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Arene ruthenium bis-saccharinato complexes: Synthesis, molecular structure and catalytic oxidation properties in aqueous solution

Trieu-Tien Thai, Bruno Therrien, Georg Süss-Fink*

Institut de Chimie, Université de Neuchâtel, Case postale 158, CH-2009 Neuchâtel, Switzerland

A B S T R A C T

Arene ruthenium complexes [(η^6-arene)Ru(sacc)$_2$(OH$_2$)] (arene = *para*-cymeme, benzene) containing an aqua and two saccharinato ligands have been synthesized from [(η^6-arene)RuCl$_2$]$_2$ and sodium saccharinate in a water-ethanol mixture (1:1). The aqua complex [(η^6-MeC$_6$H$_4$Pr^i)Ru(sacc)$_2$(OH$_2$)] reacts with acetonitrile to give the acetonitrile complex [(η^6-MeC$_6$H$_4$Pr^i)Ru(sacc)$_2$(NCMe)]. The corresponding benzene derivative [(η^6-C$_6$H$_6$)Ru(sacc)$_2$(NCMe)] was obtained from [(η^6-C$_6$H$_6$)RuCl$_2$]$_2$ and saccNa in an acetonitrile-methanol mixture (1:1). All new complexes show a piano-stool geometry with two monohapto nitrogen-bonded saccharinato ligands in addition to a H$_2$O or MeCN ligand. All complexes of the type [(η^6-arene)Ru(sacc)$_2$(OH$_2$)] and [(η^6-arene)Ru(sacc)$_2$(NCMe)] were found to catalyze the oxidation of secondary alcohols with *tert*-butyl hydroperoxide (Bu^{t}OOH) to give the corresponding ketones in aqueous solution.

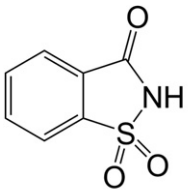
Keywords

Arene, Ruthenium, Saccharinato, Alcohol oxidation, tert-Butyl hydroperoxide, Aqueous solution

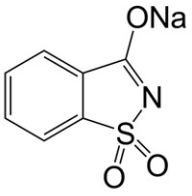
1. Introduction

In recent years, environmental concern pushed chemical industry to look for “green” solutions in production, in particular avoiding toxic organic solvents. As the most abundant liquid that occurs on Earth, water is a cheap and non-toxic solvent, so it can be used in large amounts without any associated hazard [1]. Water is not only a solvent but also plays a fundamental role in coordination chemistry. Water-soluble organometallic complexes attract continuously growing interest for applications in catalysis, because of environmentally friendly processing, simple product separation and pH dependent selectivity in aqueous media [2]. Based on an early observation by M. Baird [3], we found in the 1990s that chloride or tetrafluoroborate salts of cationic arene ruthenium complexes are well soluble in water, the arene ruthenium bond being robust towards hydrolysis [4–6], which resulted in a rapid development of arene ruthenium chemistry in aqueous solution [7]. Recently, we reported the synthesis of arene ruthenium oxinato complexes [(η^6-arene)Ru(η^2-*N,O*-L)(Cl)] and [(η^6-arene)Ru(η^2-*N,O*-L)(OH$_2$)]$^+$, which catalyze the hydrogenation of carbon dioxide in aqueous solution in presence of KOH to give the formate, with catalytic turnovers up to 400 [8].

Saccharin, discovered by Remsen and Fahlberg in 1879, is about 500 times sweeter than sugar [9]. Its water-soluble sodium salt therefore is widely used as artificial sweetener for diabetics as well as an additive in dietetic products. Recently, it has also been used for ionic liquids [10]. The saccharinate anion has been shown to coordinate to Cr, Zn, V, Pb, Hg, Mn, Co, and the complexes [M(sacc)$_2$(OH$_2$)$_4$] (M = Cr, Zn) [11]; [V(sacc)$_2$(OH$_2$)$_4$] · 2H$_2$O, [V(sacc)$_2$(py)$_4$] · 2 py (py = pyridine) [12]; [Pb(sacc)$_2$] · H$_2$O [13]; [HgCl(py)(sacc)]$_2$ [14]; [Mn(phen)$_2$(sacc)(OH$_2$)](sacc), [Co(bipy)2-(sacc)(OH$_2$)](sacc) (phen = phenanthroline, bipy = bipyridine) [15]; [Zn(sacc)$_2$(im)$_2$], [Zn(sacc)$_2$(bzim)$_2$]$_2$ · EtOH · H$_2$O (im = imidazole, bzim = benzimidazole) [16] have been reported.



saccharin
(saccH)



sodium saccharinate
(saccNa)

The oxidation of alcohols to give carbonyl compounds such as aldehydes, ketones and carboxylic acids is an important transformation in organic synthesis [17] as well as for industrial manufacturing. There are many publications for this reaction using molecular oxygen [18–22] or hydrogen peroxide [23–35] as oxidants. As far as this reaction in aqueous media is concerned, the oxidation of alcohols with H$_2$O$_2$ under phase-transfer conditions has

* Corresponding author. Tel.: +41 32 718 2405; fax: +41 32 718 2511.
E-mail address: georg.suess-fink@unine.ch (G. Süss-Fink).

been proposed [36–39]. Noyori [40–43] reported a combined system composed of Na_2WO_4 and $[CH_3(n\text{-}C_8H_{17})_3N][HSO_4]$ as a transfer phase catalyst, which efficiently catalyses the oxidation of alcohols to the corresponding carbonyl compounds with high yields. Trakarnpruk [44] and Punniyamurthy [45] compared the oxidation activity of H_2O_2 and *tert*-butyl hydroperoxide, another cheap and easy-to-use peroxide. A number of catalysts for the use of Bu^tOOH have been reported [46–58]. Watanabe [59] and Muharashi [60] used the ruthenium complex $[RuCl_2(PPh_3)_3]$ that catalyses the oxidation with high conversion (>92%). Recently, Singh et al. [61,62] used arene ruthenium complexes of the type $[(\eta^6\text{-arene})Ru(L)Cl][PF_6]$ (arene = *para*-cymene, benzene) (L = *N*-[2-(arylchalcogeno) ethyl]morpholines with aryl = Ph or 2-pyridine for S, Ph for Se, 4-$MeOC_6H_4$ for Te) as catalysts for alcohol oxidation, using *N*-methylmorpholine *N*-oxyde (NMO), Bu^tOOH, $NaIO_4$ and NaOCl as oxidants.

Herein, we report the synthesis of arene ruthenium complexes containing saccharinato ligands, and their catalytic potential for the oxidation of secondary alcohols with *tert*-butyl hydroperoxide in aqueous solution.

2. Results and discussion

2.1. Synthesis of the aqua complexes $[(\eta^6\text{-arene})Ru(sacc)_2(OH_2)]$ (**1**, **2**)

The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = *para*-cymeme, benzene) react in a water-ethanol mixture (1:1) under reflux with an excess of sodium saccharinate salt to give the corresponding complexes $[(\eta^6\text{-arene})Ru(sacc)_2(OH_2)]$. The hexamethylbenzene complex $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ failed to give the corresponding aqua complex $[(\eta^6\text{-}C_6Me_6)Ru(sacc)_2(OH_2)]$; no reaction was observed under these conditions. The reaction of $[(\eta^6\text{-arene})RuCl_2]_2$ with only two equivalents of saccNa in a water-ethanol mixture (1:1) results in a mixture of $[(\eta^6\text{-arene})Ru(sacc)_2(OH_2)]$ and $[(\eta^6\text{-arene})RuCl_2]_2$ instead of giving a monosaccharinato arene ruthenium complex.

The aqua complexes **1**–**2** have been isolated by crystallization in a water–ethanol mixture (1:1) and washed with water; they form air-stable, yellow to red crystalline solids which are well soluble in dichloromethane, chloroform, acetone and ethanol. The spectroscopic and analytical data are given in Section 3.

2.2. Synthesis of the acetonitrile complexes $[(\eta^6\text{-arene})Ru(sacc)_2(NCMe)]$ (**3**, **4**)

The *para*-cymene ruthenium complex bis-saccharinato $[(\eta^6\text{-}MeC_6H_4Pr^i)Ru(sacc)_2(OH_2)]$ reacts with acetonitrile to give the acetonitrile complex $[(\eta^6\text{-}MeC_6H_4Pr^i)Ru(sacc)_2(NCMe)]$ (**3**). The corresponding benzene complex $[(\eta^6\text{-}C_6H_6)Ru(sacc)_2(NCMe)]$ cannot be prepared by this method, presumably because it is not soluble in acetonitrile. However, it can be synthesized directly from the dinuclear benzene ruthenium complex $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, which reacts in an acetonitrile–ethanol mixture (1:1) under reflux with an excess of sodium saccharinate salt to give $[(\eta^6\text{-}C_6H_6)Ru(sacc)_2(NCMe)]$ (**4**).

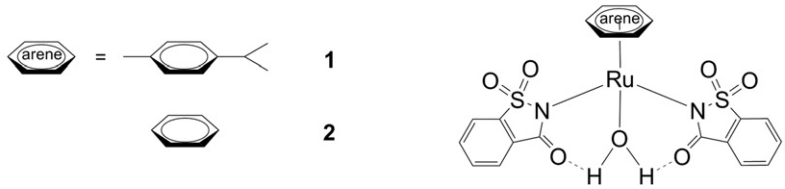
Complex **3** was isolated by crystallization in acetonitrile and washed with acetonitrile, complex **4** was isolated by crystallization from an acetonitrile–ethanol mixture (1:1) and washed with acetonitrile. Both compounds form air-stable, yellow, crystalline solids which are well soluble in dichloromethane, chloroform, acetone and ethanol. The spectroscopic and analytical data are given in Section 3.

2.3. Molecular structure of the complexes $[(\eta^6\text{-arene})Ru(sacc)_2(OH_2)]$ (**1**, **2**)

The molecular structures of **1** and **2** have been established by single-crystal X-ray structure analysis. Both complexes show a typical piano-stool geometry with the metal center being coordinated by an arene ligand, two saccharinato and a water molecule. The saccharinato ligand is bound to the ruthenium atom by its nitrogen, the most common coordination mode of the saccharinato ligand [63]. Strong hydrogen bonds are observed between oxygen atoms of the saccharinato ligands and the coordinated water molecule. ORTEP drawings with the atom labelling scheme for complexes **1** and **2** are shown in Fig. 1, while the intramolecular hydrogen-bonded networks of **1** and **2** are presented in Fig. 2. Selected bond lengths and angles for these two bis-saccharinato complexes are listed in Table 1.

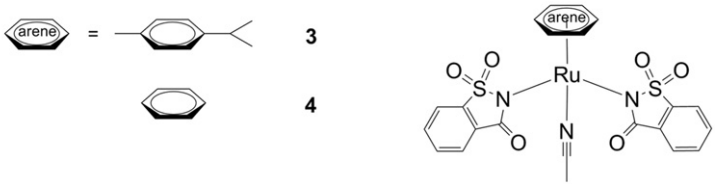
The geometrical parameters of **1** and **2** are comparable to those observed in other *N,N,O* (η^6-arene) ruthenium complexes [64,65].

$$[(\eta^6\text{-arene})RuCl_2]_2 + 4\ saccNa + 2\ H_2O \longrightarrow 2\ [(\eta^6\text{-arene})Ru(sacc)_2(OH_2)] + 4\ NaCl$$



$$[(\eta^6\text{-}MeC_6H_4Pr^i)Ru(sacc)_2(OH_2)] + MeCN \longrightarrow [(\eta^6\text{-}MeC_6H_4Pr^i)Ru(sacc)_2(NCMe)] + H_2O$$

$$[(\eta^6\text{-}C_6H_6)RuCl_2]_2 + 4\ saccNa + 2\ MeCN \longrightarrow 2\ [(\eta^6\text{-}C_6H_6)Ru(sacc)_2(NCMe)] + 4\ NaCl$$



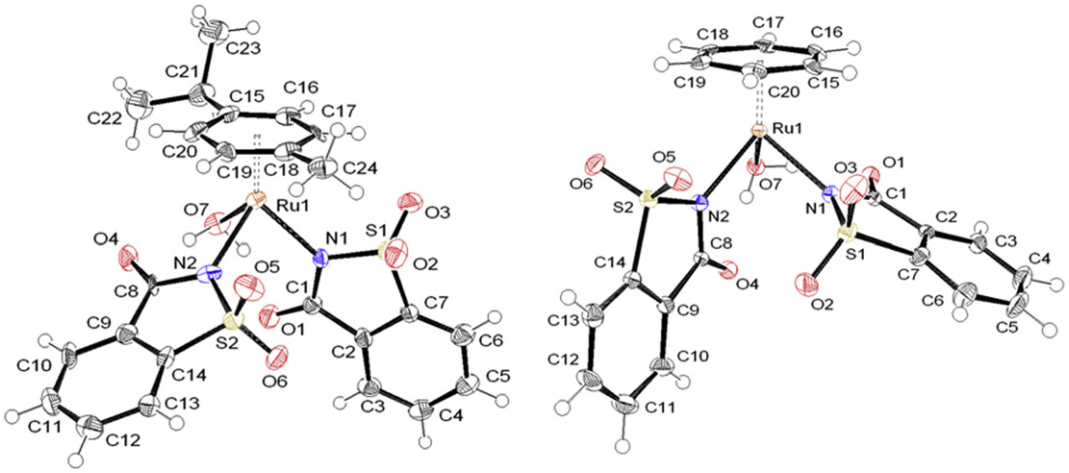


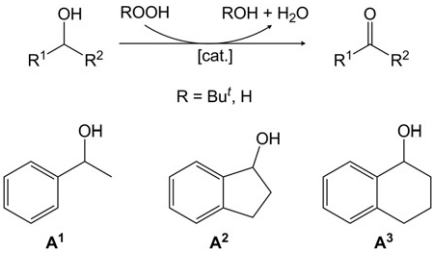
Fig. 1. ORTEP diagrams of **1** (left) and **2** (right) with 50% probability thermal ellipsoids.

In **1**, the ruthenium atom is situated 1.676 Å away from the centroid of the *para*-cymene ligand, while in **2** the distance between the centroid of the benzene ligand and Ru is slightly shorter (1.662 Å). This difference is consistent with a higher electron-donating ability of the *para*-cymene ring as compared to that of benzene.

In both compounds, strong intramolecular hydrogen bonds are observed (Fig. 2). The coordinated water molecule interacts with the oxygen atom of the C═O moiety of each neighbouring saccharinato ligands. The O···OH_2 separations are all comprised between 2.6 and 2.7 Å with O—H···O angles >153.0°. In addition to these intramolecular hydrogen bonds, a series of intermolecular hydrogen bond interactions are observed in the crystal packing of **1** and **2**, thus forming a very closed packing arrangement in the solid state.

*2.4. Catalytic application of complexes **1**–**4** for the oxidation of secondary alcohols with Bu^{t}OOH and H_2O_2 in aqueous solution*

Based on a study of Singh et al. on using arene ruthenium complexes for alcohol oxidation with Bu^{t}OOH in dichloromethane [61,62], we decided to use our arene ruthenium bis-saccharinato complexes as catalysts for the oxidation of secondary alcohols with H_2O_2 or Bu^{t}OOH to give the corresponding ketones in aqueous solution, thus avoiding dichloromethane as solvent. The alcohols studied as substrates for this reaction are 1-phenylethanol (**A^1**), indanol (**A^2**) and tetralol (**A^3**).



In a preliminary series, the oxidation of alcohols **A^1**, **A^2** and **A^3** has been studied with complex **1** under various conditions (Table 2) : With a substrate to catalyst ratio (S/C) varying from 1000 to 10,000, the reaction is quantitative at room temperature (25 °C) for all alcohols (conv. > 99%) using Bu^{t}OOH as oxidant in aqueous solution. Without solvent, the reaction works also well at 100 °C (entries 1, 2). The oxidation activities of H_2O_2 and Bu^{t}OOH have also been compared; the results show that Bu^{t}OOH is more efficient than H_2O_2. For the further catalytic study, it was decided to oxidize the alcohols with Bu^{t}OOH in aqueous solution, the S/C ratio being 100,000.

The results obtained (Fig. 3) show that the conversion increases linearly with the increase of the molar ratio of oxidant and substrate. The pH-dependence of the catalytic activity of **1** was studied for the oxidation of 1-phenylethanol to give acetophenone. The reaction works at various pH (3, 5, 9 and 12), the catalytic activity being maximal for pH 9 (Fig. 4). The conversion depends also on temperature: With **1** as catalyst, we found the conversion to

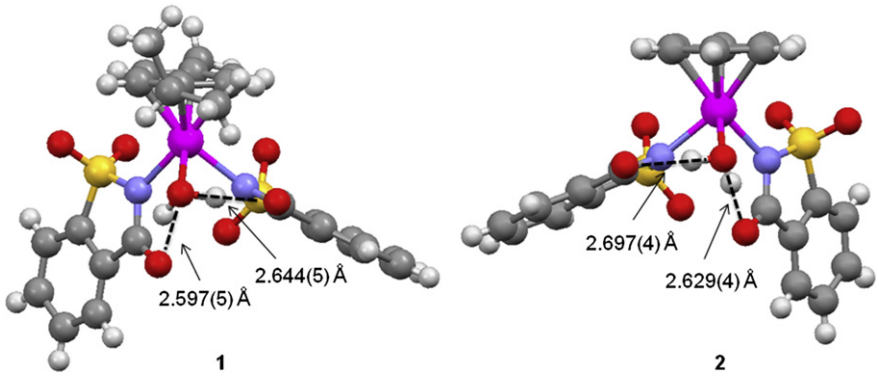


Fig. 2. Intramolecular hydrogen-bonded networks observed in **1** and **2**.

Table 1
Selected bond lengths and angles for **1** and **2**. Ru-centroid.

	1	2
Interatomic distances (Å)		
Ru-N1	2.151(4)	2.140(3)
Ru-N2	2.146(4)	2.137(3)
Ru-O7	2.154(3)	2.147(2)
O7···O1	2.597(5)	2.697(4)
O7···O4	2.644(5)	2.629(4)
Ru-centroid	1.676	1.662
Angles (°)		
N1-Ru-N2	87.03(15)	86.80(11)
N1-Ru-O7	84.37(14)	83.08(10)
N2-Ru-O7	81.96(14)	84.94(11)
O7-H···O1	153.8	153.3
O7-H···O4	164.4	157.6

be maximum at 80 °C (Fig. 5), because Bu^{t}OOH is not heat-resistant and its boiling point is 96.2 °C. The time-dependence of the catalytic activity of **1** for the oxidation of 1-phenylethanol (Fig. 6) shows that the conversion increases linearly with time. These results are available for the oxidation of 1-phenylethanol (**A^1**) catalyzed by **1**.

All complexes **1**–**4** are found to catalyze the oxidation of secondary alcohols **A^1**–**A^3**, the results obtained are shown in Table 3. We found that the best result is obtained at pH 7 with the aqua complex **2** as the catalyst for all alcohols with high conversion (>95%), the turnover frequencies varying from 31,733 to 33,033 h^{-1} (entries 3, 11 and 19). All complexes show higher activities for the oxidation of **A^2** than for the oxidation of **A^1** and **A^3**. In addition, within the series of the acetonitrile complexes **3** and **4**, the benzene ruthenium complex **4** is more active than **3**.

A tentative catalytic cycle for the oxidation of secondary alcohols in aqueous solution with Bu^{t}OOH or H_2O_2 as oxidants involving the aqua complexes **1** or **2** is shown in Scheme 1. The aqua ligand may be replaced by an oxo ligand upon reaction with ROOH, thus increasing the oxidation state of ruthenium from II to IV. The oxo complex may then be reduced by the alcohol to give the ketone and the aqua complex. A similar reaction cycle may be considered for the acetonitrile complexes **3** and **4**.

The oxidation of ruthenium (II) to ruthenium (IV) may be initiated by a proton transfer from the aqua ligand to the oxo groups of the saccharinato ligands, which may be facilitated at pH = 9, the optimal pH for the catalytic reaction.

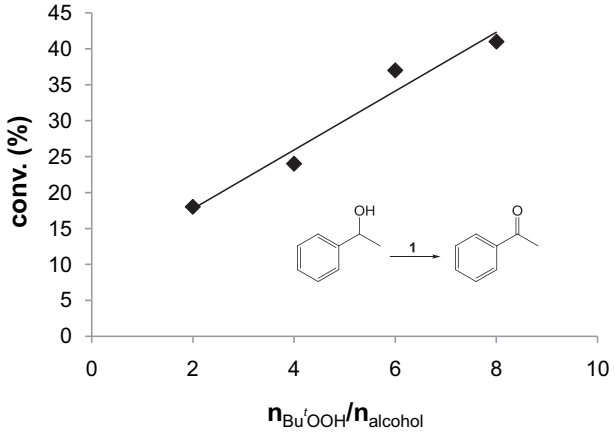


Fig. 3. Molar ratio between Bu^{t}OOH and alcohol-dependence of conversion for the oxidation of 1-phenylethanol catalyzed by **1** in aqueous solution. Conditions: 0.01 μmol catalyst **1**, 1 mmol of 1-phenylethanol, Bu^{t}OOH (2–8 mmol), 5 mL of water, at room temperature (25 °C), the reaction was stirred for 3 h.

3. Experimental

3.1. General

All manipulations were carried out in an inert atmosphere using standard Schlenk techniques and pure solvents. The starting materials $[(\eta^6\text{-arene})RuCl_2]_2$ were prepared according to the published methods [66]. All other reagents were commercially available and were used without further purification. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Microanalyses were carried out by the Mikroelementaranalytisches Laboratorium, ETH Zürich (Switzerland).

3.2. General procedure for the synthesis of complex $[(\eta^6\text{-arene})Ru(sacc)_2(OH_2)]$ (*1*, *2*)

To a solution of $[(\eta^6\text{-arene})RuCl_2]_2$ (0.082 mmol) in 20 mL of water–ethanol mixture (1:1), 4 equiv. of solid saccNa was added and the reaction mixture was heated under reflux for 2 h. Then the solution was cooled to room temperature and the solvent was reduced to a half of its volume. The crystals formed overnight were washed with water and dried under vacuum.

Table 2
Oxidation of alcohols catalyzed by **1**.[a]

Entry	S/C	Alcohol	Oxidant	$n_{oxidant}$ (mmol)	Solvent	pH	T (°C)	Conv[b](%)	TON[b,c]	TOF[b,d] (h^{-1})
1	1000	**A^1**	Bu^{t}OOH	4	–	–	RT	77.8	778	257
2	1000	**A^1**	Bu^{t}OOH	4	–	–	100	90.7	907	302
3	1000	**A^1**	Bu^{t}OOH	4	H_2O	7	RT	99.6	996	332
4	1000	**A^1**	Bu^{t}OOH	4	H_2O	7	100	99.1	991	330
5	10,000	**A^1**	Bu^{t}OOH	4	H_2O	7	RT	99.5	9950	3317
6	10,000	**A^2**	Bu^{t}OOH	4	H_2O	7	RT	100	10,000	3333
7	10,000	**A^3**	Bu^{t}OOH	4	H_2O	7	RT	99.4	9940	3313
8	100,000	**A^1**	Bu^{t}OOH	4	H_2O	7	RT	24.0	24,000	8000
9	10,000	**A^1**	H_2O_2	5	H_2O	7	RT	1.7	170	57
10	100,000	**A^1**	H_2O_2	5	H_2O	7	RT	1.7	1700	567
11	10,000	**A^1**	H_2O_2	5	H_2O	7	70	10.4	1040	347
12	100,000	**A^1**	H_2O_2	5	H_2O	7	70	4.2	4200	1400
13	10,000	**A^3**	H_2O_2	5	H_2O	7	70	3.9	390	130
14	100,000	**A^3**	H_2O_2	5	H_2O	7	70	3.1	3100	1033

[a] Conditions: H_2O (5 mL), alcohol (1 mmol), 3 h.
[b] Determined by Gas Chromatography (GC) or GC–MS.
[c] Turnover number: mol of product (ketone)/mol of catalyst.
[d] Mean turnover frequency: mol of product/(mol of catalyst × h) determined after 3 h.

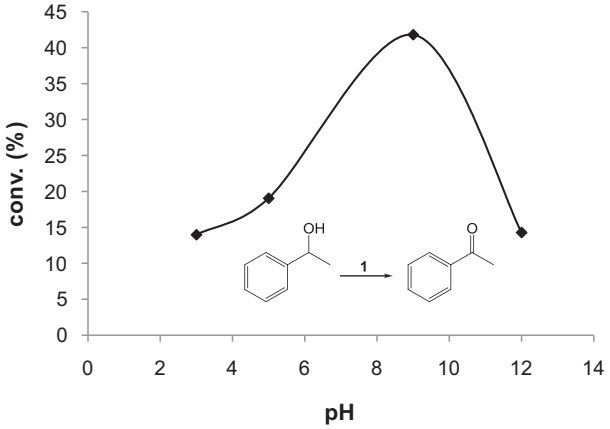


Fig. 4. pH-dependence of conversion for the oxidation of 1-phenylethanol catalyzed by **1** in aqueous solution. Conditions: 0.01 μmol catalyst **1**, 1 mmol of 1-phenylethanol, 4 mmol of Bu^{t}OOH, 5 mL of aqueous solution with desired pH, at room temperature (25 °C), the reaction was stirred for 3 h The pH was adjusted by addition of HCl 1 M or KOH 1 M.

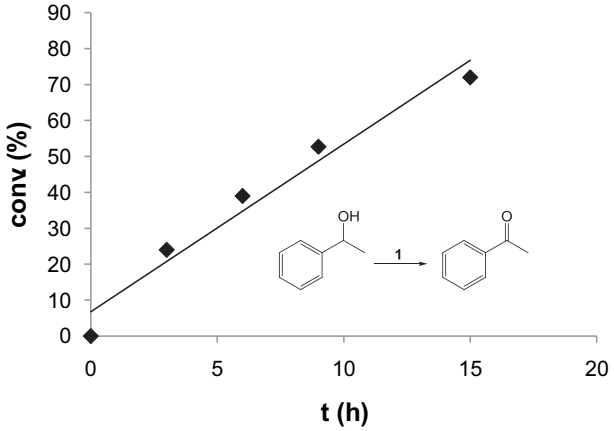


Fig. 6. Time-dependence of conversion for the oxidation of 1-phenylethanol catalyzed by **1** in aqueous solution. Conditions: 0.01 μmol catalyst **1**, 1 mmol of 1-phenylethanol, 4 mmol of Bu^{t}OOH, 5 mL of water, at room temperature (25 °C), the reaction was stirred for the desired time.

*3.2.1. [(η^6-MeC$_6$H$_4$Pr^i)Ru(sacc)$_2$(OH$_2$)] (**1**) yield: 85% (86.1 mg)*

Anal. Calc. for **1**, $C_{24}H_{24}N_2O_7S_2Ru$: C, 46.67; H, 3.92; N, 4.54. Found: C, 46.56; H, 4.02; N, 4.51%. ^{1}H NMR (400 MHz, CD_2Cl_2) : δ 1.32 (d, J = 8 Hz, 6 H, −CH(C*H*$_3$)$_2$), 2.11 (s, 3 H, C*H*$_3$), 3.20 (sept, 1 H, −C*H*(CH$_3$)$_2$), 5.73 (d, J = 8 Hz, 2 H, C$_6$H$_4$), 6.28 (d, J = 8 Hz, 2 H, C$_6$H$_4$), 7.61–7.77 (m, 8 H, H$_{sacc}$). ^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2): δ 19.03 (1 C, CH$_3$), 22.58 (2 C, −CH(*C*H$_3$)$_2$), 30.76 (1 C, −*C*H(CH$_3$)$_2$), 77.45 (2 CH, C$_6$H$_4$), 85.13 (2 CH, C$_6$H$_4$), 102.77 (1 C, C$_6$H$_4$), 103.77 (1 C, C$_6$H$_4$), 119.92 (2 C, CH$_{sacc}$), 123.37 (2 C, CH$_{sacc}$), 131.31 (2 C, C$_{sacc}$), 132.92 (2 C, CH$_{sacc}$), 133.00 (2 C, CH$_{sacc}$), 141.86 (2 C, C$_{sacc}$), 172.79 (2 C, C═O).

*3.2.2. [(η^6-C$_6$H$_6$)Ru(sacc)$_2$(OH$_2$)] (**2**) yield: 74% (68.2 mg)*

Anal. Calc. for **2**, $C_{20}H_{16}N_2O_7S_2Ru$: C, 42.78; H, 2.87; N, 4.99. Found: C, 42.68; H, 2.89; N, 4.95%. ^{1}H NMR (400 MHz, CD_2Cl_2) : δ 6.17 (s, 6 H, C$_6$H$_6$), 7.63–7.80 (m, 8 H, 2 (−C$_7$H$_4$)). ^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2): δ 84.00 (6 C, C$_6$H$_6$), 120.34 (2 CH, CH$_{sacc}$), 123.78 (2 CH, CH$_{sacc}$), 131.38 (2 C, C$_{sacc}$), 133.36 (2 CH, CH$_{sacc}$), 133.43 (2 CH, CH$_{sacc}$), 141.82 (2 C, C$_{sacc}$), 172.74 (2 C, C═O).

*3.3. Synthesis of complex [(η^6-MeC$_6$H$_4$Pr^i)Ru(sacc)$_2$(NCCH$_3$)] (**3**)*

Acetonitrile was added to the *para*-cymene ruthenium aqua complex [(η^6-MeC$_6$H$_4$Pr^i)Ru(sacc)$_2$(OH$_2$)] (**1**) (0.065 mmol) and the reaction mixture was stirred for 2 h at room temperature. Then the solvent was reduced to a half of its volume. The crystals formed overnight were washed with acetonitrile and dried under vacuum.

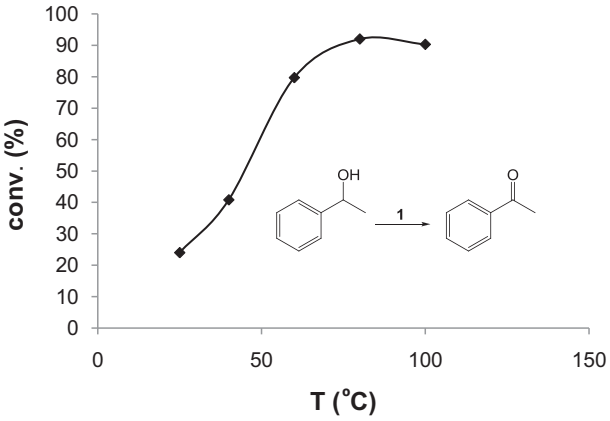


Fig. 5. Temperature-dependence of conversion for the oxidation of 1-phenylethanol catalyzed by **1** in aqueous solution. Conditions: 0.01 μmol catalyst **1**, 1 mmol of 1-phenylethanol, 4 mmol of Bu^{t}OOH, 5 mL of water, at desired temperature, the reaction was stirred for 3 h.

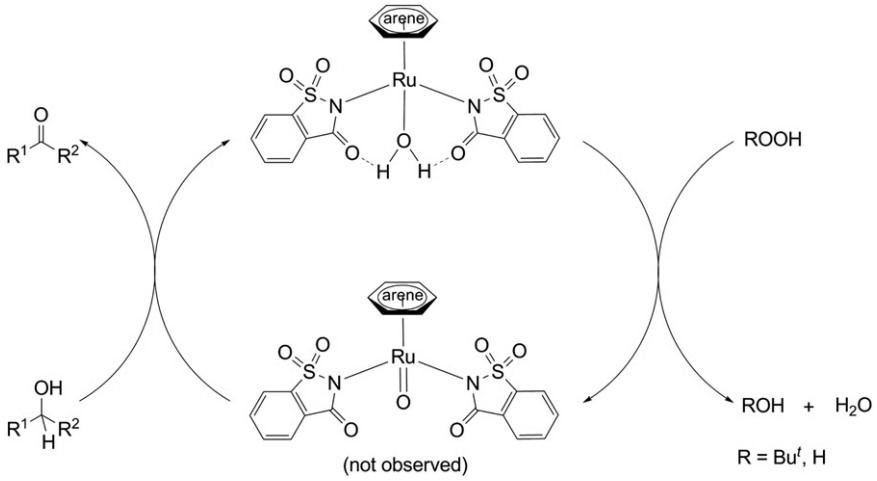
*3.3.1. [(η^6-MeC$_6$H$_4$Pr^i)Ru(sacc)$_2$(NCCH$_3$)] (**3**) yield: 90% (37.5 mg)*

Anal. Calc. for **3** · 0.5 CH$_3$CN, $C_{27}H_{26.5}N_{3.5}O_6S_2Ru$: C, 49.04; H, 4.04; N, 7.41. Found: C, 49.17; H, 4.20; N, 7.15%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.36 (d, J = 8 Hz, 6 H, −CH(C*H*$_3$)$_2$), 2.00 (s, 3 H, C*H*$_3$CN), 2.14 (s, 3 H, C*H*$_3$), 3.22 (sept, 1 H, −C*H*(CH$_3$)$_2$), 5.76 (d, J = 4 Hz, 2 H, C$_6$H$_4$), 6.30 (d, J = 4 Hz, 2 H, C$_6$H$_4$), 7.65–7.80 (m, 8 H, H$_{sacc}$). ^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2): δ 17.30 (1 C, CH$_3$), 20.85 (2 C, −CH(*C*H$_3$)$_2$), 29.04 (1 C, −*C*H(CH$_3$)$_2$), 75.77 (2 CH, C$_6$H$_4$), 83.37 (2 CH, C$_6$H$_4$),

Table 3
Oxidation of secondary alcohols catalyzed by **1**–**4** in aqueous solution.[a]

Entry	Catalyst	Substrate	pH	Conv.[b] (%)	TON[b,c]	TOF[b,d] (h^{-1})
1	**1**	**A^1**	7	24.0	24,000	8000
2	**1**	**A^1**	9	41.8	41,800	13,933
3	**2**	**A^1**	7	95.2	95,200	31,733
4	**2**	**A^1**	9	29.4	29,400	9800
5	**3**	**A^1**	7	29.6	29,600	9867
6	**3**	**A^1**	9	28.9	28,900	9633
7	**4**	**A^1**	7	31.2	31,200	10,400
8	**4**	**A^1**	9	59.7	59,700	19,900
9	**1**	**A^2**	7	61.4	61,400	20,467
10	**1**	**A^2**	9	65.5	65,500	21,833
11	**2**	**A^2**	7	99.1	99,100	33,033
12	**2**	**A^2**	9	72.2	72,200	24,067
13	**3**	**A^2**	7	45.8	45,800	15,267
14	**3**	**A^2**	9	71.8	71,800	23,933
15	**4**	**A^2**	7	43.2	43,200	14,400
16	**4**	**A^2**	9	70.5	70,500	23,500
17	**1**	**A^3**	7	96.9	96,900	32,300
18	**1**	**A^3**	9	16.2	16,200	5400
19	**2**	**A^3**	7	97.3	97,300	32,433
20	**2**	**A^3**	9	38.5	38,500	12,833
21	**3**	**A^3**	7	32.7	32,700	10,900
22	**3**	**A^3**	9	38.3	38,300	12,767
23	**4**	**A^3**	7	36.6	36,600	12,200
24	**4**	**A^3**	9	40.3	40,300	13,433

[a] Conditions: H$_2$O (5 mL), **A** (1 mmol), Bu^{t}OOH (4 mmol), catalyst (0.01 μmol), room temperature (25 °C), 3 h.
[b] Determined by Gas Chromatography (GC) or GC–MS.
[c] Turnover number: mol of product (ketone)/mol of catalyst.
[d] Mean turnover frequency: mol of product/(mol of catalyst × h) determined after 3 h.



Scheme 1. Postulated catalytic cycle for the oxidation of secondary alcohols in aqueous solution using arene ruthenium bis-saccharinato complexes with Bu^tOOH or H_2O_2 as oxidants.

103.18 (1 C, C_6H_4), 103.53(1 C, C_6H_4), 118.19 (2 C, CH_{sacc}), 121.64 (2 C, CH_{sacc}), 129.59 (2 C, C_{sacc}), 131.18 (2 CH, CH_{sacc}), 131.26 (2 C, CH_{sacc}), 140.15 (2 C, C_{sacc}), 171.06 (2 C, C═O).

3.4. Synthesis of complex $[(\eta^6\text{-}C_6H_6)Ru(sacc)_2(NCCH_3)]$ (**4**)

To a solution of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.082 mmol) in 20 mL of acetonitrile–methanol mixture (1:1), 4 equiv. of solid saccNa was added and the reaction mixture was heated under reflux for 2 h. Then the solution was cooled to room temperature and the solvent was reduced to a half of its volume. The crystals formed overnight were washed with acetonitrile and dried under vacuum.

3.4.1. $[(\eta^6\text{-}C_6H_6)Ru(sacc)_2(NCCH_3)]$ (**4**) yield: 65% (62.4 mg)

Anal. Calc. for **4**, $C_{22}H_{17}N_3O_6S_2Ru$: C, 45.20; H, 2.93; N, 7.19. Found: C, 45.15; H, 3.04; N, 7.10%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.00 (s, 3 H, CH_3CN), 6.19 (s, 6 H, C_6H_6), 7.67–7.82 (m, 8 H, H_{sacc}). ^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2): δ 84.02 (6 C, C_6H_6), 120.35 (2 C, CH_{sacc}), 123.80 (2 C, CH_{sacc}), 131.40 (2 C, C_{sacc}), 133.37 (2 C, CH_{sacc}), 133.44 (2 C, CH_{sacc}), 141.84 (2 C, C_{sacc}), 171.68 (2 C, C═O).

Table 4
Crystallographic and structure refinement parameters for complexes **1** and **2**.

	1	**2**
Chemical formula	$C_{24}H_{24}N_2O_7RuS_2$	$C_{20}H_{16}N_2O_7RuS_2$
Formula weight	617.64	561.54
Crystal system	Triclinic	Monoclinic
Space group	*P*–1(no.2)	*P* $2_1/c$ (no. 14)
Crystal colour and shape	Red block	Red block
Crystal size	0.27 × 0.22 × 0.19	0.25 × 0.22 × 0.16
a (Å)	8.0016(9)	12.5341(10)
b (Å)	11.3618(12)	12.9820(11)
c (Å)	13.9339(15)	13.3197(11)
α (°)	97.663(13)	90
β (°)	98.766(13)	106.747(9)
γ (°)	101.197(13)	90
V (Å^3)	1210.7(2)	2075.4(3)
Z	2	4
T (K)	173(2)	173(2)
D_c (g cm^{-3})	1.694	1.797
μ (mm^{-1})	0.869	1.004
Scan range (°)	$2.64 < \theta < 26.20$	$2.24 < \theta < 26.21$
Unique reflections	4437	4103
Observed refls [I > 2σ(I)]	3731	2736
R_{int}	0.0336	0.0657
Final *R* indices [I > 2σ(I)][a]	0.0355, wR_2 0.0869	0.0337, wR_2 0.0602
R indices (all data)	0.0489, wR_2 0.1265	0.0652, wR_2 0.0550
Goodness-of-fit	1.194	0.850
Max, Min $\Delta\rho$/e (Å^{-3})	1.497, −1.934	0.650, −1.475

[a] Structures were refined on F_0^2: $wR_2 = [\Sigma[w\ (F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

3.5. X-ray crystallography

Crystals of complexes **1** and **2** were mounted on a Stoe Image Plate Diffraction system equipped with a φ circle goniometer, using Mo-Kα graphite monochromated radiation (λ = 0.71073 Å) with φ range 0–200°. The structures were solved by direct methods using the program SHELXS-97, while the refinement and all further calculations were carried out using SHELXL-97 [67]. The H-atoms were found on Fourier difference map or included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Crystallographic details are summarized in Table 4. Fig. 1 was drawn with ORTEP [68], while Fig. 2 was drawn with Mercury [69].

3.6. Oxidation of secondary alcohols

The oxidation of secondary alcohols $\mathbf{A^1}$–$\mathbf{A^3}$ (1 mmol), using **1**–**4** (0.01–1 μmol) as catalysts and Bu^tOOH (4 mmol) or H_2O_2 (5 mmol) as oxidants, was carried out in aqueous solution (5 mL) under inert atmosphere. The appropriate pH of the solution was adjusted with HCl (1 M) or KOH (1 M). The solution was then stirred for the given time at the given temperature. Then the organic products were extracted by ligroin and identified after filtration through silica gel by GC on CP-wax 52-CB (25 m × 0.32 mm) capillary column or by GC–MS on ZB-5MS (Zebron, 30 m × 0.25 μm) capillary column for all alcohols. The conversion was determined by integration of the signals. The pH was monitored using a pH meter (Mettler Toledo InLab 413).

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Appendix A. Supplementary material

CCDC-811946 **1** and 811947 **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.

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