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

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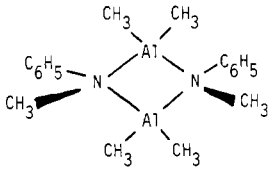
The solution properties of $[(CH_3)_2MN(CH_3)(C_6H_5)]_2$ (M = Al, Ga, In) and the crystalline state of the indium derivative have been investigated. All compounds exist in solution as mixtures of cis and trans geometrical isomers. The cis isomer is the predominant species for the aluminum and gallium 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 $P\bar{1}$ (No. 2) with a = 7.3202 (15) Å, b = 7.6095 (21) Å, c = 8.9800 (27) Å, α = 83.194 (24)°, β = 81.800 (21)°, γ = 81.986 (19)°, V = 487.8 (2) Å^3, and ρ(calcd) = 1.71 g cm^{-3} for Z = 1 (dimeric unit) with molecular weight 502.1. Diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer, and the structure was solved by 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 2θ = 3.0–55.0° (Mo Kα radiation). The dimeric molecule lies on a crystallographic center of symmetry. The In–N (bridging) distances are In–N(1) = 2.280 (2) Å and In–N(1′) = 2.284 (2) Å, the In···In′ distance is 3.363 Å, and the indium–methyl bond lengths are defined by In–C(1) = 2.156 (4) Å and In–C(2) = 2.149 (4) Å. The dimerization and/or isomerization reactions in solution were investigated by ^{1}H 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.

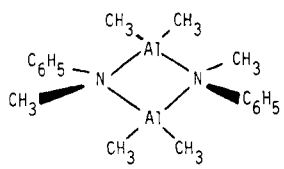
Introduction

The synthetic scheme[1] for the preparation of semiconductor 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 polymers[2] with the simplest formulas R_2(group 3)–(group 5)R'_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 reaction[3] 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



cis isomer



trans isomer

interest to note that the 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 $[2_{\pi_s} + 2_{\pi_s}]$ 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 compared to its aluminum and gallium analogues, 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 ^{1}H NMR spectroscopy.

Experimental Section

All compounds were manipulated in a vacuum line or a purified argon atmosphere. The solvents, benzene, toluene, and methylene chloride, were purified by being refluxed 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) iodide[5]

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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 molar ratio of methyl groups per mole 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 cryoscopically in benzene by using an instrument similar to that described by Shriver.[7]

The infrared spectra were recorded in the range 4000–250 cm^{-1} by means of a Perkin-Elmer Model 457 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 (τ).

Preparation of $(CH_3)_2MN(CH_3)(C_6H_5)$ (M = Ga and In). The gallium and indium amide derivatives were prepared from stoichiometric quantities of *N*-methylaniline and $Ga(CH_3)_3$ or $In(CH_3)_3$ by a pyrolytic method using a sealed tube equipped with a break-seal sidearm. In the case of $(CH_3)_2GaN(CH_3)(C_6H_5)$, 0.1133 g (0.9872 mmol) of $Ga(CH_3)_3$ was reacted with 0.1058 g (0.9887 mmol) of $N(CH_3)(C_6H_5)H$ at 130 °C for 24 h. After reaction was complete, 1.01 mmol of CH_4 was removed and measured by means of a Toepler pump–gas burette assembly. The product was purified by vacuum sublimation at 120 °C. The indium derivative was prepared by the identical procedure. Reaction conditions of 60 °C for 8–10 h led to the formation of 1.00 mol of CH_4/mol of $In(CH_3)_3$. 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 $(CH_3)_2GaN(CH_3)(C_6H_5)$. The gallium–nitrogen product was fully characterized. The colorless, crystalline solid has a melting point of 112–114 °C. In a microscopic examination of a typical sample, all crystals appeared identical in shape. Two different crystalline 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, [calculated 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, reference tetramethylsilane) and assignment. Benzene-d_6 solution: CH_3Ga (10.12, cis; 9.98, trans; 9.82, cis), CH_3N (7.11, cis; 7.21, trans). Toluene-d_8 solution: CH_3Ga (10.02, cis; 9.88, trans; 9.73, cis), CH_3N (7.06, trans; 7.01, cis). CH_2Cl_2 solution: CH_3Ga (10.60, cis; 10.35, trans; 9.95, cis), CH_3N (7.02, cis; 7.08, trans). The relative intensities of lines due to the different isomers are given in the appropraite 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) cm^{-1}. 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 crystalline 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, reference tetramethylsilane) and assignment. Benzene-d_6 solution: CH_3In (10.06, trans; 10.05, cis; 10.00, cis), CH_3N (7.03, cis; 6.99, trans). Toluene-d_8 solution: CH_3In (10.03, trans; 9.97, cis; 9.83, cis), CH_3N (6.97, cis; 6.96, trans). Methylene chloride solution: CH_3In (10.32, cis; 10.25, trans; 10.17, cis), CH_3N (6.90, cis; 6.86, trans). The relative intensities of lines due to the different isomers are given in the appropriate table. It is of interest to note that the indium derivative is significantly less soluble than the aluminum or gallium analogues. 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) cm^{-1}. Anal. Calcd for $(CH_3)_2InN(CH_3)(C_6H_5)$: In, 45.7; moles of $InCH_3$/moles of In, 2.00. Found: In, 44.7; moles of $InCH_3$/moles of In 2.00.

The high melting point and limited solubility of this compound with the simplest formula $(CH_3)_2InN(CH_3)(C_6H_5)$ led 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.

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

cryst system: triclinic	a = 7.3202 (15) Å
space group: $P\bar{1}$ [C_i^1; No. 2]	b = 7.6095 (21) Å
V = 487.8 (2) Å^3	c = 8.9800 (27) Å
Z = 1 (dimeric unit)	α = 83.194 (24)°
fw 502.1	β = 81.800 (21)°
ρ_{calcd} = 1.71 g cm^{-3}	γ = 81.986 (19)°

B. Collection of Intensity Data

diffractometer	Syntex $P2_1$
radiation	Mo Kα (λ 0.710 730 Å)
monochromator	highly oriented graphite, equatorial geometry; 2θ(mono) = 12.2°
rflctns measd	$+h,\pm k,\pm l$
scan type	coupled θ(crystal)–2θ(counter)
2θ range	3.0–55.0°
scan speed	4.0°/min (in 2θ)
scan width	$[2.0 + \Delta(\alpha_2{-}\alpha_1)]$°
rflctns collected	2479 total data, 2259 independent data
standards	3 collected every 97 data; no significant decay
abs coeff	μ = 23.5 cm^{-1}; empirical correction based upon ψ scans of the $4\bar{1}0$ (2θ = 24.08°; T_{max}/T_{min} = 1.270) and $5\bar{3}1$ (35.45°; 1.270) reflections

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 24 reflections with 2θ = 20–30°.

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 × 0.25 × 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 $P2_1$ 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 by 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 nonhydrogen 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).

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

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(7) Shriver, D. F. "The Manipulation of Air Sensitive Compounds"; McGraw-Hill: New York, 1969; p 95.
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Table II. Final Positional and Thermal Parameters[a]

atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
In	0.00891 (2)	0.20272 (2)	0.40374 (2)		H(1C)	−0.253 (12)	0.462 (13)	0.344 (12)	12.5 (27)
N(1)	−0.0621 (3)	−0.0684 (3)	0.3625 (2)		H(2A)	0.379 (7)	0.220 (8)	0.318 (6)	7.5 (13)
C(1)	−0.2386 (6)	0.3934 (5)	0.4141 (5)		H(2B)	0.280 (7)	0.206 (7)	0.191 (6)	5.9 (11)
C(2)	0.2684 (5)	0.2632 (5)	0.2771 (4)		H(2C)	0.254 (7)	0.383 (8)	0.245 (6)	6.8 (12)
C(3)	−0.2632 (4)	−0.0541 (4)	0.3514 (4)		H(3A)	−0.312 (6)	−0.171 (6)	0.366 (5)	4.9 (9)
C(11)	0.0522 (3)	−0.1498 (3)	0.2401 (3)		H(3B)	−0.328 (5)	0.004 (5)	0.440 (5)	4.1 (8)
C(12)	0.2456 (4)	−0.1669 (4)	0.2347 (3)		H(3C)	−0.297 (5)	0.011 (6)	0.261 (5)	4.6 (8)
C(13)	0.3636 (5)	−0.2421 (5)	0.1182 (4)		H(12)	0.300 (5)	−0.127 (5)	0.307 (5)	3.9 (8)
C(14)	0.2930 (5)	−0.3056 (5)	0.0033 (4)		H(13)	0.498 (6)	−0.253 (7)	0.106 (5)	6.1 (11)
C(15)	0.1026 (6)	−0.2922 (5)	0.0765 (4)		H(14)	0.381 (5)	−0.363 (5)	−0.080 (5)	4.5 (8)
C(16)	−0.0183 (4)	−0.2148 (4)	0.1231 (3)		H(15)	0.057 (7)	−0.329 (6)	−0.040 (6)	5.8 (11)
H(1A)	−0.337 (11)	0.362 (11)	0.446 (10)	11.0 (23)	H(16)	−0.171 (5)	−0.200 (5)	0.124 (4)	4.1 (7)
H(1B)	−0.236 (8)	0.471 (8)	0.497 (7)	7.1 (13)					

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)	4.84 (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 (10)
C(16)	3.83 (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 $\exp[-1/4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

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 nonhydrogen atoms. Continued full-matrix, least-squares refinement of positional and anisotropic thermal parameters for all nonhydrogen 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 Å.[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 $\sum w(|F_o| - |F_c|)^2$ 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 aluminum[4] 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 cyroscopic molecular weight studies of little use), and it has a relatively high melting point, 179–181 °C. 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 Waals distances (see Figure 1). The atomic numbering

Table III. Intramolecular Distances (Å) for $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$

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 (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)

(10) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

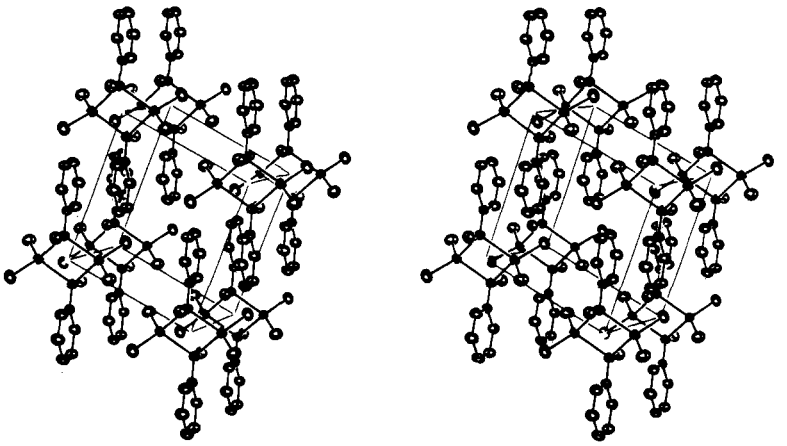

Figure 1. Stereoscopic packing diagram for $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ (ORTEP-II diagram; 30% ellipsoids; hydrogen atoms omitted).

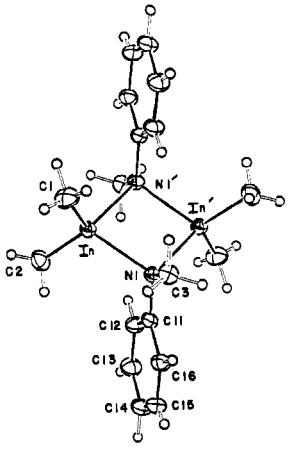

Figure 2. Labeling of atoms in the $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ molecule. The molecule lies on an inversion center. Atoms in the basic asymmetric unit are labeled normally. Atoms in the "other half" of the molecule are labeled with a prime; their positions are related to atoms in the basic asymmetric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

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)° to N(1)–In–N(1′) = 85.08 (7)°; the nitrogen–indium–carbon angles are more typical, with values lying between 109.10 (11)° and 112.24 (11)° (see Table IV). The indium–methyl bond lengths, In–C(1) = 2.156 (4) Å and In–C(2) = 2.149 (4) Å (average 2.153 [5] Å), suggest a covalent radius of 1.38 Å for indium(III) in this type of environment. The $In(\mu\text{-}N)_2In'$ system is required to be precisely planar; the bond lengths are In–N(1) = In′–N(1′) = 2.280 (2) Å and In–N(1′) = In′–N(1) = 2.284 (2) Å (average 2.282 [3] Å).[11] The obtuse In–N(1)–In′ angle of 94.92 (7)° and the long In···In′ distance of 3.363 (0) Å confirm that there is no direct indium–indium bonding.

As shown in Figure 2, the bridging $\mu\text{-}N(CH_3)(C_6H_5)$ groups take up a mutually trans arrangement. The dihedral angle between the $In(\mu\text{-}N)_2In'$ and phenyl planes is 91.3° (see Table V and Figure 3). Angles around N(1) range from In–N(1)–In′ = 94.92 (7)° to In–N(1)–C(11) = 115.19 (15)°. The nitrogen–methyl bond length [N(1)–C(3) = 1.478 (3) Å] is some 0.048 (4) Å longer than the nitrogen–phenyl bond length [N(1)–C(11) = 1.430 (3) Å], reflecting, principally, the difference in covalent radius of an sp^3- vs. an sp^2-hybridized carbon atom.

Carbon–carbon distances around the phenyl ring range from C(14)–C(15) = 1.379 (6) Å to C(16)–C(11) = 1.401 (4) Å, the average values being 1.389 [9] 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 sub-

Table V. Least-Squares Planes[a]

atom	dev, Å	atom	dev, Å
	(A) $In(\mu\text{-}N)_2In'$ plane		
	$0.8852X - 0.3043Y - 0.3502Z = -1.1254$[b]		
In	0.000	In′	0.000
N(1)	0.000	N(1′)	0.000
	(B) Phenyl Ring		
	$0.0566X + 0.8483Y - 0.5265Z = -1.8666$[b]		
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)

[a] Dihedral angle between planes A and B is 91.30° (88.70°). [b] Orthonormalized (Å) coordinates.

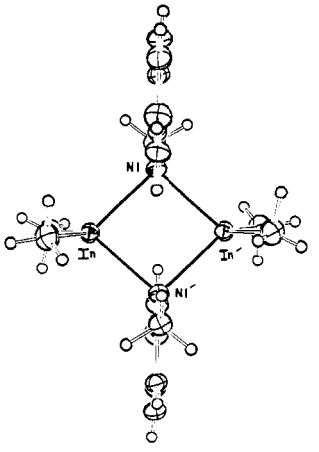

Figure 3. $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ molecule projected onto its $In(\mu\text{-}N)_2In'$ plane. Note the near orthogonality of the phenyl groups with this plane (ORTEP-II diagram; 30% probability ellipsoids for nonhydrogen atoms).

(11) Esd's on average values are shown in square brackets and are calculated by the scatter formula

$$[\sigma] = [\sum_{i=1}^{i=N} (\bar{d} - d_i)/(N-1)]^{1/2}$$

(12) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1630.

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]

bond or contact	distance, Å	
	$[(CH_3)_2InN(CH_3)(C_6H_5)]_2$	$[(CH_3)_2InN(CH_3)_2]_2$[a]
In···In′	3.363 (0)	3.278 (2)
In-N	2.280 (2)	2.225 (13)
	2.284 (2)	2.247 (13)
In-CH_3	2.149 (4)	2.168 (19)
	2.156 (4)	2.170 (18)
N-CH_3	1.478 (3)	1.444 (15)
		1.505 (19)
N-C_6H_5	1.430 (3)	-
	angle, deg	
atoms	$[(CH_3)_2InN(CH_3)(C_6H_5)]_2$	$[(CH_3)_2InN(CH_3)_2]_2$[a]
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)

[a] See ref 13.

Table VII. Effect of Solvent on the Percentage Cis Isomer

	C_6H_6	$C_6H_5CH_3$	CH_2Cl_2
$[(CH_3)_2AlN(CH_3)(C_6H_5)]_2$[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

[a] See ref 4.

Table VIII. 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		

[a] See ref 4.

stantially reduced from 120° [C(16)-C(11)-C(12) = 117.11 (24)°] as is that at the para carbon [C(13)-C(14)-C(15) = 118.39 (33)°]; these reductions are compensated for by significant expansions of the angles at the ortho carbon atoms [C(11)-C(12)-C(13) = 121.89 (28)° and C(15)-C(16)-C(11) = 120.23 (27)°] and at the meta carbon atoms [C(12)-C(13)-C(14) = 120.62 (32)° and C(14)-C(15)-C(16) = 121.75 (33)°].

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(CH_3)(C_6H_5) distances of 2.282 [3] Å (average) are significantly longer (by 0.046 Å) than the In-(μ-N(CH_3)$_2$) 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)° vs. 94.3 (3)°, respectively). (3) The In-CH_3 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 ~0.016 Å *shorter* than the In-CH_3 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 CH_3-In-CH_3 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 by 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 Al > Ga > In. For the aluminum 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 0.36 D, respectively). Upon changing to the most polar solvent, CH_2Cl_2 (1.60 D), 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-CH_3 lines with increasing field is cis, cis, trans. The spectra of the aluminum and gallium derivatives in all solvents are identical in appearance with that observed for the indium compound in CH_2Cl_2 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. Our 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

(13) Mertz, K.; Schwarz, W.; Eberwein, B.; Weidlein, J.; Hess, H.; Hausen, H. D. *Z. Anorg. Allg. Chem.* **1977**, *429*, 99.

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

	M in $[(CH_3)_2MN(CH_3)(C_6H_5)]_2$		
	Al[a]	Ga	In
ΔH, kJ/mol	−4.47	+4.16	−1.94
ΔS, J/mol K	−1.74	+21.8	−10.3
$T\Delta S_{298}$, kJ/mol	−0.52	+6.50	−3.07
ΔG_{298}, kJ/mol	−3.95	−2.34	+1.13
r_b[2]	0.9885	0.9676	0.9781

[a] Reference 4. [b] Least-squares plot of ln K vs. $1/T$.

trans isomer is consistent with a stepwise dimerization reaction. Kinetic control in a concerted cycloaddition reaction would have led to the cis isomer.

The measurements of cis/trans ratios or equilibrium constants (K = [cis]/[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 min 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 being 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.

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Registry No. *trans*-$[(CH_3)_2GaN(CH_3)(C_6H_5)]_2$, 77590-13-7; *cis*-$[(CH_3)_2GaN(CH_3)(C_6H_5)]_2$, 77646-77-6; *trans*-$[(CH_3)_2InN(CH_3)(C_6H_5)]_2$, 77590-14-8; *cis*-$[(CH_3)_2InN(CH_3)(C_6H_5)]_2$, 77646-78-7; *trans*-$[(CH_3)_2AlN(CH_3)(C_6H_5)]_2$, 56604-60-5; *cis*-$[(CH_3)_2AlN(CH_3)(C_6H_5)]_2$, 56649-31-1; $Ga(CH_3)_3$, 1445-79-0; $In(CH_3)_3$, 3385-78-2.

Supplementary Material Available: Listings of data-processing formulas and observed and calculated structure factor amplitudes for $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$ (14 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto di Chimica Generale ed Inorganica, University of Venice, 30100 Venice, Italy, and the William Ramsay and Ralph Forster Laboratories, University College London, London, England

Nucleophilic Substitution Reactions of Chloro-, Iodo-, and Aquo(1,5-diamino-3-methyl-3-azapentane)platinum(II) Cations. A New Nucleophilicity Scale for Cationic Platinum(II) Complexes and a Comparison of the Leaving Group Effects of Chloride and Iodide

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The kinetics of the replacement of X from $[Pt(Medien)X]^{n+}$ (Medien = 1,5-diamino-3-methyl-3-azapentane; X = Cl or I (n = 1), H_2O (n = 2)) by a variety of nucleophiles (Cl^-, Br^-, N_3^-, SCN^-, I^-, $SeCN^-$, $(NH_2)_2CS$, H_2O) have been studied in water at 25.0 °C. There is a good linear relationship between log $k_2°$ for the 1+ cationic substrates ($k_2°$ is the second-order rate constant at μ = 0) and log $k_2°$ for the reaction of the same nucleophile with $[Pt(NH_3)(en)Cl]^+$ (en = 1,2-diaminoethane) which is taken as a standard for a new nucleophilicity scale that is appropriate to the 1+ substrates. The slopes of these plots are 1.05 and 1.15 for the replacement of chloride and iodide, respectively, but lines cross and the rate constant for the aquation of the iodo complex is smaller than that for the chloro species. The factors causing the large difference in nucleophilic discrimination are discussed. The rate constants for the displacement of water from the corresponding dicationic species do not follow a similar linear relationship, but when they are plotted against log $k_2°$ for a standard 2+ cationic substrate $[Pt(dien)H_2O]^{2+}$ (dien = 1,5-diamino-3-azapentane), the linearity returns. The behavior of the Medien complex is compared with that of the corresponding dien species.

Introduction

In a recent paper[3] we observed that many of the departures from a linear relationship between the $n_{Pt}°$ value of a particular nucleophile and log k_2 for its reaction with a particular substrate could be eliminated if we used as our standard a reference substrate of the same charge type as that being investigated. For a 1+ cation we used, as reference, $[Pt(en)(NH_3)Cl]^+$ (en = 1,2-diaminoethane) in its reactions of the type $[Pt(en)(NH_3)Cl]^+ + Y^{n-} \rightarrow [Pt(en)(NH_3)Y]^{(2-n)+} + Cl^-$ (in water at 25 °C). In that paper we were able to investigate the cis effect (relative to NH_3) of $(CH_3)_2SO$, and we have since

(1) University of Venice.
(2) University College London.
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