Iron-catalyzed hydrosilylation of CO2: CO2 conversion to formamides and methylamines

Xavier Frogneux, Olivier Jacquet, Thibault Cantat

To cite this version:

Xavier Frogneux, Olivier Jacquet, Thibault Cantat. Iron-catalyzed hydrosilylation of CO2: CO2 conversion to formamides and methylamines. Catal. Sci. Technol., 2014, 4, pp.1529-1533. <10.1039/c4cy00130c>. <hal-01157655>

HAL Id: hal-01157655

https://hal.archives-ouvertes.fr/hal-01157655

Submitted on 17 Nov 2015

Catalysis Science & Technology

COMMUNICATION

View Article Online
View Journal | View Issue

Iron-catalyzed hydrosilylation of CO_2: CO_2 conversion to formamides and methylamines†

Cite this: *Catal. Sci. Technol.*, 2014, 4, 1529

Received 31st January 2014,
Accepted 15th February 2014

DOI: 10.1039/c4cy00130c

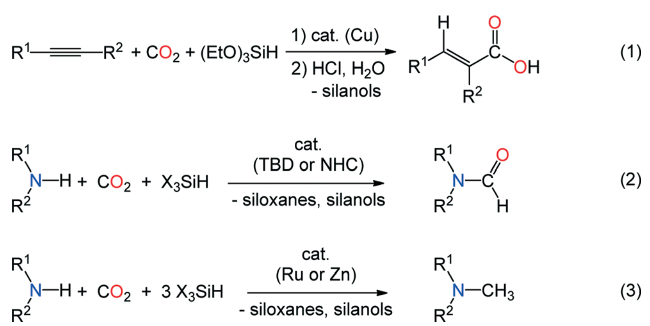
www.rsc.org/catalysis

Xavier Frogneux, Olivier Jacquet and Thibault Cantat*

Catalytic hydrosilylation of CO_2 is an efficient and selective approach to form chemicals. Herein, we describe the first iron catalysts able to promote the reductive functionalization of CO_2 using hydrosilanes as reductants. Iron(II) salts supported by phosphine donors enable the conversion of CO_2 to formamide and methylamine derivatives under mild reaction conditions.

Catalytic hydrosilylation reactions are attractive alternatives to classical reduction methods with hydrogen or metal hydrides because they usually operate under mild conditions with superior chemoselectivity.[1] Indeed, hydrosilanes possess a reduction potential similar to H_2 and a Si–H bond that is kinetically more reactive because of its polarity and lower bond dissociation energy (92 kcal mol^{-1} in SiH_4 *vs.* 104 kcal mol^{-1} in H_2).[2] In addition, they circumvent the problematic sensitivity of aluminium and boron hydrides to moisture. As a result, catalytic hydrosilylation can achieve highly chemo- and regio-selective transformations of a wide range of carbonyl groups such as ketones, carboxylic acids, esters, amides and ureas.[3] Importantly, in 1981, Hirai *et al.* extended hydrosilylation strategies to reduce CO_2 using $RuCl_2(PPh_3)_3$ as a catalyst,[4] and a variety of organic and organometallic catalysts have been shown to promote the direct hydrosilylation of CO_2 since then.[5] CO_2 reduction to formic acid and methanol has limited economical interest because these molecules are produced at low cost and on large scales that are incompatible with the availability of hydrosilanes. In contrast, CO_2 conversion to fine and bulk chemicals has the advantage of creating added value for niche applications. In this respect, the unique reducing properties of hydrosilanes have been exemplified, over the last 4 years, with the design of novel catalytic transformations to convert CO_2 to carboxylic acids, formamides and methylamines (Scheme 1).[6] These new advances have motivated the search for novel efficient catalysts able to facilitate the hydrosilylation of CO_2.[5b–e,g,i,j,7] From another standpoint, remarkable efforts have recently demonstrated the potential of iron complexes as earth abundant and cost efficient metal catalysts in hydrosilylation reactions.[8] For example, Sortais, Darcel *et al.* have utilized well-defined iron carbene complexes for the chemoselective reduction of esters to aldehydes.[9] In 2009, Beller *et al.* and Nagashima *et al.* showed independently that iron carbonyl complexes were potent hydrosilylation catalysts for the reduction of amides to amines.[10] Recently, our group reported the first examples of urea reduction to formamidines, using iron complexes as hydrosilylation catalysts.[3k] Yet, so far, iron catalysts have never been utilized in CO_2 hydrosilylation reactions and, herein, we describe the first iron complexes able to promote the reductive functionalization of CO_2 using hydrosilanes. In this contribution, Fe^{II} salts supported by phosphine donors are shown to catalyze the conversion of CO_2 to formamide and methylamine derivatives under mild reaction conditions.

Using CO_2 and hydrosilanes for the formylation of amines affords an attractive route to formamides and this transformation was unveiled for the first time in 2012 in our



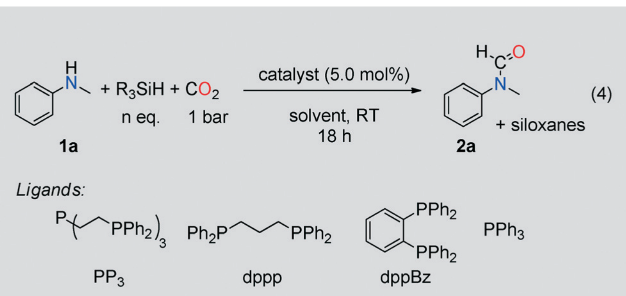
Scheme 1 Reductive functionalization of CO_2 to α,β-unsaturated carboxylic acids, formamides and methylamines using hydrosilane reductants.

CEA, IRAMIS, SIS2M, CNRS UMR 3299, CEA/Saclay, 91191 Gif-sur-Yvette, France. E-mail: thibault.cantat@cea.fr; Fax: +33 1 6908 6640; Tel: +33 1 6908 4338

† Electronic supplementary information (ESI) available: General experimental details, synthetic procedures and data for **2r** and **2v**. See DOI: 10.1039/c4cy00130c

laboratories (eqn (2) in Scheme 1).[6b,d] This catalytic reaction was found to be robust and a large scope of N–H bonds in amines, anilines, hydrazines and N-heterocycles were successfully formylated with hydrosilanes, such as $PhSiH_3$, Ph_2SiH_2, $(EtO)_3SiH$ or polymethylhydrosiloxane (PMHS). Interestingly, while organic catalysts (guanidines and N-heterocyclic carbenes (NHCs)) were originally utilized, Baba *et al.* showed that copper(II) diphosphine complexes were also active catalysts in this transformation.[7] As such, the formylation of *N*-methylaniline (**1a**) with CO_2 and phenylsilane was selected as a benchmark reaction to test the catalytic activity of a variety of iron complexes in CO_2 hydrosilylation. In the presence of a catalytic amount of $FeCl_2$, $FeCl_3$, $Fe(SO_4)\cdot 7H_2O$, $Fe(acac)_2$ or $Fe(acac)_3$ (5.0 mol%), addition of 1 equiv. of $PhSiH_3$ to a THF solution of **1a** under an atmosphere of CO_2 (1 bar) led to no reaction and the starting materials were recovered unreacted after 18 h at 100 °C. Notably, Beller *et al.* have shown that iron(II) phosphine complexes are able to promote the hydrogenation of the kinetically stable CO_2 molecule to formate derivatives[11] and we have found recently that $Fe(acac)_2$ in combination with tris[2-(diphenylphosphino)ethyl]phosphine (PP_3) can catalyze the hydrosilylation of organic ureas to formamidines.[3k] Supporting phosphine ligands were therefore screened so as to form complexes with $Fe(acac)_2$ and generate active catalysts in the formylation of **1a** (entries 1–6, Table 1 and ESI†). While PPh_3, 1,3-bis(diphenylphosphino)propane (dppp), 1,1′-bis(diphenylphosphino)ferrocene (dppf), 1,2-bis(diphenylphosphino)benzene (dppBz) and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) did not improve the reactivity of $Fe(acac)_2$, an equimolar mixture of PP_3 (5.0 mol%) and $Fe(acac)_2$ allowed for the quantitative conversion of **1a** to its formamide **2a** at RT after 18 h (entry 1, Table 1). After usual work-up aimed at eliminating the siloxanes by-products, **2a** was successfully isolated in 92% yield. Importantly, the presence of both $Fe(acac)_2$ and the supporting ligand is necessary to obtain catalytic activity in the conversion of **1a to 2a** (entries 2 and 3). Replacing $Fe(acac)_2$ with $Fe(BF_4)_2\cdot 6H_2O$ lowers the conversion yield of **2a** to 13% (entry 7, Table 1).

Table 1 Iron-catalyzed formylation of **1a** using CO_2



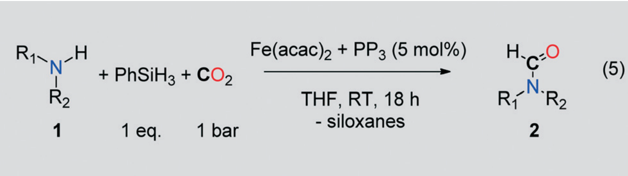
Entry[a]	Catalyst[a]	Solvent	R_3SiH (*n*)	Yield[b] (%)
1	$Fe(acac)_2 + PP_3$ (1 : 1)	THF	$PhSiH_3$ (1)	>95 (92)[c]
2	$Fe(acac)_2$	THF	$PhSiH_3$ (1)	<1
3	PP_3	THF	$PhSiH_3$ (1)	<1
4	$Fe(acac)_2 + PPh_3$ (1 : 4)	THF	$PhSiH_3$ (1)	<1
5	$Fe(acac)_2$ + dppp (1 : 2)	THF	$PhSiH_3$ (1)	<1
6	$Fe(acac)_2$ + dppBz (1 : 2)	THF	$PhSiH_3$ (1)	<1
7	$Fe(BF_4)_2\cdot 6H_2O + PP_3$ (1 : 1)	THF	$PhSiH_3$ (1)	13
8	$Fe(acac)_2 + PP_3$ (1 : 1)	CH_3CN	$PhSiH_3$ (1)	>95
9	$Fe(acac)_2 + PP_3$ (1 : 1)	CH_2Cl_2	$PhSiH_3$ (1)	>95
10	$Fe(acac)_2 + PP_3$ (1 : 1)	Toluene	$PhSiH_3$ (1)	63
11	$Fe(acac)_2 + PP_3$ (1 : 1)	1,4-Dioxane	$PhSiH_3$ (1)	48
12	$Fe(acac)_2 + PP_3$ (1 : 1)	THF	Et_3SiH (3)	<1
13	$Fe(acac)_2 + PP_3$ (1 : 1)	THF	TMDS (1.5)	<1
14	$Fe(acac)_2 + PP_3$ (1 : 1)	THF	PMHS (3)	<1[d]

[a] Reaction conditions: *N*-methylaniline (**1a**, 0.250 mmol), hydrosilane R_3SiH (3 eq. Si–H), catalyst (0.0125 mmol, 5.0 mol%), solvent (0.7 mL), CO_2 (1 bar), 18 h, RT. [b] Determined by GC/MS using mesitylene as the internal standard after calibration. [c] Isolated yield. [d] 70 °C.

It is noteworthy that the polarity of the solvent has a significant impact on the activity of the iron catalytic system. While toluene and 1,4-dioxane ($\varepsilon_0 < 2.4$) impair the formylation of **1a**, polar solvents with a dielectric constant ε_0 greater than 7.5 (THF, CH_2Cl_2, and CH_3CN) lead to the quantitative formation of **2a** (entries 1, 8–11 in Table 1). CO_2 reductive functionalization to **2a** also depends on the nature of the reductant and less reactive hydrosilanes, such as Et_3SiH, 1,1,4,4-tetramethyldisiloxane (TMDS) and PMHS, are unreactive in eqn (4), even at 70 °C (entries 12–14, Table 1). As a result, $Fe(acac)_2 + PP_3$ is superior to 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) which operates at 100 °C and affords **2a** in a modest 39% yield after 24 h with 1 equiv. of $PhSiH_3$.[6b] For comparison, low catalyst loadings of $Cu(OAc)_2$ + 1.5 dppBz (0.07 mol%) were shown to convert **1a to 2a** in 87% yield after 30 h at 80 °C. In fact, the catalytic activity of the iron(II) system resembles that of free NHCs which are able to promote the formylation of N–H bonds of amines, anilines, hydrazines and hydrazones at room temperature.[6d]

The scope of active amine substrates in the iron(II) catalyzed formylation reaction was then explored (eqn (5) and Table 2). Using 5.0 mol% of $Fe(acac)_2 + PP_3$ with $PhSiH_3$, aliphatic secondary amines **1b**, **1d**, **1e** and **1h** proved to be highly active in this reaction, providing quantitative conversions to the desired formamides after 18 h at RT under 1 bar CO_2 (entries 1, 3, 4, 7, Table 2). Under the same conditions, the sterically hindered di-iso-propylamine **1c** was successfully converted to **2c** in a modest 40% yield determined by GC/MS (entry 2, Table 2). Nonetheless, while **1a** is an active substrate, the presence of two aromatic rings on the nitrogen atom completely shuts down the formylation of the N–H bond in **1g** (entry 6, Table 2). This reaction can also be applied with good success to convert primary amines and formanilide **2i** was obtained in good conversion (79%) from aniline **1i** (entry 8, Table 2). Despite the presence of two iso-propyl substituents at the α-position, **1j** was transformed to **2j** in 38% conversion. Interestingly, the introduction of an electron donating group at the *para* position of aniline hampers the formylation rate and *p*-anisidine (**1k**) afforded **2k** in a modest 34% yield, while conversions greater than 62% were observed starting from aniline (**1i**) or *p*-chloroaniline (**1l**). In contrast

Table 2 Formylation of various amines with the described system



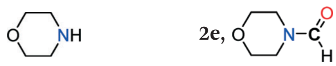
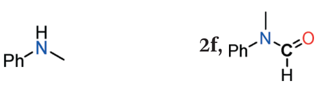
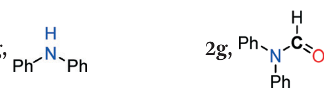
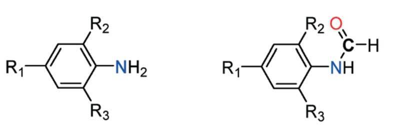
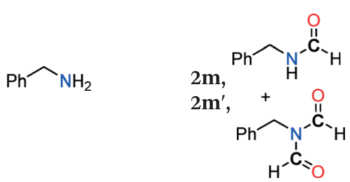
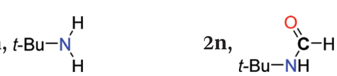
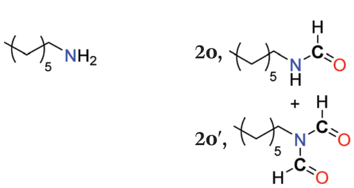
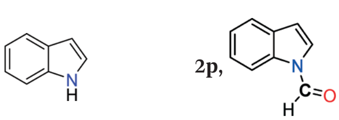
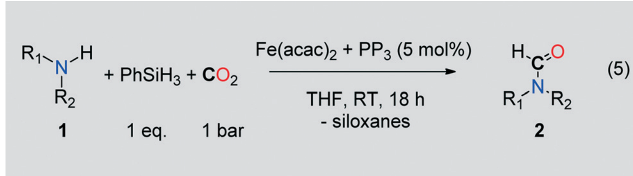
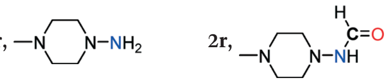
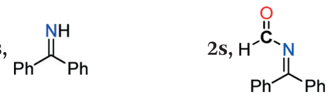
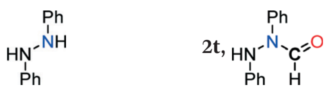
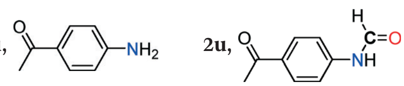
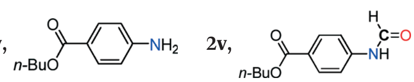
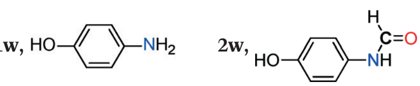
Entry[a]	Substrate (1)	Product (2)	Yield[b] (%)
1	1b 	2b	>95
2	1c 	2c	40
3	1d 	2d	>95
4	1e 	2e	>95
5	1f 	2f	>95
6	1g 	2g	<1
7	1h 	2h	>95
8			
	1i R_1=H, R_2=H, R_3=H	2i R_1=H, R_2=H, R_3=H	79
	1j R_1=H, R_2=*i*Pr, R_3=*i*Pr	2j R_1=H, R_2=*i*Pr, R_3=*i*Pr	38
	1k R_1=OMe, R_2=H, R_3=H	2k R_1=OMe, R_2=H, R_3=H	34
	1l R_1=Cl, R_2=H, R_3=H	2l R_1=Cl, R_2=H, R_3=H	62
9	1m 	2m, 2m′	76/17
10	1n 	2n	70
11	1o 	2o, 2o′	45/25
12	1p 	2p	<1

Table 2 *(continued)*



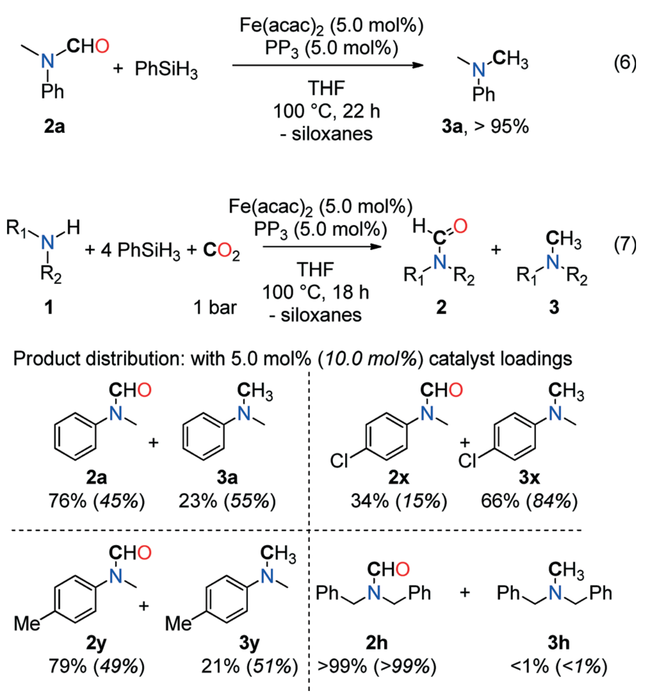
Entry[a]	Substrate (1)	Product (2)	Yield[b] (%)
13	1q 	2q	<1
14	1r 	2r	24
15	1s 	2s	8
16	1t 	2t	26
17	1u 	2u	65
18	1v 	2v	58
19	1w 	2w	<1

[a] Reaction conditions: amine (0.250 mmol), $PhSiH_3$ (0.250 mmol), catalyst (0.0125 mmol), solvent (0.7 mL), CO_2 (1 bar), 18 h, RT. [b] Determined by GC/MS using mesitylene as the internal standard after calibration.

to the results obtained with NHCs, the bis-formylated products are not observed when aniline derivatives are reacted with $PhSiH_3$ and CO_2 in the presence of Fe(acac)$_2$ + PP_3.[6d] Yet, starting with aliphatic primary amines, a competition between mono- and bis-formylation appears and, although the monoformamides **2m** and **2o** are obtained as major products from benzylamine (**1m**) and *n*-heptylamine (**1o**), respectively, significant amounts of **2m′** and **2o′** were also detected (up to 25%) (entries 9 and 11, Table 2). This product distribution was left unchanged after longer reaction times (36 h). For sterically hindered substrates such as *tert*-butylamine **1n**, no trace of bis-formylated products were detected (entry 10) and the formamide was obtained in a good 70% GC yield.

The N–H bonds in less basic substrates such as imidazoles (**1q**) or indoles (**1p**) are resistant to formylation (Entries 12 and 13). Benzophenone imine (**1s**) and aliphatic and aromatic hydrazines (**1r** and **1t**) display a low reactivity and the corresponding formyl products were obtained in low yields, ranging from 8 to 26% (entries 14–16, Table 2). An important advantage of hydrosilylation over classical reduction methods (with hydrogen or metal hydrides) is the enhanced chemoselectivity, enabled by the use of a mild and polarized hydrosilane reductant. This benefit translates well into the present iron-catalyzed formylation of amines and **1u** and **1v** are successfully formylated to **2u** and **2v**, respectively, with no reduction of the additional ketone or ester functionality (entries 17 and 18, Table 2). Nevertheless, the system is incompatible with the presence of a hydroxyl group (entry 19, Table 2).

In 2013, we designed a novel catalytic reaction to utilize CO_2 as a C_1-building block in the methylation of amines.[6c] Using zinc catalysts and hydrosilanes as reductants, CO_2 was shown to undergo a complete deoxygenation *via* a 6-electron reduction pathway coupled to the formation of a C–N bond (eqn (3) in Scheme 1). Shortly afterwards, Beller *et al.* reported an efficient ruthenium phosphine catalyst for this transformation.[12] Both the Zn and Ru catalytic systems operate at 100 °C with $PhSiH_3$. From a mechanistic standpoint, it was shown that the zinc-catalyzed methylation of N–H bonds involves two steps with opposite electronic demand at the nitrogen centre and the amine substrate is first converted to its formamide, which is subsequently hydrosilylated to the corresponding methylamine. In order to evaluate the potential of $Fe(acac)_2$ + PP_3 in the catalytic methylation of amines with CO_2, the reduction of formamide **2a** was first tested in the presence of a stoichiometric amount of $PhSiH_3$. As depicted in eqn (6) (Scheme 2), the iron catalyst can promote the quantitative hydrosilylation of formamide **2a to 3a**, albeit at 100 °C. As a consequence, raising the reaction temperature to 100 °C enables the utilization of the iron catalyst in the direct methylation of *N*-methylaniline with CO_2. In fact, using 1 bar CO_2 and 4 equiv. of $PhSiH_3$, $Fe(acac)_2$ + PP_3 (5.0 mol%) is able to convert directly **1a** to *N*,*N*-dimethylaniline (**3a**) in 23% yield after 18 h (eqn (7), Scheme 2). As such, the iron catalyst exhibits a somewhat lower activity than the zinc carbene or ruthenium phosphine complexes utilized previously by Cantat *et al.* and Beller *et al.*, respectively.[6c,12] As expected, formamide **2a** accumulates in the methylation of **1a** and its reduction to **3a** is rate limiting. Increasing the catalyst loading to 10.0 mol% is beneficial to the conversion to methylamines and **3a**, **3x** and **3y** are obtained in good yields, ranging from 51 to 84%, from **1a**, **1x** and **1y**, respectively (eqn (7), Scheme 2). Under the same conditions, the aliphatic dibenzylamine (**1h**) yields selectively formamide **2h**. Although modest, the catalytic activity of $Fe(acac)_2$ + PP_3 in the methylation of amines establishes the potential of iron complexes to promote the 6-electron reduction of CO_2 and further efforts are underway in our laboratories to improve the catalytic activity of the iron system and to utilize inexpensive hydrosilanes, such as PMHS and TMDS, in this transformation.



Scheme 2 Iron-catalyzed reduction of **2a to 3a** and methylation of *N*-methylanilines.

Conclusions

In the search for earth abundant and cost efficient catalysts for the reduction of CO_2, we have reported herein the first examples of iron catalysts able to promote the hydrosilylation of CO_2. Iron(II) salts supported by a tetraphosphine ligand are able to transform CO_2 to formamides in the presence of amines and $PhSiH_3$ at room temperature. The reaction is chemoselective and tolerant to ketone and ester functionalities. At 100 °C, the catalytic system is also active in the methylation of aniline derivatives.

Acknowledgements

For financial support of this work, we acknowledge the CEA, the CNRS, the CHARMMMAT Laboratory of Excellence and the European Research Council (ERC Starting Grant Agreement no. 336467). T.C. thanks the Fondation Louis D. – Institut de France for its formidable support.

Notes and references

1 (*a*) *Modern Reduction Methods*, ed. E. A. Andersson and I. J. Munslow, Wiley-VCH, Weinheim, 2008; (*b*) *Hydrosilylation: A Comprehensive Review on Recent Advances*, ed. B. Marciniec, Springer, New York, 2009; (*c*) *Silicon in Organic, Organometallic and Polymer Chemistry*, ed. M. A. Brook, Wiley, New York, 2000; (*d*) J. Y. Corey, *Chem. Rev.*, 2011, **111**, 863–1071; (*e*) G. L. Larson and J. L. Fry, *Organic Reactions*, ed. S. E. Denmark, Wiley, Hoboken, 2008; (*f*) B. Marciniec, *Coord. Chem. Rev.*, 2005, **249**, 2374–2390; (*g*) B. Marciniec, J. Gulinsky, W. Urbaniak and Z. W. Kornetka, *The Chemistry of Organic Silicon Compounds*, ed. B. Marciniec, Pergamon Press, Oxford, 1992; (*h*) V. B. Pukhnarevich, E. Lukevics, L. T. Kopylova and M. G. Voronkov, *Perspectives of Hydrosilylation*, ed. E. Lukevics, Institute of Organic Synthesis, Riga, 1992.

2 R. Walsh, *Acc. Chem. Res.*, 1981, **14**, 246–252.

3 (*a*) D. Addis, S. Das, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2011, **50**, 6004–6011; (*b*) D. Bezier, S. Park and M. Brookhart, *Org. Lett.*, 2013, **15**, 496–499; (*c*) D. Bezier, G. T. Venkanna, L. C. M. Castro, J. X. Zheng, T. Roisnel, J. B. Sortais and C. Darcel, *Adv. Synth. Catal.*, 2012, **354**, 1879–1884; (*d*) L. C. M. Castro, J. B. Sortais and C. Darcel, *Chem. Commun.*, 2012, **48**, 151–153; (*e*) C. Cheng and M. Brookhart, *Angew. Chem., Int. Ed.*, 2012, **51**, 9422–9424; (*f*) S. Das, D. Addis, S. L. Zhou, K. Junge and M. Beller, *J. Am. Chem. Soc.*, 2010, **132**, 4971–4971; (*g*) S. Das, Y. H. Li, K. Junge and M. Beller, *Chem. Commun.*, 2012, **48**, 10742–10744; (*h*) S. Das, K. Moller, K. Junge and M. Beller, *Chem.–Eur. J.*, 2011, **17**, 7414–7417; (*i*) K. Junge, B. Wendt, S. L. Zhou and M. Beller, *Eur. J. Org. Chem.*, 2013, 2061–2065; (*j*) K. Matsubara, T. Iura, T. Maki and H. Nagashima, *J. Org. Chem.*, 2002, **67**, 4985–4988; (*k*) J. Pouessel, O. Jacquet and T. Cantat, *ChemCatChem*, 2013, **5**, 3552–3556; (*l*) K. Miyamoto, Y. Motoyama and H. Nagashima, *Chem. Lett.*, 2012, **41**, 229–231.

4 H. Koinuma, F. Kawakami, H. Kato and H. Hirai, *J. Chem. Soc., Chem. Commun.*, 1981, 213–214.

5 (*a*) A. Berkefeld, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2010, **132**, 10660–10661; (*b*) A. Berkefeld, W. E. Piers, M. Parvez, L. Castro, L. Maron and O. Eisenstein, *Chem. Sci.*, 2013, **4**, 2152–2162; (*c*) O. Jacquet, C. D. Gomes, M. Ephritikhine and T. Cantat, *ChemCatChem*, 2013, **5**, 117–122; (*d*) M. Khandelwal and R. J. Wehmschulte, *Angew. Chem., Int. Ed.*, 2012, **51**, 7323–7326; (*e*) R. Lalrempuia, M. Iglesias, V. Polo, P. J. S. Miguel, F. J. Fernandez-Alvarez, J. J. Perez-Torrente and L. A. Oro, *Angew. Chem., Int. Ed.*, 2012, **51**, 12824–12827; (*f*) T. Matsuo and H. Kawaguchi, *J. Am. Chem. Soc.*, 2006, **128**, 12362–12363; (*g*) S. Park, D. Bézier and M. Brookhart, *J. Am. Chem. Soc.*, 2012, **134**, 11404–11407; (*h*) S. N. Riduan, Y. G. Zhang and J. Y. Ying, *Angew. Chem., Int. Ed.*, 2009, **48**, 3322–3325; (*i*) W. Sattler and G. Parkin, *J. Am. Chem. Soc.*, 2012, **134**, 17462–17465; (*j*) K. Motokura, D. Kashiwame, A. Miyaji and T. Baba, *Org. Lett.*, 2012, **14**, 2642–2645.

6 (*a*) T. Fujihara, T. H. Xu, K. Semba, J. Terao and Y. Tsuji, *Angew. Chem., Int. Ed.*, 2011, **50**, 523–527; (*b*) C. D. Gomes, O. Jacquet, C. Villiers, P. Thuery, M. Ephritikhine and T. Cantat, *Angew. Chem., Int. Ed.*, 2012, **51**, 187–190; (*c*) O. Jacquet, X. Frogneux, C. D. Gomes and T. Cantat, *Chem. Sci.*, 2013, **4**, 2127–2131; (*d*) O. Jacquet, C. D. Gomes, M. Ephritikhine and T. Cantat, *J. Am. Chem. Soc.*, 2012, **134**, 2934–2937.

7 K. Motokura, N. Takahashi, D. Kashiwame, S. Yamaguchi, A. Miyaji and T. Baba, *Catal. Sci. Technol.*, 2013, **3**, 2392–2396.

8 M. Zhang and A. Q. Zhang, *Appl. Organomet. Chem.*, 2010, **24**, 751–757.

9 H. Q. Li, L. C. M. Castro, J. X. Zheng, T. Roisnel, V. Dorcet, J. B. Sortais and C. Darcel, *Angew. Chem., Int. Ed.*, 2013, **52**, 8045–8049.

10 (*a*) Y. Sunada, H. Kawakami, T. Imaoka, Y. Motoyama and H. Nagashima, *Angew. Chem., Int. Ed.*, 2009, **48**, 9511–9514; (*b*) S. Zhou, K. Junge, D. Addis, S. Das and M. Beller, *Angew. Chem., Int. Ed.*, 2009, **48**, 9507–9510.

11 C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 9777–9780.

12 Y. H. Li, X. J. Fang, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2013, **52**, 9568–9571.