Rethinking Basic Concepts - Hydrogenation of Alkenes Catalyzed by Bench-Stable Alkyl Mn(I) Complexes

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ABSTRACT: An efficient additive-free manganese-catalyzed hydrogenation of alkenes to alkanes with molecular hydrogen is described. This reaction is environmentally benign and atom economic, implementing an inexpensive, earth abundant non-precious metal catalyst. The most efficient pre-catalyst is the bench-stable alkyl bisphosphine Mn(I) complex *fac*-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$)]. The catalytic process is initiated by migratory insertion of a CO ligand into the Mn-alkyl bond to yield an acyl intermediate which undergoes rapid hydrogenolysis to form the active 16e Mn(I) hydride catalyst [Mn(dippe)(CO)$_2$(H)]. A range of mono- and disubstituted alkenes were efficiently converted into alkanes in good to excellent yields. The hydrogenation of 1-alkenes and 1,1-disubstituted alkenes proceeds at 25 °C, while 1,2-disubstituted alkenes require a reaction temperature of 60°C. In all cases, a catalyst loading of 2 mol % and a hydrogen pressure of 50 bar was applied. A mechanism based on DFT calculations is presented.

One of the fundamental research goals in modern chemistry is the development of sustainable, efficient and selective syntheses. Accordingly, it is quite important to perform reactions under catalytic conditions and to replace precious metal catalysts by Earth abundant non-precious metal catalysts.[1] In particular base metals such as iron and manganese are promising candidates as these belong to the most abundant metals in the Earth crust, are inexpensive, and exhibit a low environmental impact. In this context, atom-efficient and clean processes which permit access to a green synthesis of valuable products such as alkanes, alcohols and amines is the hydrogenation of olefins, alkynes, carbonyl compounds, imines and nitriles with molecular hydrogen are of paramount importance.[2,3] While iron, cobalt, and nickel hydrogenation catalysts had been subject of intense investigation over the past decade,[4-13] low valent Mn(I) catalysts just appeared in 2016 as new but very powerful players in this field.[8,9,10,11,15] The latter are typically substitutionally inert 18e complexes bearing two or three CO ligands and bi- and tridenate N, C, S, and P-donor ligands, respectively (Scheme 1) where substrate binding occurs in an outer-sphere fashion. Thus, these types of complexes are active only for the hydrogenation of polar multiple bonds such as nitriles, imines, and carbonyl compounds, while alkenes are not hydrogenated. In fact, examples of manganese catalysts which are capable of hydrogenating unactivated C=C double bonds are exceedingly rare.[16]

Scheme 1. Structural Motifs of Most Mn(I) (De)hydrogenation Catalysts (X = Cl, Br, H)
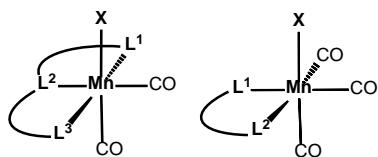

We describe here the synthesis and catalytic activity of new well-defined and bench-stable alkyl carbonyl Mn(I) complexes of the type *fac*-[Mn(dpre)(CO)$_3$(R)] (dpre = 1,2-bis(di-*n*-propylphosphino)ethane, R = CH$_3$, CH$_2$CH$_3$, CH$_2$CH$_2$CH$_3$) and *fac*-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$) (dippe = 1,2-bis(di-*iso*-propylphosphino)ethane) for the hydrogenation of alkenes with molecular hydrogen. We take advantage of the fact that (i) CO ligands of Mn(I) alkyl carbonyl complexes are known to undergo migratory insertions to form acyl complexes if strong field ligands such as CO or tertiary phosphines are present - *a well-known textbook reaction*.[17] and (ii) that hydrogenolysis of a transition-metal acyl complexes affords aldehydes and metal hydride complexes - *typically the final step in both stoichiometric and catalytic hydroformylations of alkenes*.[18] Accordingly, the catalytic process is initiated by migratory insertion of a CO ligand into the Mn-alkyl bond to yield acyl intermediates which undergo rapid hydrogenolysis to create the active 16e Mn(I) hydride catalysts (Scheme 2).

Scheme 2. Formation of a Coordinatively Unsaturated Mn(I) Hydride Species *via* Alkyl Migration and Hydrogenolysis of an Acyl Intermediate
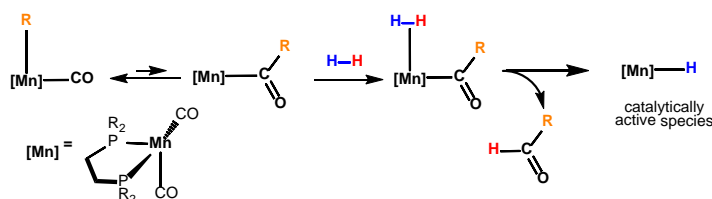
The new alkyl Mn(I) complexes *fac*-[Mn(dpre)(CO)$_3$(R)] (R = CH$_3$ (**3**), CH$_2$CH$_3$ (**4**), CH$_2$CH$_2$CH$_3$ (**5**)) and *fac*-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] (**6**) were obtained by treatment of *fac*-[Mn(dpre)(CO)$_3$(Br)] (**1**) and *fac*-[Mn(dippe)(CO)$_3$(Br)] (**2**) with NaK (3 equiv) and subsequent addition of CH$_3$I, CH$_3$CH$_2$Br, and CH$_3$CH$_2$CH$_2$Br, respectively, in moderate to good isolated yields (Scheme 3). All complexes are bench-stable for at least 4 weeks in the presence of air. They were fully characterized by ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR and IR spectroscopy, and high-resolution mass spectrometry. In addition, the molecular structure of **6** was determined by X-ray crystallography. A structural view is depicted in Scheme 3 with selected bond distances and angles given in the caption.

Scheme 3. Synthesis of *fac*-[Mn(R$_2$PCH$_2$CH$_2$PR$_2$)(CO)$_3$(R')] (3-6) and Structural View of 6 showing 50 % Ellipsoids (Most H Atoms Omitted for Clarity).^{a}
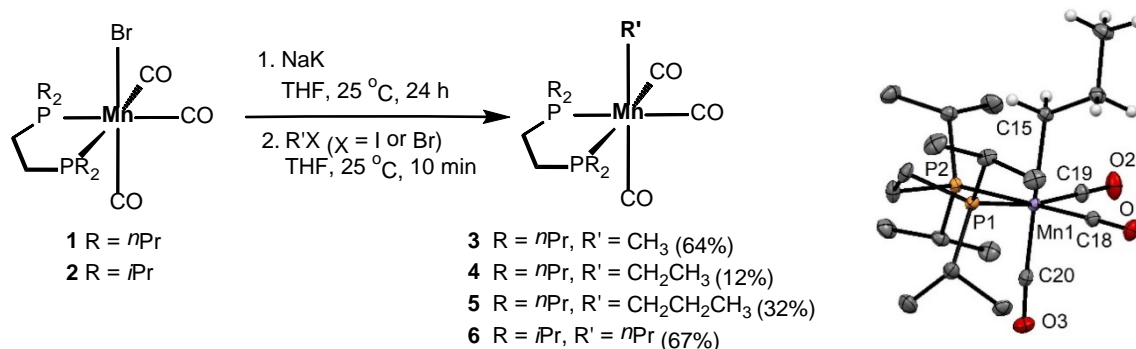

^{a} Selected bond distances (Å) and angles (°): Mn1-C15 2.187(1), Mn1-C18 1.803(1), Mn1-C19 1.799(1), Mn1-C20 1.798(1), Mn1-P1 2.3224(5), Mn1-P2 2.3324(5), P1-Mn1-P2 85.53(2).

The catalytic performance of complexes **3-6** and the known Mn(I) complexes *fac*-[Mn(dippe)(CO)$_3$(H)] (**7**),[19] [Mn(CO)$_5$(CH$_3$)] (**8**)[20] and *fac*-[Mn(bipy)(CO)$_3$(CH$_3$)] (**9**)[21] as well as *fac*-[Mn(dpre)(CO)$_3$(H)] (**10**)[22] was then investigated for the hydrogenation of 1-dodecene (**11**) as model substrate (Scheme 4). Selected optimization experiments are depicted in Table 1. With complexes **3-6** as pre-catalysts and a catalyst loading of 2 mol% at 100°C and a hydrogen pressure of 50 bar H$_2$ in toluene for 18 h, dodecane was obtained in essentially quantitative yield (Table 1, entries 1-4). Under the same reaction conditions complexes **7-10** were catalytically inactive and no reaction took place even when the catalyst loading was increased to 4 mol% (Table 1, entries 5-8). This clearly emphasizes that strongly electron donating co-ligands such as aliphatic bisphosphines are required to achieve high catalytic activity. Moreover, coordinatively saturated and inert hydride complexes **7** and **10** are inactive due to the lack of a vacant coordination site and are no intermediates in the catalytic process. At 40 °C and a catalyst loading of 2 mol% in diethyl ether as solvent complex **3** was no longer catalytically active, while complexes **4-6** were still efficient to convert 1-dodecene to dodecane in quantitative yield (Table 1, entries 9-12). It has to be noted that the rate of alkyl migration follows the order *n*Pr > Et > Me as established by Moss and co-workers some years ago.[23] Finally, at 25 °C complexes **3-5** were no longer active, whereas with complex **6** dodecane was isolated in 99% yield (Table 1, entries

13-15) suggesting that sterically demanding and very electron rich bisphosphines facilitate the catalytic reaction. Lowering the catalyst loading of **6** to 1 mol% led to a slight decrease in catalytic activity yielding dodecane in 87% yield (Table 1, entry 16).

Scheme 4. Mn(I) Complexes Tested as Catalysts
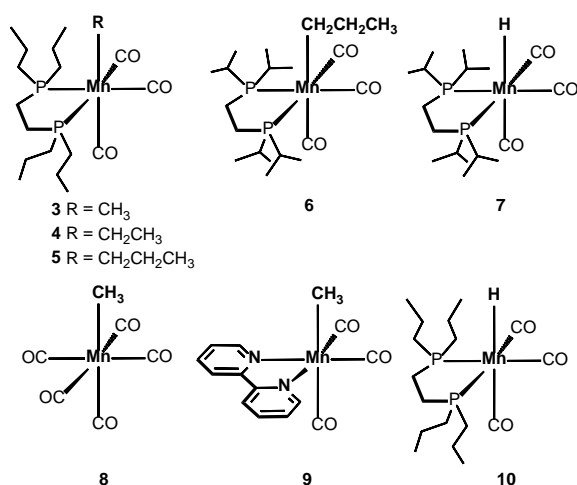
Having determined **6** as the most active catalyst and to prove its general applicability, various substrates have been tested to establish scope and limitations (Table 2). The substrate scope was expanded to a variety of monosubstituted alkenes, 1,1-disubstituted alkenes and *cis*- and *trans*-1,2-disubstituted alkenes. Tri- and tetrasubstituted alkenes could not be hydrogenated. Terminal alkenes and allylic alcohols **12-22** as well as the 1,1-disubstituted alkanes **23** and **26** were already reduced to the corresponding alkanes in 83-99% yields at 25 °C with a catalyst loading of 2 mol%, 50 bar hydrogen pressure, reaction times between 18 to 24 h in diethyl ether as solvent (Table 2). The only exception is 4-vinylpyridine (**24**) where the yield was only 39%. There was no indication of polymerization of this thermally unstable substrate underlining the mild reaction conditions of the catalytic protocol. In the case of **26**, only the terminal double bond was hydrogenated. Complete hydrogenation of internal alkenes such as *trans*- and *cis*-stilbenes (**28**, **29**) and cyclic substrates such as 1*H*-indene (**27**), furan-2,5-dione (**31**), 2-ethoxy-3,4-dihydro-2*H*-pyran (**27**) and 1,5-cyclooctadiene (**33**) could be achieved although a higher temperature (60 °C) was required. In the case of (*E*)-4-phenylbut-3-en-2-one (**34**) also the carbonyl moiety was hydrogenated. The catalytic protocol shows high functional group tolerance and halides, hydroxy groups, ethers, esters and even very sensitive anhydrides were well tolerated. No reaction took place with alkenes bearing carboxylic acid (**35**) and nitrile (**36**) moieties, respectively.

The reaction mechanism was explored in detail by means of DFT calculations,[24] with propene taken as substrate and **6** (**A** in the calculations) as pre-catalyst. The free energy profile for the initiation process, where the active catalyst is formed, is depicted in Figure 1. The first step is the migration of the $CH_2CH_2CH_3$ ligand in complex **A** to the carbonyl C-atom of an adjacent CO ligand. This occurs in an easy step with a barrier of only 11 kcal/mol producing intermediate **B**, an acyl species stabilized by an agostic C-H bond. This transformation is slightly endergonic by 6 kcal/mol. Addition of dihydrogen affords complex **D** bearing a κ^2-H_2 ligand. Coordination of H_2 has a barrier of 9 kcal/mol (**TS$_{CH}$**) and a free energy balance of $\Delta G = 7$ kcal/mol, from the pair of molecules in **C** to the dihydrogen complex **D**. Finally, H-atom transfer from dihydrogen to the C-atom of the acyl ligand produces **E**, a C-H σ-complex of butanal. This last step has a barrier of only 3 kcal/mol and it is thermoneutral. The catalytically active species **F** results from ligand exchange from butanal to one molecule of propene which is thermodynamically very favorable by –15 kcal/mol.
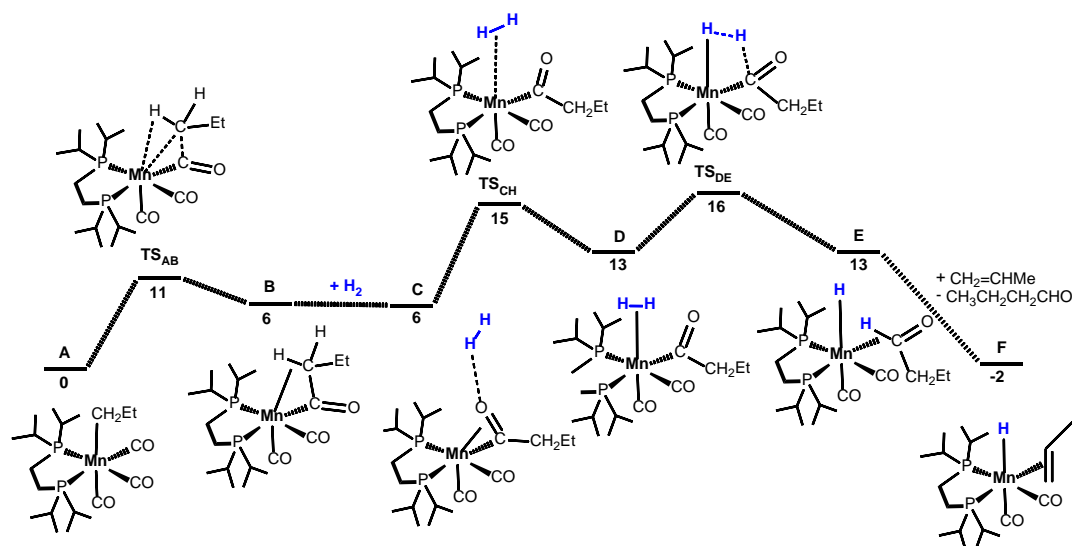
Figure 1. Free Energy Profile Calculated for the Formation and Hydrogenolysis an Acyl Intermediate. Free Energies (kcal/mol) are Referred to *fac*-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] (**6**) (**A** in the calculations).

The free energy profile calculated for the catalytic reaction is depicted in Figure 2. Starting point is the hydride olefin complex **F** which is the active species of the catalytic reaction. In the first step of the reaction the hydride migrates to the internal olefin C-atom resulting in an alkyl complex stabilized by a C-H agostic interaction in intermediate **G**. This is a very facile step with a barrier of merely 1 kcal/mol and a favorable free energy balance of ΔG = –5 kcal/mol. The following step corresponds to dihydrogen coordination restoring a saturated coordination environment around the metal in intermediate **I**. The overall barrier for H$_2$ coordination from intermediate **G** to the dihydrogen complex **I** is 12 kcal/mol which is the highest one along the path. In the last step of the mechanism H-atom transfer from the dihydrogen ligand to the alkyl C-atom (a formal protonation) regenerates a hydride and forms the final product that remains weakly coordinated as a C-H σ-ligand in intermediate **J**. This last step has negligible barrier (5 kcal/mol) and is strongly exergonic with ΔG = -25 kcal/mol. Closing of the catalytic cycle brings **J** back to **F** with liberation of propane and coordination of a new propene molecule in a favorable process with ΔG = –13 kcal/mol.
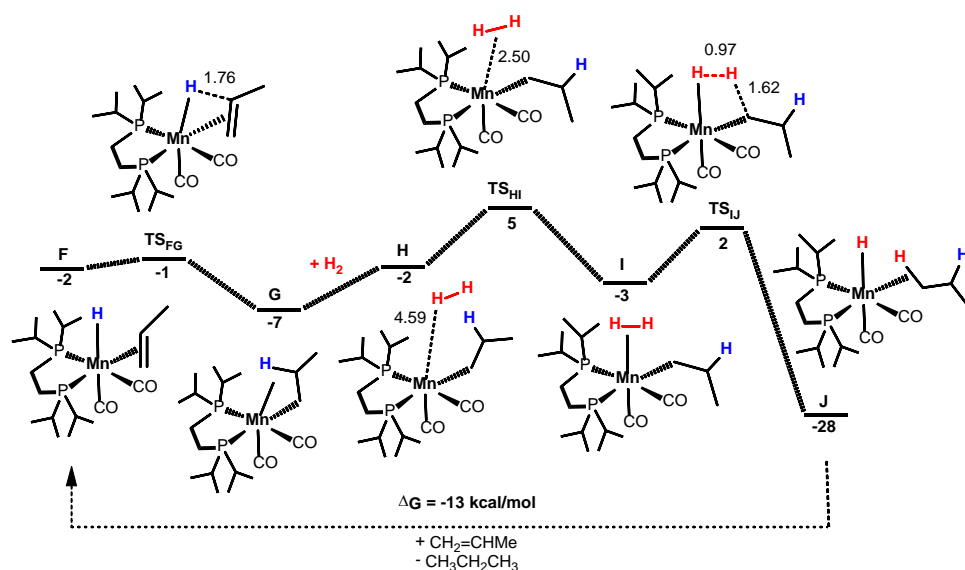

Figure 2. Free Energy Profile Calculated for the Hydrogenation of Propene. Free Energies (kcal/mol) are Referred to *fac*-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] (**6**) (**A** in the calculations)

In sum, an efficient additive-free manganese-catalyzed hydrogenation of alkenes to alkanes with molecular hydrogen is described. To the best of our knowledge, this is the first example of a well-defined Mn(I)-based catalyst for the reduction of unactivated C=C bonds with dihydrogen. The most efficient pre-catalyst is the alkyl bisphosphine Mn(I) complex fac-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] which is air-stable for several weeks. The catalytic process is initiated by migratory insertion of a CO ligand into the Mn-alkyl bond to yield an acyl intermediate which undergoes rapid hydrogenolysis to form the active 16e$^-$ Mn(I) hydride catalyst [Mn(dippe)(CO)$_2$(H)] - a conceptually new approach in Mn(I) hydrogenation chemistry. We were able to hydrogenate a range of mono- and disubstituted alkenes to afford alkanes in good to excellent yields with high functional group tolerance. The hydrogenation of monosubstituted alkenes and 1,1-disubstituted alkenes proceeds at 25 °C, while 1,2-disubstituted alkenes require a reaction temperature of 60 °C. In all cases, a catalyst loading of 2 mol % and a hydrogen pressure of 50 bar was applied. DFT calculations disclosed a typical *inner shell* mechanism with all reacting fragments coordinated to the metal. The path involves protonation of the internal C=C carbon atom followed by hydride insertion into the Mn–C bond of the resulting alkyl.
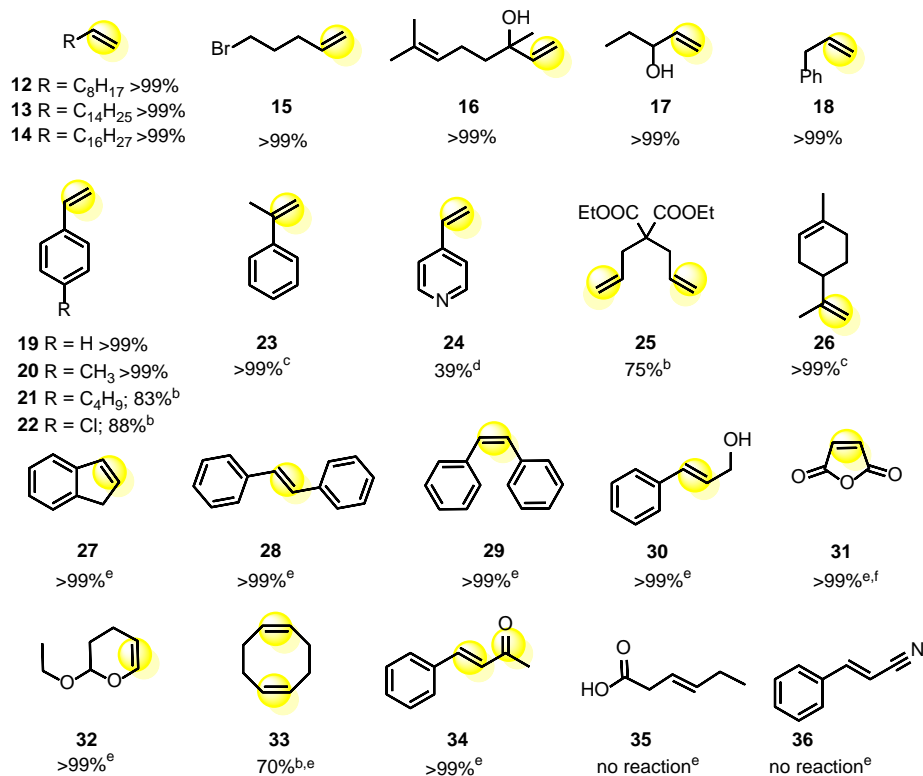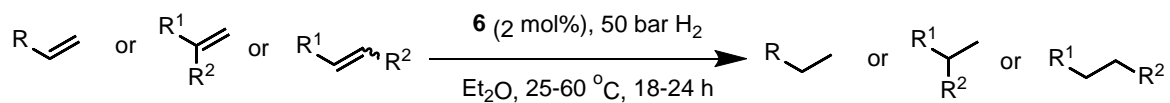
**Table 1 Catalyst Screening for the Synthesis of Dodecane from 1-Dodecene[a]**
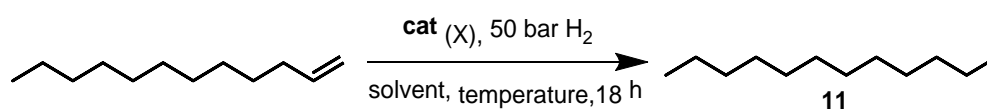
entry	catalyst	X (mol%)	solvent	T (°C)	yield (%)[b]
1	fac-[Mn(dpre)(CO)$_3$(CH$_3$)] (**3**)	2	toluene	100	99
2	fac-[Mn(dpre)(CO)$_3$(CH$_2$CH$_3$)] (**4**)	2	toluene	100	99
3	fac-[Mn(dpre)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] (**5**)	2	toluene	100	99
4	fac-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] (**6**)	2	toluene	100	99
5	fac-[Mn(dippe)(CO)$_3$(H)] (**7**)	4	toluene	100	
6	[Mn(CO)$_5$(CH$_3$)] (**8**)	4	toluene	100	
7	fac-[Mn(bipy)(CO)$_3$(CH$_3$)] (**9**)	4	toluene	100	
8	fac-[Mn(dpre)(CO)$_3$(H)] (**10**)	4	toluene	100	
9	fac-[Mn(dpre)(CO)$_3$(CH$_3$)] (**3**)	2	Et$_2$O	40	
10	fac-[Mn(dpre)(CO)$_3$(CH$_2$CH$_3$)] (**4**)	2	Et$_2$O	40	99
11	fac-[Mn(dpre)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] (**5**)	2	Et$_2$O	40	99
12	fac-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] (**6**)	2	Et$_2$O	40	99
13	fac-[Mn(dpre)(CO)$_3$(CH$_2$CH$_3$)] (**4**)	2	Et$_2$O	25	
14	fac-[Mn(dpre)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] (**5**)	2	Et$_2$O	25	
15	fac-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] (**6**)	2	Et$_2$O	25	99
16	fac-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] (**6**)	1	Et$_2$O	25	87

[a]Reaction conditions: 1-dodecene (0.56 mmol), 50 bar H$_2$, 5 mL toluene or diethyl ether, 18 h. [b]Yield determined by ^{1}H NMR analysis using methyl benzoate as standard.

Table 2 Hydrogenation of Various Alkenes Catalyzed by *fac*-[Mn(dippe)(CO)₃(CH₂CH₂CH₃)] (6)^a

$$R\diagup\!\!=\quad \text{or} \quad R^1{=}\diagdown_{R^2} \quad \text{or} \quad R^1\diagdown\!\!\sim\!\!R^2 \xrightarrow[\text{Et}_2\text{O, 25-60 }^\circ\text{C, 18-24 h}]{\textbf{6}\ (2\ \text{mol\%}),\ 50\ \text{bar H}_2} R\diagup\!\!\diagdown \quad \text{or} \quad R^1\diagup\!\!\diagdown_{R^2} \quad \text{or} \quad R^1\diagdown\!\!\diagup_{R^2}$$

12 R = C₈H₁₇ >99%
13 R = C₁₄H₂₅ >99%
14 R = C₁₆H₂₇ >99%

15 >99%

16 >99%

17 >99%

18 >99%

19 R = H >99%
20 R = CH₃ >99%
21 R = C₄H₉; 83%^{b}
22 R = Cl; 88%^{b}

23 >99%^{c}

24 39%^{d}

25 75%^{b}

26 >99%^{c}

27 >99%^{e}

28 >99%^{e}

29 >99%^{e}

30 >99%^{e}

31 >99%^{e,f}

32 >99%^{e}

33 70%^{b,e}

34 >99%^{e}

35 no reaction^e

36 no reaction^e

^{a}Reaction conditions: substrate (0.56 mmol), *fac*-[Mn(dippe)(CO)₃(CH₂CH₂CH₃)] (**6**) (2 mol%), 5 mL of diethyl ether, 50 bar H₂, 25 °C, 18 h, isolated yields. ^{b}Conversion determined by GC-MS. ^{c}24 h. ^{d}Yield determined by ¹H NMR analysis using methyl benzoate as standard. ^{e}60°C, 24 h. ^{f}THF/CH₂Cl₂ (1:1) as solvent.
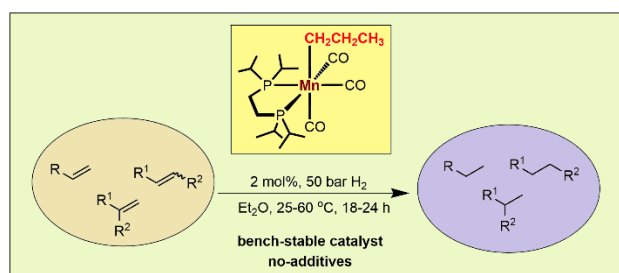
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

X-ray crystallographic data for **6** (CCDC entry 1920413). (CIF)

Synthetic procedures, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{H} NMR spectra of all compounds, crystallographic data and complete computational details (PDF)

Cartesian coordinates for DFT-optimized structures (XYZ)

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Notes

The authors declare no competing financial interest.

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(diethyl ether) using the PCM/SMD model. A full account of the computational details and a complete list of references are provided as SI.