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CNN pincer ruthenium complexes for efficient transfer hydrogenation of biomass-derived carbonyl compounds†

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The ligand HCNN^{OMe} (6-(4-methoxyphenyl)-2-aminomethylpyridine) is easily prepared from the commercially available 6-(4-methoxyphenyl)pyridine-2-carbaldehyde by the reaction of hydroxylamine and hydrogenation (H_2, 1 atm) with Pd/C. The pincer complexes *cis*-[RuCl(CNN^{OMe})(PPh_3)$_2$] (**1**) and [RuCl(CNN^{OMe})(PP)] (PP = dppb, **2**; and dppf, **3**) are synthesized from [$RuCl_2(PPh_3)_3$], HCNN^{OMe} and PP (for **2** and **3**) in 2-propanol with NEt_3 at reflux and are isolated in 85–93% yield. Carbonylation of **1** (CO, 1 atm) gives [RuCl(CNN^{OMe})(CO)(PPh_3)] (**4**) (79% yield) which cleanly reacts with Na[BAr$^f_4$] and PCy_3, affording the cationic *trans*-[Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)][BAr$^f_4$] (**5**) (92% yield). These robust pincer complexes display remarkably high catalytic activity in the transfer hydrogenation (TH) of lignocellulosic biomass carbonyl compounds, using 2-propanol at reflux in a basic medium (NaOiPr or K_2CO_3). Thus, furfural, 5-(hydroxymethyl)furfural and Cyrene are reduced to the corresponding alcohols with **2** and **3**, at S/C in the range of 10 000–100 000, within minutes or hours (TOF up to 1 500 000 h^{-1}). The monocarbonyl complex **5** was found to be extremely active in the TH of cinnamaldehyde, vanillin derivatives and ethyl levulinate at S/C in the range of 10 000–50 000. Vanillyl alcohol is also obtained by the TH of vanillin with **5** (S/C = 500) in 2-propanol in the presence of K_2CO_3.

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Introduction

The development of simple and environmentally friendly processes for the production of valuable chemicals from biosourced compounds has become a necessity for a sustainable economy, as it will reduce the dependence on fossil resources.[1–3] Carbohydrates and lignin are inexpensive and globally accessible biomass feedstocks which can be employed for the production of building blocks and biofuels[1,4–10] *via* hydrolysis, pyrolysis, defunctionalization and enzymatic degradation reactions.[1,11–14] In addition to the use of lignocellulosic biomass for conventional production, an emerging strategy is the preparation of new biomass-based platform chemicals.[3] The search for clean and efficient processes that involve the use of non-toxic renewable reagents and solvents, without the formation of side-products and waste, is a prerequisite for reducing environmental impact, in agreement with the principles of green chemistry.[15,16] In this context, catalysis will play a leading role in the production of either bulky compounds (biofuels), using heterogeneous catalysts, or biomass-derived platform chemicals through selective transformations with well-defined homogeneous catalysts.[17–20] Hydrogenation (HY)[21–24] and transfer hydrogenation (TH)[25–29] of carbonyl compounds by means of ruthenium complexes[30] are industrially widely accepted processes for the synthesis of alcohols using H_2 or 2-propanol as reducing agents, instead of $NaBH_4$ and $LiAlH_4$.[31] The high control of selectivity imparted by the metal complexes, associated with the high atom economy with respect to the classical methods, makes this approach a sustainable pathway for carbonyl reduction in organic synthesis. A particularly successful outcome was the introduction of the Noyori–Ikariya bifunctional amino ruthenium catalysts *trans*-[$RuCl_2$(PP)(diamine)] (PP = diphosphine) and [RuCl(arene)(NN)] in HY and TH reactions, respectively (Fig. 1).[32,33]

The isolation of *cis*-[$RuCl_2$(ampy)(PP)][34–37] and the related pincer complexes [RuCl(CNN)(PP)][38–42] and [RuCl(CNN)(PPh_3)(CO)][43] containing the 2-(aminomethyl)pyridine (ampy) motif[44] led to a class of extremely active TH and HY catalysts, which are complementary to the renowned Noyori–Ikariya

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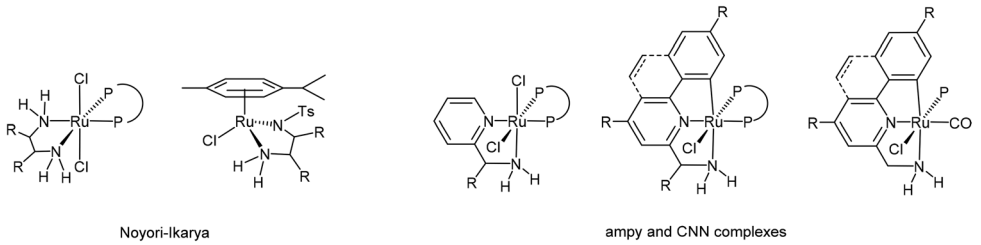


Fig. 1 The structure of amino- and ampy-type ruthenium complexes.

catalysts[32,33] (Fig. 1). In addition to high selectivity, the pincer complexes show a remarkably high productivity (S/C up to 100 000), which is a critical parameter for the catalytic C═O reduction. In particular, the pincer complexes have allowed the clean reduction of commercial-grade ketones and even aldehydes,[38,45,46] which can easily undergo aldol condensation,[47] Claisen–Tishchenko,[48–54] Cannizzaro[55] and decarbonylative side-reactions.[56–61] Furthermore, the pincer CNN Ru complexes have been found to be active in dehydrogenation,[62] racemization and deuteration of alcohols,[63] as well as imine hydrogenation.[64] It is worth pointing out that the HCNN ligands have been prepared through rather cumbersome procedures, namely starting from 6-arylpyridines and benzo[*h*] quinolones, *via* the formation of the *N*-oxide and cyano intermediates,[41,65] entailing chemoenzymatic synthesis[66] and heterocyclization of 1-naphthylamine.[38]

We report herein a straightforward synthesis of several pincer Ru complexes, prepared from the easily accessible 6-(4-methoxyphenyl)-2-aminomethylpyridine ($HCNN^{OMe}$) ligand, in combination with phosphines and carbon monoxide. The robust pincer complexes [RuCl(CNN^{OMe})(PP)] and *trans*-[Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)][BAr^f_4] exhibit high rate and selectivity in the TH of ketones and aldehydes available from lignocellulosic biomass to the corresponding alcohols in 2-propanol. High selectivity was attained for 5-HMF, Cyrene, ethyl levulinate, cinnamaldehyde and vanillin derivatives with an unprecedentedly high productivity (S/C up to 100 000).

Results and discussion

Synthesis of the $HCNN^{OMe}$ ligand

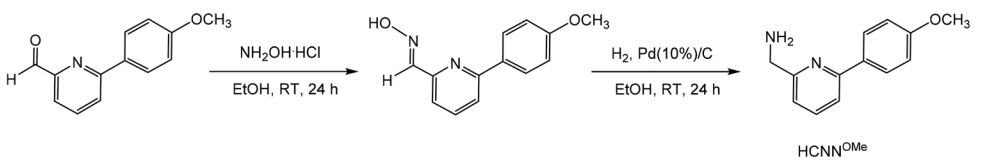
The 2,6 functionalized pyridine $HCNN^{OMe}$ ligand is easily synthesized on a g-scale by treatment of the commercially available 6-(4-methoxyphenyl)pyridine-2-carbaldehyde with $NH_2OH{\cdot}HCl$, resulting in the quantitative formation of the corresponding (*E*)-oxime, as inferred from the low field HC═N ^1H NMR signal at δ 8.18 ppm, which is consistent with the related (*E*)-oxime pyridine derivatives.[67,68] This intermediate is selectively hydrogenated with H_2 (1 atm) using 10% Pd/C at room temperature in ethanol (89% yield) (Scheme 1).

While the formation of the oxime occurs cleanly, the use of a diluted solution of oxime in ethanol under low hydrogen pressure in the presence of a palladium catalyst is crucial to avoiding the formation of both 6-(4-methoxyphenyl)-2-methylpyridine, *via* C–N cleavage, and the secondary amine bis((6-(4-methoxyphenyl)pyridin-2-yl)methyl)amine, through the nucleophilic attack of the formed amine towards the intermediate imine. The reported synthesis represents a more straightforward route to prepare HCNN pincer ligands on a g-scale, with respect to those previously reported, involving the formation of pyridine oxide and the use of Me_3SiCN with dimethylcarbamoyl chloride as the cyanation agent in the 2 position, followed by reduction with $LiAlH_4$ or H_2.[41]

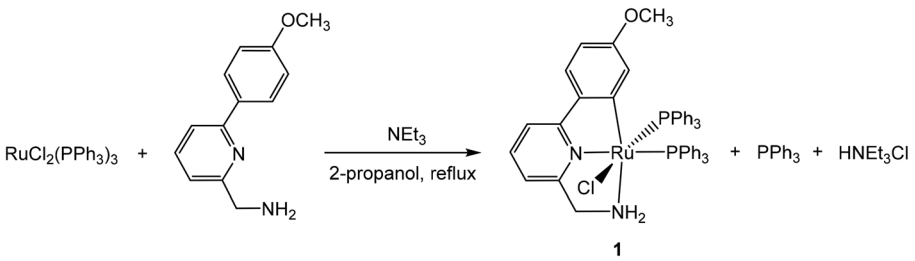
Synthesis of the pincer ruthenium complexes

The treatment of [$RuCl_2(PPh_3)_3$] with 1.2 equiv. of the ligand $HCNN^{OMe}$, in the presence of NEt_3 (10 equiv.) in 2-propanol at reflux (2 h), promptly affords the pincer complex *cis*-[RuCl(CNN^{OMe})(PPh_3)$_2$] (**1**) in 93% yield, through the elimination of one PPh_3 and orthometalation reaction (Scheme 2).

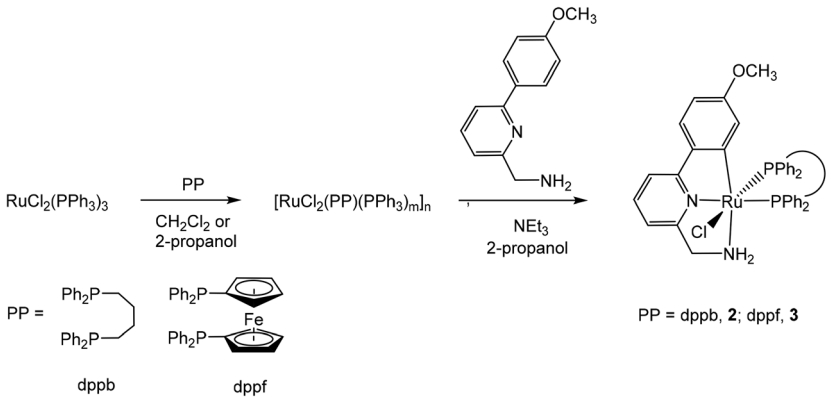
The $^{31}P\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 shows two doublets at δ 54.6 and 49.4 ppm, with a $^2J_{PP}$ of 32.8 Hz, whereas the cyclometalated carbon atom appears in the $^{13}C\{^1H\}$ NMR spectrum at δ 183.7 ppm (dd with a $^2J_{CP}$ of 13.8 Hz and 8.2 Hz). In addition, the CH_2N proton signals of **1** appear in the ^1H NMR spectrum as a doublet of doublets at δ 4.04 (dd, $^2J_{HH}$ = 16.2 Hz, $^3J_{HH}$ = 5.9 Hz) and a multiplet at δ 3.38, whereas the NH_2 signals are found at δ 3.65 and 1.87 ppm. The related diphosphine pincer derivative [RuCl(CNN^{OMe})(dppb)] (**2**) is isolated in 91% yield through a one-pot synthesis starting from [$RuCl_2(PPh_3)_3$] and 1,4-bis(diphenylphosphino)butane (dppb)



Scheme 1 Synthesis of the ligand $HCNN^{OMe}$.



Scheme 2 Synthesis of the complex *cis*-[RuCl(CNN^{OMe})(PPh$_3$)$_2$] (**1**).

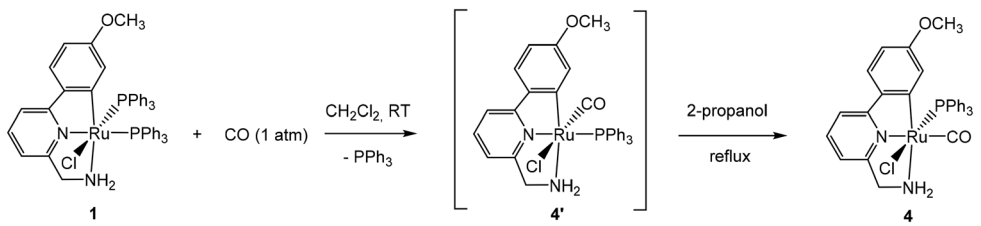


Scheme 3 Synthesis of the diphosphine complexes [RuCl(CNN^{OMe})(PP)] (PP = dppb, **2**; and dppf, **3**).

in 2-propanol at reflux (2 h), *via* the intermediate [RuCl$_2$(dppb)(PPh$_3$)], followed by reaction with HCNN^{OMe} and NEt$_3$ in 2-propanol at reflux (2 h) (Scheme 3).

Alternatively, **2** is prepared by reacting [RuCl$_2$(dppb)(PPh$_3$)][69] with HCNN^{OMe} and NEt$_3$ in 2-propanol at reflux, and isolated in 88% yield. The ^{31}P{^{1}H} NMR spectrum of **2** shows two doublets at δ = 56.9 and 41.0 ppm, with $^2J_{PP}$ = 37.7 Hz, whereas the ^{13}C{^{1}H} NMR doublet at δ 52.3 ppm ($^3J_{CP}$ = 2.7 Hz) corresponds to the *C*H$_2$N group and the doublet of doublets at δ 184.9 ppm ($^2J_{CP}$ = 16.0 and 7.7 Hz) corresponds to the orthometalated carbon atom. The ^{1}H NMR spectrum of **2** shows a doublet of doublets at δ 4.15 ppm and a triplet of doublets at δ 3.75 ppm corresponding to the CH$_2$N protons, whereas the NH$_2$ signals are found at δ 3.45 and 2.03 ppm, as inferred from the ^{1}H–^{15}N HSQC 2D NMR spectrum (see ESI, Fig. S22†), according to the related derivative [RuCl(CNN)(dppb)].[41,42] Similarly, the dppf complex [RuCl(CNN^{OMe})(dppf)] (**3**, 85% yield) has been obtained from [RuCl$_2$(PPh$_3$)$_3$] and 1,1′-bis(diphenylphosphino)ferrocene (dppf) in dichloromethane at RT (2 h), followed by reaction with the ligand HCNN^{OMe} in the presence of NEt$_3$ in 2-propanol at reflux, without the isolation of the intermediate [RuCl$_2$(dppf)(PPh$_3$)$_m$]$_n$ (Scheme 3).[63,69] The spectroscopic data of **3** are similar to those of **2**, with two ^{31}P{^{1}H} NMR doublets at δ = 61.5 and 44.1 ppm ($^2J_{PP}$ = 35.6 Hz) and the ^{13}C{^{1}H} NMR orthometalated signal at δ 182.5 (dd, $^2J_{CP}$ = 14.9 and 8.2 Hz). The monocarbonyl derivative [RuCl(CNN^{OMe})(PPh$_3$)(CO)] (**4**) has been isolated in 79% yield by the reaction of **1** with CO (1 atm) in CH$_2$Cl$_2$ at RT (12 h), followed by a 48 h treatment of the crude product with 2-propanol at reflux (Scheme 4).

Control experiments show that during carbonylation of **1** at RT both **4** and its isomer **4′** (δ_P 48.8 ppm, 2 : 1 ratio) are formed, the latter being completely converted into the thermodynamically most stable complex **4** in 2-propanol at reflux. The ^{31}P{^{1}H} NMR



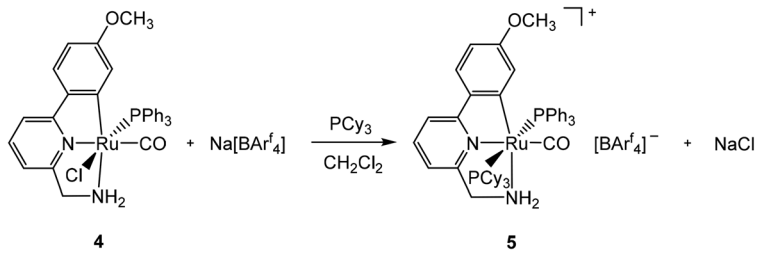
Scheme 4 Synthesis of the monocarbonyl complex [RuCl(CNN^{OMe})(CO)(PPh$_3$)] (**4**).

spectrum of **4** in CD_2Cl_2 shows a singlet at δ 56.7 ppm, the ^1H NMR signals for the diastereotopic methylene are found at δ 4.23 and 3.41 and the NH_2 protons are found at δ 3.87 and 2.79 ppm. In the $^{13}C\{^1H\}$ NMR spectrum the cyclometalated carbon gives a doublet at δ 179.0 ($^2J_{CP}$ = 12.6 Hz), whereas the doublet at δ 207.1 ($^2J_{CP}$ = 17.7 Hz) corresponds to the CO ligand, which exhibits an IR ν_{CO} absorption band at 1913 cm^{-1}.[43] The treatment of **4** with $Na[BAr^f_4]$ (Ar^f = 3,5-$(CF_3)_2C_6H_3$) in the presence of one equiv. of the bulky phosphine PCy_3 in CH_2Cl_2 at RT quickly affords the cationic complex *trans*-$[Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)][BAr^f_4]$ (**5**), isolated in 92% yield, *via* the substitution of Cl with the PCy_3 ligand (Scheme 5).

The $^{31}P\{^1H\}$ NMR spectrum of **5** in CD_2Cl_2 shows two doublets at δ 34.2 and 22.0 ppm with $^2J_{PP}$ = 250.9 Hz, which is in agreement with a *trans* arrangement of the two phosphorus atoms. In the ^1H NMR spectrum of **5** the two diastereotopic CH_2N protons appear as a doublet of doublets at δ 4.28 ppm ($^2J_{HH}$ = 16.3 Hz and $^3J_{HH}$ = 6.5 Hz) and as a multiplet in the range δ 3.62–3.46 ppm, partially overlapped with one NH_2 proton, while the other is at δ 2.83. The cyclometalated carbon atom gives a doublet of doublets at δ 175.3 ppm ($^2J_{CP}$ = 10.9 Hz and 8.9 Hz) in the $^{13}C\{^1H\}$ NMR spectrum, whereas the triplet at δ 206.1 ppm ($^2J_{CP}$ = 15.3 Hz) corresponds to the coordinated CO, which exhibits an IR stretching absorption at 1919 cm^{-1}. All these data are consistent with those found for the related bis PPh_3 complex *trans*-$[Ru(CNN)(PPh_3)_2(CO)][BAr^f_4]$.[43] It is worth pointing out that although several homoleptic ruthenium(II) complexes showing the *trans*-$Ru(CO)(P)_2$ core have been described, only few examples containing two phosphines, exerting a different *trans* influence, have been reported so far.[70–74]

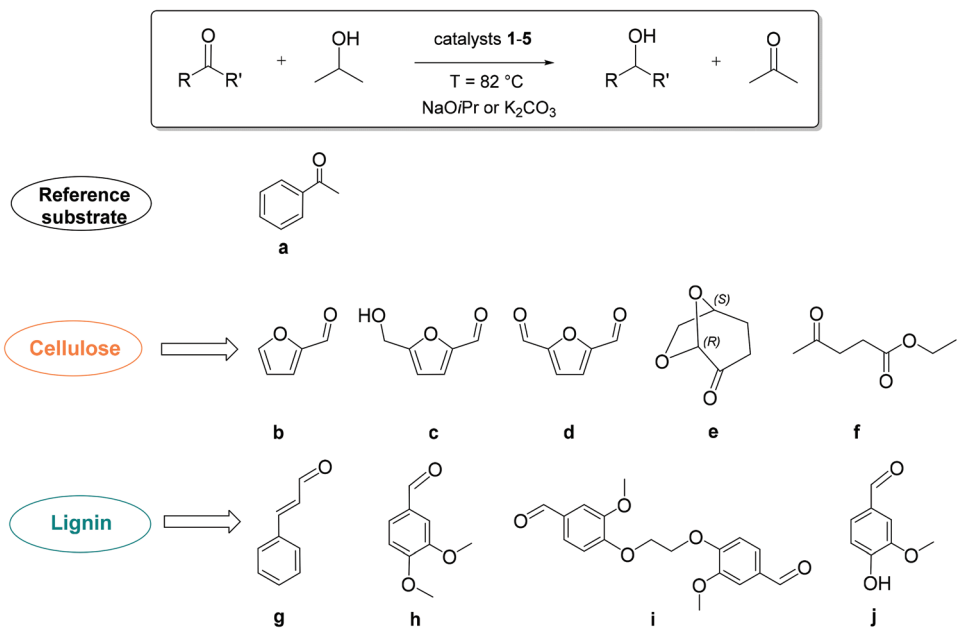
Reduction of aldehydes and ketones *via* TH catalyzed by the CNN^{OMe} pincer ruthenium complexes

The easily prepared pincer CNN^{OMe} ruthenium complexes **1–5** have been investigated in the reduction of the model substrate acetophenone **a** *via* TH with 2-propanol in the presence of a base. These complexes have been found to be extremely productive, affording quantitative conversion of **a** at S/C = 10 000–100 000 (S/C = substrate/catalyst molar ratio) and TOF up to 1 100 000 h^{-1}. This protocol has been subsequently applied to the TH of carbonyl compounds obtained from lignocellulosic biomass (Scheme 6).



4 **5**

Scheme 5 Synthesis of the cationic carbonyl complex $[Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)][BAr^f_4]$ (**5**).



Scheme 6 Reduction of carbonyl compounds *via* TH catalyzed by complexes **1–5**.

Table 1 Catalytic TH of acetophenone **a** (0.1 M) with complexes **1–5** (S/C = 10 000–100 000) and NaOiPr (2 mol%) in 2-propanol at 82 °C

Entry	Complex	S/C	Time [min]	Conv.[a] [%]	TOF[b] [h^{-1}]
1	**1**	10 000	8 h	97	1200
2	**2**	20 000	5	99	1 100 000
3	**2**	50 000	20	99	450 000
4	**3**	20 000	15	99	260 000
5	**3**	50 000	60	98	100 000
6	**4**	20 000	20	99	95 000
7	**4**	50 000	120	98	60 000
8	**5**	10 000	20	99	150 000
9	**5**	20 000	40	99	110 000
10	**5**	50 000	240	99	92 000
11	**5**	100 000	8 h	98	42 000

[a] Conversions have been determined by GC analyses. [b] Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion.

Complex **1** at a S/C of 10 000 shows poor activity in the TH of **a**, affording 97% conversion after 8 h with NaOiPr (2 mol%) in 2-propanol at 82 °C (Table 1, entry 1). On the other hand, the diphosphine dppb derivative **2** leads to complete conversion of **a** into 1-phenylethanol at S/C = 20 000 and 50 000 in 5 and 20 min with TOF values of 1 100 000 and 450 000 h^{-1}, respectively (Table 1, entries 2 and 3), indicating that **2** is a highly productive catalytic TH system with an activity comparable to that observed for the related CNN pincer complexes.[42]

Complex **3**, containing the robust dppf ligand, also allows the reduction of **a** at S/C = 20 000 and 50 000, although with longer reaction times (15 and 60 min) (Table 1, entries 4 and 5), which is in line with the analogous pincer 2-aminomethylbenzo[*h*]quinoline derivatives [RuCl(CNN^{R})(dppf)].[38] Interestingly, the monocarbonyl complex **4**, obtained from **1** by the substitution of one PPh_3 with CO, shows a higher activity with respect to **1**, affording a quantitative reduction of **a** in 20 and 120 min at S/C = 20 000 and 50 000, respectively, even if the rate is slower than those for the diphosphine derivatives **2** and **3** (entries 6 and 7). Finally, the cationic complex **5**, formed from **4** by the replacement of the chloride ion with PCy_3, shows complete reduction of **a** at S/C = 10 000–50 000, with a higher rate with respect to **4** (TOFs up to 150 000 h^{-1}, entries 8–10). It is worth noting that **5**, unlike complexes **1–4**, is highly soluble in alcohols, stable in diluted 2-propanol solution for days and much less oxygen sensitive, and allows the TH of **a** even at S/C = 100 000, showing that **5** is a practical and productive catalyst for the carbonyl reduction (entry 11). Control experiments, carried out under the same catalytic conditions and without ruthenium, show a small conversion of **a** (9%) in 12 h, indicating that the base NaOiPr is a poor catalyst.[75] The high performance of the monocarbonyl pincer **5**, containing the PCy_3 phosphine, is in line with our studies on the systems [$RuCl_2$(HCNN)$(CO)_2$]/phosphines and the related pincer complex [Ru(CNN)$(PPh_3)_2$(CO)][BAr^f_4].[43] As a matter of fact, for this class of pincer carbonyl ruthenium complexes the use of the more basic phosphine PCy_3, with respect to PPh_3, resulted in an enhancement of the catalytic activity. Therefore, it is likely that during the TH complex **5** undergoes a substitution of PPh_3, generating a robust catalytically active hydride species H-Ru(CNN)(CO)(PCy_3), which is less sensitive towards catalyst deactivation.[76–78]

On the basis of the results obtained with the model substrate **a**, the most promising complexes **2**, **3** and **5** have been investigated in the TH of both aldehydes and ketones available from the cellulose and lignin biomass, using 2-propanol as the hydrogen donor, in the presence of NaOiPr or K_2CO_3 (Scheme 6). The reduction of furfural (FAL) **b** to furfuryl alcohol has been achieved with **2** and **3** at S/C = 10 000 and 1000 with NaOiPr (2 mol%), affording selective reduction to the corresponding alcohol (94 and 92%) in 30 and 2 min, respectively (Table 2, entries 1 and 2). Conversely, with **5** at S/C = 10 000 the formation of furfuryl alcohol (90%) has been achieved in 10 min, with a small amount of uncharacterized side products (4%) (entry 3). The use of potassium carbonate as the weak base under the same catalytic conditions results in poor conversion with the Ru catalysts (47% in 24 h with **2**, see ESI; Table S1,† entry 2). The catalytic HY of **b** has been reported for Ru bis(diimine) complexes[79] and Ru(III)–acetylacetonate/dppb at 100–140 °C with H_2 under pressure.[80]

The substrate 5-(hydroxymethyl)furfural (5-HMF) **c**, available from the cellulose biomass (C6 sugars), can be hydrogenated to 2,5-bis(hydroxymethyl)furan (BHMF) which is a building block for the environment friendly polyurethanes and polyesters[81,82] and for the synthesis of 1,6-hexanediol used in adhesives.[83] In spite of the vast literature on the heterogeneous catalysis of **c**, only very recently has homogeneous TH emerged as a viable and easy to apply route for the reduction of **c** to BHMF.[84] Complex **2** efficiently catalyzes the selective reduction of **c** to BHMF at S/C = 10 000 and 20 000 in 5 and 10 min, respectively (entries 4 and 5). With **3** and **5** complete conversion is observed at S/C = 10 000 and 50 000 (10 min–8 h) (entries 6–9), whereas at S/C = 1000 the reduction occurs with **3** in 1 min (see ESI; Table S1,† entry 3), indicating that these pincer complexes are among the most active and productive catalysts for the TH of **c** with 2-propanol.[85] Using complex **2** as the catalyst (3.1 mg, S/C = 10 000), BHMF (4.57 g) has been prepared in 90% yield (99% purity), starting from 5.00 g of **c** in 2-propanol at reflux in 30 min. With **2** and **3** in the presence of NaOiPr, incomplete reduction of 2,5-diformylfuran (DFF) **d** to BHMF is observed, whereas with the weak base K_2CO_3 (5 mol%) **3** affords only 4% conversion to the diol in 3 h (see ESI; Table S1,† entry 4). Interestingly, complex **5** at S/C = 1000 with K_2CO_3 affords the quantitative formation of BHMF in 60 min (entry 10). To the best of our knowledge, no examples of TH of **d** with 2-propanol have been reported in the literature so far. The bicyclic ketone Cyrene (dihydrolevoglucosenone) **e**, obtained by the HY of levoglucosenone from cellulosic materials (*e.g.* Furacell process),[86] is emerging as a green, non-toxic dipolar aprotic solvent in place of *N*-methylpyrrolidone, DMF or sulfolane.[87] The HY of **e** over the supported metal catalysts led to levoglucosanol as a mixture of *erythro* and *threo* diastereoisomers[88,89] and 1,6-hexanediol through ring opening.[90] Conversely, no examples of homogeneous catalysts for the TH of **e** have been

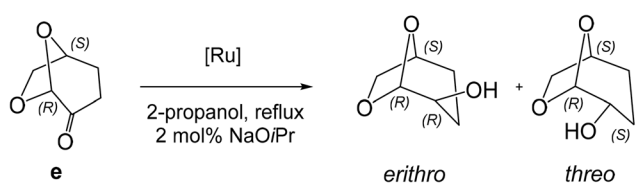
Table 2 Catalytic TH of lignocellulosic biomass carbonyl compounds (0.1 M) to alcohols with complexes 2, 3, and 5 (S/C = 500–100 000) in 2-propanol at 82 °C

Entry	Substrate	Complex	S/C	Base[a]	Time [min]	Conv.[b] [%]	Alcohol [%]	By-prod. [%]
1	**b**	**2**	10 000	NaOiPr	30	94	94	—
2	**b**	**3**	1000	NaOiPr	2	92	92	—
3	**b**	**5**	10 000	NaOiPr	10	94	90	4
4	**c**	**2**	10 000	NaOiPr	5	99[c]	99	—
5	**c**	**2**	20 000	NaOiPr	10	99[c]	96	3
6	**c**	**3**	10 000	NaOiPr	10	99[c]	94	5
7	**c**	**3**	50 000	NaOiPr	60	99[c]	94	5
8	**c**	**5**	10 000	NaOiPr	30	99[c]	98	< 1
9	**c**	**5**	50 000	NaOiPr	8 h	99[c]	98	1
10	**d**	**5**	1000	K_2CO_3	60	99[c]	95	4
11	**e**	**2**	1000	NaOiPr	1	99	99[d]	—
12	**e**	**2**	10 000	NaOiPr	2	99	99[d]	—
13	**e**	**3**	10 000	NaOiPr	1	99	99[e]	—
14	**e**	**3**	50 000	NaOiPr	5	98	98[e]	—
15	**e**	**5**	50 000	NaOiPr	150	98	98[f]	—
16	**e**	**5**	100 000	NaOiPr	7 h	99	99[f]	—
17	**f**	**2**	1000	NaOiPr	60	95	92[g]	3[h]
18	**f**	**2**	1000	K_2CO_3	20	99	97[g]	2[h]
19	**f**	**3**	1000	NaOiPr	15	60	58[g]	2[h]
20	**f**	**3**	1000	K_2CO_3	15	99	98[g]	1[h]
21	**f**	**5**	10 000	K_2CO_3	30	98	96[g]	2[h]
22	**g**	**2**	10 000	K_2CO_3	8 h	98	94	4[i]
23	**g**	**3**	10 000	K_2CO_3	8 h	99	92	7[i]
24	**g**	**5**	10 000	K_2CO_3	60	99	90	9[i]
25	**g**	**5**	20 000	K_2CO_3	120	98	91	7[i]
26	**g**	**5**	50 000	K_2CO_3	8 h	99	91	8[i]
27	**h**	**3**	25 000	K_2CO_3	3	99[c]	98	1
28	**h**	**5**	25 000	K_2CO_3	30	99[c]	99	—
29	**h**	**5**	25 000	NaOiPr	15	99[c]	95	4
30	**i**	**3**	25 000	NaOiPr	4	99[c]	99	—
31	**j**	**5**	500	K_2CO_3	36 h	96[c]	96	—

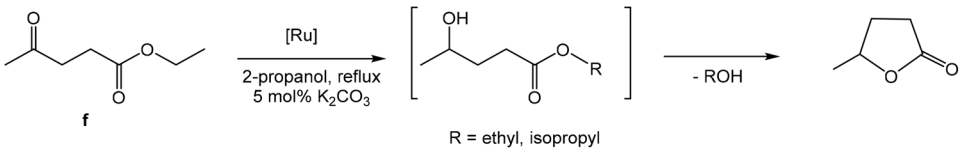
[a] Base: NaOiPr (2 mol%) or K_2CO_3 (5 mol%). [b] Conversions have been determined by GC analyses. [c] Conversions have been determined by NMR analyses. [d] *erythro*/*threo* ratio 1 : 1.2. [e] *erythro*/*threo* ratio 1.4 : 1. [f] *erythro*/*threo* ratio 1 : 5.7. [g] % of γ-valerolactone (GVL). [h] Isopropyl 4-hydroxypentanoate. [i] 3-Phenylpropan-1-ol.

previously reported. Interestingly, we have found that **e** is easily reduced *via* TH in 2-propanol using complexes **2**, **3** and **5** with NaOiPr (2 mol%) as the base (Scheme 7).

With **2** at S/C = 10 000 **e** is quantitatively reduced to alcohol in 2 min with an *erythro*/*threo* ratio of 1/1.2. Conversely, **3** affords complete reduction at S/C = 10 000 and 50 000 in 1 and 5 min, respectively, affording a TOF of 1 500 000 h^{-1} with *erythro*/*threo* = 1.4/1, as confirmed by ^1H and $^{13}C\{^1H\}$ NMR measurements (entries 11–14).[89,91] Although **5** shows a lower rate for the TH of **e** with respect to **2** and **3**, complex **5** leads to complete conversion at S/C = 50 000 and 100 000 in 150 min and 7 h, respectively, with *erythro*/*threo* = 1/5.7 (entries 15 and 16, and see ESI, Fig. S46†). Notably, the diastereomerically pure *threo* alcohol has been recently isolated by selective reduction of **e** using baker's yeast (*Saccharomyces cerevisiae*).[91,92] The HY of levulinic acid (LA) and levulinate esters,[93–97] which are directly accessible from lignocellulosic biomass,[95] is an attractive process for the synthesis of γ-valerolactone (GVL) which has wide applications as a solvent, fuel additive and monomer for polymer synthesis.[98] Most of the processes involve the HY of LA to GVL at high temperatures and H_2 pressure.[97,99–102] Recently, Ir and Ru complexes based on phosphine and dipyridylamine ligands have been reported to efficiently hydrogenate LA to GVL with formic acid as the hydrogen donor and in the presence of H_2.[103,104] In addition, the TH of LA and levulinate derivatives has been described using the Shvo catalyst,[105] $Fe(OTf)_2$/tetraphos[105] with formic acid and the Casey's iron catalyst[94] with 2-propanol at S/C = 100, but no examples of Ru complexes for the TH of levulinate esters with 2-propanol have been reported to date. The pincer complex **2** (S/C = 1000) catalyzes efficiently the TH of ethyl levulinate **f** to GVL (92%) in 60 min with NaOiPr (2 mol%) (entry 17, and Scheme 8). Interestingly, the use of the weak base K_2CO_3 (5 mol%) as the co-catalyst results in a higher conversion and selectivity to GVL (97%) in a shorter reaction time (20 min) (entry 18).



Scheme 7 Reduction of Cyrene **e** to levoglucosanol *via* TH catalyzed by complexes **2**, **3** and **5**.



Scheme 8 Conversion of ethyl levulinate to GVL *via* TH catalyzed by complexes **2**, **3** and **5**.

A similar behavior has been observed for the dppf derivative **3**, leading to 99% conversion with K_2CO_3, whereas with NaOiPr only 60% of GVL was attained in 15 min (entries 19 and 20). Unlike **2** and **3**, complex **5** has been proved to be active at a lower loading, affording complete conversion of **f** at S/C = 10 000 in the presence of K_2CO_3 (5% mol) in 30 min, with a TOF of 20 000 h^{-1}. To the best of our knowledge, the cationic monocarbonyl PCy_3 pincer complex **5** is one of the most active systems for the TH of **f** (entry 21). Control ^1H NMR experiments show that the reaction proceeds *via* the reduction of **f** to a mixture of ethyl and isopropyl 4-hydroxyvalerate, generated in the 2-propanol basic medium, followed by an intramolecular cyclization to GVL and alcohol elimination, in accordance with the literature data (Scheme 8 and see ESI, Fig. S40†).[104] The HY of *trans*-cinnamaldehyde **g**, which can be obtained from lignin defunctionalization, leads to 3-phenylpropanal, 3-phenylpropan-1-ol and 3-phenyl-2-propenol (cinnamyl alcohol), which can find applications as feedstocks in pharmaceuticals, cosmetics and fine chemicals.[106–108] The chemoselective reduction of the C=O bond is more challenging because the HY of the C=C bond is thermodynamically more favorable than that of the carbonyl group and many efforts have been devoted to improve the selectivity towards cinnamyl alcohol with metal based catalysts.[109] Nevertheless, we have found that **g** can be easily reduced *via* TH to the corresponding allylic alcohol with complexes **2** and **3** (S/C = 10 000) leading to 94 and 92% conversion, respectively, in the presence of K_2CO_3, with the formation of 3-phenylpropan-1-ol as a by-product in 4 and 7% yield in 8 h, as a result of the concomitant reduction of the C=C bond (entries 22 and 23). Control experiments with **2** at a higher loading (S/C = 1000) gives cinnamyl alcohol (94%) in 5 min, while after a prolonged reaction time (1 h) 3-phenylpropan-1-ol is formed in up to 35% yield (see ESI; Table S1, entry 7 and Fig. S41†). Complex **5** has been proved to catalyze the TH of **g** at higher S/C ratios, namely 10 000, 20 000 and 50 000, with the formation of 7–8% of 3-phenylpropan-1-ol (1–8 h, entries 24–26). The functionalized vanillin derivatives 3,4-dimethoxybenzaldehyde (veratraldehyde) **h**, 4,4′-[ethane-1,2-diylbis(oxy)]bis(3-methoxybenzaldehyde) **i** and also vanillin **j** have been reduced to the corresponding alcohols with the pincer ruthenium complexes. For these bio-derivatives, no examples of TH Ru catalysts have been previously reported. Veratraldehyde **h** is promptly converted to veratryl alcohol (3,4-dimethoxybenzyl alcohol) by using complex **3** (S/C = 25 000) in 3 min (entry 27). By using the cationic complex **5** (S/C = 25 000) the quantitative reduction occurs in 30 and 15 min, in the presence of K_2CO_3 (5 mol%) and NaOiPr (2 mol%), respectively (entries 28 and 29). The dialdehyde **i** is rapidly and selectively reduced to the corresponding dibenzyl alcohol in 99% yield with **3** (S/C = 25 000) in the presence of NaOiPr in 4 min, with a remarkably high TOF value of 500 000 h^{-1} and without the formation of the monoalcohol or by-products of the aldol condensation, due to the high reaction rate (entry 30). Interestingly, vanillin **j**, which is an acidic phenolic compound, is selectively reduced to vanillyl alcohol (96%) with **5** (S/C = 500) in the presence of K_2CO_3 (5 mol%) in 36 h at 82 °C, while complex **3** shows no conversion under these catalytic conditions (entry 31). To the best of our knowledge, complex **5** is the first example of a catalyst for the selective TH of vanillin to the corresponding alcohol. The use of $[RuCl_2(PPh_3)_3]$ in the HY of **j** (S/C = 30 and 33 atm of H_2) leads to the formation of vanillyl alcohol, 2-methoxy-4-methylphenol and 2-methoxy-phenol, as a result of hydrogenation and decarbonylative aldehyde reactions,[110] whereas with the Shvo catalyst (S/C = 200 and 10 atm of H_2) under acidic conditions the alcohol product is formed at 145 °C.[111] Conversely, the TH of **j** with formic acid on palladium results in the exclusive formation of 2-methoxy-4-methylphenol.[112]

Conclusions

In summary, a straightforward synthesis of a series of pincer CNN^{OMe} ruthenium complexes is reported from a $HCNN^{OMe}$ ligand prepared in high yield from the commercially available 6-(4-methoxyphenyl)pyridine-2-carbaldehyde, by reaction with hydroxylamine and subsequent hydrogenation. These pincer complexes are highly productive catalysts for the transfer hydrogenation (TH) of several biomass-derived carbonyl compounds with 2-propanol as the hydrogen source, affording an unprecedented activity (S/C ratio up to 100 000 and TOF up to 1 500 000 h^{-1}). Interestingly, the derivatives $[RuCl(CNN^{OMe})(PP)]$ (PP = dppb and dppf) display high catalytic activity in the reduction of furfural, 5-HMF and Cyrene. Conversely, the monocarbonyl *trans*-$[Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)][BAr^f{}_4]$ shows an unprecedentedly high productivity in the TH of ethyl levulinate, cinnamaldehyde and vanillin derivatives. These results indicate that since no universal catalyst can be designed for the TH of carbonyl compounds, specific substrates can be efficiently reduced by pincer ruthenium complexes through a suitable tuning of the ancillary ligands. Further studies on the development of highly active pincer catalysts for the C–H bond formation reactions of biomass relevant products, including asymmetric transformations, are underway.

Experimental

General

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were carefully dried by standard methods and distilled under argon before use. The substrate **i** was synthetized following a previously reported method.[113,114] The ruthenium complexes $[RuCl_2(PPh_3)_3]$[115] and $[RuCl_2(dppb)(PPh_3)]$[69] were prepared according to literature procedures, whereas all other chemicals were purchased from Aldrich and Strem and used without further purification. NMR measurements were recorded on a Bruker Avance III HD NMR 400 spectrometer. Chemical shifts (ppm) were relative to TMS for ^1H and $^{13}C\{^1H\}$, whereas H_3PO_4 was used for $^{31}P\{^1H\}$. Infrared measurements were performed using a Bruker Vector 22 FTIR spectrometer. Elemental analyses (C, H, and N) were carried out with a Carlo Erba 1106 analyzer, whereas GC analyses were performed with a Varian CP-3380 gas chromatograph equipped with a 25 m length MEGADEX-ETTBDMS-β chiral column with hydrogen (5 psi) as the carrier gas and a flame ionization detector (FID). ESI-MS analysis and multi-stage mass spectrometry (MS^n) experiments were performed using a Finnigan LXQ Linear Ion Trap (Thermo Scientific, San Jose, CA, USA) fitted with an ESI source operating in positive mode. The data acquisition was under the control of Xcalibur software (Thermo Scientific).

Synthesis of (*E*)-6-(4-methoxyphenyl)pyridine-2-carbaldehyde oxime. Hydroxylamine hydrochloride (0.57 g, 8.2 mmol) was carefully added to a solution of commercially available 6-(4-methoxyphenyl)pyridine-2-carbaldehyde (1.50 g, 7.04 mmol) in a mixture of acetonitrile (47.5 mL), methanol (82.5 mL) and water (3.75 mL), which was heated up and turned yellow. The obtained clear solution was then stirred for 30 min at room temperature. The solvents were evaporated off and the residue was dissolved in 100 mL of ethyl acetate and extracted with 5% aqueous $NaHCO_3$ (2 × 50 mL). The organic phase was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure to obtain the oxime as a white solid. Yield 1.53 g (95%). Elemental analysis calcd (%) for $C_{13}H_{12}N_2O_2$: C 68.41, H 5.30, N 12.27; found: C 68.37, H 5.39, N 12.21. MS (*m*/*z*, ESI^+): 251.16 [M + Na], 229.18 [M + H]. ^1H NMR (400.1 MHz, CD_3OD, 25 °C): δ = 8.18 (s, 1H; HC═N), 7.95 (ddd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.9 Hz, $^5J_{HH}$ = 2.1 Hz, 2H; aromatic protons), 7.81 (pseudo-t, $^3J_{HH}$ = 7.9 Hz, 1H; aromatic proton), 7.75–7.72 (m, 2H; aromatic protons), 7.02 (ddd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.9 Hz, $^5J_{HH}$ = 2.1 Hz, 2H; aromatic protons), 3.85 ppm (s, 3H; CH_3O); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_3OD, 25 °C): δ = 160.9 (s; C*C*OCH$_3$), 157.0 (s; N*C*C), 152.1 (s; N*C*CH═N), 149.1 (s; C*C*H═N), 137.4–113.7 (m; aromatic carbon atoms), 54.4 ppm (s; *C*H$_3$O).

Synthesis of 6-(4-methoxyphenyl)-2-aminomethylpyridine $HCNN^{OMe}$. A solution of (*E*)-6-(4-methoxyphenyl)pyridine-2-carbaldehyde oxime (1.5 g, 6.58 mmol) in absolute ethanol (450 mL) was introduced into a 500 mL three neck round bottomed flask under stirring and an inert atmosphere. After the addition of 10% Pd/C (150 mg), the reaction mixture was hydrogenated (1 atm of H_2) at room temperature overnight, leading to complete conversion as found by TLC analysis. The catalyst was removed from the reaction mixture by filtering through a Celite pad and was thoroughly washed with absolute EtOH. The resulting clear solution was concentrated to dryness under reduced pressure, affording 1.45 g of crude product as an off-white solid. The residue was purified by silica gel flash chromatography (eluent: Et_2O/MeOH/NH_4OH (94 : 5 : 1)), affording the pure compound as a colorless powder. Yield 1.25 g (89%). Elemental analysis calcd (%) for $C_{13}H_{14}N_2O$: C 72.87, H 6.59, N 13.07; found: C 72.85, H 6.63, N 13.01. MS (*m*/*z*, ESI^+): 215.20 [M + H]. ^1H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 8.05 (ddd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 3.0 Hz, $^5J_{HH}$ = 2.0 Hz, 2H; aromatic protons), 7.72 (t, $^3J_{HH}$ = 7.7 Hz, 1H; aromatic proton), 7.59 (d, $^3J_{HH}$ = 7.8 Hz, 1H; aromatic proton), 7.20 (d, $^3J_{HH}$ = 7.6 Hz, 1H; aromatic proton), 7.03 (ddd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 3.0 Hz, $^5J_{HH}$ = 2.1 Hz, 2H; aromatic protons), 4.00 (s, 2H; CH_2N), 3.89 (s, 3H; CH_3O), 1.77 ppm (s, 2H; NH_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ = 162.0 (s; N*C*C), 160.5 (s; C*C*OCH$_3$), 156.0 (s; N*C*CH$_2$), 137.1–113.9 (m; aromatic carbon atoms), 55.3 (s; *C*H$_3$O), 47.9 ppm (s; *C*H$_2$N).

Synthesis of *cis*-$[RuCl(CNN^{OMe})(PPh_3)_2]$ (1). The ligand $HCNN^{OMe}$ (54 mg, 0.252 mmol, 1.2 equiv.) and NEt_3 (291 μL, 2.09 mmol, 10 equiv.) were added to $[RuCl_2(PPh_3)_3]$ (200.0 mg, 0.209 mmol) in 2-propanol (5 mL) and the mixture was stirred at reflux for 2 h. The resulting suspension was filtered, obtaining a yellow solid, which was washed with 2-propanol (2 × 3 mL), methanol (2 × 3 mL), and *n*-heptane (2 × 5 mL) and dried under reduced pressure. Yield: 170 mg (93%). Elemental analysis calcd (%) for $C_{49}H_{43}ClN_2OP_2Ru$ (874.36): C 67.31, H 4.96, N 3.20; found: C 67.22, H 5.01, N 3.16. ^1H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 8.02 (dt, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.6 Hz, 1H; aromatic proton), 7.77 (m, 1H; aromatic proton), 7.63 (d, $^3J_{HH}$ = 2.2 Hz, 1H; aromatic proton), 7.53–7.01 (m, 13H; aromatic protons), 6.98–6.79 (m, 18H; aromatic protons), 6.61 (d, $^3J_{HH}$ = 7.5 Hz, 1H; aromatic proton), 6.41 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.6, 1H; aromatic proton), 4.04 (dd, $^2J_{HH}$ = 16.1 Hz, $^3J_{HH}$ = 6.0 Hz, 1H; CH_2N), 3.68 (s, 3H; CH_3O), 3.74–3.60 (m, 1H; NH_2), 3.38 (m, 1H; CH_2N), 1.87 ppm (m, 1H; NH_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $C_2D_2Cl_4$, 25 °C): δ = 183.7 (dd, $^2J_{CP}$ = 13.2 Hz, $^2J_{CP}$ = 8.9 Hz; CRu), 163.0 (s; N*C*C), 157.2 (s; C*C*OCH$_3$), 156.8 (s; N*C*CH$_2$), 142.2–109.0 (m; aromatic carbon atoms), 55.1 (s; *C*H$_3$O), 50.8 ppm (d, $^2J_{CP}$ = 1.8 Hz; *C*H$_2$N). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ = 54.6 (d, $^2J_{PP}$ = 32.8 Hz), 49.4 (d, $^2J_{PP}$ = 32.8 Hz).

Synthesis of $[RuCl(CNN^{OMe})(dppb)]$ (2)

Method A. The complex $[RuCl_2(PPh_3)_3]$ (200 mg, 0.209 mmol) and dppb (98 mg, 0.230 mmol, 1.10 equiv.) were suspended in 2-propanol (4.0 mL), and the mixture was stirred at reflux for 3 h. The ligand $HCNN^{OMe}$ (54 mg, 0.252 mmol, 1.21 equiv.) and NEt_3 (291 μL, 2.09 mmol, 10 equiv.) were added and the mixture was refluxed for 2 h. The suspension was cooled to room temperature, obtaining a yellow precipitate, which was filtered, washed with 2-propanol (3 mL), MeOH (2 × 3 mL), and *n*-heptane (2 × 5 mL) and dried under reduced pressure. Yield: 147 mg (91%). Elemental analysis calcd (%) for $C_{41}H_{41}ClN_2OP_2Ru$ (776.26): C

63.34, H 5.27, N 3.65. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 8.21 (tt, $^3J_{HH}$ = 9.2 Hz, $^4J_{HH}$ = 1.5 Hz, 2H; aromatic protons), 7.78 (tt, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.3 Hz, 2H; aromatic protons), 7.58–7.41 (m, 7H; aromatic protons), 7.41–7.32 (m, 6H; aromatic protons), 7.30 (d, $^3J_{HH}$ = 8.5 Hz, 1H; aromatic proton), 7.19 (t, $^3J_{HH}$ = 7.8 Hz, 1H; aromatic proton), 7.00 (d, $^3J_{HH}$ = 8.1 Hz, 1H; aromatic proton), 6.88 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1H; aromatic proton), 6.67 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz, 1H; aromatic proton), 6.64 (d, $^3J_{HH}$ = 7.1 Hz, 1H; aromatic proton), 6.53 (dd, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 2.5 Hz, 1H; aromatic proton), 6.06 (t, $^3J_{HH}$ = 8.1 Hz, 2H; aromatic protons), 4.15 (dd, $^2J_{HH}$ = 15.5 Hz, $^3J_{HH}$ = 4.6 Hz, 1H; CH_2N), 3.75 (td, $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 4.7 Hz, 1H; CH_2N), 3.61 (s, 3H; CH_3O), 3.45 (td, $^2J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 5.4 Hz, 1H; NH_2), 3.16 (pseudo-q, J_{HH} = 12.3 Hz, 1H; CH_2P), 3.03 (tt, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 3.3 Hz, 1H; CH_2P), 2.33 (dd, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 9.0 Hz, 1H; CH_2P), 2.24 (t, $^2J_{HH}$ = 14.6 Hz, 1H; CH_2P), 2.08–1.85 (m, 3H; C$H_2$$CH_2P$ and NH_2), 1.79–1.65 (m, 1H; CH_2CH_2P), 1.65–1.56 (m, 1H; CH_2CH_2P), 1.25–1.06 ppm (m, 1H; CH_2CH_2P). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ = 184.9 (dd, $^2J_{CP}$ = 16.0 Hz, $^2J_{CP}$ = 7.7 Hz; CRu), 162.9 (s; N*C*C), 157.7 (s; C*C*OCH_3), 155.9 (s; N*C*CH_2), 144.3–107.3 (m; aromatic carbon atoms), 54.6 (s; *C*H_3O), 52.2 (d, $^3J_{CP}$ = 2.7 Hz; *C*H_2N), 32.7 (dd, $^1J_{CP}$ = 24.7 Hz, $^3J_{CP}$ = 1.5 Hz; *C*H_2P), 30.7 (d, $^1J_{CP}$ = 31.5 Hz; *C*H_2P), 26.5 (d, $^2J_{CP}$ = 1.6 Hz; *C*H_2CH_2P), 21.8 ppm (d, $^2J_{CP}$ = 1.2 Hz; *C*H_2CH_2P). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C) δ 56.9 (d, $^2J_{PP}$ = 37.7 Hz), 41.0 ppm (d, $^2J_{PP}$ = 37.7 Hz).

Method B. To a suspension of [$RuCl_2(PPh_3)$(dppb)] (100 mg, 0.116 mmol) in 2-propanol (3.0 mL) the ligand $HCNN^{OMe}$ (28 mg, 0.131 mmol, 1.13 equiv.) and triethylamine (162 μL, 1.16 mmol, 10 equiv.) were added. The mixture was stirred under reflux conditions for 2 h, obtaining a yellow precipitate, which was filtered, washed with 2-propanol (2 × 2 mL), methanol (2 × 2 mL), and *n*-heptane (2 × 5 mL) and dried under reduced pressure. Yield: 80.1 mg (89%).

Synthesis of [RuCl(CNN^{OMe})(dppf)] (3). The complex [$RuCl_2(PPh_3)_3$] (200 mg, 0.209 mmol) and dppf (128 mg, 0.230 mmol, 1.10 equiv.) were dissolved in dichloromethane (4.0 mL) and the solution was stirred for 3 h at room temperature. The solvent was evaporated under reduced pressure and the ligand $HCNN^{OMe}$ (54 mg, 0.252 mmol, 1.21 equiv.) dissolved in 2-propanol (4.0 mL) and NEt_3 (291 μL, 2.09 mmol, 10 equiv.) were added. The mixture was refluxed for 3 h obtaining a yellow precipitate, which was filtered, washed with 2-propanol (2 × 4 mL), methanol (2 × 4 mL), and *n*-heptane (2 × 5 mL) and dried under reduced pressure. Yield: 161 mg (85%). Elemental analysis calcd (%) for $C_{47}H_{41}ClFeN_2OP_2Ru$ (904.17): C 62.43, H 4.57, N 3.10; found: C 62.36, H 4.50, N 3.02. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 8.51 (t, $^3J_{HH}$ = 8.3 Hz, 2H; aromatic protons), 8.06 (t, $^3J_{HH}$ = 7.4 Hz, 2H; aromatic protons), 8.01 (d, $^4J_{HH}$ = 1.6 Hz, 1H; aromatic proton), 7.73 (t, $^3J_{HH}$ = 8.5 Hz, 1H; aromatic proton), 7.54 (d, $^3J_{HH}$ = 7.2 Hz, 1H; aromatic proton), 7.49 (t, $^3J_{HH}$ = 8.3 Hz, 2H; aromatic protons), 7.41 (d, $^3J_{HH}$ = 7.3 Hz, 1H; aromatic proton), 7.37 (t, $^3J_{HH}$ = 7.2 Hz, 2H; aromatic protons), 7.31 (d, $^3J_{HH}$ = 8.5 Hz, 1H; aromatic proton), 7.28–7.15 (m, 4H; aromatic protons), 6.99 (d, $^3J_{HH}$ = 8.2 Hz, 1H; aromatic proton), 6.95 (d, $^3J_{HH}$ = 7.2 Hz, 1H; aromatic proton), 6.75–6.69 (m, 4H; aromatic protons), 6.55 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.2 Hz, 1H; aromatic proton), 6.49 (t, $^3J_{HH}$ = 8.5 Hz, 2H; aromatic protons), 5.37 (s, 1H; C_5H_4), 4.90 (s, 1H; C_5H_4), 4.39 (s, 1H; C_5H_4), 4.27 (s, 1H; C_5H_4), 4.21 (s, 1H; C_5H_4), 4.14 (dd, $^2J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 4.8 Hz, 1H; CH_2N), 4.00 (s, 1H; C_5H_4), 3.90 (s, 1H; C_5H_4), 3.79 (s, 3H; CH_3O), 3.67–3.57 (m, 1H; NH_2), 3.47 (ddd, $^2J_{HH}$ = 16.7 Hz, $^3J_{HH}$ = 11.8 Hz, $^3J_{HH}$ = 5.6 Hz, 1H; CH_2N), 3.21 (s, 1H; C_5H_4), 2.06 ppm (dd, $^2J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 5.3 Hz, 1H; NH_2). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ = 182.5 (dd, $^2J_{CP}$ = 14.9 Hz, $^2J_{CP}$ = 8.2 Hz; CRu), 163.1 (s; N*C*C), 156.7 (s; C*C*OCH_3), 156.6 (s; N*C*CH_2), 143.6–108.0 (m; aromatic carbon atoms), 87.4 (dd, $^1J_{CP}$ = 38.3 Hz, $^3J_{CP}$ = 4.3 Hz; *ipso*-C_5H_4), 86.3 (d, $^1J_{CP}$ = 49.6 Hz; *ipso*-C_5H_4), 77.4 (d, $^2J_{CP}$ = 13.2 Hz; C_5H_4), 76.4 (d, $^2J_{CP}$ = 7.7 Hz; C_5H_4), 75.5 (d, $^3J_{CP}$ = 2.5 Hz; C_5H_4), 73.4 (d, $^2J_{CP}$ = 6.8 Hz; C_5H_4), 73.1 (d, $^3J_{CP}$ = 4.8 Hz; C_5H_4), 69.2 (d, $^3J_{CP}$ = 1.3 Hz; C_5H_4), 69.1 (br s; C_5H_4), 68.7 (d, $^2J_{CP}$ = 5.0 Hz; C_5H_4), 54.9 (s; *C*H_3O), 51.3 ppm (d, $^3J_{CP}$ = 2.1 Hz; *C*H_2N). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ = 61.5 (d, $^2J_{PP}$ = 35.6 Hz), 44.1 ppm (d, $^2J_{PP}$ = 35.6 Hz).

Synthesis of [RuCl(CNN^{OMe})(CO)(PPh_3)] (4). The complex *cis*-[RuCl(CNN^{OMe})(PPh_3)$_2$] (**1**) (251.9 mg, 0.29 mmol) was suspended in dichloromethane (5 mL) and the mixture was stirred under a CO atmosphere (1 atm) overnight at room temperature. The obtained yellow solution was concentrated to about 1 mL by evaporation of the solvent under reduced pressure. The addition of *n*-heptane (10 mL) afforded a light-yellow precipitate, which was washed with diethyl ether (3 × 5 mL) and *n*-heptane (3 × 10 mL) and dried under reduced pressure. The residue was suspended in 2-propanol (5 mL) and stirred at reflux for 48 h providing the product as a single isomer. Yield: 115 mg (79%). Anal. calcd (%) for $C_{32}H_{28}ClN_2O_2PRu$ (640.08): C 60.05, H 4.41, N 4.38; found: C 60.09, H 4.36, N 4.42. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 7.51 (t, $^3J_{HH}$ = 7.8 Hz, 1H; aromatic proton), 7.45–7.37 (m, 3H; aromatic protons), 7.35–7.16 (m, 14H; aromatic protons), 7.04 (d, $^4J_{HH}$ = 1.8 Hz, 1H; aromatic proton), 6.65 (d, $^3J_{HH}$ = 7.5 Hz, 1H; aromatic proton), 6.36 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.4 Hz, 1H; aromatic proton), 4.23 (dd, $^2J_{HH}$ = 16.4 Hz, $^3J_{HH}$ = 6.4 Hz, 1H; CH_2N), 3.87 (dd, $^2J_{HH}$ = 16.5 Hz, $^3J_{HH}$ = 9.0 Hz, 1H; NH_2), 3.70 (s, 3H; CH_3O), 3.41 (ddd, $^2J_{HH}$ = 16.5 Hz, $^3J_{HH}$ = 10.5 Hz, $^3J_{HH}$ = 6.1 Hz, 1H; CH_2N), 2.79 ppm (dd, $^2J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 6.8 Hz, 1H; NH_2). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ = 207.1 (d, $^2J_{CP}$ = 17.7 Hz; CO), 179.0 (d, $^2J_{CP}$ = 12.6 Hz; CRu), 161.6 (s; N*C*C), 159.2 (s; C*C*OCH_3), 156.6 (s; N*C*CH_2), 138.4–108.6 (m; aromatic carbon atoms), 54.7 (s; *C*H_3O), 50.9 (s; CH_2N). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ = 56.7 ppm (s). IR (Nujol): $\tilde{\nu}$ = 1913 (s) (C≡O) cm^{-1}.

Synthesis of *trans*-[Ru(CNN^{OMe})(CO)(PCy_3)(PPh_3)][BAr^f_4] (5). Na[BAr^f_4] (60.0 mg, 0.0677 mmol) and PCy_3 (17.6 mg, 0.0628 mmol) were added to [RuCl(CNN^{OMe})(CO)(PPh_3)] (**4**) (40.0 mg, 0.0625 mmol) in dichloromethane (5 mL). The reaction mixture was stirred for 30 min at room temperature and filtered to remove NaCl. The obtained solution was concentrated (1 mL) and the addition of *n*-heptane (5 mL) afforded a light-yellow precipitate, which was filtered, washed with

n-heptane (3 × 5 mL) and dried under reduced pressure. Yield 100.5 mg (92%). Anal. calcd (%) for $C_{82}H_{73}BF_{24}N_2O_2P_2Ru$ (1748.29): C 56.34, H 4.21, N 1.60; found: C 56.38, H 4.26, N 1.65. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 7.79 (m, 8H; aromatic protons), 7.66 (t, $^3J_{HH}$ = 8.0 Hz, 1H; aromatic proton), 7.62 (br s, 4H; aromatic protons), 7.52 (d, $^3J_{HH}$ = 7.9 Hz, 1H; aromatic proton), 7.50 (d, $^3J_{HH}$ = 8.7 Hz, 1H; aromatic proton), 7.44–7.39 (m, 3H; aromatic protons), 7.34–7.26 (m, 6H; aromatic protons), 7.25–7.17 (m, 6H; aromatic protons), 6.84 (m, 1H; aromatic proton), 6.77 (d, $^3J_{HH}$ = 7.5 Hz, 1H; aromatic proton), 6.51 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.5 Hz, 1H; aromatic proton), 4.28 (dd, $^2J_{HH}$ = 16.3 Hz, $^3J_{HH}$ = 6.5 Hz, 1H; CH_2N), 3.67 (s, 3H; CH_3O), 3.62–3.46 (m, 2H; CH_2N and NH_2), 2.83 (m, 1H; NH_2), 2.15 (m, 3H; PCH), 2.00–1.72 (m, 10H; CH_2 of Cy), 1.71–1.56 (m, 5H; CH_2 of Cy), 1.55–1.27 (m, 4H; CH_2 of Cy), 1.20 (q, J_{HH} = 10.3 Hz, 4H; CH_2 of Cy), 1.05 (q, J_{HH} = 13.1 Hz, 4H; CH_2 of Cy), 0.81–0.64 ppm (m, 3H; CH_2 of Cy). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ = 206.1 (t, $^2J_{CP}$ = 15.3 Hz; CO), 175.3 (dd, $^2J_{CP}$ = 10.9 Hz, $^2J_{CP}$ = 8.9 Hz; CRu), 162.8 (s; N*C*C), 161.8 (q, $^1J_{CB}$ = 50.1 Hz; CB), 160.0 (s; C*C*OCH$_3$), 157.1 (s; N*C*CH$_2$), 137.9–109.2 (aromatic carbon atoms), 124.6 (q, $^1J_{CF}$ = 272.3 Hz; *C*F$_3$), 54.7 (s; *C*H$_3$O), 50.4 (s; CH$_2$N), 35.6 (dd, $^1J_{CP}$ = 15.7 Hz, $^3J_{CP}$ = 1.5 Hz; P*C*H), 30.5 (s; CH_2 of Cy), 28.7 (d, J_{CP} = 2.9 Hz; CH_2 of Cy), 27.5 (d, J_{CP} = 12.3 Hz; CH_2 of Cy), 27.4 (d, J_{CP} = 9.5 Hz CH_2 of Cy), 26.8 (d, J_{CP} = 11.8 Hz; CH_2 of Cy), 26.0 ppm (s; CH_2 of Cy). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ = 34.2 (d, $^2J_{PP}$ = 250.9 Hz), 22.0 ppm (d, $^2J_{PP}$ = 250.9 Hz). IR (Nujol): $\tilde{\nu}$ = 1919 (s) (C≡O) cm^{-1}.

Catalytic TH of ketones and aldehydes in the presence of NaOiPr

The ruthenium catalyst solution used for TH was prepared by dissolving the ruthenium complexes **1–5** (2.0 μmol) in 2 mL of 2-propanol. A 0.1 M solution of NaOiPr (200 μL, 20 μmol) in 2-propanol and the catalyst solution (1 mL, 1.0 μmol) were added to the ketone or aldehyde solution (1.0 mmol) in 2-propanol (final volume 10 mL) and the resulting mixture was heated under reflux conditions. The reaction was sampled by removing an aliquot of the reaction mixture (0.5 mL), which was quenched by adding diethyl ether (1 : 1 v/v), filtered through a short silica pad and subjected to GC analysis. The addition of the base was considered the start time of the reaction. The S/C molar ratio was 1000/1, whereas the base concentration was 2 mol% with respect to the substrate (0.1 M). The same procedure was followed for TH reactions at other S/C ratios (in the range of 1000–100 000) using the appropriate amount of catalysts. For solid and high-boiling compounds, the solvent was evaporated under vacuum and the crude mixture was dissolved in $CDCl_3$ and analyzed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

Catalytic TH of ketones and aldehydes in the presence of K_2CO_3

When potassium carbonate was used as the base in place of NaOiPr, the substrate (1 mmol), K_2CO_3 (6.9 mg, 0.05 mmol) and 2-propanol were introduced into a Schlenk tube and heated at reflux. The catalyst solution of complexes **2**, **3** and **5** in 2-propanol (1 mL, 1.0 μmol Ru) was added to the mixture to reach a final volume of 10 mL. The addition of the Ru complex was considered the start time of the catalysis. The TH reductions were monitored analogously as described previously by removal of an aliquot of the reaction mixture (approximately 0.5 mL) followed by the addition of diethyl ether (1 : 1 v/v). After filtration through a short silica pad, the conversion was determined by GC analysis. The S/C molar ratio was 1000/1, whereas the base concentration was 5 mol% with respect to the substrate (0.1 M). The same procedure was followed for TH reactions at other S/C ratios (in the range of 500–50 000) using the appropriate amount of catalysts.

Preparation of 2,5-bis(hydroxymethyl)furan (BHMF)

5-HMF (5.00 g, 39.6 mmol) and the complex **2** (3.1 mg, 4.0 μmol) were dissolved in 2-propanol (388 mL) in a 1 L three-neck round bottom flask equipped with a magnetic stirrer and a condenser. A 0.1 M solution of NaOiPr (7.9 mL, 0.79 mmol) in 2-propanol was added and the resulting mixture was refluxed for 30 min. The S/C molar ratio was 10 000/1, whereas the base concentration was 2 mol% with respect to the substrate (0.1 M). The obtained solution was cooled to room temperature and diethyl ether (300 mL) was added. After filtration through a short silica pad, the solution was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was dissolved in distilled water (25 mL), extracted with ethyl acetate (2 × 100 mL) and diethyl ether (100 mL). The organic layers were combined, dried over anhydrous Na_2SO_4 and evaporated to dryness, affording the product as a white solid with 99% purity, as inferred from NMR analysis (see ESI, Fig. S44 and S45†). Yield 4.57 g (90%).

Conflicts of interest

The authors declare no competing financial interests.

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