

AD-A096 596

STATE UNIV OF NEW YORK AT BUFFALO DEPT OF CHEMISTRY F/6 11/9
THE NATURE OF THE DIMETHYL-ALUMINUM (-GALLIUM AND -INDIUM) METH--ETC(U)
MAR 81 O T BEACHLEY, C BUENO, M R CHURCHILL N00014-78-C-0562

UNCLASSIFIED

NL

1 OF 1
AD-A
036596

END
DATE
FILMED
4-81
DTIC

AD A 096596

DOC FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 6	2. GOVT ACCESSION NO. AD-A096596	3. RECIPIENT'S CATALOG NUMBER (7)
4. TITLE (and Subtitle) The Nature of the Dimethyl-aluminum (-gallium and -indium) Methylphenylamide Dimers in Solution and the Molecular Structure of $((CH_3)_2InN(CH_3)(C_6H_5))_2$		5. TYPE OF REPORT & PERIOD COVERED Technical Report
6. PERFORMING ORG. REPORT NUMBER O. T. Beachley, Jr. Clifford Bueno Melvyn Rowen/Churchill Robert B./Hallock and Randall G./Simmons		7. CONTRACT OR GRANT NUMBER(s) N 00014-78-C-0562
8. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-053-686
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy, Arlington, Va. 22217		12. REPORT DATE March 26, 1981
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 14 TR-6		13. NUMBER OF PAGES 31
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Approved for Public Release, Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)
Prepared for Publication in Inorganic Chemistry

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Aluminum, Gallium, Indium
Inorganic polymers
Metal-nitrogen compounds
X-ray crystal study

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
The solution properties of $((CH_3)_2MN(CH_3)(C_6H_5))_2$ (M=Al, Ga, In) and the crystalline state of the indium derivative have been investigated. All compounds exist in solution as mixtures of cis and trans geometrical isomers. The cis isomer is the predominant species for the aluminum and gallium compounds, whereas the trans isomer is more abundant in the case

DTIC
ELECTE
MAR 20 1981
A

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

400352 81 3 19 010

of indium. An X-ray structural study of the indium derivative identified the trans isomer in the solid state. The complex $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (No. 2) with $a = 7.3202(15)\text{\AA}$, $b = 7.6095(21)\text{\AA}$, $c = 8.9800(27)\text{\AA}$, $\alpha = 83.194(24)^\circ$, $\beta = 81.800(21)^\circ$, $\gamma = 81.986(19)^\circ$, $V = 487.8(2)\text{\AA}^3$ and $\rho(\text{calcd}) = 1.71\text{ g cm}^{-3}$ for $Z = 1$ (dimeric unit) with molecular weight 502.1. Diffraction data were collected with a Syntex P2₁ automated four-circle diffractometer and the structure was solved using Patterson, Fourier, and full-matrix least-squares refinement techniques. The resulting discrepancy indices were $R_F = 2.7\%$ and $R_{WF} = 3.3\%$ for all 2259 reflections with $2\theta = 3.0\text{--}55.0^\circ$ (MoK α radiation). The dimeric molecule lies on a crystallographic center of symmetry. The In-N (bridging) distances are $In-N(1) = 2.280(2)\text{\AA}$ and $In-N(1') = 2.284(2)\text{\AA}$, the $In\cdots In'$ distance is $3.363\text{\AA}$, and the indium-methyl bond lengths are defined by $In-C(1) = 2.156(4)\text{\AA}$ and $In-C(2) = 2.149(4)\text{\AA}$. The dimerization and/or isomerization reactions in solution were investigated by 1H NMR spectroscopy by evaluating the effects of solvent and temperature on the cis/trans isomer ratios. All data are consistent with the hypotheses that the aluminum-nitrogen dimer is formed by a concerted π -cycloaddition reaction but the gallium and indium dimers are formed by a series of metal-nitrogen bond forming reactions. The influence of these proposed dimerization reactions on the potential for polymer formation are discussed.

Accession For	
CR&I	☒
T&B	☐
Assignment	☐
Publication	☐
Availability Codes	
Dist	Avail and/or
A	

OFFICE OF NAVAL RESEARCH
Contract N-00014-78-C-0562
Task No. NR 053-686
TECHNICAL REPORT NO. 6

The Nature of the Dimethyl-aluminum (-gallium and
-indium) Methylphenylamide Dimers in Solution and the
Molecular Structure of $[(CH_3)_2InN(CH_3(C_6H_5))]_2$

by

O. T. Beachley, Jr.,* Clifford Bueno, Melvyn Rowen Churchill*
Robert B. Hallock and Randall G. Simmons

Prepared for Publication

in

Inorganic Chemistry

State University of New York at Buffalo
Department of Chemistry
Buffalo, New York 14214

16, March 1981

Reproduction in whole or in part is permitted for
any purpose of the United States Government

*This document has been approved for public release
and sale; its distribution is unlimited

[Contribution from the Department of Chemistry, State
University of New York at Buffalo, Buffalo, New York 14214].

The Nature of the Dimethyl-aluminum (-gallium and
-indium) Methylphenylamide Dimers in Solution and the
Molecular Structure of $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$

by

O. T. Beachley, Jr.,* Clifford Bueno, Melvyn Rowen Churchill*

Robert B. Hallock and Randall G. Simmons

Abstract

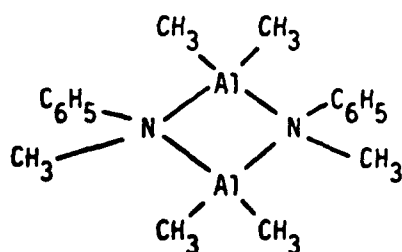
The solution properties of $[(CH_3)_2MN(CH_3)(C_6H_5)]_2$ ($M=Al, Ga, In$) and the crystalline state of the indium derivative have been investigated. All compounds exist in solution as mixtures of cis and trans geometrical isomers. The cis isomer is the predominant species for the aluminum and gallium compounds, whereas the trans isomer is more abundant in the case of indium. An X-ray structural study of the indium derivative identified the trans isomer in the solid state. The complex $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ crystallizes in the centrosymmetric triclinic space group PT (No. 2)

with $a = 7.3202(15)\text{\AA}$, $b = 7.6095(21)\text{\AA}$, $c = 8.9800(27)\text{\AA}$, $\alpha = 83.194(24)^\circ$, $\beta = 81.800(21)^\circ$, $\gamma = 81.986(19)^\circ$, $V = 487.8(2)\text{\AA}^3$ and $\rho(\text{calcd}) = 1.71\text{ g cm}^{-3}$ for $Z = 1$ (dimeric unit) with molecular weight 502.1. Diffraction data were collected with a Syntex P2₁ automated four-circle diffractometer and the structure was solved using Patterson, Fourier, and full-matrix least-squares refinement techniques. The resulting discrepancy indices were $R_F = 2.7\%$ and $R_{WF} = 3.3\%$ for all 2259 reflections with $2\theta = 3.0\text{--}55.0^\circ$ (MoK α radiation). The dimeric molecule lies on a crystallographic center of symmetry. The In-N (bridging) distances are In-N(1) = $2.280(2)\text{\AA}$ and In-N(1') = $2.284(2)\text{\AA}$, the In...In' distance is $3.363\text{\AA}$, and the indium-methyl bond lengths are defined by In-C(1) = $2.156(4)\text{\AA}$ and In-C(2) = $2.149(4)\text{\AA}$. The dimerization and/or isomerization reactions in solution were investigated by ^1H NMR spectroscopy by evaluating the effects of solvent and temperature on the cis/trans isomer ratios. All data are consistent with the hypotheses that the aluminum-nitrogen dimer is formed by a concerted π -cycloaddition reaction but the gallium and indium dimers are formed by a series of metal-nitrogen bond forming reactions. The influence of these proposed dimerization reactions on the potential for polymer formation are discussed.

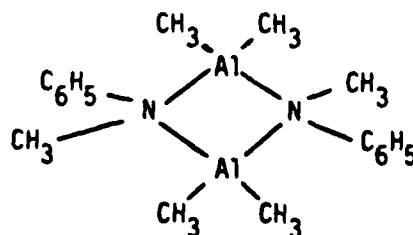
Introduction

The synthetic scheme¹ for the preparation of semi-conductor materials such as GaAs, GaP and InP involves an elimination-condensation reaction sequence between appropriate Lewis acids and bases. This fundamental reaction has also been used for the attempted preparation of inorganic polymers² with the simplest formulas $R_2III-VR'_2$. However, the potential of this reaction sequence has not been realized because small molecules, typically dimers but occasionally trimers, are the usual products.² A variety of factors, including steric effects, valency angle strain and reaction mechanism, have been used to account for the nature of a specific product.² Since none of these explanations have been completely satisfactory, a goal of our research has been to elucidate how the small molecules are formed.

The kinetics of the elimination reaction³ between dimethylalane $(CH_3)_2AlH$ and N-methylaniline $N(CH_3)(C_6H_5)H$ have been investigated and a mechanism has been proposed to explain all experimental observations. The product of the elimination-condensation reaction sequence is the dimer, $[(CH_3)_2AlN(CH_3)(C_6H_5)]_2$ which exists in solution as a mixture of cis and trans geometrical isomers. It is of interest to note that the



cis isomer



trans isomer

cis isomer is the predominant species in solution and its relative concentration compared to the trans isomer is essentially independent of the nature of the nonreactive solvent.^{3,4} Thus, $[(CH_3)_2AlN(CH_3)(C_6H_5)]_2$ exists as an 83%/17% mixture of cis/trans isomers in benzene, toluene or methylene chloride solutions. There are two significant features of the proposed reaction mechanism which were used to explain all experimental observations. (1) The elimination reaction is a second order reaction between monomeric alane $(CH_3)_2AlH$ and $N(CH_3)(C_6H_5)H$. Adduct formation is a "dead-end" path for the elimination reaction.³ (2) The dimeric aluminum-nitrogen product might be formed by a concerted $2\pi_s + 2\pi_a$ cycloaddition reaction between two monomeric $(CH_3)_2AlN(CH_3)(C_6H_5)$ species. Thus, kinetic factors could favor the formation of the cis isomer by minimizing the steric interactions between bulky phenyl groups. These conclusions also lead to the speculation that the proposed concerted cycloaddition reaction might preclude the formation of polymeric aluminum-nitrogen species.³

The observations and hypotheses defined for the $(CH_3)_2AlN(CH_3)(C_6H_5)$ system lead us to question the nature of the corresponding gallium and indium compounds. A linear polymer or a smaller oligomer might be formed if a concerted π -cycloaddition reaction did not occur. However, if dimers were the observed products, the unsymmetrical substitution about the nitrogen atoms would provide NMR probes to learn more about their formation and isomerization reactions.

In this paper we report the syntheses and characterizations of the new compounds, $(CH_3)_2GaN(CH_3)(C_6H_5)$ and $(CH_3)_2InN(CH_3)(C_6H_5)$. Since the

indium compound had unusual physical properties in comparison with the aluminum and gallium analogs, the crystalline state was defined by an X-ray structural study. Dimeric molecules in the trans conformation were observed for $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$. Consequently, the effects of solvent and temperature on the cis/trans isomer ratio of the aluminum, gallium and indium derivatives were investigated by 1H NMR spectroscopy.

Experimental

All compounds were manipulated in a vacuum line or a purified argon atmosphere. The solvents, benzene, toluene and methylene chloride were purified by refluxing with sodium ribbon, sodium sand or phosphorus pentoxide, respectively. The solvents were distilled prior to use under an argon atmosphere or at high vacuum. The preparation of $[(CH_3)_2AlN(CH_3)(C_6H_5)]_2$ has been previously described.^{3,4} Trimethylgallium was purchased from Alfa Inorganics and used as received. Trimethylindium was prepared from InI_3 by a standard Grignard reaction in diethyl ether. The indium(III) iodide⁵ was prepared from indium metal and iodine in diethyl ether. The diethyl ether was removed from $In(CH_3)_3 \cdot O(C_2H_5)_2$ by refluxing with benzene and subsequent fractional distillation. N-methylaniline was dried over KOH pellets and distilled just before use.

Compounds were analyzed for gallium or indium, after hydrolysis in dilute HNO_3 , by EDTA titration. The mole ratio of methyl groups per mol of metal was determined by quantitatively converting the ligand to CH_4 by acid hydrolysis. The CH_4 was measured by means of a Toepler pump-gas burette assembly. Molecular weight measurements were obtained cryo-

scopically in benzene by using an instrument similar to that described by Shriver.⁷

The infrared spectra were recorded in the range $4000\text{--}250\text{ cm}^{-1}$ by means of a Perkin-Elmer Model 456 spectrometer. The spectra were recorded as Nujol mulls by using CsI plates. The ^1H NMR spectra were recorded at 90 MHz by using a Varian Model EM-390 spectrometer equipped with a variable temperature probe. The spectrometer was locked on the benzene signal at 2.73 ppm(π).

Preparation of $(\text{CH}_3)_2\text{MN}(\text{CH}_3)(\text{C}_6\text{H}_5)$ (M=Ga and In). The gallium- and indium-amide derivatives were prepared from stoichiometric quantities of N-methylaniline and $\text{Ga}(\text{CH}_3)_3$ or $\text{In}(\text{CH}_3)_3$ by a pyrolytic method using a sealed tube equipped with a break-seal sidearm. In the case of $(\text{CH}_3)_2\text{GaN}(\text{CH}_3)(\text{C}_6\text{H}_5)$, 0.1133 g (0.9872 mmol) of $\text{Ga}(\text{CH}_3)_3$ was reacted with 0.1058 g (0.9887 mmole) of $\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{H}$ at 130°C for 24 hrs. After reaction was complete, 1.01 mmol CH_4 was removed and measured by means of a Toepler pump-gas burette assembly. The product was purified by vacuum sublimation at 120° . The indium derivative was prepared by the identical procedure. Reaction conditions of 60° for 8-10 hrs. lead to the formation of 1.00 mole CH_4 per mole $\text{In}(\text{CH}_3)_3$. Crystals of suitable quality for the X-ray structural study were obtained from the preparative reaction. Other samples were purified by vacuum sublimation at 100°C .

Characterization of $(\text{CH}_3)_2\text{GaN}(\text{CH}_3)(\text{C}_6\text{H}_5)$. The gallium-nitrogen product was fully characterized. The colorless, crystalline solid has a melting point of $112\text{--}114^\circ\text{C}$. In a microscopic examination of a typical

sample, all crystals appeared identical in shape. Two different crystal-line forms, indicative of different isomers, were not apparent. The following experimental cryoscopic molecular weight data in benzene solution were observed: $[(CH_3)_2GaN(CH_3)(C_6H_5)]_2$ - formula weight - 206: [Calc. molality, (observed molecular weight)] 0.1718 (410); 0.1690 (401); 0.1060 (404); 0.0772 (394). The 1H NMR spectra were observed in benzene, toluene and methylene chloride solutions. The spectra had no concentration dependence. The following give the chemical shift data (τ , ppm, reference tetramethylsilane) and assignment: Benzene- d_6 solution - CH_3 -Ga (10.12 - cis; 9.98 - trans, 9.82 - cis); CH_3 -N (7.11 - cis; 7.21 - trans). Toluene- d_8 solution - CH_3 -Ga (10.02 - cis, 9.88 - trans; 9.73 - cis); CH_3 -N (7.06 - trans; 7.01 - cis), CH_2Cl_2 solution - CH_3 -Ga (10.60 - cis, 10.35 - trans, 9.95 - cis); CH_3 -N - (7.02 - cis; 7.08 - trans). The relative intensities of lines due to the different isomers are given in the appropriate table. The following infrared spectral bands were observed: 1590(s), 1575(m); 1548(w), 1490(vs), 1458(s); 1378(m); 1295(w), 1202(m); 1198(s), 1160(m); 1151(m); 1080(w); 1042(w); 1020(m), 1000(w); 898(w); 789(s); 764(vs), 731(s); 701(s); 588(m); 562(s); 535(s); 439(s). Anal. Calcd. for $(CH_3)_2GaN(CH_3)(C_6H_5)$: Ga 33.89; Found: Ga, 33.85.

Characterization of $(CH_3)_2InN(CH_3)(C_6H_5)$. The indium-nitrogen product was a colorless, crystalline solid and had a melting point of 179-181°C. All crystals in a typical sample had the identical crystal-line form according to microscopic examination. The 1H NMR spectra were observed in benzene, toluene and methylene chloride solutions. The

spectra had no concentration dependence. The following give the chemical shift data, (τ , ppm, reference tetramethylsilane) and assignment:

Benzene- d_6 solution - CH_3 -In (10.06-trans; 10.05-cis; 10.00-cis);

CH_3 -N (7.03, cis; 6.99, trans). Toluene- d_9 solution - CH_3 -In (10.03 trans, 9.97 - cis; 9.83 - cis); CH_3 -N (6.97, cis; 6.96, trans).

Methylene chloride solution - CH_3 -In (10.32 - cis; 10.25 - trans; 10.17 - cis); CH_3 -N (6.90, cis; 6.86, trans). The relative intensities of lines due to the different isomers is given in the appropriate table.

It is of interest to note that the indium derivative is significantly less soluble than the aluminum or gallium analogs. The following infrared spectral bands were observed: 1595(s), 1570(m); 1485(s); 1335(vw), 1295(w); 1230(s); 1190(m); 1165(m); 1155(w), 1090(vw); 1040(w); 1020(m); 1000(m); 890(vw); 785(m), 765(s); 700(s); 585(m); 510(m); 490(m); 410(m). Anal. Calcd for $(CH_3)_2InN(CH_3)(C_6H_5)$: In, 45.7; mol $InCH_3$ /mol In, 2.00. Found: In, 44.7; mol $InCH_3$ /mol In 2.00.

The high melting point and limited solubility of this compound with the simplest formula $(CH_3)_2InN(CH_3)(C_6H_5)$ lead to speculation that it might exist in the solid state as a polymer, a smaller oligomer or a dimer. Consequently, an X-ray structural study was initiated.

Collection and Treatment of the X-ray Diffraction Data for

$[(CH_3)_2InN(CH_3)(C_6H_5)]_2$. A crystal of dimensions 0.41 x 0.25 x 0.10 mm was handled in a modified KSE inert-atmosphere drybox and was carefully inserted into a thin-walled, glass capillary, which was flame-sealed, set into an aluminum pin with beeswax, and mounted into a eucentric

goniometer on our Syntex P2₁ diffractometer. Determinations of the crystal class (triclinic), the orientation matrix and accurate cell dimensions, and data collection (via the θ - 2θ scan technique) were carried out as described previously;⁸ details appear in Table I.

Data were corrected for absorption by an empirical method, based on a series of ψ -scans (see Table I), and were converted to unscaled $|F_o|$ values following correction for Lorentz and polarization effects. Any reflection with $I < 0$ was assigned a value of $|F_o| = 0$.

Solution and Refinement of the Structure. The structure was solved using our in-house Syntex XTL system which consists of (i) a Data General Nova 1200 computer (with 24K of 16 bit word memory and with a parallel floating-point processor for 32- or 64-bit arithmetic) (ii) a Diablo moving-head disk unit with a storage capacity of 1.2 million 16-bit words, (iii) a Versatec electrostatic printer/plotter, and (iv) a locally modified version of the XTL conversational program package. Scattering factors for neutral indium, nitrogen, carbon and hydrogen were used in their analytical form;^{9a} the contributions of all non-hydrogen atoms were corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.^{9b} The function minimized during the least-squares refinement process was $\sum w(|F_o| - |F_c|)^2$; the weights used (w) are the stochastic $\sigma(|F_o|)$ values modified by an "ignorance factor" (p) as shown in eq. 1 (p was set at 0.03).

$$w = [\sigma(|F_o|)^2 + (p|F_o|)^2]^{-1} \quad (1)$$

Data were converted to an approximately absolute scale by means of a Wilson plot. The position of the indium atom was determined from a three-dimensional Patterson synthesis.

Full-matrix least-squares refinement of positional and isotropic thermal parameters for the indium atom led to $R_F = 25.9\%$ and $R_{WF} = 34.5\%$. A difference-Fourier synthesis confirmed that the true space group was the assumed $P\bar{1}$ (rather than $P1$) and led to the unambiguous location of all remaining non-hydrogen atoms. Continued full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms led to convergence with $R_F = 2.8\%$ and $R_{WF} = 3.4\%$. A second difference-Fourier synthesis resulted in the location of the hydrogen atoms of the phenyl ring. The methyl hydrogen atoms were then included in their idealized (staggered) positions with $d(C-H) = 0.95\text{\AA}$.¹⁰ All positional and anisotropic (isotropic for hydrogen atoms) thermal parameters were refined, leading to final convergence with $R_F = 2.7\%$, $R_{WF} = 3.3\%$, and $GOF = 0.912$ for all 2259 reflections (none rejected). It may be noted that the discrepancy indices for those 2144 reflections with $|F_O| > 3\sigma(|F_O|)$ were $R_F = 2.5\%$ and $R_{WF} = 3.2\%$. The NO:NV ratio was 2259: 156 or approximately 14.5:1.

The function $\Sigma w(|F_O| - |F_C|)^2$ showed no major trends as a function of $|F_O|$, $(\sin\theta)/\lambda$, sequence number, parity or identity of crystallographic indices. The weighting scheme is therefore acceptable. Final positional and thermal parameters are collected in Table II.

Results and Discussion

The dimethylaluminum (-gallium and -indium)-methylphenylamide derivatives are readily prepared from the appropriate organometallic compound ($M(CH_3)_3$) and N-methylaniline by a stoichiometric reaction. The aluminum⁴ and gallium compounds exist in solution as dimers, according to cryoscopic molecular weight measurements. The indium-nitrogen compound had two properties which led us to suspect, incorrectly, that it might exist as a polymer. The compound has limited solubility, in nonreactive solvents which makes cryoscopic molecular weight studies of little use, and it has a relatively high melting point, 179-181°. Therefore, an X-ray structural study was undertaken.

The compound, $(CH_3)_2InN(CH_3)(C_6H_5)$, exists in the solid state as a dimeric molecule in the trans conformation. The dimeric molecule lies on a center of symmetry (at 0, 0, 1/2) in a unit cell belonging to the triclinic space group, $P\bar{1}$. The crystal consists of discrete ordered dimeric units of $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ which are separated by normal van der Waal's distances (see Figure 1). The atomic numbering scheme is shown in Figure 2, while interatomic distances and angles are collected in Tables III and IV.

The indium(III) ion is in a rather distorted tetrahedral environment, with interligand angles ranging from $C(1)-In-C(2) = 122.41(15)^\circ$ to $N(1)-In-N(1') = 85.08(7)^\circ$; the nitrogen-indium-carbon angles are more typical, with values lying between $109.10(11)^\circ$ and $112.24(11)^\circ$ (see Table IV). The indium-methyl bond lengths, $In-C(1) = 2.156(4)$ and $In-C(2) = 2.149(4)\text{\AA}$ (average = $2.153[5]\text{\AA}$) suggest a covalent radius of

1.38 Å for indium(III) in this type of environment. The $\text{In}(\mu\text{-N})_2\text{In}'$ system is required to be precisely planar; bond lengths are $\text{In}-\text{N}(1) = \text{In}'-\text{N}(1') = 2.280(2)\text{Å}$ and $\text{In}-\text{N}(1') = \text{In}'-\text{N}(1) = 2.284(2)\text{Å}$ (average = $2.282[3]\text{Å}$).¹¹ The obtuse $\text{In}-\text{N}(1)-\text{In}'$ angle of $94.92(7)^\circ$ and the long $\text{In}\cdots\text{In}'$ distance of $3.363(0)\text{Å}$ confirm that there is no direct indium-indium bonding.

As shown in Figure 2, the bridging $\mu\text{-N}(\text{CH}_3)(\text{C}_6\text{H}_5)$ groups take up a mutually trans arrangement. The dihedral angle between the $\text{In}(\mu\text{-N})_2\text{In}'$ and phenyl planes is 91.3° (see Table V and Figure 3). Angles around N(1) range from $\text{In}-\text{N}(1)-\text{In}' = 94.92(7)^\circ$ to $\text{In}-\text{N}(1)-\text{C}(11) = 115.19(15)^\circ$. The nitrogen-methyl bond length ($\text{N}(1)-\text{C}(3) = 1.478(3)\text{Å}$) is some $0.048(4)\text{Å}$ longer than the nitrogen-phenyl bond length ($\text{N}(1)-\text{C}(11) = 1.430(3)\text{Å}$), reflecting, principally, the difference in covalent radius of an sp^3 -versus an sp^2 - hybridized carbon atom.

Carbon-carbon distances around the phenyl ring range from $\text{C}(14)-\text{C}(15) = 1.379(6)\text{Å}$ to $\text{C}(16)-\text{C}(11) = 1.401(4)\text{Å}$, the average values being $1.389[9]\text{Å}$. The C_6 skeleton of this system has only C_{2v} symmetry and not D_{6h} symmetry. The bonding of the C_6H_5 moiety to the electronegative nitrogen atom causes systematic variations in internal angles within the six-membered ring.¹² The angle at the ipso-carbon is substantially reduced from 120° ($\text{C}(16)-\text{C}(11)-\text{C}(12) = 117.11(24)^\circ$) as is that at the para-carbon ($\text{C}(13)-\text{C}(14)-\text{C}(15) = 118.39(33)^\circ$); these reductions are compensated for by significant expansions of the angles at the ortho-carbon atoms ($\text{C}(11)-\text{C}(12)-\text{C}(13) = 121.89(28)^\circ$ and $\text{C}(15)-\text{C}(16)-\text{C}(11) = 120.23(27)^\circ$) and at the meta-carbon atoms ($\text{C}(12)-\text{C}(13)-\text{C}(14) = 120.62(32)^\circ$ and $\text{C}(14)-\text{C}(15)-\text{C}(16) = 121.75(33)^\circ$).

The only reported structural study of an indium(III) complex with similar features to our present molecule is that of the species $[(CH_3)_2InN(CH_3)_2]_2$.¹³ This structural study is not as accurate as our present study of $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$, but relevant parameters are compared in Table VI. The principal significant differences are as follows.

- (1) The In-(μ -N(CH₃)(C₆H₅)) distances of 2.282[3]Å (average) are significantly longer (by 0.046Å) than the In-(μ -N(CH₃)₂) distances, which average 2.236[16]Å.
- (2) The In...In distance of 3.363(0)Å in $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ is 0.085[2]Å longer than the corresponding distance in $[(CH_3)_2InN(CH_3)_2]_2$. This is principally a result of the different In-(μ -N) distances, since the In-N-In' angles are fairly similar (*viz.*, 94.92(8)° versus 94.3(3)°, respectively).
- (3) The In-CH₃ bond lengths in $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ are 2.149(4) and 2.156(4)Å (average = 2.153[5]Å) and are ~ 0.016Å shorter than the In-CH₃ bond lengths in $[(CH_3)_2InN(CH_3)_2]_2$ (2.168(19) and 2.170(18)Å; average = 2.169[1]Å). This, presumably, results as part of an internal mechanism to compensate for the contrary difference in In-(μ -N) distances (see 1).
- (4) The CH₃-In-CH₃ angle of 122.41(15)° in $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ is substantially less obtuse than the corresponding angle of 131.3(10)° in $[(CH_3)_2InN(CH_3)_2]_2$.
- (5) All other differences are relatively small.

The aluminum-,⁴ gallium- and indium-methylphenylamide derivatives

exist in solution as mixtures of cis and trans geometrical isomers of the four membered ring dimers. The effects of solvent (Table VII) and temperature (Table VIII) on the isomer ratio have been investigated using ^1H NMR spectroscopy. The solvents included benzene, toluene and methylene chloride. The variable temperature study, 34 to -45°C , employed methylene chloride solutions. The lowest temperature studied was determined by the solubility limit of a compound.

The investigation of the effects of the solvent on the ratio of cis/trans isomers for the three compounds leads to two generalities. (1) The cis/trans isomer ratio observed for a given solvent decreases in the order $\text{Al} > \text{Ga} > \text{In}$. For the aluminium and gallium compounds, the cis isomer predominates whereas the trans isomer is more abundant for the indium derivative. (2) The cis/trans isomer ratio for the aluminum compound is essentially independent of the dipole moment of the solvent. In contrast, both the gallium and indium compounds exhibit a solvent dependence. In the case of the gallium derivative, the cis/trans ratio increases as the solvent polarity increases. For the indium compound, there is no simple change in isomer ratio with solvent polarity. The fraction of the more abundant trans isomer is essentially the same for benzene and toluene solutions, dipole moments of 0 and 0.36D, respectively. Upon changing to the most polar solvent, CH_2Cl_2 (1.60D), the relative amount of cis isomer decreases, an unexpected change. However, there is also a change in the overall appearance of the spectrum which suggests a change in the nature of solvation. In CH_2Cl_2 solution, the In-CH_3 line for the trans isomer separates the two In-CH_3 lines assigned

to the cis isomer. In the aromatic solvents, the sequence of the three In-CH₃ lines with increasing field is cis, cis, trans. The spectra of the aluminum and gallium derivatives in all solvents are identical in appearance to that observed for the indium compound in CH₂Cl₂ solution. These observations suggest that the three solvents do not solvate the three derivatives similarly. Consequently, caution must be exercised in the interpretation of the data.

The mechanism for dimer formation and/or isomerization must be consistent with the observed solvent effects for a given derivative. The aluminum-nitrogen dimer is believed to be formed by a concerted π -cycloaddition reaction,³ whereas the gallium and indium derivatives are more likely formed by a series of metal-nitrogen bond making reactions. One new metal-nitrogen bond is formed from the monomers and then ring closure occurs. These conclusions are based on the following. Thermodynamic and kinetic factors can influence the cis/trans isomer ratio for a given derivative. The lack of a solvent effect for the aluminum-nitrogen compound suggests that kinetic effects are important. In a concerted π -cycloaddition reaction, steric effects in the transition state lead to the predominance of the cis isomer.³ In contrast the solvent effects observed for the gallium and indium compounds suggest that a dimerization path other than a concerted π -cycloaddition reaction is occurring. A stepwise process seems most likely. π bonding interactions would be expected to decrease significantly in the order Al-N >> Ga-N > In-N. The observation that the indium derivative exists in the solid state as only the trans isomer is consistent with a stepwise

dimerization reaction. Kinetic control in a concerted cycloaddition reaction would have lead to the cis isomer.

The measurements of cis/trans ratios or equilibrium constants ($K = [\text{cis}]/[\text{trans}]$) at various temperatures permit the calculation of ΔH and ΔS for the trans to cis isomerization reaction. The results of these calculations are given in Table IX. The isomerization reaction is slow on the NMR time scale but equilibrium was clearly established in 10-15 minutes at all temperatures studied. The calculated enthalpy and entropy changes are small. There are no simple, consistent changes in ΔH or ΔS from the aluminum- to gallium- to indium-nitrogen compounds. For the aluminum compound, as T decreases, the concentration of the cis isomer increases. Thus, the cis isomer is thermodynamically more stable and more readily formed by the concerted π -cycloaddition reaction, but there is an increase in entropy from the cis to the trans isomer. The situation is reversed for the gallium compound. The trans isomer is more stable but the entropy change favors the more abundant cis isomer. The $T\Delta S$ term is responsible for the predominance of the cis isomer at all temperatures studied. These conclusions suggest that the ring of the cis isomer might be bent in solution. In the case of the indium compound, the $T\Delta S$ term is also the most important factor for the temperatures studied, but it favors the trans isomer. The cis isomer is thermodynamically more stable, apparently better solvated by the polar solvent CH_2Cl_2 . All of the conclusions suggest that very subtle factors influence the cis/trans isomer ratio. It is obvious that no one simple factor will give a periodic trend.

In conclusion, the experimental data are consistent with the hypothesis that the aluminum-nitrogen dimer is formed by a concerted π -cycloaddition reaction. Thus, polymers are precluded by the reaction mechanism. In the case of the gallium and indium derivatives, the dimers are most likely formed from the monomers by a series of metal-nitrogen bond forming reactions. Concerted processes are inconsistent with the experimental data. Thus, inorganic polymers are potential products in gallium- and indium-nitrogen chemistry. However, the metal-nitrogen bonds must be strong enough to overcome the negative entropy change expected for polymer formation from the simple monomer. Consequently, small molecules are observed.

Acknowledgments. This work was supported in part by the Office of Naval Research and the National Science Foundation.

Supplementary Material Available. A listing of data-processing formulas and observed and calculated structure factor amplitudes for $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ (14 pages). For ordering information, see any masthead page.

Table I. Experimental Data for the X-ray Diffraction Study of
 $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$

A. Crystal Parameters at 24°C

crystal system:	triclinic	
space group:	$P\bar{1}$ [C_1 ¹ ; No. 2]	
a = 7.3202(15)Å		V = 487.8(2)Å ³
b = 7.6095(21)Å		Z = 1 (dimeric unit)
c = 8.9800(27)Å		formula wt = 502.1
α = 83.194(24)°		ρ _{calc} = 1.71 g cm ⁻³
β = 81.800(21)°		
γ = 81.986(19)°		

B. Collection of Intensity Data

diffractometer:	Syntex P2 ₁
radiation:	MoKα (λ 0.710 730Å)
monochromator:	highly oriented graphite, equatorial geometry; 2θ(mono) = 12.2°
reflections measured:	+h, ±k, ±l
scan type:	coupled θ (crystal) - 2θ (counter)
2θ range:	3.0 - 55.0°
scan speed:	4.0°/min (in 2θ)
scan width:	[2.0 + Δ(α ₂ -α ₁)]°
reflections collected:	2479 total data, 2259 independent data
standards:	3 collected every 97 data; no significant decay
absorption coeff:	μ = 23.5 cm ⁻¹ ; empirical correction based upon ψ-scans of the 410 (2θ = 24.08°; T _{max} /T _{min} = 1.270) and 531 (35.45°; 1.270) reflections.

^aUnit cell parameters were derived from a least squares fit to the setting angles of the unresolved MoKα components of 24 reflections with 2θ = 20-30°.

Table II

Final Positional and Thermal Parameters ^a

Atom	x	y	z	B (Å ²)
IN	0.00891(2)	0.20272(2)	0.40374(2)	
N(1)	-0.0621(3)	-0.0684(3)	0.3625(2)	
C(1)	-0.2386(6)	0.3934(5)	0.4141(5)	
C(2)	0.2684(5)	0.2632(5)	0.2771(4)	
C(3)	-0.2632(4)	-0.0541(4)	0.3514(4)	
C(11)	0.0522(3)	-0.1498(3)	0.2401(3)	
C(12)	0.2456(4)	-0.1669(4)	0.2347(3)	
C(13)	0.3636(5)	-0.2421(5)	0.1182(4)	
C(14)	0.2930(5)	-0.3056(5)	0.0033(4)	
C(15)	0.1026(6)	-0.2922(5)	0.0765(4)	
C(16)	-0.0183(4)	-0.2148(4)	0.1231(3)	
H(1A)	-0.337(11)	0.362(11)	0.446(10)	11.0(23)
H(1B)	-0.236(8)	0.471(8)	0.497(7)	7.1(13)
H(1C)	-0.253(12)	0.462(13)	0.344(12)	12.5(27)
H(2A)	0.379(7)	0.220(8)	0.318(6)	7.5(13)
H(2B)	0.280(7)	0.206(7)	0.191(6)	5.9(11)
H(2C)	0.254(7)	0.383(8)	0.245(6)	6.8(12)
H(3A)	-0.312(6)	-0.171(6)	0.366(5)	4.9(9)
H(3B)	-0.328(5)	0.004(5)	0.440(5)	4.1(8)
H(3C)	-0.297(5)	0.011(6)	0.261(5)	4.6(8)
H(12)	0.300(5)	-0.127(5)	0.307(5)	3.9(8)
H(13)	0.498(6)	-0.253(7)	0.106(5)	6.1(11)
H(14)	0.381(5)	-0.363(5)	-0.080(5)	4.5(8)
H(15)	0.057(7)	-0.329(6)	-0.040(6)	5.8(11)
H(16)	-0.171(5)	-0.200(5)	0.124(4)	4.1(7)

Atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
IN	2.909(9)	2.699(9)	2.566(9)	-0.193(5)	-0.183(5)	-0.313(5)
N(1)	2.44(7)	3.09(8)	2.59(8)	-0.17(6)	-0.25(6)	-0.58(6)
C(1)	4.99(16)	3.88(14)	4.34(15)	1.25(12)	-0.93(12)	-0.86(12)
C(2)	3.79(13)	4.64(15)	4.12(14)	-1.20(11)	0.19(11)	-0.03(12)
C(3)	2.65(10)	4.00(12)	3.65(12)	-0.26(8)	-0.43(8)	-0.41(10)
C(11)	2.92(9)	2.66(9)	2.33(9)	-0.26(7)	-0.15(7)	-0.29(7)
C(12)	2.99(10)	4.13(12)	3.38(11)	-0.39(9)	-0.06(8)	-1.09(9)
C(13)	3.50(12)	4.04(15)	4.11(14)	-0.13(10)	0.41(10)	-1.03(11)
C(14)	5.29(15)	4.03(13)	2.94(12)	-0.06(11)	0.70(10)	-0.74(10)
C(15)	6.07(17)	4.32(14)	2.49(11)	-1.07(12)	-0.53(11)	-0.93(12)
C(16)	3.03(12)	3.93(12)	2.68(10)	-0.78(10)	-0.58(8)	-0.46(8)

^a The anisotropic thermal parameters enter the expression for the calculated structure factor in the form $\exp[-1/4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hlc^*a^*B_{13} + 2klb^*c^*B_{23})]$.

Table III Intramolecular Distances ($\text{\AA}$) for $[(\text{CH}_3)_2\text{InN}(\text{CH}_3)(\text{C}_6\text{H}_5)]_2$

Atoms	dist	Atoms	dist
(A) Distances from the indium atom			
In-N(1)	2.280(2)	In-C(1)	2.156(4)
In-N(1')	2.284(2)	In-C(2)	2.149(4)
In...In'	3.363(0)		
(B) Nitrogen-Carbon Distances			
N(1)-C(3)	1.478(3)	N(1)-C(11)	1.430(3)
(C) Carbon-Carbon Distances			
C(11)-C(12)	1.398(4)	C(14)-C(15)	1.379(6)
C(12)-C(13)	1.383(5)	C(15)-C(16)	1.394(5)
C(13)-C(14)	1.380(5)	C(16)-C(11)	1.401(4)
(D) Carbon-Hydrogen Distances			
C(1)-H(1A)	0.79(8)	C(3)-H(3B)	0.99(4)
C(1)-H(1B)	1.01(6)	C(3)-H(3C)	0.94(4)
C(1)-H(1C)	0.78(10)	C(12)-H(12)	0.91(4)
C(2)-H(2A)	0.94(6)	C(13)-H(13)	0.97(4)
C(2)-H(2B)	0.92(5)	C(14)-H(14)	1.02(4)
C(2)-H(2C)	0.92(6)	C(15)-H(15)	0.68(5)
C(3)-H(3A)	0.99(4)	C(16)-H(16)	1.10(4)

Table IV Selected Intramolecular Angles (in deg)

Atoms	Angle	Atoms	Angle
N(1)-In-N(1')	85.08(7)	In-N(1)-In'	94.92(7)
N(1)-In-C(1)	109.84(12)	In-N(1)-C(3)	109.00(16)
N(1)-In-C(2)	112.24(11)	In-N(1)-C(11)	115.19(15)
C(1)-In-C(2)	122.41(15)	In'-N(1)-C(3)	108.75(16)
N(1')-In-C(1)	111.99(12)	In'-N(1)-C(11)	114.10(15)
N(1')-In-C(2)	109.10(11)	C(3)-N(1)-C(11)	113.32(21)
N(1)-C(11)-C(12)	119.11(23)	N(1)-C(11)-C(16)	123.78(23)
C(16)-C(11)-C(12)	117.11(24)	C(13)-C(14)-C(15)	118.39(33)
C(11)-C(12)-C(13)	121.89(28)	C(14)-C(15)-C(16)	121.75(33)
C(12)-C(13)-C(14)	120.62(32)	C(15)-C(16)-C(11)	120.23(27)

Table V Least-Squares Planes

Atom	dev., Å	Atom	dev., Å
(A) The $\text{In}(\mu\text{-N})_2\text{In}'$ plane			
Eq: $0.8852X - 0.3043Y - 0.3520Z = -1.1254^a$			
In	0.000	In'	0.000
N(1)	0.000	N(1')	0.000
(B) The Phenyl Ring			
Eq: $0.0566X + 0.8483Y - 0.5265Z = -1.8666^a$			
C(11)	0.003(2)	C(14)	0.003(3)
C(12)	-0.006(3)	C(15)	-0.006(3)
C(13)	0.003(4)	C(16)	0.002(3)
(C) Dihedral Angle			
A/B	91.30°	(88.70°)	

^aOrthonormalized (Å) coordinates.

Table VI. Comparison of Intramolecular Parameters for $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ and $[(CH_3)_2InN(CH_3)_2]_2^a$

	$[(CH_3)_2InN(CH_3)(C_6H_5)]_2$	$[(CH_3)_2InN(CH_3)_2]_2^a$
Bond or contact	dist, Å	dist, Å
In...In'	3.363(0)	3.278(2)
In-N	$\begin{Bmatrix} 2.280(2) \\ 2.284(2) \end{Bmatrix}$	$\begin{Bmatrix} 2.225(13) \\ 2.247(13) \end{Bmatrix}$
In-CH ₃	$\begin{Bmatrix} 2.149(4) \\ 2.156(4) \end{Bmatrix}$	$\begin{Bmatrix} 2.168(19) \\ 2.170(18) \end{Bmatrix}$
N-CH ₃	1.478(3)	$\begin{Bmatrix} 1.444(15) \\ 1.505(19) \end{Bmatrix}$
N-C ₆ H ₅	1.430(3)	-
Atoms	angle, deg.	angle, deg.
N-In-N'	85.08(7)	85.7(4)
CH ₃ -In-CH ₃	122.41(15)	131.3(10)
In-N-In'	94.92(8)	94.3(3)

^aSee ref. 13.

Table VII The Effect of Solvent on the Percentage Cis Isomer

	<u>C₆H₆</u>	<u>C₆H₅CH₃</u>	<u>CH₂Cl₂</u>
$[(CH_3)_2AlN(CH_3)(C_6H_5)]_2^a$	84.2	83.7	83.3
$[(CH_3)_2GaN(CH_3)(C_6H_5)]_2$	64.5	65.7	71.7
$[(CH_3)_2InN(CH_3)(C_6H_5)]_2$	43.5	43.0	39.2

^aSee Reference 4.

Table VIII The Effect of Temperature on the Cis/Trans Ratio (K)
in Methylene Chloride Solution.

$[(CH_3)_2AlN(CH_3)(C_6H_5)]_2$		$[(CH_3)_2GaN(CH_3)(C_6H_5)]_2$		$[(CH_3)_2InN(CH_3)(C_6H_5)]_2$	
T(K)	K ^a	T(K)	K ^a	T(K)	K ^a
296°	5.00	307°	2.53	307°	0.632
279	5.76	288	2.50	278	0.674
268	5.82	278	2.33	268	0.688
257	6.40	268	2.11	258	0.713
244	7.59	258	2.02	238	0.796
229	8.34	248	1.83	228	0.809
		228	1.48		

^aSee Reference 4

Table IX Thermodynamic Parameters for the Effect of T on the Trans to Cis Equilibrium

	$[(CH_3)_2MN(CH_3)(C_6H_5)]_2$		
	M=Al ^a	Ga	In
$\Delta H(\text{kJ/mole})$	-4.47	+4.16	-1.94
$\Delta S(\text{J/mol K})$	-1.74	+21.8	-10.3
$T\Delta S_{298}(\text{kJ/mol})$	-0.52	+6.50	-3.07
$\Delta G_{298}(\text{kJ/mol})$	-3.95	-2.34	+1.13
r_b^2	0.9885	0.9676	0.9781

^aReference 4

^bLeast squares plot of $\ln K$ vs $1/T$.

Captions to Figures

Figure 1. Stereoscopic packing diagram for $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$
(ORTEP-II diagram; 30% ellipsoids; hydrogen atoms omitted).

Figure 2. Labeling of atoms in the $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ molecule.
The molecule lies on an inversion center. Atoms in the
basic asymmetric unit are labelled normally. Atoms in the
"other half" of the molecule are labelled with a prime;
their positions are related to atoms in the basic asymmetric
unit by the transformation $[x', y', z'] = [-x, -y, 1-z]$.
This is an ORTEP-II diagram with 30% probability ellipsoids
for all non-hydrogen atoms.

Figure 3. The $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ molecule, projected onto its
 $In(\mu-N)_2In'$ plane. Note the near orthogonality of the
phenyl groups with this plane. [ORTEP-II diagram; 30%
probability ellipsoids for non-hydrogen atoms.]

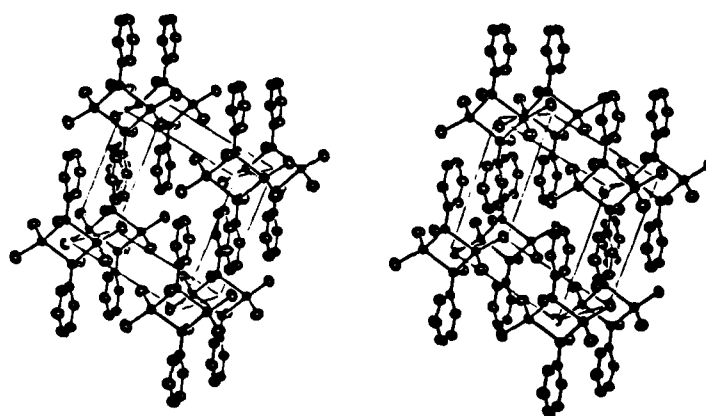


Figure 1

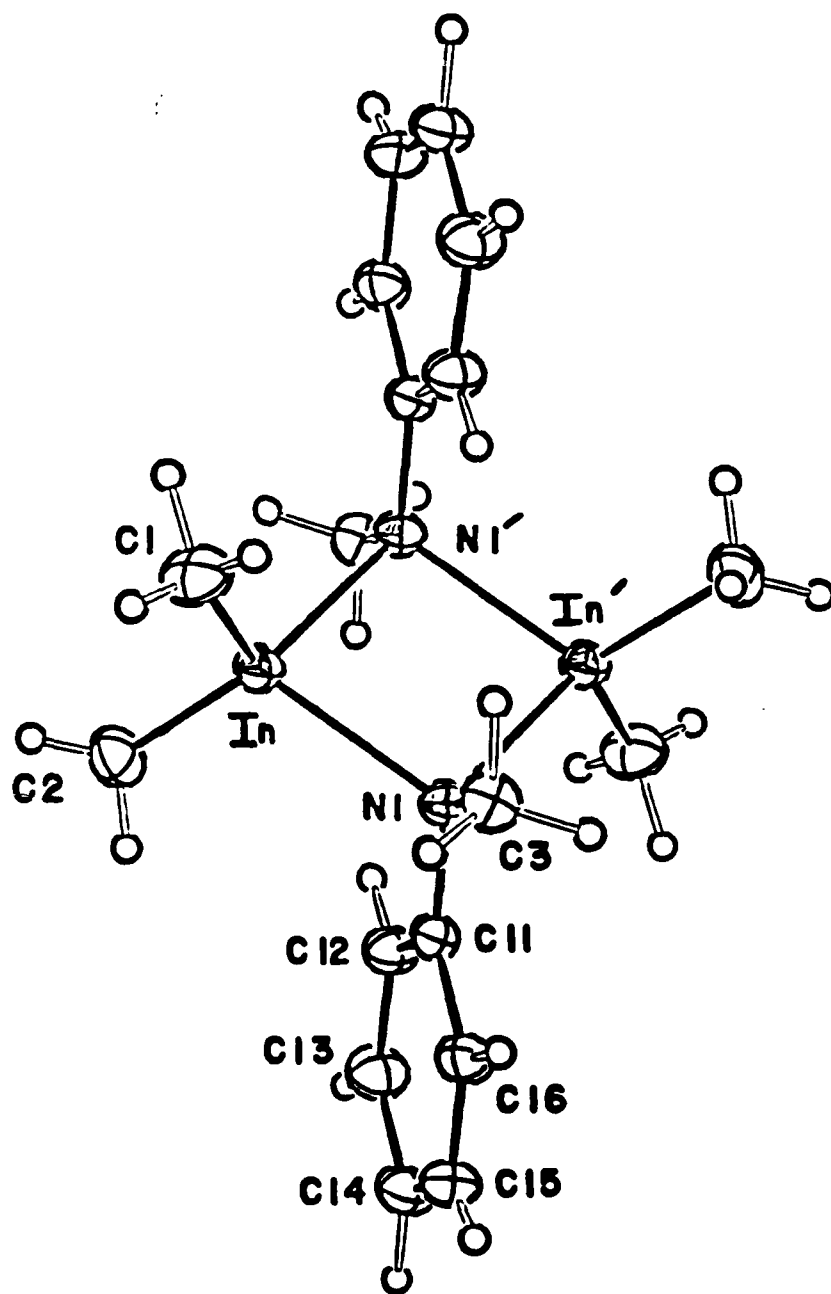


Figure 2

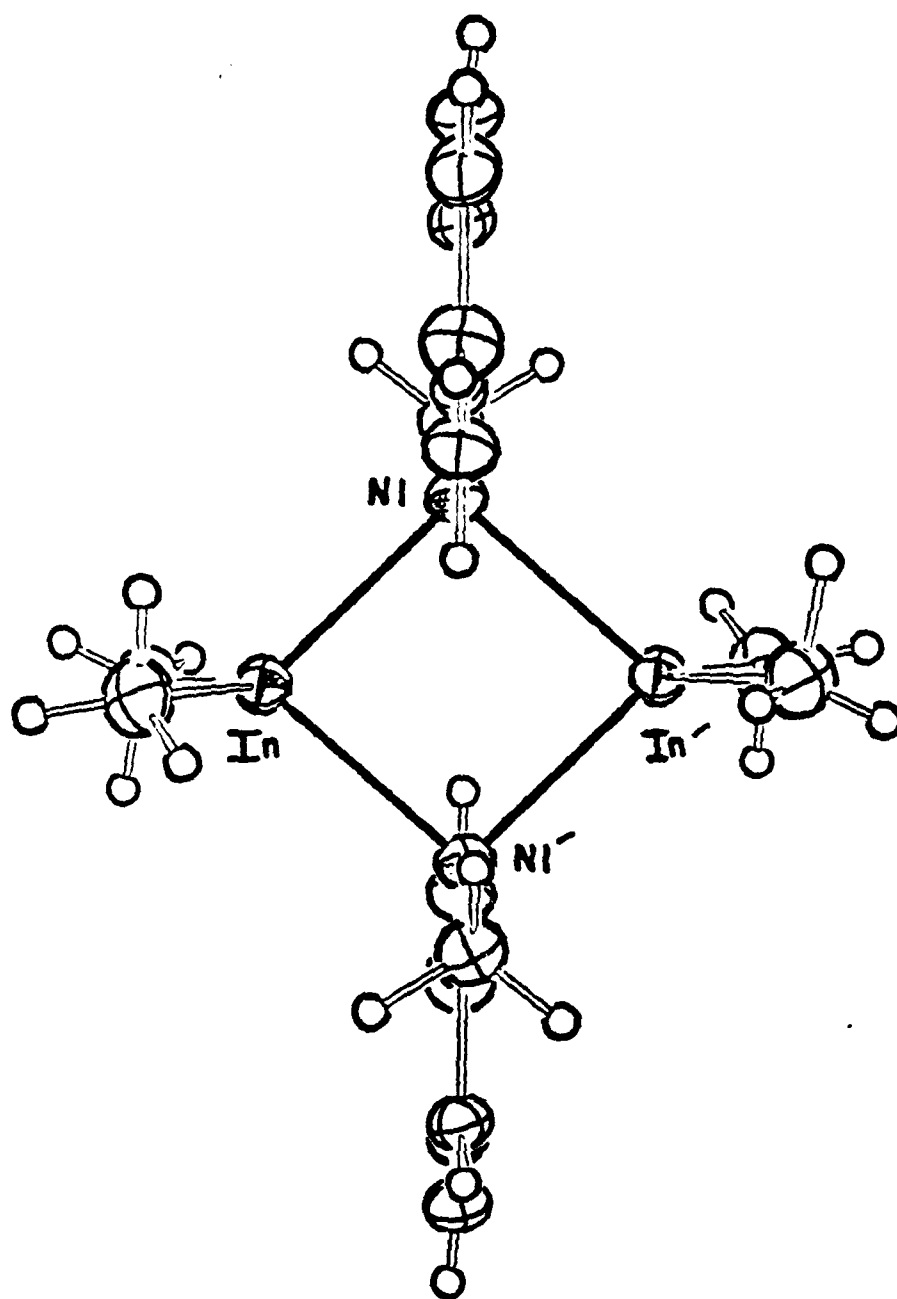


Figure 3

References

1. Manasevit, H. M.; Simpson, W. I. J. Electrochem. Soc. 1979, 116, 1725.
2. Coates, G. E.; Green, M.L.H.; Wade, K. "Organometallic Compounds", 3rd ed., Methuen: London, 1967; Vol. 1, Chapter 3.
3. Beachley, O. T., Jr.; Tessier-Youngs, C. Inorg. Chem. 1979, 18, 3188.
4. Wakatsuki, K.; Tanaka, T. Bull. Chem. Soc. Jpn. 1975, 48, 1475.
5. Gyanne, M.J.S.; Wilkinson, M.; Worrall, I. J. Inorg. Nucl. Chem. Lett. 1973, 9, 765.
6. Beachley, O. T., Jr.; Coates, G. E. J. Chem. Soc. 1965, 3241.
7. Shriver, D. F. "The Manipulation of Air Sensitive Compounds"; McGraw-Hill: 1969, p. 95.
8. Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. Inorg. Chem. 1977, 16, 265.
9. "International Tables for X-Ray Crystallography", Kynoch Press, Birmingham, England, 1974; Vol. 4 (a) pp 99-101 (b) pp 149-150.
10. Churchill, M. R. Inorg. Chem. 1973, 12, 1213.
11. Esd's on average values are shown in square brackets and are calculated by the scatter formula
$$[\sigma] = \left[\sum_{i=1}^{i=N} (\bar{d} - d_i) / (N-1) \right]^{1/2}$$
12. Domenicano, A.; Vaciago, A.; Coulson, C. A. Acta. Crystallogr., Sect. B 1975, 31, 1630.
13. Mertz, K.; Schwarz, W.; Eberwein, B.; Weidlein, J.; Hess, H.; Hausen, H. D. Z. Anorg. Allg. Chem. 1977, 429, 99.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D. C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D. C. 20380	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D. C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D. C. 20360	1	Naval Ship Research & Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D. C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GENNo.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco, Calif. 96503 1

Mr. James Kelly
DTNSRDC Code 2804
Annapolis, Maryland 21402 1

TECHNICAL REPORT DISTRIBUTION LIST, 053

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. R. N. Grimes Department of Chemistry University of Virginia Charlottesville, Virginia 22901	1	Professor H. Abrahamson Department of Chemistry University of Oklahoma Norman, Oklahoma 73019	1
Dr. M. F. Hawthorne Department of Chemistry University of California Los Angeles, California 90024	1	Dr. M. H. Chisholm Department of Chemistry Indiana University Bloomington, Indiana 47401	1
Dr. D. B. Brown Department of Chemistry University of Vermont Burlington, Vermont 05401	1	Dr. B. Foxman Department of Chemistry Brandeis University Waltham, Massachusetts 02154	1
Dr. W. B. Fox Chemistry Division Naval Research Laboratory Code 6130 Washington, D. C. 20375	1	Dr. T. Marks Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. J. Adcock Department of Chemistry University of Tennessee Knoxville, Tennessee 37916	1	Dr. G. Geoffrey Department of Chemistry Pennsylvania State University University Park, Pennsylvania 16802	1
Dr. A. Cowley Department of Chemistry University of Texas Austin, Texas 78712	1	Dr. J. Zuckerman Department of Chemistry University of Oklahoma Norman, Oklahoma	1
Dr. W. Hatfield Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1	Professor P. S. Skell Department of Chemistry The Pennsylvania State University University Park, Pennsylvania 16802	1
Dr. D. Seyferth Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Professor K. M. Nicholas Department of Chemistry Boston College Chestnut Hill, Massachusetts 02167	1
Professor Ralph Rudolph Department of Chemistry University of Michigan Ann Arbor, Michigan 48109	1	Professor R. Neilson Department of Chemistry Texas Christian University Fort Worth, Texas 76129	1
Professor Richard Eisenberg Department of Chemistry University of Rochester Rochester, New York 14627	1	Professor M. Newcomb Texas A&M University Department of Chemistry College Station, Texas 77843	1

DATE
FILMED
-8