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Sulfur, tin and gold derivatives of 1-(2′-pyridyl)-*ortho*-carborane, 1-R-2-X-1,2-$C_2B_{10}H_{10}$ (R = 2′-pyridyl, X = SH, $SnMe_3$ or $AuPPh_3$)

Andrei S. Batsanov,[a] Mark A. Fox,*[a] Thomas G. Hibbert,[a] Judith A. K. Howard,[a] Raikko Kivekäs,[b] Anna Laromaine,†[c] Reijo Sillanpää,[d] Clara Viñas*[c] and Kenneth Wade[a]

[a] *Department of Chemistry, University of Durham, South Road, Durham, UK, DH1 3LE. E-mail: m.a.fox@durham.ac.uk*
[b] *Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014, Finland*
[c] *Institut de Ciència de Materials de Barcelona (CSIC), Campus de la U.A.B., E-08193, Bellaterra, Spain. E-mail: clara@icmab.es; Fax: + 34 93 5805729; Tel: + 34 93 5805729*
[d] *Department of Chemistry, University of Jyväskylä, FIN-40351, Finland*

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Reaction of the lithium salt of 1-(2′-pyridyl)-*ortho*-carborane, Li[1-R-1,2-$C_2B_{10}H_{10}$] (R = 2′-NC_5H_4), with sulfur, followed by hydrolysis, gave the mercapto-*o*-carborane, 1-R-2-SH-1,2-$C_2B_{10}H_{10}$ which forms chiral crystals containing helical chains of molecules linked by intermolecular S–H ··· N hydrogen bonds. The cage C(1)–C(2) and *exo* C(2)–S bond lengths (1.730(3) and 1.775(2) Å, respectively) are indicative of *exo* S=C π bonding. The tin derivative 1-R-2-$SnMe_3$-1,2-$C_2B_{10}H_{10}$, prepared from Li[1-R-1,2-$C_2B_{10}H_{10}$] and Me_3SnCl, crystallises with no significant intermolecular interactions. The pyridyl group lies in the C(1)–C(2)–Sn plane, oriented to minimise the N ··· Sn distance (2.861(3) Å). The tin environment is distorted trigonal bipyramidal with axial N and Me. The gold derivative 1-R-2-$AuPPh_3$-1,2-$C_2B_{10}H_{10}$, prepared from Li[1-R-1,2-$C_2B_{10}H_{10}$] and AuCl(PPh_3), reveals no N ··· Au interaction in its crystal structure.

Derivatives of *ortho*-carborane of formula 1-R-1,2-$C_2B_{10}H_{11}$, bearing a nitrogen-containing substituent R on one cage carbon atom, have attracted much recent attention as potential medicinal agents for use in boron neutron capture therapy (BNCT)[1,2] and as potentially-chelating carboranyl ligand precursors.[3–8] For example many metal complexes 1-R-2-ML_n-1,2-$C_2B_{10}H_{10}$ (with an *exo*-cluster C–M bond) or 1-R-2-X-3-ML_n-1,2-$C_2B_9H_9$ (where ML_n replaces one boron vertex) have been prepared from dialkylaminomethyl-*ortho*-carborane (**1**, R = Me or Et)[4–6] (Fig. 1) or from 1-(2′-picolyl)-*ortho*-carborane (**2**).[7] When a metal atom is linked to amino or picolyl nitrogen atoms in these derivatised carboranes, five-membered C_3NM rings are formed if a *closo*-C_2B_{10} cage is retained; four-membered C_2NM rings are found in MC_2B_9 systems in which the ML_n unit occupies a cage site.

We have previously reported the syntheses of 1-(2′-pyridyl)-*ortho*-carborane **3** which resembles **1** in the proximity of its nitrogen atom to the cage.[9,10] Compound **3** has two notable properties. Firstly, it contains a strong intramolecular hydrogen bond between the pyridyl nitrogen atom and the acidic hydrogen atom bonded to the cage carbon (C2), significantly stronger than the comparable intramolecular hydrogen bonds in compounds **1** and **2**.[9] Secondly, substitution on the cage carbon (C2) of compound **3**, to form 1-(2′-pyridyl)-2-aryl-*ortho*-carboranes, with aryl bromides or iodides in the presence of a copper catalyst is facile.[10] By contrast, attempted reaction of 1-phenyl-*ortho*-carborane with aryl bromides or iodides in presence of a copper catalyst did not afford 1,2-diaryl-*ortho*-carboranes. The formation of 1-(2′pyridyl)-2-aryl-*ortho*-carboranes from **3** was believed to proceed through a copper intermediate **4** (M = Cu) involving an intramolecular Cu ··· N interaction. A copper derivative 1-R-2-Cu-1,2-$C_2B_{10}H_{10}$ synthesised from the lithio derivative of **1** (R = Et) with copper(I) chloride was found to be air-sensitive and believed to contain a Cu ··· N interaction.[4] With **1** (R = Me) instead of **1** (R = Et), a stable compound 2,2′-(1-R-1,2-$C_2B_{10}H_{10}$)$_2$Cu was obtained with two Cu ··· N interactions. Copper carboranes are apparently more stable when two or more cage C–Cu bonds are present.[11,12] The only crystal structures of *ortho*-carboranes with cage C–Cu single bonds are found in salts of $[\{(C_2B_{10}H_{10})_2\}_2Cu]^-$ and $[\{(C_2B_{10}H_{10})_2\}_2Cu]^{2-}$ where the copper atom is bonded to four cage carbons with C–Cu bond lengths between 2.01 and 2.07 Å.[12]

Here, we report the synthesis, spectroscopic and structural characterisation of three new derivatives 1-(2′-pyridyl)-*ortho*-carborane **3**. One of these is the 2-mercapto derivative (**5**), which we believe to be the first derivative of *ortho*-carborane containing a mercapto group –SH to be structurally characterised. It was expected (rightly, in the event) to be of interest in connection with its hydrogen bonding, and can also be seen as a potential precursor for chelated metal complexes containing six-membered C_3NMS rings (*cf*. the related thiol of **1** (R = Me) which has been previously studied[8]). The second derivative we describe here is compound **6**, the first *ortho*-carborane with a trimethylstannyl (as opposed to an organotin halide[6]) substituent to be structurally characterised. It was seen as a possible model for the copper intermediate **4** (M = Cu) though it was appreciated that the very weak Lewis acidity and relative bulk of the $SnMe_3$ residue might discourage chelation

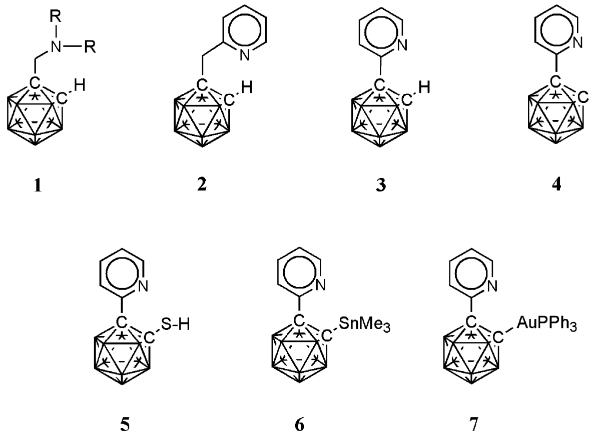

Fig. 1 Compounds **1**–**7** discussed in this study. Each naked cluster vertex represents BH.

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and force the pyridyl ring plane out of the C–C(1)–C(2) plane. The third derivative is the gold compound **7,** also structurally characterised. We assess the effect of the pyridyl group on the cage geometry by comparing with several known gold carborane complexes of formula 1-R-2-AuL-1,2-$C_2B_{10}H_{10}$ (L = PPh_3, $AsPh_3$). Compound **7** is also a possible model for the copper intermediate **4** (M = Cu) though it is appreciated that gold is a weaker acceptor than copper towards pyridyl nitrogen.

Experimental

All manipulations were carried out under dry, oxygen-free N_2. Commercial grade acetonitrile, pentane, *n*-butyllithium in hexanes and resublimed sulfur were used without further purification. Dry Et_2O and THF were obtained by reflux and distillation over Na wire. Demineralised water was used in the aqueous stages of syntheses. Compound **3** was prepared by the literature methods.[7,9]

Infrared spectra were recorded as KBr discs using a Perkin Elmer 1720X FTIR spectrometer. Elemental analyses were performed using Exeter Analytical CE-440 apparatus. ^1H, ^{11}B, ^{31}P, ^{13}C and ^{119}Sn NMR spectra were recorded as room temperature solutions on Varian Unity 300 MHz spectrometer equipped with the appropriate decoupling accessories. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$, those for ^1H, $^1H\{^{11}B\}$ and $^{13}C\{^1H\}$ NMR spectra were referenced to $SiMe_4$, and for the ^{119}Sn NMR spectrum was referenced to $SnMe_4$. ^1H NMR spectra were referenced to residual protio impurity in the solvent ($CDCl_3$, 7.26 ppm). ^{13}C NMR spectra were referenced to the solvent resonance ($CDCl_3$, 77.0 ppm; $(CD_3)_2CO$, 30.0 ppm; C_6D_6, 128.0 ppm). ^{31}P NMR spectrum was referenced to external 85% H_3PO_4. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in Hertz.

Preparation of 1-(2′-pyridyl)-2-mercapto-*ortho*-carborane (5)

To a solution of **3** (117 mg, 0.53 mmol) in dry Et_2O (20 cm^3) at 0 °C was added 1.6 M n-BuLi in hexanes (0.35 cm^3, 0.56 mmol). After stirring for *ca.* 20 min resublimed sulfur (51 mg, 1.59 mmol, 200% excess) was added and the reaction mixture was stirred at room temperature for 24 h. Water (20 cm^3) was then added and stirring continued for 1 h. Unreacted sulfur was then removed by filtration and the Et_2O solution was sequentially extracted with 1 M HCl solution (3 × 40 cm^3) and water (3 × 40 cm^3). The combined aqueous fractions were extracted with Et_2O (40 cm^3) and the recombined Et_2O fractions were then dried over $MgSO_4$. Filtration, followed by removal of the Et_2O *in vacuo* gave **5** as a white powder, recrystallised from acetone. Yield: 114 mg, 85%. $C_7H_{15}B_{10}NS$ requires: N, 5.5; C, 33.2; H, 6.0; S, 12.7. Found: N, 5.3; C, 33.4; H, 6.2; S, 12.4%. IR: ν/cm^{-1} 2935 (C_{aryl}–H), 2644 (S–H); 2596, 2584, 2572 (B–H); 1585 (C=N); 1463, 1433 (C–N); 885 (S–H); 740, 725 (C_{aryl}–H). $^1H\{^{11}B\}$ NMR ($CDCl_3$): δ 8.68 (d, 1H, $^3J_{HH}$ = 4.4, H6′), 7.80 (m, 2H, H3′, H4′), 7.43 (dd, 1H, $^3J_{HH}$ = 4.4, $^4J_{HH}$ = 1.4, H5′), 3.77 (s, SH, 1H), 2.95 (br s, BH, 2H), 2.61 (br s, BH, 2H), 2.52 (br s, BH, 3H), 2.29 (br s, BH, 1H), 2.21 (br s, BH, 2H). ^{11}B NMR ($CDCl_3$): δ −2.0 (d, $^1J_{BH}$ = 164, 1B), −4.3 (d, $^1J_{BH}$ = 134, 1B), −7.8 (d, $^1J_{BH}$ = 177, 2B), −9.5 (d, $^1J_{BH}$ = 187, 4B), −10.0 (d, $^1J_{BH}$ = 142, 2B). $^{13}C\{^1H\}$ NMR (d_6-acetone): δ 149.5 (C2′), 148.6 (C6′), 137.7 (C4′), 126.1 (C3′), 125.5 (C5′), 85.8 (C1), 77.6 (C2).

Preparation of 1-(2′-pyridyl)-2-(trimethylstannyl)-*ortho*-carborane (*6*)

To a solution of **1** (221 mg, 1.00 mmol) in dry THF (30 cm^3) at 0 °C was added 2.42 M n-BuLi in hexanes (0.42 cm^3, 1.02 mmol). After stirring at 0 °C for 30 min Me_3SnCl (200 mg, 1.00 mmol) was added and the reaction mixture was stirred for a further hour, and allowed to warm to room temperature. The nascent LiCl was removed by filtration and the THF removed *in vacuo* giving a tacky yellow solid. This solid was triturated with pentane (2 × 20 cm^3) and recrystallised from Et_2O. Yield: 285 mg, 74%. Mp 195–196 °C. $C_{10}H_{23}B_{10}NSn$ requires: C, 31.4; H, 6.1; N 3.7. Found: C, 31.4; H, 6.0; N, 3.0%. IR: ν/cm^{-1} 2986w, 2916w, 2876w (pyridyl/CH_3 str.) 2597vs, 2558sh (BH) 1636m, 1591m, 1471m, 1432vs (pyridyl skel.) 1079m, 1061m, 1003m, 825w, 765s, br (BH wag). $^1H\{^{11}B\}$ NMR ($CDCl_3$): δ 8.15 (d, 1H, $^3J_{HH}$ = 5, H6′), 7.65 (d, 1H, $^3J_{HH}$ = 8, H4′), 7.51 (d, 1H, $^3J_{HH}$ = 8, H3′), 7.25 (dd, 1H, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, H5′), 2.43 (br s, 2H, BH), 2.31 (br s, 4H, BH), 2.11 (br s, 2H, BH), 1.94 (br s, 2H, BH), 0.20 (br s + d, 9H, J_{SnH} = 54, $SnCH_3$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −1.3 (d, $^1J_{BH}$ = 145, 1B), −1.7 (d, $^1J_{BH}$ = 155, 1B), −5.9 (d, $^1J_{BH}$ = 149, 2B), −8.9 (d, 4B), −10.1 (d, $^1J_{BH}$ = 156, 2B); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 151.8 (C2′), 145.9 (C6′), 137.5 (C4′), 123.9 (C5′), 122.5 (C3′), 77.3 (C1), 67.5 (C2), −3.2 (CH_3); ^{119}Sn NMR ($CDCl_3$): δ 21.9.

Preparation of 1-(2′-pyridyl)-2-($AuPPh_3$)-*ortho*-carborane (*7*)

To a stirring solution of [1-(2′-pyridyl)-1,2-$C_2B_{10}H_{11}$] (15.5 mg, 0.07 mmol) in 4 ml of dry diethyl ether at 0 °C, was added dropwise, 0.044 ml of a 1.6 M of *n*-BuLi (0.07 mmol). After addition the reaction mixture was stirred at 0 °C for 30 min then at ambient temperature for 30 min, then 35 mg of $AuCl(PPh_3)$ (0.07 mmol) was added. After stirring for 30 min, the solid was filtered off and recrystallized from chloroform and hexane, to obtain an orange solid in 85% yield (40 mg, 0.059 mmol). $C_{25}H_{29}B_{10}NPAu$ requires C, 44.2, H, 4.3, N, 2.1. Found: C, 44.0; H, 4.3, N, 2.1%. $H\{^{11}B\}$ NMR ($CDCl_3$): 8.06–7.10 (m, 19H, PPh_3, C_5H_4N), 2.83 (br s, 2H, B–H), 2.37 (br s, 8H, B–H). ^{11}B NMR ($CDCl_3$): δ −3.5 (d, $^1J_{BH}$ = 119, 2B), −9.3 (m, 8B). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.8 (s, C2′), 136.3 (s, C6′), 134.1 (d, ^2J(C, P) = 12, C_{PPh_3}), 131.8 (d, ^3J(C, P) = 29, C_{PPh_3}), 130.0 (s, C4′), 129.1 (d, ^4J(C, P) = 8, C_{PPh_3}), 123.5 (s, C5′), 123.3 (s, C3′). ^{31}P NMR ($CDCl_3$): δ 36.4 (s, PPh_3).

X-Ray crystallography

Single crystals of **5** and **7** (colourless) were grown from acetone, those of **6** (pale yellow) from Et_2O, at room temperature. X-ray experiments for **5**–**7** were carried out at low temperatures, using Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostats. Compound **5** was studied also at room temperature; this structure (**5a**) is practically identical with the (more precise) low-temperature one (**5**), which is referred to in the discussion. Diffraction data were collected on an Enraf Nonius Kappa diffractometer (for **5** and **7**) or Bruker SMART three-circle diffractometer (for **5a** and **6**) equipped with CCD area detectors. Graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) was used.

Reflection intensities were corrected for absorption by numerical integration (based on crystal face-indexing) for **6** and by the empirical method for **7**. All structures were solved by direct methods; carbon and boron atoms of the carborane cage could be reliably distinguished by the bond distances and electron density concentration. All non-hydrogen atoms were refined with anisotropic displacement parameters and H atoms ‘riding’ in idealised positions (except the H atom bonded to S in **5** and **5a**, which was refined in isotropic approximation), by full-matrix least squares against F^2 of all reflections, using SHELXL programs.[13] The absolute configuration of **5** was determined by refinement of Flack *x* parameter[14] converging at 0.02(8). The crystal data and experimental details are listed in Table 1.

CCDC reference numbers 245430 (**5**), 239447 (**5a**), 239448 (**6**) and 245431 (**7**).

See http://www.rsc.org/suppdata/dt/b4/b411099d/ for crystallographic data in CIF or other electronic format.

Computational section

The *ab initio* computations were carried out with the Gaussian 98 package.[15] The two minima of **5** discussed here were optimised at

Table 1 Crystal data

Compound	**5**	**6**	**7**
Formula	$C_7H_{15}B_{10}NS$	$C_{10}H_{23}B_{10}NSn$	$C_{25}H_{29}B_{10}NPAu$
M	253.36	384.08	679.53
T/K	173	150	173
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$ (no. 4)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	8.3207(2)	10.009(1)	12.6732(3)
b/Å	8.1789(2)	13.544(1)	15.8053(6)
c/Å	10.5083(2)	13.516(1)	14.3786(5)
β/°	109.596(1)	107.28(1)	103.159(2)
U/Å^3	673.71(3)	1749.6(3)	2804.46(16)
Z	2	4	4
D_c/g cm^{-3}	1.249	1.458	1.609
μ/mm^{-1}	0.21	1.45	5.32
Reflections measured	2547	8408	14188
Unique reflections	2547	3149	4914
R_{int}	—	0.043	0.036
$R\,[F^2 \geq 2\sigma(F^2)]$	0.036	0.031	0.047
$wR\,(F^2)$, all data	0.087	0.074	0.049

the HF/6–31G* level with no symmetry constraints. Frequency calculations were computed on these optimised geometries at the HF/6–31G* level and revealed no imaginary frequencies. Optimisation of these geometries were then carried out at the MP2/6–31G* level. Selected parameters for minimum (total energy at −974.79590 au) of similar geometry to experimental: C(1)–C(2) 1.692 Å, N–C(12)–C(1)–C(2) −70.7°, H(2)–S–C(2)–C(1) 81.2°, N···H 3.056 Å, for less stable minimum (−974.79491 au) C(1)–C(2) 1.697 Å, N–C(12)–C(1)–C(2) 77.2°, H(2)–S–C(2)–C(1) 106.6°. The shorter C(1)–C(2) bond lengths in these optimised geometries compared to experimental are partly due to the different orientations of the SH and pyridyl groups.[26,28]

Results and discussion

Synthetic and spectroscopic aspects

1-(2′-Pyridyl)-2-mercapto-*ortho*-carborane (**5**) was prepared from compound **3**: the second cage carbon atom of the parent pyridyl carborane was lithiated using butyllithium, sulfur was inserted into the carbon–lithium bond by reaction with elemental sulfur, and the thiol liberated by working up the product with aqueous acid. The IR spectrum of **5** as a KBr disc has an absorption at 2644 cm^{-1}, consistent with the presence of a hydrogen bonded S–H moiety.[16]

Compound **6**, 1-(2′-pyridyl)-2-(trimethylstannyl)-*ortho*-carborane, was also prepared from compound **3** *via* the lithio derivative. With trimethyltin chloride, this lithio derivative afforded **6** and lithium chloride. The tin atom in compound **6** has a tetrahedral arrangement in solution, indicated by the ^{119}Sn chemical shift of 21.9 and the $^2J(^{119}Sn–C^1H_3)$ coupling constant of 54 Hz in chloroform.[6,17] A related compound, 1-phenyl-2-(trimethylstannyl)-*ortho*-carborane (*i.e.* with a phenyl group in place of the pyridyl group in **6**), has a $^2J(^{119}Sn–C^1H_3)$ coupling constant of 58 Hz in chloroform.[18] A low-temperature (−60 °C in CD_2Cl_2 solution) ^{1}H NMR study of **6** was carried out to explore whether the Sn···N interaction might be strong enough to lock the trimethyltin residue in a particular orientation at lower temperatures, so rendering the tin-attached methyl groups inequivalent. However, these methyl groups remained equivalent, consistent with free rotation of the $SnMe_3$ group about the *exo*-cluster C–Sn bond, implying that any Sn···N interactions are very weak, as expected in view of the low Lewis acidity of the $SnMe_3$ residue.

Compound **7**, 1-(2′-pyridyl)-2-(triphenylphosphine)gold-*ortho*-carborane, was also prepared from the lithio derivative of compound **3**. With $AuCl(PPh_3)$, this lithio derivative afforded **7** and lithium chloride. Comparison of the NMR data for **7** with those reported for 1-phenyl-2-(triphenylphosphine)gold-*ortho*-carborane[19] indicates little Au···N interaction is present in solutions of **7**. The ^{31}P chemical shifts are 36.4 ppm and 38.6 ppm respectively.

Structural aspects

Compound **5** crystallises in a chiral space group $P2_1$, hence it deserves checking for non-linear optical (NLO) properties, for which a non-centrosymmetric structure is a prerequisite.[20] Previous studies of carborane derivatives for NLO purposes have been reported.[21] The crystal structure of **5** shows no intramolecular S–H···N interactions; the torsion angle C(2)–C(1)–C(12)–N is 96.4(2)°. Instead, the molecules (Fig. 2) are linked by S–H···N hydrogen bonds into helices, spiralling around a 2_1 screw axis (Fig. 3).

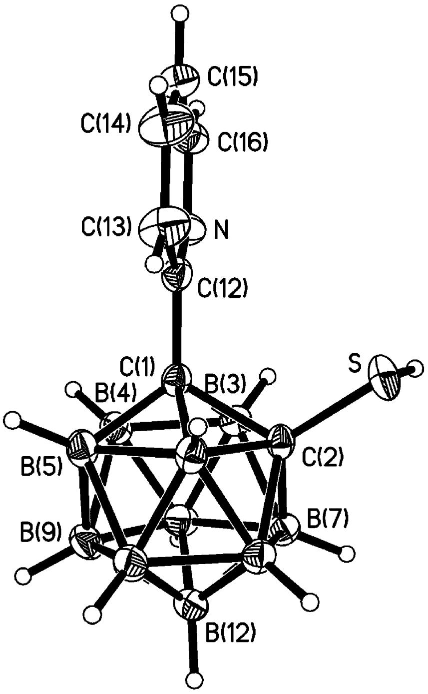

Fig. 2 Molecular structure of 1-(2′-pyridyl)-2-mercapto-*ortho*-carborane **5**. Selected bond distances (Å) and torsion angles (°): C(1)–C(2) 1.730(3), C(1)–C(12) 1.507(3), C(2)–S 1.775(2); N–C(12)–C(1)–C(2) 96.4(2), H(2)–S–C(2)–C(1) −99(2).

Within the helices, the hydrogen-bonded S···N distance of 3.445(2) Å and the S–H···N angle of 152(2)° lie within the ranges of 3.4–3.7 Å and 140–152° typical of S–H···N

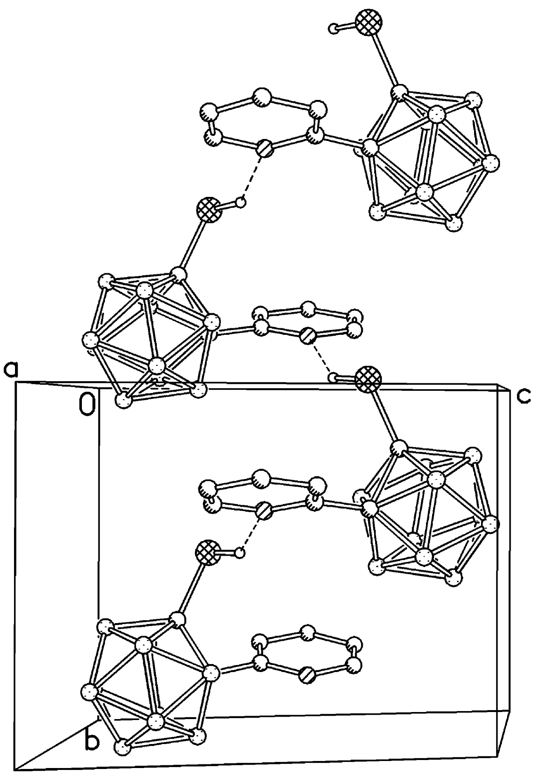

Fig. 3 Intermolecular hydrogen bonds in the crystal of **5**. Hydrogen bond distances (Å) and angles (°), S–H 1.27(3), H · · · N 2.17(3), S · · · N 3.445(2), S–H · · · N 152(2).

systems. It is interesting that the S–H · · · N hydrogen bonding in **5** is exclusively *inter*molecular, in marked contrast to the exclusively *intra*molecular C–H · · · N hydrogen bonding in the parent 1-(2′-pyridyl)-*ortho*-carborane **3**. In crystalline **3**, the pyridine ring is locked in an orientation coplanar with the C(1)–C(2)–H plane by intramolecular C(2)–H · · · N hydrogen bonding, involving the protic hydrogen on C(2). A similar orientation of the pyridine ring in **5** might have permitted S–H · · · N hydrogen bonding within a six-membered C_3SH · · · N ring in place of the five-membered C_3H · · · N ring in **3**. However, there is no *intra*molecular S–H · · · N hydrogen bonding in the crystals of **5**, in which the pyridyl and thiol substituents are orientated in planes roughly perpendicular to the C(12)–C(1)–C(2)–S plane, orientations incompatible with intramolecular S–H · · · N interactions.

Further discussions of hydrogen bonding interactions in organonitrogen derivatives of *ortho*-carborane, including the *inter*- and *intra*-molecular N · · · H–C interactions in **2** (which contains dimeric 1-(2′-picolyl)-1,2-$C_2B_{10}H_{11}$ units in the crystal) and also in an isomer of **5** (again with dimeric 1-(2′-pyridyl)-2-SH-1,2-$C_2B_{10}H_{10}$ units in the crystal) are to be found elsewhere.[9,22,23] Calculations on **5** optimised at the MP2/6–31G* level of theory have revealed two minima, one minimum comparable to that found experimentally and a slightly less stable minimum (*ca* 0.7 kcal mol^{-1}). The latter minimum has the hydrogen atom at sulfur pointing away from the pyridyl nitrogen. The experimental and computed geometries of **5** suggest intramolecular H-bonding is not favourable in **5** due to the lack of flexibility along the S–C–C–C–N link compared to the C–C–C–C–N link in **2**.

The π orbital overlap between phenyl group and tangential cluster orbitals has been invoked to explain the cage C–C lengthening in aryl-*ortho*-carborane derivatives.[24,25] This was further explored by *ab initio* RHF/6–31G* and MP2/6–31G* calculational studies on 1-phenyl-*ortho*-carborane and other aryl-carboranes in order to probe the orientational preferences of aryl groups attached to the carbon atoms of *ortho*-carborane.[26,27] These calculations have indicated that, although the overall energy of an aryl-carborane may vary only slightly with the aryl group orientation, the latter does have a perceptible influence on the C(1)–C(2) bond distance, which is greatest when the aryl group is aligned perpendicular to the aryl C–C(1)–C(2) plane. This is because this orientation optimises transfer of electronic charge from the filled π orbitals of the aryl group into a cage LUMO that is σ-antibonding with respect to the cage bond C(1)–C(2). Similar calculations on hydroxyl, amino or thiolato derivatives of *ortho*-carborane show that such derivatives also experience C(1)–C(2) bond elongation as the substituent orientation changes from coplanar to perpendicular, so increasing the capacity for dative π-bonding from what would otherwise be a lone pair p orbital on the *exo*-atom.[28] The sulfur 'lone-pair' orbital of the SH group has a similar influence on the C(1)–C(2) bond to the π orbitals of the phenyl group. Molecular orbital computations on the crystal structure of 1,2-$(SPh)_2$-1,2-$C_2B_{10}H_{10}$ indicate the transfer of electron density from the lone pairs at the sulfur atoms to the cage as mainly responsible for its long C(1)–C(2) bond length (1.798(3) Å) perhaps reinforced by the lone-pair repulsion between the two neighbouring sulfur atoms.[29,30]

These *exo*-dative π-bonding effects are believed to be responsible for the length of the cage C(1)–C(2) bond in compound **5**, which at 1.730(3) Å is *ca* 0.1 Å longer than its counterpart in pyridyl-*ortho*-carborane **3**. Even longer cage C(1)–C(2) bonds have been found in anionic thiolate compounds $[1\text{-R-2-S-1,2-}C_2B_{10}H_{10}]^-$ (R = Ph[31] or Me[32]) in which the absence of the proton on sulfur allows even stronger S–C(2) *exo* dative π-bonding than in **5**. Relevant data are listed in Table 2, which shows how the cage C(1)–C(2) bond lengthens as the *exo* C(2)–S bond shortens. The data in Table 2 also show that the cage bond-lengthening effect of a pyridyl or phenyl group or a thiolate residue at C(1) is far less than that of a pyridyl or phenyl group at C(1) and a thiolate residue at C(2).[9,33–35] It has to be pointed out that, unlike in the disubstituted carboranes, the groups at C(1) of the monosubstituted derivatives are not orientated to maximise *exo*-dative π-bonding.

The crystal structure of compound **6** (see Fig. 4) differs markedly from that of **5** in that there are no significant

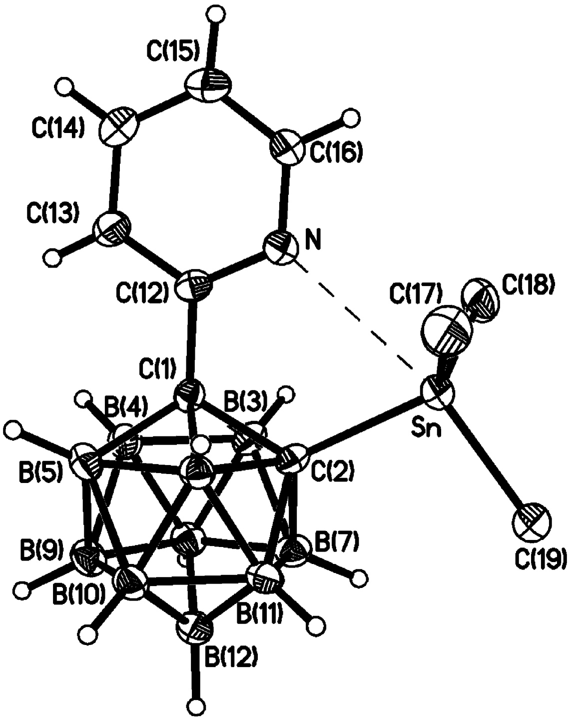

Fig. 4 Molecular structure of 1-(2′-pyridyl)-2-trimethylstannyl-*ortho*-carborane **6**. Selected bond distances (Å) and torsion angles (°): C(1)–C(2) 1.668(5), C(1)–C(12) 1.512(5), C(2)–Sn 2.207(4), N–C(12)–C(1)–C(2) −0.4(4). Methyl hydrogens are omitted for clarity.

Table 2 Bond distances (Å) in *ortho* carborane derivatives 1-R-2-X-1,2-$C_2B_{10}H_{10}$

R	X	*d*(C(1)–C(2))	*d*(C(1)–R)	*d*(C(2)–X)	Ref.
H	H	1.620(3)			33
2′-Pyridyl	H	1.632(3)	1.513(3)		9
H	S-2′-pyridyl	1.643(3)		1.778(2)	22
Ph	H	1.649(2)	1.511(2)		34
2′-Pyridyl	2′-Pyridyl	1.689(3)	1.505(4)	1.506(3)	35
2′-Pyridyl	SH	1.730(3)	1.507(3)	1.775(2)	This work
Me	S^-	1.792(5)	1.510(5)	1.735(4)	32
Ph	S^-	1.836(5)	1.495(5)	1.729(4)	31

*inter*molecular interactions. The pyridyl ring orientation is that which minimises the N···Sn distance: the C(2)–C(1)–C(12)–N torsion angle is zero within experimental error, and the tin atom lies within 0.10 Å from the pyridyl ring plane. The Sn···N distance, 2.861(3) Å, though shorter than the sum of the van der Waals radii of Sn and N (3.75 Å), is understandably longer than the sum of their covalent radii (2.15 Å), as expected in view of the low Lewis acidity of species Me_3SnR.[36] The coordination at tin is distorted from four-coordinate tetrahedral towards five-coordinate trigonal bipyramidal (TBP) in which the axial positions are occupied by the nitrogen atom and a methyl carbon atom, C(19), the N–Sn–C(19) angle being 168.1(1)°. The two geometries can be distinguished by the difference between the average equatorial and average apical angles, zero for a tetrahedron, 30° for an ideal TBP.[37] In **6** this difference (for C–C–C angles only), is 8.8(2)°, *i.e.* closer to tetrahedron than TBP. The most pronounced distortion is the widening to 118.0(2)° of the C(17)–Sn–C(18) angle, into which the pyridyl group is 'wedged'.

Conversely, **6** may be compared with an extensively studied series of systems R_3SnNX with a hypervalent interaction along the N···Sn···X axis,[38,39] (the path for nucleophilic substitution of X) with Sn···N distances ranging from 2.37 to 2.65 Å.[39] These additional intramolecular interactions can have important chemical effects, such as enhanced reactivity of Sn–C bonds[40] or stabilisation toward hydrolytic decomposition[41] and may afford unique synthetic routes to particular organotin compounds.[42] Most such studies have involved systems in which X is a relatively electronegative ligand, *e.g.* a halogen. Tetraorganotin compounds are very weak Lewis acids and only one case of additional N···SnR_4 coordination seem to have been studied structurally, a pyrazine–trimethyltin derivative with a long Sn···N distance of 3.101(5) Å and only very slight elongation of the Sn–CH_3 bond trans to the latter (2.171 Å) compared to the two *cis* (pseudo-equatorial) bonds, averaging 2.134 Å.[41] In **6** the Sn···N distance is shorter; however, the pseudo-apical Sn–C(19) bond (2.153(4) Å) is not significantly longer than the pseudo-equatorial bonds Sn–C(17), 2.134(4) Å and Sn–C(18), 2.141(4) Å. The pyridine group tilts slightly toward the tin atom, apparently due to the Sn···N attraction, but the tilt is small with the B(12)–C(1)–C(12) angle in **6** being 176.6(3)°.

Of more relevance to **6**, perhaps, is the crystal structure of a dimeric carborane assembly consisting of two 1-Me_2NCH_2-2-$SnMe_2$-1,2-$C_2B_{10}H_{10}$ moieties linked by a Sn–Sn bond.[6] This was made from **1**, BuLi and Me_2SnBr_2 followed by reduction with sodium metal. In this structure the Sn···N distances are long, averaging 3.640(8) Å, and the coordination environment of the tin atom is effectively tetrahedral.

The gold carborane **7** crystallises in a form where no *inter*molecular interactions are detected. Both the Au···N distance of 3.192(3) Å and the orientation of the pyridyl group imply weak attraction between the two atoms (Fig. 5). As there are five crystal structures in the literature[19,43–45] of the formula 1-R-2-AuL-1,2-$C_2B_{10}H_{10}$ (L = PPh_3, $AsPh_3$), selected data are listed in Table 3 for comparison with **7**. On close inspection of the table, it appears that the more electron-withdrawing the R group is, the longer the Au–C(2) bond becomes. A second trend is the more bulky the R group is, the cage C(1)–C(2) bond

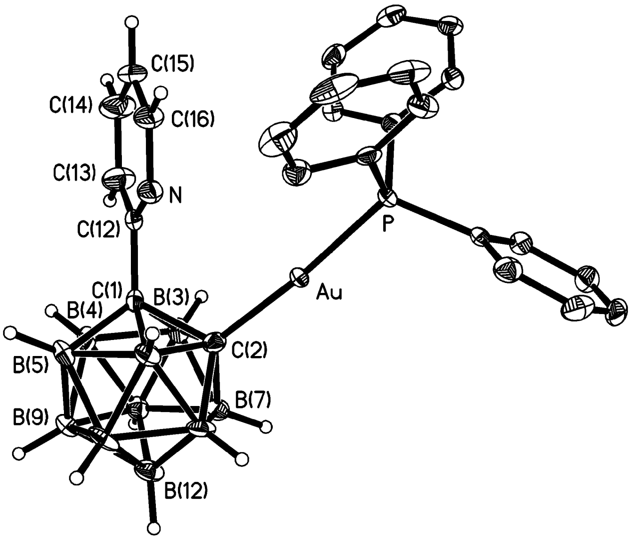

Fig. 5 Molecular structure of 1-(2′-pyridyl)-2-$AuPPh_3$-*ortho*-carborane **7**. Selected bond distances (Å) and torsion angles (°); C(1)–C(2) 1.684(5), C(1)–C(12) 1.518(5), C(2)–Au 2.069(3), Au–P 2.272(1), N–C(12)–C(1)–C(2) −64.3(4). Phenyl hydrogens are omitted for clarity.

Table 3 Bond distances (Å) in *ortho* carborane derivatives 1-R-2-AuL-1,2-$C_2B_{10}H_{10}$

R	L	*d*(C(2)–Au)	*d*(C(1)–C(2))	Ref.
H	PPh_3	2.039(8)	—[a]	43
$MeOCH_2$	$AsPh_3$	2.039(8)	1.667(11)	19
$AuPPh_3$	PPh_3	2.044(15)[b]	1.71(2)	44
$SiMe_2{}^tBu$	PPh_3	2.050(4)	1.706(6)	45
2′-Pyridyl	PPh_3	2.069(3)	1.684(5)	This work
$CB_{10}H_{10}CAu(PPh_3)$	PPh_3	2.11(3)[b]	—[c]	44

[a] Cage disorder present in crystal. [b] Averaged. [c] Values of 1.595 and 1.655 for the two C(1)–C(2) bonds suggest poor quality data. The parent bis(carborane) has a C(1)–C(2) bond length of 1.625 Å.[28]

length increases. These trends thus may reflect electronic and steric effects respectively.

The C(1)–C(2) bond distance of 1.668(5) Å in **6** is about 0.04 Å longer than in **3** but 0.06 Å shorter than in **5**. The shortening of the bond compared to **5** can be attributed in part to the parallel orientation between the pyridyl ring and the C(1)–C(2) bond[26] but more importantly to the absence of *exo* C(2)–S π bonding in **6**. However, the lengthening of the cage C–C bond in **6** compared to that in **3** is probably due to steric effects between the two bulky substituents as found elsewhere.[46] The C(1)–C(2) bond distance of 1.684(5) Å in **7** is only 0.01 Å longer than in **6** (possibly due to the different orientation of the pyridyl group). The similarities in the [1-(2′-pyridyl)-1,2-$C_2B_{10}H_{10}$] moiety for **6** and **7** suggest this carborane geometry is present in the copper intermediate **4** (M = Cu). Stronger metal$\cdots$nitrogen intramolecular interaction in **4** (M = Cu) is likely as copper is a better ligand acceptor than trimethyltin and gold moieties.

Conclusions and further work

Here we have described the syntheses and structural characterisation of three compounds made from 1-(2′-pyridyl)-*ortho*-carborane **3**. The pyridyl group in these carboranes appears to facilitate growth of suitable crystals for X-ray crystallography.

For 1-(2′-pyridyl)-2-mercapto-*ortho*-carborane **5**, the pyridyl nitrogen is involved in intermolecular hydrogen bonding—of a type which may be a suitable candidate for NLO materials—and gives the first structurally determined example of an *ortho*-carborane with a thiol substituent.

For 1-(2′-pyridyl)-2-(trimethylstannyl)-*ortho*-carborane **6**, the pyridyl nitrogen interacts weakly with the tin atom. This is the first structurally determined example of an *ortho*-carborane with a $SnMe_3$ substituent.

Compounds **3** and **5** are potential chelating ligands in transition metal complexes. Thus, 1-(2′-pyridyl)-*ortho*-carborane **3** can chelate a metal atom through an *exo*-cluster bond C–M and a (pyridyl)N→M bond whereas the thiol **5** can chelate a metal atom through a S–M bond and a N→M bond. In fact, we have recently found that the thiol **5** gives complexes of the type 1-(C_5H_4N)-2-SML_n-1,2-$C_2B_{10}H_{10}$ with the metal atom chelated by the S and N atoms of **5**.[47] We are also looking at the possibility of preparing 1-(2′-pyridyl)-2-X-3-ML_n-1,2-$C_2B_9H_9$ (where ML_n replaces a BH unit on one vertex) containing a (pyridyl)N→M bond from 1-(2′-pyridyl)-*ortho*-carborane **3**.

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