Addition of methyllithium to disilyne RSi$\equiv$SiR (R = Si*i*Pr[CH(SiMe$_3$)$_2$]), giving a disilenyllithium, and its unexpected isomerization to a disilacyclopropylsilyllithium†‡

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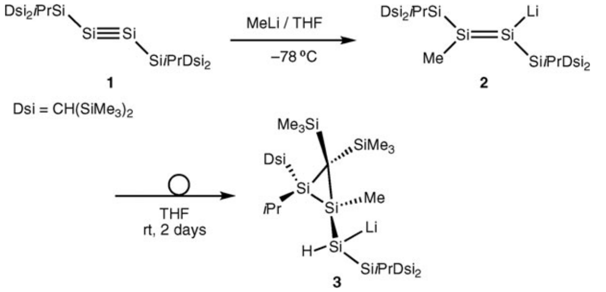
The reaction of the isolable disilyne 1, RSi$\equiv$SiR (R = Si*i*Pr[CH(SiMe$_3$)$_2$]), with MeLi produced the methyl-substituted disilenyllithium 2 as the primary product. However, 2 is not thermally stable at room temperature in THF, and slowly isomerized to the unexpected disilacyclopropylsilyllithium, which was characterized by NMR spectroscopy as well as by X-ray crystallography.

The synthesis, characterization, and reactivity of compounds with multiple bonds between heavier main group elements are of considerable interest because of their unusual structures and bonding.[1] Numerous alkene analogues of heavier group 14 elements have been isolated and characterized by taking advantage of kinetic stabilization using bulky substituents.[1] However, much less is known about the heavier group 14 congeners of alkynes, although a few papers have described the synthesis and structure of alkyne analogues.[2] In 2004, we[3] and Wiberg's group[4] reported the synthesis of triply bonded silicon species, disilynes, which are stabilized by very bulky silyl groups. Later, Tokitoh's group reported the aryl-substituted disilyne by the use of very bulky aryl groups.[5]

The first isolated and fully characterized disilyne was RSi$\equiv$SiR (R = Si*i*Pr[CH(SiMe$_3$)$_2$]$_2$) **1**; its *trans*-bent structure was unequivocally determined by X-ray crystallography[3] as well as a solid-state ^{29}Si NMR study.[6] To study the reactivity of the Si$\equiv$Si triple bond, we have investigated various reactions of **1** with *t*BuLi,[7] alkali metals,[7,8] alkenes,[9] alkynes,[9] nitriles[10] and silylcyanides.[11] Among them, an interesting reactivity of **1** is the reaction with *t*BuLi, giving hydrogen-substituted disilenyllithium, (Dsi$_2$*i*PrSi)(H)Si=Si(Li)(Si*i*PrDsi$_2$) (Dsi = CH(SiMe$_3$)$_2$).[7,12] This reaction involves the one-electron transfer reaction from *t*BuLi to **1**, giving the anion radical of **1** and the *tert*-butyl radical, followed by hydrogen abstraction of the resulting anion radical from the *tert*-butyl radical to produce the disilenyllithium.[7] Very recently, we also reported the addition reaction of secondary amines and hydroborane toward **1**, giving R$_2$N- or R$_2$B-substituted disilenes.[13] The addition reactions toward disilyne **1** provide a new route for the synthesis of heteroatom-substituted disilenes. Thus, it is quite reasonable to assume that organolithium reagents (RLi) also undergo the addition reaction toward **1** if R is a small group that allows the addition reaction. We report here the reaction of **1** with MeLi to produce the methyl-substituted disilenyllithium **2** as the primary product; however, the resulting disilenyllithium unexpectedly underwent isomerization to disilacyclopropylsilyllithium, which is the first example of an isolable silyllithium derivative bearing a disilacyclopropyl group, whose structure was fully characterized by NMR spectroscopy and X-ray crystallography.

Based on the previous report of the formation of an sp^3-type silyllithium by the 1,2-addition reaction of methyllithium across the Si=Si double bond of a disilene,[14] we carried out the reaction of the disilyne **1** with MeLi in the hope of obtaining a methyl-substituted disilenyllithium. As shown in Scheme 1, one equivalent of MeLi was added to the THF solution of the disilyne **1** at −78 °C. A color change from green to red was immediately observed, and the methyl-substituted disilenyllithium **2** was formed as the 1,2-addition product of MeLi across the Si$\equiv$Si triple bond of **1**. This result is different from the case of the reaction with *t*BuLi, which affords H-substituted disilenyllithium *via* one-electron reduction followed by hydrogen abstraction.[7] The small size of MeLi relative to *t*BuLi apparently allows a 1,2-addition reaction.

The disilenyllithium **2** was characterized by NMR spectroscopy. The ^{1}H NMR signal of the methyl group attached to an sp^2-Si atom was observed at 1.03 ppm (in THF-d_8), which is low-field shifted relative to a normal methyl group at the Si atom because of the deshielding effect of the Si=Si double bond. A similar situation is observed in the case of the previously reported methyl-substituted disilene R^{1}R^{2}Si=SiR^{1}Me (R^1 = SiMe*t*Bu$_2$, R^2 = SiMeR$^1_2$) (1.37 ppm in C$_6$D$_6$).[14b] The ^{29}Si NMR signals of the sp^2-Si atoms of **2** were observed at 114.1 and 143.4 ppm (in THF-d_8), and the values are similar to



Scheme 1 Reaction of **1** with MeLi to give **2** and the isomerization of **2** to **3**.

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those of the previously reported H-substituted disilenyllithium, (Dsi$_2$*i*PrSi)(H)Si=Si(Li)(Si*i*PrDsi$_2$), (124.7 and 165.0 ppm in C_6D_6).[7]

Although the reaction of a disilene with MeLi has been known to afford the silyllithium $R_2MeSiSiR_2Li$ as a 1,2-addition product,[14] further addition of MeLi toward **2** did not occur. **2** was stable below −30 °C in THF, but unstable at room temperature and gradually isomerized to the hydrogen-substituted silyllithium **3** bearing a disilacyclopropyl group in 80% yield (Scheme 1).[15]

Pale yellow single crystals of **3** were obtained from C_6D_6 solution in the NMR tube. The structure of **3** was determined by X-ray crystallography and NMR spectroscopic data. In the crystalline form, the contact ion pair **3** exists as a monomer, in which the lithium atom is coordinated by two THF molecules (Fig. 1). The long distance of H1···Li1 (3.33 Å) indicated that there is no Si–H···Li agostic interaction. The Si1–Li1 bond length is 2.640(7) Å, which is close to the Si–Li bond length of the previously reported H-substituted silyllithium dimer, [(*t*BuMe$_2$Si)$_2$SiHLi]$_2$ (2.644(4), 2.667(4) Å).[16a] The Si1–Si3 bond length of 2.4017(13) is slightly elongated by the steric repulsion of the bulky Si*i*Pr[CH(SiMe$_3$)$_2$]$_2$ group. The Si2–Si4 bond length of the disilacyclopropane unit is 2.2748(13) Å, which is normal compared with the Si–Si single bond lengths of the previously reported disilacyclopropanes (2.272(2),[17a] 2.2749(10) Å[17b]). The bond length of Si2–C25 (2.004(3) Å) is slightly longer than that of Si4–C25 (1.938(3) Å) because of the steric repulsion between the SiMe$_3$ groups at the C25 atom and the bulky SiH[Li(thf)$_2$]Si*i*Pr[CH(SiMe$_3$)$_2$]$_2$ group at the Si2 atom.

The ^{29}Si NMR signals of the Si atoms of the disilacyclopropyl skeleton of **3** are observed at high field (−62.4 ppm (*Si*Me) and −16.2 ppm (*Si**i*Pr)). The broad signal assigned to *Si*Li of **3** is observed at −160.5 ppm and the chemical shift is similar to the previously reported hydrogen-substituted silyllithiums with two silyl substituents [(*t*BuMe$_2$Si)$_2$SiHLi: −188.8 ppm ($^1J_{\mathrm{Si-H}}$ = 75 Hz in toluene-*d*$_8$),[16a] (*t*Bu$_3$Si)$_2$SiHLi: −175.5 ppm ($^1J_{\mathrm{Si-H}}$ = 94.6 Hz in THF-*d*$_8$)].[16b] Although the ^{1}H NMR signal of Si(Li)*H* could not be identified in THF-*d*$_8$ because it is overlapped with the signals of the *i*Pr groups, the Si–H coupling constant ($^1J_{\mathrm{Si-H}}$ = 88 Hz) can be identified by a ^{29}Si NMR measurement. The small coupling constant indicates the large p-character of the Si–H bond.

A plausible mechanism for the formation of **3** is illustrated in Scheme 2. Because the bond energy of Si–H is lower than that of C–H, the deprotonation of C–H by a silyl anion is generally an endothermic process. However, in the case of **2**, the acidity of the methyne proton of –C*H*(SiMe$_3$)$_2$ is relatively high because of the effect of the three silyl groups. In addition, the –C*H*(SiMe$_3$)$_2$ group and the sp^2-silyl anion are relatively close, and therefore the sp^2-Si anion in **2** can abstract the methyne proton of –C*H*(SiMe$_3$)$_2$. Finally, the subsequent reaction of C–Li with the Si=Si double bond would give the disilacyclopropylsilyllithium **3**.

In summary, MeLi undergoes an addition reaction to the disilyne **1** to produce a disilenyllithium derivative, (Dsi$_2$*i*PrSi)(Me)Si=Si(Li)(Si*i*PrDsi$_2$), which isomerizes to the unexpected disilacyclopropylsilyllithium.

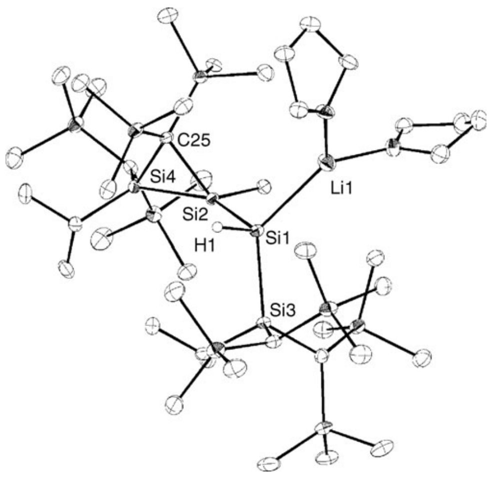
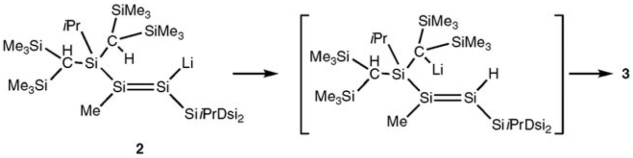


Fig. 1 ORTEP drawing of **3** (30% thermal ellipsoids). Hydrogen atoms except for the H atom on the Si1 atom and the benzene molecules as a crystallization solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si2 = 2.3737(13), Si1–Si3 = 2.4017(13), Si2–Si4 = 2.2748(13), Si2–C25 = 2.004(3), Si4–C25 = 1.938(3), Si1–Li1 = 2.640(7), Si1–H1 = 1.46(3). Si2–Si1–Si3 = 113.13(5), Si2–Si1–Li1 = 107.68(7), Si3–Si1–Li1 = 128.45(17), Si2–Si1–H1 = 101.5(12), Si3–Si1–H1 = 96.7(12), C25–Si2–Si4 = 53.42(10), C25–Si4–Si2 = 56.11(10), Si4–C25–Si2 = 70.47(12).



Scheme 2 Plausible mechanism for the isomerization of **2** to **3**.

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Experimental

All experiments were performed using high-vacuum line techniques or in an argon atmosphere using an MBraun MB 150B-G glove box. All solvents were dried and de-gassed over potassium mirror in vacuum prior to use. NMR spectra were recorded on a Bruker AV-400FT NMR spectrometer (^{1}H NMR at 400 MHz; ^{13}C NMR at 100.6 MHz; ^{29}Si NMR at 79.5 MHz).

Preparation of 2

MeLi (1.09 M in ether, 60 μL, 0.064 mmol) was added to a THF (1 mL) solution of the disilyne **1** (48 mg, 0.057 mmol) at −78 °C. The color of the reaction mixture immediately changed from green to red. After stirring for 5 min at −78 °C, the solvent was removed *in vacuo*. The NMR spectra of the red residue showed the quantitative formation of **2**. ^{1}H NMR (THF-*d*$_8$, δ) −0.06 (s, 2H), 0.00 (s, 2H), 0.17 (s, 18H), 0.24 (s, 18H), 0.25 (s, 18H), 0.33 (s, 18H), 1.03 (s, 3H, Si=SiC*H*$_3$), 1.18 (d, ^{3}J = 7 Hz, 6H), 1.20 (d, ^{3}J = 7 Hz, 6H), 1.41 (sep, ^{3}J = 7 Hz, 1H), 1.47 (sep, ^{3}J = 7 Hz, 1H); ^{13}C NMR (THF-d_8, δ) 6.03 (CH_3), 6.05 (CH_3), 6.5 (CH_3), 6.6 (CH_3), 8.1 (CH), 8.9 (CH), 12.5 (Si=Si*C*H_3), 17.5 (CH), 18.9 (CH), 22.9 (CH_3), 23.0 (CH_3); ^{29}Si NMR (THF-d_8, δ) −3.4 (*Si*Me$_3$), −3.3 (*Si*Me$_3$), −3.0 (*Si*Me$_3$), −2.9 (*Si*Me$_3$), 4.4 (*i*Pr*Si*), 12.8 (*i*Pr*Si*), 114.1 (Li–Si=Si), 143.4 (Li–Si=Si).

Isomerization of 2 to 3

The silyllithium **2** was prepared by the above procedure. The THF solution of **2** was allowed to stand for two days at room temperature. The NMR analysis showed the disappearance of **2** and the formation of **3**. After removal of the solvent, **3** was obtained as an air- and moisture-sensitive pale yellow solid (48 mg, 80%). Mp 69–71 °C (dec); ^{1}H NMR (THF-d_8, δ) −0.29 (s, 1H), −0.28 (s, 1H), −0.22 (s, 1H), 0.16 (s, 9H), 0.18 (s, 18H), 0.20 (s, 9H), 0.25 (s, 9H), 0.26 (s, 9H), 0.28 (s, 9H), 0.32 (s, 9H), 0.47 (s, 3H), 1.04 (d, ^{3}J = 8 Hz, 3H), 1.17 (sep, ^{3}J = 8 Hz, 1H), 1.25 (d, ^{3}J = 8 Hz, 3H), 1.28 (d, ^{3}J = 8 Hz, 3H), 1.29 (d, ^{3}J = 8 Hz, 3H), 1.45 (sep, ^{3}J = 8 Hz, 1H). The chemical shift of the Si*H* cannot be measured precisely because of its overlap with the signals of the *i*Pr groups; however, from the HMQC 2-D NMR spectrum the signal is deduced to occur at 1.1–1.3 ppm. ^{13}C NMR (THF-d_8, δ) −0.9 (C), 0.4 (CH), 4.7 (CH_3), 4.9 (CH_3), 5.9 (CH_3), 6.09 (CH_3), 6.14 (CH_3), 6.4 (CH_3), 6.8 (CH_3), 8.96 (CH_3), 9.1 (CH_3), 9.02 (CH), 11.3 (CH), 16.2 (CH), 19.1 (CH), 22.2 (CH_3), 22.4 (CH_3), 23.3 (CH_3), 23.9 (CH_3); ^{29}Si NMR (THF-d_8, δ) −160.5 (*Si*Li), −62.4 (*Si*Me), −16.2 (^{i}Pr*Si*), −7.3 (*Si*Me$_3$), −6.7 (*Si*Me$_3$), −2.1 (*Si*Me$_3$), −1.5 (*Si*Me$_3$), −1.1 (*Si*Me$_3$), −0.7 (*Si*Me$_3$), 0.5 (*Si*Me$_3$), 0.7 (*Si*Me$_3$), 25.0 (*i*Pr*Si*).

X-Ray analysis of 3

Single crystals of **3** for X-ray diffraction analysis were grown from a benzene solution. Diffraction data were collected at 150 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo-Kα radiation (λ = 0.71070 Å). The structure was solved by the direct method using the SIR-92 program[18] and refined by the full-matrix least-squares method by the SHELXL-97 program.[19] Crystal data for **3**(thf)$_2$(C_6H_6)$_3$: $C_{61}H_{127}LiO_2Si_{12}$, MW = 1236.65, monoclinic, *C*2/*c*, a = 53.017(2), b = 14.9830(5), c = 19.9430(9) Å, β = 100.564(3)°, V = 15573.3(11) Å^3, Z = 8, D_c = 1.055 g cm^{-3}, R = 0.0632 ($I > 2\sigma(I)$), R_w = 0.1738 (all data), GOF = 0.907 for 17550 reflections and 690 parameters.†

References

1 For recent reviews on silenes, see: (*a*) T. Müller, W. Ziche and N. Auner, in *The Chemistry of Organic Silicon Compounds*, ed. Y. Apeloig and Z. Rapport, Wiley, Chichester, 1998, vol. 2, part 2, ch. 16, p. 855; (*b*) T. L. Morkin and W. J. Leigh, *Acc. Chem. Res.*, 2001, **34**, 129; (*c*) L. E. Gusel'nikov, *Coord. Chem. Rev.*, 2003, **244**, 149; (*d*) H. Ottosson and P. G. Steel, *Chem.–Eur. J.*, 2006, **12**, 1576; (*e*) H. Ottosson and A. M. Eklöf, *Coord. Chem. Rev.*, 2008, **252**, 1287; (*f*) For recent reviews on disilenes, see: R. Okazaki and R. West, *Adv. Organomet. Chem.*, 1996, **39**, 231; (*g*) M. Weidenbruch, in *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, Chichester, 2001, vol. 3, ch. 5, p. 391; (*h*) M. Kira and T. Iwamoto, *Adv. Organomet. Chem.*, 2006, **54**, 73; (*i*) For recent reviews on the multiple bonding in main group elements, see: P. P. Power, *Chem. Rev.*, 1999, **99**, 3463; (*j*) P. P. Power, *Chem. Commun.*, 2003, 2091; (*k*) Y. Wang and G. H. Robinson, *Chem. Commun.*, 2009, 5201.

2 (*a*) Pb analogue: L. Pu, B. Twamley and P. P. Power, *J. Am. Chem. Soc.*, 2000, **122**, 3524; (*b*) Ge analogue: A. D. Phillips, R. J. Wright, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2002, **124**, 5930; (*c*) Y. Sugiyama, T. Sasamori, Y. Hosoi, Y. Furukawa, N. Takagi, S. Nagase and N. Tokitoh, *J. Am. Chem. Soc.*, 2006, **128**, 1023; (*d*) Sn analogue: M. Stender, A. D. Phillips, R. J. Wright and P. P. Power, *Angew. Chem., Int. Ed.*, 2002, **41**, 1785; (*e*) R. C. Fischer, L. Pu, J. C. Fettinger, M. A. Brynda and P. P. Power, *J. Am. Chem. Soc.*, 2006, **128**, 11366.

3 (*a*) A. Sekiguchi, R. Kinjo and M. Ichinohe, *Science*, 2004, **305**, 1755; (*b*) A. Sekiguchi, M. Ichinohe and R. Kinjo, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 825; (*c*) A. Sekiguchi, *Pure Appl. Chem.*, 2008, **80**, 447.

4 N. Wiberg, S. K. Vasisht, G. Fischer and P. Mayer, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1823.

5 T. Sasamori, K. Hironaka, Y. Sugiyama, N. Takagi, S. Nagase, Y. Hosoi, Y. Furukawa and N. Tokitoh, *J. Am. Chem. Soc.*, 2008, **130**, 13856.

6 V. Kravchenko, R. Kinjo, A. Sekiguchi, M. Ichinohe, R. West, Y. S. Balazs, A. Schmidt, M. Karni and Y. Apeloig, *J. Am. Chem. Soc.*, 2006, **128**, 14472.

7 R. Kinjo, M. Ichinohe and A. Sekiguchi, *J. Am. Chem. Soc.*, 2007, **129**, 26.

8 A. Sekiguchi, R. Kinjo and M. Ichinohe, *Synth. Met.*, 2009, **159**, 773.

9 R. Kinjo, M. Ichinohe, A. Sekiguchi, N. Takagi, M. Sumimoto and S. Nagase, *J. Am. Chem. Soc.*, 2007, **129**, 7766.

10 K. Takeuchi, M. Ichinohe, A. Sekiguchi, J.-D. Guo and S. Nagase, *Organometallics*, 2009, **28**, 2658.

11 (*a*) K. Takeuchi, M. Ichinohe and A. Sekiguchi, *J. Am. Chem. Soc.*, 2008, **130**, 16848; (*b*) K. Takeuchi, M. Ichinohe, A. Sekiguchi, J.-D. Guo and S. Nagase, *J. Phys. Org. Chem.*, in press.

12 (*a*) For the synthesis and reactivities of disilenyllithium derivatives, see: D. Scheschkewitz, *Angew. Chem., Int. Ed.*, 2004, **43**, 2965; (*b*) M. Ichinohe, K. Sanuki, S. Inoue and A. Sekiguchi, *Organometallics*, 2004, **23**, 3088; (*c*) S. Inoue, M. Ichinohe and A. Sekiguchi, *Chem. Lett.*, 2005, **34**, 1564; (*d*) M. Ichinohe, K. Sanuki, S. Inoue and A. Sekiguchi, *Silicon Chem.*, 2007, **3**, 111; (*e*) D. Scheschkewitz, *Angew. Chem., Int. Ed.*, 2005, **44**, 2954; (*f*) T. I. Nguyen and D. Scheschkewitz, *J. Am. Chem. Soc.*, 2005, **127**, 10174; (*g*) K. Abersfelder, D. Güclü and D. Scheschkewitz, *Angew. Chem., Int. Ed.*, 2006, **45**, 1643; (*h*) I. Bejan and D. Scheschkewitz, *Angew. Chem., Int. Ed.*, 2007, **46**, 5783; (*i*) S. Inoue, M. Ichinohe and A. Sekiguchi, *Angew. Chem., Int. Ed.*, 2007, **46**, 3346; (*j*) I. Bejan, D. Güclü, S. Inoue, M. Ichinohe, A. Sekiguchi and D. Scheschkewitz, *Angew. Chem., Int. Ed.*, 2007, **46**, 3349; (*k*) I. Bejan, S. Inoue, M. Ichinohe, A. Sekiguchi and D. Scheschkewitz, *Chem.–Eur. J.*, 2008, **14**, 7119; (*l*) T. Iwamoto, M. Kobayashi, K. Uchiyama, S. Sasaki, S. Nagendran, H. Isobe and M. Kira, *J. Am. Chem. Soc.*, 2009, **131**, 3156; (*m*) K. Abersfelder and D. Scheschkewitz, *J. Am. Chem. Soc.*, 2008, **130**, 4114; (*n*) Recent review on disilenides and related compounds: D. Scheschkewitz, *Chem.–Eur. J.*, 2009, **15**, 2476.

13 K. Takeuchi, M. Ikoshi, M. Ichinohe and A. Sekiguchi, *J. Am. Chem. Soc.*, 2010, **132**, 930.

14 (*a*) M. Kira and T. Iwamoto, *J. Organomet. Chem.*, 2000, **611**, 236; (*b*) M. Ichinohe, R. Kinjo and A. Sekiguchi, *Organometallics*, 2003, **22**, 4621.

15 The H-substituted disilenyllithium, (Dsi$_2$*i*PrSi)(H)-Si=Si(Li)(Si*i*PrDsi$_2$), is stable in THF at room temperature for a few days and it slowly decomposes to a complicated mixture.

16 (*a*) T. Iwamoto, J. Okita, C. Kabuto and M. Kira, *J. Am. Chem. Soc.*, 2002, **124**, 11604; (*b*) N. Wiberg, W. Niedermayer, H. Nöth and M. Warchhold, *J. Organomet. Chem.*, 2001, **628**, 46.

17 (*a*) S. Masamune, S. Murakami, H. Tobita and D. J. Williams, *J. Am. Chem. Soc.*, 1983, **105**, 7776; (*b*) B. Gehrhus and P. B. Hitchcock, *Organometallics*, 2004, **23**, 2848.

18 A. Guagliardi, M. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

19 G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure-Refinement*, University of Göttingen, Germany, 1997.