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Communication

Arene ruthenium oxinato complexes: Synthesis, molecular structure and catalytic activity for the hydrogenation of carbon dioxide in aqueous solution

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ABSTRACT

Two families of arene ruthenium oxinato complexes of the types $[(\eta^6\text{-arene})Ru(\eta^2\text{-}N,O\text{-L})Cl]$ and $[(\eta^6\text{-arene})Ru(\eta^2\text{-}N,O\text{-L})(OH_2)]^+$ have been synthesized from the dinuclear precursors $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = *para*-cymeme or hexamethylbenzene) and the corresponding oxine LH (LH = 8-hydroxyquinoline, 5-chloro-8-hydroxyquinoline, 5,7-dichloro-8-hydroxyquinoline, 5-nitro-8-hydroxyquinoline, 5,7-dimethyl-8-hydroxyquinoline, 5,7-dichloro-2-methyl-8-hydroxyquinoline). The molecular structures of the neutral chloro complexes $[(\eta^6\text{-}C_6Me_6)Ru(\eta^2\text{-}N,O\text{-L})Cl]$ (LH = 8-hydroxyquinoline, 5,7-dichloro-2-methyl-8-hydroxyquinoline) and $[(\eta^6\text{-}MeC_6H_4Pr^i)Ru(\eta^2\text{-}N,O\text{-L})Cl]$ (LH = 5,7-dichloro-2-methyl-8-hydroxyquinoline) as well as those of the cationic aqua derivatives $[(\eta^6\text{-}MeC_6H_4Pr^i)Ru(\eta^2\text{-}N,O\text{-L})(OH_2)]^+$ (LH = 8-hydroxyquinoline, 5,7-dimethyl-8-hydroxyquinoline), isolated as the tetrafluoroborate salts, show in all cases a piano-stool arrangement with the arene ligand, the chelating oxinato ligand and the chloro or the aqua ligand surrounding the ruthenium center in a pseudo-tetrahedral fashion. The analogous reaction of $[(\eta^6\text{-}MeC_6H_4Pr^i)RuCl_2]_2$ with other *N,O*-chelating ligands such as 2-pyridinemethanol or tetrahydrofurfurylamine did not give the expected analogs but resulted in the formation of the complexes $[(\eta^6\text{-}MeC_6H_4Pr^i)Ru(\eta^2\text{-}NC_5H_4CH_2OH)Cl]^+$ and $[(\eta^6\text{-}MeC_6H_4Pr^i)Ru(\eta^1\text{-}NHCH_2C_4H_3O)Cl_2]$. The neutral and cationic complexes of the types $[(\eta^6\text{-arene})Ru(\eta^2\text{-}N,O\text{-L})Cl]$ and $[(\eta^6\text{-arene})Ru(\eta^2\text{-}N,O\text{-L})(OH_2)]^+$ have been found to catalyze the hydrogenation of carbon dioxide to give formate in alkaline aqueous solution with catalytic turnovers up to 400.

1. Introduction

The first arene ruthenium complex was obtained from the reaction of $RuCl_3 \cdot nH_2O$ with 1,3-cyclohexadiene and reported by Winkhaus and Singer in 1967 as a polymeric material, $[(\eta^6\text{-}C_6H_6)RuCl_2]_n$ [1]. Later studies by Zelonka and Baird [2] and by Bennett and Smith [3] showed this complex to be a dimer, $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$. Since these early reports, the chemistry of arene ruthenium complexes has been steadily developed [4,5]. A new impetus came into this field in 1988, when Ludi, Merbach, Bürgi and co-workers showed that arene ruthenium aqua complexes previously observed by NMR spectroscopy [2] can be isolated under certain conditions; the characterization of the cation $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ by single-crystal X-ray structure analysis of the sulfate salt can be considered as a breakthrough [6]. In the 1990s we found that the chloride or tetrafluoroborate salts of cationic arene ruthenium complexes are well soluble in water, the arene ruthenium bond being robust toward hydrolysis [7–9], which resulted in a rapid development of arene ruthenium chemistry in aqueous solution [10], especially as far as water-soluble catalysts for transfer hydrogenation reactions in aqueous solution are concerned [11–21].

The hydrogenation of carbon dioxide to give formic acid in aqueous solution is an attractive approach to the use of carbon dioxide as an economical and ecological C_1 source [22]. This reaction, first reported in 1976 by Inoue and co-workers, is catalyzed by various group VIII metal phosphine complexes in benzene in the presence of water and base [23]. The direct formation of formic acid from CO_2 and H_2 in supercritical carbon dioxide using ruthenium catalysts was pioneered by Noyori and Jessop [24–28], while the hydrogenation of carbon dioxide in water, catalyzed by water-soluble rhodium or ruthenium complexes was developed by Gassner and Leitner [29] and by Joó and Laurenczy [30–33]. Himeda carefully studied the influence of the pH on this reaction and designed rhodium, iridium and ruthenium complexes containing chelating *N,N*-ligands that can be deprotonated and that are highly active in basic solution [34]. The aqueous hydrogenation of carbon dioxide under acidic conditions, catalyzed by water-soluble arene ruthenium or pentamethylcyclopentadienyl iridium complexes, was pioneered by Ogo and Fukuzumi [35–37].

Based on our work on water-soluble organometallic complexes containing chelating ligands for catalytic transfer hydrogenation

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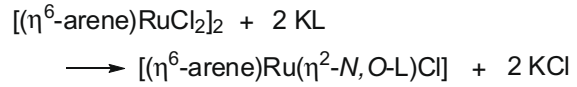
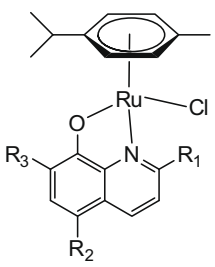
reactions using sodium formate and water as hydrogen source [11–12], we intended to develop a complementary catalyst for the hydrogenation of CO_2 to give $HCOO^-$, which can be coupled to the NADH-regenerating (η^5-C_5Me_5)Rh(*ortho*-phenanthroline) catalyst for the chemoenzymatic enantioselective reduction of ketones (Scheme 1), catalyst using formate as a hydrogen source to give carbon dioxide [13]. We decided to synthesize and to test (η^6-arene)Ru(oxinato) complexes for this purpose. The first arene ruthenium complexes containing oxinato ligands have been synthesized by Kirchner and co-workers, who structurally characterized the *para*-cymene complex [(η^6-$MeC_6H_4Pr^i$)Ru(η^2-*N,O*-L)Cl] (LH = 8-hydroxyquinoline) (**1**) [38]. In this paper we report the synthesis of a whole series of *para*-cymene ruthenium chloro complexes containing substituted oxinato ligands, the hexamethylbenzene analogs, the corresponding cationic aqua complexes and their catalytic properties for the hydrogenation of carbon dioxide in aqueous solution.

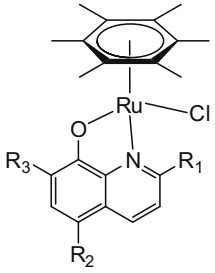
2. Results and discussion

2.1. Synthesis of the chloro complexes [(η^6-arene)Ru(η^2-N,O-L)Cl] (**2**–**11**)

The *para*-cymene ruthenium complex [(η^6-$MeC_6H_4Pr^i$)$RuCl_2$]$_2$ reacts in tetrahydrofuran solution at room temperature with potassium 8-hydroxyquinolate to give the known [38] 8-hydroxyquinolinato complex **1**. This reaction reported by Kirchner and co-workers [38] also works with various substituted 8-hydroxyquinolates. However, for the analogous reactions of the hexamethylbenzene precursors [(η^6-C_6Me_6)$RuCl_2$]$_2$ chloroform has to be used as solvent for solubility reasons.







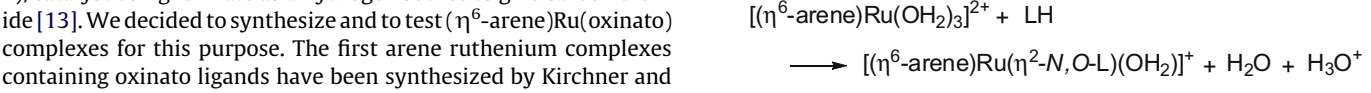
1 R_1 = H, R_2 = H, R_3 = H [38]
2 R_1 = H, R_2 = Cl, R_3 = Cl
3 R_1 = H, R_2 = Cl, R_3 = H
4 R_1 = H, R_2 = NO_2, R_3 = H
5 R_1 = Me, R_2 = Cl, R_3 = Cl

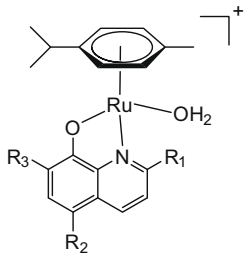
6 R_1 = H, R_2 = H, R_3 = H
7 R_1 = H, R_2 = Cl, R_3 = Cl
8 R_1 = H, R_2 = Cl, R_3 = H
9 R_1 = H, R_2 = NO_2, R_3 = H
10 R_1 = H, R_2 = Me, R_3 = Me
11 R_1 = Me, R_2 = Cl, R_3 = Cl

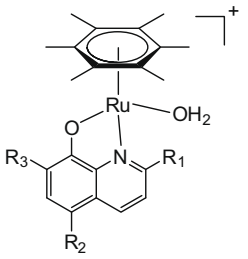
All chloro complexes **1**–**11** have been isolated by precipitation with diethyl ether and purified by column chromatography on silica gel, they form air-stable, orange to red crystalline solids which are well soluble in dichloromethane, chloroform and acetone. The spectroscopic (MS, ^{1}H and ^{13}C NMR) and analytical data are given in Section 3.

2.2. Synthesis of the aqua complexes [(η^6-arene)Ru(η^2-N,O-L)(OH_2)]$^+$ (**12**–**19**)

In contrast to arene ruthenium chloro complexes containing chelating *N,N*-ligands, which hydrolyze in water to give the corresponding cationic aqua complexes [11,12,39], the hydrolysis of the chloro complexes **1**–**11** does not give the expected aqua complexes. We therefore prepared these cationic complexes by reacting the triaqua complexes [(η^6-arene)Ru(OH_2)$_3$]$^{2+}$ in aqueous solution with the corresponding 8-hydroxyquinoline derivatives.







12 R_1 = H, R_2 = H, R_3 = H
13 R_1 = Me, R_2 = Cl, R_3 = Cl
14 R_1 = H, R_2 = Cl, R_3 = H
15 R_1 = H, R_2 = Me, R_3 = Me

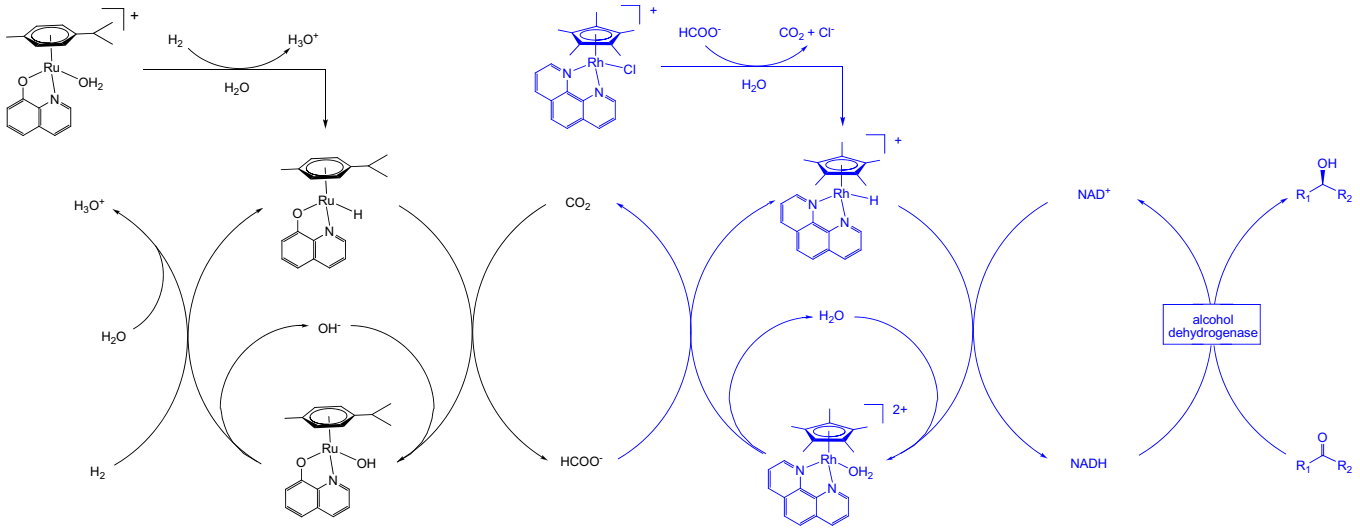
16 R_1 = H, R_2 = H, R_3 = H
17 R_1 = Me, R_2 =Cl, R_3 = Cl
18 R_1 = H, R_2 = NO_2, R_3 = H
19 R_1 = H, R_2 = Me, R_3 = Me

The cationic complexes **12**–**19** can be isolated as the tetrafluoroborate salts that form air-stable orange-red solids, well soluble in water, methanol and acetonitrile. The spectroscopic (MS, ^{1}H and ^{13}C NMR) and analytical data are given in Section 3.

2.3. Molecular structures of the complexes [(η^6-$MeC_6H_4Pr^i$)Ru(η^2-N,O-L)Cl] (**5**), [(η^6-C_6Me_6)Ru(η^2-N,O-L)Cl] (**6**, **11**) and [(η^6-$MeC_6H_4Pr^i$)Ru(η^2-N,O-L)(OH_2)]$^+$ (**12**, **15**)

The *para*-cymene chloro complex **5** crystallizes in the monoclinic centrosymmetric space group $P2_1/n$. The asymmetric unit comprises only one molecule, the molecular structure of which is depicted in Fig. 1. Crystallographic details are given in Table 8, and significant bond lengths and bond angles are listed in Table 1. The hexamethylbenzene chloro complex **6** crystallizes also in the monoclinic centrosymmetric space group $P2_1/c$, the asymmetric unit comprising only one molecule. The molecular structure of **6** is depicted in Fig. 2, crystallographic details are given in Table 8, and significant bond lengths and bond angles are listed in Table 2. The 5,7-dichloro-2-methyl-substituted analog **11** crystallizes in the monoclinic centrosymmetric space group $P2_1/a$, the asymmetric unit comprising only one molecule. The molecular structure of **11** is depicted in Fig. 3, crystallographic details are given in Table 8, and significant bond lengths and bond angles are listed in Table 3. In the chloro complexes **5**, **6** and **11**, the ruthenium atom is coordinated to the η^6-arene ligand, to the oxygen atom and the nitrogen atom of the η^2-oxinato ligand, as well as to the chlorine atom, the coordination geometry of ruthenium center being pseudo-tetrahedral. The Ru–N and Ru–O distances are similar to those found in **1** [38].

The tetrafluoroborate salt of the aqua complex **12** crystallizes in the orthorhombic centrosymmetric space group *Pcab*. The asymmetric unit comprises one molecule of the cationic complex and one tetrafluoroborate counter-anion. The molecular structure of **12** is depicted in Fig. 4. Crystallographic details are given in Table 8, and significant bond lengths and bond angles are listed in Table 4. The 5,7-dimethyl-substituted analog **15**[BF_4] crystallizes in the triclinic centrosymmetric space group $P\bar{1}$. The asymmetric unit



Scheme 1. Coupling of CO_2-hydrogenating catalyst system to the CO_2-evolving catalyst system in the catalytic regeneration of NADH [13].

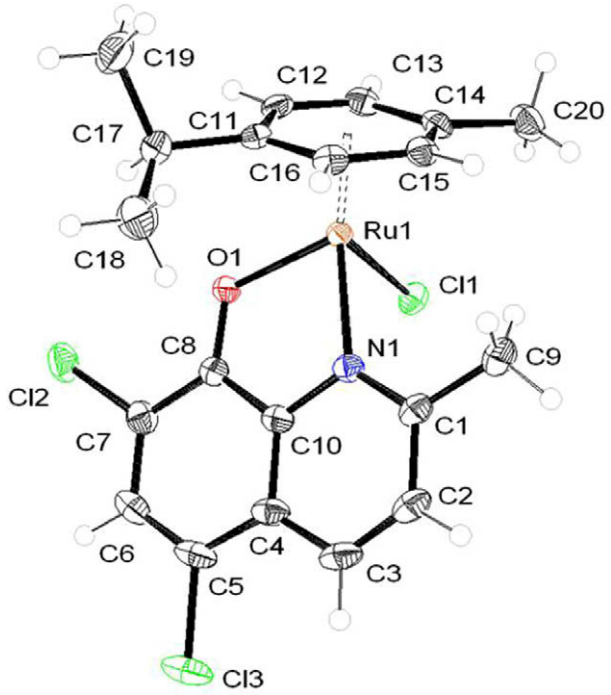


Fig. 1. Molecular structure of **5**.

Table 1
Selected bond lengths (Å) and angles (°) in **5**.

Interatomic distances		Bond angles	
Ru(1)–Cl(1)	2.4130(6)	N(1)–Ru(1)–O(1)	78.55(6)
Ru(1)–N(1)	2.1455(17)	N(1)–Ru(1)–Cl(1)	82.42(5)
Ru(1)–O(1)	2.0633(14)	O(1)–Ru(1)–Cl(1)	87.85(4)
Ru(1)–C(11)	2.175(2)		
Ru(1)–C(12)	2.172(2)		
Ru(1)–C(13)	2.185(2)		
Ru(1)–C(14)	2.215(2)		
Ru(1)–C(15)	2.203(2)		
Ru(1)-C(16)	2.164(2)		

comprises four cationic complexes, four tetrafluoroborate counteranions and a water molecule. The molecular structure of **15** is depicted in Fig. 5, crystallographic details are given in Table 8, and significant bond lengths and bond angles are listed in Table 5. In both cationic aqua complexes **12** and **15**, the ruthenium atom is coordinated to the η^6-$MeC_6H_4Pr^i$ ligand, to the oxygen atom and the nitrogen atom of the η^2-oxinato ligand, as well as to the oxygen atom of a water ligand, the coordination geometry of ruthenium being pseudo-tetrahedral. The Ru–N and Ru–O distances are also similar to those found in **1** [38].

2.4. Catalytic application of the η^2-oxinato complexes for the hydrogenation of carbon dioxide in aqueous solution

Based on the studies of Himeda [34], Ogo and Fukuzumi [35–37] on the use of the water-soluble arene ruthenium complexes containing bipyridine (bipy) as ligand for the hydrogenation of carbon dioxide to give formic acid in aqueous solution, we checked the catalytic potential of the η^2-oxinato complexes **1**, **4**, **9**, **10** and **12**[BF_4] for this reaction. They do indeed catalyze this reaction in alkaline aqueous solution to give formate, the highest activity being observed for **12**[BF_4] (Table 6).

$$CO_2 + H_2 \rightarrow HCOOH$$

The pH dependence of the catalytic activity of **12**[BF_4] was studied for the hydrogenation of carbon dioxide to give formic acid. Under acidic conditions, the reaction does not work, the catalytic activity is maximal for pH 14 (Table 7). The temperature dependence of the catalytic activity of **12**[BF_4] was also studied: the maximum turnover was obtained at 100 °C (Fig. 6). The kinetic plot shows that under these conditions the reaction is almost complete after 10 h when formic acid starts to decompose. The maximum turnover frequency (97 h^{-1}) was observed after 2 h (Fig. 7).

In accordance with observations by Ogo and Fukuzumi for (η^6-arene)Ru(bipyridine) complexes [35,36], we believe the catalytic cycle for carbon dioxide hydrogenation by (η^6-arene)Ru(oxinato) complexes to involve a hydrido complex formed *in situ* from the corresponding aqua or chloro complexes (Scheme 2). The hydrido complex may insert CO_2 to give the corresponding formyl complex, which will then react with hydroxide to give the formate anion and a hydroxo complex that can be converted with molecular hydrogen into the catalytically active hydrido complex, see Scheme 2.

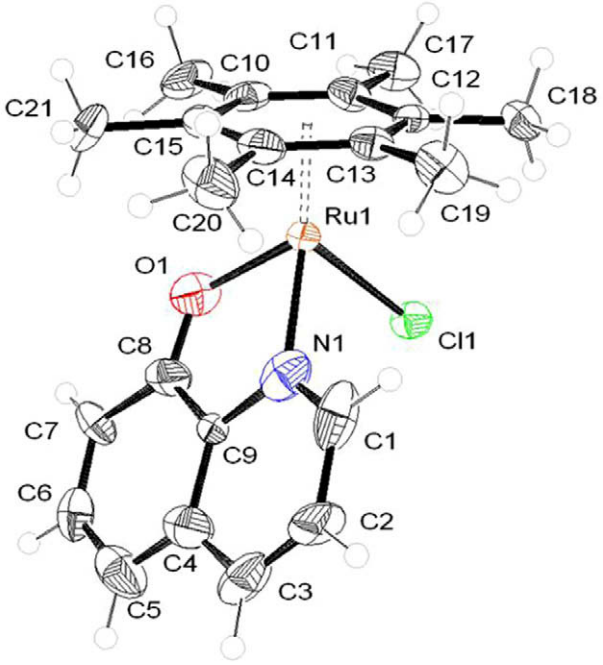


Fig. 2. Molecular structure of **6**.

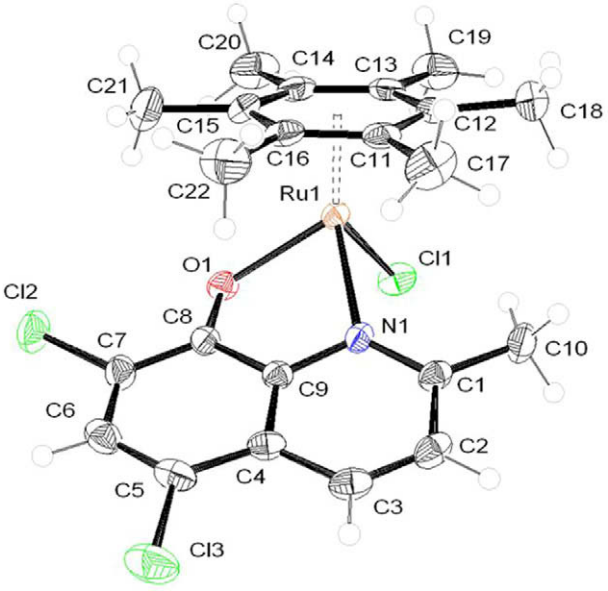


Fig. 3. Molecular structure of **11**.

Table 2
Selected bond lengths (Å) and angles (°) in **6**.

Interatomic distances		Bond angles	
Ru(1)–Cl(1)	2.4108(13)	N(1)–Ru(1)–O(1)	79.1(2)
Ru(1)–N(1)	2.088(5)	N(1)–Ru(1)–Cl(1)	83.31(13)
Ru(1)–O(1)	2.107(4)	O(1)–Ru(1)–Cl(1)	86.23(11)
Ru(1)–C(10)	2.190(5)		
Ru(1)–C(11)	2.214(5)		
Ru(1)–C(12)	2.210(4)		
Ru(1)–C(13)	2.226(5)		
Ru(1)–C(14)	2.185(6)		
Ru(1)–C(15)	2.181(6)		

Table 3
Selected bond lengths (Å) and angles (°) in **11**.

Interatomic distances		Bond angles	
Ru(1)–Cl(1)	2.4055(11)	N(1)–Ru(1)–O(1)	76.82(10)
Ru(1)–N(1)	2.139(3)	N(1)–Ru(1)–Cl(1)	87.40(8)
Ru(1)–O(1)	2.099(3)	O(1)–Ru(1)–Cl(1)	89.52(8)
Ru(1)–C(11)	2.182(4)		
Ru(1)–C(12)	2.246(4)		
Ru(1)–C(13)	2.216(4)		
Ru(1)–C(14)	2.189(4)		
Ru(1)–C(15)	2.197(4)		
Ru(1)–C(16)	2.189(4)		

The results obtained (Table 7) clearly demonstrate that it is in principle possible to regenerate the formate anion consumed in the catalytic regeneration of NADH in aqueous solution [13] by using the oxinato complex $[(\eta^6\text{-}MeC_6H_4Pr^i)Ru(\eta^2\text{-}NC_9H_6O)(OH_2)]^+$ (**12**). However, **12**$[BF_4]$ cannot simply be coupled to the $[(\eta^5\text{-}C_5Me_5)Rh(phen)(OH_2)]^{2+}$ (phen = *ortho*-phenanthroline) catalyst, since the latter one is active at pH 7, whereas **12**$[BF_4]$ requires pH 14 despite a much lower catalytic activity.

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 [40]. Complex $[(\eta^6\text{-}MeC_6H_4Pr^i)Ru(\eta^2\text{-}NC_9H_6O)Cl]$ (**1**) was synthesized according to the literature report [38]. All other reagents were commercially available and were used without further purification. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Electro-spray mass spectra were obtained in positive- or negative-ion mode with an LCQ Finnigan mass spectrometer. Microanalyses were carried out by the Mikroelementaranalytisches Laboratorium, ETH Zürich (Switzerland).

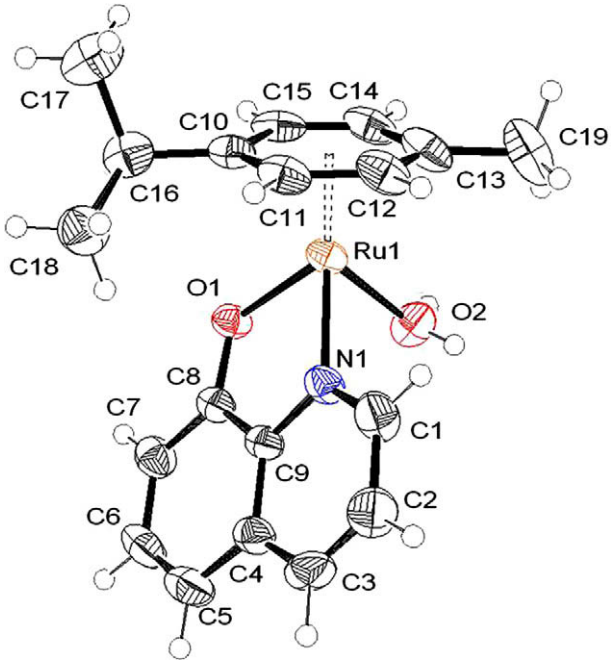


Fig. 4. Molecular structure of cation **12**.

Table 4
Selected bond lengths (Å) and angles (°) in **12**[BF_4].

Interatomic distances		Bond angles	
Ru(1)–O(1)	2.066(3)	N(1)–Ru(1)–O(1)	79.07(12)
Ru(1)–N(1)	2.085(3)	N(1)–Ru(1)–O(2)	82.14(14)
Ru(1)–O(2)	2.132(3)	O(1)–Ru(1)–O(2)	82.68(13)
Ru(1)–C(10)	2.152(4)		
Ru(1)–C(11)	2.145(4)		
Ru(1)–C(12)	2.172(4)		
Ru(1)–C(13)	2.191(4)		
Ru(1)–C(14)	2.174(4)		
Ru(1)–C(15)	2.168(4)		

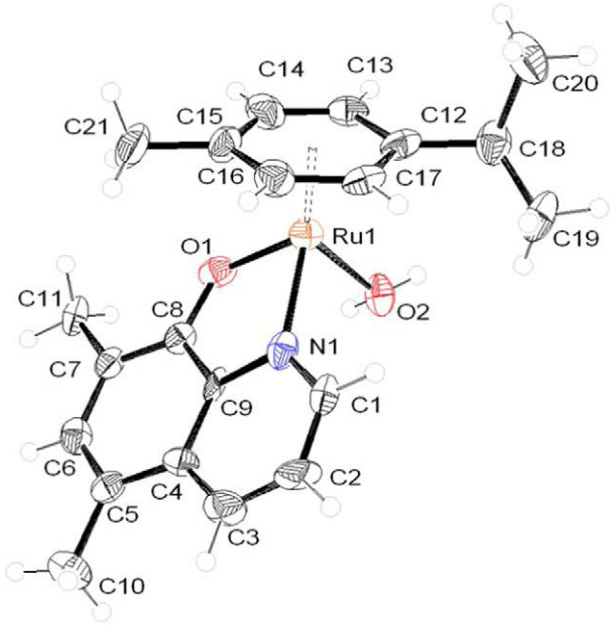


Fig. 5. Molecular structure of cation **15**.

Table 5
Selected bond lengths (Å) and angles (°) in **15**[BF_4].

Interatomic distances		Bond angles	
Ru(1)–O(1)	2.048(6)	N(1)–Ru(1)–O(1)	78.7(3)
Ru(1)–N(1)	2.063(7)	N(1)–Ru(1)–O(2)	84.6(2)
Ru(1)–O(2)	2.140(6)	O(1)–Ru(1)–O(2)	83.9(2)
Ru(1)–C(12)	2.210(9)		
Ru(1)–C(13)	2.188(8)		
Ru(1)–C(14)	2.151(10)		
Ru(1)–C(15)	2.146(10)		
Ru(1)–C(16)	2.134(10)		
Ru(1)–C(17)	2.167(9)		

3.2. General procedure for the synthesis of complex [(η^6-$MeC_6H_4Pr^i$)Ru(η^2-N,O-L)Cl] (**2**–**5**)

The potassium oxinates KL (L = $NC_9H_4Cl_2O$, NC_9H_5ClO, $NC_9H_5(NO_2)O$, $NC_9H_3MeCl_2O$) have been synthesized by adding KOH to a solution of the oxine in ethanol; after filtration the solution was reduced to dryness [38]. To a solution of [(η^6-$MeC_6H_4Pr^i$)$RuCl_2$]$_2$ (50 mg, 0.082 mmol) in THF (8 mL), 2 equiv. of solid KL (L = $NC_9H_4Cl_2O$, NC_9H_5ClO, $NC_9H_5(NO_2)O$, $NC_9H_3MeCl_2O$) (0.163 mmol) was added and the reaction mixture stirred for 2 h at room temperature. When the volume was reduced to 2 mL under high vacuum, an orange precipitate formed. Then the precipitation was completed by addition of diethyl ether (5 mL). The solid was isolated by decanting and dissolved in dichloromethane (5 mL). The solution was filtered and then concentrated to 1 mL. Upon addition of diethyl ether an orange precipitate formed, which was isolated by decanting and washed with Et_2O (3 × 2 mL). The product was purified by column on silica gel (CH_2Cl_2:acetone from 97:3 to 80:20) and dried *in vacuo*.

Table 6
Hydrogenation of carbon dioxide to give formic acid (as formate) using **1**, **4**, **9**, **10** and **12**[BF_4] as catalyst precursors in aqueous solution.[a]

Catalyst	TON[b,c]	Yield (mmol)
1	77	0.185
4	60	0.123
9	94	0.204
10	122	0.260
12[BF_4]	128	0.264

[a] Conditions: 50 mL reaction vessel, 20 mL KOH 1 M, 2 μmol catalyst, 20 bar H_2, 20 bar CO_2, 20 h at 80 °C.
[b] Turnover number = mol of product (formate)/mol of catalyst. TON is a unitless parameter.
[c] Determined by ^{1}H NMR measurement of the resulting solution with TSP (3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt) in D_2O as the reference and the internal standard.

Table 7
pH dependence for the hydrogenation of carbon dioxide of **12**[BF_4] in aqueous solution.[a]

pH	TON[b,c]	Yield (mmol)
3	0	0
9	3	0.007
14 (KOH 1 M)	128	0.264

[a] Conditions: 50 mL reaction vessel, 20 mL aqueous solution with pH desired, 2 μmol catalyst, 20 bar H_2, 20 bar CO_2, 20 h at 80 °C.
[b] Turnover number = mol of product (formate)/mol of catalyst. TON is a unitless parameter.
[c] Determined by ^{1}H NMR measurement of the resulting solution with TSP (3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt) in D_2O as the reference and the internal standard.

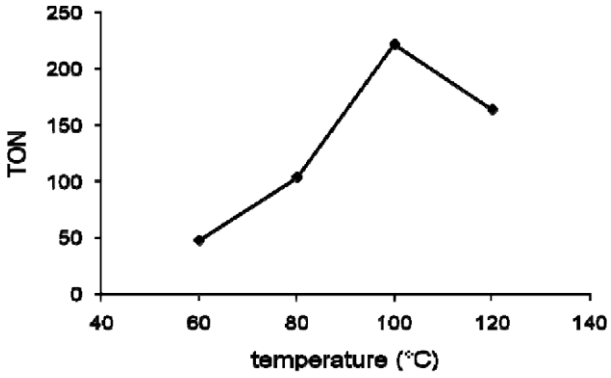


Fig. 6. Temperature-dependence of TON for the hydrogenation of carbon dioxide catalyzed by **12**[BF_4] in aqueous solution. (Conditions: 2 μmol catalyst, 25 bar of H_2, 25 bar of CO_2, 50 mL reaction vessel, 20 mL aqueous Et_3N solution (0.25 M) at the desired temperature, the reaction was stirred for 20 h.)

3.2.1. [(η^6-$MeC_6H_4Pr^i$)Ru(η^2-$NC_9H_4Cl_2O$)Cl]: (**2**) yield: 72% (56.7 mg)

Anal. Calc. for $C_{19}H_{18}NOCl_3Ru$: C, 47.17; H, 3.75; N, 2.90. Found: C, 47.51; H, 3.88; N, 2.91%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.14 (d, J = 8 Hz, 3H, CH-(CH_3)$_2$), 1.22 (d, J = 8 Hz, 3H, CH-(CH_3)$_2$), 2.33 (s, 3H, CH_3), 2.84 (m, 1H, CH-(CH_3)$_2$), 5.36 (d, J = 8 Hz, 1H, C_6H_4),

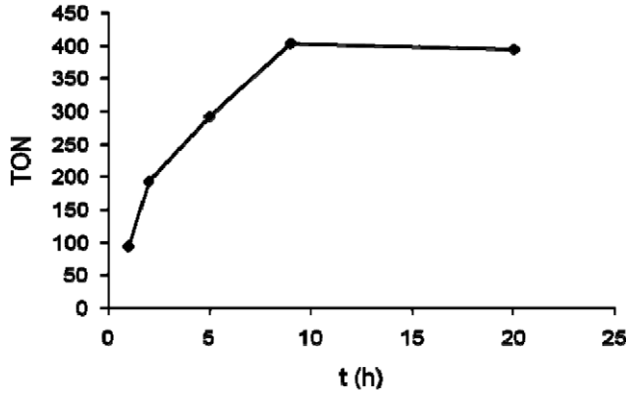


Fig. 7. Time-dependence of TON for the hydrogenation of carbon dioxide catalyzed by **12**[BF_4] in aqueous solution. (Conditions: 2 μmol catalyst, 50 bar of H_2, 50 bar of CO_2, 50 mL reaction vessel, 20 mL aqueous Et_3N solution (0.25 M) at 100 °C, the reaction was stirred for desired time.)

5.46 (m, 2H, C_6H_4), 5.68 (d, J = 8 Hz, 1H, C_6H_4), 7.43 (m, 1H, C_9H_4), 7.51 (s, 1H, C_9H_4), 8.36 (d, J = 8 Hz, C_9H_4), 8.96 (d, J = 4 Hz, C_9H_4). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 18.77 (CH_3), 22.27 (1C, CH-(CH_3)$_2$), 22.45 (1C, CH-(CH_3)$_2$), 31.15 (1C, CH-(CH_3)$_2$), 80.57 (1CH, C_6H_4), 81.92 (1CH, C_6H_4), 82.08 (1CH, C_6H_4), 82.75 (1CH, C_6H_4), 98.90 (1C, C_6H_4), 101.76 (1C, C_9H_4), 112.14 (CH, C_9H_4), 118.75 (1C, C_9H_4), 122.53 (1CH, C_9H_4), 126.38 (1C, C_9H_4), 130.21 (1CH, C_9H_4), 135.14 (1CH, C_9H_4), 144.76 (1C, C_9H_4), 149.77 (1CH, C_9H_4), 163.16 (1C, C_9H_4). MS (ESI) m/z = 448 [M−Cl]$^+$.

*3.2.2. [(η^6-$MeC_6H_4Pr^i$)Ru(η^2-NC_9H_5ClO)Cl]: (**3**) yield: 74% (54.2 mg)*

Anal. Calc. for $C_{19}H_{19}NOCl_2Ru$: C, 50.79; H, 4.26; N, 3.12. Found: C, 50.93; H, 4.45; N, 3.09%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.16 (d, J = 4 Hz, 6 H, CH-(CH_3)$_2$), 2.31 (s, 3 H, CH_3), 2.78 (m, 1H, CH-(CH_3)$_2$), 5.31 (d, J = 4 Hz, 1H, C_6H_4), 5.43 (d, J = 4 Hz, 1H, C_6H_4), 5.49 (d, J = 4 Hz, 1H, C_6H_4), 5.60 (d, J = 4 Hz, 1H, C_6H_4), 6.92 (d, J = 8 Hz, 1H, C_9H_5), 7.36 (d, J = 8 Hz, 1H, C_9H_5), 7.44 (m, 1H, C_9H_5), 8.38 (d, J = 8 Hz, 1H, C_9H_5), 8.94 (d, J = 4 Hz, C_9H_5). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 18.85 (CH_3), 22.23 (CH-(CH_3)$_2$), 22.57 (CH-(CH_3)$_2$), 31.12 (CH-(CH_3)$_2$), 80.80 (1CH, C_6H_4), 81.32 (1CH, C_6H_4), 82.00 (1CH, C_6H_4), 82.80 (1CH, C_6H_4), 99.10 (1C, C_6H_4), 101.57 (1C, C_6H_4), 112.39 (1C, C_9H_5), 114.62 (1CH, C_9H_5), 122.68 (1CH, C_9H_5), 127.47 (1C, C_9H_5), 130.04 (1CH, C_9H_5), 134.99 (1CH, C_9H_5), 144.83 (1C, C_9H_5), 148.86 (1CH, C_9H_5), 168.04 (1C, C_9H_5). MS (ESI) m/z = 414 [M−Cl]$^+$.

*3.2.3. [(η^6-$MeC_6H_4Pr^i$)Ru(η^2-$NC_9H_5(NO_2)O$)Cl]: (**4**) yield: 67% (50.3 mg)*

Anal. Calc. for $C_{19}H_{19}N_2O_3ClRu$: C, 49.62; H, 4.16; N, 6.09. Found: C, 50.09; H, 4.37; N, 5.85%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.21 (d, J = 8 Hz, 6 H, CH-(CH_3)$_2$), 2.33 (s, 3H, CH_3), 2.82 (m, 1H, CH-(CH_3)$_2$), 5.38 (d, J = 4 Hz, 1H, C_6H_4), 5.49 (d, J = 4 Hz, 1H, C_6H_4), 5.56 (d, J = 4 Hz, 1H, C_6H_4), 5.66 (d, J = 4 Hz, 1H, C_6H_4), 6.89 (d, J = 8 Hz, 1H, C_9H_5), 7.62 (m, 1H, C_9H_5), 8.54 (d, J = 8 Hz, 1H, C_9H_5), 9.00 (d, J = 4 Hz, 1H, C_9H_5), 9.50 (d, J = 8 Hz, 1H, C_9H_5). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 18.87 (CH_3), 22.31 (CH-(CH_3)$_2$), 22.47 (CH-(CH_3)$_2$), 31.22 (CH-(CH_3)$_2$), 80.90 (1CH, C_6H_4), 81.96 (1CH, C_6H_4), 82.55 (1CH, C_6H_4), 82.85 (1CH, C_6H_4), 99.39 (1C, C_6H_4), 102.53 (1C, C_6H_4), 113.58 (1CH, C_9H_5), 125.70 (1CH, C_9H_5), 126.07 (1C, C_9H_5), 129.24 (1C, C_9H_5), 132.34 (1CH, C_9H_5), 135.95 (1CH, C_9H_5), 143.38 (1C, C_9H_5), 149.61 (1CH, C_9H_5), 176.85 (1C, C_9H_5). MS (ESI) m/z = 425 [M−Cl]$^+$.

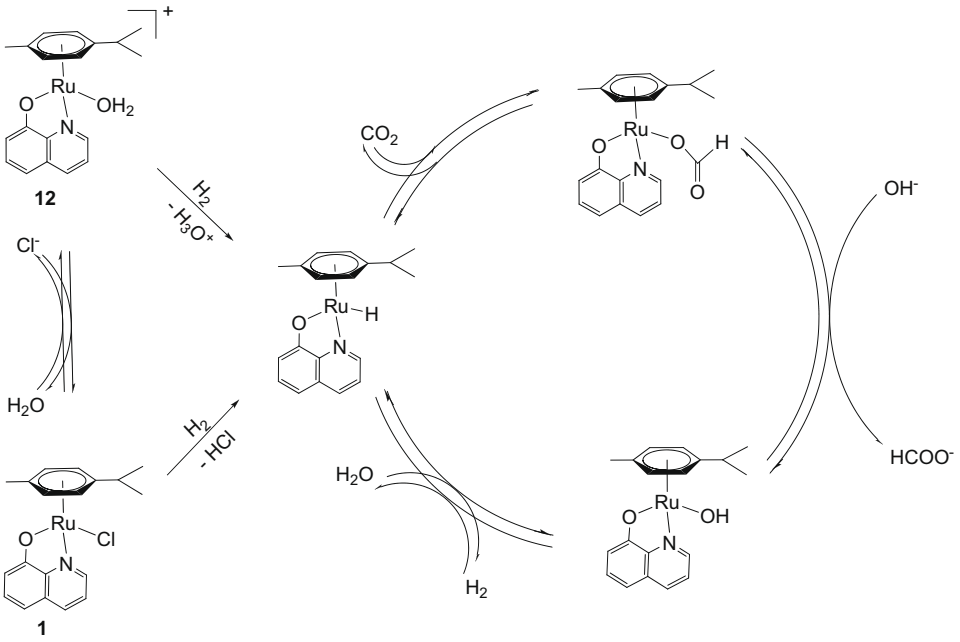
*3.2.4. [(η^6-$MeC_6H_4Pr^i$)Ru(η^2-$NC_9H_3MeCl_2O$)Cl]: (**5**) yield: 76% (61.4 mg)*

Anal. Calc. for $C_{20}H_{20}NOCl_3Ru$: C, 48.25; H, 4.05; N, 2.81. Found: C, 48.45; H, 4.02; N, 2.81%. ^1H NMR (400 MHz, CD_2Cl_2): δ 0.95 (d, J = 8 Hz, 3H, CH-(CH_3)$_2$), 1.11 (d, J = 4 Hz, 3H, CH-(CH_3)$_2$), 2.29 (s, 3H, CH_3), 2.62 (m, 1H, CH-(CH_3)$_2$), 3.16 (s, 3H, CH_3), 5.27 (d, J = 4 Hz, 1H, C_6H_4), 5.54 (m, 2H, C_6H_4), 5.70 (d, J = 4 Hz, 1H, C_6H_4), 7.40 (s, 1H, C_9H_3), 7.42 (d, J = 8 Hz, 1H, C_9H_3), 8.23 (d, J = 8 Hz, 1H, C_9H_3). ^{13}C {^1H} NMR (100 MHz, CD_2Cl_2): δ 18.67 (CH_3), 21.75 (1C, CH-(CH_3)$_2$), 22.05 (1C, CH-(CH_3)$_2$), 28.66 (Me), 30.99 (CH-(CH_3)$_2$), 79.56 (1CH, C_6H_4), 79.72 (1CH, C_6H_4), 80.74 (1CH, C_6H_4), 86.34 (1CH, C_6H_4), 100.47 (1C, C_6H_4), 101.90 (1C, C_6H_4), 111.80 (1C, C_9H_3), 118.33 (1C, C_9H_3), 124.18 (1CH, C_9H_3), 124.59 (1C,

Table 8
Crystallographic and structure refinement parameters for complexes **5**, **6**, **11**, **12**[BF_4] and **15**[BF_4]·0.25H_2O.

	5	**6**	**11**	**12**[BF_4]	**15**[BF_4]·0.25H_2O
Chemical formula	$C_{20}H_{20}Cl_3NORu$	$C_{21}H_{24}ClNORu$	$C_{22}H_{24}Cl_3NORu$	$C_{19}H_{22}BF_4NO_2Ru$	$C_{21}H_{26.5}BF_4NO_{2.25}Ru$
Formula weight	497.79	442.93	525.84	484.26	516.81
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/a$ (no. 14)	$Pcab$ (no. 61)	$P\bar{1}$ (no. 2)
Crystal color and shape	Orange block	Orange block	Orange block	Red plate	Orange block
Crystal size	0.27 × 0.22 × 0.19	0.25 × 0.22 × 0.16	0.16 × 0.14 × 0.11	0.20 × 0.18 × 0.17	0.25 × 0.22 × 0.17
a (Å)	14.513(1)	13.936(2)	14.399(2)	14.3671(9)	9.8825(7)
b (Å)	8.1149(6)	7.7228(7)	9.0695(10)	16.1713(8)	19.9322(15)
c (Å)	16.678(1)	17.189(2)	16.991(3)	16.8419(9)	23.578(2)
α (°)	90	90	90	90	74.572(9)
β (°)	102.190(9)	96.086(15)	114.650(15)	90	80.207(9)
γ (°)	90	90	90	90	85.036(9)
V (Å^3)	1919.9(3)	1839.6(3)	2016.7(5)	3913.0(4)	4407.6(6)
Z	4	4	4	8	8
T (K)	203(2)	203(2)	203(2)	203(2)	203(2)
D_c (g cm^{-3})	1.722	1.599	1.732	1.644	1.558
μ (mm^{-1})	1.244	1.006	1.189	0.852	0.763
Scan range (°)	2.05 < θ < 26.05	2.38 < θ < 26.08	2.60 < θ < 26.07	2.25 < θ < 29.31	2.08 < θ < 26.08
Unique reflections	3754	3607	3919	5315	15 849
Reflections used [$I > 2\sigma(I)$]	3118	1775	2643	3049	5579
R_{int}	0.0294	0.1102	0.0679	0.1471	0.1389
Final R indices [$I > 2\sigma(I)$][a]	0.0217, wR_2 0.0507	0.0405, wR_2 0.0610	0.0352, wR_2 0.0698	0.0495, wR_2 0.0907	0.0529, wR_2 0.0958
R indices (all data)	0.1090, wR_2 0.0691	0.0599, wR_2 0.0741	0.1093, wR_2 0.1044	0.1591, wR_2 0.1096	0.0292, wR_2 0.0521
Goodness-of-fit	0.948	0.703	0.906	0.911	0.734
Max, Min $\Delta\rho/e$ (Å^{-3})	0.721, −0.717	0.732, −0.672	0.943, −1.226	0.787, −0.742	0.542, −0.642

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



Scheme 2. Postulated catalytic cycle for the hydrogenation of carbon dioxide in water using a 8-hydroxyquinoline complex under basic conditions.

C_9H_3), 128.55 (1CH, C_9H_3), 134.74 (1CH, C_9H_3), 144.54 (1C, C_9H_3), 160.19 (1C, C_9H_3), 162.79 (1C, C_9H_3). MS (ESI) m/z = 462 $[M-Cl]^+$.

3.3. General procedure for the synthesis of complex [(η^6-C_6Me_6)Ru(η^2-N,O-L)Cl] (**6**–**11**)

The sodium oxinates NaL (L = NC_9H_6O, $NC_9H_4Cl_2O$, NC_9H_5ClO, $NC_9H_5(NO_2)O$, $NC_9H_4Me_2O$, $NC_9H_3MeCl_2O$) have been synthesized by adding MeONa to a solution of the oxine LH in methanol; after filtration the solution was reduced to dryness [38]. To a solution of $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ (55 mg, 0.082 mmol) in chloroform (10 mL), 2 equiv. of solid NaL (0.163 mmol) was added and the reaction mixture was heated under reflux for 2 h. The solution was cooled to room temperature and then the solvent was reduced to 1 mL, precipitation was completed by addition of Et_2O, the solid was washed by Et_2O (2 × 2 mL) and dried under vacuum. The product was purified by the column on silica gel (CH_2Cl_2:acetone from 95:5 to 80:20) and dried *in vacuo*.

3.3.1. [(η^6-C_6Me_6)Ru(η^2-NC_9H_6O)Cl]: (**6**) yield: 74% (53.4 mg)

Anal. Calc. for $C_{21}H_{24}NOClRu$: C, 56.94; H, 5.46; N, 3.16. Found: C, 56.70; H, 5.62; N, 3.01%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13 (s, 18H, $C_6(CH_3)_6$), 6.74 (d, J = 8 Hz, 1H, C_9H_6), 6.99 (d, J = 8 Hz, 1H, C_9H_6), 7.28 (d, J = 4 Hz, 1H, C_9H_6), 7.30 (d, J = 4 Hz, 1H, C_9H_6), 7.98 (d, J = 8 Hz, 1H, C_9H_6), 8.59 (d, J = 4 Hz, 1H, C_9H_6). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.63 (6C, $C_6(CH_3)_6$), 91.53 (6C, $C_6(CH_3)_6$), 109.84 (1CH, C_9H_6), 115.13 (1CH, C_9H_6), 121.73 (1CH, C_9H_6), 130.27 (1CH, C_9H_6), 130.47 (1C, C_9H_6), 137.18 (1CH, C_9H_6), 145.76 (1C, C_9H_6), 146.61 (1CH, C_9H_6), 168.27 (1C, C_9H_6). MS (ESI) m/z = 407 $[M-Cl]^+$.

3.3.2. [(η^6-C_6Me_6)Ru(η^2-$NC_9H_4Cl_2O$)Cl]: (**7**) yield: 72% (59.7 mg)

Anal. Calc. for $C_{21}H_{22}NOCl_3Ru$: C, 49.28; H, 4.33; N, 2.74. Found: C, 48.85; H, 4.53; N, 2.61%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.11 (s, 18H, $C_6(CH_3)_6$), 7.47 (s, 1H, C_9H_4), 7.48 (t, J = 4 Hz, J = 8 Hz, 1H, C_9H_4), 8.31 (d, J = 8 Hz, 1H, C_9H_4), 8.66 (d, J = 4 Hz, 1H, C_9H_4). ^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2): δ 15.25 (6C, $C_6(CH_3)_6$), 91.73 (6C, $C_6(CH_3)_6$), 111.01 (1C, C_9H_4), 117.57 (1C, C_9H_4), 122.55 (1CH, C_9H_4), 126.36 (1C, C_9H_4), 129.53 (1CH, C_9H_4), 134.34 (1CH, C_9H_4), 145.68 (1C, C_9H_4), 148.13 (1CH, C_9H_4), 162.46 (1C, C_9H_4). MS (ESI) m/z = 476 $[M-Cl]^+$.

3.3.3. [(η^6-C_6Me_6)Ru(η^2-NC_9H_5ClO)Cl]: (**8**) yield: 50% (38.5 mg)

Anal. Calc. for $C_{23}H_{28}NOClRu$: C, 52.83; H, 4.86, N, 2.93. Found: C, 52.91; H, 4.97; N, 2.88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13 (s, 18H, $C_6(CH_3)_6$), 6.90 (d, J = 8 Hz, 1H, C_9H_5), 7.32 (d, J = 8 Hz, 1H, C_9H_5), 7.43 (t, J = 4 Hz, J = 8 Hz, 1H, C_9H_5), 8.31 (d, J = 8 Hz, 1H, C_9H_5), 8.63 (d, J = 4 Hz, 1H, C_9H_5). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.64 (6C, $C_6(CH_3)_6$), 91.67 (6C, $C_6(CH_3)_6$), 111.60 (1C, C_9H_5), 114.55 (1CH, C_9H_5), 122.47 (1CH, C_9H_5), 127.55 (1C, C_9H_5), 129.87 (1CH, C_9H_5), 134.43 (1CH, C_9H_5), 146.03 (1C, C_9H_5), 146.96 (1CH, C_9H_5), 167.61 (1C, C_9H_5). MS (ESI) m/z = 442 $[M-Cl]^+$.

3.3.4. [(η^6-C_6Me_6)Ru(η^2-$NC_9H_5(NO_2)O$)Cl]: (**9**) yield: 65% (51.7 mg)

Anal. Calc. for $C_{21}H_{23}N_2O_3ClRu$: C, 51.69; H, 4.75; N, 5.74. Found: C, 51.52; H, 4.87; N, 5.45%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.12 (s, 18H, $C_6(CH_3)_6$), 6.79 (d, J = 8 Hz, 1H, C_9H_5), 7.65 (m, 1H, C_9H_5), 8.47 (d, J = 8 Hz, 1H, C_9H_5), 8.69 (d, J = 4 Hz, 1H, C_9H_5), 9.41 (d, J = 8 Hz, 1H, C_9H_5). ^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2): δ 15.39 (6C, $C_6(CH_3)_6$), 92.15 (6C, $C_6(CH_3)_6$), 112.85 (1CH, C_9H_5), 125.63 (1CH, C_9H_5), 126.18 (1C, C_9H_5), 128.52 (1C, C_9H_5), 131.94 (1CH, C_9H_5), 134.95 (1CH, C_9H_5), 144.40 (1C, C_9H_5), 147.78 (1CH, C_9H_5), 176.51 (1C, C_9H_5). MS (ESI) m/z = 453 $[M-Cl]^+$.

3.3.5. [(η^6-C_6Me_6)Ru(η^2-$NC_9H_4Me_2O$)Cl]: (**10**) yield: 80% (62 mg)

Anal. Calc. for $C_{23}H_{28}NOClRu$: C, 58.65; H, 5.99, N, 2.97. Found: C, 58.41; H, 6.06; N, 2.84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.10 (s, 18H, $C_6(CH_3)_6$), 2.44 (s, 6 H, 2Me), 7.07 (s, 1H, C_9H_4), 7.27 (t, J = 4 Hz, J = 8 Hz, 1H, C_9H_4), 8.05 (d, J = 8 Hz, 1H, C_9H_4), 8.59 (d, J = 4 Hz, 1H, C_9H_4). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 15.23 ($C_6(CH_3)_6$), 16.04 (1C, Me), 16.83 (1C, Me), 91.15 (6C, $C_6(CH_3)_6$), 115.34 (1C, C_9H_4), 120.01 (1CH, C_9H_4), 123.30 (1C, C_9H_4), 126.93 (1C, C_9H_4), 132.50 (1CH, C_9H_4), 133.78 (1CH, C_9H_4), 144.58 (1C, C_9H_4), 146.14 (1CH, C_9H_4), 163.58 (1C, C_9H_4). MS (ESI) m/z = 436 $[M-Cl]^+$.

*3.3.6. [(η^6-C_6Me_6)Ru(η^2-$NC_9H_3MeCl_2O$)Cl]: (**11**) yield: 85% (72.5 mg)*

Anal. Calc. for $C_{22}H_{24}NOCl_3Ru$: C, 50.25; H, 4.60; N, 2.66. Found: C, 50.45; H, 4.67; N, 2.65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 18H, $C_6(CH_3)_6$), 3.08 (s, 3H, CH_3), 7.32 (d, J = 8 Hz, 1H, C_9H_3), 7.39 (s, 1H, C_9H_3), 8.16 (d, J = 8 Hz, C_9H_3). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 16.02 (6C, $C_6(CH_3)_6$), 27.99 (1C, Me), 91.76 (6C, $C_6(CH_3)_6$), 111.37 (1C, C_9H_3), 119.26 (1C, C_9H_3), 123.58 (1CH, C_9H_3), 124.57 (1C, C_9H_3), 128.50 (1CH, C_9H_3), 134.36 (1CH, C_9H_3), 145.69 (1C, C_9H_3), 160.33 (1C, C_9H_3), 162.55 (1C, C_9H_3). MS (ESI) m/z = 490 [M−Cl]$^+$.

*3.4. Preparation of the aqua complexes [(η^6-arene)Ru(η^2-N,O-L)(OH_2)][BF_4] (**12**[BF_4]–**19**[BF_4])*

A mixture of [(η^6-arene)$RuCl_2$]$_2$ (0.082 mmol) and 2 equiv. of silver sulfate (0.163 mmol) in water (10 mL) was stirred for 2 h in the dark at room temperature. After this time, the yellow solution was filtered and then added the neat oxine LH (L = NC_9H_6O, $NC_9H_4Cl_2O$, NC_9H_5ClO, $NC_9H_5(NO_2)O$, $NC_9H_4Me_2O$, $NC_9H_3MeCl_2O$) (0.163 mmol). Then the solution was again stirred for 2 h in the dark at room temperature, during this time the color changed from yellow to orange or red. The product was precipitated by adding a saturated aqueous solution of $NaBF_4$. The tetrafluoroborate salt was obtained by crystallization from water as orange-red crystals.

*3.4.1. [(η^6-$MeC_6H_4Pr^i$)Ru(η^2-NC_9H_6O)(OH_2)][BF_4]: **12**[BF_4] yield: 89% (71 mg)*

Anal. Calc. for $C_{19}H_{22}BF_4NO_2Ru$: C, 47.12; H, 4.58; N, 2.89. Found: C, 47.32; H, 4.74; N, 2.95%. ^{1}H NMR (400 MHz, D_2O): δ 0.98 (d, J = 8 Hz, 6 H, CH-(CH_3)$_2$), 2.17 (s, 3H, CH_3), 2.59 (m, 1H, CH-(CH_3)$_2$), 5.74 (d, J = 8 Hz, 2H, C_6H_4), 5.95 (d, J = 8 Hz, 2H, C_6H_4), 7.03 (d, J = 8 Hz, 1H, C_9H_6), 7.16 (d, J = 8 Hz, 1H, C_9H_6), 7.44 (t, 1H, C_9H_6), 7.63 (t, 1H, C_9H_6), 8.40 (d, J = 8 Hz, 1H, C_9H_6), 8.49 (d, J = 4 Hz, 1H, C_9H_6). ^{13}C {^{1}H} NMR (100 MHz, D_2O): δ 17.77 (CH_3), 21.30 (2C, CH-(CH_3)$_2$), 30.61 (1C, CH-(CH_3)$_2$), 79.98 (2CH, C_6H_4), 82.75 (2CH, C_6H_4), 98.16 (1C, C_6H_4), 100.05 (1C, C_6H_4), 114.11 (1CH, C_9H_6), 114.60 (1CH, C_9H_6), 123.23 (1CH, C_9H_6), 130.04 (1CH, C_9H_6), 130.21 (1C, C_9H_6), 139.56 (1CH, C_9H_6), 142.55 (1C, C_9H_6), 151.95 (1CH, C_9H_6), 164.98 (1C, C_9H_6). MS (ESI) m/z = 380 [M−BF_4−H_2O]$^+$.

*3.4.2. [(η^6-$MeC_6H_4Pr^i$)Ru(η^2-$NC_9H_3MeCl_2O$)(OH_2)][BF_4]: **13**[BF_4] yield: 83% (74.6 mg)*

Anal. Calc. for $C_{20}H_{22}BCl_2F_4NO_2Ru$: C, 42.35; H, 3.91; N, 2.4. Found: C, 42.57; H, 3.72; N, 2.57%. ^{1}H NMR (400 MHz, D_2O): δ 0.90 (d, J = 4 Hz, 6 H, CH-(CH_3)$_2$), 2.24 (s, 3H, CH_3), 2.41 (m, 1H, CH-(CH_3)$_2$), 3.34 (s, 3H, CH_3), 5.86 (d, J = 4 Hz, 2H, C_6H_4), 6.08 (d, J = 8 Hz, 2H, C_6H_4), 7.61 (s, 1H, C_9H_3), 7.71 (d, J = 8 Hz, 1H, C_9H_3), 8.49 (d, J = 8 Hz, 1H, C_9H_3). ^{13}C {^{1}H} NMR (100 MHz, D_2O): δ 17.77 (1CH, CH_3), 21.08 (2CH, CH-(CH_3)$_2$), 28.57 (1CH, CH_3), 30.37 (1CH, CH-(CH_3)$_2$), 79.33 (2CH, C_6H_4), 81.67 (1CH, C_6H_4), 85.99 (1CH, C_6H_4), 96.80 (1C, C_6H_4), 101.53 (1C, C_6H_4), 115.39 (1C, C_9H_3), 118.61 (1C, C_9H_3), 124.59 (1C, C_9H_3), 125.12 (1CH, C_9H_3), 128.33 (1CH, C_9H_3), 136.22 (1CH, C_9H_3), 143.93 (1C, C_9H_3), 160.31 (1C, C_9H_3), 163.72 (1C, C_9H_3). MS (ESI) m/z = 462 [M−BF_4−H_2O]$^+$.

*3.4.3. [(η^6-$MeC_6H_4Pr^i$)Ru(η^2-NC_9H_5ClO)(OH_2)][BF_4]: **14**[BF_4] yield: 75% (63.5 mg)*

Anal. Calc. for $C_{19}H_{21}BClF_4NO_2Ru$: C, 43.99; H, 4.08; N, 2.70. Found: C, 43.74; H, 4.25; N, 2.79%. ^{1}H NMR (400 MHz, D_2O): δ 1.01 (d, J = 4 Hz, 6 H, CH-(CH_3)$_2$), 2.19 (s, 3H, CH_3), 2.61 (m, 1H, CH-(CH_3)$_2$), 5.77 (d, J = 4 Hz, 2H, C_6H_4), 5.98 (d, J = 8 Hz, 2H, C_6H_4), 6.97 (d, J = 8 Hz, 1H, C_9H_5), 7.51 (d, J = 8 Hz, 1H, C_9H_5), 7.77 (m, 1H, C_9H_5), 8.65 (d, J = 8 Hz, 1H, C_9H_5), 9.57 (d, J = 4 Hz, 1H, C_9H_5). ^{13}C {^{1}H} NMR (100 MHz, D_2O): δ 17.64 (CH_3), 21.17 (2C, CH-(CH_3)$_2$), 30.49 (1C, CH-(CH_3)$_2$), 79.88 (2CH, C_6H_4), 82.76 (2CH, C_6H_4), 98.30 (1C, C_6H_4), 100.06 (1C, C_6H_4), 114.04 (1CH, C_9H_5), 115.41 (1C, C_9H_5), 123.81 (1CH, C_9H_5), 127.21 (1C, C_9H_5), 129.42 (1CH, C_9H_5), 136.34 (1CH, C_9H_5), 143.04 (1C, C_9H_5), 152.32 (1CH, C_9H_5), 164.56 (1C, C_9H_5). MS (ESI) m/z = 414 [M−BF_4−H_2O]$^+$.

*3.4.4. [(η^6-$MeC_6H_4Pr^i$)Ru(η^2-$NC_9H_4Me_2O$)(OH_2)][BF_4]: **15**[BF_4] yield: 99% (83.1 mg)*

Anal. Calc. for **15**[BF_4]·H_2O, $C_{21}H_{28}BF_4NO_3Ru$: C, 47.56; H, 5.32; N, 2.64. Found: C, 47.82; H, 5.30; N, 2.72%. ^{1}H NMR (400 MHz, D_2O): δ 0.98 (d, J = 4 Hz, 6 H, CH-(CH_3)$_2$), 2.21 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 5.75 (d, J = 8 Hz, 2H, C_6H_4), 5.95 (d, J = 8 Hz, 2H, C_6H_4), 7.24 (s, 1H, C_9H_4), 7.61 (m, 1H, C_9H_4), 8.49 (d, J = 8 Hz, 1H, C_9H_4), 9.50 (d, J = 4 Hz, 1H, C_9H_4). ^{13}C {^{1}H} NMR (100 MHz, D_2O): δ 15.71 (CH_3), 16.08 (CH_3), 17.79 (CH_3), 21.24 (2C, CH-(CH_3)$_2$), 30.56 (CH-(CH_3)$_2$), 80.33 (2CH, C_6H_4), 82.74 (2CH, C_6H_4), 97.54 (1C, C_6H_4), 100.09 (1C, C_6H_4), 120.97 (1C, C_9H_4), 121.58 (1CH, C_9H_4), 124.37 (1C, C_9H_4), 127.29 (1C, C_9H_4), 132.48 (1CH, C_9H_4), 136.53 (1CH, C_9H_4), 142.51 (1C, C_9H_4), 151.51 (1CH, C_9H_4), 160.80 (1C, C_9H_4). MS (ESI) m/z = 408 [M−BF_4−H_2O]$^+$.

*3.4.5. [(η^6-C_6Me_6)Ru(η^2-NC_9H_6O)(OH_2)][BF_4]: **16**[BF_4] yield: 73% (61 mg)*

Anal. Calc. for $C_{21}H_{26}BF_4NO_2Ru$: C, 49.23; H, 5.12; N, 2.73. Found: C, 49.19; H, 5.00; N, 2.86%. ^{1}H NMR (400 MHz, D_2O): δ 2.12 (s, 18H, $C_6(CH_3)_6$), 7.01 (d, J = 8 Hz, 1H, C_9H_6), 7.07 (d, J = 8 Hz, 1H, C_9H_6), 7.40 (t, 1H, C_9H_6), 7.63 (m, 1H, C_9H_6), 8.32 (d, J = 8 Hz, 1H, C_9H_6), 9.09 (d, J = 4 Hz, 1H, C_9H_6). ^{13}C {^{1}H} NMR (100 MHz, D_2O): δ 14.93 (6CH, $C_6(CH_3)_6$), 91.68 (6C, $C_6(CH_3)_6$), 113.33 (1CH, C_9H_6), 114.20 (1CH, C_9H_6), 123.01 (1CH, C_9H_6), 129.96 (1C, C_9H_6), 130.18 (1CH, C_9H_6), 138.96 (1CH, C_9H_6), 143.78 (1C, C_9H_6), 150.05 (1CH, C_9H_6), 165.01 (1C, C_9H_6). MS (ESI) m/z = 408 [M−BF_4−H_2O]$^+$.

*3.4.6. [(η^6-C_6Me_6)Ru(η^2-$NC_9H_3Cl_2MeO$)(OH_2)][BF_4]: **17**[BF_4] yield: 90% (88 mg)*

Anal. Calc. for $C_{22}H_{26}BCl_2F_4NO_2Ru$: C, 44.39; H, 4.40; N, 2.35. Found: C, 44.40; H, 4.41; N, 2.41%. ^{1}H NMR (400 MHz, D_2O): δ 1.99 (s, 18H, $C_6(CH_3)_6$), 3.16 (s, 3H, CH_3), 7.35 (s, 1H, C_9H_3), 7.66 (d, J = 8 Hz, 1H, C_9H_3), 8.37 (d, J = 8 Hz, 1H, C_9H_3). ^{13}C {^{1}H} NMR (100 MHz, D_2O): δ 15.19–15.29 (6C, $C_6(CH_3)_6$), 27.73 (1C, CH_3), 91.78 (6C, $C_6(CH_3)_6$), 114.80 (1C, C_9H_3), 118.41 (1C, C_9H_3), 124.35 (1C, C_9H_3), 124.73 (1CH, C_9H_3), 127.61 (1CH, C_9H_3), 135.40 (1CH, C_9H_3), 144.72 (1C, C_9H_3), 145.74 (1C, C_9H_3), 163.28 (1C, C_9H_3). MS (ESI) m/z = 490 [M−BF_4−H_2O]$^+$.

*3.4.7. [(η^6-C_6Me_6)Ru(η^2-$NC_9H_5(NO_2)O$)(OH_2)][BF_4]: **18**[BF_4] yield: 61% (56 mg)*

Anal. Calc. for $C_{21}H_{25}BF_4N_2O_4Ru$: C, 45.26; H, 4.52; N, 5.03. Found: C, 45.03; H, 4.80; N, 5.24%. ^{1}H NMR (400 MHz, D_2O): δ 2.12 (s, 18H, $C_6(CH_3)_6$), 6.93 (d, J = 8 Hz, 1H, C_9H_5), 7.88 (m, 1H, C_9H_5), 8.52 (d, J = 8 Hz, 1H, C_9H_5), 9.17 (d, J = 4 Hz, 1H, C_9H_5), 9.39 (d, J = 8 Hz, 1H, C_9H_5). ^{13}C {^{1}H} NMR (100 MHz, D_2O): δ 14.93 (6CH, $C_6(CH_3)_6$), 92.38 (6C, $C_6(CH_3)_6$), 113.00 (1CH, C_9H_5), 125.61 (1C, C_9H_5), 126.71 (1CH, C_9H_5), 130.33 (1C, C_9H_5), 132.46 (1CH, C_9H_5), 136.11 (1CH, C_9H_5), 150.90 (1CH, C_9H_5), 174.88 (1C, C_9H_5). MS (ESI) m/z = 453 [M−BF_4−H_2O]$^+$.

*3.4.8. [(η^6-C_6Me_6)Ru(η^2-$NC_9H_4Me_2O$)(OH_2)][BF_4]: [**19**][BF_4] yield: 98% (87 mg)*

Anal. Calc. for $C_{23}H_{30}BF_4NO_2Ru$: C, 51.12; H, 5.60; N, 2.59. Found: C, 50.93; H, 5.70; N, 2.70%. ^{1}H NMR (100 MHz, D_2O): δ 2.12 (s, 18H, $C_6(CH_3)_6$), 2.36 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 7.23 (s, 1H, C_9H_4), 7.65 (m, 1H, C_9H_4), 8.45 (d, J = 8 Hz, 1H, C_9H_4), 9.09 (d, J = 4 Hz, 1H, C_9H_4). ^{13}C {^{1}H} NMR (100 MHz, D_2O): δ 14.52

(6CH, $C_6(CH_3)_6$), 15.00 (1CH, CH_3), 15.84 (1CH, CH_3), 91.38 (6C, $C_6(CH_3)_6$), 117.18 (1C, C_9H_4), 119.81(1C, C_9H_4), 121.30 (1CH, C_9H_4), 123.80 (1C, C_9H_4), 126.78 (1C, C_9H_4), 131.92 (1CH, C_9H_4), 135.67 (1CH, C_9H_4), 149.68 (1CH, C_9H_4), 160.24 (1C, C_9H_4). MS (ESI) m/z = 436 $[M-BF_4-H_2O]^+$.

3.5. X-ray crystallography

Crystals of complexes **5**, **6**, **11**, **12**[BF_4] and **15**[BF_4] 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 [41]. Refinement and all further calculations were carried out using SHELXL-97 [42]. The H-atoms were 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 8. Figures of complexes **5**, **6**, **11**, **12**[BF_4] and **15**[BF_4] were drawn with ORTEP-32 [43].

3.6. Hydrogenation of carbon dioxide

The hydrogenation of carbon dioxide using **1**, **4**, **9**, **10** or **12**[BF_4] as catalyst (2 μmol) was carried out in aqueous solution (20 mL) under basic conditions. The solution was pressurized in an autoclave with H_2 and CO_2 and stirred for the time indicated at the given temperature. The reaction was finished by cooling the autoclave to 0 °C. After pressure release, the yield of formic acid was determined by ^{1}H NMR measurement of the resulting solution with TSP (3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt) in D_2O as the reference and the internal standard.

4. Supplementary material

CCDC 703775, 703776, 703777, 703778, and 703779 contain the supplementary crystallographic data for complex **5**, **6**, **11**, **12**[BF_4] and **15**[BF_4]·0.25H_2O. 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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