Two New Ruthenium(II) Complexes with Cyclometalated 2-Phenylpyridine Ligands

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The reaction of $Ru_3(CO)_{12}$ and 2-phenylpyridine (Hppy) in hot methanol yields the dinuclear ruthenium(II) complex $[Ru(OCH_3)(ppy)(CO)_2]_2$ (**3**) in moderate yield. Heating of $Ru_3(CO)_{12}$ and Hppy in a cyclohexane–dimethoxyethane mixture generates the mononuclear complex [Ru-*cis*-$(ppy)_2$-*cis*-$(CO)_2$] (**2**). When **2** is treated with methanol at elevated temperature, only partial conversion into **3** can be achieved. The structures of complexes **2** (two polymorphs) and **3** were established by X-ray diffraction analysis.

Key words: Cyclometalated Ligands, Metallacycles, N Ligands, Ruthenium, Organometallic Compounds, Polymorphism

Introduction

2-Phenylpyridine (Hppy) is a convenient precursor for metal complexes containing the cyclometalated 2-(2-pyridyl)phenyl (ppy) ligand, and a variety of transition metal complexes containing this ligand and ring-substituted derivatives thereof are known. In all cases, complexation of the metal with the nitrogen donor and metalation at an *ortho*-position of the phenyl ring gives rise to a five-membered chelate ring. The first ruthenium complexes containing the cyclometalated ppy ligand, $[Ru(bipy)_2(L)]^+$ (HL = 2-(4-nitrophenyl)pyridine) [1] and $[Ru(bipy)_2(ppy)]^+$ [2], were prepared two decades ago. At that time, it was already known that benzo[*h*]quinoline, a sterically rigid relative of 2-phenylpyridine, was easily cyclometalated by several transition metals including ruthenium [3], and the structure of a ruthenium(II) complex incorporating two benzo-[*h*]quinolin-10-yl (bq) ligands, $[Ru(bq)_2(CO)_2]$, was firmly established [4]. Notably, an analogous complex incorporating the parent ppy ligand, *i. e.* $[Ru(ppy)_2(CO)_2]$, has not been reported up to now.

Ruthenium(II) complexes with chelating 2,2′-bipyridine (bpy) and related ligands, *e. g.* $[Ru(bpy)_3]^{2+}$, have attracted wide attention because of their photophysical, photochemical and electrochemical properties [5]. In contrast, the interest in ruthenium complexes with cyclometalated 2-phenylpyridine ligands has been growing only recently [6 – 14]. A motivation for studying Ru–ppy complexes comes from the fact that the replacement of a neutral bpy by an anionic cyclometalated ppy ligand, due to the strong σ-donation of the latter, increases the electron density around the metal and the ligand field strength and thus enhances the $d \rightarrow \pi^*$ back donation. These particular ligand effects contribute to various properties such as a significant cathodic shift of the $Ru^{II/III}$ oxidation potential [2, 12b, 13, 15, 16], enhanced metal-to-ligand charge-transfer character [12a], and stabilization of the Ru^{IV} oxidation state, *e. g.* in the cation $[(Cp^*Ru(\mu\text{-ppy})RuCp^*Cl_2]^+$ [11] and in the Ru^{III}/Ru^{IV} complex $[\{Ru(ppy)(phen)Cl\}_2(\mu\text{-O})]PF_6$ [15]. Furthermore, various Ru(II)–ppy complexes are highly efficient mediators for several oxidoreductases [16]. The remarkable stability of the metal–carbon bond in the Ru(II)–ppy complexes in combination with the directing effect of the metal has allowed the regioselective functionalization of the phenyl ring with various electrophilic reagents [8, 17]. Finally, ruthenium(II) complexes containing the ppy unit incorporated in a terdentate CNN ligand have recently been identified as superior catalysts for transfer hydrogenation of ketones with 2-propanol [18].

Ru(II)–ppy complexes are usually prepared by direct cyclometalation of a 2-phenylpyridine ligand using an electrophilic Ru(II) complex [1, 2, 7] or by transmetalation of the *ortho*-mercurated complex $Hg(ppy)_2$ with, *e. g.*, $RuHCl(CO)(PPh)_3$ [8], [(η^6-cym-

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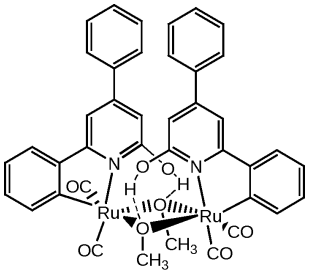


1

Fig. 1.

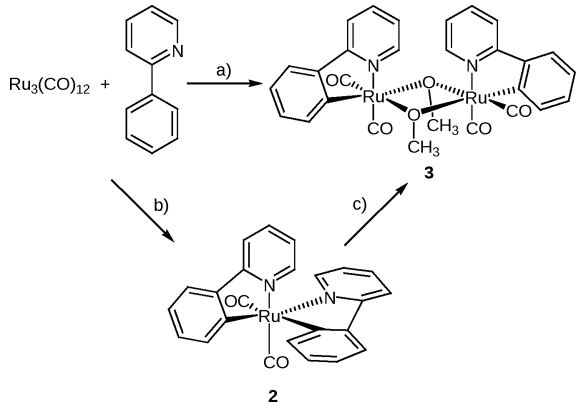
ene)$RuCl_2]_2$ [10], or [$Cp^*Ru(NO)Cl_2$] [11]. We have found that the reaction of 2-hydroxy-4,6-diphenylpyridine with $Ru_3(CO)_{12}$ in boiling methanol provides the dinuclear Ru(II)–bpy complex **1** (Fig. 1), in which the two ruthenium subunits are bridged by two methoxy groups both of which maintain a O···H–O hydrogen bond with the hydroxy substituent at the pyridine ring [19]. We report now that an analogous reaction occurs when 2-phenylpyridine is used, and that the so far unknown complex [$Ru(ppy)_2(CO)_2$] is a possible intermediate in this transformation.

Results and Discussion

Syntheses

When triruthenium-dodecacarbonyl and 2-phenylpyridine (Hppy) in a 1 : 6 molar ratio were heated in a mixture of methanol and toluene (4 : 1 v/v) at 100 °C for 3 d, an off-white solid could be isolated which was well soluble in common organic solvents with the exception of pentane, cyclohexane, and methanol. An X-ray crystal structure determination revealed the structure of the dinuclear ruthenium(II) complex **3**, which consists of two identical [$Ru(OCH_3)(ppy)(CO)$] fragments mutually connected by ruthenium–oxygen coordination (Scheme 1 and Fig. 3). The ^1H and ^{13}C NMR spectra confirm the symmetrical constitution of the complex. Thus, the structure of **3** is analogous to that of **1** (see Introduction), but the ^1H NMR spectra of **3** indicate the presence of only one species in solution, in contrast to the mixture of different species in solution which had been observed for **1** [19].

It should be noted that the formation of **3** occurs less smoothly and less effectively than in the case of **1**, where 2-hydroxy-4,6-diphenylpyridine was a reaction partner (CH_3OH, 65 °C, 2 d, 64 % yield [19]). When $Ru_3(CO)_{12}$ and Hppy were kept in methanol at reflux (65 °C) for 3 d, the conversion was only 50 % and the



2 **3**

Scheme 1. Synthesis of complexes **2** and **3**. Conditions: a) 2-phenylpyridine (6 equiv.), methanol–toluene (4 : 1 v/v), 100 °C, 3 d (50 % yield); b) 2-phenylpyridine (9 equiv.), DME–cyclohexane (2 : 7 v/v), 135 °C, 3 d (67 % yield); c) DME–methanol (1 : 1 v/v), 135 °C (microwaves), 30 min, incomplete conversion.

TLC control indicated not only the presence of **3** but also of a second compound which later was identified as the mononuclear complex **2** by an independent synthesis (*vide infra*). Under the optimized reaction conditions mentioned above, only traces of **2** and $Ru_3(CO)_{12}$ were detected when the reaction was stopped.

The mononuclear complex **2** could be prepared in 67 % yield from $Ru_3(CO)_{12}$ and Hppy, when the reaction was conducted in a boiling mixture of cyclohexane and 1,2-dimethoxyethane (DME) rather than in methanol. Complex **2** is soluble in chloroform, but barely soluble even in hot methanol. In the IR spectrum, two strong and sharp carbonyl stretching vibrations are seen (ν = 1989 and 1931 cm^{-1}) which indicate the presence of two *cis*-coordinated carbonyl ligands. The ^1H NMR spectrum shows 16 signals of equal intensity which in the COSY spectrum are recognized as belonging to four groups consisting each of four spin-coupled nuclei. These data in combination with elemental analyses and mass spectra suggested the structure of a non-symmetrical mononuclear complex [$Ru(ppy)_2$-*cis*-$(CO)_2$]. The X-ray crystal structure determination confirmed the structural proposal: it showed that complex **2** has the two carbonyl ligands in a *cis*-relationship and the two ppy ligands in a (mutually orthogonal) arrangement which places one of the carbonyl ligands *trans* to the Ru–N bond of the first ppy ligand and the other one *trans* to the Ru–C_{aryl} bond of the second ppy ligand (Scheme 1 and Fig. 2).

It is interesting to note that analogous conditions (octane–DME) were used to prepare the related com-

	Polymorph **A**	Polymorph **B**		Polymorph **A**	Polymorph **B**
Distances (Å)					
Ru1–N1	2.146(1)	2.154(2)	Ru1–C23	1.927(2)	1.936(3)
Ru1–N2	2.177(2)	2.168(2)	Ru1–C24	1.857(2)	1.853(3)
Ru1–C11	2.068(2)	2.066(2)	C23–O1	1.141(3)	1.132(3)
Ru1–C22	2.112(2)	2.112(2)	C24–O2	1.149(3)	1.150(3)
Angles (deg)					
N1–Ru1–C11	78.98(8)	78.62(9)	N2–Ru1–C11	166.17(7)	163.17(8)
N1–Ru1–N2	91.74(7)	89.00(7)	N2–Ru1–C22	77.76(7)	77.58(8)
N1–Ru1–C22	88.01(7)	89.25(7)	N2–Ru1–C23	99.97(9)	99.97(9)
N1–Ru1–C23	92.41(8)	91.68(9)	N2–Ru1–C24	95.33(8)	98.29(9)
C23–Ru1–C24	91.55(9)	91.31(10)			
Torsion angles (deg)					
N1–C5–C6–C11	−3.5(3)	−2.7(3)	N2–C16–C17–C22	−1.2(3)	−2.2(3)

Table 1. Selected bond lengths, angles, and torsion angles for the two polymorphs of complex **2** with estimated standard deviations in parentheses.

plex [Ru(bq)-*cis*-$(CO)_2$] (bq = benzo[*h*]quinolin-10-yl) [3, 13], which in contrast to **2** has the two chelating bq ligands with the N atoms *trans* to each other [4]. It should also be mentioned that for some cyclometalation reactions leading to Ru–bpy complexes, a polar solvent such as methanol led to improved yields [12b, 20]. As we show here, this does not apply to the synthesis of complex **2**.

The presence of small amounts of the mononuclear complex **2** in all preparations directed to the synthesis of the dinuclear complex **3** seems to suggest that **2** is an intermediate in the formation of **3**. Therefore, we checked whether the conversion of **2** into **3** was possible under conditions corresponding to the direct preparation of **3** from $Ru_3(CO)_{12}$ and Hppy in hot methanol. We found that heating of **2** in methanol-toluene (4 : 1) at 80 °C even for 5 d resulted only in a partial conversion (**2** : **3** : Hppy = 2 : 1 : 5.3) besides the formation of decomposition products. In spite of several variations (temperature, cosolvents such as water and DME), no conditions for the clean and complete conversion of **2** into **3** were found. In our hands, microwave heating (135 °C, 30 min) of **2** in a DME-methanol mixture gave the best conversion under relatively moderate thermal impact (see Experimental Section). These results let us conclude that **2** is a possible, but not a necessary intermediate in the formation of **3** from $Ru_3(CO)_{12}$ and Hppy in hot methanol. Nevertheless, it is remarkable that a Ru–C bond in **2** can be cleaved by methanol, since for other Ru–ppy complexes, this bond has been described as rather robust, tolerating for example the conditions of various electrophilic substitution reactions at the phenyl ring [8]. An effort towards demetalation of [Ru(5-Br-ppy)Cl(CO)$(PPh_3)_2$] with concentrated hydrochloric acid yielded the free ligand in only 25 % yield [8a].

*Solid-state structures of complexes **2** and **3***

The structures of **2** and **3**, as determined by X-ray crystal structure analysis, are shown in Figs. 2 and 3. Relevant data on the molecular geometry are presented in Tables 1 and 2. For complex **2**, two polymorphs were found both of which crystallized in the monoclinic space group $P2_1/c$ but were obtained as rod-shaped (herein called polymorph **A**) and prismatic (polymorph **B**) crystals, respectively. Both polymorphs of **2** show the same molecular structure of the complex and similar molecular geometry data (Table 1); therefore, only the values for polymorph **A** are cited in the following discussion.

In the mononuclear complex **2**, the ruthenium atom has a distorted octahedral coordination, with the three types of bonds (Ru–C(O), Ru–C_{aryl}, Ru–N) in a pairwise *cis*-coordination. Distinct bond-length differences are observed for each pair of these bond types, since each atom coordinated to the metal has a different ligand situated in *trans*-position. Thus, the Ru1–N2 bond

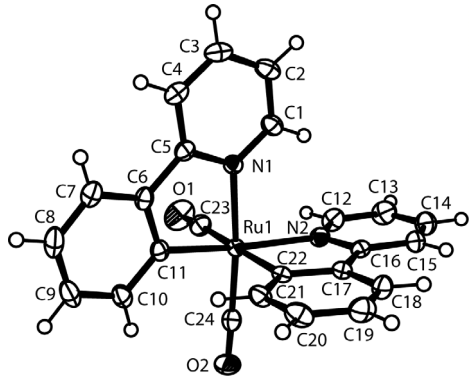


Fig. 2. Molecular structure of **2** (polymorph **A**) in the crystal. Displacement ellipsoids are shown at the 50 % probability level.

Table 2. Selected bond lengths, angles, and torsion angles for complex **3** with estimated standard deviations in parentheses.

Distances (Å)			
Ru1–N1	2.113(3)	Ru2–N2	2.128(3)
Ru1–O1	2.179(2)	Ru2–O1	2.117(2)
Ru1–O2	2.099(2)	Ru2–O2	2.156(2)
Ru1–C3	1.862(4)	Ru2–C5	1.863(4)
Ru1-C4	1.876(4)	Ru2–C6	1.866(5)
Ru1-C13	2.056(4)	Ru2–C24	2.064(4)
Angles (deg)			
N1–Ru1–O1	88.76(11)	N2–Ru2–O1	87.37(10)
N1–Ru1–O2	85.92(11)	N2–Ru2–O2	87.64(11)
N1–Ru1–C3	89.62(15)	N2–Ru2–C5	91.11(16)
N1–Ru1–C4	173.10(14)	N2–Ru2–C6	172.22(14)
N1–Ru1–C13	79.07(15)	N2–Ru2–C24	79.24(14)
O1–Ru1–O2	75.66(9)	O1–Ru2–O2	75.80(9)
Ru1–O1–Ru2	101.15(10)	Ru1–O2–Ru2	102.48(10)
Torsion angles (deg)			
N1–C11–C12–C13	−1.8(5)	N2–C22–C23–C24	2.6(5)

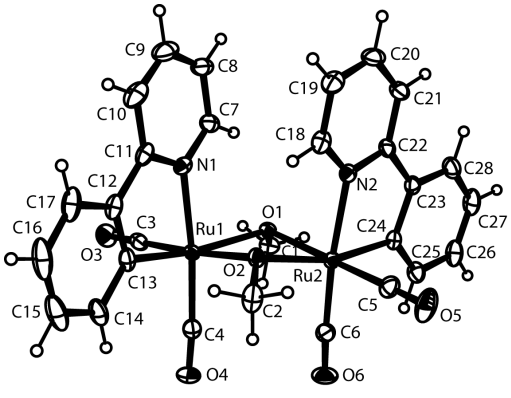


Fig. 3. Molecular structure of **3** in the crystal. Displacement ellipsoids are shown at the 30 % probability level.

(2.177(2) Å, *trans* to Ru–C_{aryl}) is much longer than the Ru1–N1 bond (2.146(2) Å, *trans* to Ru–$C_{carbonyl}$). Analogously, the Ru–C_{aryl} bond *trans* to a CO ligand is markedly longer than the one *trans* to a pyridyl ligand (Ru1–C22: 2.112(2) Å; Ru1–C11: 2.066(2) Å), and the bond length difference is even larger when a Ru–$C_{carbonyl}$ bond is situated *trans* to a Ru–C_{aryl} bond rather than to a Ru–N bond (Ru1–C23: 1.927(2) Å; Ru1–C24: 1.857(2) Å). These bond-length variations underline again the strong labilizing effect of the metal–carbon σ bond on a *trans*-positioned bond, as was already observed in related ruthenium complexes [1b, 12, 13, 15]. The *trans* influence of the carbonyl ligand is obviously smaller, although the Ru1–C22 bond is not much shorter than in the complex [Ru(bq)$_2$-(CO)$_2$] which contains two mutually *trans*-oriented Ru–C_{aryl} bonds (2.12 – 2.13(1) Å) [4].

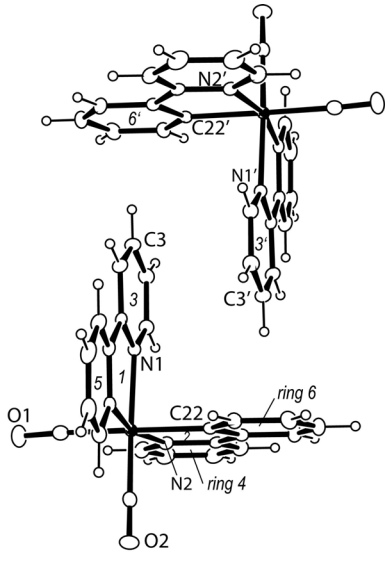


Fig. 4. The centrosymmetrical coordination motif found in both polymorphs of complex **2**. The ring numbering scheme is given by italic numbers.

In both polymorphs, the two ppy ligands deviate slightly from coplanarity: the dihedral angles between the phenyl and the pyridyl ring planes are 5.8 and 1.2° in **A**, and 3.9 and 7.7° in **B**.

The molecular structure of complex **3** is quite similar to that of **1** [19], with the exception of the missing OH substituent (Fig. 3). One sees again a dimeric complex with a non-crystallographic C_2-symmetric molecular topology. The four-membered ring Ru1–-O1–Ru2–O2 in **3** is sligthly more folded than in **1** (21.1(1) *vs.* 15.3(9)° around the O1···O2 axis), and the bonds Ru1–N1, Ru1–O1 and Ru1–O2 are longer in **3** than in **1** (Δd = 0.019, 0.033 and 0.028 Å, respectively).

The molecular packing in the crystal structure of polymorphs **A** and **B** of complex **2** is shown in Figs. 5 and 6, respectively. Both structures contain a centrosymmetrical coordination unit in which two molecules are held together by edge-to-face $C_{pyridyl}$–H···π_{phenyl} contacts and show a close facial $\pi\cdots\pi$ alignment for the pyridine rings of the two molecules (Fig. 4 and Table 3). The distance between the two parallel pyridine rings and the geometry of their slipped stacking are in a range that is often found in crystal structures containing facially arranged N-heteroaromatic ring systems [21].

In the crystal structure of polymorph **2B**, the two ppy ligands of a complex molecule are not only involved in the dimeric coordination motif shown

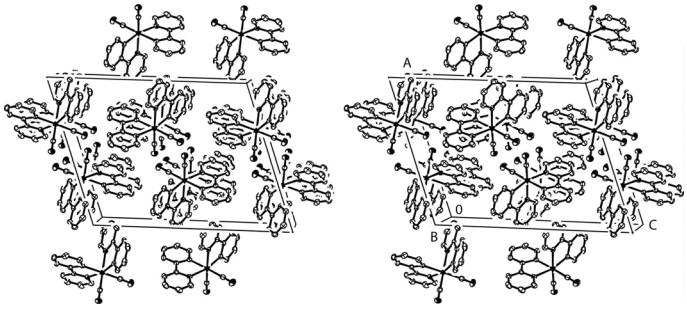


Fig. 5. Stereo view of the molecular packing in the crystal of complex **2**, polymorph **A**. Hydrogen atoms are not shown.

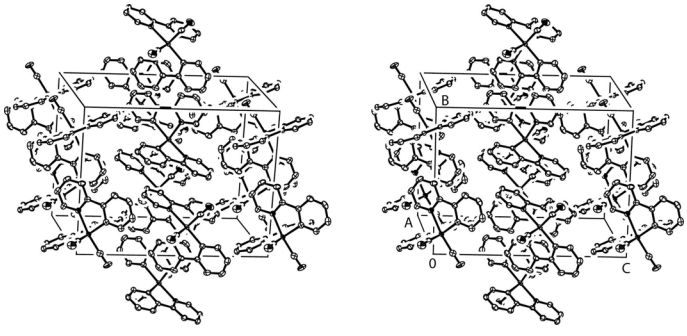


Fig. 6. Stereo view of the molecular packing in the crystal of complex **2**, polymorph **B**. Hydrogen atoms are not shown.

Table 3. Geometry of close intermolecular C–H$\cdots\pi$ and $\pi\cdots\pi$ contacts in the two polymorphs of complex **2**[a].

	Polymorph **A**		Polymorph **B**		
C–H$\cdots\pi$ contacts					
C–H$\cdots$A	C3–H3$\cdots$*Cg*(6′)	C18–H18$\cdots$*Cg*(5″)	C3–H3$\cdots$*Cg*(6′)		
C–H (Å)	0.95	0.95	0.95		
C$\cdots$A (Å)	3.503	3.693	3.580		
H$\cdots$A (Å)	2.56	2.86	2.64		
C–H$\cdots$A (deg)	172	140	172		
∠(C–H), A ring plane (deg)	84	62	84		
Facial ring–ring contacts with a Cg(a)–Cg(b) distance less than 4.0 Å					
Contact	ring 3 – ring 3′		ring 3 – ring 3′	ring 3 – ring 5″ [b]	ring 4 – ring 6‴ [c]
Distance *Cg*(a) – *Cg*(b) (Å)	3.666		3.705	3.943	3.959
Angle between ring planes (deg)	0.0		0.0	3.9	7.7
Perpendicular distance (Å)	3.375		3.399	3.480, 3.437	3.428, 3.274
Offset angle (deg)[d]	23.0		23.4	29.3, 28.0	34.2, 30.0

[a] For each of the two polymorphs, the values given in the first column refer to the centrosymmetrical coordination motif depicted in Fig. 4. *Cg*(6′), for example, designates the center of gravity of ring number 6′ as shown in Fig. 4. Symmetry codes for polymorph **A**: rings 3′ and 6′: $-x$, $2-y$, $-z$; ring 5″: x, $1.5-y$, $0.5+z$. For polymorph **B**: rings 3′ and 6′: $2-x$, $1-y$, $-z$; rings 3″ and 5″: $1-x$, $1-y$, $-z$; rings 4‴ and 6‴: $2-x$, $-y$, $-z$; [b] same geometry for ring 5 – ring 3″ contacts; [c] same geometry for ring 6 – ring 4‴ contacts; [d] angle between vector *Cg*(a)–*Cg*(b) and normal to plane *a*, and *vice versa*.

in Fig. 4, but also in a face-to-face arrangement with the ppy ligands of inversion-related neighboring molecules. Close contacts corresponding to a slipped pyridyl–phenyl π-stacking geometry can be observed (Fig. 6 and Table 3). In the crystal structure of polymorph **2A**, on the other hand, non-perpendicular edge-to-face arrangements of the aromatic rings of two neighboring molecules are found which give rise to some short C–H$\cdots\pi$ contacts (Fig. 5 and Table 3). In combination with C–H$\cdots$O interactions (C13–H13$\cdots$O2 (x, $1+y$, z): C–O 3.329 Å, H$\cdots$O 2.58 Å, ∠C–H$\cdots$O 135°), they could contribute to the stabilization of the crystal packing.

Conclusion

In contrast to the growing number of ruthenium complexes containing one bidentate 2-(2-pyridyl)-phenyl (ppy) ligand, complexes featuring two such ligands are still rare. We present here the new mononuclear ruthenium(II) complex [Ru-*cis*-(ppy)$_2$-

cis-$(CO)_2$] (**2**), which is easily prepared from $Ru_3(CO)_{12}$ and 2-phenylpyridine in a boiling cyclohexane–dimethoxyethane mixture. This synthesis is analogous to that of the complex $[Ru(bq)_2(CO)_2]$ which instead of the cyclometalated ppy ligand carries the analogous, but sterically more rigid benzo[*h*]quinolin-10-yl (bq) ligand [3, 13]. Surprisingly however, the two bq ligands in the latter (octahedral) complex are arranged *trans* to each other, while they are in a *cis* geometry in complex **2**. As a consequence of different *trans* influences, two distinctly different Ru–C_{ppy} bond lengths (2.112 *vs*. 2.068 Å) are found. Perhaps, the significant lengthening of one of these bonds facilitates its cleavage by methanol at elevated temperature, leading to replacement of one ppy ligand by a methanolate ligand and formation of the dinuclear complex $[Ru(OCH_3)(ppy)(CO)_2]_2$ (**3**). However, a complete conversion of **2** into **3** could not be achieved because of accompanying thermal degradation reactions.

Experimental Section

General information

Dodecacarbonyl-triruthenium was prepared by a published procedure [22]; 2-phenylpyridine was purchased and used as received. Solvents were dried by the usual methods. NMR spectra were recorded using a Bruker DRX 400 spectrometer (^{1}H: 400.13 MHz, ^{13}C: 100.62 MHz); the solvent signal served as the internal standard [^{1}H: δ(C*H*Cl$_3$) = 7.26 ppm; ^{13}C: δ(*C*DCl$_3$) = 77.0 ppm]. IR spectra: Bruker Vector 22 FTIR instrument. ESI mass spectra: Waters Micromass ZMD instrument. Differential scanning calorimetry (DSC): Perkin Elmer DSC 7 instrument. Microwave irradiation was carried out in a μ-Prep MW oven (MLS, Leutkirch, Germany) (frequency 2.45 GHz, continuous irradiation). *In situ* temperature control was obtained using a fibre optical sensor (ATC-FO sensor, MLS). Microanalyses were carried out with a Heraeus CHN-O-Rapid instrument in the Institute for Analytical Chemistry, University of Ulm.

Syntheses

*cis-(Dicarbonyl)-cis-bis[2-(pyridin-2-yl-κN)phenyl-κC^1] ruthenium, [Ru(ppy)$_2$(CO)$_2$] (**2**)*

A thick-walled Schlenk tube with a screw cap was flushed with argon and charged with $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol), 2-phenylpyridine (219 mg, 1.41 mmol), dry 1,2-dimethoxyethane (2 mL), and cyclohexane (7 mL) and was closed. The mixture was heated at 135 °C for 3 d. A gray solid, accompanied by small amounts of a black solid, gradually separated from the hot yellow solution. The mixture was then kept at 7 °C overnight, and the formed precipitate was isolated by filtration and washed with methanol (1 mL). In order to remove the black impurities, the solid was dissolved in dichloromethane (2 mL), and the solution was passed through a syringe filter (0.45 μm). The solvent was evaporated, and the residue was dried at 110 °C/0.001 mbar for 1 h to furnish 146 mg (0.31 mmol, 67 % yield based on Ru) of complex **2** as a gray powder. DSC determination of the melting points showed peaks at 275 and 282 °C, corresponding to the presence of two polymorphs (see the section on crystal structure determination). – IR (KBr): ν = 1989 (s, CO), 1931 (s, CO), 1600 (m), 1578 (m), 1475 (m), 751 (s) cm^{-1}. – ^{1}H NMR (CDCl$_3$): δ = 6.67 – 6.70 (m, 1 H), 6.75 – 6.77 (m, 1 H), 6.81 (virtual t, *J* = 7.1, 7.1 Hz, 1 H), 6.89 (virtual t, *J* = 7.1, 7.3 Hz, 1 H), 7.10 (virtual t, *J* = 7.3, 7.3 Hz, 1 H), 7.22 – 7.26 (m, 3 H), 7.51 (virtual t, *J* = 7.6, 7.6 Hz, 1 H), 7.67 (d, *J* = 7.8 Hz, 1 H), 7.79 (d, *J* = 7.8 Hz, 1 H), 7.83 (d, *J* = 8.1 Hz, 1 H), 7.91 (virtual t, *J* = 7.6, 7.6 Hz, 1 H), 8.00 (d, *J* = 8.1 Hz, 1 H), 8.10 (d, *J* = 7.3 Hz, 1 H), 9.07 (d, *J* = 5.1 Hz, 1 H); all multiplet lines are further split into doublets or broadened by long-range coupling, $J \leq 0.8$ Hz. – MS (ESI): *m/z* (%) = 464.8 [M]$^+$. – ^{13}C NMR (CDCl$_3$): δ = 118.9, 119.7, 120.3, 121.5, 122.5, 123.2, 123.5, 124.1, 129.1, 129.7, 136.6, 137.6, 137.7, 139.8, 142.7, 145.5, 146.7, 153.2, 164.6, 165.6, 177.2, 178.3, 194.6, 202.9. – $C_{24}H_{16}N_2O_2Ru$ (465.5): calcd. C 61.93, H 3.46, N 6.02; found C 61.92, H 3.45, N 6.01.

*cis-(Dicarbonyl)-di-μ-methoxy-bis[2-(pyridin-2-yl-κN) phenyl-κC^1] diruthenium, [Ru(OCH$_3$)(ppy)(CO)$_2$]$_2$ (**3**)*

$Ru_3(CO)_{12}$ (100 mg, 0.16 mmol), 2-phenylpyridine (146 mg, 0.94 mmol), dry methanol (8 mL), and dry toluene (2 mL) were placed in an argon-purged and flame-dried thick-walled Schlenk tube with a screw cap. The mixture was heated at 100 °C. After 1 h, dissolution of $Ru_3(CO)_{12}$ was complete, and after 2 d, the color of the solution gradually changed from dark-red to orange. The solution was allowed to cool, and the tube was carefully opened to relief the built-up pressure of carbon monoxide. TLC control at this point indicated the presence of complexes **2** and **3** [R_f = 0.81 and 0.65, respectively (silica gel, ethyl acetate/cyclohexane = 1/1)]. Heating was continued for another 24 h, then the solution was kept at 7 °C overnight. A white precipitate was formed which was isolated by filtration, washed with methanol (1 mL) and dried at 110 °C/0.001 mbar for 1 h, yielding 80 mg (0.12 mmol, 50 % based on Ru) of complex **3** as an off-white powdery solid. M. p. > 220 °C (dec.). – IR (KBr): ν = 2787 (m), 2028 (s), 2010 (s), 1964 (s), 1946 (s), 1603 (m), 1479 (m), 1050 (m), 753 (m) cm^{-1}. – ^{1}H NMR (CDCl$_3$): δ = 3.52 (s, 6 H, OCH$_3$), 6.49 – 6.53 (m$_c$, 2 H), 7.12 (dt, *J* = 7.4 and 1.3 Hz, 2 H), 7.18 (dt, *J* = 7.3 and 1.5 Hz, 2 H), 7.68 – 7.72 (m$_c$, 2 H), 7.75 (dd, *J* = 7.3 and 1.5 Hz, 2 H), 7.86 – 7.90 (m, 6 H). – ^{13}C NMR (CDCl$_3$): δ = 67.7 (OCH$_3$), 118.6, 120.9, 123.1, 124.1, 129.7, 137.6, 140.1, 143.4, 148.3,

Table 4. Summary of crystallographic data and structure refinement details for compounds **2** and **3**.

	2 Polymorph **A** (m. p. 280 °C)	**2** Polymorph **B** (m. p. 275 °C)	**3**
Formula	$C_{24}H_{16}N_2O_2Ru$	$C_{24}H_{16}N_2O_2Ru$	$C_{28}H_{22}N_2O_6Ru_2$
M_r	465.46	465.46	684.62
Cryst. size, mm^3	$0.38 \times 0.19 \times 0.08$	$0.38 \times 0.31 \times 0.12$	$0.38 \times 0.23 \times 0.15$
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	14.423(2)	8.898(1)	10.160(2)
b, Å	7.526(1)	13.172(1)	11.280(2)
c, Å	18.539(2)	16.334(2)	12.824(2)
α, deg	90	90	112.91(2)
β, deg	108.97(2)	98.84(2)	95.57(2)
γ, deg	90	90	100.86(2)
V, Å^3	1903.1(5)	1891.6(4)	1305.8(3)
Z	4	4	2
D_{calcd}, g cm^{-3}	1.624	1.634	1.741
$\mu(MoK_\alpha)$, cm^{-1}	8.47	8.52	12.02
$F(000)$, e	936	936	680
hkl range	$\pm17, \pm8, \pm22$	$\pm10, \pm16, \pm20$	$\pm11, \pm13, \pm15$
θ_{min}, θ_{max}, °	2.32, 25.93	2.00, 25.97	2.02, 25.89
Refls. measured	14419	18148	10219
Refls. unique (R_{int})	3517 (0.0311)	3664 (0.0374)	4700 (0.0613)
Param. refined	262	262	345
$R(F)$/w$R(F^2)$ (all reflections) [a]	0.0276 / 0.0496	0.0341 / 0.0613	0.0429 / 0.0869
Goodness of fit (GoF) [b]	0.955	0.974	0.969
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	$0.32/-0.29$	$0.35/-0.62$	$0.51/-0.65$

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma(w({F_o}^2 - {F_c}^2)^2)/2\Sigma w({F_o}^2)^2]^{1/2}$; [b] GoF = $[\Sigma w(|F_o| - |F|_c)^2/(N_{obs} - N_{param})]^{1/2}$.

164.1, 170.9, 196.3 (CO), 202.0 (CO). – MS (ESI): *m/z* (%) = 685.1 $[M]^+$. – $C_{28}H_{22}N_2O_6Ru_2$ (684.6): calcd. C 49.12, H 3.24, N 4.09; found C 49.06, H 3.27, N 4.11.

Conversion ***2*** $\rightarrow$ ***3***

a) Complex **2** (30 mg), dry methanol (2 mL), and dry toluene (0.5 mL) were heated at 80 °C for 5 d in a closed thick-walled Schlenk tube. After evaporation of the solvents, the residue was analyzed by ^{1}H NMR, which indicated an approximate composition of **2** : **3** : Hppy = 2 : 1 : 5.3 besides unidentified decomposition product(s).

b) A mixture of complex **2** (31 mg), methanol (2 mL) and 1,2-dimethoxyethane (2 mL) was placed in a 9 mL glass vessel which was closed and exposed to microwave irradiation at a controlled temperature of 135 °C (heating up with a maximum of 300 W for 5 min, then with 158 W for 25 min). The clear solution which had been formed on warming was then kept at 7 °C overnight, but no precipitate appeared. After addition of water, an off-white solid separated which was filtered off and dried (15 mg). According to ^{1}H NMR integration, the composition of the solid was **2** : **3** = 1 : 2.25.

X-Ray crystal structure determination

Slow evaporation of the solvent from a dichloromethane solution of **2** during several days yielded rod-shaped colorless crystals with a black hue (polymorph **A**). Crystallization of **2** from dichloromethane–pentane by the diffusion method gave a mixture of rod-shaped and prismatic crystals (polymorphs **A** and **B**, respectively) which were separated manually. DSC measurements (nitrogen atmosphere, heating rate 10 °C min^{-1} up to 250 °C and 5 °C min^{-1} in the range 250 – 300 °C) showed melting points at 280 °C (**A**) and 275 °C (**B**). Colorless single crystals of **3** were obtained by crystallization from methanol. Data collection was performed at 190 K on an image-plate diffractometer (Stoe IPDS) using monochromated MoK_α radiation (λ = 0.71073 Å). Both structures were solved by Direct Methods and refined (F^2 values) using a full-matrix least-squares method. For **2**, an empirical absorption correction was applied using the program DIFABS [23]. Hydrogen-atom positions were calculated geometrically and treated as riding on their bond neighbors in the refinement procedure. Software for structure solution and refinement: SHELXL-97 [24]; molecule plots: ORTEP-3 [25]; geometrical analysis: PLATON [26]. Further details are provided in Table 4.

CCDC-684363 (**2**, polymorph **A**), CCDC-684364 (**2**, polymorph **B**) and CCDC-684365 (**3**) 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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