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Fast transfer hydrogenation using a highly active orthometalated heterocyclic carbene ruthenium catalyst

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Abstract

The free carbene 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene reacts with *trans*,*cis*-RuHCl(PPh_3)$_2$(ampy) (ampy = 2-(aminomethyl)pyridine) affording an orthometalated N-heterocyclic carbene complex characterized by an X-ray diffraction study. This compound in presence of NaOH shows very high catalytic activity for the transfer hydrogenation of several ketones to alcohols using 2-propanol as hydrogen source, affording TOF values up to 120,000 h^{-1} (at 50% conversion).

Keywords: Ruthenium; Carbene; Orthometalation; Transfer hydrogenation; X-ray structure

1. Introduction

The isolation of stable free N-heterocyclic carbenes (NHCs) by Arduengo et al. [1] in 1991 led to a new attention to the carbene chemistry and in particular for the use of these ligands in homogeneous catalysis [2]. NHC transition metal complexes, in which the carbene ligands are two electron donors with slight π-back-bonding, are thermally stable and robust to degradation favoring the generation of efficient and long-living catalysts. As regards ruthenium, most of the known NHC-catalysts have been applied to olefin metathesis [3], C–C alkyne coupling [4] and hydrogenation [5] reactions. It should be noted that, despite ruthenium complexes have proven to be excellent catalysts for hydrogen transfer reactions from alcohols to ketones [6], only a few ruthenium based catalysts, containing carbene ligands, have been reported [7]. For these systems high concentration of ruthenium pre-catalysts or base co-catalysts and long reaction times are required. Related carbene complexes of rhodium and iridium also show catalytic activity in transfer hydrogenation [8].

In a recent work, we have isolated highly efficient catalysts for transfer hydrogenation bearing 2-(aminomethyl)pyridine (ampy) in combination with a diphosphine [PP] [9a] or a cyclometalated phosphine $[PC]^-$ ligand, namely $[(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2]^-$ [9b,9c]. For the latter system, displaying a metal-carbon σ bond, the formation of a five-membered metallacycle [10] leads to a robust complex with an electron rich metal center. Apparently, the ampy ligand shows a high ligand acceleration in the transfer hydrogenation catalyzed by phosphino ruthenium(II) complexes, with respect to the other nitrogen ligands [9a,9b]. On the other hand, the NHC carbenes are considered to behave similarly to tertiary phosphines, but bind to the metal center more strongly and are excellent electron donors. Moreover, it is now well-established that aryl- and alkyl-substituted N-heterocyclic carbene ligands undergo facile intramolecular C–H bond activation, leading to cyclometalated $[EC]^-$ complexes (E = C of

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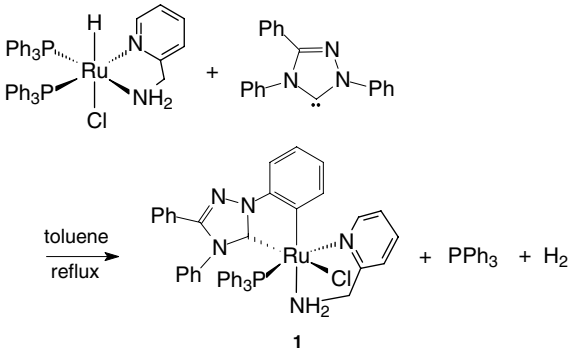
carbene) [11]. Although different $[CC]^-$ ruthenium complexes have been isolated [11a], only the arene species RuCl[CC](*p*-cymene) is catalytically active for alkene and alkyne C–C coupling reactions [12].

In view of these findings, we wished to examine whether the combination of ampy with NHC ligands in a ruthenium complex would afford active hydrogen transfer catalysts and we have investigated the coordination chemistry of the commercially available free carbene 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene. As a matter of fact, with this ligand in combination with ampy we have obtained a new orthometalated $[CC]^-$ ruthenium complex that is an extremely active catalyst for the transfer hydrogenation of ketones (TOF up to 120,000 h^{-1}).

2. Results and discussion

Treatment of the monohydride complex *trans*,*cis*-$RuHCl(PPh_3)_2$(ampy) [9a] with an equimolar amount of the free carbene 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene in refluxing toluene afforded the cyclometalated heterocyclic carbene derivative **1** which was isolated in high yield (Eq. 1)



(1)

1

In this reaction one PPh_3 is displaced by the carbene with concomitant orthometalation of a phenyl group and dihydrogen extrusion. The formation of the five-membered chelate ring leads to the thermally stable complex **1**. In order to establish the former formulation with six different donor ligands coordinated to the metal center, an X-ray structural analysis has been carried out on a single crystal of **1** and a perspective view of the complex is depicted in Fig. 1.

The ruthenium atom is in a distorted octahedral environment with PPh_3 *trans* to the pyridine nitrogen and the NH_2 group *trans* to the orthometalated carbon. The Ru–C(1) and Ru–C(12) lengths are typical for Ru-heterocyclic carbene and Ru-aryl bond distances. The ampy ligand presents a Ru–N(4) distance of 2.144(2) Å for the pyridine nitrogen, and a relatively long Ru–N(5) distance (2.221(2) Å) for the NH_2 group, in agreement with the *trans* influence [13] of the phenyl ligand. Complex **1** shows small N(4)–Ru–N(5) (76.16(8)°) and C(1)–Ru–C(12) (78.96(9)°) angles for the two five-membered cycles with a relatively large P–Ru–N(5) 102.94(6) angle for the weakly coordinated amino nitrogen.

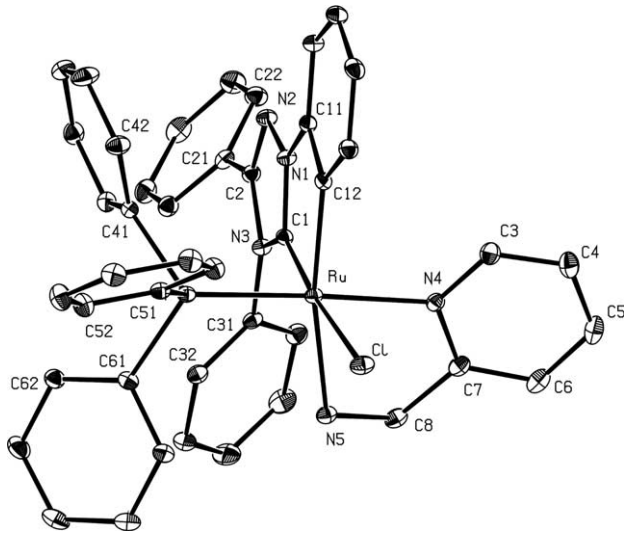
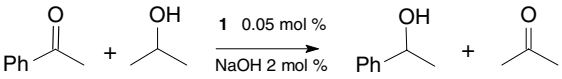


Fig. 1. ORTEP drawing of complex **1** in the solid state, using thermal ellipsoids at the 20% probability level for clarity. Selected bond length (Å) and angles (°): Ru–Cl 2.5040(6), Ru–P 2.2818(6), Ru–N(4) 2.144(2), Ru–N(5) 2.221(2), Ru–C(1) 1.970(2), Ru–C(12) 2.070(2), and Cl–Ru–P 93.86(2), Cl–Ru–N(4) 81.67(5), Cl–Ru–N(5) 81.63(6), Cl–Ru–C(1) 175.12(7), Cl–Ru–C(12) 98.96(6), P–Ru–N(4) 175.52(5), P–Ru–N(5) 102.94(6), P–Ru–C(1) 90.48(6), N(4)–Ru–N(5) 76.16(8), P–Ru–C(12) 88.06(6), N(4)–Ru–C(1) 94.00(8), N(4)–Ru–C(12) 92.95(8), N(5)–Ru–C(1) 99.56(8), N(5)–Ru–C(12) 168.94(8), C(1)–Ru–C(12) 78.96(9).

In the ^1H NMR spectrum of **1** two broad doublets at δ 4.22 and 3.20 (J(HH) = 17.6 Hz) are for the nonequivalent geminal CH_2 protons, whereas the signals at δ 2.59 and 2.05 are for the NH_2 protons, as proven by the addition of a D_2O solution of NaOH to **1** ($CDCl_3$) that leads quickly to the disappearance of the amino protons, indicating that a fast H/D exchange occurs. In the $^{13}C\{^1H\}$ NMR spectrum the low-field signals at δ 199.3 and 170.6 are for the Ru–C carbene and the orthometalated carbon, respectively, in agreement with other $[CC]^-$ ruthenium systems [14]. The CH_2 signal of the ampy ligand is at δ 48.3, very close to that of related ampy complexes [9] and the free ligand (δ 47.8).

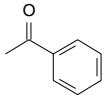
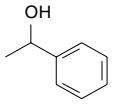
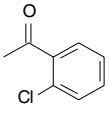
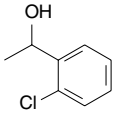
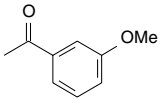
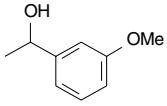
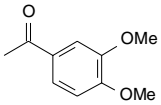
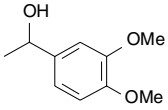
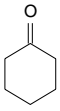
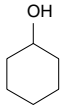
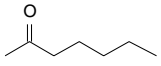
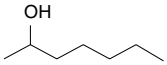
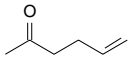
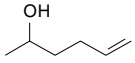
The orthometalated heterocyclic carbene compound **1** is an efficient catalytic precursor for the transfer hydrogenation of ketones to alcohols with 2-propanol as hydrogen donor and in presence of a base (Eq. 2)



(2)

Thus, when **1** (0.05 mol%) is used with NaOH as co-catalyst (2 mol%), acetophenone (0.1 M solution) is quickly reduced to 1-phenylethanol at reflux, with a TOF value of 110,000 h^{-1} at 50% conversion (Table 1).

Table 1
Catalytic transfer hydrogenation of ketones using complex **1**[a]

Ketone	Alcohol	Conversion % (min)[b]		TOF (h^{-1})[c]
		99	(5)	110000
		90	(10)	50000
		98	(10)	70000
		98	(2)	120000
		99	(5)	100000
		96	(10)	70000
		96	(15)	50000

[a] Conditions: reactions were carried out at 82 °C, ketone 0.1 M in 2-propanol, ketone/Ru/NaOH = 2000/1/40.
[b] The conversion was determined by GC.
[c] Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion.

Following this protocol a number of different ketones, i.e., alkylaryl, cyclic and dialkyl substrates, can be quantitatively converted to the corresponding alcohols within a few minutes and with TOF values that are among the highest reported in the literature [9,15]. Particularly fast reduction is achieved with 3′,4′-dimethoxyacetophenone and cyclohexanone, which show TOF values of 120,000 and 100,000 h^{-1}, respectively, the first being converted in less than 2 min. It should be noted that 5-hexen-2-one is selectively reduced at the carbonyl group without hydrogenation or isomerization of the carbon–carbon double bond, allowing this procedure to be applied for the synthesis of unsaturated alcohols. Since complex **1** can be easily obtained from the commercially available free carbene and displays a significantly higher performance (TOF values) respect to the reported metal carbene hydrogen transfer catalysts [7,8], it holds promise for a broad application in the reduction of carbonyl compounds. As example, 3′-methoxy-1-phenylethanol has been easily obtained in 83% isolated yield, starting from 1.50 g of 3′-methoxyacetophenone (0.2 M in 2-propanol) and using the complex **1** (0.05 mol%). The catalytic activity of **1** has also been compared with that of the related ruthenium derivatives containing the ampy ligand [9a,9b]. Under identical catalytic conditions, the precursor *trans*,*cis*-RuHCl-$(PPh_3)_2$(ampy) exhibits a lower activity for the reduction of acetophenone (TOF = 28,000 h^{-1}) [9a] than **1**. The latter is also more active than the cyclometalated phosphine derivative RuCl(CO)[(2-CH_2-6-MeC_6H_3)PPh_2]-(ampy) (TOF = 60,000 h^{-1}) [9b], suggesting that the bidentate carbene $[CC]^-$ with the ampy ligand is a particular favorable combination for obtaining a highly active catalytic species. Under our standard conditions (NaOH 2 mol% relative to acetophenone), control experiments in the absence of **1** result in about 2% reduction of the ketone after 1 h. Furthermore, when the catalysis with **1** is carried out at 25 °C instead of 82 °C, 1-phenylethanol is formed in small amount (3% conv. after 1 h). As regards the mechanism, it is likely that in the basic 2-propanol media the complex **1** leads to the corresponding monohydride derivative through the isopropoxide/β-elimination route, as reported for other ruthenium chloride catalytic precursors [9a,16], since in absence of base no activity for **1** has been observed. Furthermore, the high performance of **1** can be attributed to the presence of the RuH/NH_2 motif [17] in addition to the orthometalated heterocyclic carbene that allows stability to the ruthenium center, avoiding facile oxidation or degradation and favoring long-living catalytic species.

In conclusion, we have successfully isolated a new heterocyclic carbene ruthenium catalyst capable of performing the transfer hydrogenation of several ketones with very high activity. Work is currently in progress to expand the chemistry of ruthenium complexes containing ancillary orthometalated heterocyclic carbenes for homogeneous catalysis.

3. Experimental

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were carefully dried by conventional methods and distilled under argon before use, whereas chemicals were purchased from Aldrich and used without further purification. The complex *trans*,*cis*-RuHCl$(PPh_3)_2$(ampy) [9a] and 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene [18] were prepared according to the procedures reported in the literature. NMR measurements were carried out using a Bruker AC 200 spectrometer. Chemical shifts, in ppm, are relative to TMS for ^1H and ^{13}C, and to external 85% H_3PO_4 for ^{31}P. Elemental analysis (C, H, N) was performed by the Microanalytical Laboratory of the Technische Universität München.

3.1. Synthesis of complex 1

A suspension of *trans*,*cis*-$RuHCl(PPh_3)_2$(ampy) (242 mg, 0.314 mmol) and 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene (103 mg, 0.346 mmol) was stirred at −60 °C in 6 mL of toluene for 20 min. The mixture was then stirred at room temperature for 2 h and refluxed for 1.5 h. Cooling the suspension to −30 °C afforded a precipitate which was collected by filtration and washed once with 4 mL of toluene and twice with 5 mL diethyl ether and recrystallized from chloroform to give a yellow crystalline product. Yield: 209 mg (83%). *Anal*. Calc. for $C_{44}H_{37}ClN_5PRu$: C, 65.79; H, 4.64; N, 8.72. Found: C, 66.01; H, 4.67; N, 8.93%. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 8.73 (s, 1H; NCH), 7.81–6.51 (m, 32H, aromatic protons), 4.22 (br d, $^2J(HH) = 17.6$ Hz, 1H; CH_2), 3.20 (br d, $^2J(HH) = 17.6$ Hz, 1H; CH_2), 2.59 (br, 1H; NH_2), 2.05 (br, 1H; NH_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 199.3 (s; Ru–C carbene), 170.6 (s; Ru–C phenyl), 166.3, 162.6, 151.8, 150.4, 142.7, 138.0–119.6, 111.0 (aromatic carbons), 48.3 (d, $^3J(CP) = 5.3$ Hz; CH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 50.4 (s).

3.2. Single crystal X-ray structure determination of compound 1 · 2CDCl3

Crystal data and details of the structure determination are presented in Table 2. Suitable single crystals for the X-ray diffraction study were grown from $CDCl_3$. A clear yellow prism was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR951) and graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 8202 reflections. Data collection was performed at 173 K (OXFORD CRYOSYSTEMS) within a θ-range of $1.67° < \theta < 25.28°$, measured with nine data sets in rotation scan modus with $\Delta\varphi/\Delta\omega = 1.0°$. A total number of 51,646 intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects. After merging ($R_{int} = 0.041$) a sum of 8208 (all data) and 7239 [$I > 2\sigma(I)$], respectively, remained and all data were used. The structure was solved by a combination of direct methods and difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found and refined with individual isotropic displacement parameters. The deuterium atoms of the two disordered solvent molecule $CDCl_3$ were placed in ideal positions (riding model). Full-matrix least-squares refinements with 734 parameters were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err <0.001. The final residual electron density map showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. All calculations were performed on an Intel Pentium II PC, with the STRUX-V system, including the programs PLATON, SIR92, and SHELXL-97 [19]. A disorder over two positions (1/2:1/2 each) of both solvent molecules $CDCl_3$ could be resolved clearly. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-279017 [**1** · $2CDCl_3$]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Table 2
Crystallographic data for **1** · $2CDCl_3$

	1 · $2CDCl_3$
Formula	$C_{46}H_{37}D_2Cl_7N_5PRu$
Fw	1044.02
Color habit	Yellow/prism
Crystal dimensions (mm^3)	$0.30 \times 0.38 \times 0.46$
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a (Å)	12.9019(1)
b (Å)	13.2558(1)
c (Å)	15.3039(1)
α (°)	98.4528(3)
β (°)	109.8214(3)
γ (°)	107.0775(2)
V ($Å^3$)	2263.51(3)
Z	2
T (K)	173
D_{calc} ($g\,cm^{-3}$)	1.532
μ (mm^{-1})	0.835
$F(000)$	1056
θ Range (°)	1.67–25.28
Index ranges (h, k, l)	±15, ±15, ±18
No. of rflns. collected	51,646
No. of indep. rflns./R_{int}	8208/0.041
No. of obsd. rflns. ($I > 2\sigma(I)$)	7239
No. of data/restraints/params	8208/0/724
$R_1/wR_2(I > 2\sigma(I))$[a]	0.0277/0.0642
R_1/wR_2 (all data)[a]	0.0341/0.0670
GOF (on F^2)[a]	1.036
Largest diff. peak and hole (e $Å^{-3}$)	+0.46/−0.44

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; GOF = $\{\sum[w(F_o^2F_c^2)^2]/(n-p)\}^{1/2}$.

3.3. Catalytic activity of complex 1

The ruthenium complex **1** (4.0 mg 5.0 μmol) was dissolved in 5 mL of 2-propanol. The ketone (2 mmol) was

dissolved in 18.6 mL of 2-propanol and the solution was heated to reflux under argon. By addition of 0.4 mL of a 0.1 M solution of NaOH in 2-propanol and 1 mL of the solution containing the ruthenium complex the reduction of the ketone starts immediately (complex **1** 0.05 mol%, NaOH 2 mol%) and the yield was determined by GC analysis.

*3.4. Preparation of 3′-methoxy-1-phenylethanol using complex **1***

3′-methoxyacetophenone (1.50 g, 10 mmol) was dissolved in 46 mL of 2-propanol and refluxed under argon. By addition of 1 mL of a 2-propanol solution of **1** (4.0 mg 5.0 μmol) and 2 mL of a 0.1 M solution of NaOH, the reaction starts immediately and was completed after 15 min. The solution was concentrated and the residue was dissolved in 20 mL of ether, dried over Na_2SO_4 and purified through silica gel chromatography. The product was obtained pure as pale yellow oily liquid. Yield: 1.26 g (83%).

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