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Hydrogenation of carboxylic esters catalyzed by phosphine-free bis-N-heterocyclic carbene manganese complexes

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ABSTRACT: As an earth-abundant transition metal, manganese is now recognized as a good candidate for the development of catalysts for reduction-type reactions. It is often associated with a non-innocent tridentate ligand, featuring an acidic NH moiety. We report here that a simple bidentate and phosphine-free bis-N-heterocyclic ligand associated with manganese in [Mn(bis-NHC^{Mes})(CO)₃Br] complex could catalyze the hydrogenation of carboxylic esters in the presence of KBHET₃ as an activator at 100-120 °C under 50 bar of H₂ at 1 mol% catalyst loading in 2-Me-THF.

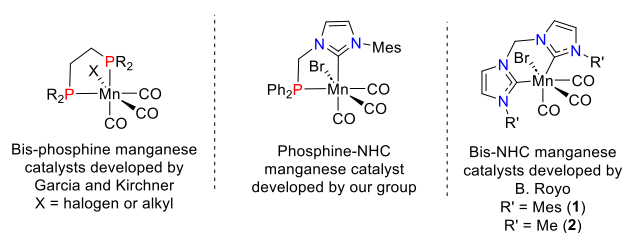
INTRODUCTION

The development of earth-abundant-based catalysts is drawing an increasing attention since the beginning of the 21st century in the general context of the global awareness of the end of the abundance of non-renewable resources. Precious transition metals are essential raw materials that are part of these non-renewable resources. Their prices are subject to market volatility and their availability is highly dependent on geopolitical constraints.¹ As a consequence, it is preferable to develop catalysts based on abundant 3d metals. Manganese, which is the third most abundant transition metal in the earth's crust, is a good candidate, as is iron, for the development of catalysts.²

In the field of reduction reactions,³ within a few years, since the first example from Beller's group for the hydrogenation of nitriles, ketones and aldehydes in 2016,⁴ an increasing number of manganese-based catalysts have been developed,⁵ including several from our group.⁶ In particular, Garcia and Kirchner developed manganese catalysts based on bidentate phosphines (Chart 1, left) for the hydrogenation of nitriles,⁷ carbon dioxide,⁸ ketones,⁹ alkenes,¹⁰ alkynes,¹¹ for transfer hydrogenation and hydration of nitriles.¹² The Mn-alkyl derivatives of the aforementioned catalyst were also applied with success in hydroboration and hydrosilylation reactions.¹³ In parallel, we have developed a new family of manganese catalysts for hydrogenation of ketones featuring a mixed phosphine-NHC ligand, [Mn(P-NHC)(CO)₃Br] (Chart 1, middle).¹⁴ The stoichiometric activation of H₂ was shown to proceed through the deprotonation of the methylene bridge with a non-conventional phosphine ylide intermediate. In the course of H₂ activation, the three carbonyl ligands remained coordinated to the metal centre, which contrasts with the active species relying on unsaturated dicarbonyl 16 electrons complex [Mn(P)(CO)₂H] in the case of bidentate phosphines. Even though

the exact mechanism for the hydrogenation has not yet been fully rationalized, we assumed that the presence of the phosphine moiety was thus mandatory to obtain an active catalyst in hydrogenation due to the acidity of protons in alpha to the phosphorus atom.

Chart 1: Manganese complexes with bidentate ligands



Based on structural analogy from bisphosphine to NHC-phosphine complexes, we thus were curious to explore the potential of bis-NHC manganese complexes in hydrogenation. Besides, NHC-Mn complexes are less common than phosphine ones in catalysis.¹⁵ We selected [Mn(bis-NHC^{Mes})(CO)₃Br] **1** and [Mn(bis-NHC^{Me})(CO)₃Br] **2** (Chart 1, right) which were first reported by Royo for the reduction of CO₂¹⁶ and applied in hydrosilylation reactions for the reduction of ketones,¹⁷ sulfoxides¹⁸ and, most interestingly, esters into alcohols in the presence of an inexpensive silane (PMHS).¹⁹ It is also worth noting that Ke applied the same catalysts in hydrogen borrowing reactions for the alkylation of anilines²⁰ and alcohols,²¹ and Kundu in the transformation of α,β -unsaturated ketones to α -methylated ketones using methanol.²²

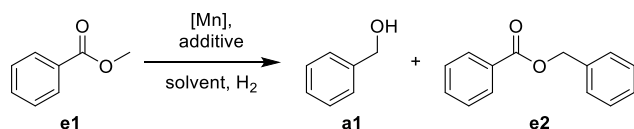
While the hydrogenation of carbonyl derivatives with manganese complexes is now well established, there are only a few catalysts that are capable of reducing carboxylic

esters, which represent an important class of reducible functional groups. The catalysts developed to date are mostly based on tridentate ligands,²³ with one exception.²⁴ In all cases, the catalysts are featuring an acidic “NH” moiety. We report herein that air-stable phosphine-free, and “NH” free bis-NHC manganese complexes can be used as efficient catalysts for the hydrogenation of esters upon activation with KBHET₃.

RESULTS AND DISCUSSION

Complexes **1** and **2** were prepared according to Royo’s methods.¹⁶⁻¹⁷ They were evaluated in the catalytic hydrogenation of esters using methylbenzoate **e1** as model substrate in reaction conditions previously optimized with the NHC-P manganese complex.¹⁴ In toluene, using KHMDs as base, no conversion was observed (Table 1, entry 1). In alcoholic solvent, in the presence of *t*-BuOK, only products resulting from trans-esterification with the solvent was detected (entries 2-4). Encouraging results were obtained with *t*-BuOK in THF, as benzylbenzoate **e2**, resulting from trans-esterification of starting material **e1** with the desired alcohol **a1**, was detected in 40% yield (entry 5). We have also tested 2-Me-THF as a more sustainable ethereal solvent, which was found to have a beneficial effect on several catalytic reactions implying transition metal-based catalysts.²⁵ With *t*-BuOK as base, a mixture of alcohol **a1** and ester **e2** was obtained (entry 6). Changing the additive to triethylborohydride had a drastic effect on the activity. Indeed, with NaBHET₃, the alcohol was formed in 78% yield (entry 7). The effect of the cation was noticeable, as lithium salt led to low conversion (entry 8), while the potassium salt gave almost complete conversion (95%) and a 89% yield of benzyl alcohol (entry 9). Among the different solvent tested, 2-MeTHF is the more suitable for this hydrogenation (entries 9-12). Increasing the catalyst loading from 0.5 to 1 mol% increased the yield in benzylalcohol from 89% to 96% (entries 9 and 13). The impact of temperature and H₂ pressure was also investigated. Lowering the temperature to 80 °C significantly altered the activity of the catalytic system, as only 46% of alcohol was obtained while increasing to 120 °C led to a full conversion of the starting ester into the alcohol **a1** (entries 13-15). The activity of the catalytic system is less impacted by the pressure than by the temperature since at 30 bars of pressure, the alcohol **a1** was obtained in 88% yield against 100% under 50 bars (entries 15-16). A series of control experiments proved that both manganese catalyst and KBHET₃ are required in this transformation (entries 17-18). Complex [Mn(bis-NHC^{Me})(CO)₃Br] **2** based on less bulky N-methyl imidazol-2-ylidene moieties was found to be less active than **1** (entry 21).

Table 1: Optimization of the parameters of the hydrogenation of methylbenzoate **e1 catalyzed by manganese complex **1**** ^[a]



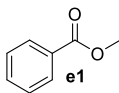
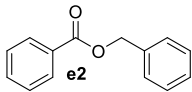
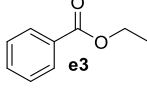
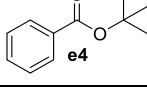
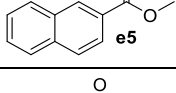
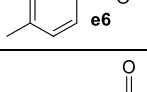
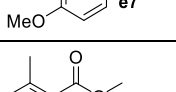
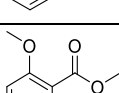
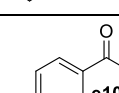
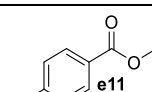

Entry	Additive (%)	Solvent	Temp. (°C)	Yield ^[b]	
				a1	e2
1 ^[c]	KHMDs	Toluene	100	4	0
2	<i>t</i> -BuOK	<i>t</i> -AmOH	100	0	0
3	<i>t</i> -BuOK	EtOH	100	0	0
4	<i>t</i> -BuOK	MeOH	100	1	0
5	<i>t</i> -BuOK	THF	100	7	40
6	<i>t</i> -BuOK	2-Me-THF	100	16	10
7	NaBHET ₃	2-Me-THF	100	78	-
8	LiBHET ₃	2-Me-THF	100	13	2
9	KBHET ₃	2-Me-THF	100	89	6
10	KBHET ₃	CPME	100	71	18
11	KBHET ₃	THF	100	14	7
12	KBHET ₃	Toluene	100	52	18
13 ^[d]	KBHET ₃	2-Me-THF	100	96	-
14 ^[d]	KBHET ₃	2-Me-THF	80	46	16
15 ^[d]	KBHET ₃	2-Me-THF	120	100	-
16 ^[d,e]	KBHET ₃	2-Me-THF	120	88	-
17 ^[f]	KBHET ₃	2-Me-THF	100	1	7
18	-	2-Me-THF	100	0	0
19 ^[g]	KBHET ₃	2-Me-THF	100	25	4
20 ^[h]	KBHET ₃	2-Me-THF	100	50	10
21 ^[i]	KBHET ₃	2-Me-THF	100	31	25

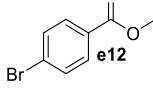
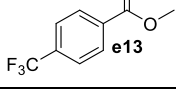
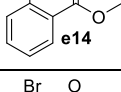
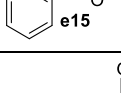
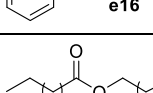
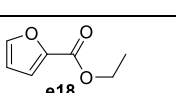
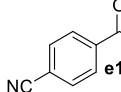
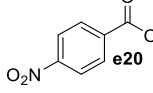
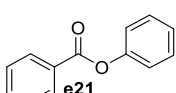
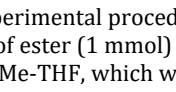
[a] Experimental procedure: an autoclave was loaded, in that order, with a solution of methylbenzoate **e1** (1 mmol) in solvent (1 mL) and a solution of catalyst **1** (0.5 mol%) in solvent (0.5 mL), which was firstly pre-activated with the additive (10 mol%) for 30 min, then the autoclave was immediately pressurized with hydrogen (50 bar) and kept under stirring for 24 h at the indicated temperature. [b] Yield determined by ¹H NMR spectroscopy. [c] KHMDs (2 mol%, 0.5 M in toluene). [d] complex **1** (1 mol%). [e] H₂ (30 bar). [f] no catalyst. [g] KBHET₃ (1 mol%, 1M in THF). [h] 2 h. [i] complex **2** (0.5 mol%).

With the optimized conditions in hand, we then explored the scope of the esters amenable for this hydrogenation. We first investigated the influence of the alkyl group of alkylbenzoate (Table 2, entries 1-4) at 100 °C with 1 mol% catalyst for 24 h (conditions A). An increase of the steric hindrance of these alkyl groups results in a dramatic decrease of the yield going from methyl (**e1**, 96%) to ethyl (**e3**, 62%), benzyl (**e2**, 58%), and tert-butyl (**e4**, 16%). At 120 °C (conditions B), good yields were obtained for **e1-e3**, but with the bulky *t*-Bu group, the conversion remained low (29%). Electron donating groups (entries 5-9) were well tolerated in para or ortho positions, although methyl 2-methoxybenzoate **e9** led to a lower yield, probably due to poisoning of the catalyst by chelation of the 1,3-dioxygenated motif. Halogenated groups did not hamper the reduction, as methyl para-fluoro (**e10**), chloro (**e11**), bromo (**e12**) and, para-trifluoromethyl (**e13**) benzoate as well as ortho-substituted esters (**e14**, **e15**) were reduced in good yields (entries 10-15). Benzylformate (**e16**), aliphatic hexylhexanoate (**e17**)

and ethyl furan-2-carboxylate (**e18**) as a model heterocyclic compound, were also reduced in good yields (entries 16-18). Methyl 4-cyanobenzoate **e19** was reduced in a low yield. Methyl 4-nitrobenzoate **e20** and phenyl benzoate **e21** inhibited the reduction. In the latter two cases, competitive experiments (i.e. reduction of methyl benzoate **e1** in the presence of 1 equiv. of nitrobenzene and phenol respectively), showed that nitro-group and phenol were responsible of the inhibition as no conversion (<5%) of methyl benzoate **e1** was detected in both cases.

Table 2: Scope of the hydrogenation of carboxylic esters catalyzed by manganese complex **1^[a]**

Entry	Substrate	Conditions	Conv. (%)	Yield (%)
1		A	96	96
		B	>98	97 (92)
2		A	58	58
		B	>98	>98 (93)
3		A	63	62
		B	>98	99 (99)
4		A	17	16
		B	29	29
5		B	> 98	100 (99)
6		B	>98	100 (97)
7		C	91	88 (81)
8		B	92	92 (89)
9		C	43	24
10		D	90	88 (80)
11		D	95	95 (92)

12		D	>98	99 (98)
13		E	63	55 (49)
14		E	90	82 (60)
15		D	97	97 (94)
16		F	>98	97 (91)
17		D	80	80 (53)
18		D	52	52
19		D	39	15
20		C	2	2
21		G	0	0

[a] Experimental procedure: an autoclave was loaded with a solution of ester (1 mmol) in 2-Me-THF (0.7 ml) and a solution of **1** in 2-Me-THF, which was firstly pre-activated with KBHET₃ (10 mol%, 1 M in THF) for 30 min, in this order, then the autoclave was immediately pressurized with hydrogen (50 bar) and kept under stirring in an oil bath. Conversion and yield were determined by ¹H NMR, isolated yield in brackets. [b] Conditions: A = catalyst 1 mol% at 100 °C for 24 h; B = catalyst 1 mol% at 120 °C for 24 h; C = catalyst 2 mol% at 140 °C for 24 h; D = catalyst 2 mol% at 120 °C for 24 h; E = catalyst 2 mol% at 120 °C for 2 h; F = catalyst 1 mol% at 140 °C for 24 h; G = catalyst 1 mol% at 100°C for 2 h.

In order to get insights into the mechanism of this hydrogenation with a priori innocent bis-NHC ligand,²⁶ a series of control experiments were conducted. First, in the presence of mercury (300 equiv. with respect to manganese catalyst, Scheme 1), the reduction of methylbenzoate **e1** led to the corresponding alcohol **a1** in 94% yield under conditions B of Table 2. The formation of manganese nanoparticles is therefore unlikely.²⁷

Scheme 1: Mercury poisoning test



Then, in a Young-type NMR tube, complex **1** was reacted with KBHET_3 (5 equiv.) in $\text{THF-}d_8$ and the reaction monitored by NMR spectroscopy (Scheme 2 a and see S.I., figures S5-S9). At r.t., the system evolved slowly (Figure S5 and S6). After 22 h (Figure S8), complex **1** was fully consumed and four hydridic signals were detected, a major one (sharp signal, $\nu_{1/2} = 3\text{ Hz}$, at -6.91 ppm, ca 64%) and three broad minor signals ($\nu_{1/2} = 35$ Hz) at -9.60 , -9.87 and -14.14 ppm (ca 12%, 4%, and 20%, respectively).²⁸ At 60 °C, the same signals were observed after only one hour, along with a complete conversion (Figure S7). The signal at -6.91 ppm is very similar to the one reported by Royo in 2018 for $[\text{Mn}(\text{BisNHC}^{\text{Me}})(\text{CO})_3\text{H}]$ complex ($\delta = -6.82$ ppm in CD_3CN)^{17a} and to the one recently reported by Kundu and attributed to the parent $[\text{Mn}(\text{BisNHC}^{\text{Et}})(\text{CO})_3\text{H}]$ complex ($\delta = -6.90$ ppm in CD_3CN).²² The three other hydride signals could not be assigned with certainty.²⁹ In order to confirm the structure of manganese hydride complex $[\text{Mn}(\text{BisNHC}^{\text{Mes}})(\text{CO})_3\text{H}]$ **3**, **1** was reacted with NaBH_4 in EtOH at 85 °C (Scheme 2 b). Within a few minutes, **1** was converted quantitatively in **3** as a single hydride compound characterized by a negative signal in ^1H NMR at -6.89 ppm (in $\text{THF-}d_8$). **3** was fully characterized by spectroscopic methods. Besides, the molecular structure of **3** was ascertained by X-ray diffraction studies on single crystals (Figure 1).

Scheme 2: Synthesis of manganese hydride complex **3**.

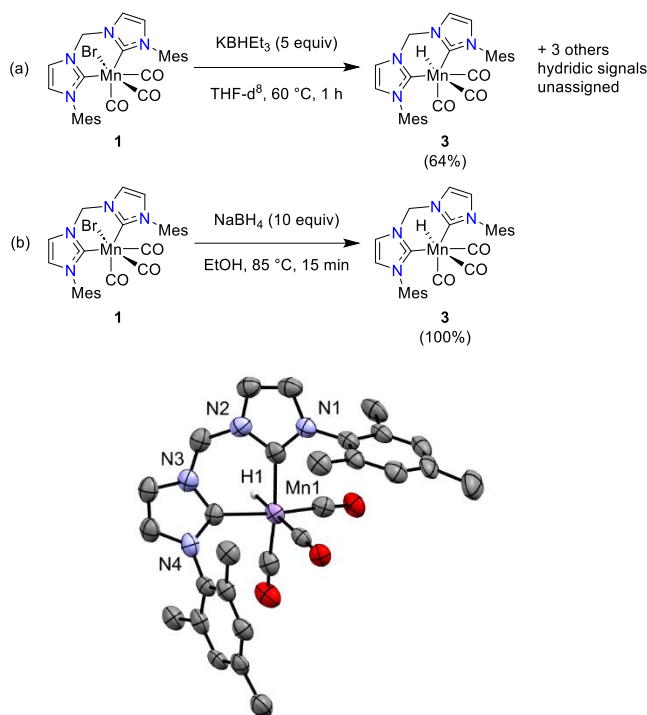


Figure 1: Molecular structure of complex **3** (ellipsoids drawn at the 50% probability level). 2 molecules of THF and H atoms (except H1) have been omitted for clarity.

The reactivity of the complex $[\text{Mn}(\text{Bis-NHC}^{\text{Mes}})(\text{CO})_3\text{H}]$ **3** toward esters was then explored. First, complex **3** was stable at 80 °C in the presence of methylbenzoate **e1** in $\text{THF-}d_8$ for 24 hours, showing no insertion of the ester in the Mn-H bond (Figure S10). When the same mixture was exposed to hydrogen, 4 bars, no evolution was detected after 24 hours (Figure S11). To confirm the inactivity of **3** as catalyst, a typical catalysis was performed in an autoclave and no conversion was detected in the absence of additives. However, in the presence of KBHET_3 (10 mol%), the activity was restored (79% conversion, Figure S4.). These results suggested that the manganese hydride is not the active catalyst in this transformation and that KBHET_3 may play a key role.³⁰ Full rationalization of the mechanism is still under investigation and will be reported in due time.

CONCLUSION

In summary, the hydrogenation of carboxylic esters was accomplished in the presence of manganese catalysts featuring phosphine-free and NH-free ligands upon activation with KBHET_3 . The alcohols were obtained in good yield using an acceptable catalyst loading (1 mol%). It is worth noting that bis-NHC ligands are simple and easily accessible ligands in one step from *N*-substituted imidazoles. The resulting manganese complexes are fairly stable, handleable under air in a solid state.

EXPERIMENTAL SECTION

General information: All manipulations were carried out using Schlenk techniques under an atmosphere of dry argon or in an argon-filled glovebox (MBraun Unilabplus Eco. Dry and oxygen-free organic solvents (THF, Et_2O , CH_2Cl_2 , toluene, pentane) were obtained using LabSolv (Innovative Technology) solvent purification system. Organic solvents used for column chromatography and water were degassed by argon bubbling during 15 min. Deuterated toluene, THF, and CD_2Cl_2 for NMR experiments were degassed prior to use and 2-Me-THF for catalytic experiments was distilled and kept over 4Å molecular sieves. Liquid esters and CDCl_3 were passed through a short column of basic alumina, deoxygenated by three freeze-pump-thaw cycles. Column chromatography purification of organic substrates was performed on Organics Ultrapure silica gel (size 40-63 μm), KBHET_3 (1M in THF) was purchased from Aldrich and used as received. *N*-mesitylimidazole,³¹ 3,3'-methylenebis[1-methyl-3-imidazolium bromide],³² 3,3'-methylenebis[1-(2,4,6-trimethylphenyl)-3-imidazolium bromide],³² $[\text{Mn}[\text{bis-NHC}^{\text{Mes}}](\text{CO})_3\text{Br}]$ **1**^{17a} and $[\text{Mn}(\text{bis-NHC}^{\text{Me}})(\text{CO})_3\text{Br}]$ **2**^{17a} were prepared according to known methods. All other reagent grade chemicals purchased from commercial sources were used as received. IR spectra in solution were recorded in 0.1 mm CaF_2 cells using a Perkin Elmer Frontier FT-IR spectrometer and given in cm^{-1} . ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra were recorded on Bruker Avance 300, Bruker Avance 400, Avance III HD 400, and Bruker Avance NEO 600 and referenced against the residual signals of deuterated solvents (^1H and ^{13}C), $\text{BF}_3\cdot\text{OEt}_2$ (^{19}F , external standard) and 85% H_3PO_4 (^{31}P , external standard), respectively. When necessary, signal attribution in ^{13}C spectra was based on decoupled $^{13}\text{C}\{^{31}\text{P}, ^1\text{H}\}$ and 2D ^{13}C - ^1H HMQC/HMBC experiments. High-resolution mass spectra (ESI positive mode) were obtained using a Xevo G2 QTof (Waters) spectrometer. Elemental analyses were carried out at the LCC-CNRS (Toulouse) using a Perkin Elmer 2400 series II analyzer. Non-stirred 'Autoclave Maxitech' autoclaves (50 mL) were used for the hydrogenation reactions.

General procedure for the hydrogenation reactions:

Under argon, an autoclave was charged with a solution of ester (1 mmol) in 2-Me-THF (0.7 mL) and a solution of **1** which was prepared in 2-Me-THF (0.7 mL) and activated with KBH₄ (0.1 mL, 1.0 M in THF, 0.1 mmol, 10 mol%) for 30 min in this order, then the autoclave was immediately pressurized with hydrogen (50 bar) and kept under stirring in an oil bath at the required temperature. Once the reactor has cooled down to room temperature and the pressure of hydrogen has been released, the reaction mixture was diluted with CH₂Cl₂ (2.0 mL) and filtered through a small pad of Celite (2 cm in a Pasteur pipette). The Pasteur pipette was then flushed with an additional volume of CH₂Cl₂. The filtrate was evaporated under vacuum and the crude product was purified by column chromatography on silica (size 40-63 μm) using pentane/ethyl acetate mixtures as eluent to afford the corresponding alcohols.

Synthesis and characterization of [Mn(Bis-NHC^{Mes})(CO)₃H]**3**

To a solution of complex **1** (50 mg, 0.08 mmol) in degassed ethanol (15 mL, ethanol 96%), NaBH₄ (30 mg, 0.8 mmol, 10 equiv.) was added and the reaction mixture was stirred at 85 °C. The solution turned from yellow to colorless and the reaction was monitored by IR after 10 min. If the conversion is not full, NaBH₄ (30 mg, 0.8 mmol, 10 equiv.) was added again and the conversion was checked by IR. Two alternative work-up were carried out.

1) After cooling down to r.t., ethanol was evaporated. The compound was extracted from the solid residue with toluene (3 x 10 mL). The solvent was evaporated under vacuum. The residue was washed with pentane (10 mL) and dried to afford hydride complex **3** as a white solid (47 mg, 100%).

2) After cooling down to r.t., ethanol was evaporated. The solid residue was redissolved in 2-Me-THF (3 mL) and washed with degassed water (3 x 3 mL). The organic phase was dried over MgSO₄ and evaporated affording hydride complex **3** as a pale yellow solid (28 mg, 63 %).

Single crystal suitable for X-ray diffraction analysis were obtained by diffusion of *n*-hexane in a THF solution of **3**. CCDC-2262076 contains the supplementary crystallographic data for complex **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

¹H NMR (600 MHz, THF-*d*₈) δ 7.46 (d, *J* = 2.0 Hz, 2H, CH_{im}), 6.92-6.91 (m, 4H, CH_{Mes} + CH_{im}), 6.89 (br. s, 2H, CH_{Mes}), 6.16 (d, *J* = 11.7 Hz, 1H, CH₂), 5.95 (d, *J* = 11.7 Hz, 1H, CH₂), 2.28 (s, 6H, CH_{3Mes}), 2.04 (s, 6H, CH_{3Mes}), 1.89 (s, 6H, CH_{3Mes}), -6.89 (s, 1H, Mn-H).

¹³C{¹H} NMR (151 MHz, THF-*d*₈) δ 226.4 (2CO), 222.4 (CO), 207.4 (NCN), 138.8 (C_{Mes}), 138.0 (C_{Mes}), 136.9 (C_{Mes}, 2C), 129.6 (CH_{Mes}), 129.5 (CH_{Mes}), 122.9 (CH_{im}), 121.0 (CH_{im}), 63.3 (CH₂), 21.2 (CH_{3Mes}), 18.7 (CH_{3Mes}), 18.6 (CH_{3Mes}).

HR-MS (ESI) : *m/z* calcd for C₂₈H₂₈MnN₄O₃⁺ ([M-H]⁺): 523.1542, found : 523.1544 er 0.4 ppm

IR ν_{CO} (THF) = 1975, 1886, 1872 cm⁻¹

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Description and spectra of the products of catalysis and mechanistic studies (PDF)

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Notes

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(29) When compound 3 (pure) was reacted with an excess of KBHET₃ (6 equiv.) in THF-*d*₈, no reaction took place after 1 h at 60 °C or 4 days at r.t. and no new hydridic signals were detected by NMR spectroscopy, See S.I. figures S12 to S14.

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