Homogeneous Catalysis

DOI: 10.1002/anie.200906348

Copper-Catalyzed Hydrosilylation with a Bowl-Shaped Phosphane Ligand: Preferential Reduction of a Bulky Ketone in the Presence of an Aldehyde**

*Tetsuaki Fujihara, Kazuhiko Semba, Jun Terao, and Yasushi Tsuji**

Ligands play a crucial role in the efficiency and selectivity of homogeneous catalysts;[1] therefore, much effort has been given to their development. Bowl-shaped tris(3,5-diarylphenyl)phosphanes (**1**–**3**, Figure 1a)[2] have a unique structure

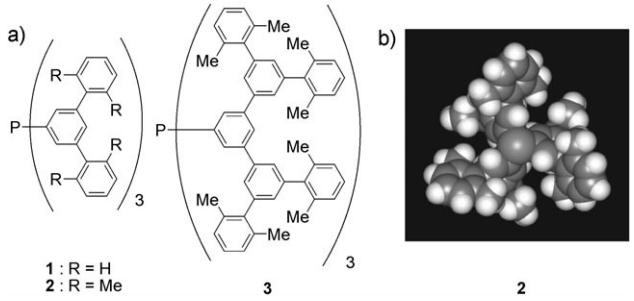
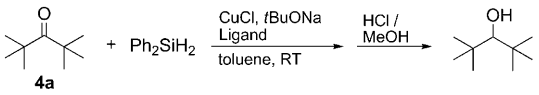


Figure 1. a) Bowl-shaped phosphanes **1**–**3**. b) An optimized structure of **2** calculated by the HF/6-31G(d)-CONFLEX/MM3 method.[2]

that consists of a bulky periphery (the rim of the bowl has a diameter of 2.0–2.6 nm) and substantial empty space around the phosphorus atom (Figure 1b). We have recently reported that **2** and **3** are particularly effective ligands in the rhodium-catalyzed hydrosilylation reaction of ketones[2a,b] and the palladium-catalyzed Suzuki–Miyaura coupling of aryl chlorides.[2c] Herein, we report the use of extremely active copper catalysts[3] that contain bowl-shaped phosphane (bsp) ligands (**2** or **3**) in the hydrosilylation reaction of ketones. These catalysts afford the unprecedented preferential reduction of a bulky ketone substrate in the presence of an unprotected aldehyde.

First, the hydrosilylation of the poorly reactive ketone[4] 2,2,4,4-tetramethyl-3-pentanone (**4a**) with Ph_2SiH_2 was investigated at room temperature (Table 1). A CuCl/*t*BuONa catalyst system with conventional phosphane ligands, such as

Table 1: Effect of phosphanes on the copper-catalyzed hydrosilylation of **4a**.[a]



Entry	Ligand	Yield [%][b] after 20 min	after 5 h
1	PPh_3	<1	2
2	P(*o*-Tol)$_3$	<1	<1
3	P(Mes)$_3$	<1	2
4	P(*t*Bu)$_3$	9	11
5	**1**	7	25
6	**2**	43	92
7	**3**	99	99
8	bdp	<1	4
9	(*S*)-dtbm-segphos	<1	1
10[c]	**2**	<1	5

[a] **4a** (2.0 mmol), Ph_2SiH_2 (2.4 mmol), CuCl (0.02 mmol, 1.0 mol%), phosphane (0.02 mmol, 1.0 mol%), *t*BuONa (0.12 mmol, 6.0 mol%), toluene (2.0 mL), RT. [b] Yield of alcohol determined using a GC internal standard. [c] [{RhCl(C_2H_4)$_2$}$_2$] (0.01 mmol, 1.0 mol%) and **2** (0.02 mmol, 1.0 mol%) were used as the catalyst. Tol = methylphenyl, Mes = mesityl, bdp = 1,2-bis(diphenylphosphino)benzene, dtbm-segphos = (4,4′-bi-1,3-benzodioxole)-5,5′-diylbis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphane.

PPh_3, P(*o*-Tol)$_3$,[5] P(Mes)$_3$,[5] and P(*t*Bu)$_3$, afforded the corresponding alcohol after hydrolysis in only 2%, <1%, 2%, and 11% yields, respectively (5 h; Table 1, entries 1–4). In contrast, **2** was remarkably effective in this reaction, affording the product in 92% after 5 h (Table 1, entry 6). Furthermore, **3** was a more efficient ligand, providing the alcohol in quantitative yield after only 20 min (Table 1, entry 7). Bidentate phosphane ligands, such as bdp[5] and (*S*)-dtbm-segphos,[5] which are very effective ligands in copper-catalyzed hydrosilylation reactions,[6] were unsuccessful (Table 1, entries 8 and 9). Under the same reaction conditions as in Table 1, entry 6 (5 h), other silanes, such as Et_3SiH, $MePh_2SiH$, and $Me(OEt)_2SiH$, afforded the product in trace, 2%, and 51% yields, respectively. An excess (5 equiv) of silane only slightly improved the yield, namely trace amounts with Et_3SiH and 8% using $MePh_2SiH$. Nolan et al. reported that N-heterocyclic carbene (NHC) ligands, such as ICy (*N*,*N*′-bis(cyclohexyl)imidazol-2-ylidene), IMes (*N*,*N*′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), and IPr (*N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), were highly efficient in the copper-catalyzed hydrosilylation reactions of bulky ketones.[4c,7] Under the same reaction conditions as in Table 1, entry 7 (20 min), the ICy ligand afforded

[*] Prof. Dr. T. Fujihara, K. Semba, Prof. Dr. J. Terao, Prof. Dr. Y. Tsuji
Department of Energy and Hydrocarbon Chemistry
Graduate School of Engineering, Kyoto University
Kyoto 615-8510 (Japan)
Fax: (+81) 75-383-2514
E-mail: ytsuji@scl.kyoto-u.ac.jp
Homepage: http://twww.ehcc.kyoto-u.ac.jp/

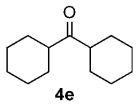
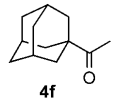
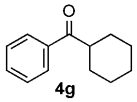
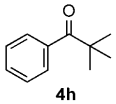
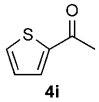
[**] This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas ("Synergy of Elements" and "Chemistry of Concerto Catalysis") from the Ministry of Education, Culture, Sports, Science, and Technology (Japan).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200906348.

the alcohol in a poor yield (6%), whereas IMes and IPr afforded high yields (84% and 94%, respectively). Conversely, a rhodium catalyst with bsp ([{RhCl(C_2H_4)$_2$}$_2$] with **2**; 1.0 mol% rhodium, P/Rh = 1)[2a,b] was not as effective for the bulky ketone (Table 1, entry 10).

The efficacy of the bsp ligands was further confirmed using various ketones (Table 2). The results using PPh_3 were also listed for comparison, because PPh_3 represents the core

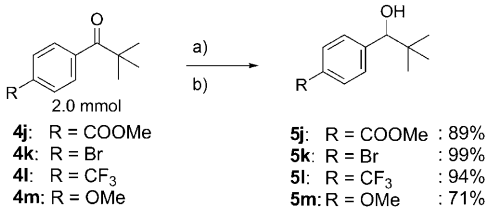
Table 2: Hydrosilylation of various ketones.[a]

Entry	Substrates	Ligand	*t* [min]	Yield [%][b]
1	 **4b**	**1**	10	98
2		**3**		68
3		PPh_3		23
4	 **4c**	**2**	360	28[c]
5		**3**		98[d]
6		PPh_3		< 1
7	 **4d**	**2**	20	99
8		**3**		99 (83)[e]
9		PPh_3		8
10	 **4e**	**2**	40	79
11		**3**		95 (89)[e]
12		PPh_3		3
13	 **4f**	**2**	90	53
14		**3**		83 (75)[e]
15		PPh_3		4
16	 **4g**	**2**	60	77
17		**3**		(93)[e]
18		PPh_3		2
19	 **4h**	**2**	10	95
20		**3**		99 (87)[e]
21		PPh_3		9
22	 **4i**	**1**	20	84 (69)[e]
23		**3**		24
24		PPh_3		5

[a] Ketone **4** (2.0 mmol), Ph_2SiH_2 (2.4 mmol), CuCl (0.02 mmol, 1.0 mol%), phosphane (0.02 mmol, 1.0 mol%), *t*BuONa (0.12 mmol, 6.0 mol%), toluene (2.0 mL), RT. [b] Yield of alcohol determined using a GC internal standard. [c] *cis*/*trans* = 44:56. [d] *cis*/*trans* = 58:42. [e] Yield of isolated product.

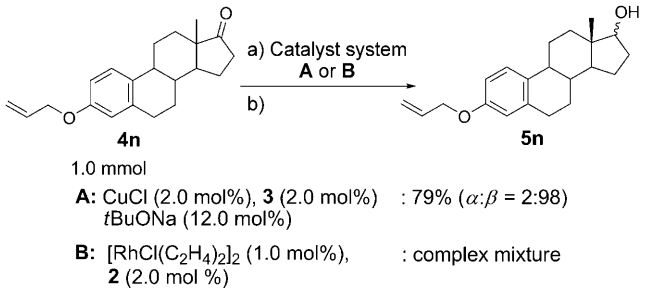
part of all the bsp ligands (**1**–**3**). The less-bulky cyclohexanone (**4b**) was easily reduced in 10 min to cyclohexanol in 98% and 68% yields using ligands **1** and **3**, respectively (Table 2, entries 1 and 2), whilst the yield with PPh_3 was only 23% (Table 2, entry 3). The more bulky 2-*tert*-butylcyclohexanone (**4c**) afforded its corresponding alcohol in 98% yield (ligand **3**; Table 2, entry 5). The highly congested 2,2,6,6-tetramethylcyclohexanone (**4d**) readily afforded the corresponding alcohol in almost quantitative yield in 20 min with either **2** or **3** as the ligand (Table 2, entries 7 and 8, respectively). Dicyclohexyl ketone (**4e**) and 1-adamantyl methyl ketone (**4f**) were also readily reduced to their corresponding alcohols by the Cu–bsp catalyst systems (Table 2, entries 10, 11, and 14). Aromatic ketones, such as cyclohexyl phenyl ketone (**4g**), *tert*-butyl phenyl ketone (**4h**), and 2-acetylthiophene (**4i**), were smoothly reduced in high yields (Table 2, entries 17, 19, 20, and 22), whereas the attempted hydrosilylation reactions of methyl 2,4,6-trimethylphenylketone was unsuccessful using ligands **1**–**3**.

Bulky ketones bearing multiple substituents (**4j**–**4m**) were converted into their corresponding alcohols in 15 min at room temperature whilst retaining their functionalities in excellent to good isolated yields (Scheme 1). Furthermore,



Scheme 1. Reduction of ketones **4j**–**4m** to alcohols. Reaction conditions: a) CuCl (1.0 mol%), **3** (1.0 mol%), *t*BuONa (6.0 mol%), Ph_2SiH_2 (2.4 mmol), toluene, RT, 15 min; b) HCl/MeOH.

the Cu–bsp catalyzed hydrosilylation of estrone derivative (**4n**), which contains an allyl ether functionality, proceeded chemoselectively toward the carbonyl moiety, affording the isolated allyloxy product in 79% yield (Scheme 2). In

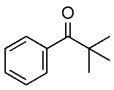
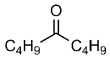
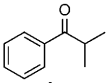


Scheme 2. Reduction of ketone **4n** containing an allyl ether. Reaction conditions: a) Catalyst system **A** or **B**, Ph_2SiH_2 (1.2 mmol), toluene, RT, 8 h; b) K_2CO_3/MeOH.

contrast, the rhodium catalyst system[2a,b] with a bsp ligand provided a mixture of products from the hydrosilylation of both the allyl and the carbonyl functional groups.

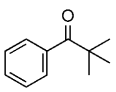
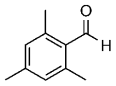
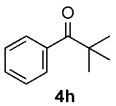
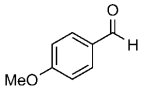
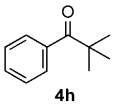
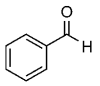
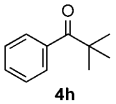
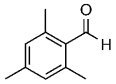
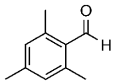
Initial rates of reaction for the hydrosilylations of **4h**, isopropyl phenyl ketone (**4o**), and acetophenone (**4p**) with Ph_2SiH_2 were found to be 1.1, 4.9×10^{-1}, and 8.5×10^{-2} mol L^{-1} h^{-1}, respectively,[5] which indicates that the reaction was much faster with a more bulky substrate. This intriguing difference between the rates of reaction was investigated using a competition reaction between equimolar amounts of two ketones that have substituents of different bulkiness (A: more bulky, B: less bulky) in the presence of half an equivalent of Ph_2SiH_2 at room temperature (Table 3). In the competition reaction between **4h** and **4p**, the more

Table 3: Competitive hydrosilylation between two substrates (A and B) of different bulkiness.[a]

Entry	Substrates A	Substrates B	*T* [°C]	*t* [h]	Yield [%][b] A	Yield [%][b] B
1	 **4h**	 **4p**	RT	0.2	88	2
2[c]					87	3
3	 **4d**	 **4b**	RT	0.3	89	11
4[d]					21	79
5	 **4a**	 **4q**	RT	0.5	71	17
6[e]	 **4o**	 **4p**	RT	0.2	99	11
7[e]	 **6a**	$C_6H_{13}CHO$ **6b**	−40	3	87	13
8[e]	 **6c**	$C_6H_{13}CHO$ **6b**	−40	1	78	25

[a] Bulky substrate A (2.0 mmol), less bulky substrate B (2.0 mmol), Ph_2SiH_2 (2.0 mmol), CuCl (0.02 mmol), **3** (0.02 mmol), *t*BuONa (0.12 mmol), toluene (2.0 mL). [b] Yield of alcohol determined using a GC internal standard. [c] **2** was used instead of **3**. [d] PPh_3 was used instead of **2**. [e] Toluene (4.0 mL).

Table 4: Hydrosilylation of bulky ketones in the presence of aldehydes.[a]

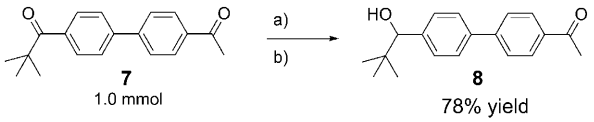
Entry	Substrates A	Substrates C	*t* [h]	Yield [%][b] A	Yield [%][b] C
1	 **4h**	 **6d**	3	90	5
2[c]				8	86
3[d]				41	46
4[e]				56	41
5[f]				55	43
6	 **4h**	 **6e**	2.5	92	6
7	 **4h**	 **6f**	12	81	12
8	 **4h**	$C_6H_{13}CHO$ **6b**	3	87	12
9	 **4d**	 **6d**	2	92	9
10	 **4d**	$C_6H_{13}CHO$ **6b**	3	72	21
11	 **4a**	 **6d**	1	62	28

[a] Bulky ketone A (2.0 mmol), aldehyde (2.0 mmol), Ph_2SiH_2 (2.0 mmol), CuCl (0.02 mmol), **3** (0.02 mmol), *t*BuONa (0.12 mmol), toluene (4.0 mL) at −40 °C. [b] Yield of alcohol determined using a GC internal standard. [c] PPh_3 was used instead of **3**. [d] ICy was used instead of **3**. [e] IMes was used instead of **3**. [f] IPr was used instead of **3**.

bulky **4h** was preferentially reduced using either **3** or **2** as the ligand (Table 3, entries 1 and 2). Similarly, the more bulky **4d** was reduced preferentially over **4b** using ligand **3** (Table 3, entry 3). However, when PPh_3 was used as the ligand, the less bulky **4b** was preferentially reduced, as expected (Table 3, entry 4). Higher reactivity of the more bulky **4a** over the less bulky 5-nonanone (**4q**) was also observed (Table 3, entry 5). In the competition reaction between **4o** and **4p** (isopropyl ketone versus methyl ketone), the alcohol from the isopropyl ketone substrate was obtained as the major product (Table 3, entry 6). Even when two competing aldehydes were employed, the more bulky substrates (**6a** and **6c**) were predominantly reduced over heptanal (**6b**; Table 3, entries 7 and 8).

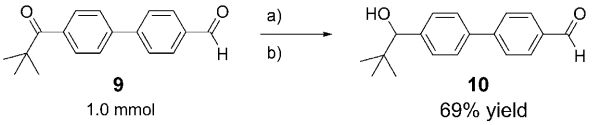
The most remarkable feature of this bsp catalyst system is the preferential reduction of a ketone (**4**) in the presence of an aldehyde (**6**). The hydrosilylation reaction of an equimolar mixture of **4h**, 2,4,6-trimethylbenzaldehyde (**6d**), and Ph_2SiH_2, using **3** as the ligand, afforded the corresponding alcohol from the ketone in 90% yield and the corresponding alcohol from the aldehyde in only 5% yield (Table 4, entry 1). When PPh_3 was used instead of **3**, the alcohol from the aldehyde was predominantly obtained (Table 4, entry 2). NHC ligands, such as ICy, IMes, and IPr, were highly efficient in the copper-catalyzed hydrosilylation of bulky ketones.[4c,7] However, when these ligands were used, no selectivity in hydrosilylation was observed between ketone and aldehyde substrates (Table 4, entries 3–5). In the reactions of **4h** with 4-methoxybenzaldehyde (**6e**), benzaldehyde (**6f**), and even **6b**, the alcohol from **4h** was obtained preferentially in 92%, 81%, and 87% yields, respectively (Table 4, entries 6–8). Surprisingly, even highly congested ketones, such as **4d** and **4a**, were preferentially reduced in the presence of aldehydes (**6b** or **6d**) to their corresponding alcohols in 92%, 72%, and 62% yields, respectively (Table 4, entries 9–11). To the best of our knowledge, there have been only six precedents for the preferential reduction of a ketone in the presence of an aldehyde.[10] However, all of these previous reactions necessitated the prior in situ protection of the more reactive aldehyde, followed by the reduction of the unprotected ketone and successive deprotection of the aldehyde during work-up. However, in these reactions, the in situ protections were significantly affected by subtle changes in the reaction conditions, thus making these methods unreliable.

The hydrosilylation of diketone **7** was carried out as shown in Scheme 3. After 3 h, almost all of **7** had been consumed, and the reaction mixture contained **8** as the major



Scheme 3. Reduction of diketone **7**. Reaction conditions: a) CuCl (2.0 mol%), **3** (2.0 mol%), *t*BuONa (12.0 mol%), Ph_2SiH_2 (1.0 mmol), toluene, RT, 3 h; b) HCl/MeOH.

product (78% yield) with a small amount of the corresponding diol from the reduction of the both keto groups (5% yield). Thus, the more bulky ketone functionality of **7** was preferentially reduced during the reaction. In the hydrosilylation reaction of **9**, which has both ketone and the formyl substituents (Scheme 4), **9** was fully consumed within 17 h and



Scheme 4. Reduction of ketoaldehyde **9**. Reaction conditions: a) CuCl (2.0 mol%), **3** (2.0 mol%), *t*BuONa (12.0 mol%), Ph_2SiH_2 (1.0 mmol), toluene/CH_2Cl_2, −40 °C, 17 h; b) K_2CO_3/MeOH.

the resulting reaction mixture contained **10** as the major product, with a small amount of the corresponding diol from the reduction of both the keto and the formyl moieties (3% yield) and the mono alcohol bearing a keto functionality from the reduction of only the formyl moiety (3% yield). The pure compound **10** was isolated in 69% yield from the reaction mixture, thereby indicating that the keto functionality had been preferentially reduced.

It is well-known that copper complexes are easy to aggregate.[11] Indeed, it was reported that the copper tetramer with a cubane structure, $[\{CuCl(PPh_3)\}_4]$, was obtained from the reaction of an equimolar mixture of CuCl and PPh_3.[12] In contrast, when the similar reaction of an equimolar mixture of CuCl and **2** was carried out, a lower-nuclearity complex, the copper dimer $[\{CuCl(\mathbf{2})\}_2]$ was obtained in 54% yield; the structure was confirmed by X-ray crystallography (Figure 2).[8] These results suggest that the unique steric bulk of **2** could suppress the aggregation of copper centers.

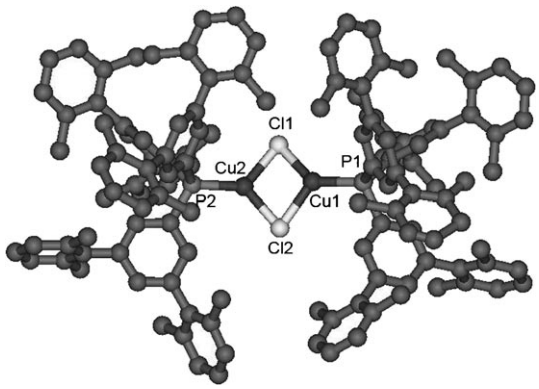


Figure 2. Crystal structure of $[\{CuCl(\mathbf{2})\}_2]$.

A possible catalytic cycle for this hydrosilylation reaction is shown in Figure 3. The key intermediates in the cycle are the bsp-bearing copper hydride species **11** and alkoxide **12**.

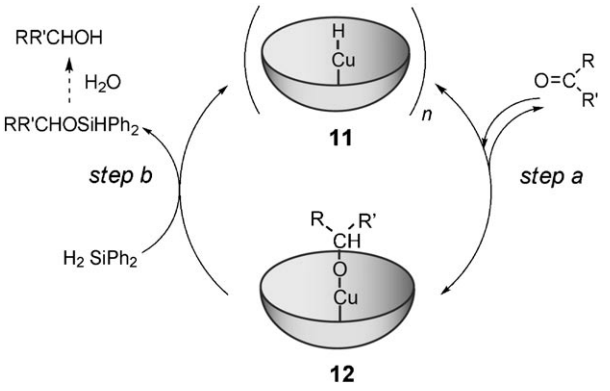


Figure 3. Plausible reaction mechanism.

Typically, copper hydrides prefer to aggregate; indeed, the copper hydride complex with PPh_3 was isolated as the hexamer $[(Ph_3PCuH)_6]$.[12] In this cycle, the complexation of **11** with a ketone or an aldehyde would reversibly afford **12** (step a). Here, **12** from bulky ketones could be of much lower nuclearity (possibly, mono) owing to the bulkiness of the bsp and bulky alkoxide moieties. Such a highly unsaturated complex **12** would be extremely reactive for σ-bond metathesis[13] with a silane to afford the product and regenerate **11** (step b). Conversely, following complexation with a less bulky ketone or aldehyde, **12** might be susceptible to aggregation owing to the smaller alkoxide moieties, thus their relative reactivity in step b would be low.

In conclusion, we have developed a highly active copper catalyst using a bsp ligand for the hydrosilylation reaction of ketones, and these reactions proceed faster with more bulky ketone substrates. It is noteworthy that the present catalysts afford the unprecedented preferential reduction of a bulky ketone in the presence of an unprotected aldehyde. Further studies on the reaction mechanism and characterization of the catalytic species are underway.

Received: November 11, 2009
Revised: December 3, 2009
Published online: January 25, 2010

Keywords: aldehydes · copper · hydrosilylation · ketones · P ligands

[1] a) P. W. N. M. van Leeuwen, *Homogeneous Catalysis*, Kluwer Academic, Dordrecht, **2004**; b) *Comprehensive Organometallic Chemistry III*, *Vol. 10 and 11* (Eds.: I. Ojima, T. Hiyama), Elsevier Science, Amsterdam, **2006**.

[2] For catalytic reactions using bsp as the ligand, see: a) O. Niyomura, M. Tokunaga, Y. Obora, T. Iwasawa, Y. Tsuji, *Angew. Chem.* **2003**, *115*, 1325–1327; *Angew. Chem. Int. Ed.* **2003**, *42*, 1287–1289; b) O. Niyomura, T. Iwasawa, N. Sawada, M. Tokunaga, Y. Obora, Y. Tsuji, *Organometallics* **2005**, *24*,

3468 – 3475; c) H. Ohta, M. Tokunaga, Y. Obora, T. Iwai, T. Iwasawa, T. Fujihara, Y. Tsuji, *Org. Lett.* **2007**, *9*, 89 – 92.
[3] a) C. Deutsch, N. Krause, B. H. Lipshutz, *Chem. Rev.* **2008**, *108*, 2916 – 2927; b) S. Rendler, M. Oestreich, *Angew. Chem.* **2007**, *119*, 504 – 510; *Angew. Chem. Int. Ed.* **2007**, *46*, 498 – 504.
[4] To date, only two catalyst systems have been reported for the hydrosilylation of **4a**: a) G. Hamasaka, A. Ochida, K. Hara, M. Sawamura, *Angew. Chem.* **2007**, *119*, 5477 – 5479; *Angew. Chem. Int. Ed.* **2007**, *46*, 5381 – 5383; b) G. Hamasaka, S. Kawamorita, A. Ochida, R. Akiyama, K. Hara, A. Fukuoka, K. Asakura, W. J. Chun, H. Ohmiya, M. Sawamura, *Organometallics* **2008**, *27*, 6495 – 6506; c) S. Díez-González, H. Kaur, F. K. Zinn, E. D. Stevens, S. P. Nolan, *J. Org. Chem.* **2005**, *70*, 4784 – 4796.
[5] See the Supporting Information.
[6] a) B. A. Baker, Z. V. Boskovic, B. H. Lipshutz, *Org. Lett.* **2008**, *10*, 289 – 292; b) B. H. Lipshutz, J. M. Servesko, B. R. Taft, *J. Am. Chem. Soc.* **2004**, *126*, 8352 – 8353; c) B. H. Lipshutz, K. Noson, W. Chrisman, A. Lower, *J. Am. Chem. Soc.* **2003**, *125*, 8779 – 8789.
[7] a) S. Díez-González, E. D. Stevens, N. M. Scott, J. L. Petersen, S. P. Nolan, *Chem. Eur. J.* **2008**, *14*, 158 – 168; b) S. Díez-González, N. M. Scott, S. P. Nolan, *Organometallics* **2006**, *25*, 2355 – 2358; c) H. Kaur, F. K. Zinn, E. D. Stevens, S. P. Nolan, *Organometallics* **2004**, *23*, 1157 – 1160.
[8] CCDC 753994 ($[CuCl(\mathbf{2})]_2 \cdot 1.5(C_4H_{10}O) \cdot 0.5(CH_2Cl_2)$), 753995 (**8**), and 753996 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For further details, see the Supporting Information.
[9] a) J.-L. Luche, A. L. Gemal, *J. Am. Chem. Soc.* **1979**, *101*, 5848 – 5849; b) A. L. Gemal, J.-L. Luche, *J. Org. Chem.* **1979**, *44*, 4187 – 4189; c) M. P. Paradisi, G. P. Zecchini, G. Ortar, *Tetrahedron Lett.* **1980**, *21*, 5085 – 5088; d) T. Chihara, T. Wakabayashi, K. Taya, H. Ogawa, *Can. J. Chem.* **1990**, *68*, 720 – 724; e) J. H. An, T. B. Sim, J. Choi, N. M. Yoon, *Bull. Korean Chem. Soc.* **1997**, *18*, 111 – 113; f) A. Clerici, N. Pastori, O. Porta, *Eur. J. Org. Chem.* **2002**, 3326 – 3335.
[10] G. van Koten, J. G. Noltes in *Comprehensive Organometallic Chemistry*, *Vol. 2* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1982**; pp. 709 – 763.
[11] a) G. Costa, E. Reisenhofer, L. Stefani, *J. Inorg. Nucl. Chem.* **1965**, *27*, 2581 – 2584; b) M. R. Churchill, K. Kalra, *Inorg. Chem.* **1974**, *13*, 1065 – 1071.
[12] a) W. S. Mahoney, D. M. Brestensky, J. M. Stryker, *J. Am. Chem. Soc.* **1988**, *110*, 291 – 293; b) W. S. Mahoney, J. M. Stryker, *J. Am. Chem. Soc.* **1989**, *111*, 8818 – 8823.
[13] a) T. Gathy, D. Peeters, T. Leyssens, *J. Organomet. Chem.* **2009**, *694*, 3943 – 3950; b) S. Rendler, O. Plefka, B. Karatas, G. Auer, R. Fröchlich, C. Mück-Lichtenfeld, S. Grimme, M. Oestreich, *Chem. Eur. J.* **2008**, *14*, 11512 – 11528.

