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# Towards ligand simplification in manganese-catalyzed hydrogenation and hydrosilylation processes

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**Abstract.** Rapidly emerging application of organometallic manganese complexes incorporating less elaborated mono- and bidentate donor ligands in catalytic hydrogenation, transfer hydrogenation, hydrogen-borrowing and hydrosilylation processes is comprehensively reviewed. Special attention is devoted to the influence of the nature of donor moieties (P-, N- and C-donors) on the catalytic activity and/or selectivity, the comparison with structurally related polydentate systems and mechanistic aspects.

**Keywords:** Manganese complexes, Bidentate ligands, Hydrogenation, Transfer Hydrogenation, Hydrogen borrowing, Hydrosilylation

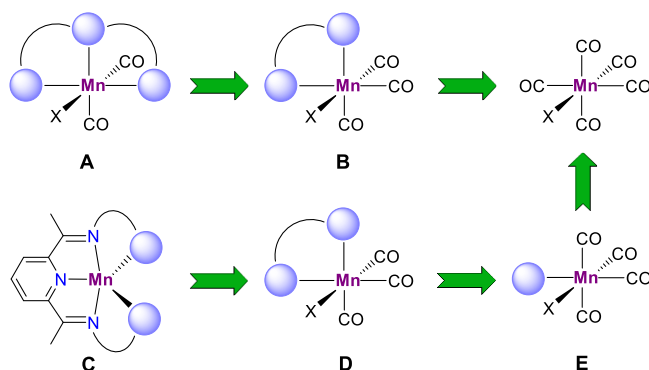
**List of abbreviations:** DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DFT, Density functional theory; Dipp, 2,6-diisopropylphenyl; KIE, kinetic isotope effect; LPO, dilauroyl peroxide ( $nC_{11}H_{23}COO$ )<sub>2</sub>; Mes, 2,4,6-trimethylphenyl; MP, N-methylpyrrolidine; NHC, N-heterocyclic carbene; Oct, 1-octyl; PDI, pyridine-diimine; PMHS, polymethylhydrosiloxane; Pent, 1-pentyl; Pr, 1-propyl; *i*Pr, 2-propyl; Py, pyridyl; SET, single electron transfer; TEMPO, 2,2,6,6-tetramethylpiperidine-1-oxyl; TfO<sup>-</sup>, trifluoromethylsulfonate; TMS, trimethylsilyl; TOF, turnover frequency; Tol, tolyl; TON, turnover number.

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- Acknowledgements
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## 1. Introduction

Homogeneous catalysis using organometallic manganese complexes have gained a tremendous progress during last decade [1-5] and continues to attract considerable attention from academic research community. In particular, since the seminal discovery of first efficient Mn-based (de)hydrogenation catalytic systems by Beller [6] and Milstein [7] in the beginning of 2016, this topic became one of the most rapidly emerging areas in catalysis using Earth-abundant transition metal complexes. Despite many impressive results obtained to date, the initial development of Mn(I)-based reduction catalysis was mainly performed using the transposition of chemical concepts previously applied for catalysts containing isoelectronic Fe(II) and Co(I) metal centers, namely the use of pincer-type ligands with phosphine donor extremities [8-22] capable to activate inert chemical bonds *via* a metal-ligand cooperation [23-26] (**A**, Scheme 1). However, the analysis of recent literature provides growing evidence that tridentate ligand architectures are not mandatory for the design of efficient manganese (de)hydrogenation catalysts, as complexes bearing less elaborated bidentate ligands (**B**, Scheme 1) can be competitive or sometimes even superior in terms of catalytic activity and/or application scope. In addition, some of these successful Mn(I) catalytic systems contain only spectator donor ligands or even are based uniquely on metal carbonyl precursors, thus indicating the existence of unconventional reaction mechanisms undoubtedly arising from the specificity of organometallic manganese chemistry. Indeed, a similar trend can be also evidenced for Mn-catalyzed hydrosilylation-type processes: the evolution from the state-of-the-art Mn(II) catalysts developed by Trovitch [27-29] incorporating polydentate PDI-type scaffolds (**C**, Scheme 1) to the catalytic systems based on simpler bi- (**D**) and monodentate (**E**) donor ligands or even manganese carbonyl  $\text{Mn}_2(\text{CO})_{10}$ .



**Scheme 1.** Evolution of the ligand design in Mn-catalyzed hydrogenation and hydrosilylation.

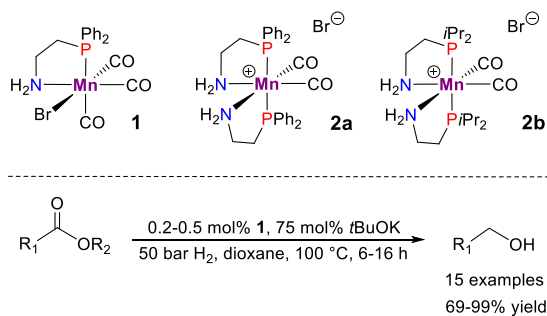
While Mn-catalyzed hydrogenation-type processes have been extensively reviewed [8-22], these contributions have been essentially focused on the most popular pincer-type systems with a particular attention devoted to the comparison between manganese and their 3d metal congeners – iron and cobalt [10-13]. In contrast, this article is focusing on a systematic overview of the catalytic properties of manganese complexes bearing bidentate donor ligands in (de)hydrogenation processes including the analysis of their relative performance depending on the nature of donor moieties (P-, N- and C-donors) and the comparison, when possible, with structurally related pincer scaffolds. The literature is covered until the end of September 2021. The application of Mn(I) complexes **B** in the catalysis of electro- and photochemical  $\text{CO}_2$  reduction [30-32] is out of scope of this contribution. As several excellent review articles on Mn-catalyzed hydrosilylation are available [33-38], in this account we aim to mainly show the recent evolution of ligand design in Mn-catalyzed hydrosilylative transformations of more challenging substrates (carboxylic acid derivatives, alkenes, alkynes).

Mechanistic aspects of these reactions and the influence of auxiliary ligands on the catalytic activity and/or chemoselectivity are presented in detail.

## 2. Manganese complexes bearing bidentate donor ligands in hydrogenation-type reactions

### 2.1. Hydrogenation of unsaturated C=O, C=N and C=C double bonds

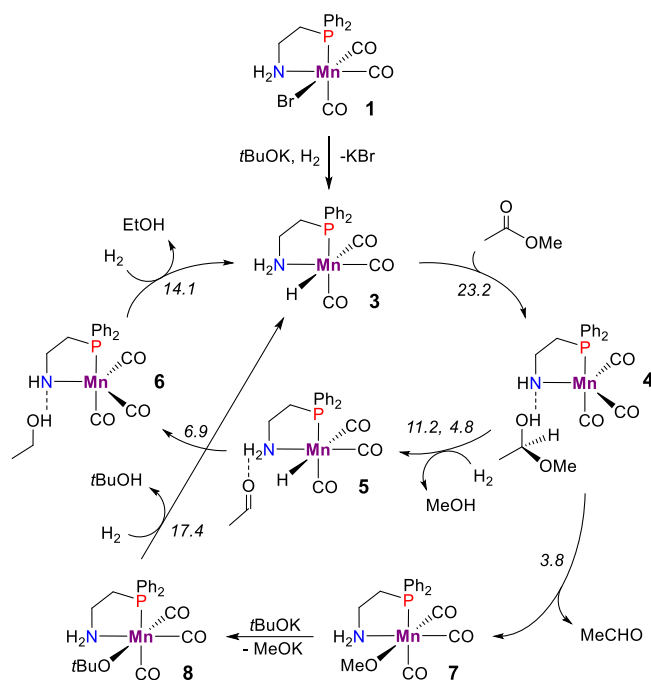
Though the first precedents of catalytic hydrogenation using Mn(0) carbonyl complexes  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$  have been reported more than 40 years ago by the groups of Wender [39] and Cremer [40], these catalytic systems worked only under very harsh conditions (70-200 bar  $\text{H}_2$ , 160-200 °C) with low efficiency (TON of 67 for 1-octene and of 20 for acridine). Later, it was demonstrated by Atwood and coll. [41] that Mn(I) complex *cis*-( $\text{PPh}_3$ )(CO) $_4$ MnH under UV irradiation was able to hydrogenate 1-octene at room temperature and atmospheric hydrogen pressure, albeit the isomerization of the substrate to the mixture of 2-octenes was the major process. However, the first efficient hydrogenation reaction catalyzed by Mn(I) complexes bearing bidentate ligands was reported by Pidko and coll. in 2017. [42] Neutral (**1**) and cationic (**2a-b**) complexes incorporating phosphine-amine ligands were shown to be active in ester hydrogenation (Scheme 2). Upon initial screening pre-catalyst **1** containing one  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NH}_2$  ligand was found to be *ca.* two times more active in the reduction of methyl benzoate than **2a** incorporating two bidentate ligands (75 vs. 43% of substrate conversion), whereas the replacement of Ph substituents at the phosphorus atom by *i*Pr ones resulted in further detrimental effect for the catalytic activity (13% conversion for **2b**). Notably, catalytic system generated *in situ* from  $\text{Mn}(\text{CO})_5\text{Br}$  and one equivalent of PN ligand provided similar activity as for isolated complex **1**. Under optimized conditions a variety of aliphatic and aromatic esters was successfully converted to the corresponding alcohols using only 0.2 mol% of catalyst (TON of 350-500), albeit in the presence of very high amount of base – 75 mol% *t*BuOK. The catalytic system tolerates well terminal and internal alkene moieties, but the conjugated C=C bond in methyl cinnamate was fully reduced to form *in fine*  $\text{Ph}(\text{CH}_2)_3\text{OH}$ .



**Scheme 2.** Hydrogenation of esters catalyzed by Mn(I) PN complexes **1** and **2**.

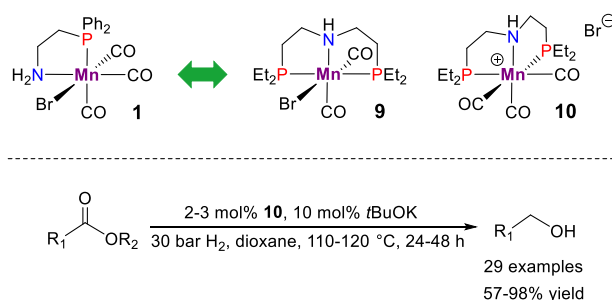
The reaction mechanism for model substrate  $\text{MeCO}_2\text{Me}$  was studied in detail by DFT calculations [42, 43] allowing in particular to clarify the critical importance of the strong excess of base for reaction efficiency especially in the case of esters containing small alkyl substituents. The key step of the catalytic cycle includes concerted hydride/proton transfer between the hydride complex **3** and ester to afford the intermediate **4**, in which the hemiacetal moiety is hydrogen-bonded to deprotonated PN ligand (Scheme 3). The subsequent hydrogenative cleavage of C–O bond affords methanol and acetaldehyde complex **5**, which is then easily reduced to **6** followed by the regeneration of the starting hydride complex **3** in the presence of dihydrogen. Importantly, the alternative amide-assisted fragmentation of hemiacetal intermediate **4** leads to the formation of methoxide species **7** resistant to hydrogenolysis to form **3** and thus representing the main catalyst deactivation pathway. It

was shown that high concentration of *t*BuOK, besides a transformation of **7** into more reactive *tert*-butoxide species **8**, additionally increases the polarity of reaction medium making each step in the sequence **7**→**8**→**3** more thermodynamically favorable.



**Scheme 3.** Simplified catalytic cycle for the hydrogenation of methyl acetate catalyzed by Mn(I) complex **1** based on DFT study (activation energy barriers are given in kcal/mol, in case of two-step process both values separated by comma are given).

Similar Mn-catalyzed ester hydrogenation protocol with an ample substrate scope was originally introduced by the group of Beller using complexes **9** and **10** exhibiting PNP pincer ligands (Scheme 4) [44], which can be formally considered as an extension of PN-type ligand with a second  $\text{CH}_2\text{CH}_2\text{PR}_2$  arm. Both neutral and cationic pre-catalysts showed identical results assuming *in situ* formation of the same catalytically competent dicarbonyl hydride species  $(\text{PNP})\text{Mn}(\text{CO})_2\text{H}$ . Importantly, in this case the use of small ethyl substituents at the phosphorous atoms was found to be crucial, as analogous manganese bromide complexes  $(\text{PNP})\text{Mn}(\text{CO})_2\text{Br}$  with more common bulkier *i*Pr and Cy groups showed negligible catalytic activity.

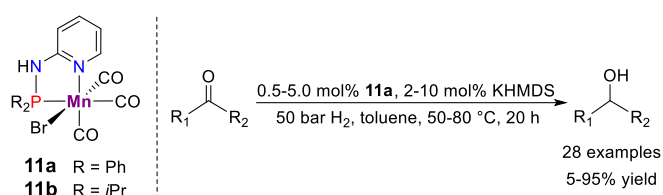


**Scheme 4.** Hydrogenation of esters catalyzed by related Mn(I) PNP complexes **9** and **10**.

The reaction proceeding under similar conditions as in the case of complex **1**, demonstrates the same chemoselectivity *vs.* isolated/conjugated  $\text{C}=\text{C}$  bonds and according to DFT study goes *via* a conceptually close sequence of outer-sphere reduction of ester and aldehyde molecules. While the typical catalyst charge for PNP complex **10** is ten times higher compared to simpler PN congener **1**, this fact is counterbalanced by a significantly lower amount of base required for efficient substrate

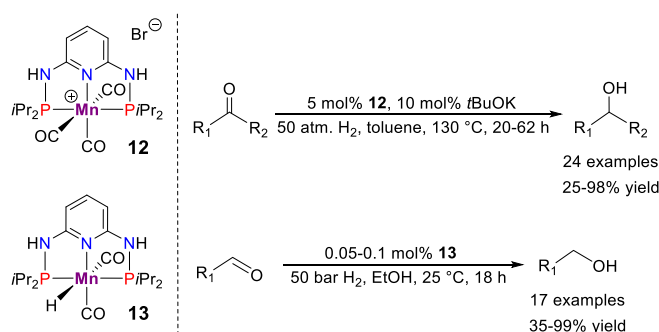
conversion (10 vs. 75%). Though it is difficult to benchmark precisely the relative performance of PN and PNP Mn(I) catalysts due to some fluctuations in reaction conditions (50 vs. 30 bar H<sub>2</sub> / 20 vs. 24 h of reaction time for **1** and **10**, respectively), the reduction of methyl benzoate at 100 °C with the same charge of catalyst (2 mol%) and base (10 mol%) reveals a small preference for pincer-type system affording 97% GC yield of BnOH compared to 80% obtained in the case of its bidentate analogue.

The application of pyridinyl-phosphine manganese complexes **11a-b** in ketone hydrogenation was reported in 2018 by Sortais and coll. (Scheme 5) [45]. As in the case of PN complexes **2a-b**, pre-catalysts **11a** containing Ph<sub>2</sub>P donor moiety was more active than its *i*Pr<sub>2</sub>P analogue **11b** (90 and 65% of acetophenone conversion using 1.0 mol% of catalysts at 80 °C). Aliphatic and aromatic ketones can be smoothly reduced at 50 °C using 0.5 mol% of complex **11a** and 2 mol% of KHMDS or *t*BuOK as a base (TON of 50-190). Noteworthy, this catalytic system tolerates many functional groups including all types of halogens, CF<sub>3</sub>, ester, amide, terminal alkene as well as pyridine and unprotected aromatic amine. The hydrogenation of aromatic enones can be selectively performed at conjugated C=C bonds to form the corresponding saturated ketones isolated in excellent yields, which could be fully reduced at 80-100 °C using higher charge of catalyst and base (5 mol% **11a**, 10 mol% *t*BuOK). The identified scope limitations include sterically bulky substrates as well as nitro, CN and thiophene moieties.



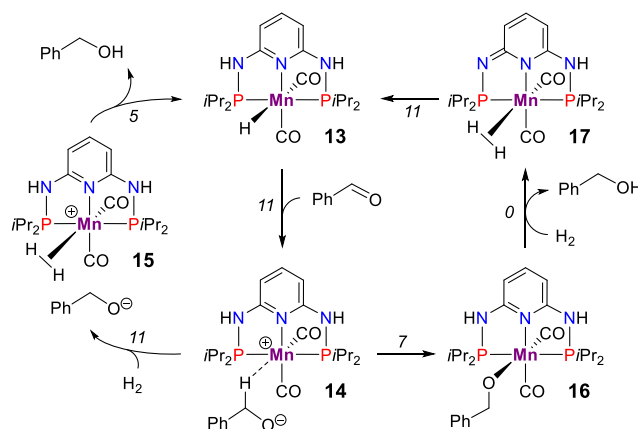
**Scheme 5.** Hydrogenation of ketones catalyzed by Mn(I) PN complexes **11**.

Remarkably, the catalytic activity of cationic tricarbonyl Mn(I) complex **12** based on structurally related PN<sup>3</sup>P pincer-type ligand in ketone hydrogenation was far below the bidentate system **11a** (Scheme 6) [46]. Indeed, in this case the utilization of 5.0 mol% of catalyst and heating at 130 °C was required to achieve reasonable substrate conversion. However, it was shown that the corresponding dicarbonyl neutral hydride derivative **13** was very efficient in hydrogenation of aldehydes at room temperature (Scheme 6) [47]. The selective reduction of aldehyde moiety readily proceeds using 0.05-0.1 mol% of catalyst **13** under base-free conditions and tolerates numerous functional groups including heterocycles and even conjugated C=C bond. The addition of 3 equivalents of DBU as base allowed to further decrease the amount of catalyst to 50 ppm providing TON up to 10400 for *p*-FC<sub>6</sub>H<sub>4</sub>CHO.



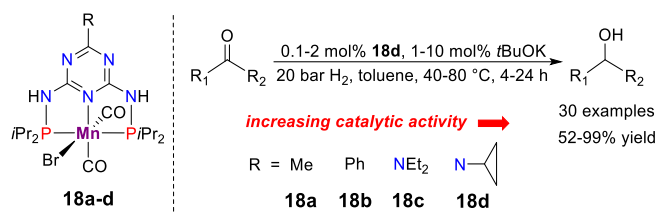
**Scheme 6.** Hydrogenation of ketones and aldehydes catalyzed by Mn(I) PN<sup>3</sup>P complexes **12** and **13**, respectively.

Mechanistic studies revealed the importance of both NH functions in complex **13** and ethanol as solvent for the catalytic cycle. Indeed, the corresponding NMe congener was completely inactive and metal alkoxide intermediate (PN<sup>3</sup>P)(CO)<sub>2</sub>MnOCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>F, which can be reversibly formed upon the reaction of **13** with excess of aldehyde in THF or benzene failed to react with dihydrogen. DFT calculations showed that reduction of PhCHO can proceed *via* two distinct reaction pathways (Scheme 7) characterized by similar energy barriers and implying the participation of ethanol as proton shuttle. Both of them include the direct hydride-ion transfer to aldehyde to form the common zwitterionic intermediate **14** containing C–H bound benzylate anion. This species can either directly react with dihydrogen to give the cationic  $\eta^2$ -H<sub>2</sub> complex **15** producing upon deprotonation with BnO<sup>−</sup> the starting hydride **13** and BnOH, or isomerize to the alkoxide complex **16**. The hydrogenolysis of the latter proceeds *via* a bifunctional mechanism with a participation of acidic NH function to form the neutral  $\eta^2$ -H<sub>2</sub> complex **17** featuring a dearomatized pyridine moiety affording finally **13** upon cooperative H–H bond activation. Curiously, complex **13** being unable to hydrogenate ketones, esters and nitriles acts as efficient catalyst for hydrogenation of *a priori* less reactive CO<sub>2</sub> occurring in THF/H<sub>2</sub>O at 100 °C in the presence of DBU as base and LiOTf as Lewis acid activator with TON up to 31600 [48].



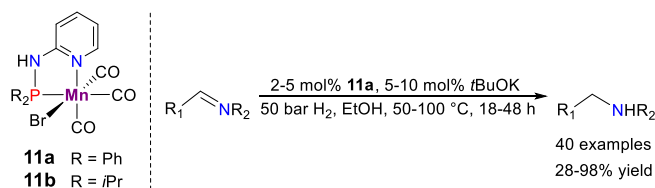
**Scheme 7.** Simplified mechanism for the hydrogenation of benzaldehyde catalyzed by Mn(I) PN<sup>3</sup>P complex **13** based on DFT calculations (activation energy barriers are given in kcal/mol).

The nature of central heterocyclic core in PNP pincer systems plays a crucial role for the catalytic performance, since the replacement of pyridine to more electron-rich *para*-substituted 2,4,6-triazine resulted in PN<sup>5</sup>P complexes **18**, which are very efficient for the hydrogenation of ketones at 80 °C (TON up to 950) using catalyst charge in a range of 0.1-1.0 mol% and ten-fold amount of *t*BuOK as a base (Scheme 8) [49]. The electronic properties of the triazine substituent in *para*-position also strongly affects the catalyst productivity with NHC<sub>3</sub>H<sub>5</sub> affording the best results. In contrast to bidentate PN catalyst **11a** sterically bulky substrates and aromatic ketones bearing NO<sub>2</sub> or CN groups could be efficiently reduced to the corresponding alcohols albeit with higher 1.0-2.0 mol% catalyst charge.



**Scheme 8.** Hydrogenation of ketones catalyzed by Mn(I) PN<sup>5</sup>P complexes **18**.

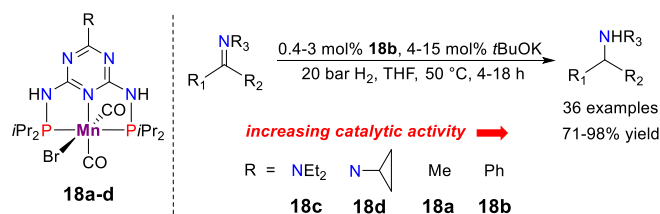
Pyridinyl-phosphine manganese complexes **11a-b** were also shown to be viable catalysts for the hydrogenation of aldimines (Scheme 9) [50]. Complex bearing Ph<sub>2</sub>P moiety was again *ca.* 2 times more active than its *i*Pr<sub>2</sub>P analogue affording 74 and 40% product yield in hydrogenation of model Ph(H)C=NPh under standard conditions using 2 mol% **11a** and **11b**, respectively. Noticeably, this catalytic system is water-tolerant, because the starting aldimines were obtained *in situ* by the condensation of aldehydes with 1.2 equivalents of the corresponding primary amines. This protocol showed a large substrate scope and target amine products were typically obtained in >90% yield. Other reducible functional groups (ketone, ketimine, ester, amide, alkene) remained completely intact and a variety of heterocyclic functions was well-tolerated. Importantly, the hydrogenation of aldimines derived from β- or γ-aminoalcohols did not produce any side products from the competitive N-alkylation processes. The use of enantiomerically pure aminoalcohols and aminoesters in this Mn-catalyzed reductive amination did not lead to the erosion of optical purity in the final products.



**Scheme 9.** Hydrogenation of aldimines catalyzed by Mn(I) PN complexes **11**.

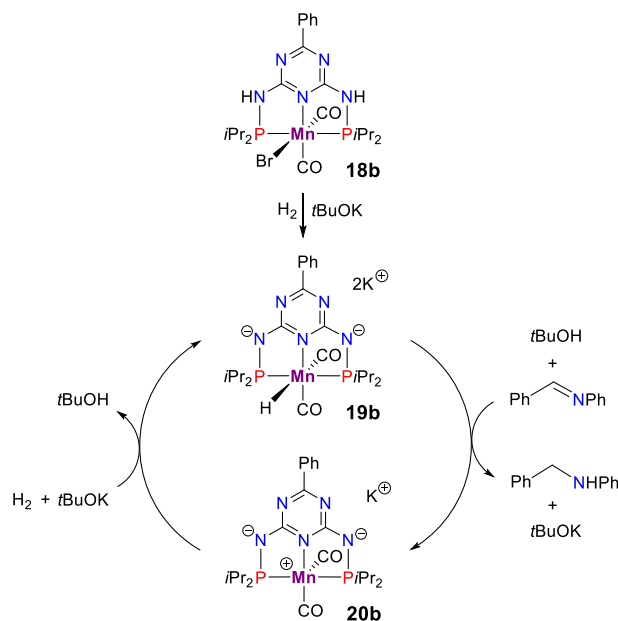
While PN<sup>3</sup>P pincer analogue of complex **11b** showed negligible activity in hydrogenation of Ph(H)C=NPh, PN<sup>5</sup>P complexes **18** exhibiting triazine core represent the most active to date Mn-based systems for C=N bond hydrogenation (Scheme 10) [51]. Contrary to ketone hydrogenation catalysis (Scheme 8) *para*-amino substituted species **18c-d** were *ca.* 2 times less efficient than complexes bearing Me and especially Ph group supposing in the latter case the positive role of electron-withdrawing substituents. However, further increase of the accepting character of aryl using *p*-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub> led to poor results. A variety of aldimines can be readily reduced using 0.4 mol% of **18b** and ten-fold excess of *t*BuOK in only 4 hours at 50 °C. The presence of coordinating CN, pyridine, thiophene and SMe groups did not affect the reduction rate, while NO<sub>2</sub> derivatives react more slowly (18 h) and require 0.6 mol% of catalyst to reach good conversion. Though, PN<sup>5</sup>P complex **18b** was also active for ketone hydrogenation (Scheme 8), selective reduction of the C=N bond in aldimine was achieved in the presence of diarylketone moiety, thus illustrating a relevant example of selectivity control upon the change of solvent (toluene *vs.* THF) and reaction temperature (80 °C *vs.* 50 °C). Importantly, five examples of challenging ketimines incorporating CN, pyridine and pyrazine functions were efficiently reduced in 71-85% isolated yield using 1-3 mol% of **18b** and 5-15 mol% of *t*BuOK under mild conditions (20 bar H<sub>2</sub>, 50 °C, 18 h).





**Scheme 10.** Hydrogenation of imines catalyzed by Mn(I) PN<sup>5</sup>P complexes **18**.

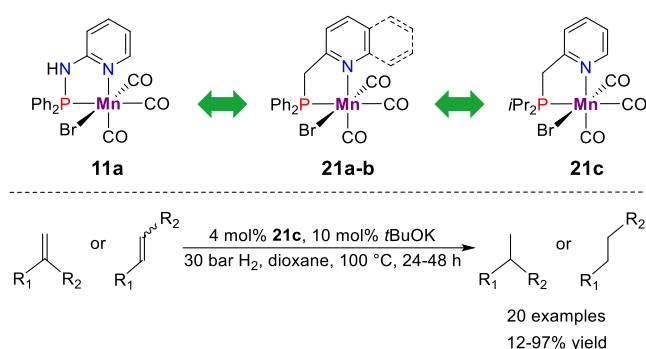
Interestingly, detailed mechanistic investigations revealed the dianionic hydride complex **19b** having bis-deprotonated PN<sup>5</sup>P scaffold to be the key intermediate of this catalytic process (Scheme 11). Indeed, the reduction of C=N bond proceeds *via* the concerted outer-sphere hydride transfer to the substrate with concomitant protonation by *t*BuOH to form the target amine and mono-anionic 16-electron species **20b** regenerating the starting hydride **19b** upon H<sub>2</sub> activation in the presence of base.



**Scheme 11.** Reaction mechanism for the hydrogenation of Ph(H)C=NPh catalyzed by Mn(I) PN<sup>5</sup>P complex **18b** based on stoichiometric experiments and kinetic studies.

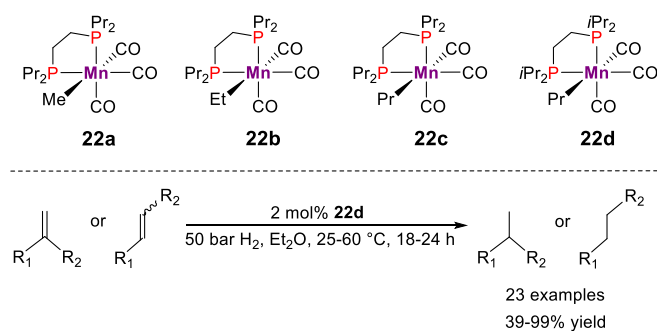
The bridge between phosphine and pyridine in PN complexes also directly influences catalytic activity (Scheme 12). Complex **21a** containing CH<sub>2</sub> unit instead of NH in **11a** was less active in hydrogenation of acetophenone (Scheme 5) [45] and Ph(H)C=NPh (Scheme 9) [50] providing under standard conditions only 15% and 17% conversion, respectively. The replacement of pyridine moiety with quinoline in complex **21b** did not affect the efficiency of ketone reduction, but almost inhibited the activity in the hydrogenation of aldimines. The same trend was observed in the tridentate series, where PNP complex (*i*Pr<sub>2</sub>PCH<sub>2</sub>PyCH<sub>2</sub>P*i*Pr<sub>2</sub>)Mn(CO)<sub>2</sub>H was by far less active in hydrogenation of aldehydes (Scheme 6) [47] than its PN<sup>3</sup>P analogue **13** (TON 21 vs. 2000 for *p*-FC<sub>6</sub>H<sub>4</sub>CHO under the same conditions). However, the group Khusnutdinova has recently shown that PN complex **21c** featuring a CH<sub>2</sub> bridge between two donor units was able to catalyze the hydrogenation of alkenes (Scheme 12) [52]. The catalytic system showed a moderate efficiency for styrenes and terminal aliphatic alkenes (TON 8-24). The incorporation of electron-withdrawing groups or sterically bulky substituents at the C=C double bond led to further drop in yields to 23-34%. While 1,1-disubstituted styrenes can be reduced with reasonable efficiency (25-76%), internal alkenes were almost unreactive. Besides alkenes, this protocol was successfully applied to the hydrogenation of 1,5-

cyclooctadiene and 1-pentadecyne selectively affording cyclooctene and pentadecane in 92% and 99% yield, respectively.



**Scheme 12.** Hydrogenation of alkenes catalyzed by Mn(I) PN complex **21c**.

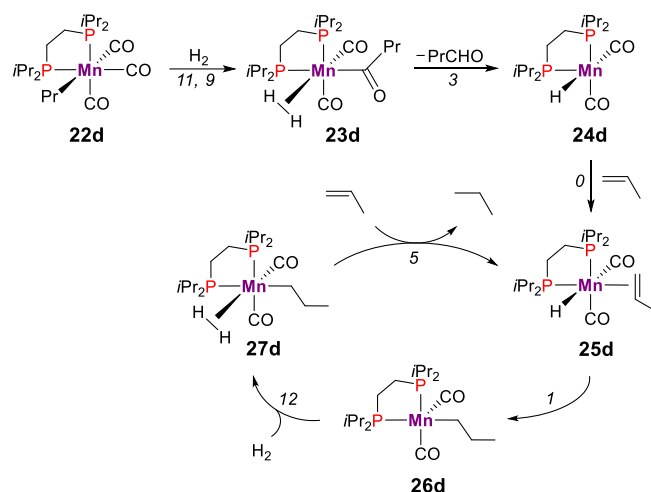
Kirchner and co-workers have shown that alkene hydrogenation can be performed with much higher efficiency using  $\sigma$ -alkyl Mn(I) complexes **22** bearing aliphatic chelating diphosphines (Scheme 13) [53]. Though all complexes **22** were competent as catalysts for the hydrogenation of 1-dodecene under base-free conditions providing full substrate conversion, only **22d** was active at room temperature, whereas **22a** and **22b-c** required heating at 100 °C and 40 °C, respectively. Broad scope of mono- and 1,1-disubstituted alkenes was reduced at 25 °C in most cases in quantitative yield. In contrast to PN complex **21c**, internal alkenes could be easily hydrogenated in excellent yields at slightly higher temperature (60 °C). This protocol was shown to tolerate tri- and tetra-substituted alkene fragments and unprotected alcohols. While esters and anhydride functions remained intact during hydrogenation process,  $\alpha,\beta$ -unsaturated ketone (*E*)-PhCH=CHCOCH<sub>3</sub> was reduced quantitatively at both C=C and C=O bonds. The reduction of pyridinyl alkene derivative was rather sluggish resulting in only 39% conversion, whereas the presence of nitrile or carboxylic groups totally inhibited the reaction.



**Scheme 13.** Hydrogenation of alkenes catalyzed by Mn(I) diphosphine complexes **22**.

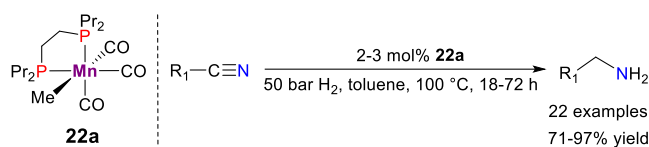
The reaction mechanism was investigated in detail by DFT calculations for the most active catalyst (Scheme 14) [53]. It was shown that the activation of starting  $\sigma$ -alkyl complex **22d** proceeds as a sequence of migratory CO insertion across Mn–alkyl bond with concomitant H<sub>2</sub> coordination, followed by hydrogenative cleavage of Mn–acyl bond in the resulting intermediate **23d** to form 1-butanal and 16-electron hydride complex **24d**. This proposition was in full agreement with more difficult activation of complexes **22a** vs. **22b-c** due to the increase of the activation barrier for migratory insertion in Me>Et>Pr row and with the absence of catalytic activity for the corresponding tricarbonyl hydrides. Coordination of the substrate to the latter leads to the formation of  $\eta^2$ -alkene complex **25d** being probably the resting state of this catalytic cycle. The alkene insertion across Mn–H bond in **25d** followed by H<sub>2</sub> coordination affords alkyl-dihydrogen intermediate **27d** liberating

the propane *via* a formal Mn–C bond protonation and the binding of next substrate molecule to close the catalytic cycle.



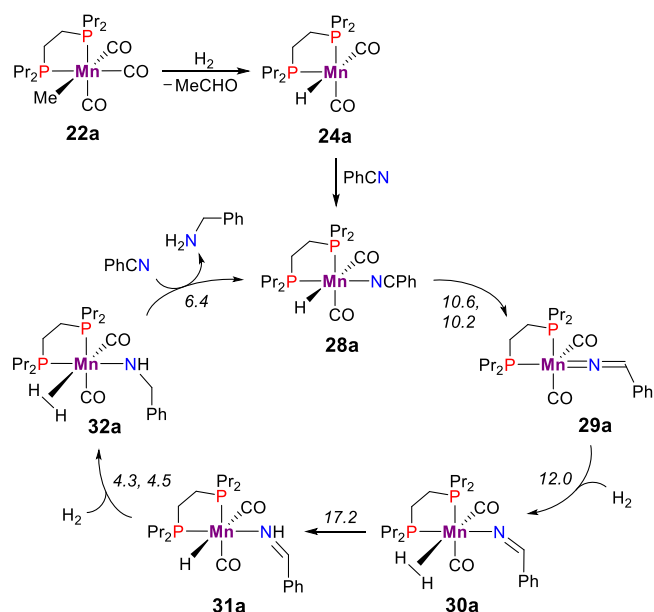
**Scheme 14.** Simplified activation scheme of pre-catalyst **22d** and catalytic cycle for propene hydrogenation based on DFT study (activation energy barriers are given in kcal/mol, in case of two-step process both values separated by comma are given).

Complex **22a** was also active in the hydrogenation of nitriles in the absence of base (Scheme 15) [54]. Aliphatic nitriles and their aromatic analogues bearing electron-donating or electron-withdrawing substituents were readily reduced to the corresponding amines using typically 2 mol% of catalyst. The catalytic system tolerated also halogen substituents, NH<sub>2</sub>, CF<sub>3</sub> and heterocyclic moieties and failed only for nitro derivatives.



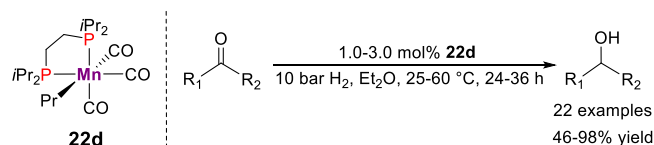
**Scheme 15.** Base-free hydrogenation of nitriles catalyzed by Mn(I) diphosphine complex **22a**.

DFT calculations of reaction mechanism (Scheme 16) [54] revealed the same activation mode for pre-catalyst **22a** affording upon substrate coordination nitrile-hydride complex **28a**. Intramolecular hydride transfer to the nitrile carbon atom in the latter leads to azavinylidene species **29a** transforming in the presence of dihydrogen into the  $\sigma$ -iminyl derivative **30a** and then by the protonation to the imine intermediate **31a**. The reduction of coordinated imine in **31a** proceeds *via* stepwise hydride transfer, hydrogenolysis of Mn–N bond in amide complex **32a** and the coordination of next nitrile molecule.



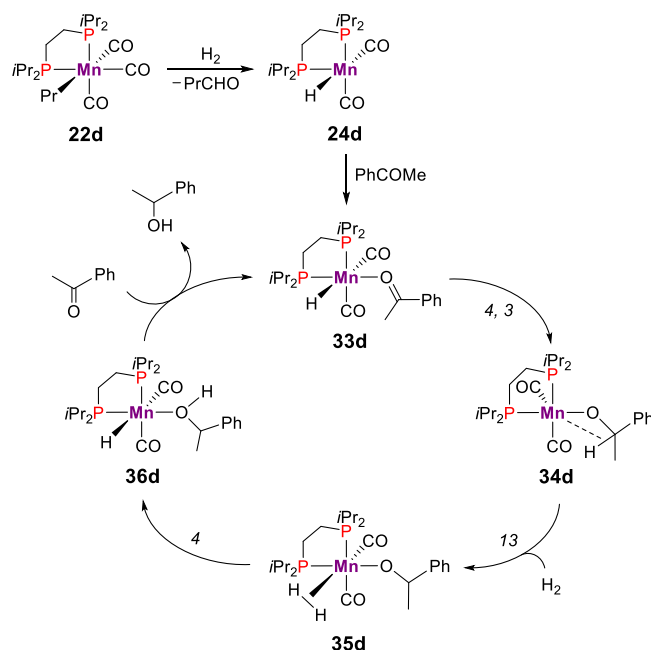
**Scheme 16.** Simplified catalytic cycle for PhCN hydrogenation by complex **22a** based on DFT study (activation energy barriers are given in kcal/mol, in case of two-step process both values separated by comma are given).

It was also shown that diphosphine Mn(I) complex **22d**, which can be activated under very mild conditions, was able to catalyze base-free ketone hydrogenation at room temperature using only 10 bar hydrogen pressure (Scheme 17) [55]. Though the typical catalytic charge (3 mol%) remains quite elevated, this reaction represents a sole example of Mn-based ketone hydrogenation in the absence of base known to date. This catalytic protocol allowed to reduce a variety of aromatic and aliphatic ketones with a good tolerance to halogen, NH<sub>2</sub> and heterocyclic moieties, but was found to be completely inefficient for nitro- and cyano-containing aromatic ketones. Interestingly, the chemoselectivity for hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes and ketones using complex **22d** was strongly dependent on the reaction temperature. It was demonstrated that uniquely C=O bonds were reduced at 25 °C to give the corresponding allylic alcohols being opposite to the behavior of related PN system **11a** (Scheme 5) [45]. In contrast, at 60 °C the conjugated C=C bonds seemed to be hydrogenated before C=O ones affording *in fine* fully saturated products.



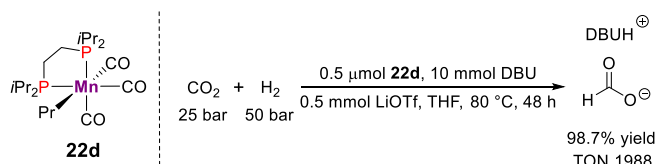
**Scheme 17.** Room temperature hydrogenation of ketones catalyzed by Mn(I) diphosphine complex **22d** under base-free conditions.

The proposed catalytic cycle based on DFT calculations (Scheme 18) includes the initial O-coordination of acetophenone to the unsaturated species **24d** followed by inner-sphere reduction of C=O bond in the resulting complex **33d** to form alkoxide intermediate **34d** stabilized by a C–H agostic interaction. The subsequent coordination of H<sub>2</sub> molecule to the latter, intramolecular proton transfer to form the intermediate **36d** and the displacement of the final product by another acetophenone molecule ends up the catalytic cycle.



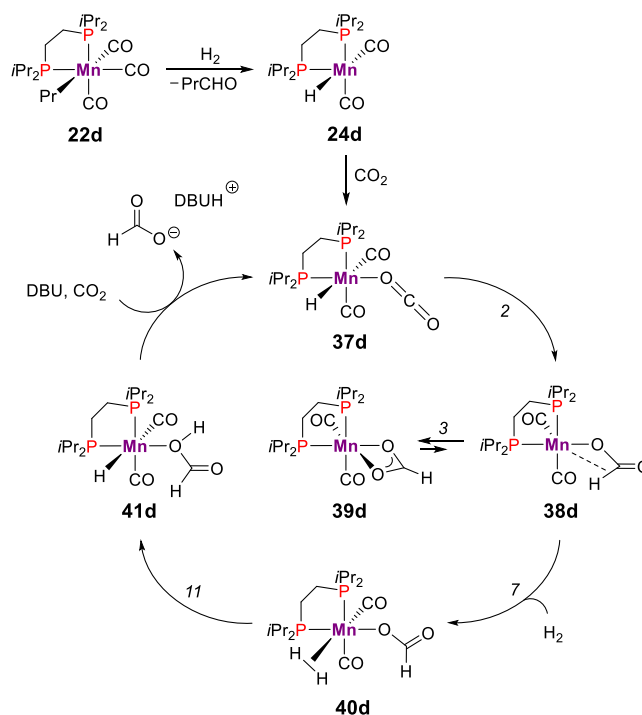
**Scheme 18.** Simplified catalytic cycle for acetophenone hydrogenation by complex **22d** based on DFT study (activation energy barriers are given in kcal/mol, in case of two-step process both values separated by comma are given).

The application of Mn(I) diphosphine complex **22d** for CO<sub>2</sub> hydrogenation to formate was recently reported by Kirchner, Gonsalvi and co-workers (Scheme 19) [56]. Under optimized conditions formate salt was obtained with TON values up to *ca.* 1000 after 24 h at 80 °C in the presence of DBU as base. The utilization of lithium triflate as Lewis acid promoter and extension of the reaction time to 48 h allowed to double the TON value leading to almost quantitative CO<sub>2</sub> conversion.



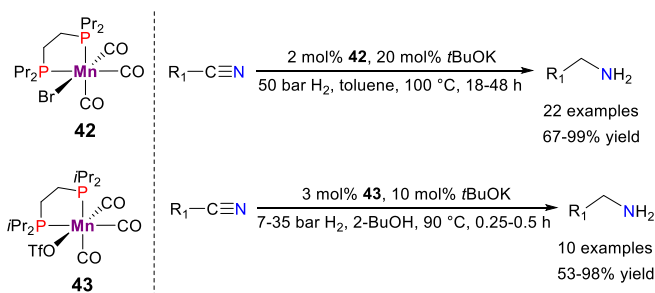
**Scheme 19.** Hydrogenation of CO<sub>2</sub> to formate catalyzed by Mn(I) diphosphine complex **22d**.

The proposed catalytic cycle (Scheme 20) includes the inner-sphere hydride transfer in O-coordinated CO<sub>2</sub> complex **37d** to afford  $\kappa^1$ -O bound formate intermediate **38d** stabilized by a C–H agostic interaction. The latter is in equilibrium with slightly more stable  $\kappa^2$ -O form **39d** representing a catalyst resting state. The catalytic cycle is completed by the coordination of dihydrogen to complex **38d**, intramolecular proton transfer in the resulting  $\eta^2$ -H<sub>2</sub> intermediate **40d** and base-assisted liberation of formic acid from hydride species **41d**.



**Scheme 20.** Simplified catalytic cycle for CO<sub>2</sub> hydrogenation by complex **22d** based on DFT study (activation energy barriers are given in kcal/mol).

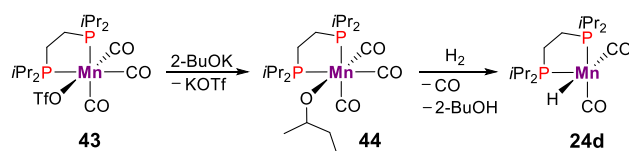
The groups of Kirchner [57] and García [58] have independently demonstrated that nitrile hydrogenation can be also efficiently catalyzed by other Mn(I) diphosphine derivatives **42** and **43** under similar conditions, but uniquely in the presence of base (Scheme 21). Both catalytic systems were able to reduce aliphatic, aromatic and heteroaromatic nitriles in good yields in the presence of other potentially reducible functional groups (ester, conjugated alkene, internal alkyne). It was shown that for complex **43** using secondary alcohols as solvents nitrile reduction can partially proceed as transfer hydrogenation (*vide infra* Scheme 62) and its relative contribution decreased with higher dihydrogen pressure and replacement of *i*PrOH with 2-BuOH. Despite higher catalyst loading complex **43** bearing diphosphine ligand with *i*Pr groups seemed to be more active than its Pr-substituted analogue **42**. As a representative example, the reduction of less reactive *p*-MeOC<sub>6</sub>H<sub>4</sub>CN using pre-catalyst **43** proceeded at lower temperature (90 °C *vs.* 100 °C), hydrogen pressure (7 *vs.* 50 bar), amount of base (3.3 *vs.* 5 equiv.) and revealed much higher TOF values (*ca.* 130 *vs.* 2.2 h<sup>-1</sup>).



**Scheme 21.** Hydrogenation of nitriles catalyzed by Mn(I) diphosphine complexes **42** and **43**.

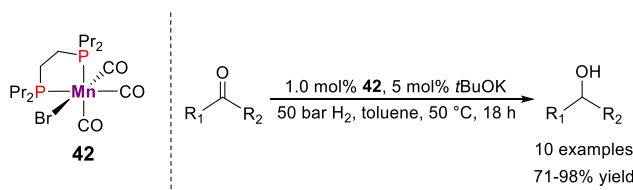
While the formation of the corresponding hydride complexes *fac*-(R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)Mn(CO)<sub>3</sub>H was evidenced in both cases by NMR spectroscopy of the reaction mixtures [57, 58], it was demonstrated that at least one of them (R = *i*Pr) was totally inactive under catalytic conditions and was proposed to be a catalyst deactivation product [58]. Unlike the case of  $\sigma$ -alkyl diphosphine

complexes **22a-d** (Schemes 16, 18, 20), the exact mechanism of nitrile hydrogenation catalyzed by Mn(I) bromide or triflate derivatives **42** and **43** remained unclear to date. While Kirchner and co-workers proposed the existence of base-assisted outer-sphere hydride transfer from *fac*-(Pr<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPr<sub>2</sub>)Mn(CO)<sub>3</sub>H to the substrate [57], García and coll. postulated that catalyst activation included triflate ligand substitution in **43** with 2-BuOK, decarbonylation of the corresponding alkoxide derivative **44** and hydrogenative cleavage of the Mn-alkoxide bond with release of 2-butanol leading to the unsaturated hydride species **24d** (Scheme 22) [58], which can then coordinate the molecule of nitrile and perform the catalytic hydrogenation similarly as depicted in Scheme 16.



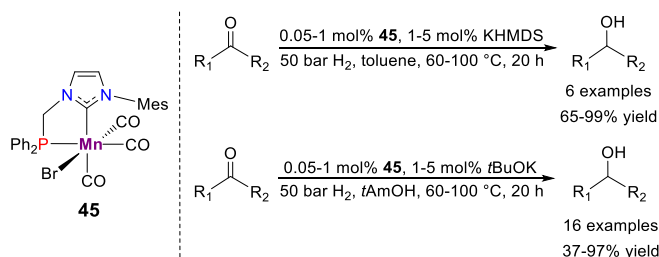
**Scheme 22.** Plausible route for the activation of Mn(I) diphosphine complex **43** in the presence of base.

Complex **42** was also active in ketone hydrogenation providing good yields for aromatic and cyclic aliphatic substrates (Scheme 23) [57]. The comparison of the catalytic activity of diphosphine complex **42** with its phosphine-pyridine analogue **11a** operating under very similar conditions (Scheme 5) revealed slightly higher performance of the PN-based system (TON 180 vs. 94 in hydrogenation of acetophenone using **11a** and **42**, respectively).



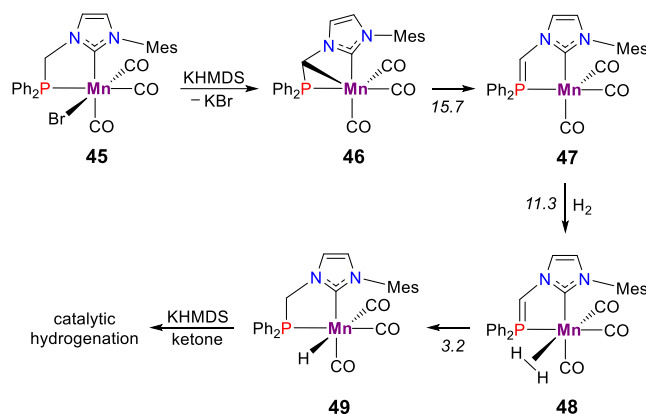
**Scheme 23.** Hydrogenation of ketones catalyzed by Mn(I) diphosphine complex **42**.

The association of phosphine and NHC donors in bidentate ligand was shown to boost significantly the catalytic activity in Mn-catalyzed ketone hydrogenation (Scheme 24) [59]. Indeed, complex **45** afforded quantitative conversion of acetophenone using only 0.1 mol% catalyst loading at 60 °C in toluene and the amount of catalyst may be even reduced to 0.05 mol% at higher temperature (100 °C). Importantly, this reaction can be even better performed in *t*AmOH providing TON up to 6200 at 100 °C using 0.01 mol% of **45** and 1 mol% of *t*BuOK as base. A variety of aromatic and aliphatic ketones was efficiently reduced with this system using typically 0.1-0.5 mol% catalyst charge. In contrast to PN complex **11a** sterically demanding substrates can be readily hydrogenated in 72-85% yield on 0.5 mol% amount of **45**. Halogens, CF<sub>3</sub> and pyridine groups were well tolerated, whereas the reduction of thiophene- and pyrrole-containing ketones was found to be rather sluggish.

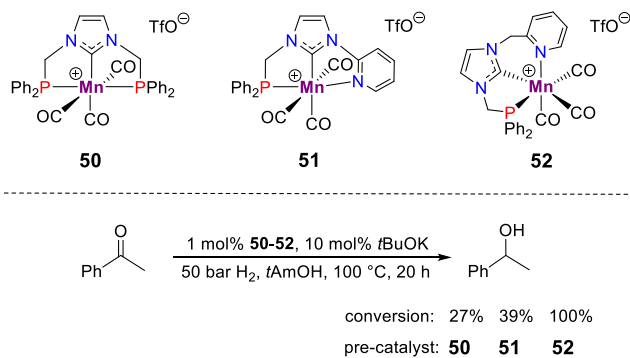


**Scheme 24.** Hydrogenation of ketones catalyzed by Mn(I) phosphine-NHC complex **45**.

Stoichiometric experiments revealed that complex **45** in the presence of a strong base transformed to 18-electron cyclometallated species **46** easily activating H<sub>2</sub> even at low temperature to form hydride product **49** (Scheme 25). DFT calculations showed that this process proceeds *via* initial isomerization of complex **46** into non-classical NHC-phosphonium ylide intermediate **47**, followed by H<sub>2</sub> coordination and cooperative H–H bond activation in the resulting  $\eta^2$ -H<sub>2</sub> complex **48**. It was found that hydride complex **49** was inactive in hydrogenation of acetophenone under base-free conditions even at 5 mol% charge, but can readily re-enter into the catalytic cycle in the presence of base.

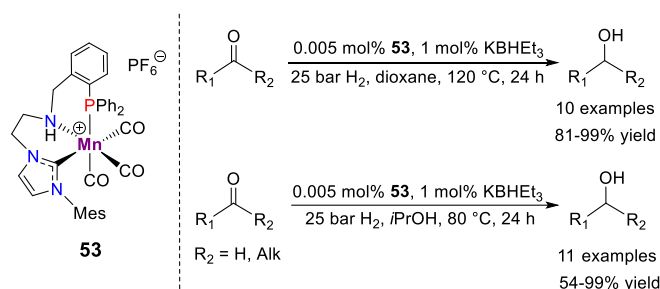
**Scheme 25.** Simplified mechanism of cooperative H<sub>2</sub> activation by NHC-phosphine complex **45** in the presence of KHMDS based on DFT calculations (activation energy barriers are given in kcal/mol).

With the aim to improve the catalytic performance of **45**, the modification of this pre-catalyst by anchoring an additional phosphine or pyridine donor moiety to NHC core was then performed (Scheme 26) [60]. However, the resulting cationic Mn(I) tricarbonyl pincer-type complexes **50-52** were much less active in acetophenone hydrogenation than parent bidentate derivative **45**. The catalytic activity of these systems seemed to correlate with relative rigidity of the pincer ligand, the best results being obtained for PCN complex **52** exhibiting 5,6-membered chelating system. Since the corresponding neutral bidentate complexes *fac*-(Ph<sub>2</sub>PCH<sub>2</sub>NHC–L)Mn(CO)<sub>3</sub>Br displayed very similar results with cationic pincer derivatives **50-52**, it can be reasonably concluded that the same catalytically competent species were formed. Better results obtained for complex **52** may be ascribed to the easier decoordination of the pyridine moiety in a less thermodynamically stable 6-membered metallacycle.

**Scheme 26.** Hydrogenation of acetophenone catalyzed by Mn(I) pincer complexes **50-52** incorporating phosphine-NHC moiety.

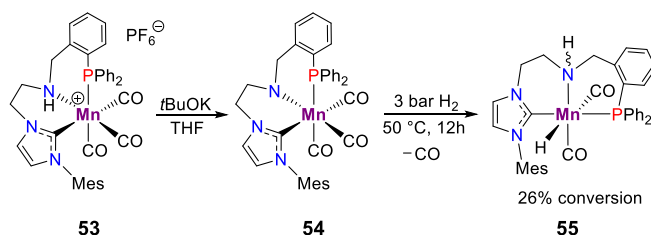


Remarkable potential of NHC-phosphine containing ligands in Mn-catalyzed hydrogenation was further demonstrated by the group of Pidko (Scheme 27) [61]. It was found that cationic complex **53** bearing NHC-amine-phosphine ligand was extremely efficient in the hydrogenation of carbonyl derivatives and aldimines providing excellent levels of conversions at 0.005-0.02 mol% (50-200 ppm) catalyst loading. Interestingly, the use of KBHET<sub>3</sub> as base provided much better results than conventional *t*BuOK, namely 3-7 fold rate acceleration and the absence of an induction period, which was rationalized in terms of more efficient pre-catalyst activation (*vide infra*). Under optimized conditions, acetophenone could be fully reduced after 9 h using only 5 ppm of catalyst charge in dioxane at 120 °C providing TON of *ca.* 200000. Detailed kinetic studies revealed that this catalytic system was on the first order on the pre-catalyst **53** and had a TOF value more than 40000 h<sup>-1</sup>. A variety of arylketones was successfully hydrogenated using 50 ppm of catalyst including sterically hindered substrates. Interestingly, the reduction of dialkylketones and related compounds containing amino groups was possible at lower temperature (80 °C) in isopropanol. While potentially reducible ester group was tolerated under the latter conditions albeit with full transesterification,  $\alpha,\beta$ -unsaturated ketone such as benzylideneacetone was unexpectedly found to be totally unreactive. Aromatic and heteroaromatic aldehydes could be selectively hydrogenated in *i*PrOH without any undesired condensation processes. Alkyl formates were also amenable substrates for this catalytic system leading to full conversion in dioxane at 120 °C with only 0.02 mol% of catalyst charge. Finally, catalyst **53** remained for the moment the most productive for hydrogenation of aromatic aldimines (TON of 900 *vs.* 245 for Ph(H)C=NPh using **53** and **18b**, respectively).

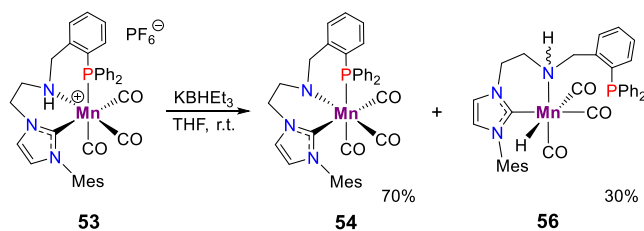


**Scheme 27.** Hydrogenation of aldehydes and ketones catalyzed by Mn(I) pincer complex **53**.

Mechanistic experiments revealed the significant difference in the activation of complex **53** using *t*BuOK and KBHET<sub>3</sub>. It was shown that neutral amide species **54** obtained in a quantitative manner upon deprotonation of the starting material with *t*BuOK (Scheme 28) reacted with dihydrogen very sluggishly to form pincer hydride species **55** even at 50 °C. In contrast the reaction of **53** with KBHET<sub>3</sub> instantaneously led to the formation of **54** and tricarbonyl hydride product **56** bearing bidentate NHC-amine ligand with pendant phosphine moiety. Noteworthy, NMR monitoring of the stoichiometric reaction between the mixture **55/56** and acetophenone showed higher reactivity of the bidentate complex. Though a slow decarbonylation of **56** into **55** was possible, the realization of two distinct catalytic cycles involving hydride intermediates with both bi- and tridentate ligand coordination modes cannot be excluded.

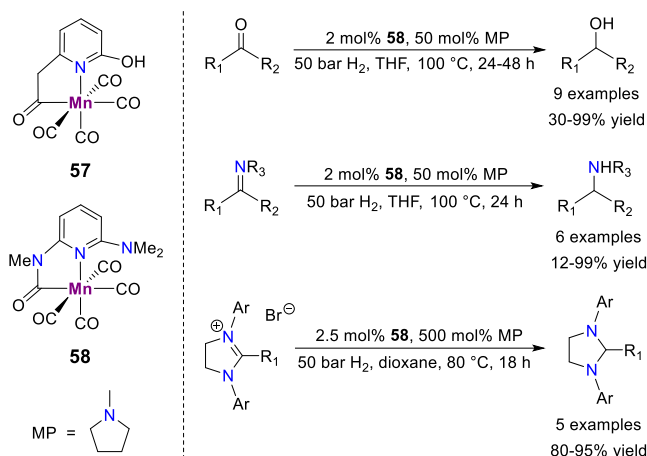


**Scheme 28.** Activation of Mn(I) pincer complex **53** using *t*BuOK.



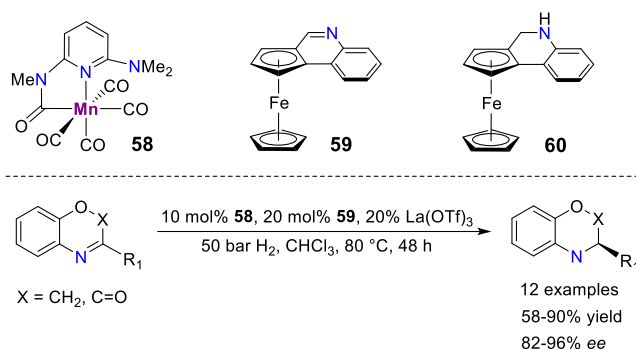
**Scheme 29.** Activation of Mn(I) pincer complex **53** using  $\text{KBHET}_3$ .

The group of Hu has found that bidentate ligands incorporating carbon-based donors applicable in Mn-catalyzed hydrogenation are not restricted to NHCs (Scheme 30) [62,63]. It was shown that Mn(I) tetracarbonyl complexes **57** and **58** bearing chelating pyridine-acyl and pyridine-carbamoyl ligands, respectively demonstrated modest activity in hydrogenation of aldehydes and ketones in the presence of *N*-methylpyrrolidine (MP) weak base. Despite complex **57** contains non-innocent 2-hydroxypyridine fragment, its analogue **58** having *a priori* no cooperative functionalities was much more active in hydrogenation of ketones and imines providing *ca.* 2-, 7- and 9.5-fold increase of TON values for the reduction of acetophenone,  $\text{Ph(H)C=NPh}$  and  $\text{Ph(Me)C=NPh}$ , respectively. Though the activity of catalyst **58** was far below the best Mn-based catalytic systems, it was capable to catalyze efficiently the hydrogenation of aryl-substituted imidazolium salts failed for Mn(I) complexes **1** (Scheme 2) and **9** (Scheme 4,  $\text{R} = i\text{Pr}$ ) bearing PN and PNP ligands, respectively.



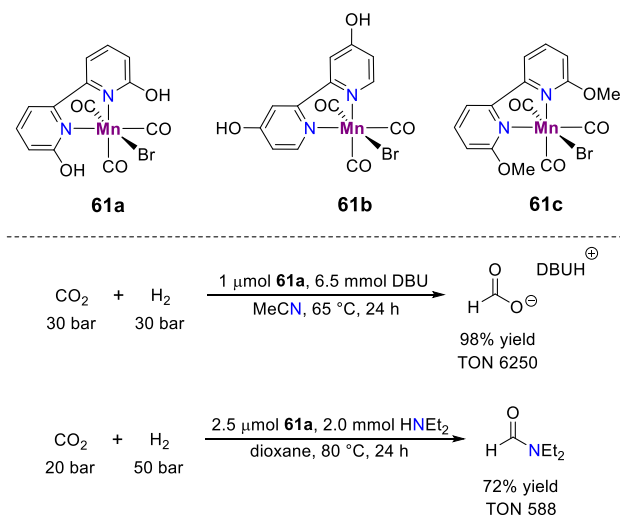
**Scheme 30.** Hydrogenation of aldehydes, imines and imidazolium salts using Mn(I) complex **58**.

Such C=N bond hydrogenation was then used as one of key steps for the asymmetric relay hydrogenation of benzoxazinones and benzoxazines using a combination of catalyst **58** with planar-chiral ferrocene derivative **59** (Scheme 31) [63]. The reduction of the latter produced the saturated compound **60** capable to perform the enantioselective hydride transfer to these substrates in the presence of  $\text{La(OTf)}_3$  as Lewis acid. This protocol allowed to get the target products in good-to-excellent yields and useful level of enantioselectivity.



**Scheme 31.** Relay hydrogenation of benzoxazinones and benzoxazines using the combination of Mn(I) complex **58** and planar-chiral ferrocene-based imine **59**.

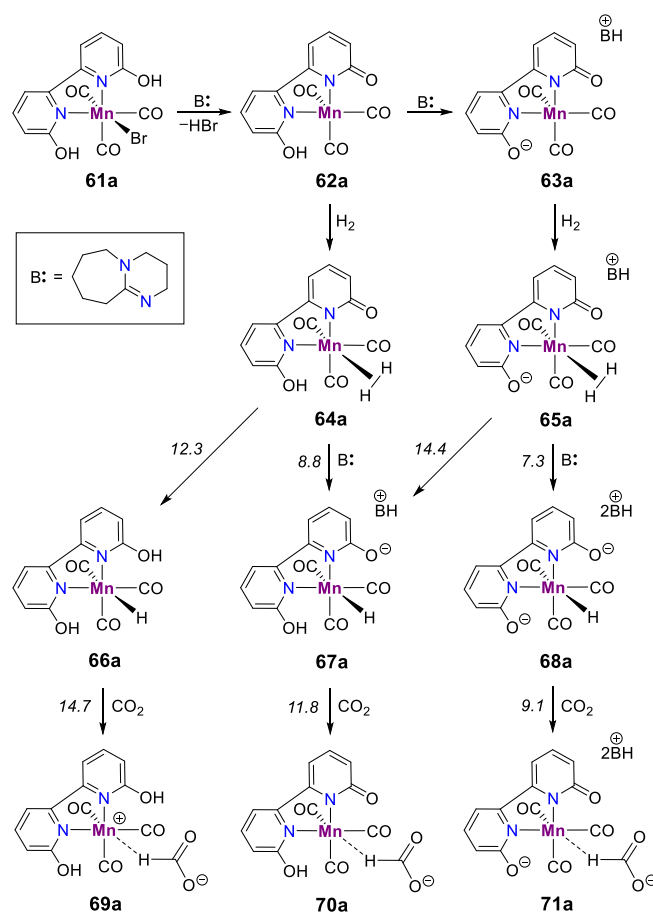
The association of two 2-hydroxypyridine units in the bidentate NN ligand was successfully used by Khusnutdinova, Nervi and co-workers for Mn-catalyzed CO<sub>2</sub> hydrogenation to formate or diethylformamide (Scheme 32) [64]. Under optimized conditions up to 6250 TON for the formation of DBU formate salt was achieved with complex **61a** in acetonitrile at 65 °C. The corresponding cationic complex [(NN)Mn(CO)<sub>3</sub>(MeCN)](OTf) displayed the same performance thus assuming a facile dissociation of the bromide ligand in **61a** in highly polar medium. This Mn(I) NN system was *ca.* 3 times superior in terms of TON than PP complex **22d** (Scheme 19) [56] under lower temperature and optimal H<sub>2</sub>/CO<sub>2</sub> ratio (1:1 vs. 2:1 for **61a** and **22d**, respectively). The presence of hydroxyl groups in the proximity to the metal center in complex **61a** was shown to be a critical factor since its *para*-hydroxylated **61b** or methylated **61c** analogues revealed negligible catalytic activity (TON 18 and 160, respectively). Importantly, diethylformamide could be also prepared using this catalytic system with TON up to 588, but higher temperature and dihydrogen pressure were necessary in this case.



**Scheme 32.** Hydrogenation of CO<sub>2</sub> to formate and diethylformamide catalyzed by Mn(I) complex **61a** bearing bidentate NN ligand.

The mechanism of this reaction was studied by DFT calculations by the groups of Pati [65] and Yang [66] (Scheme 33). It was proposed that pre-catalyst **61a** in the presence of large excess of DBU could undergo single or double deprotonation to afford neutral **62a** and anionic **63a** intermediates, respectively each of them containing one dearomatized pyridine moiety. Both compounds in the presence of dihydrogen transform into the corresponding η<sup>2</sup>-H<sub>2</sub> complexes **64a** and **65a**, which can undergo either a cooperative H–H bond activation assisted by the pendant aryloxide moiety or the H–H bond deprotonation with external molecule of DBU to afford hydride complexes **66a-68a**

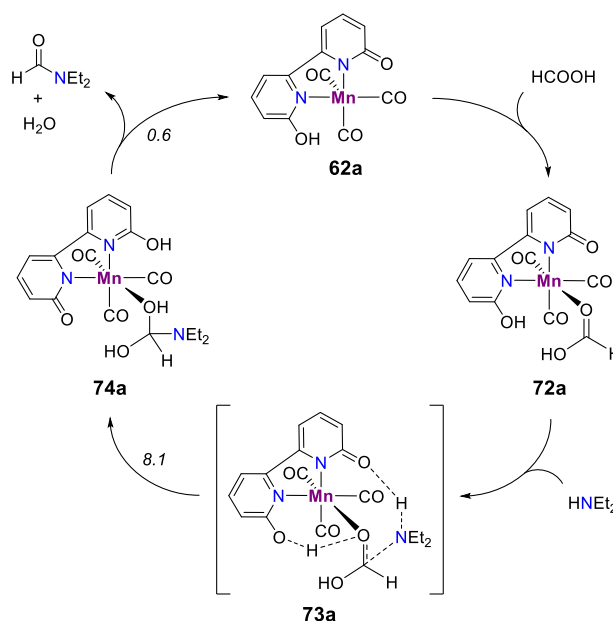
differing in the overall molecule charge. The activation barriers for DBU-assisted routes are lower than for cooperative activation, especially for monoanionic complex **65a**. Direct hydride transfer from complexes **66a-68a** to CO<sub>2</sub> afforded the intermediates **69a-71a** exhibiting a formate anion hydrogen-bonded to Mn(I) center regenerating the corresponding dihydrogen complexes by the subsequent release of the product. The energy barriers for CO<sub>2</sub>-to-formate conversion gradually decreased in **66a**→**67a**→**68a** row being consistent with the increased hydricity of anionic species. While the lowest energy profile **63a**→**65a**→**68a**→**71a** includes the double deprotonation of NN ligand, the formation of anionic complex **63a** was not detected by IR spectroscopy in the reaction of **61a** with six equivalents of DBU. Though this pathway can not be totally excluded, it is more probable that the catalytic cycle is mainly operating *via* monodeprotonated intermediate **62a** presented in high concentration along the sequence **62a**→**64a**→**67a**→**70a** being only marginally higher in energy than the previous one.



**Scheme 33.** Different mechanistic pathways for CO<sub>2</sub> hydrogenation to formate in acetonitrile catalyzed by Mn(I) complex **61a** based on DFT calculations (activation energy barriers are given in kcal/mol).

It was also shown by Yang and coworkers that hydroxyl groups in complex **61a** play a critical role in the transformation of CO<sub>2</sub> into diethylformamide (Scheme 34) [66]. The catalytic cycle in this case consists in the O-coordination of formic acid molecule obtained from CO<sub>2</sub> as shown in the Scheme 33 to Mn(I) complex **62a** followed by the nucleophilic attack of diethylamine to the resulting intermediate **72a** *via* the transition state **73a**, in which both oxygen atoms simultaneously participate in N–H bond deprotonation and O–H bond formation. The resulting intermediate **74a** easily loses the target diethylformamide and water with regeneration of starting complex **62a**. Importantly, the

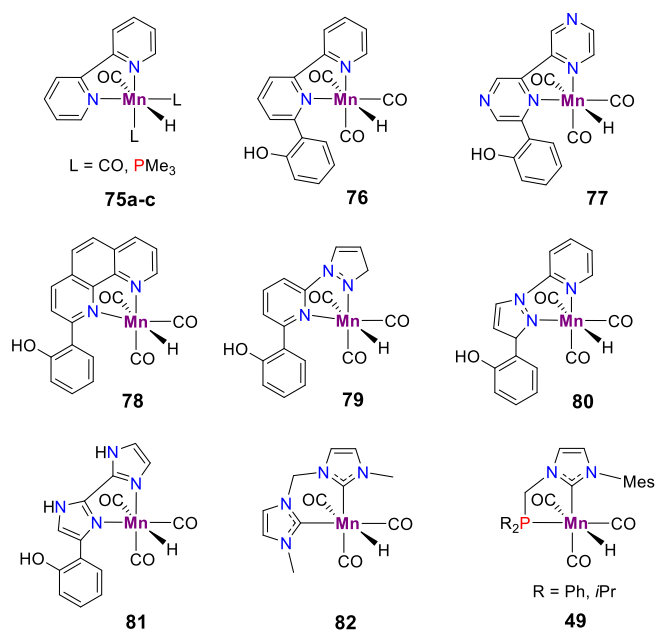
presence of two proton relay sites in **72a** leads to a very low activation barrier (8.1 kcal/mol), whereas alternative mechanisms for Mn-catalyzed process without direct participation of NN ligand or direct reaction between HCOOH and HNEt<sub>2</sub> are much more energy demanding (>40 kcal/mol).



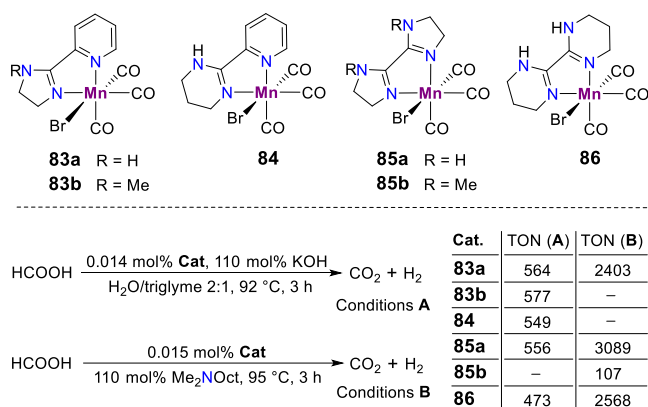
**Scheme 34.** Simplified mechanism for CO<sub>2</sub> hydrogenation to formamide catalyzed by Mn(I) complex **61a** (activation energy barriers are given in kcal/mol).

The relevance of related Mn(I) hydride complexes bearing aromatic nitrogen-based (**75-81**), [67,68] phosphine-NHC (**49**) [69] and bis(NHC) (**82**) [70] ligands for CO<sub>2</sub> hydrogenation was predicted by DFT calculations (Scheme 35), but to date none of them have been tested experimentally.

Interestingly, it was recently shown by Beller and co-workers that Mn(I) complexes bearing bidentate NN ligands were highly active in the reverse reaction – dehydrogenation of formic acid to form CO<sub>2</sub> and H<sub>2</sub> (Scheme 36) [71,72]. The catalytic system was initially optimized for aqueous triglyme medium (conditions **A**) [71] and it was found that the presence of at least one cyclic N=C–N fragment in ligand structure was crucial for good catalytic activity. The methylation of non-coordinated nitrogen atom of the imidazoline did not significantly alter the catalytic activity, as catalysts **83a** and **83b** displayed similar performance. Importantly, the activity of well-defined Mn(I) complex **83a** was identical to the catalytic system prepared *in situ* from Mn(CO)<sub>5</sub>Br and pyridine-imidazoline. Kinetic experiments revealed a strong decrease of the reaction rate catalyzed by **83a** after *ca.* 30 min corresponding to *ca.* 8% of formic acid conversion, which was attributed to the increasing pH of the medium. Since low pH values due to excess of formic acid were also detrimental for catalysis, this problem was solved by continuous slow addition of HCOOH revealing a maximal TON value of 5763 after 45 h of reaction time corresponding to 67% of substrate conversion.



**Scheme 35.** Mn(I) complexes bearing bidentate ligands studied by DFT calculations as CO<sub>2</sub> hydrogenation catalysts.

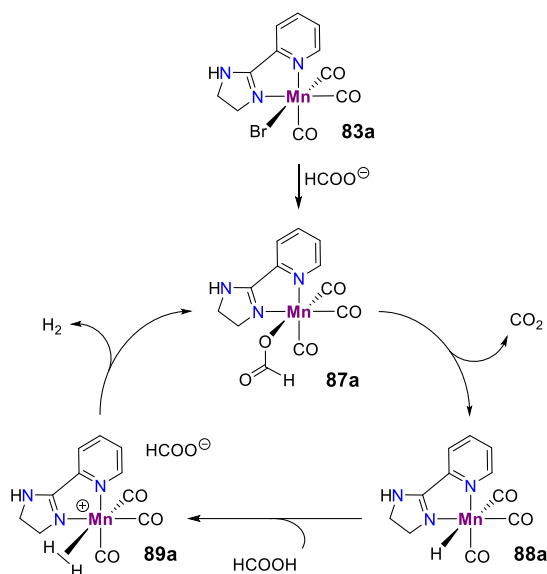


**Scheme 36.** Formic acid dehydrogenation catalyzed by Mn(I) complexes **83-86** bearing bidentate NN ligands.

Later on it was found that the replacement of KOH base by dimethyl(octyl)amine allowed to achieve better substrate conversion without slow addition of formic acid due to more efficient pH control (conditions **B**) [72]. Under these conditions bis-imidazoline complex **85a** was more active than previously used **83a** providing TON of 3089 and 6738 after 3 h and 12 h, respectively, corresponding in the latter case to full conversion. The stability of this catalytic system was also demonstrated by a long-term experiment using the regular addition of new portions of HCOOH (12 cycles during 4 days) revealing an almost unchanged H<sub>2</sub> evolution rate with a final TON value of 7883. Notably, CO content in the resulting CO<sub>2</sub>/H<sub>2</sub> mixture under these conditions (39-60 ppm) was much lower than using catalyst **83a** (757-832 ppm, conditions **A**), which is of critical importance for application in fuel cells.

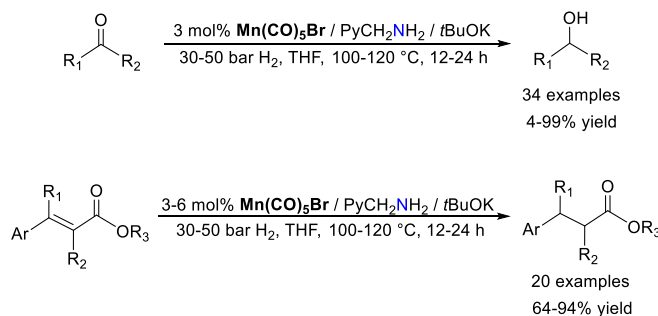
The proposed mechanism of formic acid dehydrogenation (Scheme 37) included the initial formation of formate complex **87a**, detected by NMR in the reaction mixture and characterized by X-ray diffraction in the case of pre-catalyst **83a**. The decarboxylation of the latter species led to the hydride **88a**, further undergoing the protonation to  $\eta^2\text{-H}_2$  intermediate **89a** and dihydrogen loss closing the catalytic cycle. The observation of significant KIE for DCOOD/DCOOK using both H<sub>2</sub>O

(1.89) and D<sub>2</sub>O (2.08) was consistent with decarboxylation of complex **87a** as a rate determining step. This mechanism clearly explained the critical role of pH in order to maintain in the reaction medium sufficient concentration of both formate anion required for the formation of **87a** and free acid necessary for the efficient decomposition of the hydride **88a**.



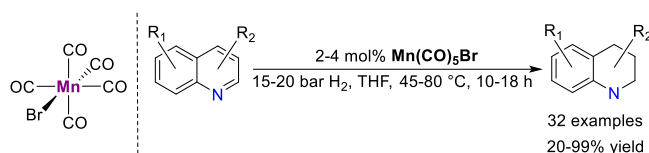
**Scheme 37.** Mechanism for formic acid dehydrogenation catalyzed by Mn(I) complex **83a** bearing pyridine-imidazoline ligand.

Very recently, Topf and coll. showed that catalytic system generated *in situ* from Mn(CO)<sub>5</sub>Br and 2-picolylamine in the presence of base was active for hydrogenation of ketones and alkenes bearing electron-withdrawing groups (Scheme 38) [73]. The 1:1 metal/ligand ratio was found to be optimal providing 99% product yield upon hydrogenation of acetophenone under rather harsh conditions (3 mol% of catalyst, 3 mol% *t*BuOK, 50 bar H<sub>2</sub>, THF, 120 °C, 12 h), whereas two-fold excess of diamine ligand led to inferior results (25% alcohol yield). Interestingly, the catalytic activity of well-defined diamine complex (NN)Mn(CO)<sub>3</sub>Br at the same catalytic charge was much lower affording only 8% product yield. Though a variety of non-functionalized aromatic and aliphatic ketones was reduced in nearly quantitative yield using 3 mol% catalyst, this system remains significantly less active compared to the Mn(I) complexes bearing PN, PP and PC ligands (*vide supra*). While F, Cl, CF<sub>3</sub> and CN groups were well tolerated the hydrogenation of bromo- and iodo-substituted aromatic ketones led to only 4-23% yields. The reduction of  $\alpha,\beta$ -unsaturated esters proceeds selectively at the C=C bond to form the target products in good-to-excellent yields, albeit two-fold increase of catalyst charge was required in some cases.



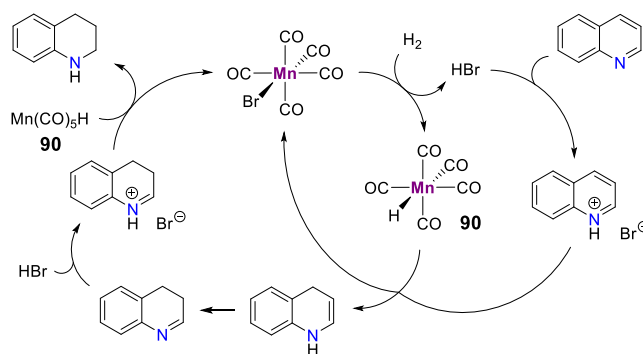
**Scheme 38.** Hydrogenation of ketones and  $\alpha,\beta$ -unsaturated esters catalyzed by Mn(I) catalyst generated *in situ* from Mn(CO)<sub>5</sub>Br and equimolar amount of 2-picolylamine and *t*BuOK.

Interestingly, Beller and co-workers have demonstrated that hydrogenation of quinolines can be performed efficiently using simple  $\text{Mn}(\text{CO})_5\text{Br}$  precursor without any auxiliary ligands (Scheme 39) [74]. A variety of diversely-substituted tetrahydroquinolines was obtained under mild conditions (typically 15 bar of  $\text{H}_2$ , 45 °C, 18 h) using 2 mol% of pre-catalyst. Halogens, triflate,  $\text{CF}_3$ , pyrazole or unprotected OH groups were readily tolerated and this protocol could be also extended to the reduction of other fused N-heterocycles, namely isoquinoline, quinoxaline, acridine and naphthyridine. Importantly, this catalytic system was particularly chemoselective for hydrogenation of quinoline ring leaving intact other reducible fragments including ketones, esters, nitriles and conjugated C=C bonds. Only for 3-acetoxy- and 3-cyanoquinolines small amounts of over-reduction products were detected affording however acceptable yields of target tetrahydroquinolines (47 and 65%, respectively). It is noteworthy that the use of 2.5 mol% of Mn(I) PNP complex  $(\text{HN}(\text{CH}_2\text{CH}_2\text{P}i\text{Pr}_2)_2)\text{Mn}(\text{CO})_2\text{Br}$  for hydrogenation of quinoline provided only 9% yield even under more forcing conditions (50 bar  $\text{H}_2$ , THF, 140 °C, 18 h) thus demonstrating remarkable advantage of using auxiliary ligand-free Mn-based catalytic system.



**Scheme 39.** Hydrogenation of quinolines catalyzed by  $\text{Mn}(\text{CO})_5\text{Br}$ .

The catalytic cycle for quinoline hydrogenation based on detailed mechanistic studies is shown in Scheme 40. The key step of this transformation involved the hydrogenative cleavage of Mn–Br bond in  $\text{Mn}(\text{CO})_5\text{Br}$  to form the corresponding Mn(I) hydride **90** and HBr instantaneously trapped with basic substrate. The reduction of the resulting activated quinolinium salt was likely to proceed as 1,4-hydride addition with concomitant regeneration of starting  $\text{Mn}(\text{CO})_5\text{Br}$  to form 1,4-dihydroquinoline. The latter undergoes the rearrangement into 3,4-dihydroquinoline followed by protonation and the reduction of activated C=N bond. It was also shown that  $\text{Mn}(\text{CO})_5\text{Br}$  partially disproportionated under reaction conditions to  $\text{Mn}_2(\text{CO})_{10}$  – an additional source of  $\text{Mn}(\text{CO})_5\text{H}$  by hydrogenative metal-metal bond cleavage and  $\text{MnBr}_2$ , which could serve as Lewis acid additive for substrate activation.

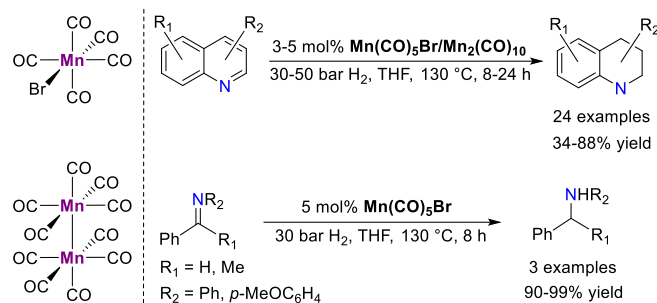


**Scheme 40.** Proposed catalytic cycle for hydrogenation of quinolines catalyzed by  $\text{Mn}(\text{CO})_5\text{Br}$ .

Shortly after the publication of Beller, the group of Wang independently reported the hydrogenation of quinolines and imines catalyzed by  $\text{Mn}(\text{CO})_5\text{Br}$  and  $\text{Mn}_2(\text{CO})_{10}$  (Scheme 41) [75]. The use of 3 mol%  $\text{Mn}_2(\text{CO})_{10}$  also led to a full quinoline conversion, thus showing that acidic activation of the substrate with HBr (Scheme 40) was not mandatory under harsh conditions. Importantly, aromatic aldimines and ketimines could be hydrogenated with excellent yields (Scheme



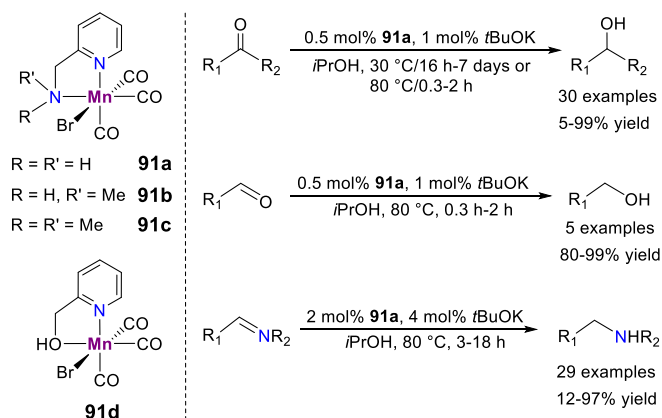
41). Though catalyst charge remained quite elevated at the moment, this system clearly illustrates the potential of simple acidic Mn(I) carbonyl hydrides for the hydrogenation of C=N bonds in the presence of Brønsted or Lewis acid as activators.



**Scheme 41.** Hydrogenation of quinolines and imines catalyzed by  $\text{Mn}(\text{CO})_5\text{Br}$  and  $\text{Mn}_2(\text{CO})_{10}$ .

## 2.2. Transfer hydrogenation processes

The first example of transfer hydrogenation catalyzed by Mn(I) complexes **91** bearing bidentate 2-picolyamine ligands was reported in 2017 by Sortais and coll. (Scheme 42) [76]. Acetophenone could be quantitatively reduced to the corresponding alcohol using isopropanol as a hydrogen donor only after 15 min of heating at 80 °C in the presence of 0.5 mol% of pre-catalyst **91a** and two-fold excess of *t*BuOK as base. The amount of catalyst could be divided by ten still affording 58% conversion in 10 min and a complete consumption of the starting material after 2 h. A series of experiments at 0.01-0.1 mol% catalyst loading revealed the average TOF of 3600 h<sup>-1</sup> and maximum TON of 2000 in this reaction. While complex **91b** bearing *N*-methylated ligand containing NHMe moiety was only slightly less performant than **91a**, the analogous derivatives **91c** and **91d** incorporating NMe<sub>2</sub> and OH donor extremities, respectively showed negligible catalytic activity.



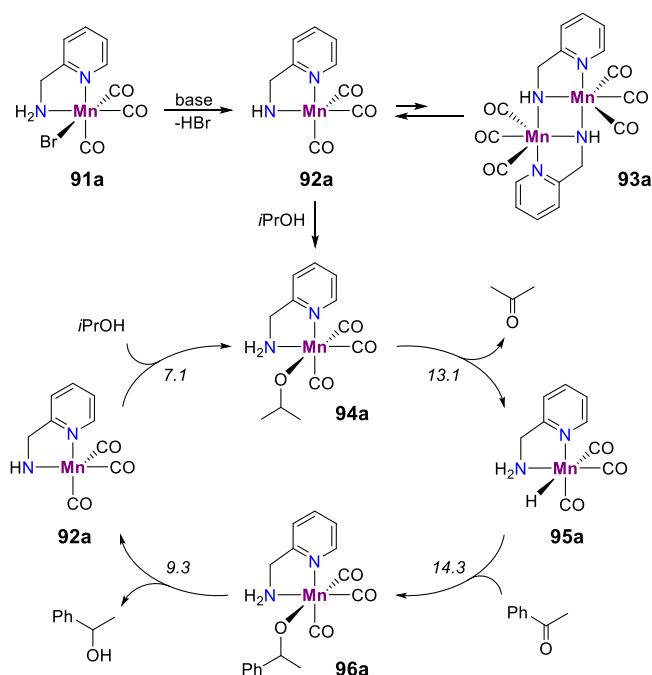
**Scheme 42.** Transfer hydrogenation of ketones, aldehydes and imines catalyzed by Mn(I) complex **91a** bearing 2-picolyamine ligand.

This protocol showed a spectacular application scope and functional group tolerance. Both aromatic and aliphatic ketones were readily reduced including sterically bulky and highly electron-rich substrates. Aldehydes could also serve as suitable substrates providing the primary alcohol products with low amounts (up to 5-7%) of aldol-like condensation products. Remarkably, the reaction can readily proceed even at 30 °C, albeit much more slowly (16 h), with similar or sometimes even better efficiency. Halogens, CF<sub>3</sub>, aromatic amines and heterocycles were well-tolerated and pre-catalyst **91a** was exceptionally selective for activated C=O bonds, as other potentially reducible fragments such as ester, amide, CN, NO<sub>2</sub>, terminal alkyne and even conjugated C=C bond were

almost not affected. The identified limitations of this catalytic system include 2-acetylpyridine or 2-acetylfuran and 1,3-diketones, probably due to catalyst poisoning by strong chelating coordination. Finally, an equimolar mixture of  $\text{Mn}(\text{CO})_5\text{Br}$  and 2-picolylamine could be readily used instead of well-defined pre-catalyst **91a** affording similar levels of conversion [77].

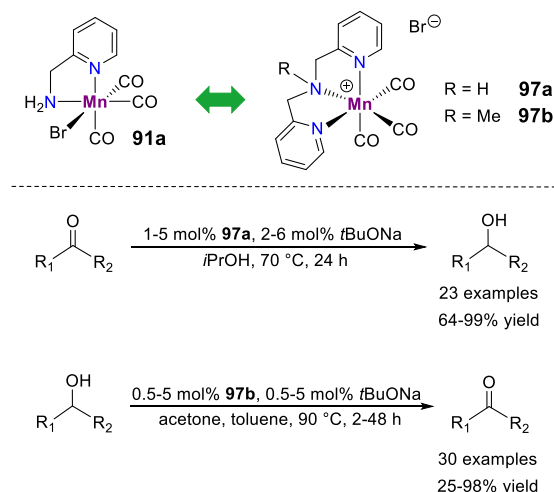
The same Mn(I) complex **91a** was also found to be active in transfer hydrogenation of aldimines under similar conditions (Scheme 42), though the use of higher catalyst charge (2 mol%) was required in this case [78]. The reduction of aromatic aldimines with this catalytic system was rather efficient to give the amines in excellent yields, whereas the transformations for the substrates derived from aliphatic amines proceeded sluggishly (12-38% yield) and ketimines were found to be unreactive at all. Similar functional group tolerance as in the previous case [76] was observed with notable exceptions of  $\text{NO}_2$ -containing substrate totally deactivating the catalyst and highly efficient reduction of 2-iminosubstituted nitrogen heterocycles.

The mechanism of the transfer hydrogenation of ketones using Mn(I) complex **91a** (Scheme 43) was studied experimentally [76] and by DFT calculations [79]. The deprotonation of **91a** led to the formation of Mn(I) amide intermediate **92a**, which can either rapidly form the corresponding alkoxide complex **94a** upon reaction with isopropanol or dimerize to the binuclear species **93a**, isolated in the absence of *i*PrOH and characterized by X-ray diffraction [76]. Importantly, well-defined dimer **93a** was shown to be a competent catalyst under base-free conditions requiring however some induction period to dissociate into the mononuclear species. Alkoxide complex **94a** underwent a  $\beta$ -hydride elimination to form acetone with an activation barrier of 13.1 kcal/mol resulting in the thermodynamically favorable formation of the hydride intermediate **95a**, which regenerated the amido complex **92a** upon the reaction with acetophenone followed by elimination of the product. According to DFT calculations low efficiency of the complex **91d** bearing N,O donor extremities was explained by much greater stability of the alkoxide complex **94d** making the formation of the key hydride intermediate **95d** highly endothermic process.



**Scheme 43.** Simplified mechanism of transfer hydrogenation of acetophenone catalyzed by Mn(I) complex **91a** based on DFT calculations (activation energy barriers are given in kcal/mol).

Interestingly, the formal substitution of one hydrogen atom in NH<sub>2</sub> moiety of Mn(I) complex **91a** by a second 2-picolylyl fragment was shown to produce a detrimental effect to the activity in transfer hydrogenation (Scheme 44) [80]. Indeed, for cationic Mn(I) complex **97a** bearing tridentate NNN ligand prolonged heating at 70 °C was required to achieve 96% conversion of acetophenone using 1 mol% of catalyst (TOF of 4 h<sup>-1</sup> vs. ca. 3600 h<sup>-1</sup> for less elaborated **91a**). The substrate scope was quite large, but for many acyclic aliphatic or heteroaromatic ketones increased catalyst charge (5 mol%) was required to access good levels of conversion. In contrast to the bidentate series **91a-c**, the presence of NH moiety in the coordination sphere of manganese was not mandatory for NNN ligands as complexes **97a** and **97b** showed virtually the same catalytic performance thus presuming the existence of another mechanism for the transfer hydrogenation of ketones.

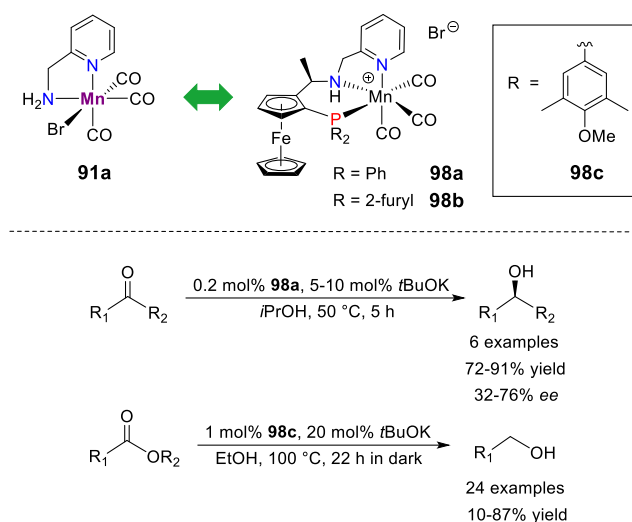


**Scheme 44.** Transfer hydrogenation of ketones and transfer dehydrogenation of secondary alcohols catalyzed by Mn(I) NNN complexes **97**.

It is noteworthy, that both Mn(I) NNN complexes **97** were able to catalyze more efficiently the reverse reaction, namely the transfer dehydrogenation of secondary alcohols using acetone as hydrogen acceptor (Scheme 44) [81]. The use of well-defined complexes **97** or their generation *in situ* from Mn(CO)<sub>5</sub>Br and the corresponding bis(picolylyl)amines afforded the same results. Remarkably, in this transformation, NH-containing complex **97a** was slightly less active than its analogue **97b** bearing uniquely tertiary amine donors affording 78% and 97% yield of acetophenone after 30 min of reaction, respectively. Alkyl(aryl)-substituted alcohols were more easily dehydrogenated using this protocol (2 h of reaction using 0.5 mol% of **97b**), whereas fully aliphatic derivatives required 10-fold increase of both catalyst charge and reaction time. The reaction tolerated halogens, primary and tertiary amines, esters and  $\alpha,\beta$ -unsaturated C=C bonds providing in the latter case excellent yields of target products without any side processes.

In 2019, Clark and coll. have demonstrated that cationic complexes **98** incorporating chiral ferrocenyl phosphine arm in picolylylamine scaffold could be successfully applied in asymmetric transfer hydrogenation of ketones (Scheme 45) [14]. This system was capable to operate at relatively low catalyst loading at 50 °C with TOF values (1024-1360 h<sup>-1</sup> at 50 °C) comparable to those of NN prototype **91a** (ca. 3600 h<sup>-1</sup> at 80 °C), but required much higher amount of base (2 vs. 25-50 equivalents for **91a** and **98**, respectively). Despite relatively modest enantiomeric induction levels were obtained in ketone reduction using Mn(I) complexes **98**, these species were shown to be much more performant in hydrogenation processes using molecular dihydrogen [14].

Importantly, PNN complexes **98** were shown to catalyze transfer hydrogenation of esters using ethanol as hydrogen donor (Scheme 45) [82]. The presence of the additional phosphine moiety in complexes **98** was crucial in this case as complex **91a** showed very low activity (15% conversion and 2% yield of the target alcohol), which can be tentatively attributed to higher nucleophilic character of the corresponding PNN hydride intermediate facilitating the reaction with less active carbonyl substrate. The replacement of ethanol by methanol led to much lower conversion mostly affording trans-esterification product, whereas the use of secondary alcohol 2-butanol as hydrogen donor was completely inefficient. Under optimal conditions, a variety of alkyl esters (Me, Et, *i*Pr) derived from aromatic or aliphatic acids was reduced with good efficiency. While this protocol tolerated halogens or heterocyclic moieties, the substrates bearing free OH, NH<sub>2</sub> and CN groups were identified as limitation. The use of optically pure  $\alpha$ -substituted and  $\alpha,\beta$ -unsaturated esters led to chiral center racemization and fully reduced products, respectively.

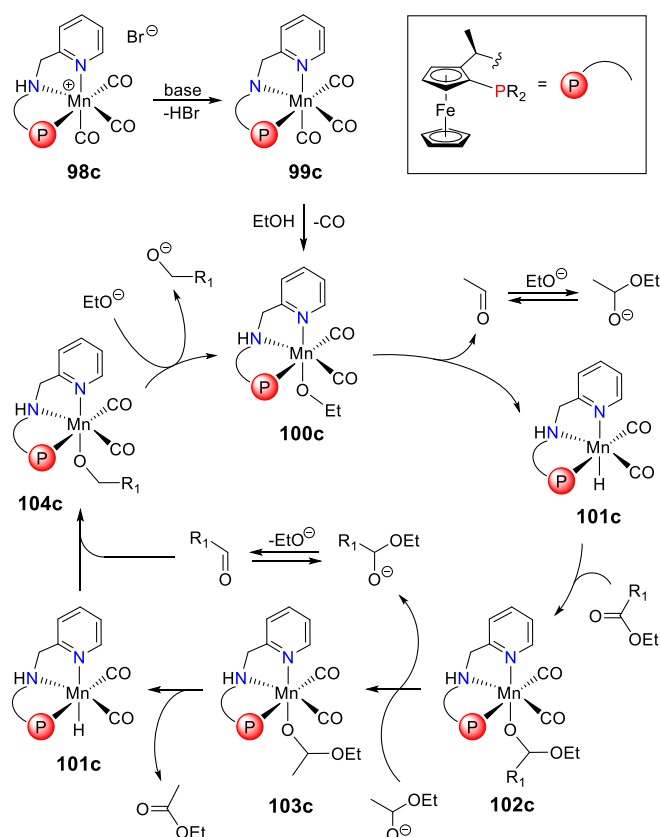


**Scheme 45.** Transfer hydrogenation of ketones and esters catalyzed by Mn(I) complexes **98** bearing PNN-type ligands.

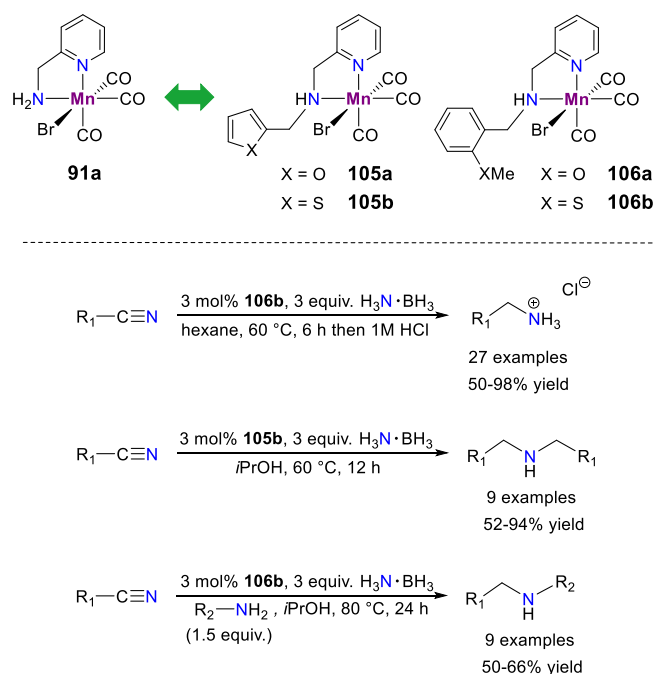
The proposed reaction mechanism (Scheme 46) includes the deprotonation of the starting complex **98c** into the corresponding amido species **99c**, which undergoes a sequence of decarbonylation, EtOH activation and  $\beta$ -elimination processes to give the hydride intermediate **101c** and acetaldehyde being in the equilibrium with the corresponding anionic acetal derivative. Nucleophilic attack of the hydride in **101c** to the ester substrate affords the Mn(I) hemiacetal intermediate **102c** forming by a similar sequence of transformations the corresponding aldehyde finally hydrogenated to the target primary alcohol products.

Very recently, the group of Maji demonstrated that the association of picolylamine motif with hemilabile O- or S-based arms in Mn(I) complexes **105-106** provided excellent results in external base-free transfer hydrogenation of nitriles using ammonia-borane as hydrogen donor under mild conditions (Scheme 47) [83]. The outcome of the reaction for aromatic nitriles ArCN depended drastically on the nature of solvent affording selectively primary amines ArCH<sub>2</sub>NH<sub>2</sub> in hexane and secondary amines (ArCH<sub>2</sub>)<sub>2</sub>NH in isopropanol, the latter product arisen from the condensation between the transient imine intermediates ArCH=NH and ArCH<sub>2</sub>NH<sub>2</sub> being facilitated in this polar solvent. Noticeably, the realization of the latter reaction in the presence of slight excess (1.5 equivalents) of the external aliphatic or aromatic amines RNH<sub>2</sub> led to the exclusive formation of unsymmetrical amines ArCH<sub>2</sub>NHR. Aliphatic nitriles could be also efficiently reduced to primary

amines in excellent yields. This protocol tolerated well the presence of halogen or ester groups, but ketone function was found to be reduced under these reaction conditions.



**Scheme 46.** Proposed mechanism for transfer hydrogenation of esters catalyzed by Mn(I) complex **98c** bearing PNN-type ligand.

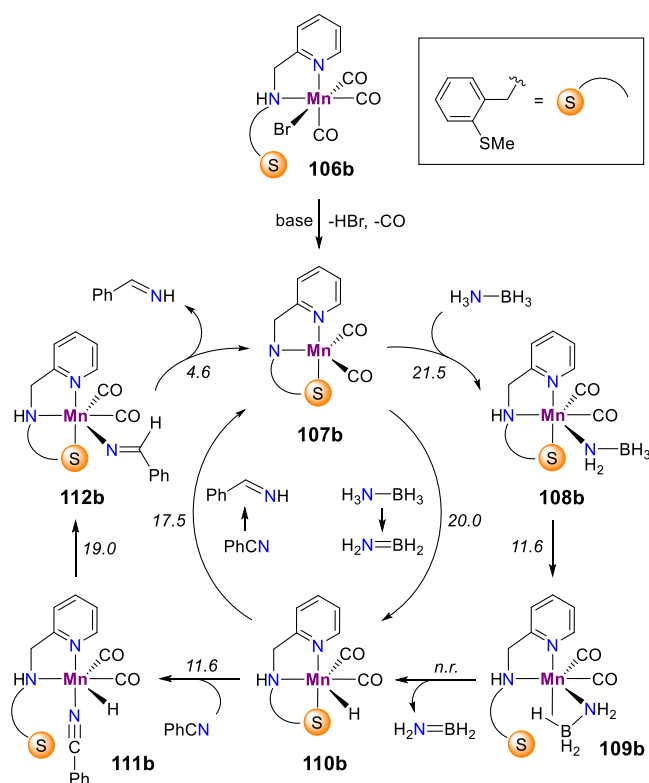


**Scheme 47.** Chemo-divergent transfer hydrogenation of nitriles with ammonia-borane catalyzed by Mn(I) complexes **105-106** bearing hemilabile SNN-type ligands.

Though all Mn(I) pre-catalysts **105-106** were active in both reaction media, their relative performance were rather different with a net preference for SNN-based ligands. Indeed, complexes

**105b** and **106b** were almost equally active in transfer hydrogenation of PhCN in hexane being *ca.* 3 times more efficient in terms of product yield than O-based analogues **105a** and **106a**. For the synthesis of symmetrical secondary amines, the use of **105b** exhibiting thiophene arm was found to be optimal (91% *vs.* 47-60% yield for other pre-catalysts), whereas pre-catalyst **106b** provided remarkable selectivity for the transfer hydrogenation process in the presence of external primary amine.

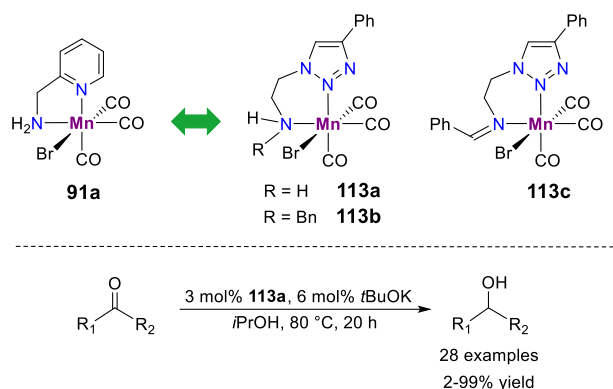
The reaction mechanism (Scheme 48) was investigated in detail experimentally and by DFT calculations for complex **106b** [83]. The reaction started by the deprotonation of the latter by traces of NH<sub>3</sub> present in ammonia borane and decarbonylation to give 16-electron complex **107b** bearing SNN pincer ligand. The latter can dehydrogenate H<sub>3</sub>N–BH<sub>3</sub> to form the hydride species **110b** and H<sub>2</sub>N=BH<sub>2</sub> either *via* concerted outer-sphere process or *via* stepwise inner-sphere mechanism including cooperative activation of the N–H bond, decoordination of the sulphur moiety to form the intermediate **109b** exhibiting agostic B–H interaction and β-hydride elimination. While the calculated activation energies for both pathways were very similar revealing maximal barriers of 20.0 and 21.5 kcal/mol for outer- and inner-sphere processes, KIE measurements clearly showed the implication of B–H and N–H bond activation processes in rate-determining step thus being consistent with concerted ammonia-borane dehydrogenation. Similarly, the hydrogenation of nitrile to imine can proceed by simultaneous hydride/proton transfer or as a sequence of the S-arm dissociation with concomitant binding of PhCN molecule to the metal, intramolecular hydride transfer in the resulting **111b** with a re-coordination of S-donor and finally imine liberation upon proton transfer in **112b** from NH moiety of the pincer ligand. While again, calculations data did not allow to distinguish between two mechanisms (17.5 *vs.* 19.0 kcal/mol maximal activation barriers for outer- and inner-sphere



**Scheme 48.** Simplified mechanism for the transfer hydrogenation of benzonitrile with ammonia-borane catalyzed by Mn(I) complex **106b** based on DFT study and KIE measurements (activation energy barriers are given in kcal/mol, n.r. – transition state was not located).

processes, respectively), catalytic tests in the presence of coordinating ligands (pyridines, PPh<sub>3</sub>) revealed a significant drop of activity. Taking into account that addition of PPh<sub>3</sub> did not affect the step of amine-borane dehydrogenation in the absence of nitrile, these data showed that nitrile reduction proceeded at least partially *via* inner-sphere mechanism highlighting the vital importance of hemilabile S-donor group for the catalytic cycle. Finally, the chemo-divergent character of this transfer hydrogenation protocol can be rationalized in terms of relative difference in the reaction rates between the hydrogenation of imine intermediates ArCH=NH and their condensation with primary amines ArCH<sub>2</sub>NH<sub>2</sub> depending on the solvent polarity and the nature of Mn(I) catalyst.

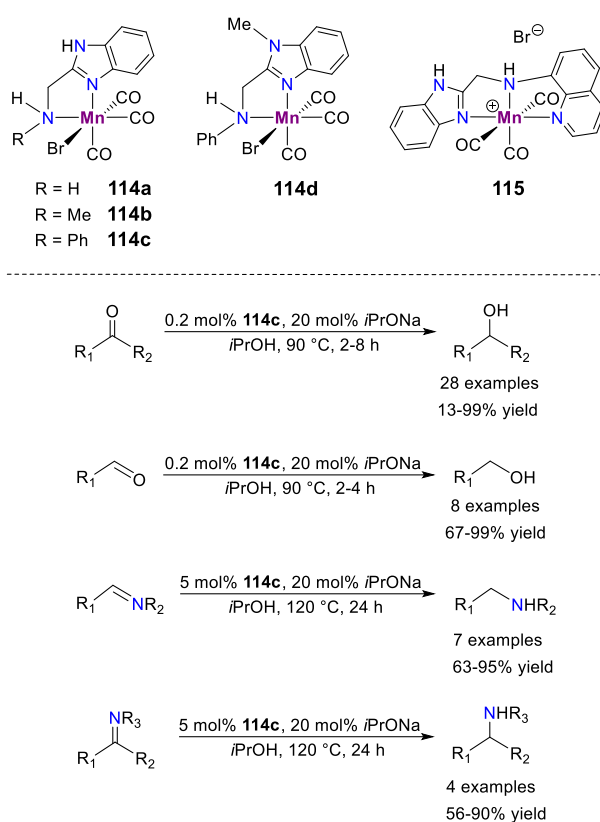
The simplicity of picolylamine ligand scaffold and the efficiency of the corresponding Mn(I) complex **91a** in transfer hydrogenation inspired many research groups to develop similar catalytic systems by the replacement of the pyridine moiety by another donor fragment. In 2018 Leitner and coll. reported Mn(I) complexes **113** based on aminotriazole ligands active in transfer hydrogenation of ketones (Scheme 49) [84]. Similarly, as it was observed for picolylamine derivatives **91** the presence of the NH moiety coordinated to the metal was essential for catalytic activity (complex **113c** was almost inactive) and the alkylation of the NH<sub>2</sub> group resulted in slightly lower efficiency (90% *vs.* 83% of acetophenone conversion using complexes **113a** and **113b**, respectively). While the catalytic system based on complex **113a** readily reduced aromatic ketones, transfer hydrogenation of aliphatic substrates worked in less efficient manner affording only 47-76% conversion. In contrast to catalyst **91a** the presence of nitro group in aromatic ketones induced a serious drop in the reaction efficiency (19-31% yield). Interestingly, for  $\alpha,\beta$ -unsaturated ketones *E*-ArCH=CHCOMe bearing phenyl and 2-furfuryl groups different chemoselectivity of the C=C/C=O bonds reduction was observed giving fully saturated and allylic alcohols in 85 and 88% yield, respectively. The comparison between aminopicolyl and aminotriazole Mn(I) complexes **91a** and **113a** revealed significant decrease of catalytic activity in the latter case (TOF of 1.5 h<sup>-1</sup> *vs.* 3600 h<sup>-1</sup> for the reduction of acetophenone at 80 °C), which can be attributed not only to the pyridine-to-triazole change, but also to the increasing size of chelating system (five- *vs.* six-membered metallacycle, respectively).



**Scheme 49.** Transfer hydrogenation of ketones catalyzed by Mn(I) complexes **113** bearing aminotriazole ligands.

Later in 2019 the group of Kundu prepared a series of Mn(I) complexes **114** based on various amino-benzimidazole ligands having five-membered metallacycle similarly as in the prototype **91a** (Scheme 50) [85]. Unlike picolylamine (Scheme 42) and amino-triazole (Scheme 49) systems, the mono-methylation of the NH<sub>2</sub> moiety had a slightly positive effect to the catalytic performance being even more pronounced for phenyl-substituted ligand affording in the reduction of acetophenone 62%, 68% and 96% yields for **114a**, **114b** and **114c**, respectively). Noteworthy, the N–H bond in the

benzimidazole seemed to play a role in catalysis since the complex **114d** was found to be *ca.* two times less active than **114c**. As in the case of picolyamine-based NN and NNN ligands (Scheme 44), the introduction of additional nitrogen substituent into amino-benzimidazole scaffold in complex **115** almost killed any catalytic activity.



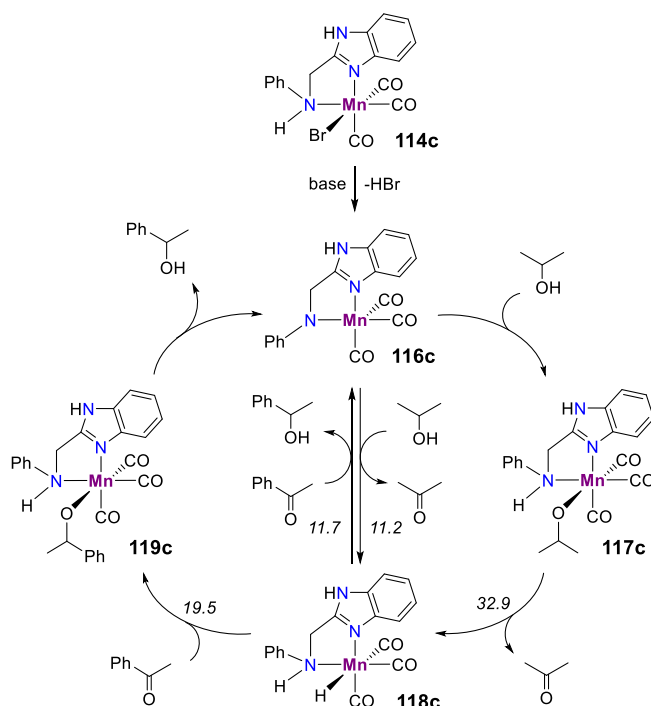
**Scheme 50.** Transfer hydrogenation of ketones, aldehydes and aldimines catalyzed by Mn(I) complex **114c** bearing amino-benzimidazole ligand.

Interestingly, significant TOF (*ca.* 200-250 h<sup>-1</sup>) and TON (450-500) values were achieved for **114c** regardless some contribution of background Meerwein-Ponndorf-Verley reduction (25% conversion without Mn(I) catalyst under the same conditions). Under optimized conditions, a variety of ketones was successfully reduced at 90 °C using only 0.2 mol% of pre-catalyst **114c**, but the presence of large excess of *i*PrONa as base (20 mol%, 100 equivalents) was essential. Aromatic and aliphatic aldehydes could also serve as good substrates for this reaction, the latter however being more impacted by aldol-type side reactions due to a higher amount of base present in solution. This catalytic system displayed similar functional group tolerance as picolyamine catalyst **91a** allowing in particular a net preservation of the conjugated C=C bonds. Importantly, complex **114c** was active in transfer hydrogenation of imines albeit in much higher catalyst charge (5 mol%) and under more forcing conditions. Unlike catalyst **91a** (Scheme 42) aldimines derived from aliphatic amines and aromatic ketimines could be efficiently reduced with **114c** being actually a sole Mn-catalyst capable to perform transfer hydrogenation of the latter substrates.

DFT calculations of transfer hydrogenation mechanism for the pre-catalyst **114c** (Scheme 51) showed that both key steps of the process namely *i*PrOH dehydrogenation with amido species **116c** and acetophenone hydrogenation with the hydride **118c** proceeded *via* concerted outer-sphere pathway with low activation barriers of about 11.2 and 11.7 kcal/mol, respectively. In contrast, inner-sphere mechanism operating in the case of picolyamine complex **91a** (Scheme 43) was found to be



unlikely for amino-benzimidazole system due to much higher activation energies for  $\beta$ -hydride elimination from the alkoxide **117c** and direct reaction of hydride **118c** with acetophenone to form **119c** (32.9 and 19.5 kcal/mol, respectively). These results may explain the beneficial role of the phenyl substituent in **114c** in catalysis due to the increase of the N–H bond acidity facilitating a concerted proton/hydride transfer.

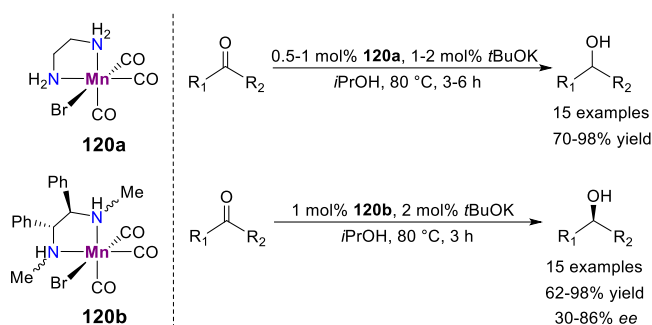


**Scheme 51.** DFT modelling of two possible mechanisms for transfer hydrogenation of acetophenone catalyzed by Mn(I) complex **114c** (activation energy barriers are given in kcal/mol).

The next important step towards NN ligand design in Mn(I)-catalyzed transfer hydrogenation was realized by Sortais and coll. by the extensive screening of various diamine ligands in combination with  $\text{Mn}(\text{CO})_5\text{Br}$  forming catalytically active species *in situ* upon heating to 80 °C (Scheme 52) [77]. While the suppression or elongation of the alkyl spacer in picolyamine ligand led to poor results (0% and 7% of acetophenone conversion for 2-aminopyridine and  $\text{PyCH}_2\text{CH}_2\text{NH}_2$ , respectively) thus confirming the importance of metallacycle size, it was found that simple aliphatic diamines could be valuable alternatives. Remarkably, the best results were obtained for ubiquitous ethylenediamine and after optimization of the reaction conditions complex **120a** was shown to reduce a variety of aromatic ketones including sterically demanding representatives typically in a nearly quantitative yield (Scheme 52). The low price of this diamine ligand coupled with *in situ* catalyst generation and easy product isolation by the filtration through a short plug of silica makes this catalytic procedure an attractive alternative to classic stoichiometric ketone reduction with  $\text{NaBH}_4$  from both economical and practical (no hydrolysis/extraction work-up) points of view.

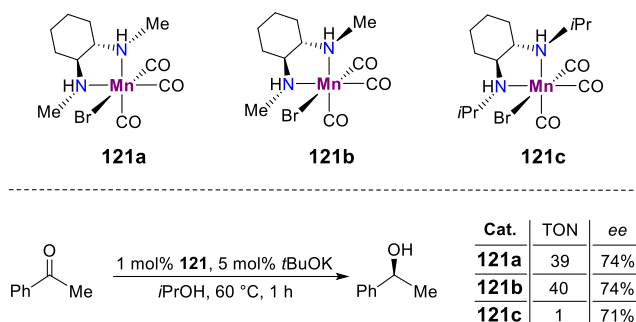
The extension of this methodology to commercially available chiral diamines allowed to detect two structural families based on 1,2-diphenyl-1,2-ethanediamine and 1,2-diaminocyclohexane motifs combining good catalytic activity with promising levels of enantiomeric induction (36% and 52% *ee* for acetophenone reduction, respectively). Interestingly, the methylation of  $\text{NH}_2$  moieties in both NN ligands considerably improved enantioselectivity levels providing the best results for complex **120b** with 64% *ee* (Scheme 52). The evaluation of the application scope of asymmetric transfer hydrogenation with generated *in situ* complex **120b** revealed that *ortho*-substituted acetophenones or

their analogues with larger alkyl substituents afforded the target secondary alcohols with 68-90% optical purity, whereas *ee* values significantly drops to 30-46% for *para*-substituted acetophenones.



**Scheme 52.** Transfer hydrogenation of ketones catalyzed by Mn(I) complexes **120** generated *in situ* from Mn(CO)<sub>5</sub>Br and equimolar amount of the corresponding aliphatic diamine.

Later Pidko and coll. evaluated the application of well-defined Mn(I) diamine complexes **121** (Scheme 53) in asymmetric transfer hydrogenation of acetophenone and studied in detail the mechanism of this reaction [86]. It was found that isolated complexes **121a** and **121b** differing only in the configuration of *N*-methyl groups afforded 74% *ee* at 60 °C, which was slightly better than the value obtained using *in situ* generated system (69% *ee*). The complex **121c** bearing bulkier isopropyl groups at the nitrogen atoms was almost inactive under these conditions.

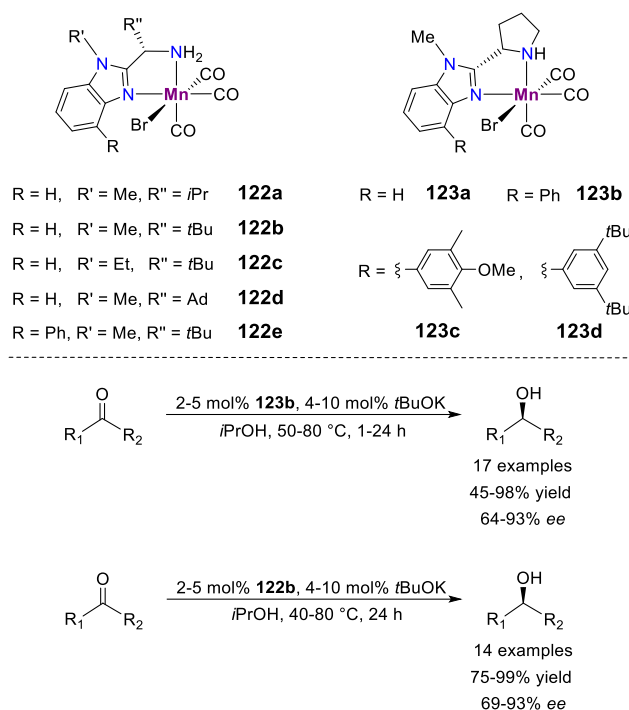


**Scheme 53.** Well-defined Mn(I) complexes **121** bearing chiral aliphatic diamines tested in asymmetric transfer hydrogenation of acetophenone.

DFT study revealed that transfer hydrogenation in this case proceeds through inner-sphere mechanism similarly to picolylamine system (Scheme 43) with the  $\beta$ -hydride elimination from the corresponding isopropoxide intermediate as the rate-determining step. The results of this theoretical investigation were consistent with kinetic measurements data and the observation of a strong primary KIE of 2.7 in the case of fully deuterated isopropanol.

Very recently, the group of Sun evaluated a series of well-defined Mn(I) complexes **122-123** bearing aminoacid-derived benzimidazole-amine ligands in asymmetric transfer hydrogenation of ketones (Scheme 54) [87]. Initial catalyst screening for the reduction of acetophenone (2 mol% cat., 4 mol% *t*BuOK, 80 °C, 20 min) revealed that in complexes **122a-d** the increase of steric volume of the alkyl group R'' at the stereogenic carbon atom was beneficial for the enantioselectivity (42%, 65% and 66% *ee* for *i*Pr, *t*Bu and Ad, respectively) providing in the best cases similar values obtained in the case of *in situ* generated complex **120b** (Scheme 52) [77]. In contrast, the replacement of the methyl substituent at benzimidazole nitrogen atom by an ethyl one led to serious drop of *ee* (65% vs. 24% for **122b** and **122c**, respectively). While the introduction of Ph group at the adjacent position of the aromatic benzimidazole ring in NH<sub>2</sub>-containing complexes **122** totally inhibited the catalytic

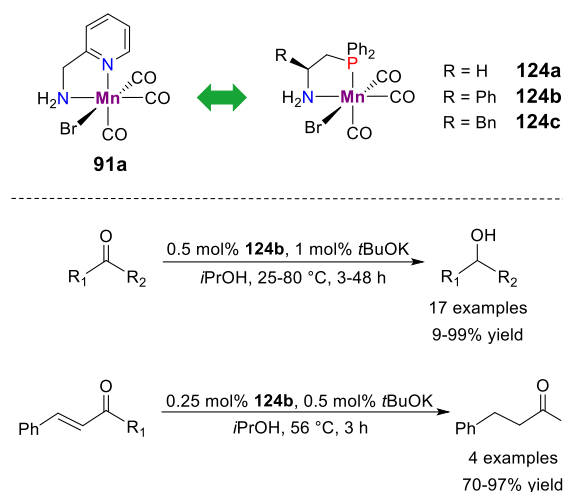
activity (complex **122e**), this strategy allowed to improve significantly the efficiency of proline derived analogues **123** (48% vs. 82% *ee* for **123a** and **123b**, respectively). Importantly, transfer hydrogenation may be also performed at 40-50 °C for 24 h achieving excellent levels of substrate conversion and slightly better enantiomeric induction.



**Scheme 54.** Transfer hydrogenation of ketones catalyzed by well-defined Mn(I) complexes **122** and **123** bearing chiral NN ligands.

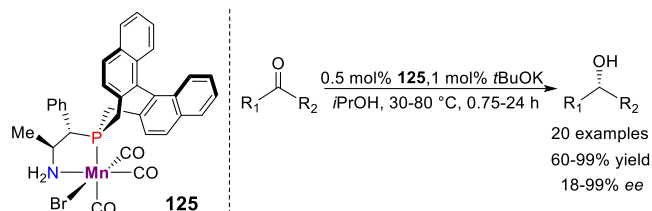
Diversely substituted acetophenone derivatives were typically reduced at 50 °C using 2 mol% of complex **123b** with excellent yield and *ee* in a range of 85-90%. Unlike the case of complex **120b** the introduction of the substituents at the *para*-position of aromatic ring did not lead to the decrease of enantioselectivity. In contrast, complex **123b** displayed slightly lower performance for furan- and thiophene derived ketones (51-53% yield, 69-71% *ee*) and was inefficient for the substrates bearing bulky aliphatic groups (8% yield and 77% *ee* for PhCO*t*Bu). However, such substrates could be readily reduced using complex **122b** even at 40 °C providing the target *t*Bu-substituted secondary alcohols in 76-94% yield and 89-93% *ee*. As expected, the decrease of steric volume of alkyl groups led to lower levels of enantiomeric induction being the worse for long-chain and cyclic alkyls (69-71% *ee*).

A formal change of pyridine moiety in picolylamine system by phosphine was reported by the group of Lacy in 2019 (Scheme 55) [88]. It was shown that complexes **124** bearing PN ligands easily available from optically pure amino-acids were competent catalyst for transfer hydrogenation of various ketones typically at 60 °C using 0.5 mol% catalyst loading albeit with negligibly low enantiomeric induction (11% *ee* max). The reaction afforded good-to-excellent product yields and well tolerated halogens, heterocycles, NO<sub>2</sub> groups and failed completely only for phenol-containing substrates. Interestingly, this catalytic system allowed the selective reduction of C=C bond in chalcone derivatives to give the corresponding saturated ketones, which could be readily transformed to secondary alcohols using higher amount of catalyst and longer reaction time.



**Scheme 55.** Transfer hydrogenation of ketones and chalcones catalyzed by Mn(I) complexes **124** bearing phosphine-amine ligands.

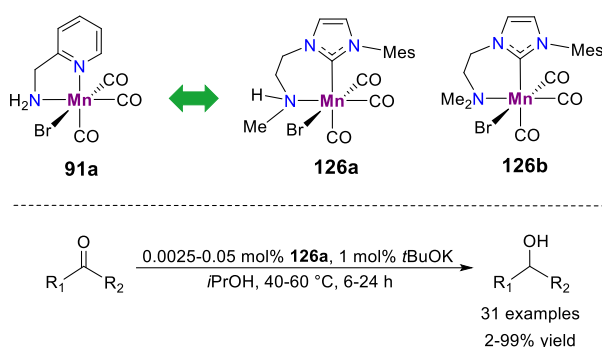
The potential of phosphine-amine ligands for asymmetric transfer hydrogenation of ketones was recently demonstrated by Bastin, Sortais and coll. (Scheme 56) [89]. The key to success in this reaction seemed to be the use of the axially chiral binepine phosphorous scaffold in well-defined Mn(I) complex **125** allowing a relatively fast reaction rate at 30 °C for aromatic ketones and giving generally *ca.* 10-15% higher *ee* values than those observed for related diamine analogue **120b** (Scheme 52). In contrast to NN-based system **120b**, the deleterious effect of *para*-substituent of the aryl on the enantiomeric induction was less pronounced here providing in most cases *ee* values higher than 55%. Though aliphatic ketones could be also reduced using this synthetic protocol the enantioselectivity was very low (90% conversion and 18% *ee* for CyCOMe at 50 °C).



**Scheme 56.** Asymmetric transfer hydrogenation of ketones catalyzed by well-defined Mn(I) complex **125** bearing chiral phosphine-amine ligand.

While the use of phosphine-amine ligands more donating than NN analogues in Mn(I)-catalyzed transfer hydrogenation of ketones did not improve the overall catalyst performance, the situation changed dramatically for NHC-amine complexes **126** developed by Pidko and co-workers (Scheme 57) [90]. While complex **126b** without coordinated NH moiety was inactive as expected, its analogue **126a** was highly efficient in acetophenone reduction with TOF up to 10800 h<sup>-1</sup>. Importantly, the reaction efficiency in this case was strongly dependent on temperature especially for low catalyst loading. The analysis of kinetic data for acetophenone transfer hydrogenation catalyzed by 50 ppm of **126b** at 60 and 70 °C revealed that despite faster initial reaction rate in the latter case TON value after 6 h (11100) was inferior to the one obtained at lower temperature (15100). This difference became even more spectacular for 25 ppm catalyst loading (3100 vs. 17300 TON for 70 and 60 °C, respectively) clearly showing faster catalyst deactivation at higher temperatures. Taking into account this information, the evaluation of substrate scope was performed at 40 °C using 0.05 mol% of catalyst affording in most cases more than 80% product yields for various aromatic and aliphatic

ketones. The identified limitations included sterically bulky ketones such as MesCOMe or Cy<sub>2</sub>CO, phenol- and nitrogen heterocycles containing compounds. Aromatic substrates bearing NH<sub>2</sub>, CN and NO<sub>2</sub> groups were reduced with lower 12-27% yield, which could be surely improved at higher catalyst loading and/or more elevated temperature.

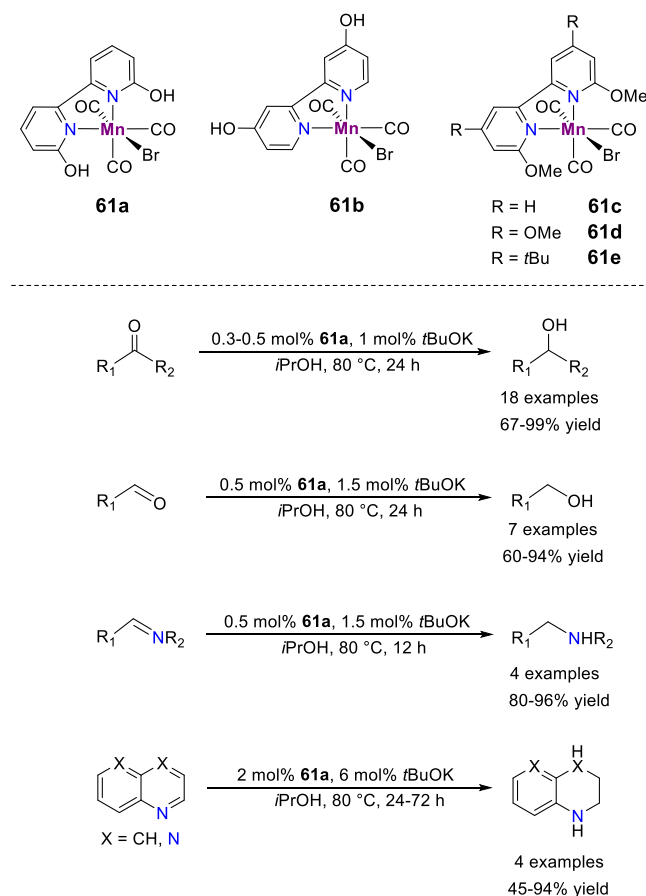


**Scheme 57.** Transfer hydrogenation of ketones catalyzed by Mn(I) complex **126a** bearing NHC-amine ligand.

Recently, Khusnutdinova and coll. demonstrated the viability of another strategy for the design of Mn(I)-based catalysts bearing bidentate NN ligands for transfer hydrogenation involving no amine/amide ligand cooperativity (Scheme 58) [91]. A series of bipyridine complexes **61** was initially tested in the reduction of acetophenone at 80 °C using 0.3 mol% catalyst charge in the presence of 1 mol % of *t*BuOK. As could be expected complex **61a** bearing hydroxyl groups in the close proximity to metal center and successfully used in CO<sub>2</sub> hydrogenation (Scheme 32) [64] was the most active in this transformation providing a quantitative conversion after 24 h. Surprisingly, its isomer **61b** exhibiting distal hydroxyl groups and poorly active in CO<sub>2</sub> hydrogenation afforded similar results being even slightly more productive after 1 h of reaction at 80 °C (88 vs. 93% yield for **61a** and **61b**, respectively). Moreover, in contrast to completely inactive *fac*-(bipy)Mn(CO)<sub>3</sub>Br, complexes **61c-e** containing *ortho*-methoxy-substituted bipy ligands also led to full substrate conversion at 1 mol% catalyst charge in the presence of 3 mol% of *t*BuOK (background base-assisted reaction in the presence 5 mol% of *t*BuOK gave only 20% conversion under these conditions) providing the evidence that cooperative OH fragment was not strictly required for catalytic turnover. The TON values of *ca.* 215/175/95 obtained for **61c-e** at lower catalyst loading (0.3 mol%) showed that complex **61c** was the most active in the methylated series. The comparison of kinetic data for transfer hydrogenation of acetophenone at 50 °C revealed much higher performance of complex **61a** displaying first-order behavior over **61b** with more complicated kinetic pattern, whereas catalysts **61c-d** were inactive under these conditions.

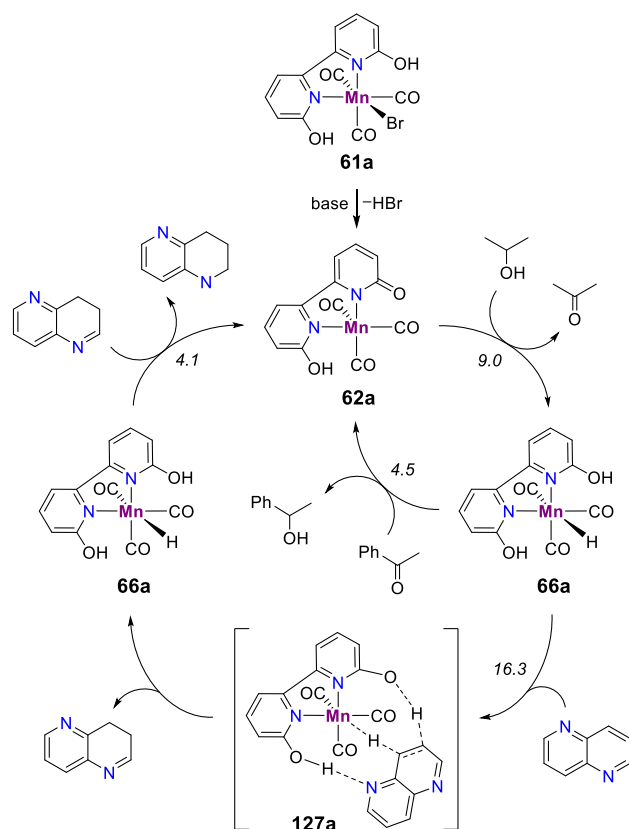
Both aromatic and aliphatic ketones were reduced in excellent yield using 0.3 mol% of catalyst **61a** and the reaction tolerated some potentially coordinating functional groups (CN, SMe, furan). Curiously, the reduction of aldehydes was slower and slight increase of catalyst charge to 0.5 mol% was required to get good product yields. Importantly, this catalytic system provided highest TON known to date in transfer hydrogenation of aromatic aldimines (for example TON values observed for *p*-ClC<sub>6</sub>H<sub>4</sub>CH=NPh reduction were *ca.* 46, 17 and 170 for Mn(I) NN complexes **91a**, **114c** and **61a**, respectively), though the synthetic scope was not developed. The potential of complex **61a** for transfer hydrogenation of *N*-heterocycles was also highlighted. While the reduction of quinoline was relatively sluggish (45% yield after 72 h of reaction), the reaction for acridine, quinoxaline and 1,5-naphthhydrine afforded excellent isolated yields being comparable in term of TON with Mn(CO)<sub>5</sub>Br-

catalyzed direct hydrogenation procedure developed by Beller (Scheme 39) [74]. Noticeably, complex **61c** bearing a methoxy group was almost unreactive for *N*-heterocycles showing the importance of free OH groups for the catalytic cycle.



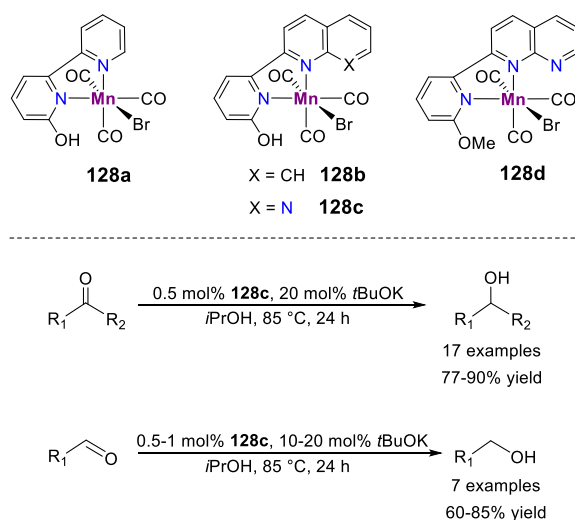
**Scheme 58.** Transfer hydrogenation of ketones, aldehydes, aldimines and *N*-heterocycles using Mn(I) complex **61a** bearing bipyridine ligands.

Reaction mechanism of transfer hydrogenation of acetophenone and 1,5-naphthydrine with complex **61a** based on DFT calculations and deuterium-labelling experiments is shown in the Scheme 59 [91]. It was demonstrated that the isopropanol dehydrogenation with monodeprotonated intermediate **62a** proceeds as concerted outer-sphere process with activation barrier of only 9.0 kcal/mol to form the hydride complex **66a** destabilized by 6.3 kcal/mol relative to **62a**. The hydrogenation of acetophenone and *N*-heterocycles with **66a** also proceeds in concerted manner regenerating the initial deprotonated species **62a**. Importantly, in the case of 1,5-naphthydrine the second OH group is also directly involved into the first-rate determining C=C bond reduction step (transition state **127a**) forming a hydrogen bond with the nitrogen atom of neighboring heterocyclic ring. This additional interaction allows to decrease the activation barrier (16.3 kcal/mol) compared to quinoline (24.3 kcal/mol) thus explaining the lower efficiency of the catalyst **61a** for transfer hydrogenation of this substrate.



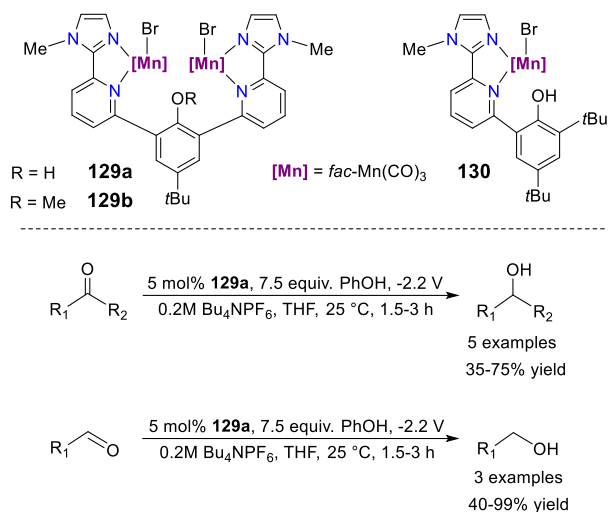
**Scheme 59.** Simplified reaction mechanism for transfer hydrogenation of acetophenone and 1,5-naphthydrine using Mn(I) complex **61a** based on DFT calculations (activation energy barriers are given in kcal/mol).

In 2019, the group of Xia reported the application of structurally similar Mn(I) complexes **128** based on heteroaromatic NN systems containing a single OH group in the proximity to metal center in transfer hydrogenation of aldehydes and ketones (Scheme 60) [92]. Though these catalytic systems were significantly less efficient than those based on complexes **61** and required strong excess of base, it was found that fusion of the second nitrogen ring in complex **128a** was slightly beneficial for catalytic performance. Interestingly, complex **128d** lacking cooperative OH moiety displayed the same activity as **128b** in acetophenone reduction, which again may indicate the existence of an unconventional reaction mechanism.



**Scheme 60.** Transfer hydrogenation of ketones and aldehydes catalyzed by Mn(I) complexes **128** bearing heteroaromatic NN ligand.

The unusual example of Mn-catalyzed transfer hydrogenation of carbonyl compounds using phenol as hydrogen donor under controlled potential electrolysis was recently reported by Siewert and coll. (Scheme 61) [93]. It was found that binuclear complex **129a** containing two Mn(I) units based on pyridine-imidazole ligand and proximal OH group was moderately active for the reduction of aliphatic aldehydes and ketones with Faradaic efficiency (FE) 60-93%.



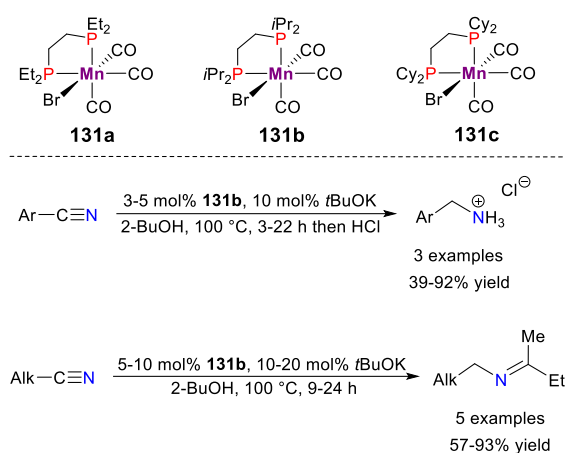
**Scheme 61.** Electrochemical hydrogenation of ketones and aldehydes using phenol as hydrogen donor catalyzed by Mn(I) complex **129a** bearing bidentate pyridine-imidazole ligand.

The reaction tolerated isolated C=C bonds leading however to the decrease of both Faradaic and isolated product yields (for example 1-pentanal and 1-pent-4-enal were reduced with 99% (FE 93%) and 40% (FE 47%) yields, respectively). It was proposed that the reaction mechanism involves the reduction of (NN)(CO)<sub>3</sub>Mn–Br units in **129a** into the corresponding anionic metallates (NN)(CO)<sub>3</sub>Mn<sup>–</sup> followed by their protonation with phenol to form hydride species (NN)(CO)<sub>3</sub>MnH capable to hydrogenate C=O bond. Interestingly, the presence of hydroxyl group and the second metal center was crucial for the catalysis since both complexes **129b** and **130** were completely inefficient.

Though nitrogen donors present in most Mn-based catalysts for transfer hydrogenation known to date, other bidentate ligand architectures can be efficient as well. In particular, García and co-workers have shown that complexes **131** bearing chelating aliphatic diphosphines are active in transfer hydrogenation of nitriles using 2-butanol as hydrogen donor (Scheme 62) [94]. Under these conditions, a mixture of target primary amine RCH<sub>2</sub>NH<sub>2</sub> and the product of its condensation with 2-butanone RCH<sub>2</sub>N=C(Me)Et were formed, the latter being the major component for aliphatic nitriles. The catalytic performance increased in **131a**→**131c**→**131b** row order affording 58%, 94% and full conversion of benzonitrile after 3 h at 100 °C, respectively. While the reduction of electron-rich aromatic nitriles readily proceeded with 3 mol% of **131b**, more electron-poor *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN and aliphatic substrates required higher amounts of catalyst (5-10 mol%) to achieve synthetically useful yields. It is important to note that despite the implication of the same alkoxide and hydride intermediates in the catalytic cycle (Scheme 22), transfer hydrogenation catalyzed by complex **131b** was much slower than direct nitrile hydrogenation using closely related Mn(I) triflate complex *fac*-(*i*Pr<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P*i*Pr<sub>2</sub>)Mn(CO)<sub>3</sub>(OTf) **43** (Scheme 21) [58] (for example TOF of *ca.* 10 and 120 h<sup>–1</sup>



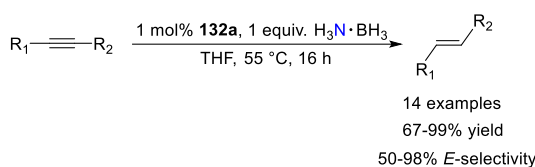
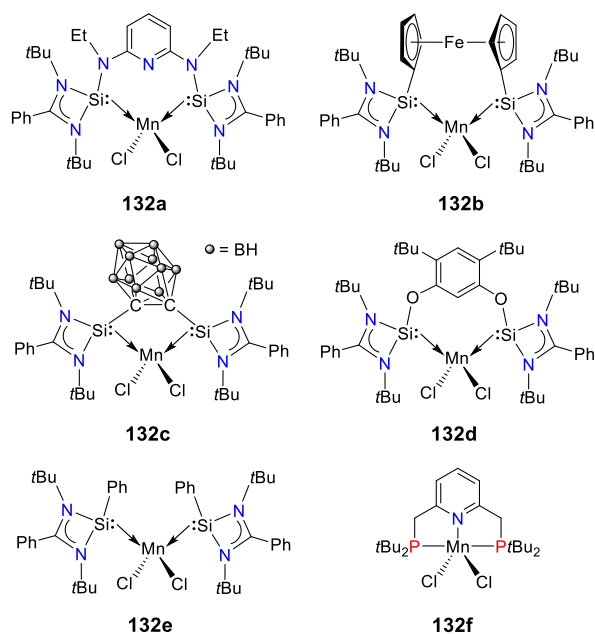
were observed for the reduction of PhCN using 3 mol% of **131b** and **43** at 100 °C and 90 °C, respectively).



**Scheme 62.** Transfer hydrogenation of nitriles catalyzed by Mn(I) complexes **131** bearing diphosphine ligands.

In 2018, Driess and coworkers shown that Mn(II) complexes bearing more exotic *N*-heterocyclic silylene ligands were able to perform transfer semi-hydrogenation of internal alkynes using ammonia-borane as hydrogen donor (Scheme 63) [95]. While well-defined tetrahedral Mn(II) complexes **132a-b** and **132e** provided a quantitative conversion at 1 mol% catalyst loading, catalytic systems **132c-d** generated *in situ* from MnCl<sub>2</sub> and equimolar amount of the corresponding disilylene were much less efficient (41-48% conversion). Importantly, both bidentate coordination and the nature of the bridge between two silylene moieties directly affected the stereoselectivity of this transformation being the best for pre-catalyst **132a**. This protocol was shown to be very efficient for diaryl-, arylalkyl and arylsilyl internal alkynes affording the target alkenes with typically more than 90% *E*-selectivity. The reaction tolerated halogens, thiophene, OMe and ester groups leading however to lower stereoselectivities for the two latter cases (60-82%). The reduction of aliphatic 6-dodecyne was more sluggish (67% conversion) and non-stereoselective, whereas disilylate alkyne Me<sub>3</sub>SiC≡CSiMe<sub>3</sub> was unreactive at all.

The mechanism of this reaction is not clear for the moment. Since the addition of TEMPO did not affect the reaction outcome the formation of free radicals seems to be unlikely. Taking into account the reduction properties of ammonia-borane and the possibility to create an efficient catalytic system from diaminopyridine-based disilylene and Mn(CO)<sub>5</sub>Br, the formation of Mn(I) complexes from **132a** cannot be excluded. Such reduction mechanism was recently inferred from DFT calculations by Azofra, El-Sepelgy and coworkers for highly *Z*-selective transfer semi-hydrogenation of internal alkynes catalyzed with PNP pincer Mn(II) complex under similar conditions (1 mol% of (*i*Pr<sub>2</sub>PCH<sub>2</sub>PyCH<sub>2</sub>P*i*Pr<sub>2</sub>)MnCl<sub>2</sub>, 1 equiv. H<sub>3</sub>N•BH<sub>3</sub>, MeOH, 60 °C, 20 h) [96]. However, generated *in situ* structurally similar PNP complex **132f** under the conditions of Driess was poorly active and displayed no stereoselectivity thus the oxidation state of catalytically competent manganese disilylene species remains the open question.

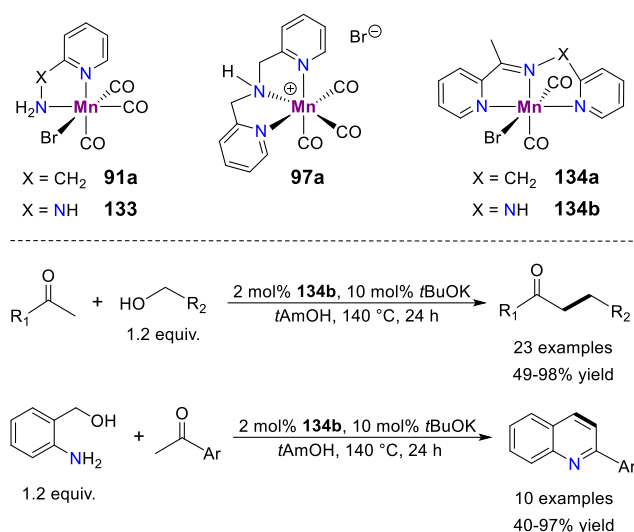


**Scheme 63.** Transfer semi-hydrogenation of alkynes catalyzed by Mn(II) complexes **132** bearing *N*-heterocyclic silylene ligand.

### 2.3. Hydrogen-borrowing transformations

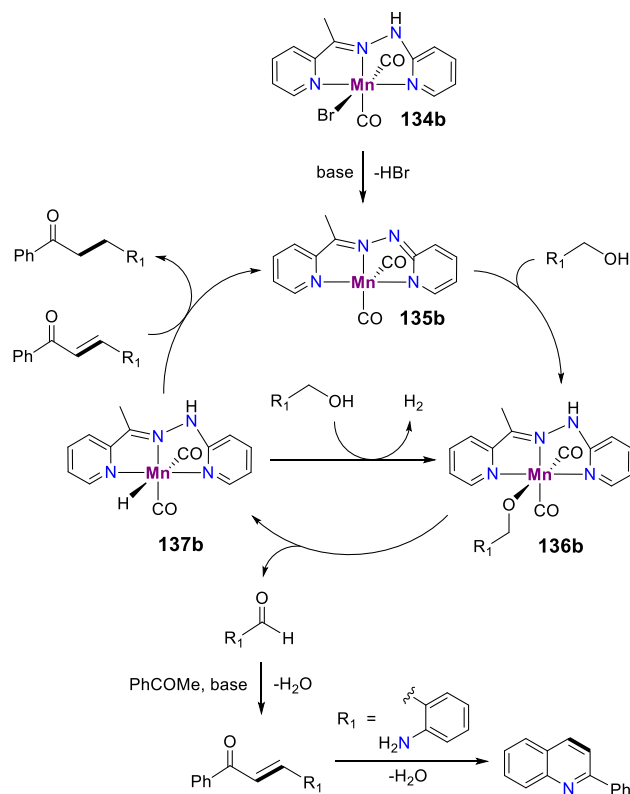
Since its discovery in 2016, various phosphine-based PNP [7, 97], PN<sup>3</sup>P [98], PN<sup>5</sup>P [99] and PNN [100] pincers were shown to be dominant ligand structures in the area of Mn-catalyzed hydrogen-auto transfer reactions [9-13, 15-17, 19, 22]. The first evaluation of Mn(I) complexes bearing bidentate ligands in hydrogen-borrowing processes was mentioned in the report of Maji [101] dealing with  $\alpha$ -alkylation of arylmethylketones with primary alcohols (Scheme 64), originally introduced by Beller and coll. [102]. Initial catalyst screening (2.5 mol% cat., 20 mol% *t*BuOK, *t*AmOH, 120 °C, 24 h) for the alkylation of acetophenone with BnOH revealed that *in situ* generated picolylamine complex **91a** was moderately active providing 31% GC product yield, whereas the corresponding tridentate analogue **97a** was found to be slightly more performant (42% yield). Though the complex **133** based on 2-hydrazinylpyridine was low-efficient (10% yield), it was shown that incorporation of an additional pyridine moiety to the ligand resulted in highly active catalyst **134b** affording 89% GC yield of the product, which can be further improved to almost quantitative yield at higher temperature (140 °C) using only 10 mol% of base. Importantly, the presence of NH moiety in this ligand was critical, because structurally close catalyst **134a** containing CH<sub>2</sub> linker was only moderately active (29% yield). Under optimized conditions a variety of aryl(methyl)ketones was alkylated with benzylic alcohols in good-to-excellent yields. Similarly as it was found in the case of Mn(I) PNP complexes [103], the application of 2-aminobenzyl alcohols smoothly afforded the corresponding quinolines in more than 70% yield. The use of aliphatic alcohols and ketones was also possible, but methanol cannot be activated with this catalytic system in contrast to those based on PNP [104] and PN<sup>3</sup>P [105] ligands. While the reaction was tolerant for the presence of halogens, CF<sub>3</sub>

and various heterocyclic fragments (pyridine, furan, thiophene) it failed completely for nitrile- and ester-containing substrates.



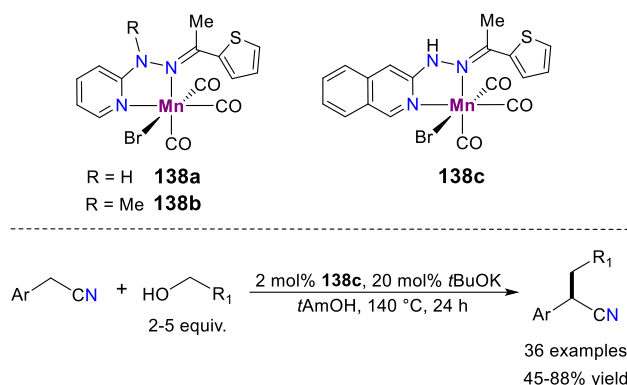
**Scheme 64.** Alkylation of ketones with primary alcohols and Friedländer synthesis of quinolines catalyzed by generated *in situ* Mn(I) complexes bearing NN and NNN ligands.

The proposed reaction mechanism (Scheme 65) includes the deprotonation of *in situ* generated complex **134b** to form the intermediate **135b** with dearomatized pyridine fragment, which then reacts with alcohol to form the alkoxide species **136b**. The latter undergoes the β-hydride elimination to form manganese hydride **137b** and the aldehyde participating in base-induced condensation with ketone to afford enone, which can either be further hydrogenated with **137b** to form the saturated ketone or cyclized with pendant amine function to provide quinoline.



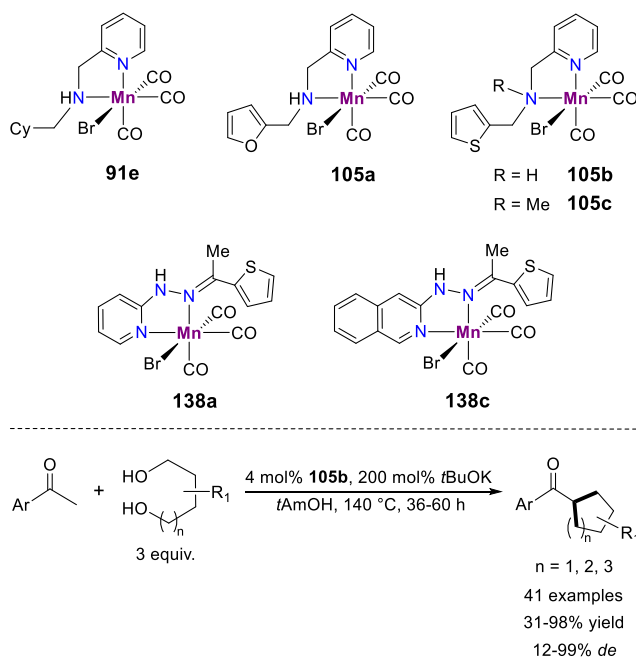
**Scheme 65.** Proposed mechanism for alkylation of acetophenone with primary alcohols catalyzed by generated *in situ* Mn(I) complex **134b** bearing NNN ligand.

Later on the same group reported selective monoalkylation of arylacetonitriles with primary alcohols catalyzed by Mn(I) complexes **138** bearing similar hydrazine-containing NN ligands (Scheme 66) [106]. Well-defined Mn(I) catalysts **138a** and **138c** afforded similar results being marginally better for the latter one, whereas the N-methylated complex **138b** displayed very low efficiency thus showing the importance of NH moiety for alcohol dehydrogenation step. This protocol showed a wide substrate scope and provided the target products in moderate-to-high yields for both aliphatic (besides methanol) and aromatic alcohols. The mechanistic studies revealed that the coordination of thiophene moiety is not directly implicated in the catalytic cycle and the key step of alcohol dehydrogenation proceeds *via* an outer-sphere process.



**Scheme 66.** Alkylation of nitriles with primary alcohols catalyzed Mn(I) complexes **138** based on NN ligand bearing a thiophene arm.

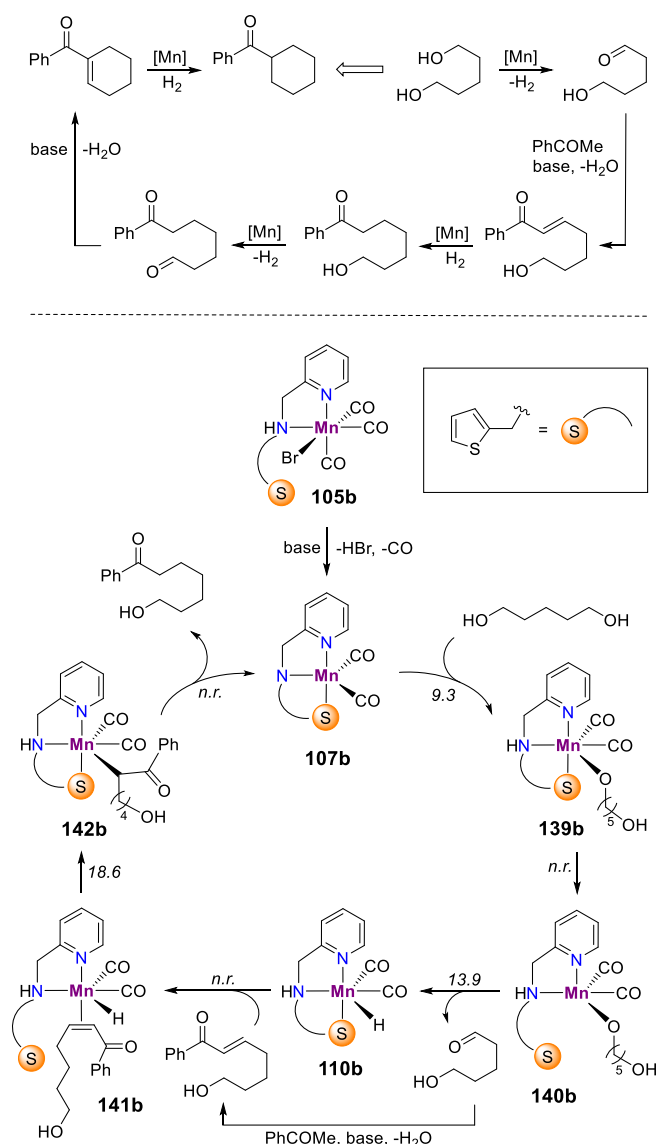
In contrast to previous systems **138** the hemilabile properties of sulphur-containing arm was shown to be more important for the Mn(I)-catalyzed assembly of cycloalkane scaffolds by the double alkylation of aryl(methyl)ketones with 1,n-aliphatic diols (Scheme 67) [107]. While all Mn(I) complexes bearing bidentate picolylamine (**91e**, **105a**) and picolyhydrazine (**138a**, **138c**) ligands at 4 mol% charge were active in the annulation of  $\text{C}_6\text{Me}_5\text{COMe}$  with  $\text{HO}(\text{CH}_2)_n\text{OH}$  affording the final product in a similar 45-62% yield range, the use of the same amount of catalyst **105b** led to a



**Scheme 67.** Stereoselective synthesis of aryl(cycloalkyl)ketones from 1,n-aliphatic diols catalyzed by Mn(I) complexes **105** bearing hemilabile NNS ligand.

significant improvement (88% yield). This protocol showed an ample substrate scope and appeared to be the most efficient for the formation of six-membered rings (60-to-98% yield). The formation of cyclopentyl- and cycloheptyl-substituted ketones proceeded generally with 20-30% lower yields still being attractive from a synthetic point of view. Both ketone and diol partners involved in this process could possess various substitution patterns and contain halogen and methoxy groups. Importantly, the employment of 3-substituted 1,5-pentandiols led to the formation of *trans*-isomers of 1,4-disubstituted cyclohexanes with 97-99% diastereoselectivity.

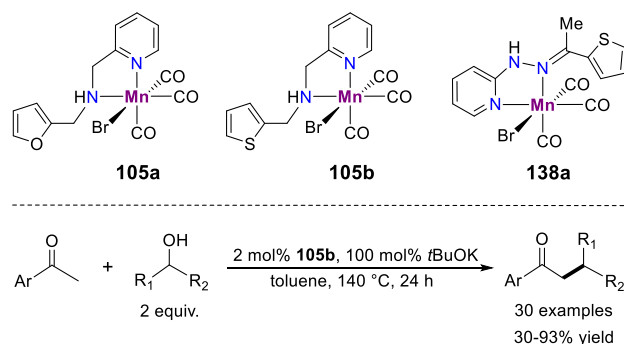
The reaction mechanism supported by isotope-labelling experiments and DFT calculations is shown on Scheme 68. The initial pre-catalyst **105b** first transforms into the pincer-type species **107b** upon a sequence of deprotonation and CO loss. Then the cooperative Mn-amido type activation of O–H bond in the diol takes place (N-methylated complex **105c** was totally inactive) to form the alkoxide intermediate **139b**. The  $\beta$ -hydride elimination in the latter leads to the formation of hydride complex **110b** and aldehyde, which undergoes a base-assisted condensation with ketone to get the



**Scheme 68.** Reaction scheme for the condensation of acetophenone with 1,5-pentanediol catalyzed by Mn(I) NNS complex **105b** (up) and the simplified mechanism of the key diol dehydrogenation and enone hydrogenation steps based on DFT calculations (down, activation energy barriers are given in kcal/mol, n.r. transition states were not localized).

corresponding enone product. The reaction of the latter with hydride **110b** proceeds as a sequence of C=C bond coordination to form  $\eta^2$ -alkene complex **141b**, hydride insertion and Mn-alkyl bond cleavage in the resulting  $\sigma$ -alkyl species **142b** to give the initial amide **107b** and saturated  $\omega$ -hydroxyketone undergoing similar series of steps to produce the final aryl(cycloalkyl)ketone. Noticeably, the hemilability of a pendant thiophene arm was shown to be important for the realization of alcohol dehydrogenation and enone hydrogenation steps, which was confirmed by poisoning experiments in the presence of auxiliary L-type ligands such as PPh<sub>3</sub> or pyridine.

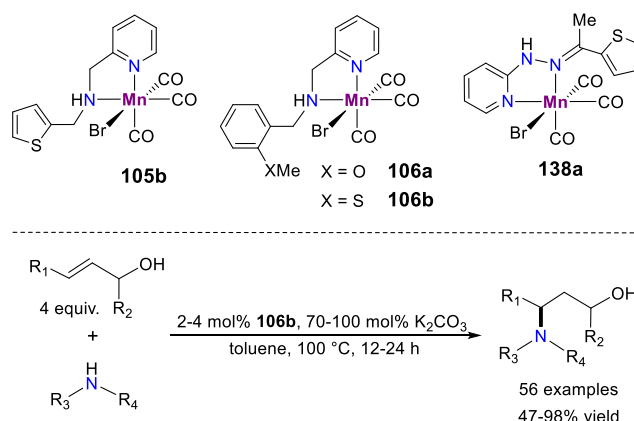
It was also shown by Maji and coll. that Mn(I) NN complex **105b** was efficient in  $\alpha$ -alkylation of aromatic ketones with secondary alcohols (Scheme 69) [108]. In this case the presence of both picolylamine core and hemilabile thiophene moiety was even more important for catalytic performance since the corresponding furan- (**105a**) and picolylhydrazine-containing (**138a**) analogues were much less efficient (85%, 25% and >10% product yield in the alkylation of C<sub>6</sub>Me<sub>5</sub>COMe with cyclohexanol using 2 mol% of **105b**, **105a** and **138a**, respectively). This protocol was successfully applied to a variety of cyclic or acyclic aliphatic alcohols as well as to a series of 1-[hetero]arylethanol derivatives. Interestingly, very high *cis*-diastereoselectivity was observed for 4-substituted cyclohexanols, which was rationalized as a result of equatorial attack of Mn(I) hydride to the conjugated enone at the final reaction step. The reaction tolerated various heterocyclic moieties and internal aromatic alkyne, albeit with lower yield in the latter case. The reaction mechanism is similar to that proposed for the alkylation of aromatic ketones with primary alcohols (Scheme 65) with alcohol dehydrogenation as rate-determining step (KIE  $k_H/k_D = 2.14$  for alkylation of C<sub>6</sub>Me<sub>5</sub>COMe with Me(Ph)CDOH). The addition of 10-fold excess of coordinating additives was shown to significantly slow down the reaction between C<sub>6</sub>Me<sub>5</sub>COMe and Me(Ph)CHOH (45% and 11% yield for pyridine and 4-picoline, respectively *vs.* 85% under optimal conditions) thus demonstrating the importance of hemilabile coordination of thiophene fragment for this process.



**Scheme 69.** Alkylation of aromatic ketones using secondary alcohols catalyzed by Mn(I) NNS complex **105b**.

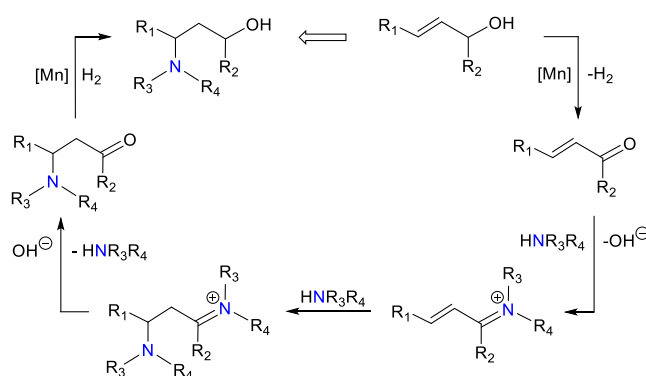
Very recently, the same research group reported the application of Mn(I) complexes with bidentate NN ligands in a formal *anti*-Markovnikov hydroamination of allylic alcohols in the presence of a weak base – K<sub>2</sub>CO<sub>3</sub> (Scheme 70) [109]. The presence of the picolylamine ligand scaffold was again found to be critical for the occurrence of this transformation since picolylhydrazine-containing complex was almost inactive. The complex **106b** bearing thioether arm was more active than its thiophene- and methoxy-containing analogues (92% *vs.* 78% *vs.* 60% yield in the amination of allylic alcohol with N-methylaniline for **106b**, **105b** and **106a**, respectively). The reaction can be applied to a wide variety of secondary aromatic or aliphatic amines with complete regioselectivity and typical product yield higher than 90%. Primary aromatic amines could be also

employed but with slightly reduced efficiency (55-60% yields). This protocol well tolerated numerous functional groups including halogens, CF<sub>3</sub>, heterocycles, amide, alkene, secondary hydroxyl group and was successfully applied for the derivatization of several complex organic molecules.



**Scheme 70.** Formal *anti*-Markovnikov hydroamination of allylic alcohols catalyzed by Mn(I) complexes bearing hemilabile NNS ligands.

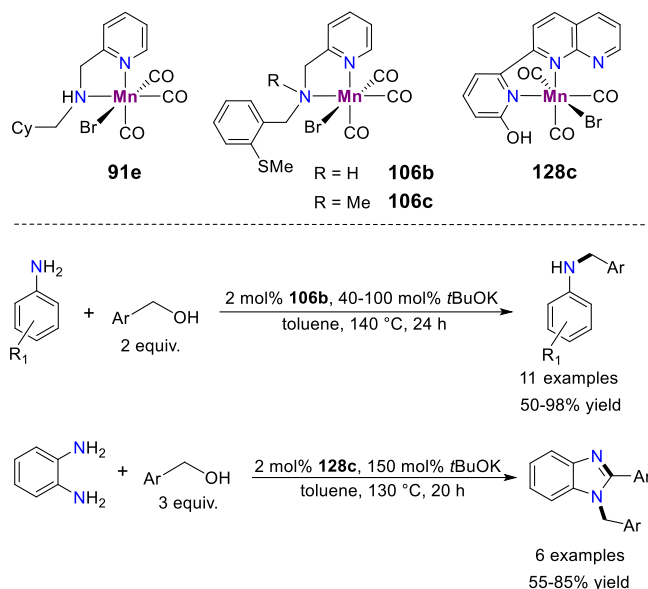
The reaction mechanism (Scheme 71) includes the Mn-catalyzed dehydrogenation of allylic alcohol into the  $\alpha,\beta$ -unsaturated carbonyl compound, which undergoes a condensation with amine to form the corresponding iminium species. The Michael addition of the second amine molecule to the latter, followed by hydrolysis and the hydrogenation of resulting ketone intermediate leads to the formation of the final  $\gamma$ -amino-alcohol product. The formation of allyl-substituted iminium salt and  $\beta$ -aminoketone was confirmed by HRMS spectra of reaction mixtures. According to the results of deuterium-labelling experiments (KIE  $k_H/k_D = 3.43$ ) inner-sphere alcohol dehydrogenation seems to be implicated into the rate-determining step of the process. The potential role of the S-based donor as hemilabile ligand was confirmed by the reduced reaction efficiency in the presence of exogenous phosphine donor ligands (37% and 16% yields in the presence of PPh<sub>3</sub> and PCy<sub>3</sub>, respectively).



**Scheme 71.** Reaction scheme for the amination of allylic alcohols with primary or secondary amines catalyzed by Mn(I) NNS complex **106b**.

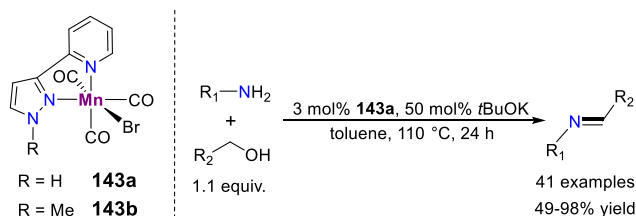
It was also shown by Maji that well-defined Mn(I) picolyamine complexes can catalyze monoalkylation of anilines with benzylic alcohols (Scheme 72) [110]. The complex **106b** having additional S-donor moiety was found again more active than its analogue **91e** affording 91% and 40% yields for the reaction between aniline and BnOH in the presence of 40 mol% of *t*BuOK as base. Interestingly, *N*-methylated catalyst **106c** was still able to perform some catalytic turnover (18% yield). This protocol showed only moderate efficiency being far below the best Mn(I) catalytic systems for N-amine alkylation with alcohols based on PNP [111] and PN<sup>3</sup>P [112] ligands. In

addition, the use of stoichiometric amount of base was required in most cases to achieve reasonable product yield. The alkylation of aromatic primary *ortho*-diamines catalyzed by Mn(I) NN complex **128c** exhibiting different type of cooperativity to form the corresponding substituted benzimidazoles under similar reaction conditions was reported by Chen, Xia and coll. (Scheme 72) [92]. The reaction typically proceeded with 75-80% yield but required an excess of strong base thus limiting the application for the substrates bearing functional groups.



**Scheme 72.** Alkylation of aromatic amines with benzylic alcohols catalyzed by Mn(I) complexes bearing bidentate NN and hemi-labile NNS ligands.

The use of different nitrogen heterocycles in the design of Mn(I) complexes with NN ligands was also evaluated. In particular, Chai and coll. reported that complexes **143** bearing pyridine-pyrazole ligands were able to perform the dehydrogenation of benzylic alcohols in the presence of primary amines (Scheme 73) [113]. While both catalysts displayed similar conversion in the reaction between PhNH<sub>2</sub> and BnOH, it was remarkable that complex **143b** containing N-methylated pyrazole moiety was more efficient in the C=N bond hydrogenation (77:23 ratio between PhN=NBn and PhNHBn), whereas **143a** provided 98% selectivity of imine formation. Negligible activity of **143a** in hydrogenation reactions was exploited for the development of selective imine synthesis with ample substrate scope. Both aromatic and aliphatic amines incorporating halogens, CF<sub>3</sub> and various heterocyclic fragments can be engaged in this process to form the target products in typically 80-90% isolated yields.

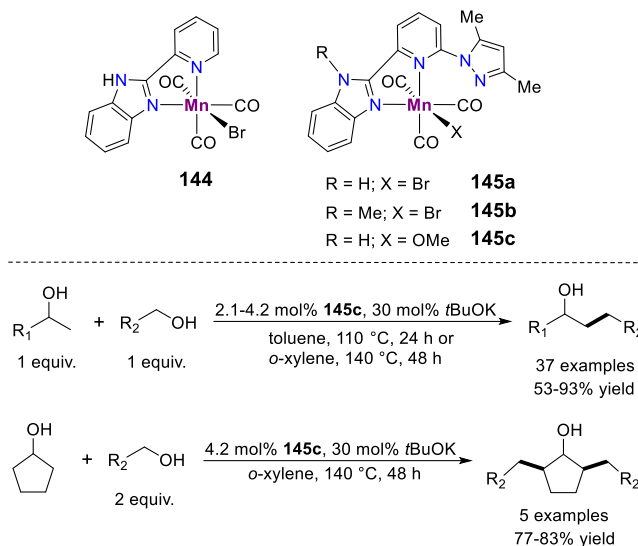


**Scheme 73.** Synthesis of imines from primary alcohols catalyzed by Mn(I) complex **143a** bearing pyridine-pyrazole ligand.

The influence of a pendant pyrazole group in Mn(I) complexes based on pyridine-benzimidazole ligands on the selectivity in  $\beta$ -alkylation of secondary alcohols with primary alcohols was studied by Yu and coll. (Scheme 74) [114]. While the use of 2.1 mol% of complex **144** afforded

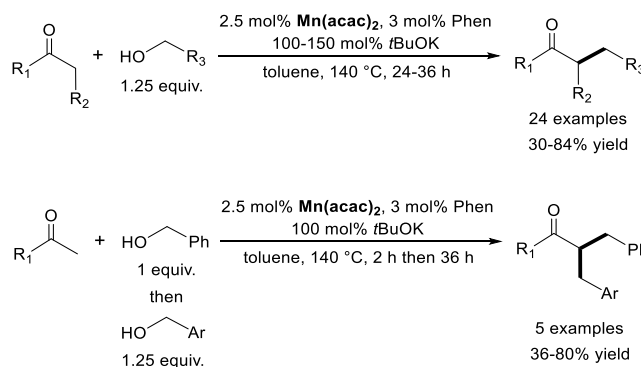


higher amount of target alcohol product in the reaction of Ph(Me)CHOH with BnOH at 110 °C (92% conversion, 78% selectivity) than its analogues **145a-b** (84-86% conversion, 53-67% selectivity), the catalysts **145c** combining the pyrazole-containing NN ligand and methoxide led to significantly improved results (96% conversion, 94% selectivity). A variety of substituted secondary alcohols can be obtained from both aromatic and aliphatic substrates requiring however the two-fold increase of catalyst charge and reaction temperature to 140 °C in the latter case. The efficient double alkylation of cyclopentanol with benzylic alcohols was also developed. The presence of halogens, CF<sub>3</sub> and pyridine groups was well tolerated, but unexpectedly the tri-substituted C=C double bond in cholesterol was fully hydrogenated under reaction conditions.



**Scheme 74.** Selective  $\beta$ -alkylation of secondary alcohols with primary alcohols catalyzed by Mn(I) complex **145c** bearing pyridine-benzimidazole ligand.

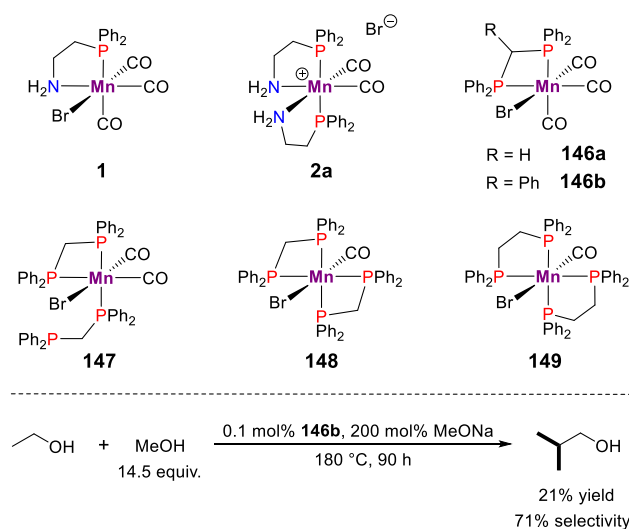
Finally, it was demonstrated that even Mn(II) precursors in combination with bidentate nitrogen ligands could be applied to the  $\alpha$ -alkylation of ketones (Scheme 75) [115]. The application of catalytic system generated *in situ* from Mn(acac)<sub>2</sub> and 1,10-phenanthroline to the reaction between propiophenone with BnOH led to the preferential formation of alkylated ketone accompanied by its hydrogenation product (80% and 20% GC yields, respectively). The utilization of other tertiary aromatic and aliphatic diamines under the same conditions led to lower conversions and significantly higher amounts of secondary alcohol by-products. The reaction was found to be the most efficient for benzylic alcohols to give branched ketone products in 70-80% typical yield and may be



**Scheme 75.** Alkylation of ketones with primary alcohols catalyzed by the catalyst generated *in situ* from Mn(acac)<sub>2</sub> and 1,10-phenanthroline.

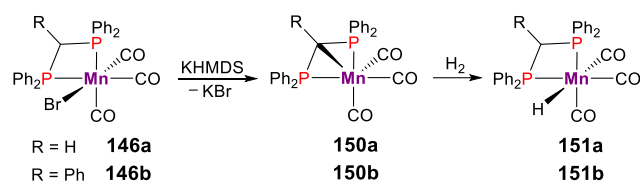
even used for one-pot double alkylation of acetophenones *via* the consecutive addition of two different alcohol components. The use of aliphatic and heterocycle-containing substrates was also possible, but the product yields dropped to 30-50%. Though isotope-labelling control experiments were in agreement with a realization on Mn-catalyzed alcohol dehydrogenation, the nature of the catalytic species and corresponding metal oxidation state are not clear for the moment.

In 2020, Wass and coll. evaluated the catalytic activity of Mn(I) complexes based on PN and PP bidentate ligands for synthesis of isobutanol from ethanol and methanol using Guerbet reaction (Scheme 76) [116], previously described by Liu [117] and Jones [118] for Mn(I) PNP complexes. While complex **1** containing single phosphinoamine ligand showed low activity (TON 12), the introduction of the second PN ligand in **2a** led to better results (TON 87). The inversed trend was observed for PP ligands, since pre-catalyst **148** bearing two chelating dppm ligands was less productive than **146a** (TON 22 and 67, respectively). Though the replacement of dppm ligands in **146** with dppe afforded very similar results (**149**: TON 26), better performance was achieved for complex **147** exhibiting three coordinated and one pendant phosphine moiety (TON 113).



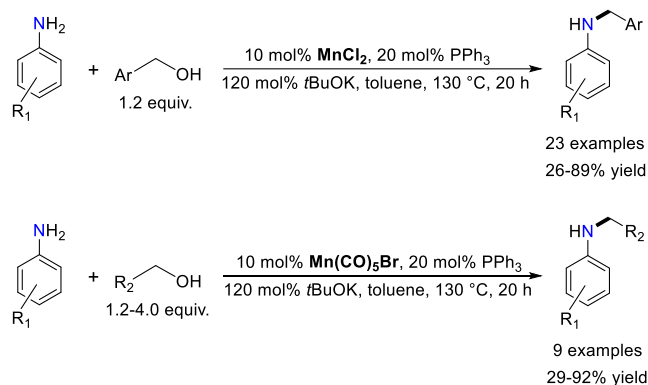
**Scheme 76.** Selective synthesis of isobutanol by Guerbet reaction catalyzed by Mn(I) complexes **146** bearing dppm-type diphosphine ligand.

Finally, it was shown that the introduction of phenyl moiety into the dppm bridge in **146a** was the optimal strategy since the activity of the resulting catalyst **146b** was increased by *ca.* three times (TON 206) keeping the same level of selectivity (*n*-propanol and 2-butanol were systematically detected as by-products). These results are in accord with a recent observation of the strongly beneficial effect of dppm bridge substitution in complexes **146** for cooperative dihydrogen activation (Scheme 77) [119]. Indeed, it was shown that diphosphinomethanide complex **150b** obtained by the deprotonation of the bromide precursor **146b** was capable to activate H<sub>2</sub> under very mild conditions (1 atm H<sub>2</sub>, 25 °C, 5 min) to give the corresponding hydride **151b** in 89% yield, whereas the reaction from its non-substituted analogue **150a** required more drastic conditions (50 atm. H<sub>2</sub>, 50 °C, 16 h) and was less efficient (50% yield of **151a**). Though the exact role of dppm bridge modification in the Guerbet reaction is not clear for the moment, it can be proposed that the presence of Ph substituent increases the acidity of the adjacent C–H bond thus facilitating hydrogenation/dehydrogenation steps involved in this process.



**Scheme 77.** Simplified scheme of cooperative hydrogen activation with Mn(I) dppm complexes **146**.

Later on Peng and coll. have shown that catalytic systems generated *in situ* from  $\text{MnCl}_2$  or  $\text{Mn}(\text{CO})_5\text{Br}$  with simple triphenylphosphine were able to perform the N-alkylation of anilines with primary alcohols (Scheme 78) [120]. The combination of 10 mol%  $\text{MnCl}_2$  with two-fold excess of  $\text{PPh}_3$  was found to be optimal, whereas the use of more electron-donating triaryl- ( $\text{ToI}_3\text{P}$ ,  $\text{Mes}_3\text{P}$ ) and trialkylphosphines ( $\text{PEt}_3$ ,  $\text{PCy}_3$ ,  $\text{PtBu}_3$ ) provided a deleterious effect for the catalytic activity. A variety of anilines was alkylated in moderate-to-good yield using slight excess of benzylic alcohols and sur-stoichiometric amount of strong base. While, halogens and various heterocycles were tolerated in this protocol, the substrates bearing CN, ester,  $\text{NO}_2$  and OH functions afforded no desired products. In contrast to  $\text{MnCl}_2/2\text{PPh}_3$  combination and Mn(I) complexes with NN ligands (Scheme 72), the catalytic system derived from  $\text{Mn}(\text{CO})_5\text{Br}$  was able to activate aliphatic primary alcohols (besides methanol) thus showing the preference of P-based ligands over bidentate amines in such type of processes.

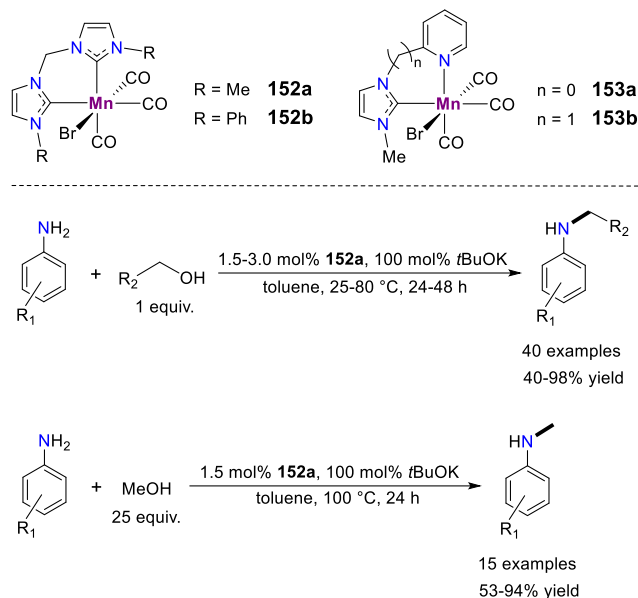


**Scheme 78.** Alkylation of aromatic amines with primary alcohols catalyzed by the combination of  $\text{MnCl}_2$  or  $\text{Mn}(\text{CO})_5\text{Br}$  with two equivalents of  $\text{PPh}_3$ .

Similarly to hydrogenation and transfer hydrogenation processes, some remarkable results by using Mn(I) complexes bearing NHC-containing ligands were recently obtained. In 2019, the group of Ke reported highly efficient alkylation of anilines with alcohols catalyzed by bis(NHC) complexes **152** (Scheme 79) [121]. Complex **152a** was found to be highly active under very mild conditions (100 mol%  $t\text{BuOK}$ ,  $25^\circ\text{C}$ , 24 h) leading to 85% product yield in a model reaction between  $\text{PhNH}_2$  and  $\text{BnOH}$  at 1.5 mol% catalyst loading, whereas its analogue **152b** based on more bulky bis(NHC) ligand was less efficient (58% yield). Importantly, the presence of two NHC donor moieties was critical since the related complexes **153** bearing pyridine-NHC ligands were practically inactive under these conditions.

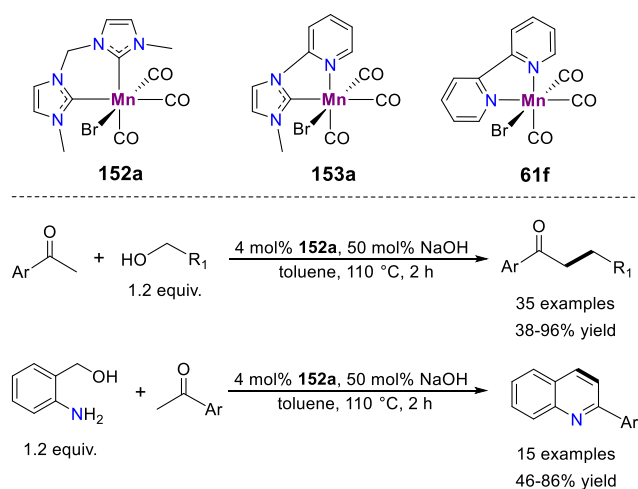
The unique catalytic properties of complex **152a** constituted a highly efficient protocol for aniline alkylation using only stoichiometric amount of alcohol, which represents the first example of such process catalyzed by a 3d transition metal complex at room temperature. Both benzylic and aliphatic alcohols can be successfully employed to form the products in good-to-excellent yields. The reaction was compatible with numerous functional groups including halogens,  $\text{CF}_3$  and alkenes as

well as coordinating SMe, thiophene and pyridine moieties requiring however for the latter the increase of catalyst charge to 3 mol%. High activity of catalyst **152a** also allowed to use of methanol as alkylating agent at higher temperature (100 °C) to afford the target products typically in 70-90% yield keeping similar functional group tolerance. Stoichiometric experiments and DFT calculations revealed that both alcohol dehydrogenation and imine hydrogenation steps are likely to proceed *via* an outer-sphere mechanism with the last step being kinetically rate-determining.



**Scheme 79.** Selective mono-alkylation of aromatic amines with alcohols catalyzed by Mn(I) complexes **152** bearing bis(NHC) ligand.

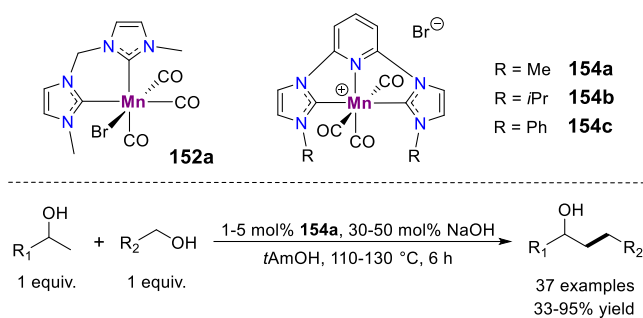
Shortly after the same group has shown the application of complex **152a** for the  $\alpha$ -alkylation of ketones and Friedländer's quinoline synthesis (Scheme 80) [122]. Unlike the previous case, complexes **152a** and **61f** exhibiting NHC-pyridine and bipyridine ligands also displayed some catalytic activity in acetophenone alkylation with BnOH being *ca.* 2 times lower than bis(NHC) system (27-30% *vs.* 64% yield). Under optimized conditions the reaction possessed a wide substrate scope with functional group tolerance similar to that previously observed in the work of Maji (Scheme 64) [101]. Despite the catalyst charge for bis(NHC) complex **152a** in this case was higher than for NNN pincer-type



**Scheme 80.** Alkylation of ketones with primary alcohols and Friedländer synthesis of quinolines catalyzed by Mn(I) complex **152a** bearing bis(NHC) ligand.

complex **134b** (4 vs. 2 mol%), the bidentate system operated at lower temperature (110 vs. 140 °C) in shorter reaction time (2 vs. 24 h) using weaker base (NaOH vs. *t*BuOK). Though it is difficult to benchmark precisely the activity of CC and NNN systems due to different reaction conditions, it can be noted that the former one is more efficient in terms of TOF (11.3 and 1.9 h<sup>-1</sup> for **152a** and **134b**, respectively) in the representative reaction involving acetophenone and BnOH.

The comparison of bidentate and pincer-type Mn(I) complexes containing NHC donor units in  $\beta$ -alkylation of secondary alcohols was recently performed by Ke and coll. (Scheme 81) [123]. It was shown that complex **152a** at 2 mol% charge was superior to bulkier CNC pincer-type derivatives **154b-c** both in terms of activity (82% vs. 45-56% yield for acetophenone alkylation with BnOH) and selectivity towards the formation of ketone products (93% vs. 78-81%). However, pre-catalyst **154a** bearing methyl groups at the nitrogen atoms was found to be much efficient resulting in 93% of the target product with more than 99% selectivity even at 1 mol% catalytic charge. A variety of aromatic ketones can be alkylated with benzylic alcohols in good-to-excellent yields using typically 1 mol% of **154a** in the presence of cheap base NaOH. Aliphatic alcohols were employed as well with good efficiency, however five-fold amount of catalyst was required in that case. The presence of coordinating N- or S- groups in the substrates has a deleterious effect to the catalytic activity, but still 30-50% product yields could be achieved using 2 mol% catalytic charge.



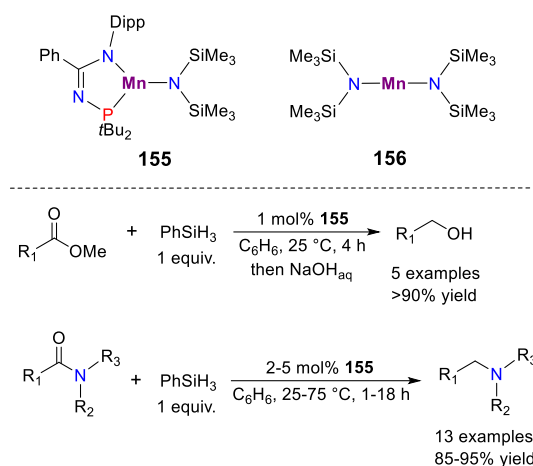
**Scheme 81.** Selective  $\beta$ -alkylation of secondary alcohols with primary alcohols catalyzed by Mn(I) complex **154a** bearing NHC-pyridine-NHC ligand.

As in the previous case the performance of NHC-containing system was found to be better than for the related amine-based complex **145c** described by Yu and coll. (Scheme 74) [114] revealing TOF 14.8 and 1.8 h<sup>-1</sup> respectively in the alkylation of acetophenone with BnOH at the same temperature and base amount. The last three examples clearly highlight the great potential of Mn(I) NHC complexes for the future design of hydrogenation catalysts.

### 3. Evolution of the ligand design in Mn-based hydrosilylation catalysis

Hydrosilylation of activated carbonyl derivatives using Mn(I) and Mn(II) complexes bearing different types of donor ligands has already been well developed [33-38] providing in particular several catalytic systems working at room temperature, under solvent-free conditions with outstanding TOF numbers up to 297000 h<sup>-1</sup> [29], 76800 h<sup>-1</sup> [27] and 19800 h<sup>-1</sup> [28] for aldehydes, ketones and alkylformates, respectively. In contrast, only few Mn-based catalytic systems for efficient and chemoselective reduction of carboxylic acid derivatives as well as for hydrosilylation of multiple C-C (alkenes, alkynes) and C-N (imines, nitriles) bonds are known in literature. A rapid progress in this area achieved during the last five years owing to the utilization of simpler manganese complexes is performed in this final section.

The first example of hydrosilylation of esters catalyzed by Mn(II) complexes bearing bidentate ligands was reported in 2017 by Sydora, Stradiotto, Turculet and coll. (Scheme 82) [124]. It was shown that well-defined complex **155** based on *N*-phosphinoamidinate ligand was capable to reduce methyl benzoates with phenylsilane at room temperature with more than 90% conversion after 4 h. Aliphatic methyl heptanoate was also reduced in almost quantitative manner under these conditions. While Cl and CF<sub>3</sub> substituents in *para*-position of the aromatic ring were well tolerated the reaction failed for NO<sub>2</sub> or pyridine containing esters as well as for lactones like phthalide. The catalytic activity of complex **155** was comparable with state-of-the-art Mn(II) pre-catalysts based on multidentate PDI ligands developed by Trovitch [27].

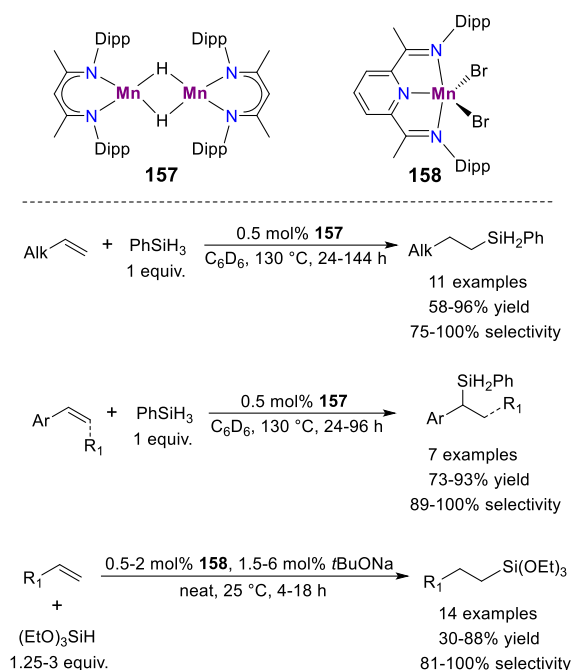


**Scheme 82.** Hydrosilylative reduction of esters and tertiary amides catalyzed by Mn(II) complex **155** bearing *N*-phosphinoamidinate ligand.

The same catalyst **155** could be employed in the hydrosilylative reduction of tertiary amides with phenylsilane to form the corresponding amines (Scheme 82) [124]. Typically high conversions were observed for aromatic and aliphatic derivatives using only 2 mol% of catalyst at room temperature for 18-48 h, while in some cases increase of catalyst loading to 5 mol% and heating at 75 °C was required. Though halogens, OMe, and thiophene moieties were compatible with this protocol, the presence of CN or NO<sub>2</sub> groups led to complex mixtures of products. The catalytic system was also not applicable to secondary and primary amide substrates. Interestingly, it was demonstrated that simple bis(amido) complex Mn(N(SiMe<sub>3</sub>)<sub>2</sub>) **156** could also catalyze amide reduction at 75 °C but with lower efficiency thus demonstrating the importance of bidentate PN ligand [124, 125].

Later, Trovitch and coll. demonstrated that binuclear Mn(II) hydride complex **157** bearing bulky β-ketiminate ligands was efficient for alkene hydrosilylation (Scheme 83) [126]. Only phenylsilane was found to be suitable for this transformation, whereas less active secondary (Ph<sub>2</sub>SiH<sub>2</sub>) or tertiary (Ph<sub>3</sub>SiH, (EtO)<sub>3</sub>SiH) silanes gave no conversion. Though this reaction proceeded under rather harsh conditions (prolonged heating at 130 °C in benzene), it was found to afford excellent regioselectivity. Indeed, for the aliphatic terminal alkenes the exclusive formation of *anti*-Markovnikov addition product – linear silane was observed in good yield. Disubstituted geminal alkenes, cyclic alkenes and dienes were also reactive, but longer reaction time was typically required in these cases. This difference in relative reaction rate allowed in particular to perform fully selective hydrosilylation of terminal alkene in myrcene in 96% yield keeping intact geminal and trisubstituted moieties. In contrast the reaction of styrene derivatives under these conditions led to the preferential formation (89-100% selectivity) of branched silanes resulting from Markovnikov addition. Interestingly, the presence of coordinating PPh<sub>2</sub> group in styrene substrate did not strongly affect the catalytic process and the corresponding product was isolated in 78% yield as a single

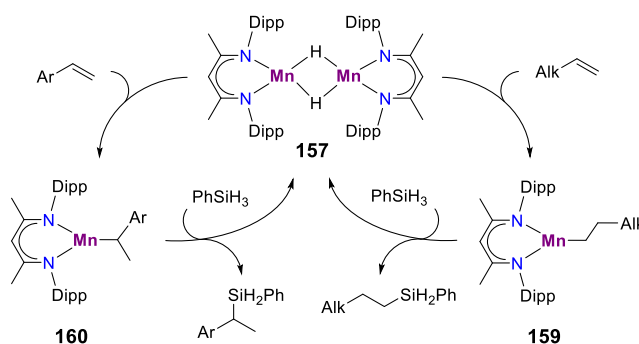
isomer. The catalyst **157** was also successfully used to form silicones from 1,2,4-trivinylcyclohexane and PMHS under solvent-free conditions at 0.05 mol% catalyst charge.



**Scheme 83.** Hydrosilylation of aliphatic and aromatic alkenes catalyzed by Mn(II) complexes **157** and **158** bearing β-ketiminate and PDI ligands, respectively.

The comparison of β-dekeniminate catalyst **157** with catalytic system based on a combination of the Mn(II) complex **158** bearing tridentate PDI ligand and *t*BuONa activator (Scheme 83) [127] shows the superiority of the latter for the hydrosilylation of terminal aliphatic alkenes. In this case the reaction proceeds rapidly at room temperature with *anti*-Markovnikov selectivity and can be employed for less reactive tertiary silanes. However, styrene substrates afforded only *ca.* 30% yields of linear silanes under these conditions thus showing that the use of less active bidentate catalytic system can be complementary to selectively achieve the alternative isomer.

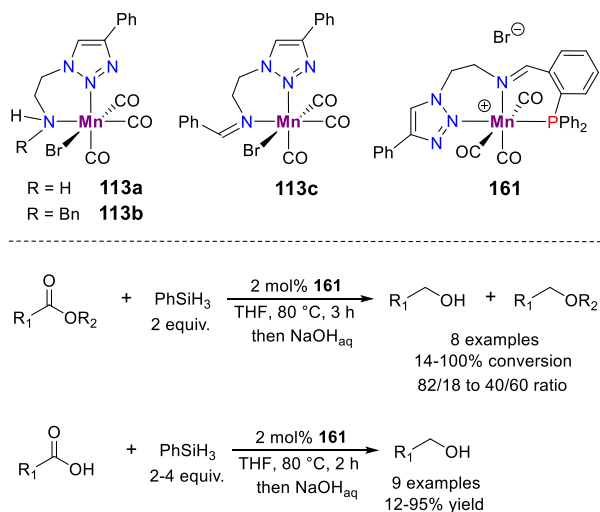
The reaction mechanism for alkene hydrosilylation catalyzed by Mn(II) complex **157** based on stoichiometric experiments is shown in Scheme 84 [126]. It was demonstrated that contrary to classic Chalk-Harrod mechanism implicating Si-H bond activation binuclear catalyst **157** undergoes dissociation and alkene insertion processes leading to σ-alkyl intermediates **159** and **160** (the structure of **160** derived from 4-*t*Bu-styrene was confirmed by X-ray diffraction), which then form the final products and starting hydride complex **157** upon σ-bond metathesis with silane. While the formation of primary



**Scheme 84.** Simplified reaction mechanism for Markovnikov and *anti*-Markovnikov alkene hydrosilylation catalyzed by Mn(II)  $\beta$ -keteniminato complex **157**.

alkyl species **159** is expected for aliphatic alkenes, styrenes are typically prone to react at the benzylic position to form secondary alkyl intermediate of type **160** thus explaining the observed regioselectivity trend.

The evaluation of more stable carbonyl Mn(I) complexes bearing bidentate NN ligands in the hydrosilylation of esters and carboxylic acids was first reported by Werlé, Leitner and coll. (Scheme 85) [128]. It was demonstrated that the hydrosilylation of ethyl benzoate catalyzed by imino-triazole complex **113c** (2 mol% cat, 2 eq. PhSiH<sub>3</sub>, THF, 80 °C, 3 h) led to 53% of substrate conversion providing the ether BnOEt with 94% selectivity. Similar bidentate complex **113a** bearing amine-triazole ligand was slightly more active under the same conditions (67% conversion) affording equal amount of ether and alcohol products after hydrolysis, whereas the use of its benzyl-substituted analogue **113b** led to only 18% conversion with preferential formation of alcohol product. The activity of pincer-type analogue **161** obtained by a formal addition of phosphine arm to **113c** was found to be superior leading to a full substrate conversion to form both products with a ratio dependent on the reaction temperature and the rate of silane addition. This reduction protocol was applicable for both benzoic and aliphatic ester derivatives to form generally alcohols as major products. Interestingly, the reduction of benzoic acid using complexes **113c** and **161** afforded almost exclusively the benzylic alcohol with again higher activity of the PNN system compared to the NN one (50 vs. 28% conversion). Simple aliphatic and aromatic carboxylic acids were readily reduced in good-to-excellent yield, while in the case of *m*-nitrobenzoic acid 12% of the target product was only obtained.

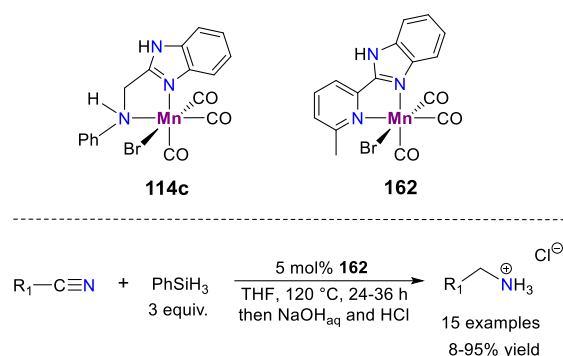


**Scheme 85.** Hydrosilylation of esters and carboxylic acids catalyzed by Mn(I) complexes bearing triazole-amine ligands.

The hydrosilylation of nitriles to amines catalyzed by Mn(I) complexes based on bidentate diamine ligands was reported by the group of Kundu (Scheme 86) [129]. Complex **162** exhibiting the benzimidazole-pyridine scaffold was more efficient than its secondary amine analogue **114c** in the reduction of PhCN both in terms of conversion (>99% vs. 80%) and product selectivity towards benzylamine (25% of imine BnN=C(H)Ph was formed in the latter case). The reduction of numerous aromatic and benzylic nitriles was successfully achieved with a tolerance to halogen, OMe, CF<sub>3</sub>, SMe

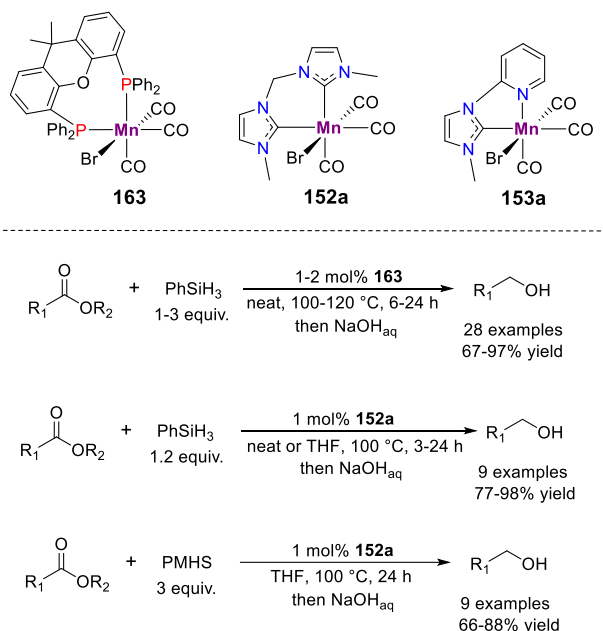


and thiophene groups. In contrast 3-cyanopyridine was reacted sluggishly to afford only 8% yield and PentCN was found to be unreactive at all.



**Scheme 86.** Hydrosilylation of nitriles catalyzed by Mn(I) complex **162** bearing benzimidazole-pyridine ligands.

The replacement of nitrogen donor moieties in Mn(I) complexes by phosphines [130] and NHCs [131] in the context of ester hydrosilylation (Scheme 87) was recently performed in the groups of Bagh and Royo, respectively. Both catalytic systems led to the selective formation of alcohols. In particular, complex **163** derived from Xantphos was capable to reduce a variety of esters in high yield under solvent free conditions using 1 mol% of catalyst and one equivalent of phenyl silane per ester moiety. Secondary ( $\text{Ph}_2\text{SiH}_2$ ) or tertiary ( $\text{Ph}_3\text{SiH}$ ,  $\text{Et}_3\text{SiH}$ ) silanes could also be employed with similar efficiency, but longer reaction time was required to achieve a full conversion (12 h *vs.* 6 h for  $\text{PhSiH}_3$  for  $\text{PhCO}_2\text{Bn}$  reduction). This process was equally efficient for the substrates containing aliphatic or aromatic groups at both carboxylic acid and alcohol components including lactones and even poly(1,6-hexamethyleneadipate). The list of functional group compatibility included halogens, furan, terminal or internal alkene and free hydroxyl in the  $\alpha$ -position to the ester moiety.

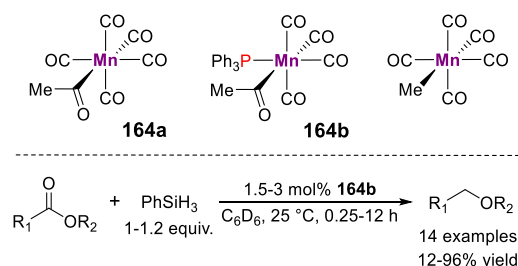


**Scheme 87.** Hydrosilylation of esters to alcohols catalyzed by Mn(I) complexes **163** and **152a** bearing diphosphine and bis(NHC) ligands, respectively.

NHC-containing Mn(I) complexes reported by Royo et al. were operating under similar conditions with bis(NHC) catalyst **152a** being slightly more active than its pyridine-NHC congener

**153a** requiring 3 and 6 hours, respectively for the quantitative reduction of methyl benzoate at 1 mol% catalyst charge. Interestingly, complex **152a** can be reused by five successive additions of ester and silane leading after 4 days to a TON of 485 for the reduction of PhCO<sub>2</sub>Me. Importantly, high activity of this system allowed to replace phenylsilane with 3 equivalents of cheaper PMHS resulting in comparable product yields. While simple aromatic and aliphatic esters could be readily reduced using complex **152a**, the reaction of substrates containing NO<sub>2</sub>, NH<sub>2</sub>, pyridine, CN and conjugated alkene groups led to the formation of complex product mixtures.

Selective hydrosilylative transformation of esters to ethers catalyzed by Mn(I)  $\sigma$ -acyl complex **164b** supported by PPh<sub>3</sub> was reported in early work of Cutler et al. (Scheme 88) [132]. It was shown that the conversion of EtOAc to Et<sub>2</sub>O with 85% NMR yield could be achieved within 15 min using 3 mol% of catalyst **164b** at room temperature in the presence of PhSiH<sub>3</sub>, whereas for less reactive silanes such as Ph<sub>2</sub>SiH<sub>2</sub> or Ph<sub>2</sub>MeSiH the reaction stopped at the formation of the corresponding silylacetals isolated in 89-95% yield. Phosphine-free acyl complex **164a** in combination with PhSiH<sub>3</sub> worked much slower under these conditions requiring 1.5 h for full conversion. Curiously, even simple carbonyl derivatives such as Mn(CO)<sub>5</sub>Me and Mn(CO)<sub>5</sub>Br were catalytically active in the reduction of ethyl acetate to form Et<sub>2</sub>O in 85 and 55% NMR yield, respectively after 4 h. This protocol was found to be very efficient for the aliphatic esters besides very bulky and phenol-derived ones, in which the mixtures of ethers and silylacetals were formed.

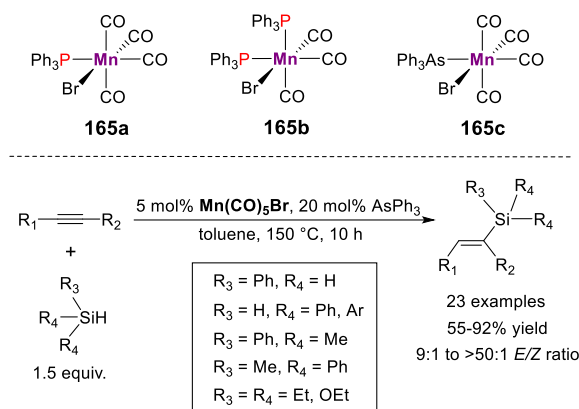


**Scheme 88.** Hydrosilylation of esters to ethers catalyzed by Mn(I)  $\sigma$ -acyl complex **164b** bearing monodentate PPh<sub>3</sub> ligand.

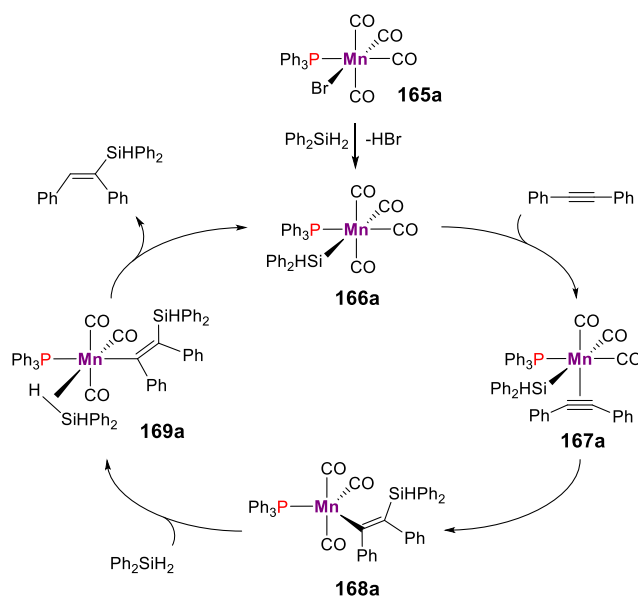
The potential of Mn(I) carbonyl complexes incorporating simple monodentate phosphines in hydrosilylation of alkynes was demonstrated by Wang and coll. (Scheme 89) [133]. While the hydrosilylation of diphenylacetylene with PhSiH<sub>3</sub> at 150 °C catalyzed with 5 mol% of Mn(CO)<sub>5</sub>Br led to only 25% combined yield of the corresponding vinylsilanes with 1.3:1 *E/Z* ratio, the addition of PPh<sub>3</sub> or AsPh<sub>3</sub> greatly improved both yields (60-85%) and *E*-stereoselectivity (14:1 to 43:1). Curiously, the addition of PCy<sub>3</sub>, dppe or bipy-type ligands totally inhibited the catalytic activity. Both well-defined and generated *in situ* complexes **165** showed comparable product yields, but the *E*-stereoselectivity was found to be slightly better in the presence of an excess of monodentate ligand. Finally, the catalytic system generated *in situ* from 5 mol% of Mn(CO)<sub>5</sub>Br and 20 mol% of AsPh<sub>3</sub> revealed to be the most efficient in terms of yield and stereoselectivity was observed with a variety of internal alkynes and silanes. Diaryl alkynes could be stereoselectively hydrosilylated in high yield using primary, secondary and tertiary silanes. The reaction for arylalkyl-substituted internal alkynes proceeded with synthetically useful level of regioselectivity (1:5 to 1:13) favoring the addition of silyl fragment to the adjacent position of the alkyl group. Halogens, CF<sub>3</sub> and thiophene functions were well tolerated and nitrile group remained completely untouched.

The reaction mechanism proposed based on extensive stoichiometric studies with phosphine complexes is presented in Scheme 90. The catalytic cycle starts with formation of  $\sigma$ -silyl intermediate

**166a** from the reaction of the bromide precursor **165a** with diphenylsilane. The latter is transformed *via* thermal CO ligand substitution with diphenylacetylene to the  $\eta^2$ -alkyne complex **167a**, which undergoes the alkyne insertion across Mn–Si bond to form  $\sigma$ -vinyl derivative **168a**. The coordination of silane molecule followed by  $\sigma$ -bond metathesis leads to the formation of the final product and the regeneration of silyl intermediate **166a**.



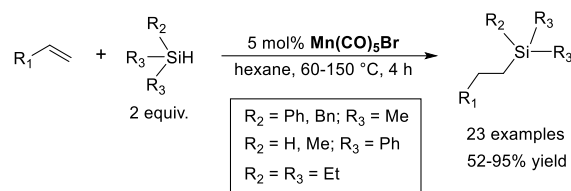
**Scheme 89.** *E*-selective hydrosilylation of alkynes catalyzed by well-defined or generated *in situ* Mn(I) complexes **165**.



**Scheme 90.** Proposed reaction mechanism for *E*-selective hydrosilylation of diphenylacetylene with  $\text{Ph}_2\text{SiH}_2$  catalyzed by Mn(I) complex **165a**.

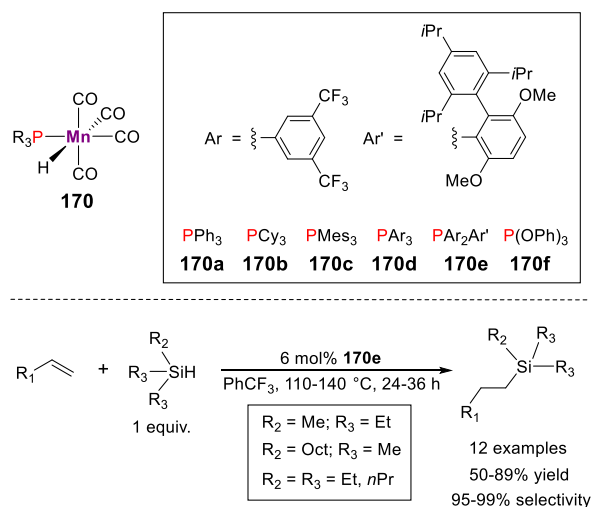
While singular low-efficient examples of hydrosilylation of terminal aliphatic alkenes using simple carbonyl complexes  $(\text{CO})_5\text{MnSiPh}_3$  [134] and  $\text{Mn}_2(\text{CO})_{10}$  [135] were known in literature, this reaction was generalized by Wang and coll. only in 2018 using  $\text{Mn}(\text{CO})_5\text{Br}$  (Scheme 91) [136]. The optimization of the reaction between styrene and  $\text{Me}_2\text{BnSiH}$  to avoid dehydrogenative alkene silylation (*vide infra*) revealed that heating in hexane in the presence of 5 mol% of catalyst and two equivalents of tertiary silane was required to provide quantitatively *anti*-Markovnikov addition product with excellent selectivity. It was also shown that both  $\text{Mn}(\text{CO})_5\text{Br}$  and  $\text{Mn}_2(\text{CO})_{10}$  complexes under UV irradiation at room temperature gave similar results but with slightly lower conversions. A vast variety of styrenes and tertiary silanes was readily employed at 60 °C using this catalytic system to form the target products in 80% average yield. The scope for terminal aliphatic alkenes was less

extended and heating up to 150 °C was sometimes required. Importantly, the presence of halogen, CF<sub>3</sub>, C<sub>6</sub>F<sub>5</sub>, pyridine and even reducible ester groups was perfectly tolerated providing much larger scope than for Mn(II) catalysts **157** and **158** bearing β-ketenimate and PDI ligands (Scheme 83).



**Scheme 91.** Hydro-silylation of alkenes catalyzed by Mn(CO)<sub>5</sub>Br.

Very recently, the group of Xie studied in detail the role of monodentate phosphine additives in *anti*-Markovnikov alkene hydro-silylation in the presence of an equimolar amount of silane catalyzed by hydride complexes **170** generated *in situ* from Mn<sub>2</sub>(CO)<sub>10</sub>, phosphine and silane (Scheme 92) [137]. It was shown on the model reaction between TolCH=CH<sub>2</sub> and Et<sub>3</sub>SiH that the reaction efficiency was improved with the increase of both steric volume of the phosphine ligand (10%, 35% and 55% for **170a-c**, respectively) and their accepting properties (59%, 79% and 80% for **170d-f**, respectively). Among all ligands JackiePhos-derived complex **170e** was selected to evaluate the substrate scope being optimal in terms of yield and chemoselectivity vs. dehydrogenative silylation process. Despite the reaction yields were close to simpler system of Wang, it is notable that ketone group was also tolerated in such process and hydro-silylation of 1,2,4-trivinylcyclohexane with PMHS led to silicone material in 76% yield.

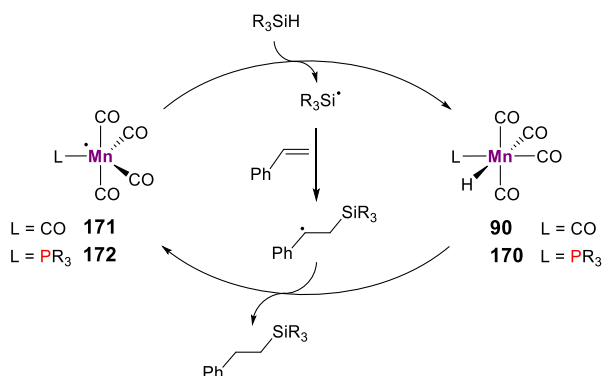


**Scheme 92.** Hydro-silylation of alkenes catalyzed by generated *in situ* Mn(I) hydride complexes **170** bearing monodentate phosphine ligands.

The proposed reaction mechanism for styrene hydro-silylation with simple Mn(I) carbonyl complexes (Scheme 93) includes the formation of 17-electron manganese radicals **171-172** upon thermal or photochemical cleavage of Mn–Mn or Mn–Br bonds. These species abstract hydrogen atom from silane to form the corresponding Mn(I) hydride complexes and the silyl radical. The latter undergoes the addition across C=C alkene bond to form benzyl radical reacting with hydride complexes to afford the final product and the starting 17-electron organometallic species.

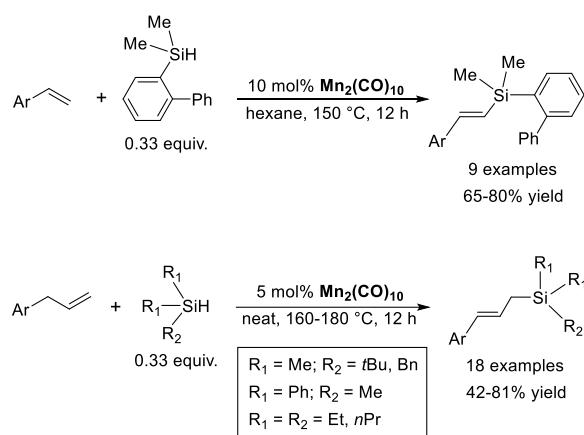
The formation of minor amounts of vinylsilane byproducts in alkene hydro-silylation catalyzed by Mn(I) carbonyl complexes *via* the dehydrogenative silylation motivated the group of Wang to search the optimal conditions for the realization of this highly challenging transformation as a major

reaction pathway. This goal was initially achieved for a series of styrenes using 10 mol% of  $\text{Mn}_2(\text{CO})_{10}$  at high temperature in the presence of sub-stoichiometric amount of particular tertiary silane (Scheme 94) [136].



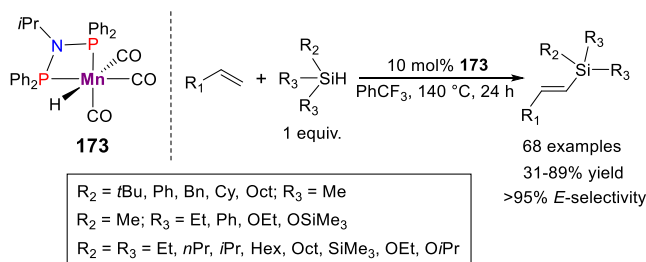
**Scheme 93.** Simplified mechanism of hydrosilylation of styrene with tertiary silanes catalyzed by  $\text{Mn}(\text{CO})_5\text{Br}$  and phosphine-based  $\text{Mn}(\text{I})$  complexes **170**.

Later, the group of Yang showed that this transformation can be generalized for allylarenes to form allylsilane products in moderate-to-good yield (Scheme 94) [138]. The key factor here allowing to control the selectivity for other tertiary silanes was the solvent-free conditions at more elevated temperature. Despite harsh conditions several functional groups such as  $\text{CF}_3$ , halogens,  $\text{NO}_2$ , CN, thioether, furan, thiophene were well-tolerated.



**Scheme 94.** Dehydrogenative silylation of styrenes and allylarenes catalyzed by  $\text{Mn}_2(\text{CO})_{10}$ .

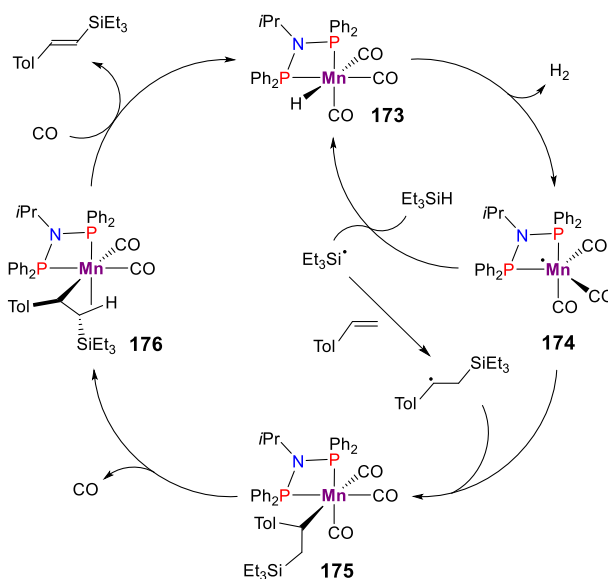
The real breakthrough in this area was found later by Xie and coll., who showed that the application of generated *in situ* complex **173** bearing short-bite diphosphine ligand led to the development of extremely general and robust procedure for dehydrogenative silylation of diverse terminal alkenes (Scheme 95) [137] outperforming all transition metal catalysts known to date.



**Scheme 95.** Highly versatile dehydrogenative silylation of alkenes catalyzed by Mn(I) hydride complex **173** *in situ* from  $\text{Mn}_2(\text{CO})_{10}$  and short-bite diphosphine ligand.

Remarkably, the reaction was extremely specific to this ligand providing only traces of desired product for structurally similar  $\text{Ph}_2\text{PNHPPPh}_2$  and  $\text{dppm}$  ligands. The substrate scope for both tertiary silanes and alkenes was extremely vast including not only regular aromatic and aliphatic olefins, but also conjugated dienes and even simplest C2-C4 alkenes. Functional group tolerance was remarkable as well since this protocol was fully compatible with OH, CN, ketone, ester, amine, numerous types of heterocycles and can be applied for the direct functionalization of several drugs and natural products.

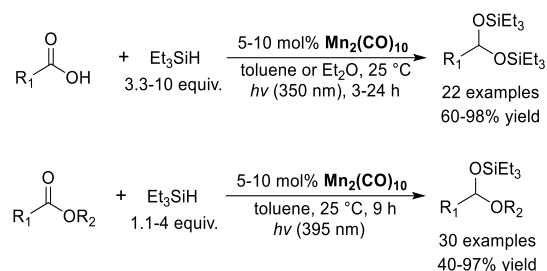
The reaction mechanism based on DFT calculations is shown in Scheme 96. The hydride complex **173** formed *in situ* from  $\text{Mn}_2(\text{CO})_{10}$  and the corresponding diphosphine undergoes at high temperature an homolytic Mn–H bond cleavage to form dihydrogen and 17-electron radical **174**, which is capable to abstract hydrogen atom from tertiary silane to regenerate again hydride species. The subsequent recombination of Mn-centered radical **174** and alkyl radical obtained from  $\text{Et}_3\text{Si}^\cdot$  and alkene leads to the formation of  $\sigma$ -alkyl intermediate **175**. The decarbonylation of the latter to the complex **176** stabilized by an agostic C–H interaction followed by  $\beta$ -hydride elimination afforded the final vinylsilane closing the catalytic cycle. It was found that the origin of chemoselectivity in this process resides in the lower energetic barrier for the reaction of alkyl radical with metallo-radical **174** (23.9 kcal/mol) than hydrogen abstraction from hydride **173** (27.9 kcal/mol) due to the bulky nature of diphosphine ligand.



**Scheme 96.** Simplified mechanism of dehydrogenative silylation of  $\text{TolCH=CH}_2$  with  $\text{Et}_3\text{SiH}$  catalyzed by Mn(I) complex **173** based on DFT calculations.

The application of  $\text{Mn}_2(\text{CO})_{10}$  under photochemical activation for the selective transformation of carboxylic acids to bis-silylacetals, which could be either isolated or hydrolyzed to the corresponding aldehydes was first reported by Sortais and coll. (Scheme 97) [139]. The chemoselectivity of this transformation was perfectly controlled by the choice of appropriate reducing agent leading to aldehyde derivatives for tertiary silanes ( $\text{Et}_3\text{SiH}$ ,  $\text{Ph}_2\text{MeSiH}$ ,  $\text{PhMe}_2\text{SiH}$ ) and to alcohols with more reactive silanes ( $\text{Ph}_2\text{SiH}_2$ ,  $\text{Et}_2\text{SiH}_2$ , TMDs). This protocol was very efficient for the reduction of aliphatic carboxylic acids besides sterically bulky ones such as 2-phenylpropionic acid. Benzoic acids reacted more sluggishly (30-40% yield), whereas stronger trifluoroacetic acid was totally unreactive. The

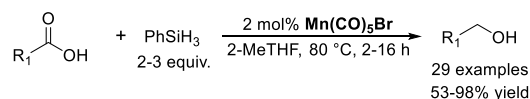
reaction tolerated the presence of halogens, CF<sub>3</sub>, unprotected aromatic amine or indole and thiophene moieties and failed for nitro-substituted derivatives. While internal alkene moiety was fully tolerated, the terminal one in hept-6-enoic acid underwent partial hydrosilylation to form the 2:1 mixture between unsaturated and saturated products. The reduction of phenol- or conjugated C=C bond containing substrates was accompanied by OH group silylation and hydrogenation, respectively.



**Scheme 97.** Chemoselective reduction of carboxylic acids and esters to silylacetals catalyzed by Mn<sub>2</sub>(CO)<sub>10</sub> under photochemical activation.

Similar protocol was later applied by the same group for the selective transformation of esters to mixed silylalkylacetals (Scheme 97) [140]. A variety of esters derived was reduced with excellent selectivity using only slight excess of Et<sub>3</sub>SiH. The reaction was almost insensitive to the nature of alcohol fragment and to steric crowding comparing to the reduction of carboxylic acids providing 70-90% yields for benzoic or 2-phenylbutanoic acid derivatives. As in the previous case halogens, CF<sub>3</sub>, internal alkene and furan moieties were well tolerated.

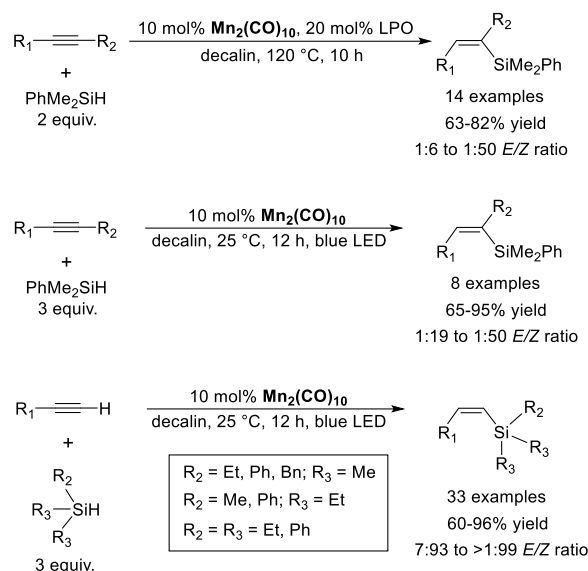
The hydrosilylative reduction of carboxylic acids to alcohols using Mn(CO)<sub>5</sub>Br under thermal conditions was recently reported by Werlé and coll. (Scheme 98) [141]. This process readily proceeded only with 2.5 equivalents of phenylsilane, whereas the use of less active Ph<sub>2</sub>SiH<sub>2</sub> or PMHS afforded *ca.* 30% yield for the reduction of 3-cyclohexylpropanoic acid using 6 and 10-fold excess of silane, respectively. Both aliphatic and aromatic carboxylic acids were smoothly converted to the corresponding alcohols with the tolerance to halogen, CF<sub>3</sub>, OH, thiophene and indole groups. As for others Mn-based catalytic systems for the reduction of carboxylic acid derivatives the presence of nitro group resulted in complete inhibition of the process. The reaction for levulinic acid led to the formation of the corresponding diol due to concomitant reduction of ketone group. Interestingly, the group of Garcia showed that the same transformation under more forcing conditions (2.5 mol% Mn(CO)<sub>5</sub>Br, 100 °C, toluene, 24 h) afforded 2-methyltetrahydrofuran in good yield [142].



**Scheme 98.** Hydrosilylative reduction of carboxylic acids to alcohols with phenylsilane catalyzed by Mn(CO)<sub>5</sub>Br.

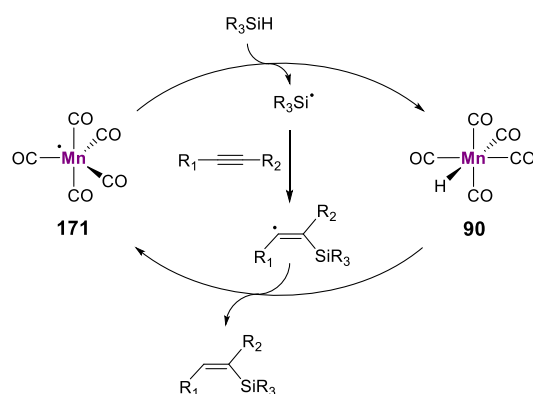
The hydrosilylation of alkynes with PhMe<sub>2</sub>SiH catalyzed by Mn<sub>2</sub>(CO)<sub>10</sub> in the presence of peroxide activator under thermal conditions was initially reported by the group of Wang (Scheme 99) [133]. In contrast to the results obtained with phosphine/arsine derivatives of Mn(CO)<sub>5</sub>Br (Scheme 89), under these conditions the reaction was found to be highly *Z*-selective. A series of vinylsilanes was obtained in good yield from diaryl- and alkylaryl-substituted acetylenes, being perfectly regioselective in the latter case for the formation of products, in which silyl group was attached to the alkyl end. Terminal alkynes such as 3-ethynylthiophene were also smoothly reacted to form the product in 78% yield.

Later, Zhang and coll. have shown that similar transformation can be performed at room temperature under UV irradiation and further expanded the application scope (Scheme 99) [143]. In a complement to the results of Wang, it was demonstrated that aliphatic internal alkynes were also suitable substrates. This protocol was highly efficient for hydrosilylation of a broad scope of non-functionalized aromatic and aliphatic terminal alkynes using different tertiary silanes to form the corresponding vinylsilanes in excellent yields and 93-99% *Z*-selectivity. Reducible ketone and ester groups remained intact during the transformation and this method was successfully applied to the modification of complex natural products.



**Scheme 99.** *Z*-selective hydrosilylation of alkynes catalyzed by  $\text{Mn}_2(\text{CO})_{10}$  under thermal and photochemical activations.

The reaction mechanism for both processes (Scheme 100) includes the homolytic cleavage of Mn–Mn bond in  $\text{Mn}_2(\text{CO})_{10}$  either in the presence of peroxide at high temperature [133] or *via* photochemical activation [143]. The resulting 17-electron complex **171** abstracts a hydrogen atom from tertiary silane to form Mn(I) hydride **90** and silyl radical. The reaction of the latter with alkynes followed by hydrogen atom transfer from **90** to the resulting radical affords the final product with concomitant regeneration of starting odd-electron complex **171**. The observed *Z*-selectivity in product formation is caused by the preferential *trans*-arrangement of alkene substituent and bulky silyl group in vinyl radicals to minimize steric constraints.



**Scheme 100.** Proposed reaction mechanism for *Z*-selective hydrosilylation of alkynes catalyzed by  $\text{Mn}_2(\text{CO})_{10}$ .



## 4. Conclusions

The results collected in this contribution demonstrate that manganese complexes bearing bidentate ligands are more efficient in transfer hydrogenation than their pincer-type analogues, show a comparable performance in hydrogenation processes and are generally less active for hydrogen borrowing reactions. In addition, there is also growing evidence of the importance of the hemilability phenomenon in tridentate Mn(I) catalysts being one of the key factors in the design of several systems with outstanding performance in (transfer) hydrogenation. Another important message arisen from the recent results in manganese catalysis clearly illustrates that cooperative ligands are not necessarily required for the design of efficient hydrogenation catalysts based on first row transition metals. Similar trend was evidenced in parallel in the area of Mn-catalyzed hydrosilylation showing that the evolution from highly sensitive Mn(II) catalysts bearing elaborated polydentate ligands to air-stable Mn(I) complexes containing simple mono- or bidentate donor ligands, often resulted in higher activity and/or chemoselectivity. Finally, in some reduction catalytic processes the utilization of trivial carbonyl derivatives such as  $\text{Mn}(\text{CO})_5\text{Br}$  or  $\text{Mn}_2(\text{CO})_{10}$  led to remarkable results.

One of the direct consequences for this rather counterintuitive aspect of manganese reduction catalysis, which can be shortly formulated as “simpler is sometimes better” could play an important role for the development of real sustainable 3d metal catalysis. Taking into account that the relative price of both metal and auxiliary ligands is equally important, manganese offers an unique opportunity to replace elaborated and expensive pincer ligands often unavoidable in Fe- or Co-based hydrogenation-type catalysts with ubiquitous phosphine ligands or bi- or tridentate scaffolds based on nitrogen-, carbon- or sulphur-based donor moieties. Reinvestigation of basic organometallic manganese chemistry in the context of search for new reaction pathways and unconventional catalyst activation modes will surely provide additional opportunities for the future development of greener homogeneous reduction catalysis attractive for industrial applications.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgements

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