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The First Thiolate-Bridged Dinuclear Indacarboranes with σ-Coordination

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The good yield preparation and the structural analysis of three novel thiolate-bridged dinuclear σ-bonded indacarboranes $[(C_2B_9H_{11})In^{III}\{S(CH_2)_2S(CH_2)_2S\}]_2 \cdot (BzNMe_3)_2$ (**2**$\cdot(BzNMe_3)_2$), $[(C_2B_9H_{11})In^{III}(SPh)_2]_2 \cdot PPN2$ (**3**$\cdot(PPN_2)$), and $[(C_2B_9H_{11})In^{III}(SCH_2CH_2S)]_2 \cdot (PPh_3$-*p-xylyl*-$PPh_3)$ (**4**$\cdot(PPh_3$-*p-xylyl*-$PPh_3)$) which constitute the first examples of dimeric thiolatoindacarboranes are reported. The complex **2**$\cdot(BzNMe_3)$ was prepared by reacting $[(C_2B_9H_{11})InCl_2(THF)] \cdot (BzNMe_3)$ with sodium salt of bis-2-mercaptoethyl sulfide. The other two compounds were synthesized by utilizing the reactivity of indiumhalothiolate with $Tl_2(C_2B_9H_{11})$ in the presence of a suitable countercation. All three compounds crystallize in the triclinic space group $P\bar{1}$. Other crystallographic data are given in the order of the compound: unit cell parameters; V; Z; unique data ($F_o > 4.0\sigma(F_o)$); R_1. **2**$\cdot(BzNMe_3)_2$: $a = 8.608(2)$ Å, $b = 11.886(3)$ Å, $c = 13.283(4)$ Å, $\alpha = 79.39(2)°$, $\beta = 76.71(2)°$, $\gamma = 73.82(2)°$, 1259.7(6) Å^3; 1; 2489; 4.45%. **3**$\cdot(PPN)_2$: $a = 11.664(4)$ Å, $b = 11.981(4)$ Å, $c = 18.454(6)$ Å, $\alpha = 82.66(2)°$, $\beta = 81.03(2)°$, $\gamma = 86.22(2)°$; 2523.7(15) Å^3; 1; 5682; 4.50%. **4**$\cdot(PPh_3$-*p-xylyl*-$PPh_3)$: $a = 10.605(1)$ Å, $b = 12.088(2)$ Å, $c = 12.923(2)$ Å, $\alpha = 103.51(1)°$, $\beta = 94.37(1)°$, $\gamma = 105.83(2)°$; 1532.3(4) Å^3; 1; 2776; 4.13%. For all three compounds, the dimeric nature centers around a crystallographic inversion center, resulting in the rhomboid InSInS core with the S−In−S angle being acute for **2** and **3** while obtuse for **4** and the two bridging thiolate groups are arranged in *anti*-position across the planar InSInS rhomboid. All indium metal centers basically adopt distorted tetrahedral geometry with two bridging sulfur atoms, one terminal sulfur atom, and the unique boron atom although two additional weak coordinations to the indium center from the sulfide sulfur atom and the cage boron atom adjacent to the unique boron are conceivable in the case of complex **2**. In all cases, the extreme "slip distortion" of the indium center toward the unique boron atom occurs, resulting in the interaction of the InS_3 moiety with the *nido*-C_2B_9 cage via the σ-In−B10 bond in *endo*-fashion.

Introduction

The richness of the heterocarborane chemistry of the s- and p-block elements has emerged in the form of large number of examples with unique synthetic use and structural novelty.[1] In particular, the importance of the development of the convenient synthetic routes to heterocarboranes of p-block elements was pointed out owing to their potential practical uses in materials science.[1,2] However, the incidence of well-characterized indacarboranes, among others, is surprisingly very low and the examples are limited to small carborane. To date, C_2B_4−In^{III} is the only reported fragment in indacarborane complexes[3,4] where the indium metal is bonded to the open C_2B_3 face in an η^3 interactions,[4] resulting in the π-coordination, a rather ubiquitous coordination pattern observed for carborane complexes of the main group elements.[1,2,5−8] In addition, organoindium compounds containing sulfur are gathering continuing interest due to their potential application as single-source precursors for the MOCVD growth of semiconductor thin films.[9,10] Prompted by the paucity described above, attempts to explore the chemistry of indacarboranes containing sulfur were made by employing the larger carborane cage *nido*-7,8-$C_2B_9H_{11}{}^{2-}$ and thiolates, well-known for their bridging ability which can lead to multinuclear species. Here, we report the good yield preparation and the structural analysis of three novel thiolate-bridged dinuclear σ-bonded indacarboranes $[(C_2B_9H_{11})In^{III}\{S(CH_2)_2S(CH_2)_2S\}]_2 \cdot (BzNMe_3)_2$ (**2**$\cdot(BzNMe_3)_2$), $[(C_2B_9H_{11})In^{III}(SPh)_2]_2 \cdot PPN_2$ (**3**$\cdot(PPN_2)$), and $[(C_2B_9H_{11})In^{III}(SCH_2CH_2S)]_2 \cdot (PPh_3$-*p-xylyl*-$PPh_3)$ (**4**$\cdot(PPh_3$-*p-xylyl*-$PPh_3)$) which constitute the first examples of dimeric thiolatoindacarboranes.

Experimental Section

All manipulations were carried out under dinitrogen by using standard Schlenk techniques. Reagent grade solvents were distilled from

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appropriate drying agents,[11] and deuterated solvents were dried before use by trap-to-trap distillation from 3 Å activated molecular sieves. The chemicals $InCl_3$, phenyl disulfide, ethylene dithiol, bis-2-mercaptoethyl sulfide, bis(triphenylphosphoranylidene)ammonium chloride (PPNCl), $[PPh_3$-*p*-*xylyl*-$PPh_3]Br_2$, trimethylbenzylammonium chloride ($BzNMe_3Cl$), thallium acetate, and KOH were purchased from Aldrich and used as received. $[Tl_2C_2B_9H_{11}]$[12] and $[In(SPh)_2I]$[13] were prepared according to the reported procedures.

Physical Measurements. Infrared spectra were measured as KBr pellets on a Bomem MB-100 FTIR spectrometer. ^1H NMR spectra were obtained either at 200.13 MHz on a Bruker AC 200 or 300.13 MHz on a Bruker AM 300 spectrometer and were referenced to internal solvents peaks. ^{11}B NMR spectra were recorded at 96.295 MHz on a Bruker AM 300 instrument and referenced to external $BF_3 \cdot OEt_2$. All chemical shifts downfield of the reference are designated as positive. Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of the Korea Basic Science Institute.

$[(C_2B_9H_{11})In\{S(CH_2)_2S(CH_2)_2S\}]_2 \cdot (BzNMe_3)_2$ [2·$(BzNMe_3)_2$]. A 65 mg (0.35 mmol) amount of $NaS(CH_2)_2S(CH_2)_2SNa$ was added to a colorless solution of $[(C_2B_9H_{11})InCl_2(THF)] \cdot BzNMe_3$ (**1**·$BzNMe_3$)[14] generated in situ from the reaction mixture of 75 mg (0.33 mmol) of $InCl_3$, 180 mg (0.33 mmol) of $Tl_2C_2B_9H_{11}$ and 60 mg (0.33 mmol) of $BzNMe_3Cl$ in 20 mL of THF. The reaction mixture was stirred for 12 h at 30 °C, and then filtered. The volume of the filtrate was reduced to ca. 5 mL by evaporation in vacuo, and then the resulting content were treated with excess Et_2O, causing gradual formation of white crystalline solid which was collected and washed with Et_2O. The white solid was recrystallized from $THF/CH_3CN/Et_2O$, affording analytically pure colorless crystals in a yield of 63% (115 mg). Anal. Calcd for $C_{32}H_{70}N_2B_{18}S_6In_2$: C, 34.96; H, 6.42; N, 2.55. Found. C, 35.59; H, 6.62; N, 2.93. IR (KBr, cm^{-1}): $\nu_{BH} = 2567$ (s), 2542 (s), 2529 (s), 2507 (s), 2483 (s), 2474 (s), 2418 (s). ^1H NMR (ppm, CD_3CN): 1.75 (br, 2H, carboranyl CH), 3.1−2.9 (br, 13H, *Me*$_3NCH_2Ph$ + $-SCH_2CH_2S-$), 4.37 (s, 2H, Me_3NCH_2Ph), 7.4−7.6 (m, 5H, Me_3NCH_2Ph). $^{11}B\{^1H\}$ NMR (ppm, THF/10% CD_3CN): −16.2, −17.1, −20.4, −29.4, −36.7 (2:3:2:1:1).

$[(C_2B_9H_{11})In(SPh)_2]_2PPN_2$ (3·PPN_2). An equimolar slurry of 140 mg (0.30 mmol) of $In(SPh)_2I$, 165 mg of $Tl_2C_2B_9H_{11}$, and 170 mg of PPNCl in 20 mL of THF was stirred at ambient temperature for 12 h. The reaction mixture was filtered over a Celite pad, and the volume of the filtrate was reduced to ca. 5 mL in vacuo. Addition of excessive Et_2O gave white solid which was collected, washed with Et_2O, and dried in vacuo. Recrystallization from THF/Et_2O solution afforded analytically pure colorless crystals in a yield of 43% (130 mg). Anal. Calcd for $C_{100}H_{102}N_2B_{18}P_4S_4In_2$: C, 59.81; H, 5.12; N, 1.39. Found. C, 60.22; H, 5.44; N, 1.25. IR (KBr, cm^{-1}): $\nu_{BH} = 2544$ (s), 2524 (s), 2510 (s), 2493 (s), 2455 (s). ^1H NMR (ppm, CD_3CN): 1.45 (br, 2H, carboranyl CH), 7.1−7.7 (m, 40H, phenyl). $^{11}B\{^1H\}$ NMR (ppm, THF/10% CD_3CN): −15.4, −16.8, −20.5, −31.2, −35.8 (2:3:2:1:1).

$[(C_2B_9H_{11})In(SCH_2CH_2S)]_2 \cdot (PPh_3$-*p*-*xylyl*-$PPh_3)$ (4·(PPh_3-*p*-*xylyl*-PPh_3)). A mixture of 135 mg (0.60 mmol) of $InCl_3$, 85 mg (0.60 mmol) of $NaSCH_2CH_2SNa$, and 240 mg (0.30 mmol) of $[PPh_3$-*p*-*xylyl*-$PPh_3]Br_2$ in 20 mL of DMF was stirred at ambient temperature for 12 h and filtered. A 325 mg (0.60 mmol) amount of $Tl_2C_2B_9H_{11}$ was added to the filtrate, and the resulting solution was stirred for 5 h and then filtered. The resulting colorless filtrate was reduced in volume, and addition of Et_2O afforded white solid, which was collected, washed with THF, and dried in vacuo. Recrystallization from $DMF/CH_3CN/Et_2O$ solution afforded analytically pure colorless crystals in a yield of 54% (210 mg). Anal. Calcd for $C_{52}H_{68}B_{18}P_2S_4In_2$: C, 47.77; H, 5.24. Found. C, 47.58; H, 5.34. IR (KBr, cm^{-1}): $\nu_{BH} = 2578$ (s), 2531 (s), 2518 (sh), 2500 (s), 2475 (s). ^1H NMR (ppm, DMSO-d_6): 1.48 (br, 4H, carboranyl CH), 2.79 (s, 8H, $-SCH_2CH_2S-$), 5.07 (d, 4H, $PPh_3-CH_2C_6H_4CH_2-PPh_3$), 6.75 (s, 4H, $PPh_3-CH_2C_6H_4CH_2-PPh_3$), 7.56−7.92 (m, 30H, $PPh_3-CH_2C_6H_4CH_2-PPh_3$). $^{11}B\{^1H\}$ NMR (ppm, DMF/10% CD_3CN): −15.7, −20.7, −32.3, −36.1 (5: 2:1:1).

X-ray Structural Determination. Reflection data were collected on an Enraf-Nonius CAD4TSB diffractometer equipped with graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation at 20 °C. Accurate cell parameters and orientation matrixes for **2**·$(BzNMe_3)_2$, **3**·PPN_2, and **4**·(PPh_3-*p*-*xylyl*-PPh_3) were determined from the least-squares fit of 25 accurately centered reflections in the range of $5° \le \theta \le 13°$, $6° \le \theta \le 12°$, and $8.5° \le \theta \le 14°$, respectively. Totals of 2836, 6150, and 3335 reflections were scanned in the ranges $1.59° < \theta < 24.98°$, $1.13° < \theta < 22.51°$, and $2.02° < \theta < 21.98°$ for **2**·$(BzNMe_3)_2$, **3**·PPN_2, and **4**·(PPh_3-*p*-*xylyl*-PPh_3), respectively. All data were collected with the $\omega/2\theta$ scan mode and corrected for *Lp* effects. Ψ-scan absorption corrections were applied.

The structures of all compounds were solved by Patterson's heavy atom methods (SHELXS-86).[15] Non-hydrogen atoms were refined by full-matrix least-squares techniques (SHELXL-93)[16] with anisotropic displacement parameters. The phenyl rings were refined as rigid groups with fixed bond lengths ($d_{C-C} = 1.390$ Å) and angles (120.0°). Carboranyl hydrogen atoms were included in the located positions. Phenyl, methyl, and methylene hydrogen atoms were placed at their geometrically calculated positions ($d_{CH} = 0.930$ Å for phenyl, 0.960 Å for methyl, and 0.970 Å for methylene) and refined riding on the corresponding carbon atoms with isotropic thermal parameters ($U = 1.2U(C_{phenyl})$, $1.5U(C_{methyl})$, and $1.2U(C_{methylene})$. The goodness of fit for all observed reflections was 1.112 for **2**·$(BzNMe_3)_2$, 1.072 for **3**·PPN_2, and 1.045 for **4**·(PPh_3-*p*-*xylyl*-PPh_3). Maximum and minimum peaks in the final difference synthesis were 1.383 and −0.667 e Å^3 for **2**·$(BzNMe_3)_2$, 1.314 and −0.878 e Å^3 for **3**·PPN_2, and 0.682 and −0.490 e Å^3 for **4**·(PPh_3-*p*-*xylyl*-PPh_3).The final R_1 and weighted wR_2 were 0.0445 and 0.0905 for 2489 reflections with $|F_o| > 4.0\sigma(F_o)$ in **2**·$(BzNMe_3)_2$, 0.0450 and 0.1167 for 5682 reflections in **3**·$(PPN)_2$, and 0.0413 and 0.0842 for 2776 reflections in **4**·(PPh_3-*p*-*xylyl*-PPh_3), respectively. Details of other crystallographic data for three complexes are given in Table 1.

Results and Discussion

Reactions. Aside from its renown as an excellent ligand, the dicarbollide moiety is remarkable for its ability to stabilize both high[17] and low[18] metal oxidation states. It is noticeable in possessing physicochemical and coordination properties that are more diverse than those of any other cluster. In our earlier work,[14] we observed that the chlorides in $[(C_2B_9H_{11})InCl_2(THF)] \cdot BzNMe_3$ (**1**·$BzNMe_3$) were labile enough to undergo nucleophilic substitution with various nucleophiles such as $[TlC_2B_9H_{11}]^-$ and $[HBPz^*{}_3]^-$ (Pz* = 3,5-dimethylpyrazolyl) to form stable complexes $[In(C_2B_9H_{11})_2]^-$ and $[(HBPz^*{}_3)In(C_2B_9H_{11})]$, respectively. Thus, the use of monoanionic chloroindacarborane **1** as a synthon in deriving thiolatoindacarborane was attempted as outlined in Scheme 1. When **1**·$BzNMe_3$, generated in situ from the one-pot reaction of $InCl_3$, $Tl_2C_2B_9H_{11}$, and $BzNMe_3Cl$ in an 1:1:1 molar ratio, was reacted with 1 equiv of $NaS(CH_2)_2S(CH_2)_2SNa$ in THF, the thiolate-bridged dinuclear complex **2**·$(BzNMe_3)_2$ was formed. The reaction temperature seems to be crucial in this reaction system since no reaction was observed at temperatures under 20 °C. On the other hand, analogous reactions of **1** with NaSPh or $NaS(CH_2CH_2)SNa$ did

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Table 1. Crystallographic Data for $[(C_2B_9H_{11})In(S(CH_2)_2S(CH_2)_2S]_2\cdot(BzNMe_3)_2$ (**2**·$(BzNMe_3)_2$), $[(C_2B_9H_{11})In(SPh)_2]_2\cdot(PPN_2)$ (**3**·(PPN_2)), and $[(C_2B_9H_{11})In(S(CH_2)_2S)]_2\cdot(Ph_3P\text{-}p\text{-xylyl-}PPh_3)$ (**4**·$(Ph_3P\text{-}p\text{-xylyl-}PPh_3)$)

	2·$(BzNMe_3)_2$	**3**·(PPN_2)	**4**·$(Ph_3P\text{-}p\text{-xylyl-}PPh_3)$
empirical formula	$C_{32}H_{70}N_2B_{18}S_6In_2$	$C_{100}H_{102}N_2B_{18}P_4S_4In_2$	$C_{52}H_{68}B_{18}P_2S_4In_2$
fw	1099.48	2008.18	1307.46
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
λ (Å)	0.710 73	0.710 73	0.710 73
a (Å)	8.608(2)	11.664(4)	10.605(1)
b (Å)	11.886(3)	11.981(4)	12.088(2)
c (Å)	13.283(4)	18.454(6)	12.923(2)
α (deg)	79.39(2)	82.66(2)	103.51(1)
β (deg)	76.71(2)	81.03(2)	94.37(1)
γ (deg)	73.82(2)	86.22(2)	105.83(1)
V (Å^3)	1259.7(6)	2523.7(15)	1532.3(4)
Z	1	1	1
D_{calc} (g/cm^3)	1.449	1.321	1.417
μ (mm^{-1})	1.192	0.650	0.977
T (°C)	20	20	20
R1 ($\lvert F_o\rvert > 4\sigma(F_o)$)[a]	0.0445	0.0450	0.0413
wR2 ($\lvert F_o\rvert > 4\sigma(F_o)$)[b]	0.0905	0.1167	0.0842
x	0.0282	0.0707	0.0402
y	2.5875	3.9626	1.7076

[a] $R1 = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$.

Scheme 1

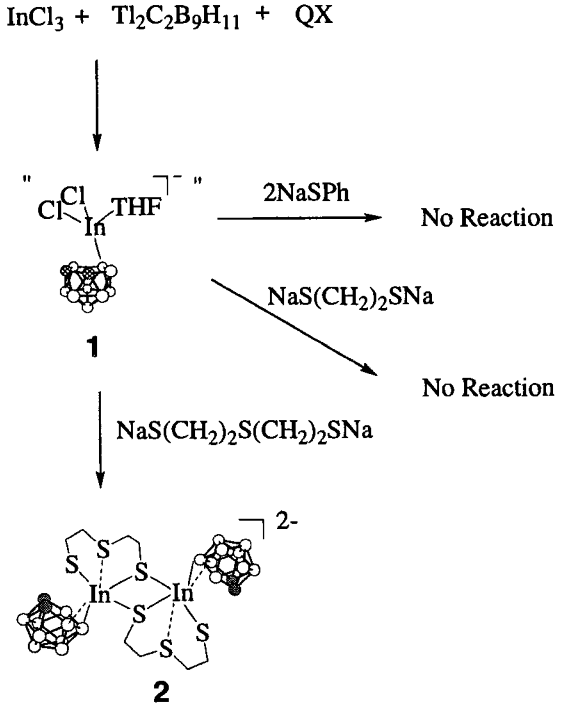

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**, **3**, and **4**

	2	**3**	**4**
In−In′	3.879 (1)	3.844 (1)	3.621 (1)
In−S1	2.541(2)	2.655(2)	2.613(2)
In−S2	2.442(2)	2.453(2)	2.418(2)
In−S1′	2.747(2)	2.606(2)	2.577(2)
In−S3	3.098(2)		
In−B9	2.553(8)	2.587(6)	2.595(7)
In−B10	2.354(8)	2.263(6)	2.281(7)
In−B11	2.755(10)	2.662(6)	2.602(8)
In−C7	3.102(7)	3.094(6)	3.038(7)
In−C8	3.001(7)	3.069(5)	3.044(6)
C7−C8	1.558(9)	1.543(8)	1.558(9)
C7−B11	1.609(8)	1.608(8)	1.620(10)
C8−B9	1.642(9)	1.619(9)	1.607(10)
B9−B10	1.807(9)	1.834(8)	1.822(11)
B10−B11	1.771(10)	1.816(9)	1.806(11)
S1−In−S2	116.03(8)	100.68(5)	88.42(6)
S1−In−S1′	85.71(6)	86.12(5)	91.53(6)
S1−In−B10	108.6(2)	105.92(15)	110.1(2)
S2−In−B10	135.30(2)	137.8(2)	143.0(2)
S2−In−S1′	82.99(6)	100.82(5)	101.21(7)
B10−In−S1′	99.21(16)	113.0(2)	109.6(2)
In−S1−In′	94.29(6)	93.88(5)	88.47(6)
In−B10−B9	74.4(3)	77.5(3)	77.6(4)
In−B10−B11	82.5(4)	80.7(3)	78.1(4)

not proceed to generate the desired thiolatoindacarboranes as confirmed by in situ $^{11}B\{^1H\}$ NMR spectra of the reaction mixtures. The preparation of **3**·$(PPN)_2$ and **4**·$(PPh_3$-*p-xylyl*-$PPh_3)$ was achieved by utilizing the corresponding indiumhalothiolates as outlined in Scheme 2.

Structures. The molecular structures of **2, 3**, and **4**, displayed in Figures 1, 2, and 3, respectively, reveal the dimeric nature centered around a crystallographic inversion center. The resulting InSInS cores are rhomboids with the S−In−S angle being acute for **2** and **3** while obtuse for **4**. The values for the selected bond distances and angles, listed in Table 2, indicate that the extent of obliqueness of the rhomboids is small. The $In^{III}-In^{III}$ distances of 3.879 (1), 3.844 (1) and 3.621(1) Å in **2**, **3**, and **4**, respectively, can be compared with that (3.696(1) Å) found in $[1\text{-}(CHMe_2)\text{-}1\text{-}In^{III}\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2$,[4a] that (3.591(4) Å) observed in $[Li(tmeda)_2][Me_3In-H-InMe_3]$[19] and the sum (3.8 Å) of the van der Waals radius[20] for two indium atoms.

In all three compounds, the two bridging thiolate groups are arranged in *anti*-position across the planar InSInS rhomboid and the indium metal centers basically adopt distorted tetrahedral geometry with two bridging sulfur atoms, one terminal sulfur atom, and the unique boron atom. In the case of the complex **2**, two additional weak coordination to the indium center from the sulfide sulfur atom and the cage boron atom adjacent to the unique boron, indicated as dotted lines in Figure 1, are conceivable based on the comparison of the geometric values (vide infra).

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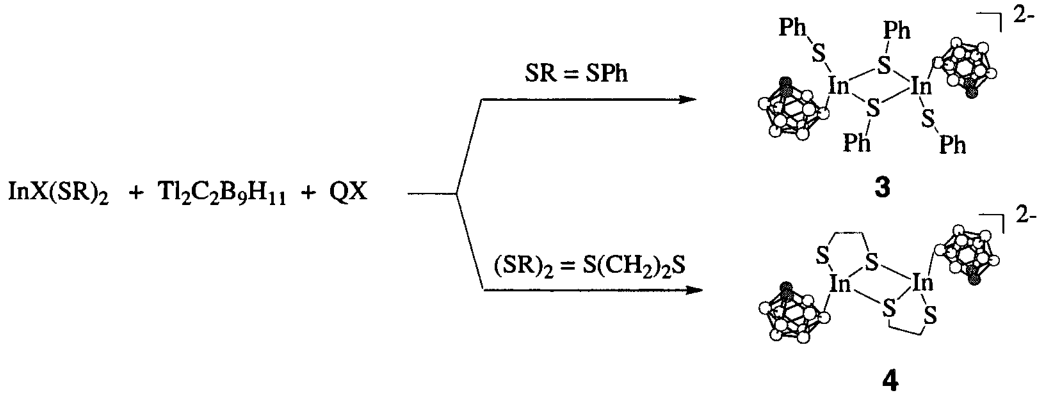
Scheme 2



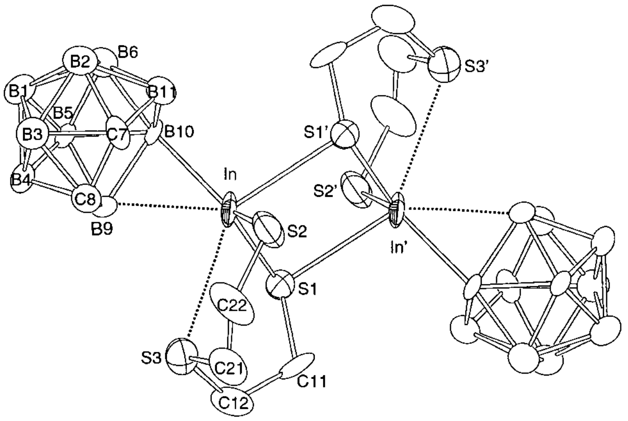


Figure 1. ORTEP drawing of **2**. All hydrogen atoms have been omitted for clarity.

The bond distances between indium and terminal thiolate sulfur atom for three compounds are in the range of 2.418−2.453 Å (Table 2) which is in good agreement with the sum (2.46 Å) of Shannon's ionic radii[21] of tetrahedral In(III) and S^{2-} as well as with the average In−S distances observed in $[BrIn(SPh)_3]^-$ (2.450 Å)[22] and $[In(SC_6H_3\text{-}2,6\text{-}Me_2)_4]^-$ (2.464 Å).[23] The bridging thiolate sulfur atoms interact asymmetrically with indium metal centers, giving two sets of In−S distances. The difference between two sets is only about 0.05 Å for **3** and **4** but is significantly large as 0.21 Å for **2**. Sulfide sulfur atom of the bis-2-mercaptoethyl sulfide ligand in **2** does not seem to behave as a simple spectator since it has an interatomic distance of 3.100 Å with indium (In−S3) which is shorter than the sum (3.7 Å) of van der Waals radii[20] for In and S. It is interesting to note that such a weak interaction behavior of bis-2-mercaptoethyl sulfide ligand has not been precedented in transition metal complexes but was observed in main group element complexes of $Ge(S(CH_2)_2S(CH_2)_2S)Cl_2$ (3.005 Å),[24] $Sn(S(CH_2)_2S(CH_2)_2S)Cl_2$ (2.760 Å),[25] $As(S(CH_2)_2S(CH_2)_2S)Cl$ (2.719 Å),[26] and $Sb(S(CH_2)_2S(CH_2)_2S)(p\text{-}C_6H_4NO_2)$ (3.189 Å).[27] The analysis of the torsional angles in **2** shows that the octagon thioether−In ring has the boat−chair conformation.

The consideration of the electron configuration of the indium atoms deserves comment since it would provide reasons for the presence of the dimeric nature and the asymmetric interaction of the bridging thiolate sulfur atoms with indium atoms. In counting the electrons for the indium atoms in the crystallographic asymmetric monomer units in **2**, **3**, and **4**, presumably the cage and the two thiolate sulfurs, S1 and S2, are each providing one electron each and indium atom also provides three electrons to give a total of 6 electrons at the indium atom. Then the two additional electrons needed for an octet at the indium atom are supplied by a S1′ → In dative bond, leading to the dimeric nature and possibly to the asymmetric interaction of the bridging thiolate sulfur atoms with indium atoms. The extent of asymmetry is relatively small for the compounds **3** and **4** but large for **2**. The large asymmetry seen in **2** might be ascribed to the additional two weak interactions between indium atom and S3 and B9 atoms as indicated by the analysis of geometric parameters.

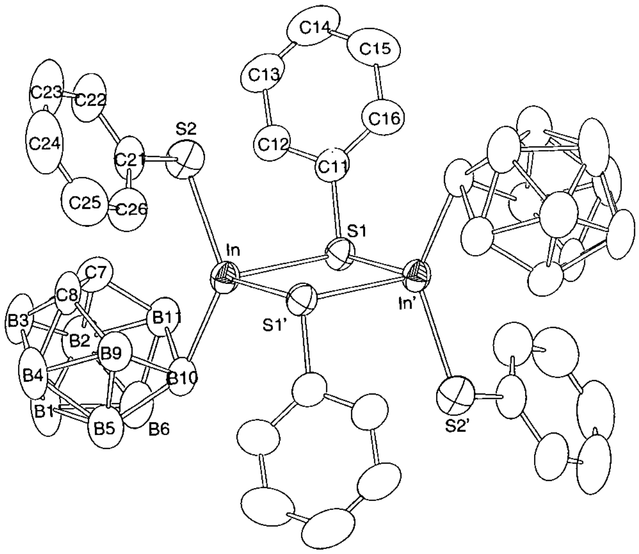


Figure 2. ORTEP drawing of **3**. All hydrogen atoms have been omitted for clarity.

As can be seen in Figure 4, the coordination leads to an extreme "slip distortion" of the indium center toward the unique boron atom in **3** and **4**, resulting in the interaction of the InS_3 moiety with the *nido*-C_2B_9 cage via a σ-In−B10 bond in *endo*-fashion. The slip parameter Δ,[28] which quantifies the extent of the slip distortion, is 1.056 and 0.949 Å for **3** and **4**, respectively. These values are consistent with the reported values of 0.91,

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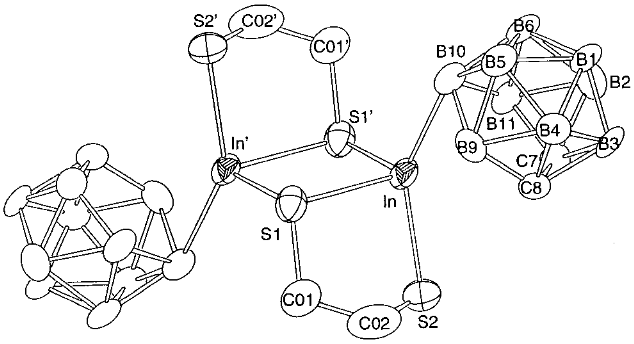
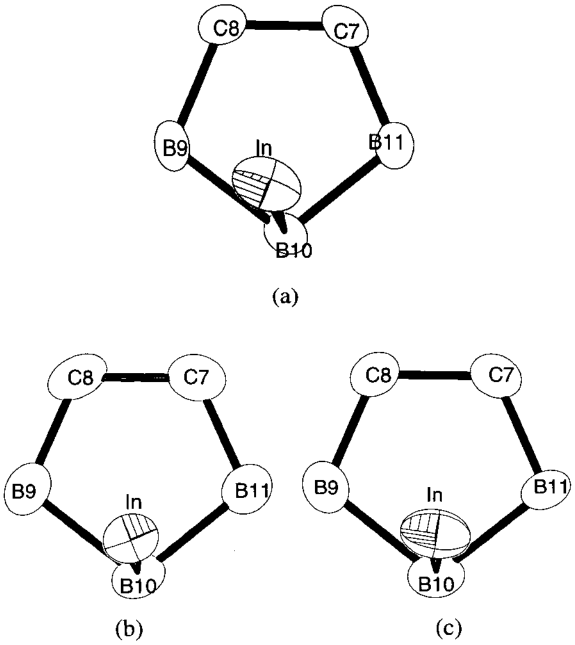


Figure 3. ORTEP drawing of **4**. All hydrogen atoms have been omitted for clarity.



(a)

(b)

(c)

Figure 4. Projection of (a) the indium atom in **2**, (b) the indium atom in **3**, and (c) the indium atom in **4** onto the open C_2B_3 pentagonal plane.

0.87, 0.92, 1.257, and 0.96 Å for σ-bonded heterocarboranes [10-*endo*-L-7,8-*nido*-$C_2B_9H_{11}$] (L = H,[29] Ph_3PAu,[30] Ph_3PHg[31]), [10-*endo*-$SnPh_3$-10-μ-*H*-7,8-*nido*-$C_2B_9H_{11}$]$^-$,[32] and [*endo*-10-{$AlEt(PEt_3)_2$}-7,8-$C_2B_9H_{11}$],[7a] respectively. In **2**, the indium atom also shows extreme slip distortion to the unique boron atom B10. But the shorter In−B9 distance of 2.553(8) Å compared to the In−B11 distance of 2.755(10) Å and the shorter In−B10 distance of 2.354(7) Å compared to the In−B9 distance imply the asymmetric shift of the indium atom toward B9 boron atom and thus the presence of an asymmetric *endo*-η^2 bonding. This structural feature is depicted in Figures 1 and 4a. The compound **2** constitutes the first example of the *endo*-η^2 bonding mode in the C_2B_9 carborane system.[33,34] The metal slip distortion is a common observation in the main group metallacarborane chemistry,[1,2,5−8,35] but η^1 σ-coordination and η^2 bonding are still relatively rare. The compounds **2**, **3**, and **4** constitute not only the new addition to the list of examples with the *endo*-η^1 or η^2 type interaction but also the first indacarboranes with the C_2B_9 cage to the best of our knowledge.

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Supporting Information Available: Tables listing details of the crystallographic data collection, positional and equivalent isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles for **2**, **3**, and **4** (20 pages). Ordering information is given on any current masthead page.

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