Notes

Thiosemicarbazone Complexes of Indium with New Modes of Coordination: X-ray Crystal Structure of $\{(Me_2In)_2[NC_5H_4CMeNNC(S)NC_6H_5]_2\}(InMe)$

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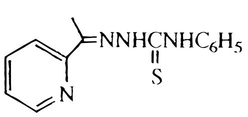
*Summary: The trinuclear complex $\{(Me_2In)_2[NC_5H_4CMeNNC(S)NC_6H_5]_2\}(InMe)$ (**3**) has been prepared. X-ray analysis reveals that the two indium moieties are coordinated to the three nitrogen atoms in the ligand and the one indium moiety is attached to the two nitrogen and two sulfur atoms of the two ligands. The trinuclear nature and unusual distorted-square-pyramidal coordination geometry of the indium centers for **3** were confirmed through single-crystal X-ray diffraction analyses.*

α-N-Heterocyclic carboxaldehyde thiosemicarbazones and bis(thiosemicarbazones) comprise two interesting classes of experimental cancer chemotherapeutic agents.[1] Extensive studies on the antitumor properties of metal complexes of heterocyclic carboxaldehyde thiosemicarbazones have been well-documented.[2] Radioactive congeners of gallium (^{67}Ga, ^{68}Ga) and indium (^{111}In, ^{113}In) are γ-ray emitters with energies which make them useful for medical imaging.[3] Although the coordination chemistry of heterocyclic carboxaldehyde thiosemicarbazones with gallium and indium remains relatively unexplored,[4] the potential for the development of materials for medical imaging has been recognized. Recently, we have prepared a series of dinuclear aluminum and gallium heterocyclic carboxaldehyde thiosemicarbazone complexes[5] and trinuclear aluminum and gallium complexes of bis(thiosemicarbazones).[6] As part of our continuing studies into the synthetic utility and the understanding of the uncommon coordination geometry of these important ligands with indium, we attempted to synthesize trinuclear neutral indium complexes using thiosemicarbazone ligands **1** and **2**, which we have used successfully for opening up a new field of multinuclear organoindium derivatives. We report here the synthesis and characterization of indium heterocyclic carboxaldehyde thiosemicarbazone and bis(thiosemicarbazone) complexes.



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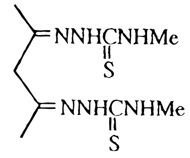

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Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free dinitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. Toluene and hexane were freshly distilled from sodium/benzophenone prior to use. All ^1H and ^{13}C NMR spectra were measured on a Bruker WH-300 spectrometer. Chemical shifts were referenced relative to either TMS (^1H) or benzene-d_6 (^1H, δ 7.155; $^{13}C\{^1H\}$, δ 128.00). IR spectra were recored on a Shimadzu FT IR-8501 spectrometer. Mass spectra were recorded on a high-resolution VG 70-VSEG instrument, and elemental analyses were performed by the Basic Science Center. The ligands $[NC_5H_4CCH_3NNHC(S)NHC_6H_5]$ and bis(thiosemicarbazone) were prepared according to the literature methods.[7] $AlMe_3$ and $GaMe_3$ were purchased from Strem Chemicals.

Synthesis of $\{(Me_2In)_2[NC_5H_4CMeNNC(S)NC_6H_5]_2\}(InMe)\cdot THF$ (3). A solution of $InMe_3$ (0.48 g, 3 mmol) in toluene (10 mL) was added over 10 min to a solution of **1** (0.27

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Table 1. Crystallographic Data for the Structural Studies of Compounds 3 and 4

	3	**4**
empirical formula	$C_{37}H_{47}N_8OS_2In_3$	$C_{22}H_{45}N_6S_2O_2In_3$
fw	1027.88	833.85
cryst syst	monoclinic	orthorhombic
space group	*C*2/*c*	*P*2$_1$2$_1$2$_1$
cell constants		
a, Å	22.783(1)	15.096(3)
b, Å	7.079(0)	16.922(3)
c, Å	29.177(1)	12.706(2)
β, deg	96.940(2)	
V, Å^3	4671.4(2)	3245.8(1)
Z	4	4
D_{calcd}, g cm^{-3}	1.56	1.69
F(000)	254	316
λ(Mo Kα), cm^{-1}	0.710 69	0.710 69
μ, mm^{-1}	15.91	22.67
no. of processed rflns	16 438	12 100
total no. of unique rflns	4166	3317
no. of obsd rflns	3111	2532
R_{merge}	0.05	0.06
goodness of fit	1.69	1.69
R1[a]	0.036	0.043
wR2[a]	0.047	0.048

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum w[(F_o{}^2 - F_c{}^2)^2]/\sum[wF_o{}^2]\}^{1/2}$.

g, 1 mmol) in toluene (10 mL). After 5 h at room temperature the volatiles were removed in vacuo, to yield a white solid. This was recrystallized as yellow prisms overnight at −20 °C from THF (5 mL) and hexane (2 mL) (0.32 g, 62% yield). Mp: 216−218 °C dec. ^{1}H NMR (300 MHz, C_6D_6): δ 7.40−6.88 (m, 18H, C_6H_5 and NC_5H_4), 3.57 (m, 2H, OC_4H_8), 1.48 (m, 2H, OC_4H_8), 1.23 (s, 6H, CCH_3), 0.43 (s, 12H, $InCH_3$), 0.27 (s, 3H, $InCH_3$). ^{13}C NMR (C_6D_6): δ 176.36 (*C*S), 167.07 (*C*N), 144.66, 140.63, 129.00, 128.65, 125.05, 123.21, 122.41, 120.48, 118.80, 106.19 (C_6H_5 and NC_5H_4), 67.50 (OC_4H_8), 31.66 (OC_4H_8), 22.74 (CCH_3), 1.06 ($InCH_3$), −4.26 ($InCH_3$). IR (as KBr pellet; cm^{-1}): 2992 (w), 2968 (w), 1594 (m), 1546 (w), 1502 (s), 1472 (s), 1368 (w), 1342 (w), 1292 (w), 1192 (s), 1151 (m), 1100 (w), 1072 (m), 1025 (w), 998 (w), 943 (m), 901 (w), 810 (w), 782 (m), 740 (w), 698 (s), 675 (m), 648 (w), 638 (w), 560 (w), 508 (m), 480 (w), 408 (w). MS (CI): *m/z* 956 (M$^+$). Anal. Calcd for $C_{37}H_{47}N_8OS_2In_3$: C, 43.22; H, 4.57. Found: C, 42.76; H, 4.32.

Synthesis of {((THF)Me$_2$In)$_2$[CH$_2$(MeCNNC(S)NMe)$_2$]}(InMe) (4). To a solution of **2** (0.38 g, 1.38 mmol) in toluene (10 mL) at room temperature was added $InMe_3$ (0.662 g, 4.14 mmol) in toluene (10 mL) via syringe. The reaction mixture was stirred for 5 h at room temperature. All volatiles were removed under reduced pressure to give a residue, from which the product was extracted with THF (10 mL). A 2 mL volume of hexane was layered on this solution, and this mixture was then set aside in the freezer (−20 °C) for 2 days to give yellow crystals in 48% yield. Mp: 146−148 °C dec. ^{1}H NMR (300 MHz, C_6D_6): δ 3.74 (d, *J* = 12.68 Hz, 1H, C*H*), 3.57 (m, 4H, OC_4H_8), 3.26 (s, 3H, NCH_3), 3.04 (s, 3H, NCH_3), 1.65 (d, *J* = 12.68 Hz, 1H, C*H*), 1.48 (s, 3H, CCH_3), 1.43 (m, 4H, OC_4H_8), 1.38 (s, 3H, CCH_3), 0.23 (s, 6H, $InCH_3$), 0.18 (s, 6H, $InCH_3$), 0.15 (s, 3H, $InCH_3$). ^{13}C NMR (300 MHz, C_6D_6): δ 182.01 (*C*S), 179.84 (*C*S), 143.28 (*C*(CH$_3$)N), 141.83 (*C*(CH$_3$)N), 68.42 (OC_4H_8), 41.32 (CH_2), 38.01 (NCH_3), 36.00 (NCH_3), 25.51 (OC_4H_8), 24.79 (CCH_3), 18.62 (CCH_3), −2.71 ($InCH_3$), −4.18 ($InCH_3$), −6.81 ($InCH_3$). IR (as KBr pellet; cm^{-1}): 3382 (m), 2946 (w), 1612 (m), 1526 (s), 1492 (s), 1432 (w), 1404 (m), 1355 (w), 1278 (w), 1253 (w), 1242 (m), 1168 (m), 1092 (w), 1047 (w), 1012 (w), 942 (w), 848 (w), 782 (m), 696 (s), 625 (w), 600 (w), 504 (m), 448 (m). MS (CI): *m/z* 834 (M$^+$). The moisture sensitivity prevented elemental analysis.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3

In(1)−S(1)	2.491(2)	In(2)−C(21)	2.143(7)
In(1)−N(9)	2.394(4)	S(11)−C(10)	1.746(5)
In(1)−C(19)	2.10(1)	N(8)−N(9)	1.370(5)
In(2)−N(1)	2.418(4)	N(8)−C(7)	1.296(6)
In(2)−N(8)	2.317(4)	N(9)−C(10)	1.389(6)
In(2)−N(12)	2.298(4)	N(12)−C(10)	1.291(7)
In(2)−C(20)	2.151(7)		
S(11)−In(1)−S(11*)	109.38(8)	N(9)−In(1)−C(19)	108.0(1)
S(11)−In(1)−N(9)	64.3(1)	N(1)−In(2)−N(8)	68.1(1)
S(11)−In(1)−N(9*)	94.4(1)	N(1)−In(2)−N(12)	137.4(1)
S(11)−In(1)−C(19)	125.31(4)	N(8)−In(2)−N(12)	69.3(1)
S(11)−In(1)−N(9)	64.3(1)	C(20)−In(2)−C(21)	139.7(3)
N(9)−In(1)−N(9*)	144.1(2)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for 4

In(1)−S(11)	2.550(4)	In(3)−N(17)	2.19(1)
In(1)−N(1)	2.16(1)	In(3)−C(21)	2.13(1)
In(1)−N(4)	2.30(1)	In(3)−C(22)	2.13(2)
In(1)−N(9)	2.271(9)	S(11)−C(10)	1.75(1)
In(1)−C(12)	2.17(4)	S(14)−C(2)	1.77(1)
In(2)−S(14)	2.561(4)	N(1)−C(2)	1.31(2)
In(2)−O(1)	2.57(1)	N(3)−N(4)	1.38(1)
In(2)−N(3)	2.33(1)	N(3)−C(2)	1.36(2)
In(2)−C(18)	2.13(4)	N(4)−C(5)	1.28(1)
In(2)−C(19)	2.18(2)	N(8)−N(9)	1.36(1)
In(2)−O(2)	2.572(8)	N(8)−C(7)	1.29(1)
In(2)−N(8)	2.358(9)	N(9)−C(10)	1.36(1)
S(11)−In(1)−N(1)	96.8(3)	S(14)−In(2)−O(1)	82.2(3)
S(11)−In(1)−N(4)	132.4(2)	S(14)−In(2)−N(3)	63.9(3)
S(11)−In(1)−N(9)	64.9(3)	S(14)−In(2)−C(18)	119.5(4)
S(11)−In(1)−C(12)	119.5(4)	S(14)−In(2)−C(19)	112.5(5)
N(1)−In(1)−N(4)	72.0(4)	O(1)−In(2)−N(3)	145.8(4)
N(1)−In(1)−N(9)	124.0(4)	O(2)−In(3)−N(8)	161.4(3)
N(4)−In(1)−N(9)	83.1(3)	N(8)−In(3)−N(17)	71.7(3)

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **3** and **4** are given in Table 1. The crystals of **3** and **4** were grown from toluene/hexane solution at −15 °C. The crystals of **3** and **4** were mounted in thin-walled glass capillaries and sealed under argon. The data sets of **3** and **4** were collected using a Rigaku/RAXIS IIa area detector employing graphite-monochromated Mo Kα radiation (λ = 0.710 96 Å) at a temperature of 253 K. The structures were solved by direct methods. Refinements were by full-matrix least-squares techniques based on *F* to minimize the quantity $\sum w(|F_o| - F_c|)^2$ with $w = 1/\sigma^2(F)$. Non-hydrogen atoms of **3** and **4** were anisotropically refined, and hydrogen atoms were isotropically refined. The hydrogen atoms of **3** and **4** were included as constant contributions to the structure factors. The refinement of **3** converged to R1 = 0.036 and R2 = 0.047 and that of **4** converged to R1 = 0.043 and R2 = 0.048. Selected bond distances for **3** and **4** are given in Tables 2 and 3, respectively. The molecular structures of compounds **3** and **4** are given in Figures 1 and 3, respectively.

Results and Discussion

Synthesis and Characterization. The reaction of 2-acetylpyridine 4-phenylthiosemicarbazone with trimethylindium in toluene affords the organoindium complex, in which four hydrogen atoms have been lost from the aza hydrogen atoms via the methane elimination reaction. The yellow complex **3** was isolated as air-sensitive crystalline solids. This complex is readily soluble in benzene, toluene, and THF. Complex **3** is thermally robust and shows no sign of decomposition after 12 h at 60−80 °C in toluene. The initial indication of the trinuclear formulation for **3** stemmed from the observation of a parent peak at *m/z* 956 in the CI mass spectrum. Such a view was supported by the presence of two signals, in a ratio of 4:1, at δ 0.43 and 0.27 in the region expected for a σ-bonded species due to the

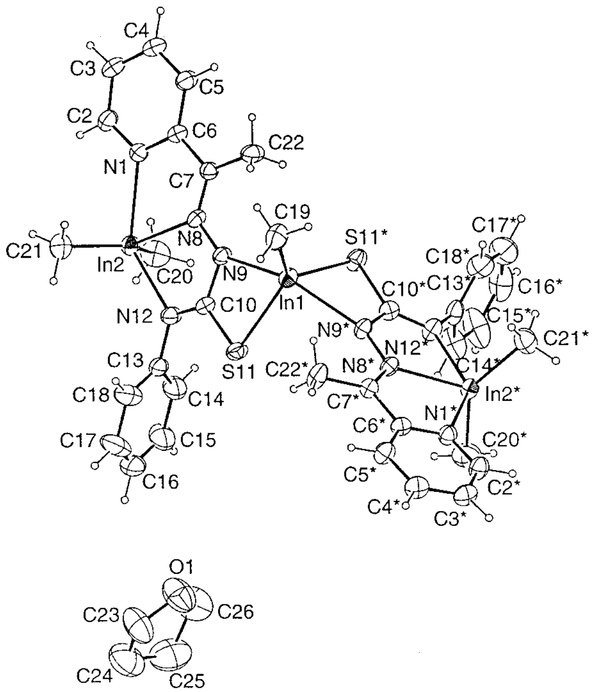


Figure 1. Molecular structure of {(Me$_2$In)$_2$[NC$_5$H$_4$CMeNNC(S)NC$_6$H$_5$]$_2$}(InMe)·THF (**3**). The thermal ellipsoids are drawn at the 30% probability level.

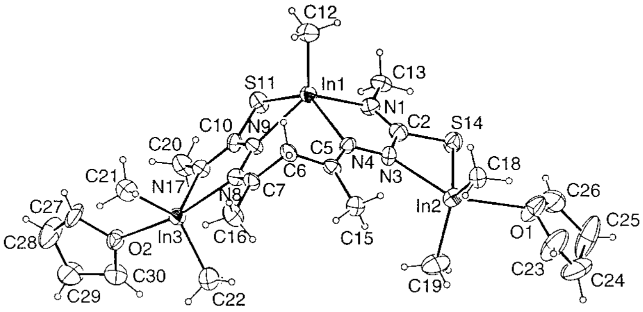
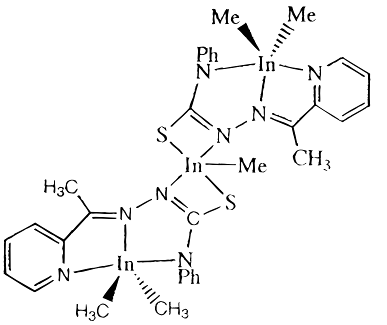


Figure 3. Molecular structure of {((THF)Me$_2$In)$_2$[CH$_2$(MeCNNC(S)NMe)$_2$]}(InMe) (**4**). The thermal ellipsoids are drawn at the 30% probability level.

hydrogen atoms of the In−Me groups[8] in the ^{1}H NMR spectrum. The carbons (C(10), C(7)) attached to the imine groups appear at 176.36 and 160.07 ppm in the ^{13}C NMR spectrum. In the infrared spectrum of **3**, the stretching mode of ν(CS) at 780 cm^{-1} is significantly decreased. This could involve a tautomerism for semicarbazone-3-thiol, i.e., a 1,3-proton shift (**1** ↔ **5**).

Colorless crystalline **4** was produced in 62% yield in a manner similar to that described for **3**. A parent peak corresponding to a trinuclear nature was detected in the CI mass spectrum (m/z 834). The methyl groups of the indium moieties in **4** give rise to three signals in the ^{1}H and ^{13}C{H} NMR spectra. Accordingly, the trinuclear nature and the chelating coordination mode of the indium centers for both **3** and **4** have been confirmed through single-crystal X-ray diffraction analyses.



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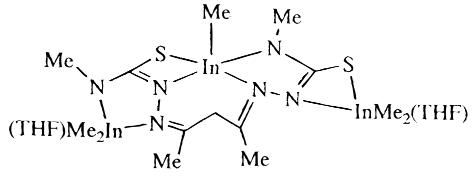

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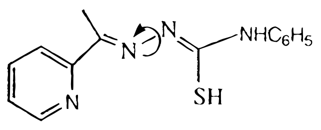
Description of the Molecular Structure of 3. Crystals of **3** suitable for an X-ray diffraction study were grown from THF/hexane at −20 °C, and the structure of **3** was determined from data collected at −120 °C. A summary of the data collection and crystallographic parameters is given in Table 1. Selected bond lengths and angles are given in Table 2. An ORTEP diagram of the solid-state structure giving the atom-numbering scheme used in the tables is shown in Figure 1. The packing diagram of compound **3** (view down the C axis) is shown in Figure 2 (Supporting Information). The molecule of **3** possesses a 2-fold rotation axis on which the In(1) and C(19) atoms lie. The structure consists of discrete trinuclear units with the indium atoms in unusual distorted-square-based-pyramidal environments (N(9)−In(1)−N(9*) = 144.1(2)°, S(11)−In(1)−S(11*) = 109.38(8)°, N(1)−In(2)−N(12) = 137.4(1)°, N(8)−In(2)−C(20) = 111.2(2)°). The geometry of In(1) consists of the two nitrogen and two sulfur atoms of the two acetylpyridine thiosemicarbazones with an apical methyl group completing the coordination sphere. Within a given complex, the two nitrogen atoms as well as the two thiolato atoms are oriented in a trans configuration. A THF molecule is included in the cavity of **3**. The In(1)−S(11) distance (2.491(2) Å) in **3** is comparable to those found in the tris-chelate complex of indium [In(2-C$_5$H$_4$NS)$_3$] (2.531(2) Å),[9] In(SPh)$_3$·2py (2.458 Å),[10] and K$_8$(In$_4$S$_{10}$) (2.453−2.479 Å),[11] In(SMes*)$_3$ (2.403 Å),[12] and Ph$_4$P[BrIn(SPh)$_3$] (2.435−2.470 Å).[13] The In(1)−N(9) distance (2.394(4) Å) is very similar to that in MeIn(C$_6$H$_5$CH$_2$NNC$_5$H$_4$)$_2$ (2.349(3) Å)[14] and InCl(BTA-TM) (2.322(10) Å).[15] The pyridyl In(2)−N(1) distance (2.418(4)



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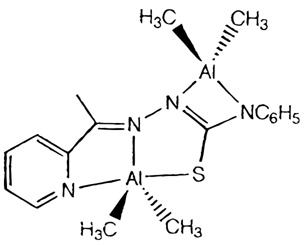
Å) is slightly longer than the amido In(2)−N(8) distance (2.317(4) Å) and In(2)−N(12) distance (2.317(4) Å), a feature consistent with the literature.[16] The In(1)−C(19) bond distance (2.10(1) Å) falls well within the range common for five-coordinate indium complexes.[16] An interesting structural aspect in **3** is that the In(2) center is coordinated to the three nitrogen atoms in the ligand **1**. In most cases, the ligand **1** coordinates to the metal ions *via* an N,N,S coordination mode. Accordingly, N,N,N chelation in **3** may be attributable to the result of the strong affinity of the In metal for S in the rotational conformer of the isomer. The ligand **1** (*E* isomer) contains one semicarbazone with a thiol group or alternatively one donor entity HN−C=S.[2] It is also interesting to note that the interaction of $AlMe_3$ with ligand **1** afforded the dinuclear aluminum complex **6** with different coordination modes. The principal structural difference between **3** and **6** is attributable to the increased radius of indium with respect to that of aluminum and the strong bond of In−S in the four-membered InNCS rings. Another conspicuous structural feature is that three of the pentacoordinate indium atoms are in distorted-square-pyramidal environments. The literature reveals many other structural reports of neutral five-coordinate organoindium complexes with trigonal-bipyramidal coordination.[16,17] Of these complexes, a few organoindium complexes have had square-pyramidal coordination.[13] The unusual arrangement observed for **3** is similar to that recently reported for the monomeric structure of $MeIn(C_6H_5CH_2NNC_5H_4)_2$.[13] It appears that only when the associated ligands are sufficiently rigid will square-pyramidal coordination be favored.



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Molecular Structure Description of 4. A crystal of **4** suitable for an X-ray diffraction study was grown from THF/hexane at −20 °C. A summary of the data collection and crystallographic parameters for **4** is given in Table 1. The relevant bond lengths and angles are shown in Table 3. The molecular structure of **4** is given in Figure 3.

Several points are worthy of note regarding the structure and bonding in the novel compound **4**. Compound **4** contains three types of methylindium fragments. In(1) is included in the InNCS four-membered ring and the InN_2C_2 five-membered ring. The geometry about the indium center In(1) is best described as a distorted-square-pyramidal environment (N(9)−In(1)−N(1) = 124.0(4)°, S(11)−In(1)−N(4) = 132.4(2)°) consisting of the three nitrogen atoms and one sulfur atom of the 2,4-bis(4-*N*-methylthiosemicarbazono)pentane anion with an apical methyl group completing the coordination sphere. A feature of particular interest is the arrangement of the four-membered In(2)SCN ring and the five-membered In(3)NCNN ring. In both indium atoms, a THF molecule is coordinated as part of the five-coordinate structure on the basis of X-ray crystallographic data. The In(2)−O(1) bond distance in **4** (2.57(1) Å) is comparable to those observed in other structurally characterized compounds showing In−THF interactions ($InCl_3$·2THF, 2.257(9) Å;[18] $InMes_3$·THF, 2.414(4) Å;[19] $[{}^iPr_2In(THF)_2][BF_4]$, 2.309(5) and 2.416(5) Å).[20] The indium in the four-membered ring, In(2), is in a distorted-square-pyramidal environment (S(14)−In(2)−C(19) = 112.5(5)°, O(1)−In(2)−N(3) = 145.8(4)°). However, the indium atom In(3) of the terminal dimethylindium unit is found in a distorted-trigonal-bipyramidal geometry (O(2)−In(3)−N(8) = 161.4(3)°). Moreover, the axial In(3)−N(8) bond length (2.358(9) Å) is longer than that of the equatorial In(3)−N(17) bond distance (2.19(1) Å). Although direct comparisons are difficult due to the lack of known In bis(thiosemicarbazone) complexes, the In−N and In−C bond distances of **4** correlate favorably with the reported values for five-coordinate TBP complexes. In summary, the synthetic utility points toward the view that the ligands **1** and **2** are very useful for synthesizing multinuclear complexes incorporating group 13 elements.

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Supporting Information Available: Tables of crystal data, structure refinement details, bond distances, bond angles, atomic coordinates, and thermal parameters for **3** and **4** and a packing diagram for **3** (13 pages). Ordering information is given on any current masthead page.

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