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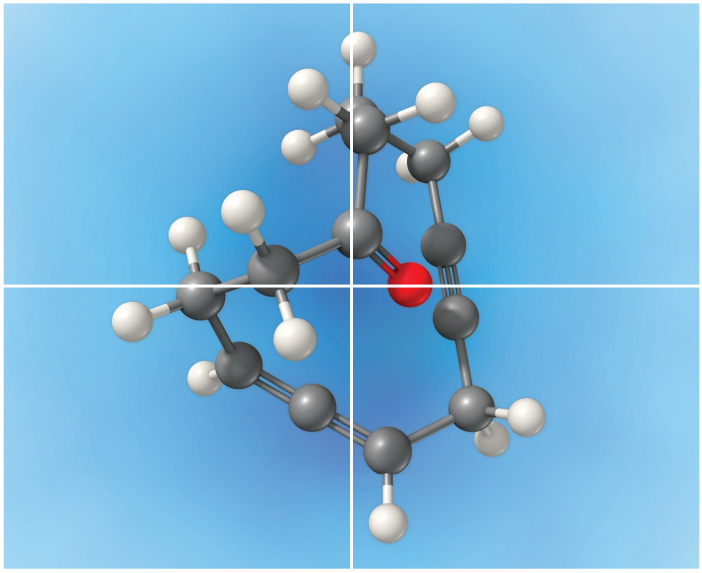

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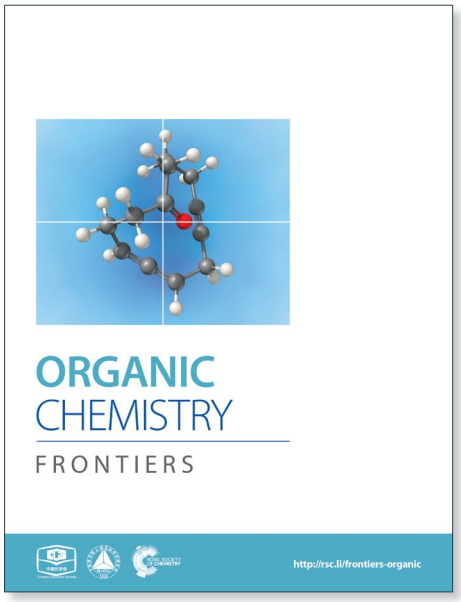

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Organic Chemistry Frontiers

ARTICLE

Ruthenium complexes with a N-heterocyclic carbene NNC-pincer ligand: preparation and catalytic properties.

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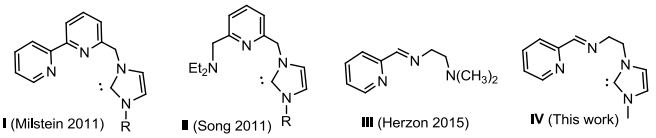
1-Methyl-3-(2-((pyridin-2-ylmethylene)amino)ethyl)-1*H*-imidazol-3-ium bromide was prepared and used as a N-heterocyclic carbene NNC-pincer ligand precursor. Depending on the coordination strategy, a monometallic [Ru(NNC)(CO_3)(PPh_3)] complex, or the [Ru(μ-Cl)(NNC)]$_2$($2Cl^-$) dimer were obtained. A di-silver complex in which two ligands are monocoordinated to the metal center through the NHC groups was also obtained and characterised. The dimetalic ruthenium complex reacts with alcohols yielding a monohydride species. The preliminary studies on the catalytic activity of the ruthenium dimer indicate that the complex is active in the reduction of ketones and aldehydes under transfer hydrogenation conditions.

Introduction

Transition metal complexes containing pincer-type ligands have attracted increasing attention due to the unusual properties of the metal center imparted by the *mer*-coordination of the tridentate ligands.[1] The tridentate coordination mode of pincer ligands renders high thermal stability to the product complexes, and this is why pincer complexes are often used as catalysts for endothermic reactions, such as dehydrogenations of organic substrates.[2] Ruthenium pincer complexes[3] proved to be excellent catalysts for alcohol dehydrogenation and also for hydrogenation of organic carbonyl compounds.[2b] Reactivity patterns such as the deprotonation-dearomatization, metal-ligand cooperativity, and the unusual electronic structures of ruthenium pincer complexes make this type of compounds efficient catalysts for several synthetic methods that include important green transformations. Among prominent examples are the hydrogenations of carboxylic acid esters,[4] nitriles[5] or CO_2,[6] where catalysts based on ruthenium have played a predominant role,[4a-k] although osmium[4a, 4c] and iron[4l, 4m, 7] have also provided useful catalysts. Some efficient hydrogenation catalysts have incorporated NNC-pincer ligands with N-heterocyclic carbenes, as in the relevant examples reported by Milstein,[4f, 8] Song[9] and others.[10] The introduction of NHCs into the structure of pincer ligands is expected to bring catalytic benefits by the presence of the strong electron-donor NHC group, and also by increased thermal stability of the resulting metal complexes,[11] compared to the related complexes containing coordinated phosphines or amines.



Scheme 1

Based on these previous findings, and in our experience in the chemistry of ruthenium complexes with NHC-based pincer ligands,[12] we now report the preparation of ligand **IV**, which we used for the syntheses of two new ruthenium-NNC pincer complexes. The new ligand **IV** is somewhat related to the NNN-pincer ligand **III** recently reported by Herzon and co-workers, which was used for making a Ru complex that was highly active in the reductive hydration of terminal alkynes.[13] The coordination properties of **IV** will be described, together with the preliminary studies on the catalytic activity of the product ruthenium complexes in the reduction of ketones by transfer hydrogenation.

Results and discussion

Preparation of the new compounds

The imidazolium salt **1** was prepared in high yield by condensation of 3-(2-aminoethyl)-1-methylimidazolium bromide (i) and 2-pyridinecarboxaldehyde in *i*PrOH at room temperature, as shown in Scheme 2. The details of the preparation of the aminoethyl-methylimidazolium salt may be found in the experimental section of this article.

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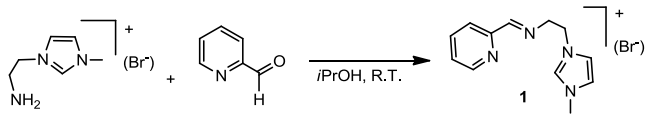
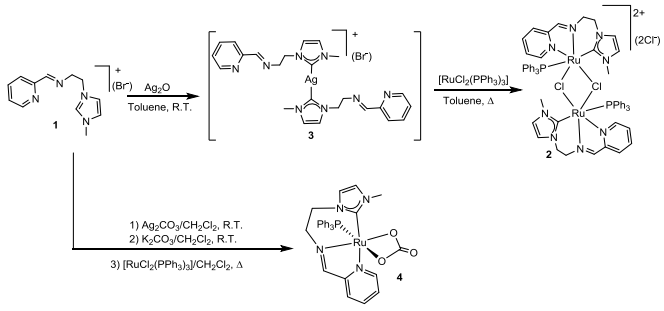
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



Scheme 2

For coordination of **1** to Ru, we tried standard strategies, but all of them afforded products in low yield. For one example, the transmetallation from a preformed silver-NHC complexes by reaction of **1** with Ag_2O and subsequent addition of $[RuCl_2(PPh_3)_3]$ in toluene allowed the formation of the di-ruthenium complex **2**, as a red solid in *ca*. 30% yield (Scheme 3). The Ag-NHC intermediate could be isolated by reaction of **1** with 0.5 equivalents of Ag_2O in CH_2Cl_2 at room temperature, yielding the $[Ag(NHC)_2]^+(Br^-)$ complex **3**, in 50 % yield.

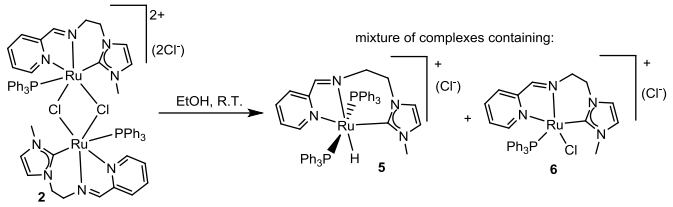


Scheme 3

When the reaction is performed between **1** and $[RuCl_2(PPh_3)_3]$ in the presence of Ag_2CO_3 and K_2CO_3 in refluxing CH_2Cl_2, the monometallic complex **4** with a coordinated carbonate ligand is obtained as the only isolable complex, in 9 % yield.

Complexes **2**-**4** were characterized by means of NMR spectroscopy and mass spectrometry, and gave satisfactory elemental analyses. The ^{13}C NMR spectrum of the silver di-NHC complex **3**, displayed the diagnostic signal due to the carbene-carbon atoms as a singlet at 182 ppm. The ^1H NMR spectra of **2** and **4** are consistent with formation of NHC species, as seen by the disappearance of the signal due to the NC*H*N proton of the imidazolium fragment of **1**. The ^{13}C NMR spectrum of **2** revealed the characteristic signal due to the carbene carbon at 184.5 ppm. Although we recorded the ^{13}C NMR spectrum of **4**, we were unable to locate the signal of the carbene carbon, probably due to the low concentration at which we had to carry the NMR study of the complex, which was obtained only in small amounts.

Upon prolonged standing, alcohol (EtOH or *i*PrOH) solutions of **2**, produced a hydride species that we tentatively formulate as **5** (Scheme 4). The presence of the hydride was confirmed by ^1H NMR spectroscopy, which revealed a triplet at -9.6 ppm. Although we have not been able to isolate this species, by mass spectrometry we could detect a mass peak at m/z = 841.3 assigned to $[\mathbf{5}]^+$, together with a peak at m/z = 613.2, which may be attributed to the ruthenium complex **6** (Scheme 4). The spontaneous formation of this ruthenium-hydride species under alcoholic conditions is an indication that complex **2** may be a good candidate for catalyzing processes involving alcohol dehydrogenation and transfer hydrogenation.[14]



Scheme 4

The molecular structures of complexes **2** and **4** were confirmed by single-crystal X-ray diffraction studies. The molecular structure of **2** (Figure 1) exhibits two octahedral metal fragments connected by bridging chloride ligands. The NNC-pincer ligand and the phosphine complete the coordination sphere about ruthenium in **2**. The PPh_3 ligand is *trans* to a bridging chloride, and the two pincer ligands adopt a relative *anti* conformation, with the two imidazolylidenes (or the two pyridines) occupying opposite sites on each metal fragment. The NNC-pincer bite angle is 170.5(3)° and the distance of the Ru-$C_{carbene}$ bond is 2.041Å. All other angles and distances lie in the expected range.

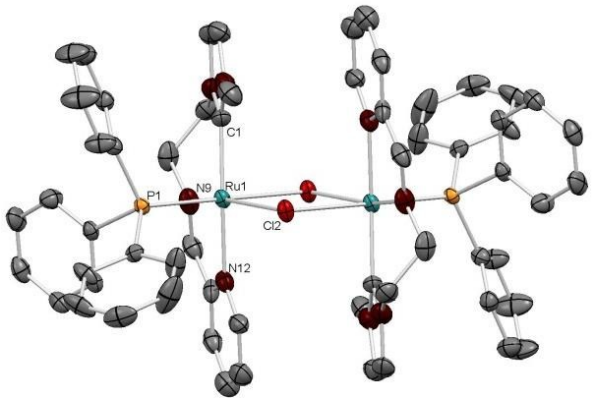


Figure 1. Molecular diagram of complex **2**. Hydrogen atoms, counter-anions (two chlorides) and solvent (five molecules of $CHCl_3$) have been omitted for clarity. Ellipsoids at the 30% probability level. Selected bond distances (Å) and bond angles (deg): Ru(1)-C(1) = 2.041(7); Ru(1)-P(1) = 2.3066(15); Ru(1)-N(9) = 2.015(6); Ru(1)-N(12) 2.144(6); Ru(1)-Cl(2) = 2.4527(14); C(1)-Ru(1)- P(1) = 92.3(2); C(1)-Ru(1)- Cl(2) = 95.1(2); C(1)-Ru(1)- N(9) = 94.6(3); C(1)-Ru(1)- N(12) = 170.5(3); N(9)-Ru(1)- N(12) = 77.2(3).

The molecular structure of complex **4** (Figure 2), consists of a ruthenium center in a pseudo-octahedral environment, with the *mer*-tridentate NNC ligand, a chelating carbonate, and PPh_3 (*trans* to one of the oxygen atoms of the carbonate) completing the coordination sphere. The bite angle of the NNC-pincer ligand is 167.5(7)°, slightly smaller than that shown by **2**. The length of the Ru-$C_{carbene}$ bond is 2.1020(2) Å. All other distances and angles are unexceptional.

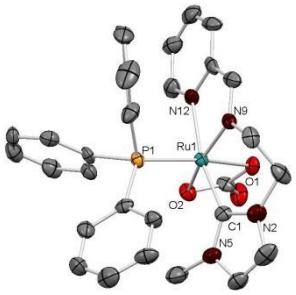


Figure 2. Molecular diagram of complex **4**. Hydrogen atoms and solvent molecules (two molecules of H_2O and one CH_2Cl_2) have been omitted for clarity. Thermal ellipsoids are at the 50% probability level. Selected bond distances (Å) and bond angles (deg): Ru(1)-C(1) = 2.020(2); Ru(1)-P(1) = 2.272(5); Ru(1)-N(9) = 1.988(16); Ru(1)-N(12) 2.150(16); Ru(1)-O(1) = 2.134(13); Ru(1)-O(2) = 2.120(13); C(1)-Ru(1)- P(1) = 93.3(6); C(1)-Ru(1)- O(1) = 89.4(7); C(1)-Ru(1)- O(2) = 94.7(7); C(1)-Ru(1)- N(9) = 91.8(7); C(1)-Ru(1)- N(12) = 167.5(7); N(9)-Ru(1)- N(12) = 78.6(7).

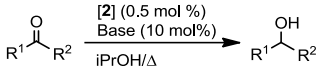
Catalytic properties

Complex 2 was evaluated for activity in the transfer hydrogenation of ketones in refluxing iPrOH (82 °C). In order to optimize the reaction conditions, we first tested the reduction of acetophenone using 0.5 mol% of 2 and 10 mol% of different bases, and a 6 h reaction time. As can be seen from the results in Table 1, the best results are obtained with NaOtBu (entry 7), although the base alone is capable of reducing the ketone yielding 23% of 1-phenylethanol (entry 3). For this reason, and in order to minimize the background activity of the base,15 we considered more adequate to use KOH, which under the same reaction conditions afforded almost quantitative yields of the alcohol (entry 5), while providing negligible amounts of product in the absence of 2 (entry 1). Then catalyst 2 was used for the reduction of other ketones (benzophenone, cyclohexanone, 3-hexanone and phenylhexanone) and aldehydes (benzaldehyde, 4-bromobenzaldehyde and 3-phenyl-propionaldehyde) in refluxing *i*PrOH in the presence of KOH (entries 10-19). As can be seen from the results shown in Table 1, all five ketones were efficiently reduced under the reaction conditions used. While benzophenone was the substrate to afford lower yields to the final product, cyclohexanone afforded quantitative yields to cyclohexanol in just ten minutes.

The reduction of the two aldehydes (benzaldehyde and 4-bromobenzaldehyde) afforded the resulting alcohols, together with the formation of the products resulting from the base-catalysed aldol condensation between the arylaldehydes and acetone. This process has been already described for the reduction of arylaldehydes by Ru(II) catalysts using similar reaction conditions.[16]

A study of the time-dependent reaction profiles of the reduction of acetophenone, benzophenone and cyclohexanone (Figure 3) reveals that there is no detectable non-productive lag phase, which suggests that generation of the active catalytic species must be fast. The reaction rates corresponding to the reduction of each of the ketones are consistent with the final thermodynamic data shown in Table 1, implying that the different activities shown for each type of ketone are of kinetic nature.

Table 1. Reduction of ketones and aldehydes by transfer hydrogenation.



Entry	Cat.	Base	Time	substrate	Conv.%[b]	Yield %
1	none	KOH	6h	acetophenone	9	4
2	none	Cs_2CO_3	6h	acetophenone	8	3
3	none	NaO*t*Bu	6h	acetophenone	36	23
4	none	KO*t*Bu	6h	acetophenone	9	4
5	**2**	KOH	6h	acetophenone	94	86
6	**2**	Cs_2CO_3	6h	acetophenone	25	19
7	**2**	NaO*t*Bu	6h	acetophenone	94	90
8	**2**	KO*t*Bu	6h	acetophenone	85	79
9	none	KOH	1h	acetophenone	1	1
10	**2**	KOH	1h	acetophenone	94	88
11	**2**	KOH	1h	benzophenone	99	68
12	**2**	KOH	10 min	cyclohexanone	99	99
13	**2**	KOH	6h	3-hexanone	85	82[b]
14	**2**	KOH	6h	phenylhexanone	93	93
16	**2**	KOH	1h	benzaldehyde	98	33(30)[c]
17	**2**	KOH	6h	benzaldehyde	99	37(31)[c]
18	**2**	KOH	6h	4-Bromo-benzaldehyde	98	75(20)[c]
19	**2**	KOH	6h	3-phenyl-propionaldehyde	99	38(61)[c]

Conditions: substrate (1 mmol), base (0.1 mmol), **2** (0.5 mol%) in 3 mL of *i*PrOH at reflux temperature. [a]Conversions and yields determined by GC. [b]Yield determined by ^{1}H NMR. [c]Value in parenthesis refers to aldol condensation product.

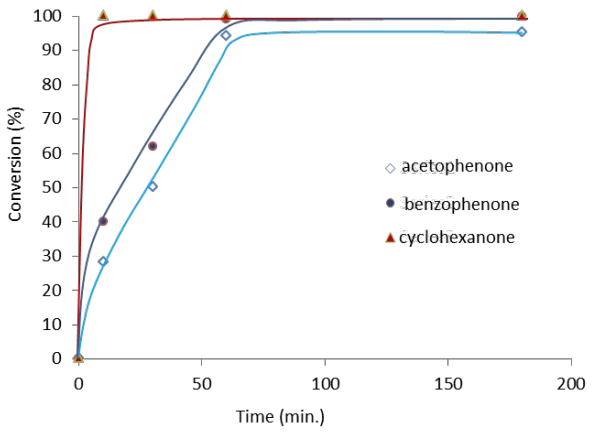


Figure 3. Time-dependent reaction profiles of the reduction of ketones by transfer hydrogenation. Reaction conditions: Ketone (1 mmol), base (0.1 mmol), 2 (0.5 mol%) in 3 mL of *i*PrOH at reflux.

Conclusions

We have prepared a new NNC-pincer ligand with one NHC donor group. The new ligand was coordinated to ruthenium. Depending on the coordination strategy, we were able to obtain two significantly different complexes. While the transmetallation of the ligand from a preformed silver-NHC complex to $[RuCl_2(PPh_3)_3]$ afforded the diruthenium complex **2** with two bridging chloride ligands, the reaction of the ligand precursor with Ag_2CO_3, Na_2CO_3 and the same ruthenium source gave the monometallic carbonate pincer complex **4**. The stability of the dimetallic complex **2** is high, however it forms a ruthenium hydride species in alcoholic solutions. This reactivity indicates that the complex may easily generate monometallic species that may be active in transfer hydrogenation.

The preliminary studies on the catalytic activity of **2** indicate that the complex is active in the reduction of ketones and aldehydes under transfer hydrogenation conditions. While the catalyst is very active in the reduction of ketones to the corresponding secondary alcohols, the reduction of aldehydes affords the related primary alcohols together with the product resulting from the aldol condensation between the aldehyde and acetone. The catalyst is extraordinarily active in the reduction of cyclohexanone. These promising results indicate that the catalyst may have potential for more challenging reactions, such as the reduction of carboxylic esters in the presence of molecular hydrogen. Further studies in this direction are underway.

Experimental Section

General methods. All operations were carried out under nitrogen atmosphere unless otherwise stated using standard Schlenk techniques. Solvents were dried using a solvent purification system (MBraun SPS). All reagents were used as received from commercial suppliers. NMR spectra were recorded either on a Varian Mercury 300 or Varian NMR System 500 MHz spectrometers and referenced (^1H, ^{13}C) as follows: CD_3OD (δ 3.31, 49.00), CD_2Cl_2 (δ 5.32, 54.00), $CDCl_3$ (δ 7.26, 77.16). Electrospray mass spectra (ESIMS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. Accurate mass measurements were performed by use of a Q-TOF premier mass spectrometer with electrospray source (Waters, Manchester, UK) operating at a resolution of ca. 16000 (fwhm). Elemental analyses were carried out on a EuroEA3000 Eurovector Analyzer.

Synthesis of compound 1.

3-(2-phthalimidoethyl)-1-methylimidazolium bromide was prepared by adapting a reported method in the literature.[17] N-(2-Bromoethyl)phthalimide (10.5 g, 41.3 mmol) and 1-methylimidazole (3.2 g, 39.0 mmol) were sealed in a pressure tube in 40 mL of toluene and stirred at 120 °C for 70 h. After cooling to room temperature, the product was filtered, washed with toluene and diethyl ether, and dried under vacuum. Yield: 11.87 g (90%) of a white solid. ^1H NMR (400 MHz, DMSO-d^6) δ 3.83 (s, 3H, CH_3), 4.01 (m, 2H, CH_2), 4.45 (m, 2H, CH_2), 7.70 (br t, J=1.6, 1H, CH), 7.86 (overlapped, 5H, CH), 9.22 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d^6) δ 35.77 (CH_3), 38.04 (CH_2), 47.83 (CH_2), 122.85 (CH), 123.22 (2CH), 123.57 (CH), 131.51 (2C), 134.53 (2CH), 137.12 (CH), 167.65 (2CO).

The NMR data of the product match the corresponding data reported in the literature.[18]

3-(2-aminoethyl)-1-methylimidazolium bromide (i) was prepared by adapting a reported method in the literature.[17] A solution of 3-(2-phthalimidoethyl)-1-methylimidazolium bromide (11.78 g, 35.0 mmol) and hydrazine hydrate (7.0 g, 50%, ca. 109 mmol) in 80 mL of ethanol in a 250 mL flask was heated at 80 °C overnight. A bulky amorphous white solid formed in the flask. After cooling, 100 mL of ethanol was added into the flask and the solid was crashed into a cottage-cheese like paste; this was transferred into a fritted funnel and the product solution was vacuum-filtered into a 500 mL flask; the solid was washed with additional 2 × 50 mL portions of ethanol. The ethanol solution was rotary-evaporated, and the crude product was dried under vacuum of an oil pump at 50 °C for 30 min to yield a pale-yellow oil that was used without further purification in the next step. Yield: 7.23 g (100%). ^1H NMR (400 MHz, DMSO-d^6) δ 2.48 (br, NH_2), 2.89 (t, J=5.8, 2H, CH_2), 3.86 (s, 3H, CH_3), 4.13 (t, J=5.8, 2H, CH_2), 7.72 (br t, J=1.6, 1H, CH), 7.86 (br t, J=1.6, 1H, CH), 9.19 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d^6) δ 35.67 (CH_3), 41.30 (CH_2), 51.85 (CH_2), 122.47 (CH), 123.24 (CH), 136.72 (CH). According to the ^1H NMR spectrum, the isolated material contained ca. 5 mol% of an aromatic impurity, presumably N,N'-phthaloylhydrazine. The NMR data of the product match the corresponding data reported in the literature.[19]

A solution of 3-(2-aminoethyl)-1-methylimidazolium bromide (i) (5.87 g, 28.5 mmol) in 2-propanol (30 mL) and 2-pyridinecarboxaldehyde (3.05 g, 28.5 mol) was stirred overnight (16 h) at room temperature. Then the solvent was removed, and the resulting oil was dried under vacuum to give a grey solid. The product was recrystallized from CH_2Cl_2 (150 mL) to yield 7.1 g (85 %) of a hygroscopic solid. 1H NMR (300 MHz, DMSO-d^6) δ (ppm) 9.33 (m, 1H, CHPy), 8.62 (d, J = 4.6 Hz, 1H, CHPy), 8.34 (s, 1H, NCH), 7.92 (m, 2H, CHPy), 7.76 (s, 1H, CHPy), 7.45 (m, 2H, CHImid), 4.57 (t, J = 5.2 Hz, 2H, CH_2), 4.06 (t, J = 5.2 Hz, 2H, CH_2), 3.87 (s, 3H, CH_3), $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d^6): δ (ppm) 164.5 (NCH), 164.4 (NC), 153.5 (CPy), 149.3 (CPy), 136.9 (CPy), 125.4 (CPy), 123.4 (CPy), 122.6 (CImid), 120.6 (CImid), 58.5 (NCH_2), 49.5 (NCH_2), 35.7 (CH_3). HRMS ESI-TOF-MS (positive mode): monosiotopic peak 215.1294, calcd 215.1297.

Synthesis of compound 2. 70 mg of **1** (0.24 mmol), 35 mg of Ag_2O (0.15 mmol) and 189 mg (0.20 mmol) of $[RuCl_2(PPh_3)_3]$ were dried under vacuum for approximately one hour. The solid mixture was dissolved with 10 mL of anhydrous toluene and stirred at room temperature overnight in absence of light. Then, the reaction was heated to reflux under nitrogen during 1 day. The mixture was cooled to RT and filtered over Celite, washed with Toluene and the residue redissolved in MeOH. The solvent was removed under reduced pressure. Red crystals of **4** were obtained by slow evaporation in $CHCl_3$, 0.87 g (27.9

%). ^{1}H NMR (300 MHz, CD2Cl2): δ (ppm) 9.51 (d, J = 5.2 Hz, 2H, CHPy), 8.62 (s, 2H, NCH), 7.65 (bs, 6H, CHPy), 7.37-6.93 (m, 34H, P($C_{18}H_{15}$), CHImid), 3.68 (m, 8H, NCH_2), 3.44 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ (ppm) 184.54 (d, J = 13.9 Hz, P-Ru-Ccarbene), 165.6 (NCH), 157.3 (NC), 152.8 (CPy), 135.4 (d, J = 14.0 Hz, P-CPy), 134.2 (d, J = 9.2 Hz, P-$CPPh_3$), 133.4 (d, J = 14.0 Hz, P-CPy), 129.7 ($CPPh_3$), 128.1 (d, J = 9.0 Hz, P-$CPPh_3$), 125.7 (CPy), 125.1 (CPy), 123.3 (CImid), 122.8 (CImid), 61.5 (NCH_2), 49.8 (NCH_2), 39.0 (CH_3). ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ (ppm) 48.81. Electrospray MS (20 V, m/z): 613.2 $[M]^+$. Elemental analysis calcd (%) for $C_{60}H_{58}N_8P2Cl_4Ru_2.3CHCl_3$: C 45.7; H 3.7; N 6.7; found C 45.5; H 4.4; N 6.2.

Synthesis of compound 3. To a solution of 50 mg of **1** (0.17 mmol) in CH_2Cl_2 (10 mL) were added in absence of light 25 mg (0.11 mmol) of Ag_2O and stirred at room temperature for 5 h. The crude mixture was filtered over Celite, and the solvent was removed under reduced pressure. Precipitation from CH_2Cl_2/diethyl ether gave **3** as a yellow solid, 0.50 g (47.9 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.60 (bs, 2H, CHPy), 8.21 (s, 2H, NCH), 7.99 (bs, 2H, CHPy), 7.75 (m, 2H, CHPy), 7.47 (m, 2H, CHPy), 7.03 (bs, 2H, CHImid), 6.89 (bs, 2H, CHImid), 4.63-4.36 (m, 4H, NCH_2), 4.10-3.92 (m, 4H, NCH_2), 3.79 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 181.88 (Ag-Ccarbene), 164.3 (NCH), 153.6 (NC), 149.5 (CPy), 136.8 (CPy), 125.2 (CPy), 121.9 (CImid), 121.8 (CImid), 61.5 (NCH_2), 52.3 (NCH_2), 38.8 (CH_3). Electrospray MS (20 V, m/z): 535.1 $[M]^+$. Elemental analysis calcd (%) for $C_{24}H_{28}N_8AgBr$: C 46.8; H 4.6; N 18.2; found C 47.3; H 3.9; N 18.4.

Synthesis of compound 4. In the absence of light, a round bottomed flask protected from light, was loaded with 100 mg of **1** (0.34 mmol), 77 mg of Ag_2CO_3 (0.28 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred during 5 min prior the addition of K_2CO_3 (691 mg, 5 mmol). then for another 1.5 h, At this point, $RuCl_2(PPh_3)3$ (320 mg, 0.33 mmol) was added and the mixture was heated under reflux for 1h, allowed to warm to room temperature and filtered through Celite. The solvent was removed under reduced pressure. The solid residue was washed with diethyl ether, redissolved in CH_2Cl_2 and precipitated with diethyl ether to obtain 20 mg of a purple solid (9 %).1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.81 (m, 1H, CHPy), 8.74 (s, 1H, NCH), 7.69 (m, 1H, CHPy), 7.64 (m, 6H, $CHPPh_3$), 7.26 (m, 6H, $CHPPh_3$), 6.82 (m, 6H, $CHPPh_3$), 6.54 (bs, 2H, CHImid), 4.26 (bs, 4H, CH2), 3.15 (s, 3H, CH_3). 13C{1H} NMR (75 MHz, $CDCl_3$): δ (ppm) 168.4 (CO_3), 162.0 (NCH), 155.8 (NC), 150.6 (CPy), 134.7 (CPy), 132.7 ($CPPh_3$), 132.6 ($CPPh_3$), 129.0 ($CPPh_3$), 127.9 ($CPPh_3$), 127.8 ($CPPh_3$), 125.1 (CPy), 124.8 (CPy), 122.2 (CImid), 121.3 (CImid), 61.4 (NCH_2), 50.9 (NCH_2), 36.2 (CH_3). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ (ppm) 54.35. Electrospray MS (20 V, m/z): 289.2 $[M\text{-}CO_3]^{2+}$, 309.7 $[M\text{-}CO_3{}^{+}MeCN]^{2+}$, 330.2 $[M\text{-}CO_3{}^{+}2MeCN]^{2+}$, 639.1 $[M]^+$. Elemental analysis calcd (%) for $C_{31}H_{29}N_4O_3PRu.CH_2Cl_2$: C 53.2; H 4.3; N 7.8; found C 52.9; H 4.4; N 8.2.

General Procedure for Tranfer Hydrogenation of Ketones to Alcohols. In a 50 mL high-pressure Schlenk tube, ketone (1 mmol), catalyst (0.5 mol %), Base (0.1 mmol) and *i*PrOH (3 mL) were placed. The mixture was stirred and heated to 85 ºC for 1h. The reaction yields were calculated by GC using Anisole as internal standard.

X-Ray Crystallography.

Single crystals of **2** and **4** suitable for X-ray crystallographic analysis were obtained as described above. Diffraction data were collected on a Agilent SuperNova diffractometer equipped with an Altas CCD detector using Cu Kα radiation (λ = 1.54184 Å). Single mounted on a MicroMount polymer tip (MiteGen) in a random orientation. The crystals were kept at 293 K during data collection for **2** and at 290 K for **4**. The structures were solved by direct methods in SHELXS-97[20] and refined by the full-matrix method based on F2 with the program SHELXL-97 using the OLEX software package.[20-21] Further crystallographic data may be found in the corresponding CIF files which were deposited at the Cambridge Crystallographic Data Centre CCDC, Cambridge, UK. The reference number for **2** and **4** were assigned as 1060997, 1060998 respectively.

Crystal data, data collection and structure refinement details for **2** and **4**:

Compound ***2***: $C_{70}H_{66}Cl_{34}N_8P_2Ru_2$ (*M* = 2488.68): monoclinic, space group $P2_1/a$, *a* = 13.2500(2)Å, *b* = 16.9695(3) Å, *c* = 23.3436(4) Å, α = 90°*β* = 103.9482(18)° γ = 90°, *V* = 5093.95(17) $Å^3$, *Z* = 2, *T* = 293(2) K, μ(CuKα) = 11.254 mm^{-1},*Dcalc* = 1.623g/cm^3, 44887 reflections measured (7.38 ≤ 2Θ ≤ 131.968), 8883 unique (R_{int} = 0.0512, R_{sigma} = 0.0321), which were used in all calculations. The final R_1 was 0.0721 (I>=2u(I)) and wR_2 was 0.2154 (all data).

Compound **4**: $C_{32}H_{35}Cl_2N_4O_5PRu$ (*M* =758.58): monoclinic, space group $P2_1/c$, *a* = 18.2792(3)Å, *b* = 11.74106(11) Å, *c* = 17.1049(2)Å, *V* = 3259.49(9) $Å^3$, *Z* = 4, *T* = 199.95(10) K, μ(CuKα) = 1.54184 mm^{-1}, *Dcalc* = 1.546 g/mm^3, 27673 reflections measured (9.296 ≤ 2Θ ≤ 139.32), 6075 unique (R_{int} = 0.0499, R_{sigma} = 0.0291) which were used in all calculations. The final R_1 was 0.2354 (I > 2σ(I)) and wR_2 was 0.5147 (all data).

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Ruthenium complexes with a N-heterocyclic carbene NNC-pincer ligand: preparation and catalytic properties.

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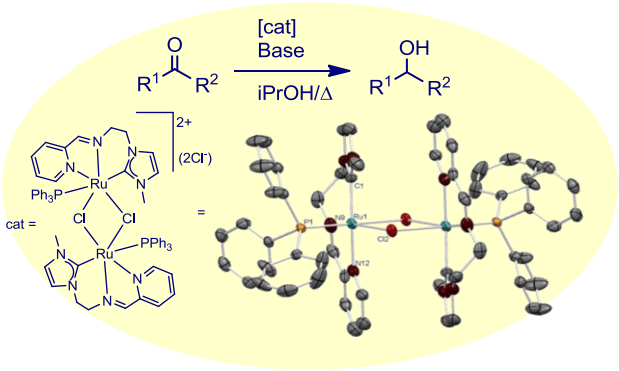

A NNC NHC-based pincer-type Ru(II) complex was obtained and tested in the reduction of carbonyl groups.