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Halfsandwich complexes of ruthenium(II), rhodium(III) and iridium(III) with *N*-substituted 3-hydroxy-2-methyl-4-pyridone ligands

Roland Lang [a], Kurt Polborn [b], Theodor Severin [a], Kay Severin [c,*]

[a] *Institut für Pharmazie der Ludwig-Maximilians-Universität, Butenandtstr. 5–13, D-81377 Munich, Germany*
[b] *Institut für Organische Chemie der Ludwig-Maximilians-Universität, Butenandtstr. 5–13, D-81377 Munich, Germany*
[c] *Institut für Anorganische Chemie der Ludwig-Maximilians-Universität, Butenandtstr. 5–13, D-81377 Munich, Germany*

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Abstract

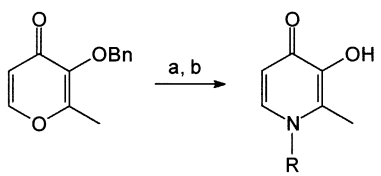
The synthesis and characterization of (*p*-cymene)Ru^{II}, Cp*Rh^{III} and Cp*Ir^{III} complexes with *N*-alkyl and *N*-aryl substituted 3-hydroxy-2-methyl-4-pyridone ligands is reported. All compounds display an unusually high solubility in water. With the chiral ligand *N*-(*o*-$C_6H_4CO_2Me$)-3-hydroxy-2-methyl-4-pyridone two isomers were obtained but no diastereoselectivity was observed. The structure of [(*p*-cymene)$Ru(C_9H_{12}NO_2)Cl$] (**2**) was determined by single crystal X-ray diffraction. Reactions of [(*p*-cymene)$Ru(C_7H_8NO_2)Cl$] (**1**) with *n*-butylamine and triphenylphosphine were shown to result in substitution of the chloride ligand.

Keywords: Crystal structures; Ruthenium complexes; Rhodium complexes; Iridium complexes; Hydroxypyridone complexes

1. Introduction

When maltose or lactose is heated with primary aliphatic amines in neutral aqueous solutions 3-hydroxy-2-methyl-4-pyridones are formed among other products in low yields [1]. This was reported as early as 1954 [1c] but access to this class of compounds based on this convenient synthetic method is often inefficient. Hydroxypyridones are readily prepared in moderate yields by heating maltol with primary aliphatic amines in aqueous solution. Later it was shown that *N*-alkyl and *N*-aryl substituted pyridones can be prepared in good yields by reaction of benzylated maltol with primary amines and subsequent hydrogenolysis (Scheme 1) [2].

Recently, there has been a significant interest in these compounds as sequestering agents for various metal ions [2a, 3–5]. The focus of attention has been particularly on Fe^{III} since very stable 3:1 complexes are formed. Being orally available 3-hydroxy-2-methyl-4-pyridones have emerged as promising candidates for the treatment of iron-overload [5]. To the best of our knowledge, no organometallic complexes with these ligands have been reported. Given the extensive coordination chemistry of γ-pyridones this is somewhat surprising, especially since the reactivities and the catalytic properties of organometallic complexes should differ notably from comparable complexes with other *O*,*O*-chelate ligands such as acetyl acetonate. Due to the unique electronic structure of the pyridone ligand the metal center in *O*,*O*-chelate complexes is predicted to be very electron rich (Scheme 2). Amongst other effects this may facilitate (catalytic) reactions which require the formation of cationic complexes or intermediates.



Scheme 1. Synthesis of *N*-substituted 3-hydroxy-2-methyl-4-pyridones from 3-*O*-benzylmaltol: (a) R-NH_2, (EtOH, H_2O), 8–10 h; (b) Pd/C, H_2, MeOH/EtOH, 12 h.

* Corresponding author. Fax: +49-89-2180 7866.
E-mail address: kse@cup.uni-muenchen.de (K. Severin)

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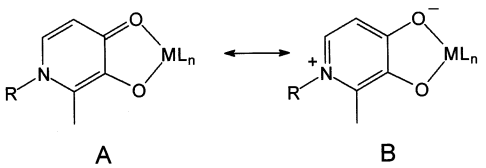


Scheme 2. Mesomeric forms which contribute to the electronic structure of coordinated 3-hydroxy-2-methyl-4-pyridone ligands.

In this paper (*p*-cymene)Ru^{II}, Cp*Rh^{III} and Cp*Ir^{III} complexes with *N*-substituted 3-hydroxy-2-methyl-4-pyridone ligands are described. These organometallic fragments were chosen because they are known to form monomeric complexes with bidentate, monoanionic ligands such as acetyl acetonate [6] and α-amino acid anions [7]. Furthermore, highly reactive catalysts for a variety of different transformations were found among complexes of this kind. For example (*p*-cymene)Ru^{II} complexes were used as catalysts for hydrogen transfer reactions [8], for the oligomerization of α-amino acid esters [9], for olefin cyclopropanations [10] and for isomerization reactions [11]; Cp*Rh and Cp*Ir complexes were utilized as catalysts for Diels–Alder [12] and hydrogenation reactions [13].

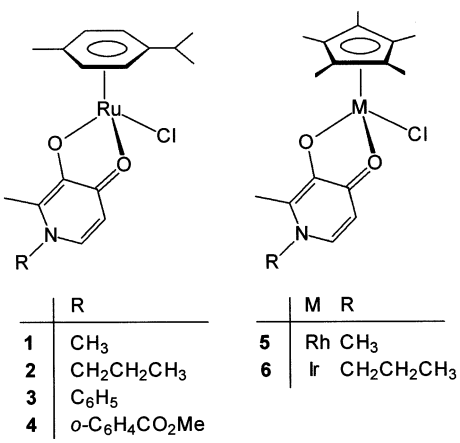
2. Results and discussion

2.1. Synthesis

Racemic mixtures of the ruthenium complexes **1**–**4** were prepared by reaction of [(*p*-cymene)RuCl$_2$]$_2$ with the sodium salts of the corresponding *N*-alkyl and *N*-aryl substituted 3-hydroxy-2-methyl-4-pyridones in dichloromethane. The orange products are soluble in chloroform, methanol and water (see Section 2.3) but insoluble in diethyl ether and hexanes. All complexes are chiral with the ruthenium atom being the stereogenic center and the pyridone ligands acting as bidentate *O*,*O*′-chelates. Consequently the ^{1}H NMR spectra ($CDCl_3$) show two doublets for the methyl groups (i-Pr) and four doublets for the aromatic protons of the cymene ligand. To elucidate the configurational stability of the metal center ^{1}H NMR spectra of **1** in the more polar solvent CD_3OD were recorded in the temperature range of −60 to +23°C. The results indicate that epimerization is fast on the NMR time scale: even at −20°C only one doublet for the methyl group (i-Pr) and two doublets for the aromatic protons were observed. This contrasts to other [(*p*-cymene)Ru(A–B)Cl] complexes for which epimerization in methanol was detected only at elevated temperatures [14]. Interestingly, at −60°C, signals of two isomers were recorded the relative ratio of which was determined to be 2.8:1. Most likely, a cationic solvate complex and the neutral chloro complex coexist at this temperature. The coexistence of such species in CD_3OD was previously postulated for a (η^6-benzene)Ru complex with a pyrrolcarbaldiminato ligand [15].

The *N*-aryl substituted complex **4** is obtained as a mixture of two diastereoisomers. In solution the relative ratio is 1:1 as determined by integration of selected ^{1}H NMR signals ($CDCl_3$). The formation of isomers is caused by hindered rotation of the C(arene)–N(pyridone) bond. For *ortho* substituted aryl groups this barrier is known to be sufficiently high to allow the separation of rotational isomers [16].

Similarly to **1**–**4**, the rhodium and iridium complexes **5** and **6** were obtained in good yields using the chloro-bridged dimers [Cp*RhCl$_2$]$_2$ or [Cp*IrCl$_2$]$_2$. The ^{1}H and ^{13}C NMR spectroscopic data are in agreement with the structures depicted. Both complexes show good solubility in polar organic solvents *and* water. Epimerization processes could not be studied because the enantiomeric forms are indistinguishable by NMR. Contrary to **1**, at −60°C (and above) only one isomer was observed for **5** and **6** in CD_3OD.



	R
1	CH_3
2	$CH_2CH_2CH_3$
3	C_6H_5
4	*o*-$C_6H_4CO_2Me$

	M	R
5	Rh	CH_3
6	Ir	$CH_2CH_2CH_3$

2.2. Structural analysis

Single crystals of **2** suitable for X-ray structural analysis were obtained by slow diffusion of hexane into a solution of **2** in chloroform. The geometry around the ruthenium atom can be described as a distorted tetrahedron with the η^6-arene ring and the other donor atoms adopting a 'piano stool' configuration (Fig. 1). The Ru–Cl bond length, 242.8(1) pm, is similar to that found in related molecules [14,17]. As a result of the constrained geometry of the chelate ligand the O1–Ru–O2 angle (79.41°) is smaller than the O2–Ru–Cl angle (85.50°) and the O1–Ru–Cl angle (86.74°).

Of special interest are the bond lengths of the pyridone ligand. The relatively long C–O2 bond distance, 129.5(4) pm, as well as the bond lengths within the six-membered ring (Fig. 2) indicate that the zwitterionic form 'B' (Scheme 2) contributes significantly to the electronic structure of **2**. Based on X-ray structural

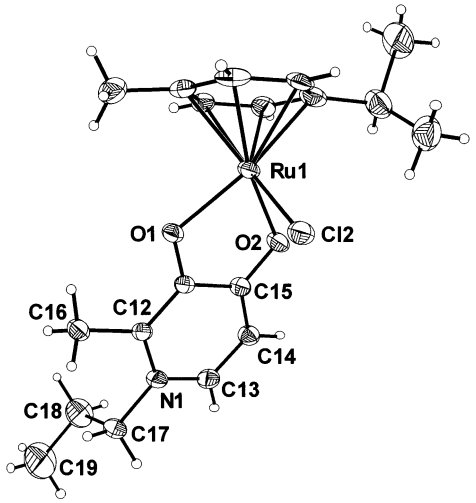


Fig. 1. Molecular structure of complex **2**.

analyses similar conclusions were drawn for some homoleptic pyridone complexes of Al^{3+} and Ga^{3+} [4].

2.3. Reactivity

The electron donating character of the pyridone ligand is expected to facilitate substitution reactions at the remaining coordination site. And indeed, the chloro ligand in **1** is easily replaced by the neutral *N*- and *P*-donor ligands *n*-$BuNH_2$ and PPh_3 (Scheme 3). Analogous reactions with PPh_3 occur with the rhodium and iridium compounds **5** and **6** as shown by in situ NMR experiments (^1H and ^{31}P, $CDCl_3$). The high lability of the chloro ligand contrasts to the behavior of other halfsandwich complexes with monoanionic chelate ligands for which silver salts such as $AgBF_4$ were used as chloride abstracting agents [6,18]. A substitution reaction of the chloro ligand with a neutral solvent molecule may also account for the good solubility of all complexes in water which is unusual for this type of compound.

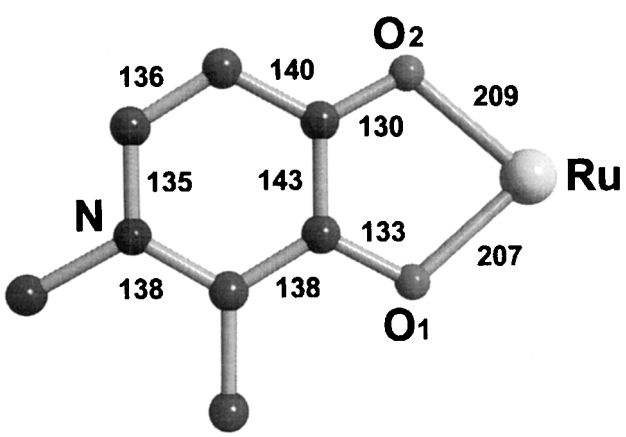
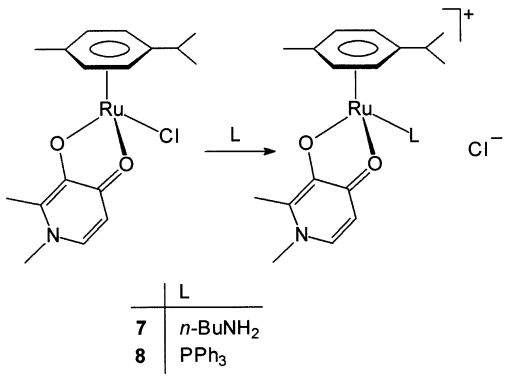


Fig. 2. Selected bond lengths (pm) of complex **2**. Only the parts of the pyridone ligand and the ruthenium atom are shown.



Scheme 3. Reaction of **1** with *n*-butylamine and triphenylphosphine.

It should be noted that the reaction of *n*-$BuNH_2$ with **1** does not afford a *N,O*-chelating pyridonimine [2a] despite the fact that metal assisted condensation reactions of primary amines with anionic ligands containing α-keto groups in the coordination sphere of (*p*-cymene)Ru(II) complexes are well known [19]. This result is in agreement with the phenolate character of the carbonyl group deduced from the X-ray structural analysis.

3. Experimental

3.1. General

All solvents were of analytical grade quality, obtained commercially and used without further purification. The complexes $[(p\text{-cymene})RuCl_2]_2$ [20], $[Cp^*RhCl_2]_2$ [21], and $[Cp^*IrCl_2]_2$ [21] were prepared as described in the literature. The pyridone ligands were synthesized according to published procedures. Infrared spectra were measured with Perkin–Elmer 841 or Nicolet 520 instruments. The NMR spectra were obtained on a JEOL EX 400 or GSX 270 with the solvent as internal standard.

3.2. 3-Hydroxy-2-methyl-1-propyl-4-pyridone

A total of 2.52 g maltol (20 mmol) and 2.36 g *n*-propylamine (40 mmol) in 50 ml water are heated under reflux for 4 h. After evaporation under reduced pressure the residue is crystallized from methanol. According to spectral data the product is identical to a substance prepared from *O*-benzylmaltol as described in Ref. [2a].

3.3. General procedure for the synthesis of *1–6*

A solution of 0.4 mmol NaOMe in methanol (2 M) was added to a suspension of 0.4 mmol *N*-substituted 3-hydroxy-2-methyl-4-pyridone in 10 ml of dichlo-

romethane. The resulting clear solution was subsequently added to 0.2 mmol of [(*p*-cymene)$RuCl_2]_2$, $[(Cp^*)RhCl_2]_2$, or $[(Cp^*)IrCl_2]_2$ dissolved in 10 ml of dichloromethane. After 2 h the solvent was removed in vacuo. The products were extracted with 30 ml of diethyl ether/dichloromethane (1:2). Yellow or orange powders were obtained after evaporation of the solvent under reduced pressure and drying in vacuo at 50°C.

3.4. [(*p*-Cymene)$Ru(C_7H_8NO_2)Cl$] (**1**)

Yield: 85%, m.p. 247–249°C (dec.). IR (KBr): $\nu =$ 1599 cm^{-1} (s), 1543 (s), 1506 (s). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.22$ [d, $^3J = 6.8$ Hz, 3H, $CH(CH_3)_2$], 1.27 [d, $^3J = 7.0$ Hz, 3H, $CH(CH_3)_2$], 2.26 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.84 (sept., $^3J = 7.2$ Hz, 1H, $CH(CH_3)_2$], 3.52 (s, 3H, NCH_3), 5.18 (d, $^3J = 5.1$ Hz, 1H, CH, cymene), 5.24 (d, $^3J = 5.6$ Hz, 1H, CH, cymene), 5.37 (d, $^3J = 5.5$ Hz, 1H, CH, cymene), 5.44 (d, $^3J = 5.8$ Hz, 1H, CH, cymene), 6.30 (d, $^3J = 6.6$ Hz, 1H, C_5H_2N), 6.86 (d, $^3J = 7.2$ Hz, 1H, C_5H_2N). ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 12.20$ (N–C(CH_3)=C), 18.68 (CH_3, cymene), 22.36, 23.50 [$CH(CH_3)_2$], 31.07 [$CH(CH_3)_2$], 42.47 (NCH_3), 77.60, 78.56, 79.22, 79.58, 95.50, 99.05 (cymene), 109.19, 132.22, 132.38 (N–CH=CH, N–*C*(CH3)=C), 160.99, 175.30 (CO). *Anal.* Calc. for $C_{17}H_{22}ClNO_2Ru$ (408.89): C, 49.94; H, 5.42; N, 3.43. Found: C, 49.31; H, 5.33; N, 3.24%.

3.5. [(*p*-Cymene)$Ru(C_9H_{12}NO_2)Cl$] (**2**)

Yield: 82%, m.p. 215–217°C (dec.). IR (KBr): $\nu =$ 1600 cm^{-1} (s), 1538 (s), 1507 (s). ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.94$ (t, $^3J = 7.4$ Hz, 3H, $CH_2CH_2CH_3$], 1.27 [d, $^3J = 6.9$ Hz, 3H, $CH(CH_3)_2$], 1.32 [d, $^3J = 7.0$ Hz, 3H, $CH(CH_3)_2$], 1.65–1.79 (m, 2H, $CH_2CH_2CH_3$), 2.31 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.93 (sept., $^3J = 6.9$ Hz, 1H, $CH(CH_3)_2$], 3.74–3.80 (m, 2H, $CH_2CH_2CH_3$), 5.23 (d, $^3J = 5.8$ Hz, 1H, CH, cymene), 5.28 (d, $^3J = 5.4$ Hz, 1H, CH, cymene), 5.42 (d, $^3J = 5.7$ Hz, 1H, CH, cymene), 5.48 (d, $^3J = 5.4$ Hz, 1H, CH, cymene), 6.41 (d, $^3J = 6.5$ Hz, 1H, C_5H_2N), 6.90 (d, $^3J = 6.8$ Hz, 1H, C_5H_2N). ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 10.99$, 11.80 (N–C(CH_3)=C, CH_2CH_2-CH_3), 18.61 (CH_3, cymene), 22.40, 23.51 [$CH(CH_3)_2$], 24.07 ($CH_2CH_2CH_3$), 31.06 [$CH(CH_3)_2$], 56.25 ($CH_2CH_2CH_3$), 77.66, 78.58, 79.28, 79.68, 95.33, 99.06 (cymene), 109.69, 131.47, 131.69 (N–CH=CH, N–*C*(CH3)=C), 161.07, 175.07 (CO). *Anal.* Calc. for $C_{19}H_{26}ClNO_2Ru$ (436.94): C, 52.23; H, 6.00; N, 3.21. Found: C, 52.32; H, 6.10; N, 3.09%.

3.6. [(*p*-Cymene)$Ru(C_{12}H_{10}NO_2)Cl$] (**3**)

Yield: 75%, m.p. 226–228°C (dec.). IR (KBr): $\nu =$ 1584 cm^{-1} (s), 1534 (s), 1496 (s). ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.26$ [d, $^3J = 6.9$ Hz, 3H, $CH(CH_3)_2$], 1.31 [d, $^3J = 6.6$ Hz, 3H, $CH(CH_3)_2$], 2.09 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.90 (sept., $^3J = 6.9$ Hz, 1H, $CH(CH_3)_2$], 5.23 (d, $^3J = 6.0$ Hz, 1H, CH, cymene), 5.29 (d, $^3J = 5.9$ Hz, 1H, CH, cymene), 5.43 (d, $^3J = 5.5$ Hz, 1H, CH, cymene), 5.48 (d, $^3J = 5.5$ Hz, 1H, CH, cymene), 6.47 (d, $^3J = 6.9$ Hz, 1H, C_5H_2N), 6.94 (d, $^3J = 6.8$ Hz, 1H, C_5H_2N), 7.16–7.19 (m, 2H, C_6H_5), 7.43–7.45 (m, 3H, C_6H_5). ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 13.87$ (N–C(CH_3)=C), 18.67 (CH_3, cymene), 22.47, 22.56 [$CH(CH_3)_2$], 31.11 [$CH(CH_3)_2$], 78.66, 79.26, 79.70, 95.46, 99.26 (cymene), 109.40, 126.37, 129.45, 129.75, 132.20, 132.50, 142.18 (N–CH=CH, N–*C*(CH3)=C, C_6H_5), 160.67, 176.19 (CO). *Anal.* Calc. for $C_{22}H_{24}ClNO_2Ru$ (470.96): C, 56.11; H, 5.14; N, 2.97. Found: C, 55.37; H, 5.14; N, 2.77%.

3.7. [(*p*-Cymene)$Ru(C_{14}H_{12}NO_4)Cl$] (**4**)

Yield: 82%, m.p. 185–187°C (dec.). IR (KBr): $\nu =$ 1716 cm^{-1} (s, CO_2Me), 1591 (s), 1536 (s), 1506 (s). ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.19$–1.39 [m, 12H, $CH(CH_3)_2$], 2.00 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.85–2.96 (m, 2H, $CH(CH_3)_2$], 3.58 (s, 3H, CO_2CH_3), 3.65 (s, 3H, CO_2CH_3), 5.21–5.51 (m, 8H, CH, cymene), 6.47 (d, $^3J = 6.4$ Hz, 1H, C_5H_2N), 6.50 (d, $^3J = 6.3$ Hz, 1H, C_5H_2N), 6.86 (d, $^3J = 6.8$ Hz, 1H, C_5H_2N), 6.87 (d, $^3J = 6.8$ Hz, 1H, C_5H_2N), 7.26–7.28 (m, 2H, $C_6H_4CO_2Me$), 7.55–7.68 (m, 4H, $C_6H_4CO_2Me$), 8.04–8.07 (m, 2H, $C_6H_4CO_2Me$). ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 13.45$ (N–C(CH_3)=C), 18.57, 18.82 (CH_3, cymene), 22.08, 22.58, 22.72 [$CH(CH_3)_2$], 31.08, 31.65 [$CH(CH_3)_2$], 52.65, 53.69 (CO_2CH_3), 77.78, 78.50, 78.73, 79.18, 79.27, 79.42, 80.26, 95.38, 95.79, 99.13, 99.26 (cymene), 109.26, 109.41, 127.87, 127.96, 128.57, 128.77, 129.98, 131.87, 132.48, 133.10, 133.36, 133.73, 140.97, 141.23 (N–CH=CH, N–*C*(CH3)=C, $C_6H_4CO_2Me$), 160.35, 160.50, 164.89, 165.34, 176.38, 176.77 (CO, CO_2). *Anal.* Calc. for $C_{24}H_{26}ClNO_4Ru$ (528.99): C, 54.49; H, 4.95; N, 2.65. Found: C, 54.27; H, 4.89; N, 2.55%.

3.8. [$Cp^*Rh(C_7H_8NO_2)Cl$] (**5**)

Yield: 85%, m.p. 217–220°C (dec.). IR (KBr): $\nu =$ 1596 cm^{-1} (s), 1541 (s), 1504 (s). ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.70$ (s, 15H, Cp^*), 2.37 (s, 3H, N–C(CH_3)=C), 3.56 (s, 3H, NCH_3), 6.29 (d, $^3J = 7.0$ Hz, 1H, C_5H_2N), 6.87 (d, $^3J = 6.8$ Hz, 1H, C_5H_2N). ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 8.92$ [$C_5(CH_3)_5$], 12.31 (N–C(CH_3)=C), 42.40 (NCH_3), 90.59 [d, $^1J_{RhC} = 9.3$ Hz, $C_5(CH_3)_5$], 109.60 (d, $^3J_{RhC} = 1.6$ Hz, N–CH=*C*H), 131.52 (N–*C*H=CH), 132.08 (d, $^3J_{RhC} = 2.0$ Hz, N–*C*(CH3)=C), 161.55, 175.73 (CO). *Anal.* Calc. for $C_{17}H_{23}ClNO_2Rh{\cdot}0.5H_2O$ (420.74): C, 48.53; H, 5.75; N, 3.33. Found: C, 48.80; H, 5.51; N, 3.22%.

3.9. [Cp*Ir($C_9H_{12}NO_2$)Cl] (6)

Yield: 78%, m.p. 235–237°C (dec.). IR (KBr): $\nu =$ 1600 cm^{-1} (s), 1540 (s), 1505 (s). ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.94$ (t, $^3J = 7.4$ Hz, 3H, $CH_2CH_2CH_3$], 1.65–1.76 (m, 2H, $CH_2CH_2CH_3$), 1.69 (s, 15H, Cp*), 2.43 (s, 3H, N–C(CH_3)=C), 3.77–3.83 (m, 2H, $CH_2CH_2CH_3$), 6.40 (d, $^3J = 6.8$ Hz, 1H, C_5H_2N), 6.94 (d, $^3J = 6.5$ Hz, 1H, C_5H_2N). ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 9.22$ [$C_5(CH_3)_5$], 11.07, 11.95 (N–C(CH_3)=C, $CH_2CH_2CH_3$), 24.16 ($CH_2CH_2CH_3$), 56.26 ($CH_2CH_2CH_3$), 81.60 [$C_5(CH_3)_5$], 109.66, 131.21, 132.11 (N–CH=CH, N–C(CH3)=C), 163.28, 176.45 (CO). *Anal.* Calc. for $C_{19}H_{26}ClIrNO_2$ (529.10): C, 43.13; H, 5.14; N, 2.65. Found: C, 42.87; H, 5.22; N, 2.56%.

3.10. [(p-Cymene)Ru($C_7H_8NO_2$)($C_4H_9NH_2$)]Cl (7)

A total of 82 mg (0.2 mmol) **1** and 30 μl (0.3 mmol) *n*-butylamine in 5 ml of methanol were stirred for 3 h. After removal of the solvent under reduced pressure the product was washed with 30 ml of diethyl ether and dried in vacuo. Yield: 92%. IR (KBr): $\nu = 1601$ cm^{-1} (s), 1547 (s), 1503 (s). ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.66$ (t, $^3J = 7.0$ Hz, CH_3, Bu), 1.00 (sext., $^3J = 7.2$ Hz, CH_2, Bu), 1.23 [d, $^3J = 6.7$ Hz, 3H, $CH(CH_3)_2$], 1.25 [d, $^3J = 6.8$ Hz, 3H, $CH(CH_3)_2$], 1.29–1.50 (m, 2H, CH_2, Bu), 2.14–2.43 (m, 2H, NCH_2, Bu), 2.20 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.84 (sept., $^3J = 7.0$ Hz, 1H, $CH(CH_3)_2$], 3.08 (br, NH), 3.70 (s, 3H, NCH_3), 4.84 (s, 3H, NCH_3), 5.42 (d, $^3J = 5.8$ Hz, 1H, CH, cymene), 5.59–5.61 (m, 3H, CH, cymene), 6.30 (d, $^3J = 6.6$ Hz, 1H, C_5H_2N), 7.18 (d, $^3J = 6.8$ Hz, 1H, C_5H_2N). ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 11.81$, 13.63 (N–C(CH_3)=C, CH_3, Bu), 18.01, 19.89 (CH_3, cymene, CH_2, Bu), 22.53, 22.66 [$CH(CH_3)_2$], 31.19 [$CH(CH_3)_2$], 33.69 (CH_2, Bu), 42.78 (NCH_3), 44.20 (NCH_2, Bu), 79.65, 80.25, 80.59, 80.92 (cymene), 109.39, 133.97, 133.83 (N–CH=CH, N–C(CH3)=C), 160.27, 174.84 (CO). *Anal.* Calc. for $C_{22}H_{35}ClN_2O_2Ru{\cdot}0.5H_2O$ (491.04): C, 51.37; H, 6.98; N, 5.70. Found: C, 51.22; H, 6.80; N, 5.58%.

3.11. [(p-Cymene)Ru($C_7H_8NO_2$)PPh_3]Cl (8)

A total of 82 mg (0.2 mmol) **1** and 52 mg (0.2 mmol) PPh_3 in 7 ml of dichloromethane were stirred for 4 h. After removal of the solvent under reduced pressure the product was dried in vacuo. Yield: 98%. IR (KBr): $\nu = 1602$ cm^{-1} (s), 1544 (s), 1505 (s). ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.11$ [d, $^3J = 6.7$ Hz, 3H, $CH(CH_3)_2$], 1.13 [d, $^3J = 6.7$ Hz, 3H, $CH(CH_3)_2$], 1.80 (s, 3H, CH_3, cymene), 2.05 (s, 3H, N–C(CH_3)=C), 2.53 (sept., $^3J = 6.7$ Hz, 1H, $CH(CH_3)_2$], 3.59 (s, 3H, NCH_3), 4.92 (d, $^3J = 5.9$ Hz, 1H, CH, cymene), 5.12 (d, $^3J = 6.2$ Hz, 1H, CH, cymene), 5.31 (d, $^3J = 5.9$ Hz, 1H, CH, cymene), 5.43 (d, $^3J = 5.9$ Hz, 1H, CH, cymene), 5.97 (d, $^3J = 7.0$ Hz, 1H, C_5H_2N), 7.14 (d, $^3J = 6.8$ Hz, 1H, C_5H_2N), 7.24–7.43 (m, 15H, PPh_3). ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 11.50$ (N–C(CH_3)=C), 18.00 (CH_3, cymene), 22.04, 22.35 [$CH(CH_3)_2$], 30.96 [$CH(CH_3)_2$], 42.59 (NCH_3), 85.60 (d, $^2J_{PC} = 2.8$ Hz, CH, cymene), 86.04 (CH, cymene), 86.37 (d, $^2J_{PC} = 3.9$ Hz, CH, cymene), 87.68 (d, $^2J_{PC} = 5.2$ Hz, CH, cymene), 97.24 (C, cymene), 108.72 (d, $^2J_{PC} = 5.1$ Hz, C, cymene), 109.73, 128.28, 128.422, 129.48, 130.13, 130.88, 130.91, 133.28, 134.09, 134.24, 134.89 (N–CH=CH, N–C(CH3)=C, PPh_3), 160.66, 175.39 (CO). ^{31}P NMR (109 MHz, $CDCl_3$): $\delta = 30.06$ (PPh_3). *Anal.* Calc. for $C_{35}H_{37}ClNO_2PRu{\cdot}1.5H_2O$ (698.2): C, 60.21; H, 5.77; N, 2.01. Found: C, 60.47; H, 5.67; N, 1.95%.

Table 1
Crystallographic data of complex **2**

Empirical formula	$C_{19}H_{26}ClNO_2Ru$
Molecular weight (g mol^{-1})	436.93
Crystal size (mm^{-1})	$0.10 \times 0.37 \times 0.53$
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	7.654(2)
b (Å)	9.8818(13)
c (Å)	13.920(2)
α (°)	104.149(10)
β (°)	103.910(14)
γ (°)	98.976(13)
Volume ($Å^3$)	964.8(3)
Z	2
Density (g cm^{-3})	1.504
Absorption coefficient (mm^{-1})	0.961
θ range (°)	2.80–23.96
Index ranges	$-8 \rightarrow 8$, $-11 \rightarrow 0$, $-15 \rightarrow 15$
Reflections collected	3227
Independent reflections	3024
Absorption correction	semi-empirical
Max. and min. transmission	0.9998 and 0.8381
Weights	$w = 1/(\sigma^2(F_o^2) + (0.0344P)^2 + 0.7624P]$; $P = (F_o^2 + 2F_c^2)/3$
Data/restraints/parameters	2764/0/222
Goodness-of-fit on F^2	1.117
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0277$, $wR_2 = 0.0674$
R indices (all data)	$R_1 = 0.0325$, $wR_2 = 0.0708$
Largest difference peak/hole (e $Å^{-3}$)	0.643/−0.720

3.12. X-ray crystallographic investigations

An Enraf–Nonius CAD 4 diffractometer was employed for data collection using Mo Kα radiation ($T =$ 295 K). The structure was solved by direct methods (SHELXS-86) [22] and was refined by means of the full-matrix least-squares procedures using SHELXL-93 [23] (Table 1). All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was employed.

4. Conclusions

We have shown that chiral halfsandwich complexes of ruthenium, rhodium and iridium with *O*,*O*′-coordinating *N*-substituted 3-hydroxy-2-methyl-4-pyridone ligands can be obtained in good yields by reaction of $[(p\text{-cymene})RuCl_2]_2$, $[Cp^*RhCl_2]_2$ or $[Cp^*IrCl_2]_2$ with the corresponding chelate anions. The electron donating character of the pyridone ligands is manifested in the low configurational stability of the stereogenic ruthenium center of **1**–**4**, the good solubility of all complexes in water and the lability of the chloro ligand towards substitution with neutral donor ligands. Currently, we are further exploring the organometallic chemistry of these interesting ligands.

5. Supplementary material

Further details of the crystal structure determination may be obtained from the Cambridge Crystallographic Data Centre. Any request for this material should quote the full literature citation and the reference number CCDC-125745.

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