Transfer Hydrogenation of Carbonyl Derivatives Catalyzed by an Inexpensive Phosphine-Free Manganese Precatalyst

Antoine Bruneau-Voisine, Ding Wang, Vincent Dorcet, Thierry Roisnel, Christophe Darcel, Jean-Baptiste Sortais

Transfer hydrogenation of carbonyl derivatives catalyzed by an inexpensive phosphine-free manganese pre-catalyst.

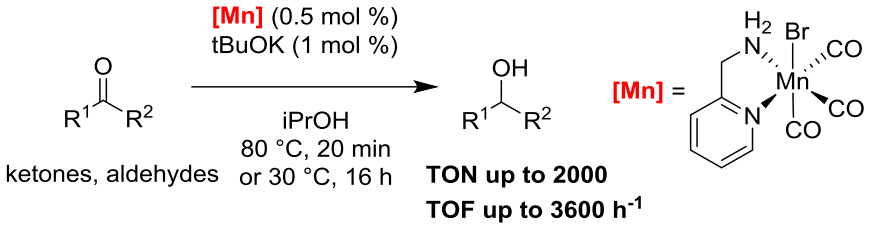
Antoine Bruneau-Voisine,[a] Ding Wang,[a] Vincent Dorcet,[b] Thierry Roisnel,[b] Christophe Darcel,[a] Jean-Baptiste Sortais [a,c,†*].

[a] Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Team Organometallics: Materials and Catalysis, 263 avenue du Général Leclerc, 35042 Rennes Cedex, France.

[b] Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Centre de Diffractométrie X, 263 avenue du Général Leclerc, 35042 Rennes Cedex, France.

[c] Institut Universitaire de France, 1 rue Descartes, 75231 Paris Cedex 05, France.

Supporting Information Placeholder



ABSTRACT: A very simple and inexpensive catalytic system based on abundant manganese as transition metal and on an inexpensive phosphine-free bidendate ligand, 2-aminomethylpyridine, has been developed for the reduction of a large variety of carbonyl derivatives with isopropanol as hydrogen donor. Remarkably, the reaction proceeds at room temperature, with low catalyst loading (down to 0.1 mol %) and exhibits a good tolerance toward functional groups. High TON (2000) and TOF (3600 h^{-1}) were obtained.

The development of non-noble metal based catalytic systems has been increasing for more than a decade, notably in the field of reduction reactions or hydroelementation.[1] Tremendous progress have been accomplished in the case of iron[2] and cobalt.[3] In the case of manganese,[4] which is the third most abundant transition metal after iron and titanium, until recently the reduction of C=O bond was limited to the hydrosilylation of carbonyl derivatives,[5] the hydroboration,[6] and electrochemical reduction of CO_2.[7]

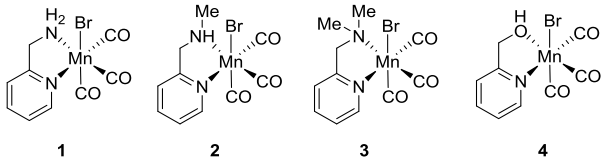
The development of efficient catalytic systems based on manganese for reduction reactions was opened by Beller in 2016, who reported the first examples of hydrogenation of ketones, esters and nitriles using a tridendate aliphatic $[(iPr)_2PCH_2CH_2]_2NH$ ligand.[8] In the case of hydrogen transfer reactions, Beller has recently reported that dipicolylamine manganese pincer complex could promote the hydrogen transfer of ketones in isopropanol at 70 °C in 24 h.[9] The potential of pincer type ligands with manganese in redox reactions was reinforced mainly by the studies of Milstein,[10] Kempe,[11] Kirchner,[12] Boncella[13] and us,[14] with pyridinyl-core PNP and PN^3P ligands and triazinyl-core PN^5P ligands. However, one major drawback of these phosphorus pincer type ligands used in catalysis with non-precious metals is the cost of the ligand which is overwhelming the price of the metal precursors.

In the quest for simple and inexpensive catalytic systems, we were looking for alternative ligands, suitable to promote bi-functional catalysts.[15] We were inspired by ruthenium catalysis, and in particular the work of Baratta who demonstrated that simple bidendate aminomethylpyridine ligand (ampy) could significantly improve the activity and the robustness of ruthenium hydrogen transfer catalysts, reaching very high TON and TOF.[16]

In the present contribution, we have demonstrated that well-defined manganese complexes featuring a bidentate ampy ligand are highly efficient catalysts for hydrogen transfer of ketones and aldehydes at room temperature, with TOF up to 3600 h^{-1} and TON up to 2000.

We have first prepared a series of four manganese complexes, bearing as ligand 2-hydroxymethylpyridine, 2-aminomethylpyridine, 2-(*N*-methyl-aminomethyl)-pyridine and 2-(*N*,*N*-dimethyl-aminomethyl)pyridine (Scheme 1). The synthesis of the complexes is straightforward: for aminomethylpyridine derivatives, complexes **1**-**3** were obtained as yellow solids with good yields (93-95%) by reaction of one equivalent of the ligand with one equivalent of $Mn(CO)_5Br$ in toluene at 110 °C for 4 h. Complex **4** was prepared in hexane at 70 °C as described by Miguel.[17] Complexes **1**-**3** were fully characterized by NMR spectroscopies, IR and elemental analysis. The molecular structures were confirmed by X-Ray diffraction studies on single crystals (Figure 1).[18] These complexes are fairly stable under air, but slowly decompose under exposure to light.

Scheme 1. Well-defined Manganese complexes used in this study.



1 2 3 4

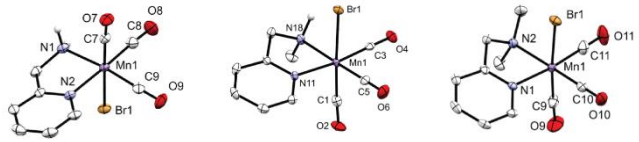
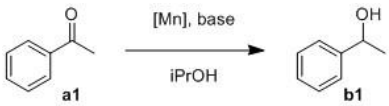


Figure 1: Perspective views of the molecular structures of complexes **1** (left), **2** (middle) and **3** (right), with thermal ellipsoids drawn at 50% probability. Hydrogens, except the NH, were omitted for clarity.

We then explored the catalytic activities of complex **1** for the reduction of acetophenone **a1** in the presence of isopropanol as the hydrogen source. To our delight, with 1 mol % of **1**, 2 mol % of tBuOK as the base, at 80 °C, within 5 min, we observed a full reduction of the ketone to the corresponding 1-phenylethanol **b1** (Table 1, entry 1). The catalyst loading was then decreased to 0.1 mol %, leading to a conversion of 31% and 58%, after 5 and 10 min respectively (TOF = 3720 and 3480 h^{-1}, respectively). An average TOF of 3600 h^{-1} was obtained, demonstrating the high activity of complex **1**. With a very low catalyst loading of 0.01 mol %, a TON of 2000 was achieved after 16 h (entry 5). Encouraged by these results, the temperature was then decreased to room temperature. With 0.5 mol % of catalyst, after 3 h, 50% of the ketone was reduced and a full conversion was obtained after 16 h (entry 7). Even with a substrate: catalyst ratio of 1000, the reduction of acetophenone was still achieved in 90% conversion (entry 8). Control experiments (entries 9-12) demonstrated that all the components of the catalytic system were crucial to obtain high activities.[19] Compared to catalyst **1**, catalyst **2**, bearing one methyl substituent on the amine moieties, was found slightly less active (See S.I.) than **1** and catalysts **3** and **4** showed very low activities (entries 14, 15). These results show that the presence of NH moieties on the ligand is crucial for the hydrogen transfer to occur.

Table 1: Optimization of the reaction parameters[a]

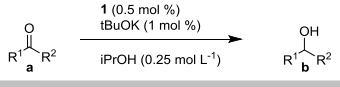


entry	cat. (mol %)	tBuOK (mol %)	temp (°C)	time	conv (%)
1	**1** (1)	2	80	5 min	> 97
2	**1** (0.5)	1	80	15 min	> 97
3	**1** (0.1)	0.2	80	5 min	31
				10 min	58
				2 h	> 97
4	**1** (0.05)	0.1	80	2 h 30	80
5	**1** (0.01)	0.02	80	16 h	20
6	**1** (0.5)	1	60	1 h	96
7	**1** (0.5)	1	30	3 h	50
				16 h	97
8	**1** (0.1)	0.2	30	19 h	90
9	**1** (1)	-	80	1 h	0
10	-	10	80	1 h	5
11	Ampy (1)	2	80	1 h	0
12	$Mn(CO)_5Br$ (1)	2	80	1 h	< 1
13	**2** (0.5)	1	80	15 min	97
14	**3** (0.5)	1	80	30 min	8
15	**4** (0.5)	1	80	20 min	6

[a] Typical conditions: To a Schlenk tube, under argon, were added in this order: catalyst precursor, iPrOH (2 mL), acetophenone (0.5 mmol) and tBuOK. The conversion was determined by GC and ^{1}H NMR.

The generality of the reaction was then probed using two optimal conditions: 80 °C, 20 min or 30 °C, 16 h, 0.5 mol % of **1** and 1 mol % of tBuOK (Table 2). In general, the reaction proceeded well with a large range of substrates. Steric hindrance was well tolerated as from acetophenone to pivalophenone or 2-methylacetophenone, high yield of the corresponding alcohols were obtained (entries 1-6). Aromatic ketones bearing electron donating groups (entries 6-9) were reduced with high yield. Interestingly, aromatic aldehydes were also converted nicely to the corresponding benzylalcohols (entries 10-11), with almost no side reactions[16d] (in the case of 4-phenylbenzaldehyde, less than 5% of the product of the aldol condensation of the aldehyde with acetone was detected in the crude NMR). Halogen-containing substrates are suitable for this reduction without formation of dehalogenated products (entries 12-17). Functional group tolerance was then evaluated: cyano, nitro, amino, amido and ester were tolerated (entries 18-24). In the case of ethyl levunilate (entry 24, 98% conversion), a mixture of cyclic γ-valerolactone (84%) and linear isopropyl-4-hydroxy-pentanoate (16 %), resulting from trans-esterification, was obtained. Aliphatic and cyclic ketones were fully converted to the corresponding alcohols (entries 25-29). Conjugated α,β-unsaturated ketones were reduced to the corresponding unsaturated alcohols with high selectivity, as the sole reduction of the carbonyl moieties was observed in the case of β-ionone (entry 31), and only 5% of the saturated alcohol was detected in the case of cinnamyl-ketone (entry 30). For very challenging cinnamaldehyde (entry 32), the chemoselectivity was perfect toward the allylic alcohol and less than 7% of aldol consendation by-products were detected after 2 h at 80 °C. Finally, heteroaromatic ketones were tested: thiophenyl derivative was fully reduced to the corresponding alcohol (entry 33), while 4-acetyl pyridine led to moderate conversion at 80 °C and almost no conversion at 30 °C (entry 34). The bidentate 2-acetyl-pyridine poisoned the catalyst, and little conversion was observed under both conditions (entry 35). The same limitation was observed in the case of 2-acetylfurane and several 1,3-diketones.[20]

Table 2: Scope of the hydrogen transfer of ketones to give alcohols under the catalysis of 1.[a]

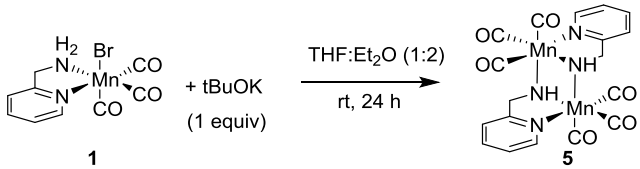


entry	substrate	product		conv (yield) at 80 °C, 20 min	conv (yield) at 30 °C, 16 h
1			**b1**, X = H, Y = Me	> 99 (93)	> 99
2			**b2**, X = H, Y = Et	99	99 (84)
3			**b3**, X = H, Y = iPr	> 99 (95)	> 99
4			**b4**, X = H, Y = tBu	92	99 (99)
5			**b5**, X = H, Y = cyclopropyl	77 (62)	50
6			**b6**, X = 2-Me, Y = Me	94 (88)	75
7			**b7**, X = 4-Me, Y = Me	95 (87)	87
8			**b8**	97	94 (89)
9			**b9**, X = 4-OMe Y = Me	83	66
10			**b10**, X = 3,4,5-$(OMe)_3$ Y = H	> 99 (99)	62[b]
11			**b11**, X = 4-Ph, Y = H	> 99[c] (92)	99
12			**b12**, X = 4-I, Y = Me	26	> 99 (99)[d]
13			**b13**, X = 4-Br, Y = Me	98	98 (87)
14			**b14**, X = 2-Cl, Y = Me	> 99	> 99 (99)
15			**b15**, X = 4-F, Y = Me	96(85)	91
16			**b16**, X = 4-CF_3, Y = Me	> 99	> 99 (96)
17			**b17**, X = H, Y = CF_3	> 99 (58)	20
18			**b18**, X = 4-CN, Y = Me	> 99	89 (78)
19			**b19**, X = 4-NO_2, Y = Me	97	> 99 (99)
20			**b20**, X = 4-N⟨⟩O Y = Me	73	30
21			**b21**, X = NEt_2, Y = H	97 (83)	74
22			**b22**, X = NH_2, Y = Me	82	58[e]
23			**b23**, X = NHC(O)CH_3, Y = H	95 > 99 (90)[c, f]	26
24			**b24**	98[g]	41[g]
25			**b25**	95 (93)	80
26			**b26**, n = 1	> 99 (99)	> 99
27			**b27**, n = 2	96	94 (94)
28			**b28**	73 > 99 (99)[h]	25
29			**b29**	67	50
30			**b30**	90[i]	92 (87)
31			**b31**	81 100 (90)[f]	87
32			**b32**	92 (80) [j]	5
33			**b33**	94 96 (96)[f]	80
34			**b34**, 4-acetyl	56	11
35			**b35**, 2-acetyl	13	10

[a] Typical conditions: To a Schlenk tube, under argon, were added in this order: catalyst **1**, iPrOH (0.25 $molL^{-1}$), ketone or aldehyde (0.5 or 2 mmol) and tBuOK. The conversion was determined by ^1H NMR on the crude mixture. Isolated yield in parentheses; [b] selectivity alcohol: aldol by-products of 67:33. [c] 5% of aldol condensation by-product were detected in the crude mixture; [d] one week, due to low solubility of the starting material; [e] 72 h; [f] 1 h; [g] selectivity γ-valerolactone/Isopropyl-4-hydroxypentanoate 84/16 at 80 °C and 77/23 at 30 °C; [h] 2 h, iPrOH 4 mL; [i] enol 95%, 4-phenylbutan-2-ol 5%; [j] 2 h, 7 % aldol condensation by-products were detected in the crude mixture.

Then, to gain insight into the nature of the catalytic active species, we performed stoichiometric reactions between complex **1** and the base.[21] After 24 h at room temperature, the dimeric manganese complex **5,** resulting from the deprotonation of the NH moieties, could be isolated in 42% yield. (Scheme 2).[5k] A similar dimer was obtained by Miguel starting from 2-pyridinemethanol.[17] The molecular structure of **5** was confirmed by X-Ray diffraction studies (Figure 2).[22] Unfortunately, further reactions of **5** with isopropanol or **1** with $NaBH_4$, did not allow the characterization of any manganese hydride intermediate.

Scheme 2. Synthesis of dimer 5.



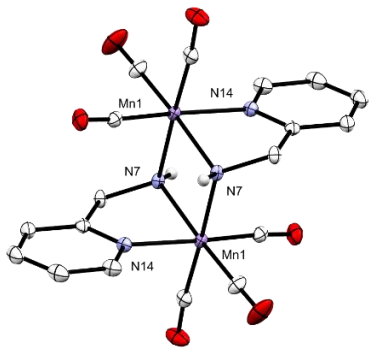


Figure 2: Perspective view of the molecular structure of complex **5**, with thermal ellipsoids drawn at 50% probability. Hydrogens, except the NH, were omitted for clarity.

Finally, complex **5**, was tested as catalyst without addition of external base under standard conditions: with 0.5 mol % of **5**, at 80 °C after 90 min, acetophenone was fully reduced to 1-phenylethanol. The corresponding deprotonated monomer, formed by the dissociation of the dimer, is likely the intermediate of the catalytic cycle, which is in line with mechanism of ligand-assisted hydrogen transfer reactions.

In conclusion, we have developed an highly efficient and simple catalytic system for the reduction by hydrogen transfer of ketones and aldehydes, including α,β-unsaturated aldehydes, at room temperature, based on phosphine-free bidendate aminomethyl pyridine ligand. High TON (2000) and TOF (3600 h^{-1}) were achieved with this catalytic system.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Experimental procedures, full characterization data, including X-Ray data and NMR spectra of all the compounds (PDF)

AUTHOR INFORMATION

Corresponding Author

Jean-Baptiste Sortais, jean-baptiste.sortais@lcc-toulouse.fr

Present Addresses

† LCC-CNRS, Université de Toulouse, INPT, UPS, 205 route de Narbonne 31077 Toulouse Cedex 4, France.

Author Contributions

The manuscript was written through contributions of all authors.

ACKNOWLEDGMENT

We thank the Centre National de la Recherche Scientifique (CNRS), the Université de Rennes 1, Fonds Européens de développement économique régional (FEDER founds), INCREASE FR-CNRS 3707, la Fondation Rennes 1 (grant to D.W.) and the Agence National de la Recherche (ANR agency, program JCJC ANR-15-CE07-0001 "Ferracycles").

REFERENCES

(1). (a) Bullock, M., *Catalysis without Precious Metals*. Wiley-VCH: Weinheim, 2010; (b) Bullock, R. M., *Science* **2013,** *342*, 1054-1055.

(2). (a) Bauer, E., *Iron catalysis II*. Springer: Heidelberg, 2015; Vol. 50; (b) Bauer, I.; Knölker, H.-J., *Chem. Rev.* **2015,** *115*, 3170-3387; (c) Misal Castro, L. C.; Li, H.; Sortais, J.-B.; Darcel, C., *Green Chem.* **2015,** *17*, 2283-2303; (d) Morris, R. H., *Acc. Chem. Res.* **2015,** *48*, 1494-1502.

(3). (a) Chirik, P. J., *Acc. Chem. Res.* **2015,** *48*, 1687-1695; (b) Gandeepan, P.; Cheng, C.-H., *Acc. Chem. Res.* **2015,** *48*, 1194-1206; (c) Gao, K.; Yoshikai, N., *Acc. Chem. Res.* **2014,** *47*, 1208-1219.

(4). (a) Valyaev, D. A.; Lavigne, G.; Lugan, N., *Coord. Chem. Rev.* **2016,** *308*, 191-235; (b) Khusnutdinov, R. I.; Bayguzina, A. R.; Dzhemilev, U. M., *Russ. J. Org. Chem.* **2012,** *48*, 309-348.

(5). (a) Mukhopadhyay, T. K.; Flores, M.; Groy, T. L.; Trovitch, R. J., *J. Am. Chem. Soc.* **2014,** *136*, 882-885; (b) Trovitch, R. J., *Synlett* **2014,** *25*, 1638-1642; (c) Ghosh, C.; Mukhopadhyay, T. K.; Flores, M.; Groy, T. L.; Trovitch, R. J., *Inorg. Chem.* **2015,** *54*, 10398-10406; (d) Zheng, J.; Chevance, S.; Darcel, C.; Sortais, J.-B., *Chem. Commun.* **2013,** *49*, 10010-10012; (e) Zheng, J.; Elangovan, S.; Valyaev, D. A.; Brousses, R.; César, V.; Sortais, J.-B.; Darcel, C.; Lugan, N.; Lavigne, G., *Adv. Synth. Catal.* **2014,** *356*, 1093-1097; (f) Valyaev, D. A.; Wei, D.; Elangovan, S.; Cavailles, M.; Dorcet, V.; Sortais, J.-B.; Darcel, C.; Lugan, N., *Organometallics* **2016,** *35*, 4090-4098; (g) Mao, Z.; Gregg, B. T.; Cutler, A. R., *J. Am. Chem. Soc.* **1995,** *117*, 10139-10140; (h) DiBiase Cavanaugh, M.; Gregg, B. T.; Cutler, A. R., *Organometallics* **1996,** *15*, 2764-2769; (i) Son, S. U.; Paik, S.-J.; Lee, I. S.; Lee, Y.-A.; Chung, Y. K.; Seok, W. K.; Lee, H. N., *Organometallics* **1999,** *18*, 4114-4118; (j) Arias-Ugarte, R.; Sharma, H. K.; Morris, A. L. C.; Pannell, K. H., *J. Am. Chem. Soc.* **2012,** *134*, 848-851; (k) Mukhopadhyay, T. K.; Rock, C. L.; Hong, M.; Ashley, D. C.; Groy, T. L.; Baik, M.-H.; Trovitch, R. J., *J. Am. Chem. Soc.* **2017,** *139*, 4901-4915.

(6). Zhang, G.; Zeng, H.; Wu, J.; Yin, Z.; Zheng, S.; Fettinger, J. C., *Angew. Chem. Int. Ed.* **2016,** *55*, 14369-14372.

(7). (a) Mukhopadhyay, T. K.; MacLean, N. L.; Gan, L.; Ashley, D. C.; Groy, T. L.; Baik, M.-H.; Jones, A. K.; Trovitch, R. J., *Inorg. Chem.* **2015,** *54*, 4475-4482; (b) Bourrez, M.; Molton, F.; Chardon-Noblat, S.; Deronzier, A., *Angew. Chem. Int. Ed.* **2011,** *50*, 9903-9906; (c) Smieja, J. M.; Sampson, M. D.; Grice, K. A.; Benson, E. E.; Froehlich, J. D.; Kubiak, C. P., *Inorg. Chem.* **2013,** *52*, 2484-2491; (d) Franco, F.; Cometto, C.; Ferrero Vallana, F.; Sordello, F.; Priola, E.; Minero, C.; Nervi, C.; Gobetto, R., *Chem. Commun.* **2014,** *50*, 14670-14673; (e) Walsh, J. J.; Neri, G.; Smith, C. L.; Cowan, A. J., *Chem. Commun.* **2014,** *50*, 12698-12701; (f) Takeda, H.; Koizumi, H.; Okamoto, K.; Ishitani, O., *Chem. Commun.* **2014,** *50*, 1491-1493; (g) Sampson, M. D.; Nguyen, A. D.; Grice, K. A.; Moore, C. E.; Rheingold, A. L.; Kubiak, C. P., *J. Am. Chem. Soc.* **2014,** *136*, 5460-5471; (h) Cheung, P. L.; Machan, C. W.; Malkhasian, A. Y. S.; Agarwal, J.; Kubiak, C. P., *Inorg. Chem.* **2016,** *55*, 3192-3198; (i) Sampson, M. D.; Kubiak, C. P., *J. Am. Chem. Soc.* **2016,** *138*, 1386-1393.

(8). (a) Elangovan, S.; Topf, C.; Fischer, S.; Jiao, H.; Spannenberg, A.; Baumann, W.; Ludwig, R.; Junge, K.; Beller, M., *J. Am. Chem. Soc.* **2016,** *138*, 8809-8814; (b) Elangovan, S.; Garbe, M.; Jiao, H.; Spannenberg, A.; Junge, K.; Beller, M., *Angew. Chem. Int. Ed.* **2016,** *55*, 15364-15368; (c) Elangovan, S.; Neumann, J.; Sortais, J.-B.; Junge, K.; Darcel, C.; Beller, M., *Nat. Commun.* **2016,** *7*, 12641; (d) Peña-López, M.; Piehl, P.; Elangovan, S.; Neumann, H.; Beller, M., *Angew. Chem. Int. Ed.* **2016,** *55*, 14967-14971; (e) Andérez-Fernández, M.; Vogt, L. K.; Fischer, S.; Zhou, W.; Jiao, H.; Garbe, M.; Elangovan, S.; Junge, K.; Junge, H.; Ludwig, R.; Beller, M., *Angew. Chem. Int. Ed.* **2017,** *56*, 559-562; (f) Neumann, J.; Elangovan, S.; Spannenberg, A.; Junge, K.; Beller, M., *Chem. Eur. J.* **2017,** *23*, 5410-5413; (g) Papa, V.; Cabrero-Antonino, J. R.; Alberico, E.; Spanneberg, A.; Junge, K.; Junge, H.; Beller, M., *Chem. Sci.* **2017**; (h) Nguyen, D. H.; Trivelli, X.; Capet, F.; Paul, J.-F.; Dumeignil, F.; Gauvin, R. M., *ACS Catal.* **2017,** *7*, 2022-2032.

(9). Perez, M.; Elangovan, S.; Spannenberg, A.; Junge, K.; Beller, M., *ChemSusChem* **2017,** *10*, 83-86.

(10). (a) Mukherjee, A.; Nerush, A.; Leitus, G.; Shimon, L. J. W.; Ben David, Y.; Espinosa Jalapa, N. A.; Milstein, D., *J. Am. Chem. Soc.* **2016,** *138*, 4298-4301; (b) Espinosa-Jalapa, N. A.; Nerush, A.; Shimon, L. J. W.; Leitus, G.; Avram, L.; Ben-David, Y.; Milstein, D., *Chem. Eur. J.* **2017,** *23*, 5934-5938; (c) Chakraborty, S.; Gellrich, U.; Diskin-Posner, Y.; Leitus, G.; Avram, L.; Milstein, D., *Angew. Chem. Int. Ed. Engl.* **2017,** *56*, 4229-4233.

(11). (a) Kallmeier, F.; Irrgang, T.; Dietel, T.; Kempe, R., *Angew. Chem. Int. Ed.* **2016,** *55*, 11806-11809; (b) Deibl, N.; Kempe, R., *Angew. Chem. Int. Ed.* **2017,** *56*, 1663-1666.

(12). (a) Mastalir, M.; Glatz, M.; Gorgas, N.; Stöger, B.; Pittenauer, E.; Allmaier, G.; Veiros, L. F.; Kirchner, K., *Chem. Eur. J.* **2016,** *22*, 12316-12320; (b) Mastalir, M.; Glatz, M.; Pittenauer, E.; Allmaier, G.; Kirchner, K., *J. Am. Chem. Soc.* **2016,** *138*, 15543-15546.

(13). (a) Tondreau, A. M.; Boncella, J. M., *Organometallics* **2016,** *35*, 2049-2052; (b) Tondreau, A. M.; Boncella, J. M., *Polyhedron* **2016,** *116*, 96-104.

(14). (a) Bruneau-Voisine, A.; Wang, D.; Dorcet, V.; Roisnel, T.; Darcel, C.; Sortais, J.-B., *J. Catal.* **2017,** *347*, 57-62; (b) Bruneau-Voisine, A.; Wang, D.; Roisnel, T.; Darcel, C.; Sortais, J.-B., *Catal. Commun.* **2017,** *92*, 1-4.

(15). (a) Doucet, H.; Ohkuma, T.; Murata, K.; Yokozawa, T.; Kozawa, M.; Katayama, E.; England, A. F.; Ikariya, T.; Noyori, R., *Angew. Chem. Int. Ed.* **1998,** *37*, 1703-1707; (b) Noyori, R.; Yamakawa, M.; Hashiguchi, S., *J. Org. Chem.* **2001,** *66*, 7931-7944; (c) Zhao, B.; Han, Z.; Ding, K., *Angew. Chem. Int. Ed.* **2013,** *52*, 4744-4788.

(16). (a) Putignano, E.; Bossi, G.; Rigo, P.; Baratta, W., *Organometallics* **2012,** *31*, 1133-1142; (b) Zhang, S.; Baldino, S.; Baratta, W., *Organometallics* **2013,** *32*, 5299-5304; (c) Chelucci, G.; Baldino, S.; Baratta, W., *Coord. Chem. Rev.* **2015,** *300*, 29-85; (d) Baldino, S.; Facchetti, S.; Zanotti-Gerosa, A.; Nedden, H. G.; Baratta, W., *ChemCatChem* **2016,** *8*, 2279-2288; (e) Solinas, M.; Sechi, B.; Baldino, S.; Baratta, W.; Chelucci, G., *ChemistrySelect* **2016,** *1*, 2492-2497; (f) Baratta, W.; Rigo, P., *Eur. J. Inorg. Chem.* **2008,** *2008*, 4041-4053; (g) Baratta, W.; Herdtweck, E.; Siega, K.; Toniutti, M.; Rigo, P., *Organometallics* **2005,** *24*, 1660-1669.

(17). Alvarez, C. M.; Carrillo, R.; Garcia-Rodriguez, R.; Miguel, D., *Chem. Commun.* **2012,** *48*, 7705-7707.

(18). CCDC numbers 1545746 for 1, 1545749 for 2 and 1545748 for 3

(19). Ouali, A.; Majoral, J.-P.; Caminade, A.-M.; Taillefer, M., *ChemCatChem* **2009,** *1*, 504-509.

(20). Wei, D.; Roisnel, T.; Darcel, C.; Clot, E.; Sortais, J.-B., *ChemCatChem* **2017,** *9*, 80-83.

(21). Spasyuk, D.; Smith, S.; Gusev, D. G., *Angew. Chem. Int. Ed.* **2012,** *51*, 2772-2775.

(22). CCDC number 1545747.