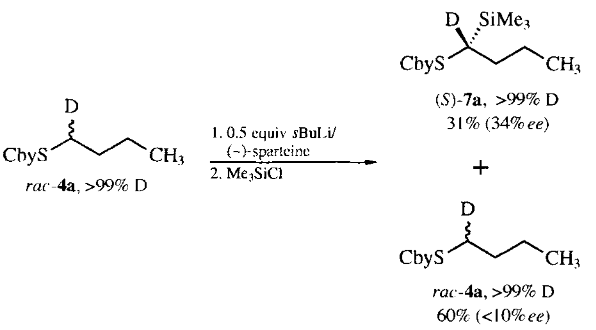
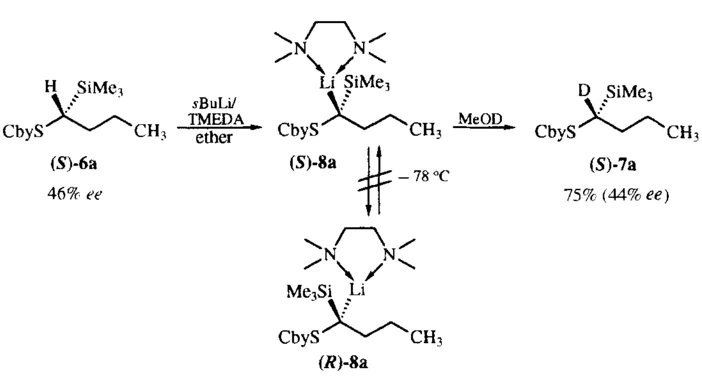
presence of only 0.5 equivalents of chiral base, and the carbanions formed in this way were trapped with chlorotrimethylsilane. In the starting material isolated at the end of the experiment (60%) the enantiomer ratio (*R*)-**4a**:(*S*)-**4a** was determined to be 45:55 by ^{1}H NMR spectroscopy;[14] the removal of the *pro-S* proton in **2** is thus only slightly preferred.



Since the lithiated primary thiocarbamates of type **3** are not configurationally stable in ether at −78 °C, we thought that a more sterically demanding group at the carbanionic center might lead to higher configurational stability. Thus, (*S*)-**6a** (46% *ee*) was deprotonated with *s*BuLi/TMEDA under the conditions described above, left at −78 °C for 2.5 h, and the ion pair thus formed trapped with [D$_1$]methanol. The α-deuterated silane (*S*)-**7a** was obtained with 44% *ee*.[15] Even though the negative charge on the carbanion is stabilized by the trimethylsilyl group, synthetically useful configurational stability was observed. Thus, the formation of a configurationally stable, enantiomerically enriched α-thioalkyllithium compound has been achieved for the first time.



Experimental Procedure

To a solution of (−)-sparteine (352 mg, 1.5 mmol) or TMEDA (174 mg, 1.5 mmol) in 10 mL of ether cooled to −78 °C was added dropwise 1.25 mmol of an approximately 1.4 M solution of *sec*-butyllithium in isopentane/cyclohexane. The reaction mixture was stirred for 10 min at −78 °C, then 1.0 mmol of the carbamate (**2a**–**c**, **4a**, **6a**) was slowly added dropwise and the solution stirred for a further 2.5 h. Finally, 3.0 mmol of the desired electrophile was added by syringe and the mixture stirred a further 4 h at −78 °C. The workup consisted of pouring the solution into a mixture of 20 mL of 2 N HCl and 20 mL of ether. The product was purified in the usual fashion. The resulting carboxylic acids were treated with diazomethane to provide the methyl esters **5a**–**c**.

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[1] H. J. Reich, M. D. Bowe, *J. Am. Chem. Soc.* **1990**, *112*, 8994; b) H. J. Reich, R. R. Dykstra, *ibid.* **1993**, *115*, 7041; c) T. Cohen, M. Bhupathy, *Acc. Chem. Res.* **1989**, *22*, 152; d) K. Brinckmann, R. Brückner, *Chem. Ber.* **1993**, *126*, 1227; e) P. G. McDougal, B. D. Condon, *Tetrahedron Lett.* **1989**, *30*, 789; f) T. Ruhland, R. Dress, R. W. Hoffmann, *Angew. Chem.* **1993**, *105*, 1487; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1467; R. W. Hoffmann, M. Julius, F. Chemla, T. Ruhland, G. Frenzen, *Tetrahedron* **1994**, *50* 6049; g) H. J. Reich, R. R. Dykstra, *Angew. Chem.* **1993**, *105*, 1489; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1469; H. J. Reich, J. B. Borst, R. R. Dykstra, *Tetrahedron* **1994**, *50*, 5869.

[2] For a short review see: V. K. Aggarwal, *Angew. Chem.* **1994**, *106*, 185; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 175.

[3] a) D. Hoppe, F. Hintze, P. Tebben, *Angew. Chem.* **1990**, *102*, 5872; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1422; b) A. Carstens, *Tetrahedron* **1994**, *50*, 6097; c) for a short review see: P. Knochel, *Angew. Chem.* **1992**, *104*, 1486; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1459; d) D. Hoppe, F. Hintze, P. Tebben, M. Paetow, H. Ahrens, J. Schwerdtfeger, P. Sommerfeld, J. Haller, W. Guarnieri, S. Kolczewski, T. Hense, I. Hoppe, *Pure Appl. Chem.* **1994**, *66*, 1479; for applications of α-amino-substituted: e) S. T. Kerrick, P. Beak, *J. Am. Chem. Soc.* **1991**, *113*, 9708; D. J. Gallagher, S. T. Kerrick, P. Beak, *ibid.* **1992**, *114*, 5872.

[4] F. Hintze, D. Hoppe, *Synthesis* **1992**, 1216.

[5] Thiocarbamates **2a** (95%), **2b** (87%), and **2c** (88%) were prepared from the corresponding alkanethiols with 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carbonyl chloride by the sodium hydride route [4].

[6] All the products were fully characterized spectroscopically. Correct elemental analyses were also obtained for each product.

[7] a) For stereochemical correlation methyl (*S*)-lactate was converted to methyl (*R*)-(2-acetylthio)propanoate by using a Mitsunobu reaction [7b], the *S*-acetyl group removed [7c], and the enantiomeric excess of the known [7d] (*R*)-2-sulfanylpropanoic acid measured using correlated specific rotation as >95% *ee*. Finally, the carbamate group was introduced (cesium carbonate/THF). The specific rotation $[\alpha]_D^{20} = +36.4$ ($c = 1.41$, CH_2Cl_2)) for *ent*-**5b** (85% *ee*) corresponds well to that of the sample **5b** obtained by deprotonation (47% *ee*): $[\alpha]_D^{20} = -19.4$ ($c = 1.33$, CH_2Cl_2); b) R. P. Vollante, *Tetrahedron Lett.* **1981**, *22*, 3119; c) L. N. Owen, M. B. Rahman, *J. Chem. Soc. C* **1971**, 2432; d) B. Strijtveen, R. M. Kellog, *J. Org. Chem.*, **1986**, *51*, 3664.

[9] D. Hoppe, M. Paetow, F. Hintze, *Angew. Chem.* **1993**, *105*, 430; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 394.

[10] The extent of deuteration was determined by GC-MS using NH_3 for chemical ionization.

[11] a) J. M. Lehn, G. Wipff, J. Demuynck, *Helv. Chim. Acta* **1977**, *60*, 1239; b) F. Bernardi, A. Bottoni, A. Venturini, A. Mangini, *J. Am. Chem. Soc.* **1986**, *108*, 8171.

[12] J. March, *Advanced Organic Chemistry*, 4th ed., Wiley, New York, **1992**, Chapter 1.

[13] O. Zschage, J.-R. Schwark, T. Krämer, *Tetrahedron* **1992**, *48*, 8377.

[14] ^{1}H NMR conditions: 360 MHz, 10 mg of **4a** + 0.9 mg of tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) [Eu(hfc)$_3$] in 0.6 mL of $CDCl_3$; the signal of the α proton at $\delta = 6.4$ is split by roughly 0.02 ppm.

[15] $[\alpha]_D^{20} = 5.3$ ($c = 1.90$ in CH_2Cl_2, 44% *ee*); ^{1}H NMR conditions: 10 mg of **6a** + 10 mg of [Pr(hfc)$_3$] in 0.6 mL of $CDCl_3$.

[Fe(2,4,6-tBu$_3$C$_6$H$_2$)$_2$], a Monomeric Diaryl Complex with Two-Coordinate Iron(II)**

Hardy Müller, Wolfgang Seidel,* and Helmar Görls

Homoleptic organo transition metal compounds with low coordination numbers are rare. This is especially true for neutral complexes of the type [MR$_n$] ($n < 4$) which are expected to exhibit interesting chemical properties based on their coordinatively unsaturated character. To date tetramesityldiiron[1] serves as the only example of a structurally characterized neutral

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iron(II) complex with organic ligands. In this complex the metal atom is three-coordinate; the same coordination number is found in the analogous Co(II) complex[2a] and in [$\{Mn(mes)_2\}_3$] (mes = 2,4,6-$Me_3C_6H_2$).[2b] Even though two-coordinate iron(II) species are rare, Power et al. were able to show that they can be prepared by employing bulky amido ligands such as $[N(SiMePh_2)_2]^-$, $[N(SiMe_2Ph)_2]^-$, and $(NmesBmes_2)^-$.[3] In the crystal, these compounds have a N-Fe-N bond angle of approximately 170°. For the vaporizable iron(II) amide [$Fe\{N(SiMe_3)_2\}_2$] in the gas phase, the two-coordinate nature of the central metal and a N-Fe-N bond angle of 180° was confirmed by electron diffraction studies.[4] Furthermore, Power et al. recently also reported the synthesis and characterization of thiolato complexes with two-coordinate iron(II).[5]

We therefore decided to investigate whether monomeric two-coordinate iron complexes of type [FeR_2] could be obtained by the use of aryl ligands with bulkier substituents than those found in the three-coordinate tetramesityldiiron [$\{Fe(mes)(\mu\text{-}mes)\}_2$]. We applied 2,4,6-$i$$Pr_3C_6H_2$ (trip), 2,4,6-$Ph_3C_6H_2$ (triph), and 2,4,6-$t$$Bu_3C_6H_2$ (mes*) as aryl ligands.

The corresponding compounds were synthesized analogously to the preparation of tetramesityldiiron; stoichiometric amounts (1:2) of [$FeBr_2(thf)_2$] (**1**) and Grignard reagent were allowed to react in tetrahydrofuran, after that the magnesium halides were precipitated by addition of dioxan. The reaction with (trip)MgBr afforded a brown, crystalline substance of composition **2**. This compound is a dimer and structurally similar to tetramesityldiiron.[6]

[$\{Fe(trip)(\mu\text{-}trip)\}_2$] **2**

In contrast, treatment of the iron halide with (triph)MgBr does not afford the corresponding diaryliron complex. Instead, a colorless precipitate forms which presumably is an adduct of the reactants. No change in the nature of this precipitate is observed upon treatment with dioxan.

A similar colorless, fine-crystalline precipitate of the composition **3** is initially obtained when **1** is treated with two equivalents of (mes*)MgBr in tetrahydrofuran [Eq. (a)]. Addition of dioxan, followed by removal of the solvent and extraction of the residue with n-pentane yielded an air- and moisture-sensitive yellow product **4** [Eq. (b)]. Its magnetic moment of 4.77 μ_B at room temperature is appropriate for an iron(II) high-spin complex. Notably, [$\{Fe(mes)(\mu\text{-}mes)\}_2$] and **2** show a markedly smaller magnetic moment.

$$\underset{\mathbf{1}}{2\,[FeBr_2(thf)_2]} + 4\,(mes^*)MgBr \xrightarrow{THF} \underset{\mathbf{3}}{[Fe_2Mg_3Br_6(mes^*)_4(thf)_2]} + MgBr_2 \qquad (a)$$

$$\underset{\mathbf{3}}{[Fe_2Mg_3Br_6(mes^*)_4(thf)_2]} \xrightarrow{THF/dioxan} \underset{\mathbf{4}}{2\,[Fe(mes^*)_2]} + 3\,MgBr_2(dioxan)_2 \qquad (b)$$

The homoleptic diaryliron(II) compounds prepared dissolve readily in apolar solvents. The increase in size of the substituents on the aryl ligands has a decisive influence on the reactivity. The adduct formation with nitrogen bases and concurrent cleavage of the respective dimer has been reported for **2**[6] and [$\{Fe(mes)(\mu\text{-}mes)\}_2$];[7] however, no such reaction is observed for **4**. Moreover, whereas tetramesityldiiron rapidly undergoes an insertion reaction with isocyanate or CO,[8] the same reaction occurs at a much slower rate with **4**. Complex **4** is thermally surprisingly stable (decomposition occurs at 179 °C); this is a result of the steric shielding of the central atom, which in turn kinetically disfavors the decomposition reaction.

Single crystals of **4** suitable for an X-ray structure analysis were obtained from n-heptane.[9] The crystal structure analysis of **4** shows the presence of two-coordinate iron(II) centers in the C_2-symmetric molecules (Fig. 1). The Fe–C1 distance (2.051(5) Å) is comparable with the terminal Fe–C distances in tetramesityldiiron and those in **2**. The C1-Fe-C1A bond angle of 158.9(3)° is about 11° smaller than the corresponding angles in the aforementioned amides and about 17° smaller than that in [$Cu(mes^*)SMe_2$][10] which serves as the only known compound of a 3d element with a (mes*) group. The neutral dialkylmanganese compound [$Mn\{C(SiMe_3)_3\}_2$][11] in which the manganese(II) center is two-coordinate has a linear structure with an Mn–C bond length of 2.102 Å. The bent geometry at the iron center in **4** is most likely a result of packing effects; intermolecular interactions can be excluded. Larger deviations from a linear arrangement of ligands have also been reported for two-coordinate phosphane complexes of type [$M(PR_3)_2$] (e.g. M = Pd, R = c-C_6H_{11}).[12]

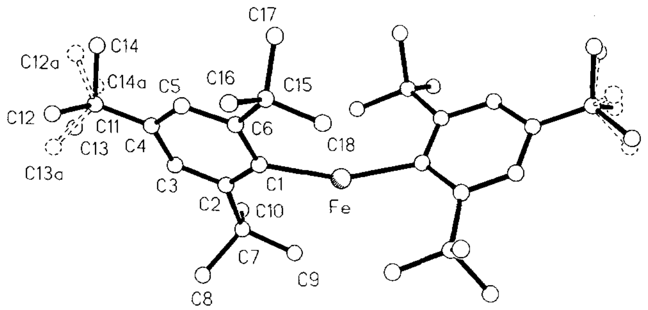

Fig. 1. Molecular structure of **4** in the crystal; selected bond lengths [Å] and angles [°]: Fe-C1 2.051(5), C1-C2 1.426(7), C1-C6 1.413(7), C2-C3 1.400(7), C3-C4 1.376(7), C4-C5 1.388(7), C5-C6 1.389(7), Fe···C18 2.822(8), Fe···C9 2.744(6), Fe···H9b 2.16#, Fe···H18c 2.33(1)#; C1-Fe-C1A 158.9(3), Fe-C1-C2 119.4(4), Fe-C1-C6 122.7(3), C1-C2-C7 124.3(4), C1-C6-C15 122.9(4), C1-C2-C3 120.2(5), C2-C3-C4 123.2(5), C3-C4-C5 116.2(5), C4-C5-C6 123.2(5), C1-C6-C5 120.8(4). Distances marked with a # were calculated based on the covalent radius of the hydrogen atom.

An Fe···H distance of 2.1–2.3 Å can be calculated from the Fe···C9 and Fe···C18 distances of 2.744(6) Å and 2.822(8) Å, respectively. However, no evidence of agostic interactions in **4** was apparent from the IR spectrum (between 2700 and 2350 cm^{-1}) or from ^1H NMR investigations. The ^1H NMR spectrum in [D_8]toluene shows three paramagnetically shifted signals which are assigned to protons of the *para-* and *ortho-*tBu groups and to aromatic protons. No splitting of these signals is observed even at temperatures as low as −80 °C; similar results have also been reported for thiolatoiron(II) complexes[5] and trimesitylrhodium.[13]

Experimental Procedure

All reactions were carried out under anaerobic and anhydrous conditions.

4: A solution of (mes*)MgBr (34.2 mmol, 103.5 mL) in THF was added dropwise over a period of 2.5 h to a stirred suspension of **1** (6.15 g, 17.08 mmol) in THF (30 mL). Stirring was continued for an additional 1.5 h, whereupon 1,4-dioxan (12 mL) in THF (15 mL) was slowly added to precipitate the $MgBr_2(dioxan)_2$. After 15 h the solution was evaporated to dryness and the residue was treated with n-pentane. After one hour the magnesium salts were collected on a filter and washed with the filtrate so to completely extract the products. The filtrate was then reduced in volume to about 30–40 mL. Crystallization was accomplished by cooling to −30 °C, and agitating the filtrate until the yellow compound started to crystallize. After 48 h the product was collected by filtration. Crystals suitable for a X-ray structure analysis were obtained upon cooling a saturated solution (n-heptane; 50 °C) to room temperature. Yield: 5.9 g (63%).

$C_{36}H_{58}Fe$ (546.67 g mol^{-1}): elemental analysis: found C 80.51, H 10.12, Fe 10.16%; calcd C 79.09, H 10.69, Fe 10.22%; χ_{mol}(corr.) = 9.703 × 10^{-3} cm^3 mol^{-1} (291 K): μ_{eff} = 4.77 μ_B; IR (Nujol): $\tilde{\nu}$ = 1590 (m), 1522 (m), 1385 (s), 1362 (s), 1343 (s), 1247 (s), 1209 (m), 1168 (m), 1122 (m), 1023 (m), 934 (s), 899 (m), 879 (m), 743 (s), 715 (s), 646 (s), 569 (m), 471 (s) cm^{-1}; ^{1}H NMR ([D$_8$]toluene, 25 °C): δ = 18.6 (s, 18 H), 53 (s, 36 H), 115 (s, 4 H); m.p. 179 °C (exothermic).

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[1] H. Müller, W. Seidel, H. Görls, *J. Organomet. Chem.* **1993**, *445*, 133–136.
[2] a) K. H. Theopold, J. Silvestre, E. K. Byrne, D. S. Richeson, *Organometallics* **1989**, *8*, 2001–2009; b) S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Chem. Soc. Chem. Commun.* **1983**, 1128–1129.
[3] a) R. A. Bartlett, P. P. Power, *J. Am. Chem. Soc.* **1987**, *109*, 7563–7564; b) H. Chen, R. A. Bartlett, H. V. Rasika Dias, M. M. Olmstead, P. P. Power, *ibid.* **1989**, *111*, 4338–4345; c) H. Chen, R. A. Bartlett, M. M. Olmstead, P. P. Power, S. C. Shoner, *ibid.* **1990**, *112*, 1048–1055.
[4] R. A. Andersen, K. Faegri, J. C. Green, A. Haaland, M. F. Lappert, W.-P. Leung, K. Rypdal, *Inorg. Chem.* **1988**, *27*, 1782–1786.
[5] J. J. Ellison, K. Ruhlandt-Senge, P. P. Power, *Angew. Chem.* **1994**, *106*, 1248–1250; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1178–1180.
[6] a) H. Müller, Dissertion, Universität Jena, **1993**; b) The synthesis and structure of **2** has recently been reported: A. Klose, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, N. Re, *J. Am. Chem. Soc.* **1994**, *116*, 9123–9135.
[7] W. Seidel, K.-J. Lattermann, *Z. Chem.* **1983**, *23*, 31.
[8] H. Müller, W. Seidel, H. Görls, *J. Organomet. Chem.* **1994**, *472*, 215–220.
[9] Crystal data: Mo$_{K\alpha}$, λ = 0.71069 Å, θ-2ω scan, solution: heavy atom methods (SHELXS 86), refinement with MOLEN, hydrogen atoms calculated on ideal positions, $C_{36}H_{58}Fe$, M = 546.7 g mol^{-1}, $C2/c$, a = 17.935(4), b = 8.644(1), c = 23.591(5) Å, β = 109.89(1)°, V = 3439(1) Å^3, Z = 4, ρ_{calcd} = 1.06 g cm^{-3}, μ = 4.6 cm^{-1}, T = 293 K, 6427 measured reflections, 5961 symmetry-independent reflections of which 1806 were observed ($I > 2\sigma(I)$), 165 refined parameters, R = 0.073, R_w = 0.081 ($w = 1/\sigma^2(F_0)$), residual electron density 0.58 e Å^{-3}. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-58691.
[10] X. He, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1992**, *114*, 9668–9670.
[11] N. H. Buttrus, C. Eaborn, P. B. Hitchcock, J. D. Smith, A. C. Sullivan, *J. Chem. Soc. Chem. Commun.* **1985**, 1380–1381.
[12] A. Immirzi, A. Musco, *J. Chem. Soc. Chem. Commun.* **1974**, 400–401.
[13] R. S. Hay-Motherwell, B. Hussain-Bates, M. B. Hursthouse, G. Wilkinson, *J. Chem. Soc. Chem. Commun.* **1990**, 1242–1243.

Compounds with Planar Tetracoordinate Boron Atoms: Anti van't Hoff/Le Bel Geometries without Metal Centers[**]

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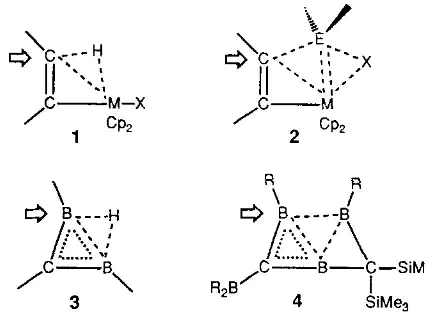
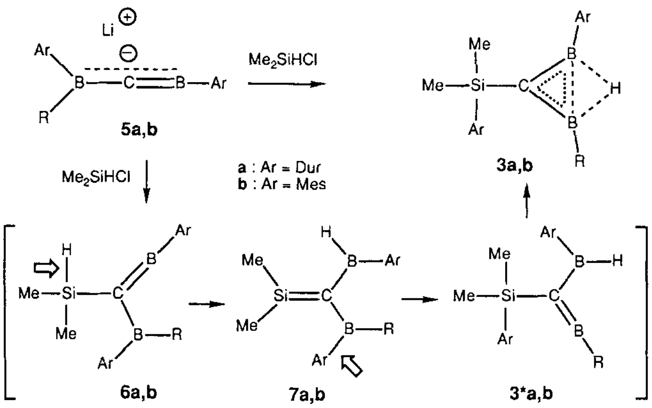
Dedicated to Prof. Paul von Ragué Schleyer on the occasion of his 65th birthday

Numerous compounds **1**[3, 4] and **2**[5] have anti van't Hoff/Le Bel geometries[1, 2] with planar tetracoordinate carbon atoms; all of them contain at least one metal atom (M = Ti, Zr, Hf...; E = H, B), and most contain even two (E = Al, Ga, Zr...) (Scheme 1). We show here by crystal structure analyses that compounds **3a** and **3c** contain planar tetracoordinate boron atoms. Compounds **3** and **4**[6] are examples of compounds having anti van't Hoff/Le Bel geometries *without* metal centers.



Scheme 1. **1**, **2**: M = Ti, Zr, Hf...; **1**: X = +, Cl, Br, CH_3; **2**: X = H, Cl, CH_3, C≡CR; E = B, Al, Ga, Zr...; **4**: R = 2,3,5,6-Me_4C_6H.

The H-bridged borylmethyleneboranes **3a, b** are obtained from the reaction of borylborataalkynes **5a, b**[6] with chlorodimethylsilane at 25 °C (Scheme 2). In these reactions a hydrogen atom is transferred from a silicon atom to a boron atom, and an aryl group from a boron atom to a silicon atom. Primary products are probably silylmethyleneboranes **6a, b**, which then give the diborylsilaethenes **7a, b** by means of a 1,3 shift of the hydrogen atom from the tetracoordinate silicon atom to the dicoordinate boron atom. The 1,3 shift of the aryl group from the boron atom with the bis(trimethylsilyl)methyl substituent R to the tricoordinate silicon atom formally leads to the classical borylmethyleneboranes **3*a, b**, which have the β-agostic[6] structure **3a, b**. Compound **3c** is formed by melting **9** (150 °C),[7] which in turn is accessible from **8a**[6] and diethylborane. In the reaction giving **3c** two boron atoms connected to the carbon atom framework change places—possibly by a double 1,2 rearrangement (Scheme 3). The respective substituents migrate together with the boron atoms.



Scheme 2. R = $CH(SiMe_3)_2$; Dur = 2,3,5,6-Me_4C_6H; Mes = 2,4,6-$Me_3C_6H_2$.

Figure 1 shows the X-ray crystal structures of **3a** and **3c**;[8] the corresponding constitution of **3b** is deduced from the similarity of its NMR data to that of the framework atoms of **3a** and **3c** (Table 1).

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