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Synthesis, characterization and catalytic activity of dinuclear half-sandwich Ru(II), Rh(III) and Ir(III) complexes

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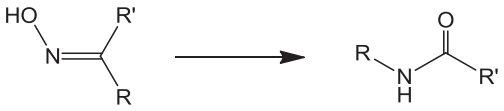
ABSTRACT

The reaction in dichloromethane between the chloro-bridged complexes $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})_2\text{Ru}_2(\mu\text{-Cl})_2\text{Cl}_2]$, $[(\eta^5\text{-}C_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2]$ and $[(\eta^5\text{-}C_5\text{Me}_5)_2\text{Ir}_2(\mu\text{-Cl})_2\text{Cl}_2]$, and the ligand precursor, 3,3′-[(1*E*,1′*E*)-{(methylenebis(4,1-phenylene))bis(azanylylidene)}bis(ethan-1-yl-1-ylidene)]bis(4-hydroxy-6-methyl-2H-pyran-2-one) (LH_2), has yielded the corresponding neutral dinuclear Ru(II), Rh(III) and Ir(III) complexes of the formula $[\{(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}\}_2\text{L}]$ (**1**), $[\{(\eta^5\text{-}C_5\text{Me}_5)\text{RhCl}\}_2\text{L}]$ (**2**) and $[\{(\eta^5\text{-}C_5\text{Me}_5)\text{IrCl}\}_2\text{L}]$ (**3**). The complexes were characterized by elemental analysis, infrared, ^{1}H NMR, ^{13}C NMR, ESI mass spectrometry, and complexes **2** and **3** by single-crystal X-ray structure analysis. All complexes were used as catalysts under different reaction conditions for the formation of amides from aldehydes in the presence of $NH_2OH\cdot HCl$ and $NaHCO_3$. All complexes show good conversion with catalytic turnover numbers up to 500.

Introduction

The amide bond formation is one of the most important reactions in organic chemistry. The formation of an amide bond is often seen as a contemporary challenge due to the occurrence of amide functions in chemicals of biological and industrial importance [1–3]. Several synthetic strategies have been developed to generate amide functions; the coupling of carboxylic acids or carboxylic acid derivatives with amines [4], the reaction of azides with water [5], the reaction of aromatic halides with an amino carbonyle [6], the reaction of alcohols with amines [7], the reaction of alcohols with a hydroxylamine hydrochloride [8], the Schmidt reaction [9], the Beckmann rearrangement [10], the conversion of aldoximes to amides [11], and the oxidative amidation of aldehydes [12]. Transition metal complexes based on manganese [13], iron [14], nickel [15], copper [16], zinc [17], zirconium [18], ruthenium [19], rhodium [20], palladium [21], silver/gold [22], and iridium [8] have been also used to synthesize amides catalytically. Mostly, these catalytic reactions require large amount of catalysts and are generally performed at high temperature.

The Beckmann rearrangement remains a traditional strategy for the preparation of amides from ketoximes in the presence of a Lewis acid catalyst (Scheme 1). However, due to an inactive migration of the hydrogen from an aldehyde/aldoxime during the amide formation, exploiting the Beckmann rearrangement is not always ideal for the synthesis of amides [23,24]. A successful modification of the standard Beckmann rearrangement conditions has been introduced by Williams using half-sandwich complexes as catalysts in the presence of *p*-toluenesulfonic acid [25], or cesium carbonate [8]. Other groups also modified the reaction conditions to increase the Beckmann rearrangement adding aluminum oxide [26], or $NaHCO_3$ [12,27] to catalysts and substrates. However, despite these modifications, in most cases the catalyst loading remains high, while for others, additives and high temperatures are also required.



Scheme 1. Beckmann rearrangement of oximes to form amides [28].

Therefore, in view of optimizing the reaction conditions of the Beckmann rearrangement in the presence of half-sandwich ruthenium(II), rhodium(III) and iridium(III) catalysts, a series of dinuclear complexes has been prepared: Dinuclear catalysts being potentially beneficial over mononuclear complexes [29]. All complexes were used as efficient catalysts for the aldehyde to amide transformation

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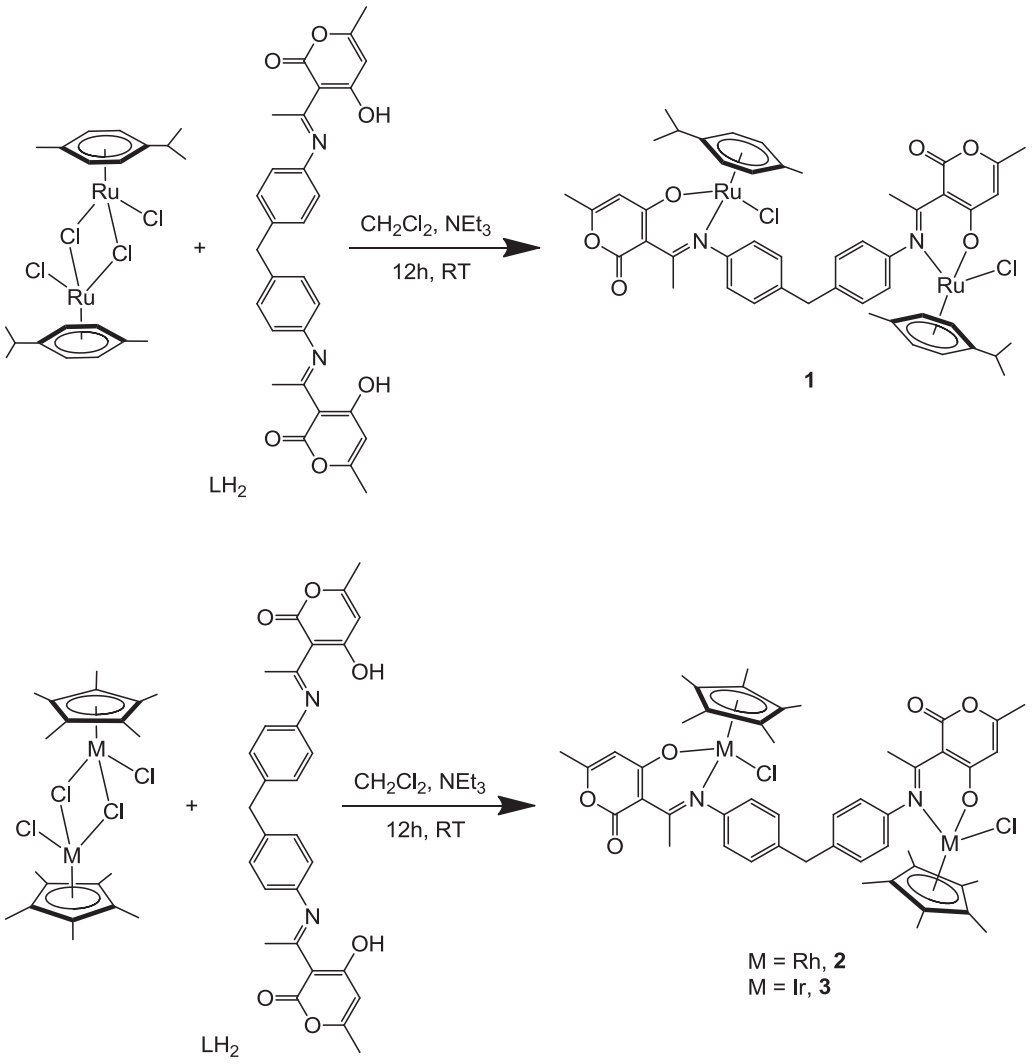
in a one pot procedure in the presence of $NaHCO_3$ and $NH_2OH{\cdot}HCl$. Under these conditions, the conversion from aldehyde to amide requires a low catalyst loading and gives good yields.

Results and discussion

One equivalent of the ligand precursor 3,3′-[(1*E*,1′*E*)-{(methylenebis(4,1-phenylene))bis(azanylylidene)}bis(ethan-1-yl-1-ylidene)]bis(4-hydroxy-6-methyl-2H-pyran-2-one) (LH_2) reacts with the chloro-bridged complexes $[(\eta^6\text{-}p\text{-}^i PrC_6H_4Me)_2Ru_2(\mu\text{-}Cl)_2Cl_2]$, $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}Cl)_2Cl_2]$ and $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu\text{-}Cl)_2Cl_2]$ in the presence of triethylamine to afford in good yields the dinuclear half-sandwich complexes $[\{(\eta^6\text{-}p\text{-}^i PrC_6H_4Me)RuCl\}_2L]$ (**1**), $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2L]$ (**2**) and $[\{(\eta^5\text{-}C_5Me_5)IrCl\}_2L]$ (**3**), respectively (see Scheme 2). All complexes are air stable solids and they have been characterized by elemental analysis, infrared, UV–visible, ^1H NMR, ^{13}C NMR spectroscopy and ESI mass spectrometry (see Experimental part).

The infrared spectra of the complexes show strong stretching vibrations in the frequency range 1993–1996 cm^{-1}. The presence of this strong $\nu_{C=O}$ stretching frequency confirms that the free lactone group is not involved in the coordination of L to the metal centers. In addition, a ν_{C-O} stretching frequency, which is observed at 1329 cm^{-1} in the ligand precursor, appears shifted to higher frequency 1347–1350 cm^{-1} after the complexation, confirming the coordination of L via the enolic oxygen. Similarly, the $\nu_{C=N}$ stretching frequency in the complexes is shifted to lower frequency as compared to the ligand precursor (LH_2), indicating the coordination of the imine nitrogen towards the metals. The electronic spectra of complexes **1**–**3** show two to three absorption bands in the UV–visible region: The intense absorption observed in the range 445–488 nm is assigned to MLCT transitions, while the band around 272–296 nm corresponds to n–π^* or π–π^* transitions.

The ^1H NMR spectra of complexes **1**–**3** also confirm the double N∩O chelating coordination mode of L. Upon coordination, the signal associated with the azomethine protons is upfield shifted as compared to the ligand precursor by almost 1 ppm, while the two doublets associated to the equivalent aromatic protons of the phenyl groups are now split due to the diastereotopic nature of complexes **1**–**3**. Indeed, the double N∩O coordination of L to the metal centers generates two chiral-at-the-metal centers, thus giving rise to potentially three species; a pair of enantiomers (*R*,*R* and *S*,*S*) and the *meso* form (*R*,*S*). However, the ^1N NMR spectra show only one set of signals for all complexes, suggesting that the *racemic* or *meso* form is not obtained. The chirality of the dinuclear complexes is clearly evidenced in complex **1** in which the methyl



Scheme 2. Synthesis of the dinuclear half-sandwich complexes **1**–**3**.

protons of the isopropyl group of the *p*-cymene ligand are now observed as two distinct doublets, while the aromatic protons of the *p*-cymene appear as four multiplets. The electrospray ionization (ESI) mass spectra of **1**–**3**, obtained in positive mode, give peaks at m/z = 1003.4, 1007.9 and 1205.4 respectively. These peaks correspond to $[M - Cl]^+$ for complexes **1** and **2**, while for **3** the peak corresponds to $[M - Cl + H_2O]^+$. The loss of one chloride atom for half-sandwich complexes is quite common under ESI-MS conditions [30–32].

Furthermore, the molecular structures of complexes **2** and **3** have been established by single-crystal X-ray structure analysis. Both complexes crystalize in the monoclinic space group *C* 2/*c*, showing the *R*,*R* and *S*,*S* enantiomers. Both metal centers adopt an archetypical piano-stool geometry with the metals being coordinated by a pentamethylcyclopentadienyl ligand, a chlorido ligand, and an imine nitrogen atom and a phenolic oxygen from L. The Ortep drawings of the two complexes are presented in Fig. 1, while selected bond lengths and angles are listed in Table 1.

As emphasized in Fig. 1, the two structures are almost undistinguishable, the intramolecular metal–metal distance being respectively 8.9110(9) Å in **2** and 8.9004(12) Å in **3**. Similarly, the Rh–Cl distance is 2.460(1) Å, while the Ir–Cl distance is 2.450(4) Å. Overall, the geometrical parameters of the two complexes are quite similar (Table 1), and are comparable to those observed in analogous half-sandwich Rh(III) and Ir(III) complexes with N∩O chelating ligands [31–32]. The molecular arrangement in **2** and **3** of the two pentamethylcyclopentadienyl rings suggested that the *meso* isomer was not formed for steric reasons, being in agreement with the ^{1}H NMR data where only one set of signals was observed.

Then, all complexes were tested as catalysts for aldehyde to amide transformations. The reaction conditions were optimized with benzaldehyde in the presence of $NH_2OH{\cdot}HCl$, by varying the nature of the base ($NaHCO_3$, Cs_2CO_3, NEt_3), the reaction time (1–24 h), the substrate to catalyst ratio (100:1 to 1500:1), the temperature and the solvent (acetonitrile, methanol, toluene). The best conversion of benzaldehyde to benzamide was obtained in toluene at reflux after 12 h with $NaHCO_3$, and with a substrate to catalyst ratio of 500:1 (Scheme 3). It is worth mentioning that without complexes, benzamide was not observed.

Following the optimization process with benzaldehyde, other aldehyde derivatives were tested; naphthaldehyde, 4-tolylaldehyde, 4-anisaldehyde, 4-chlorobenzaldehyde, 4-bromo

Table 1
Selected bond lengths and angles for complexes **2**·H_2O and **3** (i = $-x$, y, ½ − z).

	2·H_2O	**3**
Interatomic distances		
M–N1	2.118(3)	2.122(11)
M–O1	2.046(3)	2.052(11)
M–Cl1	2.4604(10)	2.450(4)
M–centroid	1.788	1.785
N1–C8	1.311(5)	1.29(2)
C8–C10	1.458(5)	1.47(2)
C10–C11	1.419(6)	1.43(2)
C11–O1	1.270(5)	1.26(2)
C10–C15	1.442(6)	1.46(2)
C15–O3	1.187(7)	1.15(3)
C15–O2	1.401(5)	1.41(2)
C13–O2	1.356(6)	1.34(2)
Angles		
N1–M–O1	86.05(11)	85.7(4)
N1–M–Cl1	84.48(9)	83.0(3)
O1–M–Cl1	88.01(10)	85.1(3)
M–N1–C8	127.4(2)	127.5(10)
M–O1–C11	128.3(3)	130.2(10)
N1–C8–C10	122.8(3)	124.6(13)
C8–C10–C11	123.8(3)	122.5(13)
C10–C11–O1	126.6(3)	126.0(14)
C2–C1–C2^i	113.8(4)	113.0(17)

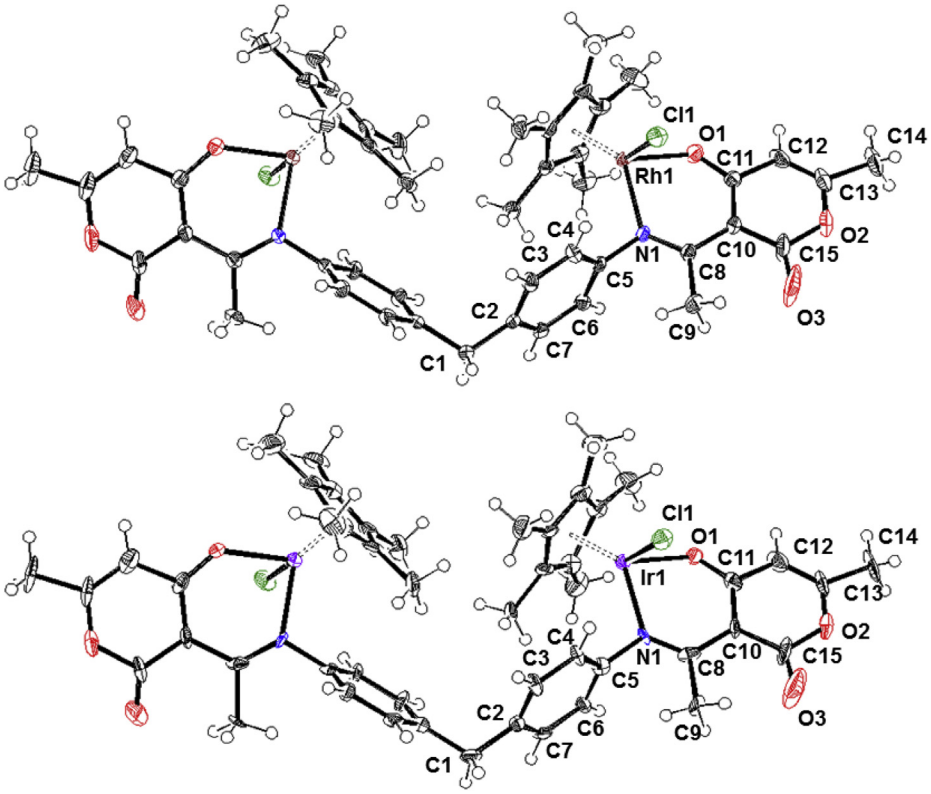
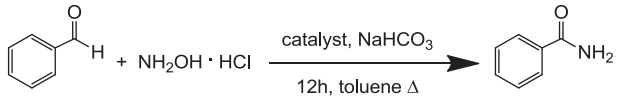


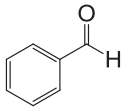
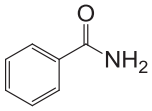
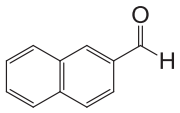
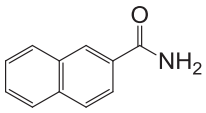
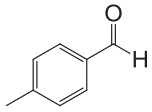
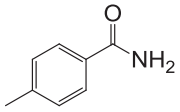
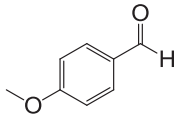
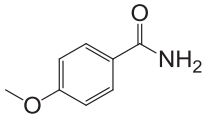
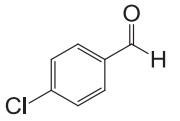
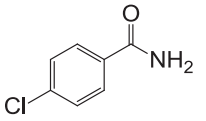
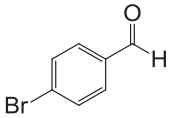
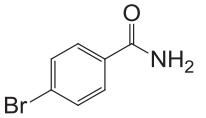
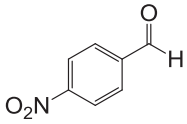
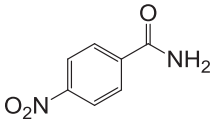
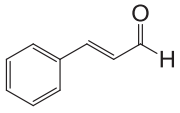
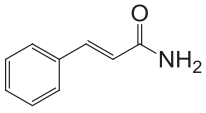
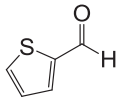
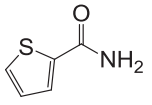
Fig. 1. Ortep diagrams of **2** (top) and **3** (bottom) with 50% probability ellipsoids (symmetry code = $-x$, y, ½ − z).



Scheme 3. Optimized conditions for the benzaldehyde to benzamide conversion using complexes **1**–**3**.

benzaldehyde, 4-nitrobenzaldehyde, *trans*-cinnamaldehyde and 2-thiophenecarboxaldehyde. At the end of each reaction, the amides were purified by column chromatography (see Supporting information), and the yields are reported in Table 2. These results show that all complexes are active catalysts for the formation of amides from aldehydes.

Table 2
One pot conversion of aldehydes to amides using complexes **1**–**3**.[a]

Entry	Aldehyde	Amide	Yield[b]		
			1	**2**	**3**
1			65	92	55[d]
2			55	64	77
3			80	98	98[c]
4			77	96	71
5			92	97[c]	25[c]
6			80	83[c]	76
7			92	33	43[c]
8			71	99	51[c]
9			95	89	94

[a] Conditions: aldehyde (1.0 mmol), complex **1**–**3** (0.002 mmol), $NaHCO_3$ (1.0 mmol), $NH_2OH{\cdot}HCl$ (1.0 mmol), toluene (2 mL), temperature 110 °C, time 12 h. C/S ratio 1:500.
[b] Isolated yields (%) after recrystallization or column chromatography.
[c] Isolated yield after 24 h.
[d] Isolated yield without addition of $NaHCO_3$.

Interestingly, the presence of electron withdrawing or electron donating group in the *para*-position of the benzaldehyde (entries 3–7) has a different effect on the yield of reaction depending on the catalyst used. For example, with 4-nitrobenzaldehyde (entry 7), only the ruthenium catalyst gives a good conversion, while for 4-chlorobenzaldehyde (entry 5) the iridium derivative remains almost inactive but excellent conversions are observed with the rhodium and ruthenium analogs. Surprisingly, complex **3** produces benzamide only in the absence of the base (entry 1), in only 55% yield, but on the other hand, with naphthaldehyde as substrate (entry 2) and $NaHCO_3$ as the base, the same iridium complex **3** is now the most active catalyst. Overall, except for 4-nitrobenzaldehyde, the rhodium catalyst appears to be the best catalyst for the conversion of aldehyde to amide, with even a quantitative conversion of *trans*-cinnamaldehyde (entry 8) under the catalytic conditions used.

Consequently, to better understand the catalytic mechanism and to potentially identify intermediate species produced during the catalytic reactions, a new experiment has been performed in which the reaction in toluene between 4-bromobenzaldehyde, $NH_2OH{\cdot}HCl$, $NaHCO_3$ and catalyst **2** was stopped at an early stage (12 h instead of 24 h). This experiment has allowed the isolation of (4-bromophenyl)methanimine: The structure of (4-bromophenyl) methanimine being confirmed by ^1H, $^{13}C\{^1H\}$ and 2D NMR spectroscopy (see Supporting information). The presence of an imine intermediate suggests that after coordination of the oxime to the rhodium center a rearrangement occurs, in which the oxygen atom of the oxime is replaced by a hydrogen, and the corresponding imine can be released. However, when the reaction is allowed to proceed for a prolonged period, the imine seems to be reinserted in the catalytic cycle and able to generate the expected amide. Based on these findings and using the catalytic cycle previously suggested by Crabtree [27], a catalytic cycle incorporating the release and reinsertion of the imine intermediate was proposed (Scheme 4). Despite the presence of two metal centers in catalysts **1**–**3** (L_n—M), we assumed only one catalytic center in this proposed mechanism, having no evidence at this early stage of our investigation if both metals were catalytically active simultaneously.

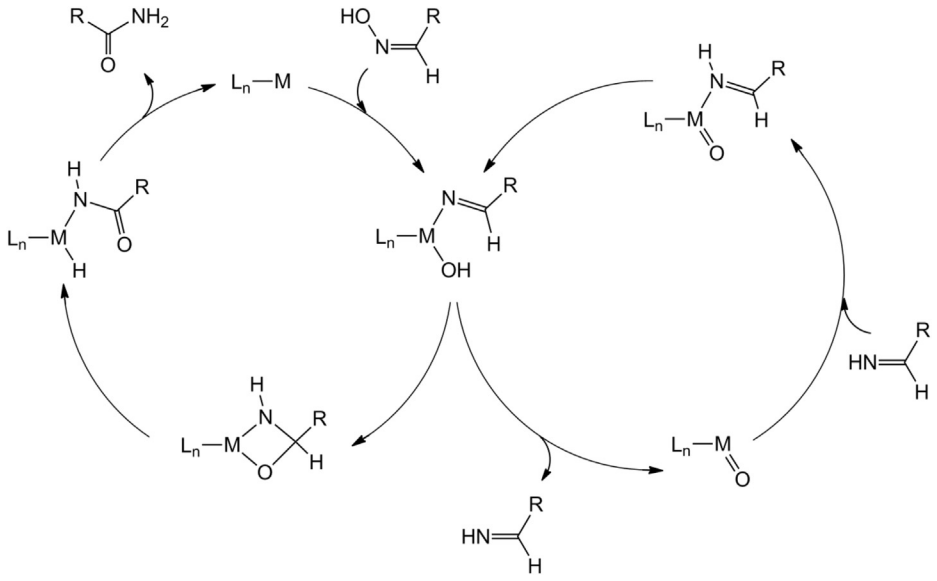
Conclusion

A series of half-sandwich complexes has been synthesized and fully characterized. The complexes appear to efficiently catalyze the formation of amides from aldehydes in the presence of $NH_2OH{\cdot}HCl$ and $NaHCO_3$ in toluene at reflux. It was also shown that imine intermediates are formed at the early stage of the catalytic reaction without however affecting the activity of the complexes. All complexes show good conversion with catalytic turnover numbers up to 500.

Experimental

Materials and methods

$RuCl_3{\cdot}nH_2O$, $RhCl_3{\cdot}nH_2O$ and $IrCl_3{\cdot}nH_2O$ were obtained from Johnson Matthey. α-Phellandrene, 1,2,3,4,5-pentamethylcyclo pentadiene, hydroxylamine hydrochloride, 4,4′-methylenedianiline, 3-acetyl-2-hydroxy-6-methyl-4*H*-pyran-4-one, benzaldehyde, naphthaldehyde, 4-anisaldehyde, *trans*-cinnamaldehyde, 2-thiophenecarboxaldehyde and sodium bicarbonate were obtained from Sigma Aldrich, while 4-nitrobenzaldehyde and 4-tolylaldehyde were purchased from Fluka and 4-bromobenzaldehyde from Acros. All reagents were of analytical reagent grade and



Scheme 4. Proposed mechanism for the catalytic rearrangement of aldoximes to amides (left cycle) from complexes **1**–**3** (M = Ru, Rh, Ir; L_n = ligands), showing the release and reinsertion of an imine intermediate (right cycle).

used as received. The starting materials $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu\text{-}Cl)_2Cl_2]$, $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}Cl)_2Cl_2]$ and $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu\text{-}Cl)_2Cl_2]$ were prepared according to published methods [33,34]. The ^1H, $^{13}C\{^1H\}$ and 2D NMR spectra were recorded with a Bruker Avance II 400 MHz spectrometer. Infrared spectra were recorded in the range of 4000–400 cm^{-1} as KBr pellets with a Perkin–Elmer FTIR 1720 X spectrometer. Electrospray mass spectra were obtained in positive ion mode with a LCQ Finnigan mass spectrometer. Microanalyzes were carried out by the Mikroelementaranalytisches Laboratorium, ETH Zürich (Switzerland). UV–visible absorption spectra were recorded with an Uvikon 930 spectrophotometer (10^{-4} M in CH_2Cl_2).

General procedure for the synthesis of the ligand precursor (LH_2)

The ligand precursor 3,3′-[(1*E*,1′*E*)-{(methylenebis(4,1-phenylene))bis(azanylyli-dene)}bis(ethan-1-yl-1-ylidene)]bis(4-hydroxy-6-methyl-2H-pyran-2-one) (LH_2) was synthesized by treating a methanolic solution of 4,4′-methylenedianiline and 2 equivalents of 3-acetyl-2-hydroxy-6-methyl-4*H*-pyran-4-one at reflux for 2 h. The product was obtained as a white solid, and purified using column chromatography (silica gel, hexane:chloroform, 3:1). Yield: 80%. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) = 7.27 (d, $^3J_{HH}$ = 8.4 Hz, 4H, H_{ar}), 7.12 (d, 4H, H_{ar}), 5.76 (s, 2H, CH), 4.05 (s, 2H, CH_2), 2.60 (s, 6H, CH_3), 2.16 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) = 184.9 (C–O), 175.3 (C=N), 163.4 (C=O), 140.4 (C_{ar}), 134.7 (C_{ar}), 130.0 (C_{ar}), 125.8 (C_{ar}), 107.1 ($C_{lactone}$), 97.4 ($C_{lactone}$), 40.9 (CH_2), 20.3 (CH_3), 19.9 (CH_3). MS (ESI positive mode): *m*/*z* 521.6 $[M + Na]^+$.

*General procedure for the synthesis of complexes **1**–**3***

A dichloromethane solution of the ligand precursor LH_2 (1 mmol) was stirred with triethylamine (1 mL) for 1 h. Then to the solution, the corresponding chloro bridged dimeric complex (1 mmol) was added and the mixture was stirred for another 11 h at room temperature. A color change of the solution from dark red to yellow was observed. The solution was concentrated to 2 mL, and hexane was added to initiate precipitation of the complex. The yellow–red powder was filtered and washed with hexane, and purified using column chromatography.

Complex **1**, yellow solid (silica gel, chloroform:methanol, 9.9:0.1). Yield: 84%. IR (KBr, ν, cm^{-1}): 1562 (CH=N), 1350 (C–O). ^1H NMR (400 MHz, MeOD, 25 °C): δ (ppm) = 7.49 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H_{ar}), 7.39 (s, 4H, H_{ar}), 7.23 (d, 2H, H_{ar}), 6.00 (s, 2H, CH), 5.46 (d, $^3J_{HH}$ = 4.8 Hz, 4H, $H_{p\text{-}cym}$), 5.06 (d, 2H, $H_{p\text{-}cym}$), 4.24 (d, 2H, $H_{p\text{-}cym}$), 4.17 (s, 2H, CH_2), 2.56 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CH(CH_3)_2$), 2.14 (s, 6H, CH_3), 2.12 (s, 6H, CH_3), 1.92 (s, 6H, CH_3), 1.16 (d, 6H, $CH(CH_3)_2$), 1.09 (d, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, MeOD, 25 °C): δ (ppm) = 178.0 (C–O), 170.2 (C=N), 165.2 (C=O), 161.6 (C_{ar}), 153.8 (C_{ar}), 139.6 (C_{ar}), 129.5 (C_{ar}), 128.8 (C_{ar}), 105.9 ($C_{lactone}$), 102.6 ($C_{p\text{-}cym}$), 100.4 ($C_{p\text{-}cym}$), 95.3 ($C_{p\text{-}cym}$), 85.9 ($C_{p\text{-}cym}$), 84.6 ($C_{p\text{-}cym}$), 80.5 ($C_{p\text{-}cym}$), 40.2 (CH_2), 30.1 ($CH(CH_3)_2$), 22.7 (CH_3), 21.3 (CH_3), 20.2 (CH_3), 17.8 (CH_3), 16.8 (CH_3). MS (ESI positive mode): *m*/*z* 1003.4 $[M - Cl]^+$. Anal. Calcd for $C_{49}H_{52}Cl_2N_2O_6Ru_2$: C, 56.70; H, 5.05; N 2.70. Found: C, 56.70; H, 5.05; N 2.81.

Complex **2**, reddish-brown solid (silica gel, chloroform:methanol, 9.5:0.5). Yield 85%. FTIR (KBr, ν, cm^{-1}): 1554 (CH=N), 1347 (C–O). ^1H NMR (400 MHz, MeOD, 25 °C): δ (ppm) = 7.41 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H_{ar}), 7.33 (d, 4H, H_{ar}), 7.24 (d, 2H, H_{ar}), 6.06 (s, 2H, CH), 4.07 (d, 2H, CH_2), 2.18 (s, 6H, CH_3), 2.17 (s, 6H, CH_3), 1.31 (s, 30H, H_{cp^*}). $^{13}C\{^1H\}$ NMR (100 MHz, MeOD, 25 °C): δ (ppm) = 178.9 (C–O), 172.0 (C=N), 165.7 (C=O), 161.6 (C_{ar}), 149.4 (C_{ar}), 139.9 (C_{ar}), 129.7 (C_{ar}), 128.7 (C_{ar}), 125.3 (C_{ar}), 124.56 (C_{ar}), 107.2 ($C_{lactone}$), 106.7 ($C_{lactone}$), 94.2 (C_{cp^*}), 40.2 (CH_2), 24.3 (CH_3), 22.2 (CH_3), 19.2 (CH_3), 17.9 (CH_3), 7.2 (C_{cp^*}). MS (ESI positive mode): *m*/*z* 1007.9 $[M - Cl]^+$. Anal. Calcd for $C_{49}H_{54}Cl_2O_6Rh_2 \cdot 0.5H_2O$: C, 55.91; H, 5.27; N 2.66. Found: C, 55.85; H, 5.22; N 2.72.

Complex **3**, yellow solid (silica gel, chloroform). Yield 70%. FTIR (KBr, ν, cm^{-1}): 1554 (CH=N), 1347(C–O). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) = 7.96 (s, 2H, H_{ar}), 7.17 (d, $^3J_{HH}$ = 7.2 Hz, 4H, H_{ar}), 6.75 (d, 2H, H_{ar}), 5.93 (s, 2H, CH), 4.01 (d, 2H, CH_2), 2.22 (d, 6H, CH_3), 2.09 (s, 6H, CH_3), 1.26 (s, 30H, H_{cp^*}). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) = 177.3 (C–O), 169.8 (C=N), 164.4 (C=O), 161.2 (C_{ar}), 150.5 (C_{ar}), 139.5 (C_{ar}), 129.8 (C_{ar}), 125.6 (C_{ar}), 106.9 ($C_{lactone}$), 102.4 ($C_{lactone}$), 85.6 (C_{cp^*}), 40.2 (CH_2), 25.6 (CH_3), 19.6 (CH_3), 8.5 (C_{cp^*}). MS (ESI positive mode): *m*/*z* 1205.4 $[M - Cl + H_2O]^+$. Anal. Calcd for $C_{49}H_{54}Cl_2Ir_2N_2O_6 \cdot 2H_2O$: C, 46.77; H, 4.65; N 2.23. Found: C, 46.47; H, 4.41; N 2.25.

Table 3
Crystallographic and structure refinement parameters for complexes **2**·H_2O and **3**.

	2·H_2O	**3**
Chemical formula	$C_{49}H_{56}Cl_2N_2O_7Rh_2$	$C_{49}H_{54}Cl_2N_2O_6Ir_2$
Formula weight	1061.68	1222.24
Crystal system	Monoclinic	Monoclinic
Space group	*C* 2/*c* (no. 15)	*C* 2/*c* (no. 15)
Crystal color and shape	Red block	Yellow block
Crystal size	0.22 × 0.19 × 0.17	0.19 × 0.17 × 0.16
a (Å)	33.249(3)	33.1075(19)
b (Å)	10.0527(8)	10.0748(4)
c (Å)	13.8955(10)	13.9307(8)
β (°)	93.921(7)	93.838(4)
V (Å^3)	4633.6(6)	4636.2(4)
Z	4	4
T (K)	173(2)	173(2)
D_c (g cm^{-3})	1.522	1.751
μ (mm^{-1})	0.881	5.900
Scan range (°)	$2.12 < \theta < 29.26$	$2.11 < \theta < 29.22$
Unique reflections	6284	6281
Observed refls [$I > 2\sigma(I)$]	4607	5195
R_{int}	0.0671	0.0796
Final *R* indices [$I > 2\sigma(I)$][a]	0.0525, wR_2 0.1000	0.1020, wR_2 0.1982
R indices (all data)	0.0849, wR_2 0.1089	0.1288, wR_2 0.2098
Goodness-of-fit	1.054	1.236
Max, min $\Delta\rho$/e (Å^{-3})	0.980, −1.196	6.993, −7.943

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

General procedure for the catalytic transformation of aldehydes to amides

The complexes (**1**–**3**) (0.002 mmol), the aldehyde (1 mmol), NH_2OH·HCl (1 mmol) and $NaHCO_3$ (1 mmol) were introduced in a dried schlenk tube and purged with N_2. Then, to the mixture, dried and degassed toluene (2 mL) was added, and the solution was refluxed for 12 h. The mixture was cooled to room temperature and the products were extracted with methanol and dichloromethane before being filtered through Celite to remove the remaining complex. The amide was purified using column chromatography, and dried under vacuum. Characterization details for each amide are given in the Supporting information.

Single-crystal X-ray structure analyses

Crystals of complexes **2**·H_2O and **3** were obtained by diffusion of pentane in a dichloromethane solution of **2** and **3**. Crystals were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo-Kα graphite monochromated radiation (λ = 0.71073 Å) with ϕ range 0–200°. The structures were solved by direct methods using the program SHELXS-97, while the refinement and all further calculations were carried out using SHELXL-97 [35]. The H-atoms were found on Fourier difference map or included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Crystallographic details are summarized in Table 3. Fig. 1 was drawn with Ortep [36].

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Appendix A. Supplementary material

CCDC 980659 (**2**·H_2O) and 980660 (**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.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.04.024.

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