OL | Organic Letters

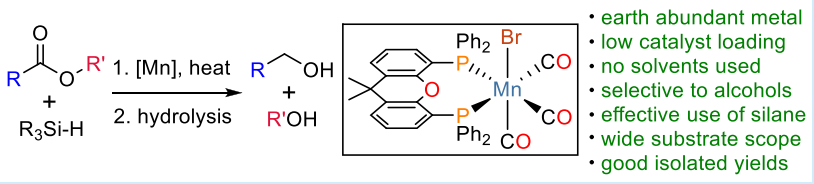
pubs.acs.org/OrgLett Letter

Hydrosilylation of Esters Catalyzed by Bisphosphine Manganese(I) Complex: Selective Transformation of Esters to Alcohols

Rakesh R. Behera, Rahul Ghosh, Surajit Panda, Subrat Khamari, and Bidraha Bagh*

Cite This: https://dx.doi.org/10.1021/acs.orglett.0c01144 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information



ABSTRACT: Selective and efficient hydrosilylations of esters to alcohols by a well-defined manganese(I) complex with a commercially available bisphosphine ligand are described. These reactions are easy alternatives for stoichiometric hydride reduction or hydrogenation, and employing cheap, abundant, and nonprecious metal is attractive. The hydrosilylations were performed at 100 °C under solvent-free conditions with low catalyst loading. A large variety of aromatic, aliphatic, and cyclic esters bearing different functional groups were selectively converted into the corresponding alcohols in good yields.

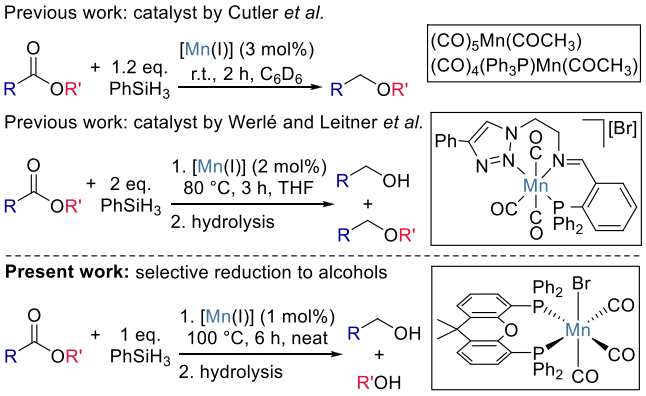
The reduction of carboxylic acids and esters to the corresponding alcohols is one of the most important transformations in synthetic chemistry. The conventional method of using a stoichiometric amount of reactive hydrides such as $LiAlH_4$, $LiBH_4$, and DIBALH is an efficient but tricky reaction.[1] In addition, the formation of a stoichiometric amount of byproducts is detrimental. Therefore, catalytic hydrogenation is often desirable. However, hydrogenation of esters by molecular hydrogen suffers from poor selectivity, and drastic reaction conditions (high temperature and high hydrogen pressure) are required.[2] Transfer hydrogenation (TH) and hydrosilylation are gaining a lot of attention as easy alternatives to classical hydrogenation. Although transition-metal (TM)-catalyzed THs of aldehydes and ketones are abundant,[3] the number of TM catalysts for TH of esters is small. To the best of our knowledge, only three examples of TH of esters have been reported.[4] In 2015, cationic half-sandwich Ru complexes ($[Cp(PiPr_3)Ru(CH_3CN)_2][PF_6]$, $[Cp^*(phen)Ru(CH_3CN)][PF_6]$) were reported as efficient catalysts for the TH of esters with isopropanol as sacrificial hydrogen source.[4a] Thereafter, Ru-SNS[4b] and Fe-PNP[4c] pincer complexes were also effectively utilized for the reduction of ester. Besides TH, hydrosilylation of esters to the corresponding alcohols is an area of growing interest. In the 1990s, titanocene dichloride and titanium alkoxides were reported as effective catalysts for the hydrosilylation of esters to alcohol.[5] MoO_2Cl_2 was also utilized for the same purpose.[6] Besides early TMs, noble metals such as rhodium,[7] palladium,[8] and ruthenium[9,10] were also reported.

Although the utilization of earth-abundant, nonprecious TMs as catalysts is sustainable and thus desirable, the reports on the catalytic hydrosilylation of esters by base metals are extremely limited. Few iron complexes were utilized for the hydrosilylation of esters to ethers, aldehydes, and alcohols.[11] Whereas the use of manganese catalysts for the hydrosilylation of carbonyls is well established,[12] only a few reports have described the hydrosilylation of carboxyl substrates. The reduction of carboxylic acids by $Mn_2(CO)_{10}$ yielded aldehydes rather than alcohols.[13] However, Mn(II) complexes with pentadentate redox-active bis(imino)pyridine based ligand[14] and *N*-phosphinoamidinate (potentially redox-active) ligand[15] were utilized as active catalysts for the reduction of ester to alcohol. To the best of our knowledge, there are only two reports on the hydrosilylation of esters catalyzed by Mn(I) complexes. In the mid-1990s, hydrosilylation of esters to ethers was reported by using Mn(I)−acetyl complexes $(L)(CO)_4Mn(COCH_3)$ (L = CO, PPh_3) (Scheme 1).[16] Very recently, Mn(I) complexes with triazole-based ligands were utilized for the hydrosilylation of esters, yielding a mixture of alcohols and ethers (Scheme 1).[17] In the last 8−10 years, Mn(I) complexes have gained immense interest for their catalytic applications in a variety of chemical transformations.[18,19] Herein we address the use of a readily available Mn(I) complex with a commercially available bisphosphine ligand as an effective catalyst for the selective hydrosilylation of a large variety of esters to the corresponding alcohols under solvent-free

Received: March 30, 2020

https://dx.doi.org/10.1021/acs.orglett.0c01144
Org. Lett. XXXX, XXX, XXX−XXX

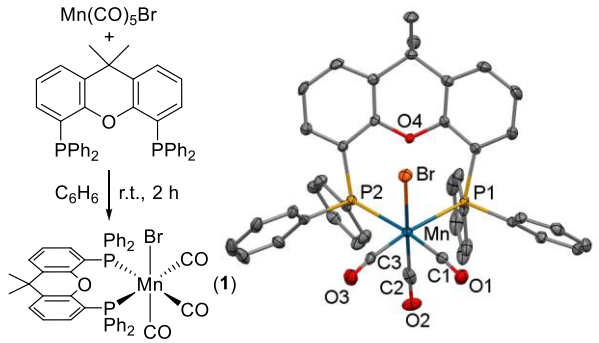
Scheme 1. Hydrosilylation of Esters by Mn(I) Catalysts



conditions (Scheme 1). Thus pyrophoric hydride reagents for conventional reduction can be avoided by using silane as a much milder reagent. Because classical hydrogenation requires an expensive high-pressure reactor, the present hydrosilylation protocol is much more economical and is safer. In addition, this hydrosilylation is highly selective, whereas the hydrogenation of ester suffers poor selectivity.

We selected xantphos for the synthesis of the corresponding Mn(I) complex because it is readily available and is one of the most used ligands for the development of a large variety of metal catalysts.[20] The neutral Mn(I) complex *fac*-[Mn(xantphos)$(CO)_3$Br] (**1**) was synthesized in high isolated yield (95%) by reacting the commercially available precursor $Mn(CO)_5Br$ with the commercially available bisphosphine ligand xantphos at r.t. (Scheme 2). The resulting yellow-orange

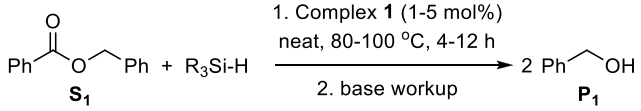
Scheme 2. Synthesis of *fac*-[Mn(xantphos)$(CO)_3$Br] (1) (Molecular Structure Showing 50% Ellipsoid)



complex **1** is diamagnetic and was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The NMR spectra of **1** are consistent with the overall C_s symmetry. The bisphosphine ligand framework was clearly seen in the ^1H and ^{13}C NMR spectra of **1**. A broad resonance at 26.14 ppm appears in the ^{31}P NMR spectrum, which is shifted downfield compared with the free xantphos ligand (−17.97 ppm). Complex **1** was also characterized by IR spectroscopy. Three strong CO stretching vibrations at 2023, 1950, and 1909 cm^{-1} were observed in the IR spectrum, which is consistent with the previous reports.[21] The mass analysis of **1** shows that the peak at 716.1161 corresponds to $[M^+ - Br]$. Complex **1** was further characterized by single-crystal X-ray analysis (Scheme 2). The geometry around manganese in **1** is distorted octahedral, and the bond distances and bond angles are consistent with similar complexes *fac*-[Mn(iPr$_2$P(CH$_2$)$_2$PiPr$_2$)$(CO)_3$Br and *fac*-[Mn(nPr$_2$P(CH$_2$)$_2$PnPr$_2$)$(CO)_3$Br].[21]

We set out to examine the catalytic activity of **1** under various reaction conditions for the hydrosilylation of ester, using benzyl benzoate as the standard substrate (Table 1). A

Table 1. Performance of 1 for the Hydrosilylation of Benzyl Benzoate under Different Reaction Conditions[a]



en.	1 (mol %)	silane (equiv)	temp (°C)	time (h)	yield (%)[b]
1	**2**	$PhSiH_3$ (2)	100	6	>99 (92)[c]
2	**1**	$PhSiH_3$ (2)	100	6	>99 (91)[c]
3	1	$PhSiH_3$ (2)	100	**5**	>99 (91)[c]
4	1	$PhSiH_3$ (2)	100	**4**	95
5	1	**Ph_2SiH_2** (2)	100	4	51 (>99)[d]
6	1	**Ph_3SiH** (2)	100	4	45 (>99)[d]
7	1	**Et_3SiH** (2)	100	4	46 (>99)[d]
8	1	$PhSiH_3$ (2)	**80**	4	46 (>99)[d]
9	1	$PhSiH_3$ (2)	**90**	4	53 (>99)[d]
10	1	$PhSiH_3$ (**1**)	100	5	>99 (92)[c]
11	1	$PhSiH_3$ (**1**)	100	4	93

[a]Reactions conducted in a pressure tube (10 mL) with 0.5 mmol S_1, 0.5/1.0 mmol of silane, and 1/2 mol % of **1**. [b]Yields of P_1 were determined by ^1H NMR spectroscopy using ferrocene (0.1 mmol) as an external standard. [c]Isolated yields of P_1. [d]NMR yields of P_1 for 12 h reaction. Key parameters for each entry are indicated in bold.

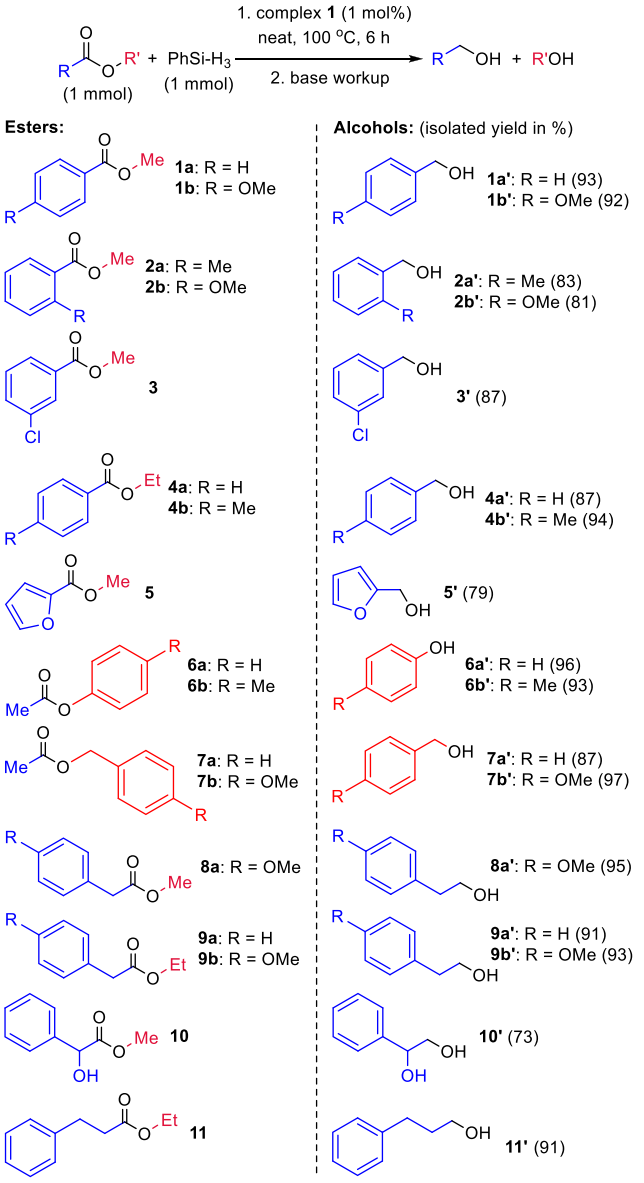
complete conversion of benzyl benzoate (S_1) to benzyl alcohol (P_1) was observed when S_1 (0.5 mmol) was heated with phenylsilane (1.0 mmol) to 100 °C for 6 h in the presence of 2 mol % catalyst **1** (entry 1). Reducing the catalyst loading to 1 mol % (entry 2) led to the complete conversion of S_1 to P_1 in just 6 h with >90% isolated yield. Decreasing the reaction time to 4 h gave P_1 in 95% NMR yield (entry 4). We also tested various secondary and tertiary silanes such as diphenylsilane (entry 5), triphenylsilane (entry 6), and triethylsilane (entry 7), and we obtained P_1 in approximately 40−50% yield in 4 h. Therefore, phenylsilane proved to be the best one under the reaction conditions. Thereafter, the hydrosilylation of S_1 was tested at lower temperatures. Upon lowering the temperature to 80 (entry 8) and 90 °C (entry 9), a poorer yield (approximately 40−50%) of P_1 was obtained in 4 h. Thereafter, we varied the amount of silane used for the hydrosilylation of S_1. The use of 1 equiv of phenylsilane led to the complete conversion of S_1 to P_1 (92% isolated yield) in just 5 h at 100 °C with 1 mol % catalyst loading (entry 10).

Thereafter, we explored various additional esters for the hydrosilylation of esters to alcohols based on the optimized conditions (1 mol % catalyst loading, neat, 100 °C, 6 h) to expand the substrate scope (Scheme 3).

First, we tested various aromatic esters. Methyl and ethyl benzoate derivatives (**1a**, **1b**, **2a**, **2b**, **3**, **4a**, **4b**) were reduced to benzyl alcohol derivatives in high isolated yields (**1a′**: 93%, **1b′**: 92%, **2a′**: 83%, **2b′**: 81%, **3′**: 87%, **4a′**: 87%, **4b′**: 94%). Another aromatic ester, methyl 2-furoate (**5**), was also easily reduced to furfuryl alcohol (**5′**: 79%). This catalytic system is also very effective for the reduction of phenyl acetates (**6a**, **6b**) to phenols (**6a′**: 96%, **6b′**: 93%). Therefore, the catalytic system is compatible with both electron-donating and electron-

https://dx.doi.org/10.1021/acs.orglett.0c01144
Org. Lett. XXXX, XXX, XXX−XXX

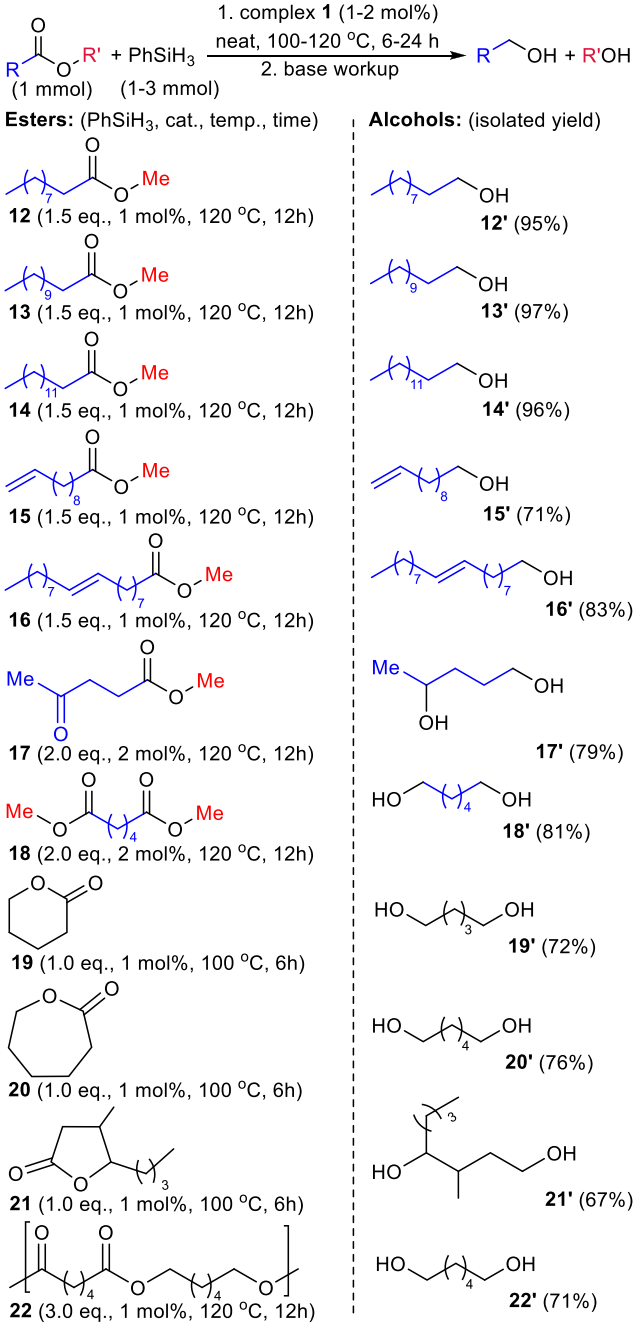
Scheme 3. Hydrosilylation of Various Esters to Alcohols Catalyzed by 1



withdrawing functionalities. Thereafter, more challenging aliphatic esters were tested. We were pleased to see that benzyl acetate derivatives (**7a**, **7b**) were reduced to benzyl alcohols (**7a′**: 87%, **7b′**: 97%) in excellent yield. This catalytic system is equally effective for methyl and ethyl phenyl acetates (**8a**, **9a**, **9b**) to give corresponding 2-phenylethanols (**8a′**: 95%, **9a′**: 91%, **9b′**: 93%). Similarly, methyl 2-hydroxy-2-phenylacetate (**10**) gave 1-phenyl-1,2-ethanediol (**10′**: 73%) in good yield. A high yield was also obtained for the reduction of ethyl 3-phenylpropionate (**11**) to 3-phenyl-1-propanol (**11′**: 91%). To test the robustness of the present catalytic system, the hydrosilylation of methyl 4-methoxybenzoate (**1b**) and 4-methoxybenzyl acetate (**7b**) was scaled up 10 times, and we obtained almost quantitative yields of 4-methoxybenzyl alcohol (96 to 97%).

The reduction of esters for the production of alcohols is an extremely important process for the chemical industry. For example, long-chain fatty alcohols are widely utilized in consumer products such as lubricants, surfactants, plasticizers, flavorings, and solvents for paints, and the global demand is drastically increasing. Presently, a major portion of fatty alcohols is produced through the hydrogenation of fatty esters derived from coconut and palm oil using a heterogeneous catalyst under harsh reaction conditions (250−300 °C and 2000−3000 psig of H_2 pressure).[22] CE-1270, an industrial sample obtained from coconut oil, contains mostly methyl laurate, **13** (∼71−75%), and methyl myristate, **14** (∼24−29%), with a small portion of methyl caprate, **12** (∼1%). We set out to reduce those fatty esters by using **1** (Scheme 4). Hydrosilylation of **12**, **13**, and **14** gave the corresponding fatty alcohols in almost quantitative yields (**12′**: 95%, **13′**: 97%, **14′**: 96%). Under identical reaction conditions, methyl 10-

Scheme 4. Catalytic Hydrosilylation of Esters with Practical Implications



https://dx.doi.org/10.1021/acs.orglett.0c01144
Org. Lett. XXXX, XXX, XXX−XXX

undecenoate (**15**) underwent the reduction of only the ester moiety, whereas the terminal alkene moiety remained intact (**15′**: 71%). A gram-scale hydrosilylation of **13** (10.0 mmol, 2.14 g) was also successfully accomplished (in almost quantitative yield). Thereafter, we focused our attention on methyl oleate (**16**), methyl levulinate (**17**), and dimethyl adipate (**18**) due to their relevance in biomass conversion and renewable chemistry.[23] Again, only the ester moiety of **16** was selectively reduced (**16′**: 83%), whereas the alkene part was unaltered. Thereafter, methyl levulinate (**17**) was subjected to hydrosilylation. It was not surprising that both keto and ester functionalities were reduced to the corresponding diol **17′** (79%). Similarly, dimethyl adipate (**18**) was cleanly reduced to the 1,6-hexanediol (**18′**: 81%). A higher temperature, higher silane amount, and longer reaction time were required for the fatty esters due to their unreactive nature. We also applied this hydrosilylation method for the reduction of lactones, which can be derived from natural sources. The six- and seven-membered lactones, *δ*-valerolactone (**19**) and *ε*-caprolactone (**20**), were reduced to the corresponding diols in good yields (**19′**: 72%, **20′**: 76%). Using the same protocol, whiskey lactone (**21**) was also reduced to the desired diol **21′** (77%). Because the present catalyst is very effective for the reduction of various esters, we targeted polyester as a potential substrate relevant to polymer recycling. The number of homogeneous catalysts for this purpose is very scarce.[4c,24] We choose the industrial sample dynacoll-7360, or poly(1,6-hexamethylene adipate) (**22**), which is produced by the condensation polymerization of 1,6-hexanediol and adipic acid. We were pleased to see that 1,6-hexanediol was obtained as a recycled product in good yield (71%) if **22** was submitted to the present catalytic protocol.

In conclusion, we have developed a readily accessible base-metal catalyst that is very efficient for the selective hydrosilylation of esters to alcohols. The substrate scope includes various aromatic, aliphatic, and cyclic esters. Industrially valuable fatty alcohols were also obtained under much milder reaction conditions from fatty esters. Furthermore, the catalytic system is also applicable to important substrates relevant to renewable chemistry and recycling of plastic waste. Previously reported Mn(I)−acetyl complexes[16] catalyzed the hydrosilylation of esters to ether as a partially reduced product, and Mn(I)−triazole complexes[17] converted esters to a mixture of alcohol and ethers; the complete reduction of esters could not be achieved. Compared with those previous reports, the present catalyst is much more active and selective for the reduction of esters to alcohols. Previously known Mn(II)−bis(imino)pyridine complexes[14] showed high activity only for the reduction of formates, however, they displayed sluggish reactivity for other simple esters such as phenyl acetate (1 mol % cat., r.t., 10 days) and *tert*-butyl acetate (1 mol % cat., 80 °C, 10 day). In the other report of the Mn(II)−phosphinoamidinate catalyst,[15] the reduction of methyl benzoate derivatives was only considered. For the hydrosilylation of esters to alcohols, all known Mn catalysts (including Mn(II) species) were highly air-sensitive, involved a complex ligand synthesis, and showed a very limited (5 to 8) substrate scope with simple esters such as formats, acetates, and methyl benzoates. In contrast, we synthesized a readily available Mn(I) catalyst (air-sensitive in solution, but stable for days in solid) by using a cheap and commercially available ligand with a wide substrate scope (28), including relatively unreactive substrates such as fatty esters and polyesters. Another advantage of this catalytic protocol is the solvent-free hydrosilylation. Further investigations will involve the utilization of this catalyst for the hydrosilylation of various other substrates such as alkynes and in different hydrofunctionalization reactions such as hydrogenation and hydroboration.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01144.

Experimental procedures, spectral data, and copies of ^{1}H and ^{13}C NMR spectra of the products of hydrosilylations, mechanistic analysis, and crystal data of manganese complex (**1**) (PDF)

Accession Codes

CCDC 1982008 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Bidraha Bagh − *School of Chemical Sciences, National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar, Odisha 752050, India;* orcid.org/0000-0003-0489-3312; Email: bidraha@niser.ac.in

Authors

Rakesh R. Behera − *School of Chemical Sciences, National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar, Odisha 752050, India*

Rahul Ghosh − *School of Chemical Sciences, National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar, Odisha 752050, India*

Surajit Panda − *School of Chemical Sciences, National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar, Odisha 752050, India*

Subrat Khamari − *School of Chemical Sciences, National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar, Odisha 752050, India*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c01144

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank SERB New Delhi (ECR/2018/000003), DAE, and NISER for financial support. R.R.B. thanks UGC for a research fellowship, and R.G. and S.P. acknowledge NISER for research fellowships.

■ REFERENCES

(1) Ege, S. N. *Organic Chemistry*; D. C. Health Company: Lexington, MA, 1989; p 596.

(2) For selected papers, see: (a) van Putten, R.; Uslamin, E. A.; Garbe, M.; Liu, C.; Gonzalez-de-Castro, A.; Lutz, M.; Junge, K.; Hensen, E. J. M.; Beller, M.; Lefort, L.; Pidko, E. A. Non-Pincer-Type Manganese Complexes as Efficient Catalysts for the Hydrogenation of

Esters. *Angew. Chem., Int. Ed.* **2017**, *56*, 7531−7534. (b) Espinosa-Jalapa, N. A.; Nerush, A.; Shimon, L. J. W.; Leitus, G.; Avram, L.; Ben-David, Y.; Milstein, D. Manganese-Catalyzed Hydrogenation of Esters to Alcohols. *Chem. - Eur. J.* **2017**, *23*, 5934−5938. (c) Widegren, M. B.; Harkness, G. J.; Slawin, A. M. Z.; Cordes, D. B.; Clarke, M. L. A Highly Active Manganese Catalyst for Enantioselective ketone and Ester Hydrogenation. *Angew. Chem., Int. Ed.* **2017**, *56*, 5825−5828. (d) Chen, J.; Zhu, H.; Chen, J.; Le, Z.-G.; Tu, T. Synthesis, Characterization and Catalytic Application of Pyridine Bridged N-Heterocyclic Carbene−Ruthenium Complexes in the Hydrogenation of Carbonates. *Chem. - Asian J.* **2017**, *12*, 2809−2812. (e) Henrion, M.; Roisnel, T.; Couturier, J.-L.; Dubois, J.-L.; Sortais, J.-B.; Darcel, C.; Carpentier, J.-F. Ruthenium complexes bearing amino-bis-(phosphinite) or amino-bis(aminophosphine) ligands: Applications in catalytic ester hydrogenation. *Mol. Catal.* **2017**, *432*, 15−22. (f) Kim, D.; Le, L.; Drance, M. J.; Jensen, K. H.; Bogdanovski, K.; Cervarich, T. N.; Barnard, M. G.; Pudalov, N. J.; Knapp, S. M. M.; Chianese, A. R. Ester Hydrogenation Catalyzed by CNN-Pincer Complexes of Ruthenium. *Organometallics* **2016**, *35*, 982−989. (g) Srimani, D.; Mukherjee, A.; Goldberg, A. F. G.; Leitus, G.; DiskinPosner, Y.; Shimon, L. J. W.; Ben David, Y.; Milstein, D. Cobalt-Catalyzed Hydrogenation of Esters to Alcohols: Unexpected Reactivity Trend Indicates Ester Enolate Intermediacy. *Angew. Chem., Int. Ed.* **2015**, *54*, 12357−12360. (h) Chakraborty, S.; Dai, H.; Bhattacharya, P.; Fairweather, N. T.; Gibson, M. S.; Krause, J. A.; Guan, H. Iron-Based Catalysts for the Hydrogenation of Esters to Alcohols. *J. Am. Chem. Soc.* **2014**, *136*, 7869−7872. (i) Carpenter, I.; Eckelmann, S. C.; Kuntz, M. T.; Fuentes, J. A.; France, M. B.; Clarke, M. L. Convenient and improved protocols for the hydrogenation of esters using Ru catalysts derived from (P,P), (P,N,N) and (P,N,O) ligands. *Dalton Trans* **2012**, *41*, 10136−10140. (j) Fogler, E.; Balaraman, E.; Ben-David, Y.; Leitus, G.; Shimon, L. J. W.; Milstein, D. New CNN-Type Ruthenium Pincer NHC Complexes. Mild, Efficient Catalytic Hydrogenation of Esters. *Organometallics* **2011**, *30*, 3826−3833. (k) Sun, Y.; Koehler, C.; Tan, R.; Annibale, V. T.; Song, D. Ester hydrogenation catalyzed by Ru-CNN pincer complexes. *Chem. Commun.* **2011**, *47*, 8349−8351. (l) Ito, M.; Ootsuka, T.; Watari, R.; Shiibashi, A.; Himizu, A.; Ikariya, T. Catalytic Hydrogenation of Carboxamides and Esters by Well-Defined Cp*Ru Complexes Bearing a Protic Amine Ligand. *J. Am. Chem. Soc.* **2011**, *133*, 4240−4242.

(3) For selected reviews, see: (a) Ai, W.; Zhong, R.; Liu, X.; Liu, Q. Hydride Transfer Reactions Catalyzed by Cobalt Complexes. *Chem. Rev.* **2019**, *119*, 2876−2953. (b) Zhang, Z.; Butt, N. A.; Zhou, M.; Liu, D.; Zhang, W. Asymmetric Transfer and Pressure Hydrogenation with Earth-Abunant Transition Metal Catalysts. *Chin. J. Chem.* **2018**, *36*, 443−454. (c) Morris, R. H. Mechanisms of the H_2- and transfer hydrogenation of polar bonds catalyzed by iron group hydrides. *Dalton Trans* **2018**, *47*, 10809−10826. (d) Matsunami, A.; Kayaki, Y. Upgrading and expanding the scope of homogeneous transferhydrogenation. *Tetrahedron Lett.* **2018**, *59*, 504−513. (e) Stefane, B.; Pozgan, F. Metal-Catalysed Transfer Hydrogenation of Ketones. *Top. Curr. Chem.* **2016**, *374*, 1−67. (f) Echeverria, P.-G.; Ayad, T.; Phansavath, P.; Ratovelomanana-Vidal, V. Recent Developments in Asymmetric Hydrogenation and Transfer Hydrogenation of Ketones and Imines through Dynamic Kinetic Resolution. *Synthesis* **2016**, *48*, 2523−2539. (g) Foubelo, F.; Nájera, C.; Yus, M. Catalytic asymmetric transfer hydrogenation of ketones: Recent advances. *Tetrahedron: Asymmetry* **2015**, *26*, 769−790. (h) Morris, R. H. Exploiting Metal−Ligand Bifunctional Reactions in the Design of Iron Asymmetric Hydrogenation Catalysts. *Acc. Chem. Res.* **2015**, *48*, 1494−1502. (i) Wang, D.; Astruc, D. The Golden Age of Transfer Hydrogenation. *Chem. Rev.* **2015**, *115*, 6621−6686. (j) Li, Y. Y.; Yu, S. L.; Shen, W. Y.; Gao, J. X. Iron-, Cobalt-, and Nickel-Catalyzed Asymmetric Transfer Hydrogenation and Asymmetric Hydrogenation of Ketones. *Acc. Chem. Res.* **2015**, *48*, 2587−2598. (k) Vaclavik, J.; Kacer, P.; Kuzma, M.; Cerveny, L. Opportunities Offered by Chiral η^6-Arene/N-Arylsulfonyldiamine-Ru^{II} Catalysts in the Asymmetric Transfer Hydrogenation of Ketones and Imines. *Molecules* **2011**, *16*, 5460−5495. (l) Robertson, A.; Matsumoto, T.; Ogo, S. The development of aqueous transfer hydrogenation catalysts. *Dalton Trans* **2011**, *40*, 10304−10310. (m) Malacea, R.; Poli, R.; Manoury, E. Asymmetric hydrosilylation, transferhydrogenation and hydrogenation of ketones catalyzed by iridium complexes. *Coord. Chem. Rev.* **2010**, *254*, 729−752.

(4) (a) Lee, S.-H.; Nikonov, G. I. Transfer Hydrogenation of Ketones, Nitriles, and Esters Catalyzed by a Half-Sandwich Complex of Ruthenium. *ChemCatChem* **2015**, *7*, 107−113. (b) Dubey, A.; Khaskin, E. Catalytic Ester Metathesis Reaction and Its Application to Transfer Hydrogenation of Esters. *ACS Catal.* **2016**, *6*, 3998−4002. (c) Farrar-Tobar, R. A.; Wozniak, B.; Savini, A.; Hinze, S.; Tin, S.; de Vries, J. G. Base-Free Iron Catalyzed Transfer Hydrogenation of Esters Using EtOH as Hydrogen Source. *Angew. Chem., Int. Ed.* **2019**, *58*, 1129−1133.

(5) (a) Berk, S. C.; Kreutzer, K. A.; Buchwald, S. L. A Catalytic Method for the Reduction of Esters to Alcohols. *J. Am. Chem. Soc.* **1991**, *113*, 5093−5095. (b) Berk, S. C.; Buchwald, S. L. An Air-Stable Catalyst System for the Conversion of Esters to Alcohols. *J. Org. Chem.* **1992**, *57*, 3751−3753. (c) Barr, K. J.; Berk, S. C.; Buchwald, S. L. Titanocene-Catalyzed Reduction of Esters Using Polymethylhydrosiloxane as the Stoichiometric Reductant. *J. Org. Chem.* **1994**, *59*, 4323−4326. (d) Reding, M. T.; Buchwald, S. L. An Inexpensive Air-Stable Titanium-Based System for the Conversion of Esters to Primary Alcohols. *J. Org. Chem.* **1995**, *60*, 7884−7890. (e) Verdaguer, X.; Hansen, M. C.; Berk, S. C.; Buchwald, S. L. Titanocene-Catalyzed Reduction of Lactones to Lactols. *J. Org. Chem.* **1997**, *62*, 8522−8528.

(6) Fernandes, A. C.; Romão, C. C. Silane/MoO_2Cl_2 as an efficient system for the reduction of esters. *J. Mol. Catal. A: Chem.* **2006**, *253*, 96−98.

(7) Ohta, T.; Kamiya, M.; Nobutomo, M.; Kusui, K.; Furukawa, I. Reduction of Carboxylic Acid Derivatives Using Diphenylsilane in the Presence of a Rh−PPh3 Complex. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1856−1861.

(8) Nakanishi, J.; Tatamidani, H.; Fukumoto, Y.; Chatani, N. A New Synthesis of Aldehydes by the Palladium-Catalyzed Reaction of 2-Pyridinyl Esters with Hydrosilanes. *Synlett* **2006**, *2006*, 869−872.

(9) Igarashi, M.; Mizuno, R.; Fuchikami, T. Ruthenium complex catalyzed hydrosilylation of esters: a facile transformation of esters to alkyl silyl acetals and aldehydes. *Tetrahedron Lett.* **2001**, *42*, 2149−2151.

(10) Matsubara, K.; Iura, T.; Maki, T.; Nagashima, H. A Triruthenium Carbonyl Cluster Bearing a Bridging Acenaphthylene Ligand: An Efficient Catalyst for Reduction of Esters, Carboxylic Acids, and Amides by Trialkylsilanes. *J. Org. Chem.* **2002**, *67*, 4985−4988.

(11) (a) Bézier, D.; Venkanna, G. T.; Castro, L. C. M.; Zheng, J.; Roisnel, T.; Sortais, J.-B.; Darcel, C. Iron-Catalyzed Hydrosilylation of Esters. *Adv. Synth. Catal.* **2012**, *354*, 1879−1884. (b) Das, S.; Li, Y.; Junge, K.; Beller, M. Synthesis of ethers from esters via Fe-catalyzed hydrosilylation. *Chem. Commun.* **2012**, *48*, 10742−10744. (c) Junge, K.; Wendt, B.; Zhou, S.; Beller, M. Iron-Catalyzed Reduction of Carboxylic Esters to Alcohols. *Eur. J. Org. Chem.* **2013**, *2013*, 2061−2065. (d) Li, H.; Misal Castro, L. C.; Zheng, J.; Roisnel, T.; Dorcet, V.; Sortais, J.-B.; Darcel, C. Selective Reduction of Esters to Aldehydes under the Catalysis of Well-Defined NHC−Iron Complexes. *Angew. Chem., Int. Ed.* **2013**, *52*, 8045−8049.

(12) (a) Hanna, P. K.; Gregg, B. T.; Cutler, A. R. Manganese Carbonyl Compounds as Hydrosilation Catalysts for Organoiron Acyl Complexes. *Organometallics* **1991**, *10*, 31−33. (b) DiBiase Cavanaugh, M.; Gregg, B. T.; Cutler, A. R. Manganese Carbonyl Complexes as Catalysts for the Hydrosilation of Ketones: Comparison with $RhCl(PPh_3)_3$. *Organometallics* **1996**, *15*, 2764−2769. (c) DiBiase Cavanaugh, M.; Gregg, B. T.; Chiulli, R. J.; Cutler, A. R. The reactions of hydrosilanes with the methoxycarbonyl complexes Cd(L)(CO)-MCO_2Me (M = Fe, Ru; L = CO, PPh_3) and $(L)(CO)_XMCO$, Me (M = Co, Mn; L = CO, PPh_3; x = 3, 4, with and without catalysis. *J. Organomet. Chem.* **1997**, *547*, 173−182. (d) Mao, Z.; Gregg, B. T.; Cutler, A. R. Manganese- and Rhodium-Catalyzed Phenylsilane

https://dx.doi.org/10.1021/acs.orglett.0c01144
Org. Lett. XXXX, XXX, XXX−XXX

Hydrosilation-Deoxygenation of Iron Acyl Complexes Cp(L)(CO)-FeC(O)R (L = CO, PPh_3, $P(OMe)_3$, $P(OPh)_3$; R = CH_3, Ph, $CHMe_2$, CMe_3). *Organometallics* **1998**, *17*, 1993−2002. (e) Son, S. U.; Paik, S.-J.; Lee, I. S.; Lee, Y.-A.; Chung, Y. K.; Seok, W. K.; Lee, H. N. Chemistry of [(1H-hydronaphthalene)$Mn(CO)_3$]: The Role of Ring-Slippage in Substitution, Catalytic Hydrosilylation, and Molecular Crystal Structure of $[(\eta^3\text{-}C_{10}H_9)Mn(CO)_3P(OMe)_3]$. *Organometallics* **1999**, *18*, 4114−4118. (f) Son, S. U.; Paik, S.-J.; Chung, Y. K. Hydrosilylation of ketones catalyzed by tricarbonyl naphthalene manganese cation. *J. Mol. Catal. A: Chem.* **2000**, *151*, 87−90. (g) Riener, K.; Högerl, M. P.; Gigler, P.; Kühn, F. E. Rhodium-Catalyzed Hydrosilylation of Ketones: Catalyst Development and Mechanistic Insights. *ACS Catal.* **2012**, *2*, 613−621. (h) Chidara, V. K.; Du, G. An Efficient Catalyst Based on Manganese Salen for Hydrosilylation of Carbonyl Compounds. *Organometallics* **2013**, *32*, 5034−5037. (i) Zheng, J.; Elangovan, S.; Valyaev, D. A.; Brousses, R.; César, V.; Sortais, J.-B.; Darcel, C.; Lugan, N.; Lavigne, G. Hydrosilylation of Aldehydes and Ketones Catalyzed by Half-Sandwich Manganese(I) N-Heterocyclic Carbene Complexes. *Adv. Synth. Catal.* **2014**, *356*, 1093−1097. (j) Trovitch, R. *Synlett* **2014**, *25*, 1638−1642. (k) Ghosh, C.; Mukhopadhyay, T. K.; Flores, M.; Groy, T. L.; Trovitch, R. Comparing Well-Defined Manganese, Iron, Cobalt, and Nickel Ketone Hydrosilylation Catalysts. *Inorg. Chem.* **2015**, *54*, 10398−10406. (l) Ghosh, C.; Mukhopadhyay, T. K.; Flores, M.; Groy, T. L.; Trovitch, R. J. A Pentacoordinate Mn(II) Precatalyst That Exhibits Notable Aldehyde and Ketone Hydrosilylation Turnover Frequencies. *Inorg. Chem.* **2015**, *54*, 10398−10406. (m) Valyaev, D. A.; Wei, D.; Elangovan, S.; Cavailles, M.; Dorcet, V.; Sortais, J.-B.; Darcel, C.; Lugan, N. Half-Sandwich Manganese Complexes Bearing Cp Tethered N-Heterocyclic Carbene Ligands: Synthesis and Mechanistic Insights into the Catalytic Ketone Hydrosilylation. *Organometallics* **2016**, *35*, 4090−4098. (n) Trovitch, R. J. The Emergence of Manganese-Based Carbonyl Hydrosilylation Catalysts. *Acc. Chem. Res.* **2017**, *50*, 2842−2852. (o) Ma, X.; Zuo, Z.; Liu, G.; Huang, Z. Manganese-Catalyzed Asymmetric Hydrosilylation of Aryl Ketones. *ACS Omega* **2017**, *2*, 4688−4692. (p) Wenz, J.; Vasilenko, V.; Kochan, A.; Wadepohl, H.; Gade, L. H. Coordination Chemistry of the PdmBOX Pincer Ligand: Reactivity at the Metal and the Ligand. *Eur. J. Inorg. Chem.* **2017**, *2017*, 5545−5556.

(13) Zheng, J.; Chevance, S.; Darcel, C.; Sortais, J.-B. Selective reduction of carboxylic acids to aldehydes through manganese catalysed hydrosilylation. *Chem. Commun.* **2013**, *49*, 10010−10012.

(14) (a) Mukhopadhyay, T. K.; Flores, M.; Groy, T. L.; Trovitch, R. J. A Highly Active Manganese Precatalyst for the Hydrosilylation of Ketones and Esters. *J. Am. Chem. Soc.* **2014**, *136*, 882−885. (b) Mukhopadhyay, T. K.; Rock, C. L.; Hong, M.; Ashley, D. C.; Groy, T. L.; Baik, M.-H.; Trovitch, R. J. Mechanistic Investigation of Bis(imino)pyridine Manganese Catalyzed Carbonyl and Carboxylate Hydrosilylation. *J. Am. Chem. Soc.* **2017**, *139*, 4901−4915. (c) Mukhopadhyay, T. K.; Ghosh, C.; Flores, M.; Groy, T. L.; Trovitch, R. J. Hydrosilylation of Aldehydes and Formates Using a Dimeric Manganese Precatalyst. *Organometallics* **2017**, *36*, 3477−3483.

(15) Kelly, C. M.; McDonald, R.; Sydora, O. L.; Stradiotto, M.; Turculet, L. A Manganese Pre-Catalyst: Mild Reduction of Amides, Ketones, Aldehydes, and Esters. *Angew. Chem., Int. Ed.* **2017**, *56*, 15901−15904.

(16) Mao, Z.; Gregg, B. T.; Cutler, A. R. Catalytic Hydrosilation of Organic Esters Using Manganese Carbonyl Acetyl Complexes, $(L)(C0)_4MnC(O)CH_3$ (L = CO, PPh_3). *J. Am. Chem. Soc.* **1995**, *117*, 10139−10140.

(17) Martínez-Ferraté, O.; Chatterjee, B.; Werlé, C.; Leitner, W. Hydrosilylation of carbonyl and carboxyl groups catalysed by Mn(I) complexes bearing triazole ligands. *Catal. Sci. Technol.* **2019**, *9*, 6370−6378.

(18) For selected reviews, see: (a) Bhunia, M.; Sreejyothi, P.; Mandal, S. K. Earth-abundant metal catalyzed hydrosilylative reduction of various functional groups. *Coord. Chem. Rev.* **2020**, *405*, 213110. (b) Maji, B.; Barman, M. K. Recent Developments of Manganese Complexes for Catalytic Hydrogenation and Dehydrogenation Reactions. *Synthesis* **2017**, *49*, 3377−3393. (c) Valyaev, D. A.; Lavigne, G.; Lugan, N. Manganese organometallic compounds in homogeneous catalysis: Past, present, and prospects. *Coord. Chem. Rev.* **2016**, *308*, 191−235. (d) Carney, J. R.; Dillon, B. R.; Thomas, S. P. Recent Advances of Manganese Catalysis for Organic Synthesis. *Eur. J. Org. Chem.* **2016**, *2016*, 3912−3929. (e) Garbe, M.; Junge, K.; Beller, M. Homogeneous Catalysis by Manganese-Based Pincer Complexes. *Eur. J. Org. Chem.* **2017**, *2017*, 4344−4362. (f) Yang, X.; Wang, C. Manganese-Catalyzed Hydrosilylation Reactions. *Chem. - Asian J.* **2018**, *13*, 2307−2315. (g) Filonenko, G. A.; van Putten, R.; Hensen, E. J. M.; Pidko, E. A. Catalytic (de)hydrogenation promoted by non-precious metals − Co, Fe and Mn: recent advances in an emerging field. *Chem. Soc. Rev.* **2018**, *47*, 1459−1483. (h) Gorgas, N.; Kirchner, K. Isoelectronic Manganese and Iron Hydrogenation/Dehydrogenation Catalysts: Similarities and Divergences. *Acc. Chem. Res.* **2018**, *51*, 1558−1569. (i) Hu, Y.; Wang, C. Manganese-Catalyzed C-H Olefination Reactions. *ChemCatChem* **2019**, *11*, 1167−1174.

(19) For selected recent papers, see: (a) Yadav, V.; Landge, V. G.; Subaramanian, M.; Balaraman, E. Manganese-Catalyzed α-Olefination of Nitriles with Secondary Alcohols. *ACS Catal.* **2020**, *10*, 947−954. (b) Sousa, S. C. A.; Carrasco, C. J.; Pinto, M. F.; Royo, B. A Manganese N-Heterocyclic Carbene Catalyst for Reduction of Sulfoxides with Silanes. *ChemCatChem* **2019**, *11*, 3839−3843. (c) Tan, Y.-X.; Liu, X.-Y.; Zhao, Y.-S.; Tian, P.; Lin, G.-Q. Arylation/Intramolecular Conjugate Addition of 1,6-Enynes Enabled by Manganese(I)-Catalyzed C−H Bond Activation. *Org. Lett.* **2019**, *21*, 5−9. (d) El-Sepelgy, O.; Matador, E.; Brzozowska, A.; Rueping, M. C-Alkylation of Secondary Alcohols by Primary Alcohols through Manganese-Catalyzed Double Hydrogen Autotransfer. *ChemSusChem* **2019**, *12*, 3099−3102. (e) Hammarback, L. A.; Robinson, A.; Lynam, J. M.; Fairlamb, I. J. S. Delineating the critical role of acid additives in Mn-catalysed C−H bond functionalisation processes. *Chem. Commun.* **2019**, *55*, 3211−3214. (f) Kaithal, A.; Gracia, L.-L.; Camp, C.; Quadrelli, E. A.; Leitner, W. Direct Synthesis of Cycloalkanes from Diols and Secondary Alcohols or Ketones Using a Homogeneous Manganese Catalyst. *J. Am. Chem. Soc.* **2019**, *141*, 17487−17492. (g) Dutta, P. K.; Chauhan, J.; Ravva, M. K.; Sen, S. Directing-Group-Assisted Manganese-Catalyzed Cyclopropanation of Indoles. *Org. Lett.* **2019**, *21*, 2025−2028. (h) Ling, F.; Hou, H.; Chen, J.; Nian, S.; Yi, X.; Wang, Z.; Song, D.; Zhong, W. Highly Enantioselective Synthesis of Chiral Benzhydrols via Manganese Catalyzed Asymmetric Hydrogenation of Unsymmetrical Benzophenones Using an Imidazole-Based Chiral PNN Tridentate Ligand. *Org. Lett.* **2019**, *21*, 3937−3941. (i) Kaplaneris, N.; Rogge, T.; Yin, R.; Wang, H.; Sirvinskaite, G.; Ackermann, L. Late-Stage Diversification through Manganese-Catalyzed C-H Activation: Access to Acyclic, Hybrid, and Stapled Peptides. *Angew. Chem., Int. Ed.* **2019**, *58*, 3476−3480. (j) Zhang, L.; Tang, Y.; Han, Z.; Ding, K. Lutidine-Based Chiral Pincer Manganese Catalysts for EnantioselectiveHydrogenation of Ketones. *Angew. Chem., Int. Ed.* **2019**, *58*, 4973−4977. (k) Bruneau-Voisine, A.; Pallova, L.; Bastin, S.; César, V.; Sortais, J.-B. Manganese catalyzed α-methylation of ketones with methanol as a C1 source. *Chem. Commun.* **2019**, *55*, 314−317. (l) Das, U. K.; Kumar, A.; Ben-David, Y.; Iron, M. A.; Milstein, D. Manganese Catalyzed Hydrogenation of Carbamates and Urea Derivatives. *J. Am. Chem. Soc.* **2019**, *141*, 12962−12966. (m) Gawali, S. S.; Pandia, B. K.; Gunanathan, C. Manganese(I)-Catalyzed α-Alkenylation of Ketones Using Primary Alcohols. *Org. Lett.* **2019**, *21*, 3842−3847. (n) Waiba, S.; Barman, M. K.; Maji, B. Manganese-Catalyzed Acceptorless Dehydrogenative Coupling of Alcohols With Sulfones: A Tool To Access Highly Substituted Vinyl Sulfones. *J. Org. Chem.* **2019**, *84*, 973−982. (o) Ali, S.; Huo, J.; Wang, C. Manganese-Catalyzed Aromatic C−H Allylation of Ketones. *Org. Lett.* **2019**, *21*, 6961−6965. (p) Rana, J.; Gupta, V.; Balaraman, E. Manganese-catalyzed direct C−C coupling of α-C−H bonds of amides and esters with alcohols via hydrogen autotransfer. *Dalton Trans* **2019**, *48*, 7094−7099. (q) Thorve, P. R.; Guru, M. M.; Maji, B. Manganese-Catalyzed Divergent Markovnikov Addition and

https://dx.doi.org/10.1021/acs.orglett.0c01144
Org. Lett. XXXX, XXX, XXX−XXX

[2 + 2+2] Cycloaddition of 2-Carbonyl Indanone with Terminal Alkyne. *J. Org. Chem.* **2019**, *84*, 8185−8193. (r) Borghs, J. C.; Azofra, L. M.; Biberger, T.; Linnenberg, O.; Cavallo, L.; Rueping, M.; El-Sepelgy, O. Manganese-Catalyzed Multicomponent Synthesis of Pyrroles through Acceptorless Dehydrogenation Hydrogen Autotransfer Catalysis: Experiment and Computation. *ChemSusChem* **2019**, *12*, 3083−3088. (s) Wei, D.; Bruneau-Voisine, A.; Dubois, M.; Bastin, S.; Sortais, J.-B. Manganese-Catalyzed Transfer Hydrogenation of Aldimines. *ChemCatChem* **2019**, *11*, 5256−5259. (t) Ryabchuk, P.; Stier, K.; Junge, K.; Checinski, M. P.; Beller, M. Molecularly Defined Manganese Catalyst for Low-Temperature Hydrogenation of Carbon Monoxide to Methanol. *J. Am. Chem. Soc.* **2019**, *141*, 16923−16929. (u) Weber, S.; Veiros, L. F.; Kirchner, K. Old Concepts, New Application − Additive-Free Hydrogenation of Nitriles Catalyzed by an Air Stable Alkyl Mn(I) Complex. *Adv. Synth. Catal.* **2019**, *361*, 5412−5420. (v) Weber, S.; Stoeger, B.; Veiros, L. F.; Kirchner, K. Rethinking Basic Concepts-Hydrogenation of Alkenes Catalyzed by Bench-Stable Alkyl Mn(I) Complexes. *ACS Catal.* **2019**, *9*, 9715−9720.

(20) van Leeuwen, P. W. N. M.; Kamer, P. C. J. Featuring Xantphos. *Catal. Sci. Technol.* **2018**, *8*, 26−113.

(21) (a) Weber, S.; Stöger, B.; Kirchner, K. Hydrogenation of Nitriles and Ketones Catalyzed by an Air-Stable Bisphosphine Mn(I) Complex. *Org. Lett.* **2018**, *20*, 7212−7215. (b) Garduño, J. A.; Flores-Alamo, M.; García, J. J. Manganese-Catalyzed Transfer Hydrogenation of Nitriles with 2-Butanol as the Hydrogen Source. *ChemCatChem* **2019**, *11*, 5330−5338.

(22) Rieke, R. D.; Thakur, D. S.; Roberts, B. D.; White, G. T. Fatty Methyl Ester Hydrogenation to Fatty Alcohol Part II: Process Issues. *J. Am. Oil Chem. Soc.* **1997**, *74*, 333−339.

(23) (a) Werpy, T.; Petersen, G. *Top Value-Added Chemicals from Biomass: Vol. I-Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; DOE/GO-102004-1992; National Renewable Energy Laboratory, U.S. Department of Energy (DOE): Golden, CO, 2004. (b) Holladay, J. E.; White, J. F.; Bozell, J. J.; Johnson, D. *Top Value-Added Chemicals from Biomass: Vol. II-Results of Screening for Potential Candidates from Biorefinery Lignin*; PNNL-16983; Pacific Northwest National Laboratory, U.S. Department of Energy (DOE): Richland, WA, 2007. (c) Corma, A.; Iborra, S.; Velty, A. Chemical Routes for the Transformation of Biomass into Chemicals. *Chem. Rev.* **2007**, *107*, 2411−2502. (d) Belgacem, M. N.; Gandini, A. *Monomers, Polymers and Composites from Renewable Resources*; Elsevier: Amsterdam, 2008. (e) Goldbach, V.; Roesle, P.; Mecking, S. Catalytic Isomerizing ω-Functionalization of Fatty Acids. *ACS Catal.* **2015**, *5*, 5951−5972. (f) Li, X.; Jia, P.; Wang, T. Furfural: A Promising Platform Compound for Sustainable Production of C_4 and C_5 Chemicals. *ACS Catal.* **2016**, *6*, 7621−7640.

(24) (a) Westhues, S.; Idel, J.; Klankermayer, J. Molecular catalyst systems as key enablers for tailored polyesters and polycarbonate recycling concepts. *Sci. Adv.* **2018**, *4*, eaat9669−9676. (b) Fuentes, J. A.; Smith, S. M.; Scharbert, M. T.; Carpenter, I.; Cordes, D. B.; Slawin, A. M. Z.; Clarke, M. L. On the Functional Group Tolerance of Ester Hydrogenation and Polyester Depolymerisation Catalysed by Ruthenium Complexes of Tridentate Aminophosphine Ligands. *Chem. - Eur. J.* **2015**, *21*, 10851−10860. (c) Krall, E. M.; Klein, T. W.; Andersen, R. J.; Nett, A. J.; Glasgow, R. W.; Reader, D. S.; Dauphinais, B. C.; McIlrath, S. P.; Fischer, A. A.; Carney, M. J.; Hudson, D. J.; Robertson, N. J. Controlled hydrogenative depolymerization of polyesters and polycarbonates catalyzed by ruthenium(II) PNN pincer complexes. *Chem. Commun.* **2014**, *50*, 4884−4887.

https://dx.doi.org/10.1021/acs.orglett.0c01144
Org. Lett. XXXX, XXX, XXX−XXX