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# Acceptorless and base-free dehydrogenation of alcohols mediated by a dipyridylamine-Ir(III) catalyst

Harikrishnan Jayaprakash, Liwei Guo, Shengdong Wang, Christian Bruneau, Cédric Fischmeister\*

Dedication ((optional))

**Abstract:** Several dipyridylamine-Ir(III) and dipyridylamine-Ru(II) complexes have been evaluated in the acceptorless dehydrogenation of alcohols in the absence of base additives. Iridium catalysts were found superior to ruthenium complexes and the nature of the bridging nitrogen in dipyridylamine ligands was also evidenced as a key parameter. Catalytic reactions were conducted in toluene but more sustainable solvents such as anisole and *p*-cymene were found suitable for this transformation.

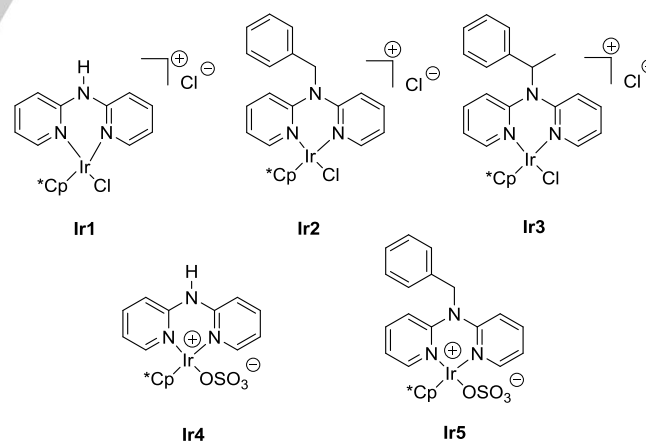
## Introduction

The catalytic dehydrogenation of alcohols<sup>[1]</sup> often quoted as oxidant free oxidation is for many reasons a very appealing oxidation process. Following the pioneering studies made by Robinson,<sup>[2]</sup> this reaction was quickly identified as a valuable route for the production of hydrogen.<sup>[3-5]</sup> The dehydrogenation of alcohols for the production of carbonyl compounds is more recent and has found numerous interesting applications in tandem and hydrogen-borrowing reactions for the synthesis of organic compounds<sup>[6]</sup> but also as a catalytic tool for the production of (bio)-alcohols via the Guerbet reaction.<sup>[7]</sup> The oxidation of alcohols through acceptorless dehydrogenation is a clean process as dihydrogen is the unique coproduct of the reaction. This reaction proceeds therefore with high atom economy unlike many stoichiometric oxidants (Cr and Mn compounds, Dess-Martin, Swern reagents..) used in organic synthesis and it does not require any oxidant (O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, RCO<sub>3</sub>H,...) when compared to other catalytic oxidation processes. A number of transition metal catalysts are known to promote the acceptorless dehydrogenation of alcohols<sup>[8-15]</sup> leading to ketone from secondary alcohols whereas primary alcohols do not always deliver the expected aldehydes and rather furnish ester derivatives. Among the catalyst reported so far, those operating under base- and additive-free conditions<sup>[9,11,13,15]</sup> are the most attractive as they generate less wastes and they tolerate reagents bearing base-sensitive functional groups. A survey of the catalysts operating under

base-free conditions shows that bifunctional catalysts bearing basic ligands such as pincer, carboxylate and other chelating ligands are employed. Alternatively, Kanai reported an original process for the room temperature acceptorless dehydrogenation of alcohols using a hybrid ternary catalytic system.<sup>[16]</sup> Recently, we have been interested in the synthesis of catalysts bearing chelating dipyridylamine ligands<sup>[17,18]</sup> in a number of catalytic transformations. 2,2-Dipyridylamine is a non-expensive commercially available compound and 2,2'-dipyridylamine derived ligands are easily accessible using simple synthetic procedures. We have developed a number of dpa-based catalysts that showed very good performances in hydrogenation reactions<sup>[19]</sup> and base-free dehydrogenation of formic acid<sup>[20]</sup> and nitrogen heterocycles.<sup>[21]</sup> These previous studies clearly demonstrated the high efficiency of this type of catalysts in hydrogenation and dehydrogenation processes and prompted us to investigate their potential in the acceptorless and base-free dehydrogenation of secondary and primary alcohols.

## Results and Discussion

The iridium-chloro catalysts **Ir1-3** and the zwitterionic iridium complexes **Ir4-5** were first evaluated as catalysts for the dehydrogenation of the model substrate 1-phenylethanol (Figure 1).



**Figure 1.** Ir-dpa complexes evaluated in the dehydrogenation of 1-phenylethanol

These catalysts were first screened in the base-assisted dehydrogenation of 1-phenylethanol at 130 °C in toluene (Scheme 1). This first set of experiments revealed the modest activity of these catalysts in particular for **Ir1**, **Ir4** and **Ir5** and

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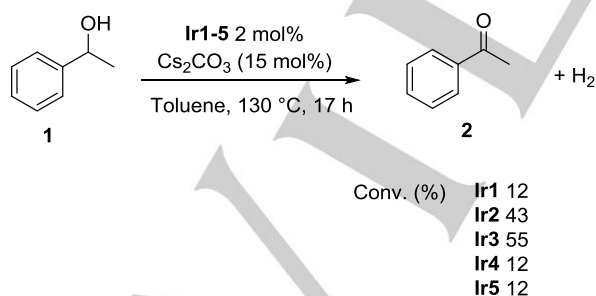
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**Table 1.** Dehydrogenation of 1-phenylethanol with **Ir2**. Screening of bases<sup>[a]</sup>

Entry	Base	Conversion (%) <sup>[b]</sup>
1	Cs <sub>2</sub> CO <sub>3</sub>	45
2	Na <sub>2</sub> CO <sub>3</sub>	29
3	K <sub>2</sub> CO <sub>3</sub>	20
4	KOAc	20
5	NaOAc	11
6	K <sub>3</sub> PO <sub>4</sub>	No conversion

[a] Reaction conditions: 1-phenylethanol (40 mg, 0.33 mmol), **Ir2** (4 mg, 0.006 mmol, 2 mol%), base (15 mol%), toluene (3 mL), 130 °C (oil bath), 17 h, argon flow. [b] Determined by gas chromatography. [c] A mixture of acetophenone **2** and 1,3-diphenylbutan-1-one was obtained in a 34/66 ratio as determined by gas chromatography.

demonstrated that Ir-Cl complexes **Ir2** and **Ir3** were more efficient than their Ir-OSO<sub>3</sub> counterparts. This result contrasts with our previous studies on the dehydrogenation reactions of formic acid and *N*-heterocycles for which Ir-OSO<sub>3</sub> catalysts surpassed their Ir-Cl counterparts.<sup>[20,21]</sup> The nature of the reagent may of course have a strong influence on the catalytic pathway but other parameters should also be considered as key parameters. Indeed, previous studies on formic acid and *N*-heterocycle dehydrogenations were conducted in water where ligand exchange (OSO<sub>3</sub>/H<sub>2</sub>O) was likely proceeding whereas decoordination of the -OSO<sub>3</sub> ligand might be more difficult in toluene. These results also emphasized the deleterious influence of a bridging N-H vs N-R in the dipyriddyamine ligand (**Ir1** and **Ir5**) hence also contrasting with the dehydrogenation of formic acid where the N-H moiety was necessary to ensure the best catalytic performances.<sup>[20]</sup>

**Scheme 1** Dehydrogenation of 1-phenylethanol (Conversion determined by gas chromatography)

Another parameter to consider to rationalize these results is the reaction pH. Whereas the dehydrogenation of formic acid was

performed under acidic conditions,<sup>[20]</sup> the dehydrogenation of 1-phenylethanol is conducted under alkaline media likely leading to the deprotonation of the bridging N-H hence transforming the neutral dipyriddyamine ligand into an anionic dipyriddyamine<sup>[22]</sup> and consequently to a new catalytic species. However, as reported hereafter in the base-free dehydrogenation study, this hypothesis may not be the unique answer to the poor activity of **Ir1** and **Ir4** since these two complexes presented again poor performances under base-free conditions (vide infra)

Having identified **Ir2** and **Ir3** as the most potent catalysts for the dehydrogenation of 1-phenylethanol, we turned our attention to the nature of the base. As depicted in Table 1, none of the inorganic bases tested led to better results than Cs<sub>2</sub>CO<sub>3</sub>. The same conclusion was obtained when **Ir3** was evaluated with the same inorganic bases (see ESI).

As emphasized in the introduction, base-free dehydrogenation of alcohols is strongly desired as these conditions guarantee the integrity of base-sensitive functional groups while minimizing wastes production. The dehydrogenation of 1-phenylethanol was attempted under base-free conditions and considering the issues raised here above, i.e. deprotonation of bridging N-H in dipyriddyamine ligand, all the catalysts were again evaluated under these pH neutral conditions. Our investigations demonstrated that the base-free dehydrogenation of 1-phenylethanol could be achieved with high conversion provided a higher reaction temperature and a longer reaction time were implemented. All reactions were conducted under a flow of argon as a simple open system failed to furnish good results (see ESI). This experimental observation is consistent with a gas (H<sub>2</sub>) release from the reaction medium. Of note, **Ir2** led to full conversion of 1-phenylethanol in refluxing toluene for 24 h (Table 2). It should be noted that despite the neutral condition, **Ir1**, and **Ir4** bearing the *NH*-dipyriddyamine ligand were yet inefficient as the zwitterionic *Bn*-dipyriddyamine **Ir5**. These results confirmed that zwitterionic complexes were not suitable for this transformation and that the NH-dipyriddyamine ligand was also unsuitable. In the latter case this result can no longer be explained by the deprotonation of the NH-dipyriddyamine ligand but may be related to the lower electron density at the metal in **Ir1** vs **Ir2** and **Ir3**, which was identified as an important parameter for the dehydrogenation of formic acid.<sup>[20]</sup> This result provides some hints for a possible reaction mechanism in which the basicity of the dipyriddyamine ligand would be a key parameter.

**Table 2.** Base-free dehydrogenation of 1-phenylethanol<sup>[a]</sup>

Entry	Catalyst	Conversion (%) <sup>[b]</sup>
1	<b>Ir1</b>	7
2	<b>Ir2</b>	100 (94) <sup>[c]</sup> (97) <sup>[d]</sup>
3	<b>Ir3</b>	80
4	<b>Ir4</b>	1
5	<b>Ir5</b>	7

[a] Reaction conditions: 1-phenylethanol (40 mg, 0.33 mmol), Catalyst (0.006 mmol, 2 mol%), refluxing toluene (140 °C, oil bath temperature), 24 h, argon flow. [b] Determined by gas chromatography. [c] 17 h at 140°C. [d] 17 h at 150 °C in xylenes.

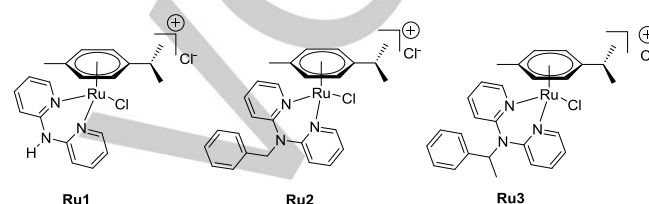
Further tests were performed with **Ir2** in order to identify the optimized reaction conditions (Table 3). This series of experiments demonstrated that 2 mol% of catalyst was the lowest catalyst loading acceptable to ensure high conversion in a reasonable amount of time and that a 1 M concentration of substrate was also an important requirement (Table 3, entries 4-6). Finally, greener and more sustainable solvents<sup>[23]</sup> such as anisole and *p*-cymene were evaluated and found to be suitable for this transformation whereas the reaction conducted in cyclopentylmethyl ether (CPME) led to poor conversion of 1-phenylethanol (Table 3, entries 7-9).

**Table 3.** Experimental condition optimisation<sup>[a]</sup>

Entry	Catalyst (mol%)	[1] (mol.L <sup>-1</sup> )	t (h)	Conversion (%) <sup>[b]</sup>
1	2	0.1	24	100
2	1	0.1	24	85
3	0.5	0.1	24	54
4	2	0.1	17	69
5	2	0.01	17	33
6	2	1	17	99
7 <sup>[c]</sup>	2	0.1	17	12
8 <sup>[d]</sup>	2	0.1	17	92
9 <sup>[e]</sup>	2	0.1	17	75

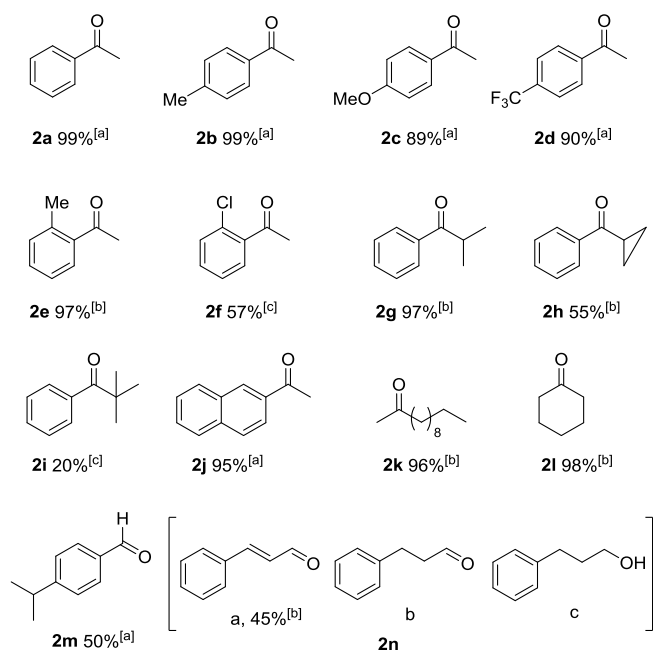
[a] Reaction conditions: 1-phenylethanol (40 mg, 0.33 mmol), **Ir2**, solvent, 140 °C (oil bath temperature), 24 h, argon flow. [b] Determined by gas chromatography. [c] CPME (110 °C) [d] Anisole [e] *p*-cymene

of alcohols. However due to the high cost of iridium metal, less expensive transition metals should also be amenable to perform this reaction. A few examples of ruthenium catalysts promoting the dehydrogenation of alcohols under base-free conditions have been reported.<sup>[11]</sup> They require in general high temperature (up to 165 °C) and long reaction times (up to 5 days) to reach high conversions. The ruthenium catalysts **Ru1-3** were evaluated in the base-free and base-assisted dehydrogenation of 1-phenylethanol (Figure 2). Under both type of experimental conditions, these catalysts displayed poor performances (see ESI). These results are in agreement with our previous studies on hydrogenation and dehydrogenation reactions where iridium catalysts always surpassed ruthenium catalysts.

**Figure 2** Ruthenium complexes

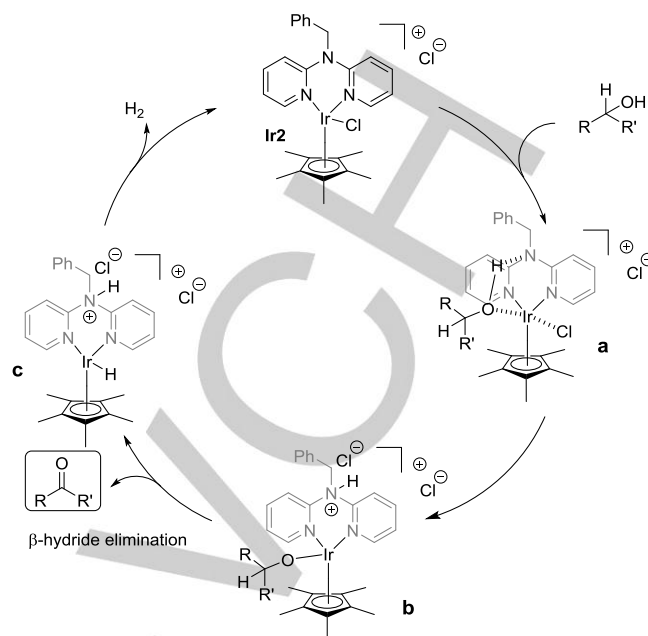
The scope and limitations of the base-free dehydrogenation of alcohols with **Ir2** was then investigated using a range of secondary alcohols. As depicted in Figure 3, 1-phenylethanol derivatives bearing an electron-donating or an electron-withdrawing group at the *para*-position were efficiently transformed into the corresponding alcohols (Figure 3, **2a-2d**) whereas steric hindrance at the *ortho*-position was problematic only with an electron-withdrawing substituent. Steric hindrance on the aliphatic side chain also showed some limitations upon moving from an isopropyl to a very bulky *t*-butyl substituent (Figure 3, **2g-2i**). To the best of our knowledge, the synthesis of compound **2i** by dehydrogenation of alcohol is unprecedented. Despite full conversion of the hydroxyl-precursor, the synthesis of **2h** was hampered by side reactions thus leading to a moderate yield of 55%. Notably, aliphatic secondary alcohols were efficiently converted to the corresponding ketones ((Figure 3, **2k-2l**). The challenging dehydrogenation of primary alcohols was also investigated. In this case, **2m** was obtained in a modest 50% yield whereas cinnamyl alcohol was fully converted but with poor selectivity as 2 products resulting from partial (**2nb**) of full reduction (**2nc**) of the expected product (**2na**) were detected by GC/MS leading to the isolation of **2na** in a modest 45% yield.

With respect to other transition metals, iridium-based complexes are in general the most performing catalysts in dehydrogenation



**Figure 3** Reaction scope with isolated yields (Reaction condition: substrate (0.33 mmol), Catalyst (2 mol%), argon flow. [a] refluxing toluene (140 °C, oil bath temperature), 24 h; [b] refluxing toluene, 17 h; [c] anisole, 150 °C, 24 h)

Based on the experimental results obtained during the screening of the various catalysts implemented in this study, a possible reaction mechanism is presented in Figure 4. As reported earlier in this manuscript, the activity of the catalyst was drastically improved when the dipyriddyamine ligand was made of a bridging tertiary amine vs secondary amine. This prompted us to propose a mechanism in which the basicity of the bridging nitrogen was a key parameter. Just like other bifunctional catalysts based on pincer ligands, the bridging nitrogen would play the role of a base abstracting the acidic proton of the alcohol thus leading to the possible intermediate **b**. Subsequent  $\beta$ -hydride elimination would release the ketone product leading to **c** and hydrogen extrusion would then regenerate **Ir2**. Another mechanism involving the decooordination of one of the pyridine ring that would act as a basic centre is also conceivable. Further experimental and theoretical studies will be necessary to shed light on the mechanism



**Figure 4** Proposed mechanism

## Conclusions

In conclusion, we have implemented an iridium catalyst for the acceptorless and base-free dehydrogenation of alcohols. This catalyst displays high efficiency in a number of alcohol dehydrogenation reactions performed under experimental conditions similar to those reported until now. However, by contrast to many of the recently reported catalysts based on complex ligand architectures, this catalyst is easily prepared from accessible compounds. Of note, the nature of dipyriddyamine ligand, particularly the substitution pattern at the bridging nitrogen turned to be a key parameter, as previously observed in the dehydrogenation of formic acid. We will take advantage of the tunability of the dipyriddyamine ligand to further improve the catalyst performances in organic media and in water.

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**Keywords:** dehydrogenation • alcohol • acceptorless • base-free • iridium

- [1] a) T. C. Johnson, D. J. Morris, M. Wills, *Chem. Soc. Rev.*, **2010**, 39, 81; b) G. E. Dabereiner, R. H. Crabtree, *Chem. Rev.*, **2010**, 110, 681.  
 [2] a) A. Dobson, S. D. Robinson, *J. Organomet. Chem.*, **1975**, 87, c52; b) A. Dobson, S. D. Robinson, *Inorg. Chem.*, **1977**, 16, 137.

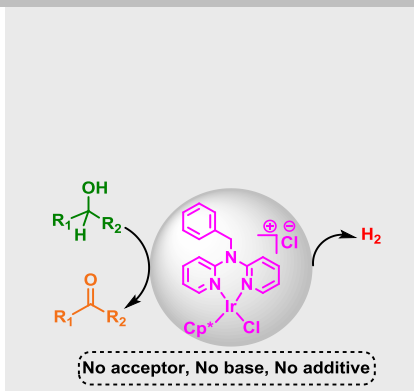
- [3] a) D. Morton, D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, **1987**, 249; b) D. Morton, D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, **1988**, 1155.
- [4] a) H. Junge, M. Beller, *Tetrahedron Lett.*, **2005**, *46*, 1031; b) H. Junge, B. Loges, M. Beller, *Chem. Commun.*, **2007**, 522; c) M. Nielsen, A. Kamer, D. Cozzula, H. Junge, S. Gladiali, M. Beller, *Angew. Chem. Int. Ed.*, **2011**, *50*, 9593; P. Sponholz, D. Mellmann, C. Cordes, P. G. Alsaheb, B. Li, Y. Li, M. Nielsen, H. Junge, P. Dixneuf, M. Beller, *ChemSusChem*, **2014**, *7*, 2419-2422.
- [5] a) A. Friedrich, S. Schneider, **2009**, *1*, 72; b) M. Trincado, D. Banerjee, H. Grützmacher, *Energy Environ. Sci.* **2014**, *7*, 2464; c) K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller, G. Laurenczy, *Chem. Rev.*, **2018**, *118*, 372-433.
- [6] For reviews, see: a) S. Bähn, S. Imm, L. Neubert, M. Zhang, H. Neumann, M. Beller, *ChemCatChem*, **2011**, *3*, 1853-1864; b) G. Guillena, D. J. Ramon, M. Yus, *Chem. Rev.*, **2010**, *110*, 1611-1641; c) M. H. S. A. Hamid, P. A. Slatford, J. M. J. Williams, *Adv. Synth. Catal.*, **2007**, *349*, 1555-1575; d) A. Quintard, J. Rodriguez, **2016**, *9*, 28-30; e) F. Huang, Z. Liu, Z. Yu, *Angew. Chem. Int. Ed.*, **2016**, *55*, 862-875.
- [7] H. Aitchison, R. L. Wingad, D. F. Wass, *ACS Catal.*, **2016**, *6*, 7125-7132.
- [8] Iridium catalysts: a) K.-E. Fujita, T. Yoshida, Y. Imori, N. T., R. Yamaguchi, *Org. Lett.*, **2011**, *13*, 2278-2281; b) S. Musa, I. Shaposhnikov, S. Cohen, D. Gelman, *Angew. Chem. Int. Ed.*, **2011**, *50*, 3533-3537; c) A. V. Polukeev, P. V. Petrovskii, A. S. Peregudov, M. G. Ezernitskaya, A. A. Koridze, *Organometallics*, **2013**, *32*, 1000-1015; d) S. Gilcernal, D. Gilcernal, G. F. S. Whitehead, J. Xiao, *Chem. Eur. J.* **2016**, *22*, 10513-10522; e) K.-i. Fujita, R. Tamura, Y. Tanaka, M. Yoshida, M. Onoda, R. Yamaguchi, *Organometallics*, **2017**, *7*, 7226-7230;
- [9] Iridium catalysts operating under base-free conditions: a) K.-E. Fujita, N. T., R. Yamaguchi, *Org. Lett.*, **2007**, *9*, 109-111; b) A. H. Ngo, M. J. Adams, L. H. Do, *Organometallics*, **2014**, *33*, 6742-6745; c) R. Kawahara, K.-E. Fujita, R. Yamaguchi, *Angew. Chem. Int. Ed.* **2012**, *51*, 12790-12794; d) G. Gonzalez Miera, E. Martínez-Castro, B. Martín-Matute, *Organometallics*, **2018**, *37*, 636; e) R. G. Alabau, M. A. Esteruelas, A. Martínez, M. Olivan, E. Oñate, *Organometallics*, **2018**, *37*, 2732-2740; f) Q. Wang, C.-H. Guo, X. Zhang, M. Zhu, H. Jiao, H.-S. Wu, *Eur. J. Org. Chem.*, **2019**, 3929-3936.
- [10] Ruthenium catalysts: a) G. B. W. L. Lighthart, R. H. Meijer, M. P. J. Donners, J. Meuldijk, J. A. J. M. Vekemans, L. A. Hulshof, *Tetrahedron Lett.*, **2003**, *44*, 1507-1509; b) J. Zhang, M. Gandelman, L. J. W. Shimon, H. Rozenberg, D. Milstein, *Organometallics*, **2004**, *23*, 4026-4033; c) G. R. A. Adait, J. M. Williams, *Tetrahedron Lett.*, **2005**, *46*, 8233-8235; d) W. Baratta, G. Bossi, E. Putignano, P. Rigo, *Chem. Eur. J.*, **2011**, *17*, 3474-3481; e) S. Shahane, C. Fischmeister, C. Bruneau, *Catal. Sci. Technol.*, **2012**, *2*, 1425-1428; f) J. Yuan, Y. Sun, G.-A. Yu, C. Zhao, N.-F. She, S.-L. Mao, P.-S. Huang, Z.-J. Han, J. Yin, S.-H. Liu, *Dalton Trans.*, **2012**, *41*, 10309-10316; g) I. Dutta, A. Sarbajna, P. Pandey, S. M. Wahidur Rahman, K. Singh, J. K. Bera, *Organometallics*, **2016**, *35*, 1505-1513; h) Z. Wang, B. Pan, Q. Liu, E. Yue, G. A. Solan, Y. Maa, W.-H. Sun, *Catal. Sci. Technol.*, **2017**, *7*, 1654-1661.
- [11] Ruthenium and osmium catalysts operating under base-free conditions: a) J. van Buijtenen, J. Meuldijk, J. A. J. M. Vekemans, L. A. Hulshof, H. Kooijman, A. L. Spek, *Organometallics*, **2006**, *25*, 873; b) J. Zhang, E. Balaraman, G. Leitus, D. Milstein, *Organometallics*, **2011**, *30*, 5716-5724; c) S. Muthaiah, S. H. Hong, *Adv. Synth. Catal.* **2012**, *354*, 3045-3053; d) K.-N. T. Tseng, J. W. Kampf, N.K. Szymczak, *Organometallics*, **2013**, *32*, 2046-2049; e) M. Delgado-Rebollo, D. Canseco-Gonzalez, M. Hollering, H. Mueller-Bunz M. Albrecht, *Dalton Trans.*, **2014**, *43*, 4462-4473; f) M. L. Buil, M. A. Esteruelas, M. Pilar Gay, M. Gomez-Gallego, A. I. Nicasio, E. Oñate, A. Santiago, M. A. Sierra, *Organometallics*, **2018**, *37*, 603-617;
- [12] Rhodium catalyst: a) X. Wang, C. Wang, Y. Liua, J. Xiao, *Green Chem.*, **2016**, *18*, 4605-4610; b) L. Munjanja, H. Yuan, W. W. Brennessel, W. D. Jones, *J. Organomet. Chem.*, **2017**, *847*, 28-32.
- [13] Cobalt catalysts, see: a) S. Xu, L. M. Althlhol, K. Paudel, E. Reinheimer, D. L. Tyer, D. K. Taylor, A. M. Smith, J. Holzmann, E. Lozano, K. Ding, *Inorg. Chem.* **2018**, *57*, 2394-2397.
- [13] Cobalt catalysts operating under base-free conditions, see: a) G. Zhang, K. V. Vasudevan, B. L. Scott, S. K. Hanson, *J. Am. Chem. Soc.*, **2013**, *135*, 8668-8681; b) G. Zhang, S. K. Hanson, *Org. Lett.*, **2013**, *15*, 650-653; c) S. Xu, L. M. Althlhol, K. Paudel, E. Reinheimer, D. L. Tyer, D. K. Taylor, A. M. Smith, J. Holzmann, E. Lozano, K. Ding, *Inorg. Chem.* **2018**, *57*, 2394-2397.
- [14] Iron catalysts, see: a) H. Song, B. Kang, S. H. Hong, *ACS Catal.*, **2014**, *4*, 2889-2895; b) S. Sinha, S. Das, R. Sikari, S. Parua, P. Brandaó, S. Demeshko, F. Meyer, N. D. Paul, *Inorg. Chem.* **2017**, *56*, 14084-14100.
- [15] Iron catalyst operating under base-free conditions: a) S. Chakraborty, P. O. Lagaditis, M. Förster, E. A. Bielinski, N. Hazari, M. C. Holthausen, W. D. Jones, S. Schneider, *ACS Catal.*, **2014**, *4*, 3994-4003.
- [16] H. Fuse, H. Mitsunuma, M. Kanai, *J. Am. Chem. Soc.* **2020**, *142*, 4493-4499.
- [17] S. Wang, C. Bruneau, J.-L. Renaud, S. Gaillard, C. Fischmeister, *Dalton Trans.* **2019**, *48*, 11599-11621.
- [18] For early reports on dpa-based catalysts, see: a) Courtois, R. Barhdadi, S. Condon, M. Troupel, *Tetrahedron Lett.*, **1999**, *40*, 5993-5996; b) K. Bolm, J.-C. Frison, J. L. Paih, C. Moessner, G. Raabe, *J. Organomet. Chem.*, **2004**, *689*, 3767-3777; c) Y. Hu, Y. Yu, Z. Hou, H. Li, X. Zhao, B. Feng, *Adv. Synth. Catal.*, **2008**, *350*, 2077-2085; d) P. Haquette, B. Dumat, B. Talbi, S. Arbabi, J.-L. Renaud, G. Jaouen, M. Salmain, *J. Organomet. Chem.* **2009**, *694*, 937-941; e) C. Romain, S. Gaillard, M. K. Elmekdem, L. Toupet, C. Fischmeister, C. M. Thomas, J.-L. Renaud, *Organometallics*, **2010**, *29*, 1992-1995.
- [19] a) S. Wang, V. Dorcet, T. Roisnel, C. Bruneau, C. Fischmeister, *Organometallics*, **2017**, *36*, 708-713; b) S. Wang, H. Huang, V. Dorcet, T. Roisnel, C. Bruneau, C. Fischmeister, *Organometallics*, **2017**, *36*, 3152-3162; c) S. Wang, H. Huang, C. Bruneau, C. Fischmeister, *ChemSusChem*, **2017**, *10*, 4150-4154; d) S. Wang, H. Huang, C. Bruneau, C. Fischmeister, *Catal. Sci. Technol.* **2019**, *9*, 4077-4082.
- [20] S. Wang, H. Huang, T. Roisnel, C. Bruneau, C. Fischmeister, *ChemSusChem*, **2019**, *12*, 179-184.
- [21] S. Wang, H. Huang, C. Bruneau, C. Fischmeister, *ChemSusChem*, **2019**, *12*, 2350-2354.
- [22] a) E. Sauvageot, P. Lafite, E. Duverger, R. Mariona, M. Hamelf, S. Gaillard, J.-L. Renaud, R. Daniellou, *J. Organomet. Chem.* **2016**, *808*, 122-127.
- [23] a) C. M. Alder, J. D. Hayler, R. K. Henderson, A. M. Redman, L. Shukla, L. E. Shuster, H. F. Sneddon, *Green Chem.* **2016**, *18*, 3879-3890; b) D. Prat, O. Pardigon, H.-W. Flemming, S. Letestu, V. Ducandas, P. Isnard, E. Guntrum, T. Senac, S. Ruisseau, P. Cruciani, P. Hosek, *Org. Process Res. Dev.* **2013**, *17*, 1517-1525; c) F. G. Delolo, E. N. dos Santos, E. V. Gusevskaya, *Green Chem.* **2019**, *21*, 1091-1098; d) A. V. Granato, A. G. dos Santos, *ChemSusChem*, **2017**, *10*, 1832-1837.

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