/AgCl.

TEM studies were carried out with a JEOL-2100F electron microscope operated at 200 kV (Advanced Instrumentation Research Facility at Jawaharlal Nehru University Delhi, India). The specimens for TEM were prepared by dispersing the powder in chloroform by ultrasonic treatment, dropping onto a porous carbon film supported on a copper grid, and then drying in air. The nano-structural phase morphology was observed by using a Carl Zeiss EVO50 Scanning Electron Microscope (SEM). Nanostructures observed by SEM were analyzed for their elemental composition by

EDX system model QuanTax 200 which is based on the SDD technology and provides an energy resolution of 127 eV at Mn K α . The samples were scanned in different regions in order to minimize the error in the analysis for evaluating the morphological parameters. Samples were mounted on a circular metallic sample holder with a sticky carbon tape.

Single crystal diffraction studies were carried out with a Bruker AXS SMART Apex CCD diffractometer using Mo $K\alpha$ (0.71073 Å) radiation at 100(2) (for **1**)/298(2) (for **2**) K. The software SADABS was used for absorption correction (if needed) and SHELXTL for space group, structure determination, and refinements [58,59]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they are attached. The least-squares refinement cycles on F^2 were performed until converged. The figures of molecular structures of **1**, **2** and secondary interactions were drown using Diamond programme [60]. Powder X-ray diffraction studies were carried out on a Bruker D8 Advance Diffractometer with Ni-filtered Cu $K\alpha$ X-rays of wavelength (λ) = 1.54065 Å. The data were recorded in a 2θ range of 10–70° with the step size of 0.05° and step time of 1 s.

All DFT calculations were carried out at Supercomputing Facility for Bioinformatics and Computational Biology of the department with the GAUSSIAN-03 [61] program with an objective of calculating the partial charges present on various atoms in **1** and **2**. The geometry of all the compounds was optimized at the B3LYP [62] level using an SDD basis set for metal atom, and 6–31G* basis sets for C, N, H, S, O and Cl. Geometry optimizations were carried out without any symmetry restriction. Harmonic force constants were computed at the optimized geometries to characterize the minima. The molecular orbital plots were made using the Chemcraft program package.

2.2. Chemicals and reagents

Thiophenol, (2-chloroethyl)morpholine hydrochloride, NH_4PF_6 , KOH and all other chemicals procured from Sigma–Aldrich (USA) were used as received. The solvents were dried and distilled before use by standard procedures [63]. The $[(\eta^6-p\text{-}cymene)RuCl(\mu\text{-}Cl)]_2$ was prepared by procedure reported in literature [64]. The ligand **L** was synthesized by an earlier reported procedure [8].

2.3. Synthesis of half-sandwich complexes 1 and 2

The solid $[\{(\eta^6-p-cymene)RuCl(\mu-Cl)\}_2]$ (0.12 g, 0.2 mmol) was added to the solution of **L** (0.045 g, 0.2 mmol) made in CH₃OH (15 cm³). The mixture was stirred for 24 h at room temperature. The solid NH₄PF₆ (0.16 g, 10 mmol) was added to the above mixture which was further stirred at room temperature for 2 h. The precipitate formed was filtered, washed with cold methanol (10 cm³) and dried in *vacuo*. This resulted in **1** as a red microcrystalline solid. In the filtrate kept aside for slow evaporation orange crystals of **2** appeared which were separated out and found suitable for X-ray diffraction. The single crystals of **1** suitable for X-ray diffraction were obtained by diffusion of diethyl ether into its solution (1 cm³) made in a mixture of CH₃OH and CH₃CN (1:4, v/v).

1 Yield: 0.095 g, 70%. m.p. 178 °C. $\Lambda_{\rm M}$ = 144.8 S cm² mol⁻¹. Anal. Calc. for C₂₂H₃₁Cl₂NORuS·PF₆: C, 39.18; H, 4.63; N, 2.08%. Found: C, 39.10; H, 4.60; N, 2.15%. IR (KBr, $\nu_{\rm max}/{\rm cm}^1$): 3034 (m; $\nu_{\rm C-H(aromatic)}$), 2970, 2860 (s; $\nu_{\rm C-H(aliphatic)}$), 1630 (m; $\nu_{\rm C-C(aromatic)}$), 1203, 1115 (w; $\nu_{\rm C-N}$), 845 (s; $\nu_{\rm P-F}$), 748 (m; $\nu_{\rm C-H(aromatic)}$). UV–vis. in CH₃CN, $\lambda_{\rm max}/{\rm nm}$ ($\epsilon/{\rm M}^{-1}$ cm⁻¹): 250 (6209), 325 (849), 409 (538).

2 Yield: 0.014 g, 15%. m.p. 155 °C. $\Lambda_{\rm M} = 155.5$ S cm² mol⁻¹. Anal. Calc. for C₁₀H₂₀ClN₂Ru·PF₆: C, 26.71; H, 4.48; N, 6.23%. Found: C, 26.70; H, 4.40; N, 6.29%. ¹H NMR (CD₃CN, 25 °C, vs Me₄Si): δ (ppm):

 $\begin{array}{l} 1.18-1.20 \ (d,\,^{3}J_{HH}=6.6 \ Hz,\, 3H,\, CH_{3} \ of \ i-Pr),\, 1.89 \ (s,\, 6H,\, NH_{3}),\, 2.00 \ (s,\\ 3H,\, CH_{3} \ p \ to \ i-Pr),\, 2.74 \ (sp,\, 1H,\, CH \ of \ i-Pr),\, 5.33-5.72 \ (m,\, 4H,\, Ar-H \\ of \ p-cymene). \, ^{13}C\{^{1}H\} \ NMR \ (CD_{3}CN,\, 25 \ ^{\circ}C,\, vs \ Me_{4}Si): \ \delta \ (ppm): \, 18.4 \\ (CH_{3}, \ p \ to \ i-Pr),\, 22.4 \ (CH_{3} \ of \ i-Pr),\, 31.5 \ (CH \ of \ i-Pr),\, 81.3-104.2 \ (Ar-C \\ of \ p-cymene). \ IR \ (KBr, \ \nu_{max}/cm^{1}): \ 3288 \ (m; \ \nu_{N-H}),\, 3018 \ (s; \\ \nu_{C-H(aromatic)}),\, 1596 \ (m; \ \nu_{C-C(aromatic)}),\, 1441 \ (w; \ \nu_{N-H}) \ 848(s; \ \nu_{P-F}), \\ 744 \ (m; \ \nu_{C-H(aromatic)}). \end{array}$

2.4. Isolation of Ru–RuS₂ nano-particles

A solution of the ketone (acetophenone, 4-chloro/bromoacetophenone or benzophenone) (1 mmol), KOH (0.2 cm³ of a 0.2 M solution in 2-propanol) and the complex **1** (1 mmol) were heated under reflux (80 °C) in 10 cm³ of 2-propanol for 1 h and thereafter cooled to room temperature. The solvent was decanted and black residue of Ru–RuS₂ nano-particles was washed with 4 cm³ of acetone and 1 cm³ of water.

3. Results and discussion

The syntheses of **L**, **1** and **2** are shown in Scheme 1. When amount of NH₄PF₆ used was not in excess (i.e. upto equimolar amount only) Ru(II) complex, $[(\eta^6-p-cymene)RuCl_2(L)]$ was major product (small amount of $[(\eta^6-p-cymene)RuCl(L)][PF_6]$ was also formed) rather than **1** and largely NH₄PF₆ remained unconsumed. The yield of **2** was not complementary to that of **1** as side reaction and escape of NH₃ was unavoidable. The **L** in the monochloro complex behaves as (S, N) donor rather than a monodentate ligand (as in **1**). Probably following set of reactions feasible under ambient conditions and in the presence of excess of NH₄PF₆ result in Ru(III) species.

 $\begin{array}{l} \mathsf{NH}_4\mathsf{PF}_6 \rightleftharpoons \mathsf{NH}_3 + \mathsf{HPF}_6 \\ \mathsf{HPF}_6 \rightleftharpoons \mathsf{PF}_6^- + \mathsf{H}^+ \\ \mathsf{4Ru}(\mathsf{II}) + \mathsf{4H}^+ + \mathsf{O}_2 \!\rightarrow\! \mathsf{4Ru}(\mathsf{III}) + \mathsf{2H}_2\mathsf{O} \end{array}$

The solubility of L, 1 and 2 in common organic solvent was found to be good but in hexane, diethyl ether and petroleum ether both complexes could not be dissolved significantly. The solution of **1** in DMSO showed the sign of decomposition after 24 h. The L was authenticated with ¹H and ¹³C{¹H} NMR and IR spectra. The EPR spectrum (Figure S4 in Supplementary Information) of 1 (paramagnetic complex) in solid state was recorded at room temperature and X-band frequencies. The spectrum is very broad and unsymmetrical and therefore it can not be converted to very accurate parameters. However there are two maxima and approximate 'g' values calculated using magnetic field 'H' at these two maxima are \sim 2.07 and \sim 2.73. Further position of EPR signal of **1** appears to be consistent with its low spin octahedral geometry [57.65.66]. The molar conductance value of 1 (144.8 S cm² mol⁻¹) was found consistent with its 1:1 electrolytic nature. UV-visible spectrum of 1 recorded in CH₃CN (conc. 1–2 mmol) shows bands at 250, 325 and 409 nm. Their corresponding extinction coefficients $(\varepsilon/L \text{ M}^{-1} \text{ cm}^{-1})$ are ~6209, ~849 and ~538 respectively (Figures S6.1–S6.2 in Supplementary Information), characteristic of Ru(III) species [65]. The presence of L and p-cymene in 1 is supported by its IR spectrum. The formation of **2** suggests that NH₄PF₆ has a role in the oxidation of Ru(II) to Ru(III) and is also a source of NH₃ for it. IR and NMR spectra of 2 were found characteristic. The molecular structures of 1 and 2 based on single crystal diffraction studies made on them are shown in Figs. 1 and 2 along with important bond lengths and angles. For details of crystal data and refinement parameters of 1 and 2 see Tables S1 and S2 in Supplementary Information. In cations of 1 and 2, there is a pseudooctahedral "Piano-Stool" disposition of donor atoms around



Fig. 1. ORTEP diagram of cation of **1** with 50% probability ellipsoids; H-atoms and PF_{6}^{-} are omitted for clarity. Bond length (Å): Ru(1)-S(1) 2.413(3), Ru(1)-Cl(1) 2.400(3), Ru(1)-Cl(2) 2.419(3), Ru(1)-C 2.175(13)-2.226(13); bond angle (°): Cl(1)-Ru(1)-S(1) 85.05(12), Cl(2)-Ru(1)-S(1) 88.15(11), Cl(1)-Ru(1)-Cl(2) 88.50(11).

ruthenium. The *p*-cymene ring occupies one face of octahedron and co-ligands the other one. In case of **1**, co-ligands are **L** (bonded through S alone) and two Cl atoms. The data for Ru(III)–S bond distances in molecular species are not easily available therefore comparisons are made with Ru(II)–S bond lengths. The Ru–S bond length of cation of **1** is 2.413(3) Å, which is longer than the value 2.3815(12) Å reported for Ru(II) species, $[(\eta^6-benzene)RuCl(L)][PF_6]$ [8] (L = N-{2-(phenylthio)ethyl}morpholine). This is not surprising as sulfur ligand in **1** is monodentate whereas it is bidentate in the later complex. Unexpectedly Ru–S bond distance of cation of **1** is also longer than the reported values 2.3978(7) Å for $[(\eta^6-p-cymene) RuCl_2(MeSC_3H_5)]$ [5] and 2.3881–2.3833(7) Å for $[(\eta^6-p-cymene) RuCl(SMe_2)_2]$ [SbF₆] [5]. The steric factor of **L** may be responsible for



Fig. 2. ORTEP diagram of **2** with 30% probability ellipsoids; H-atoms are omitted for clarity. Bond length (Å): Ru(1)–N(1) 2.149(3), Ru(1)–N(2) 2.141(3), Ru(1)–Cl(1) 2.4137(9), Ru(1)–C 2.156(3)–2.206(3); bond angle (°): N(1)–Ru(1)–N(2) 82.83(12), Cl(1)–Ru(1)–N(1) 84.53(9), Cl(1)–Ru(1)–N(2) 84.26(9).

it. The Ru—S bond distance, 2.3409(12) Å for $[\eta^5$ -Cp*Ru(III)(tpdt)] [14] (tpdt = 3-thiapentane-1,5-dithiolate) is significantly shorter than that of **1** as tpdt is behaving as a chelating ligand. Two Ru—N bond lengths of cation of **2** are 2.149(3) and 2.141(3) Å, are shorter than the values reported for Ru(II) species, 2.192(4) Å for $[(\eta^6-p$ cymene)RuCl(L)][PF₆] [6] (L = N-{2-(phenylthio)ethyl}pyrrolidine) and 2.208(3) Å for $[(\eta^6-\text{benzene})\text{RuCl}(\mathbf{L})][\text{PF}_6]$ [8] ($\mathbf{L} = N-\{2-(\text{phe}-\text{phe})\}$ nvlthio)ethyl}morpholine). The reason for these shorter bond lengths in 2 may be due to the strong coordination behavior of NH₃ (less sterically demanding) than the N of pyrrolidine and morpholine rings. The two Ru—Cl bond lengths of cation of 1 (2.400(3) and 2.419(3) Å) are longer than the sum of covalent radii of Ru(III) and Cl (2.20 Å) and the values 2.321(1)-2.351(1) reported for trans-[Ru(DMSO)₃Cl₃] [67]. These present values are also consistent with the reduction of the covalent radius (0.04 Å) when Ru(II) changes to Ru(III) [68]. The Ru—Cl(terminal) bond distances, 2.3851(8) Å for $[(\eta^5-Cp)Ru(III)Cl_2]_2$ [29] and 2.418(2) Å for $[\eta^5-Cp^*Ru(III)Cl_2]_2$ [69,70], are consistent with the bond length of **1**. The Ru—Cl bond length of cation of 2, 2.4137(9) Å is also consistent with earlier reports on Ru(II)—Cl bond distances [6–8], for example 2.4108(8) Å for [(η⁶-*p*-cymene)RuCl₂(MeSC₂H₄Ph)] [5], 2.4104(7) Å for [(η⁶-*p*cymene)RuCl₂(MeSC₃H₅)] [5] and 2.3944(7) Å for $[(\eta^6-p-cymene)]$ RuCl(SMe₂)₂][SbF₆] [5]. The Ru—C bond lengths of cations of **1–2** (2.156(3)-2.226(13) Å) are consistent with earlier reports [4,6-9,12,14,18,69-71]. The C-Ru-C bond angles for 1 and 2 are also normal.

There are interesting secondary interactions in the crystal of **1**. The C—H···· π interaction results in chain formation (Figures S1 and S2 in Supplementary Information) and each PF₆ is involved with in secondary interaction with six cations as shown in Fig. 3 (Figures S3.1 and S3.2 in Supplementary Information). The cyclic voltammetric curve of complex **1** (Figures S5.1 and S5.2 in Supplementary Information) is not of high quality but appears to be of Ru(II)/Ru(III) couple, as Ru(III) on applying the potential to begin experiment may not survive and most likely reduced to Ru(II). The $E_{1/2}$ value 0.650 V (vs. Ag/AgCl) (Table S4) implies that both species, Ru(II) and Ru(III), are equally stabilized by the same set of ligands. The short lived reduced state of the metal ion is probably responsible for the nature of CV curve [72], which shows some signs of reversibility of Ru(II)/Ru(III) process.

The DFT studies reveal that partial atomic charge for **1** and **2** are -0.240 e and -0.045 e respectively (Figures S7 and S8 in Supplementary Information). This supports the easy conversion of Ru(III) to Ru(II) in CV experiment. The sulphur is softer donor than nitrogen and its presence in **1** appears to result in the present variation of atomic charges.

3.1. Formation of nanosized Ru-RuS₂

The attempt was made to catalyze with complex **1** transfer hydrogenation of ketones (acetophenone, 4-chloro or bromoacetophenone and benzophenone) with 2-propanol in the presence of KOH at 80 °C. The products of transfer hydrogenation reaction could not be unequivocally detected. The complex decomposes (almost completely in 1 h) in the course of such an attempt. The resulting black residue was found amorphous in nature by powder X-ray diffraction studies. The amorphous powder was annealed in argon atmosphere at 800 °C for 6 h which led to the formation of crystalline Ru–RuS₂ nano-particles. The powder X-ray diffraction pattern of these nano-particles (Table S5 and Figure S9 in Supplementary Information) was indexed on the basis of primitive hexagonal unit cell [73] (JCPDS # 06-0663) with the refined lattice



Fig. 3. Secondary interactions of PF_6^- anion.



Fig. 4. HR-TEM image of Ru-RuS₂ nano-particles obtained from 1; showing the average size to be 5-8 nm and the fringe width 0.164 nm.

parameter; a = 2.705, c = 4.281 Å (for Ru phase) and primitive cubic unit cell [74] (JCPDS # 73-1677) with the refined lattice parameter; a = 5.609 Å (for RuS₂ phase). The *d* values (Å) (*hkl*)/2 θ (°) are: 3.2385 (111)/27.52, 2.8046 (200)/31.88, 2.5088 (210)/35.76, 2.3435 (100)/38.38, 2.2900 (211)/39.31, 2.1420 (002)/42.15, 2.0551 (101)/ 44.03, 1.9835 (220)/45.70, 1.8699 (221)/48.66, 1.6919 (311)/54.17, 1.6196 (222)/56.80, 1.5808 (102)/58.33, 1.5555 (023)/59.37, 1.4992 (321)/61.83, 1.4023 (400)/66.64, 1.3606 (410)/68.96, 1.3530 (110)/ 69.41. SEM and SEM-EDX (Figures S10.1–S10.3 in Supplementary Information) and HR-TEM (Fig. 4 and Figure S11) and TEM-EDX (Figure S12 in Supplementary Information) have been used to characterize these nano-particles. These studies have revealed that they are spherical and block shaped Ru-RuS₂ nano-particles of average size 5-8 nm. TEM-EDX (Figure S12 in Supplementary Information) analyses further indicate composition of Ru-RuS₂ nano-particles as: Ru nano-particles = 70 (wt.%) and RuS₂ nanoparticles = (30 wt.%). The SEM-EDX studies (Figure S10 in Supplementary Information) also reveal very similar composition of these Ru-RuS₂ nano-particles.

4. Conclusion

Half-sandwich $17e^-$ Ru(III) complex having η^6 -p-cymene has been unexpectedly formed when NH₄PF₆ is used in excess. The Ru(III) species has been authenticated by EPR and DFT calculations. The attempt to use it as a transfer hydrogenation catalyst resulted in Ru-RuS₂ (70:30 wt.%) nano-particles of size 5-8 nm. The formation of such nano-particles is observed for the first time.

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Appendix A. Supplementary material

CCDC reference numbers 806931 (1) and 831534 (2) contain 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.

Appendix B. Supplementary information

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2012.05.022.

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