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Active ruthenium-(*N*-heterocyclic carbene) complexes for hydrogenation of ketones

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Four ruthenium-*N*-heterocyclic carbene complexes (3–6) have been prepared and the new compounds characterized by C, H, N analyses, ^{1}H-NMR and ^{13}C-NMR. The reduction of ketones to alcohols via transfer hydrogenation was achieved with catalytic amounts of complexes 3–6 in the presence of *t*-BuOK. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: imidazolin-2-ylidene; *N*-heterocyclic carbene; benzimidazolin-2-ylidene; transfer hydrogenation

INTRODUCTION

Metal complexes of *N*-heterocyclic carbenes (NHCs) were first reported independently by Wanzlick and Öfele in 1968.[1,2] Both reports used the deprotonation of an imidazolium salt by a basic metal precursor to form the imidazolin-2-ylidene complexes. These type of complexes were later studied extensively by Lappert *et al*.[3–6] However, it was only during the last decade that a renewed interest in these complexes occurred with the isolation by Bertrand[7] of stable phosphinocarbenes and by Arduengo of *N*-heterocyclic carbenes.[8]

Homogeneous organometallic catalysis has long depended on phosphine ligands.[9,10] Despite their effectiveness in controlling reactivity and selectivity, phosphine-based catalysts require air-free handling to prevent the oxidation of the ligand and have been subject to P-C activation at elevated temperatures. Recently, nucleophilic *N*-heterocyclic carbenes (NHCs),[11] with stronger σ-donor electronic properties than bulky tertiary phosphines,[12] have emerged as a new family of ligands. In contrast to metal complexes of phosphines, the metal–NHC complexes appear to be extraordinarily stable towards heat, air and moisture owing to high dissociation energies of their metal–carbon bonds.[13] The precursor imidazolium salts are often easier to obtain than phosphines, but preparation of the metal complexes from these salts can be more difficult.[14] The most common method is direct complexation of the free NHC, either isolated,[15–18] or generated *in situ*[19] formed by deprotonation of the imidazolium salts. Oxidative addition of an imidazolinium carbon–hydrogen bond[20,21] to a low valent metal center and addition of an electron-rich olefin with C=C bond cleavage[22,23] can also lead to metal–NHC carbene complexes in certain cases.

Carbene complexes of late transition metals have been used in many types of homogeneous catalytic reactions including Heck and Suzuki coupling reactions,[24,25] olefin metathesis,[26,27] hydroformylation, hydrogenation and hydrosilylation,[28,29] and the copolymerization of ethene and CO.[30]

We have previously reported the use of an *in situ* formed imidazolidin-2-ylidene, tetrahydropyrimidin-2-ylidene and tetrahydrodiazepin-2-ylidenepalladium(II) systems that exhibit high activity for various coupling reactions of aryl bromides and aryl chlorides.[31–33] In order to obtain more stable, efficient and active systems, we have also investigated benzo-annelated derivatives.[34–36] Recently our group reported that novel complexes of rhodium(I) 1,3-dialkyimidazolidin-2-ylidenes gave secondary alcohols in good yields by the addition of phenylboronic acid to aldehydes.[37]

Catalytic transfer hydrogenation with the aid of a stable hydrogen donor is a useful alternative method for catalytic hydrogenation by molecular hydrogen.[38,39] In transfer hydrogenation, organic molecules such as primary and secondary alcohols[40] or formic acid and its salts[41–43] have been employed as the hydrogen source. The use of a hydrogen donor has some advantages over the use of molecular hydrogen since it avoids the risks and the

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constraints associated with hydrogen gas as well as the necessity for pressure vessels and other equipment. Although metal catalyzed transfer hydrogenation using a stable H-donor has been found to be reliable, the current emphasis on cleaner methods for chemical transformations requires high selectivity, low cost and the production of minimum waste.

Transition-metal catalyzed transfer hydrogenation using 2-propanol as a hydrogen source has become an efficient method in organic synthesis as illustrated by several useful applications reported in recent years.[44,45] The reaction conditions for this important process are economic, relatively mild and environmentally friendly. The most commonly used catalysts for this reaction are ruthenium(II) complexes, but some rhodium and iridium derivatives have also been used.[46–49]

The use of NHCs in transfer hydrogenation reactions has so far been limited. Only a few examples of transfer hydrogenation reactions mediated by organometallic complexes containing NHCs have been reported. The use of transition-metal–NHC complexes in catalytic transfer hydrogenation was pioneered by Nolan.[50] The cationic iridium–NHC complex was found to be highly active for reduction of ketones. Crabtree also developed new, air stable iridium(III) bis(carbene) complexes, which were active for transfer hydrogenation of ketones.[51] Danopoulos reported tridentate pyridinobis(carbine)ruthenium(II) complexes for the transfer hydrogenation of ketones.[52]

Based on these findings and our, continuing interest in developing more efficient and stable catalysts, we wished to examine whether we could influence the catalytic activity of ruthenium-imidazolidin-2-ylidine and benzimidazolin-2-ylidene complexes for the transfer hydrogenation of ketones. (Scheme 1).

We now report: (i) the straightforward preparation of new $RuCl_2$(NHC) (hexamethylbenzene) (**3–6**) complexes; and (ii) their efficient catalysis for transfer hydrogenation of ketones.

EXPERIMENTAL

Materials

Methylene chloride was purchased from Merck and distilled from P_2O_5 prior to use. Toluene and hexane were purchased from Aldrich or Merck and distilled from Na/benzophenone. 2-Propanol was purchased from Aldrich or Across Chemicals. AgOTf was purchased from Aldrich. All manipulations were prepared using standard Schlenk techniques under an inert atmosphere of nitrogen or argon. The complex $[RuCl_2(hexamethylbenzene)]_2$[53] 1,3-dialkylimidazolidin-2-ylidene (**1**) and 1,3-dialkylbenzimidazolin-2-ylidene (**2**) were prepared according to known methods.[54]

Spectroscopic analyses

FT-IR spectra were recorded as KBr pellets in the 400–4000 cm^{-1} range on a ATI UNICAM 2000 spectrometer. All ^1H and ^{13}C-NMR were performed in $CDCl_3$ and recorded on a Bruker AM 400 WB FT spectrometer. ^1H-NMR spectra were collected 400.0 MHz and ^{13}C NMR spectra were collected 100.0 MHz and chemical shifts referenced to residual solvent $CDCl_3$. Microanalyses were performed by the TÜBITAK Analyses Center.

Preparation of NHC–Ru(II) complex (3)

A solution of 1,3-bis(2-picoly)imidazolin-2-ylidene (0.13 g, 0.25 mmol) and $[RuCl_2(C_6(CH_3)_6)]_2$ (0.14 g, 0.22 mmol) was heated at 100 °C for 4 h. Upon cooling, orange crystals precipitated. These crystals were filtered, washed with hexane (15 ml) and dried under vacuum. Yield; 0.22 g, 87%; m.p. 219–220 °C; $\nu_{(NCN)} = 1508\ cm^{-1}$.

Anal. found: C, 55.65; H, 5.61; N, 9.63. Calcd for $C_{27}H_{34}N_4RuCl_2$: C, 55.29; H, 5.80; N, 9.55%.

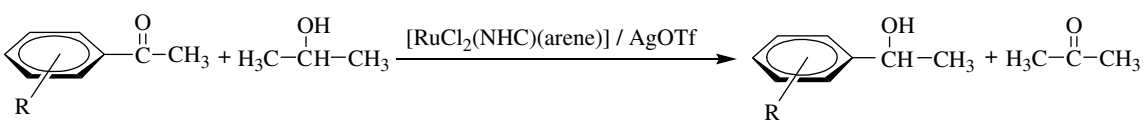
^1H NMR (δ, $CDCl_3$): 3.35, 3.79, 3.88 and 4.40 [ku, 4H, $J = 10.5$ Hz, NCH_2CH_2N]; 4.29, 5.63 and 4.62, 5.15 [d, 4H, $J = 16.0$ Hz, $J = 14.0$ Hz, $CH_2C_5H_4N$]; 7.14, 7.24, 7.56 and 7.78 [t, 4H, $J = 6.9$ Hz, $J = 6.1$ Hz, $J = 7.7$ Hz, $J = 7.8$ Hz, $CH_2C_5H_4N$]; 7.34, 8.07 and 8.47, 8.72 [d, 4H, $J = 7.8$ Hz, $J = 7.5$ Hz, $J = 4.6$ Hz, $CH_2C_5H_4N$]; 1.97 [s, 18 H, $C_6(CH_3)_6$]. ^{13}C {H} NMR (δ, $CDCl_3$): 211.8 [$C_{carbene}$]; 49.8 and 51.9 [NCH_2CH_2N]; 53.0 and 55.9 [$CH_2C_5H_4N$]; 123.3, 123.5, 124.8, 126.6,137.7, 139.4, 149.3, 156.1, 156.4, 158.5 [$CH_2C_5H_4N$]; 16.6 [$C_6(CH_3)_6$]; 97.5 [$C_6(CH_3)_6$].

Preparation of NHC–Ru(II) complex (4)

Compound **4** was prepared in a similar way to **3**, from 1,3-bis(6-methyl-2-picolyl)imidazolin-2-ylidene (0.15 g, 0.26 mmol) and $[RuCl_2(C_6(CH_3)_6)]_2$ (0.15 g, 0.22 mmol), to give orange crystals (yield; 0.19 g, 73%; m.p. 125–126 °C; $\nu_{(NCN)} = 1510\ cm^{-1}$.

Anal. found: C, 56.75; H, 6.16; N, 9.18. Calcd for $C_{29}H_{38}N_4RuCl_2$: C, 56.67; H, 6.18; N, 9.12%.

^1H NMR (δ, $CDCl_3$): 3.42, 3.75, 3.86 and 4.44 [ku, 4H, $J = 10.0$ Hz, NCH_2CH_2N]; 4.21, 4.46, 5.25 and 5.47 [d, 4H, $J = 16.0$ Hz, $J = 17.2$ Hz, $J = 14.8$ Hz, $J = 16.4$ Hz, $CH_2C_5H_3N(CH_3)$-6]; 2.48 and 2.98 [s, 6H, $CH_2C_5H_3N(CH_3)$-6]; 6.98, 7.13, 7.23 and 7.82 [d, 4H, $J = 8.0$ Hz, $J = 6.0$ Hz, $CH_2C_5H_3N(CH_3)$-6]; 7.43 and 7.62 [t, 2H, $J = 8.0$ Hz,



Scheme 1.

$J = 7.6$ Hz, $CH_2C_5H_3N(CH_3)$-6]; 2.03 [s, 18 H, $C_6(CH_3)_6$]. ^{13}C {H} NMR (δ, $CDCl_3$): 210.9 [$C_{carbene}$]; 50.5 and 51.7 [NCH_2CH_2N]; 54.7 and 55.9 [$CH_2C_5H_3N(CH_3)$-6]; 24.5 and 29.2 [$CH_2C_5H_3N(CH_3)$-6]; 120.6, 122.8, 124.9, 127.0,137.7, 137.8, 155.6, 157.9, 158.1, 165.1 [$CH_2C_5H_3N(CH_3)$-6]; 16.6 [$C_6(CH_3)_6$]; 97.5 [$C_6(CH_3)_6$].

Preparation of NHC-Ru(II) complex (5)

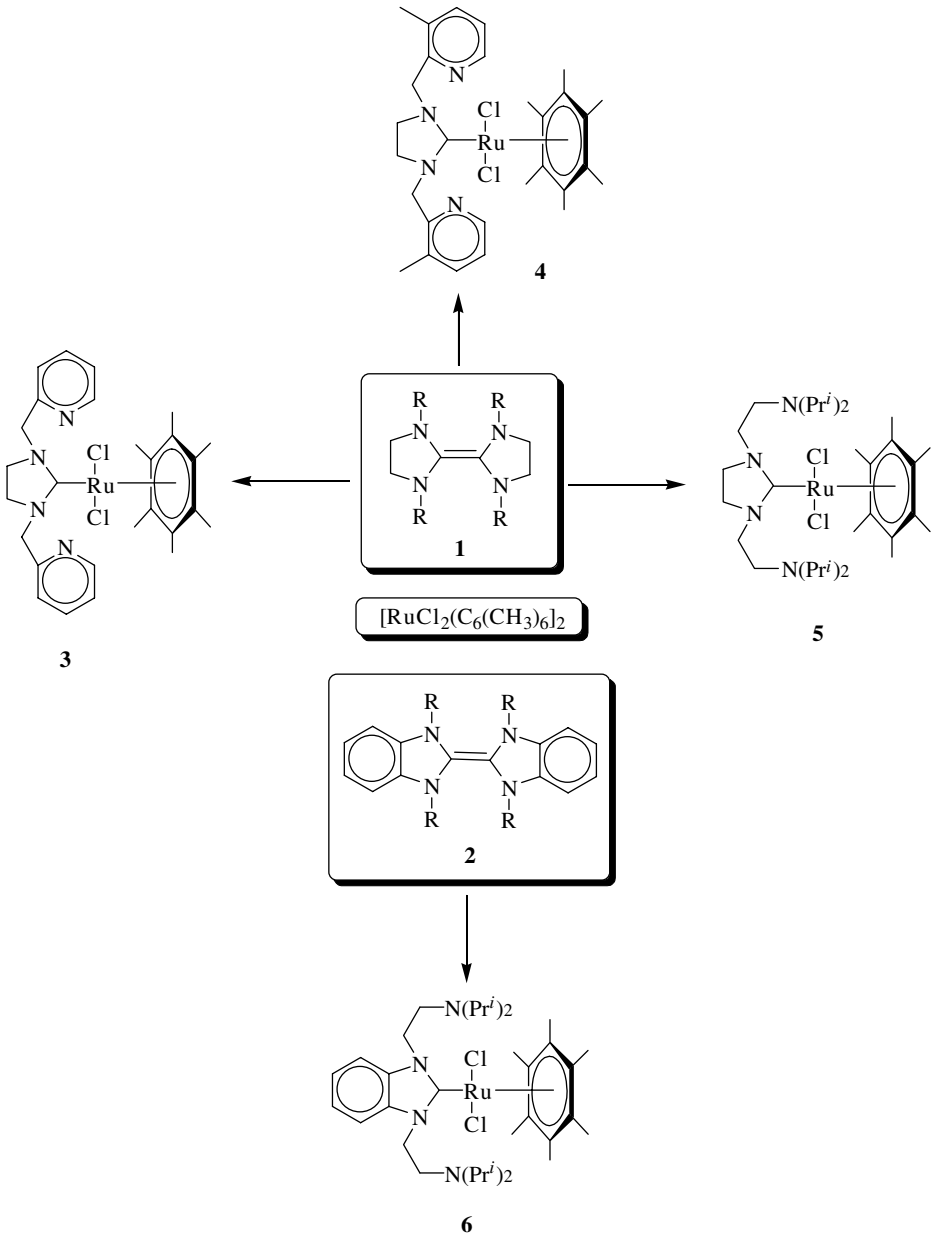
Compound **5** was prepared in a similar way to **3**, from 1,3-bis(2-diisopropylaminoethyl)imidazolin-2-ylidene (0.33 g, 0.51 mmol) and $[RuCl_2(C_6(CH_3)_6)]_2$ (0.34 g, 0.51 mmol), to give orange crystals (yield; 0.49 g, 74%; m.p. 250–251 °C; $\nu_{(NCN)} = 1488\ cm^{-1}$.

Anal. found: C, 56.60; H, 8.92; N, 8.41. Calc. For $C_{31}H_{58}N_4RuCl_2$: C, 56.53; H, 8.81; N, 8.51%.

^1H NMR (δ, $CDCl_3$): 3.07 and 3.93 [s, 4H, NCH_2CH_2N]; 3.53 and 4.27 [m, 4H, $CH_2CH_2N(Pr^i)_2$]; 2.56 [m, 4H, $CH_2CH_2N(Pr^i)_2$]; 2.90 [m, 2H, $NCH(CH_3)_2$]; 1.00 [d, 12H, $J = 6.4$ Hz, $NCH(CH_3)_2$]; 1.99 [s, 18 H, $C_6(CH_3)_6$]. ^{13}C {H} NMR (δ, $CDCl_3$): 210.1 [$C_{carbene}$]; 49.9 [NCH_2CH_2N]; 53.2 [$CH_2CH_2N(Pr^i)_2$]; 44.4 [$CH_2CH_2N(Pr^i)_2$]; 48.7 [$NCH(CH_3)_2$]; 20.6 [$NCH(CH_3)_2$]; 15.8 [$C_6(CH_3)_6$]; 94.2 [$C_6(CH_3)_6$].

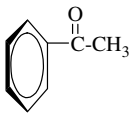
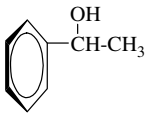
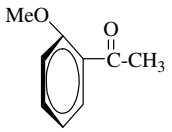
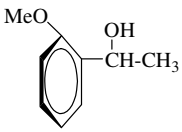
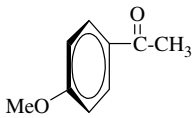
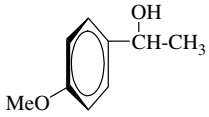
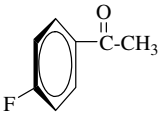
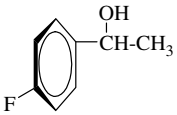
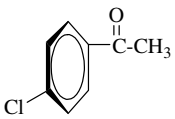
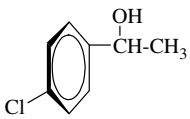
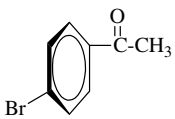
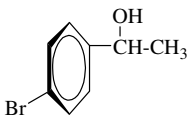
Preparation of NHC-Ru(II) complex (6)

Compound **6** was prepared in a similar way to **3**, from 1,3-bis(2-diisopropylaminoethyl)benzimidazolin-2-ylidene



Scheme 2.

Table 1. Catalytic transfer hydrogenation with Ru–NHC complexes for acetophenones with 2-propanol

Entry	Substrate	Product	Catalyst	Yield %[a,b]
1			3	97
2			4	97
3			5	98
4			6	95
5			3	86
6			4	92
7			5	97
8			6	85
9			3	93
10			4	94
11			5	96
12			6	82
13			3	97
14			4	98
15			5	99
16			6	97
17			3	92
18			4	94
19			5	96
20			6	95
21			3	67
22			4	72
23			5	78
24			6	62

[a] Catalyst (0.01 mmol), AgOTf (0.01 mmol in 3 ml CH_2Cl_2), substrate (1 mmol), ^{i}PrOH (10 ml), KOBu^{t} (5 mmol %), 80 °C, 12 h.
[b] Purity of compounds is checked by NMR and GC, yields are based on methyl aryl ketone.

(0.16 g, 0.21 mmol) and $[RuCl_2(C_6(CH_3)_6)]_2$ (0.11 g, 0.18 mmol), to give orange crystals (yield; 0.22 g, 89%; m.p. 229–230 °C; $\nu_{(NCN)} = 1471\ cm^{-1}$.

Anal. found: C, 59.21; H, 8.31; N, 7.88. Calcd for $C_{35}H_{58}N_4RuCl_2$: C, 59.49; H, 8.21; N, 7.93%.

^{1}H NMR (δ, $CDCl_3$): 7.21 and 7.45 [m, 4H, NC_6H_4N]; 3.83 and 4.98 [m, 4H, $CH_2CH_2N(Pr^i)_2$]; 2.77 and 3.28 [m, 4H, $CH_2CH_2N(Pr^i)_2$]; 3.27 [m, 2H, $NCH(CH_3)_2$]; 0.97 and 1.04 [d, 12H, $J = 6.4$ Hz, $J = 6.8$ Hz, $NCH(CH_3)_2$]; 1.87 [s, 18 H, $C_6(CH_3)_6$]. ^{13}C {H} NMR (δ, $CDCl_3$): 191.9 [$C_{carbene}$]; 109.6, 121.3 and 134.9 [NC_6H_4N]; 49.8 [$CH_2CH_2N(Pr^i)_2$]; 43.8 [$CH_2CH_2N(Pr^i)_2$]; 46.9 [$NCH(CH_3)_2$]; 19.4 and 21.6 [$NCH(CH_3)_2$]; 14.4 [$C_6(CH_3)_6$]; 93.6 [$C_6(CH_3)_6$].

Typical procedure for the transfer hydrogenation of ketones

The complexes [$RuCl_2$(NHC)(hexamethylbenzene)] (**3–6**) (0.01 mmol) and AgOTf (0.01 mmol; 2.57 mg) were introduced into a Schlenk tube under argon. Dry and degassed CH_2Cl_2 (3 ml) was added, the suspension were stirred room temperature for 30 min, and the solvent was removed by vacuum to give [RuCl(NHC) (hexamethylbenzene)]OTf (**3′–6′**). After that 2-propanol (10 ml), *t*-BuOK (5 mmol%), and the substrate (1 mmol) were added to **3′–6′**. The resulting solution was heated at 80 °C for 12 h. The solvent was then removed under reduced pressure and product distribution was determined by ^{1}H-NMR. spectroscopy and GC.

RESULTS AND DISCUSSION

The tetraaminoethenes **1** and **2** were synthesized using a method similar to that reported by Lappert *et al.*[54] The reaction of tetraaminoethenes **1** and **2** with the binuclear [$RuCl_2$(hexamethylbenzene)]$_2$ complex proceeded smoothly in refluxing toluene to give the [$RuCl_2$(NHC)(hexamethylbenzene)] (**3–6**) complexes as crystalline solids in 73–89% yields (Scheme 2).

Complexes (**3–6**), which are very stable in the solid state, were characterized by standard analytical and spectroscopic techniques. The ruthenium complexes exhibit a characteristic $\upsilon_{(NCN)}$ band typically at 1471–1510 cm^{-1}.[55–58] ^{13}C chemical shifts, which provide a useful diagnostic for metal carbene complexes, show that C_{carb} is substantially deshielded. Values for $\delta(^{13}C_{carb})$ are in the 191.9–211.8 ppm range and are similar to those found for other carbene complexes. These new complexes show typical spectroscopic signatures in line

with those recently reported for other [$RuCl_2$(NHC)(arene)] complexes.[59–64] Catalytic reduction is preferred to stochiometric reduction for large scale industrial uses of ketones hydrogenation are well known.[65]

Hydrogen gas presents considerable safety hazards especially for a large scale reactions.[66] The use of a solvent that can donate hydrogen overcomes these difficulties. 2-propanol is a popular reactive solvent for transfer hydrogenation reactions since it is easy to handle (b.p. 82 °C) and is relatively non-toxic, environmentally benign, and inexpensive. The volatile acetone by product can also be easily removed to shift unfavorable equilibria.[67]

Owing to its efficiency in the transfer hydrogenation of acetophenone, *in situ* prepared complexes **3′–6′** were further investigated in transfer hydrogenation of various methyl aryl ketones. The results were summarized in Table 1.

Complexes **3** and **6** showed high activity for most of the ketones listed in Table 1 (entries 3, 7, 11, 15, 19 and 23). The introduction of electron-withdrawing substituents, such as F and Cl, to the *para* position of aryl ring of the ketone, and since the effect of such groups the electron density on C═O bond decreases so that the activity of (entries 15, 19) was improved giving rise to the ease of hydrogenation.

CONCLUSION

From readily available starting materials, such as 1,3-dialkylimidazolidin-2-ylidene (**1**) and 1,3-dialkylbenzimidazolin-2-ylidene (**2**), four ruthenium-carbene (**3**–**6**) have been prepared and characterized. Also a convenient and highly user-friendly method for the transfer hydrogenation of ketones is presented. The procedure is simple and efficient towards various aryl ketones. Studies on the reactivity of the new complexes, extension of the methodology to other transition metals and the synthesis of other functionalized *N*-heterocyclic carbene ligands with a variety of other donor functionalities are under way.

Acknowledgments

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