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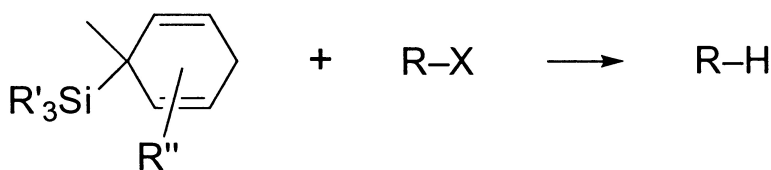
Silylated Cyclohexadienes as New Radical Chain Reducing Reagents: Preparative and Mechanistic Aspects

Armido Studer, Stephan Amrein, Florian Schleth, Tobias Schulte, and John C. Walton

(X = Cl, Br, I, SePh, OCSOPh)

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Silylated Cyclohexadienes as New Radical Chain Reducing Reagents: Preparative and Mechanistic Aspects

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Abstract: Various silylated 1,4-cyclohexadienes are presented as superior tin hydride substitutes for the conduction of various radical chain reductions. Debrominations, deiodinations, and deselenations can be performed using these environmentally benign reagents. Furthermore, *Barton–McCombie*-type deoxygenations using silylated cyclohexadienes are described. Radical cyclizations, ring expansions, and *Giese*-type addition reactions with the new tin hydride substitutes are presented. The polymerization of styrene can be regulated using silylated cyclohexadienes. Rate constants for hydrogen atom abstraction from two 1-silyl-cyclohexadienes by primary C-radicals were determined. The effects of the cyclohexadiene substituents on the reaction outcomes are discussed. Finally, qualitative EPR experiments on silyl radical expulsion from silylated cyclohexadienyl radicals are presented.

Introduction

Organotin hydrides such as Bu_3SnH, Ph_3SnH, and Me_3SnH have successfully been used to mediate preparative radical chain processes in chemistry over the last 40 years.[1] However, there are several drawbacks associated with these tin-based reagents. First of all, organostannanes are toxic.[2] In addition, special handling during disposal of tin residues is necessary, and problems with product purification are often encountered. It is therefore not surprising that many approaches have been presented to solve the so-called tin-problem in radical chemistry.[3a] For example, tris(trimethylsilyl)silane[3b] and tetraphenyldisilane[3c] have successfully been used to conduct reductive tin free radical reactions. For a more thorough compilation of tin hydride substitutes, we refer to a recently published review article on this topic.[3d]

One of us (JCW) has successfully used functionalized cyclohexadienes in radical chain reactions.[4] For example,

Scheme 1. Silylated Cyclohexadienes as Radical Chain Reducing Reagents – the Concept
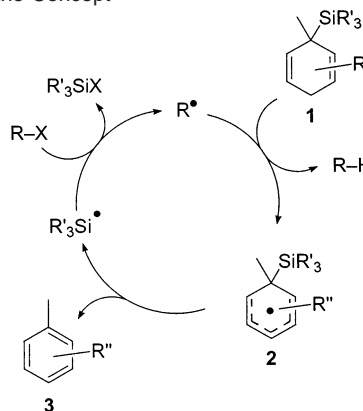
1-carbamoylcyclohexa-2,5-dienes are effective sources of aminoacyl radicals that ring close to yield β- and γ-lactams.[4d,f] On the basis of these results, the German group has introduced silylated 1,4-cyclohexadienes of type **1** as new, readily prepared radical chain reducing reagents.[5] The cyclohexadiene bis-allylic CH_2-moiety acts as the H-donor in these chain reactions. Reduction of a radical R with a reagent of type **1** affords cyclohexadienyl radical **2**. Rearomatization of **2** then provides the corresponding silyl radical, which is able to propagate the chain by reaction with a starting halide, xanthate or phenyl-selenide R–X (Scheme 1). Arene **3** is formed as the byproduct. We have also found that these silylated cyclohexadienes can be used in radical hydrosilylation reactions.[6]

Herein, we report in full detail the use of silylated cyclo-hexadienes as superior tin hydride substitutes. In addition, the

† Fachbereich Chemie der Universität Marburg.
‡ University of St. Andrews.
(1) For reviews, see: (a) Neumann, W. P. *Synthesis* **1987**, 665. (b) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987. (c) RajanBabu, T. V. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L., Ed.; Wiley: New York, 1995; Vol. 7, p 5016.
(2) (a) Ingham, R. K.; Rosenberg, S. D.; Gilman, H. *Chem. Rev.* **1960**, *60*, 459. (b) Boyer, I. J. *Toxicology* **1989**, *55*, 253.
(3) (a) Baguley, P. A.; Walton, J. C. *Angew. Chem.* **1998**, *110*, 3272; Baguley, P. A.; Walton, J. C. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3072. (b) Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188. (c) Sugi, M.; Togo, H. *Tetrahedron* **2002**, *58*, 3171, and references therein. (d) Studer, A.; Amrein, S. *Synthesis* **2002**, 835.
(4) (a) Binmore, G.; Walton, J. C.; Cardellini, L. *J. Chem. Soc., Chem. Commun.* **1995**, 27. (b) Baguley, P. A.; Binmore, G.; Milne, A.; Walton, J. C. *Chem. Commun.* **1996**, 2199. (c) Baguley, P. A.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2073. (d) Jackson, L. V.; Walton, J. C. *Chem. Commun.* **2000**, 2327. (e) Jackson, L. V.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1758. (f) Bella, A. F.; Jackson, L. V.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1839.

(5) Studer, A.; Amrein, S. *Angew. Chem.* **2000**, *112*, 3196; *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3080.
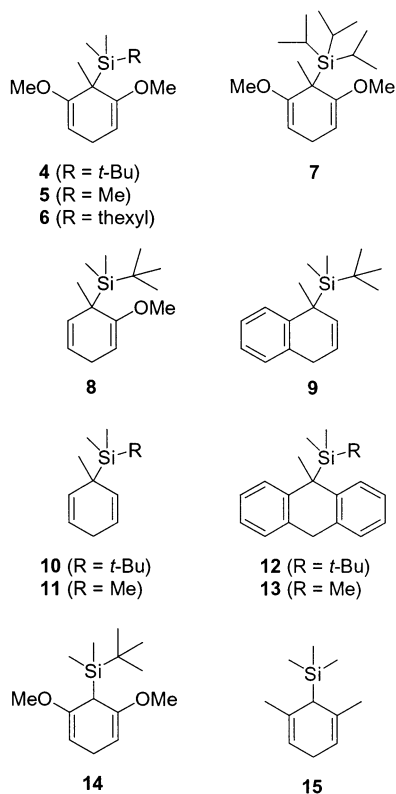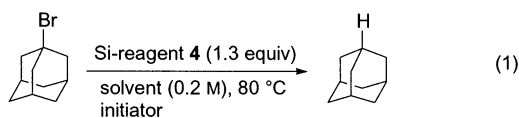
Figure 1. Various silylated cyclohexadienes studied.

Table 1. Reduction of Bromoadamantane with Reagent 4 under Different Conditions

entry	initiator	solvent	time (h)	yield (%)[a]
1	AIBN	benzene	14	88
2	AIBN	hexane	5.5	99
3	AIBN	toluene	14	28
4	AIBN	THF	14	78
5	AIBN	t-BuOH	14	42
6	AIBN	MTBE	14	60
7	Et$_3$B (0.1 equiv)/O$_2$	hexane[b]	5	82
8	Et$_3$B (0.2 equiv)/O$_2$	hexane[b]	4	99
9	Et$_3$B (0.2 equiv)/O$_2$	hexane[c]	14	-
10	air	hexane	9	99

[a] mol % adamantane determined by GC-analysis using tetradecane as internal standard. [b] Reaction was conducted at 80 °C. [c] Reaction was conducted at room temperature.

use of silylated cyclohexadienes as regulators for the radical polymerization of styrene is discussed. Moreover, we present EPR spectroscopic studies of silyl radical expulsion from the intermediate silylated cyclohexadienyl radicals.

Results and Discussion

Reductive Defunctionalizations using Silylated Cyclohexadienes. As recently described,[6c] the silylated cyclohexadienes can readily be prepared from the corresponding dienes in a one-pot silylation alkylation procedure (see also the Supporting Information). The silylated dienes **4**–**15** used for the present study are depicted in Figure 1.

Most of the initial experiments were conducted with reagent **4**, which was readily prepared on a *30*–*40 g-preparative scale*. As a test reaction, the reduction of bromoadamantane was investigated first (equation 1).

The yields were determined using GC-analysis with tetradecane as internal standard. The reduction did not go to completion in refluxing benzene (0.2 M) using α,α′-azoisobutyronitrile (AIBN) as initiator (88%, Table 1, entry 1). It is well-known that silyl radicals can add to benzene and are thus prevented from propagating the radical chain.[7] Indeed, the same

reaction in hexane provided adamantane in quantitative yield (entry 2). Reductions in toluene, THF, *tert*-butylmethyl ether (MTBE) and *t*-BuOH were not that efficient (entries 3–6). Therefore, most of the following experiments were conducted in hexane.

In addition to AIBN, other radical initiators can be used for the reduction of bromoadamantane with reagent **4**. Initiation with Et$_3$B (0.1 equiv)/O$_2$[8] afforded adamantane in 82% yield (entry 7). A quantitative conversion was observed upon using 0.2 equiv of Et$_3$B (entry 8). However, the same reaction at room temperature afforded only traces of adamantane (entry 9). As will be presented below, the silyl radical expulsion from the cyclohexadienyl radical deriving from **4** is a very fast process at ambient temperature. Therefore, the slow H-transfer step, namely the reduction of the adamantyl radical, is the reason for the failure of the room temperature reduction. Pleasingly, the reduction can be conducted perfectly well under an atmosphere of air, without using an initiator, to give adamantane in quantitative yield (entry 10).

We then examined the reduction of bromoadamantane under the optimized conditions using the Si-reagents **5**–**15** (Table 2). The thexyldimethylsilyl reagent **6** and the tri-isopropylsilylated cyclohexadiene **7** could be used as very efficient tin hydride substitutes. In both cases, quantitative reduction of bromoadamantane was obtained (entries 1,2). However, a disappointingly low conversion was obtained with the TMS-derivative **5** (35%, entry 3). We soon realized that **5** was not stable under the applied conditions. We further found that this diene slowly decomposed even at 4 °C and was therefore not a suitable tin hydride substitute. With the monomethoxy-reagent **8**, conversion was not complete under the optimized conditions (entry 4). Upon increasing the amount of AIBN (1 equiv) an 85% yield of adamantane was obtained (entry 5). The reduction with **8** could also be performed with di-*tert*-butylperoxide (DTBP) (hexane, sealed tube 140 °C, 77%, entry 6). Debromination with Si-reagent **10** (lacking the methoxy groups) under the optimized conditions provided adamantane in only 6% yield (entry 7). A 50% conversion was obtained upon increasing the amount of initiator and reagent (entry 8). We were pleased to find that a quantitative reduction was obtained with DTBP as an initiator at 140 °C (entry 9). We suspected that the diminished yields in the AIBN-experiments at 70 °C were due to inefficient initiation. Indeed, a quantitative reduction was obtained at 70 °C if di-

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(7) Cole, S. J.; Kirwan, J. N.; Roberts, B. P.; Willis, C. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 103. See also Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 3292.

(8) Miura, K.; Ichinose, Y.; Nozaki, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 143.

Table 2. Reduction of 1-Bromoadamantane with Reagents **5**−**15** in Hexane under Different Conditions

entry	Si-reagent (equiv)	initiator (equiv)	temp, time	yield (%)[a]
1	**6** (1.3)	AIBN (0.3)	80 °C, 5 h	99
2	**7** (1.3)	AIBN (0.3)	80 °C, 4.5 h	99
3	**5** (1.3)	AIBN (0.3)	80 °C, 7 h	35
4	**8** (1.3)	AIBN (0.3)	70 °C, 7 h	35
5	**8** (1.3)	AIBN (1.0)	70 °C, 7 h	85
6	**8** (1.3)	DTBP (0.3)	140 °C, 2.5 h	77
7	**10** (1.3)	AIBN (0.3)	70 °C, 5 h	6
8	**10** (2.0)	AIBN (1.0)	70 °C, 7.5 h	50
9[b]	**10** (2.0)	DTBP (0.3)	140 °C, 2.5 h	99
10	**10** (1.3)	TBHN (0.3)	70 °C, 0.8 h	99
11[b]	**11** (2.0)	DTBP (1.0)	140 °C, 1.5 h	90
12	**11** (2.0)	TBHN (1.0)	70 °C, 4.0 h	86
13	**9** (1.3)	AIBN (0.3)	80 °C, 14 h	25
14	**12** (1.3)	AIBN (0.3)	80 °C, 7 h	c
15	**13** (1.3)	AIBN (0.3)	80 °C, 7 h	c
16	**14** (1.3)	AIBN (0.3)	80 °C, 8 h	27
17	**15** (1.3)	AIBN (1.0)	70 °C, 7 h	9
18	**15** (1.3)	DTBP (0.3)	140 °C, 2.5 h	14
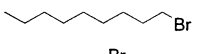
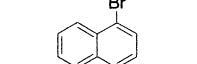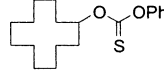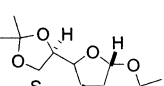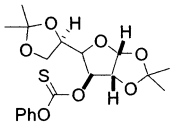[a] Determined by GC-analysis using tetradecane as internal standard. [b] Reaction was conducted in decane. [c] Zero yields also obtained with DTBP and TBHP.

tert-butylhyponitrite (TBHN)[9] was used as an initiator (entry 10). Obviously, the activating methoxy groups are necessary if AIBN is used as initiator.

In contrast to the bismethoxylated TMS-cyclohexadiene **5**, described above, the TMS-diene **11** was a stable compound and could readily be stored. As expected, reduction of bromo-adamantane with **11**, lacking the activating methoxy groups, could not be accomplished using AIBN as an initiator. However, satisfying yields were obtained with DTBP (entry 11) or TBHN (entry 12). Reduction of bromoadamantane under the optimized conditions with the benzannelated cyclohexadiene **9** provided adamantane in only 25% yield (entry 13). No further experiments were conducted with **9**. Our model reduction was intensively studied with the silylated dihydroanthracene derivatives **12** and **13**. The reduction was performed using various initiators under different conditions (entries 14, 15). However, the formation of adamantane was never observed. Finally, the silylated cyclohexadienes **14** and **15** lacking the geminal methyl group were tested as tin hydride substitutes. It turned out that the methyl group was essential for the success of the radical chain reduction. Only very low conversions were obtained with these reagents under different conditions (entries 16−18).

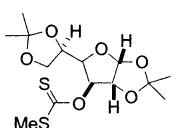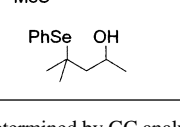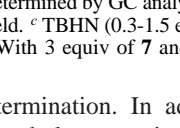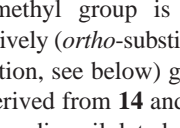From these initial experiments we concluded that the bis-methoxylated cyclohexadienes **4**, **6**, and **7** are very efficient reagents for radical debromination. For cyclohexadienes lacking the methoxy groups, such as **10** and **11**, reduction worked well only if alkoxyl radicals were used to initiate the chain reactions. As will be discussed in detail below, the methoxy groups strongly affected the rate of the rearomatization (silyl radical expulsion). Furthermore, the stability of the cyclohexadienyl radicals, and probably also the rate constant for the H-transfer step, correlated with the cyclohexadiene substituents (failed AIBN-initiation!). The cyclohexadienyl radicals generated from the silylated anthracene derivatives **12** and **13** are rather stable. Due to the low resonance energy of anthracenes, silyl radical expulsion from those radicals did not occur under the reaction conditions (see EPR experiments below) which eventually led

(9) Mendenhall, G. D. *Tetrahedron Lett.* **1983**, *24*, 451.

Table 3. Radical Reductions of Various Substrates Using 4, 7 and 10 (1.3 equiv) and AIBN (0.3 equiv) in Refluxing Hexane (0.2 M)

Entry	R–X	Si-reagent	t [h]	R–H [%][a]
1		4	3.5	99
2		7	4	99
3		4	5	98
4		7	3.5	99
5		4	18	99[b]
6		7	15	92[b]
7		7	7.5	76[b]
8		10	4	66[c]
9		7	2	99
10[d]		4	15	58
11[e]		7	16	93
12		4	15	74[b]
13		7	15	92[b]
14		4	18	91[b]
15		10	4	83[c]
16		4	18	70[b]
17		10	4	68[c]
18		4	5	63[b]

[a] Yield determined by GC analysis using tetradecane as internal standard. [b] Isolated yield. [c] TBHN (0.3-1.5 equiv). [d] With 2.0 equiv of 4 and 0.6 equiv of AIBN. [e] With 3 equiv of **7** and 1 equiv of AIBN.

to chain termination. In addition, we have shown that the geminal methyl group is essential for our reagents. The regioselectively (*ortho*-substituents in **14** and **15** efficiently block the α-position, see below) generated silylated cyclohexadienyl radicals derived from **14** and **15** underwent partial oxidation to the corresponding silylated arenes which is a chain termination process.[10]

Cyclizations and Intermolecular Additions. We then decided to study the scope and limitations of our new tin hydride substitutes. Some typical radical chain defunctionalizations were studied using Si-reagents **4**, **7**, and **10** under the conditions specified in Table 3. Primary, secondary, and aromatic halo-genides were efficiently reduced (entries 1−11). Moreover, *Barton−McCombie* type deoxygenations[11] using xanthates and thionocarbonates[12] could efficiently be conducted with our new reagents (entries 12−17). Deselenation of a tertiary phenyl-selenide worked equally well as shown in entry 18. Very recently, *Carreira* successfully used reagent **4** for a radical deselenation on the way to his synthesis of Leucascandrolide

(10) Kira, S.; Sugiyama, H.; Sakurai, H. *J. Am. Chem. Soc.* **1983**, *105*, 6436.
(11) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574.
(12) Robins, M. J.; Wilson, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 932.

Table 4. *Giese*-type Additions with Si-Reagents **4** (Ad = 1-Adamantyl)

entry	R^1–X	R^2	product	time (h)	yield (%)
1	Ad–Br	CN	**16**	7	59
2	Ad–Br	CO$_2$Me	**17**	7	42
3	Ad–I	CO$_2$Me	**17**	7	48
4	Ad–Br	COMe	**18**	3	40
5	Ad–Br	SOPh	**19**	8	16
6	Ad–Br	SO$_2$Ph	**20**	14	58
7	*t*-BuI	SO$_2$Ph	**21**	14	95
8^a	*t*-BuI	SO$_2$Ph	**21**	14	85
9^b	*t*-BuI	SO$_2$Ph	**21**	14	80
10	*i*-PrI	SO$_2$Ph	**22**	14	89
11	EtI	SO$_2$Ph	**23**	14	88

^{a} 0.15 equiv of AIBN were used. ^{b} 0.10 equiv of AIBN were used.

A.[13] This application clearly proves that our method can be applied in complex natural product syntheses.

Other common sets of synthetic reactions that utilize trialkyltin hydrides are radical cyclizations and intermolecular addition reactions. Cyclization of *o*-iodophenyl allyl ether (eq 2, 82%) and the *Beckwith–Dowd* ring enlargement reaction[14] could be conducted with Si-reagent **4** (equation 3, 49%). The *o*-iodophenyl allyl ether cyclization could also be performed with reagent **10** (1.5 equiv, TBHN (0.6 equiv), hexane (0.2 M), reflux, 65% yield). *Giese*-type additions work very well with the Si-reagent **4** (eq 4, → **16**–**23**, Table 4). The radical precursor, the Si-reagent (1.3 equiv), AIBN (0.3 equiv), and the olefin (1.3 equiv) were dissolved in hexane (1.2 M) and heated to reflux. Removal of the solvent and purification yielded the intermolecular addition products. Importantly, we did not have any problems with product purification. Bromoadamantane was successfully added to acrylonitrile (→ **16**, 59%, entry 1). We found that increasing the amount of acrylonitrile did not improve the yield. Thus, upon using 5 equiv of acrylonitrile under otherwise identical conditions a decrease of the yield was observed (30%), and hydrosilylation of acrylonitrile occurred in significant amounts (35%). Hydrosilylation was also a problem in the reaction with methyl acrylate (→ **17**, 42%, entry 2). To suppress the hydrosilylation, we repeated the reaction with methyl acrylate using iodoadamantane as radical precursor. It is known that I-abstraction is about 1 order of magnitude faster than Br-abstraction.[15] Indeed, a slightly increased yield was obtained (48%, entry 3), however, hydrosilylation could not be completely suppressed. Reductive addition of bromoadamantane to methyl vinyl ketone (→ **18**, 40%) and phenyl vinyl sulfoxide (→ **19**, 16%) occurred in moderate yields (entries 4 and 5). Phenyl vinyl sulfone turned out to be an exceptionally good acceptor. Good to excellent yields were obtained for the intermolecular reductive addition under standard conditions (0.3 equiv AIBN, 1.3 equiv olefin) using Ad-Br (→ **20**, 58%), *t*-BuI (→ **21**, 95%), *i*-PrI (→ **22**, 89%), and EtI (→ **23**, 88%, entries 6, 7, 10, 11). Finally, we also tested whether the amount of AIBN could be decreased. To this end, the reaction of *t*-BuI with phenyl vinyl sulfone was conducted with 0.15 equiv of AIBN. A slightly lower but still satisfactory yield was obtained

Table 5. Comparison of the Rate Constants for H-Atom Abstraction by Primary Alkyl Radicals from Silylated Cyclohexadienes with Those of Various Alternative Donors at 70 °C^a

H-donor	$10^{-5}k_H$/M^{-1} s^{-1}	ref
n-Bu$_3$SnH	55	18a
n-Bu$_3$GeH	2.75	18b
(Me$_3$Si)$_3$SiH	11	19
Et$_3$SiH	0.04	20
4	1.0	tw
10	0.7	tw
1-Et-1-CO$_2$H–CHD^b	0.14	4e

^{a} tw signifies this work. ^{b} H-atom abstraction from 1-ethylcyclohexa-2,5-diene-1-carboxylic acid by the ethyl radical.

(85%, entry 8). With 0.1 equiv of AIBN a further decrease of the yield was observed (80%, entry 9).

(for specification of R^1 and R^2 see Table 4)
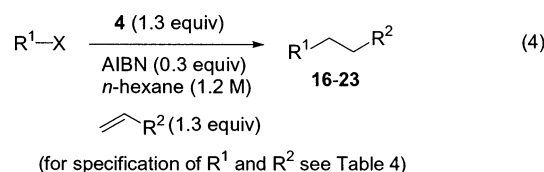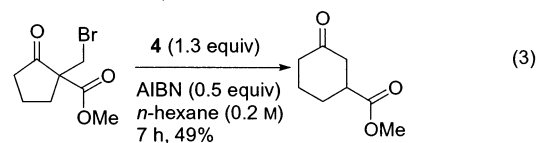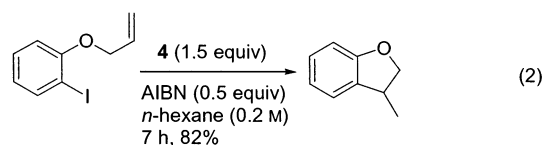
It is important to note that the syringe pump technique is not necessary to conduct these intermolecular additions. Furthermore, the olefin is used in only a small excess (1.3 equiv).

Kinetics of H-Atom Transfer from Silylated Cyclohexadienes. Hydrogen-transfer from our reagents to C-radicals is expected to be much slower than for the analogous process using the toxic Bu$_3$SnH. We determined the rates of hydrogen transfer from reagents **4** and **10** to a primary radical using the 5-*exo*-cyclization of the 5-hexenyl radical as the radical clock.[16,20] From measurements of the amounts of methylcyclopentane and 1-hexene produced in reactions at 70 °C, rate constants for abstraction of the bisallylic H-atoms by the 5-hexen-1-yl radical (k_H) were estimated (Table 5).

Rate constants for the reductions of C-radicals with cyclohexadienes have previously been determined and are in broad agreement with the values obtained in the present study.[17] It follows that the silyl substituents in our cyclohexadienes have no profound effect on the rate constant for the H-transfer reaction. Table 5 shows that **4** and **10** transfer H-atoms at least

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Table 6. Si-Reagent **4** as a Regulator for the Polymerization of Styrene

entry	4 (mol %)	AIBN (mol %)	conversion (%)	M_n	PDI
1	1	1	86	8000	2.5
2		1	>95	12 900	5.0
3	1	0.5	86	19 600	2.1
4		0.5	>95	38 600	4.2
5[a]		0.5	91	19 900	4.7
6	1	0.388	93	24 800	2.1
7		0.388	93	45 600	4.2
8	1	0.275	77	24 400	2.0
9		0.275	87	40 500	4.9
10	1	0.163	59	31 900	2.0
11		0.163	87	61 700	3.4
12	1	0.05	46	46 300	2.1
13		0.05	39	40 300	3.4

[a] Et$_3$SiH (0.5 mol %) was added.

55 times more slowly than Bu$_3$SnH,[18a] about two times more slowly than Bu$_3$GeH,[18b] and about an order of magnitude more slowly than tris(trimethylsilyl)silane ((Me$_3$Si)$_3$SiH).[19] However, the k_H values of **4** and **10** are significantly greater than k_H for Et$_3$SiH[20] and this explains why the silylated cyclohexadienes can sustain efficient chains whereas Et$_3$SiH cannot. The 2- and 6-methoxy substituents of **4** should extend the resonance stabilization in the cyclohexadienyl radical (**2**) and hence would be expected to augment the rate of H-donation. Thus, the somewhat smaller k_H value for **10** (which lacks the methoxy substituents) in comparison with **4**, is in accord with expectation. Comparison with analogous data for the 1-ethylcyclohexa-2,5-diene-1-carboxylic acid,[4e] (Table 5) shows an even smaller k_H value for this material, again suggesting that the 2,6-methoxy substituents significantly enhance the H-donation ability of **4**. This factor may contribute considerably to the efficiency of **4** as mediator of the chain reactions.

Silylated Cyclohexadienes as Regulators for the Polymerization of Styrene. The transfer reaction in radical polymerization describes a process in which further growth of the individual polymer molecule is prevented but which does not interfere with the kinetic chain. For example, the polymer radical reacts with a regulator forming a dead polymer and a new radical which can reinitiate a new chain. If the activity of the radical derived from the regulator is similar to the polymer radical, then the transfer reaction will have no influence on the overall polymerization kinetics, but the molecular weight of the polymer produced will be decreased.[21a] Thiols are often used as regulators to control the molecular weight in radical polymerizations.[21a−c] We conceived that our reagents would also be suited to this purpose because reduction/polymer chain termination with our Si-reagents will generate a silyl radical which in turn can reinitiate another polymer chain. We therefore carried out a small program along this line. The polymerizations were conducted in sealed tubes in neat styrene using varying amounts of AIBN as initiator in the presence of varying amounts of reagent **4** at 80 °C and were stopped after 6 h. The conversion was determined gravimetrically. The polydispersity indices (PDI) and the molecular weights of the polymers were analyzed using size exclusion chromatography (SEC). As control experiments the polymerizations were also conducted without Si-reagent **4**. The results are summarized in Table 6.

Using 1% of AIBN together with 1% of **4** under the conditions depicted above afforded polystyrene (PS) with an M_n of 8000 with a PDI of 2.5 (entry 1). The control experiment

without addition of the regulator provided PS with an M_n of 12 900 and a broader PDI (5.0, entry 2). Thus, reagent **4** did indeed beneficially regulate the radical polymerization of styrene leading to decreases in both M_n and PDI. The same trend was observed for all the other styrene polymerizations (compare entries 3 and 4, 6 and 7, 8 and 9, 10, and 11). In all the **4**-mediated polymerizations a comparatively low PDI (2.0−2.5) was obtained. The molecular weight of the desired PS could be adjusted depending on the AIBN/**4**-ratio. It is important to note that with Et$_3$SiH as an additive, the M_n-value could also be decreased, however, the PDI remained very high (4.7, entry 5). We also determined the chain transfer constant C$_x$ for regulator **4** according to *Mayo* at 100 °C.[21d]

$$1/M_n = 1/M_o + C_x\,[\textbf{4}]/[\text{styrene}] \qquad (2)$$

C_x is a dimensionless number and is defined by eq 2 (M_n = molecular weight obtained in the presence of regulator; M_0 = molecular weight obtained in the absence of regulator). For regulator **4** a chain transfer constant of 0.45×10^{-3} was determined (see the Supporting Information). The C_x for **4** is smaller than chain transfer rate constants obtained for thiol regulators.[21a−c] This is not surprising because H-transfer to C-centered radicals is much faster from thiols than from cyclohexadienes.[20] Importantly, along with the regulation of the molecular weight, cyclohexadiene **4** is able to significantly decrease the PDI.

Spectroscopic Study of Silyl Radical Expulsion from Silylated Cyclohexadienes. Solutions of individual silylated compounds in neat DTBP, or with DTBP diluted in cyclopropane, were photolyzed (500W Hg lamp) and radical production was monitored by EPR spectroscopy. For the 1-TMS compound **11** a spectrum with a *dtt* line structure was observed in the temperature range 150−310 K. The hyperfine splittings (hfs) [$a(1H) = 12.5$, $a(2H) = 8.4$, $a(2H) = 2.4$ G at 250 K, $g = 2.0027$] were very similar to those of structurally related cyclohexadienyl radicals;[4f,22] hence, the spectrum was easily be recognized as that of a cyclohexadienyl radical of type **2**. This spectrum weakened at higher temperatures and was replaced above ca. 350 K by a new 7-line spectrum [$g = 2.0029$, $a(6H) = 20.2$ G]. These EPR parameters were very similar to those reported for the Me$_2$C·OSiR$_3$ radical [R = Me; $a(6H) = 21.0$, R = Et; $a(6H) = 20.3$, R = Si(TMS)$_3$; $a(6H) = 20.0$ G],[23,24] and therefore, we attribute the spectrum to Me$_2$C•OSiMe$_3$ radicals formed by addition of released Me$_3$Si• radicals to acetone. Acetone would be expected to build up at higher temperatures from thermal dissociation of the initial *t*-BuO• radicals.

As a further check on radical production, samples containing **11**, DTBP and Me$_3$CBr (1 equiv) were photolyzed in the resonant cavity. The same cyclohexadienyl radical (type **2**) was

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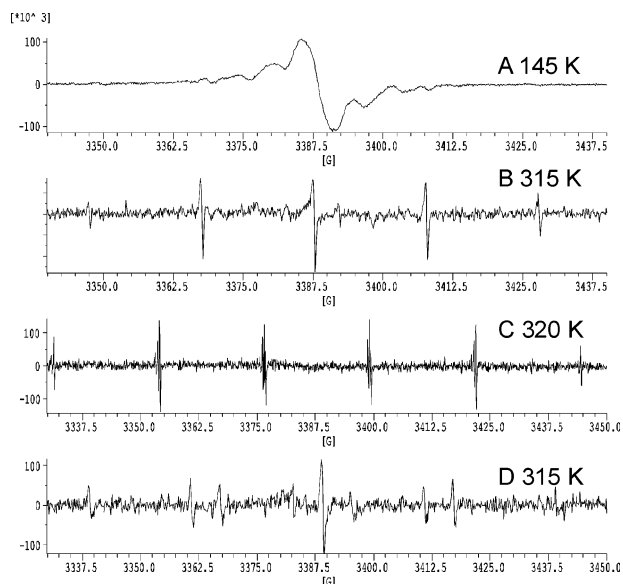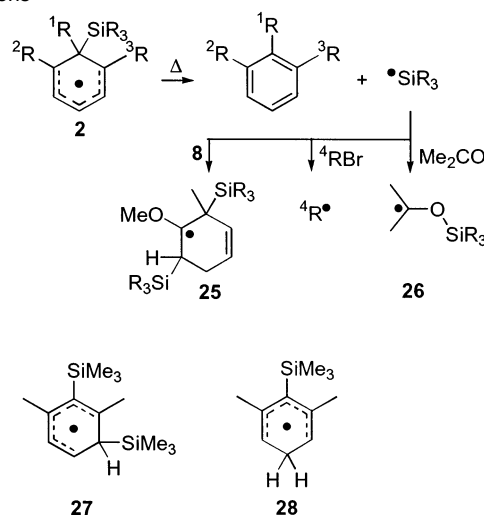
Figure 2. EPR spectra obtained on photolysis of solutions containing **4** and DTBP. A: compound **4** and DTBP at 145 K in cyclopropane. B: reagent **4** in neat DTBP at 315 K showing radical **26**. C: reagent **4**, DTBP and *t*-BuBr at 320 K showing the central 6 lines of the *t*-Bu• radical (including second order structure). D: reagent **4**, DTBP and *n*-PrBr at 315 K showing the *n*-Pr• radical.

observed up to temperatures of ca. 325 K. Above this the *t*-Bu• radical started to appear and its spectrum dominated at 350 K and above (see the Supporting Information). These observations strongly support the mechanism of Scheme 1 and indicate that dissociation of radical **2** (R″ = H) becomes rapid at 325 K and above. A very similar sequence of spectra was obtained from compound **10**, the only difference being that the spectra at 350 K (in the absence of *t*-BuBr) showed Me$_2$C•OSiMe$_2$Bu-*t*, plus additional complex spectra that were probably due to silyl radical addition to the substrate.

Somewhat different behavior was encountered with the mono-**8** and di-methoxy **4** derivatives. Photolysis of a solution of **4** and DTBP at 145 K gave rise to the spectrum shown in Figure 2 A. This consisted of 7 broad lines with a spacing of $a(6H) = 6.4$ G. The known spectrum of the Me$_3$Si• radical has $a(9H) = 6.3$ G[25] and therefore spectrum A can most likely be attributed to the *t*-BuMe$_2$Si• radical. The central line was somewhat enlarged, possibly because of overlap with adduct radicals derived from the Si-radical and substrate **4** (see below).

Even when photolysis was carried out at 100 K, with solutions of **4** in *n*-propane, no sign of the corresponding cyclohexadienyl radical **2** was obtained. Above ca. 310 K, where acetone formation became appreciable,[26] the Me$_2$C•OSiMe$_2$Bu-*t* radical (**26**) (Figure 2B) was observed, confirming the release of the silyl radical. Solutions containing **4**, DTBP and alkyl bromides were also examined. Figure 2C shows the high quality spectrum of the *t*-Bu• radical (central 6 lines only) obtained in the presence of *t*-BuBr (1 equiv). This spectrum started to appear at ca. 270 K. That the released •SiMe$_2$Bu-*t* radical could also abstract bromine from primary bromides under EPR conditions was demonstrated by the observation of the *n*-Pr• radical (Figure

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(26) The concentration of the Me$_2$C•OSiMe$_2$Bu-*t* radical in Figure 2B was ca. 10^{-7} M and hence acetone concentrations of this order of magnitude, or greater, are required for the Si-radical adducts to be detectable.

Scheme 2. Reactions of Si-centered Radicals under EPR Conditions

2D) when *n*-PrBr was present in solution. Similar results were obtained with the mono-methoxy derivative **8**. No cyclohexadienyl radical was detected, even at 145 K, however, the •SiMe$_2$-Bu-*t* radical was not observed in this case. Low-temperature spectra in cyclopropane showed a broad doublet spectrum (hfs ca. 12 G) that might be due to addition of •SiMe$_2$Bu-*t* to **8** to generate radical **25** (Scheme 2). That •SiMe$_2$Bu-*t* radicals were produced efficiently was shown by the observation of **26** at *T* > ca. 340 K, and by the observation of the *t*-Bu• radical at *T* > 270 K.

It is evident from these results that **4** and **8** are very efficient sources and that Si-radicals are released at temperatures below 270 K and probably even as low as 150 K, as judged by the absence of cyclohexadienyl type species, and the direct observation of •SiMe$_2$Bu-*t* from **4**.

EPR experiments with the benzannelated cyclohexadiene **9** showed a poorly resolved spectrum at lower temperatures that was probably due to the benzannelated cyclohexadienyl radical. Dissociation of this species required higher temperatures, as judged by the appearance of the acetone adduct **26** only above 360 K. For the silylated dihydroanthracene derivatives **12** and **13**, ill-resolved spectra that were probably the delocalized cyclohexadienyl analogues were observed at lower temperatures, but dissociation was evidently very difficult because the acetone adduct was not detected from either compound even at 360 K.

The low-temperature spectrum from the silylated cyclohexadiene **15**, lacking the geminal methyl group, was as expected for the cyclohexadienyl radical **2** (R^1=R^2=R^3= Me) [$a(2H) = 2.87$ G, $a(6H) = 7.93$ G, $a(1H) = 12.49$ G, $a(1H) = 23.13$ G at 250 K]. At higher temperatures the spectrum evolved through several stages to a complex spectrum at 345 K that probably consisted of bis-silylated radical **27** together with isomeric species (see the Supporting Information). Radical **27** could have been formed by coupling of **2** with a silyl radical and subsequent abstraction of an H-atom, or by partial oxidation to the corresponding silylated arene followed by addition of a silyl radical. By either mechanism a mixture of isomers should result. None of the acetone adduct radical **26** was detected. Radical **28,** which could easily be generated from **15** by abstraction of the bis-allylic H-atom at C(1), was not detected. However, minor amounts could easily have been hidden under the complex spectra of **2** and **27**.

Table 7. Temperature Ranges (K) over Which Cyclohexadienyl Type Radicals (CHD), Acetone Adduct Radicals **26**, and *t*-Bu• Radicals Were Spectroscopically Observed for Various Si-Reagents

Si-reagent	*T* range CHD **2**	*T* range acetone adduct **26**	*T* range *t*-Bu•
4	*a*	>310	>270
8		>340	>270
11	150−310	>350	>325
10	150−310	>350	
9	240−340	>360	
13	240→360	n.o.[b]	
12	240→360	n.o.	
15	240−340	n.o.	

a SiMe₂Bu-*t* observed at lower temps. *b* n.o. signifies not observed.

Data relevant to silyl radical release from the series of silylated reagents is collected in Table 7. These spectroscopic observations agree unequivocally with the deductions about reagent efficiency from the preparative experiments with 1-bromoadamantane. For the methoxy-substituted reagents **4** and **8**, cyclohexadienyl radicals were not observed because dissociation and release of •SiMe₂Bu-*t* was very rapid even at $T < 270$ K. This was supported by the observation of **26** and *t*-Bu• at comparatively low temperatures. This supports the classification of these two reagents as very efficient Si-radical sources. For compounds **10** and **11** cyclohexadienyl radical formation proceeded well but dissociation and silyl radical release became appreciable at somewhat higher temperatures (325 K). For the dihydroanthracene derivatives **12**, **13** silyl radical release was not observed by EPR in the accessible temperature range and this explains the zero adamantane yields of Table 2. Although H-abstraction from reagent **15** gave mainly the desired cyclohexadienyl radical **2** the reaction was diverted into other channels at higher temperatures.

Conclusions

We reported the syntheses of various silylated cylohexadienes. These dienes are readily prepared on a large scale and can be used as efficient tin hydride substitutes. Product purification is straightforward. In contrast to tris(trimethylsilyl)silane,[3b] which is probably the most successful tin hydride substitute to date, our most promising Si-reagent **4** is a solid and can be readily stored and handled. Most of the common reductive radical reactions can be conducted perfectly well with the new Si-reagents. Excellent yields are achievable with primary, secondary, and tertiary organo-iodides and -bromides. Yields approaching 90% can also be obtained with organo-chlorides and thionocarbonates. Reductions of xanthates and phenyl selenides were also realized in useful yields. The radical chain processes were tolerant of hydroxy and carbonyl functional groups. With this reagent, the alternative dissociation of intermediate **2**, releasing a methyl radical, was not observed in any case and hence product contamination with silylated-arene byproducts was nonexistent.

An advantage of silylated cyclohexadienes is that their properties can be tuned to suit particular synthetic needs. Silyl radicals of differing reactivity may be incorporated. The two key chain propagation steps, i.e., silyl radical release from radical **2** and H-atom transfer, can both be controlled to some extent by introduction of suitable substituents into the cyclohexadiene ring. The 2,6-dimethoxy substitution of **4** was particularly

effective because it led to rapid silyl radical release and simultaneously was beneficial to the H-atom transfer step. H-transfer from reagent **4** to primary C-radicals was about 10 times slower than the reduction of primary C-radicals with (Me₃-Si)₃SiH. This offers some advantages, especially for *Giese*-type addition reactions, where the direct reduction often competes with the desired intermolecular addition reaction. *Giese*-type additions with reagent **4** can be conducted without using a large excess of the olefin and without using syringe pump techniques. Similarly, reagent **4** should be effective for radical cascade (domino) sequences where a series of rearrangement steps is required to occur without reduction of the individual intermediates. We have also shown that Si-reagent **4** can be used as regulator for the polymerization of styrene. Molecular weight can be adjusted and depends on the initiator/Si-reagent-ratio. Polymerizations mediated by reagent **4** afford polystyrenes with rather narrow PDIs (∼2.0).

Our exploratory EPR experiments showed that silylated cyclohexadienes are good sources of Si-centered radicals for spectroscopic work. Direct observation of silyl radicals will not in general be possible because they react with the starting cyclohexadienes. Triethylsilane is the classic choice for use in conjunction with an alkyl bromide for EPR observation of C-centered radicals at low temperatures, whereas Me₃SnSnMe₃ has been preferred for higher temperature work.[27] Reagent **4** offers some advantages at higher temperatures (>270 K) where Et₃SiH initiated spectra often fade and when avoidance of stannanes is desirable. In addition, some C-centered radicals (particularly *σ*-radicals) abstract hydrogen from the ethyl groups of Et₃SiH, as a side reaction giving Et₂Si(H)CH•CH₃ radicals, that interfere with the desired spectrum.[28] This will not be a problem with reagent **4** because the *t*-BuMe₂Si group does not possess secondary H-atoms adjacent to silicon. Good quality spectra of various transient radicals can be obtained by use of **4** in conjunction with a reaction partner having a high affinity for Si such as an alkyl bromide or a carbonyl compound. Thus, **4** and analogues will be useful in a general sense for spectroscopic detection, characterization and monitoring of radical intermediates in various processes. EPR experiments with reagents **4**−**15** provided good support for the proposed chain mechanism and showed that Si-radical formation was most efficient for the methoxy-substituted cyclohexadienes, was difficult for the benzannelated derivative **9** and was too slow to detect for the dihydroanthracene reagents in the accessible temperature range. Reagents **4**, **7**, and **10** provide versatile and environmentally friendly additions to the toolkit of the synthetic chemist and are superior to current favorites in many applications.

Experimental Section

General. Solvents were purified by standard methods. Compounds sensitive to air and moisture were handled under argon using Schlenk techniques. FC: Merck or Fluka silica gel 60 (40−63 μm); at ca. 0.4 bar. GC: Hewlett-Packard 5890 chromatograph using Hewlett-Packard HP-5, Macherey-Nagel Optima *δ*−3, or Supelco *γ*-DEX 120 columns. Melting points: Büchi 510 apparatus; uncorrected. I. R. spectra: recorded on a Perkin-Elmer 782 or Bruker IFS-200 spectrophotometer.

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MS: Recorded on a VG Tribid, Varian CH7 (EI); IonSpec Ultima, Finnigan MAT TSQ 700 or a Finnigan MAT 95S (ESI) in *m/z* (% of basis peak). SEC: Pump: Merck Hitachi L-6200 A. Columns: Polymer Laboratories PL gel 5 μm GUARD and MIXED-C. Mobile phase: THF (1 mL/min). Detector: Shodex RI-101. Molar weights and PDI were determined using polystyrene samples of known molecular weight distribution. For data analysis Polymer Laboratories Cirrus GPC Online software (Version 1.0) was used. EPR spectra were obtained with a Bruker EMX 10/12 spectrometer operating at 9.5 GHz with 100 kHz modulation. Samples of the substrate (0.3 to 40 mg) and di-*tert*-butyl peroxide (0.01 to 0.1 mL), in 4 mm od quartz tubes were photolyzed in the resonant cavity by light from a 500 W super pressure mercury lamp. For reactions performed in cyclopropane (up to 0.5 mL), the solutions were degassed on a vacuum line using the freeze—pump—thaw technique, and tubes were flame sealed. In all cases where spectra were obtained, hfs were assigned with the aid of computer simulations using the Bruker Simfonia software package. For quantitative measurements, signals were double integrated using the Bruker WinEPR software.

Reduction of Bromoadamantane with Reagent 4 (Representative Example). 1-Bromoadamantane (107.5 mg, 0.50 mmol), Si-reagent **4** (174.5 mg, 0.65 mmol) and AIBN (24.5 mg, 0.15 mmol) were dissolved in hexane (2.5 mL) under Ar and heated to reflux. The course of the reaction was monitored by GC. The yield was determined by GC-analysis using tetradecane (130 μL, 0.50 mmol) as an internal standard. After 5.5 h, the conversion was found to be complete and the yield of adamantane was determined to be 99%.

***Barton—McCombie* Deoxygenation with Reagent 4 (Representative Example).** 1,2;5,6-Di-*O*-isopropyliden-3-*O*-phenoxythiocarbonyl-α-D-glucofuranoside (197 mg, 0.50 mmol), Si-reagent **4** (174 mg, 0.65 mmol) and AIBN (25 mg, 0.15 mmol) were dissolved in hexane (2.5 mL) under Ar. The reaction mixture was heated to reflux for 18 h. Removal of the solvent in vacuo and purification by FC (Et$_2$O/pentane 1:10) afforded 3-deoxy-1,2;5,6-di-*O*-isopropylidene-α-d-glucofuranoside (111 mg, 91%) as a colorless solid.

***Giese*-Type Addition using Reagent 4 (Representative Example).** 1-Bromoadamantane (213 mg, 1 mmol), Si-reagent **4** (349 mg, 1.3 mmol), AIBN (49 mg, 0.3 mmol), and acrylonitrile (85 μL, 1.3 mmol) were dissolved in hexane (3 mL) under Ar. The reaction mixture was heated to reflux for 4 h. Removal of the solvent in vacuo and purification by FC (Et$_2$O/pentane 1:30) afforded 3-adamantylpropionitrile **16** (112 mg, 0.59 mmol, 59%) as a colorless oil.

Polymerizations (Representative Example). In a Schlenk tube, AIBN (33 mg, 0.203 mmol) and Si-reagent **4** (141 mg, 0.524 mmol) were dissolved in freshly distilled styrene (6 mL, 52.4 mmol). The mixture was degassed with three freeze—thaw cycles. The Schlenk tube was flushed with argon, sealed and heated to 80 °C for 6 h. After cooling to room temperature, the polymer was dissolved in CH$_2$Cl$_2$ and dried at 60 °C (high vacuum, 12 h). Conversion was determined gravimetrically: 93%. The polymer was characterized by SEC (average values of three runs): M_n = 24 800; M_w = 51 000; PDI = 2.1.

Supporting Information Available: Full experimental details (including analytical data) for the preparation of **4**−**15**. Representative EPR spectra obtained from compounds **8**, **9**, **11**, **12**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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