Complexes of Organoaluminium Compounds. Part 11.[1] Nitric Oxide Complexes of Trimethyl-aluminium and -gallium and the Crystal and Molecular Structure of [$Me_3Al(ONNMeO)AlMe_2$] †

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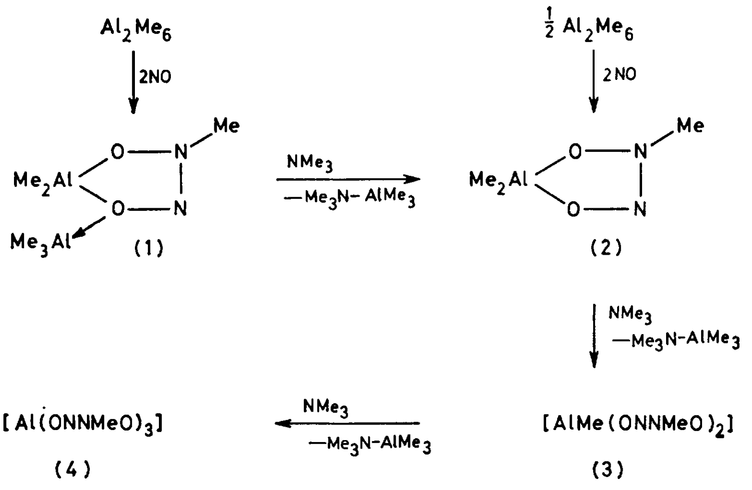
The compound [$Me_3Al(ONNMeO)AlMe_2$] (1), made from the reaction between trimethylaluminium and nitric oxide, crystallises in the triclinic system, with a = 670.6(1), b = 970.3(2), c = 1 020.9(1) pm, α = 82.37(1), β = 87.13(1), γ = 72.97(1)°, space group $P\bar{1}$, and Z = 2. The structure analysis (diffractometer data, 1 214 reflections, R = 0.092) shows that the ONNMeO ligand forms a five-membered chelate ring and that the trimethylaluminium is co-ordinated to the oxygen atom of the nitroso-group. Principal mean molecular parameters are: Al–C 195.3(11), Al–O 189.5(6), N–O 132.2(8), N–N 125.3(9) pm. The position of maximum basicity in the ring at the nitrosyl oxygen is confirmed by *ab initio* calculations. N.m.r. studies suggest that, in the presence of bases, the complex (1) rearranges to compounds [$AlMe(ONNMeO)_2$] (3) and [$Al(ONNMeO)_3$] (4) in which the co-ordination number of aluminium is five or six, respectively. The adduct [$GaMe_2(ONNMeO)$] (5) has been obtained from trimethylgallium and nitric oxide.

IN a previous publication,[2] we described the formation of the complexes (1) and [$AlMe_2(ONNMeO)$] (2), by the reaction between trimethylaluminium and nitric oxide (Scheme). We now describe an X-ray determination of the crystal and molecular structure of complex (1), the gallium complex corresponding to (2), and some n.m.r. studies on the reactions of these complexes with bases.



SCHEME

EXPERIMENTAL

Standard vacuum-line or Schlenk-tube techniques were used throughout; hydrocarbon solvents were dried over sodium and then over lithium aluminium hydride.

The ^1H n.m.r. measurements were made using a Perkin-Elmer R32 90 MHz instrument. Chemical shifts (relative intensities in parentheses) were measured from benzene (τ 2.85). A JEOL PFT-100 spectrometer at 25.15 MHz was used for ^{13}C studies.

The preparation of the aluminium compounds (1) and (2) has been described.[2] The ^{13}C n.m.r. spectra showed absorptions (p.p.m. from C_6D_6) as follows: (1) 83.1 (N–Me) and 135.5 (br) (Al–Me); (2) 84.0 (N–Me) and 136.6 (br) (Al–Me). The ^1H n.m.r. spectrum of a mixture of complex (1) and an excess of $GaMe_3$ showed, besides resonances ascribed to the $AlMe_2$ and N–Me groups, only one further peak. This indicates fast exchange, on the n.m.r. time scale, of methyl groups between uncomplexed $GaMe_3$ and the weakly complexed $AlMe_3$, as found for $GaMe_3$–Al_2Me_6 mixtures.[3,4]

(N-*Methyl*-N-*nitrosohydroxylamido*-OO′)*dimethylgallium* (5).—Nitric oxide (2.65 mmol) was sealed with a solution of $GaMe_3$ (0.152 g, 1.32 mmol) in pentane at −196 °C. A transient blue colour was observed as the solution warmed. The mixture was stirred at 20 °C for 24 h, then some of the solvent was evaporated, giving white *crystals* subliming at 20 °C (10^{-3} Torr ‡) (Found: C, 21.0; H, 5.5; N, 15.2. $C_3H_9GaN_2O_2$ requires C, 20.6; H, 5.2; N, 16.0%). The mass spectrum (only ^{69}Ga ions given; relative intensities in parentheses) showed gallium-containing ions at m/e 174 (4), 159 (44), 144 (25), 129 (22), 114 (23), 99 (100), 85 (52), and 84 (38). All these are formed by successive loss of Me or NO from the parent ion. The i.r. spectrum (Nujol mull) showed the strong peaks at 1 377, 1 292, 1 201, 1 060,

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† {[N-Methyl-N-(nitroso-O')hydroxylamido-O]dimethylaluminium-O'}trimethylaluminium.

‡ Throughout this paper: 1 Torr = (101 325/760) Pa.

and 946 cm^{-1}, which are found in the spectra of other compounds with the ONNMeO group.[2,5-7] A solution of complex (5) in toluene appeared to be indefinitely stable at 20 °C, and it became only slightly yellow after 1 week at 80 °C.

The ^1H n.m.r. spectrum of (5) showed resonances at τ 7.25 (1) and 10.04 (2). The same resonances were found, together with a new signal at τ 9.78, in spectra from samples with an excess of trimethylgallium. This suggests that (5) is insufficiently basic to complex with trimethylgallium, which is a weaker acid than is trimethylaluminium. The spectrum of a solution of (5) with an excess of trimethylaluminium showed the *N*-Me resonance at τ 7.56, *i.e.*, shifted upfield compared with (5), but like the *N*-Me resonance in complex (1). It seems that $AlMe_3$ is a sufficiently strong Lewis acid to form a complex with (5). At 36 °C there is fast exchange between the complexed $AlMe_3$ and the excess of Al_2Me_6, but at −80 °C distinct signals for both species are observed.

Structure Determination of (1).—The compound crystallised from hexane as thin plates; one of these with dimensions 0.35 × 0.2 × 0.1 mm was sealed under vacuum in a thin-walled Lindemann capillary.

Crystal data. $C_6H_{18}Al_2N_2O_2$, $M = 204.19$, Triclinic, $a = 670.6(1)$, $b = 970.3(2)$, $c = 1\,020.9(1)$ pm, $\alpha = 82.37(1)$, $\beta = 87.13(1)$, $\gamma = 72.97(1)°$, $U = 0.629\,49$ nm^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.08$ g cm^{-3}, $F(000) = 220$, Mo-K_α radiation, $\lambda = 71.069$ pm, μ(Mo-K_α) = 2.1 cm^{-1}.

Crystallographic measurements. After the crystal system was found from Weissenberg and precession photographs (Cu-K_α radiation), accurate cell parameters were obtained from setting angles of 12 reflections, using a Hilger and Watts Y290 diffractometer and Mo-K_α radiation. The intensities of 1 542 unique reflections with $2 < \theta < 20°$ were measured by ω—2θ step scans using monochromated Mo-K_α radiation and three standard reflections, measured after every 100, showed no significant alteration during data collection. However, some spurious data were obtained from an intermittent fault in the diffractometer. Although sections obviously affected were recollected, it is possible that not quite all the false data were eliminated. Thus the *R* value is probably higher than would have been obtained in the absence of trouble. Corrections were made for Lorentz and polarisation effects but not for absorption. Data with $I < 3\sigma(I)$ were rejected, leaving 1 214 reflections for use in the structure analysis.

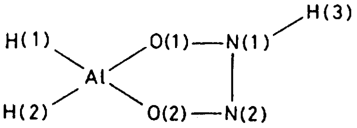
Structure solution and refinement. Initial data processing was with the University of Sussex crystallographic computer programs; the SHEL-X program of G. M. Sheldrick was used for structure solution and refinement. Atomic scattering factors and dispersion corrections were taken from ref. 8. The choice of the centrosymmetrical space group was confirmed by the subsequent successful refinement. Positions of aluminium atoms were derived from a sharpened Patterson map and those of the O, N, and C atoms from a subsequent Fourier synthesis ($R = 0.106$). Hydrogen atoms, visible on a difference-Fourier map, were included at idealised positions but not refined. With anisotropic temperature factors for non-hydrogen atoms and a weighting scheme $w = 1.11/[\sigma^2(F) + 0.010\,8\ F^2]$, full-matrix least-squares refinement was continued until the shift-to-error ratio was $\leqslant 0.2$, and $R = 0.092$ ($R' = 0.126$). A final difference Fourier was everywhere $\leqslant 0.67$ e Å^{-3}. Final positional parameters for non-hydrogen atoms are given in Table 1. Those for H atoms, together with temperature factors, observed structure amplitudes, and calculated structure factors are given in Supplementary Publication No. SUP 22853 (10 pp.).*

TABLE 1

Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	x	y	z
Al(1)	971(4)	2 202(3)	3 862(2)
Al(2)	3 727(4)	3 140(3)	938(2)
O(1)	3 968(8)	4 983(6)	1 145(5)
O(2)	2 397(8)	3 403(5)	2 621(5)
C(11)	−1 928(13)	3 427(10)	3 713(9)
C(12)	2 386(16)	2 069(13)	5 536(10)
C(13)	1 748(16)	470(10)	2 934(13)
C(21)	6 350(14)	1 614(10)	1 072(10)
C(22)	1 720(14)	3 226(11)	−396(9)
C(3)	3 181(17)	6 842(9)	2 545(9)
N(1)	3 124(10)	5 404(7)	2 268(6)
N(2)	2 266(10)	4 654(6)	3 069(6)

Calculation of Protonation Energies.—Protonation energies were calculated for compound (6), in which the three methyl groups in compound (2) are replaced by hydrogen atoms.



(6)

The Gaussian 70 package [9] was used. All calculations were minimum basis set (STO-3G). The geometry of the AlONNO ring and the bond angles at Al and N(1) were as found in the *X*-ray structure determination of (1). As in similar calculations,[10] the Al-H distance (156 pm) was taken as that in H_3Al-NMe_3 [11] and the N-H distance (101 pm) as that in ammonia.[12] The bond length to the added proton and the angles that this bond makes with the ring bonds were optimised for each protonation site with the proton constrained to lie in the plane of the ring. Details are given in SUP 22853.

RESULTS AND DISCUSSION

The Structure of $[\mathrm{Me_3Al(\overline{ONNMeO)Al}Me_2}]$ (1).—The molecular structure of complex (1) is shown in Figure 1 and bond lengths and angles are given in Table 2. The atoms Al(2), O(1), N(1), N(2), and O(2) of the five-membered ring and atoms Al(1), C(13), and C(3) are almost coplanar (Table 2). The bond distances Al(2)-O(1) and Al(2)-O(2) are significantly longer than Al-O distances in related compounds, *e.g.*, 179.8(2) pm in $[AlMe_2\{OC(Ph){=}N(Ph)\}(ONMe_3)]$,[13] 180.5(6) pm in $[\{AlMe_2[OC(Ph){=}N(Ph)]\}_2]$,[14] 185.1(7) pm in $[Me_2Al\{OC(Ph){=}N(Ph)MeCHO\}AlMe_3]$,[15] 186.7(1) pm in $[AlMe_2(ONMe_2)]_3$,[16] 185.1(3) in $[\{AlMe_2(OMe)\}_3]$,[17] and 179.5(10) pm in $[\{Me_3Si{-}O{-}AlBr_2\}_2]$.[18] The N-N and N-O distances are, however, shorter than those expected for single bonds; compare N-N 145 (N_2H_4), 140 (H_2NNO_2), 124 pm (MeN=NMe); N-O 146 (HONO), 147 pm ($HONH_2$).[12] The bond lengths and angles within the ring are similar to those in compounds containing the

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

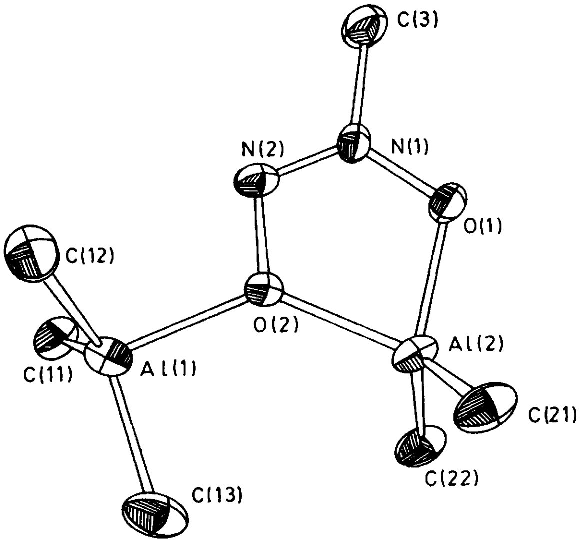


FIGURE 1 The molecular structure of $[\mathrm{Me_3Al(\overline{ONNMeO)Al}Me_2}]$, (1)

ONNPhO group, $[\mathrm{Zr(ONNPhO)_4}]$,[19] $[\mathrm{Fe(ONNPhO)_3}]$,[20] $[\mathrm{Cu(ONNPhO)_2}]$,[21] the potassium salt $\mathrm{K_2[CH_2\{N(O)\text{-}NO\}_2]}$,[22] and the hyponitrite $[\mathrm{Pt(PPh_3)_2(ONNO)}]$.[23] Except in $[\mathrm{Cu(ONNPhO)_2}]$, where the accuracy of the structure determination is lower, the two N–O bonds within each ONNRO group (R = Me or Ph) are found to be almost the same.

TABLE 2

Intramolecular distances (pm) and angles (°), with estimated standard deviations in parentheses, and displacements (pm) from the mean molecular plane in (1)

(*a*) Distances

Al(1)–O(2)	200.4(6)	Al(2)–O(1)	188.1(6)
Al(1)–C(11)	196.0(9)	Al(2)–O(2)	190.9(6)
Al(1)–C(12)	196.7(11)	Al(2)–C(21)	193.6(10)
Al(1)–C(13)	196.3(11)	Al(2)–C(22)	193.9(10)
O(1)–N(1)	131.4(8)	C(3)–N(1)	147.1(11)
O(2)–N(2)	133.0(8)	N(1)–N(2)	125.3(9)

(*b*) Angles

C(11)–Al(1)–O(2)	100.5(3)	C(22)–Al(2)–O(1)	112.6(4)
C(12)–Al(1)–O(2)	101.9(4)	N(1)–O(1)–Al(2)	111.1(4)
C(13)–Al(1)–O(2)	97.2(4)	C(21)–Al(2)–O(2)	112.0(4)
Al(2)–O(2)–Al(1)	132.9(3)	C(22)–Al(2)–O(2)	110.9(4)
N(2)–O(2)–Al(1)	111.0(4)	N(2)–O(2)–Al(2)	116.0(4)
C(12)–Al(1)–C(11)	117.1(4)	C(21)–Al(2)–C(22)	120.6(4)
C(13)–Al(1)–C(11)	117.1(5)	C(3)–N(1)–O(1)	116.7(8)
C(13)–Al(1)–C(12)	117.1(5)	N(2)–N(1)–O(1)	122.9(7)
O(2)–Al(2)–O(1)	79.8(3)	N(1)–N(2)–O(2)	110.2(6)
C(21)–Al(2)–O(1)	113.8(4)	N(2)–N(1)–C(3)	120.4(7)

(*c*) Displacements from mean plane defined by Al(2), O(1), O(2), N(1), and N(2)

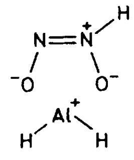
Al(2) 0.4, O(1) −0.1, O(2) −0.8, N(1) −0.4, N(2) 0.8, Al(1) 5.9, C(11) 184.2, C(12) −148.3, C(13) −14.7, C(21) −165.8, C(22) 170.7, C(3) 1.0

TABLE 3

Calculated net atomic charges and protonation energies for (6)

Charges (e)
N(1) −0.08, N(2) 0.08, O(1) −0.33, O(2) −0.30, Al 0.95, H(1) −0.29, H(2) −0.29, H(3) 0.28
Mulliken overlap populations (π contribution in parentheses)
O(1)–N(1) 0.216 (0.009), N(1)–N(2) 0.363 (0.120), O(2)–N(2) 0.262 (0.062)
Protonation energies (kJ mol^{-1})
at O(1) −977, at O(2) −994, at N(2) −816

Ab initio calculations (Table 3) for the aluminium compound (6) show (*a*) that the aluminium atom has a positive charge, (*b*) that oxygen atoms carry a greater negative charge than nitrogen atoms, (*c*) that charges on the two oxygen atoms within the AlONNO ring are similar, and (*d*) that the most important π contribution is in the N–N bond. In valence-bond terms, therefore, the structure is best described by the structure (7) with smaller contributions from (8)—(10). The positive charge on Al is consistent with the wide C–Al(2)–C angle found in (1), as in many other dimethylaluminium derivatives. The short N–N distance is also accounted for. Alternatively, in molecular-orbital terms, the 22 valence electrons of the five-membered ring may be distributed as follows: 10 into σ bonds, six into lone pairs, and six into π molecular orbitals illustrated in Figure 2. The antibonding orbital (*iv*) is unoccupied.



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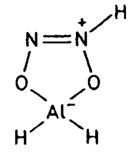

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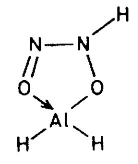

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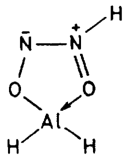

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The trimethylaluminium in (1) is co-ordinated at

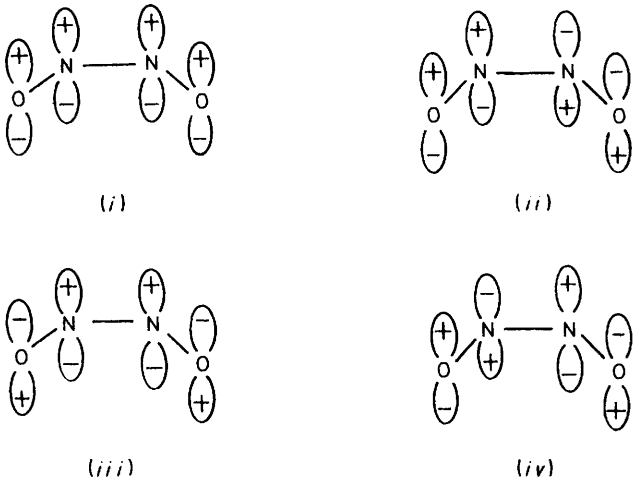


FIGURE 2 π Molecular orbitals in the ONNO portion of the chelate ring

oxygen, not, as originally proposed,[2] at nitrogen. Calculations (Table 3) indicate that the decrease in energy on protonation is greatest when the site is O(2). The difference between the basicity of the two oxygen atoms towards protons is probably not significant, but it is likely that steric effects enhance the difference towards the larger acid $AlMe_3$.

The mean Al–C distance (196.3 pm) in the $AlMe_3$ fragment, like that in $Me_3Al-OMe_2$ [24] (197.3 pm), is intermediate between the Al–C distance in monomeric $AlMe_3$ (195.7 pm) [25] and that in the stronger complex $Me_3Al-NMe_3$ (198.7 pm).[26] The Me_3Al-O bond length and the C–Al–O bond angles are similar to those in related complexes (Table 4). Larger mean C–Al–D (D = donor group) angles are associated with stronger donor–acceptor complexes Me_3Al-D.

TABLE 4

Structural data for trimethylaluminium complexes

Me_3Al-D	Al–D (pm)	C–Al–D (°)	$-\Delta H_{dis.}$ [a] (kJ mol^{-1})	Ref.
$(AlMe_3)_2$(dioxan)	202(2)	100.4(5)		*b*
$Me_3Al-OMe_2$	201.4(24)	98.7(15)	91.5(8)	*c*
(1)	200.4(6)	99.9(4)		
$Me_3Al(\overline{OCHMeNPhCPhOAl}$-$Me_2)$	192.8(6)	103.8(5)		*d*
$Me_3Al-NMe_3$	209.9(10)	102.3(3)	135.5(12)	*e*
$Me_3Al-PMe_3$	253(4)	100.0(13)	87.9(12)	*f*

[a] Solution in hexane; C. H. Henrickson, D. Duffy, and D. P. Eyman, *Inorg. Chem.*, 1968, **7**, 1047. [b] J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, 1967, **89**, 5362. [c] Ref. 24. [d] Ref. 15. [e] Ref. 26. [f] A. Almenningen, L. Fernholt, and A. Haaland, *J. Organometallic Chem.*, 1978, **145**, 109.

The only intermolecular contact <350 pm is 266 pm between O(1) and O(1^I), related by the centre of symmetry.

The Reaction between (1) *and Trimethylamine.*—Hydrogen-1 nuclear magnetic resonance spectra of solutions containing complex (1) and various quantities of trimethylamine are described in Table 5. Resonances at τ 8.3 and 10.6 are assigned to the adduct $Me_3N-AlMe_3$. These resonances remain clearly separated from all others, and at 30 °C, except with a large excess of trimethylamine, the chemical shifts are unaffected by site-exchange processes. As the NMe_3 : (1) mole ratio is increased, the *N*–Me resonance at τ 7.66, assigned to (1), is shifted to lower field and then replaced in succession by a series of new resonances until, with a large excess of NMe_3, only one *N*–Me resonance remains. At the same time, *Al*–Me resonances at τ *ca.* 10.3 disappear, leaving only the resonance at τ 10.6 assigned to $Me_3N-AlMe_3$. Discounting the signal at τ 8.3, the ratio *Al*–Me : *N*–Me remains constant at *ca.* 5 : 1 showing that methyl groups are not transferred from Al to N. The data suggest that the addition of base to complex (1) results in a reorganisation with formation of complexes (3) having five-co-ordinate aluminium (*N*–Me τ 7.17, 7.28, possibly more than one isomer) and (4) (N–Me τ 6.98) in which the aluminium is six-co-ordinate (Scheme). An ion corresponding to loss of methyl from (3) appears in the mass spectra of (1) or (2).[2] Complex (1) appears to be indefinitely stable in solution. Compound (2) could be isolated, but only in poor yield; removal of the co-ordinating $AlMe_3$ by base seems to promote the rearrangement to (3) and (4), which may themselves be stabilised by co-ordination of $AlMe_3$, as in (1). Attempts to isolate complexes (3) and (4) were unsuccessful. When solvent was removed from solutions which appeared to contain these compounds, the residues were incompletely soluble in hydrocarbon solvents. They did, however, dissolve in pyridine and also react vigorously with water to give methane. This suggests that polymeric solids, perhaps with ON(NMe)O chains linking Al atoms, are formed under the conditions of our experiments, but these materials have not been fully investigated. The compound $[Al(ONNMeO)_3]$ (4) has been referred to in a patent,[27] but has not been adequately characterised.

Similar reactions are observed when complex (1) is treated with an excess of diethyl ether or, accidentally, with traces of water vapour. Displacement of $AlMe_3$ is, however, much slower than with NMe_3, perhaps because the oxygen compounds are more weakly basic (Table 4). These displacements suggest that, in solution, the basicity of the oxygen atom in (1) is less than that in dimethyl ether and similar to that in water. The gas-phase protonation energy of (6) obtained by STO-3G calculation is almost certainly too high; for H_2O and NH_3, values obtained by this method [28] are 220—260 kJ mol^{-1} greater than the experimental values.[29] The calculated protonation energy of (6) is, however, similar to that for water, so the basicity order $NMe_3 > OMe_2 > (2) \sim H_2O$ is probably the same in the gas phase as in solution.

The *N*-methyl-*N*-nitrosohydroxylamido-*OO'* com-

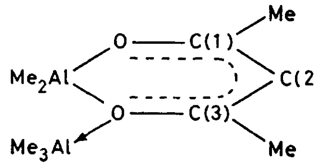
TABLE 5

Reaction between complex (1) and trimethylamine in benzene

Mole ratio	^{1}H N.m.r. (τ) [a]			Intensity ratio
NMe_3 : (1)	*N*–Me	NMe_3	*Al*–Me	*Al*–Me : *N*–Me [b]
0 : 1	7.66 (1)		10.28, 10.38 (5)	5.0 : 1
0.59 : 1	7.57 (1)	8.34 (1.8)	10.31 (2.7), 10.60 (1.8)	4.5 : 1
1.05 : 1	7.17 (0.5), 7.28 (0.5) [c]	8.32 (3)	10.35 (2.1), 10.65 (2.9)	5.0 : 1
7.0 : 1	6.98 (1) [d]	7.99 (22) [d,e]	10.73 (5) [d]	5.0 : 1

[a] Relative intensities are given in parentheses. [b] Not counting NMe_3 signal. [c] After 30 d, relative intensities changed 7.17 (0.8), 7.28 (0.2). [d] Spectrum recorded 24 h after mixing. [e] Only one signal observed for NMe_3 and $Me_3N-AlMe_3$ (T. Mole, *Chem. and Ind.*, 1964, 281) indicating fast exchange on n.m.r. time scale. Downfield shift reflects presence of uncomplexed NMe_3.

pounds resemble pentane-2,4-dione derivatives.[30] A complex (11), similar to (1), has been postulated as an



(11)

intermediate in the reaction between [AlMe$_2$(OCMeCHCMeO)] and trimethylaluminium to yield products by transfer of methyl from the co-ordinated AlMe$_3$ to C(3). Such a transfer is unlikely in complex (1) because the nitrogen N(2) adjacent to the co-ordinated oxygen is almost neutral (Table 3) and so weakly susceptible to alkylation. The compound [AlMe(OCMeCHCMeO)$_2$], with five-co-ordinate aluminium, analogous to (3), has not been detected; it appears to disproportionate more rapidly than (3) to [AlMe$_2$(OCMeCHCMeO)] and the compound [Al(OCMeCHCMeO)$_3$], with six-co-ordinate aluminium.[31]

Comparison between Aluminium and Gallium Derivatives.—The reaction between trimethylgallium and nitric oxide yields the compound (5) which is analogous to (2). The oxygen atom is sufficiently basic to co-ordinate to AlMe$_3$, but not to GaMe$_3$. In contrast to compound (2), the gallium derivative (5) does not appear to rearrange in solution giving species with six-co-ordinate gallium.

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