

Note

Ruthenium cationic species for transfer hydrogenation
of aldehydes: Synthesis and catalytic properties
of $[(PPh_3)_2Ru(CH_3CN)_3Cl]^+[A]^-$ {A = BPh₄ or ClO₄} and structure
of $[(PPh_3)_2Ru(CH_3CN)_3Cl]^+[BPh_4]^-$

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Abstract

The compounds, $[(PPh_3)_2Ru(CH_3CN)_3Cl][BPh_4]$ (**1**) and $[(PPh_3)_2Ru(CH_3CN)_3Cl][ClO_4]$ (**2**) have been synthesized from reactions of $[Ru(PPh_3)_3Cl_2]$ with $Na[BPh_4]$ and $NaClO_4 \cdot H_2O$, respectively, in acetonitrile. The compound **1** has been structurally characterized. The geometry of this complex is that of a distorted octahedral, with cationic Ru(II) center bonded two triphenylphosphine ligands in the axial position and three acetonitrile and one chloride ligands present in the basal positions. The ruthenium compounds are catalytically active for the conversion of aldehydes and ketones to alcohols at 90 °C using 2-propanol as the source of hydrogen in the presence of K_2CO_3 . © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

The structural and reactivity studies of coordinatively unsaturated complexes have received much attention due to their involvement as intermediates in transition metal catalyzed organic transformation. The ability of ruthenium to exist in variety of oxidation states as well as to assume wide range of coordination geometry are the main reasons behind ruthenium compounds being effective catalysts for variety of organic reactions including ring closing metathesis [1], C–H activation [2–4], activation of carbon–carbon multiple bonds [2], C–C bond formation [2] and Oppenauer oxidation [5], and transfer hydrogenation [6]. In most of the cases, 16 electron cationic species are predicted to be the active catalyst. Thus, in recent years, some 16 electron cationic stable species have been isolated and characterized structurally [7–9]. Transition metal catalyzed transfer hydrogenation

of ketones and aldehydes have attracted attention for the relatively benign nature of the reagents and mild reaction conditions employed [6,10–13]. In contrast to conventional hydrogenation using dihydrogen and metal catalysts, which frequently require a high hydrogen pressure [14], the transfer hydrogenation has some unique advantages in its simplicity and avoidance of cumbersome reducing agents. However, aldehydes are difficult to reduce by transfer hydrogenation catalysts [11]. It has been shown that, ruthenium complexes containing phosphine ligands and an iridium complex *N*-heterocyclic carbene are effective catalysts for reduction of aldehydes [11,13]. Recently, Yamada and Noyori has shown that, $RuCl[(R,R)\text{-}YCH(C_6H_5)CH(C_6H_5)NH_2](\eta^6\text{-arene})$ (Y = $NSO_2C_6H_4\text{-}4\text{-}CH_3$ or O) and *t*-C₄H₉OK catalyzes the asymmetric transfer hydrogenation of various benzaldehyde-1-*d*-derivatives with 2-propanol to yield (*R*)-benzyl-1-*d* alcohols in 95–99% ee and with >99% isotopic purity. Reaction of benzaldehydes with a DCO₂D-triethylamine mixture and the *R,R* catalyst affords the *S* deuterated alcohols in 97–99% ee [15].

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Another frequently encountered problem in transfer hydrogenation is the concomitant formation of alkylated products and decarbonylation [10,11]. For example, Ru(PPh₃)₃Cl₂ catalyzed reaction between butanol and acetophenone gives 1-phenylhexan-1-ol and 1-phenylhexan-1-one, rather than the expected direct transfer hydrogenation product, 1-phenylethanol [10]. It has been observed that, when primary alcohol is used as reducing agent, usually alkylated products are obtained [16].

We were interested in synthesizing simple catalytically active ruthenium(II) cationic compound containing phosphine ligands and labile N donor ligands, which can easily afford 16 electron species in solution.

Herein we report preparation, characterization, and catalytic activity of [(PPh₃)₂Ru(CH₃CN)₃Cl]⁺[BPh₄]⁻ (**1**) and [(PPh₃)₂Ru(CH₃CN)₃Cl]⁺[ClO₄]⁻ (**2**) and structure of [(PPh₃)₂Ru(CH₃CN)₃Cl]⁺[BPh₄]⁻ (**1**).

2. Experimental

All the chemicals used were reagent grade products. [Ru(PPh₃)₃Cl₂] was synthesized by reported procedure [17]. ¹H NMR spectra were recorded on Bruker AC 200, 200 MHz NMR spectrometer in CDCl₃ solutions at room temperature. IR spectra were recorded on a Thermo Nicolet Model 870 FT IR spectrometer. The UV–Vis spectra were recorded on a Shimadzu UV 600 spectrophotometer. Cyclic voltammetry experiments were performed using a fully automated CH Instruments electrochemical analyzer (Model 620a) and a three-electrode set-up consisting of a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. All experiments were performed in dry CH₃CN containing tetra-*N*-butylammonium perchlorate (0.2 mol dm⁻³) as the background electrolyte. The magnetic measurements were done using Gouy method. The C, H, and N were estimated using microanalyses on a Perkin–Elmer microanalyser, 2400.

2.1. Synthesis of [(PPh₃)₂Ru(CH₃CN)₃Cl][BPh₄] (**1**) and [(PPh₃)₂Ru(CH₃CN)₃Cl][ClO₄] (**2**)

RuCl₂(PPh₃)₃ (0.5 g; 0.520 mmol) and NaBPh₄ or NaClO₄·H₂O (0.520 mmol) were dissolved in acetonitrile (25 ml) and the reaction solution was refluxed for about 6 h. The color of the reaction solution turned to light yellow. The reaction solution was then filtered and concentrated where upon a yellow crystalline solid separated out. The separated solid was filtered and washed with hexane (3–4 times) and dried in vacuo. The compound was finally recrystallized from acetonitrile. Yield: 75%. Anal. Calcd. for C₆₆H₅₉B₁Cl₁N₃P₂Ru₁ (M_w = 1103.43): C, 71.78; H, 5.39; N, 3.81. Anal. Found: C, 71.11; H, 5.37; N, 4.05. ¹H NMR: 2.0 ppm(s); 7.27–7.79 ppm(m). IR (cm⁻¹): 3050, 2270, 1670, 1479, 1434, 696, 511. UV–Vis (nm): 330 (ε = 1270), 260 (ε = 3861). Yield: 75%. Anal. Calcd. for C₄₂H₃₉Cl₂N₃O₄P₂Ru₁ (M_w = 883.24): C, 57.06; H, 4.45; N, 4.76. Anal. Found: C, 56.78; H, 4.10;

N, 4.25. ¹H NMR: 2.1 ppm(s); 7.27–7.79 ppm(m). IR (cm⁻¹): 3055, 2265, 1675, 1485, 1440, 700, 510. UV–Vis (nm): 332 (ε = 1275), 265 (ε = 3865). Yield: 72%.

3. Hydrogenation of carbonyl compounds by 2-propanol catalyzed by **1** and **2**

The carbonyl compound (10 mmol), 2-propanol (10 cm³), solid K₂CO₃ (10 mmol), and **1** or **2** (0.05 mmol) was taken in a 25 ml schlenk flask. The reaction mixture was flushed with argon and was stirred for desired time at 90 °C. The reactions were monitored by TLC. After the completion of the reaction, the reaction mixture was added to water (50 cm³) and the organic product was extracted (4–5 times) by diethyl ether. The combined ether layer was washed with water (2/3 times), dried (Na₂SO₄) and finally the solvent was removed under vacuum to isolate the product. The products were purified by column chromatography.

4. X-ray crystallographic study

Suitable crystals of [(PPh₃)₂Ru(CH₃CN)₃Cl][BPh₄] were grown from dilute acetonitrile solution at room temperature over a period of 5–6 days. The single crystal data was collected on Bruker-Nonius Mach3 CAD4 X-ray diffractometer that uses graphite monochromated Mo Kα radiation (λ = 0.71073 Å) by ω-scan method. No absorption correction was used. The structure was solved by direct methods and refined by least square methods on F² employing WINGX [18] package and the relevant programs (SHELX-97 [19] and ORTEP-3 [20]) implemented therein. Non-hydrogen atoms were refined anisotropically and hydrogen atoms on C-atoms were fixed at calculated positions and refined using a riding model. Crystal data: Empirical formula: C₆₆H₅₉B₁Cl₁N₃P₂Ru₁, M_w = 1103.43, monoclinic, space group P2₁/c, a = 15.063(5) Å, b = 19.581(5) Å, c = 19.529(5) Å, α = 90.000°, β = 95.062(5)°, γ = 90.000°, V = 5738.4(3) Å³, Z = 4, d (calcd.) = 1.277 Mg/m³, F(000) = 2288, T = 293 K, μ = 0.418 mm⁻¹, crystal size = 0.4 × 0.4 × 0.2 mm³, data collection range 1.36 ≤ θ ≤ 25.00, 0 ≤ h ≤ 17, 0 ≤ k ≤ 23, -23 ≤ l ≤ 23, R₁ = 0.0355, wR₂ (all data) = 0.0923.

5. Results and discussion

The title compounds **1** and **2** have been prepared from a reaction of NaBPh₄ and NaClO₄·H₂O (0.520 mmol), respectively, with [(PPh₃)₃RuCl₂] (0.5 g; 0.520 mmol) in refluxing acetonitrile in high yield (ca. 75%). It was shown a few years back that, reactions of Ru₂Cl(O₂CR)₄ or Ru₂-Cl(O₂CR)₄ with PPh₃ in acetonitrile afford compounds of the type [RuCl(MeCN)₃(PPh₃)₂][Ru₂Cl₂(O₂CR)₄] or [RuCl(MeCN)₃(PPh₃)₂][Ru₂Cl₂(O₂CR)₄], two of which were structurally characterized [21]. It may be mentioned that, the yields of [RuCl(MeCN)₃(PPh₃)₂][Ru₂Cl₂(O₂CR)₄] were very poor, typically in the range of 7–10%. The highest

yield was obtained in the case of $[\text{RuCl}(\text{MeCN})_3(\text{PPh}_3)_2]_2$ - $[\text{Ru}_2\text{Cl}_2(\text{O}_2\text{CMe})_4]$ which was only 37% [21]. Fogg and James have reported the preparation of $[(\text{PPh}_3)_2\text{Ru}(\text{CH}_3\text{CN})_3\text{Cl}]^+[\text{PF}_6]^-$ from a reaction of $[(\text{PPh}_3)_3\text{RuCl}_2]$ with NH_4PF_6 in acetonitrile in 72% yield. However, this was neither characterized structurally, nor was its reactivity explored [22].

The compounds **1** and **2** have been characterized by elemental analyses, IR, UV–Vis, and ^1H NMR spectral studies, and also by electrochemical and magnetic measurements. The elemental analyses agree well with the formulations of the compounds. Cyclic voltammetry of **1** and **2** showed that the metal center undergoes a reversible ($\Delta E_p = \text{ca. } 40 \text{ mV}$), one-electron oxidation process with a half-wave potential ($E_{1/2}$) of 1.40 and 1.35 V, respectively, versus Ag/AgCl . Along with the reversible peak, the compound **1** shows an irreversible oxidative peak at 1.06 V. This is due to oxidation of BPh_4^- anion, as confirmed by cyclic voltammetry of NaBPh_4 in acetonitrile, which also shows an irreversible peak at similar position. The ^1H NMR spectra of the compounds show a singlet at δ ca. 2.0 ppm due to the $-\text{CH}_3$ protons of the bonded acetonitrile and a multiplet in the region δ ca. 7.27–7.79 ppm due to aromatic protons. The UV–Vis spectra show two bands at ca. 330 ($\epsilon = 1270$), ca. 260 ($\epsilon = 3861$). The compounds are diamagnetic in character, as expected, and clearly show the presence of ruthenium(II).

The single crystal X-ray study of **1** clearly establishes the formulation of the compound. The structure of the compound is shown in Fig. 1.

The cationic complex has a ruthenium(II) center bonded to three acetonitrile and a chloride in the equatorial plane and two triphenyl phosphines occupy the axial position in a *trans* fashion as shown earlier. The BPh_4^- anion is found outside the coordination sphere and does not show any bonding interaction with ruthenium(II) center. The ruthenium(II) center is found to be in a distorted octahedral environment. All the three Ru–N distances are not found to be equal, one of the Ru–N distance is comparatively

larger (Ru1–N1 distance = 2.034(2) Å, Ru1–N2 distance = 2.021(2) Å, and Ru1–N3 distance = 2.014(2) Å) then the other two. Similarly, $\angle\text{Ru1–N1–C1}$ and $\angle\text{Ru1–N3–C5}$ angles deviate considerably from linearity ($\angle\text{Ru1–N1–C1}$ angle = 168.6 (2)° and $\angle\text{Ru1–N3–C5}$ angle = 174.8), whereas, $\angle\text{Ru1–N2–C3}$ angle is somewhat linear ($\angle\text{Ru1–N2–C3} = 178.8(3)^\circ$). Thus, two of the three coordinated acetonitrile ligands are coordinated to ruthenium center in a highly distorted manner. Both the Ru–P distances are almost equal (Ru1–P1 distance = 2.4076(9) Å and Ru1–P2 distance = 2.4145(9) Å). The $\angle\text{N3–Ru1–N2}$ and $\angle\text{N2–Ru1–N1}$ angles are less than 90° (88.30(9)° and 87.91(9)°, respectively). Similarly, the P1–Ru1–P2 angle is found to be 177.78 (2)°. The geometry and bond lengths and bond distances are similar to those reported for $[\text{RuCl}(\text{MeCN})_3(\text{PPh}_3)_2][\text{Ru}_2\text{Cl}_2(\text{O}_2\text{CR})_4]$ [21].

Transfer hydrogenation of carbonyl compounds using 2-propanol as reducing agent as well as solvent has attracted a lot of attention over last few years due to the comparatively benign nature of the reagents [23–28]. A number of transition metal catalysts have been used for this transformation. The main focus has been on ruthenium(II) complexes [23–29]. However, in most of the cases, the reactions are effective only in the cases of ketones. Very recently, an iridium complex containing *N*-heterocyclic carbene ligand has been found to be effective in the reduction of aldehydes [11]. Encouraged by these reports, we wanted to explore the efficacy of the newly synthesized compound.

Accordingly, hydrogenation of various types of aldehydes and ketones was carried out in 2-propanol using 0.5 mol% of the newly synthesized compound, $[(\text{PPh}_3)_2\text{Ru}(\text{CH}_3\text{CN})_3\text{Cl}][\text{BPh}_4]$, (**1**) in the presence of K_2CO_3 . The products were isolated in medium to high yield and characterized by ^1H NMR spectra (Table 1). ^1H NMR spectra of the crude products showed the signals for the alcohols and the starting carbonyl compounds only. We could not observe formation of any decarbonylation or condensation product. This is also apparent from the observed values of percentage yield and conversion (Table 1).

The catalytic activity of the compound **2** has also been explored and compared with that of **1**. The results are given in Table 2. The catalytic activity of **2** is similar to that of **1** (Table 2).

Backvall and coworkers [27] have reported that, monohydrido species, $[\text{RuHCl}(\text{PPh}_3)_3]$, generated from the reaction of isopropanol and $[\text{RuCl}_2(\text{PPh}_3)_3]$, is completely inactive in the reduction of acetone to isopropanol. However, Cadierno et al. [26] have recently isolated *cis,cis*- $[\text{RuHCl}(\text{CN}-2,6\text{-C}_6\text{H}_3\text{Me}_2)_2(\text{dppf})]$ and *cis,cis,cis*- $[\text{RuH}_2(\text{CN}-2,6\text{-C}_6\text{H}_3\text{Me}_2)_2(\text{dppf})]$ [dppf = 1,1'-Bis(diphenylphosphino)ferrocene] and found that, both the monohydrido and dihydridoruthenium compounds are active in the reduction of acetophenone by isopropanol, however, the dihydrido species was found to be more active. Recently, it has been reported that, cationic complexes of the type $[\text{CpRu}(\text{P–N})(\text{CH}_3\text{CN})]^+$, where (P–N) is bidentate aminophosphine ligands, are excellent pre-catalysts for transfer hydrogenation for ketones and

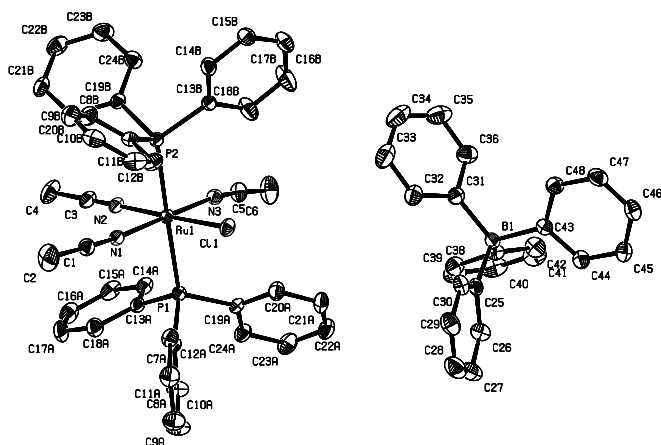


Fig. 1. ORTEP drawing of $[(\text{PPh}_3)_2\text{Ru}(\text{CH}_3\text{CN})_3\text{Cl}][\text{BPh}_4]$. The H-atoms were not shown for the sake of clarity.

Table 1

Transfer hydrogenation of carbonyl compounds catalyzed by **1** using 2-propanol and $K_2CO_3^a$

Entry	Substrates (10 mmol)	Product	Yield (%) ^b	Conversion	Turnover number ^c
1	Benzaldehyde	Benzyl alcohol	75	77	154
2	4-Methoxy-benzaldehyde	4-Methoxy-benzyl alcohol	71	73	146
3	2-Chloro-benzaldehyde	2-Chloro-benzyl alcohol	79	79	158
4	4-Chloro-benzaldehyde	4-Chloro-benzyl alcohol	80	81	162
5	4-Nitro-benzaldehyde	4-Nitro-benzyl alcohol	60	60	120
6	Acetophenone	1-Phenylethanol	68	70	140
7	Benzophenone	Diphenylmethanol	65	65	130
8	Cyclohexanone	Cyclohexanol	60	60	120

^a Reaction time = 4 h. Reaction temperature = 90 °C. Catalyst used = 0.05 mol.^b Isolated yield.^c Mol of product/mol of catalyst used.

Table 2

Comparison of transfer hydrogenation of aldehydes catalyzed by **1** and **2** using 2-propanol and $K_2CO_3^a$

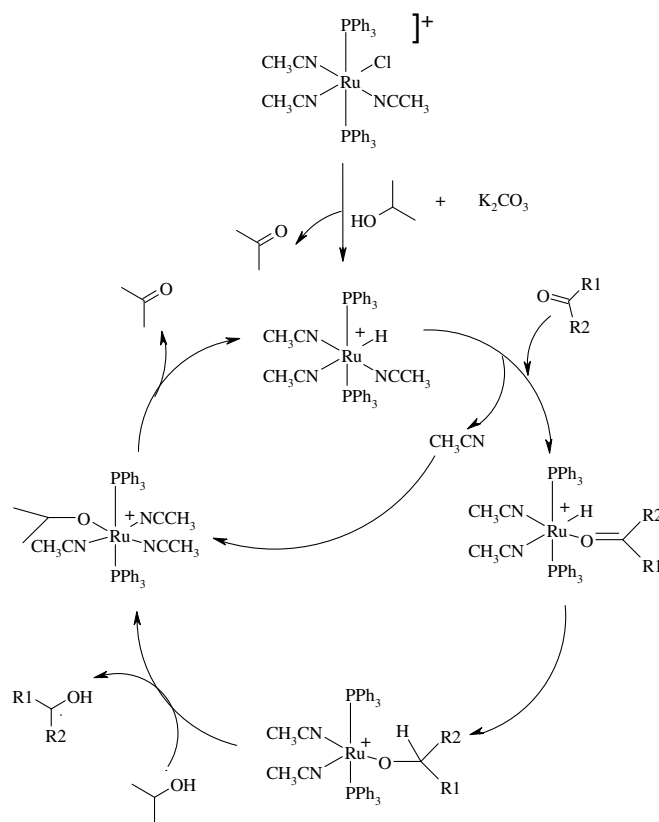
Entry	Substrates (10 mmol)	Catalyst (0.05 mmol)	Yield (%) ^b	Conversion	Turnover number ^c
1	Benzaldehyde	2	73	75	150
		1	75	77	154
2	4-Chloro-benzaldehyde	2	70	72	144
		1	80	81	162
3	4-Nitro-benzaldehyde	2	62	63	126
		1	60	60	120

^a Reaction time = 4 h. Reaction temperature = 90 °C.^b Isolated yield.^c Mol of product/mol of catalyst used.

a monohydrido Ru(II) intermediate has been proposed as the active species [30]. Similarly, the mono hydride complex, $[RuH(O_2CH)\{PPh_2(C_6H_4SO_3Na)\}_3]$ was identified to be the active species in the aqueous medium reduction of aldehydes by corresponding catalyst, $[RuCl_2L_2]$, in the presence of excess of phosphine [31,32].

Our attempts to identify the reaction intermediates by NMR spectroscopy failed. However, based on the reported mechanistic works [26–32], a possible reaction pathway has been proposed in Scheme 1.

The initial step of the reaction could be replacement of chloride by alkoxide followed by β -hydride elimination to give acetone and ruthenium monohydrido complex, which may be the active species. The next step is the replacement acetonitrile ligand by the carbonyl compound followed by the insertion of the carbonyl compound to Ru–H bond. This step is followed by proton transfer to coordinated alkoxide by isopropanol with the formation of metal hydride by β -hydride elimination to produce the active species back. Since in **1** and **2** only one Cl^- is present, formation of a monohydrido species is favored as observed earlier [30,31]. Although, a monohydrido species has been proposed as the intermediate, a dihydrido species as an intermediate cannot be ruled out completely. Also, it may be noted that, albeit monohydrido intermediate has been completely ruled out by Backvall and coworkers by isotope labeling method, the involvement of Ru(0) species has not been proved conclusively [31].



Scheme 1.

6. Conclusion

In summary, simple cationic ruthenium compounds containing labile acetonitrile ligands have been synthesized. Due to the presence of the labile acetonitrile ligands the compounds are capable of affording electronically and coordinatively unsaturated species. The compounds are effective catalysts for hydrogenation of aldehydes and ketones in isopropanol, which acts both as solvent and as hydrogen donor in this homogeneous hydrogen transfer reaction. The solvent, isopropanol, is inexpensive, and unreactive toward most organic functional groups, and employing this method, only a catalytic amount (0.5 mol%) of the ruthenium complex is necessary and high turnover numbers as well as conversions can be achieved.

7. Supplementary material

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-266619. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44 1223 336 033; deposit@ccdc.cam.ac.uk].

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