1,2-Dichalcogenins: Simple Syntheses of 1,2-Diselenins, 1,2-Dithiins, and 2-Selenathiin**

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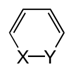
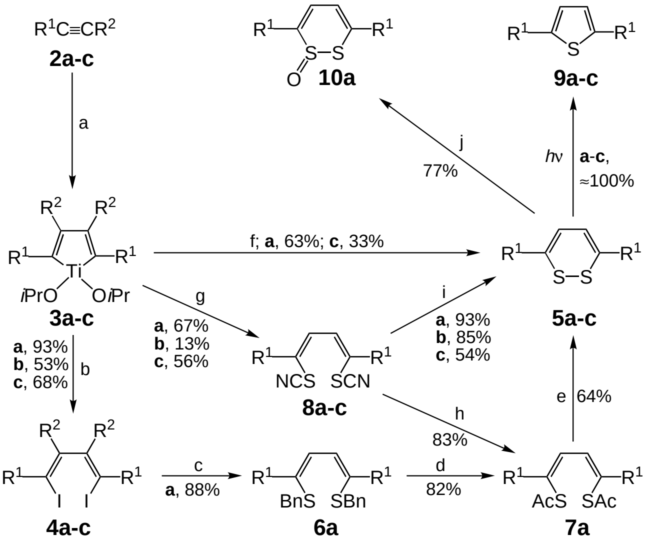
Dedicated to Professor Werner Schroth
on the occasion of his 70th birthday

Since the first reports in 1964–1967 of the synthesis of 1,2-dithiin (**1a**)[1] and isolation of 1,2-dithiin-containing thiarubrines from *Asteraceae* species,[2] synthetic and natural 1,2-dithiins have attracted considerable attention.[3] These wine-red 8π-electron heterocycles, which decompose with light or heat to thiophenes, show light-induced antibiotic or insecticidal activity with appropriate substituents.[4] The detailed study of these compounds is hampered by the lack of convenient synthetic approaches. We describe here a fundamentally new route to simple 1,2-dithiins and use this and other procedures to prepare the previously unknown 1,2-dichalcogenins (for example, **1**; X, Y = O, S, Se, Te) 1,2-diselenin (**1b**) and 2-selenathiin (**1c**), and related heterocycles.



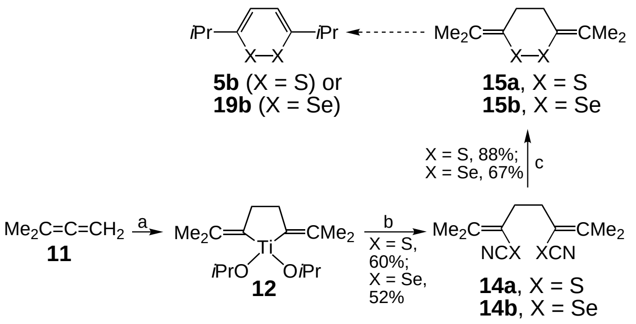
1a, X = Y = S
1b, X = Y = Se
1c, X = S, Y = Se

Titanacyclopentadienes **3** (Scheme 1), synthesized from alkynes **2** and [$(\eta^2$-propene)$\{Ti(OiPr)_2\}$], are of great utility in organic synthesis.[5] The availability of (*Z*,*Z*)-1,4-diiodo-1,3-butadienes **4** from **3**[5e] suggested a useful approach to the 1,2-dithiins **5** through lithiation followed by treatment with dibenzyl disulfide (BnSSBn) or other sulfur electrophiles. The terminal alkynes 3,3-dimethylbutyne, 3-methylbutyne, and trimethylsilylethyne (**2a–c**: R^2 = H; R^1 = *t*Bu, *i*Pr, and TMS, respectively) afford **3a–c**, which give the diiodo compounds **4a–c** on reaction with I_2. Sequential treatment of **4a** with *n*BuLi, BnSSBn, lithium dimethylaminonaphthalene (LDMAN), acetyl chloride, and KOH/MeOH affords 3,6-bis(*t*butyl)-1,2-dithiin (**5a**; 46%) via **6a** and **7a**. By using thiocyanogen ($(SCN)_2$) instead of I_2 and cyclizing with Bu_4NF or SmI_2,[6] one obtains **5a–c** from **3a–c** (62, 13, and 30%, respectively) via **8a–c**. On reaction with sulfur monochloride (S_2Cl_2) **3a** affords **5a** (63%) and thiophene **9a** (16%); similarly, **3c** gives **5c** (33%) and **9c** (33%). The dithiins **5a–c** give thiophenes **9a–c** on brief exposure to light. Oxidation of **5a** gives the *S*-oxide **10a** (77%).[7]

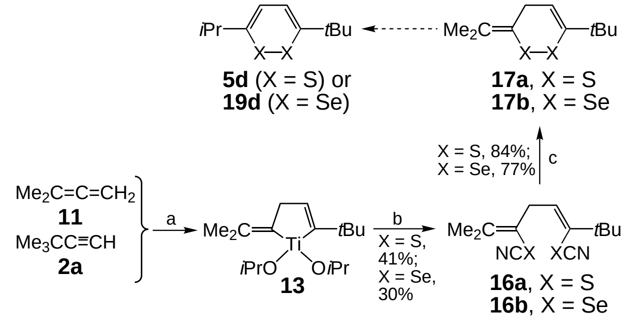


Scheme 1. Synthesis of the 1,2-dithiins **5a–c** from alkynes **2a–c** via titanacyclopentadienes **3a–c**; oxidation and photolysis of **5a–c**. **a**: R^1 = *t*Bu, R^2 = H; **b**: R^1 = *i*Pr, R^2 = H; **c**: R^1 = TMS, R^2 = H. Reagents: a) $Ti(OiPr)_4$, *i*PrMgCl; b) I_2; c) *n*BuLi, $(BnS)_2$; d) LDMAN, AcCl; e) KOH, MeOH, O_2 or I_2; f) S_2Cl_2; g) $(SCN)_2$, CH_2Cl_2; h) $LiAlH_4$, AcCl; i) TBAF or SmI_2, THF; j) *m*CPBA.

Ti-mediated cyclizations of 3-methyl-1,2-butadiene (**11**) or a mixture of **11** and **2a**, via **12** and **13**[5d] followed by trapping with $(SCN)_2$ (→**14a** and **16a**, respectively) and ring closure give **15a**[8] and **17a**, respectively, with exocyclic double bonds (Schemes 2 and 3, respectively). The reactions work equally well with **3a**, **12**, and **13** using selenocyanogen ($(SeCN)_2$)[9a] to afford 3,6-bis(*t*butyl)-1,2-diselenin (**19a**; 49%) from **2a** (**2a**→**3a**→**18**→**19a**, Scheme 4), or **15b** from **11**, and **17b** from **2a**/**11**. Visible light converts **19a** into selenophene **20**, which can also be prepared from **3a** and $Se(SeCN)_2$.[9b]



Scheme 2. Synthesis of **15a** and **15b** from **11**. Reagents: a) $Ti(OiPr)_4$, *i*PrMgCl; b) $(SCN)_2$ or $(SeCN)_2$ (X=S and Se, respectively), CH_2Cl_2; c) Bu_4NF or SmI_2.



Scheme 3. Synthesis of **17a** and **17b** from a mixture of **11** and **2a**. Reagents: a) $Ti(OiPr)_4$, *i*PrMgCl; b) $(SCN)_2$ or $(SeCN)_2$ (X = S and Se, respectively), CH_2Cl_2; c) Bu_4NF or SmI_2.

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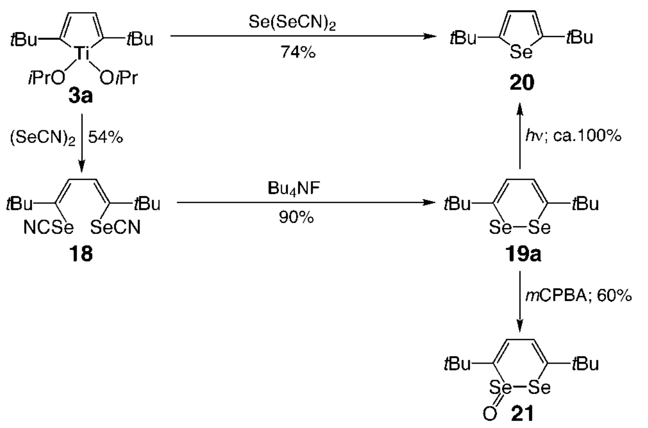
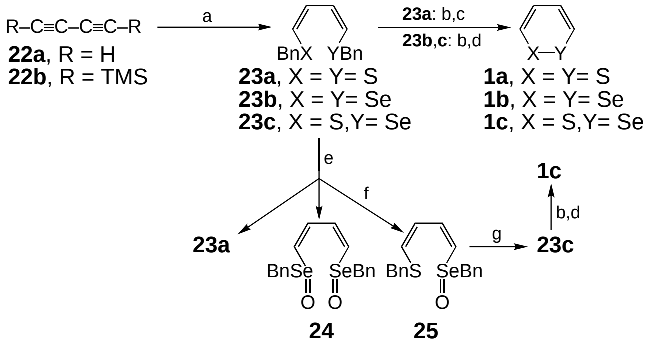


Scheme 4. Synthesis of **19a** from **3a**, as well as oxidation and photolysis of **19a**.

Oxidation of **19a** gives seleno seleninate **21** (60 %), which has NMR spectra similar to those of *S*-oxide **10**.[10]

1,2-Dithiin (**1a**), first prepared from 1,3-butadiyne (**22a**) via (*Z*,*Z*)-1,4-bis(benzylthio)-1,3-butadiene (**23a**, Scheme 5),[1b] is more easily synthesized from 1,4-bis(trimethylsilyl)-1,3-butadiyne (**22b**).[11] 1,2-Diselenin (**1b**) is readily prepared by reaction of **22b** with BnSeNa, debenzylation (Li/NH$_3$) of (*Z*,*Z*)-1,4-bis(benzylseleno)-1,3-butadiene (**23b**), removal of hydrocarbons from an aqueous solution of the dilithium salt by hexane extraction, and air oxidation in the presence of hexane/hexadecane. The volatile, but easily polymerized, **1b** is purified, after removal of hexane, by vacuum distillation from hexadecane (b.p. 250 °C) into a trap chilled with liquid N$_2$ (Figure 1). Solutions for NMR analysis are prepared by addition of CDCl$_3$ prior to vacuum transfer of **1b**. The preparation of **1c** is accomplished by treating **22b** with a mixture of BnSNa and BnSeNa and oxidizing the mixed product with excess H$_2$O$_2$. The *Se*-oxide **25** of (*Z*,*Z*)-1-benzylseleno-4-benzylthio-1,3-butadiene (**23c**) can then be separated from the bis(*Se*-oxide) **24** and unoxidized **23a**. Reduction of *Se*-oxide **25** with thiosulfate to **23c**, and treatment of **23c** with Na/NH$_3$ followed by work-up as above gives **1c**. Solutions of **1b** and **1c** in hexadecane can be used as sources of these compounds for gas-phase or matrix studies.[12]



Scheme 5. Synthesis of **1a–c** from **22a, b**. Reagents: a) BnXNa/BnYNa (X, Y = S or Se); b) Li or Na/NH$_3$; c) I$_2$; d) O$_2$, hexane/hexadecane; e) H$_2$O$_2$, THF; f) chromatography; g) Na$_2$S$_2$O$_3$, MeOH.

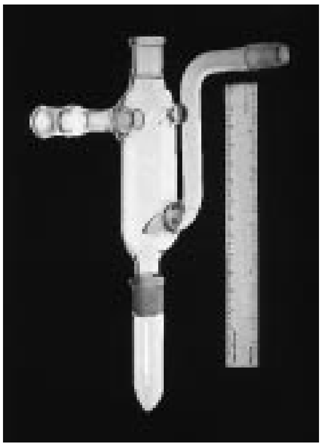
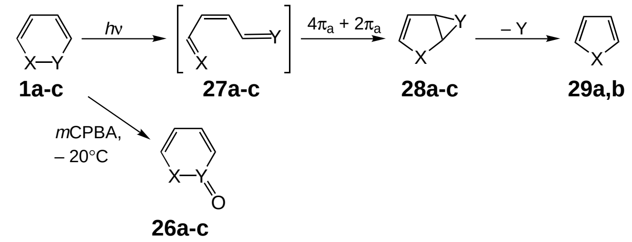


Figure 1. Small-scale apparatus for the distillation of **1a–c** from solution in hexadecane. Solutions of **1a–c** can be prepared by addition of the desired solvent to the hexadecane solution prior to distillation. The ruler is 15 cm long.

The structures of **1b** and **1c** follow from their spectroscopic data, which are surprisingly similar to those of **1a**, and by their facile oxidation to 1,2-diselenin 1-oxide (**26b**) and 2-selenathiin 2-oxide (**26c**, Scheme 6), respectively, the NMR shifts of which are quite similar to those of 1,2-dithiin 1-oxide (**26a**).[7a, 13] Light converts **1b** into selenophene **29b**, and **1c** to thiophene **29a**, presumably via intermediates **27** and **28**,[12] as seen in the photochemistry of **1a**.[3b]



Scheme 6. Photolysis and oxidation of **1a–c**. **a**: X = Y = S; **b**: X = Y = Se; **c**: X = S, Y = Se.

Comparison of the UV maxima of the parent 1,2-dithiin **1a** (457) and **5a–c** (406, 420, 478 nm, respectively) reveals an interesting hypsochromic shift for **5a,b** and a bathochromic shift for **5c** relative to **1a**. The UV maxima of **1b** (504 nm) and **1c** (488 nm) are bathochromically shifted relative to that of **1a**, as is that of **19a** (447 nm) relative to that of **5a**.[14] Bathochromic UV shifts are observed as the exocyclic positions of the two double bonds in **15a,b** are independently changed to endocyclic, for example, in the series **15a**, **17a** (both 320 nm) → **5a** and **15b** (390 nm) → **17b** (414 nm) → **19a**. There is little change in the positions of the chemical shifts of the olefinic CH ^{1}H and ^{13}C atoms in the NMR spectra of **17a,b** relative to those in **5a** and **19a**, which is consistent with the nonaromatic character of **19a**. The ^{77}Se NMR peaks in the spectra of **1b** ($\delta = 119$), **19a** ($\delta = 165$), and **1c** ($\delta = 228$) show they are strongly shielded relative to model compounds (PhSeSePh ($\delta = 464$), PhSeSPh ($\delta = 526$),[15] **15b** ($\delta = 326$), **17b** ($\delta = 287/415$), selenophene **29b** ($\delta = 565$)). Similarities in the spectroscopic data for 1,2-diselenins **1b** and

19a and 1,2-dithiins **1a** and **5a**, respectively, suggest that the structures are also quite similar, for example, *twist* conformations with ϕ(CXXC) ≈ 50° and ϕ(CCCC) ≈ 30°.[3c]

Experimental Section

Reactions were run under argon in anhydrous solvents, with $CDCl_3$ as the NMR solvent, and Na_2SO_4 or $MgSO_4$ as dessicants; **5a**, **8a**, **18**, and **23b, c** gave satisfactory CH analyses. Light-sensitive compounds **1b**, **c**, **5a**, and **19a** were handled under red light.

8a: Solutions of 3,3-dimethyl-1-butyne (15 mmol, 1.9 mL) and *i*PrMgCl (18 mmol, 9.0 mL, 2.0 M in Et_2O) were added to a stirred mixture of $Ti(OiPr)_4$ (9.0 mmol, 2.4 mL) in Et_2O (100 mL) at −78 °C. After 1 h at −78 °C and 2 h at −30 °C, $(SCN)_2$ (15 mmol; from Br_2 and $Pb(SCN)_2$ in CH_2Cl_2 at 0 °C) in CH_2Cl_2 (45 mL) was added dropwise at −78 °C. The mixture was warmed to 25 °C over 1.5 h, and stirred for 1 h before cooling to 0 °C. The mixture was quenched (saturated NH_4Cl), filtered, and extracted with Et_2O. The organic layer was washed (saturated $NaHSO_3$, $NaHCO_3$, NaCl), dried, and concentrated in vacuo. Purification by chromatography (hexane:Et_2O 80:20) gave **8a** as a light yellow solid (1.45 g, 67 %). M.p. 78–79 °C; ^{1}H NMR (300 MHz): $\delta = 1.30$ (s, 18 H), 7.13 (s, 2 H); ^{13}C NMR (75 MHz): $\delta = 28.9$, 40.4, 110.3, 131.2, 142.9; GC-MS (70 eV): *m/z*: 280 [M^+], 265, 222, 166, 149; FT-IR (KBr): $\tilde{\nu} = 2155\ cm^{-1}$ (SC≡N).

5a: Bu_4NF (0.55 mmol, 0.55 mL, 1.0 M in THF) was added slowly to **8a** (0.25 mmol, 70 mg) in THF (12 mL) at 0 °C. The mixture was stirred at 25 °C for 2 h, quenched (saturated NH_4Cl), diluted (Et_2O), washed (NH_4Cl and NaCl solutions), dried, and concentrated. Purification by chromatography (hexane) gave **5a** as a light-sensitive red solid (53 mg, 93 %). M.p. 76–77 °C; ^{1}H NMR (300 MHz): $\delta = 1.20$ (s, 18 H), 6.16 (s, 2 H); ^{13}C NMR (75 MHz): $\delta = 28.7$, 37.7, 122.0, 146.5; GC-MS (70 eV): *m/z*: 228 [M^+], 213, 196, 181, 172, 57; UV (CH_2Cl_2): $\lambda_{max} = 406$ nm ($\varepsilon = 195$).

18: $(SeCN)_2$ (12 mmol; from AgSeCN and I_2 in 25 mL THF at 0 °C)[9a] was added to the titanacyclopentadiene prepared as for **8a** from 3,3-dimethyl-1-butyne (12 mmol). Work-up afforded **18** (1.2 g, 54 %). M.p. 134–135 °C; ^{1}H NMR (300 MHz): $\delta = 1.30$ (s, 18 H), 7.05 (s, 2 H); ^{13}C NMR (75 MHz): $\delta = 29.3$, 40.8, 100.8, 133.2, 145.4; GC-MS (70 eV): *m/z*: 374 [M^+]; FT-IR (KBr): $\tilde{\nu} = 2148\ cm^{-1}$ (SeC≡N).

19a: As with **5a**, Bu_4NF (1.1 mmol) was added to **18** (0.5 mmol). Work-up gave **2** as a red solid (146 mg, 90 %). M.p. 84–85 °C; ^{1}H NMR (300 MHz): $\delta = 1.23$ (s, 18 H), 6.20 (s, 2 H); ^{13}C NMR (75 MHz): $\delta = 29.2$, 38.6, 124.7, 144.18; ^{77}Se NMR (57 MHz): $\delta = 165$; LC-MS (70 eV): *m/z*: 324 [M^+], 245, 172, 115, 73; UV (CH_2Cl_2): $\lambda_{max} = 447$ nm ($\varepsilon = 235$).

23b: A suspension of BnSeSeBn (2.0 g, 5.9 mmol) in MeOH (25 mL) at 0 °C was treated with $NaBH_4$ (1.1 g, 29.5 mmol) in small portions. Compound **22b** (0.57 g, 2.95 mmol) was then added. The mixture was refluxed for 4 h, cooled to 0 ^{C}, and filtered. Recrystallization of the precipitate (MeOH:CH_2Cl_2 5:2) afforded **23b** (0.9 g, 86 %) as off-white plates. M.p. 124–125 °C; ^{1}H NMR (300 MHz): $\delta = 3.92$ (s, 4 H), 6.44 (dd, $^3J_{cis} = 7$, $^5J = 1.9$ Hz, 2 H), 6.52 (dd, $^3J_{cis} = 7$, $^5J = 1.9$ Hz, 2 H), 7.2 (m, 10 H); ^{13}C NMR (75 MHz): $\delta = 29.2$, 123.1, 126.0, 127.6, 127.7, 127.9, 137.5; ^{77}Se NMR (57 MHz): $\delta = 315$; MS (70 eV): *m/z*: 394 [M^+].

1b: Compound **23b** (0.98 g, 2.8 mmol) was added to liquid NH_3 (70 mL) in a 100-mL 3-necked flask at −78 °C followed by the addition of lithium (0.2 g, 28 mmol) in small pieces. The blue solution was stirred for 1.5 h at −60 °C, quenched (MeOH), and evaporated. The residue was dissolved under argon in degassed aqueous 10 % KOH solution (150 mL), which was extracted with degassed hexane (3 × 20 mL) to remove toluene. The aqueous solution was then covered with hexane (70 mL) and oxygen carefully bubbled through the solution until the hexane phase turned red. The extraction process was repeated twice with fresh hexane (2 × 70 mL). After drying the hexane extract, hexadecane (15 mL) was added, and the hexane was evaporated (water pump vacuum, 15 °C). $CDCl_3$ (2 mL) was added and the volatiles were transferred at 0.02 Torr to a liquid nitrogen cooled "flash distillation" trap (Figure 1). Yield 68 % (deep red solution; by NMR with 1,4-dioxane standard); ^{1}H NMR (300 MHz): $\delta = 6.10$ (m, 2 H, H3,6), 6.27 (m, AA′BB′ multiplets with $^3J_{3,4/5,6} = 9.1$, $^4J_{3,5/6,4} = 0$, $^3J_{4,5} = 5.1$, $^5J_{3,6} = 1.9$ Hz, 2 H, H4,5); ^{13}C NMR (75 MHz): $\delta = 112.8$ (C3,6), 132.2 (C4,5); ^{77}Se NMR (57 MHz, Me_2Se): $\delta = 119$; UV (hexane): $\lambda_{max} = 504$ ($\varepsilon = 107$) nm; GC-MS (70 eV): *m/z*: 212 [M^+].

23c: As for **23b**, BnSeNa (from 8.55 g, 25 mmol BnSeSeBn) and BnSNa (from 6.2 g, 50 mmol α-toluenethiol and 150 mmol NaOMe in 120 mL MeOH) were refluxed with **22b** (7.0 g, 36 mmol) for 24 h. A precipitate containing **23a–c** in a 1:1:2 ratio (10.8 g) formed at 0 °C. Oxidation of a portion of this solid (1.22 g) in THF (11 mL) with 30 % H_2O_2 (0.6 mL) at 25 °C for 2 h precipitated **24** (0.33 g). The structure was determined from its ^{77}Se NMR ($\delta = 878$) and FT-IR spectra (film; $\tilde{\nu} = 785\ cm^{-1}$; Se=O). Chromatography of the filtrate (silica gel; CH_2Cl_2:MeOH 19:1) gave solid **25** (400 mg, yield 61 %) which was characterized from its ^{77}Se NMR ($\delta = 867$) and FT-IR spectra, $\tilde{\nu} = 802\ cm^{-1}$). Reduction of **25** (1.1 mmol) with sodium thiosulfate (0.7 mL, 1 M) in MeOH (10 mL) for 16 h gave **23c** (292 mg, yield 77 %) as off-white needles. M.p. 120–121 C; ^{1}H NMR (300 MHz): $\delta = 3.89$ (s, 2 H, SC*H*$_2$Ph), 3.92 (s, 2 H, SeC*H*$_2$Ph), 6.05 (d, 1 H, $^3J = 9.6$ Hz, SC*H*=CH), 6.17 (dd, $^3J = 10.3$, 9.6 Hz, 1 H, SCH=C*H*), 6.40 (d, $^3J = 9.4$ Hz, 1 H,SeC*H*=CH), 6.64 (dd, $^3J = 10.3$, 9.4 Hz, 1 H, SeCH=C*H*), 7.2–7.3 (m, 10 H); ^{13}C NMR (75 MHz): $\delta = 30.1$ (SCH$_2$Ph), 38.1 (SeCH$_2$Ph), 124.6 (SCH=*C*H), 126.8 (SeCH=*C*H), 127.7 (S*C*H=CH), 128.3 (Se*C*H=CH), 128.6, 128.8, 128.8, 130.2 (Ph); ^{77}Se NMR (57 MHz): $\delta = 312$; MS (70 eV): *m/z*: 346 [M^+].

1c: As for **1b**, but using sodium instead of lithium. Yield 56 % (orange solution; by NMR with 1,4-dioxane standard). ^{1}H NMR (300 MHz): $\delta = 6.00$ (dd, $^3J_{cis} = 7.9$ Hz, $^5J = 1.7$ Hz, 1 H), 6.26–6.29 (m, 3 H); ^{13}C NMR (75 MHz): $\delta = 114.0$ (Se*C*H=CH), 119.3 (S*C*H=CH), 129.7 (SCH=*C*H), 132.0 (SeCH=*C*H); ^{77}Se NMR (57 MHz, Me_2Se): $\delta = 228$; UV (hexane): $\lambda_{max} = 488$ nm; GC-MS (70 eV): *m/z*: 164 [M^+].

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[13] ^{1}H NMR (300 MHz) shifts. **26a**: $\delta = 6.98$ (dd, $^3J = 9.5$, 4.7 Hz, 1H, S(O)CH=C*H*), 7.03–7.08 (m, 2H, SC*H*=C*H*), 7.18 (dd, $^3J = 9.5$, $^5J = 1.1$ Hz, 1H, S(O)C*H*=CH); **26b**: $\delta = 6.87$ (dd, $^3J = 10.2$, $^5J = 0.9$ Hz, 1H, SeC*H*=CH), 6.95 (dd, $^3J = 10.2$, 7.2 Hz, 1H, SeCH=C*H*), 7.11 (dd, $^3J = 10.2$, 7.24 Hz, 1H, Se(O)CH=C*H*), 7.24 (dd, $^3J = 10.2$, $^5J = 0.9$ Hz, 1H, Se(O)C*H*=CH); **26c**: $\delta = 6.81$ (d, $^3J = 8.4$ Hz, 1H, SC*H*=CH), 7.01 (dd, $^3J = 8.4$, 9.6 Hz, 1H, SCH=C*H*), 7.22 (d, $^3J = 9$ Hz, 1H, Se(O)C*H*=CH), 7.36 (dd, $^3J = 9$, 9.6 Hz, 1H, Se(O)CH=C*H*).

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Lanthanide Nitrido Borates with Six-Membered B_3N_6 Rings: $Ln_3B_3N_6$[**]

Olaf Reckeweg and H.-Jürgen Meyer*

Nitrido borates of the lanthanides contain BN_x units in which boron tends to adopt coordination number three as in the structure of hexagonal boron nitride (α-BN). The coordination number four is only found for boron in the cubic form of boron nitride (β-BN). The coordination number two is reported for a large number of compounds, for example, of the type $A_3(BN_2)_2$ with A = Ca, Sr, or Ba.[1] Under pressure these compounds, together with hexagonal boron nitride, form an eutectic mixture, thus catalyzing the conversion of α-BN into its cubic modification (β-BN).[2] The BN_2^{3-} ions (16 electrons) of the $A_3(BN_2)_2$ structure type are isoelectronic and isostructural to CO_2. The same can be said of BN_3^{6-} (24 electrons)[3] and CO_3^{2-} or $B_2N_4^{8-}$ (34 electrons) and $C_2O_4^{2-}$.

Some nitrido borates of the lanthanides exhibit short metal–metal distances and interesting electric or magnetic properties. For Ln^{3+}, the compounds $Ln_3B_2N_4$ (Ln = La, Ce, Pr, Nd)[4] have one electron per formula unit in the conduction band.[5] These compounds as well as $Ce_3B_3N_6$ have been obtained as black, crystalline substances. Crystals of $La_3B_3N_6$ are colorless and transparent.

The crystal structures of the isostructural title compounds $Ln_3B_3N_6$ (Ln = La or Ce) contain the six-membered B_3N_6 ring with three exocyclic nitrogen atoms. This ring can be regarded as a fragment from a layer of hexagonal boron nitride. The triclinic crystal structures of $Ln_3B_3N_6$ are built up of lanthanide atoms and B_3N_6 rings in a rather complicated way (Figure 1).[6] The B_3N_6 units are centered in layers near $x = 0$ and 1. Two of the three crystallographically different Ln atoms in the structure build puckered layers (near $x = 0.5$) which are alternately capped from above and below by the third Ln atom. This results in a distorted square-pyramidal arrangement of metal atoms. Each of these motifs is occupied by one exocyclic N atom ($5 \times d$(La–N) = 255–265 pm, $5 \times d$(Ce–N) = 252–263 pm) of the B_3N_6 ring. This kind of square-pyramidal arrangement of metal atoms is typical for the coordination environment of terminal N atoms in various nitrido borate ions.[5, 7] The shortest Ln–Ln distances of 355 pm in $La_3B_3N_6$ and of 350 pm in $Ce_3B_3N_6$ are shorter than those in the corresponding metal (the shortest distances here are 375 pm for La and 365 pm for Ce). Short metal–metal distances have also been observed in related compounds $LnBN_2$ of the smaller lanthanides (Ln = Pr, Nd, Sm, Gd), whose structures are based on a different packing order.[7] In these structures the nitrido borate units are piled to form ${}^{1}_{\infty}[B_3N_6]$ columns with the stacking sequence like that of α-BN.

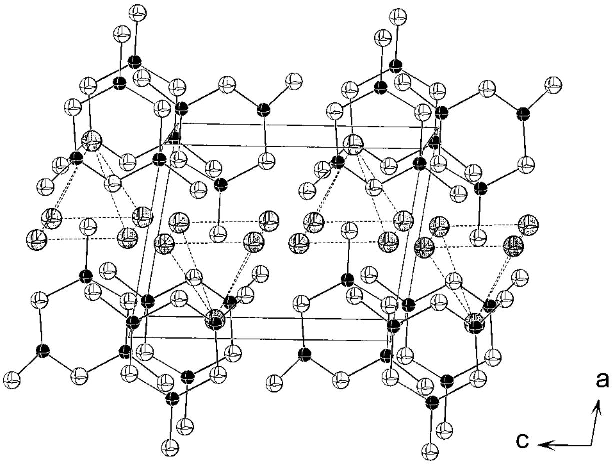

Figure 1. Section of the crystal structure of $Ln_3B_3N_6$ (Ln = La, Ce) with six-membered B_3N_6 rings.

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