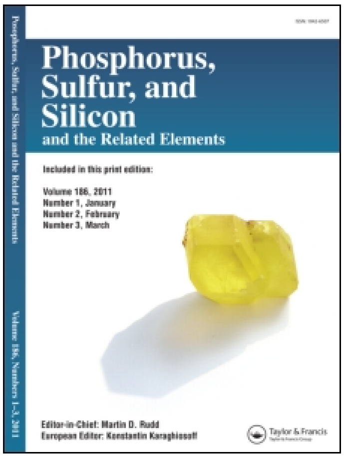

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MOLECULAR STRUCTURE OF THE SPIROCYCLIC PENTACOORDINATE INDIUM(III) COMPLEX $[(n\text{-}C_4H_9)_4N]_2\{[S_2C_2(CN)_2]_2InCl\}$ AND THE ISOMORPHOUS THALLIUM(III) COMPLEX $[(n\text{-}C_4H_9)_4N]_2\{[S_2C_2(CN)_2]_2TlBr]$

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MOLECULAR STRUCTURE OF THE SPIROCYCLIC PENTACOORDINATE INDIUM(III) COMPLEX $[(n\text{-}C_4H_9)_4N]_2\{[S_2C_2(CN)_2]_2InCl\}$ AND THE ISOMORPHOUS THALLIUM(III) COMPLEX $[(n\text{-}C_4H_9)_4N]_2\{[S_2C_2(CN)_2]_2TlBr\}$[1]

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Single-crystal X-ray diffraction analysis of the spirobis(dithia) indium(III) chloride $[(n\text{-}C_4H_9)_4N]_2\text{-}\{(S_2C_2(CN)_2]_2\text{-}InCl\}$ (**2**) and the isomorphous thallium(III) bromide $[(n\text{-}C_4H_9)_4N]_2\{[S_2C_2(CN)_2]_2TlBr\}$ (**3**) shows structures that are nearly midway along the Berry coordinate connecting idealized trigonal-bipyramidal and rectangular-pyramidal geometries. They crystallize in the monoclinic space group $P2_1/c$. **2** has a = 15.961 (3) Å, b = 12.496 (5) Å, c = 25.160 (6) Å, β = 99.59 (2)°, and Z = 4. **3** has a = 16.063 (5) Å, b = 12.565 (8) Å, c = 25.091 (7) Å, β = 100.17 (2)°, and Z = 4. The final agreement factors for **2** are R = 0.054 and R_w = 0.083 on the basis of 4503 reflections having $I \geq 2\sigma_I$; for **3** R = 0.050 and R_w = 0.062 on the basis of 4027 reflections having $I \geq 2\sigma_I$. The structures obtained follow factors important in correlating geometries observed for spirocyclic phosphoranes. The atom size and electronegativity of the central atom relative to that for the halogen atom are of particular importance in accounting for the structural similarity of **2**, **3**, and the related spirocyclic spirobis(dithia) germanium fluoride $[(CH_3)PPh_3]^+[(C_7H_6S_2)GeF]^- \cdot CH_3CN$ (**4**).

INTRODUCTION

Recently, we have extended our investigations of phosphorane chemistry[2,3] to pentacoordinate molecules of the group 4 elements silicon,[4] germanium,[5] and tin.[6] The structural principles applied to the stereochemistry of phosphoranes[2,3] generally remain intact in considering pentacoordination for these main group 4 elements,[4–6] at least as far as the investigations have been carried out. For spirocyclic derivatives of group 4, a range of structures is found that extend from the trigonal bipyramid to the square or rectangular pyramid.[4–6] Most of the group 4 compounds studied are monoanionic derivatives containing five covalent bonds. They are, therefore, isoelectronic with corresponding pentacovalent members of main group 5 elements.

It is of interest to determine the structures for related pentacoordinated complexes of the main group 3 elements and establish the extent and variation of structural principles across these series. Pentacoordinated members of the group 3 elements that are isoelectronic with groups 4 and 5 are dianionic. The only example that has been structurally characterized[7,8] is $[Et_4N]_2[InCl_5]$. The anion is square pyramidal. The latter structural form is unknown for acyclic derivatives of

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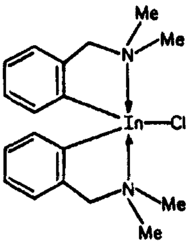
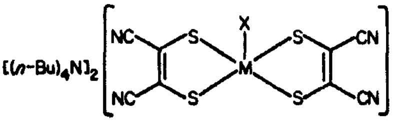


1

main groups 4 and 5, except that for $SbPh_5$.[9,10] Here the structure is thought to be a result of lattice stabilization.[11,12]

The X-ray structure of the dative-bonded five-coordinated neutral adduct $InCl_3 \cdot 2Ph_3P$[13] reveals the expected trigonal-bipyramidal geometry while the structure of the neutral dative-bonded organoindium compound **1**[14] is somewhat distorted from the trigonal bipyramid. Pentacoordination in other indium compounds studied by X-ray diffraction results from intermolecular association.[15] The structures of discrete complexes of thallium(III) do not seem to have been explored.



2, M = In, X = Cl
3, M = Tl, X = Br

We report here the X-ray structures of the first cyclic pentacoordinated anionic derivatives of indium(III) and thallium(III) halides; **2** and **3**, respectively. The complexes are formed by the 2:1 reaction of the dicyanoethylenedithiolato ligand, *cis*-$1,2\text{-}S_2C_2(CN)_2^{2-}$(mnt), with the corresponding group 3 halide.[16]

EXPERIMENTAL

X-ray studies were done at 23 ± 2°C, with an Enraf-Nonius CAD 4 diffractometer and graphite-monochromated Mo Kα radiation. Details of the experimental and computational procedures have been described previously.[6b] **2** and **3** are isomorphous, crystallizing in the monoclinic space group $P2_1/c$ [C_{2h}^5-No. 14],[17] with $Z = 4$.

Crystal data for $C_{40}H_{72}N_6S_4ClIn$ (**2**): Bright yellow crystal from MeOH–THF (0.35 × 0.38 × 0.42 mm), $a = 15.961\ (3)$ Å, $b = 12.496\ (5)$ Å, $c = 25.160\ (6)$ Å, $\beta = 99.59\ (2)°$, $\mu_{MoK\bar{\alpha}} = 0.724\ mm^{-1}$.

Crystal data for $C_{40}H_{72}N_6S_4BrTl$ (**3**): Ruby red crystal from MeOH–THF (0.25 × 0.30 × 0.30 mm), $a = 16.063\ (5)$ Å, $b = 12.565\ (8)$ Å, $c = 25.091\ (7)$ Å, $\beta = 100.17\ (2)°$, $\mu_{MoK\bar{\alpha}} = 4.30\ mm^{-1}$.

Data were collected for both compounds with use of the θ-2θ scan mode for independent reflections $(+h, +k, \pm l)$ having $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 43°$. Totals of 5694 and 5676 reflections were measured for **2** and **3**, respectively. No corrections were made for absorption. **3** was solved with use of Patterson and difference Fourier techniques. Final coordinates for **3** were used as initial coordinates for **2**. Hydrogen atoms were omitted in both cases. Anisotropic full-matrix least-squares refinement[18] was based on reflections having $I \geq 2\sigma_I$. For **3**, the final agreement factors[19] were $R = 0.050$ and $R_w = 0.062$ for 4027 reflections, and for **2**, $R = 0.054$ and $R_w = 0.083$ for 4503 reflections. Final difference Fourier synthesis showed maximum densities of 0.698 and 0.517 e/Å^3 for **3** and **2**, respectively.

RESULTS AND DISCUSSION

The atom-labeling scheme for **2** is given in Figure 1, and that for **3** is given in Figure 2. Atomic coordinates for **2** and **3** are given in Tables I and II, respectively, while bond lengths and angles for the anions of both compounds appear in Table III. Anisotropic thermal parameters and bond lengths and angles for the tetra-*n*-butylammonium ions are provided as supplementary material.

The two compounds are isostructural as can be seen in the ORTEP plots of Figures 1 and 2. Both anions have a pseudo-2-fold axis coincident with the metal-halide bond. The atom-labeling schemes are such that primed atoms go into the unprimed ones by the pseudo-2-fold axis. The geometry about the metal atoms is approximately midway between a trigonal bipyramid (TP) having S2, S2′, and halogen equatorially positioned with S1 and S1′ axially positioned and a rectangular pyramid (RP) with four basal sulfur atoms and an apical halide atom.

The geometries lie on the Berry coordinate[20] connecting the ideal TP to the RP, with the halide atom as the pivot. In terms of this coordinate **2** is displaced 49.3% (48.2% with unit vectors) from the TP toward the RP, while **3** is displaced 45.8% (46.7% using unit vectors), on the basis of the dihedral angle method.[21] As in the case of the spirocyclic phosphoranes,[3a,22] residual TP character is evident in an elongation of the metal S_{axial} bond lengths relative to the metal $S_{equatorial}$ bonds. For **2**, the axial bonds are, on the average, 0.05 Å longer than the equatorial ones, while for **3**, this value is 0.06 Å.

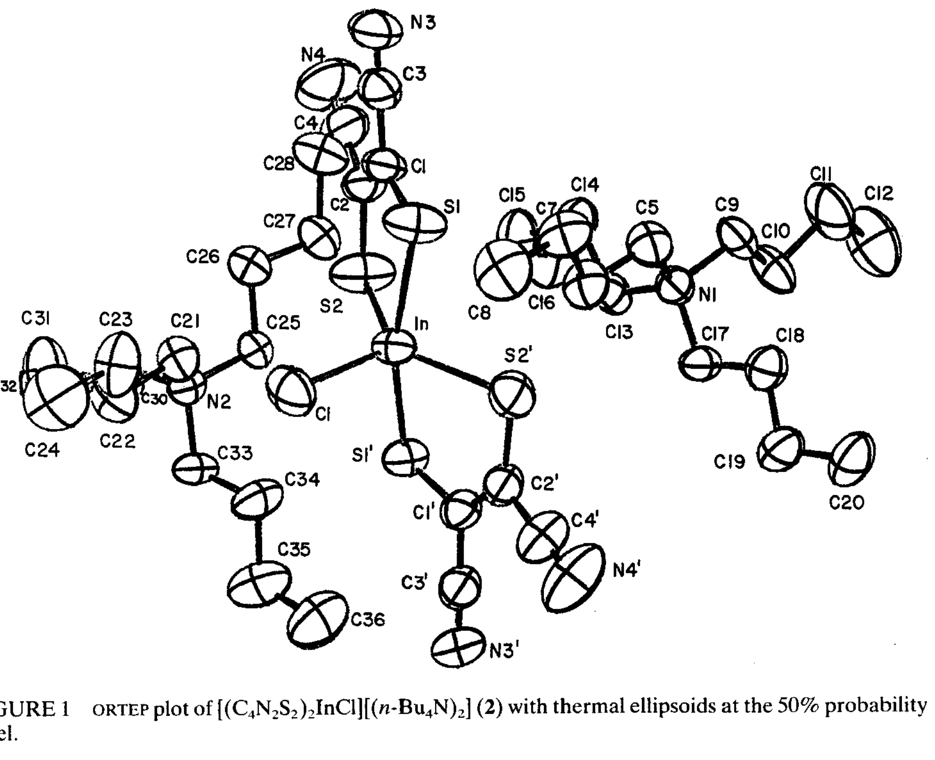


FIGURE 1 ORTEP plot of $[(C_4N_2S_2)_2InCl][(n\text{-}Bu_4N)_2]$ (**2**) with thermal ellipsoids at the 50% probability level.

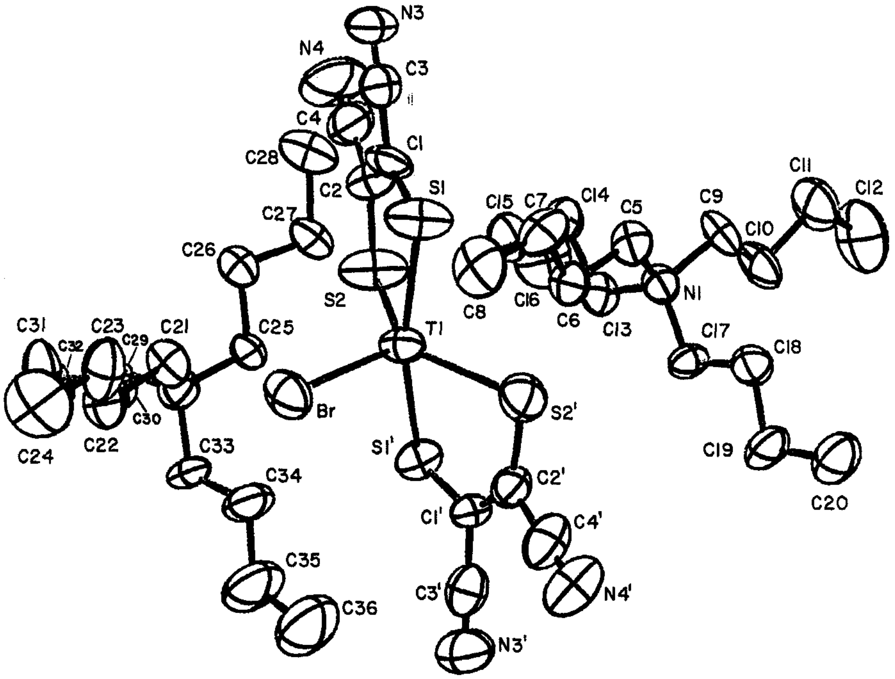


FIGURE 2 ORTEP plot of $[(C_4N_2S_2)_2TlBr][(n\text{-}Bu_4N)_2]$ (**3**) with thermal ellipsoids at the 50% probability level.

For **2**, the atoms In, Cl, S1 and S1′ are coplanar to within ±0.01 Å (Table D, supplementary material) while the atoms In, Cl, S2 and S2′ are coplanar to within ±0.05 Å. The dihedral angle between these planes is 87.8°. For **3**, the corresponding values are ±0.02 Å, ±0.07 Å, and 86.3°. Both of the dihedral angles fall in the range to be expected for geometries adhering to the C_{2v} constraint of the Berry coordinate.

It is interesting to compare bond length and angle variations within the five-membered ring in **2** and **3**. The alternation in bond length and angle size for adjacent bonds complements that found in related phosphoranes and is a manifestation of the unequal lengths associated with apical and equatorial bonds of a trigonal bipyramid.[23,24] These alternations disappear as the rectangular pyramid is approached with its equal bond character for basal bonds.

The In—Cl length in **2**, 2.418 (2) Å, is very close to the axial In—Cl distance in $[Et_4N]_2[InCl_5]$, 2.415 (2) Å.[7] The average In—Cl equatorial bond distance in the trigonal-bipyramidal adduct $InCl_3 \cdot 2Ph_3P$[13] is 2.383 (5) ± 0.05 Å. The slightly higher values for axial bonds in **2** and the $InCl_5^{2-}$ ion are appropriate for geometries nearer the square- or rectangular-pyramidal form. Relative to this discussion, the value of the equatorial In—Cl bond length for **1**,[14] 2.465 (1) Å, is unusually large. It is even longer than the basal In—Cl bonds in $InCl_5^{2-}$, 2.456 (7) Å.[7,25]

The structure of **1**[14] has an almost linear N—In—N bond angle, 178.4 (1)°, expected for an idealized trigonal bipyramid. However, the C—In—C angle is 153.3 (1)°, close to that expected for a rectangular pyramid (150°) rather than the

TABLE I

Atomic Coordinates in Crystalline $[(C_4N_2S_2)_2InCl][(n\text{-}Bu_4N)_2]$ (2)[a]

	coordinates		
atom type[b]	10^4x	10^4y	10^4z
In	2576.2 (3)	351.2 (5)	1554.6 (2)
Cl	1477 (1)	1266 (2)	1932 (1)
S1	3694 (2)	1813 (2)	1647 (1)
S2	2527 (2)	556 (2)	558 (1)
S1′	1785 (1)	−1441 (2)	1322 (1)
S2′	3478 (1)	−740 (2)	2270 (1)
C1	3636 (5)	2164 (6)	986 (3)
C2	3184 (5)	1660 (6)	542 (3)
C3	4126 (5)	3077 (7)	890 (4)
N3	4502 (5)	3814 (6)	825 (4)
C4	3263 (6)	2018 (7)	14 (4)
N4	3293 (6)	2286 (8)	−417 (4)
C1′	2077 (5)	−2028 (6)	1943 (3)
C2′	2753 (5)	−1745 (6)	2327 (3)
C3′	1526 (5)	−2905 (7)	2062 (3)
N3′	1092 (5)	−3582 (6)	2143 (4)
C4′	2863 (6)	−2286 (8)	2839 (4)
N4′	2954 (7)	−2710 (8)	3247 (4)
N1	6507 (3)	1697 (5)	4839 (2)
C5	6673 (5)	2785 (7)	5121 (3)
C6	5909 (5)	3209 (7)	5376 (4)
C7	6166 (6)	4313 (7)	5606 (4)
C8	5457 (7)	4788 (9)	5872 (5)
C9	7329 (4)	1432 (7)	4629 (3)
C10	7314 (5)	347 (8)	4332 (4)
C11	8168 (6)	252 (10)	4109 (5)
C12	8233 (7)	−868 (11)	3847 (5)
C13	5751 (4)	1753 (6)	4374 (3)
C14	5851 (5)	2611 (7)	3950 (3)
C15	5076 (5)	2530 (8)	3487 (4)
C16	5101 (7)	1562 (10)	3116 (4)
C17	6274 (5)	834 (6)	5218 (3)
C18	6968 (5)	613 (7)	5712 (3)
C19	6612 (6)	−189 (7)	6075 (4)
C20	7296 (7)	−566 (8)	6540 (4)
N2	1052 (4)	3940 (5)	3354 (2)
C21	1311 (5)	4821 (7)	3777 (3)
C22	554 (5)	5262 (7)	4025 (4)
C23	955 (6)	6105 (8)	4456 (4)
C24	262 (8)	6592 (11)	4716 (5)
C25	1867 (4)	3498 (6)	3184 (3)
C26	2341 (5)	4337 (7)	2908 (3)
C27	3092 (5)	3764 (8)	2718 (4)
C28	3642 (6)	4559 (9)	2470 (4)
C29	436 (5)	4430 (6)	2883 (3)
C30	236 (5)	3674 (7)	2404 (3)
C31	−486 (6)	4169 (9)	2002 (4)
C32	−734 (7)	3409 (10)	1503 (4)
C33	591 (5)	3019 (6)	3573 (3)
C34	1071 (6)	2547 (8)	4115 (4)
C35	489 (8)	1524 (10)	4212 (5)
C36	890 (9)	979 (12)	4613 (6)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 1.

120° equatorial angle of the trigonal bipyramid. The present structure **2** shows "axial" and "equatorial" angles of 162.2 (1) and 133.7 (1)°, respectively. These same angles for **3** are nearly the same, 162.3 (1) and 132.9 (1)°. In fact, for all pentacovalent derivatives of main-group elements studied,[1–6,21] there is a cooperative change in axial and equatorial angles, which places the structures on the Berry coordinate between the trigonal bipyramid and rectangular pyramid.[2,3a,21] In view of the presence of weak N→In dative bonds in **1**, we suggest that other structural features exert an overriding influence. Perhaps steric effects associated

TABLE II

Atomic Coordinates in Crystalline $[(C_4N_2S_2)_2TlBr][(n\text{-}Bu_4N)_2]$ (3)[a]

atom type[b]	coordinates 10^4x	 10^4y	 10^4z
Tl	2638.1 (3)	332.7 (4)	1561.1 (2)
Br	1442 (1)	1335 (1)	1963 (1)
S1	3765 (3)	1816 (4)	1653 (2)
S2	2591 (3)	550 (3)	540 (2)
S1′	1819 (2)	−1500 (3)	1313 (1)
S2′	3529 (2)	−840 (3)	2282 (2)
C1	3688 (7)	2154 (10)	979 (5)
C2	3233 (8)	1670 (10)	533 (5).
C3	4154 (8)	3086 (11)	888 (6)
N3	4513 (7)	3866 (9)	829 (5)
C4	3303 (8)	2051 (10)	6 (6)
N4	3315 (9)	2319 (12)	−412 (5)
C1′	2099 (7)	−2055 (9)	1937 (5)
C2′	2774 (8)	−1790 (10)	2328 (5)
C3′	1512 (9)	−2868 (11)	2065 (5)
N3′	1061 (8)	−3530 (10)	2136 (6)
C4′	2848 (9)	−2300 (11)	2854 (6)
N4′	2883 (9)	−2728 (11)	3261 (6)
N1	6495 (5)	1701 (8)	4851 (4)
C5	6656 (7)	2786 (9)	5128 (5)
C6	5912 (7)	3185 (9)	5368 (5)
C7	6170 (9)	4327 (10)	5609 (5)
C8	5461 (10)	4819 (12)	5870 (7)
C9	7308 (6)	1468 (11)	4628 (5)
C10	7288 (7)	367 (11)	4331 (5)
C11	8139 (9)	313 (13)	4109 (6)
C12	8191 (10)	−830 (15)	3841 (7)
C13	5722 (7)	1735 (9)	4371 (4)
C14	5821 (7)	2600 (11)	3948 (5)
C15	5054 (7)	2495 (11)	3489 (5)
C16	5068 (10)	1542 (14)	3137 (6)
C17	6281 (7)	824 (9)	5225 (4)
C18	6970 (7)	609 (10)	5720 (5)
C19	6597 (9)	208 (11)	6074 (5)
C20	7282 (9)	−597 (12)	6548 (6)
N2	1067 (6)	3961 (8)	3362 (4)
C21	1336 (7)	4827 (10)	3803 (5)
C22	577 (8)	5249 (11)	4038 (5)
C23	977 (10)	6106 (13)	4469 (6)
C24	266 (13)	6633 (16)	4738 (7)
C25	1882 (7)	3516 (9)	3197 (5)
C26	2340 (7)	4391 (10)	2923 (5)
C27	3101 (8)	3786 (11)	2729 (6)
C28	3636 (9)	4627 (13)	2477 (6)
C29	460 (7)	4478 (9)	2891 (4)
C30	224 (7)	3722 (11)	2399 (5)
C31	−479 (9)	4211 (12)	2007 (6)
C32	−725 (10)	3482 (15)	1515 (16)
C33	602 (8)	3022 (9)	3575 (5)
C34	1074 (9)	2568 (11)	4112 (6)
C35	506 (12)	1554 (15)	4189 (7)
C36	851 (15)	992 (17)	4679 (9)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 2.

with the $N(CH_3)_2$ groups are responsible for the long In—Cl bond and widened C—In—C′ angle.

Recently, we determined the structures of several related anionic pentacovalent derivatives of germanium (**4**[5b]) and tin (**5**[6] and **6**[2b]) containing sulfur ligands. The numbers in parentheses refer to unit vectors rather than actual bond distances.

One may rationalize the approach to the rectangular pyramid in unsaturated five-membered spirocyclics containing like atoms bonded to the central atom such as these in terms of decreasing electron-pair repulsion effects in a given series in

TABLE III

Bond Lengths (Å) and Bond Angles (Deg) for $[(C_4N_2S_2)_2MX]^{2-}$: **3**, M = Tl, X = Br; **2**, M = In, X = Cl[a]

	bond lengths			bond lengths	
type[b]	M = Tl, X = Br	M = In, X = Cl	type	M = Tl, X = Br	M = In, X = Cl
M-X	2.642 (2)	2.418 (2)	C1′–C2′	1.37 (2)	1.37 (1)
M-S1	2.580 (4)	2.536 (2)	C1–C3	1.43 (2)	1.43 (1)
M-S1′	2.671 (4)	2.590 (2)	C2–C4	1.43 (2)	1.43 (1)
M-S2	2.563 (4)	2.509 (3)	C1′–C3′	1.46 (2)	1.47 (1)
M-S2′	2.565 (4)	2.512 (3)	C2′–C4′	1.45 (2)	1.44 (1)
S1–C1	1.73 (1)	1.708 (8)	C3-N3	1.16 (2)	1.13 (1)
S1′–C1′	1.70 (1)	1.720 (8)	C4-N4	1.11 (2)	1.14 (1)
S2–C2	1.75 (1)	1.737 (8)	C3′-N3′	1.14 (2)	1.13 (1)
S2′–C2′	1.72 (1)	1.730 (8)	C4′-N4′	1.15 (2)	1.14 (1)
C1–C2	1.37 (2)	1.38 (1)			

	bond angles			bond angles	
type	M = Tl, X = Br	M = In, X = Cl	type	M = Tl, X = Br	M = In, X = Cl
S1-M-S1′	162.3 (1)	162.2 (1)	S1′–C1′–C2′	127 (1)	126.4 (6)
S2-M-S2′	132.9 (1)	133.7 (1)	S2–C2–C1	126 (1)	125.5 (6)
S1-M-S2′	93.3 (1)	90.9 (1)	S2′–C2′–C1′	127 (1)	126.0 (6)
S1′-M-S2	86.1 (1)	85.9 (1)	S1–C1–C3	114 (1)	115.4 (7)
S1-M-S2	84.8 (1)	85.6 (1)	S1′–C1′–C3′	114 (1)	115.0 (6)
S1′-M-S2′	81.9 (1)	83.8 (1)	S2–C2–C4	115 (1)	114.7 (7)
S1-M-X	99.7 (1)	99.7 (1)	S2′–C2′–C4′	115 (1)	115.5 (6)
S1′-M-X	98.0 (1)	98.0 (1)	C3–C1–C2	117 (1)	117.2 (8)
S2-M-X	115.8 (1)	116.1 (1)	C3′–C1′–C2′	118 (1)	118.6 (7)
S2′-M-X	110.9 (1)	110.0 (1)	C4–C2–C1	119 (1)	119.7 (7)
M-S1–C1	99.4 (4)	100.0 (3)	C4′–C2′–C1′	118 (1)	118.4 (8)
M-S1′–C1′	95.7 (4)	96.6 (3)	C1–C3-N3	177 (1)	178 (1)
M-S2–C2	100.5 (5)	100.7 (3)	C1′–C3′-N3′	176 (2)	179 (1)
M-S2′–C2′	97.6 (4)	98.2 (3)	C2–C4-N4	176 (2)	177 (1)
S1–C1–C2	129 (1)	127.5 (6)	C2′–C4′-N4′	177 (2)	180 (1)

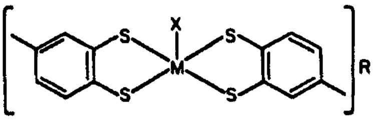
[a] Numbers in parentheses are estimated standard deviations.

[b] Atoms are labeled to agree with Figures 1 and 2.

the periodic table.[2,3a,27] For example, increasing the electronegativity of ring atoms directly bonded to the central atom and decreasing the electronegativity of the central atom or that of the acyclic atom should favor the rectangular pyramid.[2,3a] Also as one goes down a family of central atoms in the periodic table, the increase in atom size should favor reduced electron-pair repulsion effects.

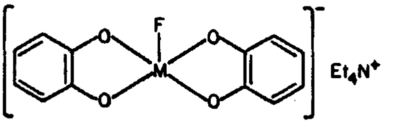
This suggestion follows the general trend of results. The tin derivatives are more rectangular pyramidal[6,26] than related germanium complexes.[5] The same holds between germanium and silicon analogues; cf. **7**[4] with **8**.[5b] The structures of spirobis(dioxa) compounds are more displaced toward the RP than the corresponding spirobis(dithia) derivatives, cf. **4** and **8**. Relative ring strain effects, reasoned to be lower for the RP compared to those for the TP,[23] also may contribute to the greater structural displacement toward the RP for the spirobis(dioxa) derivatives relative to that for the spirobis(dithia) compounds. This structural advantage should decrease as the central atom-ligand bond length increases.

The displacement in structure toward the RP as one goes down a group in the periodic table parallels the order of molecular nonrigidity, at least for the group 5



	4	5	6
M	Ge	Sn	Sn
X	F	Cl	Br
R	$CH_3P^+Ph_3\cdot CH_3CN$	Me_4N^+	$CH_3P^+Ph_3\cdot 2C_6H_6$
%(TP → RP)	47.5 (40.3)	77.2 (76.9)	93.8 $(94.6)_{av}$

elements, Sb > As > P.[2] This series is the only one that has sufficient supporting experimental evidence. Expressed differently, as molecular nonrigidity increases for pentacoordinated species, the energy difference between the TP and RP decreases.



	7	8
M	Si	Ge
%(TP → RP)	62.6 (60.8)	82.5 (80.6)

It has been more difficult to account for the structural effects of the acyclic ligand in spirocyclic derivatives, although a general correlation with the trend toward the rectangular pyramid and the presence of a bulky fifth ligand of low electronegativity exists for a specific central atom.[2,3a] If one wishes to extend this correlation to other members of a given group of the periodic table, it seems necessary to consider the relative central-atom size and electronegativity. Thus, the closeness in structure of **2** and **3** may be associated with a balance of the latter two factors. As one goes from the In—Cl to the Tl—Br bond in **2** and **3**, respectively, the step-down in the series for the metal and halogen implies a similar electronegativity difference for the M—X bond. The relative atom size[28] changes for the metal and halogen are also similar on going from In—Cl to Tl—Br. Hence, one may rationalize the structural similarity of **2** and **3** within the framework of existing factors stabilizing a rectangular pyramid.

More venturesome, in a comparison of members of different families, it is noted that the spirocyclic germanium derivative **4**[5b] has a structure close to that of **2** and **3** (the "axial" S—Ge—S and "equatorial" S—Ge—S angles are 171.06 (7) and 136.22 (9)°, respectively). Here the same diagonal relationship in the periodic table between central atom (Ge) and halogen (F) exists as is present in the dianionic species **2** and **3**.

Even though the above analysis is self-consistent, it may not accurately account for changes in other series. In particular, one needs to be aware of lattice effects and their influence on structural shape. In general, these do not dominate structure, especially for phosphoranes.[2,3a] However, as the structure of the spirocyclic silicon derivative **7**[4] shows, lattice effects enter more seriously. Further insight into the factors influencing structure for pentacoordinated derivatives of main group 3 elements should be forthcoming as additional studies are carried out in this area.

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Registry No. **2**, 80996-33-4; **3**, 38258-16-1.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes for **2** and **3**, anisotropic thermal parameters for **2** (Table A) and **3** (Table B), bond lengths and angles for the tetra-*n*-butylammonium ions in **2** and **3** (Table C), and deviations from selected least-squares mean planes for **2** and **3** (Table D) (41 pages). Ordering information is given on any current masthead page.

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