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Authors: Congyang Wang and Xiaoxu Yang

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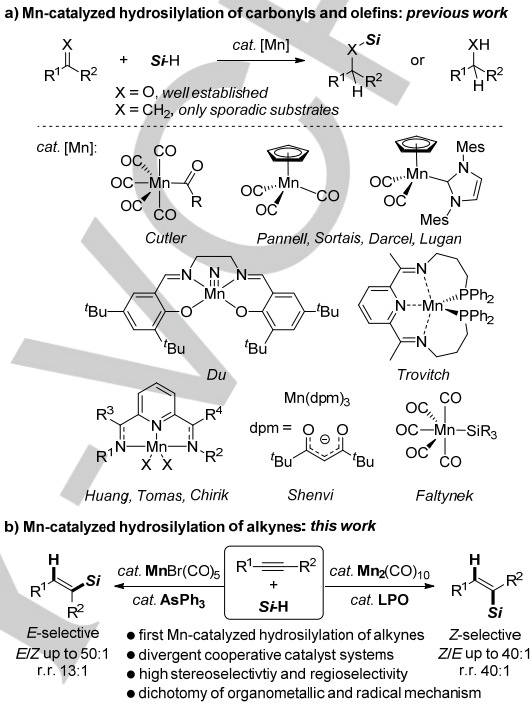
Dichotomy of Manganese Catalysis via Organometallic or Radical Mechanism: Stereodivergent Hydrosilylation of Alkynes

Xiaoxu Yang and Congyang Wang*

Abstract: Herein, we disclose the first manganese-catalyzed hydrosilylation of alkynes featuring diverse selectivities. The highly selective formation of *E*-products was achieved by using mononuclear $MnBr(CO)_5$ with the arsenic ligand, $AsPh_3$. On the contrary, the dinuclear catalyst $Mn_2(CO)_{10}$ together with LPO (dilauroyl peroxide) enabled the reversed generation of *Z*-products in good to excellent stereo- and regioselectivity. Such a way of controlling the reaction stereoselectivity is unprecedented and unique. Mechanistic experiments revealed the dichotomy of manganese catalysis *via* organometallic and radical pathways operating in the *E*- and *Z*-selective protocols respectively.

Hydrosilylation provides atom-economic methods for accessing organosilicon compounds and has wide applications in synthesis of organic molecules and functional materials.[1] Transition-metal-catalyzed hydrosilylation reactions have made great success over the past few decades.[2] In comparison with Ru, Rh, Pt, and others, manganese-catalyzed hydrosilylation has largely lagged behind (Scheme 1a). As early as in 1982, Yates, for the first time, reported $Mn_2(CO)_{10}$-catalyzed hydrosilylation of acetone, albeit only in 5% GC yield.[3] Later in 1990s, Cutler *et al.* discovered a range of acyl-manganese-complex catalyzed hydrosilylation of carbonyls including organoiron acyl complexes, ketones, and esters.[4] Since 2012, Pannell, Sortais, Darcel, Lugan and others have demonstrated hydrosilylation of DMF, carboxylic acids, aldehydes and ketones catalyzed mainly by $CpMnL(CO)_2$ (L = ligand) complex under photoirradiation.[5] Recently, Du, Trovitch and Huang have achieved pincer-type manganese catalyzed hydrosilylation of aldehydes, ketones, and esters.[6 Of note, most manganese-catalyzed hydrosilylation has been focused on the reduction of carbonyls so far, while only sporadic substrates of terminal olefin was preliminarily tried for hydrosilylation of C-C unsaturated bonds.[7]

Silyl-substituted alkenes are highly attractive building blocks owing to their non-toxicity, stability, ease of handling and diverse transformations. Among all the synthetic routes to silyl-substituted alkenes, hydrosilylation of alkynes is undoubtedly the most straightforward approach with 100% atom economy. However, manganese-catalyzed hydrosilylation of alkynes has remained elusive till now. We envision that the underlying challenges have to be met for harnessing such a process: (i) the lower polarity of the C-C triple bond compared to the C=O bond of carbonyls; (ii) the control of stereo- and regio-



Scheme 1. Mn-catalyzed hydrosilylation of unsaturated molecules.

selectivity for unsymmetrical alkynes; (iii) the undesired formation of hydrogenation byproducts. With these regard and as our continous interest on earth-abundant manganese catalysis,[8,9] herein we disclosed the first manganese-catalyzed hydrosilylation of alkynes with high stereo- and regioselectivity (Scheme 1b). Remarkably, the catalytic use of mononuclear $MnBr(CO)_5$ with the ligand of $AsPh_3$ could deliver the *E*-products in excellent stereoselectivity. On the contrary, dinuclear $Mn_2(CO)_{10}$ with LPO enabled the formation of *Z*-products in a reversed stereoselectivity. Such a control on stereodivergency highlights an unique feature of manganese catalysis, namely dichotomy of organometallic and radical mechanism.

At the outset, diphenylacetylene **1a** and phenylsilane **2a** were chosen as model substrates to screen reaction parameters (Table 1).[10] The hydrosilylation products **3aa** and **4aa** were formed in low yields with poor *E*/*Z* selectivity when **1a** was treated with **2a** in the presence of $Mn(CO)_5Br$ (**7**) (entry 1). Of note, the hydrogenation proucts **5** and **6** were also detected in noticeable yields. To our delight, the addition of PPh_3 dramatically increased the *E*/*Z* ratio to 15:1 (entry 2). The preformed $Mn(CO)_4(PPh_3)Br$ (**8**) complex showed a slightly decreased selectivity (entry 3). Other ligands had inhibitory effects on the reaction (entries 4-6).[10] Further variations on the reaction concentration and ratio of substrates gave higher yields of products, albeit with worse chemo- and stereoselectivity (entry 7). Gratifyingly, the use of triphenylarsine and triphenylantimony as ligands led to clear increasements in both the chemo- and the

[*] X. Yang, Prof. C. Wang
Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China
E-mail: wangcy@iccas.ac.cn
Homepage: http://wangcy.iccas.ac.cn/
X. Yang, Prof. C. Wang
University of Chinese Academy of Sciences, Beijing 100049, China

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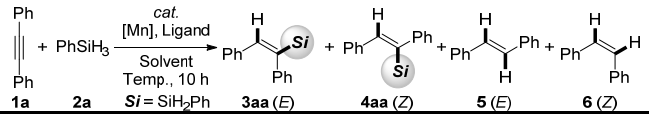
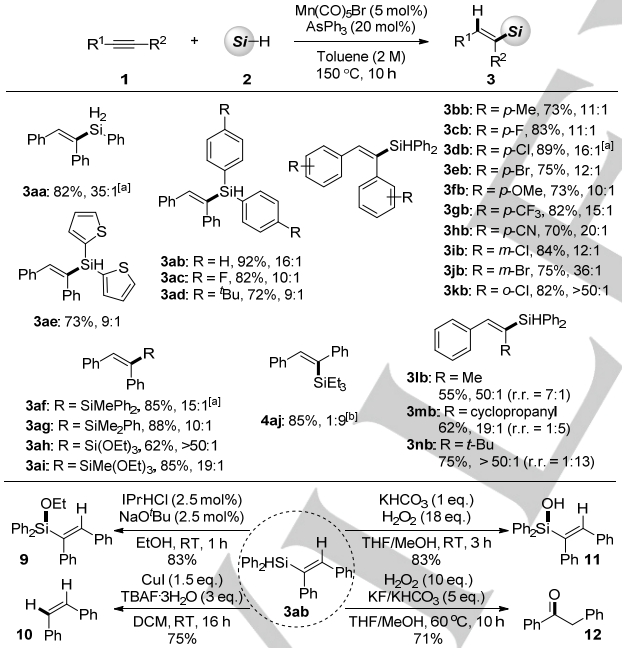
E/*Z* selectivity (entries 8-10). The optimized conditions were defined as shown in entry 8 considering the ligand econony.

Table 1. Optimization of *E*-selective hydrosilylation[a,b,c]



Entry	Cat. (5 mol%)	Ligand (20 mol%)	**5**	**6**	**3aa**	**4aa**	*E*/*Z*
1	**7**	--	6	5	14	11	1.3:1
2	**7**	PPh_3	3	3	31	2	15:1
3	**8**	--	6	6	29	3	10:1
4	**7**	PCy_3	3	3	1	<1	--
5	**7**	dppe	1	1	1	--	--
6	**7**	2,2'-bipyridine	1	1	1	<1	--
7[d]	**7**	PPh_3	12	8	61	7	8:1
8[d]	**7**	$AsPh_3$	**2**	**2**	**70**	**3**	**25:1**
9[d]	**7**	$SbPh_3$	5	4	76	4	19:1
10[d,e]	**7**	$AsPh_3$	3	2	85	2	43:1

[a] Reaction conditions unless otherwise noted: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (0.01 mmol), ligand (0.04 mmol), 150 °C, toluene (0.2 M), 12 h. [b] Yields and *E*/*Z* were determined by GC-MS. [c] **7** = $Mn(CO)_5Br$, **8** = $Mn(CO)_4(PPh_3)Br$. [d] Toluene (2 M), **1a**:**2a** = 1:1.5. [e] $AsPh_3$ (50 mol%).

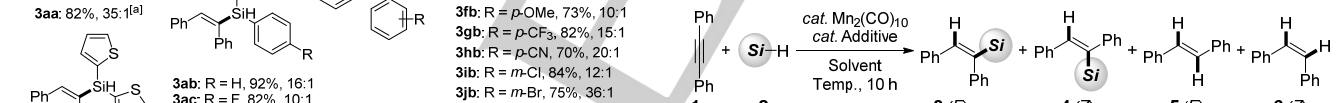


Scheme 2. Mn-catalyzed *E*-selective hydrosilylation of alkynes. Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), $Mn(CO)_5Br$ (5 mol%), $AsPh_3$ (20 mol%), toluene (2 M), 150 °C, 10 h. Combined isolated yield was shown. *E*/*Z* ratio was determined by GC-MS. r.r. = regioisomeric ratio. [a] $AsPh_3$ (50 mol%). [b] No $AsPh_3$.

Then, the substrate scope for *E*-selective hydrosilylation of alkynes was investigated (Scheme 2). A wide range of mono-, di-, and tri-substituted aromatic or aliphatic silanes was successfully applied to this protocol giving the *E*-configured products in high yields with good to excellent stereoselectivity (**3aa**-**g**). Importantly, the industrially relavent $HSi(OEt)_3$ and $HSiMe(OEt)_2$ were successfully applicable to this protocol (**3ah**, **3ai**). Suprisingly, the *Z*-configured product was formed predominantly when Et_3SiH was used in the reaction despite the underlying reason remaining unclear (**4aj**). Variations on the electronic property of alkynes had no obvious effect on the reaction outcome (**3bb**-**hb**). It is noteworthy that susceptible fluoro, chloro and bromo groups could be preserved after reaction, which provides handles for further synthetic elaborations (**3cb**-**eb**). The existence of *meta*- and *ortho*-substituents on the phenyl moiety of alkynes was well tolerated with the later showing enhanced *E*-selectivity (**3ib**-**kb**). Phenyl alkyl alkynes were also amenable to the reaction conditions leading to **3lb**-**nb** in excellent *E*/*Z* selectivity and moderate to good regioselectivity, the later of which seemed depending on the steric properties of substituents of the alkyne. The synthetic potentials of the hydrosilylation products were illustrated by derivatization reactions of **3ab**.[10]

Surprisingly, the *E*/*Z* selectivity was reversed when the dinuclear manganese catalyst, $Mn_2(CO)_{10}$ (**13**), was used in the reaction of **1a** with **2a** (Table 2, entries 1,2). The addition of PPh_3 favored the *E*-product again though the selectivity was lower than that using the mono-nuclear $MnBr(CO)_5$ catalyst (entry 3), which highlights the importance of manganese/ligand cooperation in controling the *E*-selectivity. We envisioned that the homolysis of the Mn-Mn bond in $Mn_2(CO)_{10}$ might occur in the reaction. Therefore, radical promoters were tested and, luckily, the use of a catalytic amount of dilauroyl peroxide (LPO) delivered the desired *Z*-product in enhanced yields (entries 4-6). Further variations on silanes showed that better *Z*-selectivity was obtained with more sterically bulky silanes used (entries 7-10). In view of both the yield and the selectivity, parameters of entry 9 were chosen as the optimized conditions for *Z*–selective hydrosilylation.

Table 2. Optimization of *Z*-selective hydrosilylation[a,b]



Entry	Silane	Additive (20 mol%)	**5**	**6**	**3**	**4**	*E*/*Z*
1[c,d]	$PhSiH_3$	--	13	9	13	41	1:3
2	$PhSiH_3$	--	8	6	16	60	1:4
3[c,d]	$PhSiH_3$	PPh_3	5	7	29	11	3:1
4[d]	$PhSiH_3$	AIBN	2	3	19	58	1:3
5[d]	$PhSiH_3$	LPO	5	3	18	68	1:4
6	$PhSiH_3$	LPO	1	2	19	77	1:4
7	Ph_2SiH_2	LPO	1	1	15	81	1:5
8	$PhMe_2SiH$	LPO	1	2	13	67	1:5
9	Ph_2MeSiH	LPO	**1**	**1**	**8**	**82**	**1:10**
10	$(TMS)_3SiH$	LPO	1	3	1	25	1:30

[a] Reaction conditions unless otherwise noted: **1a** (0.2 mmol), **2** (0.4 mmol), $Mn_2(CO)_{10}$ (0.02 mmol), additive (0.04 mmol), decalin (0.2 M), 120 °C, 10 h. [b] Yields and *E*/*Z* were determined by GC-MS. [c] Toluene (0.2 M). [d] **1a**:**2a** = 1:1. AIBN = azobisisobutyronitrile, LPO = dilauroyl peroxide, $(n\text{-}C_{11}H_{23}COO)_2$.

Next, the generality of *Z*-selective hydrosilylation was tested (Scheme 3). Internal alkynes bearing varied substituents are suitable for this reaction, thus leading to the *Z*-products in good yields and high *Z*/*E* selectivity (**4af**-**of**). For aryl alkyl alkynes, not

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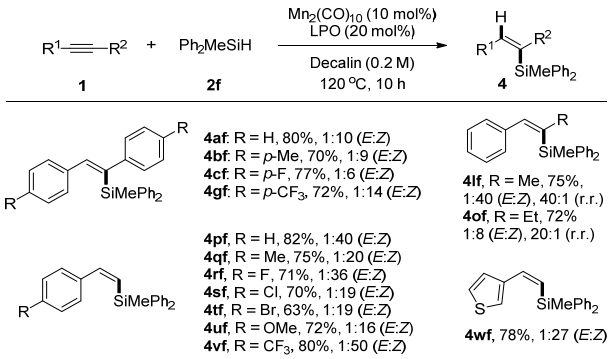
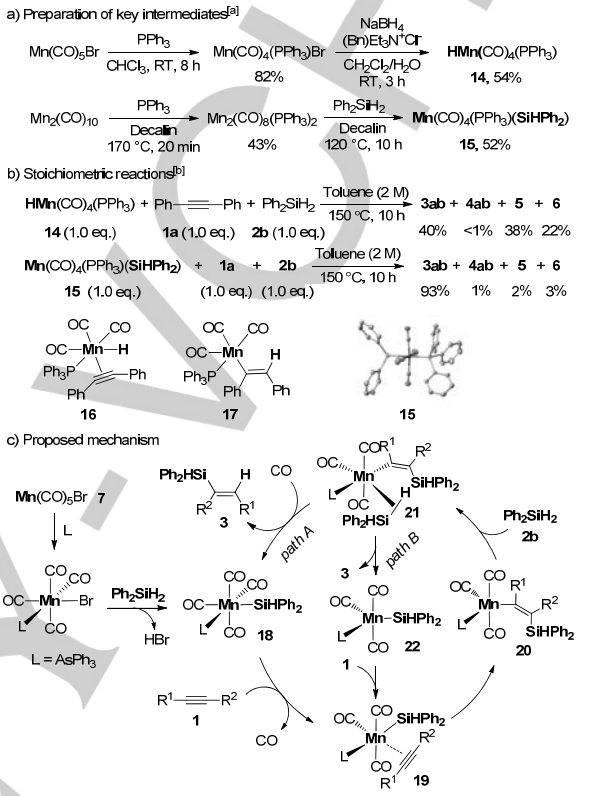
only good to excellent stereoselectivity but also very high regioselecitvity were achieved favoring products with the silyl group placed adjacent to the alkyl moiety (**4lf**, **4of**). Remarkably, a series of functional groups on the phenyl moiety of terminal alkynes including delicate halogens were amenable to this protocol affording the *Z*-products in good yields and excellent selectivity (**4pf**-**vf**). 3-Ethylylthiophene was also compatible to the reaction conditions giving **4wf** smoothly with high level of control on stereoselectivity.



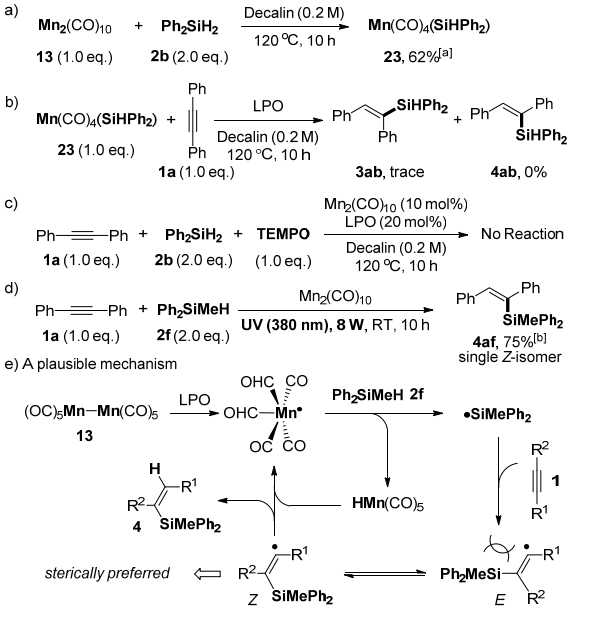
Scheme 3. Mn-catalyzed *Z*-selective hydrosilylation of alkynes. Reaction conditions: **1** (0.5 mmol), **2f** (1.0 mmol), $Mn_2(CO)_{10}$ (10 mol%), LPO (20 mol%), decalin (0.2 M), 120 °C, 10 h. Combined isolated yield was shown. *E*/*Z* ratio and regioisomeric ratio (r.r.) were detected by GC-MS.

In order to probe the possible mechanism of mononuclear $Mn(CO)_5Br$-catalyzed *E*-selective hydrosilylation reaction, a series of experiments was carried out. Firstly, **H**$Mn(CO)_4(L)$ and $Mn(CO)_4(L)$(**SiHPh$_2$**) species were assumed as the key reaction intermediates. Therefore, two representive manganese complexes **14** and **15** using PPh_3 as a ligand were prepared respectively (Scheme 4a). The structure of **15** was unambiguously confirmed by single-crystal X-ray analysis.[11] Next, we examined the stoichiometric reactions of alkyne **1a** and silane **2b** with the Mn-H species **14** and Mn-Si species **15** respectively (Scheme 4b). The hydrogenation products, stilbenes **5** and **6**, were detected as the major ones (60% GC-MS yield together), which suggested the preferred formation of hydrogenation products than hydrosilyation products from alkenyl-Mn species **17**, which was generated from **14** and **1a** through intermediate **16**. Consequently, the hydrogenation products **5** and **6** should be the major products if the Mn-H species **14** is the active species in the catalytic reaction, which is contrary to our experimental results (Table 1, entry 2). On the other hand, the Mn-Si species **15** reacted with **1a** and **2b** affording the desired hydrosilylation products **3ab** and **4ab** in excellent *E*/*Z* selectivity with the hydrogenation products **5** and **6** nicely repressed. It clearly indicated that the Mn-Si rather than Mn-H species was the active intermediate in Mn-catalyzed *E*-selective hydrosilylation reaction. Therefore, a plausible mechanism was depicted in Scheme 4c. The reaction starts with a ligand replacement and silylation giving the Mn-Si species **18**. It undergoes a CO-alkyne exchange (**19**) and insertion of alkyne into the Mn-Si bond giving a (β-silyl)alkenyl-Mn intermediate **20**. The coordination and σ-bond metathesis of **20** with silane via **21** leads to product **3** and regenerates the Mn-Si species **18**, thus closing the catalytic cycle (path A). Alternatively, species **21** could release product **3** directly affording intermediate **22**, which reacted with alkyne **1** to regenerate complex **19** (path B).

To test whether the Mn-Si species was also a key intermediate for the dinuclear $Mn_2(CO)_{10}$-catalyzed *Z*-selective hydrosilylation, the Mn-Si complex **23** was prepared from $Mn_2(CO)_{10}$ and silane **2b** in 62% isolated yield (Scheme 5a). Then a reaction of **23** and alkyne **1a** was examined, however, only a negligible amount of **3ab** were detected (Scheme 5b), which excludes **23** as a possible intermediate in *Z*-selective



Scheme 4. Mechanistic studies on *E*-selective hydrosilylation. [a] Isolated yields. [b] GC-MS yields.



Scheme 5. Mechanistic studies on *Z*-selective hydrosilylation. [a] Isolated yields. [b] GC-MS yields.

hydrosilylation reaction. We surmised that a radical mechanism might operate in the reaction based on the fact that the radical initiator, LPO, could promote the reaction. Therefore, a radical scavenger, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), was added and it completely inhibited the reaction (Scheme 5c). Besides, it was reported that $(CO)_5Mn\cdot$ was generated via homolysis of $Mn_2(CO)_{10}$ under UV irradiation.[12] As such, the *Z* hydrosilylation reaction was tested without LPO under 380 nm UV irradiation at room temperature and the hydrosilylation products were formed in 75% yield with consistent *Z*-selectivity (Scheme 5d). In view of these results, a radical mechanism was shown in Scheme 5e. The homolysis of $Mn_2(CO)_{10}$ occurs to generate $(CO)_5Mn\cdot$, which reacts with silane giving a silyl radical and $HMn(CO)_5$. The silyl radical adds to the alkyne to afford *E*- and *Z*-configured alkenyl radicals, which undergo hydrogenolysis with $HMn(CO)_5$ to form the desired product **4** and regenerate the $(CO)_5Mn\cdot$ species. The hydrogenolysis of the *Z*-alkenyl radical was preferred presumably due to the steric hindrance of the diphenylmethylsilyl group.[13]

In summary, the first manganese-catalyzed hydrosilylation of alkynes is developed, which is highlighted by divergent *E*/*Z* stereoselectivity. The cooperative use of the mononuclear $MnBr(CO)_5$ and the $AsPh_3$ ligand enables highly selective formation of *E*-products while the catalytic combination of dinuclear $Mn_2(CO)_{10}$ with LPO delivers the *Z*-products in good to excellent stereo- and regioselectivity. Mechanistically, the herein observed dichotomy of manganese catalysis through either organometallic or radical pathways is unique and holds great potentials for developing new synthetic transformations, which are underway in our laboratory.

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Keywords: hydrosilylation • alkynes • manganese • selectivity • synthetic methods

[1] a) *Comprehensive Handbook on Hydrosilylation* (Ed.: B. Marcinec), Pergamon, Oxford, **1992**; b) *Hydrosilylation: A Comprehensive Review on Recent Advances* (Ed.: B. Marciniec), Springer, Berlin, **2009**.

[2] For selected recent examples, see Ru: a) S. Ding, L. J. Song, L. W. Chung, X. Zhang, J. Sun, Y. D. Wu, *J. Am. Chem. Soc.* **2013**, *135*, 13835-13842; b) S. Ding, L. J. Song, Y. Wang, X. Zhang, L. W. Chung, Y. D. Wu, J. Sun, *Angew. Chem. Int. Ed.* **2015**, *54*, 5632-5635; *Angew. Chem.* **2015**, *127*, 5724-5727; Rh: c) A. Mori, E. Takahisa, Y. Yamanura, T. Kato, A. P. Mudalige, H. Kajiro, K. Hirabayashi, Y. Nishihara, T. Hiyama, *Organometallics* **2004**, *23*, 1755-1765; Pt: d) G. Berthon-Gelloz, J. M. Schumers, G. De Bo, I. E. Marko, *J. Org. Chem.* **2008**, *73*, 4190-4197; e) Y. Sumida, T. Kato, S. Yoshida, T. Hosoya, *Org. Lett.* **2012**, *14*, 1552-1555; Fe: f) M. D. Greenhalgh, A. S. Jones, S. P. Thomas, *ChemCatChem* **2015**, *7*, 190-222; g) X. Du, Z. Huang, *ACS Catalysis* **2017**, *7*, 1227-1243; h) A. M. Tondreau, C. C. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. Delis, P. J. Chirik, *Science* **2012**, *335*, 567-570; i) C. Belger, B. Plietker, *Chem. Commun.* **2012**, *48*, 5419-5421; j) A. J. Challinor, M. Calin, G. S. Nichol, N. B. Carter, S. P. Thomas, *Adv. Synth. Catal.* **2016**, *358*, 2404-2409; Co: k) J. Sun, L. Deng, *ACS Catalysis* **2016**, *6*, 290-300; l) Z. Mo, J. Xiao, Y. Gao, L. Deng, *J. Am. Chem. Soc.* **2014**, *136*, 17414-17417; m) C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix, P. L. Holland, *J. Am. Chem. Soc.* **2015**, *137*, 13244-13247; n) J. Guo, Z. Lu, *Angew. Chem. Int. Ed.* **2016**, *55*, 10835-10838; *Angew. Chem.* **2016**, *128*, 10993-10996; o) Z. Zuo, J. Yang, Z. Huang, *Angew. Chem. Int. Ed.* **2016**, *55*, 10839-10843; *Angew. Chem.* **2016**, *128*, 10997-11001; p) W. J. Teo, C. Wang, Y. W. Tan, S. Ge, *Angew. Chem. Int. Ed.* **2017**, *56*, 4328-4332; *Angew. Chem.* **2017**, *129*, 4392-4396; Ni: q) I. Buslov, J. Becouse, S. Mazza, M. Montandon-Clerc, X. Hu, *Angew. Chem. Int. Ed.* **2015**, *54*, 14523-14526; *Angew. Chem.* **2015**, *127*, 14731-14734; Cu: r) M. W. Gribble, Jr., M. T. Pirnot, J. S. Bandar, R. Y. Liu, S. L. Buchwald, *J. Am. Chem. Soc.* **2017**, *139*, 2192-2195.

[3] R. L. Yates, *J. Catal.* **1982**, *78*, 111-115.

[4] a) P. K. Hanna, B. T. Gregg, A. R. Cutler, *Organometallics* **1991**, *10*, 31; b) B. T. Gregg, P. K. Hanna, E. J. Crawford, A. R. Cutler, *J. Am. Chem. Soc.* **1991**, *113*, 384-385; c) Z. Mao, B. T. Gregg, A. R. Cutler, *J. Am. Chem. Soc.* **1995**, *117*, 10139; d) B. T. Gregg, A. R. Cutler, *J. Am. Chem. Soc.* **1996**, *118*, 10069-10084; e) M. DiBiase Cavanaugh, B. T. Gregg, A. R. Cutler, *Organometallics* **1996**, *15*, 2764-2769.

[5] a) R. Arias-Ugarte, H. K. Sharma, A. L. Morris, K. H. Pannell, *J. Am. Chem. Soc.* **2012**, *134*, 848-851; b) J. Zheng, S. Chevance, C. Darcel, J. B. Sortais, *Chem. Commun.* **2013**, *49*, 10010-10012; c) J. Zheng, S. Elangovan, D. A. Valyaev, R. Brousses, V. César, J.-B. Sortais, C. Darcel, N. Lugan, G. Lavigne, *Adv. Synth. Catal.* **2014**, *356*, 1093-1097; d) D. A. Valyaev, D. Wei, S. Elangovan, M. Cavailles, V. Dorcet, J.-B. Sortais, C. Darcel, N. Lugan, *Organometallics* **2016**, *35*, 4090-4098.

[6] a) V. K. Chidara, G. Du, *Organometallics* **2013**, *32*, 5034-5037; b) T. K. Mukhopadhyay, M. Flores, T. L. Groy, R. J. Trovitch, *J. Am. Chem. Soc.* **2014**, *136*, 882-885; c) T. K. Mukhopadhyay, C. L. Rock, M. Hong, D. C. Ashley, T. L. Groy, M. H. Baik, R. J. Trovitch, *J. Am. Chem. Soc.* **2017**, *139*, 4901-4915; d) X. Ma, Z. Zuo, G. Liu, Z. Huang, *ACS Omega* **2017**, *2*, 4688-4692.

[7] a) H. S. Hilal, M. Abu-Eid, M. Al-Subu, S. Khalaf, *J. Mol. Catal.* **1987**, *39*, 1-11; b) H. S. Hilal, M. A. Suleiman, W. J. Jondi, S. Khalaf, M. M. Masoud, *J. Mol. Catal. A: Chem.* **1999**, *144*, 47-59; c) S. L. Pratt, R. A. Faltynek, *J. Organomet. Chem.* **1983**, *258*, C5-C8; d) C. Obradors, R. M. Martinez, R. A. Shenvi. *J. Am. Chem. Soc.* **2016**, *138*, 4962-4971; e) J. H. Docherty, J. Peng, A. P. Dominey, S. P. Tomas, *Nat. Chem.* **2017**, *9*, 595; f) S. K. Russell, A. C. Bowman, E. Lobkovsky, K. Wieghardt, P. J. Chirik, *Eur. J. Inorg. Chem.* **2012**, 535-545.

[8] a) B. Zhou, H. Chen, C. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 1264–1267; b) R. He, Z.-T. Huang, Q.-Y. Zheng, C. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 4950–4953; *Angew. Chem.* **2014**, *126*, 5050–5053; c) R. He, X. Jin, H. Chen, Z.-T. Huang, Q.-Y. Zheng, C. Wang, *J. Am. Chem. Soc.* **2014**, *136*, 6558–6561; d) B. Zhou, Y. Hu, C. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 13659–13663; *Angew. Chem.* **2015**, *127*, 13863–13867; e) B. Zhou, Y. Hu, T. Liu, C. Wang, *Nat. Commun.* **2017**, *8*, DOI: 10.1038/s41467-017-01262-4.

[9] For selected recent examples, see: a) H. Wang, M. M. Lorion, L. Ackermann, *Angew. Chem. Int. Ed.* **2017**, *56*, 6339–6342; *Angew. Chem.* **2017**, *129*, 6436–6439; b) S.-Y. Chen, X.-L. Han, J.-Q. Wu, Q. Li, Y. Chen, H. Wang, *Angew. Chem. Int. Ed.* **2017**, *56*, 9939–9943; *Angew. Chem.* **2017**, 129, 10071–10075; c) C. Wang, A. Wang, M. Rueping, *Angew. Chem. Int. Ed.* **2017**, *56*, 9935–9938; *Angew. Chem.* **2017**, *129*, 10067–10070; d) Q. Lu, S. Greßies, F. J. R. Klauck, F. Glorius, *Angew. Chem. Int. Ed.* **2017**, *56*, 6660–6664; *Angew. Chem.* **2017**, *129*, 6760–6764; e) N. P. Yahaya, K. M. Appleby, M. Teh, C. Wagner, E. Troschke, J. T. W. Bray, S. B. Duckett, L. A. Hammarback, J. S. Ward, J. Milani, N. E. Pridmore, A. C. Whitwood, J. M. Lynam, I. J. S. Fairlamb, *Angew. Chem. Int. Ed.* **2016**, *55*, 12455– 12459; *Angew. Chem.* **2016**, *128*, 12643–12647; f) Y. Kuninobu, Y. Nishina, T. Takeuchi, K. Takai, *Angew. Chem. Int. Ed.* **2007**, *46*, 6518–6520; *Angew. Chem.* **2007**, *119*, 6638–6640; g) A. Mukherjee, A. Nerush, G. Leitus, L. J. W. Shimon, Y. B. David, N. A. E. Jalapa, D. Milstein, *J. Am. Chem. Soc.* **2016**, *138*, 4298–4301; h) S. Elangovan, J. Neumann, J.-B. Sortais, K. Junge, C. Darcel, M. Beller, *Nat. Commun.* **2016**, *7*, 12641–12648.

[10] For more details, see the Supporting Information.

[11] CCDC 1577774.

[12] B. C. Gilbert, W. Kalz, C. I. Lindsay, P. T. McGrail, A. F. Parsons, D. T. E. Whittaker, *J. Chem. Soc., Perkin Trans. 1* **2000**, 1187–1194.

[13] a) B. Kopping, C. Chatgilialoglu, M. Zehnder, B. Giese, *J. Org. Chem.* **1992**, *57*, 3994-4000; b) Y. Liu, S. Yamazaki, S. Yamabe, *J. Org. Chem.* **2005**, *70*, 556-561.

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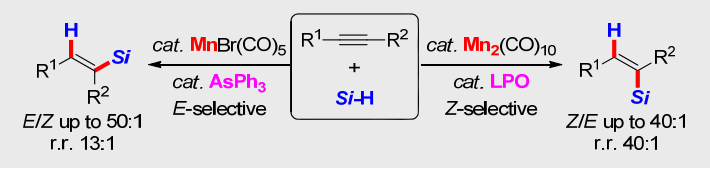

*X. Yang, C. Wang**

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Dichotomy of Manganese Catalysis via Organometallic or Radical Mechanism: Stereodivergent Hydrosilylation of Alkynes

Dichotomy of Man(ganese): The first manganese-catalyzed hydrosilylation of alkynes featuring diverse selectivities is developed. Highly selective formation of *E*-products was achieved by using mononuclear $MnBr(CO)_5$ with $AsPh_3$. On the contrary, the dinuclear catalyst $Mn_2(CO)_{10}$ together with LPO (dilauroyl peroxide) enabled the reversed generation of *Z*-products. Mechanistic experiments revealed the dichotomy of manganese catalysis *via* organometallic and radical pathways.