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# The crystal structure of $(\eta^6\text{-}C_6Me_6)Ti[(\mu\text{-}Cl)_2(AlClEt)]_2$ and the catalytic activity of the $(C_6Me_6)TiAl_2Cl_{8-x}Et_x$ $(x = 0\text{–}4)$ complexes towards butadiene

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## Abstract

The composition of $(C_6Me_6)TiAl_2Cl_{8-x}Et_x$ complexes in $(C_6Me_6)TiAl_2Cl_8 + n\ Et_3Al$ ($n = 0.5$–$6$) systems was studied by UV-Vis spectroscopy and the X-ray crystal structure of one of them, $(\eta^6\text{-}C_6Me_6)Ti[(\mu\text{-}Cl)_2(AlClEt)]_2$ (IIa-2), has been determined. The complex crystallizes in the orthorhombic space group $Pna2_1$ with $Z = 4$ and lattice parameters $a$ 15.634(3), $b$ 11.355(2), $c$ 14.417(2) Å. The ethyl groups of IIa-2 reside in outer positions of aluminate ligands farther away from the $C_6Me_6$ ligand. The other part of the complex does not differ remarkably from structures of other (arene)$Ti^{II}$ complexes. Negligible activity of $(C_6Me_6)TiAl_2Cl_8$ towards the butadiene cyclotrimerization is considerably increased by addition of 2.5–3.0 equivalents of $Et_3Al$. As follows from UV-Vis spectra, such systems contain mainly the $(C_6Me_6)TiAl_2Cl_5Et_3$ complex. It is suggested that the introduction of three Et substituents destabilizes the $Ti\text{–}(\eta^6\text{-}C_6Me_6)$ bond so that the replacement of hexamethylbenzene by butadiene in the first step of a catalytic cycle becomes more feasible.

## Introduction

The parent (arene)$Ti^{II}$ complexes, $(\eta^6\text{-benzene})Ti[(\mu\text{-}X)_2(AlX_2)]_2$ (X = Cl, Br, I), are readily obtained by reduction of titanium tetrahalides with aluminium in the presence of aluminium halides in benzene as a solvent [1–6]. The $\pi$-bonded benzene molecule can be replaced by more basic methylbenzenes up to hexamethylbenzene [7] and the halogen ligands undergo rapid exchange reactions in mix-

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tures of (arene)$Ti^{II}$ complexes [8] and in mixtures of arene complexes with different aluminium halides [5]. All the (arene)$Ti^{II}$ complexes form similar square-pyramidal structures with the titanium atom above the centre of an approximate square of bridging halogen atoms and with an arene molecule $\pi$-bonded to titanium at the apex of the pyramid. The X-ray crystal and molecular structures were determined for the following complexes: $(C_6H_6)Ti(AlCl_4)_2$ [9], $(C_6H_6)Ti(AlCl_4)_2 \cdot C_6H_6$ [10], $(C_6H_6)Ti(AlBr_4)_2 \cdot C_6H_6$ and $(C_6H_6)Ti(AlI_4)_2$ [11], $(C_6Me_6)Ti(AlCl_4)_2 \cdot C_6H_6$ [12], and (durene)$TiAl_2Cl_{4.75}I_{3.25}$ [13].

It was found that the complex $(C_6H_6)Ti(AlCl_4)_2$ (Ia) catalyzes the cyclotrimerization of butadiene to (*Z*,*E*,*E*)-1,5,9-cyclododecatriene ((*Z*,*E*,*E*)-CDT) [14] and that additions of ethylaluminium compounds to Ia further improve its catalytic properties [15,16]. Recently, the kinetics of butadiene cyclotrimerization has been thoroughly studied in systems containing $(C_6H_6)TiAl_2Cl_{8-x}Et_x$ ($x = 0$–$2$) complexes and their activity and selectivity have been found to depend on the number of Et groups ($x$) [17,18]. The ethyl-containing complexes $(C_6H_6)TiAl_2Cl_7Et$ (Ia-1) and $(C_6H_6)TiAl_2Cl_6Et_2$ (Ia-2) were formed in the Ia + $n$ $Et_yAlCl_{3-y}$ ($y = 1$–$3$) systems and numbers of Et groups in (arene)$Ti^{II}$ complexes were determined by the combination of results of UV-Vis spectroscopy of the $(C_6H_6)Ti^{II}$ complexes and of ESR spectroscopy of $Cp^*Ti^{III}Al_2Cl_{8-x}Et_x$ complexes obtained by redox reaction 1 of the $(C_6H_6)Ti^{II}$ complexes with pentamethylcyclopentadiene (Cp*H) [19,20].

$$(C_6H_6)Ti^{II} + Cp^*H \rightarrow Cp^*Ti^{III} + C_6H_6 + H^{\cdot} \qquad (1)$$

The position of a charge transfer band near 400 nm ($\epsilon \sim 2000$ cm$^2$ mmol$^{-1}$) was used for the determination of contents of Ia–Ia-2 in the catalytic systems based on Ia [17–19] and in the $TiCl_4$–$Et_yAlCl_{3-y}$ ($y = 1$–$3$) systems [21]. Complexes Ia-1 and Ia-2 were stable in benzene solution but they decomposed on an attempted precipitation of solid complexes by adding hexane. More ethylated complexes ($x > 2$) decomposed even in benzene solution [22].

The catalytic cyclotrimerization of butadiene induced by Ia was found to be blocked by mesitylene and more basic methylbenzenes [16] which are strongly bound to $Ti^{II}$ [7]. The constant of formation ($K$) of the $(C_6Me_6)Ti(AlCl_4)_2$ (IIa) complex as defined by eq. 2 was estimated from UV-Vis measurements to be at least $10^3$ while analogous equilibrium involving (*Z*,*E*,*E*)-CDT and benzene afforded $K$ close to unity.

$$(C_6H_6)Ti(AlCl_4)_2 + C_6Me_6 \overset{K}{\rightleftharpoons} (C_6Me_6)Ti(AlCl_4)_2 + C_6H_6 \qquad (2)$$

Butadiene, however, easily substitutes both benzene and (*Z*,*E*,*E*)-CDT in the first step of a catalytic cycle [18]. It can be concluded that the high stability of the $(C_6Me_6)Ti^{II}$ complexes gives us the chance to prepare stable ethyl-containing derivatives and, on the other hand, the destabilizing effect of ethylaluminium ligands can release the $Ti^{II}$–($\eta^6$-$C_6Me_6$) bond so that $C_6Me_6$ could be replaceable by butadiene.

Here we report the formation of $(C_6Me_6)TiAl_2Cl_{8-x}Et_x$ ($x = 1$–$4$) complexes in the IIa–$Et_3Al$ systems, the first crystal and molecular structure of a stable ethyl-containing $(C_6Me_6)Ti^{II}$ complex and the catalytic activity of ethyl-containing $(C_6Me_6)Ti^{II}$ complexes in the cyclotrimerization of butadiene.

## Experimental

A high-vacuum technique was used throughout the preparation of $(C_6Me_6)Ti^{II}$ complexes, in kinetic measurements of the butadiene consumption and in UV-Vis measurements as previously described for the $(C_6H_6)Ti^{II}$ complexes [17,18]. The chemicals and solvents were of the same quality as used therein.

### *Preparation of $(C_6Me_6)Ti[(\mu\text{-}Cl)_2(AlClEt)]_2$ (IIa-2)*

The benzene solution of $(C_6H_6)Ti(AlCl_4)_2$ (Ia) (0.02 *M*, 20 ml) was added to $C_6Me_6$ (0.10 g, 0.6 mmol) and after rapid shaking, during which crystalline IIa precipitated from the solution, 6 ml of 0.1 *M* solution of $Et_3Al$ in benzene was added and the mixture was further shaken until all the solid had dissolved. The electronic absorption spectrum of this solution exerted a strong charge transfer (CT) band at 400 nm in addition to other much less intense bands (Table 1). Then the volume of the solution was reduced to *ca.* 7 ml and 10 ml of hexane were added. The solution was left standing to crystallize at about 5°C with simultaneous slow distillation of the solvents to a slightly cooler ampoule. Purple crystals were separated into another ampoule equipped with a breakable seal and were sealed off. Some of the crystals were dissolved in benzene and their UV-Vis spectrum measured: $\lambda_{max}(CT) = 400$ nm.

### *Crystal structure determination of IIa-2*

An ampoule with the crystals of IIa-2 was opened in a glovebox under argon and a crystal ($0.15 \times 0.30 \times 0.40$ mm) was sealed in a capillary. Diffraction data were collected on an Enraf–Nonius CAD-4 four-circle diffractometer (Mo-$K_\alpha$, graphite monochromator, $\theta_{max} = 25°$, $T = 296$ K). Unit cell parameters were determined from 24 reflections: orthorhombic cell *a* 15.634(3), *b* 11.355(2), *c* 14.417(2) Å, space group $Pna2_1$, $Z = 4$, $V$ 2559 Å$^3$, $D_c = 1.388$ g cm$^{-3}$, $\mu = 10.3$ cm$^{-1}$. A total of 2343 independent reflections was measured; 1155 reflections with $F^2 \geqslant 2\sigma(F^2)$ were used for the solution of the structure by direct methods followed by a Fourier syntheses. Atom coordinates were refined by the full-matrix least-squares method with anisotropic thermal parameters for the Ti, Cl and Al atoms and isotropic thermal parameters for the carbon atoms. Positions of hydrogen atoms were not calculated. The final residuals for 135 refined parameters were $R = 0.075$ and $R_w = 0.079$. Important bond lengths and angles are listed in Table 2; atomic coordinates are deposited at the Cambridge Crystallographic Data Centre.

### *The catalytic systems and kinetic measurements of butadiene consumption*

The catalytic systems Ia + *m* (durene) and Ia + *m* $(C_6Me_6)$ + *n* $Et_3Al$ ($m = 3$, 25; $n = 0$–6) were prepared by mixing components in the reactor. Hexamethylben-

Table 1

Positions of the charge transfer band in the Ia + 25 $C_6Me_6$ + *n* $Et_3Al$ systems

| | $n = 0$ | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 4.0 | 6.0 |
|---|---|---|---|---|---|---|---|---|---|
| $\lambda_{max}$ (nm) | 386 | 393 | 396 | 400 | 402 | 405 | 407 | 410 | 414 |
| Assignment | IIa [a] | IIa-1 [a] | | IIa-2 [a] | | | IIa-3 | | – [b] |

[a] Broad absorption bands were further observed at 550 nm ($\epsilon \sim 100$ cm$^2$ mmol$^{-1}$) and 780–790 nm ($\epsilon \sim 30$ cm$^2$ mmol$^{-1}$). [b] The absorption band attributable to IIa-4 rapidly decayed.

Table 2

Bond distances (Å) [a] and bond angles (°) in IIa-2

| | | | |
|---|---|---|---|
| Ti–Cl(1) | 2.629(7) | Ti–C(1) | 2.50(2) |
| Ti–Cl(2) | 2.586(7) | Ti–C(2) | 2.54(2) |
| Ti–Cl(3) | 2.586(7) | Ti–C(3) | 2.47(2) |
| Ti–Cl(4) | 2.601(6) | Ti–C(4) | 2.48(2) |
| Al(1)–Cl(1) | 2.20(1) | Ti–C(5) | 2.48(2) |
| Al(1)–Cl(2) | 2.20(1) | Ti–C(6) | 2.45(2) |
| Al(1)–Cl(5) | 2.08(1) | Al(1)–C(7) | 2.03(3) |
| Al(2)–Cl(3) | 2.19(1) | Al(2)–C(9) | 2.07(3) |
| Al(2)–Cl(4) | 2.19(1) | C(7)–C(8) | 1.25(7) |
| Al(2)–Cl(6) | 2.10(1) | C(9)–C(10) | 1.31(6) |
| Cl(1)TiCl(2) | 76.8(2) | Cl(3)TiCl(4) | 76.3(2) |
| Cl(1)TiCl(3) | 79.6(3) | Cl(2)TiCl(4) | 80.6(2) |
| TiCl(1)Al(1) | 93.4(3) | TiCl(3)Al(2) | 95.0(3) |
| TiCl(2)Al(1) | 94.7(3) | TiCl(4)Al(2) | 94.6(3) |
| Cl(1)Al(1)Cl(2) | 94.8(4) | Cl(3)Al(2)Cl(4) | 94.1(4) |
| Cl(1)Al(1)Cl(5) | 108.4(5) | Cl(3)Al(2)Cl(6) | 107.6(5) |
| Cl(2)Al(1)Cl(5) | 109.5(5) | Cl(4)Al(2)Cl(6) | 110.5(5) |
| Cl(5)Al(1)C(7) | 117(1) | Cl(6)Al(2)C(9) | 112(1) |
| Al(1)C(7)C(8) | 119(3) | Al(2)C(9)C(10) | 108(3) |

[a] All bonds in the C(1)–C(6) ring are in the range 1.28–1.44 Å, average 1.39 Å.

zene (0.020 g, 0.12 mmol or 0.162 g, 1 mmol) was evacuated, dissolved in benzene and the benzene solutions of Ia (0.04 mmol in 2 ml) and $Et_3Al$ (0.02–0.24 mmol, 0.1 *M*) were added subsequently. The final volume of the catalyst solution was always 30 ml. The measurement of the kinetics of butadiene consumption was performed at constant temperature 50°C and at three butadiene concentrations $6.36 \times 10^{-2}$, $1.91 \times 10^{-1}$ and $3.18 \times 10^{-1}$ *M* which were subsequently changed to a higher value after 30 min when constant reaction rates were achieved. The evaluation of results and analyses of products were carried out as described earlier [17,18].

### *UV-Vis measurements*

The UV-Vis spectra of the above Ia + 25 $C_6Me_6$ + *n* $Et_3Al$ catalytic systems before and after the kinetic measurements and of the isolated complex IIa-2 were taken using all-sealed quartz cells $d = 1.0$ and 0.1 cm (Hellma). The catalytic systems containing only 1.5 equivalents of $C_6Me_6$ were also measured. The measurements in the region 300–1500 nm were carried out on a Varian Cary 17D spectrometer.

## Results and discussion

### *The formation of the* $(C_6Me_6)TiAl_2Cl_{8-x}Et_x$ $(x = 1–4)$ *complexes and their composition*

The ethyl-containing $(C_6Me_6)Ti^{II}$ complexes were formed from $(C_6H_6)Ti(AlCl_4)_2$ (Ia) by adding at least 1.5 equivalents of $C_6Me_6$ and *n* equivalents of $Et_3Al$ ($n = 0.5–6$), all in benzene solution. The complexes were much more soluble than $(C_6Me_6)Ti(AlCl_4)_2$ (IIa); they were freely soluble even in benzene/hexane mixtures. The UV-Vis absorption spectra of all these systems (Table 1) exerted an intense CT band near 400 nm and for $n \leqslant 1.5$ the $d$–$d$ bands of low intensity near 550 and 780 nm were also observed. Analogous spectra of $(C_6Me_6)Ti^{II}$ complexes were previously observed in the IIa–$Et_2AlCl$ systems [18]. For higher values of $n$ the $d$–$d$ bands were overlapped by a continuous absorption decreasing in intensity to longer wavelengths. The intensity of this band belonging to some by-product was noted to increase with increasing $n$. The $(C_6Me_6)Ti^{II}$ complexes were stable in solution up to $n = 4$; for $n = 6$ the CT band decreased in intensity which indicated the continuing decomposition of a $(C_6Me_6)Ti^{II}$ complex. The CT band position was constant in the range 1.5–25 equivalents of $C_6Me_6$ added to Ia which corresponded to the molar ratio of $C_6Me_6/C_6H_6 \sim 1/6000$–240. This shows that the formation constant $K$ for the IIa complexes (eq. 2) is rather close to $10^4$.

The number of Et groups in the $(C_6Me_6)Ti^{II}$ complexes contained in these systems was determined from the position of their CT band. The constant shift of this band by 7 nm per one Et group to longer wavelengths was previously found in the Ia–$Et_2AlCl$ and IIa–$Et_2AlCl$ systems for the first three members of both the Ia and IIa series [18,22] (the value of 398 nm for IIa-2 from ref. 18 was corrected to 400 nm after measurement of the solution of authentic crystals of IIa-2, *vide infra*). The application of the above constant shift value for more ethylated $(C_6Me_6)Ti^{II}$ complexes affords $\lambda_{max}(CT) = 407$ nm for $(C_6Me_6)TiAl_2Cl_5Et_3$ (IIa-3) and 414 nm for $(C_6Me_6)TiAl_2Cl_4Et_4$ (IIa-4) (see Table 1). This assignment is reasonable with respect to equilibria in the Ia or IIa–$Et_yAlCl_{3-y}$ ($y = 1$–3) systems which generally yield (arene)$Ti^{II}$ complexes containing more chlorinated aluminium ligands compared to free ethylaluminium compounds [18,22].

A fixed point for the spectroscopic determination of the number of Et groups was obtained by the X-ray analysis of crystals separated from the IIa + 1.5 $Et_3Al$ mixture (*vide infra*). The crystals were identified as $(C_6Me_6)Ti(AlCl_3Et)_2$ (IIa-2) and their benzene solution afforded $\lambda_{max}(CT) = 400$ nm, identical with that of the mother liquor. The stoichiometry of IIa-2 formation (eq. 3) is the same as for Ia-2 [22]:

$$\text{IIa} + 1.5\ Et_3Al \rightleftharpoons \text{IIa-2} + 1.0\ Et_2AlCl + 0.5\ EtAlCl_2 \qquad (3)$$

the above-mentioned general feature of these equilibria is now justified.

### *X-Ray structure of $(C_6Me_6)Ti(AlCl_3Et)_2$ (IIa-2)*

The Ia + 1.5 $C_6Me_6$ + 1.5 $Et_3Al$ system in benzene/hexane mixture afforded light purple crystals which were identified by X-ray analysis as a diethylated $(\eta^6\text{-}C_6Me_6)Ti^{II}$ complex, $(C_6Me_6)Ti[(\mu\text{-}Cl)_2(AlClEt)]_2$ (IIa-2). The structure of IIa-2 (Fig. 1) is analogous to those of IIa [12] and other (arene)$Ti^{II}$ complexes [9–11,13]. The average lengths of Ti–C(arene) (2.49 Å) and Ti–Cl (2.60 Å) bonds do not differ from the lengths of the same bonds in IIa (2.50 and 2.615 Å). The bridging Al–Cl bonds (2.195 Å) are only slightly longer compared to the same bonds in IIa (2.175 Å). The outer Al–Cl bonds lie in a molecular pseudoplane containing Al–Ti–Al skeleton and are in positions closer to the plane of the $C_6Me_6$ ligand. They have the same lengths (2.09 Å) as the outer Al–Cl bonds in IIa (2.10 Å). The ethyl groups are placed in outer positions of aluminate ligands farther from the $C_6Me_6$ plane. Their methyl groups are orientated to each other, however, one of the Me groups lies close to the molecular pseudoplane and the

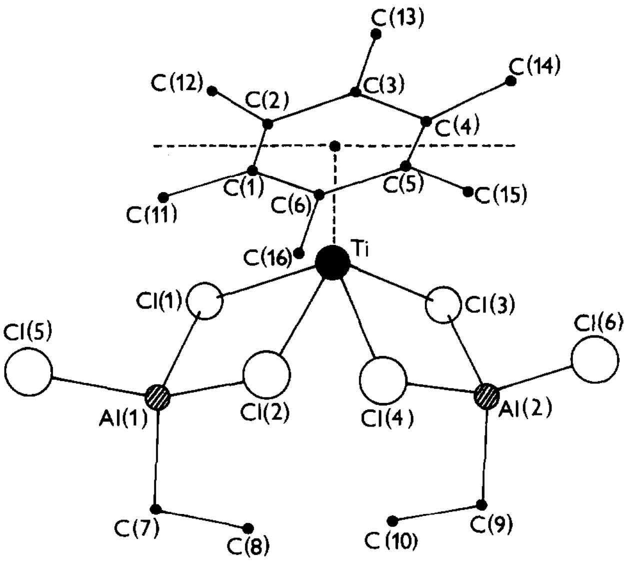

Fig. 1. The molecular structure and atom-numbering scheme for IIa-2.

other is placed farther away. This slight asymmetry is probably connected with the packing of molecules in crystal. The hexamethylbenzene ring is planar within the accuracy of the measurements and its Me groups are slightly bent above the aromatic ring plane, farther from the Ti atom. The $C_6Me_6$ ring is approximately bisected by the molecular pseudoplane in bonds; this orientation is so far known for other highly methylated (arene)$Ti^{II}$ complexes [12,13].

### *The cyclotrimerization of butadiene by the* $(C_6Me_6)Ti^{II}$ *complexes*

Kinetic parameters and the composition of products of the butadiene conversion catalyzed by the Ia + $m$ $C_6H_2Me_4$ (durene) and Ia + $m$ $C_6Me_6$ + $n$ $Et_3Al$ ($m = 0$, 3, 25; $n = 0$–6) systems are listed in Table 3. The results show that additions of $C_6Me_6$ to Ia gradually decrease the rate of butadiene consumption and change the butadiene cyclotrimerization to a Friedel–Crafts addition of butadiene to benzene, which is used as a solvent. The cationic catalysis of the formation of 1-phenyl-but-2-ene (PhB) is reflected in a very low reaction order with respect to the butadiene concentration. The qualitatively similar results were obtained with the Ia–durene system, however, a large drop in the reaction rate was accompanied by only slight increase in the production of PhB.

These results are generally in line with the conclusion drawn by Dzierzgowski *et al.* [16] that the catalytic activity of (arene)$Ti^{II}$ complexes in butadiene cyclotrimerization strongly decreases with increasing basicity of aromatic hydrocarbons. They, however, found that the (mesitylene)$TiAl_2Cl_8$ complex (in mesitylene as a solvent) is completely inactive even after addition of 4 equivalents of $Et_2AlCl$. In view of higher basicity of durene compared to mesitylene this seems to be at variance with the present results for the Ia–durene and Ia–$C_6Me_6$ systems. The discrepancy in results could originate from a much higher concentration of mesitylene compared to concentrations of durene or $C_6Me_6$ used in this work and in higher level of

Table 3

Kinetic parameters and products of the butadiene oligomerization catalyzed by the Ia + *n* $Et_3Al$ (*n* = 0, 1, 2) systems, and by the Ia + *m* $C_6H_2Me_4$ (durene) and Ia + *m* $C_6Me_6$ + *n* $Et_3Al$ (*m* = 3, 25; *n* = 0–6) systems [a]

| *m* | *n* | $v_{30}$ ($\times 10^6$ mol $l^{-1}$ $s^{-1}$) |  | Reaction order in $C_4H_6$ | Composition of oligomers (%) |  |  |  | Polymer yield (%) |
|---|---|---|---|---|---|---|---|---|---|
|  |  | ([$C_4H_6$] = 6.36 × $10^{-2}$ *M*) | ([$C_4H_6$] = 1.91 × $10^{-1}$ *M*) |  | (*Z*,*E*,*E*)-CDT | (*E*,*E*,*E*)-CDT | 1,5-COD | PhB |  |
| 0 | 0 | 320 [b] | 2580 | 1.9 | 98 | trace | 0 | 2 | 8 |
| 0 | 1 | 236 [b] | – | – | 99 | 1 | trace | 0 | 3 |
| 0 | 2 | 40 [b] | 96 | 0.8 | 96 | 3 | 1 | 0 | 5 |
| *Durene* |  |  |  |  |  |  |  |  |  |
| 3 | 0 | 104 | 983 | 2.0 | 93 | 0 | 0 | 7 | 8 |
| 25 | 0 | 15 | 89 | 1.6 | 82 | 0 | 0 | 18 | 16 |
| *Hexamethylbenzene* |  |  |  |  |  |  |  |  |  |
| 3 | 0 | 10 | 33 | 1.1 | 62 | 0 | 0 | 38 | 20 |
| 25 | 0 | 15 | 17 | 0.1 | 13 | 0 | 0 | 87 | 29 |
| 25 | 1 | 0 | 9 | – | 98 | 2 | 0 | 0 | 27 |
| 25 | 2 | 0 | 22 | – | 95 | 5 | 0 | 0 | 29 |
| 25 | 2.5 | 11 | 41 | 1.2 | 85 | 15 | 0 | 0 | 40 |
| 25 | 3 | 14 | 42 | 1.0 | 76 | 24 | 0 | 0 | 43 |
| 25 | 3.5 | 10 | 27 | 0.9 | 70 | 30 | 0 | 0 | 45 |
| 25 | 4 | 4 | 10 | 0.8 | 66 | 34 | 0 | 0 | 46 |
| 25 | 6 | inactive |  |  |  |  |  |  |  |

[a] [Ti] = $1.33 \times 10^{-3}$ mol $l^{-1}$; $v_{30}$ = rate constant after 30 min of the reaction; 1,5-COD = 1,5-cyclooctadiene; PhB = 1-phenylbut-2-ene. [b] Taken from ref. 18.

polar impurities. The latter reason follows from the comparison of electric conductivity ($\kappa$) and selectivity of CDT formation (*S*(CDT)) for Ia in benzene with those obtained by us in high-vacuum devices [17]: $\kappa = 10^{-3}$–$10^{-2}$ *vs*. $4 \times 10^{-8}$ $s^{-1}$ $m^{-1}$ and *S*(CDT) = 63 *vs*. 88%. The deactivation of impurities by adding 4 equivalents of $Et_2AlCl$ to Ia seems to be a reason for an increase in the catalytic activity by *ca*. 7 times and in *S*(CDT) to 91% in ref. 16. In contrast, we found that the "pure" Ia + 4 $Et_2AlCl$ system was slightly less active than Ia while the *S*(CDT) value was increased to 94% [18].

The results presented in Table 3 show that the negligible cyclotrimerization activity of IIa can be enhanced by additions of $Et_3Al$. The highest activity was attained in the IIa + 2.5 $Et_3Al$ and IIa + 3.0 $Et_3Al$ systems whereas addition of 1 equivalent of $Et_3Al$ only abolished the Friedel–Crafts activity of IIa. The IIa + 4 $Et_3Al$ system gave a lower activity and the IIa + 6 $Et_3Al$ system was inactive. The increase in the $Et_3Al$/IIa molar ratio led to an increase in both abundance of (*E*,*E*,*E*)-CDT (max. 34%) in the oligomer fraction and in the polymer yield (27–45%). The reaction order in butadiene was about first order and showed slight decreasing tendency with increasing *n*. The UV-Vis measurements of the final reaction mixtures afforded practically unchanged spectra of $(C_6Me_6)Ti^{II}$ complexes for *n* = 2 whereas only weak shoulders of the CT band were observed for *n* = 2.5 and 3.0. The broad absorption band decreasing in intensity to longer wavelengths became dominating with increasing value of *n*.

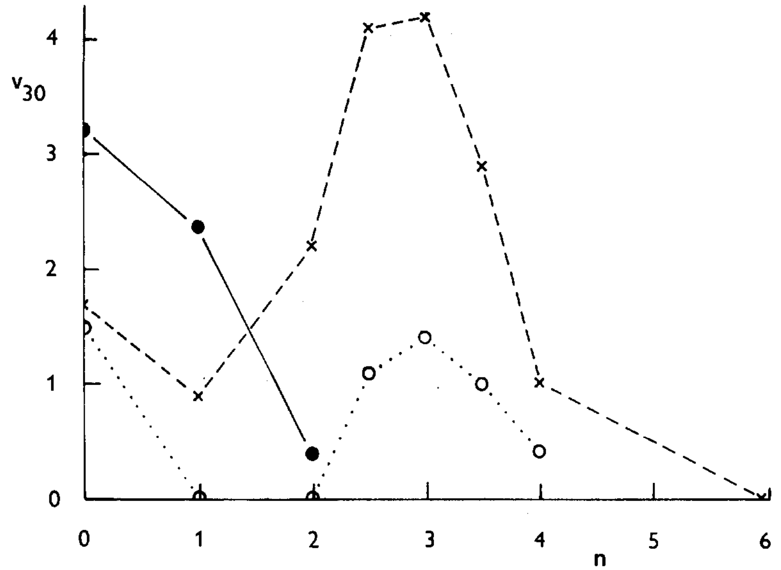

Fig. 2. The dependence of reaction rates of butadiene consumption after 30 min of the reaction on the composition of catalytic systems: Ia + $n$ $Et_3Al$ ($n$ = 0, 1, 2) at $[C_4H_6] = 6.36 \times 10^{-2}$ $M$ (●); Ia + 25 $C_6Me_6$ + $n$ $Et_3Al$ ($n$ = 0–6) at $[C_4H_6] = 6.36 \times 10^{-2}$ $M$ (o) and at $[C_4H_6] = 1.91 \times 10^{-1}$ $M$ (×). The ordinate bears the values of $v_{30}$ ($\times 10^4$ mol $l^{-1}$ $s^{-1}$) for (●) and $v_{30}$ ($\times 10^5$ mol $l^{-1}$ $s^{-1}$) for (o) and (×) taken from Table 3.

The comparison with the Ia + $n$ $Et_3Al$ systems (Table 3 and Fig. 2) shows that the latter systems are by one order more active for $n \leqslant 1$. This is because the coordinated benzene ligand in otherwise stable Ia and Ia-1 complexes is easily replaceable by butadiene in an initial step of catalytic cycle [17,18]. The Ia + 2 $Et_3Al$ system contains mainly the Ia-2 complex because more ethylated complexes are not stable. The Ia-2 complex is mostly deactivated during a rapid initial consumption of butadiene but in a later stage its low concentration is maintained by interaction between solid $TiCl_3$ or $TiCl_2$ and $EtAlCl_2$ which is always present in a low concentration. The constant reaction rate, approximate first reaction order in butadiene and a very low concentration of (arene)$Ti^{II}$ complexes (detected by UV-Vis and ESR) or its absence are typical for the Ia-2 containing systems derived from Ia [18] or $TiCl_4$ [21]. The higher yields of (*E*,*E*,*E*)-CDT and of the polymer are also encountered in these systems.

The present results show that the coordinated $C_6Me_6$ ligand is not effectively replaceable by butadiene unless the Ti–($\eta^6$-$C_6Me_6$) bond is released by ethyl substituents at aluminate ligands. The optimum $C_6Me_6$-releasing effect was obtained in the case of the $(C_6Me_6)TiAl_2Cl_5Et_3$ (IIa-3) complex which is stable in solution. Nevertheless, the abundant formation of (*E*,*E*,*E*)-CDT indicates that a trinuclear catalytic complex is in equilibrium with a probably more coordinatively unsaturated catalytic species formed by dissociation of aluminate ligands. The catalytic properties of IIa-3 are highly similar to those of Ia-2.

The initial expectation that a prolonged Ti–(arene) distance will be observed in IIa-2 compared to IIa was not fulfilled but this is not surprising in view of the facts that IIa-2 is still catalytically inactive and that this distance is practically the same for IIa and Ia. Also the geometry of the inorganic skeleton is surprisingly stable as follows from recent X-ray investigations on $CpTi^{III}(AlCl_4)_2$ and $(Bz_5C_5)Ti^{III}(AlCl_4)_2$ (Bz = benzyl) [23].

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