Sulfur and Selenium Activation by Frustrated NHC/$B(C_6F_5)_3$ Lewis Pairs; Conformational Flexibility of Products

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Frustrated Lewis pairs consisting of N-heterocyclic carbenes (NHC) and the borane $B(C_6F_5)_3$ react with elemental sulfur or selenium to give products of the type NHC-*E*-$B(C_6F_5)_3$, where *E* is S or Se. Three such products, two with sulfur and one with selenium, were characterized by X-ray diffraction and shown to exhibit considerable conformational flexibility, as revealed by differing torsion angles in the atom sequence N–C–*E*–B–C_{ipso}–C_{ortho}. In the sulfur derivatives, the S–B bonds are all long (*ca*. 2.05 Å), and the C–S bonds (*ca.* 1.73 Å) are clearly lengthened compared to imidazole-2-thiones. The Se–B distance of 2.2111 Å is the first selenone-borane bond length to be determined by X-ray analysis.

Key words: N-Heterocyclic Carbenes, Frustrated Lewis Pairs, Sulfur, Selenium

Introduction

Since 2006 a novel type of metal-free reactivity between Lewis acids and Lewis bases in the presence of dihydrogen, based on the so called *frustrated Lewis-pairs* (FLP), has been observed by Stephan and others [1 – 5]. The classical Lewis theory [6 – 8] postulates that the Lewis acid and the Lewis base form stable donor-acceptor adducts, in which the unshared pair of electrons of the base forms a covalent bond through the vacant orbital of the acid. In FLP systems, however, no such normal adduct formation is possible for steric reasons [3 – 5], but there is a great latent tendency to react when suitable substrates are available.

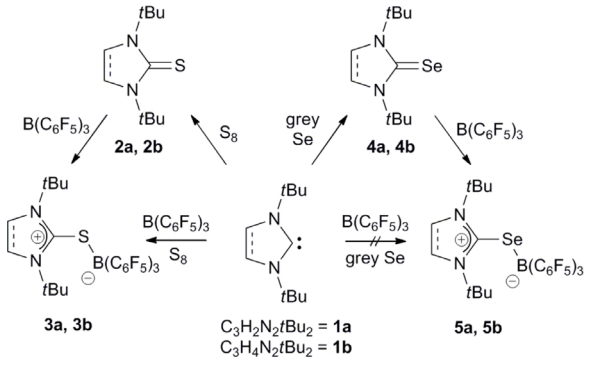
The system N-heterocyclic carbene (NHC)/$B(C_6F_5)_3$ represents the most reactive FLP combination [9]. We were able to show that 1,3-di-*tert*-butylimidazolin-2-ylidene **1a** and 1,3-di-*tert*-butylimidazolidin-2-ylidene **1b** together with $B(C_6F_5)_3$ are FLP systems for dihydrogen activation (with H^+ adding to the carbene and H^- to the borane) and for THF ring opening [10, 11]. Furthermore, sterically encumbered Lewis acids and Lewis bases react with enthalpically strong bonds such as S–S and P–P and thus with other small molecules such as organic disulfides [12, 13], polyphosphides [14] or P_4 [15]. Herein we demonstrate carbene/$B(C_6H_6)_3$ FLP reactivity towards sulfur and selenium.

The reaction behavior of free NHCs with sulfur or selenium has been studied [16 – 19]. Mixing the starting materials grey selenium or S_8 with the carbenes at r. t. in THF or toluene resulted in the formation of imidazole-2-thiones **3** [16, 17] or imidazole-2-selenones **5** [20, 21] within a few hours. After filtration and precipitation of the product from the filtrate with hexane the thiones or selenones could be obtained in almost quantitative yield. The selenium compounds are more strongly polarized than the corresponding sulfur compounds, because selenium forms only weak Se–C π bonds [22].

The system $(t\mathrm{Bu})_2PC_6F_4B(C_6F_5)_2$ is unable to form an FLP adduct with S_8; only an oxidation of the phosphane unit without further coordination of the borane to sulfur was achieved [12]. However, S–S bond cleavage in organo-disulfides with $(t\mathrm{Bu})_3P/B(C_6F_5)_3$ or carbogenic FLP combinations is known, because of the weaker non-polar covalent S–S bond in disulfides [12, 13].

Discussion

We have investigated the reactivity of the FLP combinations **1**/$B(C_6F_5)_3$ towards sulfur (S_8) and grey selenium. In the hope of splitting one S–S bond of the S_8 molecule heterolytically, the combinations **1**/$B(C_6F_5)_3$ were mixed in a toluene solution of S_8 at 0 °C. After



Scheme 1. Reactions of **1**/$B(C_6F_5)_3$ with sulfur and selenium.

about 1 h the colour of the mixture changed from yellowish to golden yellow at ambient temperature. Adding pentane and cooling to −35 °C led to precipitation of yellow products **3a,b**. **3a** was obtained after filtration in 91 % yield, whereas **3b** was isolated after crystallisation in only 41 % yield (Scheme 1). The products are pale yellow, very unpleasantly smelling solids, which decompose at room temperature and in chlorinated solvents.

The ^{11}B NMR spectrum revealed a broad singlet resonance at 10.3 ppm for **3a**, which is about 53 ppm to high field of free $B(C_6F_5)_3$. However, the signal of the saturated complex **3b** at 37.2 ppm is only moderately high-field shifted, indicating a weaker coordination of the $B(C_6F_5)_3$ moiety at sulfur. The resonances in the ^{11}B NMR spectra show in comparison to related thioborates (≈ –10 ppm) [12, 23] a distinct downfield shift consistent with the known ability of soft donors to form only weak adducts with Lewis acids [24]. The resonances of the former carbene carbon atom in the ^{13}C NMR spectra appear for **3a** at 152.0 ppm and for **3b** at 180.9 ppm, and thus are minimally shifted in contrast to the thiones (**2a**: 160.6 ppm; **2b**: 183.6 ppm; [25]). The ^{19}F NMR spectra of **3a**, **b** exhibit three broad resonances for the *ortho*-, *para*- and *meta*-positions of the C_6F_5 group. The ^1H NMR spectra show resonances of the *tert*-butyl groups and of the imidazol skeleton (see Experimental Section).

Recrystallisation from toluene/pentane solution afforded single crystals suitable for X-ray diffraction analysis. The molecular structures reveal the formation of the adducts **3a**, **b**, which contain just one sulfur atom between the former carbene and the $B(C_6F_5)_3$ unit (Figs. 1a and 2). The unsaturated compound **3a** crystallised with two molecules in the asymmetric unit, while the saturated compound **3b** crystallised with one

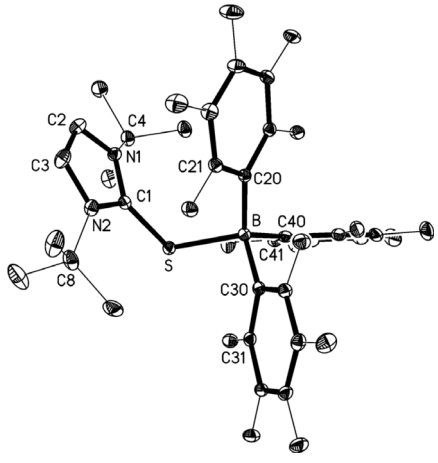


Fig. 1a. Displacement ellipsoid plot (30 %) of the first independent molecule of compound **3a**. Hydrogen atoms have been omitted for clarity.

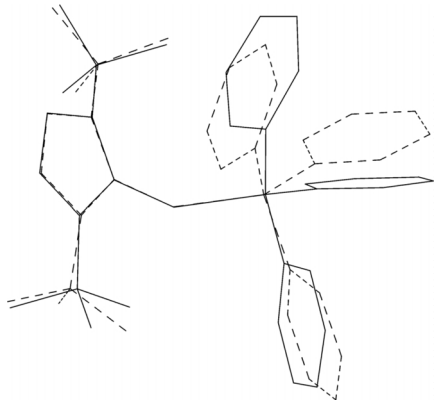


Fig. 1b. Least-squares fit of both independent molecules of compound **3a**. Full bonds: molecule 2; dashed bonds: molecule 1 (inverted). Fitted atoms: NHC ring, B, S.

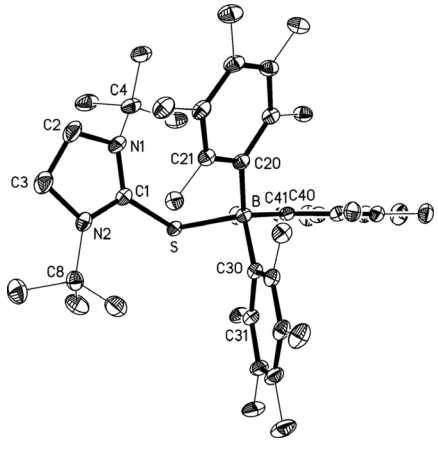


Fig. 2. Displacement ellipsoid plot (30 %) of compound **3b**. Hydrogen atoms have been omitted for clarity.

Table 1. Crystallographic data for compounds **3a**, **3b**, and **5b**.

	3a	**3b**·C_5H_{12}	**5b**·C_5H_{12}·$^1/_2C_7H_8$
Formula	$C_{29}H_{20}BF_{15}N_2S$	$C_{34}H_{34}BF_{15}N_2S$	$C_{35.5}H_{33}BF_{15}N_2Se$
M_r	724.34	798.50	862.41
Crystal size, mm^3	$0.15 \times 0.14 \times 0.11$	$0.17 \times 0.12 \times 0.07$	$0.14 \times 0.11 \times 0.09$
T, K	100(2)	100(2)	100(2)
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Cell constants			
a, Å	10.3616(6)	11.9017(8)	11.5674(4)
b, Å	13.8457(4)	12.3662(8)	12.4107(4)
c, Å	20.2999(11)	13.0292(8)	25.5403(10)
α, deg	90.557(3)	99.796(6)	90
β, deg	91.302(4)	105.035(6)	90.750(8)
γ, deg	90.907(3)	102.704(6)	90
V, $Å^3$	2911.0	1753.3	3666.2
Z	4	2	4
$F(000)$, e	1456	816	1736
μ, (CuK_α), mm^{-1}	2.1	1.8	2.4
λ, Å	1.54184	1.54184	1.54184
$2\theta_{max}$, deg	152	152	152
Transmissions	0.688, 1.000	0.884, 1.000	0.880, 1.000
Reflections meas. / indep. / R_{int}	31666 / 11660 / 0.021	25399 / 7252 / 0.032	52696 / 7624 / 0.029
Ref. parameters / restraints	893 / 24	530 / 92	439 / 0
wR (F^2, all refl.)	0.085	0.117	0.069
$R1$ [$F \geq 4\,\sigma(F)$]	0.032	0.039	0.026
S	1.02	1.09	1.06
$\Delta\rho_{max/min}$, e $Å^{-3}$	0.36 / −0.33	0.39 / −0.27	0.31 / −0.37

molecule of pentane. The tetrahedral thioborate unit shows S–B bond lengths of 2.0568 (15) and 2.0490 (15) Å for **3a** and 2.0572 (17) Å for **3b**, which are longer than those determined for $[RSB(C_6F_5)_3]^-$ anions (1.953 (13) Å and 1.991 (3) Å; [3]) reflecting the weak coordination of the borane at the sulfur atom. Even longer B–S bonds have been recorded for (tetrahydrothiophene)$B(C_6F_5)_3$ (2.0843 (16) Å; [26]) and $Me_2SB(C_6F_5)_3$ (2.091 (5) Å; [27]). The C–S distances of 1.7320 (13), 1.7335 (14) Å for **3a** and 1.7327 (15) Å for **3b** are clearly lengthened compared to related imidazole-2-thiones (1.686 (3) Å; 1.674 (4) Å), because of the loss of the partial double bond character [25]; a search of the Cambridge Database [28] revealed *ca*. 150 hits for the system C–S with three-coordinate C and one-coordinate S, with bond lengths in the range 1.60 – 1.74 Å (excluding obvious outliers such as betaines and disordered structures), av. 1.66 (3) Å. Indeed, the C–S bond lengths of **3a**, **b** correspond well with those of the zwitterionic species (NHC)-S-(4,6-dioxo-1,3-dioxanide) 1.763 (2) Å [29]. Accordingly, the angles at sulfur were found to be 108.69 (6)° and 110.88 (6)° for **3a** and 111.07 (7)° for **3b**.

It is noteworthy that no single S–S bond cleavage of the S_8 molecule to form opened S_8 bridge adducts could be observed, despite deliberate variation of the molar ratio of sulfur to the FLP combinations **1a**, **b**/$B(C_6F_5)_3$ at various temperatures; only compounds with one sulfur atom between the NHC and $B(C_6F_5)_3$ moiety could be obtained.

Because of the chemical similarity of sulfur and selenium, an obvious extension of this investigation was to the possible reactivity of the FLP combinations **1a**, **b**/$B(C_6F_5)_3$ towards grey selenium. After about 1 h the reaction mixture changed from yellowish to orange and an oily product was obtained. No adduct formation between the FLP and the selenium was observed; instead rearrangement to an abnormal carbene or selfdehydrogenation of **1a**, **b**/$B(C_6F_5)_3$ was detected [10, 11]. The failure of Se adduct formation could be a result of the high insolubility of grey selenium in toluene, which leads to fast deactivation rather than selenium activation.

However the formation of imidazole-2-selenones from free carbenes is known [20, 21], and the selenones **4a**, **b** can be prepared by the reaction of the carbenes **1a**, **b** with grey selenium. Interestingly, the ^{77}Se resonances of **4a** (188.8 ppm) and **4b** (309.0 ppm) are markedly different, and this trend is in agreement with the presence of a more strongly polarised C–Se bond in the 2-selenoimidazoline **4a** in comparison with the 2-selenoimidazolidine **4b** [30].

Compound[a]	**3a**[b]	**3b**	**5b**
E–C1	1.7320(13), 1.7335(14)	1.7327(15)	1.9187(14)
E–B	2.0568(15), 2.0490(15)	2.0572(17)	2.2111(15)
C1–*E*–B	108.69(6), 110.88(6)	111.07(7)	107.086)
B–*E*–C1–N1	−89.31(12), 86.83(12)	68.03(15)	−88.79(12)
C1–*E*–B–C20	12.79(11), −32.67(11)	−19.99(12)	44.71(10)
C1–*E*–B–C30	−111.77(9), 93.12(10)	102.92(10)	−81.79(10)
C1–*E*–B–C40	135.64(9), −154.59(9)	−145.78(10)	166.97(9)
E–B–C20–C21	−67.49(14), 66.87(14)	63.49(15)	−72.97(14)
E–B–C30–C31	−49.84(13), 51.60(14)	51.80(15)	−52.41(15)
E–B–C40–C41	−7.74(18), 8.43(8)	7.03(19)	13.64(18)
largest	C8–N2–C1–S	C4–N1–C1–S	C4–N1–C1–Se
C_{butyl}–N–C1–*E*	19.9(2), 22.0(2)	(34.22)	−28.63(18)

Table 2. Selected molecular dimensions (Å, deg) for compounds **3a**, **3b**, and **5b**[a].

[a] *E* = S or Se; [b] two independent molecules.

The complexes **5a**, **b** could be obtained by adding $B(C_6F_5)_3$ to a solution of the selenones **4a**, **b** in toluene. After 30 min stirring at r. t., the addition of pentane led to the precipitation of white solids at −35 °C, which were identified as the compounds **5a**, **b**. The solids are highly reactive and decompose over a few hours at r. t. under argon to a reddish oil. The compounds **5a**, **b** were characterised by elemental analysis, NMR and in the case of **5b** by X-ray diffraction analysis.

The ^{11}B NMR spectra revealed a broad singlet resonance for **5a** at 9.6 ppm and for the saturated imidazole complex **5b** at 24.2 ppm, similar to the complexes **3a**,**b** and indicating a weak coordination of $B(C_6F_5)_3$ at selenium (see Experimental Section). The ^{13}C NMR resonance of the former carbene carbon atom could only be detected for the molecule **5b** at 174.9 ppm, which is high-field shifted in comparison to the selenone **4b** at 180.4 ppm. The remaining spectroscopic data of the ^{1}H NMR and ^{19}F NMR spectra are in good agreement with a cationic imidazole and an anionic borate moiety (Table 1).

The expected structure of the selenium compound **5b** was also confirmed by X-ray diffraction analysis, as shown in Fig. 3. The selenium adduct of the saturated carbene crystallised with one disordered molecule of pentane and half a disordered molecule of toluene per asymmetric unit. The structural data for the tetrahedral selenoborate unit shows a C–Se distance of 1.9187 (14) Å, which is slightly longer than 1.869 (6) Å in dimethylimidazolidin-2-selenone [31], but in the range of cationic dimethylimidazolidin-2-selenonehalogen species 1.894 – 1.910 Å [32]. The Se–B distance of 2.2111 (15) Å represents the first selenone-borane bond length to be determined by X-ray diffraction analysis. The C–Se–B bond angle of 107.08 (6)° is close to a tetrahedral angle, but in comparison to the corresponding sulfur compound **3b** it

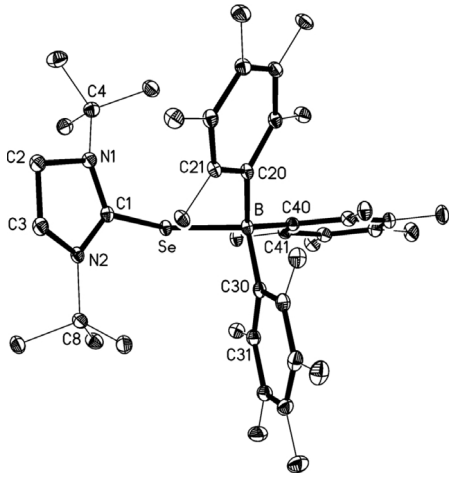


Fig. 3. Displacement ellipsoid plot (30 %) of compound **5b**. Hydrogen atoms have been omitted for clarity.

is about 4° smaller. A possible reason for the smaller angle is afforded by the VSEPR model, which states that the bond angles in compounds containing divalent chalcogen atoms decrease from sulfur to tellurium [29]. Analogous to the reaction pathway to **5a**, **b**, the sulfur adducts **3a**, **b** can be also formed through complexation of $B(C_6F_5)_3$ at the corresponding thiones **2a**, **b** (Scheme 1).

All three structures are characterised by a potentially high degree of conformational flexibility *via* the torsion angles N–C–*E*–B, C–*E*–B–C_{ipso} and *E*–B–C_{ipso}–C_{ortho} (*E* = S or Se). Selected values are given in Table 2. For **3a** and **5b**, the N–C–*E*–B angles are close to ±90°, whereas for **3b**, N1–C1–S–B is 68°. The three torsion angles C–*E*–B–C_{ipso} per structure differ, as expected, by steps of *ca.* 120°; a low absolute value means that the ring is bent back towards the NHC, often causing steric pressure against the butyl groups. These display some *E*–C–N–C_{butyl} torsion angles that differ markedly from 0°, with the central butyl

carbon being pushed back significantly out of the NHC plane (*e. g.* S–C1–N1–C4 34° for **3b**). The ring with the largest absolute value of C–*E*–B–C_{ipso} generally has the smallest value of *E*–B–C_{ipso}–C_{ortho}, *e. g.* C40 in **3b**. The variation in molecular conformation can be recognised in Figs. 1a, 2, 3, in which the $B(C_6F_5)_3$ group has been drawn with approximately the same orientation (the ring at C40 is presented horizontally and perpendicular to the plane of the paper, whereas the other two rings point out of the paper) [33]. Fig. 1b, in contrast, shows a least-squares fit of the NHC ring plus the Se and B atoms for the two independent molecules of compound **3a**; the difference in orientation of the borane moiety is obvious.

In conclusion, we have shown that carbene/$B(C_6F_5)_3$ FLP combinations are effective in the activation of sulfur and in the fixation of selenium. The weak interactions between the chalkogen atoms and FLP combinations in these systems might find application in S/Se transfer reactions.

Experimental Section

All operations with air and moisture-sensitive compounds were performed in a glovebox under a dry argon atmosphere (MBraun 200B) or on a high-vacuum line using Schlenk techniques. All solvents were purified by a solvent purification system from MBraun and stored over molecular sieve (4 Å) prior to use. The ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded on Bruker DPX 200 (200 MHz), Bruker DRX 400 (400 MHz), and Bruker DPX 600 (600 MHz) instruments. The chemical shifts are expressed in parts per million (ppm) using tetramethylsilane (TMS) as internal standard (^1H, ^{13}C) or $CFCl_3$ (^{19}F), $BF_3{\cdot}OEt_2$ (^{11}B) and Me_2Se (^{77}Se) as external standards, respectively. Coupling constants (J) are reported in Hertz (Hz), and splitting patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), sept (septet) and br (broad). Elemental analysis (C, H, N) was performed by combustion. Unless otherwise indicated, all starting materials were obtained from Aldrich and were used without further purification. 1,3-Di-*tert*-butylimidazolin-2-ylidene (**1a**) [34, 35], 1,3-di-*tert*-butylimidazolidin-2-ylidene (**1b**) [36, 37], the imidazole-2-thiones **2a** and **2b** [17, 16], the imidazole-2-selenones **4a** and **4b** [20, 21], and $B(C_6F_5)_3$ [38], were prepared according to the literature procedures.

*Synthesis of the sulfur complexes **3a** and **3b***

To 20 mL of toluene were added at 0 °C S_8 (0.14 mmol; 37 mg), $B(C_6F_5)_3$(0.98 mmol; 500 mg) and the appropriate NHC (0.98 mmol). The mixture was stirred for 2 h at r. t., the solution concentrated to 10 mL and pentane added. At −35 °C yellowish precipitates of the sulfur complexes were formed. These were isolated by filtration, immediately washed three times with 5 mL of pentane and dried *in vacuo*. The products **3** were collected as yellowish solids.

3a: Yield 645 mg (91 %). Crystals of **3a** were obtained from a mixture of toluene and pentane at −35 °C. Note: slow decomposition takes place at r. t. – ^1H NMR (400 MHz, C_6D_6): δ = 1.15 (s, 18H, CH_3), 6.11 (s, 2H, C*H*). – ^{11}B NMR (96 MHz, C_6D_6): δ = 10.3 (br. s). – ^{13}C NMR (150 MHz, C_6D_6): δ = 28.9 (CH_3), 62.8 ($C(CH_3)_3$), 117.2 ($N_2(CH)_2$), 137.2 (dm, $^1J_{CF}$ = 249 Hz, *m*-C_6F_5), 148.4 (dm, $^1J_{CF}$ = 244 Hz, *o*-C_6F_5), 152.0 (*C*SB). – ^{19}F NMR (376 MHz, C_6D_6): δ = −129.3 (br s, *o*-C_6F_5), −154.7 (br s, *p*-C_6F_5), −163.9 (br s, 6F, *m*-C_6F_5). – $C_{29}H_{20}BF_{15}N_2S$: calcd. N 3.87, C 48.09, H 2.78; found N 3.75, C 48.97, H 3.30.

3b: Yield 291 mg (41 %). Crystals of **3b** were obtained from a mixture of toluene and pentane at −35 °C. Note: decomposition takes place at r. t. and in chlorinated solvents. The yield could be increased if the thione **2b** was stirred for 30 min with $B(C_6F_5)_3$ at r. t. – ^1H NMR (400 MHz, C_6D_6): δ = 1.33 (s, 18H, CH_3), 2.66 (s, 4H, CH_2). – ^{11}B NMR (96 MHz, C_6D_6): δ = 37.22 (br s). – ^{13}C NMR (150 MHz, C_6D_6): δ = 27.18 (CH_3), 44.16 (CH_2), 57.64 ($C(CH_3)_3$), 180.9 (*C*SB). – ^{19}F NMR (376 MHz, C_6D_6): δ = −129.17 (br d, $^3J_{FF}$ = 19.7 Hz, 6F, *o*-C_6F_5), −149.18 (br s, 3F, *p*-C_6F_5), −162.34 (br s, 6F, *m*-C_6F_5). – $C_{29}H_{22}BF_{15}N_2S$: calcd. N 3.86, C 47.95, H 3.05; found N 3.77, C 48.54, H 3.53.

*NMR spectra of the selenones **4a** and **4b***

4a: ^1H NMR (300 MHz, C_6D_6): δ = 1.92 (s, 18H, CH_3), 7.01 (s, 2H, C*H*). – ^{13}C NMR (50 MHz C_6D_6): δ = 28.8 (CH_3), 60.67 ($C(CH_3)_3$), 115.8 (*C*H), 150.0 (*C*Se). – ^{77}Se NMR (57 MHz, C_6D_6): δ = 188.8 (s).

4b: ^1H NMR (300 MHz,C_6D_6): δ = 1.63 (s, 18H, CH_3), 2.69 (s, 4H, CH_2). – ^{13}C NMR (50 MHz C_6D_6): δ = 28.5 (CH_3), 44.9 (CH_2), 57.3 ($C(CH_3)_3$), 180.4 (*C*Se). – ^{77}Se NMR (57 MHz, C_6D_6): δ = 309.0 (s).

*Synthesis of the selenium complexes **5a** and **5b***

To 10 mL of a toluene solution of the appropriate selenone **5** (0.59 mmol; 136.6 mg), was added $B(C_6F_5)_3$ (0.59 mmol; 300 mg), and the mixture was stirred at r. t. for 30 min. To the reaction mixture was added pentane at −35 °C, and a yellowish precipitate of the selenium complexes was formed. The precipitate was isolated by filtration, immediately washed three times with 5 mL of pentane and dried *in vacuo*. The products **5** were collected as colourless solids. Note: prolonged stirring decreases yields; the compounds decompose over a few hours at r. t. to red oils.

5a: Yield 362 mg (89 %); an accurate elemental analysis could not be obtained due to the instability at r. t. – ^{1}H NMR (300 MHz, C_6D_6): δ = 1.15 (s,18H, CH_3), 6.11 (s, 2H, CH). – ^{13}C NMR (75 MHz, C_6D_6): δ = 29.2 (CH_3), 63.2 ($C(CH_3)_3$), 118.4 (CH). – ^{19}F NMR (376 MHz, C_6D_6): δ = −128.9 (br s, 6F, *o*-C_6F_5), −151.3 (br s, 3F, *p*-C_6F_5), −163.0 (br s, 6F, *m*-C_6F_5). – ^{11}B NMR (96 MHz, C_6D_6): δ = 9.6 (br).

5b: Yield 357 mg (87 %); an accurate elemental analysis could not be obtained due to the instability at r. t. Crystals of **5b** were obtained from a mixture of toluene and pentane at −35 °C. – ^{1}H NMR (300 MHz, C_6D_6): δ = 1.4 (s,18H, CH_3), 2.6 (s, 4H, $N_2(CH_2)_2$). – ^{13}C NMR (75 MHz, C_6D_6): δ = 28.6 (CH_3), 45.3 (CH_2), 59.3 ($C(CH_3)_3$), 135.9 (dm, *m*-C_6F_5), 149.9 (dm, *o*-C_6F_5), 174.9 (*C*SeB). – ^{19}F NMR (376 MHz, C_6D_6): δ = −130.6 (br. s, 6F, *o*-C_6F_5), −156.8 (br s, 3F, *p*-C_6F_5), −163.8 (br s, 6F, *m*-C_6F_5). – ^{11}B NMR (96 MHz, C_6D_6): δ = 24.2 (br).

X-Ray structure determinations

Crystal data and details of data collection and refinement are summarised in Table 1. Data were registered on an Oxford Diffraction Nova A diffractometer using mirror-focussed CuK_α radiation. Absorption corrections were applied using the multi-scan method. Structures were solved with routine Direct Methods and refined on F^2 using the programs SHELXS/L-97 [39]. Hydrogen atoms were included using rigid methyl groups or a riding model.

Exceptions and special features: In compound **3a** one *tert*-butyl group (atoms C9′, C10′, C11′) is disordered over two positions, while in the asymmetric unit of **3b** one pentane molecule disordered over two positions was found. Several restraints (ISOR, DELU, SAME, SADI and SIMU) were used in order to improve refinement stability of the disordered moieties. One disordered pentane molecule and one disordered half molecule of toluene were found in the asymmetric unit of **5b**, but could not be refined satisfactorily. For this reason, the program SQUEEZE (part of the PLATON program suite [40]) was used to remove mathematically the effects of the solvents.

CCDC 813555 (**3a**), 813556 (**3b**), 813557 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk /data_request/cif.

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