

Deactivation of a ruthenium(II) *N*-heterocyclic carbene *p*-cymene complex during transfer hydrogenation catalysis

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Abstract A ruthenium (II) N-heterocyclic carbene (NHC) complex was synthesized to investigate ligand dissociation as a possible deactivation pathway for the catalytic cycle of a transfer hydrogenation reaction. Diiodo(1,3-dimethylben-zimidazole-2-ylidene)(*p*-cymene)ruthenium(II) was synthesized for use as the catalytic species and characterized using physico-chemical, spectroscopic methods, and single crystal X-ray diffraction. The transfer of hydrogen from isopropanol to acetophenone was followed using ¹H NMR. We observed 94% conversion of the substrate to the alcohol product after 1 h. We also found that the *p*-cymene complex decomposed during the catalytic reaction to the extent of 80% deactivation after 1 h, based on ¹H NMR spectrometry. From Gaussian calculations, an ultraviolet–visible spectrum that is in

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excellent agreement with the actual spectrum was computed, giving insight into the nature of the absorptions observed experimentally.

Introduction

The reduction of organic compounds such as aldehydes and ketones can be performed in a variety of ways, including through the use of a stoichiometric reagent, a catalyst, electrolysis, and via hydrogen atom transfer via a radical mechanism [1]. Catalytic transfer hydrogenation reactions are an alternative to direct hydrogenation of substrates whereby the need for molecular hydrogen is avoided [2]. Transfer hydrogenation is a useful complement to catalytic reduction by molecular hydrogen since it frequently shows a different pattern of functional group selectivity [3]. In transfer hydrogenation reactions, the ionic H^+/H^- transfer from a donor to

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a substrate forms the basis for many useful C–C, C–O, and C–N bond-forming reactions [4–7].

N-heterocyclic carbenes are widely used ligands for metal complexes that have the potential to serve as homogenous catalysts. These compounds are ideal for use with larger substrates that may not be able to interact well with surfaces in heterogenous catalysis due to steric reasons [8]. *N*-heterocyclic carbenes ligands are sometimes considered phosphine alternatives, primarily because their metal complexes catalyze typical organic reactions similar to those observed for complexes possessing trialkylphosphine ligands. In addition, *N*-heterocyclic carbine complexes are not as susceptible to metal–ligand cleavage [9–11]. Nolan and co-workers first reported the first *N*-heterocyclic carbene (NHC) complex for transfer hydrogenation [12].

Common transition metal precatalysts for transfer hydrogenation contain Ir(I), Ir(III), Rh(I), Rh(III), Ru(II), and Ni(0) metal centers [12–21]. Ruthenium NHC complexes that contain arene ligands have been reported for transfer hydrogenation catalysis [15, 22].

The loss of a *p*-cymene ligand that is coordinated to a transition metal center is our proposed deactivation pathway for this catalyst. Crabtree and co-workers have reported the loss of a Cp* ligand under commonly modified transfer hydrogenation conditions [23]. Understanding the nature of catalyst decomposition is both interesting and important given that the ability to reuse a catalyst is especially important for precious metal complexes. We want to investigate the disruption of the catalytic cycle via ligand dissociation or decomposition during a transfer hydrogenation reaction. A highlight of the present work is the quantification of the loss of a *p*-cymene ligand during transfer hydrogenation catalysis when the precatalyst is a ruthenium(II) *N*-heterocyclic carbene complex that contains a *p*-cymene ligand.

Experimental

General procedures

Reagents and solvents were commercially available and were purchased from Acros Organics, Fisher Scientific, and Strem Chemicals. All chemicals were used as received. NMR spectra were recorded at 25 °C on a Bruker spectrometer at 300 MHz (¹H NMR) and 75 MHz (¹³C NMR) and referenced to DMSO (in ppm, *J* in Hz). Elemental analyses were performed by Robertson Microlit Laboratories (Ledgewood, NJ, USA). Residual solvent molecules were identified by ¹H NMR. Electrospray mass spectra were collected using a direct flow injection (injection volume = 5 µL) on an Agilent QTOF instrument in the positive ion mode. The optimized conditions were capillary = 3000 kV, cone = 10 V, source temperature = 120 °C. The ligand precursor, 1,3-dimethylbenzimidazole iodide was synthesized by a previously reported procedure [24]. UV–visible spectra were collected on a Cary 100 UV–visible spectrometer. IR spectra were collected using a Thermo Nicolet AVATAR 380 FT-IR with a SMART SPECULATR reference adaptor.

Synthesis

Synthesis of diiodo(1,3-dimethylbenzimidazole-2ylidene)(*p*-cymene)ruthenium(II)

A reaction vessel was charged with 1,3 dimethyl benzimidazole iodide (0.28 g, 1.0 mmol), silver(I) oxide (0.23 g, 1.0 mmol), and 30 mL of dichloromethane. The reaction was heated at reflux in the absence of light for 20 h. The reaction solution was filtered through Celite to remove the formed solids, and the solvent was removed under reduced pressure. Yield: 0.16 g.

Next, potassium iodide (0.66 g, 4.0 mmol) was added to the reaction vessel containing the silver benzimidazole compound (0.14 g, 0.19 mmol) and $[Ru(p-cymene)Cl_2]_2$ (Strem Chemicals) (0.093 g, 0.15 mmol) with 20 mL acetonitrile. The reaction was heated at reflux for 20 h, and the solvent was removed under reduced pressure. The product was dissolved in tetrahydrofuran, and the solution was filtered to remove undissolved solids. The tetrahydrofuran solvent was then removed under reduced pressure. Yield: 0.045 g (46%). Crystals for X-ray diffraction were grown by the slow vapor diffusion of pentane into a solution of the ruthenium complex in tetrahydrofuran. Anal. Calc. for $C_{19}H_{24}I_2N_2Ru\cdot2H_2O$ (635.29): C, 34.0; H, 4.2; N, 4.2. Found: C, 34.3; H, 3.9; N, 3.9.

¹H NMR (DMSO-d₆, 300 MHz) δ 7.75(m, 2H, benzimidazole, CH), 7.47 (m, 2H, benzimidazole, CH), $6.38 (d, (^{3}J = 6.3 Hz), 1H, p$ -cymene CH), 6.25 (m, 2H, CH)*p*-cymene CH), 6.14 (d, $({}^{3}J = 6.0 \text{ Hz})$, 1H, *p*-cymene CH), 4.20 (s, 3H, imidazole CH₃), 4.09 (s, 3H, imidazole CH₃), 3.00 (m, 1H, iPr-H), 2.19 (s, 3H, CH₃ p-cymene), 1.25 (d, $({}^{3}J = 6.9 \text{ Hz})$, 3H, *p*-cymene iPr CH₃), 1.05 (d, $({}^{3}J = 6.6 \text{ Hz}), 3H, p$ -cymene iPr CH₃). ${}^{13}C \{{}^{1}H\}$ NMR (DMSO-d₆, 75 MHz), δ 179.50 (C_{ipso}), 123.79 (benzimidazole CH), 123.40 (benzimidazole CH), 118.30 (C), 111.34 (benzimidazole CH), 111.07 (benzimidazole CH), 105.34 (C), 92.92 (p-cymene CH), 92.83 (p-cymene CH), 88.59 (p-cymene CH), 88.51 (p-cymene CH), 40.74 (imidazole CH₃), 35.94 (imidazole CH₃), 31.18 (iPr C-H), 23.56 (iPr CH₃), 20.36 (iPr CH₃), 18.40 (*p*-cymene CH₃). UV-visible data: λ (nm), (ϵ (M⁻¹cm⁻¹): 359 (6760); 297 (19600); 294 (19300); 237 (23700); 234 (23400); 218 (22400). IR data: ν (cm⁻¹, intensity, assignment); 2962.45 (m); 2360.32 (m, CO₂); 1458.68 (w); 1365.35 (w); 1342.55 (w); 1259.64 (m); 1077.29 (s); 1015.13 (s); 861.36 (w); 793.91 (vs); 747.55 (m); 666.84 (w); 627.13 (w).

Catalytic activity of the ruthenium (II) *N*-heterocyclic carbene complex

In a typical reaction, an Erlenmeyer flask was charged with KOH (0.16 g, 3.0 mmol) and 30 mL isopropanol. Next, a reaction vessel was charged with acetophenone (0.22 g, 1.8 mmol) and 1.0 mL of the prepared KOH solution (0.098 mmol) and 9 mL of isopropanol. In a separate vial, the prepared ruthenium precatalyst (0.012 g, 0.018 mmol) was dissolved in a minimal amount of tetrahydrofuran. The precatalyst solution was added to the reaction vessel and heated at reflux. Approximately 1 mL aliquots were taken from the solution after a certain period of time. Each sample was placed in approximately 20 mL hexanes, and the hexanes mixture was filtered through silica. The hexanes were removed under reduced pressure, and ¹H NMR spectra of the products were acquired in CDCl₃.

Stability of the ruthenium (II) *N*-heterocyclic carbene complex using 1,3,5-trimethoxybenzene

An Erlenmeyer flask was charged with KOH (0.010 g, 0.18 mmol) and 20 mL isopropanol. Next, a 25-mL reaction vessel was charged with acetophenone (0.023 g, 0.20 mmol) and 1,3,5-trimethoxybenzene (0.0055 g, 0.033 mmol). Next, 0.20 mL of the prepared KOH (0.0018 mmol) solution was added, along with an additional 1.8 mL isopropanol and the ruthenium precatalyst (0.022 g, 0.034 mmol). The reaction was put on reflux for a period of time. The solvent was then removed under reduced pressure, and a ¹H NMR of the product was acquired in DMSO-d₆.

Stability of the ruthenium (II) *N*-heterocyclic carbene complex using 1,3,5-trimethylbenzene

An Erlenmeyer flask was charged with KOH (0.010 g, 0.18 mmol) and 20 mL isopropanol. Next, a 25-mL reaction vessel was charged acetophenone (0.022 g, 0.19 mmol) and 1,3,5-trimethylbenzene (0.0081 g, 0.071 mmol). Next, 0.20 mL of the prepared KOH (0.0018 mmol) solution was added, along with an additional 1.8 mL isopropanol and the ruthenium precatalyst (0.022 g, 0.034 mmol). The reaction was put on reflux for a period of time. The solvent was then removed under reduced pressure, and a ¹H NMR of the product was acquired in DMSO-d₆.

Table 1 Crystal and structure refinement data for $C_{19}H_{24}I_2N_2Ru$ [1]

Formula	$C_{19}H_{24}I_2N_2Ru$
FW (g/mol)	635.29
Temperature (K)	93(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
<i>a</i> (Å)	15.6125(11)
<i>b</i> (Å)	7.8796(6)
<i>c</i> (Å)	16.7467(12)
β (°)	97.872(9)
Volume $(\text{Å})^3$	2040.8(3)
Ζ	4
r (calc) (g/cm ³)	2.068
Abs (mm ⁻¹)	3.797
<i>F</i> (000)	1208
Crystal size (mm ³)	$0.250 \times 0.190 \times 0.080$
Theta range (°)	1.317-25.092
Refl/Uniq	3599/3599
<i>R</i> (int)	0.081
Abs correction	Semi-empirical from equivalents
Max./Min.	0.751/0.453
Ref method	SHELXL-2014/7
Data/restr/par	3599/0/223
GOF on F ²	1.179
R1 indices $(I > 2 s)$	0.0377
wR2	0.1014
Peak/hole (e/Å ⁻³)	1.253 and -0.839

Crystallographic analyses

Low-temperature diffraction data (ω-scans) were collected on a Rigaku R-AXIS RAPID diffractometer coupled to an R-AXIS RAPID imaging plate detector with Mo Kα radiation ($\lambda = 0.71073$ Å) for the structure of **1**. The diffraction images were processed and scaled using the Rigaku Crystal-Clear software [25]. The structure was solved with SHELXT and was refined against F² on all data by full-matrix least squares with SHELXL [26]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of 1 can be found in the Supporting Information. Full details of the X-ray structure determination are in the CIF included as Supporting Information. CCDC number 1530788 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/ cif. All other pertinent crystallographic details such as h, k, l ranges, 2θ ranges, and R-factors can be found in Table 1.

Refinement details

These data were refined as a 2-component twin. $(1\ 0\ 0\ 0 - 1)\ 0\ 0\ 0 - 1)$ was used with an HKLF5 formatted reflection list. This twin law affected approximately 16.3(2)% of the reflections.

Gaussian calculations

Gaussian 09 [27] was used to perform a geometry optimization and time-dependent density functional theory (TD-DFT) calculation using the B3LYP hybrid functional on the subject molecule. The 6-31G(d) basis set was employed for H, C, and N, and the LANL2DZ basis set, including effective core potentials, was used for Ru and I. Symmetry was not imposed on the system. A total of 100 electronic transitions in the electronic spectrum were computed with the TD-DFT method.

Results and discussion

Synthesis and characterization

The synthesis of **1** was accomplished according to the steps shown in Scheme 1. In the preparation of **1**, 1,3-dimethyl benzimidazole iodide was generated following a published route [24] and was subsequently reacted with silver(I) oxide in dichloromethane [28, 29]. After filtering the product through Celite, the solvent was evaporated under reduced pressure. The resulting Ag(I) benzimidazole product was then reacted with potassium iodide and $[Ru(p-cymene)Cl_2]_2$ in acetonitrile to afford **1**. As such, we find that complex **1** is soluble in acetonitrile, methanol, dimethyl sulfoxide, and tetrahydrofuran. The reactions (Scheme 1) were performed in air and the ruthenium metalation proceeded with a yield of 46%. Complex **1** is air stable but may decompose in the presence of light over a period of three months. Maroon-red crystals single crystals suitable for X-ray diffraction were grown by allowing pentane vapor to slowly diffuse into a tetrahydrofuran solution containing the ruthenium(II) complex. The solid-state structure of **1** is shown in Fig. 1. The complex features an $\eta^6 p$ -cymene ligand and a ruthenium(II) center. The Ru(II) center is also coordinated to a 1,3-dimethyl-benzimidazole ligand and two iodide ligands.

Various bond lengths and angles for complex 1 are given in Table 2. The R-factor of 1 was 0.0377. The ruthenium-carbon (*N*-heterocyclic carbene) bond distance of 2.072(7) (Å) is in excellent agreement with previously published examples in the literature for related complexes [30-33]. In addition, the Ru–I bond distances of 2.7520(8) and 2.2456(8) (Å) compare well with a previously published example by Hahn and co-workers [33].

Complex 1 was characterized using 1 H, 13 C, and HSQC NMR spectroscopy. The key resonances of the product are the *p*-cymene aromatic proton resonances which appear as doublets at 6.38 (1H), 6.25 (2H), and 6.14 (1H). There is evidence for water in the 1 H NMR spectrum, which was acquired in DMSO-d₆. Also, the presence of water is consistent with the elemental analysis results of the bulk sample. Any attempts to remove the residual water from the sample were unsuccessful.

ESI-MS data for 1 were collected with a cone voltage of 10 V. The predominant feature in the mass spectrum of 1 corresponds to the $[Ru(NHC)(p-cymene)I]^+$ parent ion, indicating that one of the iodide anions dissociated during the analysis. For all of these spectra, the isotopic pattern in the mass spectrometry data fits the assigned structure.

Complex 1 was also characterized with UV-visible spectroscopy. The UV-visible spectrum for 1, which was acquired in acetonitrile, is shown in Fig. 2 (solid line). Figure 2 also contains the calculated UV-visible spectrum, which has been red-shifted by 29 nm for presentation, for 1 (dashed line).

In the UV–visible spectrum, we observe charge-transfer bands in the ultraviolet region. Consistent with previous reports [34–38] of Ru(II) piano-stool compounds, the molar absorptivities of none of the features in our experimental spectrum are consistent with the assignment of d–d bands. In the literature, absorptions in the 200–350 nm



Scheme 1 Synthesis of 1





Table 2Selected bond lengthsand angles (esd) for 1

	(1)
I(1)–Ru(1) (Å)	2.7520(8)
I(2)–Ru(1) (Å)	2.7456(8)
Ru(1)–C(11) (Å)	2.072(7)
Ru(1)–C(3) (Å)	2.180(7)
Ru(1)–C(5) (Å)	2.184(8)
Ru(1)–C(6) (Å)	2.188(8)
Ru(1)–C(4) (Å)	2.207(8)
Ru(1)–C(2) (Å)	2.255(8)
Ru(1)–C(1) (Å)	2.278(8)
C(11)–Ru(1)–I(2)	91.50(19)
C(11)–Ru(1)–I(1)	93.4(2)
I(2)–Ru(1)–I(1)	84.72(2)

range have variously been attributed to metal-to-ligand (MLCT), ligand-to-metal (LMCT), and ligand-to-ligand (LLCT, both inter- and intraligand) charge transfers. In cases where d–d transitions have been assigned [34, 36],

the absorptions were in the ca. 380–450 nm range although Gichumbi and co-workers [35] attributed the absorption feature in this range to MLCT transitions. In their report, Małecki and colleagues [36] included TD-DFT calculations that indicated that d–d transitions occurred at wavelengths greater than 400 nm and had small oscillator strengths.

Given its combination of ligands with their varied coordination modes and electron donor and acceptor attributes, assigning the electronic spectrum of the low-symmetry complex **1** can rightly be expected to be complicated. In strong agreement with the experimentally determined spectrum, our calculations show three absorption regions between 200 nm and 400 nm. The maxima of the calculated spectrum match rather well with those observed experimentally (205 vs. 234/237 nm, 264 vs. 294/297 nm, and 332 vs. 359 nm) with the peaks of the calculated spectrum occurring ca. 30 nm lower than in the experimental spectrum. The TD-DFT-computed spectrum also finds nine absorptions located between 390 nm and 620 nm although all of these are quite **Fig. 2** Experimental and calculated UV–visible spectra of 1. The calculated UV–visible spectrum was obtained using TD-DFT Gaussian 09 calculations and has been red-shifted by 29 nm in this composite image



 Table 3
 Percent orbital contributions for the metal and ligand moieties in the frontier molecular orbitals of 1

Molecular orbital	Ru	2 I	Dimethylbenzimi- dazole-2-ylidene	<i>p</i> -cymene
HOMO-10	40.7%	7.4%	36.8%	15.1%
HOMO-9	52.5	25.7	3.7	18.1
HOMO-8	38.1	43.0	3.3	15.6
HOMO-7	41.4	28.4	4.7	25.5
HOMO-6	1.9	0.6	88.5	9.1
HOMO-5	26.8	13.6	48.2	11.4
HOMO-4	41.3	31.9	7.0	19.7
HOMO-3	28.5	57.0	3.3	11.2
HOMO-2	25.8	58.2	1.5	14.5
HOMO-1	21.3	60.7	2.7	15.4
НОМО	8.1	79.9	2.3	9.7
LUMO	45.2	26.0	0.6	28.1
LUMO + 1	34.3	6.5	31.7	27.6
LUMO + 2	19.4	7.6	65.1	7.9
LUMO + 3	17.7	4.1	4.6	73.7
LUMO + 4	22.8	1.8	6.9	68.5
LUMO + 5	0.4	0.1	98.7	0.7

weak. The absorptions between 390 nm and 450 nm give rise to a weak tail in the spectrum.

Assigning the nature of the electronic transitions in the absorption spectrum necessitates review of the computed excited states and the molecular orbitals (MOs) that are involved. Full tabulations of all of the excitation energies, oscillator strengths, and orbital compositions are provided in the supplementary information. Shown in Table 3 are summations of the orbital contributions of the four fragments

(Ru, the two I atoms, the carbene ligand, and p-cymene) of **1**. All of the carbene and *p*-cymene orbital character is π -type, and all of that from the I atoms is from their valence p orbitals. As for the Ru atom, from a basic understanding of the molecular orbital theory of a d⁶ metal complex it might be supposed for 1 that the three highest occupied and the two lowest unoccupied MOs are those that should be termed the "d orbitals" and that the assignment of transitions involving the "metal" orbitals involves any of these five MOs. Review of Table 3 shows that although the two lowest unoccupied MOs do have more orbital contribution from Ru than from elsewhere, only one of the ten highest occupied MOs contains majority Ru character. In fact, orbital character from the iodine atoms makes up more than half of each of the four highest MOs; the HOMO is calculated to contain 80% I character with only 8% from Ru. Considering the Ru and I orbital contributions together, eight of the highest energy occupied molecular orbitals have majority Ru-I character; the more stable ones of these orbitals contain Ru-I-bonding character, while the ones closer in energy to the HOMO are Ru-I antibonding. The significant orbital contributions of both Ru and I in many of the frontier MOs of 1 should not be a surprise given the similar 4d5s5p valence atomic structure of these two elements, but it does mean that describing specific absorptions as resulting from metal-based d-d transitions or arising from the metal in a MLCT band cannot be precisely done for this system. Instead, the frontier "d orbitals" should really be considered to be Ru-I admixtures.

Given this caveat for **1**, we nevertheless provide some indication of the kinds of electronic transitions that give rise to the several features in the absorbance spectrum. In the 200–240 nm range, LLCT excitations from orbitals (HOMO-6 and HOMO-10) with significant carbene

character into orbitals with carbene and p-cymene character are calculated to occur. Near 260 nm, the computed excitations involve electrons going from either carbene (HOMO-5)- or Ru/I (HOMO-4 through HOMO-1)-based orbitals to carbene-based orbitals (LUMO + 2 and LUMO + 5), indicating a mixture of ligand-to-ligand and metal-to-ligand transitions. Near 330 nm, excitations are from Ru/I-based MOs (HOMO-2 and HOMO-3) with majority I character into various low-lying unoccupied MOs (LUMO through LUMO + 4), some of which have heavy Ru character while others are primarily on the *p*-cymene and carbene ligands for a mixture of what might ordinarily be termed as metal-to-metal and metal-to-ligand transitions. Lastly, in the 390-440 nm range the excitations are from the highest occupied MOs (HOMO-4 to HOMO) to the lowest unoccupied orbitals (LUMO and LUMO + 1), thereby most closely resembling an actual d-to-d charge transfer band. We see little evidence in the experimental spectrum for these "d-to-d" excitations save for a broad tail from approximately 400 to 600 nm.

Transfer hydrogenation reactivity

Having established a synthetic protocol for this organometallic complex and gained an understanding of its structural and electronic characteristics, we turned our attention to probing its catalytic activity. Complex 1 was screened for transfer hydrogenation activity for the reduction of acetophenone. The solvent for the reaction was 2-propanol, and the added base was KOH. The substrate/precatalyst/base ratio was 100:1:5. For the reduction of acetophenone, ¹H NMR spectrometry was used to follow the disappearance of the methyl protons (singlet, δ 2.6 ppm) and the appearance of the methyl protons in the alcohol product (doublet, δ 1.6 ppm). We observed 94% conversion after 1 h. This conversion corresponds to a turnover number of 94. Product formation was detected by ¹H NMR spectroscopy, by comparison with authentic material. Control reactions with substrate plus base (no precatalyst) and substrate plus precatalyst (no base) were conducted for 1 h. In both cases, less than 5% conversion was observed. Complex 1 exhibits transfer hydrogenation activity toward acetophenone which is comparable to previously published ruthenium(II) N-heterocyclic carbene complexes [15, 39–41]. Complex 1 was also screened for the catalytic reduction of an electron-poor substrate, 4-nitroacetophenone and of an electron-rich substrate, 4-methoxyacetophenone following the same catalytic conditions, which were substrate/precatalyst/base ratio of 100:1:5. Complex 1 showed less than five percent conversion of 4-nitroacetophenone and 4-methoxyacetophenone. Another objective was to obtain a ¹H NMR of the reaction mixture after 1 h of reaction time with the goal of obtaining

the ¹H NMR of the catalyst. However, the active catalyst was not observed using ¹H NMR.

The ruthenium(II) *p*-cymene complex, **1**, can withstand air and moisture. It was not necessary to run reactions using precatalyst **1** under a nitrogen atmosphere nor were dry solvents required for the reactivity experiments. Using acetophenone as a substrate, significant product conversion was observed. Conversion after three and 40 min was 28 and 92%, respectively. Conversion after five minutes and ten minutes was 50 and 70%, respectively. Conversion after 15 and 30 min was 76 and 87%, respectively. The conversion was essentially complete after 1 h.

Complex 1 could not be completely recycled for the transfer hydrogenation of acetophenone. An aliquot of the reaction mixture was removed after 1 h of transfer hydrogenation at which 94% conversion had been achieved. After 1 h of reaction time, an additional 1.8 mmol (0.22 g) of acetophenone was added. Allowing the reaction to continue for a second hour, we observed 86% conversion of acetophenone to 1-phenylethanol.

Complex deactivation

Since we have an understanding of the activity complex 1 has for the transfer hydrogenation of acetophenone, we wanted to test the stability of 1 during the catalytic reaction. Based upon electrospray mass spectrometry data, we are assuming that the precatalyst has dissociated an iodide ligand to form the active catalyst. As noted before, attempts to obtain an ¹H NMR of the catalyst after the reaction were unsuccessful. We and others have hypothesized that the loss of the *p*-cymene ligand during catalysis will cause the catalyst to deactivate, thereby hindering its reactivity [23]. We therefore wanted to determine how much p-cymene dissociated from the starting precatalyst during transfer hydrogenation. To accomplish this, we conducted the transfer hydrogenation reaction in the presence of catalyst, base, and an internal standard, 1,3,5-trimethoxybenzene. The results are summarized in Table 4. The relative integration of the methoxy protons was set to 9H at δ 3.6 ppm.

In addition, we conducted control reactions. We heated the precatalyst in DMSO- d_6 for 1 h at 85 °C. After this heating time, we acquired a ¹H NMR at room temperature

Table 4Deactivation of 1after various elapsed times inthe transfer hydrogenation ofacetophenone

Entry	Time (min)	% Decom- position of 1
1	15	47
2	30	59
3	45	65
4	60	80

(supporting information) and we did not notice any changes in the resonances of the complex compared to the initial ¹H NMR spectrum. In addition, we heated complex **1** (0.010 mmoles) in the presence of KOH (0.029 mmoles) in isopropanol for 1 h at reflux. We measured the ¹H NMR of the product in DMSO-d₆, and we noticed that the spectrum was different compared to the ¹H NMR spectrum of complex **1** (supporting information). We are assuming that the isoproxide ion is reacting with complex **1**.

We saw after 1 h of reaction time that 80% of the *p*-cymene ligand had dissociated (supporting information). This was determined with ¹H NMR spectroscopy and following the change of the *p*-cymene resonance that integrates to one proton at δ 6.38 ppm. This resonance integrated to 0.20 protons after 1 h of reaction time. One could also follow the *p*-cymene resonance that integrates to two protons at δ 6.25 ppm. This resonance integrated to 0.43 protons after 1 h of reaction time. This key experiment confirmed that the *p*-cymene ligand dissociated during catalysis. The loss of an arene ligand may be prevalent in homogenous catalysis in general. Hydrogenation of the *p*-cymene ligand during the reaction was not observed since we did not observe ¹H NMR signals for the hydrogenated product. We did notice unbound *p*-cymene at δ 5.86 ppm present in the ¹H NMR that corresponded to 1.16 protons after 1 h of reaction time. This resonance should integrate to four protons if the *p*-cymene were not coordinated to the metal center.

We also used mesitylene, 1,3,5-trimethylbenzene, instead of 1,3,5-trimethoxybenzene as an internal standard for the deactivation studies. We saw after 60 min of reaction time that 61% of the *p*-cymene ligand had dissociated (supporting information). This was determined with ¹H NMR spectroscopy and following the change of the *p*-cymene resonance that integrates to one proton at δ 6.38 ppm. This resonance integrated to 0.39 protons after 1 h of reaction time. One could also follow the *p*-cymene resonance that integrates to two protons at δ 6.25 ppm. This resonance integrated to 0.85 protons after 1 h of reaction time. We did notice unbound *p*-cymene at δ 5.86 ppm present in the ¹H NMR that corresponded to 1.54 protons after 1 h of reaction time.

Conclusions

We have reported the successful two-step synthesis of an *N*-heterocyclic carbene ruthenium(II) complex as well as its use as a catalyst in the transfer hydrogenation of acetophenone. The synthesis of the catalyst first requires the preparation of a silver(I) carbene complex followed by transmetalation with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ to form complex 1, which we have characterized with NMR spectroscopy, UV–visible spectroscopy, elemental analyses, IR spectroscopy and single crystal X-ray crystallography. Complex 1 was screened

for catalytic activity for the transfer hydrogenation of acetophenone. We achieved 94% conversion after 1 h of reaction time. To further understand the properties of **1**, we tested its stability during the catalytic reaction. We observed after 1 h of reaction time that 80% of the *p*-cymene ligand had decomposed. The loss of a *p*-cymene ligand is an important decomposition pathway that has to be considered in transition metal catalysis. A computational study of the UV–Vis spectrum of **1** shows considerable mixing of Ru and I orbital character into the frontier molecular orbitals, giving rise to the usual types of "d–d" and MLCT excitations albeit with some of the "d" and "metal" orbitals more properly viewed as Ru/I hybrids, some of which have more I character than Ru.

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