OL Organic Letters

pubs.acs.org/OrgLett Letter

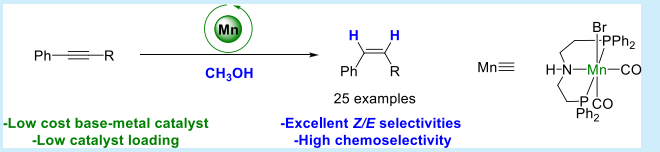
Methanol as the Hydrogen Source in the Selective Transfer Hydrogenation of Alkynes Enabled by a Manganese Pincer Complex

Jan Sklyaruk, Viktoriia Zubar, Jannik C. Borghs, and Magnus Rueping*

Cite This: https://dx.doi.org/10.1021/acs.orglett.0c02151 Read Online

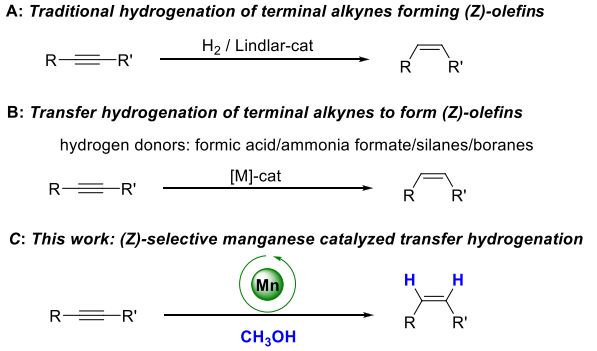
ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The first base metal-catalyzed transfer hydrogenation of alkynes with methanol is described. An air and moisture stable manganese pincer complex catalyzes the reduction of a variety of different alkynes to the corresponding (*Z*)-olefins in high yields. The reaction is stereo- and chemoselective and scalable.



Olefins play an important role in bioactive molecules, pharmaceuticals, polymers, and functional materials.[1,2] Furthermore, olefins can be functionalized into a vast variety of different compounds.[3] A common method for the synthesis of (*Z*)-olefins is the semihydrogenation of alkynes using the Pd-based Lindlar catalyst and hydrogen gas (Scheme 1A).[4] In addition, several *cis*-selective hydrogenation methods that mainly rely on the use of noble metals have been developed.[5] To avoid the use of pressurized hydrogen gas, transfer hydrogenation methods that apply hydrogen donors, such as ammonia formates,[6a] formic acid,[6b,c] silanes,[6d] and boranes,[6e] evolved as alternatives. However, these methods may have disadvantages due to functional group tolerance, their relatively high prices, and significant byproduct formation (Scheme 1B). In this regard, alcohols, especially methanol, are highly desirable as hydrogen donors.[7] Methanol is a very attractive hydrogen source, is produced on a large scale, and is one of the most important C_1 building blocks for the production of bulk and fine chemicals. The possibility of producing methanol from the greenhouse gas carbon dioxide highlights the sustainability of this hydrogen donor. In the proposed "methanol economy", methanol is considered as a promising hydrogen storage material, which can also be directly used as an alternative fuel for internal combustion and other engines, either in combination with gasoline or neat and in methanol fuel cells.[8] In the case of methanol, the dehydrogenation step is more energy demanding than for other alcohols.[9] Hence, it is challenging to develop catalysts that are active for both the dehydrogenation step of methanol and the semihydrogenation of unsaturated triple bonds to selectively form (*Z*)-olefins. This research field is so far rather underdeveloped, and to the best of our knowledge, no general studies of the base metal-catalyzed highly selective semihydrogenation of alkynes toward the formation of (*Z*)-olefins using methanol as a hydrogen source have been published.

Scheme 1. Different Methods for the (Transfer) Hydrogenation of Alkynes



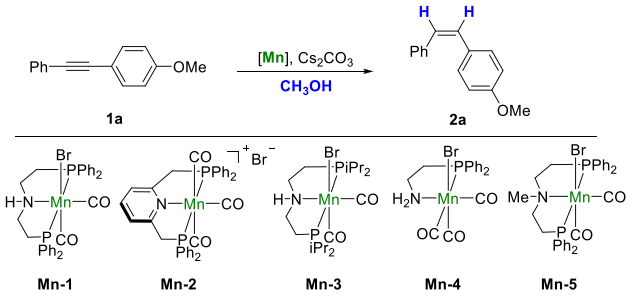
Recently, the field of manganese pincer-catalyzed (de-) hydrogenation reactions has received a great deal of attention.[9,10] Various publications described the manganese complex-catalyzed activation and synthetic utilization of methanol, whereby methanol was mainly applied as a methylating reagent.[11] However, recently reported manganese-catalyzed hydrogen borrowing and transfer hydrogenation catalysis[11,12] indicated that manganese pincer complexes may be suitable for the activation of methanol in the semitransfer hydrogenation of alkynes (Scheme 1C).

Thus, we evaluated different manganese complexes **Mn-1**−**Mn-5** as catalysts in the transfer hydrogenation of 1-methoxy-4-(phenylethynyl)benzene (**1a**) (Table 1, entries 1−5, respectively). Surprisingly, complex **Mn-1**, which is known to be active in the alkylation of ketones and nitriles,[12a,v] gave a

Received: June 29, 2020

https://dx.doi.org/10.1021/acs.orglett.0c02151
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst (mol %)	base (equiv)	yield (%)[b]	Z/E
1	**Mn-1** (2)	2	49	98/2
2	**Mn-2** (2)	2	–	–
3	**Mn-3** (2)	2	3	–
4	**Mn-4** (2)	2	–	–
5	**Mn-5** (2)	2	–	–
6[c]	**Mn-1** (2)	2	60	98/2
7	**Mn-1** (4)	2	83	98/2
8	**Mn-1** (2)	4	27	98/2
9[d]	**Mn-1** (2)	2	92	98/2
10[e]	**Mn-1** (2)	2	91	98/2
11[d]	**Mn-1** (2)	2	97	98/2
12[d]	**Mn-1** (2)	1	16	98/2
13[d]	**Mn-1** (1)	2	39	98/2
14[c]	$Mn(CO)_5Br$ (5)	2	–	–
15	**Mn-1** (2)	–	–	–
16	**L-1** (5)	3	–	–
17	–	2	–	–

[a]Reaction conditions: **1a** (0.1 mmol), [**Mn**], Cs_2CO_3, methanol (0.1 mL), 14 h, 135 °C for entries 1−10 and 150 °C for entries 11−17. [b]Yields were determined by ^1H NMR spectroscopy using acetonitrile as the internal standard. Heating inside an aluminum block. [c]Methanol (0.2 mL). [d]Toluene as the cosolvent (0.1 mL). [e]Methanol (0.2 mL) and toluene (0.2 mL).

yield of 49%, forming almost exclusively the corresponding *Z*-isomer **2a** (Table 1, entry 1).

On the other hand, the pyridyl-based complex **Mn-2**, previously used in the α-methylation of ketones,[11i] was shown to be completely inactive in this transformation (Table 1, entry 2). To evaluate the importance of the phosphine moiety, we applied the aliphatic phosphine-based complex **Mn-3** in the transformation. Although this complex is also known to be active in the alkylation of ketones,[12a] only trace amounts of product **2a** were obtained (Table 1, entry 3).

Also, the bidentate complex **Mn-4**, which is catalytically active in ester hydrogenation,[13] was inactive in the transfer hydrogenation reaction (Table 1, entry 4), highlighting the non-innocent behavior of the pincer backbone. Furthermore, N-Me-based complex **Mn-5** did not give any yield, illustrating the necessity of the NH functionality (Table 1, entry 5). The catalyst screening emphasized the importance of the aliphatic pincer backbone and the significance of aromatic phosphines in the semitransfer hydrogenation of alkynes. Increasing the amount of methanol and the amount of catalyst improved the yield (Table 1, entries 6 and 7).

In contrast, the catalytic activity decreased for a higher base loading (Table 1, entry 8). Moreover, the utilization of toluene as a cosolvent increased the yield significantly (Table 1, entry 9), while decreasing the concentration of the reaction system did not improve the yield (Table 1, entry 10). More detailed base and cosolvent screening is summarized in the Supporting Information.

Increasing the reaction temperature provided an almost quantitative yield of 97% with (*Z*)-product **2a** formed predominantly (Table 1, entry 11). Control experiments proved the efficiency of the chosen catalytic system (Table 1, entries 14−17). When other alcohols such as ethanol and isopropanol were used as hydrogen sources, quantitative yields were also obtained (see the Supporting Information). Additionally, no impact was observed when a drop of mercury was added to the reaction mixture, which suggests the homogeneous nature of the catalyst under these reaction conditions.[14]

After the kinetic profile of the reaction had been measured (see the Supporting Information), the reaction time was set to 14 h. In the further course of the work, we applied the optimized reaction conditions (Table 1, entry 11) in the transfer hydrogenation of various internal alkynes (Scheme 2). Unfortunately, terminal alkynes proved to be inactive in the transfer hydrogenation reaction.

Generally, the alkyne derivatives **1a−1x** were reduced to the corresponding olefins **2a−2x** with high selectivity in moderate to quantitative yields. Stilbene **2a** was isolated in a very good yield of 88% with a *Z*/*E* ratio of 98/2. In the further course of the evaluation of scope, both electron-donating (**2b−2g** and **2n**) and electron-withdrawing substituents (**2j−2m**) were tolerated in *ortho*, *meta*, and *para* positions of the aromatic moiety of the alkynes. Various heterocycle-containing alkynes (**1o** and **1q−1u**) were tolerated in the transformation. Also, the longer chain internal olefins **2v** and **2w** were isolated in high yields with good selectivity. It is important to note that for substrates such as **1h**, **1j**, **1l**, **1w**, and **1x** some over-hydrogenation into the corresponding diarylethanes was observed. To present the generality of the transformation, we applied our catalytic system in a gram scale synthesis of (*Z*)-stilbene (**2b**) (Scheme 3). The desired product **2b** was obtained in quantitative yield with an excellent *Z*/*E* ratio of 97/3. When (*Z*)- or (*E*)-stilbenes **2b** were used, no isomerization or hydrogenation occurred (see the Supporting Information).

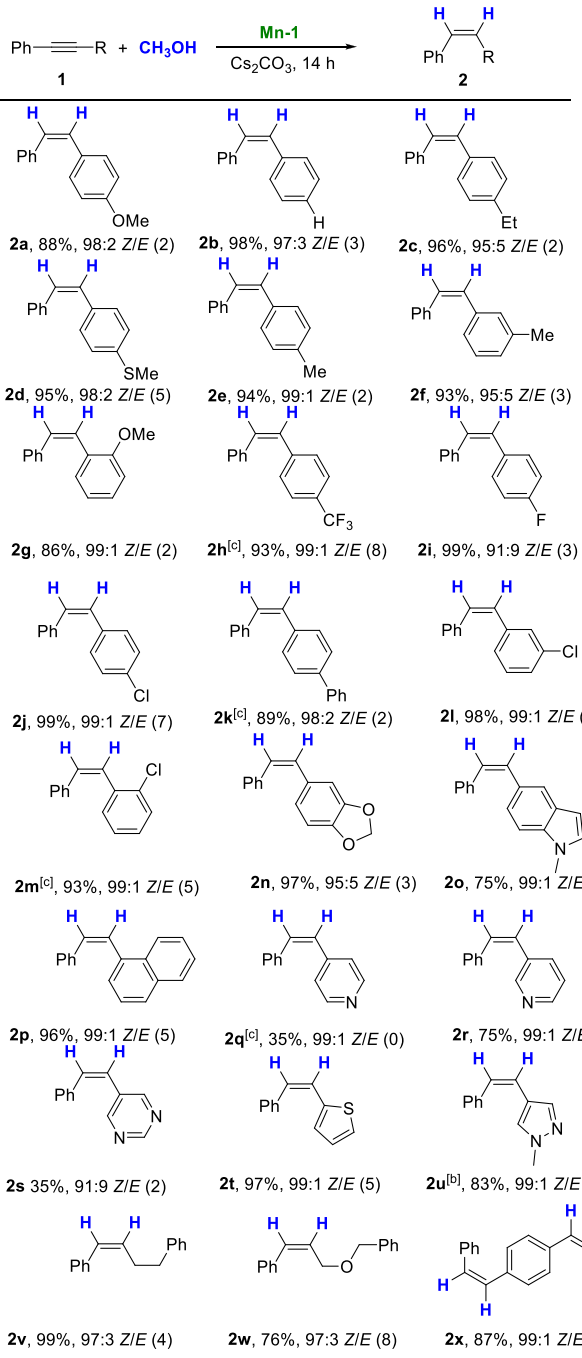
Next, we used fully deuterated methanol CD_3OD to investigate the incorporation position of hydrogen (Scheme 4).

In the olefinic position, the value of deuterium incorporation reached 94% and this result indicates the possibility of *cis*-selective deuterium incorporation. Due to the importance of deuterium-labeled compounds,[15] this transformation might be evaluated in further work (Scheme 4). Beyond that, we observed significant H/D exchange in the *ortho* position next to the methoxy group of **2a**.

On the basis of these observations, we propose the following catalytic cycle (Scheme 5). In the first step, the air and moisture stable precursor **Mn-1** is activated by a base to give the active species **Mn-1a**. Methanol coordinates to the active species **Mn-1a**, which is the deprotonated via metal ligand interactions, forming the manganese methoxide complex **Mn-1b**.[12d] The following deprotonation of the methoxide moiety results in formaldehyde elimination, so that the hydride species **Mn-1c** is obtained. Subsequent alkyne coordination and insertion into the manganese−hydride bond leads to the formation of **Mn-1d**. In the next step, the elimination of (*Z*)-stilbene occurs, to regenerate the active **Mn-1a** catalyst. However, an alternative pathway starting from **Mn-1d** is conceivable in which methanol facilitates elimination of the (*Z*)-stilbene and directly provides the **Mn-1b** intermediate.

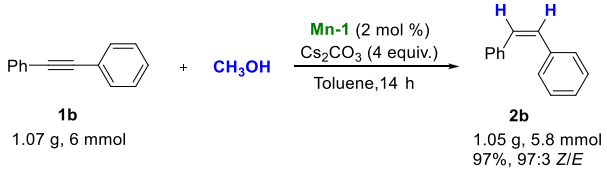
https://dx.doi.org/10.1021/acs.orglett.0c02151
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 2. Manganese-Catalyzed Transfer Hydrogenation of Alkynes[a]

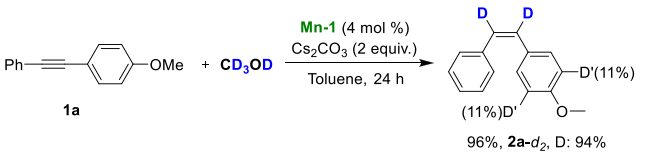


[a]Reaction conditions: **1** (0.3 mmol), Cs_2CO_3 (0.6 mmol), **Mn-1** (2 mol %) in CH_3OH (0.3 mL) and toluene (0.3 mL) at 150 °C. [b]At 130 °C. [c]**Mn-1** (4 mol %). The overhydrogenation product is presented in parentheses. Heating inside an aluminum block.

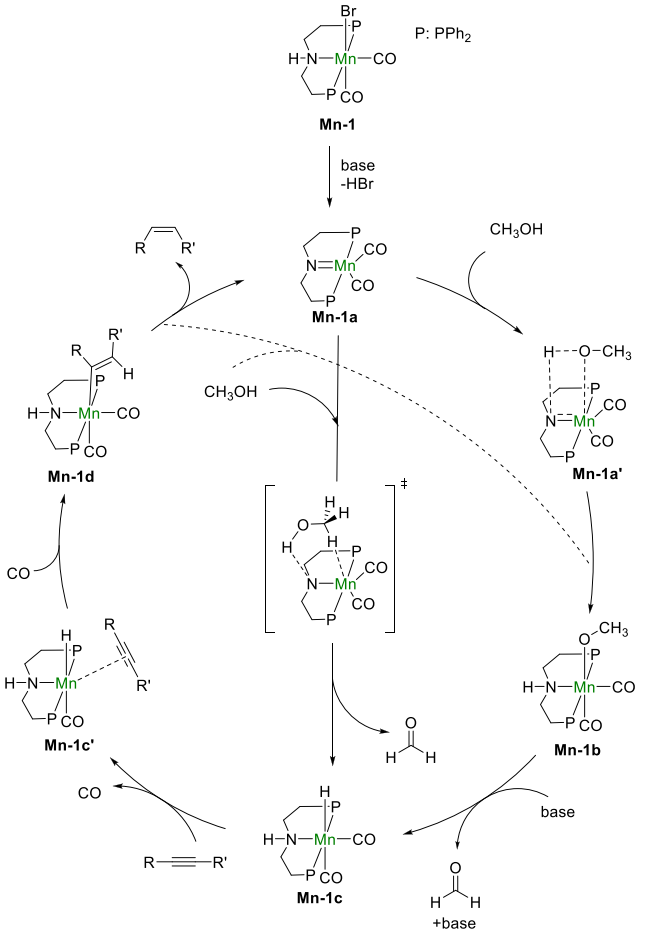
Scheme 3. Gram Scale Synthesis of (*Z*)-Stilbene (2b)



Scheme 4. Deuterium Labeling Using CD_3OD in the Transfer Deuteration of Alkynes



Scheme 5. Proposed Catalytic Cycle for the Manganese-Catalyzed Transfer Hydrogenation of Alkynes with Methanol



Alternatively, **Mn-1a** can also be directly converted to **Mn-1c** via a six-membered transition state.[12e]

In conclusion, we developed the first base metal-catalyzed semitransfer hydrogenation of alkynes, using methanol as a hydrogen donor. The applicability of this transformation was demonstrated for a variety of different alkynes, giving the corresponding (*Z*)-olefins in moderate to quantitative yields and high chemoselectivity. The reaction is scalable, and deuterium labeling experiments demonstrate the *cis*-selective hydrogen incorporation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02151.

https://dx.doi.org/10.1021/acs.orglett.0c02151
Org. Lett. XXXX, XXX, XXX−XXX

Experimental procedures and characterization of compounds (PDF)

AUTHOR INFORMATION

Corresponding Author

Magnus Rueping − *KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia;* orcid.org/0000-0003-4580-5227; Email: magnus.rueping@kaust.edu.sa

Authors

Jan Sklyaruk − *Institute of Organic Chemistry, RWTH Aachen University, 52074 Aachen, Germany*

Viktoriia Zubar − *Institute of Organic Chemistry, RWTH Aachen University, 52074 Aachen, Germany; KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia*

Jannik C. Borghs − *Institute of Organic Chemistry, RWTH Aachen University, 52074 Aachen, Germany*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c02151

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

J.S. thanks the VCI (Verband der Chemischen Industrie) for the Chemiefonds-Stipendium. J.C.B. acknowledges the DBU (Deutsche Bundesstiftung Umwelt) for the doctoral fellowship. This work was financially supported by the King Abdullah University of Science and Technology (KAUST), Saudi Arabia, Office of Sponsored Research (FCC/1/1974).

REFERENCES

(1) (a) Cushman, M.; Nagarathnam, D.; Gopal, D.; Chakraborti, A. K.; Lin, C. M.; Hamel, E. *J. Med. Chem.* **1991**, *34*, 2579−2588. (b) Sackett, D. L. *Pharmacol. Ther.* **1993**, *59*, 163−228. (c) Ohsumi, K.; Nakagawa, R.; Fukuda, Y.; Hatanaka, T.; Morinaga, Y.; Nihei, Y.; Ohishi, K.; Suga, Y.; Akiyama, Y.; Tsuji, T. *J. Med. Chem.* **1998**, *41*, 3022−3032. (d) Tron, G. C.; Pirali, T.; Sorba, G.; Pagliai, F.; Busacca, S.; Genazzani, A. A. *J. Med. Chem.* **2006**, *49*, 3033−3044. (e) Baur, J. A.; Sinclair, D. A. *Nat. Rev. Drug Discovery* **2006**, *5*, 493−506.

(2) (a) Cameron, G. G.; Grassie, N. *Makromol. Chem.* **1962**, *51*, 130−136. (b) Xu, J. F.; Chen, Y. Z.; Wu, D.; Wu, L. Z.; Tung, C. H.; Yang, Q. Z. *Angew. Chem., Int. Ed.* **2013**, *52*, 9738−9742. (c) Sakaguchi, T.; Yumoto, K.; Shiotsuki, M.; Sanda, F.; Yoshikawa, M.; Masuda, T. *Macromolecules* **2005**, *38*, 2704−2709. (d) Yamauchi, K.; Takashima, Y.; Hashidzume, A.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2008**, *130*, 5024−5025. (e) Ikejiri, S.; Takashima, Y.; Osaki, M.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2018**, *140*, 17308−17315.

(3) (a) Lane, B. S.; Burgess, K. *Chem. Rev.* **2003**, *103*, 2457−2473. (b) Yuan, Y. A.; Lu, D. F.; Chen, Y. R.; Xu, H. *Angew. Chem., Int. Ed.* **2016**, *55*, 534−538. (c) Chen, J.; Guo, J.; Lu, Z. *Chin. J. Chem.* **2018**, *36*, 1075−1109.

(4) Lindlar, H. *Helv. Chim. Acta* **1952**, *35*, 446−450.

(5) (a) Schrock, R. R.; Osborn, J. A. J. *J. Am. Chem. Soc.* **1976**, *98*, 2143−2147. (b) Sharma, V. M.; Choudary, M.; Sarma, M. R.; Rao, K. K. *J. Org. Chem.* **1989**, *54*, 2997−2998. (c) van Laren, M. W.; Elsevier, C. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 3715−3717. (d) Chernichenko, K.; Madarasz, A.; Papai, I.; Nieger, M.; Leskela, M.; Repo, T. *Nat. Chem.* **2013**, *5*, 718−723. (e) Oger, C.; Balas, L.; Durand, T.; Galano, J.-M. *Chem. Rev.* **2013**, *113*, 1313−1350 and references cited herein. (f) Gieshoff, T. N.; Welther, A.; Kessler, M. T.; Prechtl, M. H. G.; Jacobi von Wangelin, A. *Chem. Commun.* **2014**, *50*, 2261−2264. (g) Fiorio, J. L.; Goncalves, R. V.; Teixeira-Neto, E.; Ortuno, M. A.; Lopez, N.; Rossi, L. M. *ACS Catal.* **2018**, *8*, 3516−3524. (h) Reina, A.; Favier, I.; Pradel, C.; Gomez, M. *Adv. Synth. Catal.* **2018**, *360*, 3544−3552.

(6) (a) Córtese, N. A.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 3985−3987. (b) Shen, R.; Chen, T.; Zhao, Y.; Qiu, R.; Zhou, Y.; Yin, S.; Wang, X.; Goto, M.; Han, L. *J. Am. Chem. Soc.* **2011**, *133*, 17037−17044. (c) Wang, D.; Astruc, D. *Chem. Rev.* **2015**, *115*, 6621−6686. (d) Trost, B. M.; Braslau, R. *Tetrahedron Lett.* **1989**, *30*, 4657−4660. (e) Kijima, M.; Nambu, Y.; Endo, T. *Chem. Lett.* **1985**, *14*, 1851−1854.

(7) Examples, which use alcohols as a hydrogen source. Use of isopropanol: (a) Djukic, J. P.; Parkhomenko, K.; Hijazi, A.; Chemmi, A.; Allouche, L.; Brelot, L.; Pfeffer, M.; Ricard, L.; Le Goff, X. F. *J. Chem. Soc. Dalt. Trans.* **2009**, 2695−2711. (b) Belger, C.; Neisius, N. M.; Plietker, B. *Chem. - Eur. J.* **2010**, *16*, 12214−12220. (c) Horn, S.; Albrecht, M. *Chem. Commun.* **2011**, *47*, 8802−8804. (d) Kamitani, M.; Nishiguchi, Y.; Tada, R.; Itazaki, M.; Nakazawa, H. *Organometallics* **2014**, *33*, 1532−1535. (e) Payra, S.; Saha, A.; Banerjee, S. *RSC Adv.* **2016**, *6*, 52495−52499. (f) Alshakova, I. D.; Gabidullin, B.; Nikonov, G. I. *ChemCatChem* **2018**, *10*, 4874−4883. Use of glucose: (g) Manna, S.; Antonchick, A. P. *ChemSusChem* **2019**, *12*, 3094−3098. Use of ethanol: (h) Alonso, F.; Osante, I.; Yus, M. *Adv. Synth. Catal.* **2006**, *348*, 305−308. Use of methanol: (i) Tani, K.; Iseki, A.; Yamagata, T. *Chem. Commun.* **1999**, 1821−1822. Use of ethanol for the transfer hydrogenation of ylides: (j) Siva Reddy, A.; Kumara Swamy, K. C. *Angew. Chem.* **2017**, *129*, 7088−7092.

(8) (a) Olah, G. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2636−2639. (b) Olah, G. A.; Prakash, G. K. S.; Goeppert, A. *J. Am. Chem. Soc.* **2011**, *133*, 12881−12898. (c) Olah, G. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 104−107. (d) Asinger, F. *Methanol-Chemie-Und Energierohstoff*; Springer-Verlag, 1986.

(9) Crabtree, R. H. *Chem. Rev.* **2017**, *117*, 9228−9246.

(10) For reviews, see: (a) Corma, A.; Navas, J.; Sabater, M. J. *Chem. Rev.* **2018**, *118*, 1410−1459. (b) Garbe, M.; Junge, K.; Beller, M. *Eur. J. Org. Chem.* **2017**, *2017*, 4344−4362. (c) Maji, B.; Barman, M. *Synthesis* **2017**, *49*, 3377−3393. (d) Zell, T.; Langer, R. *ChemCatChem* **2018**, *10*, 1930−1940. (e) Sordakis, K.; Tang, C.; Vogt, L. K.; Junge, H.; Dyson, P. J.; Beller, M.; Laurenczy, G. *Chem. Rev.* **2018**, *118*, 372−433. (f) Filonenko, G. A.; van Putten, R.; Hensen, E. J. M.; Pidko, E. A. *Chem. Soc. Rev.* **2018**, *47*, 1459−1483. (g) Mukherjee, A.; Milstein, D. *ACS Catal.* **2018**, *8*, 11435−11469. (h) Gorgas, N.; Kirchner, K. *Acc. Chem. Res.* **2018**, *51*, 1558−1569. (i) Kallmeier, F.; Kempe, R. *Angew. Chem., Int. Ed.* **2018**, *57*, 46−60. (j) Reed-Berendt, B. G.; Polidano, K.; Morrill, L. C. *Org. Biomol. Chem.* **2019**, *17*, 1595−1607. (k) Vogiatzis, K. D.; Polynski, M. V.; Kirkland, J. K.; Townsend, J.; Hashemi, A.; Liu, C.; Pidko, E. A. *Chem. Rev.* **2019**, *119*, 2453−2523. (l) Irrgang, T.; Kempe, R. *Chem. Rev.* **2019**, *119*, 2524−2549. (m) Liu, W.; Ackermann, L. Manganese-Catalyzed C−H Activation. *ACS Catal.* **2016**, *6*, 3743−3752. (n) Li, H.; Gonçalves, T. P.; Lupp, D.; Huang, K.-W. *ACS Catal.* **2019**, *9*, 1619−1629.

(11) (a) Elangovan, S.; Neumann, J.; Sortais, J.-B.; Junge, K.; Darcel, C.; Beller, M. *Nat. Commun.* **2016**, *7*, 12641. (b) Neumann, J.; Elangovan, S.; Spannenberg, A.; Junge, K.; Beller, M. *Chem. - Eur. J.* **2017**, *23*, 5410−5413. (c) Bruneau-Voisine, A.; Wang, D.; Dorcet, V.; Roisnel, T.; Darcel, C.; Sortais, J. B. *J. Catal.* **2017**, *347*, 57−62. (d) Andérez-Fernández, M.; Vogt, L. K.; Fischer, S.; Zhou, W.; Jiao, H.; Garbe, M.; Elangovan, S.; Junge, K.; Junge, H.; Ludwig, R.; Beller, M. *Angew. Chem., Int. Ed.* **2017**, *56*, 559−562. (e) Mastalir, M.; Pittenauer, E.; Allmaier, G.; Kirchner, K. *J. Am. Chem. Soc.* **2017**, *139*, 8812−8815. (f) Natte, K.; Neumann, H.; Beller, M.; Jagadeesh, R. V. *Angew. Chem., Int. Ed.* **2017**, *56*, 6384−6394. (g) Chakraborty, S.; Gellrich, U.; Diskin-Posner, Y.; Leitus, G.; Avram, L.; Milstein, D. *Angew. Chem., Int. Ed.* **2017**, *56*, 4229−4233. (h) Wei, Z.; de Aguirre, A.; Junge, K.; Beller, M.; Jiao, H. *Catal. Sci. Technol.* **2018**, *8*, 3649−3665. (i) Sklyaruk, J.; Borghs, J.; El-Sepelgy, O.; Rueping, M. *Angew. Chem., Int. Ed.* **2019**, *58*, 775−779. (j) Bruneau-Voisine, A.; Pallova,

L.; Bastin, S.; César, V.; Sortais, J.-B. *Chem. Commun.* **2019**, *55*, 314−317.
(12) (a) Peña-López, M.; Piehl, P.; Elangovan, S.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2016**, *55*, 14967−14971. (b) Valyaev, D. A.; Lavigne, G.; Lugan, N. *Coord. Chem. Rev.* **2016**, *308*, 191−235. (c) Docherty, J. H.; Peng, J.; Dominey, A. P.; Thomas, S. P. *Nat. Chem.* **2017**, *9*, 595−600. (d) Fu, S.; Shao, Z.; Wang, Y.; Liu, Q. *J. Am. Chem. Soc.* **2017**, *139*, 11941−11948. (e) Nguyen, D. H.; Trivelli, X.; Capet, F.; Paul, J.-F.; Dumeignil, F.; Gauvin, R. M. *ACS Catal.* **2017**, *7*, 2022−2032. (f) Zhou, Y.; Mo, Z.; Luecke, M.; Driess, M. *Chem. - Eur. J.* **2018**, *24*, 4780−4784. (g) Brzozowska, A.; Azofra, L. M.; Zubar, V.; Atodiresei, I.; Cavallo, L.; Rueping, M.; El-sepelgy, O. *ACS Catal.* **2018**, *8*, 4103−4109. (h) Chakraborty, S.; Daw, P.; Ben David, Y.; Milstein, D. *ACS Catal.* **2018**, *8*, 10300−10305. (i) Liu, T.; Wang, L.; Wu, K.; Yu, Z. *ACS Catal.* **2018**, *8*, 7201−7207. (j) Yang, X.; Wang, C. *Angew. Chem.* **2018**, *130*, 935−940. (k) Carney, J. R.; Dillon, B. R.; Campbell, L.; Thomas, S. P. *Angew. Chem., Int. Ed.* **2018**, *57*, 10620−10624. (l) Kulkarni, N. V.; Brennessel, W. W.; Jones, W. D. *ACS Catal.* **2018**, *8*, 997−1002. (m) El-sepelgy, O.; Matador, E.; Brzozowska, A.; Rueping, M. *ChemSusChem* **2019**, *12*, 3099−3102. (n) Jang, Y. K.; Krückel, T.; Rueping, M.; El-Sepelgy, O. *Org. Lett.* **2018**, *20*, 7779−7783. (o) Jana, A.; Reddy, C. B.; Maji, B. *ACS Catal.* **2018**, *8*, 9226−9231. (p) Liu, T.; Wang, L.; Wu, K.; Yu, Z. *ACS Catal.* **2018**, *8*, 7201−7207. (q) Barman, M. K.; Jana, A.; Maji, B. *Adv. Synth. Catal.* **2018**, *360*, 3233−3238. (r) Banerjee, D.; Kabadwal, L. M.; Das, J. *Chem. Commun.* **2018**, *54*, 14069−14072. (s) Borghs, J. C.; Zubar, V.; Azofra, L. M.; Sklyaruk, J.; Rueping, M. *Org. Lett.* **2020**, *22*, 4222−4227. (t) Zubar, V.; Borghs, J.; Rueping, M. *Org. Lett.* **2020**, *22*, 3974−3978. (u) Brzozowska, A.; Zubar, V.; Ganardi, R.-C.; Rueping, M. *Org. Lett.* **2020**, *22*, 3765−3769. (v) Borghs, J. C.; Tran, M. A.; Sklyaruk, J.; Rueping, M.; El-Sepelgy. *J. Org. Chem.* **2019**, *84*, 7927−7935. (w) Borghs, J. C.; Azofra, L. M.; Biberger, T.; Linnenberg, O.; Cavallo, L.; Rueping, M.; El-Sepelgy, O. *ChemSusChem* **2019**, *12*, 3083−3088. (x) Matador, E.; Brzozowska, A.; El-Sepelgy, O.; Rueping, M. *ChemSusChem* **2019**, *12*, 3099−3102. (y) Borghs, J. C.; Lebedev, Y.; Rueping, M.; El-Sepelgy, O. *Org. Lett.* **2019**, *21*, 70−74. (z) Garbe, M.; Budweg, S.; Papa, V.; Wei, Z.; Hornke, H.; Bachmann, S.; Scalone, M.; Spannenberg, A.; Jiao, H.; Junge, K.; Beller, M. *Catal. Sci. Technol.* **2020**, *10*, 3994−4001.
(13) 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. *Angew. Chem., Int. Ed.* **2017**, *56*, 7531−7534.
(14) Chernyshev, V. M.; Astakhov, A. V.; Chikunov, I. E.; Tyurin, R. V.; Eremin, D. B.; Ranny, G. S.; Khrustalev, V. N.; Ananikov, V. P. *ACS Catal.* **2019**, *9*, 2984−2995.
(15) (a) Gant, T. G. *J. Med. Chem.* **2014**, *57*, 3595−3611. (b) Atzrodt, J.; Derdau, V.; Kerr, W. J.; Reid, M. *Angew. Chem., Int. Ed.* **2018**, *57*, 1758−1784.

https://dx.doi.org/10.1021/acs.orglett.0c02151
Org. Lett. XXXX, XXX, XXX−XXX