- [6] General name for these diphosphanes: (*S,S*)-2,2'-bis[(*R*)-1-(dialkylphosphino)ethyl]-1,1'-biferrocene.
- [7] *trans*-[RhCl(CO){(*R,R*)-(*S,S*)-*n*BuTRAP}] was prepared from [RhCl(CO)₂]₂ and (*R,R*)-(*S,S*)-*n*BuTRAP: m.p. 222–225 °C (decomp); $[\eta]_D^{20} = -760.1$ ($c = 0.321$ in CHCl₃); ¹H NMR (200 MHz, CDCl₃, TMS) $\delta = 0.81$ – 1.00 (m, 12H), 1.10–2.38 (m, 30H), 2.88 (quint., $J = 7$ Hz, 1H), 3.08 (quint., $J = 7$ Hz, 1H), 4.03–4.09 (m, 2H), 4.28 (s, 5H), 4.31 (s, 5H), 4.35–4.45 (m, 4H); ³¹P{¹H} NMR (81 MHz, CDCl₃, 85% H₃PO₄) $\delta = 27.27$ (dd, ² J (P,P) = 341, ¹ J (P,Rh) = 119 Hz), 32.56 (dd, ² J (P,P) = 341, ¹ J (P,Rh) = 119 Hz). Orange crystals for the X-ray crystal structure were grown from CH₂Cl₂/EtOH by solvent diffusion techniques; crystal data: orthorhombic, *P*2₁2₁2₁ (no. 19), $a = 13.74(1)$, $b = 23.34(2)$, $c = 12.96(1)$ Å, $V = 4158(7)$ Å³, $Z = 4$, $\lambda(\text{MoK}\alpha) = 0.71073$ Å; MAC Science MXC3 diffractometer. The structure was solved by direct methods and by Fourier synthesis using the Crystan-GM program package. The atoms of disordered chloro and carbonyl ligands were located at positions defined by difference Fourier synthesis for 0.55/0.45 occupancy. Hydrogen atoms were not included in the calculation. R ; $R_w = 0.069$; 0.066 for 4996 reflections. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation.
- [8] The enantioselectivities in the asymmetric hydrosilylation of simple ketones lacking secondary coordinating functional groups catalyzed by chiral rhodium–phosphane complexes still remain at most about 60%, but high enantioselectivities over 80% are obtained with α - and γ -keto esters; see: a) I. Ojima, T. Kogura, M. Kumagai, *J. Org. Chem.* **1977**, *42*, 1671–1679; b) I. Ojima, T. Kogure, *Tetrahedron Lett.* **1974**, 1889–1892; c) I. Ojima, T. Kogure, M. Kumagai, S. Horiuchi, T. Sato, *J. Organomet. Chem.* **1976**, *122*, 83–97; d) K. Yamamoto, T. Hayashi, M. Kumada, *ibid.* **1973**, *54*, C45–C47; e) T. Hayashi, K. Yamamoto, K. Kasuga, H. Omizu, M. Kumada, *ibid.* **1976**, *113*, 127–137; f) for a review see I. Ojima, K. Hirai in *Asymmetric Synthesis*, Vol. 5 (Ed.: J. D. Morrison), Academic Press, New York, **1985**, Chapter 4. For an intramolecular version see reference [5].
- [9] High enantioselectivities have been achieved in the rhodium-catalyzed asymmetric hydrosilylation of simple ketones by using nitrogen-based chiral ligands: a) H. Brunner, R. Becker, G. Rieple, *Organometallics* **1984**, *3*, 1354–1359; b) H. Brunner, A. Kürzinger, *J. Organomet. Chem.* **1988**, *346*, 413–424; c) H. Brunner, U. Obermann, *Chem. Ber.* **1989**, *122*, 499–507; d) H. Brunner, P. Brandl, *J. Organomet. Chem.* **1990**, *390*, C81–C83; e) *Tetrahedron Asymmetry* **1991**, *2*, 919–930; f) S. Gladiali, L. Pinna, G. Delogu, E. Graf, H. Brunner, *ibid.* **1990**, *1*, 937–942; g) H. Nishiyama, H. Sakaguchi, T. Nakamura, M. Horiata, M. Kondo, K. Itoh, *Organometallics* **1989**, *8*, 846–848; h) H. Nishiyama, M. Kondo, T. Nakamura, K. Itoh, *ibid.* **1991**, *10*, 500–508; i) H. Nishiyama, S. Yamaguchi, M. Kondo, K. Itoh, *J. Org. Chem.* **1992**, *57*, 4306–4309; j) H. Nishiyama, S.-B. Park, K. Itoh, *Tetrahedron Asymmetry* **1992**, *3*, 1029–1034; k) H. Nishiyama, S. Yamaguchi, S.-B. Park, K. Itoh, *ibid.* **1993**, *4*, 143–150.

naphthalenide. In a related reaction Weidenbruch et al.^[2] obtained the even more sterically crowded hexa-*tert*-butylcyclotrisilane. Hexakis(2,6-dimethylphenyl)-^[3] and hexa-*tert*-butylcyclotrigermane^[4] have also been obtained by reductive cyclization of diorganodihalogengermanes with lithium naphthalenide. To date six cyclotrisilanes^[1,2,5–7] and four cyclotrigermanes^[3,4] have been structurally characterized.^[8] Recently Baines et al.^[9] published the structure of the siladigermirane Mes₂Si(GeMes₂)₂, which was also synthesized by reductive cyclization.^[10] Three-membered ring systems containing silicon have also been thoroughly investigated by MO calculations.^[11–13]

We report here on the synthesis and structure of **1**, the first disilagermirane. Compound **1** was synthesized from germanium dichloride and tris(trimethylsilyl)silyllithium at –78 °C [Eq. (a)].^[14,15]

The reaction mechanism for the formation of **1** has not been confirmed unequivocally. It seems possible, however, that initially a germylene is formed intermediately by simultaneous LiCl elimination and migration of two Me₃Si groups. The (Me₂Si)₂Ge: then reacts with the intermediately formed disilene (Me₂Si)₂Si=Si(SiMe₃)₂ to give **1**. This seems feasible, since stable dialkylgermylenes have been synthesized and characterized previously.^[16–18] This reaction provides a novel and easy access to mixed tricyclic ring systems containing heavier elements of group 14. We are currently trying to synthesize other derivatives from the reaction of EHal₂ (E = Ge, Sn, Pb; Hal = Cl, Br) with (Me₃Si)₃ELi (E = Si, Ge, Sn).

Compound **1** has *D*_{3h} symmetry^[19] (Fig. 1). The three ring atoms lie on a crystallographic mirror plane. A threefold axis is perpendicular to the mirror plane intersecting the center of the GeSi₂ triangle. This causes a disorder of the single germanium

Synthesis and Structure of the Disilagermirane R₂Ge(SiR₂)₂ and the Solvent-Separated Ion Pair [Li{12crown-4}₂][GeR₃]; (R = SiMe₃)**

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Up until the beginning of the 1980s three-membered ring systems of the heavier elements of group 14 were considered unobtainable, and in fact even today not many of these compounds are known. However, the use of very bulky ligands stabilizes these tricyclic systems kinetically and protects the reactive center with an organic layer. This prevents further reaction and dimerization. In 1981 Masamune et al.^[1] isolated the unprecedented hexakis(2,6-dimethylphenyl)cyclotrisilane by reduction of dichlorobis(2,6-dimethylphenyl)silane with lithium

Fig. 1. Structure of **1** in the solid state. Selected bond lengths [pm] and angles [°]: Ge(1)–Si(2) 235.6(4), Ge(1)–Si(1a) 239.1(1), Si(1a)–Si(2b) 236.6(5), Si(1a)–Si(1b) 237.7(14); mean exocyclic Si–Si–Si angle 105.2(3), mean exocyclic Si–Ge–Si angle 105.8(3)°.

atom over all three ring positions; however the disorder could be solved and refined reasonable well. The site occupation factor of the Ge atom converged at 1/3. As expected the two exocyclic Ge–Si distances (235.6 pm) are shorter than the endocyclic Ge–Si distances (239.1 pm). This is also valid for the Si–Si distances (236.6 pm exocyclic, 237.7 pm endocyclic). The Si–Si and Si–Ge distances in the three-membered ring are consistent with the results of recently published ab initio calcula-

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tions.^[12] In comparison, the endocyclic Si–Si distances in hexakis(2,6-dimethylphenyl)cyclotrisilane are 238 pm and 242 pm,^[11] whereas in the sterically even more crowded hexa-*tert*-butylcyclotrisilane they are 251 pm.^[12] The Ge–Ge bond lengths in [(2,6-dimethylphenyl)₂Ge]₃^[13] and (tBuGe)₃^[14] are 254 pm and 256 pm, respectively.

In order to obtain, for example, hexakis(trimethylsilyl)-digermastannirane in analogy to the reaction described above, we synthesized tris(trimethylsilyl)germyllithium-([12]crown-4)₂ (**2**). The preparation of **2** [Eq. (b)]^[20] was carried out analogously to that of the silicon compound,^[14, 15] the only difference being the presence of [12]crown-4.

Compound **2** crystallizes as expected as a solvent-separated ion pair.^[19] In Figure 2 only the structure of the [Ge(SiMe₃)₃][−] anion is depicted. The mean Ge–Si bond length (236.7 pm) is in good agreement with the exocyclic Ge–Si bond in **1** (235.6 pm). The Ge–Si distance in [Cp*Cl₂HfGe(SiMe₃)₃] (Cp* = C₅Me₅),^[21] the only other known structurally characterized compound with this moiety, is 240.9 pm.

Fig. 2. Structure of the anion in **2**. Selected bond lengths [pm] and angles [°]: Ge(1)–Si(1) 236.6(1), Ge(1)–Si(2) 236.9(1); Si(1)–Ge(1)–Si(2) 102.66(3), Si(2)–Ge(1)–Si(2a) 100.53(4).

The most remarkable structural feature in the anion of **2** is the Si–Ge–Si angle (average of 101.6°; Ge1, Si1, and C2 lie on a crystallographic mirror plane, so that there are only two independent angles). This angle is more acute than the Si–Si–Si angle in the tris(trimethylsilyl)silyllithium derivatives R₃SiLi(thf)₃ (102.1°^[15] and R₃SiLi(dme)_{1.5} (104°),^[22] (R = SiMe₃, dme = dimethoxyethane), which both crystallize as contact ion pairs. The reason for this is the increasing energetic separation of *ns* and *np* orbitals for the heavier elements of the group. This decreases the participation of electrons in *s* orbitals in σ bonds. Therefore, in the [Ge(SiMe₃)₃][−] anion the three orthogonal *p* orbitals are chiefly used for bonding to the three Me₃Si substituents, whereas the lone pair possesses mainly *s* character. Recent investigations on Ph₃SnLi(pmdeta)^[23] and Ph₃PbLi(pmdeta),^[24] (pmdeta = (Me₂NCH₂CH₂)₂NMe) show that with increasing atomic number this effect becomes more pronounced (C–E–C angle in Ph₃E–Li; E = Sn: 96.1° and for E = Pb: 94.3°). The reduction in the Si–Ge–Si angle in the [Ge(SiMe₃)₃][−] anion is even more remarkable, because the steric demand of a (thf)₃Li group such as in (Me₃Si)₃SiLi(thf)₃ on the Si–Si–Si angle^[25] as well as a (pmdeta)Li group such as in Ph₃SnLi(pmdeta) and Ph₃PbLi(pmdeta) on the C–Sn–C and C–

Pb–C angles, respectively, are not applicable for the [Ge(SiMe₃)₃][−] anion. The Si–Ge–Si angle in (Me₃Si)₃GeLi(thf)₃ should be even smaller for these reasons. In Ge(pz)₃Na(thf)₃ (pz = pyrazol-1-yl) the germanium atom is likewise not coordinated by the alkali metal, because the sodium atom is coordinated by the three pyrazolyl ligands, which decreases the N–Ge–N angle to 96.2°.^[26]

Experimental Procedure

1: A solution of GeCl₂ (0.3 g, 2.1 mmol) in *n*-hexane (25 mL) was cooled to −78 °C and treated with (Me₃Si)₃SiLi(thf)₃ (2.0 g, 4.2 mmol). The solution was warmed to 0 °C and stirred for 12 h. The solvent was removed under reduced pressure (10^{−2} bar) and the solid residue taken up in *n*-pentane (25 mL). The insoluble components were filtered off and the solution was cooled to −90 °C. After 2 d colorless crystalline plates were obtained that were suitable for X-ray diffraction. Yield: 0.57 g (48%), decomposition at *T* ≥ 140 °C. ¹H NMR (C₆D₆, 25 °C): δ = 0.43 (s, 36 H; Si(SiMe₃)₂), 0.45 (s, 18 H; Ge(SiMe₃)₂); ²⁹Si NMR (C₆D₆, 25 °C): δ = −6.65 (Si(SiMe₃)₂), −22.1 (Ge(SiMe₃)₂), −159.98 (Si(SiMe₃)₃); IR: $\tilde{\nu}$ [cm^{−1}] = 1260 m, 1243 m, 1093 m, 1021 m, 838 vs; FI-MS: *m/z* (%): 568 (100) [*M*⁺].

2: To a solution of (1.35 g, 3.7 mmol) (Me₃Si)₄Ge in *n*-hexane (25 mL) was added [12]crown-4 (1.3 mL) and slowly methylolithium (2.5 mL, 4 mmol) in Et₂O. The white suspension was stirred for 24 h at room temperature and then THF (5 mL) was added to dissolve the white precipitate. The solution was stirred for an additional 24 h and subsequently stored at −35 °C. After approximately 7 d colorless needles were obtained that were suitable for X-ray diffraction. ¹H NMR ([D₈]toluene, 25 °C): δ = 0.27 (s, Ge(SiMe₃)₃), 3.59 (s, [O(CH₂)₂]₄); ⁷Li NMR ([D₈]toluene, 25 °C): δ = 0.27 (s).

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- [1] S. Masamune, Y. Hanzawa, S. Murakami, T. Bally, J. J. Blount, *J. Am. Chem. Soc.* **1982**, *104*, 1150.
- [2] A. Schäfer, M. Weidenbruch, K. Peters, H. G. von Schnering, *Angew. Chem.* **1984**, *96*, 311; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 302.
- [3] S. Masamune, Y. Hanzawa, D. J. Williams, *J. Am. Chem. Soc.* **1982**, *104*, 6136.
- [4] M. Weidenbruch, F.-T. Grimm, M. Herrndorf, A. Schäfer, K. Peters, H. G. von Schnering, *J. Organomet. Chem.* **1988**, *341*, 335.
- [5] J. C. Dewan, S. Murakami, J. T. Snow, S. Collins, S. Masamune, *J. Chem. Soc. Chem. Commun.* **1985**, 892.
- [6] H. Watanabe, M. Kato, T. Okawa, Y. Nagai, M. Goto, *J. Organomet. Chem.* **1984**, *271*, 225.
- [7] M. Weidenbruch, K. L. Thorn, S. Pohl, W. Saak, *J. Organomet. Chem.* **1987**, *329*, 151.
- [8] Review: T. Tsumuraya, S. A. Batcheller, S. Masamune, *Angew. Chem.* **1991**, *103*, 916; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 902.
- [9] K. H. Baines, J. A. Cooke, N. C. Payne, J. J. Vittal, *Organometallics* **1992**, *11*, 1408.
- [10] K. H. Baines, J. A. Cooke, *Organometallics* **1991**, *10*, 3419.
- [11] W. W. Schoeller, T. Dabisch, *J. Chem. Soc. Chem. Commun.* **1985**, 1706.
- [12] P. von R. Schleyer, A. F. Sax, J. Kalcher, R. Janoschek, *Angew. Chem.* **1987**, *99*, 374; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 364.
- [13] D. A. Horner, R. S. Grev, H. F. Schaefer III, *J. Am. Chem. Soc.* **1992**, *114*, 2093.
- [14] H. Gilman, C. L. Smith, *J. Organomet. Chem.* **1967**, *8*, 245; *ibid.* **1968**, *14*, 91.
- [15] A. Heine, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *Inorg. Chem.* **1993**, *32*, 2694.
- [16] D. G. Goldberg, D. H. Harris, M. F. Lappert, K. M. Thomas, *J. Chem. Soc. Chem. Commun.* **1976**, 261.
- [17] P. B. Hitchcock, M. F. Lappert, S. J. Miles, A. J. Thorne, *J. Chem. Soc. Chem. Commun.* **1984**, 480.
- [18] P. Jutzi, A. Becker, H. G. Stammer, B. Neumann, *Organometallics* **1991**, *10*, 1647.
- [19] Crystal Data of **1**: C₁₈H₄₄Si₄Ge, *M* = 567.9, rhombohedral, space group *R*3c, *a* = *b* = 1051.4(1), *c* = 5435.4(11) pm, *V* = 5.203 nm³, *Z* = 6, ρ_{calcd} = 1.087 Mg m^{−3}, *F*(000) = 1836, λ = 71.073 pm, *T* = −120 °C, $\mu(\text{MoK}\alpha)$ = 1.165 mm^{−1}, crystal size: 0.5 × 0.5 × 0.3 mm, $8^\circ \leq 2\theta \leq 55^\circ$; of the 3513 collected reflections 1339 were independent and used for refinement; largest difference peak and hole: 550 en m^{−3}, *R*1(*F* > 4 σ (*F*)) = 0.028 and *wR*2 = 0.066 (all data) with *R*1 = $\Sigma|F_o - F_c|/\Sigma F_o$ and *wR*2 = $(\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_c^2)^2)^{0.5}$; **2**: C₂₃H₅₀LiO₈Si₃Ge, *M* = 651.5, monoclinic, space group *P*2₁/m, *a* = 939.4(1), *b* = 1433.5(2), *c* = 1395.7(3) pm, β = 104.56(1)°, *V* = 1.819 nm³, *Z* = 2, ρ_{calcd} = 1.189 Mg m^{−3}, *F*(000) = 700, λ = 71.073 pm, *T* = −80 °C, $\mu(\text{MoK}\alpha)$ = 0.978 mm^{−1}, crystal size: 0.5 × 0.4 × 0.4, $8^\circ \leq 2\theta \leq 55^\circ$; of the 7864 reflections collected 4370 were independent and used for refinement, largest differ-

ence peak and hole: 310 nm^{-1} , $R1 (F > 4\sigma(F)) = 0.040$ and $wR2 = 0.095$ (all data); R values as defined above. Data of both structures were collected on a Stoe-Siemens-AED diffractometer. The intensities of the rapidly cooled crystals in an oil drop [27] were collected by the $2\theta/\omega$ method. Both structures were solved by direct methods (SHELXS-90) [28] and refined by full-matrix least-squares on F^2 [29]. The silicon/germanium disorder in **1**, which is caused by symmetry could be resolved. The refinement of occupancy for the central silicon atoms and the germanium atom resulted in values of 2/3 and 1/3, respectively. The refinement in the space group $C2/c$ was not successful. Due to the disorder of the crown ether molecule caused by the mirror plane, two crown ether molecules with an occupancy of 1/2 each were refined. 1–2 and 1–3 distances of chemically equivalent bonds were refined by using distance restraints. Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK), by quoting the full journal citation.

- [20] A. G. Brook, F. Abdesaken, H. Söllradl, *J. Organomet. Chem.* **1986**, 299, 9.
 [21] J. Arnold, D. M. Roddick, T. D. Tilley, A. C. Rheingold, S. J. Geib, *Inorg. Chem.* **1988**, 27, 3510.
 [22] G. Becker, H.-M. Hartmann, A. Münch, H. Riffel, *Z. Anorg. Allg. Chem.* **1985**, 530, 29.
 [23] D. Reed, D. Stalke, D. S. Wright, *Angew. Chem.* **1991**, 103, 1539; *Angew. Chem. Int. Ed. Engl.* **1991**, 30, 1459.
 [24] D. R. Armstrong, M. G. Davidson, D. Moncrieff, D. Stalke, D. S. Wright, *J. Chem. Soc. Chem. Commun.* **1992**, 1413.
 [25] A. Heine, D. Stalke, *Angew. Chem.* **1993**, 105, 90; *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 121.
 [26] A. Steiner, D. Stalke, *J. Chem. Soc. Chem. Commun.*, in press.
 [27] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, 26, 615.
 [28] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, 46, 467.
 [29] G. M. Sheldrick, SHELXL-93, Universität Göttingen, **1993**.

[(*N*-Lithio-*N*-mesitylsulfonyloxy-*tert*-butylcarbamate)₂·(thf)₃]: Crystal Structure of a Nitrenoid**

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Nitrenoids **1** and their reactions have been known for a very long time. In 1872 Lossen described compounds of type **1a**,^[1, 2a, b] which like compounds **1b**^[2a, b, 3] prepared by Hofmann in 1881, are converted into isocyanates **2** by the shift of the R group to the N atom and α elimination of NaX .

The observation made by Schverdina and Kotscheschkov in 1938 was particularly remarkable and long not understood: in the amination of organolithium compounds $\text{R}'\text{Li}$ the *electrophilic* species is not *O*-methylhydroxylamine (**3a**) but rather the *N*-lithiated species **3b**. Primary amines **5** are then obtained via **4**.^[4] The dimerization of a nitrenoid,^[5] which proceeds analogously, and its α elimination to provide a nitrene^[6] were

also described. What are the structural requirements for these nitrenoid reactions?

One of the insights obtained from quantum chemical calculations of **3b** and its reaction with $\text{R}'\text{Li}$ ^[7] was that the $\text{N}-\text{O}$ bond in **3b** is bridged by Li and *longer* than the related bond in its nonlithiated counterpart **3a**. This would explain the relatively facile cleavage of the $\text{N}-\text{OCH}_3$ bond in **3b**^[8] and the $\text{N}-\text{X}$ bonds in other nitrenoids such as **1a,b**. In 1991 Genet, Mallart, Greck, and Piveteau showed that nitrenoids of type **6** are also suited for the electrophilic amination of $\text{R}'\text{Li}$ to give **7**.^[9] The corresponding Boc-protected primary amine is obtained from protonation of **7**.

We report here on the crystal structure of *N*-lithium *N*-mesitylsulfonyloxy-*tert*-butylcarbamate (**6b**), which crystallizes as a dimer with three equivalents of THF, and we compare this structure to that of the dimer of the nonlithiated *N*-toluenesulfonyloxy-*tert*-butylcarbamate (**8**). Compound **6b** is the first nitrenoid characterized by X-ray structure analysis.^[10]

The two anions in $[(\mathbf{6b})_2(\text{thf})_3]$ (Fig. 1) are linked by two Li cations, such that Li1 (Li1A) is bound to N1A (N1) and O4 (O4A). The strong donor O4A prevents the bridging of, for example, the $\text{N1}-\text{O3}$ bond by Li1A . The two Li centers are tetracoordinate; each interacts with two terminal (O6 , O6A) and one shared THF molecule (O7), an unusual type of THF coordination. It is amazing that the oxygen atoms O1 (O1A) and O2 (O2A) of the sulfonyloxy unit are not bound to lithium, considering their excellent donor properties.^[18] The shortening of the $\text{N1}-\text{C10}$ bond in $[(\mathbf{6b})_2(\text{thf})_3]$ to $133.1(4) \text{ pm}$ relative to the analogous bond in $(\mathbf{8})_2$ ($\text{N1}-\text{C8}$, $140.6(7) \text{ pm}$, Fig. 2) and the lengthening of the $\text{C10}-\text{O4}$ bond in $[(\mathbf{6b})_2(\text{thf})_3]$ ($123.9(4) \text{ vs. } 120.6(7) \text{ pm}$ for $\text{C8}-\text{O4}$ in $(\mathbf{8})_2$) are as expected. In $[(\mathbf{6b})_2(\text{thf})_3]$ C10 has planar coordination, in $(\mathbf{8})_2$ C8 (sum of angles 360.0 and 359.8° , respectively). O3 in $[(\mathbf{6b})_2(\text{thf})_3]$ is almost in the plane formed by N1 , C10 , O4 , and O5 (torsion

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