

Synthesis of the First Homoleptic Trisilaallyl Chloride: 3-Chloro-1,1,2,3,3-pentakis(2',4',6'-triisopropylphenyl)trisil-1-ene

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Dedicated to Professor F. Ekkehardt Hahn on the Occasion of His 60th Birthday

Keywords: Multiple bonds; Silicon; Allylic compounds; Group 14 elements; Functional groups

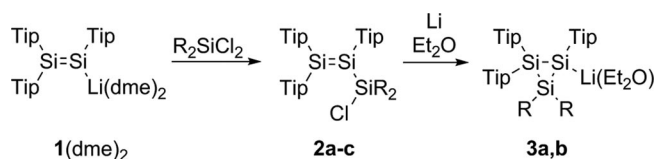
Abstract. Unsaturated silicon compounds are valuable building blocks for the synthesis of molecules with novel silicon-based structural motifs with potential applications in materials chemistry. The difficulties associated with the transfer of the Si=Si moiety to promising substrates can be explained by the lack of suitably functionalized derivatives. Herein we report the synthesis and full characterization of the first

homoleptic trisilaallyl chloride $R_2Si = Si(R) - Si(Cl)R_2$ ($R = 2,4,6$ -triisopropylphenyl) by an unprecedented nucleophilic substitution at a central silicon atom under retention of an adjacent Si=Si double bond. Attempts to reductively generate the corresponding allylic anion led to the cleavage of the Si-Si single bond and isolation of the Et₂O solvate of the corresponding disilenide.

Introduction

In organic chemistry the combination of a finite number of functional groups constitutes the basis for a virtually infinite number of compounds. The simultaneous presence of unsaturated (usually multiply bonded) moieties and functional groups is the key to that variability. Although compatibility issues may require the careful choice of reagents for further transformations and/or the utilization of protecting groups, the problem is far more severe in silicon chemistry.^[1] Due to the comparatively weak Si=Si double bond, isolable compounds with Si-Si multiple bonds require substantial kinetic protection by bulky substituents and stable derivatives have only been known since 1981.^[2] The chemistry of such disilenes has been thoroughly investigated^[3] and they show great potential with respect to future applications in silicon based materials, e.g. for photovoltaic devices.^[4] A major challenge for further developments in this regard is the high reactivity of the Si=Si double bond. The low tolerance of other functional groups in the same molecule or typical externally applied organic reagents severely constrains synthetic strategies. Therefore, the development of pro-

ocols that allow for the transformation of functional groups in the periphery of the Si=Si bond beyond the already well explored nucleophilic disilenides^[5,6] is desirable. α -Functionalized unsaturated reagents, i.e. allylic compounds, are useful reagents for organic syntheses, e.g. in the diastereoselective allylation of carbonyl compounds.^[7] In silicon chemistry, open-chained disilaallyl, cyclic trisilaallyl anions,^[8] and heteroleptic trisilaallyl chlorides^[9] have been reported. While they constitute potentially useful building blocks for molecular silicon chemistry, the transformation under retention of an allylic functionality is largely unexplored. As we have shown recently, α -chloro trisilapropenes **2a,b** are accessible from disilenide (**1**) and dichlorodimethylsilane or dichlorodiphenylsilane, respectively.^[9] Reaction of compounds **2a,b** with lithium metal in diethyl ether, however, did not yield trisilaallyl anions, but rather the isomeric trisiliranides **3a,b** (Scheme 1).



Scheme 1. Reported synthesis of trisiliranides **3a,b** from lithium disilenide **1(dme)₂** via chlorosilyl disilenes **2a,b**.^[9] Synthesis of **2c** (this work) (**2a, 3a:** $R = \text{Me}$; **2b, 3b:** $R = \text{Ph}$; **2c:** $R = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2 = \text{mesityl}$; $\text{Tip} = 2,4,6\text{-iPrC}_6\text{H}_2$).

On the basis of this observation, we anticipated that bulkier substituents at this position may provide access to stable acyclic trisilaallyl anions. Herein, we report that the peripheral chloro functionality in the known stable dichlorosilyl disilene **2d** can be replaced by the action of an aryllithium species in

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a nucleophilic substitution under preservation of the Si=Si moiety.

Results and Discussion

Reaction of disilene **1**(dme)₂^[5a] with dichlorodimesitylsilane in benzene yields chlorosilyl disilene **2c** as main product. In contrast to the preparation of chlorosilyl disilenes **2a,b** this reaction did not reach full conversion at ambient temperature but required heating to 60 °C for 8.5 h and addition of [2.1.1]cryptand in order to increase the nucleophilicity of disilene **1**. Attempts to isolate **2c** by crystallization did not succeed and chlorosilyl disilene **2c** could only be identified through its ²⁹Si NMR resonances at 100.2, 48.9 (Si=Si) and 0.6 ppm (ClSiMes₂), which are very similar to those already reported for chlorosilyl disilenes **2a,b** (Table 1).

Table 1. ²⁹Si NMR chemical shifts /ppm of trisilaallyl chlorides **2a–2e**.

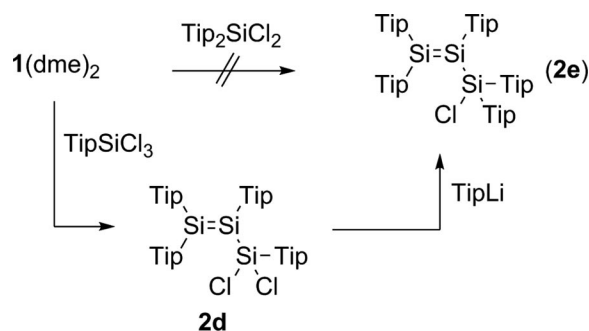
Trisilaallyl chloride	Tip ₂ Si	TipSi	RR'SiCl	R, R'
2a ^{a)}	103.0	39.9	26.2	Me, Me
2b ^{a)}	109.1	35.5	11.8	Ph, Ph
2c	100.2	48.9	0.6	Mes, Mes
2d ^{b)}	99.2	54.7	11.7	Tip, Cl
2e	105.7	47.2	−3.5	Tip, Tip

a) Ref. [9]. b) Ref. [12].

The only additional resonances of the product mixture in ²⁹Si NMR at δ = 88.5 and 43.9 ppm are assigned to 1,1,2,3,4,4-hexakis(2,4,6-triisopropylphenyl)tetrasilabutadiene,^[10] the frequently encountered oxidation product of lithium disilene **1**(dme)₂. To further increase the steric bulk of the silicon framework, lithium disilene **1**(dme)₂ was treated with Tip₂SiCl₂ under similar conditions in order to prepare the homoleptic trisilaallylchloride **2e**. In this case, no reaction occurred even in 1,2-dimethoxyethane. Prolonged heating of the reaction mixture led to decomposition of disilene **1**(dme)₂, while Tip₂SiCl₂ was partially recovered.

Despite the known reactivity of disilenes towards organolithium species,^[11] we considered a nucleophilic substitution at the peripheral dichlorosilyl group of disilene **2d**^[12] as an alternative access to **2e**. Indeed, the reaction of **2d** with TipLi yields the homoleptic trisilaallyl chloride (**2e**) (Scheme 2), which was isolated in 63% yield as intensely yellow crystals by crystallization from benzene. The highest observed peak in the mass spectrum of **2e** at 1134.8 *m/z* shows an isotopic distribution consistent with the molecular formula C₇₅H₁₁₅Si₃Cl. The ¹³C NMR exhibits a large number of well-resolved resonances probably due to hindered rotation about the Si–C_{ipso} bonds: only nine out of ten possible ¹³C signals of the aromatic CH moieties are observed probably due to coincidental overlap of two of the resonances. For the isopropyl CH₃ groups 25 signals are identified, indicating that the *para*-isopropyl groups of the Tip substituents do rotate rapidly (5 signals for 10 atoms) on the NMR time scale while the *ortho*-isopropyl do not (20 signals for 20 atoms). The ²⁹Si NMR chemical shifts of compound **2e** at 105.7, 47.2, and −3.5 ppm are in the typical range for chlorosilyl disilenes (Table 1). The

well-resolved Si–Si coupling constants (Experimental Section) in combination with 2D ¹H/²⁹Si correlations prove the connectivity of the silicon atoms in **2e**. The longest wavelength absorption in the UV/Vis spectrum is observed at λ_{max} = 418 nm (ε = 22244 L M^{−1} cm^{−1}; **2b**: λ_{max} = 427 nm, ε = 24800 L M^{−1} cm^{−1}; Tip₂Si = SiTip₂: λ_{max} = 432 nm, ε = 17500 L M^{−1} cm^{−1}^[13]).



Scheme 2. Synthesis of homoleptic trisilaallyl chloride **2e** by reaction of dichlorosilyl disilene **2d** with TipLi.

The molecular structure of **2e** was unambiguously proven by a single-crystal X-ray diffraction study (Figure 1, Table 2). The Si1–Si2 (218.60(6) pm) and Si2–Si3 bonds (236.62(6) pm) are in the typical range for Si–Si double and single bonds, respectively, and are similar to those determined for chlorosilyl disilene **2b** (Si=Si: 217.23(8) to 219.00(8), Si–Si: 231.60(8) to 232.70(8)). The Si–Cl bond vector points in the direction of the small angle of the trisilaallyl moiety for steric reasons. The tricoordinate silicon atoms exhibit an approximately planar environment (sum of angles Si1: 359.42°, Si2: 359.99°) and consequently the Si=Si double

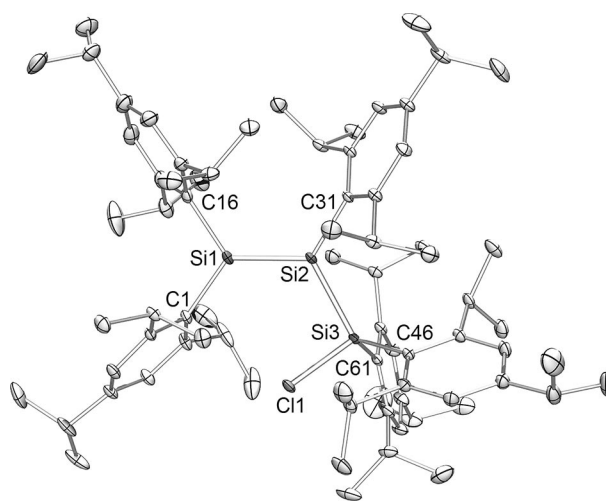


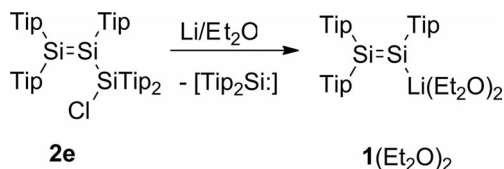
Figure 1. Molecular structure of trisilaallyl chloride **2e** in the solid state (thermal ellipsoids at 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond length /pm and angles /°: Si1–Si2 218.60(6), Si2–Si3 236.62(6), Si3–C11 192.16(6), Si1–C1 190.41(17), Si1–C16 191.37(17), Si2–C31 190.02(16), Si3–C46 191.18(17), Si3–C61 191.69(16), Si1–Si2–Si3 116.44(2), C1–Si1–Si2 125.63(5), C16–Si1–Si2 121.84(6), C1–Si1–C16 111.95(7), Si1–Si2–C31 122.10(5), C31–Si2–Si3 121.45(5), Si2–Si3–C11 96.46(2), C46–Si3–C61 108.63(7).

bond is only mildly trans-bent ($\theta_{\text{Si}1} = 6.99(7)^\circ$; trans-bent angle defined as 90° minus the angle between the Si1–Si2 bond vector and the normal of the C1–Si1–C16 plane) and just slightly twisted ($\tau = 8.00(6)^\circ$; twist angle defined as the angle between the two normals of the bonding planes of Si1 and Si2).

Table 2. Selected crystallographic details for compounds **2e** and **1(Et₂O)₂**.

	2e	1(Et₂O)₂
Formula	C ₇₅ H ₁₁₅ ClSi ₃	C ₅₃ H ₈₉ LiO ₂ Si ₂
<i>T</i> /K	173	173(2)
System	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	14.0399(4)	11.96064(17)
<i>b</i> /Å	14.7564(5)	12.85905(19)
<i>c</i> /Å	19.6116(4)	18.8888(3)
<i>a</i> /°	104.979(2)	86.8440(12)
<i>β</i> /°	93.874(2)	83.1312(13)
<i>γ</i> /°	113.243(3)	70.5368(13)
<i>V</i> /Å ³	3540.1(2)	2719.11(7)
<i>Z</i>	2	2
<i>d</i> /g·cm ⁻³	1.066	1.003
<i>μ</i> /mm ⁻¹	0.144	0.099
<i>F</i> (000)	1248	908
<i>θ</i> _{max}	31.47°	32.95°
Refl. _{total}	35175	62591
Refl. _{unique}	20046	18473
<i>S</i>	0.925	1.066
<i>R</i> ₁ (<i>I</i> > 2σ)	0.0539	0.0524
<i>wR</i> ₂ (all data)	0.1425	0.1512

With this precursor for the synthesis of an acyclic trisilaallyl anion in hand, we tested several reaction conditions for the reduction of **2e**. Mixing diethyl ether solutions of **2e** with two equivalents of lithium or potassium naphthalenide did not show any visible signs for conversion at low temperatures in either case. Warming to ambient temperature, however, resulted in the disappearance of the characteristic colors of the reducing agents. NMR spectroscopic analysis suggested in both cases that almost no conversion had taken place. In another attempt, trisilaallyl chloride **2e** was treated with a 30-fold excess of lithium powder in Et₂O at -78°C . Upon warming a color change to red was observed at -50°C which turned into orange after 2.5 h at ambient temperature. After workup and crystallization from hexane only a small amount of lithium disilene **1(Et₂O)₂** (12%) could be isolated instead of the expected trisilaallyl anion (Scheme 3). A comparison of the ¹H NMR spectroscopic data of **1(Et₂O)₂** with those of the crude product before crystallization clearly revealed that **1(Et₂O)₂** is the major product of this reaction. Since no trace of the elimin-



Scheme 3. Reaction of trisilaallyl chloride **2e** with excess lithium metal to yield disilene **1(Et₂O)₂** via proposed intermediate lithio trisilaallyl anion **4** by formal Tip_2Si^- elimination.

ated Tip_2Si fragment is detected in the ¹H NMR spectrum of the product mixture, we assume that the unstable silylene Tip_2Si actually dimerizes to *Watanabe's* disilene^[13] in solution, which is known to yield disilene **1** through Si–Tip bond cleavage by excess lithium.^[5a]

Cleavage of Si–Si bonds adjacent to Si=Si moieties with alkali metals has already been reported for tetrasilabutadienes^[14] yielding lithium and potassium disilenes, respectively. The ¹H NMR spectrum of lithium disilene **1(Et₂O)₂** in C₆D₆ is very similar to that of **1(dme)₂** with all resonances being detected at nearly the same chemical shifts. The only significant difference is the absence of dme resonances and the appearance of resonances for coordinated Et₂O at $\delta = 3.05$ and 0.81 ppm. The molecular structure of **1(Et₂O)₂** was investigated by a single-crystal X-ray diffraction study (Figure 2, Table 2).

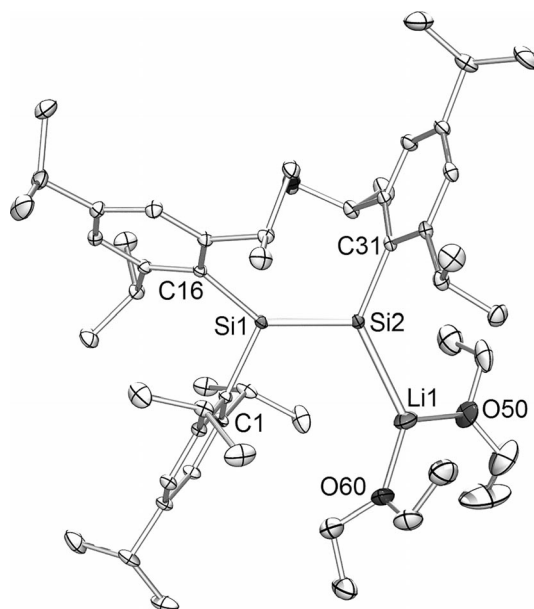


Figure 2. Molecular structure of lithium disilene **1(Et₂O)₂** in the solid state (thermal ellipsoids at 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond length /pm and angles /°: Si1–Si2 218.07(4), Si1–Cl 190.69(10), Si1–C16 191.07(10), Si2–C31 192.67(10), Si2–Li1 256.0(3), Li1–O50 196.4(5), Li1–O60 194.1(6), Si1–Si2–Si3 116.44(2), C1–Si1–Si2 125.63(5), C16–Si1–Si2 121.84(6), C1–Si1–C16 111.95(7), Si1–Si2–Li1 116.30(7), C1–Si1–Si2 114.44(3), C16–Si1–Si2 137.49(3), C1–Si1–C16 106.93(4), Si1–Si2–C31 111.04(3), C31–Si2–Li1 132.58(7).

As in the case of **1(dme)₂** a contact ion pair is present in the solid state with two equivalents of coordinating solvent. The Li–Si (256.0(3) pm) distance of **1(Et₂O)₂** is significantly shorter in comparison to that in **1(dme)₂** (285.3(3) pm) due to the coordination number of the lithium cation being reduced from five in **1(dme)₂** to three in **1(Et₂O)₂**. The Si–Si distance (218.07(4) pm) is in the typical range for Si=Si double bonds and very close to the distance in **1(dme)₂** (219.2(1) pm). The lithio disilene backbone deviates very little from planarity with small trans-bent angles ($\theta_{\text{Si}1} = 9.12(4)^\circ$, $\theta_{\text{Si}2} = 3.1(1)^\circ$) and a twist along the Si–Si bond of $\tau = 13.10(8)^\circ$.

Conclusions

The successful synthesis of the first homoleptic trisilaallyl chloride by the introduction of an additional Tip group in the periphery of the Si=Si unit is a rare example of chemistry in the periphery of the Si=Si bond.^[15] The synthetic approach, an unprecedented substitution reaction in α position to a Si=Si double bond awaits further investigation for uses in the construction of silicon-based molecules and materials.

Experimental Section

All manipulations were carried out in a protective atmosphere of argon using standard Schlenk techniques and a glovebox. Ethereal solvents were heated under reflux over sodium/benzophenone; hexane over sodium and deuterated benzene over potassium. All solvents were stored in an argon atmosphere and degassed prior to use. NMR spectra were recorded with a Bruker DRX-400 FTNMR spectrometer (¹H, 400.13 MHz) or a Bruker Avance 500 FTNMR spectrometer (¹H, 500.13 MHz, ¹³C, 125.76 MHz, ²⁹Si, 99.36 MHz). ¹H and ¹³C{¹H} NMR spectra were referenced to the peaks of residual protons of deuterated solvents (¹H) or the deuterated solvent itself (¹³C). ²⁹Si NMR spectra were referenced to external TMS. All chemical shifts are reported in ppm. UV/Vis spectra were recorded with a Perkin-Elmer Lambda 20 UV/Vis Spectrometer. Melting points were determined in an argon or nitrogen atmosphere in closed NMR tubes and are uncorrected.

3-Chloro-1,1,2,3,3-pentakis(2',4',6'-triisopropylphenyl)trisil-1-ene (2e): To a mixture of 10.95 g (12.83 mmol) **1**(dme)₂ and 4.31 g (12.77 mmol) TipSiCl₃thf (80 mL) were added at -78 °C. After 20 min the cold bath was removed and stirring was continued overnight. All volatiles are removed in vacuo and TipLi etherate (6.07 g, 21.34 mmol) was added. After the addition of 80 mL toluene the reaction mixture was stirred for 3 d. The solvent was replaced by hexane and all insoluble parts were filtered off. The filtrate was reduced to a red-brown oil and 10 mL benzene were added. Keeping the solution at 0 °C for 3 weeks gave 5.13 g (35%) pure **2e** in a first and 4.05 g (28%) in a second crystallization (combined yield: 63% of yellow crystals; mp. 220 °C, part. dec.). ¹H NMR (500.13 MHz, C₆D₆, 25 °C): δ = 7.29, 7.25, 7.15, 7.07, 7.03, 7.01, 6.91, 6.90, 6.82 (each d, altogether 10 H, Tip-H), 4.79, 4.55, 4.12, 4.01, 3.87, 3.78, 3.76, 3.64, 3.59, 3.08, 2.80, 2.70, 2.69, 2.68, 2.66 (each sept., altogether 15 H, *i*Pr-CH), 2.09, 1.571, 1.566, 1.53, 1.51, 1.471, 1.466, 1.42, 1.375, 1.371, 1.26, 1.25, 1.22, 1.16, 1.14, 1.11, 1.094, 1.088, 0.79, 0.77, 0.74, 0.61, 0.56, 0.55, 0.48, 0.45, 0.30 (each d, altogether 90 H, *i*Pr-CH₃). ¹³C NMR (125.76 MHz, C₆D₆, 25 °C): δ = 157.27, 156.07, 156.00, 155.48, 155.04, 154.55, 154.42, 154.36, 153.40, 153.07, 150.86, 150.68, 150.49, 150.42, 150.17, 139.64, 137.16, 136.49, 133.29, 130.67 (Tip-C), 124.46, 123.74, 123.55, 123.28, 123.26, 122.53, 122.51, 122.18, 121.12 (Tip-CH), 39.21, 38.90, 38.06, 38.01, 36.97, 36.23, 36.17, 34.92, 34.69, 34.62, 34.58, 34.47, 34.37, 33.76, 30.93 (*i*Pr-CH), 27.47, 27.12, 27.00, 26.67, 26.15, 25.98, 25.81, 25.48, 25.44, 25.41, 24.97, 24.92, 24.80, 24.70, 24.44, 24.27, 24.21, 24.13, 24.09, 24.05, 24.03, 23.94, 23.84, 23.22, 22.88 (*i*Pr-CH₃). ²⁹Si NMR (99.36 MHz, C₆D₆, 25 °C): δ = 105.7 [¹J(Si,Si) = 127, ²J(Si,Si) = 17 Hz, *S*Tip₂], 47.2 [¹J(Si,Si) = 127 and 97 Hz, *S*Tip], -3.5 [¹J(Si,Si) = 97, ²J(Si,Si) = 17 Hz, *S*Tip₂Cl] ppm. UV/Vis (hexane) λ_{\max} (ϵ) = 418 nm (22244 L·mol⁻¹·cm⁻¹). MS (EI) *m/z* (%) = 1134.8 (54.5, M⁺), 758.4, 469.3 (73.6), 451.3 (63.8), 433.3 (85.2), 265.1 (48.5), 231.1 (100.0), 189.1 (41.7), 43.1 (42.6).

(1,2,2-Tris(2',4',6'-triisopropylphenyl)disilyl)lithium-dietherate [1(Et₂O)₂]: To a mixture of **2e** (506 mg, 445 μ mol) and lithium powder (93 mg, 13.40 mmol) diethyl ether (20 mL) was added at -78 °C. After 5 min the cool bath was removed and stirring was continued overnight. Insoluble components were filtered off and all volatiles were removed in vacuo to yield an orange solid. Crystallization from a small amount of hexane at ambient temperature yielded 30 mg **1**(Et₂O)₂ as orange crystals (12%). ¹H NMR (400.13 MHz, C₆D₆, 25 °C): δ = 7.14 (s, 2 H, Tip-H), 7.07 (s, 4 H, Tip-H), 4.76, 4.70 (each hept., altogether 4 H, *i*Pr-CH), 4.17 (br., 2 H, *i*Pr-CH), 3.05 (q, 8 H, OCH₂), 2.89 (hept., 1 H, *i*Pr-CH), 2.77, 2.76 (each hept., altogether 2 H, *i*Pr-CH), 1.42 (mult., 18 H, *i*Pr-CH₃), 1.32 (d, 6 H, *i*Pr-CH₃), 1.20 (mult., 12 H, *i*Pr-CH₃), 1.13 (mult., 18 H, *i*Pr-CH₃), 0.81 (t, 12 H, CH₂CH₃) ppm.

Xray Crystallography: Single crystals of **1**(Et₂O)₂ and **2e** were coated with perfluorinated polyether and quickly transferred to the cold nitrogen stream at the goniometer. The accumulation of data sets was carried out with an Oxford Diffraction Xcalibur 3 diffractometer with Mo-K α radiation (λ = 0.71073 Å). Unit cells were determined using a number of representative frames. Intensities were determined from several series of frames, each covering 0.3° in \hat{E} of an entire sphere. Numerical absorption corrections were applied using SADABS. The structures were solved by direct methods or with a Patterson map and refined by least-squares on weighted F^2 values for all reflections. Refinements (SHELXL97)^[16] yielded the crystallographic parameters summarized in Table 2.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1409719 [**1**(Et₂O)₂] and CCDC-1409718 (**2e**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Plots of NMR spectra of **2e**.

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