1398 *Organometallics* **2005,** *24,* 1398−1400

Borane-Catalyzed Hydrosilylation of Thiobenzophenone: A New Route to Silicon−Sulfur Bond Formation

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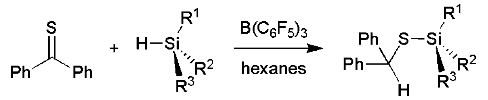
Received December 17, 2004

Summary: Clean and quantitative $B(C_6F_5)_3$-catalyzed hydrosilylation of thiobenzophenone by a variety of mono- and disilanes proceeds under mild conditions, at low catalyst loading, to furnish new silyl thioether compounds.

Hydrosilylation of ketones provides a general route for their reduction to alcohols.[1] The analogous reduction of thioketones by Si−H addition (Table 1), however, has so far been overlooked,[2] despite the potential synthetic utility of the resulting Si−S linkages in protecting and further elaborating important organosilicon or organosulfur reagents. Meanwhile, surprisingly few routes to silicon−sulfur linkages via hydrosilanes have been reported in the literature. Most of these are based on transition-metal-catalyzed dehydrocoupling of silanes and thiols.[3] Limiting the utility of such transition-metal-mediated transformations is the susceptibility of the metal to poisoning by thiol, as well as the susceptibility of other functional groups in either substrate to further reaction or degradation in the presence of transition metals. For example, our attempts to replace Si−H bonds with heteroatom substituents in oligosilanes of the formula $[-(HSiR)_n-]$ have been frustrated by Si−Si bond cleavage in these catenated chains during transition-metal-catalyzed Si−H activation reactions.[4] We have been exploring alternative, gentler strategies to generate Si−heteroatom bonds from silyl hydrides. Herein we report the first examples of Si−H addition to a thioketone: an efficient, mild route to silyl thioethers.

Table 1. Reactions of 3° Monosilanes with Thiobenzophenone in the Presence of Catalytic Amounts of $B(C_6F_5)_3$ [8]



silane	[catalyst], mol %	time,[a] h	product
Ph_3SiH	4	1.5	$Ph_2HCS-SiPh_3$ (**1**)
Ph_2MeSiH	0.01	3	$Ph_2HCS-SiMePh_2$ (**2**)
Et_3SiH	0.01	2	$Ph_2HCS-SiEt_3$ (**3**)
$PhMe_2SiH$	0.006	0.5	$Ph_2HCS-SiMe_2Ph$ (**4**)

[a] Times given are for quantitative conversions.

The Lewis acidic borane $B(C_6F_5)_3$ catalyzes both hydrosilylation of carbonyls[5] and heterodehydrocoupling of silanes with alcohols[6]. Although carbonyl complexation of the Lewis acid is typically implicated as the key mechanistic step for borane-catalyzed carbonyl transformations (e.g. $F_3{}^{\delta-}B\leftarrow O{=}C^{\delta+}RR'$),[7] Piers et al. have shown that, for $B(C_6F_5)_3$-mediated hydrosilylation, borane−carbonyl adduct formation competes with a faster pathway involving silyl hydride activation by the borane (i.e. $Ar_3{}^{\delta-}B-H\cdots Si^{\delta+}R_3$), followed by nucleophilic attack of the oxygen substrate at the nascent silylium ion. Thus, for Si−H addition to C═O in the presence of $B(C_6F_5)_3$, reaction rates diminish with increasing Lewis basicity of the carbonyl oxygen.[5] These results point to the less Lewis basic thiocarbonyl group (vide infra) as a promising candidate for hydrosilylation reactions catalyzed by $B(C_6F_5)_3$.

Hydrosilylation of thiobenzophenone by tertiary monosilanes occurs readily at room temperature in the presence of $B(C_6F_5)_3$ (Table 1). The reactions give quantitative conversion to the product silyl thioethers **1**−**4**. Not surprisingly, given the steric bulk of the substrate thioketone, the activity of this hydrosilylation reaction is quite sensitive to the size of the non-hydrogen substituents at silicon in the 3° silanes studied. Turnover frequencies range from 17 mol/(mol h) for Ph_3SiH to 30 000 mol/(mol h) for the less sterically hindered Me_2PhSiH. That Et_3SiH does not give the

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(1) Ojima, I.; Li, Z.; Zhu, J. Recent Advances in the Hydrosilylation and Related Reactions. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Chapter 29.

(2) The reduction of thiocarbonyl groups is perhaps best known in the context of Barton radical chemistry. It should be noted that silyl radicals can effect this transformation, leading to Si−S bond formation. However, the resulting reactive, carbon-based radicals can then undergo a wide range of rearrangements or further intermolecular reactions, which do not routinely preserve the initially formed $-CR_2-S-SiR'_3$ linkage. Examples of Si−S bond formation from thiocarbonyls via silyl radicals include: (a) Du, W.; Curran, D. P. *Org. Lett.* **2003**, *5*, 1765. (b) Cai, Y.; Roberts, B. P. *Tetrahedron Lett.* **2001**, *42*, 763. (c) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. *Tetrahedron* **1993**, *49*, 7193.

(3) See for example: (a) Purkayshtha, A.; Baruah, J. B. *J. Mol. Catal. A* **2003**, *198*, 47. (b) Corey, J. Y. *Adv. Silicon Chem.* **1991**, *1*, 327.

(4) (a) Rosenberg, L. *Macromol. Symp.* **2003**, *196*, 347. (b) Harrison, D. J.; Rosenberg, L. Unpublished results.

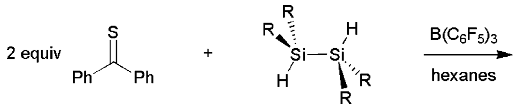
(5) (a) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440. (b) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090.

(6) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887.

(7) (a) Shambayati, S.; Crowe, W. E.; Schrieber, S. L. *Angew, Chem., Int. Ed. Engl.* **1990**, *29*, 256. (b) Shambayati, S.; Schrieber, S. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 1, pp 283−324.

10.1021/om048993n CCC: $30.25

Table 2. Reactions of 1,2-Dihydridodisilanes with 2 Equiv of Thiobenzophenone in the Presence of Catalytic Amounts of $B(C_6F_5)_3$ [8]



disilane	[catalyst], mol %	time,[a] h	product
$(HMe_2Si)_2$	0.004	0.5	$(Ph_2HCS)Me_2Si{-}SiMe_2(SCHPh_2)$ (**5**)
$(HPh_2Si)_2$	8	3	$HPh_2Si{-}SiPh_2(SCHPh_2)$ (**6**)
$(H^iPr_2Si)_2$	8	48	no reaction

[a] Times given are for quantitative conversions to products shown.

highest activities, however, suggests that the presence of at least one phenyl group at silicon also facilitates the cleavage of the Si−H bond.

The sensitivity of this catalysis to steric hindrance around the substrate Si−H bond is further illustrated by the performance of a range of disilanes in the hydrosilylation of thiobenzophenone in the presence of $B(C_6F_5)_3$ (Table 2). While 1,1,2,2-tetramethyldisilane readily reduces 2 equiv of thiobenzophenone (TOF = 50 000 mol/(mol h)) in the presence of the borane catalyst, giving the 1,2-bis(thioether)disilane **5**, the electronically similar, but much bulkier, 1,1,2,2-tetraisopropyldisilane gave no reaction with the thioketone, even at very high catalyst concentration and with prolonged reaction times. A steric and electronic balancing point is achieved with 1,1,2,2-tetraphenyldisilane: this substrate does react but requires more catalyst and longer reaction times than does 1,1,2,2-tetramethyldisilane and reacts with only 1 equiv of the thiobenzophenone to yield the unsymmetrical monosubstituted thiodisilane **6** (TOF = 9 mol/(mol h)). Of particular relevance to the potential use of these reactions in the derivatization of oligosilanes is the absence, in reactions shown in Table 2, of any products resulting from Si−Si bond cleavage. Presence of the intact Si−Si bond in compound **5** was verified by X-ray crystallography (Figure 1).[9]

The catalytic reactions described here are exceptionally clean; ^1H NMR of the crude product mixtures show only product silyl thioether or unreacted starting materials. Further, for the synthesis of compounds **2**−**5** the requisite catalyst loading is so low that the products can be used in further reactions (or submitted for microanalysis), without removal of the residual catalyst. Where higher catalyst loadings are necessary for the more sterically hindered silanes used in the synthesis of **1** and **6**, the residual $B(C_6F_5)_3$ is easily removed by filtration, as its pentane-insoluble PPh_3 adduct.

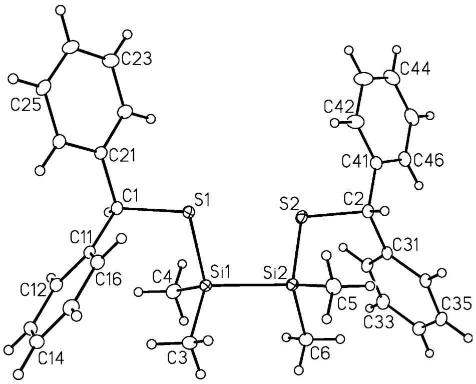


Figure 1. Molecular structure of **5**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

The silicon−sulfur bonds in **1**−**6** can be cleaved by ethanol to give diphenylmethanethiol ($HSCHPh_2$) and the corresponding ethoxysilanes. As for hydrosilylation, the rate of this ethanolysis is also sensitive to the size of substituents at silicon. Compound **1** requires 20 h in refluxing ethanol for quantitative conversion, while compound **4** reacts completely in under 16 h at room temperature. After 25 h of reflux in ethanol, compound **6** shows only 50% solvolysis of its Si−S bond. Preliminary studies indicate that diphenylmethanethiol is also produced in hydrolysis reactions of these compounds, along with silyl ethers corresponding to the condensation of product silanols.

Our preliminary investigations of the mechanism of this $B(C_6F_5)_3$-catalyzed thioketone hydrosilylation reaction have focused on the thioketone−borane interaction. If the thioketone forms a weak borane adduct relative to the corresponding ketone−borane adduct, as may be rationalized on the basis of hard and soft Lewis acid/base arguments, then our results may be consistent with a catalytic cycle in which the turnover-determining step involves Si−H activation by borane, as proposed by Piers et al.[5] Thus, a small equilibrium constant for thioketone−borane adduct formation would leave more borane available for productive catalysis and an apparent higher activity.[10] To probe the relative magnitude of the equilibrium constants for $Ph_2C{=}O{\rightarrow}B(C_6F_5)_3$ and $Ph_2C{=}S{\rightarrow}B(C_6F_5)_3$ adduct formation, we conducted a series of stoichiometric, competitive binding experiments. Complementary IR and UV spectroscopic data from these experiments suggest that in 1:1:1 mixtures of $B(C_6F_5)_3$, $O{=}CPh_2$, and $S{=}CPh_2$ the borane is largely, but not completely, complexed by the ketone. Thus, when $O{=}CPh_2$ is combined with $B(C_6F_5)_3$ in a 1:1 ratio, the strong benzophenone carbonyl stretch at 1660 cm^{-1} in the infrared spectrum disappears, consistent with borane complexation.[11] Upon addition of 1 equiv of $S{=}CPh_2$, to give a 1:1:1 $B(C_6F_5)_3/O{=}CPh_2/S{=}CPh_2$ mixture, a weak shoulder reappears at 1660 cm^{-1}. Similarly, a characteristic UV−vis absorption for thioketone (S=C $n \rightarrow \pi^*$, λ_{max} ~603 nm), which is greatly reduced by $Ph_2C{=}S{\rightarrow}B(C_6F_5)_3$ adduct formation in a 1:1

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[8] In a typical catalytic run, equimolar amounts of monosilane and thiobenzophenone (or 1:2 ratios of disilane to thiobenzophenone) were combined in pentane and the catalyst was added to the resulting blue solution. The reactions were monitored by the dissipation of the strong blue color associated with the thioketone. Conversions and product distributions were determined by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

[9] Crystal data for **5**: $C_{30}H_{34}S_2Si_2$, $M = 514.87$, triclinic, space group $P\bar{1}$, $a = 9.7665(4)$ Å, $b = 10.2755(4)$ Å, $c = 14.8114(6)$ Å, $\alpha = 85.0567(7)°$, $\beta = 75.6702(7)°$, $\gamma = 78.2575(7)°$, $V = 1409.02(10)$ Å^3, $Z = 2$, $\mu(\text{Mo K}\alpha) = 0.291$ mm^{-1}, $T = 193(2)$ K, Bruker PLATFORM/SMART 1000 CCD diffractometer, $2\theta_{max} = 52.76°$, 10 804 total data, 5735 unique data ($R_{int} = 0.0169$), refinement on F^2, final $R1(F) = 0.0315$ (for 4956 data with $F_o^2 \geq 2\sigma(F_o^2)$), $wR2(F^2) = 0.0852$ (for all unique data).

[10] This argument presumes that the rates of borane adduct formation and dissociation are not slow on the time scale of catalysis.

[11] We presume that ν_{CO} for $Ph_2C{=}O{\rightarrow}B(C_6F_5)_3$ is weaker and is shifted to lower frequency. It is apparently lost beneath another strong, broad absorption in this region of the infrared spectrum. See the Supporting Information for more details.

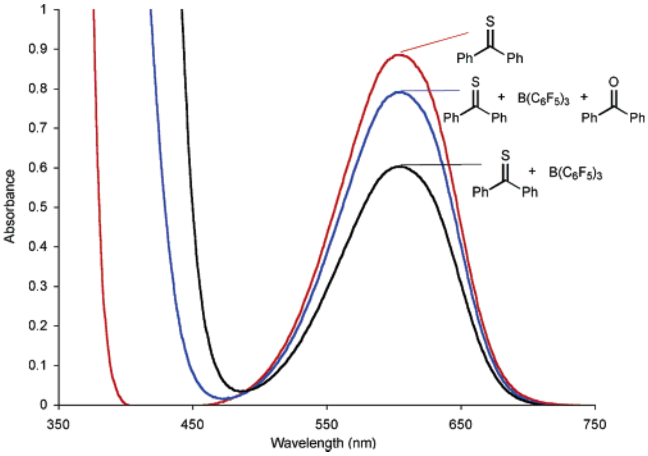

Figure 2. UV−vis spectra of free thiobenzophenone (in red), a 1:1 mixture of thiobenzophenone and $B(C_6F_5)_3$ (in black), and a 1:1:1 mixture of thiobenzophenone, $B(C_6F_5)_3$, and benzophenone (in blue).

mixture of thioketone and borane, regains most of its intensity upon the addition of 1 equiv of benzophenone (Figure 2), consistent with almost quantitative replacement of thioketone−borane adduct by ketone−borane adduct. These results support the decreased Lewis basicity of thiobenzophenone relative to its C=O analogue, which may be responsible for the high hydrosilylation activities we have observed, although they do not directly support a borane−Si−H activation mechanism for the hydrosilylation. Interestingly, preliminary experiments indicate that the hydrosilylation of benzophenone by Ph_3SiH in the presence of $B(C_6F_5)_3$ proceeds with activity comparable to or higher than that for thiobenzophenone, and if both ketone and thioketone are present, the *ketone* is selectively hydrosilylated.

The foregoing presents an exceptionally clean and mild route to new Si−S linkages. We continue to investigate the mechanism of this Lewis acid catalyzed silicon−sulfur bond formation, as well as the generality of this reaction. Exploration of other thioketones and more complex thiocarbonyl substrates is now under way,[12] the latter being of particular interest in the context of potentially chemoselective hydrosilylation of the C=S functionality.

Acknowledgment. Financial support for this work was provided by the NSERC of Canada and the University of Victoria.

Supporting Information Available: Text, tables, and figures giving full experimental details, including the preparation and characterization data of **1**−**6** and a CIF file giving complete X-ray crystallographic data for compound **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Thioketones and other C=S-containing derivatives are readily available from the corresponding C=O compounds, using Lawesson's reagent (see, for example: Varma, R. S.; Kumar, D. *Org. Lett.* **1999**, *1*, 697). A wide range of accessible thiocarbonyl compounds is also reported in the citations included in ref 2.