Switching Between Hydrogenation and Olefin Transposition Catalysis via NH Cooperativity in Mn(I) pincer complexes

Wenjun Yang,[a] Ivan Yu. Chernyshov,[b] Manuela Weber,[c] Evgeny A. Pidko,*,[a] Georgy A. Filonenko*,[a]

[a] Inorganic Systems Engineering group, Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Van der Maasweg 9, 2629 HZ, Delft, The Netherlands

[b] TheoMAT Group, ChemBio cluster, ITMO University, Lomonosova 9, St. Petersburg, 191002, Russia

[c] Institute of Chemistry and Biochemistry, Freie Universität Berlin, Fabeckstraße 34/36, Berlin, D-14195, Germany.

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ABSTRACT: While Mn-catalyzed (de)hydrogenation of carbonyl derivatives have been well established, the reactivity of Mn hydrides with olefins remains very rare. Herein we report the first Mn(I) pincer complex that effectively promotes site-controlled transposition of olefins. This new reactivity is shown to emerge once the N-H functionality within Mn/NH bifunctional complex is suppressed by alkylation. While detrimental for carbonyl (de)hydrogenation, such a masking of the cooperative NH functionality allows for the highly efficient conversion of a wide range of allylarenes to higher-value 1-propenybenzenes in near-quantitative yield with excellent stereoselectivities. The reactivity towards a single positional isomerization was also retained for longer-chain alkenes resulting in the highly regioselective formation of 2-alkenes, which are less thermodynamically stable compared to other possible isomerization products. The detailed mechanistic analysis of reaction between activated Mn catalyst and olefins points to catalysis operating via a metal alkyl mechanism - one of the three conventional transposition mechanisms previously unknown in Mn complexes.

Carbon-carbon double bonds are key skeletal units in a plethora of natural and industrial chemicals[1] as well as versatile precursors for many synthetic transformations.[2] Despite the availability of numerous protocols for installing olefin functional group (e.g., olefination, elimination, condensation, dehydrogenation), such transformations are frequently disadvantaged by low stereoselectivities or restrictions on functional groups.[3] Alternatively, transposition of pre-existing olefins offers a powerful and atom-economical route to incorporate and manipulate C=C bonds with far-reaching applications in industrial production e.g., pharmaceuticals, cosmetics, fragrances, polymers and fuels.[4] Various processes were developed with efficient catalysts based on transition metals: Ir,[5] Rh,[6] Pd,[7] Ru,[8] Cr,[9] Co,[10] Ni,[11] Fe,[12] W,[13] among others. (Figure 1a). Missing in this set of examples is a highly abundant and biocompatible manganese metal that remains unknown in olefin transposition so far.

Alkene transposition catalysis is mechanistically diverse and generally proceeds via either of the three alternative paths, namely, allyl, alkyl, or radical mechanisms with the latter two governing the activity of the vast majority of catalyst systems.[4c, 10i, 14] In both mechanisms metal hydrides are the active species, which promote the transposition reaction via an $H^-/H^\cdot$ addition to the alkene followed by the β-H elimination/ $H^\cdot$-abstraction to furnish the isomerization product.[4c]

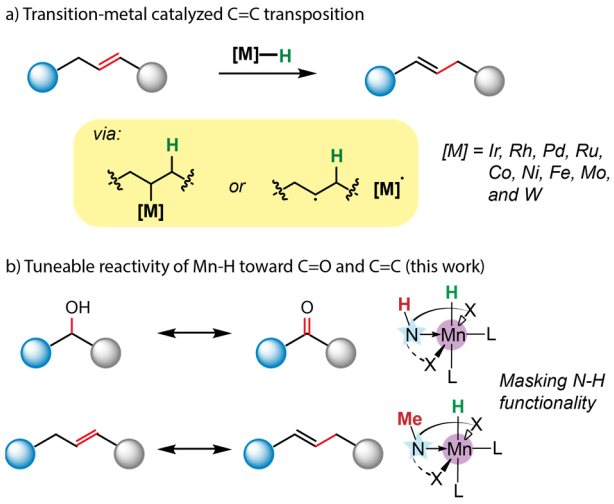


Figure 1. Metal complex-mediated olefin transpositions (a) and the reactivity discussed in this work (b).

The representative examples operating via the alkyl mechanism such as $Pd(dba)_2$ (Skrydstrup),[7a] Co-NNP complexes (Liu),[10f] and $Fe(OAc)_2$ (Koh)[12b] typically require the

in situ activation to form the catalytic metal hydride species by the reaction with such reagents as e.g., acyl chloride, ammonia borane, boryl reagent combined with base. Activation-free olefin transpositions catalysis was also demonstrated with isolated metal hydride or metal alkyl complexes.[10b, 12c] With respect to the radical-type processes, the latest advances were disclosed by Shenvi and Palmer groups employing cobalt salen[10c] and cobaloxime complexes,[10e] respectively. Upon the reductive treatement, these complexes form Co hydrides that can act as $H^{\cdot}$-donors. The central role of the metal hydrides for the catalytic C=C bond suggests a potentially broader scope of catalyst systems for this chemistry.

Manganese complexes emerged as potent carbonyl (de)hydrogenation catalysts in the last decade together with other two base metals: Fe and Co.[15] The generation of Mn hydride species has been widely accepted as a prerequisite for the (de)hydrogenation cycle.[16] However, the hydride transfer to non-polar olefins remains uncommon for Mn homogeneous catalysis. Recently a few cases of alkene hydrogenations have been reported with Mn non-pincer complexes.[17] In particular, the alkyl bisphosphine Mn (I) catalyst reported by Kirchner group forms active 16e Mn hydride under H_2 atmosphere that can reduce a range of mono- and disubstituted alkenes to alkanes.[17a]

Given these results, we envisioned that the olefin transposition reactivity could be accessible by Mn-based systems. Herein we disclose that by masking the metal/NH cooperativity one can tune the reactivity of Mn hydrides from polar C=X (X = O, N) substrates to C=C bonds. With this strategy we develop the first highly selective olefin transposition reactions catalyzed by Mn(I), specifically an N-methylated Mn-CNP complex (Figure 1b).

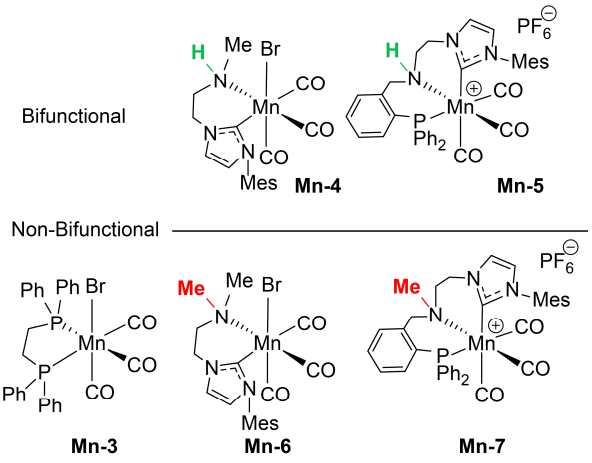
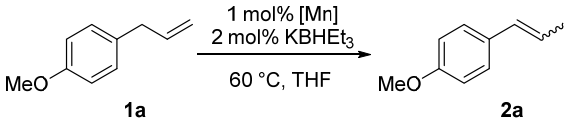


Figure 2. Mn catalysts used in this study.

At the onset of investigation we screened the activity of several well-defined Mn(I) complexes reported by our group and others (Figure 2) towards the transposition of 4-allylanisole (**1a**) model substrate. The pre-catalysts **Mn-3—5**,[16j, 18] that were reported to be efficient for carbonyl hydrogenation, surprisingly displayed no reactivity in transposition with the exception of **Mn-3** that gave 18% yield of isomerized product **2a** (Table 1, entries 1-3).

We assumed the N-H functionality might be detrimental to C=C transposition and synthesized the N-H methylated complexes **Mn-6** and **Mn-7** based on **Mn-4** and **Mn-5** (See Supporting Information for synthetic details). Interestingly, once N-H functionality is blocked, Mn complexes start exhibiting the transposition activity (entries 4, 5) with **Mn-7** giving the highest yield in the model reaction (61%). The yield and *E*-selectivity in product **2a** could be increased to 89% and 91:9 (*E*:*Z*) in a prolonged run (entry 6). Further screening of solvents and reaction temperatures confirmed the THF solvent and 60 °C temperature to be optimal for the catalytic performance of **Mn-7** (see Table S1). Control experiments indicated the necessity of the catalyst activation with $KBHEt_3$ that typically allows for more selective generation of Mn hydrides (entries 7, 8).

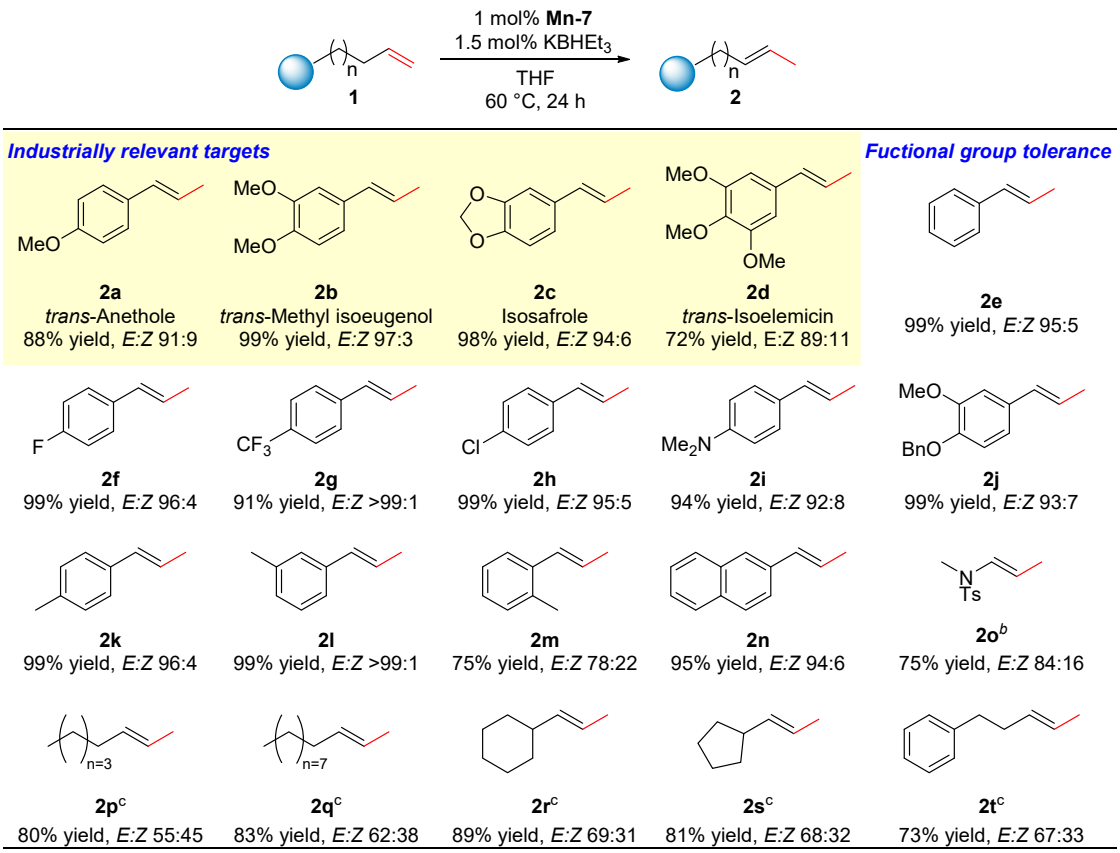
Table 1. Manganese-catalyzed transposition of 4-allylanisole model compound.[a]



Entry	[Mn]	Time (h)	Yield (%)	Z:E
1	**Mn-3**	12	18	88:12
2	**Mn-4**	12	trace	-
3	**Mn-5**	12	trace	-
4	**Mn-6**	12	27	86:14
5	**Mn-7**	12	61	85:15
6	**Mn-7**	24	89 (89)[b]	91:9
7	--	24	trace	--
8[c]	**Mn-7**	24	trace	--

a) Reaction conditions: **1a** (0.25 mmol), Mn catalyst (1 mol%), and 2 mol% $KBHEt_3$ in 0.5 mL of THF at 60 °C. b) Conversion given in parenthesis, C) $KBHEt_3$ not used for the activation of Mn catalyst.

Scheme 1. Catalytic double bond transposition with **Mn-7**.[a]



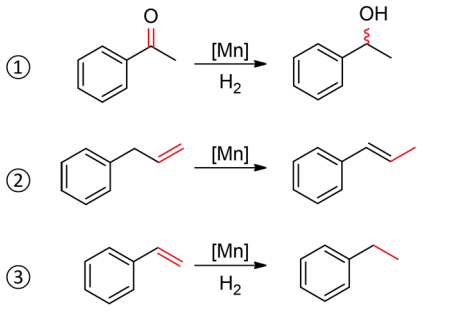
[a] Reaction conditions: substrate **1** (0.25 mmol), **Mn-7** (1 mol%), and 2 mol% $KBHEt_3$ in 0.5 mL of THF at 60 °C for 24 h. [b] 5 mol% **Mn-7** was used instead. [c] Reaction was performed with 4 mol% **Mn-7** at 70 °C in toluene instead.

With the transposition reactivity established, we sought to examine the generality of this process. A broad scope of substrates can be converted with good selectivities with complex **Mn-7** (Scheme 1). The industrially relevant anethole, isoeugenol, isosafrole, and isoelemicin (**2a-2d**) were successfully generated via the transposition reaction in excellent yields (72-99%) and *E*:*Z* ratios (>90:10). Our protocol is also efficient toward allylbenzene (**1e**) and its substituted derivatives with electron-withdrawing groups (**1f-h**), electron-donating groups (**1i-m**), and sterically hindered naphthyl (**1n**), furnishing the desired styrenyl products in ≥91% yields and ≥92% *E* selectivities.

Controlling the site selectivity is a recognized challenge for migrating the C=C bonds over extended carbon skeletons, due to the thermodynamic similarities of positionally isomerized products. **Mn-7** allows for the highly regioselective monoisomerization of longer-chain alkenes, even though further migration could be thermodynamically more favourable. Both 1-octene (**1p**) and 1-dodecene (**1t**) were isomerized to corresponding 2-alkenes in excellent yield albeit with moderate *E*:*Z* ratios. The monoisomerization process is also compatible with functionalities (**1r-1t**), including cycloalkyl and phenyl.

The N-H functionality have been broadly reported as the key structural parameter that enables the (de)hydrogenation of polar moieties and Mn/NH bifunctional behaviour in principle.[19] This was typically confirmed in the studies where alkylation of N-H functionality produced inactive (de)hydrogenation catalysts.[16h, 16i, 18a, 20] Our catalytic data (Table 1, entries 2-5) implies that for olefin transposition this structure-activity relationship is inverted.

To confirm this, we compared the C=O/C=C substrate preference using cooperative and non-cooperative Mn(I)-CNP counterparts: **Mn-5** and **Mn-7**, respectively. As depicted in Figure 3, the N-H methylation in Mn-CNPs completely suppressed the ketone hydrogenation, but enabled the transposition of allylbenzene and even the hydrogenation of styrene. Notably, **Mn-5** with the cooperative N-H functionality was inactive for either of C=C bond transformation paths. The displayed selectivity prompted a further mechanistic analysis of **Mn-7** operation in the course of reaction.



Cat.	①	②	③
Mn-5 (N-H)	Yes	No	No
Mn-7 (N-Me)	No	Yes	Yes

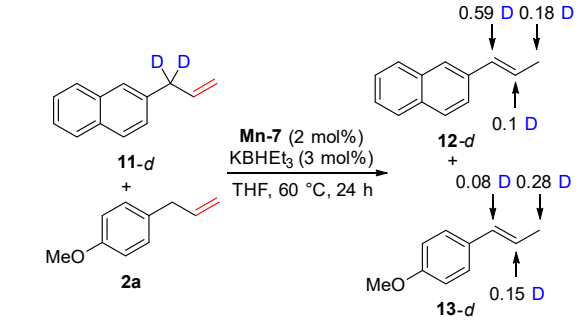
Figure 3. Reactivities of Mn(I)-CNP complexes toward C=O and C=C functionalities. See section S7 in Supporting Information for reaction details.

As a first step to the mechanistic investigation we conducted cross reactivity experiments with deuterium-labelled **11-*d*** and non-deuterated **2a** (Scheme 2). We observed both the intramolecular scrambling as well as the intermolecular crossover of the deuterium label between the olefin products. This is indicative of transposition proceeding via either alkyl or hydrogen atom transfer mechanisms, because the cross reactivity between deuterated and label-free olefins should involve a Mn-H species as a transfer medium. Together with the previous observation that $KHBEt_3$ activation was necessary for the catalytic reactivity (Table 1, entry 8), labelling data implies that the formation of Mn hydride *must* take place in the course of reaction. To verify this we monitored the $KBHEt_3$ activation of pre-catalysts **Mn-7** followed by the catalytic turnover using NMR and IR spectroscopy.

Mn-7 readily forms hydrides upon activation. At room temperature the reaction of **Mn-7** with $KBHEt_3$ in THF-d_8 gave rise to three new doublet resonances in ^{1}H NMR spectrum at -5.01, -5.65, and -6.77 ppm. with $^2J_{PH}$ = 40.0, 48.0, and 88.0 Hz, respectively (Figures 4a, b). We attributed these peaks to the isomers of tricarbonyl Mn-H species **8**, in total accounting for 97% of the activation products. The retention of three CO ligands upon the near-quantitative transformation of **7** during the activation step is confirmed by IR spectroscopy revealing three new bands at 1981, 1896, and 1876 cm^{-1} (Figure 4c). Since **8** is a tricarbonyl, monohydride complex featuring Mn-bound phosphine donor we conclude that activation of **Mn-7** leads to the dissociation of the central N-donor group rendering it hemilabile (see section S8 in Supporting Information for the structural assignments based on the exhaustive expert-bias free configurational DFT analysis). This contrasts the case of non-methylated analogue - **Mn-5**,[16j] which dissociated the phosphine arm in a similar activation step.

The dissociation of the central N-donor is the major transformation within the CN(Me)P ligand upon the activation and the hydride complex with dissociated P-donor was observed in minor amounts (3% NMR yield) (see Figure S11). The difference between Mn hydrides with dissociated N or P donor is reflected in the hydride ligand shifts in the ^{1}H NMR (Fig S11) and supported by DFT calculations (Table S4). Based on DFT analysis we assume that complex **8** might exist as an octahedral complex with facially bound P and C donor groups with isomers distinguished by hydride ligand placement *trans* to either NHC, phosphine or carbonyl ligand (**8a**, **8b** and **8c** respectively, Figure 4); all three featuring the dissociated central N donor group.

Scheme 2. Results of deuterium crossover experiments.



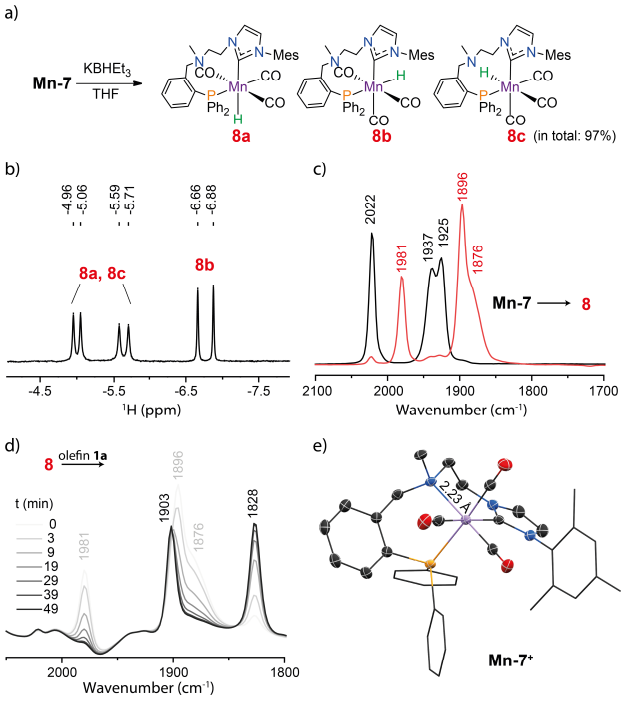


Figure 4. Activation of **Mn-7** upon the reaction with $KBHEt_3$ (a), hydride region of ^{1}H-NMR (THF-d_8) spectra (b) of *in-situ* generated complex **8** (see Figure S11 for full spectra) and IR spectra (c) of complex **Mn-7** (black) and *in-situ* generated complex **8** (red) recorded in THF. Time-dependent IR spectra evolution (d) for the reaction of complex **8** with olefin (0 to 49 min, grey to black). Molecular structure (e) of complex **Mn-7** in the solid state with thermal ellipsoids drawn at 50% probability.

Hydride complexes **8** readily reacts with olefins. A clean consumption of hydrides in **8** was observed within minutes

upon the addition of 4-allylanisole (**1a**). The analysis of this reaction with IR and NMR spectroscopy indicates the formation of the dicarbonyl Mn-alkyl species. Namely, the IR spectrum (Figure 4d) indicates the consumption of **8** and formation of two new bands at 1903, 1828 cm^{-1} typical of dicabonyl complexes. In the absence of the hydride resonance in the NMR spectrum, this suggests that reaction of **8** with olefin leads to the formation of metal-alkyl complexes with N donor group reattaching to the Mn center. As expected, the gradual production of **2a** was then detected in ^1H NMR upon the heating the reaction mixture to 60 °C (see Figure S16). This observation of hydride transfer suggests that **Mn-7** isomerizes olefins via the alkyl mechanism. Since we observe no further change in the NMR spectrum, we assume that the metal alkyl complexes likely represent the resting states in this transformation as was earlier proposed for the high-spin cobalt(II) system by Wiex, Holland and co-workers.[10b]

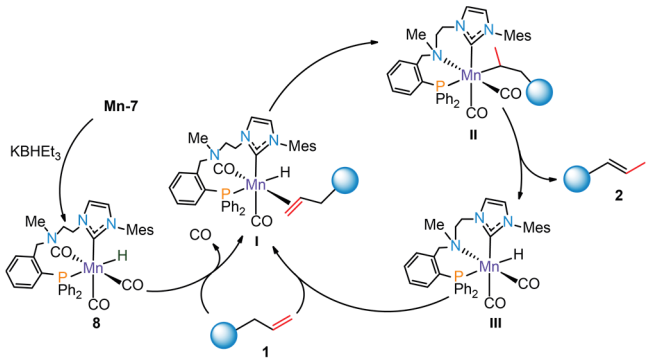


Figure 5. Mechanistic proposal for Mn-catalyzed olefin transpositions.

Table 2. Bond length of Mn-N for selected Mn complexes in the solid state calculated from X-Ray data.

Complexes	N-H		N-Me	
	Mn-4	**Mn-5**	**Mn-6**	**Mn-7**
Mn-N (Å)	2.14	2.14[a]	2.24	2.23

[a] The bond length for **Mn-5** was determined by DFT analysis previously. [16j]

Based on the results above we conclude that metal-alkyl mechanism is likely manifested in the present catalytic system (Figure 5). The activated Mn(I)-hydride precatalyst **8** enters the cycle via the reaction with alkene via the intermediate **I**. This step requires the dissociation of a CO ligand detected experimentally. Further transformation of **I** involves the hydride transfer to form Mn-alkyl species **II** aided by the reattachment of N-donor ligand. Subsequent β-hydride elimination furnishes the isomerized olefin product **2** and dicarbonyl Mn hydride **III**. The final coordination of another alkene substrate can be kinetically unfavourable due to the saturation of Mn centre with strong field ligands. However, we speculate that this step can be facilitated by the dissociation of the labile N donor within Mn-CN(Me)P complex that would liberate the vacant site for olefin coordination regenerating the species **I**.

Similar to the case of NH-cooperative Mn(I) catalyst **Mn-5** our results reveal the high extent of tridentate ligand dynamics throughout the catalyst activation. The suggested involvement of the N-donor dissociation in the catalytic cycle[21] would rationalize the selectivity flip toward C=C for Mn complexes obtained by blocking the N-H functionality (Table 1, Figure 3). Analysing the crystal structures (Figure 4e and Table 2) of methylated **Mn-6** and **7** we find that the Mn-N bonds lengths are significantly longer in these complexes compared to their NH counterparts **Mn-4, 5**.[16j, 18a] This trend further suggests that conventional pincer and tridentate ligands in Mn(I) complexes might exhibit dynamics and donor ligand lability that is not characteristic for their noble metal-based counterparts. While the catalytic functionality of this behaviour is open to debate, it clearly invites further research into ligand dissociation dynamics of catalytically relevant Mn(I) complexes.

In conclusion, this work describes the first precedent of olefin transposition catalysed by complexes based on abundant and biocompatible Mn metal. This reactivity furnishes an array of 2-alkenes in good selectivities and yields. Importantly, this activity manifests upon disabling the cooperative function in related Mn catalysts that show activity in carbonyl hydrogenation while being virtually inactive towards olefin conversion. We envision such manipulation on the metal-ligand cooperation modes may present a new design direction for controlling early transition metal catalysts and enabling multiple reactivity trains with minimal ligand modification.

AUTHOR INFORMATION

Corresponding Author

* G. A. Filonenko (G.A.Filonenko@tudelft.nl)
* E. A. Pidko (E.A.Pidko@tudelft.nl)

Present Addresses

†If an author's address is different than the one given in the affiliation line, this information may be included here.

Author Contributions

All authors have given approval to the final version of the manuscript and declare no competing interests.

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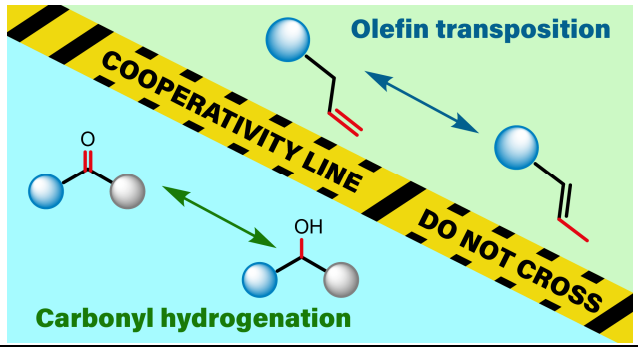
Olefin transposition
COOPERATIVITY LINE
DO NOT CROSS
O
OH
Carbonyl hydrogenation