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NITRIC OXIDE COMPLEXES OF TRIMETHYLALUMINIUM*

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Summary

Nitric oxide reacts with trimethylaluminium to give complexes Me_3AlNO and $Me_3Al(NO)_2$ which appear to be derivatives of N-methyl-N-nitrosohydroxylamine.

Nitric oxide reacts with Grignard Reagents [1-3] to give crystalline compounds which are hydrolysed to N-alkyl-N-nitrosohydroxylamines. Reactions between nitric oxide and triethylaluminium etherate [4], diethylaluminium chloride [3], or dipropylzinc [3], appear to be similar, but in these cases the organometallic intermediates have not been isolated. We have now found, however, that crystalline compounds of composition $Me_3Al.NO$(1) and $Me_3Al(NO)_2$ (2) may be easily obtained from the reaction between trimethylaluminium and nitric oxide.

Experimental

Vacuum-line and Schlenk-tube techniques were used throughout. Nitric oxide was distilled repeatedly through a trap at -78°C before use, to remove traces of moisture and nitrogen dioxide.

The compound Me_3AlNO(1).

Nitric oxide was bubbled slowly through Me_3Al (0.35 g) in hexane (20 ml) at -50°C, and the white precipitate was washed with cold hexane. M.p. 96-8°C. Found : C, 34.9; H, 8.6; N, 13.7; Al, 26.7%. C_3H_9AlNO calcd: C, 35.3; H, 8.9; N, 13.7; Al, 26.5%). The ^1H NMR spectrum (solution in benzene) showed resonances, with relative intensities 1:3:2, at 7.44, 9.86 and 10.06τ. The same

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* No reprints available.

compound was obtained (85% yield after recrystallisation) when Me_3Al was allowed to react with the stoichiometric quantity of NO in a closed section of the vacuum line.

The Compound $Me_3Al(NO)_2$(2)

A solution of Me_3Al (1.04 g, 14.4 mmol) in hexane (25 ml) was stirred at 20°C in a gas burette filled with nitric oxide. After 8 days, no further pressure change was observed; 26.5 mmol of NO had been absorbed, and a white solid had precipitated. This was incompletely soluble in boiling hexane or benzene but it could be separated at 47-52°C (0.1 Torr) into an involatile yellow residue and a white sublimate, m.p. 115-7°C (Found: C, 27.1; H, 6.8; N, 21.1%. $C_3H_9AlN_2O_2$ calcd.: C, 27.3; H, 6.8; N, 21.2%). The NMR spectrum, recorded immediately after making up a solution in benzene, showed peaks at 7.26 and 9.96τ with relative intensities 1:2.

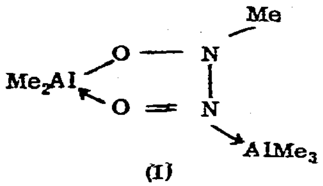
When a sample of the adduct (2) (0.108 g) was treated with 2N sulphuric acid in the vacuum line, methane (1.54 mmol) was collected. The aqueous solution was shown by gravimetric estimation (oxine) to contain 0.76 mmol of aluminium, confirming the presence of the Me_2Al group. The methane evolved was 94% of that required by the equation: $Me_2AlO_2N_2Me + 3H^+ \rightarrow Al^{3+} + 2CH_4 + [MeNH(OH)(NO)]^+$.

Reaction of (1) with Trimethylamine.

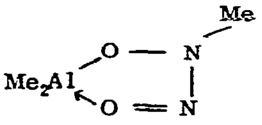
Trimethylamine (1.21 mmol) was distilled into a solution of Me_3AlNO (0.25g 2.40 mmol) in benzene (5 ml). The material volatile at 20°C condensed completely in the vacuum-line at -78°C showing that all the Me_3N had been absorbed. There were two new resonances in the NMR spectrum, at 8.06 and 10.33τ, corresponding to those in the adduct $Me_3N.AlMe_3$. This compound, which is just volatile at 20°C [5], was recovered in 85% yield. When the residue was heated at 95°C (0.7 Torr), white crystals of compound (2) (0.016 g. Yield 10%) sublimed from pale yellow involatile material. The spectra of a mixture of Me_3AlNO and Me_3AlNMe_3 showed that exchange of Me_3Al between the two complexes was slow on the NMR timescale at 30° but rapid at 120°C.

Discussion

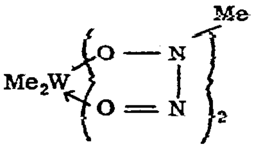
The hydrolysis and NMR spectra suggest that the trimethylaluminium adducts (1) and (2) are dimethyl(N-methyl-N-nitrosohydroxylamido)aluminium (2) and its 1:1 complex with trimethylaluminium (1).



(1)



(2)



(3)

Adduct (1) appears to be formed quantitatively. When one mol of $AlMe_3$ is removed by reaction with trimethylamine or with an excess of nitric oxide, the products are less clear cut. Although the compound (2) may be isolated as a crystalline solid, NMR spectra show, besides the expected strong peak in the N-methyl region, additional weak peaks at 6.91 and 7.03τ. These increase in intensity on standing [6], and appear to arise from further reactions involving transfer of methyl from aluminium to nitrogen.

$$2\ Me_2AlO_2N_2Me \longrightarrow MeAl(O_2N_2Me)_2 + Me_3Al$$

(2)

As far as we are aware, the only organometallic N-alkyl-N-nitrosohydroxylamido compound to be characterised by X-ray diffraction is the tungsten derivative (3), made from nitric oxide and hexamethyltungsten [7]. IR spectra of the compounds (1) - (3) and the copper derivative $Cu(O_2N_2Me)_2$ [8] are compared in Table 1.

TABLE 1

IR SPECTRA (cm^{-1})

(1) [a]	(2) [b]	(3)	$Cu(O_2N_2Me)_2$
1438sh	1495m	1485s	1475s
1417m	1420s	1420s	1440m, 1420s
1377m	1395s		1395s
1305m	1322s	1273s	1330vs
1217m		1215w	1205vs
1196s	1193s, 1187sh	1178s	
1142m, 1128s	1138vs	1160sh	1120m
1065m, 1038w	1077s	1075w	1075s
1026m		1019w	
990sh, 997s	994vs	965s	960vs
690m	698vs	706s	675vs

[a] Other peaks : 894w, 757m, 628w. [b] Other peaks : 711vs(sh), 680sh, 668sh, 621s, 570m, 384s, 305s, 240m.

When allowance is made for absorptions at ca 1420, 1190, and 660 cm^{-1}, found in other compounds with the Me_2Al-group [9], the similarity of the spectra, in the

TABLE 2

MASS SPECTRA

m/e	intensity[a]		m/e	Intensity[a]	
132	1.5	$Me_3AlN_2O_2^+$	87.0255[b]	26	Me_2AlNO^+
118	3		86.0186[b]	7	$Me_2CH_2AlNO^+$
117	100	$Me_2AlN_2O_2^+$	73	1.5	
103	1.5		72	1.5	Me_3Al^+
102	2	Me_3AlNO^+	57	2.1	Me_2Al^+

[a] As % of strongest [b] Calc. 87.0265, 86.0186, metastable peaks at 64.7 (117→87) and 72.5 (102→86).

range associated with the vibrations of the O_2N_2Me skeleton, is evident.

Mass spectra (Table 2) of compounds (1) and (2) are almost identical, and there is little difference between spectra at 70 and 10eV. The weak peak at m/e 132 and the intense peak at m/e 117 confirm the formulation of (2) as a dimer. The absence of a parent ion from this compound is not surprising; the mass spectrum of $Me_3N.AlMe_3$, even at 15eV, shows no ions containing both aluminium and nitrogen. The main fragmentation in compounds (1) and (2), partly confirmed by metastable peaks, involves elimination of methyl from the parent ion, followed by successive loss of NO, but there is also evidence for initial loss of NO and subsequent elimination of methane from the even-electron ion Me_3AlNO^+. A weak peak at m/e 177 is assigned to the ion $[Al(O_2N_2Me)_2]^+$.

Attempts to obtain complexes from the reaction between nitric oxide and other organoaluminium compounds were not successful. Triphenyl and tri-p-tolyaluminium (and also methyllithium) reacted very slowly and triethylaluminium gave an intractable brown oil. Reactions between nitric oxide and trialkylboranes are also complicated [10].

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