and C4. For **4**, the corresponding six-membered ring is in a chair conformation. Atoms C1, C2, C4, and C5 are coplanar to within $\pm$0.002 Å, with Si and C3 displaced in opposite directions from the least-squares plane by distances of 0.601 and 0.697 Å, respectively. In both **3** and **4**, the nine atom fused-ring systems are essentially planar. For **3**, the atoms Si, O1, O2, and C11–C16 are coplanar to within $\pm$0.046 Å. For **4** this value is $\pm$0.027 Å.

Despite the close similarity of **3** and **4**,[59] distortions from the ideal TBP geometry are different for the two. For **3**, distortions do not follow the Berry pseudorotation coordinate, but are "anti" Berry in nature as a consequence of the closing down of the C1–Si–C4 angle to 96.2 (2)° to accommodate the five-membered ring. This is accompanied by a nearly symmetrical opening up of the O2–Si–C angles (131.2 (2) and 132.6 (2)°). The axial atoms O1 and F are tipped toward the equatorial O2, resulting in a O1–Si–F angle of 169.2 (2)°. For **4**, distortions from the ideal TBP follow the Berry pseudorotation coordinate, where atoms C1 and C5, although chemically equivalent, play different roles in the process. By use of the dihedral angle method with unit vectors,[40] the geometry at silicon is displaced 35.5% from the TBP (O1 and F axial) toward the RP (C5 apical), where C5 is the pivotal atom in the pseudorotation process. This RP is the one that would be involved as the transition state in an exchange process leading to a TBP with an axial–equatorial ring. This relatively large displacement for **4** suggests a small strain energy difference for location of the six-membered ring at diequatorial compared to axial–equatorial positions of a TBP. As already noted, the K,18-c-6 salt of $[(CH_2)_5SiF_3]^-$, also containing a six-membered ring, has a somewhat low pseudorotational barrier, 9.3 kcal/mol.[13]

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE 88-19152) is gratefully acknowledged.

Supplementary Material Available: Tables of anisotropic thermal parameters, additional bond lengths and angles, and hydrogen atom parameters (Tables S1–S3 for **1**, Tables S4–S6 for **2**, Tables S7–S9 for **3**, and Tables S10–S12 for **4**, respectively) (25 pages); tables of calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

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(59) Although the structures are reported in different settings, **3** and **4** are isomorphous. The packing is very similar in the two, and packing effects are unlikely to account for any of the observed structural differences. The $P2_1/c$ cell for **4** can be transformed to a $P2_1/n$ setting (100, $0\bar{1}0$, $\bar{1}0\bar{1}$) with a = 10.082 (2) Å, b = 13.676 (3) Å, c = 20.288 (4) Å, and β = 106.13 (2)°, which corresponds to those of **3**. After such a unit cell transformation, the coordinates corresponding to those of **3** can be generated by $^1/_2 - x$, $^1/_2 + y$, $^1/_2 - z$.

Mesitylindium(III) Halide Compounds. X-ray Crystal Structures of $[InIMes_2]_2$ and $[InI_2Mes]_\infty$

John T. Leman,[1a] Joseph W. Ziller,[1b] and Andrew R. Barron*[,1a]

Department of Chemistry and Materials Research Laboratory, Harvard University, 12 Oxford Street,
Cambridge, Massachusetts 02138, and Department of Chemistry, University of California,
Irvine, California 94717

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The reaction of $InMes_3$ with InX_3 in 2:1 and 1:2 molar ratios yields $InXMes_2$ [X = Br (**2**), I (**3**)] and InX_2Mes [X = Br (**5**), I (**6**)], respectively. Compound **2** is a dimer in solution, whereas **3** is largely monomeric in benzene and CH_2Cl_2 but dimeric in the solid state. The dihalides **5** and **6** are polymeric in the solid state; however, **6** is a dimer in solution, while **5** is insoluble in noncoordinating solvents. The structures of **3** and **6** have been confirmed by X-ray crystallography. $[InIMes_2]_2$: monoclinic $C2/c$, a = 26.556 (4) Å, b = 17.126 (3) Å, c = 8.092 (1) Å, β = 104.70 (1)°, V = 3559.7 (9) Å^3, Z = 4, no. of observed data 3060, R = 0.032, R_w = 0.044. $[InI_2Mes]_\infty$: monoclinic $P2_1/c$, a = 8.234 (2) Å, b = 19.657 (3) Å, c = 7.703 (1) Å, β = 91.55 (2)°, V = 1246.3 (4) Å^3, Z = 4 no. of observed data 2805, R = 0.030, R_w = 0.044. Compounds **2**, **3**, **5**, and **6** are compared to their chloro analogues $InClMes_2$ (**1**) and $InCl_2Mes$ (**4**).

Introduction

The chemistry of the group 13 elements aluminum, gallium, and indium has been brought into vogue[2] by their applications as electronic material[3] and ceramic precursors,[4] as catalysts,[5] and in radiopharmaceuticals.[6] These applications notwithstanding, much research has been centered on gaining an intimate understanding of the effects, often subtle, controlling the structure,[7] bonding,[8] and reactivity[9] of their organometallic and coordination compounds. As part of this latter endeavor, we have investigated the structural chemistry of organoindium compounds containing the sterically bulky aryl group 2,4,6-$Me_3C_6H_2$ (Mes).[10]

The reaction of $InCl_3$ with 3 equiv of MesMgBr yields the monomeric $InMes_3$, whose structure has been con-

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* To whom correspondence should be addressed.

(1) (a) Harvard University. (b) University of California, Irvine.

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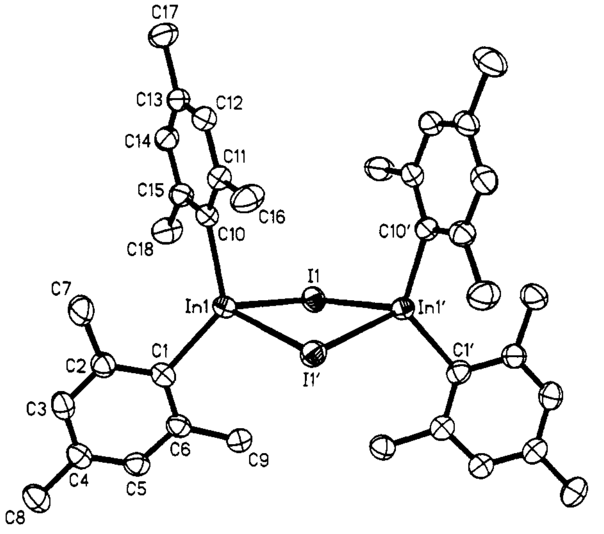

Figure 1. Structure of [$InIMes_2]_2$ (**3**). Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms are omitted for clarity.

firmed by X-ray crystallography and indicates the presence of a possible C-H—In agostic interaction.[10] In addition, we have prepared the chloro derivatives $[InClMes_2]_2$ and $[InCl_2Mes]_\infty$. We report here the synthesis and characterization of their bromo and iodo analogues, and a comparison of the homologous series.

Results

The reaction of $InMes_3$ with InX_3 in a 2:1 molar ratio yields $InXMes_2$ [X = Cl (**1**),[10] Br (**2**), I (**3**)] (eq 1). The purity of compound **2** prepared in toluene by this route is variable; Et_2O has been found to give the best results. Compound **2** can also be synthesized by the addition of 1 equiv of HBr to $InMes_3$ (eq 2).

$$2InMes_3 + InX_3 \rightarrow 3InXMe_2 \qquad (1)$$

$$X = Cl, Br, I$$

$$InMes_3 + HBr \rightarrow InBrMes_2 + MesH \qquad (2)$$

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) in $[InIMes_2]_2$ (3)

In(1)-I(1)	2.988 (1)	In(1)-C(1)	2.164 (4)
In(1)-C(10)	2.173 (4)	In(1)-I(1')	2.900 (1)
I(1)-In(1)-C(1)	114.4 (1)	I(1)-In(1)-C(10)	96.6 (1)
C(1)-In(1)-C(10)	127.7 (1)	I(1)-In(1)-I(1')	88.1 (1)
C(1)-In(1)-I(1')	106.4 (1)	C(10)-In(1)-I(1')	116.1 (1)
In(1)-I(1)-In(1')	89.5 (1)		

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) in $[InI_2Mes]_\infty$ (6)

In(1)-I(1)	2.772 (1)	In(1)-I(2)	2.760 (1)
In(1)-C(1)	2.137 (5)	In(1)-I(1')	3.192 (1)
In(1)-I(2')	3.183 (1)		
I(1)-In(1)-I(2)	99.3 (1)	I(1)-In(1)-C(1)	130.8 (1)
In(2)-In(1)-C(1)	129.9 (1)	I(1)-In(1)-I(1')	86.0 (1)
I(2)-In(1)-I(1')	93.1 (1)	C(1)-In(1)-I(1')	88.9 (1)
I(1)-In(1)-I(2')	86.7 (1)	I(2)-In(1)-I(2')	90.2 (1)
C(1)-In(1)-I(2')	94.1 (1)	I(1')-In(1)-I(2')	172.4 (1)
In(1)-In(1)-In(1')	94.0 (1)	In(1)-I(2)-In(1')	89.8 (1)

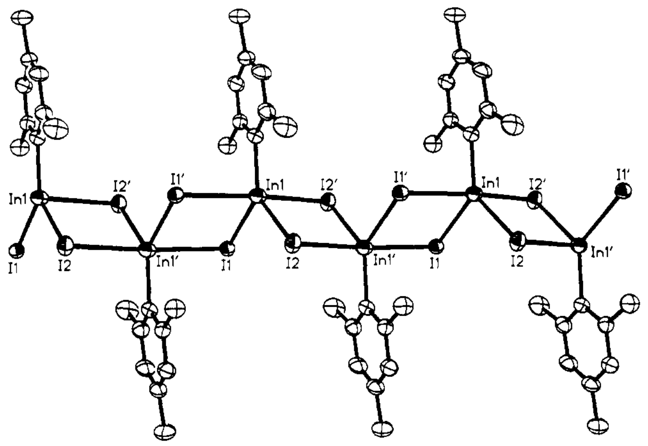

Figure 2. Structure of a section of the polymeric $[InI_2Mes]_\infty$. Inversion centers lie along the *z* axis ($^1/_2$, $^1/_2$, 0; $^1/_2$, $^1/_2$, $^1/_2$, etc.). Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms are omitted for clarity.

Compounds **1**–**3** are colorless, crystalline solids that are soluble in nonpolar organic solvents. Molecular weight determinations indicate that **1** and **2** are dimeric in solution, whereas compound **3** is largely monomeric in both benzene and CH_2Cl_2 (see Experimental Sections). However, the dimeric nature of **3** in the solid state has been determined by X-ray crystallography (see below).

The interaction of $InMes_3$ with 2 equiv of InX_3 yields InX_2Mes [X = Cl (**4**),[10] Br (**5**), I (**6**)]. Although insoluble in noncoordinating solvents, **4** and **5** dissolve readily in Et_2O and THF. The insolublility in nonpolar solvents suggests that **4** and **5** are polymeric, possibly isostructural to $[GaCl_2Mes]_\infty$, reported by Beachley, Churchill and coworkers.[11]

Unlike colorless **1**–**5**, compound **6** is pale yellow in the solid state; however, upon dissolution in nonpolar solvents a colorless solution is formed, from which the pale yellow crystals may be reobtained. Molecular weight measurements show **6** to be dimeric in both benzene and CH_2Cl_2; however, in highly polar solvents such as pyridine and nitromethane **6** is ionic. In the solid state **6**, like **4** and **5**, is polymeric (see below).

X-ray Crystallography Studies. The molecular structure of $InIMes_2$ is shown in Figure 1; selected bond lengths and angles are given in Table I. The structure

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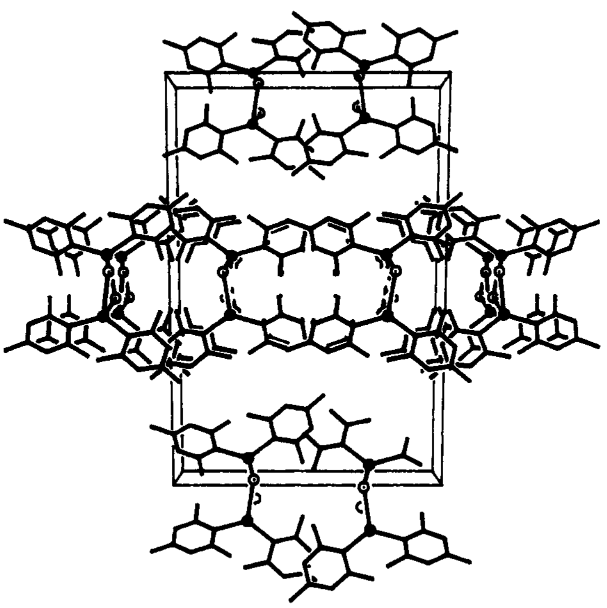


Figure 3. Unit cell packing diagram for $[InIMe_2]_2$ (3), viewed down the *z* axis.

consists of a noncentrosymmetric dimer with two bridging iodide ligands. The indium atoms are in a distorted tetrahedral geometry with the C(1)–In(1)–C(10) plane pitched 100.6° with respect to the I(1)–In(1)–I(1') plane. The In–C distances [2.164 (4) and 2.173 (4) Å] are within the range reported for terminal In–C bonds [2.093 (6)–2.26 (2) Å].[12] The In–I distances [2.988 (1) and 2.900 (1) Å] are slightly longer than found for the bridging iodines in InI_3 (2.84 Å)[13] but within the range reported for $\{InI[M(CO)_5]_2\}_2$ [M = Mn (2.951 (1) Å) and Re (2.986 (2) Å)].[14]

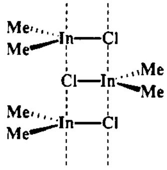
Unlike the $In(\mu\text{-}Cl)_2In$ unit in 1,[10] the iodide bridges in 3 are asymmetric. Also, unlike 1, the indium halide core is not planar but has a butterfly geometry in which the "$InMes_2$" units take the wing-tip positions. The magnitude of folding from planarity, 23.2°, may be described by the angle between the planes defined by In(1)–I(1)–I(1') and In(1')–I(1)–I(I'). The mesityl rings on each of the indium atoms are oriented almost perpendicularly (66.4°) with respect to each other, presumably in order to reduce steric interactions between the *o*-methyl groups. However, the mesityl groups above the In_2I_2 core are nearly parallel, while those below are almost coplanar, resulting in a close C(9)···C(9') intramolecular contact [3.425 (5) Å].

The crystal structure of $[InI_2Mes]_\infty$ consists of theoretically infinite strands of a one-dimensional polymer. A section of one of the strands is shown in Figure 2. Interatomic distances and angle are given in Table II. The geometry around the indium atoms is close to trigonal-bipyramidal. The axial sites are bridging iodides, while the equatorial positions are occupied by two bridging iodides and a mesityl group. The mesityl groups alternate on each side of the $[In(\mu\text{-}I)_2]_\infty$ chain, giving rise to a stair-step polymer. A similar arrangement was found in the structure of $[InCl_2(CH_2CMe_3)]_\infty$.[15]

The iodine atoms in axial positions have significantly longer In–I distances [In(1)–I(1') = 3.192 (1) Å, In(1)–I(2') = 3.183 (1) Å] than those in equatorial positions [In(1)–I(1) = 2.772 (1) Å, In(1)–I(1) = 2.760 (1) Å]. These values are on either side of that found in 3, as would be expected from a consideration of the relative In s and p character in the respective In–I bonds, i.e., five-coordinate axial (p) > four-coordinate (sp^3) > five-coordinate equatorial (sp^2).[16] In a similar manner the In–C distance in 6 [2.137 (5) Å] is shorter than found for four-coordinate mesitylindium derivatives [2.163 (5)–2.239 (11) Å].[10] The mesityl groups on each indium are oriented almost coplanar with respect to the equatorial iodides (9.8°).

Discussion

Monohalides. The solid-state structure of $InClMe_2$ as determined by X-ray crystallography[17] consists of stacked alternating molecules, which give indium an apparent coordination number of 5 (I). In the $InBrMe_2$ lattice the indium is six-coordinate with a linear Me–In–Me unit, surrounded by four equatorial bromines that are shared by neighboring metal atoms (II).[18] $InIMe_2$[19] and $InXPh_2$[20] (X = Cl, Br, I) have been shown to have structures analogous to that of $InBrMe_2$ by nuclear quadrupole resonance (NQR), Raman, and IR spectroscopy.



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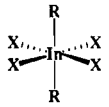

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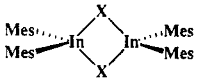

III

Both $InClMes_2$ (1)[10] and $InIMes_2$ (3) are purely dimeric in the solid state (III), as determined by X-ray crystallography, the lack of interdimer halide bridges being due to the steric bulk of the mesityl ligands. Purely dimeric structures have also been reported for $InCl[Fe(CO)_2Cp]_2$[21] and $InCl[M(CO)_5]_2$ (M = Re, Mn).[14] Due to the lack of variation in structure between 1 and 3, we propose that 2 has an analogous solid-state structure.

As is commonly observed for $In(\mu\text{-}X_2)In$ bridges, the In_2Cl_2 core of 1 is planar. However, the In_2I_2 core in 3 is significantly distorted from planarity into a butterfly geometry (see above). The ability of the In_2I_2 ring to sustain such a distortion is undoubtedly due to the more polarizable nature of the bridging iodine atoms and the diffuse nature of their valence orbitals, as compared to the analogous chloride system. It is not apparent, however, from a consideration of the structure of the dimer alone why this distortion is observed, since it apparently maximizes the steric interaction between the dimer mesityl groups. A study of the crystal packing diagram, however, reveals that the distortion within the dimer allows for interdimer stacking of the mesityl ligands. As can be seen in Figure 3, the resulting crystal structure consists of double "$InMes_2$" stacked sheets, bridged by iodine atoms.

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No such interdimer interaction is found for **1**.

Where solution molecular weight measurements have been obtained, the monohalide compounds are dimeric.[12] One exception is $InBr(Nap)_2$ ($Nap = C_{10}H_7$), which is reported to be monomeric in benzene.[22] Compounds **1** and **2** retain their solid-state dimeric structures in solution, whereas **3** is largely dissociated to a monomer (see Experimental Section). As with $InBr(Nap)_2$, the steric bulk of the aryl ligands undoubtedly contributes to the existence of a monomeric species in solution. In the case of **3**, however, this is no doubt exacerbated by a weak $In(\mu\text{-}I)_2In$ bridge, given that dimeric structures exist for **1** and **2** in which interaryl steric interaction must also be present.[10]

Dihalides. The monoalkyl dihalides of indium have solid-state structures ranging from dimers, e.g., $InCl_2Me$, through associated dimers, to polymers, e.g., $[InCl_2(CH_2CMe_3)]$.[14] For aryl compounds the dihalides are polymeric in the solid state.[20] The insolubility of compounds **4** and **5** in noncoordinating organic solvents suggests they have polymeric structures in the solid state similar to their phenyl analogues. We have been unable, however, to obtain crystals suitable for X-ray diffraction to confirm this proposal.

Although compound **6** is polymeric in the solid state, it is unlike other group 13 halide-bridged polymers in that it is soluble in aromatic hydrocarbons. Molecular weight measurements indicate that **6** is dimeric in benzene and CH_2Cl_2 (see Experimental Section). Dissolution of **6** in nitromethane or pyridine results in the formation of a 1:1 electrolyte,[23] presumably a result of a rearrangement reaction (eq 3).[24]

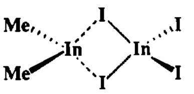
$$2InI_2Mes \rightleftharpoons InMes_2^+ + InI_4^- \qquad (3)$$

The methyl- and phenylindium diiodides have also been reported to form 1:1 electrolytes in nitromethane. Several groups[19,20,24,25] have suggested that this ionic formulation is retained in the solid state. Given the ionic nature of **6** in polar solvents, but covalent nature in nonpolar solvents and the solid state, it would seem plausible that InI_2Me and InI_2Ph could also be covalent in the solid state. Unfortunately, no structural data are available to confirm this proposition.

The most direct evidence for the ionic formulation for "InI_2Me" and "InI_2Ph" is their conductivity in nitromethane, which is found to be consistent with 1:1 electrolytes. Tuck et al.[24] reported that InI_2Et and InI_2Bu also formed conducting solutions and proposed a rearrangement similar to that shown in eq 3. As we have seen, this rearrangement does indeed occur for "covalent" iodides, indicating that the conductivity of a nitromethane solution of InI_2R cannot be used as an indication of its solid-state structure.

An IR and Raman spectroscopic study by Worrall and co-workers[25] concluded that the bands assigned to the In–C asymmetric (555 cm^{-1}) and In–C symmetric (483 cm^{-1}) stretching vibrations were characteristic of compounds containing two methyl groups attached to an indium atom. The IR spectra of **3** and **6** are remarkably similar in the metal–ligand region [(In–C) 540 (**3**), 535 cm^{-1} (**6**)] even though their solid-state structures are vastly different. Thus it would appear that IR spectral shifts are not conclusive evidence for determining the number of organo groups attached to indium.

Patterson and Carnevale[19] carried out an extensive ^{115}In nuclear quadrupole resonance (NQR) study of several methyl indium halides. On the basis of a low symmetry parameter, η, they proposed methylindium diiodide to be the ionic $[InMe_2][InI_4]$. Since η would become zero if the $[InMe_2]^+$ cation were linear, they proposed the InI_4^- anion to be coordinated to the indium cation (IV). A similar structure was proposed for the phenyl analogue.[20] It is interesting to note, however, that the ^{115}In NQR spectra for "InI_2Me" is very close to that of $InClMe_2$, in which the indium is five-coordinate trigonal-pyramidal, i.e., the same geometry found for **6** in the crystal structure. It is plausible therefore that the ^{115}In NQR data could be reinterpreted for a five-coordinate indium center in "InI_2Me".



IV

On the basis of the above arguments, and with the hindsight of the crystal structure and physical properties of **6**, we propose that the structures of InI_2Me and InI_2Ph be described as being polymeric in the solid state and dimeric in nonpolar hydrocarbons, with the ionic formulation being retained only in polar solvents.

Experimental Section

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Melting points were determined in sealed capillaries and are uncorrected. IR spectra (4000–400 cm^{-1}) were recorded on a Perkin-Elmer 137 grating spectrometer as Nujol mulls. NMR spectra were recorded on Bruker AM-250 (^1H) and AM-500 (^{13}C) spectrometers (δ in ppm relative to $SiMe_4$). Conductivities were determined by previously described methods in comparison with standard electrolytes.[26] Molecular weight measurements were made either cryoscopically in benzene or in benzene and CH_2Cl_2 by using an isopiestic instrument similar to that described by Clark.[27] The relative uncertainties in the molecular weight determination by either method are ca. ±12% of the stated values. All manipulations were carried out under nitrogen. Solvents were dried, distilled, and degassed before use. InI_3[13] and $InMes_3$[10] were prepared by following literature methods. $InBr_3$ was used as received (Strem).

$InBrMes_2$ (2). Method 1. Et_2O (50 mL) was added to a mixture of $InMes_3$ (2.00 g, 4.23 mmol) and $InBr_3$ (0.750 g, 2.12 mmol). The reactants dissolved completely over 5 min, after which the reaction was stirred for 12 h. Removal of the solvent under vacuum gave a white solid that was washed with cold pentane (20 mL): yield 2.14 g, 78%.

Method 2. $InMes_3$ (1.00 g, 2.12 mmol) was dissolved in hexane (20 mL), and a hexane solution of HBr (10.6 mL, 0.20 M) was added dropwise over 30 min at 0 °C. A white precipitate formed immediately. The reaction mixture was stirred overnight, after which the solvent was removed under vacuum and the resulting white solid washed with cold pentane (20 mL): yield 0.66 g, 72%; mp 141 °C. Anal. Calcd for $C_{18}H_{22}BrIn$: C, 49.9; H, 5.12. Found: C, 50.1; H, 5.21. Mol wt [cryoscopic (C_6H_6)]: found 803, degree of association = 1.85, at 0.025 m. IR: 1590 (m), 1540 (w), 1400 (w), 1285 (m), 1255 (m), 1085 (sh), 1070 (s), 1025 (s), 935 (w), 860 (w), 840 (s), 800 (m), 695 (w), 575 (m), 550 (w), 535 (m, In–C) cm^{-1}. NMR ($CDCl_3$): ^1H, δ 6.82 (2 H, s, C_6H_2), 2.46 (6 H, s, $o\text{-}CH_3$), 2.27 (3H, s, $p\text{-}CH_3$); ^{13}C, δ 147.5, 144.0, 139.8, 127.8 (C_6H_2), 26.0 ($o\text{-}CH_3$), 21.0 ($p\text{-}CH_3$).

$InIMes_2$ (3). Toluene (50 mL) was added to a mixture of $InMes_3$ (1.00 g, 2.12 mmol) and InI_3 (0.524 g, 1.06 mmol). After the mixture was stirred for 5 min, a clear colorless solution was

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Table III. Summary of X-ray Diffraction Data

compd	$[InIMes_2]_2$	$[InI_2Mes]_\infty$
empirical formula	$C_{36}H_{44}I_2In_2$	$C_9H_{11}I_2In$
crystal size, mm	0.33 × 0.43 × 0.50	0.26 × 0.36 × 0.46
cryst system	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$
a, Å	26.556 (4)	8.234 (2)
b, Å	17.126 (3)	19.657 (3)
c, Å	8.092 (1)	7.703 (1)
β, deg	104.70 (1)	91.55 (2)
V, Å^3	3559.7 (9)	1246.3 (4)
Z	4	4
D(calcd), mg/m^3	1.792	2.600
obs coeff, mm^{-1}	3.015	6.728
radiation (λ, Å)	Mo Kα (0.71073)/(graphite monochromator)	
temp, K	173	173
2θ range, deg	4.0–55.0	4.0–55.0
scan type	θ–2θ	θ–2θ
index range	$0 \le h \le 31, 0 \le k \le 20, -9 \le l \le 9$	$0 \le h \le 10, 0 \le k \le 25, -10 \le l \le 10$
no. of reflcns collcd	3350	3170
no. of independent reflcns	3060	2806
no. of obsd reflcns	3060	2805
weighting scheme	$w^{-1} = \sigma^2(\lvert F_o\rvert)^+ 0.005(\lvert F_o\rvert)^2$	$w^{-1} = \sigma^2(\lvert F_o\rvert) + 0.0003(\lvert F_o\rvert)^2$
final R indices (obsd data)	$R = 0.032, R_w = 0.044$	$R = 0.030, R_w = 0.044$
goodness of fit	1.56	1.92
largest diff peak, θ Å^{-3}	0.77	0.80

obtained that was further refluxed for 12 h. Removal of the solvent under vacuum gave a white solid. Extraction with boiling hexane (50 mL), filtration, and cooling to room temperature gave large colorless crystals suitable for X-ray diffraction. The solvent was removed and the crystals dried under vacuum: yield 0.76 g, 67%; mp 140–141 °C dec. Anal. Calcd for $C_{18}H_{22}IIn$: C, 45.0; H, 4.62. Found: C, 44.0; H, 4.53. Mol wt [isopiestic (CH_2Cl_2)]: found 600, degree of association = 1.25, at 0.058 m. IR: 1595 (m), 1540 (m), 1400 (w), 1290 (s), 1260 (w), 1235 (w), 1170 (w), 1030 (s), 920 (w), 880 (w), 840 (s), 700 (m), 580 (w), 540 (s, In–C), 490 cm^{-1} (w). NMR ($CDCl_3$): ^1H, δ 6.80 (2 H, s, C_6H_2), 2.48 (6 H, s, o-CH_3), 2.29 (3 H, s, p-CH_3); ^{13}C, δ 146.3, 144.0, 138.9, 127.9 (C_6H_2), 26.2 (o-CH_3), 21.1 (p-CH_3).

$InBr_2Mes$ (5). Toluene (50 mL) was added to a mixture of $InMes_3$ (0.40 g, 0.85 mmol) and $InBr_3$ (0.60 g, 1.7 mmol). The reaction mixture was refluxed overnight, during which time a white precipitate formed. The solvent was removed under vacuum, and the residue was washed with hexane (10 mL), toluene (20 mL), and again with hexane (10 mL): yield 0.55 g, 55%; mp 295 °C dec. Anal. Calcd for $C_9H_{22}Br_2In$: C, 27.4; H, 2.82. Found: C, 28.0; H, 2.83. IR: 1585 (w), 1550 (w), 1395 (w), 1285 (m), 1255 (w), 1015 (w), 1005 (w), 840 (s), 800 (w), 690 (w), 530 (m, In–C), 480 cm^{-1} (w). ^1H NMR ($CDCl_3$/THF): δ 6.81 (2 H, s, C_6H_2), 2.77 (6 H, s, o-CH_3), 2.15 (3 H, s, p-CH_3).

InI_2Mes (6). To a mixture of $InMes_3$ (1.50 g, 3.18 mmol) and InI_3 (3.14 g, 6.34 mmol) was added toluene (50 mL). The solution turned pale yellow, and a precipitate formed immediately. Upon heating, the precipitate dissolved to give a clear yellow solution. After the solution was refluxed for 24 h, the solvent was removed under vacuum to give fine yellow needles. These were found to be contaminated with unreacted $InMes_3$ (approximately 20% by ^1H NMR). The needles were therefore washed with hexane (2 × 30 mL) and then dissolved in a minimum amount of hot toluene (ca. 25 mL). Cooling to -20 °C resulted in the formation of yellow needles: yield 3.22 g, 69%; mp 213–214 °C. Anal. Calcd for $C_9H_{11}I_2In$: C, 22.2; H, 2.27. Found: C, 21.0; H, 2.24. Mol wt [cryoscopic (C_6H_6)]: found 990, degree of association = 2.03, at 0.015 m. Mol wt [isopiestic (CH_2Cl_2)]: found 941, degree of association = 1.93, at 0.020 m. Molar conductivity for 1 mM solution in $MeNO_2$: 461 Ω^{-1} cm^2. IR: 1710 (w), 1585 (w), 1550 (w), 1395 (w), 1295 (s), 1255 (m), 1170 (w), 1065 (w), 1025 (m), 1005 (s), 940 (w), 925 (w), 845 (s), 800 (w), 690 (w), 575 (w), 535 cm^{-1} (s, In–C). NMR ($CDCl_3$): ^1H, δ 6.85 (2 H, s, C_6H_2), 2.66 (6 H, s, o-CH_3), 2.30 (3 H, s, p-CH_3); ^{13}C, δ 143.9, 140.9, 137.7, 128.6 (C_6H_2), 25.8 (o-CH_3), 21.1 (p-CH_3).

Table IV. Fractional Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^4) of the Non-Hydrogen Atoms in $[InIMes_2]_2$ (3)

	x	y	z	U(eq)^a
In(1)	4271.6 (0.1)	7818.0 (0.2)	790.0 (0.1)	317 (1)
I(1)	4679.0 (0.1)	8066.2 (0.2)	4548.4 (0.4)	361 (1)
C(1)	3807 (2)	8772 (3)	-544 (5)	335 (13)
C(2)	3375 (2)	8580 (3)	-1913 (5)	350 (13)
C(3)	3042 (2)	9170 (3)	-2717 (5)	392 (14)
C(4)	3126 (2)	9954 (3)	-2239 (5)	360 (14)
C(5)	3556 (2)	10132 (3)	-921 (5)	349 (13)
C(6)	3901 (2)	9561 (2)	-83 (5)	324 (13)
C(7)	3264 (2)	7759 (3)	-2562 (7)	525 (18)
C(8)	2771 (2)	10588 (3)	-3132 (6)	463 (16)
C(9)	4371 (2)	9811 (3)	1275 (6)	388 (14)
C(10)	4038 (2)	6610 (2)	936 (5)	321 (12)
C(11)	4278 (2)	5974 (3)	389 (6)	357 (13)
C(12)	4088 (2)	5220 (3)	517 (5)	376 (14)
C(13)	3662 (2)	5093 (3)	1153 (5)	362 (13)
C(14)	3416 (2)	5723 (3)	1667 (5)	381 (14)
C(15)	3607 (2)	6489 (3)	1580 (5)	346 (13)
C(16)	4731 (2)	6065 (3)	-400 (7)	483 (18)
C(17)	3459 (2)	4266 (3)	1268 (6)	497 (17)
C(18)	3312 (2)	7150 (3)	2157 (7)	482 (18)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Fractional Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^4) of the Non-Hydrogen Atoms in $[InI_2Mes]_\infty$ (6)

	x	y	z	U(eq)^a
In(1)	4458.6 (0.5)	4578.0 (0.2)	2544.6 (0.5)	360 (1)
I(1)	3890.2 (0.4)	5833.8 (0.2)	1007.0 (0.4)	324 (1)
I(2)	7403.9 (0.4)	4849.0 (0.2)	4196.8 (0.4)	382 (1)
C(1)	3087 (6)	3656 (3)	2415 (7)	325 (14)
C(2)	1533 (6)	3677 (3)	1639 (7)	325 (15)
C(3)	651 (7)	3071 (3)	1445 (8)	390 (17)
C(4)	1293 (8)	2445 (3)	1993 (8)	419 (18)
C(5)	2839 (8)	2444 (3)	2756 (8)	429 (18)
C(6)	3755 (7)	3037 (3)	2999 (8)	382 (16)
C(7)	818 (7)	4322 (3)	933 (8)	409 (17)
C(8)	390 (10)	1788 (3)	1672 (10)	576 (24)
C(9)	5431 (8)	3000 (3)	3863 (10)	532 (22)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

X-ray Crystallographic Study. A crystal data summary is given in Table III; fractional atomic coordinates are listed in Table IV and V. X-ray data were collected on a Nicolet P3 diffractometer that is equipped with a modified LT-2 low-temperature system. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described techniques similar to those of Churchill.[28]

All data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. The systematic extinctions observed for 3 were *hkl* for $h + k = 2n + 1$ and *h*0*l* for $l = 2n + 1$; the diffraction symmetry was $2/m$. The two possible monoclinic space groups are Cc [C_s^4; No. 9] or $C2/c$ [C_{2h}^6; No. 15]. The centrosymmetric space group was chosen and later shown to be the correct choice. The systematic extinctions observed for 6 were 0*k*0 for $k = 2n + 1$ and *h*0*l* for $l = 2n + 1$; the diffraction symmetry was $2/m$. The centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] is thus uniquely defined.

All crystallographic calculations were carried out by using either the UCI modified version of the UCLA Crystallographic Computing Package[29] or the SHELXTL PLUS program set.[30] The analytical scattering factors for neutral atoms were used throughout the analysis;[31a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$)

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components of anomalous dispersion[31b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma_1(|F_o|) + X(|F_o|)^2$ [X = 0.0005 (**3**), 0.003 (**6**)].

The structure of **3** was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. The molecule is located about a 2-fold rotation axis at $^1/_2, y, ^1/_4$; no atoms lie on the axis, and thus, all site-occupancy factors are 1.0. Hydrogen atoms were included by using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. Refinement of positional and anisotropic thermal parameters led to convergence; see Table III.

The structure of **6** was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were included by using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. Refinement of positional and anisotropic thermal parameters led to convergence (see Table III). The (241) reflection was omitted because of a large discrepancy between $|F_o|$ and $|F_c|$ values. Including this reflection in the refinement resulted in a significantly increased value for R_w of 0.098.

The molecule of **6** is polymeric with repeating InI_2Mes units along the c dimension of the unit cell. The repeat units are related by inversion centers ($^1/_2, ^1/_2, -^1/_2$; $^1/_2, ^1/_2, 0$; $^1/_2, ^1/_2, ^1/_2$, etc.; see Figure 2).

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Supplementary Material Available: Listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters (5 pages); tables of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

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Two Germaoxetanes from a Germene: Formation and Structure

M. Lazraq, C. Couret,* J. Escudie,* and J. Satgé

Laboratoire de Chimie des Organominéraux, UA 477 du CNRS, Université P. Sabatier,
118 route de Narbonne, 31062 Toulouse Cedex, France

M. Dräger

Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg Universität,
Fachbereich Chemie, Joh. Joachim Becher-Weg 24, Postfach 3980, D.6500 Mainz, Germany

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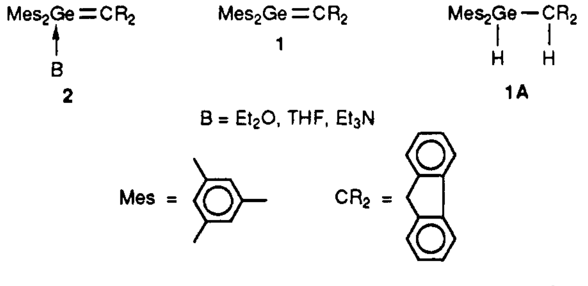
Dimesitylfluorenylidenegermane (**1**) reacts very readily with aldehydes and ketones, according to a [2 + 2] cycloaddition, leading to the corresponding germaoxetanes. These four-membered-ring heterocycles are quite stable, mainly due to the large steric hindrance of the substituents. In the case of acetone, reaction with the enolic form has been observed, followed by a germanotropic rearrangement. Germaoxetanes **3** (monoclinic, $P2_1/n$, a = 12.668 (5) Å, b = 16.794 (6) Å, c = 14.600 (5) Å, β = 90.25 (3)°, V = 3106 (2) Å^3, Z = 4, R = 0.0525) and **4** (monoclinic, $P2_1/c$, a = 22.807 (5) Å, b = 17.713 (6) Å, c = 18.425 (4) Å, β = 102.64 (2)°, V = 7263 (3) Å^3, Z = 8, R = 0.0697), obtained from benzaldehyde and benzophenone, have been characterized by X-ray diffraction methods and their data compared to those of the acyclic digermoxane **6** (triclinic, $P\bar{1}$, a = 13.002 (3), Å, b = 14.962 (2) Å, c = 16.094 (1) Å, α = 98.92 (1)°, β = 95.90 (2)°, γ = 114.52 (1)°, V = 2765 (1) Å^3, Z = 2, R = 0.0781) prepared by hydrolysis of germene **1**.

Introduction

Germenes, $R'_2Ge{=}CR_2$, compounds with a germanium–carbon double bond, have long been speculated to be reactive intermediates; they were unambiguously first evidenced by Barton,[1] and then by other groups in trapping reactions.[2,3] Owing to the large steric hindrance around the double bond and large mesomeric effects, we have recently isolated the stable germene **2** as an adduct with Lewis bases (Et_2O, THF, Et_3N).[4,5] The "free" germene **1** was further obtained by thermal decomposition of **2**.[6]



An X-ray structure determination of **1** showed the presence of a double bond between germanium and carbon (Ge=C = 1.80 Å) with a 10.4% shortening relative to the single bond in the hydrogenated derivative **1A**. The germene **1** is very reactive toward protic reagents,[4] hydrides,[4] dimethyl disulfide,[4] nitrones,[4] dienes,[4] and diazo derivatives.[7] In this paper we report the reactions of germene **1** with aldehydes and ketones and the first

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