RUTHENIUM(II)-CATALYZED TRANSFER HYDROGENATION OF AROMATIC AND HETEROAROMATIC ALDEHYDES IN AIR

Sumit S. Bhosale and Keisham S. Singh
Bioorganic Chemistry Laboratory, Council of Scientific and Industrial Research, National Institute of Oceanography, Goa, India

GRAPHICAL ABSTRACT

Abstract Aromatic and heteroaromatic aldehydes are efficiently reduced to their corresponding alcohols in the presence of \([\text{RuCl}_2(\text{p-cymene})]_2\) and KOAc in 2-propanol under air at 80 °C. The presence of KOAc in the reaction is essential; in its absence no reduction takes place. A highly efficient, external-base-free reduction of aldehydes has also been reported with \(\gamma\)-arene)ruthenium(II) complexes containing \(\text{O}^\text{O}\) chelate ligand such as \([\text{Ru(OAc)}_2(\text{p-cymene})]\) and \([\text{RuCl(KA)}(\text{p-cymene})]\), obtaining alcohol in excellent yield (OAc, acetate; KA, kojic acetate). The scope of the reaction has been extended to a broad range of aromatic and heteroaromatic aldehydes.

Keywords Heteroaldehydes; kojic acid; potassium acetate; 2-propanol; reduction; ruthenium catalysts; spectroscopic data

INTRODUCTION

Aldehydes are considered to be a key starting compound in organic synthesis. Among the prominent reactions of aldehyde, reduction to their corresponding alcohol is an important transformation in the pharmaceutical and chemical industries. There are several methods available for this reduction, among which transition metal-catalyzed transfer hydrogenation (CTH) with the aid of suitable hydrogen donor has emerged as the most feasible. Since hydrogenation using molecular hydrogen is associated with risks, requires high pressure apparatus, and needs extra care, CTH has been employed as the alternative technique for these purposes. It has long been recognized that N,N'-dimethylformamide (DMF) or

Received October 20, 2014.
Address correspondence to Keisham S. Singh, Bioorganic Chemistry Laboratory, Council of Scientific and Industrial Research, National Institute of Oceanography, Goa 403004, India. E-mail: keisham@nio.org, keisham.sarjit@gmail.com
N,N'-dimethylacetamide (DMA) solution of RuCl₃ could catalyze hydrogenation of simple olefins.[2] Over the past years, transfer hydrogenation by transition-metal catalysts using 2-propanol as a hydrogen source for reducing aldehydes and ketones has received considerable attention because of its relatively benign and green nature.[3–5]

Several transition metals have been utilized for these reactions,[6] of which ruthenium complexes appear to be the favorite candidates and the most extensively studied.[7–13] Ruthenium(II) complexes including (η⁶-arene)ruthenium (II) systems have been employed for the hydrogenation of carbonyl compounds.[13–15] For instance, oxo-tethered (η⁶-arene) ruthenium(II) complex was used as a bifunctional catalyst for asymmetric transfer hydrogenation of ketones employing formic acid / triethylamine as reducing agent.[14] Noyori et al.[15–17] have reported highly efficient chiral reduction catalysts, Ru(II)-TsDPEN (TsDPEN, N-(p-tolylsulfonyl)1,2-diphenylethlenediamine) for reduction of ketone. On the other hand, asymmetric transfer hydrogenation of ketones has been efficiently carried out with Ru(PPh₃)₂Cl₂ using either chiral bis(oxazolinylmethyl) amine[18] or chiral tridentate phosphorus ligands.[13] Other ruthenium(II) phosphate complexes such as [RuCl₂(PPh₃)(PNN')] and cationic BINAP-Ru(II) halide[20] have also been shown as efficient catalysts for stereoselective asymmetric hydrogenation of ketones. Fink et al.[21] have reported noble (η⁶-arene) ruthenium(II) complexes containing sulfonate diamine ligand, for example, [Ru(OH)L(arene)]⁺ (L = N-tosyl-trans-1,2-diaminocyclohexane). This catalyst was found to be very effective for the transfer hydrogenation of arylketones or of aryl imine in aqueous solution where sodium formate has been employed as a hydrogen source.

Although ruthenium-catalyzed hydrogenation of ketones has been extensively studied, little has been explored on the hydrogenation of aldehydes.[22,23] Recently, Basu et al.[22] reported hydrogenation of aldehyde using RuCl₃·H₂O and resin formate under a nitrogen atmosphere. Notably, transition-metal-catalyzed hydrogenation in 2-propanol is usually carried out under an inert atmosphere.[24] Unfortunately, metal-catalyzed transfer hydrogenation of aldehyde or ketones in air is less explored.[25] Moreover, in most of the reductions, the catalyst involved is mainly either RuCl₃·H₂O or ortho-metallated and cyclometallated ruthenium (III) complexes in the presence of a base and using 2-propanol as hydrogen sources.[26,27] However, as far as our knowledge goes hydrogenation of aldehydes using ruthenium(II) compounds containing O²⁻O chelate ligands of the type [RuCl

![Chemical structures of compounds 1–4.](image-url)
(O^O)(p-cymene)] has not been studied prior to this communication. Recently, (η⁶-arene) ruthenium(II) complexes bearing acetate and pyronate ligands, such as [Ru(OAc)₂(p-cymene)]²⁺ and [RuCl₂(KA)(p-cymene)], respectively, have shown to be efficient catalysts for arylation of heteroarenes. Herein, we report hydrogenation of aromatic and heteroaromatic aldehydes to their respective alcohol using [RuCl₂(p-cymene)]₂ (1)³⁰ in the presence of a base as well as a highly efficient external base-free reduction of aldehydes by ruthenium catalysts [Ru(OAc)₂(p-cymene)] (3)³¹ and [RuCl₂(KA)(p-cymene)] (4)³² (Fig. 1) under mild conditions in air.

RESULTS AND DISCUSSION

Aromatic and heteroaromatic aldehydes were reduced to their respective alcohols with [RuCl₂(p-cymene)]₂ in the presence of potassium acetate. Previously, reduction of carbonyl groups with other ruthenium complex such as RuCl₂(PPh₃)₃ using a strong base such as NaOH has been reported.³³ In contrast, hydrogenation of aldehydes with [RuCl₂(p-cymene)]₂ (1) with a weaker base such as acetate has not been explored in detail. In the present study, we described a reduction of aromatic and heteroaromatic aldehydes to their respective alcohols with [RuCl₂(p-cymene)]₂ (1) in the presence of potassium acetate and benzamide in 2-propanol or dimethylformamide (DMF) under air at 80 °C. In addition, we also disclosed a convenient reduction of aromatic and heteroaromatic aldehydes with ruthenium catalyst [Ru(OAc)₂(p-cymene)] (3) without use of external base and additive under mild condition. First, the reduction of aldehydes has been screened with [RuCl₂(p-cymene)]₂ in the presence of potassium acetate and benzamide in 2-propanol or DMF as solvent. It was found that reduction in 2-propanol was shown to be more efficient then in DMF under which a poor yield of alcohol was obtained along with unreacted starting aldehydes. The hydrogenation did not occur in the absence of ruthenium catalyst, demonstrating that catalyst played a key role for the reduction of aldehyde to alcohol (Table 1, entry 12).

To get an optimized reaction condition we have selected p-nitrobenzaldehyde as typical substrate and reduction was performed under a wide range of reaction conditions (see Table 1). First, the reduction was performed using p-nitro benzaldehyde (0.5 mmol) in the presence of [RuCl₂(p-cymene)]₂ (5 mol%), benzamide (4 equiv.) and KOAc (4 equiv.) in 2-propanol under air. Under this reaction condition the desired product, p-nitro benzyl alcohol (5a), was obtained in an isolated yield of 80% (Table 1, entry 1). The presence of acetate is critical for the reduction performed in 2-propanol, the absence of which resulted in no formation of the desired alcohol (Table 1, entry 9). However, when the solvent used was DMF, reduction occurred even in the absence of potassium acetate, giving modest yield (Table 1, entry 6). Surprisingly, in this case the yield of the product is slightly decreased in the presence of potassium acetate (Table 1, entries 4 and 6). The desired alcohol could even be formed in a trace amount by stirring aldehyde alone in DMF in the presence of 5 mol% of [RuCl₂(p-cymene)]₂ at 80 °C for 16 h.

The reduction of aldehyde to alcohol with [RuCl₂(p-cymene)]₂ in 2-propanol appeared to be excellent, and in most cases after 8 h of reaction, no unreacted aldehyde was found in the reaction mixture (thin-layer chromatography [TLC]
Table 1. Optimization studies for reduction of aldehyde to alcohol

| Entry | Ruthenium catalyst | Ligand (L)         | Additive | Solvent   | Temp. (°C) / time (h) | Yield (%) |
|-------|--------------------|--------------------|----------|-----------|-----------------------|-----------|
| 1     | [RuCl₂(p-cymene)]₂ (I) | Benzamide         | KOAc     | 2-Propanol | 80/8                  | 80        |
| 2     | [RuCl₂(p-cymene)]₂ (I) | N-Methyl benzamide | KOAc     | 2-Propanol | 80/8                  | 78        |
| 3     | [RuCl₂(p-cymene)]₂ (I) | N-Methyl benzamide | KOAc     | 2-Propanol | 80/8                  | 78        |
| 4     | [RuCl₂(p-cymene)]₂ (I) | Benzamide         | KOAc     | DMF       | 80/16                 | 69        |
| 5     | [RuCl₂(p-cymene)]₂ (I) | N-Methyl benzamide | KOAc     | DMF       | 80/16                 | 53        |
| 6     | [RuCl₂(p-cymene)]₂ (I) | Benzamide         | KOAc     | DMF       | 80/16                 | 46        |
| 7     | [RuCl₂(p-cymene)]₂ (I) | Benzamide         | KOAc     | DMF       | 80/16                 | 26        |
| 8     | [RuCl₂(p-cymene)]₂ (I) | Benzamide         | KOAc     | 2-Propanol | RT/20                 | 20        |
| 9     | [RuCl₂(p-cymene)]₂ (I) | Benzamide         | KOAc     | 2-Propanol | 80/16                 | NR        |
| 10    | [RuCl₂(p-cymene)]₂ (I) | —                  | KOAc     | 2-Propanol | 80/8                  | 70        |
| 11    | [RuCl₂(p-cymene)]₂ (I) | —                  | NaOAc    | 2-Propanol | 80/10                 | 54        |
| 12    | —                  | —                  | KOAc     | 2-Propanol | 80/16                 | NR        |
| 13    | [RuCl(dpNmei)(p-cymene)]PF₆ (2) | —      | —       | 2-Propanol | 80/16                 | NR        |
| 14    | [Ru(OAc)₂(p-cymene)] (3) | —                  | —       | 2-Propanol | 80/6                  | 84        |
| 15    | [RuCl(KA)(p-cymene)] (4) | —                  | —       | 2-Propanol | 80/6                  | 68        |
| 16    | [RuCl(KA)(p-cymene)] (4) | —                  | KOAc    | 2-Propanol | 80/6                  | 70        |

*aReaction conditions: p-nitrobenzaldehyde (0.5 mmol), catalyst (0.025 mmol, 5 mol%), amide (0.1 mmol), additive (0.1 mmol), solvent (2–3 mL), under air, temp. 80°C, time 6–16 h.

*bIsolated yield obtained after column chromatography.

*cReaction performed under a nitrogen atmosphere.
analysis: 9:1 petroleum ether / ethyl acetate). The presence of amide ligand is not essential; however, in its absence the isolated yield was slightly decreased. Thus, it is assumed that presence of amide ligand enhanced the formation of \( p \)-nitro benzyl alcohol to some extent (Table 1, entries 1 and 10). The role of amide ligand is not clear at this time; however, we believed that it enhanced in transfer hydrogenation process in association with acetate through forming an active intermediate ruthenium species. Notably, reaction of aldehyde and benzamide in 2-propanol in the absence of acetate did not form the desired alcohol, indicating benzamide alone did not produce the reduction. The addition of benzamide in association with acetate enhanced the hydrogenation process.

It is noteworthy that in the case of reactions performed in 2-propanol, no significant change was observed in the yield of the isolated alcohol when benzamide was replaced with \( N \)-methylbenzamide (Table 1, entries 1 and 2). However, the yield of the alcohol was significantly increased for the reduction performed in DMF when \( N \)-methylbenzamide was used instead of benzamide (Table 1, entries 4 and 6). The reaction can be performed either in nitrogen atmosphere or under air obtaining almost insignificantly different yields of the desired alcohols (Table 1, entries 1 and 3). Another mild base, such as sodium acetate, can also be used but it is less effective then potassium acetate (Table 1, entries 10 and 11). When the reduction was conducted at room temperature employing \([\text{RuCl}_2(p\text{-cymene})]_2\) (5 mol%), KOAc (4 equiv.) the desired alcohol was obtained in poor yield (Table 1, entry 8). In these reactions, performed in the presence of KOAc in 2-propanol, a small by product is also formed (revealed by TLC analysis), which may be probably due to unwanted reaction with aryl aldehydes. However, we did not attempt to isolate this side product and thus no clear information was obtained for these unidentified side products.

Because potassium acetate or sodium acetate is essential for the reduction of aldehyde in 2-propanol with the catalyst \([\text{RuCl}_2(p\text{-cymene})]_2\), we assumed that the active catalyst might be the \textit{in situ}–generated \([\text{Ru(OAc)}_2(p\text{-cymene})] (3). To establish this, we have conducted the reaction directly using \([\text{Ru(OAc)}_2(p\text{-cymene})] (3) (5 mol%) and aldehyde (0.5 mmol) in 2-propanol without an external base under air at 80 °C. Interestingly, this reaction gave 84% yield of alcohol much greater than the one performed with \([\text{RuCl}_2(p\text{-cymene})]_2\) (Table 1, entry 14). Inspired by this result, we became interested to evaluate other precatalyst such as \([\text{RuCl(KA)}(p\text{-cymene})] (4) containing a pyronate ligand, which is believed to behave like acetate. Reduction of \( p \)-nitrobenzaldehyde using complex 4 in 2-propanol gave the desired \( p \)-nitro-benzyl alcohol in 68% yield, demonstrating that the complex is also an effective catalyst for this reaction (Table 1, entry 15). Addition of potassium acetate (2 equiv.) slightly increased the yield of the desired alcohol (Table 1, entry 16). Although complex 4 could be used for the reduction of aldehyde, it is less effective.
Table 2. Reduction of aryl and heteroaryl aldehydes to alcohol using ruthenium(II) catalyst

| Entry | Substrate | Product | Yield (%)\(^a\) | [Ru-Cat]\(^b\) | [Ru-Cat]\(^c\) |
|-------|-----------|---------|-----------------|----------------|----------------|
| 1     | ![Substrate 1](image1) | ![Product 1](image2) | 79 | 84 |
| 2     | ![Substrate 2](image3) | ![Product 2](image4) | 68 | 81 |
| 3     | ![Substrate 3](image5) | ![Product 3](image6) | 73 | 85 |
| 4     | ![Substrate 4](image7) | ![Product 4](image8) | 57 | 80 |
| 5     | ![Substrate 5](image9) | ![Product 5](image10) | 54 | 91 |
| 6     | ![Substrate 6](image11) | ![Product 6](image12) | 57 | 59 |
| 7     | ![Substrate 7](image13) | ![Product 7](image14) | 45 | 50 |
| 8     | ![Substrate 8](image15) | ![Product 8](image16) | 15 | 49 |

(Continued)
as compared to the complex 3. Notably, when catalysts 3 and 4 were used in the
reduction, addition of benzamide did not affect the reactions at all irrespective of
the amount of ligand added. However, under similar condition, no satisfactory result
was obtained when the reduction was carried out using [RuCl(dpNmei)(p-cymene)]+ (2) [34] (see Table 1, entry 13; where dpNmei is 2-dipyridyl-N-methylimine). Thus,
the optimized reaction conditions for reduction of aldehyde in the presence of
[RuCl2(p-cymene)]2 and [Ru(OAc)2(p-cymene)], are as follows: (a) aldehyde
(0.5 mmol), [RuCl2(p-cymene)]2 (0.025 mmol, 5 mol%), benzamide (0.1 mmol),
KOAc (0.1 mmol), 2-propanol (3 mL), 80 °C, 8–16 h, under air.

With the optimized reaction condition in hands, we have extended the scope
of the reduction to other aromatic as well as heteroaromatic aldehydes, namely
4-chloro-benzaldehyde, 4-methoxybenzaldehyde, 5-nitrofurfural, 5-(2-nitrophenyl)
furfural, 5-(3-chlorophenyl) furfural, 5-nitro-2-thiophenecarboxaldehyde, and
3-methylthiophen-2-carboxaldehyde, using 5 mol% of [RuCl2(p-cymene)]2 (1) or
[Ru(OAc)2(p-cymene)] (3) (Scheme 1).

Reduction of p-chlorobenzaldehyde using catalyst 1 or 3 gave the desired
alcohol 5b in isolated yields of 68% and 81%, respectively (Table 2, entry 2).
Similarly, 2-chlorobenzaldehyde reduced readily in the presence of catalysts 1 and
3, giving the desired alcohol in good yield (Table 2, entry 3). When, p-anisaldehyde
was reduced using the catalysts 1 and 3, the desired alcohol 5d was obtained in 57%
and 80%, respectively (Table 2, entry 4). A similar trend was also observed for the
reduction of p-methoxynaphthaldehyde in which reduction performed with catalyst
3 afforded 91% yield while reduction performed with catalyst 1 gave only 54%
isolated yield of the desired alcohol (Table 2, entry 5).

Among the heteroaldehydes tested, 5-(2-nitrophenyl) furfural and 5-(3-
chlorophenyl) furfural gave excellent yield with both the catalysts 1 and 3, giving
isolated yields of 64 and 83% with [RuCl2(p-cymene)]2 and 80 and 88% yields of the desired alcohols with [Ru(OAc)2(p-cymene)] (Table 2, entries 9 and 10). Reduction of 5-nitrofurfuraldehyde and 5-nitro-2-thiophenecarboxaldehyde with both the catalysts 1 and 3 gave a modest yield (Table 2, entries 6 and 7). In contrast a methyl-substituted furfural gave much lower yield, giving only 15% with catalyst 1 and a modest yield (49%) with catalyst 3 (Table 2, entry 8). However, no satisfactory result was obtained for the reduction of 5-methyl-2-furfural. In all these reductions, [Ru(OAc)2(p-cymene)] proved to be more efficient catalyst than [RuCl2(p-cymene)]2 (see Table 2). The reduction with [Ru(OAc)2(p-cymene)] is highly efficient in that only 5 mol% of catalyst, aldehyde, and solvent were required under mild conditions, giving clean and excellent yields. This catalytic system works very well for reduction of aromatic and heteroaromatic aldehydes, obtaining good to excellent yields of the desired alcohols. However, an attempt to extend the utility of the catalytic system for reduction of ketone such as acetophenone and aliphatic aldehydes, namely 1-haptanal, to their corresponding alcohol was unsuccessful. This indicated that the catalytic system is highly efficient for reduction of only aromatic and heteroaromatic aldehydes and their derivatives.

CONCLUSION

In summary, a convenient method for the hydrogenation of aromatic and heteroaromatic aldehydes to alcohol using ruthenium catalysts, namely [RuCl2(p-cymene)]2 (1), [Ru(OAc)2(p-cymene)] (3), and [RuCl(KA)(p-cymene)] (4), is described. A weak base acetate is essential for reduction performed in 2-propanol with [RuCl2(p-cymene)]2 (1) while reduction using the catalysts [Ru(OAc)2(p-cymene)] (3) and [RuCl(KA)(p-cymene)] (4) was performed without use of an external base and additive. This catalytic system works very well in aromatic and heteromatic aldehydes but does not work for reduction of ketone or aliphatic aldehyde. The catalyst 3 is shown to be more effective than [RuCl2(p-cymene)]2 in most of the reductions. This hydrogenation of aldehydes with catalyst 3 is highly promising; it precludes use of external base and an additive, and more importantly the reaction is performed under mild conditions in air, giving excellent yields. Study on hydrogenation of carbonyl compounds catalyzed by N\(^{\text{O}}\) and O\(^{\text{O}}\) chelate ruthenium(II) catalysts in water is under way in our laboratory.

EXPERIMENTAL

Representative Procedure for [RuCl2(p-cymene)]2-Catalyzed Reduction of Aldehydes

A dried Schlenck tube was loaded with [RuCl2(p-cymene)]2 (1) (0.0153 g, 0.025 mmol, 5 mol%), p-nitrobenzaldehyde (0.5 mmol), and benzamide or N-methyl benzamide (20 mol%). Solvent (2–3 mL) was added to this reaction mixture, and then the mixture was stirred at 80 °C for 8–12 h (2-propanol) or 16 h (when solvent was DMF). After that, the reaction mixture was rotary evaporated. The residue was purified over a silica-gel column using petroleum ether and ethyl acetate as eluent to give the compound 5a as light yellow solid (0.061 g, 80%).
Representative Procedure for Reduction of Aldehydes to Alcohol Using Ruthenium Catalysts \{[\text{Ru(OAc)}_2(\text{p-cymene})] (3) and [\text{RuCl(KA)(p-cymene)}] (4)\}

A dried Schlenck tube was loaded with complexes (3 or 4) (0.025 mmol, 5 mol\%\) and p-nitrobenzaldehyde (0.5 mmol). 2-Propanol (2–3 mL) was added to this reaction mixture, and then the mixture was stirred at 80 °C for 6 h, after which the reaction mixture was rotary evaporated and the residue was purified over a silica-gel column using petroleum ether and ethyl acetate as eluent to give the compound 5a as a light yellow solid (0.064 g, 84\% yield).

FTIR (KBr, cm$^{-1}$): 3523, 3113, 1602, 1526, 1056, 736; $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.23 (d, 2H, $J = 8.7$), 7.54 (d, 2H, $J = 8.7$), 4.84 (s, 2H); $^{13}$C NMR (CDCl$_3$, 75.47 MHz): $\delta$ 148.08, 126.99, 123.73, 64.02; HRMS (ESI): calculated for C$_7$H$_7$NO$_3$Na 176.0324 [M+Na]$^+$; found: 176.0339.

FUNDING

We thank the Department of Science and Technology (Grant No. SR/FT/CS-001/2010) and the Council of Scientific and Industrial Research (PSC0105), India, for support of this work and the Director of CSIR-NIO for providing the necessary facilities.

SUPPORTING INFORMATION

General experimental procedures, characterization data ($^1$H, $^{13}$C NMR, and HRMS) for alcohols, and copies of $^1$H and $^{13}$C NMR spectra for selected alcohols for this article can be accessed on the publisher’s website.

REFERENCES

1. Samec, J. S. M.; Bäckvall, J.-E.; Andersson, P. G.; Brandt, P. Chem. Soc. Rev. 2006, 35, 237–248.
2. Halpern, J.; Harrod, J. F.; James, B. R. J. Am. Chem. Soc. 1966, 88, 5150–5155.
3. Church, T. L.; Andersson, P. G. Coord. Chem. Rev. 2008, 252, 513–531.
4. Dayan, S.; Kalaycioglu, N. O.; Daran, J.; Labande, A.; Poli, R. Eur. J. Inorg. Chem. 2013, 3224–3232.
5. Delgado-Rebollo, M.; Canseco-Gonzalez, D.; Hollering, M.; Mueller-Bunz, H.; Albrecht, M. Dalton Trans. 2014, 43, 4462–4473.
6. Wei, Y.; Xue, D.; Lei, Q.; Wang, C.; Xiao, J. Green Chem. 2013, 15, 629–634.
7. Grabulosa, A.; Mannua, A.; Albericoc, E.; Denurra, S.; Gladiali, S.; Muller, G. J. Mol. Catal. A. 2012, 363–364, 49–57.
8. Cucciolito, M. E.; Panunzi, B.; Ruffo, F.; Tuzi, A. Tetrahedron Lett. 2013, 54, 1503–1506.
9. Clapham, S. E.; Hadzovic, A.; Morris, R. H. Coord. Chem. Rev. 2004, 248, 2201–2237.
10. Indra, A.; Maity, P.; Bhat, S.; Lahiri, G. K. ChemCatChem. 2013, 5, 322–330.
11. Dayan, S.; Kayac, N.; Kalaycioglu, N. O.; Dayan, O.; Öztürk, E. C. Inorg. Chim. Acta 2013, 401, 107–113.
12. Clapham, S. E.; Hadzovic, A.; Morris, R. H. Coord. Chem. Rev. 2004, 215, 73–79.
14. Touge, T.; Hakamata, T.; Nara, H.; Kobayashi, T.; Sayo, N.; Saito, T.; Kayaki, Y.; Ikariya, T. *J. Am. Chem. Soc.* 2011, 133, 14960–14963.
15. Haack, K. J.; Hashiguci, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed. Engl.* 1997, 36, 285–288.
16. Matsumura, K.; Hashiguchi, S.; Ikariya, T.; Noyori. *J. Am. Chem. Soc.* 1997, 119, 8738–8739.
17. Hashiguchi, S.; Fujii, A.; Haack, K.-J.; Matsumura, K.; Ikariya, T. Noyori, R. *Angew. Chem., Int. Ed. Engl.* 1997, 36, 288–290.
18. Jiang, Y.; Jiang, Q.; Zhang, X. *J. Am. Chem. Soc.* 1998, 120, 3817–3818.
19. Zotto, A. D.; Baratta, W.; Ballico, M.; Herdtweck, E.; Rigo, P. *Organometallics* 2007, 26, 5636–5642.
20. Mashima, K.; Kusano, K.-H.; Sato, N.; Matsumura, Y.-I.; Nozaki, K.; Kumobayashi, H.; Sayo, N.; Hori, Y.; Ishizaki, T. *J. Org. Chem.* 1994, 59, 3064–3076.
21. Canivet, J.; Süsß-Fink, G. *Green Chem.* 2007, 9, 391–397.
22. Basu, B., Mandal, B.; Das, S.; Das, P.; Nanda, A. K. *Beilstein J. Org. Chem.* 2008, 4, 53.
23. Huo, H.; Zhou, Z.; Zhang A.; Wu, L. *Res. Chem. Intermed.* 2012, 38, 261–268.
24. Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* 2006, 35, 226–236.
25. Zhao, M.; Yu, Z.; Yan, S.; Li, Y. *Tetrahedron Lett.* 2009, 50, 4624–4628.
26. Venkatachalam, G.; Ramesh, R. *Tetrahedron Lett.* 2005, 46, 5215–5218.
27. Kannan, S.; Ramesh, R.; Liu, Y. *J. Organomet. Chem.* 2007, 692, 3380–3391.
28. Arockiam, P. B.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. *Angew. Chem. Int. Ed.*, 2010, 49, 6629–6632.
29. Singh, K. S.; Dixneuf, P. H. *ChemCatChem.* 2013, 5, 1313–1316.
30. Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* 1974, 233–241.
31. Arockiam, P.; Poirier, V.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. *Green Chem.* 2009, 11, 1871–1875.
32. Singh, K. S.; Devi, P.; Svitlyk, V.; Mozharivskyj, Y. *Inorg. Chim. Acta* 2009, 362, 5252–5258.
33. Chowdhury, R. L.; Bäckvall, Jan-E. *J. Chem. Soc., Chem. Commun.* 1991, 1063–1064.
34. Singh, K. S.; Kaminsky, W. *Inorg. Chim. Acta* 2011, 365, 487–491.