Photoinduced Reactions of Tri-*tert*-butylindium with (Diethylamino)trimethylstannane and (Di-*n*-butylamino)trimethylstannane

Daniel L. Freeman,[1a] Jerome D. Odom,*,[1a] W. Rodger Nutt,[1b] and Lukasz Lebioda[1a]

Departments of Chemistry, University of South Carolina, Columbia, South Carolina 29208, and
Davidson College, Davidson, North Carolina 28036

Received May 31, 1996⊗

The preparations of $[(t\text{-Bu})_2InNEt_2]_2$ and $[(t\text{-Bu})_2InN(n\text{-Bu})_2]_2$ by the photoinduced reactions of $(t\text{-Bu})_3In$ with Et_2NSnMe_3 and $(n\text{-Bu})_2NSnMe_3$, respectively, have been investigated. The isolation and characterization of products other than $[(t\text{-Bu})_2InNR_2]_2$ in these reactions clearly indicate that the reactions of $(t\text{-Bu})_3In$ with R_2NSnMe_3 do not proceed by simple alkyltrimethyltin elimination. A possible radical mechanism for the formation of the byproducts has been suggested. X-ray crystallographic studies indicate that both compounds are dimeric in the solid state. Crystallographic data: for $[(t\text{-Bu})_2InNEt_2]_2$, orthorhombic space group *Pbca* (No. 61), $a = 19.135(7)$ Å, $b = 19.670(6)$ Å, $c = 15.793(7)$ Å, $V = 5944.41(5)$ Å^3, $\rho(\text{calcd}) = 1.346$ g cm^{-3}; for $[(t\text{-Bu})_2InN(n\text{-Bu})_2]_2$, triclinic space group $P\bar{1}$ (No. 2), $a = 11.943(2)$ Å, $b = 15.790(1)$ Å, $c = 10.711(3)$ Å, $\alpha = 98.60(1)°$, $\beta = 103.54(2)°$, $\gamma = 94.85(1)°$, $V = 1926$ Å^3, $\rho(\text{calcd}) = 1.232$ g cm^{-3}. Mass spectrometry data indicate that both compounds exist as dimers in the gaseous state.

Introduction

As an extension of our studies of group 13/15 compounds,[2] we have begun an investigation of the alkyltrimethyltin elimination reaction (eq 1) as a low-temperature pathway to substituted

$$R_3M + R'_2NSnMe_3 \rightarrow R_2MNR'_2 + RSnMe_3 \qquad (1)$$

$$M = Ga, In$$

aminogallanes and aminoindanes. Alkyltrimethyltin elimination reactions of $(n\text{-Bu})_3B$, Ph_3B, and Et_3Al with Me_2NSnMe_3 were previously reported, and the products $(n\text{-Bu})_2BNMe_2$, Ph_2BNMe_2, and $(Et_2AlNMe_2)_2$ as well as the appropriate alkyltrimethylstannanes were isolated in good yields.[3] When $(t\text{-Bu})_3In$ was allowed to react with Et_2NSnMe_3 or $(n\text{-Bu})_2NSnMe_3$ in the absence of a solvent, $[(t\text{-Bu})_2InNEt_2]_2$ or $[(t\text{-Bu})_2InN(n\text{-Bu})_2]_2$ was isolated in 78% or 82% yield, respectively. However, the other expected product $t\text{-BuSnMe}_3$ was not observed in either reaction. The isolation and characterization of products other than $[(t\text{-Bu})_2InNR'_2]_2$ in these reactions clearly indicate that the reactions of $(t\text{-Bu})_3In$ with R'_2NSnMe_3 do not proceed by simple alkyltrimethyltin elimination. The results of these studies and the crystallographic characterizations of $[(t\text{-Bu})_2InNEt_2]_2$ and $[(t\text{-Bu})_2InN(n\text{-Bu})_2]_2$ are reported herein.

Experimental Section

Materials and General Procedures. Indium trichloride, trimethyltin chloride, lithium diethylamide, dibutylamine, and benzene-d_6 were purchased from Aldrich and used without further purification. *tert*-Butylmagnesium chloride was also purchased from Aldrich. The concentration was determined by titration with a 1.0 M solution of 2-propanol in xylene, using anhydrous 1,10-phenanthroline as an indicator.[4] The solvents diethyl ether and benzene were refluxed over sodium/benzophenone ketyl and distilled into storage flasks. Me_3SnNEt_2 and $Me_3SnN(n\text{-Bu})_2$ were prepared by published procedures.[5] All experiments were performed under a dry nitrogen or argon atmosphere by using Schlenk and glovebox techniques.[6]

The ^1H (300 MHz) and ^{13}C (75.46 MHz) NMR spectra were obtained in benzene-d_6 solutions using a Bruker AM300 FT NMR spectrometer. Standard composite-pulse proton noise-modulated decoupling was used. The ^{119}Sn (111.92 MHz) NMR spectra were obtained in a benzene-d_6 solution using a Bruker AM300 FT NMR spectrometer. Field/frequency stabilization was provided by locking to the deuterium resonance of the deuterated solvent in the 5-mm sample tube. The ^1H and ^{13}C chemical shifts are reported in parts per million (ppm) with respect to Me_4Si at 0.0 ppm. The ^1H chemical shifts were measured from the ^1H resonance of the residual C_6HD_5 (δ 7.15) solvent impurity, and the chemical shifts in the ^{13}C NMR spectra were determined from the ^{13}C resonance of the C_6D_6 solvent (δ 128.3). Mass spectra were obtained on a Finnigan VG 70SQ mass analyzer using electron impact ionization. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. Laser experiments were performed with a Coherent Inova 300 argon ion continuous-wave laser generating light at a wavelength of 488 nm (blue line) with a power output of 50 mW. Light at a wavelength of 780 nm (red line) was generated from a ILX Lightwave LDC 3742B continuous-wave laser diode with a power output of 50 mW. All elemental analyses were performed either by Robertson Microlit Laboratories, Inc., Madison, NJ, or by E+R Microanalytical Laboratory, Inc., Corona, NY.

Syntheses. Tri-*tert*-butylindium. The synthetic procedure was essentially a modification of the method described by Bradley *et al.*[7] To a suspension of $InCl_3$ (4.6 g, 21 mmol) in diethyl ether (20 mL) at 0 °C was added dropwise in the dark $t\text{-BuMgCl}$ (31.5 mL of a 2.0 M solution in ether, 63 mmol). The solvent was removed at 0 °C in vacuo, and hexane, 50 mL, was added to the residue in order to dissolve the $(t\text{-Bu})_3In$. The hexane solution was then filtered and the hexane removed at 0 °C in vacuo. The residue was heated to 45 °C (10^{-2} mmHg), and pale yellow crystals of $(t\text{-Bu})_3In$ sublimed: yield 4.3 g, 72% (based on $InCl_3$); ^1H NMR (benzene-d_6) δ 1.30 (s, t-Bu).

(Diethylamino)di-*tert*-butylindane. $(t\text{-Bu})_3In$ (0.72 g, 2.53 mmol) and Me_3SnNEt_2 (0.59 g, 2.51 mmol) were combined in a reaction tube fitted with a Teflon stopcock and side arm which could be attached to a vacuum system. The solution was freeze−pump−thaw-degassed several times, and the mixture was allowed to stand for 3 weeks at 25

⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1997.

(1) (a) University of South Carolina. (b) Davidson College.

(2) Nutt, W. R.; Blanton, J. S.; Boccanfuso, A. M.; Silks, L. A.; Garber, A. R.; Odom, J. D.; *Inorg. Chem.* **1991**, *30*, 4136.

(3) George, T. A.; Lappert, M. F. *J. Chem. Soc.* **1969**, 992.

(4) Watson, C. S.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

(5) Jones, K.; Lappert, M. F. *J. Chem. Soc.* **1965**, 1944.

(6) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds,* 2nd ed.; Wiley-Interscience: New York, 1986.

(7) Bradley, D. C.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B. *Organometallics* **1988**, *7*, 1112.

S0020-1669(96)00654-4 CCC: $14.00

Table 1. Weights of the Isolated Components from the Reaction of $(t\text{-Bu})_3In$ with R_2NSnMe_3

	R = Et_2		R = $(n\text{-Bu})_2$	
component	wt, g	mmol	wt, g	mmol
Reactants				
$(t\text{-Bu})_3In$	0.32	1.12	0.32	1.12
R_2NSnMe_3	*0.26*	1.10	*0.30*	1.08
total	0.58		0.62	
Products				
$(t\text{-Bu})_2InNR_2$	0.2627	0.876	0.2934	0.822
$(t\text{-Bu})_3In{\cdot}N(H)R_2$	0.0491	0.136	0.0764	0.184
HNR_2	trace		trace	
$SnMe_4$	0.0465	0.260	0.0442	0.247
isobutane/isobutene	0.0101	0.174	0.0121	0.210
Sn_2Me_6	trace		trace	
brown-yellow residue	*0.1603*		*0.1892*	
total	0.53		0.62	
% recovered	91.1		99.2	

°C in normal laboratory light. During this time, large crystals formed in the bottom of the reaction tube. The yellow liquid portion was removed with a syringe, leaving a crude solid (0.74 g, 2.50 mmol, 97% yield). Recrystallization of the solid from CH_2Cl_2 under an argon atmosphere gave colorless crystals of $[(t\text{-Bu})_2InNEt_2]_2$ (0.59 g, 1.97 mmol, 78%yield): mp 140−141 °C; ^{1}H NMR (benzene-d_6) δ 0.91 (t, CH_3, 6H), 1.41 (s, *t*-Bu, 18H), 3.22 (q, CH_2, 4H); ^{13}C NMR (benzene-d_6) δ 14.89 (CH_3), 33.86 (*t*-Bu), 45.02 (CH_2); mass spectrum *m/z* 545 ($M^+ - t$-Bu). Anal. Calcd for $C_{12}H_{28}InN$: C, 47.87; H, 9.30; N, 4.65; In, 38.16. Found: C, 47.81; H, 9.21; N, 4.65; In, 38.52.

Spectral data for the yellow liquid: ^{1}H NMR (benzene d_6) δ 0.07 (s), 0.24 (s) 0.62 (t), 1.40 (s), 1.52 (q); ^{119}Sn NMR (benzene d_6) δ −126.97, −108.77 (very weak intensity, $Me_3SnSnMe_3$),[8,9] 0.13 (Me_4-Sn),[8,9] 128.85; mass spectrum: *m/z* 229, 172, 115, 73, 57 at room temperature, *m/z* >700 at 190 °C.

(Di-*n*-butylamino)di-*tert*-butylindane. $(t\text{-Bu})_3In$ (0.43 g, 1.50 mmol) and $Me_3SnN(n\text{-Bu})_2$ (0.43 g, 1.50 mmol) were combined and allowed to react in accordance with the method described above. Recrystallization from CH_2Cl_2 gave $[(t\text{-Bu})_2InN(n\text{-Bu})_2]_2$ (0.44 g, 1.23 mmol, 82% yield): mp 120−121 °C; ^{1}H NMR (benzene-d_6) δ 3.36 (t, CH_2, 4H), 1.52 (s, *t*-Bu, 18H), 1.53 (mult, CH_2, 4H), 1.31 (mult, CH_2, 4H), 0.92 (t, CH_3, 6H); ^{13}C NMR (benzene-d_6) δ 52.92 (CH_2), 34.04 (*t*-Bu), 31.87 (CH_2), 21.02 (CH_2), 14.32 (CH_3); mass spectrum *m/z* 657 ($M^+ - t$-Bu). Anal. Calcd for $C_{16}H_{36}InN$: C, 53.81; H, 10.09; N, 3.90; In, 32.17. Found: C, 53.67; H, 9.98; N, 3.82; In, 32.03.

Identification of All Products Formed. In a nitrogen-filled drybox $(t\text{-Bu})_3In$ (0.320 g, 1.12 mmol) and Et_2NSnMe_3 (0.260 g, 1.10 mmol) were combined in a 50-mL reaction tube equipped with a Teflon stopcock and a side arm which could be attached to a vacuum system. The reaction tube was then attached to a vacuum system, and the reactants were freeze−pump−thaw-degassed several times. The reactants were then allowed to warm to room temperature and exposed to normal laboratory light for 2 weeks. The volatile components of the reaction mixture were separated using cold-column fractionation techniques and weighed. The first fraction collected at −120 °C (0.011 g) was identified by ^{1}H NMR spectroscopy as a mixture of isobutane and isobutene. This assignment was based on the comparison of the ^{1}H NMR spectrum of the fraction with the ^{1}H NMR spectra of the authentic compounds. The second fraction collected at −70 °C (0.047 g, 0.26 mmol 24% yield) was identified by ^{1}H, ^{13}C, and ^{119} Sn NMR spectroscopy as tetramethylstannane.[8,9] In addition, a very small fraction collected at room temperature was identified as diethylamine on the basis of its ^{1}H NMR spectrum, which was identical to the ^{1}H NMR spectrum of the authentic compound.

The nonvolatile portion of the reaction mixture contained crystals of $[(t\text{-Bu})_2InNEt_2]_2$ and a dark yellow oil. The mixture was dissolved in hexane, and the solution was cooled to −12 °C, precipitating $[(t\text{-Bu})_2InNEt_2]_2$ (0.2627 g, 0.873 mmol, 78% yield). The hexane was trap-to-trap-distilled from the filtrate, and a dark yellow oil remained. The adduct $(t\text{-Bu})_3In{\cdot}N(H)Et_2$ (0.049 g, 0.14 mmol, 12% yield) slowly sublimed from the oil at room temperature and a pressure of 10^{-2} Torr over a period of 24 h. The ^{1}H NMR spectrum of the adduct was identical to the spectrum of the autentic sample: ^{1}H NMR (benzene-d_6) δ 0.62 (t, CH_3, 6H), 1.40 (s, *t*-Bu, 27H), 1.52 (q, CH_2, 4H); mass spectrum (at room temerature) *m/z* 229, 172, 115, 73, 57. A brown-yellow residue (0.1603 g) remained: ^{119}Sn NMR (benzene-d_6) δ −126.97; 128.85; mass spectrum (at 190 °C) *m/z* >700. Anal. Found: C, 31.79; H, 6,82; Sn, 55.7. The ^{1}H NMR spectrum of the residue contained numerous peaks in the regions 0.2−0.4 and 1.1−1.4 ppm.

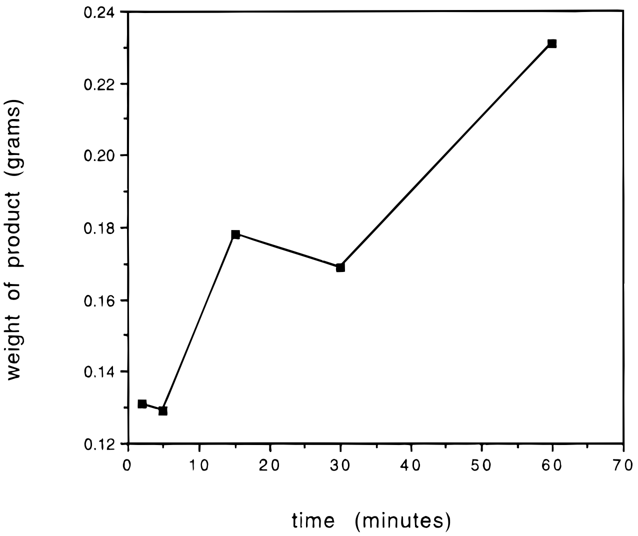


Figure 1. Graphical representation of the weight of product $[(t\text{-Bu})_2InNEt_2]_2$ formed from the reaction of $(t\text{-Bu})_3In$ with Me_3SnNEt_2 vs time of exposure to 50 mW of 488 nm laser light.

The products from the reaction of $(t\text{-Bu})_3In$ (0.320 g, 1.12 mmol) with $(n\text{-Bu})_2NSnMe_3$ (0.300 g, 1.08 mmol) were isolated and characterized in a similar manner. The results of both experiments are reported in Table 1.

Photolysis Studies. Two samples of neat Et_2NSnMe_3 and neat $(t\text{-Bu})_3In$ in a 1:1 molar ratio were prepared. Sample 1: 0.4 g (1.4 mmol) of $(t\text{-Bu})_3In$ and 0.26 g (1.4 mmol) of Et_2NSnMe_3 were placed in a 10-mL round-bottom flask that was capped with a rubber septum. Sample 2: 0.4 g (1.4 mmol) of $(t\text{-Bu})_3In$ and 0.26 g (1.4 mmol) of Et_2NSnMe_3 were placed in a 10-mL round-bottom flask that was capped with a rubber septum and covered with aluminum foil. Both the uncovered (sample 1) and covered (sample 2) flasks were placed side by side and exposed to laboratory light at room temperature. Within 2 days, a solid appeared in the flask with sample 1. After 3 weeks, the dark yellow oil was removed from the flask with sample 1 and recrystallization of the solid afforded $[(t\text{-Bu})_2InNEt_2)]_2$ (0.32 g, 1.06 mmol, 76% yield). After several months no solid was found in the covered flask with sample 2.

A flask containing $(t\text{-Bu})_3In$ (0.72 g, 2.5 mmol) and Me_3SnNEt_2 (0.59 g, 2.5 mmol) and equipped with a Teflon stopcock was exposed to 50 mW of 488-nm laser light for 60 min. After the exposure, a dark liquid was removed from the flask with a syringe, and recrystallization of the remaining solid gave $[(t\text{-Bu})_2InNEt_2)]_2$ (0.41 g, 1.4 mmol, 55% yield). In a similar experiment, the flask that contained the reaction solution was exposed to 50 mW of 780-nm laser light for 60 min. After the exposure, no solid was present in the flask and no peaks associated with $[(t\text{-Bu})_2InNEt_2)]_2$ were found in the ^{1}H NMR spectrum of the reaction solution.

A neat solution of $(t\text{-Bu})_3In$ (1.44 g, 5.1 mmol) and Me_3SnNEt_2 (1.2 g, 5.0 mmol) was prepared, and 1.0-mL aliquots of the solution were each placed in five flasks. The flasks were each exposed to 50 mW of 488- nm laser light for successively longer periods of time: 2.0, 5.0, 15.0, 30.0, and 60.0 min. After irradiation, the samples were allowed to stand in the dark for 3 days. The dark liquids were removed from the flasks with a syringe, and recrystallization of the remaining solids gave $[(t\text{-Bu})_2InNEt_2)]_2$. The yields are displayed graphically in Figure 1.

Collection of Crystallographic Data. Clear crystals of both $[(t\text{-Bu})_2InNEt_2]_2$ and $[(t\text{-Bu})_2InN(n\text{-Bu})_2]_2$ were grown by slow evaporation

---

(8) Mitchell, T. N. *J. Organomet. Chem.* **1973**, *59*, 189.

(9) Tupciauskas, A. P.; Sergeyev, N. M.; Ustynuk, Yu. A. *Org. Magn. Reson.* **1971**, *3*, 655.

Table 2. X-ray Diffraction Data for $[(t\text{-Bu})_2\text{InNEt}_2]_2$ and $[(t\text{-Bu})_2\text{InN}(n\text{-Bu})_2]_2$

	$[(t\text{-Bu})_2\text{InNEt}_2]_2$	$[(t\text{-Bu})_2\text{InN}(n\text{-Bu})_2]_2$
cryst syst	orthorhombic	triclinic
space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)
a, Å	19.135(7)	11.943(2)
b, Å	19.670(6)	15.790(1)
c, Å	15.793(7)	10.711(3)
α, deg		98.60(1)
β, deg		103.54(2)
γ, deg		94.85(1)
V, Å^3	5944.41 (3)	1926
Z	8	2
MW	602.4	714.6
ρ(calcd), g cm^{-3}	1.346	1.232
radiation (λ,Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
monochromator	graphite	graphite
2θ range, deg	4−46	4−46
scan type	$\omega/2\theta$	$\omega/2\theta$
no. of unique data	5775	5044
no. of unique data with $I > 3\sigma(I)$	3144	4783
T, °C	23	23
R^a	0.0442	0.0334
$R_w{}^b$	0.0450	0.0288
weighting scheme	$w = [\sigma^2\lvert F_o\rvert + 2 \times 10^{-4}\,\lvert F_o\rvert^2]^{-1}$	$w = [\sigma^2\lvert F_o\rvert]^{-1}$

[a] $R = \Sigma\lvert\lvert F_o - \lvert KF_c\rvert\rvert^2/\Sigma\lvert F_o\rvert$. [b] $R_w = [\Sigma w(\lvert F_o\rvert - \lvert KF_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$.

Table 3. Bond Lengths (Å), Intramolecular Distances (Å), and Selected Bond Angles (deg) for $[(t\text{-Bu})_2\text{InNEt}_2]_2$

	Distances		
In(1)···In(2)	3.381(0)	C(23)−C(24)	1.51(1)
N(1)···N(2)	3.026(5)	C(3)−C(31)	1.52(1)
In(1)−N(1)	2.270(4)	C(3)−C(33)	1.52(1)
In(1)−N(2)	2.267(4)	C(3)−C(32)	1.55(1)
In(1)−C(3)	2.254(7)	C(5)−C(51)	1.53(8)
In(1)−C(4)	2.243(6)	C(5)−C(52)	1.52(1)
In(2)−N(1)	2.272(4)	C(5)−C(53)	1.53(1)
In(2)−N(2)	2.269(4)	C(4)−C(42)	1.53(1)
In(2)−C(5)	2.254(5)	C(4)−C(41)	1.51(1)
In(2)−C(6)	2.253(7)	C(4)−C(43)	1.51(1)
N(1)−C(11)	1.498(7)	C(21)−C(22)	1.53(1)
N(1)−C(13)	1.484(8)	C(13)−C(14)	1.52(1)
N(2)−C(23)	1.491(7)	C(6)−C(62)	1.52(1)
N(2)−C(21)	1.499(6)	C(6)−C(61)	1.51(1)
C(11)−C(12)	1.52(1)	C(6)−C(63)	1.53(1)
	Angles		
In(1)−N(1)−In(2)	96.2(2)	C(3)−In(1)−N(2)	117.8(2)
C(3)−In(1)−C(4)	113.9(3)	C(4)−In(1)−N(2)	110.4(2)
C(3)−In(1)···In(2)	125.2(2)	C(13)−N(1)···N(2)	129.7(3)
C(3)−In(1)−N(1)	110.2(2)	C(11)−N(1)···N(2)	119.4(3)
C(4)−In(1)−N(1)	117.8(2)	C(31)−C(3)−In(1)	115.9(5)
C(11)−N(1)−In(1)	113.0(3)	C(32)−C(3)−In(1)	106.7(5)
C(13)−N(1)−In(1)	111.5(3)	C(33)−C(3)−In(1)	110.3(5)
C(12)−C(11)−N(1)	114.1(5)	C(41)−C(4)−In(1)	107.7(5)
C(14)−C(13)−N(1)	114.5(5)	C(42)−C(4)−In(1)	109.8(5)
N(1)−In(1)−N(2)	83.6(1)	C(43)−C(4)−In(1)	115.9(5)
C(4)−In(1)···In(2)	120.9(2)		

of solvent from a CH_2Cl_2 solution at 25 °C. Suitable crystals were mounted in glass capillary tubes with their long axis roughly parallel to the ϕ axis of the goniometer. Preliminary examination and data collection were performed with Mo Kα radiation (0.710 73 Å) on an Enraf-Nonius CAD4 computer controlled κ-axis diffractometer equipped with a graphite-crystal, incident-beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinements, using the setting angles of 25 reflections in the range 10−12°, measured by the computer-controlled diagonal-slit method of centering. Crystal data, data collection parameters, and results of the analyses are listed in Table 2 for $[(t\text{-Bu})_2\text{InNEt}_2]_2$ and $[(t\text{-Bu})_2\text{InN}(n\text{-Bu})_2]_2$ Full-matrix least-squares refinements minimized the function $w = (\sigma^2(F_o) + 2.0 \times 10^{-4}F_o{}^2)^{-1}$.

Structure Determination and Refinement. For the compound $[(t\text{-Bu})_2\text{InNEt}_2]_2$, the positions of the In atoms were obtained from a Patterson map, and the positions of the C and N atoms were taken from difference Fourier maps. The hydrogen atoms were calculated in idealized positions (C−H = 0.96 Å; H−C−H = 109.5°) and were included in the structure factor calculations, but they were not refined. The model was refined using anisotropic temperature factors for all nonhydrogen atoms. In the final cycle all shift/esd values were less than 0.005. For $[(t\text{-Bu})_2\text{InN}(n\text{-Bu})_2]_2$, the positions of the In, C, and N atoms were obtained from a Patterson map. After several cycles of a blocked full-matrix least-squares refinement with all nonhydrogen atoms anisotropic, the methyl and methylene hydrogen atoms were generated at calculated positions (C−H = 0.96 Å; H−C−H = 109.5°) with rigid geometry. Additional cycles of refinement led to convergence. All calculations were performed on a DEC VAX 8530 computer using SHELX-76,[10a] SHELX-86,[10b] and OFRRE4.[11] Scattering factors for all atoms included real and imaginary anomalous dispersion components.[12] Selected bond lengths and bond angles for $[(t\text{-Bu})_2\text{InNEt}_2]_2$ and $[(t\text{-Bu})_2\text{InN}(n\text{-Bu})_2]_2$ are given in Tables 3 and 4, respectively. Tables of observed and calculated structure factors, thermal parameters, and final positional parameters are available as Supporting Information.

Results and Discussion

When a neat solution of $(t\text{-Bu})_3\text{In}$ and $\text{Et}_2\text{NSnMe}_3$ or $(n\text{-Bu})_2\text{NSnMe}_3$ in a 1:1 mole ratio is allowed to stand at room temperature in laboratory light, $[(t\text{-Bu})_2\text{InNEt}_2]_2$ or $[(t\text{-Bu})_2\text{InN}(n\text{-Bu})_2]_2$ slowly crystallizes from the yellow liquid over a period of 2−3 weeks. The ^{119}Sn NMR spectrum of the yellow liquid exhibits resonances at 128.8, 0.13, −108.8 (very small peak), and −127.0 ppm. The peaks at 0.13 and −108.8 ppm are associated with Me_4Sn and $\text{Me}_3\text{SnSnMe}_3$.[8,9]

A more extensive investigation of these reactions revealed that isobutane, isobutene, tetramethylstannane, diethylamine or di-n-butylamine, and $(t\text{-Bu})_3\text{In}\cdot\text{N(H)Et}_2$ or $(t\text{-Bu})_3\text{In}\cdot\text{N(H)}(n\text{-Bu})_2$ were formed in addition to $[(t\text{-Bu})_2\text{InNEt}_2]_2$ or $[(t\text{-Bu})_2\text{InN}(n\text{-Bu})_2]_2$. The weights of these products are listed in Table 1. The brown-yellow residue from the reactions constituted about 30% of the products. The ^{1}H NMR spectrum of the residue contained numerous peaks in the regions 0.2−0.4 and 1.1−1.4 ppm, and the ^{119}Sn NMR spectrum exhibited two

---

(10) (a) Sheldrick, G. M. *SHELX-76 Program for Crystal Structure Determination*; Cambridge University Press: New York, 1975. (b) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: London, 1985; pp 175−189.

(11) Busing, W. R.; Martin, K. O.; Levy, H. A. *ORFFE*; Revised by F. M. Brown, C. K. Johnson, and W. E. Thiessen; Oak Ridge National Laboratory: Oak Ridge, TN, 1985.

(12) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table 4. Bond Lengths (Å), Intramolecular Distances (Å), and Selected Bond Angles (deg) for [(*t*-Bu)$_2$InN(*n*-Bu)$_2$]$_2$

Distances			
In(1)···In(2)	3.367(1)	C(5)−C(8)	1.508(9)
N(1)···N(2)	3.039(6)	C(9)−C(10)	1.547(11)
In(1)−N(1)	2.272(4)	C(9)−C(11)	1.516(10)
In(1)−N(2)	2.266(4)	C(9)−C(12)	1.531(11)
In(1)−C(1)	2.215(5)	C(13)−C(14)	1.532(10)
In(1)−C(5)	2.218(5)	C(13)−C(15)	1.505(8)
In(2)−N(1)	2.268(4)	C(13)−C(16)	1.534(9)
In(2)−N(2)	2.267(4)	C(17)−C(18)	1.523(9)
In(2)−C(9)	2.218(5)	C(18)−C(19)	1.519(10)
In(2)−C(13)	2.219(5)	C(19)−C(20)	1.510(12)
N(1)−C(17)	1.469(7)	C(21)−C(22)	1.519(8)
N(1)−C(21)	1.472(6)	C(22)−C(23)	1.509(9)
N(2)−C(25)	1.476(7)	C(23)−C(24)	1.503(14)
N(2)−C(29)	1.465(6)	C(25)−C(26)	1.515(9)
C(1)−C(2)	1.518(8)	C(26)−C(27)	1.504(10)
C(1)−C(3)	1.555(9)	C(27)−C(28)	1.509(15)
C(1)−C(4)	1.527(9)	C(29)−C(30)	1.525(8)
C(5)−C(6)	1.528(9)	C(30)−C(31)	1.487(8)
C(5)−C(7)	1.533(9)	C(31)−C(32)	1.515(13)

Angles			
In(1)−N(1)−In(2)	95.7(1)	C(22)−C(21)−N(1)	115.9(4)
C(1)−In(1)−C(5)	114.5(2)	N(1)−In(1)−N(2)	84.1(1)
C(9)−In(2)−C(13)	115.0(2)	C(5)−In(1)···In(2)	123.7(2)
C(5)−In(1)···In(2)	123.7(2)	C(21)−N(1)−C(17)	111.2(4)
C(5)−In(1)−N(1)	118.7(2)	C(25)−N(2)−C(29)	111.0(4)
C(1)−In(1)−N(1)	108.9(2)	C(2)−C(1)−In(1)	116.4(4)
C(21)−N(1)−In(1)	109.0(3)	C(3)−C(1)−In(1)	110.5(4)
C(21)−N(1)−In(2)	115.0(3)	C(4)−C(1)−In(1)	107.9(3)
C(17)−N(1)−In(1)	116.3(3)	C(6)−C(5)−In(1)	116.8(4)
C(17)−N(1)−In(2)	109.0(3)	C(7)−C(5)−In(1)	110.4(4)
C(18)−C(17)−N(1)	115.4(4)	C(8)−C(5)−In(1)	116.9(4)

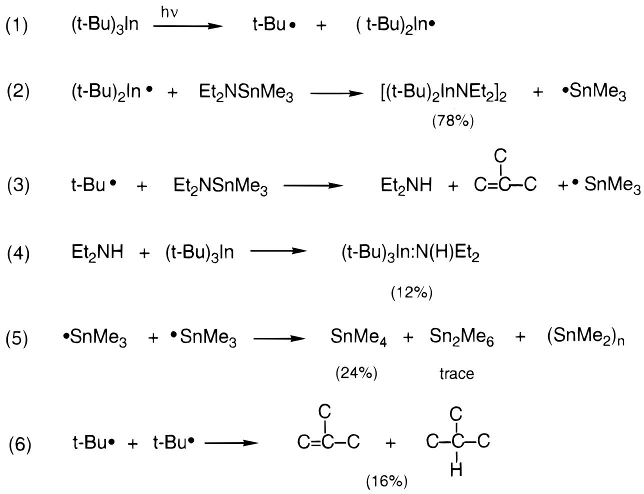
signals at −126.97 and 128.85 ppm. An elemental analysis indicated that 55.7% of the residue from the reaction of (*t*-Bu)$_3$In with Me$_3$SnNEt$_2$ is tin. The mass spectrum of the residue at 190 °C suggested that some of the tin compounds are polymeric. Fragments with *m/z* values greater than 700 were observed, and the relative intensities of the peaks were consistent with natural abundances of the tin isotopes.

These reactions are photochemically induced. A flask that contained a mixture of (*t*-Bu)$_3$In and Et$_2$NSnMe$_3$ in a 1:1 mole ratio was allowed to stand in laboratory light while a second flask that contained the same reactants in a 1:1 mole ratio was covered with aluminum foil. After 3 weeks, [(*t*-Bu)$_2$InNEt$_2$]$_2$ was isolated in a 76% yield from the flask that was exposed to light. However, no products were detected in the reaction solution from the covered flask. Similar results were observed for the reaction of (*t*-Bu)$_3$In with (*n*-Bu)$_2$NSnMe$_3$. Also, when the reactants (*t*-Bu)$_3$In and Et$_2$NSnMe$_3$ were irradiated with 50 mW of 488-nm laser light for 60 min, [(*t*-Bu)$_2$InNEt$_2$]$_2$ was obtained in a 55% yield. When laser light of 780 nm was used, no signals associated with [(*t*-Bu)$_2$InNEt$_2$]$_2$ were observed in the ^{1}H NMR spectrum of the reaction mixture.

Light is required to sustain as well as initiate the reactions. A neat solution of (*t*-Bu)$_3$In and Et$_2$NSnMe$_3$ in a 1:1 mole ratio was prepared. Each of five 1.0-mL aliquots of the solution was exposed to 488-nm laser light for a successively longer period of time and then allowed to stand in the dark for 3 days prior to the removal of the volatile components by trap-to-trap distillation. The nonvolatile mixture was dissolved in hexane, and the solution was cooled to effect precipitation of [(*t*-Bu)$_2$InNEt$_2$]$_2$. A plot of the weight of the [(*t*-Bu)$_2$InNEt$_2$]$_2$ isolated versus the time of exposure is found in Figure 1. Clearly, longer exposure times result in higher yields.

The requirement of light to effect a reaction between (*t*-Bu)$_3$In and R$_2$NSnMe$_3$ and the variety and nature of the products suggest that the reaction may proceed by a free radical mechanisim. One may infer from the products Me$_4$Sn, Me$_3$SnSnMe$_3$, and the polymeric tin compounds in the residue that the Me$_3$Sn$^•$ radical is formed initially. Self-reactions of Me$_3$Sn$^•$ have been found to yield Me$_4$Sn, Me$_3$SnSnMe$_3$, and Me$_2$Sn,[13,14] and cantenation of dialkyltin(II) can produce linear oligomers with chain lengths of 12−20.[15,16] Homolytic reactions of organotin compounds are well-known. Organotin radicals can be generated by photolysis or reactions with other radicals.[17] The CIDNP technique has been used to study the photochemical decomposition of Et$_2$NSnMe$_3$ with light from a 1000-W Hg−Xe arc lamp, and the accumulation of Me$_3$Sn$^•$ and Et$_2$N$^•$ radicals during the decomposition has been proposed as an explanation for the observed nuclear polarizations.[18] However, Me$_3$SnNEt$_2$ is stable in the presence of normal laboratory light or light emitted by an argon ion laser with 50 mW power.[19] If the photochemical decomposition of Me$_3$SnNEt$_2$ is not the source of the Me$_3$Sn$^•$ radical, then the radical must form in a reaction of the Me$_3$SnNEt$_2$ with another radical.

Scheme 1. Possible Radical Mechanism for the Formation of [(*t*-Bu)$_2$InNEt$_2$]$_2$ and Other Products in the Reaction of (*t*-Bu)$_3$In with Me$_3$SnNEt$_2$[a]



[a] Percent by weight of the recovered material, taken from Table 1, is given in parentheses.

The other reactant, (*t*-Bu)$_3$In, is known to be light sensitive. When a solution of (*t*-Bu)$_3$In in benzene was exposed to sunlight, a metallic mirror formed as well as butane, isobutane, and isobutene. Although the *t*-Bu$^•$ radical was not detected by ESR during the photochemical decomposition of (*t*-Bu)$_3$In in toluene, the radical may have formed but in concentrations too low to detect.[7] When (*t*-Bu)$_3$In was dissolved in R$_2$NSnMe$_3$ and the resulting solution was exposed to light, isobutane and isobutene were formed but a metallic mirror was not observed. It is reasonable to assume that homolytic cleavage of an In−C bond occurs and that subsequently either the *t*-Bu$^•$ or the (*t*-Bu)$_2$In$^•$ radical reacts with R$_2$NSnMe$_3$ to produce the Me$_3$Sn$^•$ radical (Scheme 1). Possible pathways to the other products are presented in Scheme 1.

The crystal and molecular structures of [(*t*-Bu)$_2$InNEt$_2$]$_2$ and [(*t*-Bu)$_2$InN(*n*-Bu)$_2$]$_2$ were determined from X-ray crystal-

---

(13) Chilton, H. T. J.; Gowenlock, B. G. *Trans. Faraday Soc.* **1953**, *49*, 1451.

(14) Clark, H. C.; Cotton, J. D.; Tsai, J. H. *Can. J. Chem.* **1966**, *44*, 903.

(15) Azuma, Y.; Newcomb, M. *Organometallics* **1984**, *3*, 9.

(16) Williams, G. H. *Advances in Free-Radical Chemistry*; LogosPress Ltd.: London, 1965; Vol. 1.

(17) Davies, A. G. *Advances in Chemistry Series*; Gould, R. F., Ed.; The Maple Press Co.: York, PA., 1976; No. 157, p 26.

(18) Lehnig, M. *Tetrahedron Lett.* **1974**, *37*, 3323.

(19) A 2.0 mL sample of Me$_3$SnEt$_2$ was irradiated for several hours with 488 nm light from an argon ion laser (50 mW power). The ^{1}H NMR spectrum of the irradiated sample in hexane was identical to the spectrum of Me$_3$SnNEt$_2$.

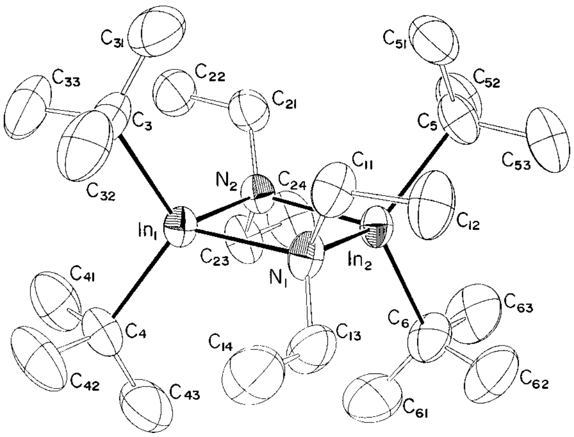


Figure 2. ORTEP drawing of $[(t\text{-Bu})_2\text{InNEt}_2]_2$.

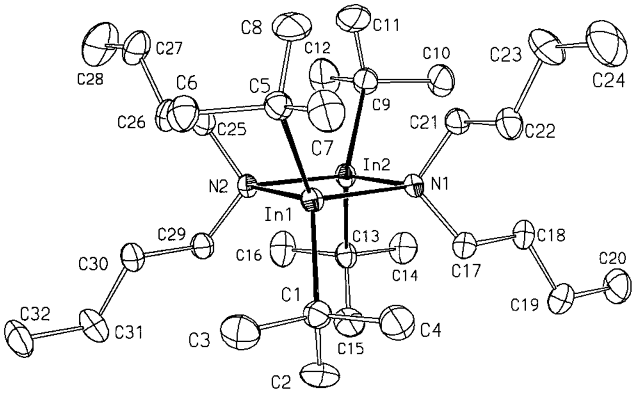


Figure 3. ORTEP drawing of $[(t\text{-Bu})_2\text{InN}(n\text{-Bu})_2]_2$.

lographic studies. Figures 2 and 3 show ORTEP drawings of the compounds. Tables 3 and 4 list selected bond distances and angles. The compound $[(t\text{-Bu})_2\text{InNEt}_2]_2$ crystallizes in the orthorhombic crystal system, and the systematic absences observed during the collection of the data were consistent with the space group *Pbca*. The structure of $[(t\text{-Bu})_2\text{InNEt}_2]_2$ consists of dimeric units with crystallographically imposed C_1 symmetry. The compound $[(t\text{-Bu})_2\text{InN}(n\text{-Bu})_2]_2$ crystallizes in the triclinic crystal system having the space group $P\bar{1}$ (No. 2). The structure of $[(t\text{-Bu})_2\text{InN}(n\text{-Bu})_2]_2$ also consists of dimeric units having crystallographically imposed C_1 symmetry. The lack of symmetry in these compounds stems from the nonplanar nature of the In_2N_2 ring. The fold angles along the In···In diagonal in $[(t\text{-Bu})_2\text{InNEt}_2]_2$ and $[(t\text{-Bu})_2\text{InN}(n\text{-Bu})_2]_2$ (5.0(2)° and 2.1(2)°) are significantly smaller than the corresponding angle (25.8°) found in $[\text{Me}_2\text{GaN(H)Dipp}]_2$[20] and probably arise from crystal-packing forces rather than steric overcrowding. A fold angle of 6.9° has been reported for $[(i\text{-Pr})_2\text{GaP}(i\text{-Pr})_2]_2$ and attributed to packing forces.[21]

A comparison of the bond lengths and bond angles common to $[(t\text{-Bu})_2\text{InNEt}_2]_2$ and $[(t\text{-Bu})_2\text{In}(n\text{-Bu})_2]_2$ (Tables 3 and 4) reveals that the molecular structures of the two dimers are very similar. Only the In−C bond distances differ. The average In−C bond length (2.251(6) Å) in $[(t\text{-Bu})_2\text{InNEt}_2]_2$ is slightly longer than the average bond length (2.217(5) Å) in $[(t\text{-Bu})_2\text{In}(n\text{-Bu})_2]_2$. However, many of the bond lengths and bond angles common to $[(t\text{-Bu})_2\text{InNEt}_2]_2$ and $[\text{Me}_2\text{InNEt}_2]_2$[22] differ significantly (Table 5). The In−N bond in $[(t\text{-Bu})_2\text{InNEt}_2]_2$ (average 2.270 (4) Å) is slightly longer than the In−N bond in $[\text{Me}_2\text{InNEt}_2]_2$ (average 2.235 (3) Å). The larger steric requirements of the *t*-Bu groups may contribute to the smaller C−In−C and N−In−N bond angles in $[(t\text{-Bu})_2\text{InNEt}_2]_2$ (average 114.0 (3) and 83.6(1)°) compared with the corresponding angles in $[\text{Me}_2\text{InNEt}_2]_2$ (average 125.9(2) and 86.0(2)°). Also, crystal-packing forces may play an important role. Smaller C−In−C and N−In−N bond angles in $[(t\text{-Bu})_2\text{InNEt}_2]_2$ would improve packing efficiency. Similar trends in C−Ga−C and N−Ga−N bond angles have been observed for $[(t\text{-Bu})_2\text{GaN(H)Ph}]_2$[23] (average 114.2 (5) and 83.5(3)°) and for $[\text{Me}_2\text{GaN(H)Ph}]_2$[20] (average 121.9 (2) and 86.4 (1)°).

Table 5. Comparison of Intramolecular Parameters for $[(t\text{-Bu})_2\text{InNEt}_2]_2$ and $[\text{Me}_2\text{InNEt}_2]_2$[22]

Bonds or Contacts (Å)

	$[(t\text{-Bu})_2\text{InNEt}_2]_2$	$[\text{Me}_2\text{InNEt}_2]_2$
In···In′	3.381(0)	3.269(1)
N−N	3.026(5)	3.050(5)
In−N	2.270(4)	2.234(3)
	2.267(4)	2.236(3)
In−C	2.254(7)	2.147(3)
	2.243(6)	2.171(4)
N−C	1.498(7)	1.481(6)
	1.484(8)	1.484(6)

Angles (deg)

	$[(t\text{-Bu})_2\text{InNEt}_2]_2$	$[\text{Me}_2\text{InNEt}_2]_2$
N−In−N′	83.6(1)	86.0(2)
C−In−C	113.9(3)	125.9(2)
In−N−In′	96.2(2)	94.0(2)
C−In−N	110.2(2)	108.4(3)
	117.8(2)	110.0(3)
C−N−C	110.9(3)	112.2(3)
	110.5(4)	
N−In−In′−N′	5.0 (2)	

The alkyltrimethyltin elimination reactions (eq 1) of Me_3Ga or Et_3Ga with $(i\text{-Bu})_2\text{NSnMe}_3$ or $(\text{C}_6\text{H}_{11})_2\text{NSnMe}_3$ have been observed. The aminogallane $[\text{R}_2\text{GaNR'}_2]_2$ and Me_4Sn or EtSnMe_3 were the only products identified in the reaction mixtures.[24] In the current study the aminoindanes $[(t\text{-Bu})_2\text{InNEt}_2]_2$ and $[(t\text{-Bu})_2\text{InN}(n\text{-Bu})_2]_2$ also were isolated from the reactions of $(t\text{-Bu})_3\text{In}$ with $\text{Et}_2\text{NSnMe}_3$ and $(n\text{-Bu})_2\text{NSnMe}_3$. However, the other product in the reactions was not the alkyltrimethyltin $(t\text{-Bu})\text{SnMe}_3$. Instead, the products isobutane, isobutene, tetramethylstannane, diethylamine or di-*n*-butylamine, and $(t\text{-Bu})_3\text{In}{\cdot}\text{NEt}_2$ or $(t\text{-Bu})_3\text{In}{\cdot}\text{N}(n\text{-Bu})_2$ were obtained. The two reaction systems differ in a second respect: Light is required to initiate and sustain the reactions of $(t\text{-Bu})_3\text{In}$ with $\text{Et}_2\text{NSnMe}_3$ and $(n\text{-Bu})_2\text{NSnMe}_3$.

Acknowledgment. The financial support from the NSF/EPSCoR (Grant ESR-9108772) is gratefully acknowledged. We also thank M. L. Myrick and J. F. Aust for the use of and help with the laser equipment and T. A. Barnard and Yan Ding for their help in obtaining the crystal structures.

Supporting Information Available: Listings of bond lengths, bond angles, selected dihedral angles, hydrogen coordinates, anisotropic temperature factors, and final positional parameters for $[(t\text{-Bu})_2\text{InNEt}_2]_2$ and $[(t\text{-Bu})_2\text{InN}(n\text{-Bu})_2]_2$ (22 pages). Ordering information is given on any current masthead page.

IC9606542

---

(20) Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.

(21) Hoffman, G. G.; Fischer, R.; Schubert, U.; Hirle, B. *J. Organomet. Chem.* **1992**, *444*, 7.

(22) Aitchison, K. A.; Julius Backer-Dirks, J. D.; Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B.; Short, R. L. *J. Organomet. Chem.* **1989**, *366*, 11.

(23) Atwood, D. A.; Jones, R. A.; Cowley, A. H.; Bott, S. G.; Atwood, J. L. *Polyhedron* **1991**, *10*, 1897.

(24) Nutt, W. R.; Murry, K. J.; Gulick, J. M.; Odom, J. D.; Ding, Y.; Lebioda, L. *Organometallics* **1996**, *15*, 1728.