

VIP Oxidation Very Important Paper

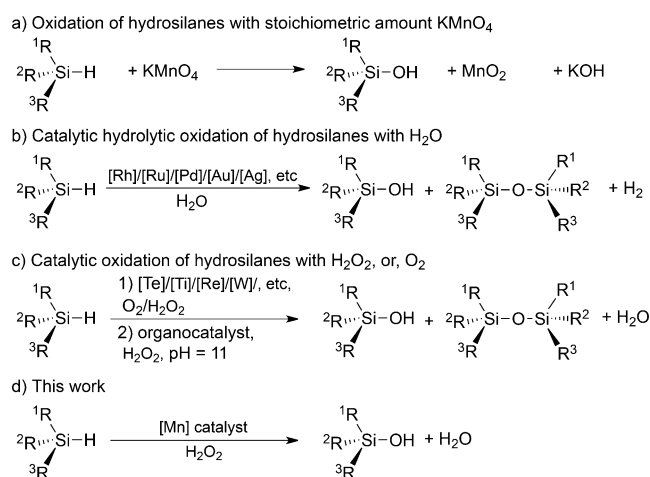
International Edition: DOI: 10.1002/anie.201900342
German Edition: DOI: 10.1002/ange.201900342

Selective Manganese-Catalyzed Oxidation of Hydrosilanes to Silanols under Neutral Reaction Conditions

Kaikai Wang, Jimei Zhou, Yuting Jiang, Miaomiao Zhang, Chao Wang, Dong Xue, Weijun Tang, Huamin Sun, Jianliang Xiao,* and Chaoqun Li*

Abstract: The first manganese-catalyzed oxidation of organosilanes to silanols with H_2O_2 under neutral reaction conditions has been accomplished. A variety of organosilanes with alkyl, aryl, alkenyl, and heterocyclic substituents were tolerated, as well as sterically hindered organosilanes. The oxidation appears to proceed by a concerted process involving a manganese hydroperoxide species. Featuring mild reaction conditions, fast oxidation, and no waste byproducts, the protocol allows a low-cost, eco-benign synthesis of both silanols and silanediols.

Silanols have found broad applications as monomers for silicon-based polymers,^[1,2] functional groups of drugs,^[1,3] directing groups for C–H functionalization,^[1,4] donors for metal-catalyzed coupling reactions,^[1,5] and organocatalysts^[1,6] (see Figure S1 in the Supporting Information). Whilst less bulky silanols can be synthesized by hydrolysis of chlorosilanes under strictly controlled conditions, it is difficult to synthesize sterically hindered silanols, silanediols, and silanols with functional groups sensitive to hydrolytic conditions.^[1,7] Silanols can also be synthesized by oxidation of organosilanes^[1a,b] with strong oxidants, such as silver salts,^[8a] permanganate,^[8b] osmium tetroxide,^[8c] dioxiranes,^[8d] peracids,^[8e] oxaziridines,^[8f] and ozone.^[8g,h] Apart from generating stoichiometric amounts of waste, these methods are often accompanied with problems of selectivity, for example, producing undesired siloxanes by condensation of two molecules of silanol, or byproducts resulting from silanol decomposition.^[8] For example, in the oxidation of organosilanes with permanganate, silanols and silanediols were obtained with poor selectivity in addition to the formation of wasteful MnO_2 (Scheme 1 a).^[8b] Furthermore, as the reaction conditions are basic, base-catalyzed rearrangement can take



Scheme 1. Synthesis of silanols by oxidation of hydrosilanes.

place.^[8b] Catalytic oxidation of Si–H bonds with a clean oxidant and high selectivity is still a challenge.

Noble metal catalysts, for example, those based on Rh,^[9a] Cu,^[9b] Re,^[9c] Ru,^[9d] Pd,^[9e] Ir,^[9f] Au,^[9g–i] and Ag,^[9j,k] have been demonstrated to promote efficient oxidation of hydrosilanes to silanols with hydrogen gas formation. However, such hydrolytic oxidation cannot completely avoid the formation of disiloxane byproducts because the silanol product itself may react with the hydrosilane (Scheme 1 b).^[9,1a] Whilst water is an ideal oxidant, O_2 and H_2O_2 are also cheap and environmentally friendly in comparison with other stoichiometric oxidants.^[8] A few catalysts based on Ti,^[10a,b] Re,^[10c,d] Te,^[10e] and W^[10f] have been explored for the oxidation of hydrosilanes by using either H_2O_2 or O_2 as the oxidant. However, disiloxanes were also formed with these catalysts (Scheme 1 c).^[10] More recently, trifluoroacetophenone was reported to catalyze the oxidation of hydrosilanes with H_2O_2 , affording a series of silanols with excellent yields and selectivities, but requiring strictly pH-controlled buffer conditions (Scheme 1 c).^[11] Clearly, although transition metal catalyzed hydrolytic oxidation and oxidation with H_2O_2 now allow oxidation of hydrosilanes to silanols, few of the reported catalytic systems can avoid the formation of disiloxane or other byproducts. Therefore, it remains valuable to develop a more efficient catalytic system that features a cheap, environmentally friendly catalyst and operates under neutral conditions for the oxidation of organosilanes to silanols.

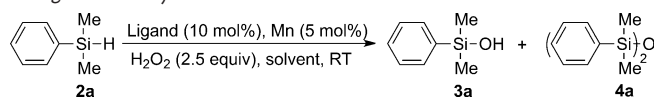
Whilst manganese-catalyzed oxidation of C=C and C(sp³)–H bonds with H_2O_2 has been studied extensively, no examples of the oxidation of organosilanes with a manganese catalyst have ever been reported.^[12] Owing to the impor-

[*] K. K. Wang, J. M. Zhou, Y. T. Jiang, M. M. Zhang, Prof. Dr. C. Wang, Prof. Dr. D. Xue, Prof. Dr. W. J. Tang, Dr. H. M. Sun, Prof. Dr. J. L. Xiao, Prof. Dr. C. Q. Li
Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education and School of Chemistry and Chemical Engineering, Shaanxi Normal University
Xi'an, 710119 (China)
E-mail: lichaoqun@snnu.edu.cn
Prof. Dr. J. L. Xiao
Department of Chemistry, University of Liverpool
Liverpool, L69 7ZD (UK)
E-mail: j.xiao@liverpool.ac.uk

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/anie.201900342>.

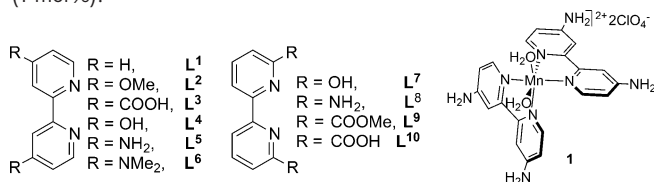
tance of silanols and our interest in catalytic oxidation,^[13] we thought it would be interesting to develop a more selective catalytic system based on cheap, eco-benign manganese as a catalyst and H₂O₂ as an oxidant for the oxidation of organosilanes (Scheme 1d). Initially, we chose dimethyl(phenyl)silane (**2a**) as the model substrate to identify possible catalysts for the oxidation using H₂O₂ in an acetone medium (Table 1). We quickly found that the simple manganese salt,

Table 1: Oxidation of dimethyl(phenyl)silane with H₂O₂ catalyzed by manganese catalysts.^[a]



Entry	Ligand	Manganese salt or complex 1	Solvent	Yield [%] 3a
1	none	Mn(ClO ₄) ₂ ·6 H ₂ O	acetone	0
2	L ¹	Mn(ClO ₄) ₂ ·6 H ₂ O	acetone	6
3	L ²	Mn(ClO ₄) ₂ ·6 H ₂ O	acetone	11
4	L ³	Mn(ClO ₄) ₂ ·6 H ₂ O	acetone	trace
5	L ⁴	Mn(ClO ₄) ₂ ·6 H ₂ O	acetone	26
6	L ⁵	Mn(ClO ₄) ₂ ·6 H ₂ O	acetone	99
7	L ⁶	Mn(ClO ₄) ₂ ·6 H ₂ O	acetone	75
8	L ⁷	Mn(ClO ₄) ₂ ·6 H ₂ O	acetone	trace
9	L ⁸	Mn(ClO ₄) ₂ ·6 H ₂ O	acetone	trace
10	L ⁹	Mn(ClO ₄) ₂ ·6 H ₂ O	acetone	trace
11	L ¹⁰	Mn(ClO ₄) ₂ ·6 H ₂ O	acetone	22
12	L ⁵	none	acetone	0
13 ^b	L ⁵	Mn(ClO ₄) ₂ ·6 H ₂ O	acetone	99
14	/	1 (1 mol%)	acetone	99

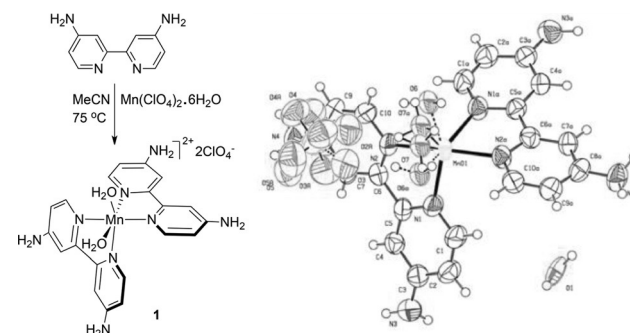
[a] General reaction conditions: **2a** (0.5 mmol), ligand (10 mol%), manganese salt (5 mol%), solvent (2 mL), room temperature in a reaction tube without nitrogen protection, 1 h, GC yield. **4a** was not observed in all the reactions. [b] **L**⁵ (2 mol%), Mn(ClO₄)₂·6 H₂O (1 mol%).



Mn(ClO₄)₂·6H₂O (5 mol%), had no catalytic activity for the target transformation (entry 1). The introduction of nitrogen ligands brought about changes. Thus, on combining the bipyridine **L**¹ (10 mol%) with Mn(ClO₄)₂·6H₂O (5 mol%), the silanol **3a** was formed in 6% yield (GC; entry 2). We then explored the electronic effect of ligand by using a range of 4,4'-disubstituted bipyridines (**L**¹–**L**⁶) and observed, remarkably, that the electron-rich 4,4'-diamino bipyridine **L**⁵ enabled an almost full oxidation of **2a** to **3a** with no formation of the disiloxane byproduct (entries 2–7). In sharp contrast, the electron-deficient **L**³ is ineffective. The steric effect is equally critical, as changing the ligand to 6,6'-disubstituted bipyridines brought about little oxidation of **2a** (entries 8–11). Further screening of other ligands as well as the combination of **L**⁵ with other manganese or iron salts demonstrated that **L**⁵, combined with Mn(ClO₄)₂, exhibits the best catalytic activity in the oxidation of **2a** with H₂O₂ (see Table A in the

Supporting Information). The catalyst loading could be lowered from 5 mol% to 1 mol% without affecting the yield of **3a** (Table 1, entry 13), but in the absence of Mn(ClO₄)₂, no reaction was observed (entry 12).

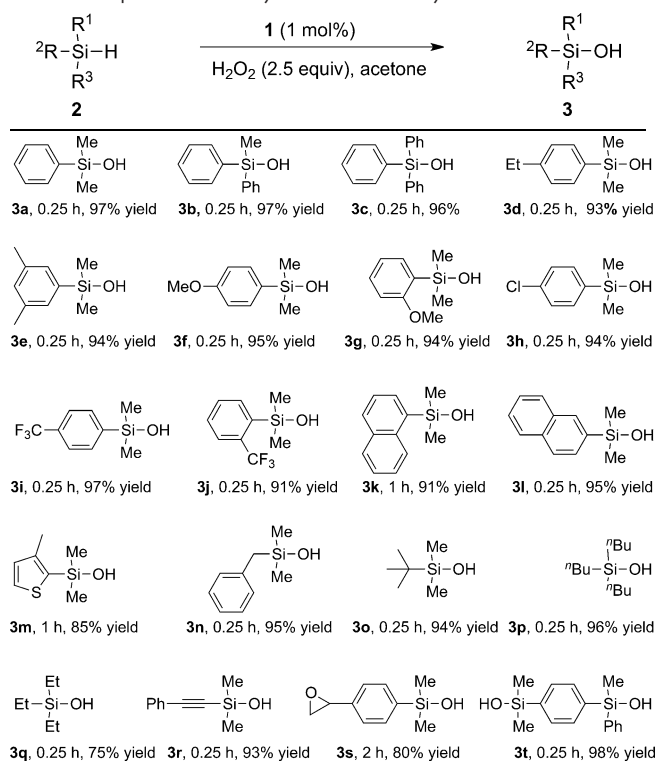
Reacting **L**⁵ with Mn(ClO₄)₂·6H₂O led to the complex **1** (Scheme 2). The structure of **1** has been determined by X-ray diffraction and shows a severely distorted octahedral geometry (see the Supporting Information for more details).



Scheme 2. Formation of **1** and its molecular structure determined by single-crystal X-ray diffraction.^[17] Thermal ellipsoids shown at 50% probability. Selected bond distances: MnO1–N1, 2.179(4) Å; MnO1–N2, 2.182(4) Å; MnO1–O6, 2.125(6) Å; MnO1–O7, 2.050(5) Å. Selected bond angles: N1–MnO1–N1a, 117.8(2)°; N1–MnO1–N2a, 100.47(16)°; N1–MnO1–N2, 74.24(16)°; N2–MnO1–N2a, 170.0(2)°.

The isolated **1** displayed a similar activity as that prepared in situ (Table 1, entries 13 and 14). Further screening led to the optimized oxidation conditions, that is, **1** (1 mol%) being the catalyst and H₂O₂ (2.5 equiv) as the oxidant in acetone at room temperature (see Table A). Under such neutral conditions, **2a** was oxidized to **3a** with high yield and no formation of any disiloxane byproduct (Table 1, entry 14). It is noted that compared with the literature reports on manganese-catalyzed oxidation reactions, acid or base additives suppressed, instead of promoted, the oxidation in question (see Table B in the Supporting Information).^[12]

Under the optimized reaction conditions, the catalytic system proved to be generally effective for the selective oxidation of various hydrosilanes into silanols in a short time (Table 2). Thus, the protocol was shown to tolerate sterically varied substituents in the substrates **2a–c**, affording the corresponding silanols **3a–c** in high yields without byproduct formation. Both electron-donating and electron-withdrawing phenyl substituents are suitable, leading to the silanol products with excellent yields (**3d–j**). Replacing the phenyl with 2-naphthyl did not affect the efficacy of the catalysis, but the sterically hindered 1-naphthyl necessitated a longer reaction time of 1 hour (**3k** vs. **3l**). A heterocyclic thiofuran-substituted silanol was also obtained in good yield in 1 hour (**3m**), as well as the benzyl- and alkyl-substituted silanols (**3n–q**). Notably, the substrate **2r**, with an alkynyl functional group was well tolerated under the oxidation conditions, affording the silanol **3r** in 93% yield. However, for the substrate **2s**, which contains a 4-vinyl substituent, both the hydride and C=C bond were oxidized, affording the silanol **3s** under the standard reaction conditions. Further-

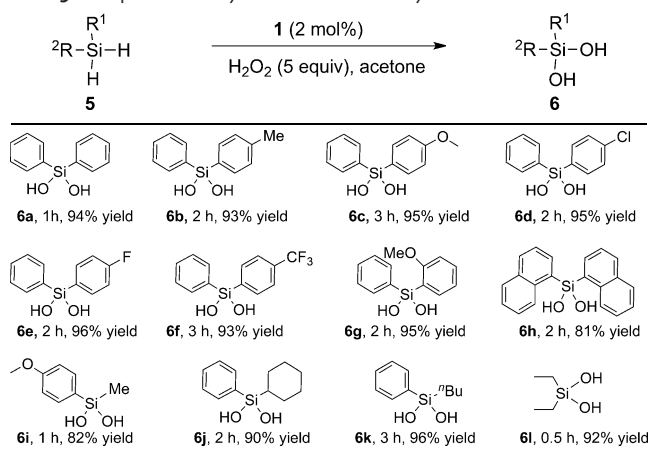
Table 2: Scope of the **1**-catalyzed oxidation of hydrosilanes.^[a]

[a] General reaction conditions: **2** (0.5 mmol), catalyst **1** (1 mol%), solvent (2 mL), room temperature in a reaction tube without nitrogen protection. Yield is that of the isolated product.

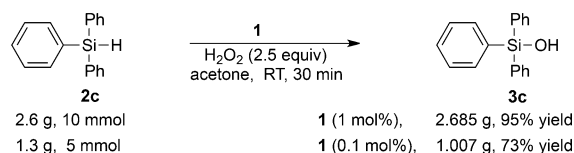
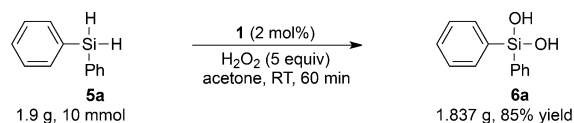
more, the substrate **2t**, with two SiH groups was completely oxidized to a silanediol in excellent yield (**3t**). The silanol **3s** with an epoxide and **3t** with two SiOH functional groups could be used as building blocks for materials synthesis.

Geminal silanediols have found applications in silicon-based materials,^[1,2] drugs,^[1,3] and organocatalysis^[1,6] (see Figure S1 in the Supporting Information). However, the synthesis of silanediols by transition metal catalyzed oxidation of dihydrosilanes is usually more difficult than that of silanols, because of the formation of disiloxanes and incomplete oxidation products.^[8–10] Our catalytic system is effective, allowing the oxidation of various substituted dihydrosilanes to silanediols. Thus, under the catalysis of **1** (2 mol%) with H₂O₂ (5 equiv) as the oxidant in acetone, dihydro diphenylsilane (**5a**) was oxidized to the silanediol **6a** in 94% yield in 1 hour (Table 3). Both electron-donating and electron-withdrawing aryl substituents are suitable, furnishing the silanediol products with excellent yields and without disiloxane formation (**6b–h**). Replacing one of the aryl substituents with an alkyl one did not significantly affect the product yields (**6i–k**). Oxidation of the less bulky dihydro diethylsilane **5l** led to the silanediol **6l**. Some of these diols have been used as organocatalysts for 1,4-addition reactions.^[6]

To further demonstrate the synthetic utility of the **1**-catalyzed oxidation of organosilanes, the bulky triphenylsilane **2c** and diphenylsilane **5a** were subjected to a gram-scale reaction. As shown in Scheme 3, the corresponding silanols **3c** and **6a** were obtained in excellent yields. Notably, this gram-

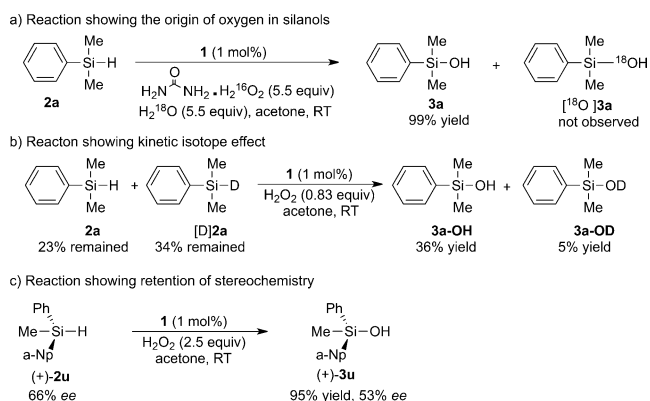
Table 3: Scope of **1**-catalyzed oxidation of dihydrosilanes.^[a]

[a] General reaction conditions: **5** (0.5 mmol), catalyst **1** (2 mol%), solvent (2 mL), room temperature in a reaction tube without nitrogen protection. Yield is that of the isolated product.

a) Catalytic oxidation of hydrosilane **2b** on gram scaleb) Catalytic oxidation of dihydrosilane **4a** on gram scale**Scheme 3.** Gram-scale oxidation of hydrosilanes.

scale oxidation could be performed at a lower catalyst loading of 0.1 mol%, as showcased by the conversion of **2c** into **3c**.

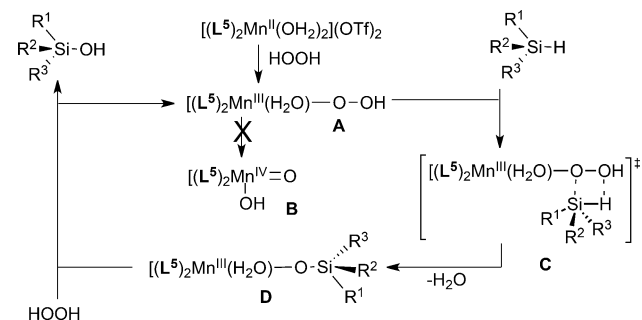
To gain insight into the oxidation mechanism, a few experiments were performed. In the absence of H₂O₂, but with the reaction open to the air, the model substrate **2a** did not undergo any oxidation in the presence of **1**, with or without water (see Table B). Upon introducing H₂¹⁸O (5.5 equiv) to the reaction under the standard conditions, **3a** was obtained in 99% yield, but no ¹⁸O-labeled silanol was observed by HRMS analysis (Scheme 4a). These observations indicate that neither molecular oxygen nor water is the oxygen source of the silanol product. A small but significant kinetic isotope effect, comparable to that observed in the polyoxotungstate-catalyzed oxidation of hydrosilanes,^[10f] could be seen in the oxidation of **2a** versus that of [D]**2a** (Scheme 4b),^[14] suggestive of the involvement of Si–H bond scission in the turnover-limiting step. To detect possible intermediate silane species, the oxidation of **2b** under the standard conditions was monitored with in situ IR spectroscopy by following the absorption at ν_{Si–H} = 806 cm^{–1} and ν_{Si–OH} = 874 cm^{–1}. The result indicates the oxidation to be complete in 20 minutes, and no other silane species accumulates during the oxidation (see Figure S1).



Scheme 4. Reactions aimed to probe the oxidation mechanism.

A more revealing experiment is the oxidation of an optically active hydrosilane (+)-**2u** (66% *ee*) with H_2O_2 under the catalysis of **1** (Scheme 4c). The reaction proceeded selectively to afford the corresponding silanol (+)-**3u** in 95% yield with 53% *ee*. Note the high degree in the retention of the configuration of silicon. This retention suggests that the oxidation in question may not involve either hetero- or homolysis of the Si–H bond before the formation of the silanol, but may rather proceed by a concerted process.^[8,10c,d,f]

Considering the observations above, we propose the following catalytic cycle for the oxidation catalyzed by **1** (Scheme 5). Initially, **1** reacts with H_2O_2 to form the active



Scheme 5. Proposed mechanism for the **1**-catalyzed oxidation of hydrosilanes.

hydroperoxide **A**. Although highly active manganese oxo species could be formed from **A** in the presence of an acid or water, the suppressing effect of acid on the oxidation (see Table B) and the lack of ^{18}O incorporation from H_2^{18}O mentioned above indicate that a species, such as **B**, is not involved in the oxidation.^[15] Instead, **A** might react directly with the hydrosilane by the transition-state **C**, involving concerted transfer of the silicon and hydride to the electrophilic hydroperoxide moiety of the manganese species to afford the siloxide **D**.^[15,16] Protonation of **D** by H_2O_2 then generates the silanol product and the active intermediate **A**, restarting the catalysis.

In conclusion, by harnessing the remarkable catalytic activity of the electron-rich manganese complex **1**, we have realized the highly efficient oxidation of organosilanes into

silanols with H_2O_2 under neutral conditions. A series of hydrosilanes and dihydrosilanes were oxidized to silanols and silanediols, respectively, within a short reaction time, with excellent yields and no waste byproduct formation. Preliminary mechanistic studies suggest that the oxidation may proceed by a concerted reaction of a $\text{Mn}^{\text{III}}\text{-OOH}$ species with the hydrosilane. Further investigations are in progress.

Acknowledgements

We gratefully acknowledge the financial support from the Fundamental Research Funds for the Central University (GK201603052), start-up funds from Shaanxi Normal University, Shaanxi Provincial Natural Science Foundation (2017JM2002), and the Program for Changjiang Scholars and Innovative Research Team in University (IRT_14R33), and the 111 project (B14041).

Conflict of interest

The authors declare no conflict of interest.

Keywords: manganese · oxidation · silanes · silanols · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2019**, *58*, 6380–6384
Angew. Chem. **2019**, *131*, 6446–6450

- [1] a) M. Jeon, J. Han, J. Park, *ACS Catal.* **2012**, *2*, 1539–1549; b) V. Chandrasekhar, R. Boomishankar, S. Nagendran, *Chem. Rev.* **2004**, *104*, 5847–5910; c) I. Ojima, Z. Li, J. Zhu in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Rappoport, Y. Apeloig), Wiley, New York, **1998**.
- [2] a) R. Murugavel, M. G. Walawalkar, M. Dan, H. W. Roesky, C. N. R. Rao, *Acc. Chem. Res.* **2004**, *37*, 763–774; b) P. D. Lickiss, *Adv. Inorg. Chem.* **1995**, *42*, 147–262.
- [3] a) A. K. Franz, S. O. Wilson, *J. Med. Chem.* **2013**, *56*, 388–405; b) R. Tacke in *Organosilicon and Bioorganosilicon Chemistry* (Ed.: H. Sakurai), Wiley, New York, **1985**.
- [4] a) M. Parasram, V. Gevorgyan, *Acc. Chem. Res.* **2017**, *50*, 2038–2053; b) M. Mewald, J. A. Schiffner, M. Oestreich, *Angew. Chem. Int. Ed.* **2012**, *51*, 1763–1765; *Angew. Chem.* **2012**, *124*, 1797–1799; c) C. Huang, B. Chattopadhyay, V. Gevorgyan, *J. Am. Chem. Soc.* **2011**, *133*, 12406–12409.
- [5] a) S. E. Denmark, A. Ambrosi, *Org. Process Res. Dev.* **2015**, *19*, 982–994; b) M. Mewald, J. A. Schiffner, M. Oestreich, *Angew. Chem. Int. Ed.* **2012**, *51*, 1763–1765; *Angew. Chem.* **2012**, *124*, 1797–1799; c) S. E. Denmark, C. S. Regens, *Acc. Chem. Res.* **2008**, *41*, 1486–1499; d) S. E. Denmark, R. F. Sweis in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**.
- [6] a) K. M. Diemoz, J. E. Hein, S. O. Wilson, J. C. Fettinger, A. K. Franz, *J. Org. Chem.* **2017**, *82*, 6738–6747; b) T. Min, J. C. Fettinger, A. K. Franz, *ACS Catal.* **2012**, *2*, 1661–1666; c) K. Motokura, N. Fujita, K. Mori, T. Mizugaki, K. Ebitani, K. Jitsukawa, K. Kaneda, *Chem. Eur. J.* **2006**, *12*, 8228–8239.
- [7] a) E. G. Rochow, W. F. Gilliam, *J. Am. Chem. Soc.* **1941**, *63*, 798–800; b) J. A. Cella, J. C. Carpenter, *J. Organomet. Chem.* **1994**, *480*, 23–26.

- [8] a) N. Duffaut, R. Calas, J.-C. Macé, *Bull. Chem. Soc. Fr.* **1959**, 1971–1973; b) P. D. Lickiss, R. Lucas, *J. Organomet. Chem.* **1995**, 521, 229–234; c) K. Valliant-Saunders, E. Gunn, G. R. Shelton, D. A. Hrovat, W. T. Borden, J. M. Mayer, *Inorg. Chem.* **2007**, 46, 5212–5219; d) W. Adam, R. Mello, R. Curci, *Angew. Chem. Int. Ed. Engl.* **1990**, 29, 890–891; *Angew. Chem.* **1990**, 102, 916–917; e) L. H. Sommer, L. A. Ulland, G. A. Parker, *J. Am. Chem. Soc.* **1972**, 94, 3469–3471; f) M. Cavicchioli, V. Montanari, G. Resnati, *Tetrahedron Lett.* **1994**, 35, 6329–6330; g) L. Spialter, J. D. Austin, *J. Am. Chem. Soc.* **1965**, 87, 4406; h) L. Spialter, L. Pazdernik, S. Bernstein, W. A. Swansiger, G. R. Buell, M. E. Freeburger, *J. Am. Chem. Soc.* **1971**, 93, 5682–5686.
- [9] a) M. Shi, K. M. Nicholas, *J. Chem. Res.* **1997**, 400–401; b) U. Schubert, C. Lorenz, *Inorg. Chem.* **1997**, 36, 1258–1259; c) E. A. Ison, R. A. Corbin, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2005**, 127, 11938–11939; d) M. Lee, S. Ko, S. Chang, *J. Am. Chem. Soc.* **2000**, 122, 12011–12012; e) G. H. Barnes, N. E. Daughenbaugh, *J. Org. Chem.* **1966**, 31, 885–887; f) Y. Lee, D. Seomoon, S. Kim, H. Han, S. Chang, P. H. Lee, *J. Org. Chem.* **2004**, 69, 1741–1743; g) T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Commun.* **2009**, 5302–5304; h) N. Asao, Y. Ishikawa, N. Hatakeyama, Menggenbateer, Y. Yamamoto, M. Chen, W. Zhang, A. Inoue, *Angew. Chem. Int. Ed.* **2010**, 49, 10093–10095; *Angew. Chem.* **2010**, 122, 10291–10293; i) J. John, E. Gravel, A. Hagege, H. Li, T. Gacoin, E. Doris, *Angew. Chem. Int. Ed.* **2011**, 50, 7533–7536; *Angew. Chem.* **2011**, 123, 7675–7678; j) T. Mitsudome, S. Arita, H. Mori, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Angew. Chem. Int. Ed.* **2008**, 47, 7938–7940; *Angew. Chem.* **2008**, 120, 8056–8058; k) Y. Kikukawa, Y. Kuroda, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **2012**, 51, 2434–2437; *Angew. Chem.* **2012**, 124, 2484–2487.
- [10] a) W. Adam, H. Garcia, C. M. Mitchell, C. R. Saha-Moller, O. Weichold, *Chem. Commun.* **1998**, 2609–2610; b) W. Adam, A. Corma, H. García, O. Weichold, *J. Catal.* **2000**, 196, 339–344; c) W. Adam, C. M. Mitchell, C. R. Saha-Moller, O. Weichold, *J. Am. Chem. Soc.* **1999**, 121, 2097–2103; d) W. Adam, C. R. Saha-Moller, O. Weichold, *J. Org. Chem.* **2000**, 65, 2897–2899; e) Y. Okada, M. Oba, A. Arai, K. Tanaka, K. Nishiyama, W. Ando, *Inorg. Chem.* **2010**, 49, 383–385; f) R. Ishimoto, K. Kamata, N. Mizuno, *Angew. Chem. Int. Ed.* **2009**, 48, 8900–8904; *Angew. Chem.* **2009**, 121, 9062–9066.
- [11] D. Limnios, C. G. Kokotos, *ACS Catal.* **2013**, 3, 2239–2243.
- [12] a) X. Engelmann, I. Monte-Perez, K. Ray, *Angew. Chem. Int. Ed.* **2016**, 55, 7632–7649; *Angew. Chem.* **2016**, 128, 7760–7778; b) M. Milan, M. Salamone, M. Costas, M. Bietti, *Acc. Chem. Res.* **2018**, 51, 1984–1995.
- [13] a) Y. Liu, C. Wang, D. Xue, M. Xiao, C. Li, J. Xiao, *Chem. Eur. J.* **2017**, 23, 3051–3061; b) Y. Liu, C. Wang, D. Xue, M. Xiao, J. Liu, C. Li, J. Xiao, *Chem. Eur. J.* **2017**, 23, 3062–3066; c) A. Gonzalez-de-Castro, C. M. Robertson, J. Xiao, *J. Am. Chem. Soc.* **2014**, 136, 8350–8360; d) A. Gonzalez-de-Castro, J. Xiao, *J. Am. Chem. Soc.* **2015**, 137, 8206–8218.
- [14] The KIE may be estimated from the remaining **2a** and [D]**2a**. The low yield of **3a-OD** is due to H–D exchange with water in the system.
- [15] a) G. Yin, M. Buchalova, A. M. Danby, C. M. Perkins, D. Kitko, J. D. Carter, W. M. Scheper, D. H. Busch, *J. Am. Chem. Soc.* **2005**, 127, 17170–17171; b) W. D. Kerber, B. Ramdhanie, D. P. Goldberg, *Angew. Chem. Int. Ed.* **2007**, 46, 3718–3721; *Angew. Chem.* **2007**, 119, 3792–3795.
- [16] Following the suggestion of a reviewer, we also carried out the **1**-catalyzed oxidation of **2a** using the single oxygen atom donors *t*BuOOH, CH₃C(O)OOH, and PhIO under the optimized reaction conditions (Table 1). The former two oxidants afforded 99% yield (GC) of **3a**, but no oxidation was observed with PhIO (see Table B). These results appear to be supportive of the concerted mechanism suggested.
- [17] CCDC 1822303 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Manuscript received: January 9, 2019

Accepted manuscript online: February 27, 2019

Version of record online: March 18, 2019