In general no sharp, symmetric signal at $g = 2.015$, such as observed in the present study, has been reported in the literature except for the work of Terenin, *et al.*[9] These authors noticed the formation of such a signal ($\Delta H = 3$ G; $g = 2.018$) in the esr spectrum by uv irradiation of a ZnO sample at 77°K. While the species responsible for the signal was not identified, it was suggested later[10] that the singlet was caused by chemisorbed oxygen atoms.

The observation made in the present study that chlorine treatment of the sample produces the sharp signal at $g = 2.015$ indicates that the signal is not caused by chemisorbed oxygen atoms. While a positive identification of this signal cannot be made at the present time, the results so far obtained suggest the presence of shallow levels on ZnO which give rise to the signal following loss of an electron to the interacting gas at the surface.

Acknowledgment. This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by the Naval Research Laboratory under Contract No. NONR 610(09).

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The Preparation and Crystal Structure of $(CH_3)_5Al_2N(C_6H_5)_2$, μ-Diphenylamino-μ-methyl-tetramethyldialuminum[1]

Sir:

In reactions of trialkyls or triaryls of group III metals such as Al, Ga, and In, with secondary aliphatic or aromatic amines, phosphines, and arsines, the resulting product is generally a dimeric or trimeric species, $[R_2M\cdot XR_2']_{2,3}$ (M = Ga, Al, In; X = N, P, As; R, R′ = alkyl, aryl).[2,3] These dimers or trimers consist of metal atoms bridged by amino, phosphino, or arsino groups which, as three electron donors, form normal Lewis electron-pair bonds. This is in contrast to the trimethylaluminum dimer in which the methyl groups occupy bridging positions and form three-center electron-deficient bonds.[4]

We wish to report here the preparation and crystal structure of a compound which simultaneously displays both types of bonding, $(CH_3)_5Al_2N(C_6H_5)_2$. This complex was prepared in our laboratory by the vacuum distillation of 20 mmoles of trimethylaluminum into a cold tube (−196°) containing 10 mmoles of diphenylamine. The reaction mixture, which was under a positive pressure of N_2, was allowed to warm slowly to room temperature and then heated to 100°. Methane was given off during the course of reaction. Excess trimethylaluminum was pumped off and the product was sublimed as clear colorless rectangular rods at 10^{-3} mm and 75°.

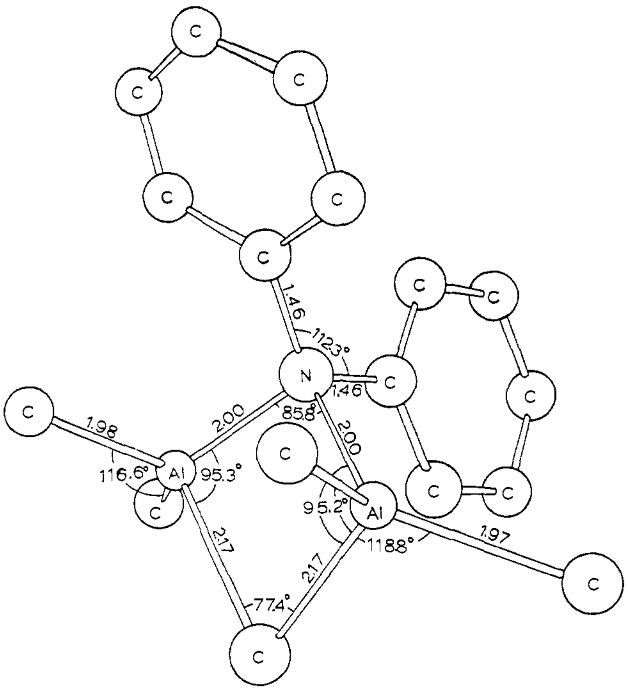

Figure 1. The molecular configuration of $(CH_3)_5Al_2N(C_6H_5)_2$.

Trimethylaluminum has been shown to crystallize as dimers with electron-deficient bridge angles (Al–C–Al) of 74.7°.[4] The X-ray structural analysis of $(CH_3)_5Al_2N(C_6H_5)_2$ shows that the crystal consists of dimeric molecules resembling those found in $[Al(CH_3)_3]_2$ but with one bridging methyl group removed and a diphenylamino group substituted in its place (Figure 1). The geometry around each Al atom is distorted from tetrahedral symmetry with exterior C–Al–C angles of 118.8 and 116.6° and interior C–Al–N angles of 95.2 and 95.3°. The Al–N–Al and Al–C–Al bridging angles are 85.8 and 77.4°, respectively. Comparison of the Al–C–Al bridging angle in this compound with $[Al(CH_3)_3]_2$ shows that this angle is only slightly larger (77.4 *vs.* 74.7°) while the Al–N–Al angle agrees favorably with other systems of this type (see below).[5,6] The average bond lengths (Al–N, 2.00 Å; Al–C (bridge), 2.18 Å; Al–C (terminal), 1.98 Å) also agree well with Pauling's sum of covalent radii[7] as well as with previous observations of bond lengths in similar systems.[4,5,8]

This work represents the first description in the solid state of a mixed electron-deficient–nonelectron-deficient bridging situation for the representative elements. Although mixed bridging systems have been previously proposed to explain proton magnetic resonance data for mixtures of $[(CH_3)_2AlN(C_6H_5)_2]_2$,[9] $[Al(C_6H_5)_3]_2$,[10] and $[(CH_3C_6H_5)_3Al]_2$[10] with $[Al(CH_3)_3]_2$, no solids were characterized. Low-temperature proton magnetic resonance studies in our laboratory have shown that $(CH_3)_5Al_2N(C_6H_5)_2$ dissolved in toluene

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[1] This research was supported by the National Science Foundation and by the Advanced Research Project Agency.

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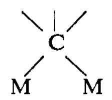
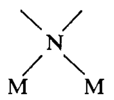
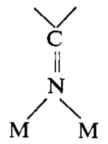
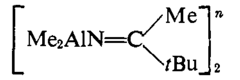
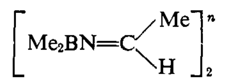
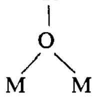
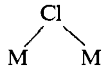
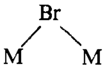
Table I. Bridge Angles (Degrees) for Four-Membered Heterocyclic Systems

					
$[Me_2Be]_n^a$	66.0	$[MeMgTrMeD_2^{h,i}]$	88.3	 $[Me_2AlN{=}C(Me)(tBu)]_2^n$	94.6
$[Me_2Mg]_n^b$	75.0	$Me_5Al_2NPh_2$	85.9	 $[Me_2BN{=}C(Me)(H)]_2^n$	93.5
$[Me_3Al]_2^c$	74.7	$[Be(N(Me)_2)_2]_3^j$	83.0		
$Me_8MgAl_2^d$	75.6	$[MeZnNPh_2]_2^k$	90.0		
$Me_5Al_2NPh_2$	78.6	$[Cl_2BNMe_2]_2^l$	86.9		
$[Et_2Mg]_n^e$	72.0	$[F_2NBMe_2]_2^m$	88.3		
$[LiAlEt_4]_n^f$	77.2				
$[Ph_3Al]_2^g$	76.5				
					
$[Br_2AlOSiMe_3]_2^o$	95.6	$[BeCl_2]_n^s$	82	$[EtMgBr\cdot NEt_3]_2^v$	87
$Mg[Al(OMe)_2Me_2]_2\cdot$dioxane^p	98.0	$[MeAlCl_2]_2^t$	91.1	$[AlBr_3]_2^w$	82
$[BrMgOtBu\cdot Et_2O]_2^q$	96.7	$[GaCl_3]_2^u$	86		
$Br_5Al_3O_6Si_4C_8H_{24}^r$	95.9, 99.4 102.2, 102.0				

[a] A. I. Snow and R. E. Rundle, *Acta Cryst.*, **4,** 348 (1951). [b] E. Weiss, *J. Organometal. Chem.* (Amsterdam), **2,** 314 (1964); also G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86,** 4825 (1964). [c] Reference 4. [d] J. L. Atwood and G. D. Stucky, unpublished results. [e] E. Weiss, *J. Organometal. Chem.* (Amsterdam), **4,** 101 (1965). [f] R. L. Gerteis, R. E. Dickerson, and T. L. Brown, *Inorg. Chem.*, **3,** 872 (1964). [g] J. F. Malone and W. S. McDonald, *Chem. Commun.*, 444 (1967). [h] Reference 5. [i] TrMeD is $Me_2N(CH_2)_2NMe$. [j] Reference 6. [k] H. M. M. Shearer and C. B. Spencer, unpublished results. [l] H. Hess, International Union of Crystallography, 6th International Congress and Symposia, Abstracts of Communications, Rome, Sept 1963, A77. [m] A. C. Hazell, *J. Chem. Soc.*, 1392 (1966). [n] H. M. M. Shearer and J. Willis, unpublished results. [o] M. Bonamico and G. Dessy, *J. Chem. Soc.*, 1786 (1967). [p] Footnote *d*. [q] P. T. Moseley and H. M. M. Shearer, *Chem. Commun.*, 279 (1968). [r] M. Bonamico and G. Dessey, *J. Chem. Soc.*, 291 (1968). [s] R. E. Rundle and P. H. Lewis, *J. Chem. Phys.*, **20,** 132 (1952). [t] G. Allegra, G. Perego, and A. Immirzi, *Makromol. Chem.*, **61,** 69 (1963). [u] S. C. Wallwork and I. J. Worall, *J. Chem. Soc.*, 1816 (1965). [v] J. D. Toney and G. D. Stucky, *Chem. Commun.*, 1168 (1967). [w] P. A. Renes and C. H. MacGillavry, *Rec. Trav. Chim.*, **64,** 275 (1945).

gives a peak corresponding to the bridging methyl proton peaks described by Jeffery, Mole, and Saunders for systems involving mixed aryl–methyl bridges.[10] Further work is in progress in this area.

The nonexistence of the dimeric electron-deficient alkyl compounds of Ga and In has been attributed to, among other things, inner-shell repulsion of the metal atoms.[4] The presence of the diphenylamino group in the bridge increases the metal–metal distance (2.72 Å in $(CH_3)_5Al_2N(C_6H_5)_2$ *vs.* 2.60 Å in $[(CH_3)_3Al]_2$) so that inner-shell repulsion should be less important in mixed bridge species of the above type. The interesting possibility thus exists that the analogous mixed bridge complexes of Ga and In can be prepared.

The crystal used in this study was grown by slow sublimation. It was mounted in a thin wall glass capillary and sealed under an argon atmosphere. X-Ray precession photographs revealed that the crystal is monoclinic and belongs to the space group $P2_1/c$. The cell dimensions as determined by least-squares treatment of the 2θ angles of 11 reflections measured on a Picker four-circle diffractometer are $a = 7.850 \pm 0.003$, $b = 10.613 \pm 0.004$, $c = 21.855 \pm 0.008$, $\beta = 91.74 \pm 0.06°$. The observed density, measured by the flotation method, of 1.08 g/cc agrees well with a density of 1.09 g/cc calculated for four molecules per unit cell. Three-dimensional intensity data were collected on a four-circle Picker diffractometer using Ni-filtered Cu Kα radiation and a 2θ scanning technique. A total of 1711 reflections lying within the range $2\theta < 100°$ was used in the subsequent analysis. The structure was solved by the symbolic addition procedure. Full-matrix least-squares refinement incorporating anisotropic temperature factors has given an R factor of 11.7%. Further refinement of the data is in progress. Attempts are being made to locate methyl hydrogen atoms by difference Fourier techniques.

It is significant that the geometries of the four-membered heterocyclic ring systems formed by group II and III metals depend in a very systematic way upon the bridging atom. This is illustrated in Table I. We note the following.

1. The bridge angle changes only slightly as the metal atom and the groups exterior to the ring are varied, with the exception of the polymeric beryllium complexes.
2. All of the oxygen-bridged structures contain planar three-coordinate oxygen.
3. The bridging angle increases approximately 11° going from C to N to O. The next member of this series is typified by Me_2AlF which is reported to be a tetramer with an Al–F–Al angle of 135°.[11] We feel that the smaller angle found for Cl- and Br-bridged dimeric compounds is due primarily to the larger anion repulsions across the ring.

Studies of the nonbonded interactions as well as simple molecular orbital calculations are currently

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(11) J. Weidlein and V. Krieg, *J. Organometal. Chem.* (Amsterdam), **11,** 9 (1968).

being made in an effort to better understand the geometries and bonding in these compounds.

[12] NASA Trainee, 1966–1968.

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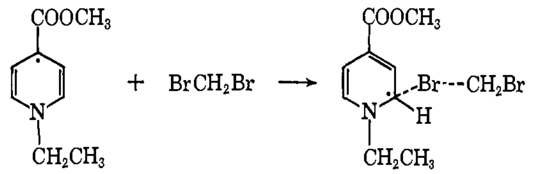
The Solvent Effect on an Electron-Transfer Reaction of Pyridinyl Radicals

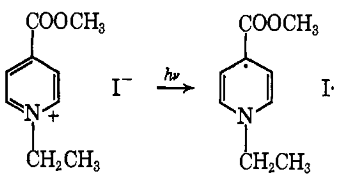
Sir:

Pyridinyl radicals react with halocarbons at rates which are very sensitive to the structure of the halocarbon.[1] Rate constants for the reaction of 1-ethyl-4-carbomethoxypyridinyl (**1**) with tetrachloromethane and dichloromethane differ by a factor of 10^8. The negligible effect of solvent polarity on the rate of reaction of **1** with dibromomethane implies an atom-transfer mechanism (eq 1). Most *para*-substituted benzyl chlorides appear to react with the pyridinyl radical **1** by the atom-transfer route judging from the rather small substituent effects observed (4-OCH_3, 4-CH_3, H, 4-Cl derivatives exhibit rate constants which differ by a factor of less than 4) (Table I). We have now found that 4-nitrobenzyl chloride reacts with **1** in acetonitrile much faster than other benzyl chlorides. The rate factor is so large that a change in mechanism must be involved, and we have confirmed that an electron-transfer process is involved by the demonstration of an enormous solvent effect on the rate of the reaction.



1 transition state (1)

Not only is the solvent effect on the reaction of **1** with 4-nitrobenzyl chloride large, but the change in rate constant for the change in solvent from 2-methyltetrahydrofuran to acetonitrile is on the order of that expected for a reaction in which an ion pair is created from a pair of neutral molecules. The fundamental process to which we can refer is that for the solvent polarity standard, **Z** value (the destruction of an ion pair through charge transfer, eq 2).[2] The operation of the Franck–Condon principle (electronic motion much faster than nuclear motion) brings about an excited state from the charge-transfer transition which is destabilized to the same extent that the ground state is stabilized. We would thus predict that creation of an ion pair in a thermal process should have a solvent sensitivity of about 0.5Δ**Z**. Data illustrating this point are given in Table I.



(2)

There seems to be only one previous report of a large solvent effect on the rate of a reaction in which electron transfer may be involved. In that case, the reaction of 4-methoxystyrene with tetracyanoethylene to form a cyclobutane has a rate which is very sensitive to solvent.[3]

A portion of the mechanism of the reaction of the pyridinyl radical **1** with 4-nitrobenzyl chloride is shown in eq 3.

Table I. Rates of Reaction of 1-Ethyl-4-carbomethoxypyridinyl (**1**)[a] with Benzyl Chlorides[b,c]

Benzyl chloride[d] (C_0)[e]	Solvent (**Z**)[f]	Radical **1** (C_0)[e]	k_2, l. mol^{-1} sec^{-1} [g]
4-CH_3O ($\sim$0.4)	CH_3CN	($\sim$0.02)	1.13×10^{-3}
4-CH_3 ($\sim$0.6)	CH_3CN	($\sim$0.025)	3.68×10^{-4}
4-H ($\sim$1.0)	CH_3CN	($\sim$0.008)	3.31×10^{-4}
4-Cl ($\sim$0.4)	CH_3CN	($\sim$0.01)	6.5×10^{-4}
4-NO_2 ($\sim10^{-5}$)	CH_3CN (71.3)	($\sim10^{-5}$)	2.4×10^4
($\sim10^{-5}$)	DMF[h] (68.4)	($\sim10^{-5}$)	1.2×10^4
($\sim10^{-5}$)	CH_3COCH_3 (65.5)	($\sim10^{-5}$)	450
($\sim10^{-4}$)	CH_2Cl_2 (64.7)	($\sim10^{-4}$)	~75
($\sim10^{-4}$)	DME[i] (59.1)	($\sim10^{-5}$)	8.3
(10^{-5}–10^{-4})	MTHF[j] (55.3)	($\sim10^{-5}$)	1.62

[a] Radical was prepared by the procedure previously reported (ref 1 and E. M. Kosower and E. J. Poziomek, *J. Am. Chem. Soc.*, **86**, 5515 (1964)) as modified by H. P. Waits and E. M. Kosower, 148th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts, S109. [b] Rates were followed spectrophotometrically in all-glass apparatus. The procedure differed from that outlined in ref 1 in that no stopcocks were used which could come into contact with the radical solution, the halide solution, and/or liquid solvent. Furthermore, the major part of the apparatus was rinsed with free-radical solution before mixing with the halide in all cases in which dilute radical solutions were used (dilute = 10^{-3} *M* or less). [c] All rate constants were measured at 25°. [d] All benzyl chlorides and solvents were subjected to rigorous purification and analysis. Details will be presented in a full publication. [e] Approximate range of concentration used in kinetic runs in moles/liter. [f] All **Z** values were new determinations, made with 1-ethyl-4-carbomethoxypyridinium iodide[2] and extrapolated to infinite dilution. [g] All rate constants are the average of two determinations, except for those for MTHF (four runs), DMF (one run), and 4-chlorobenzyl chloride (one run). Reproducibility was ±10% or better in most cases. [h] Dimethylformamide. [i] 1,2-Dimethoxyethane. [j] 2-Methyltetrahydrofuran.

A number of interesting reactions involving 4-nitrobenzyl chloride as an electron acceptor have been reported by Kornblum and coworkers.[4]

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