

would increase the likelihood of bonding through the double bond.

The acid dissociation constants for maleic acid indicate it is a considerably stronger acid than fumaric acid for the loss of the first proton and a considerably weaker acid for the loss of the second proton. Both of these facts can be explained as the result of the formation of a strong intramolecular hydrogen bond in the monoprotic anion. The formation of a similar chelate ring with Cu(II) causes an increase in the stability of the complex formed relative to that of fumaric acid. However, this chelation would hold the metal ion away from the olefinic linkage. This effect can be noted in the appreciably lower stability of the CuCl complex of maleic acid compared to that of fumaric acid.

The results of this study indicate that there is a considerably greater tendency for bonding through an olefinic linkage for Cu(I) as compared to Cu(II), which

is as expected.² However, the results also seem to indicate that bonding of Cu(II) through the olefinic linkage occurs in some cases. Silver showed surprisingly little interaction with the olefinic linkage under the conditions of our experiments. However, ligands which are selected because of their ability to form favorable chelate rings in planar, tetrahedral, or octahedral complexes would not necessarily provide the most favorable distribution of the points of attachment for silver ion, which tends to form linear complexes.

Although some indication of interaction of Cu(II) with the olefinic linkage was found, the number of metals which are known to form stable olefinic linkages was not enlarged. In aqueous solution the solvent and the carboxylate ions are probably such strong donors, compared to the olefinic linkage, that olefinic complexes are unlikely except for a few metals.

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Reactions of Triethylaluminum, Diethylaluminum Chloride, and Ethylaluminum Dichloride with Dimethyl-, Trimethyl-, and Tetramethylhydrazines

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Tetramethylhydrazine reacts with triethylaluminum, diethylaluminum chloride, and ethylaluminum dichloride to produce $(C_2H_5)_3Al \cdot N(CH_3)_2N(CH_3)_2$, $(C_2H_5)_2AlCl \cdot N(CH_3)_2N(CH_3)_2$, and $C_2H_5AlCl_2 \cdot N(CH_3)_2N(CH_3)_2$, respectively. Nuclear magnetic resonance data indicate that the two nitrogen atoms are equivalent. Molecular weight data indicate that these adducts contain one mole each of the aluminum compound and of the hydrazine per mole of adduct. Therefore, the aluminum atom is probably pentacoordinate in these compounds. The reaction of 1,1-dimethylhydrazine with diethylaluminum chloride produces ethylchloro-2,2-dimethylhydrazinoaluminum, $[C_2H_5AlClNHN(CH_3)_2]_2$. The pyrolytic condensation of ethylchloro-2,2-dimethylhydrazinoaluminum produces the polymer $[AlClN(CH_3)_2]_x$. The reaction of trimethylhydrazine with ethylaluminum dichloride produces $[Cl_2AlNCH_3N(CH_3)_2]_x$.

Recent studies by Fetter and Bartocha,¹ Laubengayer, *et al.*,² Nielsen and Sisler,³ and Paterson and Onyszchuk⁴ have extended the earlier work of Davidson and Brown⁵ concerning the reactions of alkylaluminum compounds with Lewis bases. These investigators have shown that alkylaluminum compounds react with amines and hydrazines to produce molecular addition compounds if the Lewis base contains no active hydrogen atoms. If a hydrogen atom is present on the nitrogen the reaction may proceed with the evolution of a hydrocarbon and the formation of a covalent bond between aluminum and nitrogen. The resulting amino- or hydrazinoaluminum compound may condense and form a polymeric species if another hydrogen atom is present on the nitrogen atom and another alkyl group is on the aluminum. Studies in this area have been ex-

tended by the synthesis, in our laboratory, of a variety of hydrazinoaluminum compounds, several of which apparently contain pentacoordinate aluminum.

Pentacoordinate aluminum has been proposed by Wiberg⁶ and by Ruff and Hawthorne⁷ as a result of their experiments with amine complexes of aluminum hydrides. Recently Fetter, *et al.*,⁸ have reported a series of complexes formed by reaction of trimethylaluminum and aluminum hydride trimethylamine with a variety of amines and hydrazines, and have used nuclear magnetic resonance spectra to support the postulated existence of pentacoordinate aluminum in these compounds. The existence of pentacoordinate aluminum in solid $AlH_3 \cdot 2N(CH_3)_3$ has recently been established by X-ray studies of single crystals.⁹

Before the publication of the above paper⁹ we had

(1) N. R. Fetter and B. Bartocha, *Can. J. Chem.*, **39**, 2001 (1961).
(2) A. W. Laubengayer, J. D. Smith, and G. G. Ehrlich, *J. Am. Chem. Soc.*, **83**, 542 (1961).
(3) R. P. Nielsen and H. H. Sisler, *J. Chem. Soc.*, 3818 (1962).
(4) W. G. Paterson and M. Onyszchuk, *Can. J. Chem.*, **39**, 2324 (1961).
(5) N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).

(6) E. Wiberg, H. Graf, and R. Uson, *Z. anorg. allgem. Chem.*, **272**, 221 (1958).
(7) J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 535 (1961).
(8) N. R. Fetter, B. Bartocha, F. E. Brinckman, Jr., and D. W. Moore, *Can. J. Chem.*, **41**, 1359 (1963).
(9) C. W. Heitsch, C. E. Nordman, and R. W. Parry, *Inorg. Chem.*, **2**, 508 (1963).

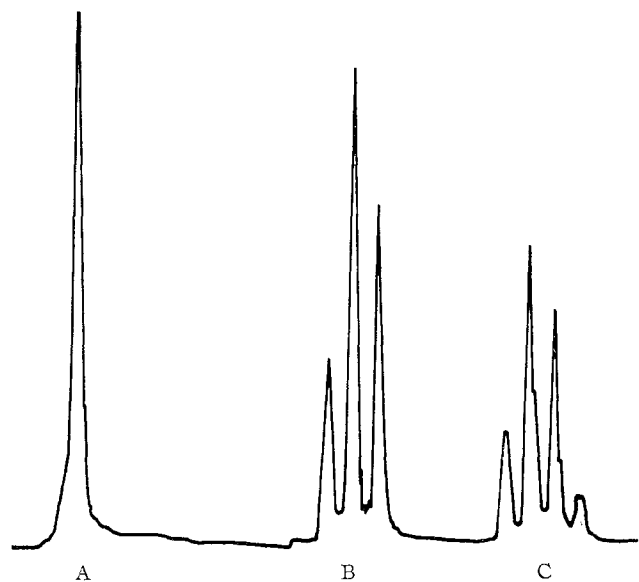


Fig. 1.— ^1H nuclear magnetic resonance spectrum of tetramethylhydrazine-diethylaluminum chloride.

prepared several new molecular addition compounds of tetramethylhydrazine with triethylaluminum, diethylaluminum chloride, and ethylaluminum dichloride and had found proton magnetic resonance spectra showing, as in the case of Fetter's compounds, that the tetramethylhydrazine is probably symmetrically bonded to the aluminum atom and that the aluminum atom is thus probably pentacoordinate. These data, along with some suggestions concerning possible bonding, are presented in this paper.

Experimental

Apparatus.—All organoaluminum compounds were handled either in a nitrogen-filled drybox or in a glass vacuum line. Molecular weights were determined cryoscopically in benzene. A standard freezing point depression apparatus was modified to provide a slow nitrogen flush so that contact of the solution with the atmosphere could be avoided.

Proton Magnetic Resonance Spectra.—The proton magnetic resonance spectra were obtained on a Varian high resolution nuclear magnetic resonance spectrometer, Model V-4300-2, provided with field homogeneity control, magnet insulation, and field stabilizer, operating at 56.4 Mc. Because of the difficulty of using a suitable internal standard with these materials, chemical shifts are reported only as differences from the $\text{N}-\text{CH}_3$ peaks in the respective spectra.

Infrared Spectra.—The infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer using sodium chloride optics. Liquid complexes were examined as thin films (prepared in a nitrogen atmosphere) and solids were made into mulls in Nujol.

Materials.—All alkylaluminum compounds were obtained from the Ethyl Corporation. Triethylaluminum was fractionally distilled and the fraction boiling at 56° (0.5 mm.) was used. Diethylaluminum chloride was similarly distilled from excess dry sodium chloride, to remove ethylaluminum dichloride as the salt $\text{NaC}_2\text{H}_5\text{AlCl}_3$, and the fraction boiling at 38° (0.25 mm.) was selected. Ethylaluminum dichloride was fractionally distilled and the fraction boiling at 47° (1.0 mm.) was used. The Olin Mathieson Co. supplied 1,1-dimethylhydrazine which had a boiling range of $62-63^\circ$ (758 mm.) when fractionated from calcium hydride. Tetramethylhydrazine was prepared from 1,1-di-

methylhydrazine by the method of Beltrami and Bissell.¹⁰ All other reagents used in this work were distilled from calcium hydride.

Analyses.—The aluminum content of a weighed sample was obtained by dissolving the sample in an acidified methanol solution and precipitating aluminum 8-hydroxyquinolate by the standard method.¹¹ The chloride content was obtained by the Volhard method. Nitrogen was determined with a Model 29 Coleman nitrogen analyzer.

The ethyl group content was determined in the vacuum line by solvolyzing a weighed sample with methanol acidified with nitric acid. The liberated ethane was collected, purified, and identified by its vapor pressures at -126.3 and -111.6° (lit.¹² 55 and 178 mm., respectively), and its volume was measured.

Reaction of Tetramethylhydrazine with Triethylaluminum.— $\text{Al}(\text{C}_2\text{H}_5)_3$ (12.4 mmoles) was transferred in a drybox to a 50-ml. single-neck, round-bottom reaction flask containing a Teflon-encapsulated magnetic stirring bar. The reaction flask was then fitted with a vacuum stopcock, attached to the manifold of the vacuum line, and the $\text{Al}(\text{C}_2\text{H}_5)_3$ was degassed. Pentane (5 ml.) was introduced into a reaction tube, attached to the manifold, degassed, and transferred to the reaction flask. A tube containing 14.0 mmoles of $\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ was attached to the manifold of the vacuum line and degassed. The $\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ was transferred to the reaction flask containing the $\text{Al}(\text{C}_2\text{H}_5)_3$ cooled with liquid nitrogen. The resulting mixture was slowly brought to ambient temperature and was then stirred for 2 hr. The pentane and excess $\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ were removed by fractional condensation.

The reaction flask containing the colorless, crude $(\text{C}_2\text{H}_5)_3\text{Al}\cdot\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ was filled with dry nitrogen and transferred, under a nitrogen stream, to a vacuum distillation apparatus. The fraction boiling at 78° (0.38 mm.) was used for analysis; yield 9.85 mmoles.

Anal. Calcd. for $(\text{C}_2\text{H}_5)_3\text{Al}\cdot\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$: Al, 13.33; N, 13.85; C_2H_5 , 43.04; mol. wt., 202. Found: Al, 13.51; N, 13.93; C_2H_5 , 43.19; mol. wt., 213.

The proton nuclear magnetic resonance spectrum of $(\text{C}_2\text{H}_5)_3\text{Al}\cdot\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ was obtained from a pure sample sealed in a glass tube. The spectrum of this compound is similar to the spectrum of $(\text{C}_2\text{H}_5)_2\text{AlCl}\cdot\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ shown in Fig. 1. The A, B, and C peaks are assigned to the $\text{N}-\text{CH}_3$, $\text{C}-\text{CH}_3$, and the CH_2 hydrogens, respectively. The ratio of the area under these peaks is 4:3:2, in accord with the formula $(\text{C}_2\text{H}_5)_3\text{Al}\cdot\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$.

Reaction of Tetramethylhydrazine with Diethylaluminum Chloride.—By the vacuum method outlined previously, 22.1 mmoles of $\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ was combined with 20.8 mmoles of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$. The resulting solution, after the excess $\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ and the solvent were removed by fractional condensation, was vacuum distilled. A yield of 19.8 mmoles of colorless product, b.p. 91° (0.28 mm.), was obtained.

Anal. Calcd. for $(\text{C}_2\text{H}_5)_2\text{AlCl}\cdot\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$: Al, 12.93; Cl, 16.99; N, 13.42; C_2H_5 , 27.85; mol. wt., 208. Found: Al, 13.09; Cl, 16.79; N, 12.87; C_2H_5 , 26.61; mol. wt., 187.

The proton nuclear magnetic resonance spectrum of $(\text{C}_2\text{H}_5)_2\text{AlCl}\cdot\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ was obtained from a pure sample sealed in a glass tube. This spectrum is shown in Fig. 1. The ratio of the areas under the $\text{N}-\text{CH}_3$, $\text{C}-\text{CH}_3$, and CH_2 hydrogen peaks is 6:3:2, in accord with the formula $(\text{C}_2\text{H}_5)_2\text{AlCl}\cdot\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$.

In order to determine if the structure of $(\text{C}_2\text{H}_5)_2\text{AlCl}\cdot\text{N}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ in benzene solution is similar to its structure in the pure liquid state, the proton magnetic resonance spectrum for this

(10) R. T. Beltrami and E. R. Bissell, *J. Am. Chem. Soc.*, **78**, 2468 (1956).

(11) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, "Applied Inorganic Analysis," John Wiley and Sons, New York, N. Y., 1953, p. 507.

(12) "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Table 1k.

complex in benzene solution was obtained. This partial spectrum showing the N-CH₃ peak is shown in Fig. 2.

This compound was also prepared at atmospheric pressure using a nitrogen atmosphere. The infrared spectrum and elemental analysis indicated that this compound was identical with the material prepared in the vacuum system.

Reaction of Tetramethylhydrazine with Ethylaluminum Dichloride.—By the vacuum method, 15.0 mmoles of N(CH₃)₂-N(CH₃)₂ was combined with 13.4 mmoles of Al(C₂H₅)₂Cl₂. The reaction mixture was allowed to warm slowly to room temperature. The resulting yellow solution was then stirred for 1 hr., during which time the color gradually changed to dark green. The excess N(CH₃)₂N(CH₃)₂ was removed by fractional condensation and the sample was transferred to a drybox. After 6 hr. the color had changed to a dark blue but no further color change was noted over a 2-month period. An attempt to distil a sample of the product yielded only decomposition products. It was noted upon dissolving a sample of the compound in benzene (approximately 3% solution) that the color change reversed over a 3-hr. period, *i.e.*, blue to green to yellow. The molecular weight determinations gave essentially the same value regardless of the color of the solution.

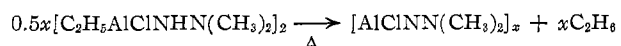
Anal. Calcd. for C₂H₅AlCl₂·N(CH₃)₂N(CH₃)₂: Al, 12.54; Cl, 32.97; N, 13.02; C₂H₅, 13.51; mol. wt., 215. Found: Al, 12.44; Cl, 32.94; N, 12.92; C₂H₅, 13.12; mol. wt., 237.

The proton nuclear resonance spectrum of this material was essentially the same as that of the two previous compounds except that the ratio of the areas under the N-CH₃, C-CH₃, and CH₂ hydrogen peaks could not be obtained accurately. This was because the latter two peaks, being small in comparison with the N-CH₃ peak, broadened and merged with the base line when an attempt was made to obtain the areas of the peaks.

Reaction of 1,1-Dimethylhydrazine with Diethylaluminum Chloride.—By the vacuum method 23.4 mmoles of N(CH₃)₂NH₂ was combined with 20.1 mmoles of Al(C₂H₅)₂Cl at liquid nitrogen temperature using toluene (5 ml.) as a solvent. The reaction mixture was allowed to warm to -78° and was stirred magnetically for 1 hr. at that temperature. The reaction mixture was then warmed to room temperature and was stirred an additional hour. In order to hasten gas evolution the toluene and excess N(CH₃)₂NH₂ were removed by fractional condensation. The resulting solution was stirred until gas evolution ceased (8 hr.). The last traces of ethane were removed by evacuation for 10 hr. The total volume of ethane evolved during the reaction was 19.9 mmoles. The resulting quantitative yield of white crystals of ethylchloro-2,2-dimethylhydrazinoaluminum melted at 95°. The molecular weight indicates that the ethyl chloro-2,2-dimethylhydrazinoaluminum is dimeric.

Anal. Calcd. for [C₂H₅AlClNHN(CH₃)₂]₂: Al, 17.92; Cl, 23.55; C₂H₅, 19.30; mol. wt., 302. Found: Al, 18.28; Cl, 23.46; C₂H₅, 19.11; mol. wt., 312.

Pyrolysis of Ethylchloro-2,2-dimethylhydrazinoaluminum.—[(C₂H₅)₂AlClNHN(CH₃)₂]₂ (13.3 mmoles) was heated in a reaction flask attached to the vacuum system for 18 hr. at temperatures up to 150°. At the end of this time the product was a light brown crystalline solid and the evolution of ethane had stopped. The total amount of ethane evolved was 11.3 mmoles, which is 85.15% of the theoretical amount present based on the equation



This material is not soluble in benzene, hexane, toluene, cyclohexane, or chloroform; m.p. 255° dec.

Anal. Calcd. for 85.15% [AlClNN(CH₃)₂]_x and 14.85% C₂H₅AlClNHN(CH₃)₂: Al, 21.73; Cl, 28.55; N, 22.56. Found: Al, 22.18; Cl, 28.44; N, 22.32.

Reaction of Trimethylhydrazine with Ethylaluminum Dichloride.—By the vacuum method 25.0 mmoles of N(CH₃)₂N(CH₃)₂ was combined with 23.4 mmoles of Al(C₂H₅)₂Cl₂ at liquid nitrogen temperature. Upon allowing the solution to warm to room temperature a slow evolution of gas commenced. After 17 hr. at room temperature the reaction flask was warmed to 60° for

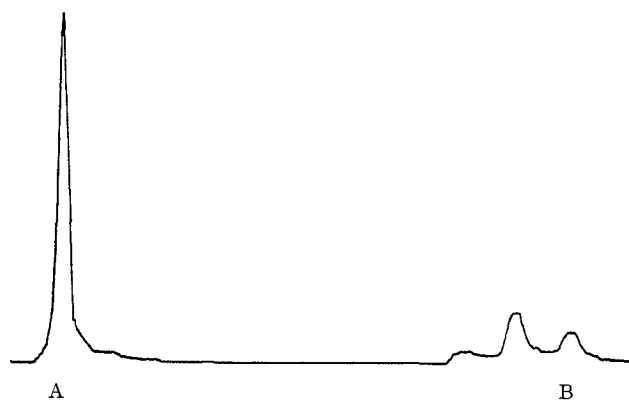
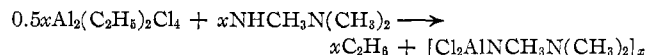


Fig. 2.—Partial (¹H) nuclear magnetic resonance spectrum of tetramethylhydrazine-diethylaluminum chloride in benzene.

2.5 hr. while under vacuum. These drastic measures produced only 91% of the theoretical amount of ethane according to the equation



The resulting tan crystalline mixture was transferred to the drybox and washed with dry benzene. Because the resulting white crystalline solid was insoluble in such solvents as hexane, toluene, benzene, cyclohexane, and chloroform, the molecular weight was not obtained; yield 85%; m.p. 165–166°.

Anal. Calcd. for Cl₂AlNCH₃N(CH₃)₂: Al, 15.78; Cl, 41.47; N, 16.38. Found: Al, 15.64; Cl, 41.40; N, 16.14.

Results and Discussion

The reactions of tetramethylhydrazine with triethylaluminum, diethylaluminum chloride, and ethylaluminum dichloride produce 1:1 molecular addition compounds. In the proton nuclear magnetic resonance spectrum of each of these compounds, there is a single N-CH₃ peak, indicating that all four of the methyl groups are equivalent. If the aluminum were bonded to only one of the nitrogens, the methyl groups attached to nitrogen would be expected to show two peaks in the spectrum because the environment of the two methyl groups attached to the quadruply bonded nitrogen should differ from that of the two attached to triply bonded nitrogen. One possible complication in the interpretation of the spectrum of the neat liquid is that the state of aggregation is not certainly known. However, a solution of tetramethylhydrazine-diethylaluminum chloride in benzene, in which molecular weight determinations indicate that a monomer is present, also shows only a single N-CH₃ peak. These results must be considered as strong evidence for the structural equivalence of the two nitrogen atoms. This indicates that the nitrogen atoms are symmetrically located with respect to the aluminum atom, and therefore the aluminum atom is pentacoordinate.

The most likely bond hybridization for the amine complexes of aluminum hydride, according to Ruff,² is sp³d with the nitrogens bonded to the apices of a trigonal bipyramid. In the tetramethylhydrazine adducts with alkylaluminum compounds the hydrazine is presumably acting as a bidentate ligand. If the bipyramidal configuration is considered there are two

TABLE I
 NUCLEAR MAGNETIC RESONANCE SPECTRA OF HYDRAZINOALUMINUM COMPLEXES

Compound	Chemical shift ^a				<i>J</i> ^b CH ₂ CH ₃
	NH	N-CH ₃ ^c	CH ₃	CH ₂	
(C ₂ H ₅) ₃ Al·N(CH ₃) ₂ N(CH ₃) ₂		0	1.54	2.72	8.1
(C ₂ H ₅) ₂ AlCl·N(CH ₃) ₂ N(CH ₃) ₂		0	1.54	2.58	7.9
C ₂ H ₅ AlCl ₂ ·N(CH ₃) ₂ N(CH ₃) ₂		0	1.59	2.47	7.3
[C ₂ H ₅ AlClNHN(CH ₃) ₂] ₂	-0.09	0	0.92	1.98	7.7

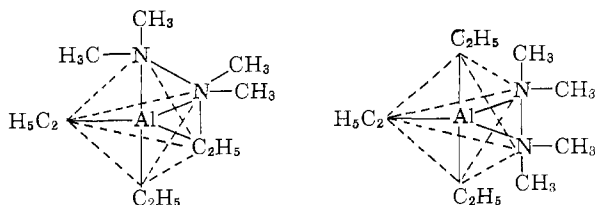
^a Chemical shift values given in parts per million. Positive shifts correspond to higher magnetic fields. ^b Spin-spin coupling constant in cycles per second. ^c The shift of this peak was arbitrarily set at 0. This coincides very nearly with the position of the CH₃ peak of ethyl alcohol.

 TABLE II
 ABSORPTIONS IN THE INFRARED SPECTRA OF HYDRAZINOALUMINUM COMPLEXES

Compound	Absorption, μ ^a
(C ₂ H ₅) ₃ Al·N(CH ₃) ₂ N(CH ₃) ₂	2.62 (vw), 2.95 (sh,w), 3.42 (vs), 3.58 (sh,s), 3.70 (sh,m), 4.72 (vw), 6.88 (vs), 6.95 (sh,s), 7.13 (s), 7.20 (sh,m), 7.35 (sh,w), 8.18 (m), 8.35 (sh,m), 8.43 (s), 8.69 (m), 8.82 (m), 8.98 (m), 9.10 (sh,m), 9.28 (m), 9.51 (m), 9.62 (m), 9.81 (s), 10.16 (vs), 10.52 (s), 10.93 (sh,m), 11.15 (s), 11.39 (m), 14.04 (s)
(C ₂ H ₅) ₂ AlCl·N(CH ₃) ₂ N(CH ₃) ₂	2.62 (vw), 2.90 (sh,w), 3.45 (vs), 3.58 (sh,s), 3.68 (sh,m), 4.28 (vw), 4.70 (vw), 6.88 (vs), 6.95 (sh,s), 7.14 (s), 7.20 (sh,m), 7.32 (m), 8.20 (m), 8.32 (s), 8.40 (sh,m), 8.69 (m), 8.83 (m), 9.15 (sh,w), 9.26 (m), 9.82 (s), 10.18 (b,s), 10.52 (s), 10.86 (w), 11.44 (s), 14.02 (b,s)
C ₂ H ₅ AlCl ₂ ·N(CH ₃) ₂ N(CH ₃) ₂	2.85 (sh,w), 3.08 (sh,w), 3.40 (vs), 3.52 (sh,s), 4.25 (vw), 4.64 (vw), 6.20 (w), 6.84 (vs), 6.90 (sh,s), 7.08 (d,s), 7.28 (sh,m), 8.19 (m), 8.30 (s), 8.38 (sh,m), 8.64 (m), 8.81 (s), 9.13 (sh,m), 9.21 (s), 9.80 (vs), 10.01 (sh,s), 10.22 (vs), 10.40 (sh,s), 10.55 (s), 10.80 (s), 11.46 (vs), 12.65 (vb,m), 13.95 (b,s)
[C ₂ H ₅ AlClNHN(CH ₃) ₂] ₂ Nujol mull	2.98 (s), 3.44 (vs), 3.69 (sh,m), 4.21 (vw), 4.68 (vw), 5.91 (vw), 6.35 (w), 6.90 (vs), 7.15 (sh,s), 7.25 (d,s), 8.18 (s), 8.39 (s), 8.61 (s), 9.02 (w), 9.19 (m), 9.70 (sh,m), 10.08 (b,vs), 10.43 (s), 10.80 (s), 11.75 (b,vs), 14.3 (vb,vs)
C ₂ H ₅ AlClNHN(CH ₃) ₂ 14.85% [AlClN(CH ₃) ₂] ₂ 85.15%	3.10 (m), 3.45 (d,vs), 3.74 (sh,m), 4.16 (w), 4.32 (w), 4.60 (w), 6.22 (m), 6.40 (sh,w), 6.49 (m), 6.54 (sh,m), 6.90 (vs), 7.16 (sh,s), 7.30 (vs), 7.45 (sh,m), 7.90 (vs), 8.19 (s), 8.48 (d,s), 8.59 (sh,m), 9.01 (m), 9.20 (m), 9.71 (b,s), 10.22 (b,s), 11.40 (b,s), 12.5 (vb,s), 13.90 (b,s)
[Cl ₂ AlNCH ₃ N(CH ₃) ₂] ₂ Nujol mull	3.39 (vs), 3.42 (sh,s), 6.82 (vs), 6.90 (sh,s), 7.12 (d,m), 7.28 (m), 8.09 (w), 8.29 (m), 8.44 (m), 8.66 (m), 8.94 (w), 9.15 (w), 9.72 (vs), 10.28 (s), 10.68 (s), 12.05 (b,vs), 14.95 (b,vs)

^a w, weak; m, medium; s, strong; v, very; sh, shoulder; d, doublet; b, broad.

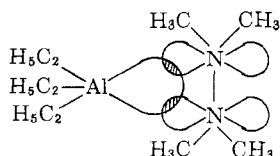
possibilities resulting in the formation of three-membered rings.



Because of the proposed bond hybridization, bond lengths, and bond angles, these structures are presumably highly strained.

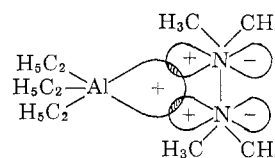
This strain would be decreased if the nitrogen sp³ lone pairs acquired more p-character, in the limit becoming pure p-orbitals, in order to point more nearly toward the aluminum atom. The N-CH₃ bonds would thereby approach sp² hybridization.

Because of the stability of sp³ hybridized aluminum complexes, a third possible structure may be considered in this connection, one in which a four-electron, three-

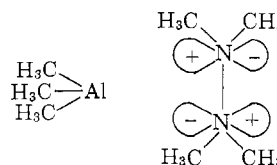


center bond is formed from the overlap of a p-orbital

from each nitrogen with the aluminum sp³ orbital. The three-center molecular orbital of lowest energy would be bonding.



That of next-lowest energy would be expected to be nonbonding between aluminum and nitrogen, and antibonding between the two nitrogens.

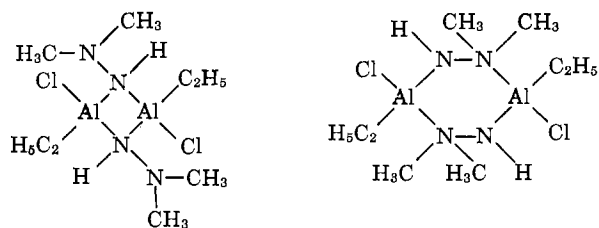


The gain in bond energy of the former should offset the loss in that of the latter, compared to the dissociated complex. These ideas are, of course, speculative.

There is a possible alternative to the explanation of the n.m.r. results that has been described above. This alternative involves the very rapid transfer of alkyl-aluminum groups from one nitrogen atom to the other nitrogen atom in the hydrazine addition compound. If the rate at which such exchange occurs were greater

than the frequency separation of the resonance peaks corresponding to the two environments of the methyl groups, then the two peaks would merge into a single one of intermediate chemical shift. It is not possible to make a very good prediction of the expected frequency difference, but it could well be of the order of 10 c.p.s., so that the average lifetime of the bond in the addition compound would then have to be of the order of 0.1 sec. or longer in order for the two peaks to be resolved. Since the rate of any exchange process should be reduced at lower temperatures, a 50% solution of tetramethylhydrazine-triethylaluminum in carbon disulfide was run at -90° . A slight broadening of the resonance of the methyl peaks was observed, but the results were not clear-cut enough to indicate that a chemical shift difference was the cause.

The compound ethylchloro-2,2-dimethylhydrazino-aluminum, $[\text{C}_2\text{H}_5\text{ClAlNHN}(\text{CH}_3)_2]_2$, can exist as either a four- or a six-membered ring. The bond angles would favor the six-membered ring as the lowest energy configuration. If we assume that the six-membered ring is formed and assume sp^3 coordination of both nitrogen



and aluminum, the ring can exist in either the chair or the boat conformation.

The pyrolysis of ethylchloro-2,2-dimethylhydrazino-aluminum produced a condensed compound which is insoluble in common organic solvents and which has a melting point 160° higher than the parent compound. Since only 85% of the theoretical amount of ethane was evolved it is postulated that the resulting polymer is end stopped with 15% of the parent compound.

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Metal-Olefin Compounds. IV. The Preparation and Properties of Some Aryl and Alkyl Platinum(II)-Olefin Compounds

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The reaction of alkyl or aryl Grignard reagents with platinum(II)-olefin compounds containing cyclic diolefins yields a series of products in which the halide groups initially present in the platinum(II)-olefin compounds are partially or completely replaced to give compounds of the type (olefin) PtR_2 or (olefin) PtRI . The methods of preparation and some physical properties of this series of compounds are reported. The chemical reactivity and spectral data are discussed, and possible structures for the compounds are proposed.

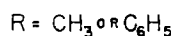
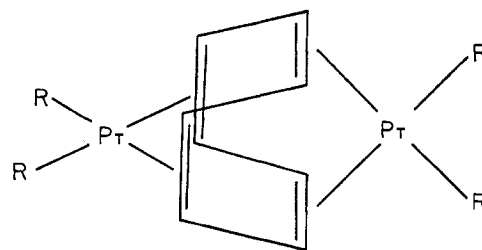
Introduction

Recently Chatt and Shaw^{2,3} predicted that platinum(II) alkyl and aryl derivatives could be stabilized by the presence of ligands that produce large crystal field splitting and using a series of substituted phosphines they succeeded in isolating a number of these compounds. They reported³⁻⁵ that the substituted phosphine derivatives of nickel(II), palladium(II), and platinum(II) containing σ -bonded *o*-substituted aryl derivatives had greater stability than the *p*-substituted analogs. The difference in stability of these compounds was believed to be due to a combination of electronic and kinetic effects.

Calvin and Coates⁶ have reported the isolation of

bismethyl-(1,5-cyclooctadiene)-palladium(II), indicating that cyclic polyolefins can also be used as stabilizing ligands.

In the previous paper in this series⁷ the binuclear



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