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Thioether–NHC bidentate manganese complexes as efficient phosphine-free catalysts for hydrogenation at room temperature†

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A series of four original phosphine-free thioether–NHC manganese complexes have been synthesised and fully characterized. These complexes have been applied as efficient catalysts for the hydrogenation of alkenes and ketones at room temperature, with low catalyst loadings (TON up to 900).

Hydrogenation or hydrogen transfer reactions using manganese complexes as pre-catalysts have developed significantly in recent years.[1] Among the advantages of these systems, the abundant and non-critical nature of manganese is an important criterion that explains the enthusiasm it has aroused in recent years for its use in sustainable catalytic systems, as is the ease with which pre-catalysts can be synthesised from the precursor $Mn(CO)_5Br$ and the stability of the resulting catalysts. These systems have mainly been investigated for the reduction of polar functional groups (ketones, imines, esters, aldehydes, nitriles, *etc.*), with tridentate ligands bearing either an acidic NH function[2] or a central N-heterocycle being involved in the cooperative metal–ligand activation of the reductant (dihydrogen or iPrOH-type hydrogen donor),[3,4] in line with the polar nature of the functional groups.

In contrast, apolar substrates, such as alkenes[5–7] and alkynes,[8,9] have been much less studied in homogeneous catalysis with manganese. In 2018, Jacobi von Wangelin used $[Mn(N(SiMe_3)_2)_2]$ in the presence of Dibal-H as a reductant to generate an Mn_6 nanocluster that proved efficient for the hydrogenation of alkenes under mild conditions (Chart 1).[10,11] A year later, the combination of the same complex with phenylacetylene also proved to be active for the hydrogenation of a few alkenes under relatively mild conditions, most probably through the generation of Mn nanoparticles.[11] The same year, Kirchner described the first well-defined Mn complex for alkene hydrogenation, an Mn-alkyl complex bearing a bis-dialkylphosphine ligand.[12] This complex, obtained following a reduction step with sodium, enables alkenes to be reduced in 24 h with a 2 mol% catalytic loading under 50 bar H_2 at 25–60 °C. In 2020, Khusnutdinova reported that bidentate pyridine–phosphine ligands can also promote this reaction, but under harsher conditions.[13] More recently, Beller's group illustrated the possibility of introducing bis-NHC as a phosphine-free ligand, which was a breakthrough, although the reaction temperature remained rather high (80–100 °C).[14] Finally, this year, Kirchner showed that catalytic loadings could be reduced to 0.25 mol% with tridentate P–NHC–P ligands, provided that the reaction temperature was held at 100 °C.[15]

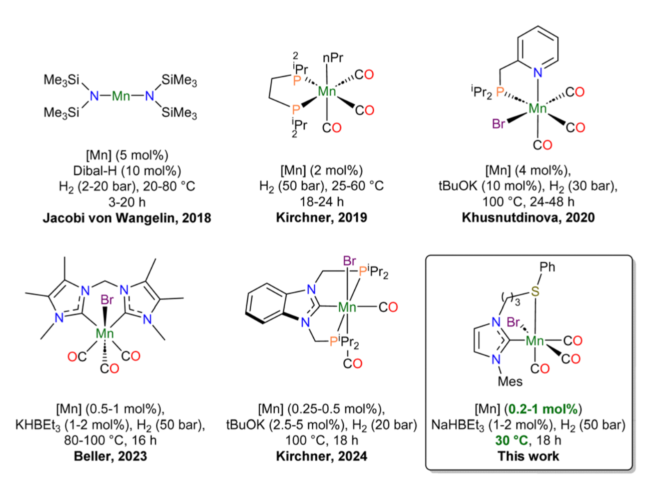

Chart 1 Manganese catalysts for hydrogenation of alkenes.

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In this article, we demonstrate that the use of NHC–thioether ligands enables the hydrogenation of alkenes at room temperature with catalytic loadings as low as 0.2 mol%. Having recently studied the catalytic activity of manganese complexes with highly coordinating bidentate NHC–phosphine[16–18] and bis-NHC[19] ligands for the hydrogenation of ketones and esters, as well as that of nickel complexes with hemilabile NHC–thioether ligands for the hydrosilylation of aldehydes,[20] we turned our attention to thioether–NHC ligands for the hydrogenation of alkenes with manganese. Our working hypothesis was that, given the potentially hemilabile character of sulphur,[20–27] it would be easier to generate a free coordination site, without loss of a CO ligand, on an active species of the $[L_2Mn(CO)_3H]$ type[14,18] and that it should therefore be possible to catalyse hydrogenation reactions under milder conditions than with P–NHC–P or bis-NHC Mn complexes, and target the reduction of alkenes.

The *S*-functionalized carbene precursors **L1.HBr–L4.HBr** were readily synthesised in two steps from *N*-substituted imidazoles (Fig. 1).[20,28–32] Next, the manganese complexes **1–4** were prepared in a two-step, one-pot procedure *via* pre-coordination of the sulphur moiety followed by deprotonation of the imidazolium group with *t*BuOK to allow carbene formation and coordination. The four complexes **1–4** were obtained in good yields (66–88%) and fully characterised by solution and solid-state IR and NMR spectroscopy, HRMS and elemental analysis. In the ^1H NMR spectra, the protons of the ethylene (**1–3**) and propylene (**4**) bridges are all diastereotopic, confirming the chelation of the ligand on the metal centre. In the IR spectra, three CO vibration bands are observed for all four complexes, which is characteristic of the facial coordination mode of the carbonyl ligands. The vibration frequencies (for example, 2014, 1932 and 1909 cm^{-1} for **1** in ATR) indicate a lower electron-donation of the thioether moieties, compared to phosphorus analogues such as $[Mes\text{-}Im\text{-}(CH_2)_2\text{-}PPh_2)Mn(CO)_3Br]$ (2005, 1925, 1907 cm^{-1}).[18]

The molecular structures of **1–4** with the facial arrangement of the carbonyl ligands and the formation of 6- (**1–3**) and 7-membered (**4**) C_{NHC},S-metallacycles were confirmed by single-crystal X-ray diffraction studies (Fig. 2). No significant variations were observed between all four complexes for the Mn–C_{NHC}, Mn–S, and Mn–Br bond distances (Table S1, ESI†). In contrast, noticeable variations were observed for the C_{NHC}–Mn–S (87.84(14) in **3** *vs.* 91.22(13) in **2**), C_{NHC}–Mn–Br (86.16(12) in **2** *vs.* 90.04(10) in **1**), and Br–Mn–S (85.00(4) in **3** *vs.* 90.44(11) in **4**) bond angles (Table S1, ESI†), but no obvious correlation can be drawn between these variations and the catalytic activities of **1–4** (*vide infra*). The main difference between complexes **1** and **4**, that only vary by the size of their metallacycle and give the highest catalytic activities (*vide infra*), is a greater distortion between the plane of the imidazolylidene ring and the Mn–S bond in **4**, the N_1C_{NHC}–MnS twist angle being +29.4(3)° and −37.0(1)°, in **1** and **4**, respectively, while the other structural parameters are similar (Table S1, ESI†).

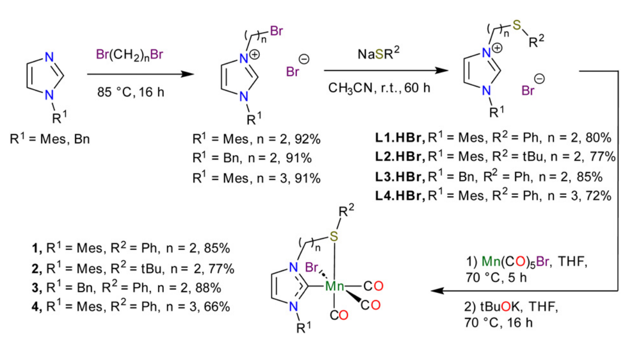


Fig. 1 Synthesis of ligands and manganese complexes **1–4**.

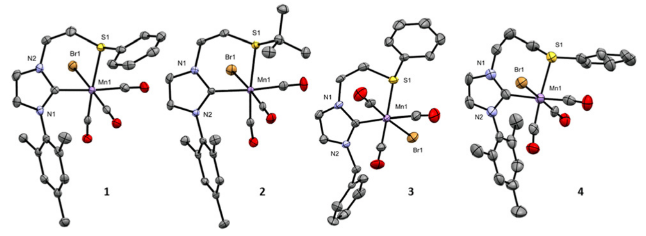
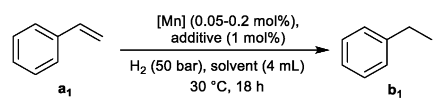


Fig. 2 Perspective view of the single-crystal X-ray structure of complexes **1–4** with thermal ellipsoids drawn at the 30% probability level.

The hydrogenation of styrene $\mathbf{a_1}$ was chosen as the model reaction to optimise the reaction conditions. Based on the conditions developed for ester hydrogenations,[18] $NaHBEt_3$ was first used to activate the pre-catalysts in 2-MeTHF. At 30 °C, in 18 h, under 50 bar of H_2, with a catalyst loading of only 0.2 mol%, styrene $\mathbf{a_1}$ was reduced to ethylbenzene $\mathbf{b_1}$ with all complexes **1–4**, without the formation of by-products (Table 1). The catalysts **1–3** incorporating an ethylene bridge led to yields of 71, 22 and 56%, respectively (entries 1–3),

Table 1 Optimisation of the parameters for the hydrogenation of styrene with pre-catalysts **1–4**



Entry	Catalyst (mol%)	Additive	Solvent	Yield (%) in b_1[a]
1	**1** (0.2)	$NaHBEt_3$	2-MeTHF	71
2	**2** (0.2)	$NaHBEt_3$	2-MeTHF	22
3	**3** (0.2)	$NaHBEt_3$	2-MeTHF	36
4	**4** (0.2)	$NaHBEt_3$	2-MeTHF	99
5	**4** (0.1)	$NaHBEt_3$	2-MeTHF	90
6[b]	**4** (0.05)	$NaHBEt_3$	2-MeTHF	38
7	**4** (0.1)	$KHBEt_3$	2-MeTHF	71
8	**4** (0.1)	$LiHBEt_3$	2-MeTHF	77
9	**4** (0.1)	KHMDS	2-MeTHF	2
10	**4** (0.1)	*t*BuOK	2-MeTHF	2
11	**4** (0.1)	$NaHBEt_3$	THF	60
12	**4** (0.1)	$NaHBEt_3$	Dioxane	35
13	**4** (0.1)	$NaHBEt_3$	Toluene	11
14[c]	**4** (0.1)	$NaHBEt_3$	2-MeTHF	26
15	—	$NaHBEt_3$	2-MeTHF	0
16	**4** (0.1)	—	2-MeTHF	0

Typical reaction conditions: to a solution of **1–4** (0.05–0.2 mol%) in solvent (4 mL) were added the additive (1 mol%) and styrene (5 mmol), in this order. The reaction mixture was transferred into an autoclave and stirred for 18 h at 30 °C under H_2 (50 bar). [a] Yield determined by GC using *n*-dodecane as an internal standard. [b] Styrene (10 mmol). [c] H_2 (10 bar).

evidencing that the presence of the *N*-mesityl and S–Ph substituents led to a higher catalytic activity than that of a *N*-benzyl or S–*t*Bu substituent. Under the same conditions, lengthening the carbon chain in complex **4** enabled full conversion of the alkene (entry 4). The latter pre-catalyst was therefore chosen for further optimisation. By lowering the catalytic loading to 0.1 mol%, good catalytic activity was maintained (90%, TON 900), but it fell to 38% when the loading was halved again (entries 5 and 6). The nature of the cation Na, K, and Li of the hydride donor was investigated, and found to have a moderate but noteworthy impact on catalysis, with yields of 90, 71 and 77%, respectively (entries 5, 7, and 8). On the other hand, the use of strong bases, such as KHMDS and *t*BuOK, did not promote the hydrogenation of styrene (entries 9 and 10). Of all the solvents tested, 2-MeTHF was by far the best for this transformation (entries 5, 11–13). Finally, control experiments confirmed that the presence of both the catalyst and the hydride, as well as a high pressure of H_2, are all necessary to achieve good yields (entries 14–16).

The scope of this transformation was then studied with a series of vinyl arenes, aliphatic alkenes, and cyclic alkenes (Fig. 3). Styrene (**a$_1$**) and styrene derivatives with either electron-donor (*p*-methylstyrene, **a$_2$**) or electron-acceptor groups (*o*-chlorostyrene, **a$_5$**) or 1,1′-disubtituted (α-methyl styrene, **a$_9$**) were fully converted within 18 h at 30 °C with optimised catalyst loadings ranging between 0.2 and 0.6 mol% and a $NaHBEt_3$ loading of 1 mol%. The catalyst loading was then set by default at 1 mol% and that of $NaHBEt_3$ at 2 mol% for the rest

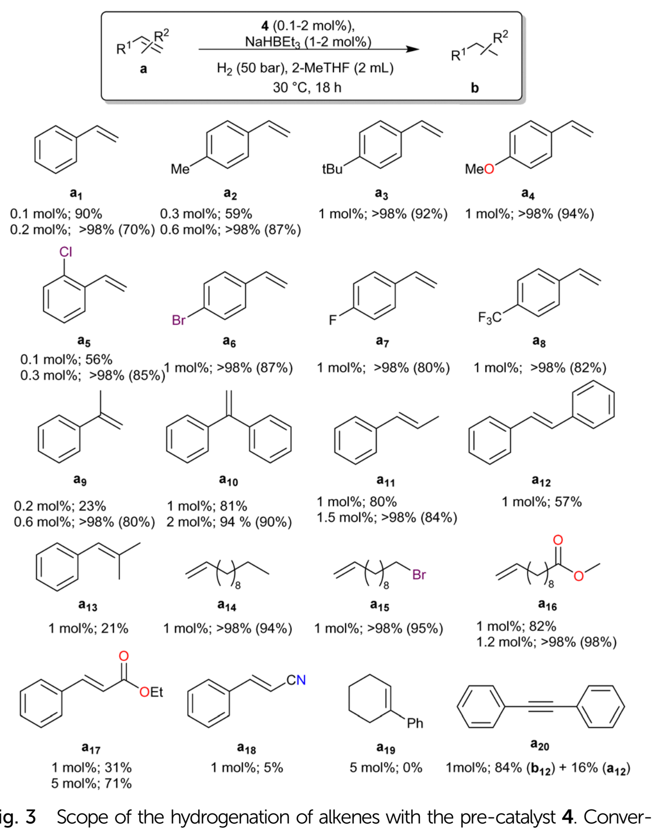


Fig. 3 Scope of the hydrogenation of alkenes with the pre-catalyst **4**. Conversion determined by GC and NMR (isolated yield). For exact conditions, see ESI.†

of the study. Under these conditions, the catalytic system was found tolerant to both electron-donating and electron-withdrawing groups as **a$_1$–a$_8$** were all fully reduced in 18 h at 30 °C under 50 bar H_2. More sterically crowded 1,1′- (**a$_9$** and **a$_{10}$**) and 1,2-disubstituted (**a$_{11}$** and **a$_{12}$**) styrenes were also reduced using this system. However, the limits of the system were reached with tri-substituted olefins such as **a$_{13}$** or **a$_{19}$**, which gave little to no conversion, respectively. The hydrogenation of the aliphatic terminal olefins **a$_{14}$–a$_{16}$** proceeded well without isomerisation of the terminal double bond[33] and showed that the catalytic system is tolerant to halogens and esters, which remained intact. The reduction of conjugated C═C bonds in ethyl cinnamate (**a$_{17}$**) and 3-phenylacrylonitrile (**a$_{18}$**) was more difficult as the loading had to be increased to 5 mol%, but the reduction of the C═C bond was selective, as no alcohol or amine was detected. Finally, diphenylacetylene (**a$_{20}$**) was chosen as a model substrate for alkynes. Under the standard conditions (1 mol% **4**, 2 mol% $NaHBEt_3$, 50 bar H_2, 30 °C, 18 h), the triple bond was reduced to 1,2-diphenylethane (**b$_{12}$**) in 84% yield, presumably *via* the transient formation of *trans*-stilbene (**a$_{12}$**), which was obtained in 16% yield at the end of the reaction.

Given the performance of this thioether–NHC based manganese catalyst for the hydrogenation of alkenes, we next studied its behaviour towards the reduction of ketones. Very few examples of hydrogenation of polar functional groups with Mn-based catalysts that are, *a priori*, non-cooperative have indeed been reported to date, the only examples being complexes bearing diphosphine,[34–38] phosphine–NHC,[16,17,19] and bis-NHC[14,18] ligands. To that end, the reaction parameters were re-optimised for the reduction of acetophenone (see Table S2, ESI†). The catalyst loading had to be increased to 3 mol% and that of $NaHBEt_3$ to 7 mol% to reach full conversion, but the hydrogenation still took place in 18 h at 30 °C under 50 bar H_2.

With these conditions in hands, the limits of the system were then evaluated (Fig. 4). Increasing the steric hindrance on the alkyl side of acetophenone (**c$_1$** to **c$_4$**) led to a moderate conversion of isobutyrophenone (**c$_3$**), but the reductions of propiophenone (**c$_2$**) and cyclopropylphenylketone (**c$_4$**) both proceeded well, and no cyclopropyl ring opening was observed in the latter case. Similarly, 2′-methylacetophenone (**c$_5$**) was fully reduced in 18 h while 2′,4′,6′-trimethylacetophenone (**c$_6$**) was only partially converted to the corresponding alcohol (80%). As for alkenes, the catalytic system was found tolerant to electron-donating and withdrawing groups (**c$_7$–c$_{11}$**). It is worth noting that 4-(methylthio)acetophenone (**c$_8$**) did not poison the catalyst and allowed the formation of the corresponding alcohol in 85% isolated yield. However, 4-cyano-acetophenone (**c$_{12}$**) only gave **d$_{12}$** in 45% yield (at 60 °C). Finally, whereas 4-phenylpropan-2-one (**c$_{13}$**), a representative example of aliphatic ketones, was fully converted to the corresponding alcohol **d$_{13}$**, the reduction of the conjugated 4-phenylbutenone (**c$_{14}$**) led to a mixture of **d$_{13}$** (33%), resulting from the full reduction of the enone, and 4-phenylprop-3-en-2-ol (**d$_{14}$**, 67%), resulting from the sole reduction of the C═O bond.

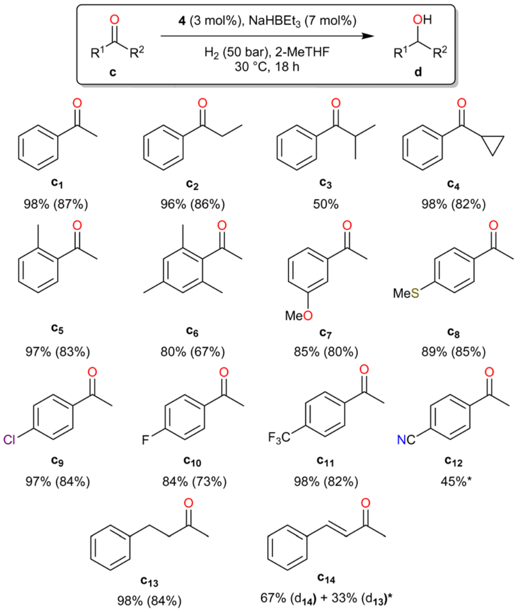


Fig. 4 Scope of the hydrogenation of ketones with the pre-catalyst **4**. Conversion determined by GC and NMR (isolated yield).* = **4** (5 mol%), 60 °C; for exact conditions, see ESI.†

In summary, we have developed a new series of phosphine-free manganese catalysts for the hydrogenation of alkenes and ketones, based on thioether–NHC ligands, able to work at room temperature with low catalyst loadings (TON up to 900 for styrene). The synthesis of ligands is straightforward in two steps and the complexes, which can be handled in air, were obtained in high yields. The scope of substrates showed a good tolerance toward several functional groups and moderate steric hindrance. The full rationalization of the operating mechanism is still under investigation and will be reported in due time.

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Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 J.-B. Sortais, *Manganese Catalysis in Organic Synthesis*, Wiley-VCH GmbH, Weinheim, Germany, 2021.
2 S. Elangovan, C. Topf, S. Fischer, H. Jiao, A. Spannenberg, W. Baumann, R. Ludwig, K. Junge and M. Beller, *J. Am. Chem. Soc.*, 2016, **138**, 8809–8814.
3 F. Kallmeier, T. Irrgang, T. Dietel and R. Kempe, *Angew. Chem., Int. Ed.*, 2016, **55**, 11806–11809.
4 A. Bruneau-Voisine, D. Wang, T. Roisnel, C. Darcel and J.-B. Sortais, *Catal. Commun.*, 2017, **92**, 1–4.
5 P. L. Bogdan, P. J. Sullivan, T. A. Donovan and J. D. Atwood, *J. Organomet. Chem.*, 1984, **269**, c51–c54.
6 T. A. Weil, S. Metlin and I. Wender, *J. Organomet. Chem.*, 1973, **49**, 227–232.
7 R. H. Fish, A. D. Thormodsen and G. A. Cremer, *J. Am. Chem. Soc.*, 1982, **104**, 5234–5237.
8 R. A. Farrar-Tobar, S. Weber, Z. Csendes, A. Ammaturo, S. Fleissner, H. Hoffmann, L. F. Veiros and K. Kirchner, *ACS Catal.*, 2022, **12**, 2253–2260.
9 H. Schratzberger, B. Stöger, L. F. Veiros and K. Kirchner, *ACS Catal.*, 2023, **13**, 14012–14022.
10 U. Chakraborty, E. Reyes-Rodriguez, S. Demeshko, F. Meyer and A. Jacobi von Wangelin, *Angew. Chem., Int. Ed.*, 2018, **57**, 4970–4975.
11 U. Chakraborty, S. Demeshko, F. Meyer and A. Jacobi von Wangelin, *Angew. Chem., Int. Ed.*, 2019, **58**, 3466–3470.
12 S. Weber, B. Stöger, L. F. Veiros and K. Kirchner, *ACS Catal.*, 2019, **9**, 9715–9720.
13 S. M. W. Rahaman, D. K. Pandey, O. Rivada-Wheelaghan, A. Dubey, R. R. Fayzullin and J. R. Khusnutdinova, *ChemCatChem*, 2020, **12**, 5912–5918.
14 N. F. Both, A. Spannenberg, H. Jiao, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2023, **62**, e202307987.
15 D. P. Zobernig, M. Luxner, B. Stöger, L. F. Veiros and K. Kirchner, *Chem. – Eur. J.*, 2024, **30**, e202302455.
16 R. Buhaibeh, O. A. Filippov, A. Bruneau-Voisine, J. Willot, C. Duhayon, D. A. Valyaev, N. Lugan, Y. Canac and J.-B. Sortais, *Angew. Chem., Int. Ed.*, 2019, **58**, 6727–6731.
17 E. S. Gulyaeva, R. Buhaibeh, M. Boundor, K. Azouzi, J. Willot, S. Bastin, C. Duhayon, N. Lugan, O. A. Filippov, J.-B. Sortais, D. A. Valyaev and Y. Canac, *Chem. – Eur. J.*, 2024, **30**, e202304201.
18 K. Azouzi, R. Pointis, R. Buhaibeh, P. H. Fernández, L. Pedussaut, M. Boundor, A. Bonfiglio, A. Bruneau-Voisine, D. Wei, T. Roisnel, C. Duhayon, M. Á. Casado, D. A. Valyaev, Y. Canac, S. Bastin, C. Raynaud and J.-B. Sortais, *J. Catal.*, 2024, **430**, 115334.
19 K. Azouzi, L. Pedussaut, R. Pointis, A. Bonfiglio, R. Kumari Riddhi, C. Duhayon, S. Bastin and J.-B. Sortais, *Organometallics*, 2023, **42**, 1832–1838.
20 F. Ulm, A. I. Poblador-Bahamonde, S. Choppin, S. Bellemin-Laponnaz, M. J. Chetcuti, T. Achard and V. Ritleng, *Dalton Trans.*, 2018, **47**, 17134–17145.
21 A. Jana, K. Das, A. Kundu, P. R. Thorve, D. Adhikari and B. Maji, *ACS Catal.*, 2020, **10**, 2615–2626.
22 K. Das, K. Sarkar and B. Maji, *ACS Catal.*, 2021, **11**, 7060–7069.
23 K. Sarkar, K. Das, A. Kundu, D. Adhikari and B. Maji, *ACS Catal.*, 2021, **11**, 2786–2794.
24 A. Jana, C. B. Reddy and B. Maji, *ACS Catal.*, 2018, **8**, 9226–9231.
25 J. Grover, S. Maji, C. Teja, S. A. Al Thabaiti, M. M. M. Mostafa, G. K. Lahiri and D. Maiti, *ACS Org. Inorg. Au*, 2023, **3**, 299–304.
26 N. F. Both, J. Fessler, A. Vicenzi, K. Andres, A. Spannenberg, K. Junge and M. Beller, *ChemCatChem*, 2024, **16**, e202301562.
27 V. Zubar, J. Sklyaruk, A. Brzozowska and M. Rueping, *Org. Lett.*, 2020, **22**, 5423–5428.
28 W. Chen, J. Egly, A. I. Poblador-Bahamonde, A. Maisse-Francois, S. Bellemin-Laponnaz and T. Achard, *Dalton Trans.*, 2020, **49**, 3243–3252.
29 V. Mechrouk, B. Leforestier, W. Chen, A. I. Poblador-Bahamonde, A. Maisse-Francois, S. Bellemin-Laponnaz and T. Achard, *Chem. – Eur. J.*, 2024, **30**, e202401390.
30 J. Egly, M. Bouché, W. Chen, A. Maisse-François, T. Achard and S. Bellemin-Laponnaz, *Eur. J. Inorg. Chem.*, 2018, 159–166.
31 J. Wolf, A. Labande, J.-C. Daran and R. Poli, *Eur. J. Inorg. Chem.*, 2007, 5069–5079.
32 C. Fliedel and P. Braunstein, *Organometallics*, 2010, **29**, 5614–5626.
33 I. Blaha, S. Weber, R. Dülger, L. F. Veiros and K. Kirchner, *ACS Catal.*, 2024, **14**, 13174–13180.
34 S. Weber, B. Stöger and K. Kirchner, *Org. Lett.*, 2018, **20**, 7212–7215.
35 S. Weber, L. F. Veiros and K. Kirchner, *Adv. Synth. Catal.*, 2019, **361**, 5412–5420.
36 S. Weber, J. Brünig, L. F. Veiros and K. Kirchner, *Organometallics*, 2021, **40**, 1388–1394.
37 J. A. Garduño, M. Flores-Alamo and J. J. García, *ChemCatChem*, 2019, **11**, 5330–5338.
38 J. A. Garduño and J. J. García, *ACS Catal.*, 2019, **9**, 392–401.