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New CNN-Type Ruthenium Pincer NHC Complexes. Mild, Efficient Catalytic Hydrogenation of Esters

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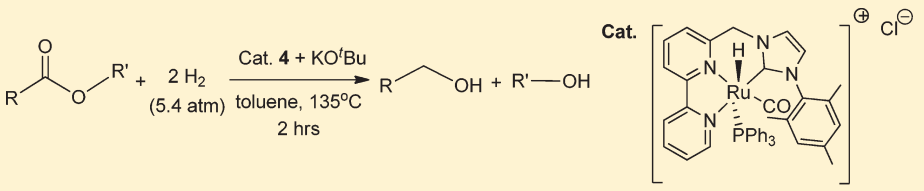
Supporting Information

ABSTRACT:



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New pincer ruthenium complexes (**2**−**6**) based on the new bipyridine-NHC ligand **1** were prepared and studied, resulting in an efficient catalytic hydrogenation of esters to the corresponding alcohols under mild conditions. Reaction of the ligand **1** with $RuH(Cl)CO(PPh_3)_3$, followed by reaction with one equivalent of the base KHMDS, gave the mixed phosphine-NHC complex **2**, incorporating a C−H-activated bipyridine ligand. Complex **2** has an octahedral structure containing two phosphorus atoms *trans* to each other, a hydride *trans* to the NHC ligand, and CO *trans* to the C−H-activated carbon of the bipyridine ligand. Using the precursor complex Ru(*p*-cymene)Cl_2(CO), reaction with **1** followed by treatment of the intermediate product with one equivalent of KHMDS resulted in formation of the dichloride pincer complexes **3a** and **3b**, which are in equilibrium, as indicated by variable-temperature ^{1}H NMR. Complex **3a** is an octahedral, neutral, and symmetric complex with the CO ligand positioned *trans* to the central pyridine group of the pincer ligand and the two chlorides *trans* to each other, as indicated by single-crystal X-ray diffraction. Complex **3b** is cationic, with an outer-sphere chloride. Reaction of the NHC ligand **1** with LiHMDS at low temperature followed by addition of $RuH(Cl)CO(PPh_3)_3$ resulted in the mixed phosphine-NHC complex **4**, which has an octahedral structure containing phosphorus *trans* to the hydride, a CO *trans* to the NHC ligand, and an outer-sphere chloride. Chloride substitution by BAr^{F-} gave the X-ray-characterized complex **5**. Deprotonation of complex **4** with KHMDS resulted in formation of the dearomatized complex **6**. The *in situ* prepared **6** (from complex **4** and an equivalent of base) is among the best catalysts known for the hydrogenation of nonactivated esters to the corresponding alcohols under mild conditions.

INTRODUCTION

PNN- and PNP-type ruthenium pincer complexes developed in our laboratory have shown substantial catalytic activity in a variety of reactions, including dehydrogenative coupling of alcohols to form esters[1−3] and H_2, the hydrogenation of esters to alcohols,[4] coupling of alcohols with amines to form amides with liberation of H_2,[5] the hydrogenation of amides to alcohols and amines,[6] the direct synthesis of imines from alcohols and amines with liberation of H_2 and H_2O,[7] dehydrogenative acylation of alcohols with esters,[8] and the dehydrogenative amidation of esters with amines.[9] A possible extension is to replace the phosphine ligand with N-heterocyclic carbenes (NHC).

While NHC ligands are often considered as simple phosphine mimics,[10] they are generally more electron-rich than phosphines and are more strongly bound to the metal. Thus, NHC complexes can exhibit different catalytic activity than their phosphine analogues.[11−18] Due to the strength of the M−C bond of the NHC ligand, dissociation is unlikely under normal conditions.[19] Among the several reported Ru-NHC complexes, probably the best known is the mixed phosphine-NHC Grubbs second-generation metathesis catalyst.[10,20] Ruthenium complexes of NHC pincer ligands were reported.[21−24] In some cases two different NHC ligands are coordinated to the same Ru center.[21]

Very recently, we have reported the PNN pincer complex **A** and the corresponding dearomatized complex **B** based on a phosphine-bipyridine ligand,[6] which efficiently catalyze amide hydrogenation to amines and alcohols. We now report the synthesis of the NHC analogue and its catalytic activity in the hydrogenation of esters to alcohols.

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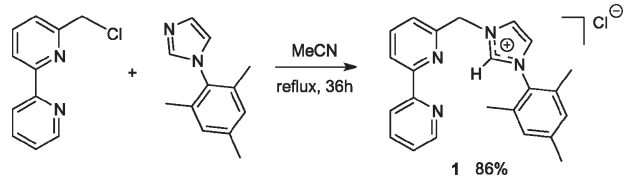
Scheme 1. Synthesis of the Bipyridine-NHC Ligand 1



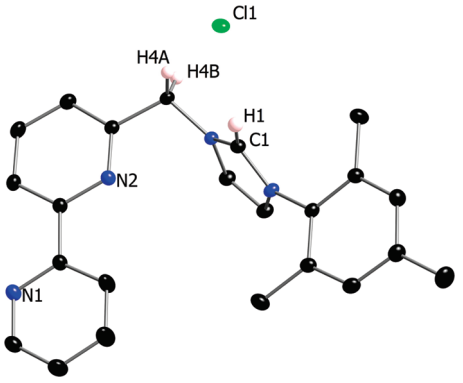
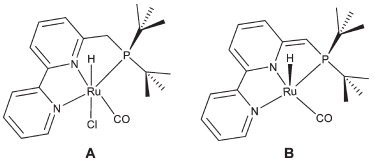


Figure 1. ORTEP plot of **1**. Most hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.



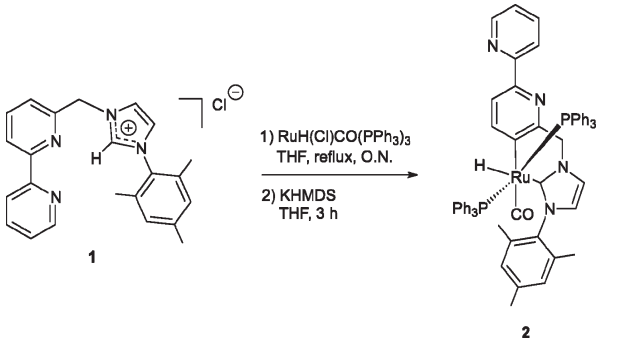
RESULTS AND DISCUSSION

Synthesis of the Bipyridine-NHC Ligand 1. Free NHC ligands can be sensitive to water; hence they were synthesized using dry solvents inside a glovebox. Reaction of 6-(chloromethyl)-2,2′-bipyridine with 1-mesityl-1*H*-imidazole in dry acetonitrile at reflux temperature under a N_2 atmosphere gave the imidazolium compound **1** in 86% yield (Scheme 1).

The fully characterized **1** gives rise to a characteristic singlet at 10.94 ppm in the ^{1}H NMR spectrum, associated with the imidazolium proton that is deprotonated upon the formation of the free NHC (H1 in the X-ray structure). Crystals of **1** suitable for single-crystal X-ray diffraction were obtained by recrystallization from hot acetonitrile (Figure 1).

Synthesis of the Ru-NHC Complexes 2−6. Trying to prepare the complex Ru(CNN)H(Cl)CO by reaction of **1** with $RuH(Cl)CO(PPh_3)_3$ in the presence of a base led to an inseparable mixture of products. Hence, we carried out a two-stage reaction, hoping for initial bipyridine complexation in the first stage, followed by deprotonation to the NHC complex. Thus, the reaction of the ligand **1** with $RuH(Cl)CO(PPh_3)_3$ in refluxing THF resulted in complete disappearance of **1** according to ^{1}H NMR, with the imidazolium proton signal at 10.94 ppm being replaced by a singlet at 10.6 ppm, indicating formation of an intermediate product, in which the NHC part was probably not coordinated. Surprisingly, reaction of the isolated product with one equivalent of the base $(Me_3Si)_2NK$ (KHMDS) resulted in formation of the NHC complex **2**, in which the bipyridine moiety underwent C−H activation and remained noncoordinated (Scheme 2).

Scheme 2. Synthesis of Complex 2



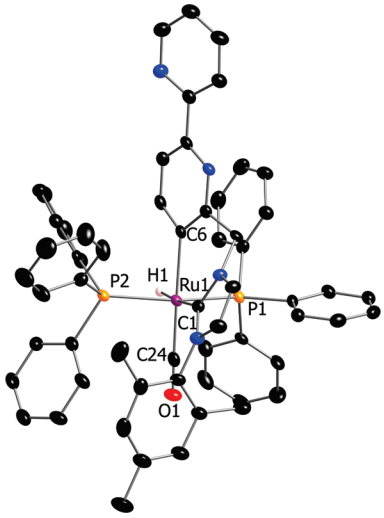


Figure 2. ORTEP plot of complex **2**. Non-hydride H atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Complex 2

Ru1−C1	2.137(3)	Ru1−H1	1.40(4)
Ru1−C24	1.885(3)	Ru1−C6	2.177(3)
Ru1−P1	2.3425(10)	Ru1−P2	2.3471(9)
C6−Ru1−C24	175.32(13)	H1−Ru1−C1	172.7(19)
P1−Ru1−P2	154.80(3)	Ru1−C24−O1	175.4(3)

The fully characterized complex **2** gives rise to a doublet at 43.22 ppm (J_{PH} = 20 Hz) in the $^{31}P\{^1H\}$NMR spectrum, and the hydride ligand appears as a triplet at −12.31 (J_{PH} = 20 Hz) in the ^{1}H NMR spectrum. The CO stretch of **2** in the IR spectrum appears at 1936 cm^{-1}. Crystals of **2** suitable for X-ray diffraction analysis were obtained by layering pentane over a concentrated dichloromethane (DCM) solution of **2**. The X-ray structure (Figure 2) exhibits an octahedral structure containing two phosphorus atoms *trans* to each other, a hydride *trans* to the

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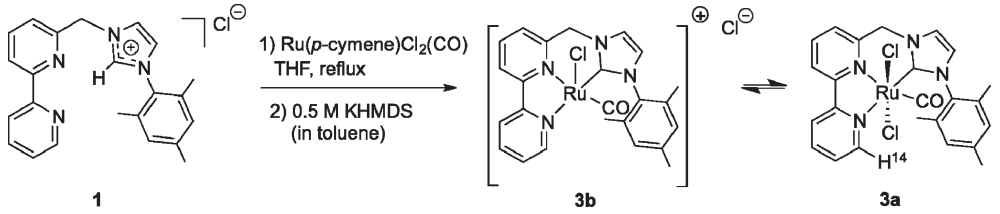
Scheme 3. Synthesis of the Ru-NHC Complexes 3a and 3b



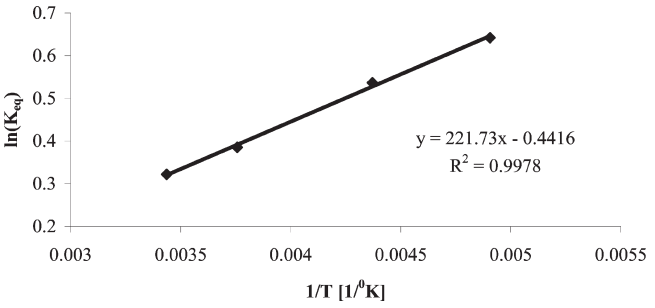


Figure 3. Van't Hoff plot for **3b** ⇌ **3a** in CD_2Cl_2.

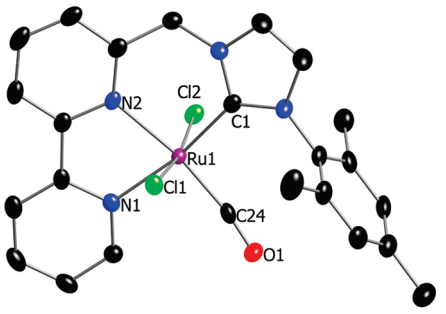


Figure 4. ORTEP plot of **3a**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

NHC ligand, and CO *trans* to the C−H-activated carbon of the bipyridine ligand.

Reported Ru(II)−C1(NHC) bond lengths of pincer complexes are in the range 1.967−2.168 Å.[10,21,25−27] The Ru−C1-(NHC) bond distance of **2** (2.137 Å) is similar to the one reported for an analogous H−Ru(II)−C(NHC) complex (2.168 Å),[26] containing a hydride ligand *trans* to the NHC ligand and two PPh_3 groups *cis* to NHC. The relatively long Ru−C1(NHC) bond is probably a result of both the *trans* effect of the hydride ligand and the steric hindrance of the two PPh_3 groups.

The unusual complex **2** might be useful for the preparation of binuclear complexes, by utilization of the noncoordinated bipyridine moiety.

Assuming that the presence of phosphine ligands hinders the coordination of the bipyridine ligand, we probed a non-phosphine complex as precursor. Thus, reaction of Ru(*p*-cymene)Cl_2-(CO) with ligand **1** was carried out under conditions similar to those leading to the formation of **2**. This resulted in formation of the dichloride pincer complexes **3a** and **3b** (Scheme 3).

Complexes **3a** and **3b** are in equilibrium, as indicated by variable-temperature ^{1}H NMR in CD_2Cl_2. The main feature in the spectrum was the bipyridine *ortho* C-*H* proton (H-14 in Scheme 3), whose chemical shift appears in the region 9−9.5 ppm.[6] Two peaks were observed in that region (9.34 and 9.10 ppm), in a temperature-dependent ratio. The peak that increases upon temperature decrease is likely to be associated with the charge-neutral complex **3a**, due to entropy considerations, assuming that CD_2Cl_2 coordination is not significant. On the basis of this data, K_{eq} was calculated at several temperatures (for example K_{eq} = 1.9 at 203.9 K), showing a linear temperature dependence. On the basis of this data, ΔH^0 = −0.44 kcal/mol; ΔS^0 = 2.16 eu for the equilibrium described in Figure 3.

Complex **3a** gives rise in the solid state to a CO stretch in the IR spectrum at 1928 cm^{-1}, indicating considerable back-bonding to this ligand. For comparison, the CO stretch of the analogous phosphine complex **A**[6] appears at 1906 cm^{-1}.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complex 3a

Ru1−C1	2.007(3)	Ru1−N1	2.114(3)
Ru1−C24	1.849(4)	Ru1−N2	2.117(3)
Ru1−Cl1	2.392(1)	Ru1−Cl2	2.4134(10)
N2−Ru1−C24	170.92(12)	N1−Ru1−C1	169.33(11)
Cl1−Ru1−Cl2	170.45(3)	Ru1−C24−O1	172.2(3)

Single crystals of **3a** suitable for X-ray diffraction were obtained by slow evaporation of a CH_2Cl_2 solution. The X-ray structure (Figure 4) shows the Ru−C1(NHC) bond distance of 2.007 Å, which is similar to the Ru(II)−C(NHC) bond length reported for a bipyridine-NHC complex.[28]

It is noteworthy that the Ru−C1(NHC) bond distance of **3a** is significantly shorter (by 0.137 Å) in comparison with the corresponding bond of complex **2**, probably due to the absence of the two bulky phosphine groups and the absence of the hydride *trans* effect in **3a**.

Next we decided to prepare a mixed phosphine-NHC complex. For this purpose, the free NHC ligand was first prepared at low temperature and then reacted with the complex precursor. Reacting a cold (−35 °C) THF suspension of **1** with a cold THF solution (−35 °C) of LiHMDS and stirring at this temperature for 4 h gave the free NHC ligand. Alternatively, the free NHC ligand was formed by mixing solid **1** and LiHMDS at −78 °C and adding cold THF (−78 °C) followed by warming to −30 °C for 4.5 h. At this stage $RuH(Cl)CO(PPh_3)_3$ was added followed by warming slowly to room temperature and then refluxing overnight in order to facilitate the coordination of the bipyridine moiety to give **4**. In practice, the second procedure gave higher yields and was easier to perform on a large scale (Scheme 4).

Scheme 4. Synthesis of Complex 4

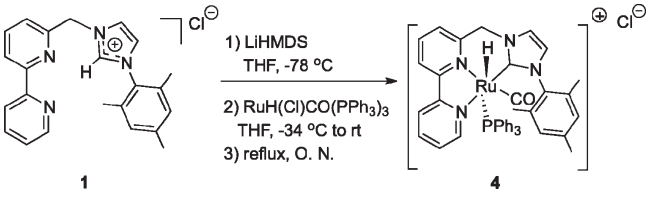


Table 3. Selected Bond Lengths (Å) and Angles (deg) of Complex 5

Ru1−C1	2.014(2)	Ru1−N1	2.116(1)
Ru1−C24	1.843(2)	Ru1−N2	2.110(2)
Ru1−P1	2.416(1)		
N2−Ru1−C24	171.15(6)	N1−Ru1−C1	160.49(6)
Ru1−C24−O1	174.53(15)		

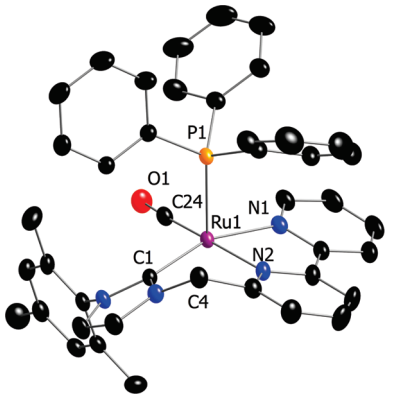


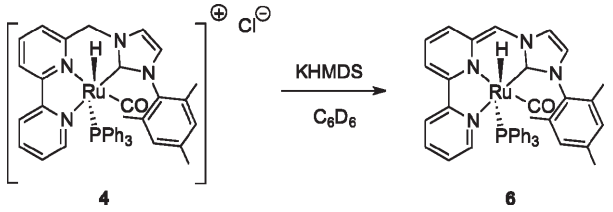
Figure 5. ORTEP plot of complex **5**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

The fully characterized **4** gives rise to a singlet at 24.03 ppm in the $^{31}P\{^1H\}$NMR spectrum, and the hydride ligand appears as a doublet at −7.96 ppm (J_{PH} = 106 Hz) in the ^1H NMR spectrum. In the $^{13}C\{^1H\}$ NMR spectrum the carbonyl ligand gives rise to a doublet at 206.63 ppm (J_{PC} = 6.2 Hz), and the NHC carbon (Ru-*C* NHC) appears at 185.05 ppm as a broad singlet. The CO stretch of **4** in the IR spectrum appears at 1932 cm^{-1}.

Treatment of **4** with $NaBAr^F$ (sodium tetrakis[(3,5-trifluoromethyl)phenylborate) gave complex **5** with no change in the spectral data. Crystals of **5** suitable for X-ray diffraction were grown from a pentane−ether solution. In 25% of the crystals the hydride was replaced by an OH group, perhaps as a result of reaction with oxygen. The hydride ligand was not detected directly by X-ray.

The X-ray structure of **5** (Table 3, Figure 5) exhibits the CO ligand *trans* to the central nitrogen atom of the pincer system, and the location of the hydride is *trans* to the phosphine. The Ru−C1(NHC) bond distance (2.014 Å) is similar to the corresponding bond in **3a** (2.007 Å) and in a reported Ru-NHC complex[28] containing a bipyridine nitrogen *trans* to the NHC ligand (1.995 Å). The Ru−P1 bond distance in **5** (2.416 Å) is significantly longer (by 0.073 Å) than the Ru−P1 bond distance in **2**, as a result of the strong *trans* effect of the hydride ligand.

Scheme 5. Synthesis of the Dearomatized Complex 6

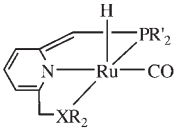


Attempted preparation of a RuNHC complex using Ag-NHC (prepared from **1** and Ag_2O) resulted in a mixture containing **2**, **4**, and a complex that is probably an isomer of **2** with CO *trans* to NHC.

Deprotonation of complex **4** with KHMDS in benzene or toluene resulted in formation of the dearomatized complex **6** as the only product. This complex was somewhat unstable at room temperature. It gives rise to a singlet at 21.62 ppm in the $^{31}P\{^1H\}$ NMR spectrum, and the hydride ligand appears as a doublet at −7.13 ppm (J_{PH} = 142 Hz) in the ^1H NMR spectrum. The "arm" vinylic proton appears as a singlet at 5.87 ppm, and the corresponding carbon exhibits a singlet at 89.68 ppm in the $^{13}C\{^1H\}$ NMR spectrum, The carbonyl ligand appears as a doublet at 209.24 ppm (J_{PC} = 5.7 Hz), and the NHC carbon (Ru-*C* NHC) appears at 179.23 ppm as a broad singlet in the $^{13}C\{^1H\}$ NMR spectrum.

Catalytic Hydrogenation of Esters. Catalytic hydrogenation of esters, particularly nonactivated ones, under mild conditions is a challenging task. In pioneering work by Elsevier et al., various aromatic and aliphatic esters were hydrogenated in hexafluoropropan-2-ol using *in situ*-prepared ruthenium complexes bearing P,P,P ligands at 86 atm of dihydrogen under basic conditions.[29] Nomura et al. reported the hydrogenation of methyl phenylacetate to a mixture of $PhCH_2CH_2OH$ and $PhCH_2CO_2$-CH_2CH_2Ph using *in situ*-prepared Ru catalyst and zinc under 20 atm of H_2.[30]

We have reported the hydrogenation of nonactivated esters to the corresponding alcohols under relatively mild and neutral conditions, catalyzed by a dearomatized PNN [2-(di-*tert*-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine] pincer-type Ru(II) complex **C** with under 5.3 atm of dihydrogen.[4]



X = P; R, R' = *i*Pr
X = N; R = Et; R' = *t*Bu

C

Following this report, Saudan et al. reported the hydrogenation of carboxylic esters to alcohols in high turnover (TON ≈ 2000) using ruthenium complexes bearing N,P ligands under 50 atm of dihydrogen in the presence of a large excess of base relative to Ru (catalyst/base = 1/100).[31] Ruthenium hydrido borohydride complexes based on bidentate phosphine and diamine ligands catalyze hydrogenation of optically active esters under 50 atm and at 16 h, as reported by Ino et al.[32,33] Methyl benzoate was hydrogenated to benzyl alcohol and methanol at 25 °C and 8 bar H_2 with a TOF of 209 h^{-1}, using a ruthenium

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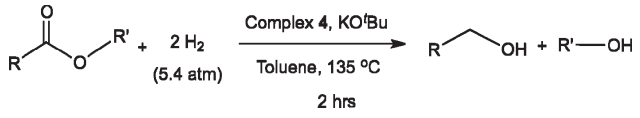
Table 4. Hydrogenation of Esters Catalyzed by Complex 4 + KO^{t}Bu[a]

entry	ester	cat. **4** (mol %)	$P(H_2)$ (atm)	time (h)	conv (%)[b]	products (yield [%])[b]
1	pentyl pentanoate	1	5.4	2	96	1-pentanol (96)
2	ethyl butyrate	1	5.4	2	98	1-butanol (97), ethanol (95)
3	benzyl benzoate	1	5.4	2	91	benzyl alcohol (89)
4	ethyl benzoate	1	5.4	2	97	benzyl alcohol (97), ethanol (94)
5[c]	ethyl benzoate	0.025	50	12	72	benzyl alcohol (71), ethanol (69)

[a] A solution of complex **4** (0.01 mmol), KO^{t}Bu (0.01 mmol), and ester (1 mmol) in toluene (2 mL) was heated at 135 ^{o}C (bath temperature) under H_2 (5.4 atm) for 2 h. [b] Conversion of esters and percentage of maximum possible amount of each of the product alcohols were determined by GC. [c] Complex **4** (0.005 mmol), KO^{t}Bu (0.005 mmol), ester (20 mmol), and toluene (5 mL) were heated at 110 ^{o}C under H_2 pressure (50 atm) in an autoclave for 12 h.

Scheme 6. Catalytic Hydrogenation of Esters by Complex 4 + KO^{t}Bu



complex bearing a chelating N-heterocyclic carbene with a primary amine donor in basic solution, as reported by Morris.[34] Ito et al. reported the Ru-catalyzed enantioselective hydrogenation of racemic lactones to chiral diols via dynamic kinetic resolution at 100 °C under 50 atm of H_2 in 2-propanol containing 25 mol % KO^{t}Bu.[35] Bergens and co-workers studied the formation of intermediates in the homogeneous hydrogenation of lactones and esters using chiral bidentate Ru(II) at −20 °C under 4 atm of H_2.[36]

We now report that complex **4** in the presence of a catalytic amount of base (one equivalent relative to Ru) is among the best catalysts for the hydrogenation of nonactivated esters to the corresponding alcohols under relatively mild conditions.[4,37−39] Thus, when a toluene solution of pentyl pentanoate (1 mmol), complex **4** (0.01 mmol), and KO^{t}Bu (0.01 mmol) was heated at 135 °C (bath temperature) for 2 h under 5.4 atm of H_2, almost quantitative formation of 1-pentanol (96%) was observed by GC with the corresponding consumption of dihydrogen (Table 4, entry 1). Hydrogenation of ethyl benzoate resulted in formation of 97% of benzyl alcohol and 94% of ethanol after 2 h (Table 4, entry 4). Using 50 atm pressure of H_2 for the same substrate, hydrogenation of ethyl benzoate resulted in the high turnover number of 2840 (Table 4, entry 5). The reaction is general and provides an attractive method for "green", mild synthesis of primary alcohols from nonactivated esters without the need for the traditionally used stoichiometric amounts of metal hydride reagents, which generate stoichiometric amounts of waste. The catalytic activity of complex **4** in other reactions is being studied.

SUMMARY

The new bipyridine-NHC ligand **1** and the Ru BPy-NHC complexes **2**, **3**, **4**, **5**, and **6** were synthesized. Ligand **1** was synthesized by reaction of 6-(chloromethyl)-2,2′-bipyridine with 1-mesityl-1*H*-imidazole, and complexes **2** and **4** were prepared by reaction of **1** with the Ru precursor $RuH(Cl)CO(PPh_3)_3$. Complex **3** was prepared by reaction of **1** with Ru precursor Ru(*p*-cymene)Cl_2(CO), complex **5** by reaction of **4** with NaBAr^F, and **6** by reaction of **4** with a base.

Complexes **2**, **3a**, and **5** were also X-ray characterized. The charge-neutral complex **3a** is in equilibrium with the cationic complex **3b** in solution.

Complex **4** in the presence of one equivalent of base (relative to Ru) is among the most active catalysts known for the rare hydrogenation of nonactivated esters to alcohols. The somewhat unstable, dearomatized pincer complex **6** is very likely an intermediate in the catalytic cycle.

EXPERIMENTAL SECTION

General Procedures. All experiments with metal complexes and the NHC ligand were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Deuterated solvents were dried over 4 Å molecular sieves.

Commercially available reagents were used as received. 6-Chloromethyl-2,2′-bipyridine (BPy-CH_2Cl) precursors,[39] 1-mesityl-1*H*-imidazole,[40] Ru(*p*-cymene)Cl_2(CO),[41] and $RuHCl(PPh_3)_3(CO)$[42] were prepared according to literature procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 300, 75, and 122 MHz, respectively, using Bruker AMX-300 and AMX-500 NMR spectrometers.

NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^{1}H NMR chemical shifts are referenced to the residual hydrogen signal of the deuterated solvent (7.15 ppm for benzene, 5.32 ppm for dichloromethane, etc.). In ^{13}C{^{1}H} NMR measurements the signals of deuterated benzene (128.0 ppm), deuterated dichloromethane (53.8 ppm), etc., were used as references. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. Abbreviations used in the description of NMR data are as follows: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; sept, septet; v, virtual; dist, distorted.

Synthesis of 3-(2,2′-Bipyridine-6-ylmethyl)-1-mesityl-1*H*-imidazolium Chloride (1). A solution of 6-(chloromethyl)-2,2′-bipyridine[39] (1 mmol, 204 mg) and 1-mesityl-1*H*-imidazole (1.35 mmol, 251 mg) in dry acetonitrile (5 mL) was refluxed under a N_2 atmosphere for 36 h. The reaction mixture was allowed to cool slowly to room temperature over 1 h. A white crystalline solid appeared, and the solvent was decanted. The product was recrystallized from hot acetonitrile and washed with dry acetonitrile in a nitrogen glovebox to yield 304 mg (85.5%) of **1** as a white solid. The crystals were suitable for X-ray analysis.

^{1}H NMR (300.1 MHz, $CDCl_3$): 10.94 (s, 1H, NC*H*N), 8.71 (d, $J_{H,H}$ = 8 Hz, 2H, Py-H1), 8.42 (d, 1H, $J_{H,H}$ = 7.8 Hz, Py-H5), 8.27 (d, 1H, $J_{H,H}$ = 8.1 Hz, Py-H7), 8−7.94(bm, Py-H4 + imidazole-C*H*C*H*N), 7.8 (m, 1H, Py-H6), 7.36 (m, 1H, Py-H3), 7.09 (bm, 1H, Py-H3), 7.01 (s, 2H, m-Ar*H*), 6.29 (s, 2H, BPyCH_2N), 2.35 (s, 3H, p-ArCH_3), 2.06 (s, 6H, o-ArCH_3). ^{13}C{^{1}H} NMR (125.75 MHz, $CDCl_3$): 156.31 (s, o-Py2),

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155.60 (s, o-Py1), 152.5 (s, o-Py2), 149.51 (s, o-Py1 *C*H), 141.46 (s, o-Ar), 139.37 (s, p-Ar), 138.86 (s, p-Py1-CH), 136.86 (s, p-Py2-CH), 134.33 (s, Py-NCHN), 130.89 (s, Ar-*C*-N), 129.98 (s, m-ArCH), 124.34 (s, m-Py1 *C*H), 124.13 (s, m-Py2 *C*H), 123.27 (s, imidazole-CHCHN), 122.54 (s, imidazole-CHCHN), 121.39 (s, m-Py1 *C*H), 120.96 (s, m-Py2 *C*H), 54.26 (s BPyCH_2N), 21.18 (s, p-ArCH_3), 17.68 (s,o-ArCH_3). HRMS: *m/z* 355.1915 (M+, calcd *m/z* 355.1923). Anal. Calcd for $C_{23}H_{23}ClN_4$: C, 70.67; H, 5.93; N, 14.33. Found: C, 70.20; H, 5.87; N, 14.46

Synthesis of Complex 2. A suspension of **1** (0.127 mmol, 50 mg) and RuH(Cl)CO(PPh_3)$_3$ (0.254 mmol, 242 mg) in dry THF (2.5 mL) was refluxed under a N_2 atmosphere overnight. The reaction mixture was allowed to cool slowly to room temperature. A yellow precipitate appeared, and the solvent was decanted. The intermediate product was washed several times with THF and pentane to yield 102 mg of a compound in which the NHC part was not coordinated, but all of the starting ligand was consumed (according to ^{1}H NMR). The above intermediate product, presumably Ru(PPh_3)$_2$(H)(CO) 3-(2,2′-bipyridin-6-ylmethyl)-1-mesityl-1*H*-imidazolium dichloride, was suspended in dry THF (2.5 mL), and 1 equiv of KHMDS (21 mg) was added, resulting in a color change to black upon stirring for 3 h at room temperature. The reaction mixture was filtered, evaporated to dryness, washed with pentane, and extracted by 4 mL of ether. The resulting solution was evaporated, and the residue was dissolved in a minimal amount of benzene. Addition of pentane resulted in precipitation of **2** as a pure, black solid (29 mg, 22%). Complex **2** was somewhat thermally unstable. Single crystals suitable for X-ray diffraction were obtained by layering pentane over a concentrated dichloromethane solution of **2**.

^{31}P{^{1}H} NMR (CD_2Cl_2): 43.22 (d, $J_{P,H}$ = 20 Hz). ^{1}H NMR (300.1 MHz, $CDCl_3$): 8.68 (bd, $J_{H,H}$ = 8 Hz, 1H, o-Py1), 8.57 (bd, $J_{H,H}$ = 8 Hz, 2H, m-Py1), 7.85 (bt, $J_{H,H}$ =7.6 Hz, 1H, m-Py2), 7.79 (bs, 12H, m-PPh_3), 7.72 (bm, 1H, p-Py2), 7.63 (bm, 1H, o-Py2), 7.2−7.45 (bm, 18H, o,p-PPh_3), 7.06−7.01 (m, 2H, m-Ar + m-Py2), 6.41 (s, 2H, BPyCH_2N), 6.37−6.30 (bm, 2H, imidazole-C*H*C*H*N), 2.39 (s, 3H, p-ArCH_3), 2.16 (s, 6H, o-ArCH_3) −12.31(t, $J_{P,H}$ = 20 Hz, 1H, Ru−H). IR: ν C═O 1936 cm^{-1}. MS: *m/z* 1009.35 (M(-H$^+$), calcd *m/z* 1009.11) *m/z* 747.20 (M(-PPh_3), calcd *m/z* 747.83).

Synthesis of Complex 3a. A suspension of **1** (0.077 mmol, 30 mg) and Ru(*p*-cymene)Cl_2(CO) (0.077 mmol, 25.6 mg) in dry THF (1.5 mL) was refluxed under an argon atmosphere overnight. A red precipitate appeared, and the solvent was decanted. The intermediate product was washed several times with THF and pentane and suspended in dry THF (2.5 mL). One equivalent of KHMDS (0.153 mL of a 0.5 M solution in toluene) was added to the reaction mixture, and it was refluxed under an Ar atmosphere for 3 days, resulting in a color change to black. The reaction mixture was filtered, the solvent was removed under vacuum, and the residue was washed by pentane and ether and extracted by THF (1 mL) to give complex **3a** as a pure, black-green solid (9 mg, 21%). Single crystals of **3a** suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution. Due to the fact that **3a** was in equilibrium in solution with the cationic **3b**, some of the NMR peaks were broad and overlapping. In addition, the material was unstable, and therefore so far we were unable to obtain a good ^{13}C NMR spectrum (at 203.8 K). Single crystals for X-ray diffraction were obtained from freshly prepared **3**.

^{1}H NMR (300.1 MHz, CD_2Cl_2, 203.8 K) of a solution of **3a** + **3b**: Peaks assigned to **3a**: 9.10 (d, 2H, $J_{H,H}$ = 5 Hz, o-Py), 8.28 (m, 4H, Ar-H), 8.21 (m, 3H, Ar-H), 8.12 (m, 3H, Ar-H), 7.91 (m, 2H, Ar-H), 7.71 (d, 2H, $J_{H,H}$ = 2 Hz, Ar-H), 7.31 (m, 3H, Ar-H), 6.99 (m, 2H, Ar-H), 6.97 (m, 2H, Ar-H), 6.93 (m, 1H, Ar-H), 6.76 (m, 1H, Ar-H), 5.72 (bs, 4H, BPyCH_2N), 2.34 (m, 12H, ArCH_3), 2.2 (m, 9H, ArCH_3), 1.51 (m, 6H, ArCH_3). Peaks assigned to **3b**: 9.34 (d, 1H, $J_{H,H}$ = 5.5 Hz, o-Py1CH), 7.44 (m, 1H, Ar-H), 7.20 (m, 1H, Ar-H), 7.13 (m, 1H, Ar-H), 7.09 (m, 1H, Ar-H), 5.80 (bs, 1H, BPyCH*H*N), 5.34 (bs, 1H, BPyCH*H*N). Spectral features of solid **3a**: IR: ν C═O 1928.3 cm^{-1}.

Table 5. K_{eq} at Various Temperatures in CD_2Cl_2

3b ⇌ 3a

K	*T* (K)
1.9	203.86
1.71	228.76
1.47	266.12
1.38	291.02

MS: *m/z* 576.93 ((M + Na)$^+$, calcd *m/z* 577.01) *m/z* 518.98 ((M − Cl$^-$)$^+$, calcd *m/z* 519.05). HRMS: *m/z* 577.0137 (M + Na − H$^+$, calcd *m/z* 577.0112). Note: in all NMR experiments the solution remained clear and no precipitate was observed. The equilibrium constants are reproducible and remained the same regardless of whether **3a** + **3b** was warmed from low temperature or cooled from ambient temperature.

Synthesis of Complex 4. A mixture of solid **1** (500 mg, 1.28 mmol) and LiHMDS (224.5 mg, 1.34 mmol) was cooled to −78 °C under Ar; then cold THF (−78°, 100 mL) was added via cannula, and the reaction mixture was stirred at the same temperature for 15 min. The reaction flask was transferred to a *calibrated* (−30 °C) ice bath containing $CaCl_2$/water/dry ice and stirred for 4.5 h. Occasionally the reaction mixture was allowed to warm to −28 °C and re-cooled to −34 °C. Then the reaction mixture was transferred via a cannula into a flask equipped with a reflux condenser containing RuHCl(CO)(PPh_3)$_3$ (1.219 g, 1.28 mmol) under Ar. The mixture was warmed slowly to room temperature under Ar and then refluxed under N_2 atmosphere overnight. After cooling to room temperature, the reaction mixture was filtered and evaporated to dryness, and the resulting solid was washed with pentane (4 × 100 mL) and extracted with 20 mL of dichloromethane. The resulting solution was filtered and concentrated under vacuum until the appearance of a yellow precipitate. Addition of pentane resulted in precipitation of an additional, impure yellow precipitate, which was dissolved in dichloromethane and precipitated again with pentane, giving **4** as a pure yellow solid (450 mg, 45%).

^{31}P{^{1}H} NMR (CD_2Cl_2): 24.03(s). ^{1}H NMR (300.1 MHz, CD_2Cl_2): 8.26 (bm, 2H, o,p-Py1), 8.17 (m, 2H, Ar-H), 8.04 (m, 2H, Ar-H) 7.88 (t, 1H, $J_{H,H}$ = 7.3 Hz, p-Py2), 7.35 (bm, 4H, Ar-H), 7.2 (m, 6H, m-Ph_3P), 7.08 (m, 1H, Ar-H), 6.85−7 (bm, 9H, o,p-Ph_3P), 6.45 (d, 1H, $J_{H,H}$ = 15.6 Hz, BPyCH*H*N), 4.45 (d, 1H, $J_{H,H}$ = 15.6 Hz, BPyCH*H*N), 2.65 (s, 3H, p-ArCH_3), 2.05 (s, 3H, o-ArCH_3), 1.87 (s, 3H, o-ArCH_3), −7.96 (d, 1H, $J_{H,P}$ =106 Hz,Ru*H*). ^{13}C{^{1}H} NMR (125.75 MHz, CD_2Cl_2): 206.63 (d, $J_{P,C}$ = 6.2 Hz,RuCO), 185.05 (bs, Ru-*C* NHC), 155.37 (s, imidazole-CHCHN), 154.42 + 154.41 (s, o-Py1+ o-Py2), 154.21 (s,Ar-*C*-N), 152.27 (s, o-Py1), 136.35 (d, $J_{P,C}$ = 11.3 Hz, PCAr), 133.05 (s, o-Ar), 132.81 (s, o-Ar), 132.54 (d, $J_{P,C}$ = 45 Hz, m-CArP), 126.29 (s, Ar CH), 125.75 (s, Ar CH), 124.88 (s, Ar CH), 122.70 (s, imidazole-CHCHN), 122.17 (s, Ar CH), 121.29 (s, imidazole-CHCHN), 28.94 (s, BPyCH_2N), 20.89 (s, p-ArCH_3), 18.96 (s, o-ArCH_3), 18.70 (s, o-ArCH_3). IR: ν C═O 1932 cm^{-1}. HRMS: *m/z* 747.1838 (M$^+$, calcd *m/z* 747.1827).

Synthesis of Complex 5 from Complex 4 by Chloride Exchange with BAr^{F-}. To an ethereal suspension (5 mL) of **4** (30 mg, 0.038 mmol) was added 1 equiv of $NaBAr^F$ (33.7 mg, 0.038 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 1 h at room temperature, and then the formed NaCl was filtered off and the solvent was removed under vacuum, to yield 53.3 mg (87%) of **5** as a pure, red solid. The spectral data are essentially identical to that of **4** except for BAr^F peaks. Single crystals suitable for X-ray diffraction were obtained by layering pentane over a concentrated ethereal solution of **5**.

Synthesis of Complex 6. A 5.7 mg amount of **4** (0.02 mmol) was suspended in 1 mL of C_6D_6, and 1 equiv of KHMDS (4.0 mg) was added to generate a dark green/black complex, **6**. Filtration into a J.Young

Table 6. Experimental Data Regarding X-ray Diffraction[a]

	1	2	3a	5
formula	$C_{23}H_{23}N_4 + Cl$	$C_{60}H_{52}N_4OP_2Ru + 0.5(CH_2Cl_2)$	$2(C_{24}H_{22}Cl_2N_4ORu) + 3(C_4H_8O)$	$C_{42}H_{37}N_4O_{1.25}PRu + C_{32}H_{12}BF_{24}$
M_w	390.90	1050.53	1317.10	1613.02
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
cryst syst	triclinic	monoclinic	triclinic	triclinic
a [Å]	8.8684(18)	12.521(3)	7.0433(14)	11.5507(3)
b [Å]	9.856(2)	16.060(3)	10.613(2)	17.3308(5)
c [Å]	12.098(2)	26.826(8)	20.980(4)	19.5847(5)
α [deg]	92.53(3)		98.10(2)	113.316(1)
β [deg]	109.86(4)	106.61(3)	94.93(3)	93.094(1)
γ [deg]	94.50(3)		103.49(5)	101.152(1)
volume [Å^3]	988.7(3)	5169(2)	1498.2(5)	3495.1(2)
Z	2	4	1	2
ρ_{calcd} [g cm^{-3}]	1.313	1.350	1.460	1.533
μ [mm^{-1}]	0.209	0.463	0.737	0.360
R_1 [$I > 2\sigma(I)$] [%]	3.88	4.86	4.09	5.15
R_1 (all data) [%]	5.24	7.05	5.73	6.98
no. of reflns (unique)	20 666 (7428)	44 708 (11 384)	15 898 (6067)	91 452 (28 402)
R_{int}	2.71	6.66	3.67	9.57
goodness of fit	1.022	1.093	1.005	1.037

[a] Crystals were coated in Hampton oil and mounted on a fiber loop.

NMR tube gave **6** as the only product. The dearomatized **6** was too unstable for isolation.

$^{31}P\{^1H\}$ NMR (C_6D_6): 21.62 (s). ^1H NMR (300.1 MHz, (C_6D_6): 8.79 (d, 1H, $J_{H,H}$ = 5.4 Hz, o-Py1), 7.25 (bs, 6H, m-Ph_3P), 6.99 (bm, 9H, o,p-Ph_3P), 6.89 (bd, 1H, $J_{H,H}$ = 4.2 Hz, Ar-H), 6.75 (d, 1H, $J_{H,H}$ = 1.7 Hz, imidazole-C*H*CHN), 6.54 (m, 1H, Ar-H), 6.43 (m, 1H, Ar-H), 6.21 (d, 1H, $J_{H,H}$ = 1.7 Hz, imidazole-CHC*H*N), 6.15 (bd, 1H, $J_{H,H}$ = 9 Hz, Ar-H), 5.96 (bm, 2H, Ar-H), 5.87 (s, 1H, BPyC*H*N), 2.20 (s, 6H, o-ArCH_3), 2.11 (s, 3H, p-ArCH_3), −7.13 (d, 1H, $J_{H,P}$ = 142 Hz, Ru*H*). $^{13}C\{^1H\}$ NMR (125.75 MHz, toluene-d_8, 228.8 K): 209.24 (d, $J_{P,C}$ = 5.7 Hz,RuCO), 179.23 (s, *C*-Ru), 157.62 (s, o-Py2), 151.27 (s, o-Py1), 150.29 (s, o-Py1CH), 141.25 (s, o-Py1), 138.60 (s, p-Ar), 138.13 (s, o-Ar), 137.91 (s, o-Ar), 134.44 (d, $J_{P,C}$ = 21.4 Hz, PCAr), 133.88 (d, $J_{P,C}$ = 20 Hz, o-CArP), 133.48 (d, $J_{P,C}$ = 12.6 Hz, m-CArP), 131.78 (s, ArCH), 129.58 (s, ArCH), 129.14 (s, ArCH), 129.02 (s, ArCH), 126.16 (s, ArCH), 125.41 (s, imidazole-CHCHN), 125.26 (s, imidazole-CHCHN), 121.26 (s, imidazole-CHCHN), 119.58 (s, imidazole-CHCHN), 118.35 (s, imidazole-CHCHN), 118.10 (s, imidazole-CHCHN), 89.68 (s, BPy-CH-imidazole), 21.18 (s, ArCH_3), 19.09 (s, ArCH_3), 17.42 (s, ArCH_3).

General Procedure for Catalytic Hydrogenation of Esters. (a) A solution of KO^{t}Bu (0.01 mmol) in toluene (1.0 mL) was transferred into a Fischer−Porter tube (100 mL) containing 0.01 mmol of complex **4**, followed by addition of the ester (1.0 mmol) in toluene (1.0 mL) in a nitrogen glovebox. The Fischer−Porter tube was flushed with dihydrogen (twice with 30 psi) and filled with H_2 (5.4 atm). The solution was heated at 135 °C (bath temperature; actual temperature is ∼100 °C) with stirring for 2 h. After cooling to ∼5 °C (with a cold water bath), excess H_2 gas was vented carefully, and the products were determined by GC analysis carried out using a Carboxen 1000 column on a HP 690 series GC system or HP-5 cross-linked 5% phenylmethylsilicone column (30 m × 0.32 mm × 0.25 μm film thickness, FID) on a HP 6890 series GC system using *m*-xylene (1.0 mmol) as an internal standard.

(b) Substrate/catalyst, 4000/1: In a nitrogen glovebox, a solution of KO^{t}Bu (0.005 mmol) in toluene (2 mL) was added to a stainless-steel 30 mL high-pressure reactor equipped with a magnetic stirring bar and containing 0.005 mmol of complex **4**. Then, the ester (20.0 mmol) in toluene (3 mL) was added. The autoclave was taken out of the glovebox, followed by three successive cycles of pressurization/venting with H_2 (3 atm), then pressurized with H_2 (50 atm) and closed. The solution was heated at 135 °C (bath temperature) with stirring. After 12 h, the autoclave was cooled in an ice/water bath, the excess H_2 was vented carefully, and the products were determined by GC. (After 5 h, the conversion of the ester was only 41%.)

Crystal data were measured at 120 K on a Bruker Kappa Apex-II CCD diffractometer equipped with (λ(Mo Kα) = 0.71073 Å) radiation, a graphite monochromator, and MiraCol optics. The data were processed with APEX-II package programs. Structures were solved by either the AUTOSOLVE module or SHELXS and refined with full-matrix least-squares refinement based on F^2 with SHELXL-97. Full details can be found in the cif files and Table 6.

■ ASSOCIATED CONTENT

Supporting Information. CIF file containing X-ray crystallographic data for complexes **2**, **3a**, and **5** as well as ligand **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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