

The reaction of tris(trimethylsilyl)silyllithium with dibenzosuberone

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Abstract

Tris(trimethylsilyl)silyllithium (**1**) reacts with dibenzosuberone in ether to give, after carbonyl addition of the lithium silanide and lithium trimethylsilylanolate elimination according to a modified Peterson mechanism, the transient silene **5** which is trapped by addition of excess **1** at the Si=C double bond to afford 2-[5H-dibenzo[a,d]cyclohepten-5-yl]-1,1,1,4,4,4-hexamethyl-2,3,3-tris(trimethylsilyl)-tetrasilane (**7**). When the same reaction is carried out in dimethoxyethane, no silene is generated, but after carbonyl addition of **1** at dibenzosuberone a 1,3-Si,O-trimethylsilyl migration occurs, producing the lithium silanide **8** which undergoes an intramolecular addition at the 10,11-C=C double bond of the dibenzocycloheptatriene system under formation of a bicyclic organolithium derivative which reacts with excess dibenzosuberone to afford the alcohol **10**. Compounds **7** and **10** were fully characterized by their IR, NMR and MS data, for **10** the results of an X-ray crystal structure analysis are also given.

Keywords: Silenes; Silaethenes; Peterson reaction; Polysilanes

1. Introduction

Silicon carbon double bond systems, known to be extremely reactive, may be stabilized kinetically by bulky substituents, so that for example some silaethenes could be isolated and structurally characterized [1]. The influence of suitable substituents on the thermodynamic stability of silaethenes has not yet been investigated thoroughly.

In the case of the chemistry of phosphalkenes, it is well known that π -donor substituents at the phosphathene carbon atom lead to a remarkable stabilization of these unsaturated systems. Thus, dialkylamino-phosphathenes are nearly stable with respect to the dimerization to 1,3-diphosphacyclobutanes without the necessity for a kinetic stabilization [2]. This was interpreted as being attributable to the contribution of resonance structures outlined in Eq. (1) [3].



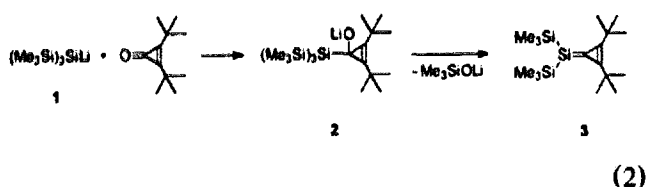
Similar π -conjugations between suitable substituents and the double bond may also be discussed for silaethenes. Theoretical studies performed by Apeloig and coworker [4] led to the conclusion that "in silenes with strong π -donors (e.g. OH) attached to carbon the natural $\text{C}^{\delta-}=\text{Si}^{\delta+}$ π -polarity is reversed". The effect is expected to lead to a weakening of the Si=C bond, which is in agreement with the comparatively long Si=C distances found by Brook and coworker [5] for stable 2-siloxysilenes, and it is very likely that the decreased polarity of the silicon carbon double bond in these silenes contributes to their stability.

In recent studies we succeeded in synthesizing 1-hydroxyalkyl-tris(trimethylsilyl)silanes, which in the presence of base eliminate trimethylsilylanolate according to a modified Peterson mechanism under formation of silaethenes. The transient silenes obtained in this way dimerize in the absence of scavenger reagents, the structures of the resulting products being dependent on the substituents at the starting alcohol, the reaction conditions and the organometallic base applied [6–9]. In continuation of these investigations, we are interested in generating silaethenes bearing π -donor substituents at the silene carbon atom according to the model discussed above and in studying the deviations of their behavior from that of previously prepared systems.

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2. Results and discussion

In 1991 Regitz and coworkers [10] described the reaction of lithium trimethylsilylphosphides with sterically congested cyclopropenones, which leads, according to a Peterson olefination process, to substituted phosphatrialfulvenes, new phosphalkene derivatives with an inverse P=C bond polarization due to the electron releasing properties of the cyclopropenylidene system, which proved to be relatively stable. These results encouraged us to study the synthesis and behavior of similarly substituted silenes (Eq. (2)).

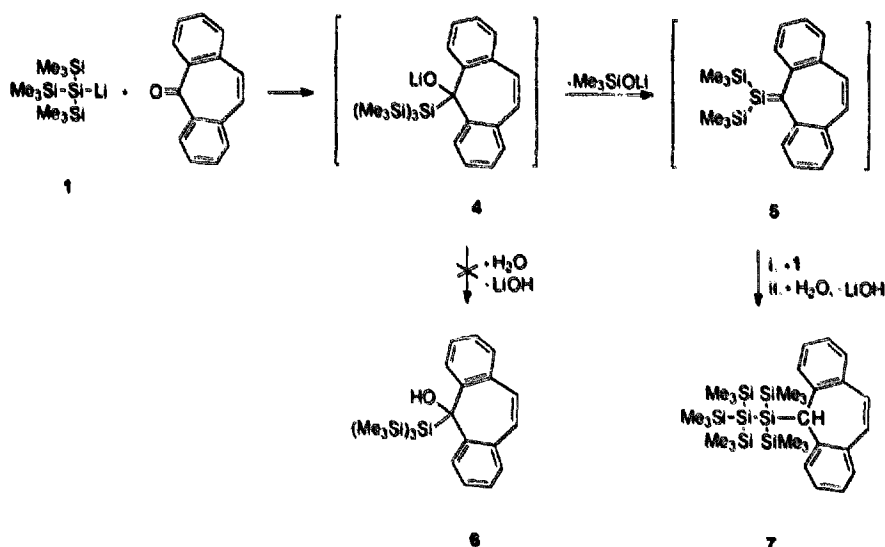


The lithiated 1-hydroxyalkyl-tris(trimethylsilyl)silane **2**, expected to be formed by reaction of tris(trimethylsilyl)silyllithium (**1**) with 2,3-di-tert-butylcyclopropenone, should decompose in situ under elimination of lithium trimethylsilylanolate to afford the silene **3**. Unfortunately the reaction led to complex mixtures of products, which could not be cleanly separated and identified.

Similar electronic effects should be expected when the silene double bond is connected with a cycloheptatriene system. Therefore we extended our studies to the reaction of **1** with dibenzosuberone. This reaction, carried out in ether at low temperature, led to a colorless crystalline product identified as 2-[5H-dibenzo[a,d]cyclohepten-5-yl]-1,1,1,4,4,4-hexamethyl-2,3,3-tris(trimethylsilyl)-tetrasilane (**7**) (Scheme 1).

As expected, the lithium silanide **1** is added at the carbonyl group of dibenzosuberone to give the lithiumoxyalkyl-tris(trimethylsilyl)silane **4**, which spontaneously eliminates lithiumtrimethylsilyloxide to afford the transient silene **5**. Consequently, the formation of the polysilane **7** is easily understood as being the result of the addition of excess lithium silanide **1** at the Si=C double bond of **5**, giving an organolithium intermediate which is hydrolysed during the aqueous work-up to give **7**. The polysilane **7** is obtained independently of the molar ratio of the components, and also regardless of whether the silanide is given to the ketone or vice versa. Obviously, owing to the steric demand of the lithium silanide **1**, the addition at the carbonyl group is a comparatively slow reaction, whereas the silanolate elimination is a very fast process. Thus, the generated silene **5** is immediately trapped by the silicon nucleophile **1**, which is always available in the reaction mixture in an apparent excess. The fact that we did not succeed in isolating the alcohol **6**, which is expected to be formed by protonation of the alkoxide **4** during the work-up, is in agreement with this interpretation. Attempts to prepare **6** by the reaction of tris(trimethylsilyl)silylmagnesium bromide with dibenzosuberone also failed. The application of the magnesium silanide instead of **1** in reactions with aldehydes or ketones generally proved to be useful, when silanolate eliminations from the metallated 1-hydroxyalkyl-tris(trimethylsilyl)silanes should be suppressed to obtain, after hydrolysis, the respective alcohols [6]. Obviously, in this particular reaction, in ether as well as in THF, the magnesium silanide was not sufficiently reactive, and in all cases the starting components were recovered unchanged.

The structure of **7** was elucidated on the basis of its rather straightforward ^1H , ^{13}C and ^{29}Si NMR spectra and MS data (see Section 3).



Scheme 1. The reaction of tris(trimethylsilyl)silyllithium (**1**) with dibenzosuberone in ether.

The addition of **1** to transient silenes generated according to the modified Peterson mechanism was observed occasionally, and appears to be typical for reactions of carbonyl compounds with excess **1** [11]. Also, in cases when sterically congested 1-hydroxyalkyl-tris(trimethylsilyl)silanes were treated with Grignard reagents to give silenes according to the Peterson mechanism, Si–C cleavage reactions occur under formation of tris(trimethylsilyl)silylmagnesium bromide, owing to steric strain, and adducts comparable with **5** were found [8].

The reaction of **1** with carbonyl compounds and the subsequent formation of silenes is generally strongly influenced by the solvent used. Actually, when the reaction of **1** with dibenzosuberone was carried out in dimethoxyethane (glyme) instead of ether, completely different results were obtained. Independent of the reaction temperature and the mode of mixing the components, we always obtained the bicyclic trisilane **10** in an almost quantitative yield. Also, $(\text{Me}_3\text{Si})_3\text{SiMgBr}$ can be used in the reaction with dibenzosuberone in glyme; the result is the same.

The structure of **10** appears to be rather complex, but the generation of the compound can easily be interpreted (Scheme 2). The alkoxide **4**, formed by addition of **1** at the carbonyl group of dibenzosuberone, does not eliminate lithium trimethylsilylanolate but undergoes a 1,3-Si,O-trimethylsilyl migration to afford the lithium silanide **8**. Such rearrangements are well known [12] and were observed generally when 1-hydroxyalkyl-tris(trimethylsilyl)silanes were treated with organometallic bases or sodium hydride in solvents of high donor capacity such as THF [6,9]. Intramolecular addition of the nucleophilic metallated silicon atom of **8** at

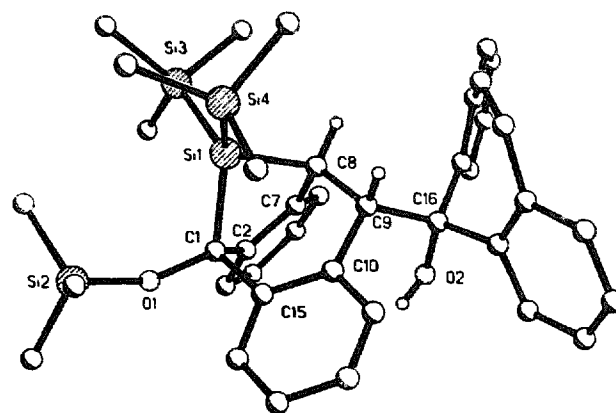
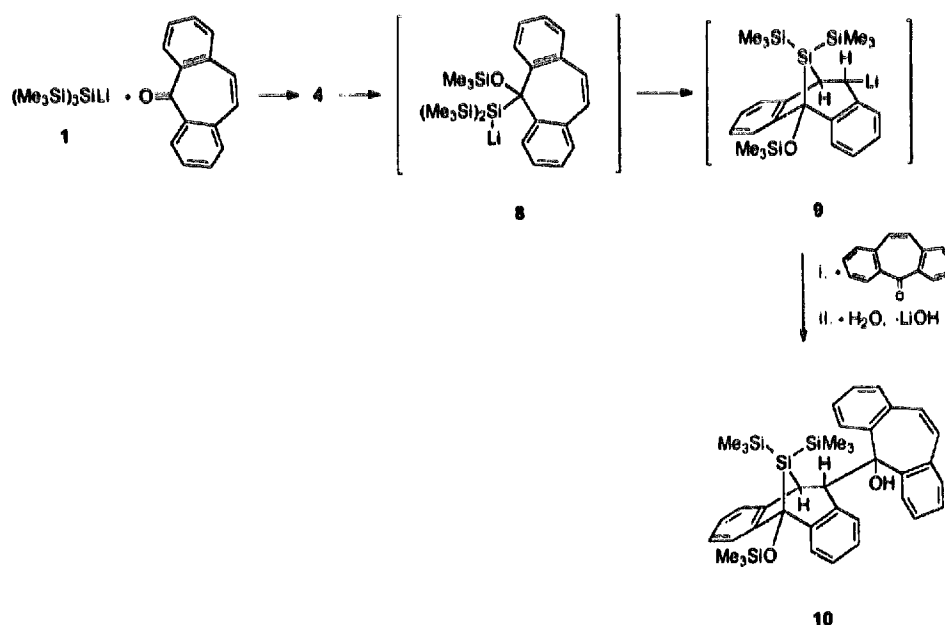


Fig. 1. Molecular structure of **10**. Selected bond distances [Å] and angles [°]: Si1–C1 1.953(6), Si1–C8 1.918(5), Si1–Si3 2.377(3), Si1–Si4 2.367(3), C7–C8 1.513(7), C8–C9 1.564(7), C9–C10 1.519(8), C9–C16 1.596(8), C1–Si1–C8 85.3(2), Si3–Si1–Si4 113.55(10), C1–Si1–Si3 115.1(2), C1–Si1–Si4 121.6(2), C2–C1–C15 109.0(4), C7–C8–C9 114.6(5), C8–C9–C10 113.5(4).

the 10,11-C=C double bond of the dibenzocycloheptatriene system gives the bridged organolithium derivative **9**. This reactive intermediate is trapped by excess dibenzosuberone under formation of an alkoxide, which after hydrolytic work-up affords the alcohol **10**.

The proposed structure of **10** was confirmed by IR, NMR, and MS data (see Section 3) and is also in full agreement with the results of an X-ray crystal structure analysis. In Fig. 1 the bicyclic nature of the molecule is clearly seen. Interestingly, the C1–Si1–C8 angle is comparatively small (85.3°) and the Si3–Si1–Si4 angle rather large (113.6°). Compared with the usual Si–C bond lengths, the Si1–C1 (1.954 Å) and Si1–C8 (1.919 Å) distances are significantly elongated.



Scheme 2. The reaction of tris(trimethylsilyl)silyllithium (**1**) with dibenzosuberone in dimethoxyethane.

To conclude the results obtained, we have to state that we did not succeed in synthesizing 5-[tris(trimethylsilyl)silyl]-dibenzo[a,d]cyclohepten-5-ol (**6**), which we expected to be a suitable precursor for the generation of silaethenes with a decreased or probably inversed polarity. Owing to the ease of the lithium trimethylsilylanolate elimination and silene formation, we are confronted with all the problems typical for in situ syntheses of silaethenes from **1** and carbonyl compounds according to the modified Peterson reaction, such as addition of excess **1** to the Si=C bond of the generated silene [6,11]. In glyme the spontaneous trimethylsilylanolate elimination can be suppressed, but under these conditions intramolecular rearrangements lead to the unexpected compound **10**.

3. Experimental section

All reactions involving organometallic reagents were carried out under purified argon. NMR: Bruker AC 250 or Bruker ARX 300, tetramethylsilane as internal standard. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402, chemical ionization with isobutane as the reactant gas. $(\text{Me}_3\text{Si})_3\text{SiLi} \cdot 3\text{THF}$ was prepared as reported in the literature [13].

3.1. Reaction of tris(trimethylsilyl)silyllithium (**1**) with dibenzosuberone in ether

0.86 g (4.15×10^{-3} mol) of dibenzosuberone, dissolved in 20 ml of ether, was added at -78°C to a stirred ethereal solution of 1.95 g (4.15×10^{-3} mol) of $(\text{Me}_3\text{Si})_3\text{SiLi} \cdot 3\text{THF}$. The violet solution was allowed to warm up to room temperature, gradually turning dark brown. After addition of water the organic layer was separated, the aqueous solution extracted several times with ether, the collected extracts dried and the solvent evaporated. Chromatographic separation of the yellow residue (silica gel/heptane) gave colorless, crystalline **7**. Yield (ref. to **1**) 0.27 g (19%), m.p. 222–225°C. ^1H NMR (benzene- d_6): $\delta = 0.12$ (s, Si(SiMe₃)₂, 18H), 0.45 (s, Si(SiMe₃)₃, 27H), 4.83 (s, SiCH, 1H), 6.75 (s, olef. CH, 2H), 6.91–7.36 (m, arom. CH, 8H). ^{13}C NMR (benzene- d_6 , DEPT): $\delta = 3.76$ [Si(SiMe₃)₂], 5.69 [Si(SiMe₃)₃], 44.80 (SiCH), 126.00 (olef. C), 129.25, 129.64, 129.87, 133.17 (arom. CH), 135.23, 141.51 (arom. quart. C). ^{29}Si NMR (benzene- d_6): $\delta = -96.2$ [Si(SiMe₃)₃], -48.7 [Si(SiMe₃)₂], -12.7 [Si(SiMe₃)], -9.6 [Si(SiMe₃)]. MS, m/z (%): 613 (0.8) [$\text{M}^+ + 1$], 597 (4.3) [$\text{M}^+ - \text{CH}_3$], 421 (100) [(Me₃Si)₃Si(Me₃Si)₂Si⁺], 365 (35) [$\text{M}^+ - \text{Si}(\text{SiMe}_3)_3$]. Anal. Found: C, 58.45; H, 9.20, C₃₀H₃₆Si₇ (613.37) Calc.: C, 58.75; H, 9.20.

3.2. Reaction of tris(trimethylsilyl)silyllithium (**1**) with dibenzosuberone in glyme

1.14 g (2.43×10^{-3} mol) of $(\text{Me}_3\text{Si})_3\text{SiLi} \cdot 3\text{THF}$, dissolved in 20 ml of glyme, was added at -78°C to a solution of 1.00 g (4.85×10^{-3} mol) of dibenzosuberone, dissolved in the same solvent. After warming the run was worked-up as described above. After evaporation of the solvent a pale yellow solid was obtained, which was recrystallized several times from n-pentane to give pure 8-bis(trimethylsilyl)-5[5-hydroxy-dibenzo[a,d]cyclohepten-5-yl]-1-trimethylsilyloxy-4,5-dihydro-dibenzo[a,d]-8-silabicyclo[3.2.1]octane (**10**). Yield 3.1 g (96%), m.p. 216–218°C. IR (Nujol): $\tilde{\nu} = 3545.6 \text{ cm}^{-1}$ (OH). ^1H NMR (benzene- d_6): $\delta = -0.16$ (s, OSiMe₃, 9H), -0.02 (s, SiSiMe₃, 9H), 0.25 (s, SiSiMe₃, 9H), 1.87 (s, COH, 1H), 2.62 (d, $^3J = 3.98 \text{ Hz}$, SiCH, 1H), 4.81 (d, $^3J = 3.98 \text{ Hz}$, CHCOH, 1H), 5.98 (d, $^3J = 7.95 \text{ Hz}$, olef. H, 1H), 6.33 (d, $^3J = 7.95 \text{ Hz}$, olef. H, 1H), 6.68–8.01 (m, arom. H, 16H). ^{13}C NMR (benzene- d_6 , DEPT): $\delta = 0.12$, 0.58 and 2.30 (SiSiMe₃ and OSiMe₃), 33.05 and 43.87 (sp³-CH).

Table 1
Crystal and structure solution data for compound **10**

Formula	C ₃₆ H ₄₈ O ₂ Si ₄
<i>M</i> [g mol ⁻¹]	661.13
<i>a</i> [Å]	10.263(1)
<i>b</i> [Å]	13.038(1)
<i>c</i> [Å]	14.900(1)
α [°]	79.25(1)
β [°]	84.35(1)
γ [°]	77.77(1)
<i>V</i> [Å ³]	1910.7(3)
ρ_{calc} [g cm ⁻³]	1.149
<i>Z</i>	2
Crystal system	triclinic
Space group (No. I.T.)	<i>P</i> $\bar{1}$ (2)
<i>F</i> (000) [e]	708
μ (Mo K α) [mm ⁻¹]	0.187
Radiation	$\lambda = 0.71073 \text{ \AA}$, (Mo K α), graphite monochromator
Diffractometer	Siemens P4
Crystal size [mm ³]	0.05 × 0.36 × 0.40
Temperature [°C]	25
Data collecting mode	ω -scan
Scan range (2 θ) [°]	3.9–44
<i>hkl</i> range	$-1/11$, $-14/14$, $-16/16$
Measured reflections	5653
Unique reflections	4686
Observed reflections	2570
Observed criterion	$I > 2\sigma(I)$
Refined parameters	407
<i>R</i> ₁ for observed reflections	0.0700
<i>R</i> ₁ for all data	0.1478
wR_2 for all data	0.1782
Restrained GoF	1.025
$\Delta\rho$ (max/min) [e Å ⁻³]	0.247 / -0.251

81.26 and 82.30 (quart. sp^3 -C), 121.13, 122.48, 125.17, 125.33, 125.90, 126.23, 126.60, 126.64, 126.96, 127.57, 127.84, 128.59, 128.98, 129.17, 129.30, 131.68, 131.81 and 132.14 (olef. and arom. CH), 132.47, 133.67, 134.27, 139.60, 149.70, 145.92, 148.39 and 154.06 (quart. arom. C). ^{29}Si NMR (benzene- d_6): -17.7 (SiSiMe₃), -14.5 (SiSiMe₃), 7.0 (SiSiMe₃), 11.4 (OSiMe₃). MS, m/z (%): 661 (0.3) [$M^+ + 1$], 645 (1.0) [$M^+ - \text{CH}_3$], 587 (0.6) [$M^+ - \text{SiMe}_3$], 571 (0.3) [$M^+ - \text{OSiMe}_3$], 453 (35) [$M^+ - \text{dibenzocycloheptatrien-5-ol}$], 207 (100) [5-hydroxy-dibenzotropylium⁺]. Anal. Found: C, 70.26; H, 7.42. C₃₉H₄₈O₂Si₄ (661.15) Calc.: C, 70.85; H, 7.32.

3.3. Crystal structure determination of 10

A crystal of **10** was measured on a Siemens P4 diffractometer after taking a rotational photograph and determining the unit cell in automatic mode. The structure was solved by direct methods (Siemens SHELXTL, Copyright 1990, Siemens Analytical X-ray Instruments Inc.) and refined by the full-matrix least-squares method of SHELXL-93 [14]. All non-hydrogen atoms were refined anisotropically. The hydrogens were put into their theoretical positions and refined using the 'riding model'. The weighting scheme was calculated according to $w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 0.00P]$, with $P = (F_o^2 + 2F_c^2)/3$. The most important data can be seen in Table 1. Further details of the structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405464, the names of the authors and the journal citation.

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References

- [1] G. Raabe and J. Michl, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds*, Wiley, New York, 1989, Part 2, Chap. 17, p. 1044.
- [2] G. Becker and O. Mundt, *Z. Anorg. Allg. Chem.*, **462** (1980) 130; H. Oehme, E. Leissring and H. Meyer, *Tetrahedron Lett.*, **21** (1980) 1141; K. Issleib, E. Leissring, M. Riemer and H. Oehme, *Z. Chem.*, **23** (1983) 99.
- [3] T.A. van der Knaap, T.C. Klebach, F. Fisser, F. Bickelhaupt, P. Ros, E.J. Baerends, C.H. Stam and M. Konijn, *Tetrahedron*, **40** (1984) 765.
- [4] Y. Apeloig and M. Karni, *J. Am. Chem. Soc.*, **106** (1984) 6676.
- [5] A.G. Brook and K.M. Baines, *Adv. Organomet. Chem.*, **25** (1986) 1.
- [6] C. Krempner, H. Reinke and H. Oehme, *Chem. Ber.*, **128** (1995) 143.
- [7] F. Luderer, H. Reinke and H. Oehme, *Chem. Ber.*, **129** (1996) 15.
- [8] F. Luderer, H. Reinke and H. Oehme, *J. Organomet. Chem.*, **510** (1996) 181.
- [9] D. Hoffmann, H. Reinke and H. Oehme, *Z. Naturforsch.*, **51b** (1996) 370.
- [10] E. Fuchs, B. Breit, H. Heydt, W. Schoeller, T. Busch, C. Krüger, P. Betz and M. Regitz, *Chem. Ber.*, **124** (1991) 2843.
- [11] H. Oehme, R. Wustrack, A. Heine, G.M. Sheldrick and D. Stalke, *J. Organomet. Chem.*, **452** (1993) 33.
- [12] A.G. Brook and J.J. Crusciel, *Organometallics*, **3** (1984) 1317.
- [13] G. Gutekunst and A.G. Brook, *J. Organomet. Chem.*, **225** (1982) 1.
- [14] G.M. Sheldrick, SHELXL-93, Universität Göttingen, 1993.