



Dehydrogenative Synthesis of Imines from Alcohols and Amines Catalyzed by a Ruthenium N-Heterocyclic Carbene Complex

Maggi, Agnese; Madsen, Robert

Published in:
Organometallics

Link to article, DOI:
[10.1021/om201095m](https://doi.org/10.1021/om201095m)

Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Maggi, A., & Madsen, R. (2012). Dehydrogenative Synthesis of Imines from Alcohols and Amines Catalyzed by a Ruthenium N-Heterocyclic Carbene Complex. *Organometallics*, 31(1), 451-455.
<https://doi.org/10.1021/om201095m>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

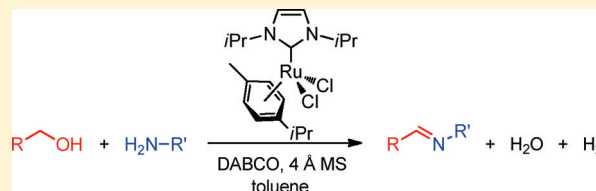
Dehydrogenative Synthesis of Imines from Alcohols and Amines Catalyzed by a Ruthenium N-Heterocyclic Carbene Complex

Agnese Maggi and Robert Madsen*

Department of Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark

S Supporting Information

ABSTRACT: A new method for the direct synthesis of imines from alcohols and amines is described where hydrogen gas is liberated. The reaction is catalyzed by the ruthenium N-heterocyclic carbene complex $[\text{RuCl}_2(\text{IiPr})(p\text{-cymene})]$ in the presence of the ligand DABCO and molecular sieves. The imination can be applied to a variety of primary alcohols and amines and can be combined with a subsequent addition reaction. A deuterium labeling experiment indicates that the catalytically active species is a ruthenium dihydride. The reaction is believed to proceed by initial dehydrogenation of the alcohol to the aldehyde, which stays coordinated to ruthenium. Nucleophilic attack of the amine affords the hemiaminal, which is released from ruthenium and converted into the imine.



INTRODUCTION

The imine is an important functional group in organic chemistry and is often used for the synthesis of amines by various addition reactions.¹ Imines are usually prepared by condensation of an aldehyde or a ketone with a primary amine but can also be formed by oxidation of secondary amines,² oxidative condensation of primary amines,³ and the aza-Wittig reaction.⁴ In addition, imines can be prepared by coupling of alcohols and amines in the presence of an oxidant.⁵

Recently, new dehydrogenative reactions have been developed for the coupling of alcohols and amines where hydrogen gas is liberated and no stoichiometric additives are necessary. These procedures constitute more environmentally benign methods for oxidative couplings and produce a minimum of waste. Ruthenium pincer complexes have been shown to mediate the coupling to form both amides⁶ and imines,⁷ depending on the structure of the ligand. An osmium pincer complex has been shown to catalyze the formation of imines,⁸ while the heterogeneous catalysts $\text{Ag}/\text{Al}_2\text{O}_3$ ⁹ and Pt/TiO_2 ¹⁰ mediate the formation of amides and imines, respectively. We have shown that ruthenium N-heterocyclic carbene complexes can catalyze the synthesis of amides from primary alcohols and amines with the extrusion of hydrogen gas.¹¹ Following our initial findings, several ruthenium N-heterocyclic carbene and related complexes have been shown to mediate the amidation.¹² Among these, the reaction is most efficiently performed with ruthenium complex **1** (Figure 1) in the presence of tricyclohexylphosphine (PCy_3) and potassium *tert*-butoxide.^{12c,d}

During the study of the mechanism of this reaction, we observed that imines in some cases were formed to a significant degree^{12d} and we speculated whether the conditions could be altered into a dehydrogenative imine synthesis. Herein, we describe a new ruthenium-catalyzed synthesis of imines from

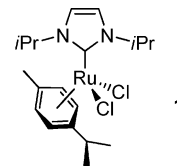
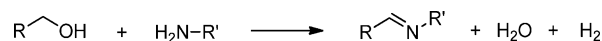


Figure 1. Structure of ruthenium N-heterocyclic carbene complex **1**.

primary alcohols and amines where hydrogen gas is liberated (Scheme 1).

Scheme 1. Dehydrogenative Imine Synthesis



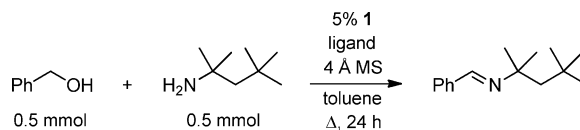
RESULTS AND DISCUSSION

For the initial studies equimolar amounts of benzyl alcohol and *tert*-octylamine were selected as test substrates (Table 1). It was quickly discovered that imine formation occurred in the absence of potassium *tert*-butoxide. The reaction was performed with 5% of complex **1** in refluxing toluene under a flow of argon. Molecular sieves were added to secure continuous removal of water during the reaction. Under these conditions a 40% yield of the imine was obtained after 24 h with 55% conversion of the alcohol (Table 1, entry 1). Only about 3% of the ester from self-condensation of the alcohol¹³ was observed as a byproduct, and no secondary amine or amide could be detected.

Imines are usually easy to reduce, and it is noteworthy that the $\text{C}=\text{N}$ bond is not saturated under the reaction conditions. To improve the conversion of the alcohol, different ligands

Received: November 8, 2011

Table 1. Optimizing Imine Formation



entry	ligand	amt of ligand (%)	BnOH conversn (%) ^a	imine yield (%) ^a
1	none		55	40
2	PCy ₃	5	67	60
3	DABCO	5	80	65
4	dppe	5	42	41
5	xantphos	5	36	32
6	phenanthroline	5	52	44
7	PPh ₃	10	17	17
8	pyridine	10	48	44
9	PCy ₃	10	84	71
10	DABCO	10	83	81
11 ^b	DABCO	10	83	74 ^c
12 ^d	DABCO	10	89	82
13 ^e	DABCO	10	48	34
14 ^f	DABCO	10	40	31
15 ^g	none		56	35 ^h

^aDetermined by GC with nonane as internal standard. ^bWithout molecular sieves. ^c9% of secondary amine was also formed. ^dWith [RuCl₂(IMe)(*p*-cymene)] (5%). ^eWith [RuCl₂(*p*-cymene)]₂ (2.5%), *i*Pr-HCl (5%), and KOtBu (5%). ^fWith [RuCl₂(*p*-cymene)]₂ (2.5%), *i*tBu-HCl (5%), and KOtBu (5%). ^gWith [RuCl₂(*p*-cymene)]₂ (2.5%). ^h15% of the secondary amine was also formed.

were investigated as additives. With 5% of PCy₃ or 1,4-diazabicyclo[2.2.2]octane (DABCO) the alcohol conversion increased (Table 1, entries 2 and 3), while bidentate ligands as well as PPh₃ and pyridine gave lower conversions (entries 4–8). A further improvement could be achieved by increasing the amount of ligand to 10% (entries 9 and 10), and since DABCO gave the best result, this ligand was selected for general use. With DABCO only a trace amount (~2%) of the secondary amine from reduction of the imine was observed as a byproduct. When the experiment in entry 10 was repeated in the absence of molecular sieves, the same conversion of benzyl alcohol was observed, but the amount of secondary amine had increased to 9% (entry 11). Hence, the molecular sieves do not influence the rate of the imination, but instead the selectivity is affected by the continuous removal of water.

The importance of the ruthenium complex was also investigated. First, the isopropyl wingtips in **1** were replaced by methyl groups and the reaction performed with the complex [RuCl₂(IMe)(*p*-cymene)] (Table 1, entry 12). This gave a slightly higher conversion than with **1**, but the product imine was obtained together with 6% of the corresponding secondary amine. Due to the lower selectivity, the methyl-substituted complex [RuCl₂(IMe)(*p*-cymene)] does not constitute a better precatalyst than the isopropyl-substituted **1**. In our amidation reaction it was possible to generate the ruthenium *N*-heterocyclic carbene complex *in situ* from [RuCl₂(*p*-cymene)]₂, 1,3-diisopropylimidazolium chloride (*i*Pr-HCl), and potassium *tert*-butoxide.¹¹ This was also attempted for the imination reaction, but a significantly lower conversion was observed as compared to the experiment with complex **1** (entries 10 and 13). The use of the more sterically hindered 1,3-di-*tert*-butylimidazol-2-ylidene as the carbene ligand gave even lower conversion (entry 14). The importance of the carbene ligand was confirmed by performing the reaction in the absence of this ligand, where a significant amount of the corresponding secondary amine was formed as a byproduct (entry 15). Thus, for general use complex **1** in the presence of DABCO

and molecular sieves presents the optimum catalyst system for the imination. The formation of hydrogen during the transformation was confirmed by collecting the argon–hydrogen gas mixture from the reaction and using it for hydrogenating an alkyne in a separate flask.

With the optimized catalyst system in place, our attention then turned to other alcohols and amines in order to investigate the scope of the imination. First, different alcohols were studied in the reaction with *tert*-octylamine (Table 2). Para-substituted benzyl alcohols with methyl, methoxy, and fluoro substituents participated well in the imine formation, and only trace amounts of the corresponding secondary amines were detected in these reactions (entries 1–4). The methoxy group could also be tolerated in the ortho position without affecting the yield of the imine (entry 5). Notably, a small amount of anisole was observed in entries 3 and 5, which presumably arises from decarbonylation of the intermediate aldehyde.¹⁴ A methyl ester in the para position gave a slightly lower yield, and with this substrate the reaction was accompanied by significant formation of both the secondary amine and the secondary amide (entry 6). *p*-Chloro- and *p*-bromobenzyl alcohol were poor substrates due to considerable dehalogenation as a side reaction (results not shown).

o-Hydroxybenzyl alcohol was also an inferior substrate since the product was obtained as a 1:1 mixture of the desired imine and the corresponding secondary amine (Table 2, entry 7). *p*-Nitrobenzyl alcohol gave the imine in moderate yield due to competing reduction of the nitro group (entry 8). Hex-5-enyl alcohol was converted into the imine with complete reduction of the olefin (entry 9). In this reaction the imine was the only product detected and the moderate yield is presumably due to the poor stability of alkylimines toward purification by flash column chromatography.

In addition to *tert*-octylamine other primary amines were also investigated as substrates, and in this case the reaction was performed with benzyl alcohol (Table 3). Cyclohexylamine gave the imine in 60% isolated yield and with only a trace

Table 2. Imination of Alcohols with *tert*-Octylamine

entry	alcohol	imine	amine conv. (%) ^a	imine yield (%) ^b
1			82	80
2			90	77
3			70	63 ^c
4			80	72
5			75	69 ^c
6 ^d			93	59 ^e
7			-	33 ^f
8			77	48 ^g
9			84	40

^aDetermined by GC with nonane as internal standard. ^bIsolated yield. ^c3% of anisole was also formed. ^dPerformed in mesitylene at 163 °C with PCy₃ instead of DABCO. ^e14% of secondary amine, 17% of amide, and 3% of methyl benzoate were also formed. ^f37% of secondary amine was also formed. ^g15% of *N*-(*p*-aminobenzylidene)-*tert*-octylamine was also formed.

amount of the secondary amine (entry 1). 1-Adamantylamine afforded the product in 70% yield together with 10% of the secondary amine (entry 2). Optically pure (*R*)-1-phenylethylamine and (*R*)-1-(1-naphthyl)ethylamine gave the corresponding imines without any sign of racemization (entries 3 and 4). The more hindered benzhydrylamine reacted very slowly and only gave 40% yield after 2 days (entry 5). Further steric hindrance inhibited the imination almost completely, as seen with tritylamine, where only a trace amount of the imine was observed together with benzyl benzoate from self-condensation of the alcohol (entry 6). These experiments indicate that the amine has to attack the ruthenium complex in order for the imination to proceed.¹⁵ Aniline reacted very sluggishly with benzyl alcohol and only gave the imine in low yield together with several byproducts (result not shown). Reacting benzyl alcohol with complex **1** in refluxing toluene in the absence of an amine gave about 10% of benzaldehyde after 2 h, as judged by GC-MS analysis, and this did not change upon prolonged treatment, where small amounts of benzyl benzoate were also observed.

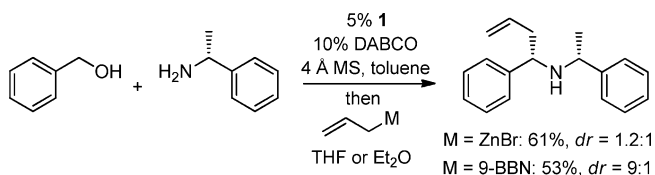
Table 3. Imination of Amines with Benzyl Alcohol

entry	amine	imine	BnOH conv. (%) ^a	imine yield (%) ^b
1			75	60
2			82	70 ^c
3			77	63 ^c
4			70	52 ^d
5 ^e			73	40 ^f
6 ^g		-	75	-

^aDetermined by GC with nonane as internal standard. ^bIsolated yield. ^c10% of secondary amine was also formed. ^d7% of secondary amine was also formed. ^eReacted for 48 h. ^f5% of secondary amine was also formed. ^gReacted for 52 h.

The imination reaction provides access to a variety of imines which may be used directly in a subsequent addition reaction. This was illustrated with the enantiomerically pure imine from Table 3, entry 3, which has previously been reacted with a variety of nucleophiles.^{1b} After the imine was formed from benzyl alcohol and (*R*)-1-phenylethylamine, the solvent was replaced with THF or Et₂O followed by addition of an allylating agent (Scheme 2). With allylzinc bromide the

Scheme 2. Sequential Imination and Allylation

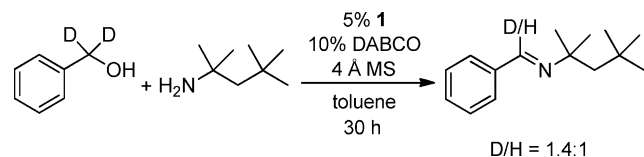


addition product was obtained in 61% overall yield from benzyl alcohol, but with almost no diastereoselectivity. With the more hindered *B*-allyl-9-BBN the product was isolated in 53% yield and with a diastereomeric ratio of 9:1.¹⁶

To obtain more information about the mechanism of the imination, two experiments with deuterium-labeled benzyl alcohol were performed. First, benzyl alcohol- α,α -*d*₂ was reacted with *tert*-octylamine under the standard conditions

(Scheme 3). Interestingly, the product imine was obtained as a 1.4:1 mixture of the deuterium-labeled imine and the

Scheme 3. Imination with Benzyl Alcohol- α,α - d_2



nonlabeled product, as shown by GC-MS analysis. This result was observed in both toluene and toluene- d_8 and is not a result of a deuterium–hydrogen exchange with the solvent. A control experiment showed that the scrambling occurred during the imination reaction and not by a competing transformation from the imine. When the product H-imine from Table 2, entry 1, was treated with PhCD_2OH under the same conditions as in Scheme 3, no deuterium incorporation in the imine was observed.

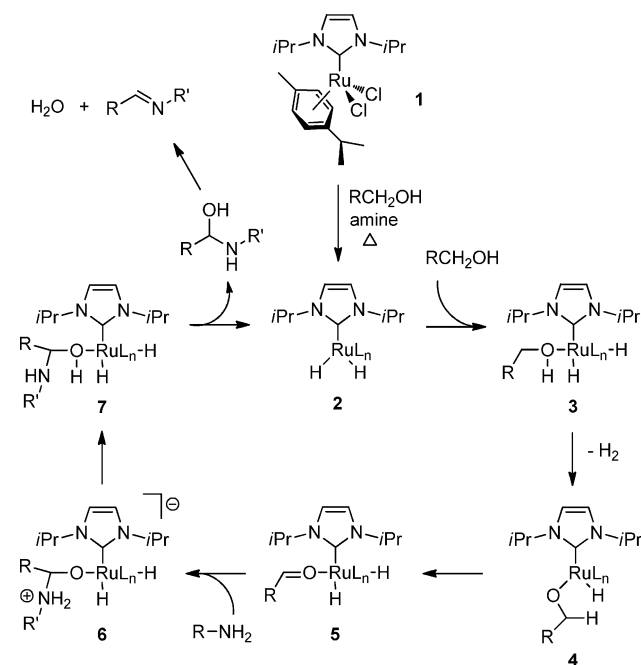
When the imination in Scheme 3 was monitored by ^1H NMR in toluene- d_8 , deuterium–hydrogen scrambling in the starting alcohol was observed already after 5 h. Reisolating the alcohol at this time showed that it consisted of PhCD_2OH (56%), PhCDHOH (34%), and PhCH_2OH (10%). This indicates that the initial β -hydride elimination to form benzaldehyde is a reversible reaction and, more importantly, the catalytically active ruthenium species is a dihydride. The same observation was made in our very recent dehydrogenative ester synthesis from primary alcohols with complex **1**.¹³

The influence of the β -hydride elimination was further probed by measuring the primary kinetic isotope effect. The initial rate was determined both with $\text{PhCH}_2\text{OH}/\text{tert-octyl-NH}_2$ and with $\text{PhCD}_2\text{OD}/\text{tert-octyl-ND}_2$, which gave a kinetic isotope effect ($k_{\text{H}}/k_{\text{D}}$) of 1.1 ± 0.3 . This negligible value indicates that β -hydride elimination from the alcohol is not the rate-determining step in the imination mechanism.

On the basis of these experiments and our previous studies on the amidation,^{12d} we propose the imination mechanism in Scheme 4. It has previously been shown by NMR that the *p*-cymene ligand in complexes such as **1** is lost upon reflux in toluene.¹⁷ This is followed by replacement of the two chloride ligands with hydride through substitution with the alcohol, release of hydrogen chloride, and β -hydride elimination. The formation of ruthenium hydrides in this way has been established for other ruthenium(II) chloride complexes.¹⁸ By this catalyst initiation small amounts of the aldehyde will be formed and converted into the imine after reaction with the amine. The catalytically active species is believed to be dihydride **2**, which coordinates the alcohol to afford complex **3**. Hydrogen gas is then liberated by hydrogen transfer to hydride, as demonstrated earlier.¹⁹ This gives rise to alkoxide complex **4**, which is then converted into aldehyde complex **5** by β -hydride elimination. It is possible that the aldehyde is released from **5** and imine formation then occurs with the amine in solution. However, since the imination is sensitive to the steric demands of the amine, it seems more reasonable that the amine attacks the coordinated aldehyde to afford hemiaminal **6** (as the zwitterion protonated at nitrogen).

This is, so far, fairly similar to the mechanism proposed for the amidation with complex **1**.^{12d} The major difference, however, is the lack of a strong base in the imination, and the more acidic environment may affect the stability of complex

Scheme 4. Proposed Mechanism for Imination



6. Recently, Crabtree and Eisenstein performed a computational study on a similar hemiaminal bonded to a ruthenium(II) hydride in order to determine whether the amide or the imine would be formed.²⁰ They showed that the amide is formed after hydrogen transfer to hydride, while imine formation requires hydrogen transfer to oxygen.²⁰ Under the more acidic conditions of the imination, hydrogen transfer to oxygen may be more facile, e.g. through an outer-sphere proton transfer, which would afford complex **7** and then the imine after decomplexation of the hemiaminal. In this way, the fate of the intermediate hemiaminal determines whether the amide or the imine is formed in the coupling. The scrambling observed in Scheme 3 can be explained by the observation that ruthenium dihydride complexes are able to scramble hydrogen and deuterium when exposed to hydrogen/deuterium gas.²¹ In combination with a reversible β -hydride elimination, this provides a route by which O–H or N–H hydrogens can be scrambled into the α positions of the alcohol.

In summary, we have presented a new method for the direct synthesis of imines from primary alcohols and amines in which water and hydrogen gas are formed as the only byproducts. The reaction is catalyzed by the ruthenium N-heterocyclic carbene complex **1**, which is easy to handle and straightforward to prepare. A mechanism is proposed with a ruthenium dihydride species as the catalytically active component.

EXPERIMENTAL SECTION

General Information. Toluene was distilled from sodium and benzophenone under an argon atmosphere. Column chromatography was performed on silica gel 60 (0.035–0.070 mm) saturated with Et_3N . NMR chemical shifts were measured with TMS or the residual solvent signal in CDCl_3 (δ_{H} 7.26 ppm, δ_{C} 77.0 ppm) as internal reference.

General Procedure for Imination. Ruthenium complex **1**^{12d} (22.9 mg, 0.05 mmol), DABCO (11.2 mg, 0.1 mmol), and 4 Å molecular sieves (150 mg) were placed in an oven-dried Schlenk flask equipped with a cold finger. Vacuum was applied, and the flask was then filled with argon (repeated twice). Toluene (1 mL), alcohol (1 mmol), amine (1 mmol), and nonane (0.2 mmol as internal standard)

were added by syringe, and the mixture was refluxed with stirring under a flow of argon for 24 h. The reaction mixture was cooled to room temperature and the solvent removed in vacuo. The residue was purified by silica gel column chromatography (hexane/Et₂O 10/0 → 9/1 with 2% Et₃N) to afford the imine.

N-(4-Methylbenzylidene)-*tert*-octylamine (Table 2, Entry 2): ¹H NMR (300 MHz, CDCl₃) δ 8.21 (s, 1H), 7.64 (d, 2H, J = 8.1 Hz), 7.21 (d, 2H, J = 8.1 Hz), 2.38 (s, 3H), 1.69 (s, 2H), 1.32 (s, 6H), 0.96 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 154.2, 140.0, 134.8, 129.1, 127.8, 60.8, 56.6, 32.0, 31.7, 29.6, 21.4; HRMS *m/z* calcd for C₁₆H₂₆N 232.2021 [M + H]⁺, found 232.2059.

N-(4-Methoxybenzylidene)-*tert*-octylamine (Table 2, Entry 3): ¹H NMR (300 MHz, CDCl₃) δ 8.18 (s, 1H), 7.70 (d, 2H, J = 8.7 Hz), 6.93 (d, 2H, J = 8.7 Hz), 3.84 (s, 3H), 1.68 (s, 2H), 1.32 (s, 6H), 0.96 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 161.0, 153.6, 130.4, 129.3, 113.8, 60.6, 56.6, 55.3, 32.0, 31.8, 29.7; HRMS *m/z* calcd for C₁₆H₂₆NO 248.1970 [M + H]⁺ found 248.2010.

N-(4-Fluorobenzylidene)-*tert*-octylamine (Table 2, Entry 4): ¹H NMR (300 MHz, CDCl₃) δ 8.21 (s, 1H), 7.76–7.70 (m, 2H), 7.10 (bt, 2H), 1.69 (s, 2H), 1.32 (s, 6H), 0.96 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 163.8 (d, J_{C-F} = 248.0 Hz), 152.9, 133.6 (d, J_{C-F} = 2.85 Hz), 129.6 (d, J_{C-F} = 8.4 Hz), 115.5 (d, J_{C-F} = 21.6 Hz), 60.9, 56.5, 32.0, 31.7, 29.6; HRMS *m/z* calcd for C₁₅H₂₃FN 236.1770 [M + H]⁺, found 236.1809.

N-(2-Methoxybenzylidene)-*tert*-octylamine (Table 2, Entry 5): ¹H NMR (300 MHz, CDCl₃) δ 8.67 (s, 1H), 7.96 (bd, 1H), 7.35 (bt, 1H), 6.98 (bt, 1H), 6.91 (bd, 1H), 3.87 (s, 3H), 1.70 (s, 2H), 1.33 (s, 6H), 0.96 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 158.6, 150.4, 131.0, 127.0, 125.8, 120.8, 110.8, 61.3, 56.6, 55.4, 32.0, 31.8, 29.8; HRMS *m/z* calcd for C₁₆H₂₆NO 248.1970 [M + H]⁺, found 248.2008.

N-(4-Carbomethoxybenzylidene)-*tert*-octylamine (Table 2, Entry 6): ¹H NMR (300 MHz, CDCl₃) δ 8.27 (s, 1H), 8.07 (d, 2H, J = 8.1 Hz), 7.80 (d, 2H, J = 8.1 Hz), 3.93 (s, 3H), 1.70 (s, 2H), 1.33 (s, 6H), 0.95 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 166.8, 153.5, 141.2, 131.1, 129.7, 127.7, 61.5, 56.5, 52.2, 32.0, 31.7, 29.5; HRMS *m/z* calcd for C₁₇H₂₆NO₂ 276.1919 [M + H]⁺, found 276.1960.

N-(4-Nitrobenzylidene)-*tert*-octylamine (Table 2, Entry 8): ¹H NMR (300 MHz, CDCl₃) δ 8.30 (s, 1H), 8.26 (d, 2H, J = 8.7 Hz), 7.91 (d, 2H, J = 8.7 Hz), 1.71 (s, 2H), 1.34 (s, 6H), 0.94 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 152.3, 142.7, 128.5, 123.8, 61.9, 56.5, 32.0, 31.7, 29.5; HRMS *m/z* calcd for C₁₅H₂₃N₂O 263.1715 [M + H]⁺, found 263.1753.

■ ASSOCIATED CONTENT

● Supporting Information

Text and figures giving experimental procedures, characterization data, and ¹H and ¹³C NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

* E-mail: rm@kemi.dtu.dk.

■ ACKNOWLEDGMENTS

We thank the Danish Council for Independent Research–Technology and Production Sciences for financial support.

■ REFERENCES

- (1) (a) Friestad, G. K.; Mathies, A. K. *Tetrahedron* **2007**, *63*, 2541–2569. (b) Alvaro, G.; Savoia, D. *Synlett* **2002**, 651–673.
- (2) (a) Jiang, G.; Chen, J.; Huang, J.-S.; Che, C.-M. *Org. Lett.* **2009**, *11*, 4568–4571. (b) So, M.-H.; Liu, Y.; Ho, C.-M.; Che, C.-M. *Chem. Asian J.* **2009**, *4*, 1551–1561. (c) Choi, H.; Doyle, M. P. *Chem. Commun.* **2007**, 745–747. (d) Wang, J.-R.; Fu, Y.; Zhang, B.-B.; Cui, X.; Liu, L.; Guo, Q.-X. *Tetrahedron Lett.* **2006**, *47*, 8293–8297. (e) Samec, J. S. M.; Éll, A. H.; Bäckvall, J.-E. *Chem. Eur. J.* **2005**, *11*, 2327–2334.
- (3) (a) Liu, L.; Zhang, S.; Fu, X.; Yan, C.-H. *Chem. Commun.* **2011**, 47, 10148–10150. (b) Lang, X.; Ji, H.; Chen, C.; Ma, W.; Zhao, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 3934–3937. (c) Patil, R. D.; Adimurthy, S. *Adv. Synth. Catal.* **2011**, *353*, 1695–1700. (d) Chu, G.; Li, C. *Org. Biomol. Chem.* **2010**, *8*, 4716–4719. (e) Yuan, Q.-L.; Zhou, X.-T.; Ji, H.-B. *Catal. Commun.* **2010**, *12*, 202–206.
- (4) Palacios, F.; Alonso, C.; Aparicio, D.; Rubiales, G.; de los Santos, J. M. *Tetrahedron* **2007**, *63*, 523–575.
- (5) (a) Jiang, L.; Jin, L.; Tian, H.; Yuan, X.; Yu, X.; Xu, Q. *Chem. Commun.* **2011**, 47, 10833–10835. (b) Sun, H.; Su, F.-Z.; Ni, J.; Cao, Y.; He, H.-Y.; Fan, K.-N. *Angew. Chem., Int. Ed.* **2009**, *48*, 4390–4393. (c) Kwon, M. S.; Kim, S.; Park, S.; Bosco, W.; Chidrala, R. K.; Park, J. *J. Org. Chem.* **2009**, *74*, 2877–2879. (d) Kim, J. W.; He, J.; Yamaguchi, K.; Mizuno, N. *Chem. Lett.* **2009**, *38*, 920–921. (e) Sithambaram, S.; Kumar, R.; Son, Y.-C.; Suib, S. L. *J. Catal.* **2008**, *253*, 269–277. (f) Blackburn, L.; Taylor, R. J. K. *Org. Lett.* **2001**, *3*, 1637–1639.
- (6) Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, *317*, 790–792.
- (7) Gnanaprakasam, B.; Zhang, J.; Milstein, D. *Angew. Chem., Int. Ed.* **2010**, *49*, 1468–1471.
- (8) Esteruelas, M. A.; Honczek, N.; Oliván, M.; Oñate, E.; Valencia, M. *Organometallics* **2011**, *30*, 2468–2471.
- (9) Shimizu, K.-i.; Ohshima, K.; Satsuma, A. *Chem. Eur. J.* **2009**, *15*, 9977–9980.
- (10) Shirashi, Y.; Ikeda, M.; Tsukamoto, D.; Tanaka, S.; Hirai, T. *Chem. Commun.* **2011**, 47, 4811–4813.
- (11) Nordström, L. U.; Vogt, H.; Madsen, R. *J. Am. Chem. Soc.* **2008**, *130*, 17672–17673.
- (12) (a) Schley, N. D.; Dobereiner, G. E.; Crabtree, R. H. *Organometallics* **2011**, *30*, 4174–4179. (b) Prades, A.; Peris, E.; Albrecht, M. *Organometallics* **2011**, *30*, 1162–1167. (c) Chen, C.; Hong, S. H. *Org. Biomol. Chem.* **2011**, *9*, 20–26. (d) Dam, J. H.; Osztrovsky, G.; Nordström, L. U.; Madsen, R. *Chem. Eur. J.* **2010**, *16*, 6820–6827.
- (13) Solhøj, A.; Madsen, R. *Organometallics* **2011**, *30*, 6044–6048.
- (14) Fristrup, P.; Kreis, M.; Palmelund, A.; Norrby, P.-O.; Madsen, R. *J. Am. Chem. Soc.* **2008**, *130*, 5206–5215.
- (15) In benzene solution tritylamine reacts readily with aldehydes to form the corresponding imines; see: Soroka, M.; Zygmunt, J. *Synthesis* **1988**, 370–372.
- (16) Addition of *B*-allyl-9-BBN to the pure imine gave a diastereomeric ratio of 97/3; see: Alvaro, G.; Boga, C.; Savoia, D.; Umani-Ronchi, A. *J. Chem. Soc., Perkin Trans. 1* **1996**, 875–882.
- (17) (a) Zhang, Y.; Chen, C.; Ghosh, S. C.; Li, Y.; Hong, S. H. *Organometallics* **2010**, *29*, 1374–1378. (b) Delaude, L.; Delfosse, S.; Richel, A.; Demonceau, A.; Noels, A. F. *Chem. Commun.* **2003**, 1526–1527.
- (18) (a) Solari, E.; Gauthier, S.; Scopelliti, R.; Severin, K. *Organometallics* **2009**, *28*, 4519–4526. (b) Aranyos, A.; Csornyik, G.; Szabó, K. J.; Bäckvall, J.-E. *Chem. Commun.* **1999**, 351–352. (c) Mizushima, E.; Yamaguchi, M.; Yamagishi, T. *Chem. Lett.* **1997**, 237–238.
- (19) Chatwin, S. L.; Davidson, M. G.; Doherty, C.; Donald, S. M.; Jazzar, R. F. R.; Macgregor, S. A.; McIntyre, G. J.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* **2006**, *25*, 99–110.
- (20) Nova, A.; Balcells, D.; Schley, N. D.; Dobereiner, G. E.; Crabtree, R. H.; Eisenstein, O. *Organometallics* **2010**, *29*, 6548–6558.
- (21) Burling, S.; Kociok-Köhn, G.; Mahon, M. F.; Whittlesey, M. K.; Williams, J. M. J. *Organometallics* **2005**, *24*, 5868–5878.