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Reactions of Halogenomethyl Complexes of Indium, X_2InCH_2X (X = Br, I), with 1,1,3,3-Tetramethyl-2-thiourea

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Summary: Indium(I) halides, InX, react with methylene dihalides CH_2X_2 *(X = Br, I) to give* X_2InCH_2X *derivatives. The bromide compound reacts with 1,1,3,3-tetramethyl-2-thiourea (tmtu) to give the thiouronium derivative* $Br_3InCH_2SC[N(CH_3)_2]_2$*, whose molecular structure has been established by X-ray crystallography: cell constants a = 12.05(2) Å, b = 16.02(1) Å, c = 7.411(3) Å; space group* $P2_12_12_1$*, R = 0.056,* $R_w = 0.053$*. The corresponding reaction with the iodide analogue yields the ionic species* $[H_2C\{SC[N(CH_3)_2]_2\}_2]^{2+}(InI_4^-)_2$ *whose structure has also been identified: cell constants a = 10.468(2) Å, b = 23.081(4) Å, c = 15.317(2) Å, β = 102.14(2)°; space group* $P2_1/n$*, R = 0.059,* $R_w = 0.070$*. The formation of the thiouronium complex confirms that the* CH_2 *group in* X_2InCH_2X *is electron-poor, in keeping with the tendency for nucleophilic ligands to react at this site.*

Introduction

We have recently demonstrated that halogenomethyl complexes of indium(III), X_2InCH_2X (X = Br, I), can be prepared by the oxidative insertion of indium monohalides, InX, into the carbon–halogen bond of the appropriate methylene dihalide.[1] The addition of halide anions X^- to these species yields the corresponding salt of $[X_3InCH_2X]^-$, but on treatment with triphenylphosphine Br_2InCH_2Br forms the phosphonium ylide derivative $Br_3InCH_2P(C_6H_5)_3$, while with the bidentate ligand *N,N,N′,N′*-tetramethylethanediamine, the product is the cyclized nitrogen ylide $\overline{Br_3InCH_2NMe_2CH_2CH_2N}Me_2$. Similar reactions occur in the system I_2InCH_2I/tmen. These results demonstrate that the reaction of X_2InCH_2X with such neutral ligands involves nucleophilic attack at the CH_2 site rather than coordination at the metal atom. We now report the reaction of the halogenomethyl complexes of indium with a thiourea ligand. Again, we find that the ligand attacks the electron-poor CH_2 group to form interesting thiouronium derivatives of indium, whose structures have been determined by X-ray crystallography.

Experimental Section

Indium monohalides were prepared by heating metal and trihalide together in a sealed tube;[2] CH_2Br_2, CH_2I_2, 1,1,3,3-tetramethyl-2-thiourea (tmtu) (Aldrich), and ethanol (95%, ACS grade, Merck) were used as supplied. Acetonitrile (ACS grade; Merck) was refluxed over calcium hydride and distilled before use. Acetone (ACS Grade; Merck) was refluxed over anhydrous calcium chloride and distilled.

Indium analysis was by back-titration of excess EDTA with thorium nitrate. In a typical analysis, ca. 50 mg of the compound was destroyed in nitric acid, the resultant solution was neutralized with sodium hydroxide, and the pH was adjusted to 3 using a buffer of potassium biphthalate (0.1 M) and HCl (0.1 M). Excess EDTA (10^{-2} M) was then added, and the mixture was titrated with a standard solution (10^{-2} M) of thorium(IV) nitrate, using xylenol orange as indicator. Halide analysis was by the Volhard method, involving silver halide precipitation and back-titration with potassium thiocyanate solution. Microanalysis was by Canadian Microanalytical Services Ltd. Conductivities were measured in a standard platinum electrode cell, standardized with 1 M aqueous KNO_3. Proton NMR spectra were recorded on a Varian EM 360 spectrometer.

All preparative work was conducted under a dry nitrogen atmosphere, using standard vacuum line techniques, up to the isolation of the products, which are air stable.

Preparation of $Br_3InCH_2SC[N(CH_3)_2]_2$. Indium monobromide (1.0 g, 5.13 mmol) and CH_2Br_2 (2.0 mL, 4.95 g, 28.5 mmol) were stirred together in acetonitrile (30 mL) at room temperature until the monobromide dissolved (ca. 4 h). Small traces of residual solid were removed by filtration, and tmtu (0.68 g, 5.13 mmol) was added to the filtrate. At this point, Br_3InCH_2(tmtu) precipitated as a colorless solid (0.38 g, 0.76 mmol), which was collected. The solution was reduced in volume by 50% in vacuo; addition of ethanol (10 mL) to turbidity, followed by cooling to 0 °C, resulted in the precipitation of a further 1.24 g (2.48 mmol) of the same compound, to give a total yield of 1.62 g, 3.24 mmol, 63%. The compound can be recrystallized from acetone:ethanol (1:1, v/v). Anal. Calcd for $C_6H_{14}Br_3N_2InS$: C, 14.4; H, 2.82; N, 5.59; In, 22.9; Br, 47.9. Found: C, 14.3; H, 2.82; N, 5.60; In, 22.5; Br, 47.6. ^{1}H NMR (acetone-d_6), δ: 2.44, s, 1H; 3.39, s, 6H (Me_4Si = 0). Molar conductivity (1 mmol L^{-1}, in CH_3CN): 3.80 Ω^{-1} cm^2 mol^{-1}.

Preparation of $[H_2C\{SC[N(CH_3)_2]_2\}_2](InI_4)_2$. Indium monoiodide (0.51 g, 2.10 mmol) and CH_2I_2 (1 mL, 3.33 g, 12.4 mmol) were stirred together for 4 h, by which point the monoiodide had completely dissolved; tmtu (0.55 g, 4.20 mmol) was then added, and the mixture was stirred for a further 12 h. A small solid residue was removed, and volatiles were pumped off to leave an oil, which on addition of ethanol (15 mL) gave $[H_2C(tmtu)_2](InI_4)_2$ as a colorless solid which was recrystallized from hot acetone:ethanol (1:2, v/v) as colorless needlelike crystals. Yield: 1.10 g, 0.72 mmol, 69% based on InI. Anal. Calcd for $C_{11}H_{26}I_8In_2N_4S_2$: C, 8.64; H, 1.71; N, 3.66; In, 15.0; I, 66.8. Found: C, 8.85; H, 1.76; N, 3.10; In, 15.6; I, 66.0. ^{1}H NMR (acetone-d_6), δ: 3.55, s, 12H; 5.15, s, 2H. Molar conductivity (1 mmol L^{-1} in CH_3CN): 265 Ω^{-1} cm^2 mol^{-1}.

Crystallographic Measurements. Suitable crystals of Br_2InCH_2Br(tmtu) (**1**) and $[H_2C(tmtu)_2](InI_4)_2$ (**2**) were mounted on glass fibers, and X-ray diffraction data were collected on a Rigaku AFC6S instrument, with graphite monochromated Mo Kα radiation (λ = 0.710 69 Å) at a temperature of 23 °C. Cell

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Table I. Summary of Crystal Data, Intensity Collection, and Structural Refinement

	1	2
formula	$C_6H_{14}N_2SBr_3In$	$C_{11}H_{26}N_4S_2I_8In_2$
fw, M_r	500.78	1523.35
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$
a, Å	12.05(2)	10.468(2)
b, Å	16.02(1)	23.081(4)
c, Å	7.411(3)	15.317(2)
β, deg		102.14(2)
V, Å^3	1431(2)	3618(2)
d_c, g cm^{-3}	2.324	2.796
Z	4	4
cryst dimens, mm	0.2 × 0.3 × 0.3	0.3 × 0.3 × 0.4
abs coeff, cm^{-1}	100.33	81.35
temp, °C	23	23
data collcn range (2θ), deg	3–50	3–45
total no. of rflcns measd	1490	5200
no. of unique data	577 ($I > 3\sigma(I)$)	2076 ($I > 3\sigma(I)$)
R $(\sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|)$	0.056	0.059
$R_w = [\sum_w(\|F_o\| - \|F_c\|)^2/\sum_w\|F_o\|^2]^{1/2}$	0.053	0.070
max Δ/δ in final cycle	0.01	0.15
ρ_{max} in final diff map, e/Å^3	1.01	1.07

Table II. Final Atomic Coordinates for Non-Hydrogen Atoms of Br_3InCH_2(tmtu), 1

atom	x	y	z
In	0.9375(2)	0.9259(2)	0.0836(4)
Br(1)	0.8010(3)	0.8079(3)	0.0420(6)
Br(2)	0.9893(4)	0.9721(3)	–0.2309(6)
Br(4)	1.1063(3)	0.8584(3)	0.2158(7)
S(1)	0.875(1)	1.1286(8)	0.162(2)
N(1)	1.033(2)	1.195(2)	–0.035(3)
N(2)	1.094(2)	1.111(2)	0.199(4)
C(1)	1.011(2)	1.137(2)	0.096(5)
C(2)	0.948(3)	1.214(3)	–0.174(5)
C(3)	1.132(3)	1.247(2)	–0.046(5)
C(4)	1.196(3)	1.085(3)	0.111(6)
C(5)	1.088(3)	1.088(3)	0.390(6)
C(6)	0.857(3)	1.022(3)	0.243(6)

constants and orientation matrices for data collection were obtained using 25 strong reflections in the range $22.54 < 2\theta < 32.35°$.

For 1, the space group was identified as $P2_12_12_1$ from the systematic absences, and this was subsequently confirmed by the successful structure refinement. The intensity of three typical reflections did not change during data collection. Absorption corrections were applied, using the program DIFABS,[3] and the data were also corrected for Lorentz and polarization effects. The structure was solved by direct methods. The indium and bromine atoms were refined anisotropically, and all others isotropically; hydrogen atoms were initially introduced in ideal positions and subsequently refined isotropically. The programs and other data used are listed in refs 4–9. A weighting scheme with $p = 0.03$ was used in the final cycles.

Essentially the same procedures were used in solving the structure of 2, except that all non-hydrogen atoms were refined anisotropically in this case. The atomic coordinates for 1 and 2 are given in Tables II and III, and the important interatomic distances and angles in Table IV. Figures 1 and 2 show the molecular structures of these substances.

Table III. Final Atomic Coordinates for Non-Hydrogen Atoms of $[H_2C(tmtu)_2](InI_4)_2$, 2

atom	x	y	z
I(1)	0.1208(3)	0.3648(1)	0.1934(2)
I(2)	0.3688(3)	0.4449(1)	0.0316(2)
I(3)	–0.0492(3)	0.4159(1)	–0.0881(2)
I(4)	0.1555(3)	0.3604(1)	0.6897(2)
I(5)	0.3724(3)	0.4337(1)	0.4984(2)
I(6)	0.2428(5)	0.2700(1)	–0.0283(2)
I(7)	0.2801(4)	0.2532(1)	0.4799(2)
I(8)	–0.0471(4)	0.3827(2)	0.4164(2)
In	0.1618(3)	0.3720(1)	0.0258(2)
In(2)	0.1858(3)	0.3576(1)	0.5176(2)
S(1)	–0.625(1)	0.5330(4)	0.2495(8)
S(2)	–0.403(1)	0.4556(4)	0.3144(7)
N(1)	–0.569(3)	0.647(1)	0.226(2)
N(2)	–0.711(4)	0.627(1)	0.314(2)
N(3)	–0.384(4)	0.358(1)	0.246(2)
N(4)	–0.268(3)	0.430(1)	0.189(2)
C(1)	–0.343(4)	0.410(2)	0.237(2)
C(2)	–0.498(4)	0.339(2)	0.267(4)
C(3)	–0.298(5)	0.313(2)	0.225(3)
C(4)	–0.187(4)	0.486(2)	0.210(3)
C(5)	–0.268(4)	0.402(2)	0.102(3)
C(6)	–0.637(4)	0.604(2)	0.262(2)
C(7)	–0.521(5)	0.635(3)	0.139(3)
C(8)	–0.518(5)	0.704(2)	0.263(3)
C(9)	–0.779(5)	0.689(2)	0.291(4)
C(10)	–0.761(6)	0.589(2)	0.379(3)
C(11)	–0.448(4)	0.524(1)	0.253(2)

Table IV. Interatomic Distances (Å) and Angles (deg) for Br_3InCH_2(tmtu), 1, and $[H_2C(tmtu)_2](InI_4)_2$, 2

	Br_3InCH_2(tmtu)		
In–Br(1)	2.525(6)	S(1)–C(1)	1.72(3)
In–Br(2)	2.523(5)	N(1)–C(1)	1.36(4)
In–Br(4)	2.504(6)	N(2)–C(1)	1.33(3)
In–C(6)	2.18(4)		
Br(1)–In–Br(2)	105.6(2)	C(1)–S(1)–C(6)	107(2)
Br(1)–In–Br(4)	104.7(2)	S(1)–C(1)–N(1)	116(2)
Br(1)–In–C(6)	108(1)	S(1)–C(1)–N(2)	122(3)
Br(2)–In–Br(4)	106.7(2)	In–C(6)–S(1)	115(2)
Br(2)–In–C(6)	114(1)		
Br(4)–In–C(6)	117(1)		
	$[H_2C(tmtu)_2](InI_4)_2$		
I(1)–In	2.696(4)	I(7)–In(2)	2.711(4)
I(2)–In	2.730(4)	I(8)–In(2)	2.664(5)
I(3)–In	2.707(4)	S(1)–C(6)	1.66(4)
I(4)–In(2)	2.721(4)	S(1)–C(11)	1.85(4)
I(5)–In(2)	2.688(4)	S(2)–C(1)	1.80(3)
I(6)–In	2.691(4)	S(2)–C(11)	1.84(3)
I(1)–In–I(2)	106.9(1)	I(4)–In(2)–I(8)	106.2(1)
I(1)–In–I(3)	111.4(1)	I(5)–In(2)–I(7)	104.6(1)
I(1)–In–I(6)	111.3(1)	I(5)–In(2)–I(8)	113.0(1)
I(2)–In–I(3)	109.0(1)	I(7)–In(2)–I(8)	113.5(2)
I(2)–In–I(6)	104.4(1)	C(6)–S(1)–C(11)	102(2)
I(3)–In–I(6)	113.3(2)	C(1)–S(2)–C(11)	105(2)
I(4)–In(2)–I(5)	109.0(1)	N(1)–C(6)–N(2)	111(3)
I(4)–In(2)–I(7)	110.5(1)	N(3)–C(1)–N(4)	131(3)

Tables of anisotropic thermal parameters for the appropriate non-hydrogen atoms, bond distances and angles, and hydrogen atom coordinates and isotropic thermal parameters are available as supplementary material.

Results and Discussion

Crystallographic Results. The reaction between InX, CH_2X_2, and tmtu clearly produces very different structures for X = Br or I. For X = Br, the product can be regarded as having a thiouronium or sulfonium ylide ligand bonded to a four-coordinate indium(III) center. The structure is very similar to that of $Br_3InCH_2{\cdot}PPh_3$,[1] the In–Br distances in the latter (2.514(2), 2.510(2), and 2.511(2) Å) are only slightly smaller than those in 1 (See Table III), and r(In–C) is the same in both molecules. The coordination at

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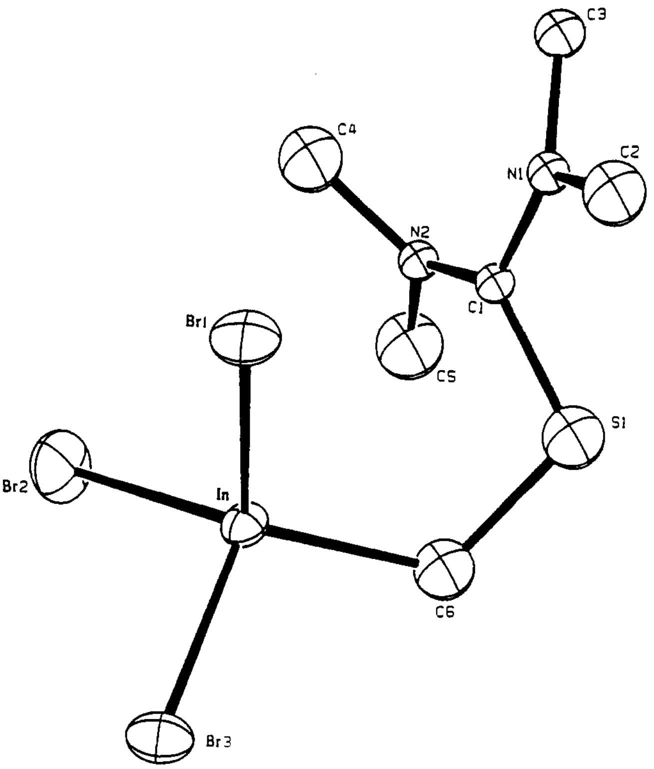

Figure 1. Molecular structure of Br_3InCH_2(tmtu), 1 (ORTEP diagram), with atoms shown as 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

indium is distorted tetrahedral, with the sum of the bond angles being 656°, and again this stereochemistry is essentially identical to that in the triphenylphosphine compound.

The structure of the parent tmtu was determined some years ago,[10] and X-ray crystallographic studies of a number of other adducts have been reported. Those most relevant to the present work include $InCl_3(tmtu)_2$[11] and $[Au(tmtu)_2Br_2]AuBr_2$ and $Au(tmtu)_2Br$.[12] Tetramethylthiourea has $r(C{=}S) = 1.68(1)$ Å, $r(C{-}N) = 1.37(1)$ Å, and $r(H_3C{-}N) = 1.46(1)$ Å, and these values imply some delocalization of electron density in the N_2CS part of the molecule. Coordination typically results in a lengthening of the C=S bond, to 1.751(7) Å in $InCl_3(tmtu)_2$, to 1.74(1) Å in $[Au(tmtu)_2Br_2]^+$, and to 1.727(9) Å in Au(tmtu)Br; comparison of the latter two values suggests that the formal oxidation state of the metal has little or no effect on $r(C{=}S)$. There is a concomitant shortening of $r(C{-}N)$, with values of 1.326(9), 1.32(1), and 1.34(1) Å, respectively, in the three molecules just discussed, while the other C—N bonds show little change. The bond length for C=S in 1 is 1.72(3) Å, longer than that in the parent ligand, but significantly shorter than that in the indium(III) complex, and close to that in Au(tmtu)Br. Similarly, the *C*—N bond (1.35(3) Å) is shorter than that in tmtu, but less so than those in the complexes of indium(III) and gold(III), and similar to that in the gold(I) adduct. These results are in keeping with a model of electron donation from the sulfur atom of tmtu to the CH_2 center in 1.

Compound 2 contains both InI_4^- anions, which have significant deviation from the expected tetrahedral symmetry, and the $[H_2C(tmtu)_2]^{2+}$ cation. The r(In–I) distances at indium(1) show one long bond (2.730(4) Å) and three others which are all almost identical and average 2.698(4) Å; at indium(2), two bonds have r(In–I) = 2.721(4) and 2.711(4) Å, and are significantly shorter at 2.688(4) and 2.664(5) Å. The average, taken over both anions, is r(In–I) = 2.70(1) Å, close to the values previously reported for this anion in $In[InI_4]$ (2.714(2) Å)[13] and $[InI_2(dmso)_4][InI_4]$ (2.71(1) Å).[14]

The cation in 2 can be viewed structurally as being the result of double nucleophilic displacement at the CH_2 site of I_2InCH_2I, resulting in the fission of both C–In and C–I bonds, although mechanistically the reaction does not appear to follow such a path. The average bond distances of 1.85(4) Å for the two resultant C–S bonds show them to be single order and, together with the S(1)–C(11)–S(2) bond angle of 105(2)°, indicate the presence of a quasi-tetrahedral H_2CS_2 center. The remaining structural features are similar to those in 1; the only unusual bond distance is C(1)–S(2) (1.80(3) Å), which is substantially larger than C(6)–S(1) (1.66(4) Å). The bond angle N(3)–C(1)–N(4) (131(3)°) is also significantly larger than the analogous value at N(1)–C(6)–N(2) (111(3)°), so that there are apparently real differences between the two regions of the molecule. Since the InI_4^- anions are also distorted (see above), this may be evidence of strong anion–cation interactions in the crystal lattice.

Spectroscopic Results. The ^1H resonance of the $N{-}CH_3$ groups of Br_3InCH_2(tmtu) at 3.39 ppm is significantly downfield from the corresponding value of 3.08 ppm in the free ligand. For the $[H_2C(tmtu)_2]^{2+}$ cation, the shift is to 3.55 ppm, and both show that the drift of charge to the CH_2 center on coordination is reflected throughout the tmtu molecule. The resonance of the CH_2 protons at 2.44 ppm in Br_3InCH_2(tmtu) is very similar to that in the triphenylphosphine analogue,[1] in keeping with the structural similarities between these two adducts. The analogous value in the $[H_2C(tmtu)_2]^{2+}$ cation is much more strongly shifted, to 5.15 ppm, close to that for CH_2Br_2 (5.0 ppm).[1]

Synthetic and Mechanistic Aspects. The reaction of InX (X = Br, I) with excess CH_2X_2 involves the oxidative addition to one C–X bond of the substrate to give X_2InCH_2X species. There are two sites of interest in such molecules, namely the indium atom, at which coordination can occur, and the CH_2 group, which has been shown in previous work to be available for nucleophilic attack.[1,15]

The reaction between Br_2InCH_2Br and tmtu is apparently very similar to that involving triphenylphosphine and the same halogenomethyl compound.[1] The formally 1:1 adduct is a nonelectrolyte whose structure in the solid state indicates that the reaction results in nucleophilic substitution of Br^- by tmtu, accompanied by bromide transfer to the indium atom. The final thiouronium product is a four-coordinate indium(III) species, and as in the triphenylphosphine case can be regarded as a derivative of the formal structure X_3InCH_2, in which CH_2 carries a small positive formal charge. Other substituted thioureas appear to follow the same reaction pathway, but the products were too unstable to be completely characterized.

In general, the behavior of these InX/CH_2X_2/tmtu systems confirms the earlier conclusion that the CH_2 site

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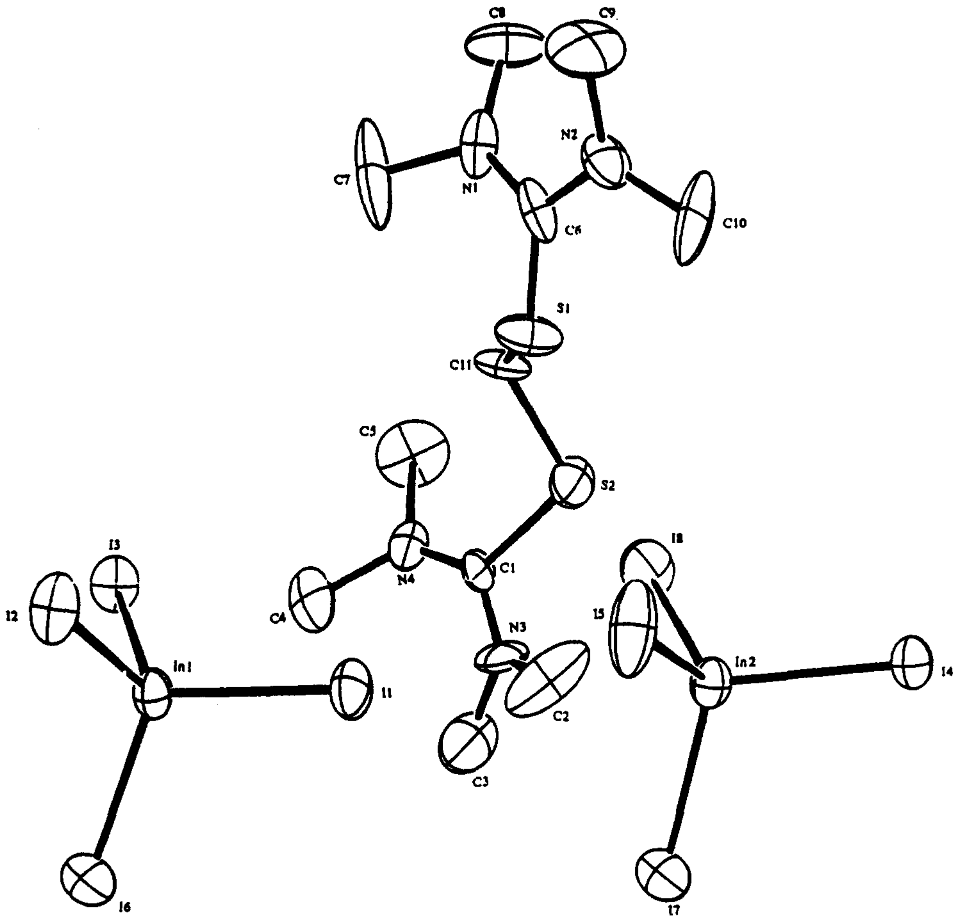

Figure 2. Molecular structure of $[H_2C(tmtu)_2](InI_4)_2$, **2**. Conditions are as in Figure 1.

of X_2InCH_2X species is electron-poor, in contrast to the electron-rich centers observed in transition metal systems.

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Supplementary Material Available: Tables of hydrogen atom coordinates, thermal parameters, and bond distances and angles (6 pages). Ordering information is given on any current masthead page.

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