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ON THE REACTIVITY OF ORGANOMETALLIC COMPOUNDS TOWARDS FUNCTIONAL SUBSTRATES
I. THE REACTION OF TRIISOBUTYLALUMINIUM WITH BENZONITRILE

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SUMMARY

The reaction between triisobutylaluminium and benzonitrile has been investigated at various temperatures (50–100°) and different reactant mole ratios (0.5–4.0). Both reduction and addition products are formed; their relative amounts were found to depend on the experimental conditions adopted, although the reduction products were always present in excess. At room temperature benzonitrile and the organoaluminium compound formed a stoichiometric complex which reacted thermally to give the reaction products. The overall experimental results are discussed and reasonable mechanisms for the addition and reduction reactions given.

INTRODUCTION

Accurate investigations of the reactivity of triisobutylaluminium (I) towards benzonitrile (II) have not to date been carried out, although reactions of other organoaluminium compounds with similar reactants have been widely investigated[1-4].

In its reaction with (II), (I) is reported to yield only reduction products at 80–90°,[2,5] and diisobutylaluminium hydride apparently reacts in a similar fashion[6].

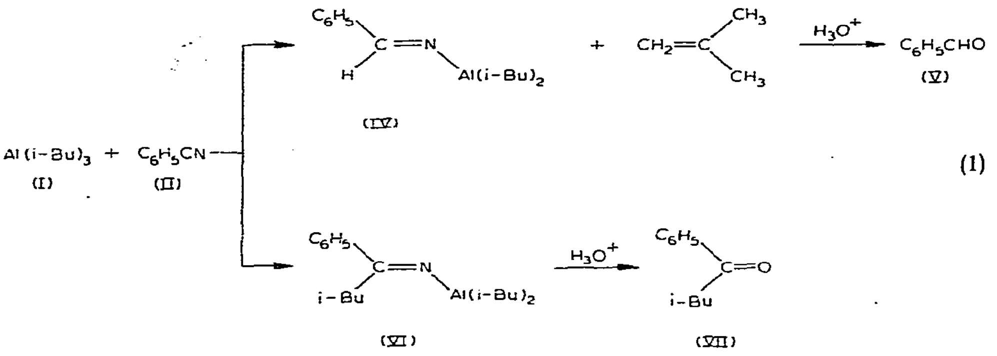
We have extended these investigations to include alkylmetal compounds of the Groups II and III elements containing a tertiary carbon atom in the β-position with respect to the metal atom, since such compounds appear interesting because of their peculiar reactivity.

The present work deals with the course and some mechanistic aspects of the reaction between triisobutylaluminium (I) and benzonitrile (II) in the absence of solvents. Additional support for the mechanisms proposed have been provided by the reaction of (II) with (+)tris[(*S*)-2-methylbutyl]aluminium (III)[7] and with (I) etherate.

RESULTS

In accordance with the behaviour of triethylaluminium[1,4], triisobutylaluminium (I) reacts with benzonitrile (II) to yield both reduction and addition products (Scheme 1). Under the temperature conditions (50–100°) and reactant mole ratio

SCHEME I



(0.5–4.0) employed, the predominant reaction occurring in the system was reduction, with benzaldehyde (V) being the only reduction product recovered after hydrolysis of the reaction mixture[2].

In Table 1 yields of aldehyde (V) and ketone (VII) are given as a function of the reactant mole ratio [(I)/(II)] at 70° (reaction time 6 h). At (I)/(II) $\leqslant$ 1.0, the extent of the addition reaction is practically negligible, being measurable only when an excess of (I) is used. The highest yield of ketone (VII) was obtained at (I)/(II) 2.0.

TABLE 1

THE YIELDS OF ALDEHYDE (V) AND KETONE (VII) AS A FUNCTION OF THE REACTANT MOLE RATIO[a]

Mole ratio $Al(i\text{-}Bu)_3/C_6H_5CN$	Yields (mole %)	
	Aldehyde (V)	Ketone (VII)
0.5	42.2	<0.1
1.0	57.6	~0.4
1.5	64.7	4.0
2.0	64.4	18.4
2.5	68.5	16.3
3.0	88.3	11.0
3.5	93.5	6.5
4.0	95.3	4.7

[a] Temperature 70°: reaction time 6 h.

TABLE 2

THE RATIO OF REDUCTION TO ADDITION PRODUCTS AS A FUNCTION OF THE REACTANT MOLE RATIO[a]

Mole ratio $Al(i\text{-}Bu)_3/C_6H_5CN$	Temperature (°C)	Product ratio reduction/addition
1.0	70	150[b]
1.5	70	16.2
2.0	70	3.5
2.5	70	4.2
3.0	70	8.0
3.5	70	14.4
4.0	70	20.2
2.0	50	3.1
4.0	50	3.2

[a] Reaction time 6 h. [b] Approximated value.

At 70°, the ratio of reduction to addition products changes in relation to the reactant mole ratio; no such dependence was found at 50° (Table 2).

At (I)/(II) 2.0 the ratio of reduction products to addition products decreased as the temperature was increased from 50° to 60° and then increased with increasing reaction temperature as shown in Table 3 and Fig. 1.

The total reaction yield as a function of the temperature is given in Fig. 2 (reaction time 2 h).

Table 4 reports the yields and optical purity of (+)(*S*)-1-phenyl-3-methyl-1-

TABLE 3

THE RATIO OF REDUCTION TO ADDITION PRODUCTS AS A FUNCTION OF THE TEMPERATURE[a]

Temperature (°C)	Yields (mole %)		Product ratio reduction/ addition
	Aldehyde (V)	Ketone (VII)	
50	13.3	3.9	3.4
60	24.4	9.8	2.5
70	54.8	16.6	3.3
80	84.6	12.1	7.0
90	93.2	6.8	13.6
100	95.5	4.5	22.0

[a] Reaction time 4 h: mole ratio $Al(i\text{-}Bu)_3/C_6H_5CN$ 2.0.

TABLE 4

REACTION BETWEEN (+)TRIS[(*S*)-2-METHYLBUTYL]ALUMINIUM[a] AND BENZONITRILE (II)[b]

Temperature (±1.0°C)	Reaction time (h)	(+)(*S*)-1-phenyl-3-methyl-1-pentanone (VIII)		
		Yields (mole %)	$[\alpha]_D^{25}$	Optical purity (%)
50	39	22.6	16.8±0.2[c]	83.0±1.0[d]
90	3	5.2	13.8±0.2[e]	66.7±0.1[f]

[a] $[\alpha]_D^{25}$ +27.87, optical purity 82.7%. [b] Mole ratio AlR_3^*/C_6H_5CN 2.0. [c] 1.904 g/100 ml, n-pentane. [d] (VIII has $[\alpha]_{D\,max}^{25}$ +20.25 (1.962 g/100 ml, n-pentane). [e] 4.922 g/100 ml, diethyl ether. [f] The optically pure (VIII) has $[\alpha]_D^{25}$ +20.70 (5.170 g/100 ml, diethyl ether)[8].

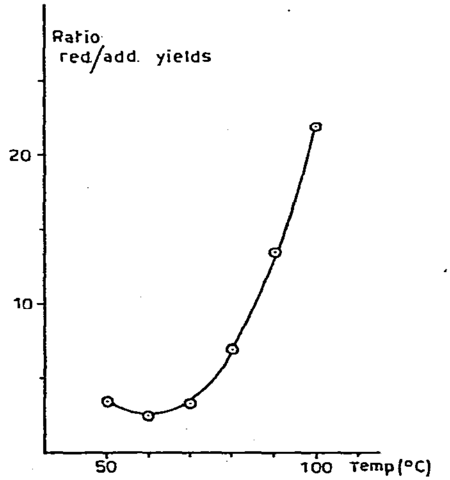


Fig. 1. The ratio of the yields of reduction to addition products as a function of the temperature at (I)/(II) 2.0 (reaction time 4 h).

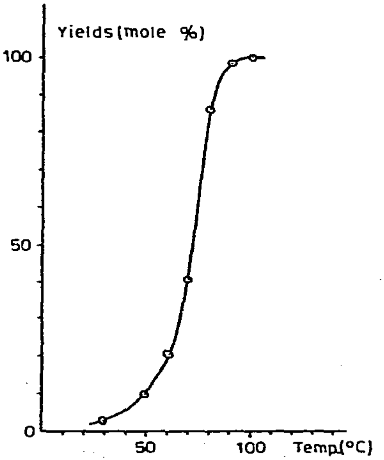


Fig. 2. Total aldehyde-ketone yields as a function of the temperature (reaction time 2 h).

TABLE 5

COMPARISON BETWEEN THE REACTIVITY OF TRIISOBUTYLALUMINIUM (I) AND THAT OF THE CORRESPONDING DIETHYL ETHERATE TOWARDS BENZONITRILE (II)[a]

Compound	Reaction time (h)	Product yields (mole %)	
		Aldehyde (V)	Ketone (VII)
triisobutylaluminium	1	89.8	5.4
	3	93.2	6.8
triisobutylaluminium—diethyl etherate	1	63.9	<0.05
	3	95.7	~ 0.05

[a] Temperature 90°: reactant mole ratio 2.0.

pentanone (VIII)[8], obtained by reacting (+)tris[(*S*)-2-methylbutyl]aluminium (III) with (II) at 50° and 90° respectively.

Finally, the reactivity of (I) is compared with that of the corresponding diethyl etherate (Table 5).

DISCUSSION

The reaction of $Al(i\text{-}Bu)_3$ (I) with benzonitrile (II) to form diisobutyl(benzylideneamino)aluminium (IV) and diisobutyl(α-isobutylbenzylideneamino)aluminium (VI) seems to occur at a relatively lower temperature than that of the corresponding reaction of (II) with triethylaluminium[1,4] (Table 3).

At 70° and a reactant mole ratio (I)/(II) $\leqslant$ 1.0, (IV) is the main product, and only

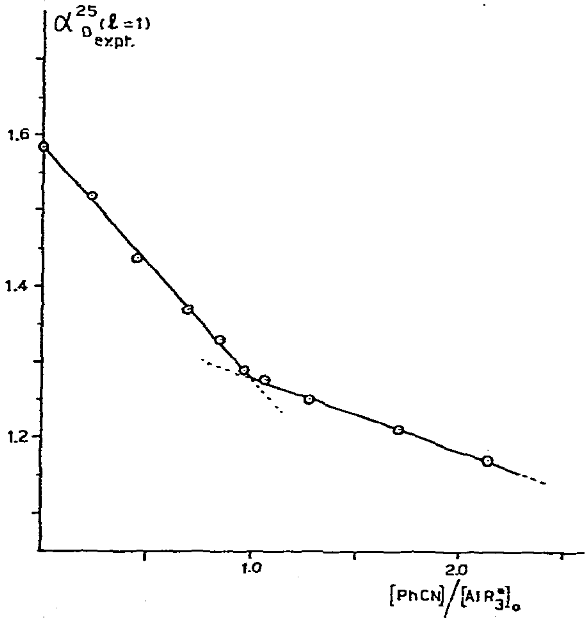
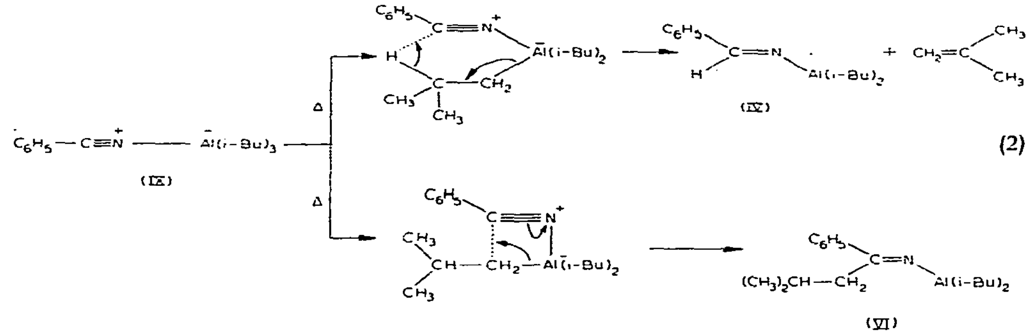


Fig. 3. Complex formation between (+)tris[(*S*)-2-methylbutyl]aluminium and benzonitrile in benzene.

small amounts of (VI) can be detected in the reaction mixture (Table 1).

In agreement with the literature^{2,4} and as indicated by the change in the optical rotation of a benzene solution of (III) as a function of the concentration of (II) (Fig. 3), it is reasonable to assume that the reaction proceeds through the formation of a 1/1 complex (IX), and that the subsequent intramolecular rearrangement^{4} of this complex, under the reaction conditions employed, leads to the formation of both a reduction (IV) and an addition product (VI) (Scheme 2).

SCHEME 2

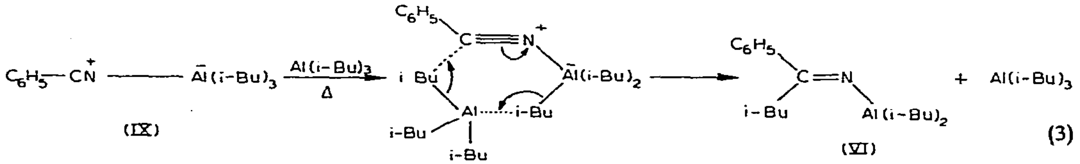


(2)

The fact that the reduction product (IV) is always in excess, together with a comparison of the present data with those of Pasynkiewicz *et al.*^{4}, confirm the greater migratory ability of the hydrogen atom bonded in the β-position relative to the aluminium atom of $Al(i\text{-}Bu)_3$^{9,10} than that of the hydrogen atom^{4} in $AlEt_3$ and of the same isobutyl group.

At 70°, the addition was found to occur with relatively higher yields when the mole ratio of $Al(i\text{-}Bu)_3$ (I) to benzonitrile (II) was 2.0 (Tables 1 and 2). This is consistent with a competitive mechanism (Scheme 3) involving the reaction of the complex (IX) with an organoaluminium molecule via a six-membered cyclic transition state^{1,4}.

SCHEME 3



(3)

This mechanism is in agreement with the observation that at 90° the reaction between (+)tris[(*S*)-2-methylbutyl]aluminium (III) and benzonitrile (II) (mole ratio 2.0) gives (+)(*S*)-1-phenyl-3-methyl-1-pentanone (VIII)^{8}, the optical purity of this compound being appreciably lower than that of the starting organoaluminium compound (Table 4).

As optically-active organoaluminium etherate compounds do not racemize at 90°^{10}, it is reasonable to assume that the same applies to the complex (IX), and thus only the uncomplexed organoaluminium compound, which reacts with (IX) as in Scheme 3, undergoes thermal racemization^{10}. The observed racemization of the recovered ketone (VIII) is, in fact, of the same order as the average racemization of (III), which can be calculated from values quoted in the literature[7,11].

The mechanism also explains the observation that at 90° triisobutylaluminium diethyl etherate reacts with (II) (mole ratio 2.0) to produce the reduction product in a large excess (Table 5). Although the organoaluminium etherate compounds form complex (IX)* [12], they do not react further with it as depicted in Scheme 3, as might have been expected from their general chemical behaviour[15].

At a ratio (I)/(II) 2.0, the yields of addition product decrease in comparison to those of the reduction product as the temperature is raised beyond 60° (Table 3 and Fig. 1).

The different effect of temperature on the rates of intramolecular reduction (Scheme 2) and of intermolecular addition (Scheme 3) does not seem to be the main reason for the increasing yield of reduction product (IV). In our opinion, these results are mainly related to the formation of dialkylaluminium hydride[9,16] and its subsequent intervention in the reduction of benzonitrile complex (IX).

Our experimental results (Table 5) show that at 90° (reaction time 1 h) and in the presence of equivalent amounts of $Al(i\text{-}Bu)_3 \cdot OEt_2$ and $Al(i\text{-}Bu)_3$, (IX) gave 63.9 and 89.8 % of benzaldehyde (V) respectively. These data are consistent with alternative mechanistic pathways; thus, when (I) is used, (IX) may also partake in a reduction reaction involving alkylaluminium hydride**. This alternative reaction does not exist of course when (I) is complexed with ether[10] and in this case only the reduction mechanism of Scheme 2 is operative. The addition reaction involving $(i\text{-}Bu)_2AlH$ and the $-C{\equiv}N$ group is very fast[17], at 24° for example, a sample of (II) in the presence of equivalent amount of (I) is quantitatively reduced to benzaldehyde (V) by diisobutylaluminium hydride within 15 min.

The reaction of (IX) with dialkylaluminium hydride (the actual concentration of the latter being dependent on that of AlR_3) also provides an explanation why the yields of addition product (VI) decreases relative to that of the reduction product (IV) at 70° when (I)/(II) is greater than 2.0 (Tables 1, 2). In fact, at 50° when hydride formation is slow[16], no apparent difference in the ratio of the yield of reduction product to addition product could be observed when the mole ratio of (I)/(II) was increased (Table 2).

From the overall results, it may therefore be concluded that in the reaction of $Al(i\text{-}Bu)_3$ with $C_6H_5{-}CN$ when the reactant mole ratio > 1.0 addition product (VI) is formed mainly by the mechanism outlined in Scheme 3[1,4], in agreement with previously reported observations on the mechanism of addition of trialkylaluminium compounds to carbonyl compounds[15,18].

On the other hand, reduction product (IV) is derived mainly from an intramolecular rearrangement of the complex $C_6H_5CN \cdot AlR_3$ (IX) (Scheme 2)[4], although

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* From a comparison of the heats of formation of triethylaluminium complexes with benzonitrile[3] and diethyl ether[13] it may be concluded that $Al(i\text{-}Bu)_3 \cdot OEt_2$ and nitriles afford (IX)[12,14]. In fact, when benzonitrile reacts with triisobutylaluminium-diethyl etherate at 0°, an equivalent amount of ether is recovered (see Experimental section).

** The discrepancy between the percentages in the reduction product when $Al(i\text{-}Bu)_3$ (I) and $Al(i\text{-}Bu)_3 \cdot OEt_2$ react with (II) (Table 5) is not completely attributable to the intervention of diisobutylaluminium hydride. In fact, it is possible that the reduction process occurs at different rates at the two reactant mole ratios of 1.0 and 2.0.

at relatively high temperatures ($\geqslant 70°$) and at (I)/(II) mole ratios $\geqslant 2.0$* the contribution of organoaluminium hydride compounds in the reaction cannot be neglected.

Further work is now in progress to investigate the kinetics of the reaction at different mole ratios and to determine its activation parameters.

EXPERIMENTAL

General

Triisobutylaluminium was obtained from the Texas Alkyl Inc. in Houston (U.S.A.), while (+)tris[(*S*)-2-methylbutyl]aluminium, $[\alpha]_D^{25}$ +27.87 (neat), was prepared as previously described[7]. Benzonitrile (C. Erba, Milan, Italy) was purified by distillation and stored over anhydrous sodium sulphate. A sample of 1-phenyl-3-methyl-1-butanone (VII) (2,4-dinitrophenylhydrazone m.p. 130–131°) was prepared according to established procedures[19]; (+)(*S*)-1-phenyl-3-methyl-1-pentanone (2,4-dinitrophenylhydrazone m.p. 138°) was obtained from (−)(*S*)-2-methyl-1-butanol[8]. Distillation and handling of all reactants was carried out under an atmosphere of dry, purified nitrogen. The reactions were performed in the absence of solvents, at various temperatures within the range 50° to 100°.

Optical rotations were measured with a Schmidt–Haensch polarimeter (sensitivity ±0.005°). GLC analyses were carried out on a C. Erba Fractovap, Mod. GT, equipped with a 2 m column of 10% butanediolsuccinate (BDS) (on Chromosorb W 60/80) at 160° and with a flow rate of 24 ml/min N_2. The reaction products were identified either through their conversion to the corresponding 2,4-dinitrophenylhydrazones or from the basis of comparative GLC retention times (benzaldehyde 3.9 min, benzonitrile 4.9 min, 1-phenyl-3-methyl-1-butanone 10.4 min), their relative percentages being determined from the areas of the corresponding chromatographic peaks.

Reactions between triisobutylaluminium (I) and benzonitrile (II)

(*a*). In a typical experiment, a weighed amount of (I) was placed in a two-necked flask (25 ml) equipped with a nitrogen inlet tube and a rubber septum fitted on a Teflon stopper. The appropriate amount of (II) was added at 0° by means of a calibrated hypodermic syringe and the vessel was then placed in a constant temperature (±0.2°) bath. After the time required for reaction (4–6 h), the flask was cooled at 0°, the mixture cautiously hydrolyzed with a 10% sulphuric acid solution and the organic products extracted with ether.

(*b*). (I) (0.39 g, 1.98 mmole) was reacted with (II) (0.05 g, 0.50 mmole) at 70° for 6 h, the mixture being then cautiously hydrolyzed with dilute sulphuric acid. The aqueous layer was made alkaline by the addition of concentrated potassium hydroxide solution and extracted with ether. No benzylamine was detected by Rimini's test or by gas chromatographic analysis. Even when (I) (1.98 mmole) was reacted with (II) (0.99 mmole) at 100° for 4 h no benzylamine was formed.

Reaction between triisobutylaluminium (I) etherate and benzonitrile (II)

(*a*). The diethyl etherate of (I) (4.32 g, 15.90 mmole) was placed in a double

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* The increase of the relative yields of reduction to addition products as the temperature is raised from 60° to 70° (Table 3) may be explained in terms of the intervention of diisobutylaluminium hydride in the reaction even at 70°.

necked 25 ml flask equipped with a magnetic stirrer. After cooling to 0°, (II) (1.07 g, 10.36 mmole) was added with stirring. Evaporation of the resulting solution at the same temperature and at reduced pressure (10 mm) gave diethyl ether (0.767 g, 10.35 mmole, 99.9% yield) containing no detectable amounts of benzonitrile.

(*b*). A measured amount of (II) was added at 0° to a weighed sample of the diethyl etherate of (I) in the reaction flask. The mixture was kept at 90 ± 1° for the required length of time (during which period the displaced diethyl ether distilled off), and then hydrolyzed with 10% sulphuric acid solution. The percentages of the components in the mixture were determined by GLC on the ether extracts.

Reduction of benzonitrile (II) by diisobutylaluminium hydride

Benzonitrile (II) (0.66 g, 6.4 mmole) was added slowly to 3.80 g of a mixture of diisobutylaluminium hydride and (I) (mole ratio 2.8/1) at 0°. After the addition the mixture was kept at 24° for 15 min and then hydrolyzed cautiously with a 10% sulphuric acid solution. The ether extracts contained 99.2% of benzaldehyde and 0.8% of unreacted (II).

The acid aqueous layer was made alkaline with 10% sodium hydroxide solution and extracted with ether. No benzylamine was detected by gas chromatographic analysis.

Reactions between benzonitrile (II) and (+)tris[(S)-2-methylbutyl]aluminium (III)

Benzonitrile (II) (1.59 g, 15.4 mmole) was added at −30° to 7.41 g (30.8 mmole) of (III) and the mixture maintained at 90 ± 1° for 3 h. After cooling to 0°, the mixture was carefully hydrolyzed with aqueous sulphuric acid and extracted with ether. On the basis of comparative GLC analysis (1-phenyl-3-methyl-1-pentanone: retention time 14.2 min) it was found that the mixture contained 94.8% of benzaldehyde and 5.2% of ketone (VIII). After removing the ether, the mixture was treated at room temperature (3 h) with a solution consisting of 3.6 g of $K_2Cr_2O_7$ and 1.3 ml of concentrated H_2SO_4 in 20 ml of water. The mixture was extracted with ether and the extracts washed with 10% sodium bicarbonate solution. After removal of the ether, 0.5 g of (VIII)[8], $[\alpha]_D^{25}$ + 13.8, (4.922 g/100 ml, ether) was obtained.

In a repeat experiment, 2.29 g (9.96 mmole) of (III) and 0.49 g (4.78 mmole) of (II) were used and the mixture kept at 50 ± 1° for 39 h. The reaction afforded 77.4% of benzaldehyde and 22.6% of ketone (by GLC analysis). After oxidation of benzaldehyde, 0.2 g of (VIII)[8], $[\alpha]_D^{25}$ + 16.8 (1.904 g/100 ml, n-pentane) was recovered.

Complex formation between (+)tris[(S)-2-methylbutyl]aluminium (III) and benzonitrile (II)

Measured volumes of a benzene solution of (II) (c 3.5870 g/10 ml) were added by means of a calibrated hypodermic 0.5 ml syringe to a benzene solution of (III) (c 0.7826 g/10 ml), in a rubber capped sealed polarimeter tube (1 dm length). The optical rotations observed *vs.* the molar ratio C_6H_5CN/AlR_3^* are reported in Fig. 3. For (+)tris[(*S*)-2-methylbutyl]aluminium: $[\alpha]_D^{25}$ + 20.2 (c 7.826 g/100 ml, benzene) and (+)tris[(*S*)-2-methylbutyl]aluminium·C_6H_5CN: $[\alpha]_D^{25}$ + 12.5 (c 10.236 g/100 ml, benzene), respectively.

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