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PAPER

Reaction of *o*-carboranes with sterically demanding *N*-heterocyclic carbene: synthesis and structural characterization of 1 : 1 adducts†

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Several *nido*-carborane–carbene 1 : 1 adducts were prepared in very high yields from the reaction of *o*-carboranes with 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene in dry THF at room temperature. Single-crystal X-ray analyses reveal that they are zwitterionic salts consisting of a *nido* carborane cage and imidazolium moiety that are linked by a five-coordinate boron atom. They are inert toward carbenes, but sensitive toward moisture and water, leading to the formation of deboration products, *nido*-C_2B_9 ions. These results shed light on the deboration reaction mechanism of *o*-carboranes.

Introduction

o-Carborane (*o*-$C_2B_{10}H_{12}$) can be reduced to *nido*-$C_2B_{10}H_{12}^{2-}$,[1] and *arachno*-$C_2B_{10}H_{12}^{4-}$,[2] be deprotonated to $LiC_2B_{10}H_{11}$ or $Li_2C_2B_{10}H_{10}$,[3] react with electrophile (E^+) to give B-substituted carboranes *o*-$C_2B_{10}H_{12-n}E_n$[4] and with nucleophiles to afford deboration species *nido*-$C_2B_9H_{11}^{2-}$.[5] In the latter reaction, it is proposed that the nucleophile first attacks the most electron deficient cage boron that is bonded to both cage carbon atoms, followed by an attack of the second equivalent of the nucleophile on the same boron atom to remove one vertex from the *o*-carborane framework.[6] Small *N*-heterocyclic carbenes (NHCs) have recently been reported to either abstract a proton from the cage C–H unit to generate ionic liquids (imidazolium salts of the carborane monoanion)[7] or attack the cage boron atom to form 1 : 2 adducts of *nido*-carborane–carbene[8] as shown in Scheme 1.

In view of the role of NHCs in the stabilization of low-valence boron compounds,[9] boryl radicals,[10] and borenium ions,[11] we wondered if a sterically demanding NHC, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, could stabilize the 1 : 1 adducts of carborane–carbene, a class of anticipated intermediates in the formation of 1 : 2 adducts. We report herein the synthesis and structural characterization of 1 : 1 *nido*-carborane–carbene adducts.

Results and discussion

Synthesis

Treatment of *o*-carborane with 2 equiv. of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**2**) in dry THF at ambient temperature gave 1 : 1 adducts **3** in 86–92% isolated yield as colorless crystals (Schemes 1 and 2). They were stable toward excess **2** due to steric reasons, which is very different from sterically less hindered NHCs.[8] However, complexes **3** were moisture sensitive, leading to the formation of deboration products **4** upon exposure to air, for example, **4a** (Scheme 3), whereas the 1 : 2 adducts were air- and moisture-stable.[8] It was noted that both *m*-carborane and *p*-carborane showed no reactivity toward **2** even under forced reaction conditions. Various cage B or C substituted carboranes were well compatible with the reaction as shown in Scheme 2. For B(3) substituted ones, **2** attacked the B(6) position owing to steric reasons.

Complexes **3** were fully characterized by various spectroscopic data and high-resolution mass spectrometry. The ^{1}H NMR spectra were in good agreement with the formulae corresponding to 1 : 1 carborane–carbene adducts. The ^{11}B NMR spectra exhibited a pattern of 1 : 2 : 3 : 2 : 2 for **3a**, 1 : 1 : 1 : 1 : 1 : 1 : 1 : 2 : 1 for **3b**, 1 : 2 : 2 : 1 : 1 : 1 : 2 for **3c**, 1 : 2 : 2 : 1 : 1 : 1 : 2 for **3d**, 1 : 2 : 2 : 1 : 1 : 2 : 1 for **3e**, 1 : 2 : 2 : 1 : 1 : 1 : 2 for **3f**, 1 : 1 : 1 : 1 : 1 : 1 : 2 : 1 : 1 for **3g**, 1 : 2 : 1 : 2 : 1 : 1 : 2 for **3h**, 1 : 2 : 1 : 2 : 4 for **3i**, and 1 : 2 : 1 : 2 : 4 for **3j**, respectively. The chemical shifts of the unique bridging B atoms fell in the range 15.9–27.8 ppm with J_{BH} = 90–115 Hz, suggesting that this boron still bonds to an *exo*-hydrogen atom. In addition, the proton coupled ^{11}B NMR spectra showed one singlet at −7.9 ppm corresponding to the *B*Cl vertex in **3c**, one resonance at −14.2 ppm assignable to the *B*Br vertex in **3d**, one peak at −29.4 ppm attributable to the *B*I in **3e**, one singlet at −9.8 ppm corresponding to the *B*Ph vertex in **3f**, one resonance at −19.8 ppm assignable to the *B*I vertex in **3i**.

Structure

The solid-state structures of complexes **3** were further confirmed by single-crystal X-ray analyses and are shown in Fig. 1. Note that as **3c**, **3d** and **3e** are isostructural and isomorphous, only a representative structure of **3c** is shown in Fig. 1c. They have a

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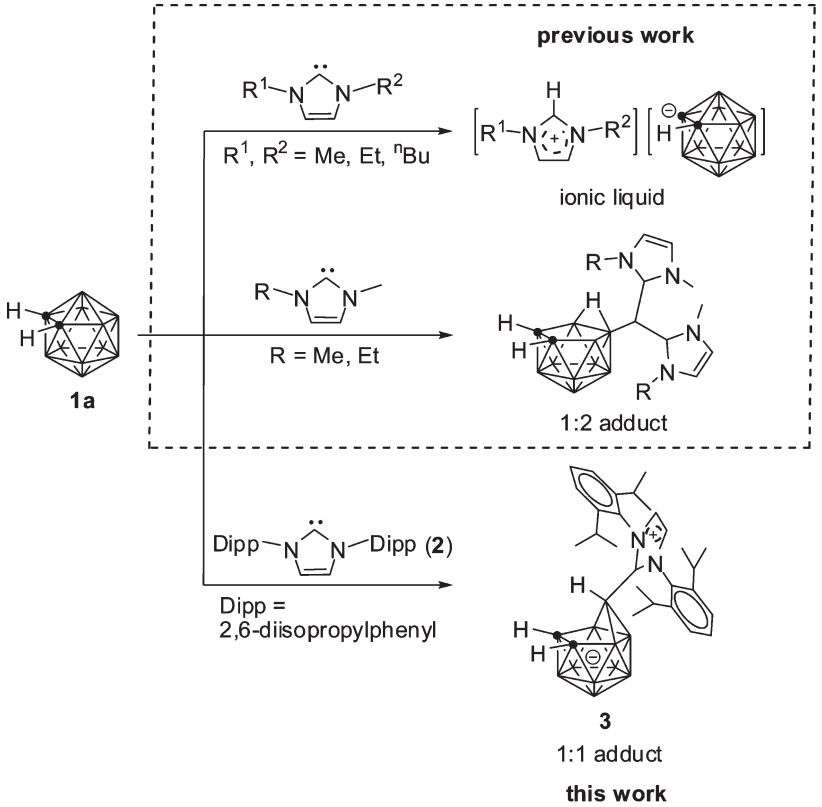
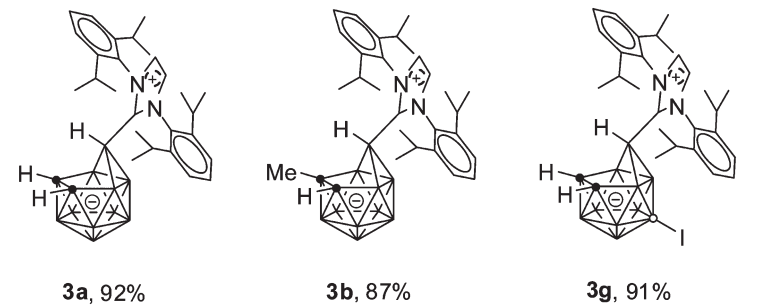
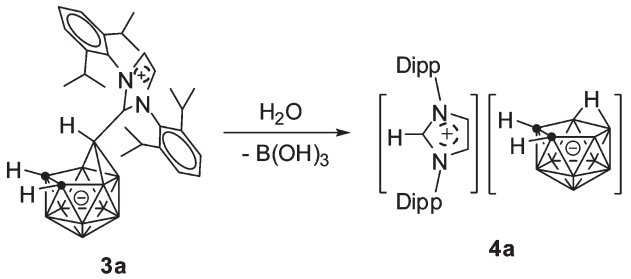
†CCDC 893415–893424 for **3a** to **3j**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31765f



Scheme 1



Scheme 2



Scheme 3

very similar *nido* cage structure with the NHC bound to the bridging boron atom that is disconnected from both cage carbon atoms. The observed geometry is close to those found in *nido*-$C_2B_{10}H_{12}$·HNP$(NMe_2)_3$[12] and [1,3-^{t}Pe$_2$-1,3-$N_2C_3H_3$][12-(1′-{1′,2′-$C_2B_{10}H_{11}$})-7,8-$C_2B_{10}H_{12}$] (Pe = pentyl).[8] As shown in Table 1, the B–C(carbene) bond distances (1.61–1.64 Å) in **3** fall in the range 1.58–1.64 Å[8,10b,13] which is normally observed in boron–carbene adducts. The B(12)–C(7)/C(8) and B(12)–B(9)/B(11) distances range from 2.54 to 2.58 Å and 1.94 to 2.01 Å, respectively, showing small variations. The B(12)–B(10) distances of 1.71–1.74 Å are in the normal range observed in *o*-carborane derivatives.[3,4,14] These data show a slip distortion of the B(12) atom towards the boron side of the C_2B_3 bonding face upon binding with NHC, cleaving the two B–C bonds and stretching the two B–B bonds. The structural parameters also indicate that both cage C and B substituents do not have obvious effects on the bonding interactions between the bridging B atom and the open C_2B_3 five-membered ring. These results suggest that **3** are best viewed as zwitterionic salts with the negative charge on the cage and positive charge on the imidazolium ring.

In summary, several 1 : 1 carborane–carbene adducts have been prepared from the reaction of *o*-carboranes with sterically demanding NHC. They are zwitterionic salts consisting of *nido* carborane cage and imidazolium unit that are linked by a five-coordinate boron atom. They do not react with an excess amount of NHC, but are sensitive to moisture and water, leading to the formation of deboration products, *nido*-C_2B_9 ions. These observations are significantly different from those of small carbenes.[7,8] The results indicate that steric factor plays a very important role in the reaction of *o*-carborane with carbenes. The isolation of 1 : 1 and 1 : 2 adducts offers a better understanding of the mechanism in the deboration process.

Experimental

General procedures

All experiments were performed under an atmosphere of dry argon with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were refluxed over sodium benzophenone ketyl for several days and freshly distilled prior to use. All chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. Compounds 1-Me-1,2-$C_2B_{10}H_{11}$,[15] 3-chloro-*o*-carborane,[16] 3-bromo-*o*-carborane,[17] 3-iodo-*o*-carborane,[18] 3-phenyl-*o*-carborane,[19] 9-iodo-*o*-carborane,[20] 1,2-$(CH_2)_3$-1,2-$C_2B_{10}H_{10}$,[21] 1,2-$(CH_2CH{=}CHCH_2)$-1,2-$C_2B_{10}H_{10}$,[22] and 1,2-[*o*-$C_6H_4(CH_2)_2$]-1,2-$C_2B_{10}H_{10}$[23] were prepared according to literature methods. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^{1}H, ^{13}C{^{1}H} and ^{11}B NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400, 100 and 128 MHz, respectively. All chemical shifts were reported in δ units with reference to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, CAS, China.

Preparation of μ-9,10,11-[2′-{1′,3′-[2″,6″-^{i}Pr$_2$(C_6H_3)]$_2$-1′,3′-$N_2C_3H_2$}]BH-7,8-$C_2B_9H_{11}$ (3a). THF solution (5 mL) of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**2**; 78 mg, 0.2 mmol) was slowly added to a stirring solution of *o*-$C_2B_{10}H_{12}$ (14 mg, 0.1 mmol) in THF (5 mL) at room temperature, and the mixture was stirred overnight. The resulting light-yellow solution was then concentrated to *ca.* 2 mL, to which hexane (10 mL) was added. The precipitate formed was filtered off and recrystallized from diethyl ether to give adduct **3a** as colorless crystals (49 mg, 92%). ^{1}H NMR (CD_2Cl_2): δ 7.53 (t, J = 7.8 Hz, 2H, C_6H_3), 7.31 (d, J = 7.8 Hz, 4H, C_6H_3), 7.14 (s, 2H, imidazolium NC*H*), 2.79 (s, 2H, cage C*H*), 2.62 (m, 4H, C*H*$(CH_3)_2$), 1.34 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.18 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 146.0, 132.5, 131.3, 124.5, 123.2 (C_6H_3 & imidazolium N*C*H), 67.1 (cage *C*), 29.4 (*C*H(CH$_3$)$_2$), 25.7, 22.4 (CH(*C*H$_3$)$_2$), the imidazolium N*C*N carbon was not observed. ^{11}B NMR (CD_2Cl_2): δ 24.0 (d, J = 115 Hz, 1B), −2.7 (d, J = 166 Hz, 2B), −7.6 (d, J = 128 Hz, 3B), −18.3 (d, J = 179 Hz, 2B), −19.9 (d, J = 141 Hz, 2B). IR (KBr, cm^{-1}): ν_{BH} 2567 (vs). HRMS: *m*/*z* calcd for $C_{29}H_{48}B_{10}N_2$ [M − H]$^+$: 531.4737. Found: 531.4744.

Preparation of 7-Me-μ-9,10,11-[2′-{1′,3′-[2″,6″-^{i}Pr$_2$(C_6H_3)]$_2$-1′,3′-$N_2C_3H_2$}]BH-7,8-$C_2B_9H_{11}$ (3b). This complex was prepared as colorless crystals from 1-Me-1,2-$C_2B_{10}H_{11}$ (16 mg, 0.1 mol) and **2** (78 mg, 0.2 mmol) in THF using the same procedure as reported for **3a**: yield 48 mg (87%). X-Ray-quality crystals were grown from a saturated diethyl ether solution at room temperature. ^{1}H NMR (CD_2Cl_2): δ 7.53 (t, J = 7.8 Hz, 2H, C_6H_3), 7.32 (m, 4H, C_6H_3), 7.15 (s, 2H, imidazolium NC*H*), 2.67 (m, 5H, C*H*$(CH_3)_2$ & cage C*H*), 1.41 (s, 3H, cage C*H*$_3$), 1.36 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.16 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 146.0, 145.8, 132.6, 131.2, 124.4, 124.3, 123.4 (C_6H_3 & imidazolium N*C*H), 29.3 (*C*H(CH$_3$)$_2$), 26.5 (cage *C*H$_3$), 25.7, 22.2, 22.1 (CH(*C*H$_3$)$_2$), the imidazolium N*C*N and cage *C* atoms were not observed. ^{11}B NMR (CD_2Cl_2): δ 21.1 (d, J = 90 Hz, 1B), −0.3 (d, J = 115 Hz, 1B), −3.0 (d, J = 154 Hz, 1B), −7.2 (d, J = 102 Hz, 1B), −7.9 (d, J = 128 Hz, 1B), −11.5 (d, J = 141 Hz, 1B), −14.7 (d, J = 154 Hz, 1B), −17.6 (d, J = 141 Hz, 2B), −19.9 (d, J = 128 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2554 (vs). HRMS: *m*/*z* calcd for $C_{30}H_{50}B_{10}N_2$ [M − H]$^+$: 545.4908. Found: 545.4910.

Preparation of 3-Cl-μ-9,10,11-[2′-{1′,3′-[2″,6″-^{i}Pr$_2$(C_6H_3)]$_2$-1′,3′-$N_2C_3H_2$}]BH-7,8-$C_2B_9H_{11}$ (3c). This complex was prepared as light-yellow crystals from 3-chloro-*o*-carborane (18 mg, 0.1 mol) and **2** (78 mg, 0.2 mmol) in THF using the same

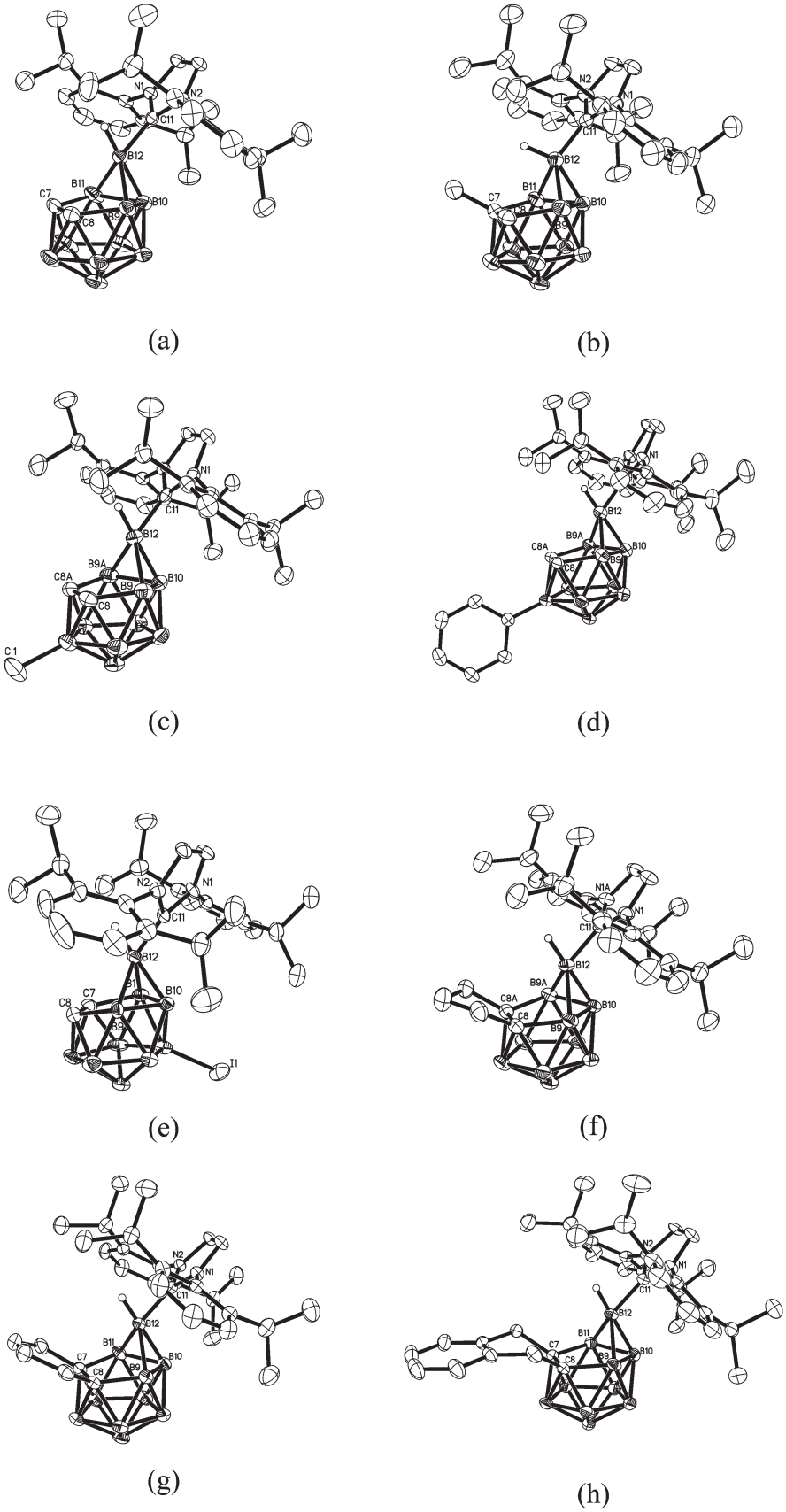
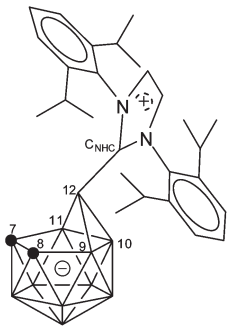


Fig. 1 Molecular structures of (a) **3a**, (b) **3b**, (c) **3c**, (d) **3f**, (e) **3g**, (f) **3h**, (g) **3i** and (h) **3j**.

Table 1 Selected bond lengths (Å) in **3**



Complex	C_{NHC}–B12	C7–C8	C7–B12	C8–B12	B9–B12	B11–B12	B10–B12
3a	1.611(3)	1.503(4)	2.566(4)	2.566(4)	1.969(4)	1.979(4)	1.718(4)
3b	1.610(4)	1.510(4)	2.579(4)	2.555(4)	1.959(5)	1.996(4)	1.718(4)
3c	1.641(8)	1.525(8)	2.559(8)	2.559(8)	1.978(6)	1.978(6)	1.728(9)
3d	1.616(5)	1.525(5)	2.570(5)	2.570(5)	1.986(4)	1.986(4)	1.720(6)
3e	1.618(5)	1.526(5)	2.557(5)	2.557(5)	1.979(4)	1.979(4)	1.713(6)
3f	1.636(5)	1.526(5)	2.578(5)	2.578(5)	1.991(4)	1.991(4)	1.739(6)
3g	1.609(10)	1.511(13)	2.549(12)	2.541(12)	1.958(11)	2.012(11)	1.728(11)
3h	1.634(4)	1.527(4)	2.563(4)	2.563(4)	1.967(4)	1.967(4)	1.708(5)
3i	1.622(3)	1.527(3)	2.537(3)	2.554(3)	1.970(4)	1.939(4)	1.734(4)
3j	1.617(5)	1.517(4)	2.552(4)	2.572(4)	1.976(5)	1.956(5)	1.724(6)

procedure as reported for **3a**: yield 51 mg (89%). X-Ray-quality crystals were grown from a saturated diethyl ether solution at room temperature. ^{1}H NMR (CD_2Cl_2): δ 7.54 (t, J = 7.8 Hz, 2H, C_6H_3), 7.32 (d, J = 8.0 Hz, 4H, C_6H_3), 7.16 (s, 2H, imidazolium NC*H*), 2.92 (s, 2H, cage C*H*), 2.58 (m, 4H, C*H*(CH_3)$_2$), 1.33 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.18 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 145.9, 132.2, 131.4, 124.5, 123.4 (C_6H_3 & imidazolium N*C*H), 71.1 (cage *C*), 29.3 (*C*H(CH_3)$_2$), 25.7, 22.3 (CH(*C*H_3)$_2$), the imidazolium N*C*N carbon was not observed. ^{11}B NMR (CD_2Cl_2): δ 26.3 (d, J = 102 Hz, 1B), −2.2 (d, J = 179 Hz, 2B), −7.1 (d, J = 179 Hz, 2B), −7.9 (s, 1B), −11.3 (d, J = 115 Hz, 1B), −18.8 (d, J = 141 Hz, 1B), −19.8 (d, J = 128 Hz, 2B). IR (KBr, cm^{-1}): ν_{BH} 2575 (vs). HRMS: *m*/*z* calcd for $C_{29}H_{47}B_{10}ClN_2$ [M − H]$^+$: 566.4338. Found: 566.4342.

Preparation of 3-Br-μ-9,10,11-[2′-{1′,3′-[2″,6″-^{i}Pr$_2$(C$_6$H$_3$)]$_2$-1′,3′-N$_2$C$_3$H$_2$}]BH-7,8-C$_2$B$_9$H$_{11}$ (3d). This complex was prepared as colorless crystals from 3-bromo-*o*-carborane (22 mg, 0.1 mol) and **2** (78 mg, 0.2 mmol) in THF using the same procedure as reported for **3a**: yield 56 mg (92%). X-Ray-quality crystals were grown from a saturated diethyl ether solution at room temperature. ^{1}H NMR (CD_2Cl_2): δ 7.54 (t, J = 7.8 Hz, 2H, C_6H_3), 7.32 (d, J = 8.0 Hz, 4H, C_6H_3), 7.17 (s, 2H, imidazolium NC*H*), 2.97 (s, 2H, cage C*H*), 2.58 (m, 4H, C*H*(CH_3)$_2$), 1.33 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.18 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 145.9, 132.2, 131.4, 124.5, 123.4 (C_6H_3 & imidazolium N*C*H), 71.3 (cage *C*), 29.3 (*C*H(CH_3)$_2$), 25.7, 22.3 (CH(*C*H_3)$_2$), the imidazolium N*C*N carbon was not observed. ^{11}B NMR (CD_2Cl_2): δ 26.3 (d, J = 90 Hz, 1B), −1.9 (d, J = 128 Hz, 2B), −6.9 (d, J = 141 Hz, 2B), −10.3 (d, J = 128 Hz, 1B), −14.2 (s, 1B), −18.3 (d, J = 154 Hz, 1B), −19.4 (d, J = 128 Hz, 2B). IR (KBr, cm^{-1}): ν_{BH} 2576 (vs). HRMS: *m*/*z* calcd for $C_{29}H_{47}B_{10}BrN_2$ [M − H]$^+$: 609.3842. Found: 609.3835.

Preparation of 3-I-μ -9,10,11-[2′-{1′,3′-[2″,6″-^{i}Pr$_2$(C$_6$H$_3$)]$_2$-1′,3′-N$_2$C$_3$H$_2$}]BH-7,8-C$_2$B$_9$H$_{11}$ (3e). This complex was prepared as colorless crystals from 3-iodo-*o*-carborane (27 mg, 0.1 mol) and **2** (78 mg, 0.2 mmol) in THF using the same procedure as reported for **3a**: yield 60 mg (91%). X-Ray-quality crystals were grown from a saturated diethyl ether solution at room temperature. ^{1}H NMR (CD_2Cl_2): δ 7.54 (t, J = 7.8 Hz, 2H, C_6H_3), 7.32 (d, J = 8.0 Hz, 4H, C_6H_3), 7.17 (s, 2H, imidazolium NC*H*), 2.99 (s, 2H, cage C*H*), 2.58 (m, 4H, C*H*(CH_3)$_2$), 1.33 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.18 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 145.9, 132.2, 131.4, 124.5, 123.4 (C_6H_3 & imidazolium N*C*H), 71.6 (cage *C*), 29.3 (*C*H(CH_3)$_2$), 25.7, 22.3 (CH(*C*H_3)$_2$), the imidazolium N*C*N carbon was not observed. ^{11}B NMR (CD_2Cl_2): δ 26.0 (d, J = 102 Hz, 1B), −1.2 (d, J = 128 Hz, 2B), −6.5 (d, J = 141 Hz, 2B), −8.4 (d, J = 128 Hz, 1B), −17.2 (d, J = 179 Hz, 1B), −18.8 (d, J = 141 Hz, 2B), −29.4 (s, 1B). IR (KBr, cm^{-1}): ν_{BH} 2575 (vs). HRMS: *m*/*z* calcd for $C_{29}H_{47}B_{10}IN_2$ [M − H]$^+$: 657.3703. Found: 657.3700.

Preparation of 3-Ph-μ-9,10,11-[2′-{1′,3′-[2″,6″-^{i}Pr$_2$(C$_6$H$_3$)]$_2$-1′,3′-N$_2$C$_3$H$_2$}]BH-7,8-C$_2$B$_9$H$_{11}$ (3f). This complex was prepared as colorless crystals from 3-phenyl-*o*-carborane (22 mg, 0.1 mol) and **2** (78 mg, 0.2 mmol) in THF using the same procedure as reported for **3a**: yield 55 mg (90%). X-Ray-quality crystals were grown from a saturated diethyl ether solution at room temperature. ^{1}H NMR (CD_2Cl_2): δ 7.55 (t, J = 7.8 Hz, 2H, C_6H_3), 7.33 (d, J = 7.8 Hz, 4H, C_6H_3), 7.30 (m, 2H, BC_6H_5), 7.16 (s, 2H, imidazolium NC*H*), 7.14 (m, 3H, BC_6H_5), 2.94 (s, 2H, cage C*H*), 2.63 (m, 4H, C*H*(CH_3)$_2$), 1.35 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.19 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 146.0, 132.8, 132.5, 131.3, 127.5, 127.4, 124.5, 123.3 (aryl &

imidazolium NCH), 70.7 (cage *C*), 29.3 (*C*H(CH_3)$_2$), 25.7, 22.4 (CH(*C*H_3)$_2$), the imidazolium NCN carbon was not observed. ^{11}B NMR (CD_2Cl_2): δ 23.5 (d, J = 90 Hz, 1B), −2.6 (d, J = 128 Hz, 2B), −7.3 (d, J = 141 Hz, 2B), −9.2 (d, J = 179 Hz, 1B), −9.8 (s, 1B), −17.7 (d, J = 141 Hz, 1B), −20.1 (d, J = 115 Hz, 2B). IR (KBr, cm^{-1}): ν_{BH} 2580 (vs). HRMS: *m*/*z* calcd for $C_{35}H_{52}B_{10}N_2$ [M − H]$^+$: 607.5050. Found: 607.5060.

Preparation of 6-I-μ-9,10,11-[2′-{1′,3′-[2″,6″-^{i}Pr$_2$(C_6H_3)]$_2$-1′,3′-$N_2C_3H_2$}]BH-7,8-$C_2B_9H_{11}$ (3g). This complex was prepared as colorless crystals from 9-iodo-*o*-carborane (27 mg, 0.1 mol) and **2** (78 mg, 0.2 mmol) in THF using the same procedure as reported for **3a**: yield 60 mg (91%). X-Ray-quality crystals were grown from a saturated diethyl ether solution at room temperature. ^{1}H NMR (CD_2Cl_2): δ 7.55 (t, J = 7.8 Hz, 2H, C_6H_3), 7.34 (m, 4H, C_6H_3), 7.20 (s, 2H, imidazolium NC*H*), 3.09 (s, 1H, cage C*H*), 2.81 (s, 1H, cage C*H*), 2.68 (m, 2H, C*H*(CH_3)$_2$), 2.53 (m, 2H, C*H*(CH_3)$_2$), 1.40 (d, J = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.38 (d, J = 7.8 Hz, 6H, CH(CH_3)$_2$), 1.18 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 146.0, 145.7, 132.3, 131.5, 124.6, 124.5, 123.8 (C_6H_3 & imidazolium N*C*H), 29.5, 29.4 (*C*H(CH_3)$_2$), 25.9, 25.8, 22.9, 22.1 (CH(*C*H_3)$_2$), the imidazolium N*C*N and cage *C* atoms were not observed. ^{11}B NMR (CD_2Cl_2): δ 23.8 (d, J = 90 Hz, 1B), −1.5 (d, J = 141 Hz, 1B), −3.6 (d, J = 179 Hz, 1B), −5.0 (d, J = 141 Hz, 1B), −6.0 (d, J = 128 Hz, 1B), −15.9 (d, J = 141 Hz, 1B), −17.1 (d, J = 154 Hz, 2B), −19.2 (d, J = 102 Hz, 1B), −19.8 (s, 1B). IR (KBr, cm^{-1}): ν_{BH} 2574 (vs). HRMS: *m*/*z* calcd for $C_{29}H_{47}B_{10}IN_2$ [M − H]$^+$: 657.3703. Found: 657.3706.

Preparation of 7,8-$(CH_2)_3$-μ-9,10,11-[2′-{1′,3′-[2″,6″-^{i}Pr$_2$(C_6H_3)]$_2$-1′,3′-$N_2C_3H_2$}]BH-7,8-$C_2B_9H_{11}$ (3h). This complex was prepared as colorless crystals from 1,2-$(CH_2)_3$-1,2-$C_2B_{10}H_{10}$ (18 mg, 0.1 mol) and **2** (78 mg, 0.2 mmol) in THF using the same procedure as reported for **3a**: yield 50 mg (88%). X-Ray-quality crystals were grown from a saturated diethyl ether solution at room temperature. ^{1}H NMR (CD_2Cl_2): δ 7.53 (t, J = 7.8 Hz, 2H, C_6H_3), 7.32 (d, J = 8.0 Hz, 4H, C_6H_3), 7.15 (s, 2H, imidazolium NC*H*), 2.67 (m, 4H, C*H*(CH_3)$_2$), 1.97 (m, 2H, CH_2), 1.86 (m, 2H, CH_2), 1.66 (m, 1H, CH_2), 1.36 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.28 (m, 1H, CH_2), 1.15 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 145.8, 132.8, 131.2, 124.3, 123.6 (C_6H_3 & imidazolium N*C*H), 67.9 (cage *C*), 36.3 (*C*H_2CH_2*C*H_2), 29.4 (*C*H(CH_3)$_2$), 26.9 (CH$_2$*C*H$_2$CH$_2$), 25.8, 25.7, 21.9 (CH(*C*H_3)$_2$), the imidazolium N*C*N carbon was not observed. ^{11}B NMR (CD_2Cl_2): δ 19.0 (d, J = 102 Hz, 1B), −1.35 (d, J = 141 Hz, 2B), −5.7 (d, J = 115 Hz, 1B), −13.2 (d, J = 141 Hz, 2B), −16.7 (d, J = 141 Hz, 1B), −18.1 (d, J = 192 Hz, 1B), −19.3 (d, J = 128 Hz, 2B). IR (KBr, cm^{-1}): ν_{BH} 2542 (vs). HRMS: *m*/*z* calcd for $C_{32}H_{52}B_{10}N_2$ [M − H]$^+$: 571.5050. Found: 571.5043.

Preparation of 7,8-(CH_2CH═CHCH_2)-μ-9,10,11-[2′-{1′,3′-[2″,6″-^{i}Pr$_2$(C_6H_3)]$_2$-1′,3′-$N_2C_3H_2$}]BH-7,8-$C_2B_9H_{11}$ (3i). This complex was prepared as colorless crystals from 1,2-(CH_2CH═CHCH_2)-1,2-$C_2B_{10}H_{10}$ (20 mg, 0.1 mol) and **2** (78 mg, 0.2 mmol) in THF using the same procedure as reported for **3a**: yield 51 mg (86%). X-Ray-quality crystals were grown from a saturated diethyl ether solution at room temperature. ^{1}H NMR (CD_2Cl_2): δ 7.54 (t, J = 7.8 Hz, 2H, C_6H_3), 7.32 (d, J = 7.8 Hz, 4H, C_6H_3), 7.13 (s, 2H, imidazolium NC*H*), 5.47 (s, 2H, CH_2C*H*═C*H*CH_2), 2.64 (m, 4H, C*H*(CH_3)$_2$), 2.45 (d, J = 16.9 Hz, 2H, CH_2CH═CHCH_2), 2.33 (d, J = 16.9 Hz, 2H, CH_2CH═CHCH_2), 1.34 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.14 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 145.9, 132.8, 131.3, 124.3, 123.4, 123.1 (C_6H_3, imidazolium N*C*H & CH_2*C*H═*C*HCH_2), 34.8 (*C*H_2CH_2═CH$_2$*C*H_2), 29.4 (*C*H(CH_3)$_2$), 25.9, 22.0 (CH(*C*H_3)$_2$), the imidazolium N*C*N and cage *C* were not observed. ^{11}B NMR (CD_2Cl_2): δ 15.9 (d, J = 115 Hz, 1B), −1.1 (d, J = 128 Hz, 2B), −7.6 (d, J = 128 Hz, 1B), −13.1 (d, J = 141 Hz, 2B), −17.6 (d, J = 115 Hz, 4B). IR (KBr, cm^{-1}): ν_{BH} 2533 (vs). HRMS: *m*/*z* calcd for $C_{33}H_{52}B_{10}N_2$ [M − H]$^+$: 583.5050. Found: 583.5045.

Preparation of 7,8-[*o*-C_6H_4(CH_2)$_2$]-μ-9,10,11-[2′-{1′,3′-[2″,6″-^{i}Pr$_2$(C_6H_3)]$_2$-1′,3′-$N_2C_3H_2$}]BH-7,8-$C_2B_9H_{11}$ (3j). This complex was prepared as light-yellow crystals from 1,2-[*o*-C_6H_4(CH_2)$_2$]-1,2-$C_2B_{10}H_{10}$ (24 mg, 0.1 mol) and **2** (78 mg, 0.2 mmol) in THF using the same procedure as reported for **3a**: yield 57 mg (90%). X-Ray-quality crystals were grown from a saturated diethyl ether solution at room temperature. ^{1}H NMR (CD_2Cl_2): δ 7.57 (t, J = 7.8 Hz, 2H, C_6H_3), 7.34 (d, J = 7.8 Hz, 4H, C_6H_3), 7.16 (s, 2H, imidazolium NC*H*), 7.05 (m, 2H, *o*-C_6H_4(CH_2)$_2$), 6.85 (m, 2H, *o*-C_6H_4(CH_2)$_2$), 3.20 (d, J = 16.5 Hz, 2H, *o*-C_6H_4(CH_2)$_2$), 2.84 (d, J = 16.5 Hz, 2H, *o*-C_6H_4(CH_2)$_2$), 2.68 (m, 4H, C*H*(CH_3)$_2$), 1.32 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.14 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 145.8, 135.2, 132.8, 131.3, 130.5, 127.1, 126.3, 124.4, 123.6 (C_6H_3, imidazolium N*C*H & *o*-C_6H_4(CH_2)$_2$), 38.9 (*o*-C_6H_4(*C*H_2)$_2$), 29.4 (*C*H(CH_3)$_2$), 25.9, 22.0 (CH(*C*H_3)$_2$), the imidazolium N*C*N and cage *C* were not observed. ^{11}B NMR (CD_2Cl_2): δ 17.8 (d, J = 90 Hz, 1B), 1.2 (d, J = 128 Hz, 2B), −6.5 (d, J = 115 Hz, 1B), −11.2 (d, J = 141 Hz, 2B), −17.6 (d, J = 128 Hz, 4B). IR (KBr, cm^{-1}): ν_{BH} 2527 (vs). HRMS: *m*/*z* calcd for $C_{37}H_{54}B_{10}N_2$ [M − H]$^+$: 633.5224. Found: 633.5233.

Preparation of [1′,3′-{2″,6″-^{i}Pr$_2$(C_6H_3)}$_2$-1′,3′-$N_2C_3H_3$]-[$C_2B_9H_{12}$] (4a). H_2O (0.1 mL) was added to a stirring solution of **3a** (53 mg, 0.1 mmol) in acetone (10 mL) at room temperature, and the mixture was stirred for 2 d. The solvent was removed *in vacuo* and the resulting light-green oil was extracted by diethyl ether (5 mL × 3). The ether solutions were combined and concentrated to 10 mL. Complex **4a** was obtained as colorless crystals after this solution stood at room temperature overnight (42 mg, 81%). ^{1}H NMR (CD_3COCD_3): δ 9.82 (s, 1H, imidazolium NC*H*N), 8.45 (s, 2H, NC*H*═C*H*N), 7.71 (t, J = 7.8 Hz, 2H, C_6H_3), 7.55 (d, J = 7.6 Hz, 4H, C_6H_3), 2.60 (m, 4H, C*H*(CH_3)$_2$), 1.31 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.26 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_3COCD_3): δ 146.1, 139.5, 133.1, 131.1, 127.4, 125.7 (C_6H_3, N*C*HN & N*C*H═*C*HN), 29.9 (*C*H(CH_3)$_2$), 24.6, 23.8 (CH(*C*H_3)$_2$), the cage *C* atoms were not observed. ^{11}B NMR (CD_3COCD_3): δ −10.0 (d, J = 128 Hz, 2B), −15.9 (d, J = 115 Hz, 2B), −16.7 (d, J = 128 Hz, 1B), −21.4 (d, J = 154 Hz, 2B), −32.3 (d, J = 128 Hz, 1B), −36.9 (d, J = 141 Hz, 1B). IR (KBr, cm^{-1}): ν_{BH} 2529 (vs). Anal. calcd for $C_{29}H_{49}B_9N_2$: C, 66.60; H, 9.40; N, 5.36. Found: C, 66.01; H, 9.33; N, 4.99.

Table 2 Crystal data and summary of data collection and refinement for **3a**·$(CH_3CH_2)_2O$, **3b**, **3c**, **3d**, and **3e**

	3a·$(CH_3CH_2)_2O$	**3b**	**3c**	**3d**	**3e**
Formula	$C_{33}H_{58}B_{10}N_2O$	$C_{30}H_{50}B_{10}N_2$	$C_{29}H_{47}B_{10}ClN_2$	$C_{29}H_{47}B_{10}BrN_2$	$C_{29}H_{47}B_{10}IN_2$
Crystal size/mm	0.50 × 0.40 × 0.30	0.50 × 0.40 × 0.30	0.40 × 0.30 × 0.20	0.40 × 0.40 × 0.30	0.40 × 0.30 × 0.20
M_r	606.9	546.8	567.2	611.7	658.7
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	*Pnma*	*Pnma*	*Pnma*
a/Å	10.715(1)	10.286(4)	19.542(4)	19.605(1)	19.826(1)
b/Å	21.911(1)	18.148(6)	16.440(3)	16.427(1)	16.333(1)
c/Å	17.309(1)	21.421(8)	10.733(2)	10.752(1)	10.784(1)
β/°	104.661(2)	90.323(7)	90	90	90
V/Å^3	3931.5(4)	3999(2)	3448.2(11)	3462.5(4)	3492.0(2)
Z	4	4	4	4	4
D_c/Mg m^{-3}	1.025	0.908	1.093	1.173	1.253
Radiation (λ(Mo Kα))/Å	0.71073	0.71073	0.71073	0.71073	0.71073
$2\theta_{max}$/°	50.5	50.5	50.5	50.5	50.5
μ/mm^{-1}	0.056	0.048	0.133	1.209	0.939
F(000)	1312	1176	1208	1280	1352
Observed reflections [$I > 2\sigma(I)$]	7108	7233	3241	3253	3280
Parameters	419	383	200	202	202
Goodness of fit on F^2	1.040	0.910	1.003	0.979	1.044
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.057	R_1 = 0.067	R_1 = 0.069	R_1 = 0.046	R_1 = 0.037
	wR_2 = 0.144	wR_2 = 0.178	wR_2 = 0.164	wR_2 = 0.118	wR_2 = 0.094

Table 3 Crystal data and summary of data collection and refinement for **3f**, **3g**, **3h**, **3i** and **3j**

	3f	**3g**	**3h**	**3i**	**3j**
Formula	$C_{35}H_{52}B_{10}N_2$	$C_{29}H_{47}B_{10}IN_2$	$C_{32}H_{52}B_{10}N_2$	$C_{33}H_{52}B_{10}N_2$	$C_{37}H_{54}B_{10}N_2$
Crystal size/mm	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.30	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.30
M_r	608.9	658.7	572.9	584.9	634.9
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pnma*	*Cc*	*Pbcm*	$P2_1/n$	*Pbca*
a/Å	21.29(3)	18.203(1)	10.726(1)	11.269(1)	18.164(2)
b/Å	17.20(2)	12.930(1)	18.193(2)	16.920(1)	19.478(2)
c/Å	10.674(2)	15.522(1)	20.347(2)	19.229(1)	22.210(2)
β/°	90	98.656(1)	90	105.086(1)	90
V/Å^3	3909(9)	3611.4(3)	3970.4(6)	3540.0(4)	7858(1)
Z	4	4	4	4	8
D_c/mg m^{-3}	1.035	1.211	0.958	1.097	1.073
Radiation (λ(Mo Kα))/Å	0.71073	0.71073	0.71073	0.71073	0.71073
$2\theta_{max}$/°	50.5	50.5	50.5	50.5	50.5
μ/mm^{-1}	0.055	0.908	0.051	0.058	0.057
F(000)	1304	1352	1232	1256	2720
Observed reflections [$I > 2\sigma(I)$]	3668	5521	3709	6411	7122
Parameters	230	379	209	406	447
Goodness of fit on F^2	1.045	0.974	0.998	1.019	1.005
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.067	R_1 = 0.052	R_1 = 0.066	R_1 = 0.059	R_1 = 0.061
	wR_2 = 0.172	wR_2 = 0.157	wR_2 = 0.174	wR_2 = 0.146	wR_2 = 0.122

X-Ray structure determination

All single crystals were immersed in Paraton-N oil and sealed under nitrogen in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation (0.71073 Å). An empirical absorption correction was applied using the SADABS program.[24] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on F^2 using the SHELXTL program package.[25] All hydrogen atoms were geometrically fixed using the riding model, so that a detailed discussion of the B-H distances was not warranted. Crystal data and details of data collection and structure refinements were given in Tables 2 and 3. Further details were deposited with Cambridge Crystallographic Data Center, CCDC reference numbers 893415–893424 for **3a** to **3j**, respectively.

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