SYNTHESIS AND STRUCTURE OF (π-ARENE)TITANIUM(II) HALOALUMINATE COMPLEXES WITH DIARYLMETHANE LIGANDS

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Novel (arene)titanium(II) haloaluminate complexes ($(\eta^6\text{-arene})Ti[(\mu\text{-}X)_2AlX_2]_2$) (X = Cl, Br) were obtained from ($(\eta^6\text{-benzene})Ti[(\mu\text{-}X)_2AlX_2]_2$) (X = Cl, Br) complexes by ligand exchange reactions with bis(pentamethylphenyl)methane and dimesitylmethane. The $[\eta^6$-1,2,3,4,5-pentamethyl-6-(2,3,4,5,6-pentamethylbenzyl)benzene]$Ti[(\mu\text{-}X)_2AlX_2]_2$ (X = Cl, Br) and $[\eta^6$-1,3,5-trimethyl-2-(2,4,6-trimethylbenzyl)benzene]$Ti[(\mu\text{-}Br)_2AlBr_2]_2$ complexes containing titanium coordinated to only one of the two phenyl rings were obtained and their crystal structures were determined. $(\eta^6\text{-Benzene})Ti[(\mu\text{-}Cl)_2AlCl_2]_2$ and dimesitylmethane afforded the $(\eta^6\text{-mesitylene})Ti[(\mu\text{-}Cl)_2AlCl_2]_2$ complex which is isotypic with the known bromo analogue. This product shows that Friedel–Crafts scission of aryl–alkyl bonds occurs in such systems even under mild conditions.

Key words: Arene complexes; Titanium; Haloaluminates; Diarylmethane ligands; Crystal structure; X-ray diffraction.

Low-valent (π-arene)titanium complexes can be obtained either by a metal atom co-deposition with the arene at low temperatures, or by the Fischer–Hafner method which consists in the reduction of metal halide with aluminium in the presence of the aluminium halide, using the arene as solvent. The first method affords an access to bis(arene)titanium(0) on laboratory scale[1]. The Fischer–Hafner synthesis is a general method for obtaining arene complexes of low-valent transition metal complexes with haloaluminate ligands[2]. The (π-arene)titanium(II) complexes are formed according to Eq. (*1*) with the arene as solvent under reflux.

$$3\ TiX_4 + 4\ AlX_3 + 2\ Al + 3\ \text{arene} \rightarrow 3\ (\eta^6\text{-arene})Ti[(\mu\text{-}X)_2AlX_2]_2 \qquad (1)$$

The complexes with more basic aromatic ligands can be obtained by performing the above reaction in liquid aromatic hydrocarbons, in benzene solution of more basic arene hydrocarbon, or by the ligand exchange of the parent benzene complexes (η^6-benzene)Ti[(μ-X)$_2$AlX$_2$]$_2$ (X = Cl (**1**), Br (**2**)) with more basic ligands in benzene solution. This exchange of η^6-benzene runs to completion for trimethyl- up to hexamethylbenzene[3]. A number of complexes obtained in this way were structurally characterised: (η^6-C_6H_5Me)Ti[(μ-Cl)$_2$AlCl$_2$]$_2$ (ref.[4a]), (η^6-$C_6H_3Me_3$)Ti[(μ-Br)$_2$AlBr$_2$]$_2$ (ref.[4b]), (η^6-C_6Me_6)Ti[(μ-Cl)$_2$AlCl$_2$]$_2$ (ref.[4c]), (η^6-C_6Me_6)Ti[(μ-Br)$_2$AlBr$_2$]$_2$ (ref.[4d]). Surprisingly, analogous complexes with fused aromatic rings, whose basicity is much higher, have not been reported yet. A probable reason is that they strongly interact with the haloaluminate ligands, that leads to the decomposition of the arene complexes, similarly to the action of σ-electron-donor ligands[2a,5].

Replacement of benzene by the methyl substituted derivatives showed a strong effect on the catalytic properties of the (π-benzene)titanium(II) complexes in the highly selective cyclotrimerisation of butadiene to (*Z*,*E*,*E*,)-cyclododeca-1,5,9-triene. The more basic was the coordinated methyl substituted arene, the slower was its exchange with buta-1,3-diene. This was, however, partly compensated by using less acid aluminates, such as ethyl(halo)aluminates[6]. In this respect, we suggest that bent arylmethane derivatives have a potential to influence catalytic complexes either by binding two Ti(II) haloaluminate complexes in one molecule or by weakly coordinating to an aluminate group within the parent complex.

Here we report structures of the products from exchange reactions of compounds **1** and **2** with bis(pentamethylphenyl)methane and bis(2,4,6-trimethylphenyl)methane, that were carried out under mild conditions. The aim of this study is to establish whether these ligands are able to bind two titanium bis(tetrahaloaluminate) moieties or whether the bent diarylmethane ligands can influence the structure of the bis(tetrahaloaluminate)-titanium skeleton.

EXPERIMENTAL

General Data and Methods

The synthesis, purification and crystallisation procedures were carried out in all-sealed glass devices equipped with magnetically breakable seals, using vacuum technique. Infrared spectra (wavenumbers in cm^{-1}) were recorded on a Mattson Galaxy 2020 FTIR single-beam spectrometer. The KBr pellets were prepared in a glovebox (labmaster 130, mBraun) and were measured in a gas-proof cuvette under a nitrogen atmosphere. The UV-VIS spectra were recorded in the range of 280 to 2 000 nm on a Varian Cary 17D spectrophotometer, using all-sealed quartz cuvettes (Hellma). Energy dispersive X-ray analyses (EDAX) were carried out on a Zeiss DSM 962 scanning electron microscope equipped with an EDAX PV9800 analyser. The acceleration voltage was 25 kV. The samples were in contact with air only shortly before the measurement. Melting points were determined in sealed capillaries on a Thiele apparatus and were not corrected.

Chemicals

The solvents hexane and benzene were purified by conventional methods, dried by refluxing over $LiAlH_4$ and stored as solutions of "dimeric titanocene" $(\mu\text{-}C_{10}H_8)[(C_5H_5)Ti(\mu\text{-}H)_2]_2$ (ref.[7]). The complexes $(\eta^6\text{-}C_6H_6)Ti(AlCl_4)_2$ (**1**) and $(\eta^6\text{-}C_6H_6)Ti(AlBr_4)_2$ (**2**) were prepared as described earlier[8] and purified by precipitation with hexane from benzene solution. Bis(pentamethylphenyl)methane and bis(2,4,6-trimethylphenyl)methane were prepared by literature procedures[9].

Reactions of **1** or **2** with Diarylmethanes

The exchange reactions of **1** or **2** with bis(pentamethylphenyl)methane or bis(2,4,6-trimethylphenyl)methane were carried out by mixing saturated benzene solutions of the reagents in 2 : 1 and/or 1 : 1 molar ratios. The reaction mixtures were heated to 70 °C for 10 min while stirring, and then cooled to room temperature. The isolation procedures differed according to the nature and appearance of the product. The structures of the crystalline products were determined by X-ray diffraction analysis. Their chemical composition was corroborated by EDAX analyses. The amounts of unreacted diarylmethanes were determined by evaporating the mother liquor *in vacuo*, followed by quenching the residue with degassed water. The organic products were extracted with diethyl ether and the crystalline diarylmethanes were weighed.

[η^6-1,2,3,4,5-Pentamethyl-6-(2,3,4,5,6-pentamethylbenzyl)benzene]titanium(II)bis(di-μ-chlorodichloroaluminium) (**3**). Saturated benzene solutions of **1** (2.0 g, 4.3 mmol) and bis(pentamethylphenyl)methane (0.67 g, 2.2 mmol) were mixed, the mixture was warmed to 70 °C for 10 min and left standing at room temperature. The intense purple colour of compound **1** in solution faded while a purple solid precipitated. The purple mother liquor was decanted and the solid was extracted twice with benzene (20 ml). The solid was then dissolved in hot benzene (80 ml) and the solution was slowly cooled to room temperature in a Dewar vessel filled with water at 70 °C. In spite of this slow crystallisation, most of the product precipitated as a purple microcrystalline solid, with only a few crystals of the size suitable for X-ray diffraction analysis. The yield of the violet crystalline product was 1.48 g (88% based on bis(pentamethylphenyl)methane). Attempted crystallisation with a smaller amount of the product did not afford more crystals suitable for the crystallographic study; however, these were easily separated from the crystalline product.

Complex **3**: IR (KBr): 1 452 (m), 1 386 (m), 1 068 (w), 1 022 (w), 1 003 (w), 818 (w), 789 (w), 710 (w), 557 (s), 515 (s), 505 (s), 440 (s). EDAX (Kα): Al, Cl, Ti. M.p.: 200 °C (decomp.).

The mother liquor was evaporated *in vacuo* and quenched with water. Extraction with diethyl ether yielded a trace of bis(pentamethylphenyl)methane.

An analogous experiment with **1** (1.0 g, 2.15 mmol) and bis(pentamethylphenyl)methane (0.61 g, 2.0 mmol) gave 1.35 g of **3** (90%). Work-up of the mother liquor afforded bis(pentamethylphenyl)methane (18 mg, 0.06 mmol).

[η^6-1,2,3,4,5-Pentamethyl-6-(2,3,4,5,6-pentamethylbenzyl)benzene]titanium(II)bis(di-μ-bromodibromoaluminium) (**4**). Benzene solutions of **2** (1.0 g, 1.22 mmol) and bis(pentamethylphenyl)methane (0.38 g, 1.22 mmol) were used for the reaction. Slow cooling to room temperature gave a violet oil which separated from an intense blue solution. The solution was concentrated to the half of the volume and decanted from the oil. The latter was dissolved in hot benzene (60 ml) and crystallised by slow cooling. The crude crystalline product was recrystallised from benzene to give blue crystals of **4**. Yield 1.05 g (82%).

Unreacted bis(pentamethylphenyl)methane: 10 mg. The reaction with reagents in 2 : 1 molar ratio gave the same yield of **4** but no unreacted diarylmethane was detected.

Complex **4**: UV-VIS (benzene): 780, 580, 390. IR (KBr): 1 450 (m), 1 385 (m), 1 263 (w), 1 097 (w), 1 068 (w), 1 022 (w), 1 001 (w), 576 (w), 542 (w), 446 (s), 413 (s). EDAX (Kα): Al, Ti, Br. M.p.: 230 °C (decomp.).

[η^6-1,3,5-Trimethyl-2-(2,4,6-trimethylbenzyl)benzene]titanium(II)bis(di-μ-bromodibromoaluminium) (**5**). The reaction of **2** (2.0 g, 2.44 mmol) and dimesitylmethane (0.34 g, 1.37 mmol) in benzene solutions gave a nearly black precipitate in a purple-blue solution. About half of the solvent was distilled off and, after standing overnight, the mother liquor was poured off. The product was washed with benzene (10 ml) and then dissolved in benzene (60 ml) at 70 °C. Large blue prismatic crystals were obtained by slow cooling of the solution. The mother liquor was concentrated to give another, minor crop of crystals. The total yield of **5** was 1.17 g (76% based on **2**). Work-up of the mother liquor did not give dimesitylmethane.

Complex **5**: IR (KBr): 1 610 (w), 1 572 (w), 1 535 (w), 1 481 (m), 1 467 (m), 1 446 (m), 1 377 (m), 1 022 (w), 897 (w), 862 (w), 451 (s), 408 (s). EDAX (Kα): Al, Ti, Br. M.p.: 205 °C (decomp.)

(η^6-1,3,5-Trimethylbenzene)titanium(II)bis(di-μ-chlorodichloroaluminium) (**6**). The reaction of **1** (1.0 g, 2.1 mmol) with dimesitylmethane (0.30 g, 1.2 mmol) turned the original purple colour of the solution to dark violet. A dark oil separated from the solution when concentrating the solution *in vacuo*, that, however, did not crystallise upon cooling. The oil was dissolved in benzene (20 ml) and then hexane was added very slowly (during 8 h). By this procedure, a dark violet crystalline material precipitated from the solution. The mother liquor was removed and the solid product was crystallised from benzene by adding hexane through the vapour phase. The yield of dark violet crystalline **6** was 0.51 g (85% based on dimesitylmethane, suggesting that the mesitylene ligand is generated from dimesitylmethane). The mother liquor was not worked up and organic products were not determined.

Complex **6**: IR (KBr): 1 564 (m), 1 460 (m), 1 383 (m), 1 307 (w), 1 037 (m), 879 (m), 683 (w), 563 (s), 499 (s), 441 (m), 434 (m). EDAX (Kα): Al, Cl, Ti. M.p.: 160 °C (decomp.).

Crystal Structure Analysis

The single crystal X-ray structure determinations were performed at room temperature on a STOE IPDS imaging plate system using graphite monochromated MoKα radiation (λ = 0.71073 Å). Crystallographic data are summarised in Table I. Suitable crystals were mounted in a glovebox (labmaster 130, mBraun) in Lindemann glass capillaries. The capillaries were closed with sealing wax. The intensity data were collected in the oscillation mode. The data reduction was performed with the program X-RED (ref.[10]). The structures were solved by direct methods[11]. The non-hydrogen atoms were localised by difference Fourier synthesis and refined anisotropically using full-matrix least-squares methods on F^2, applying variance based weighting schemes[12]. The hydrogen atoms were included in their idealised positions

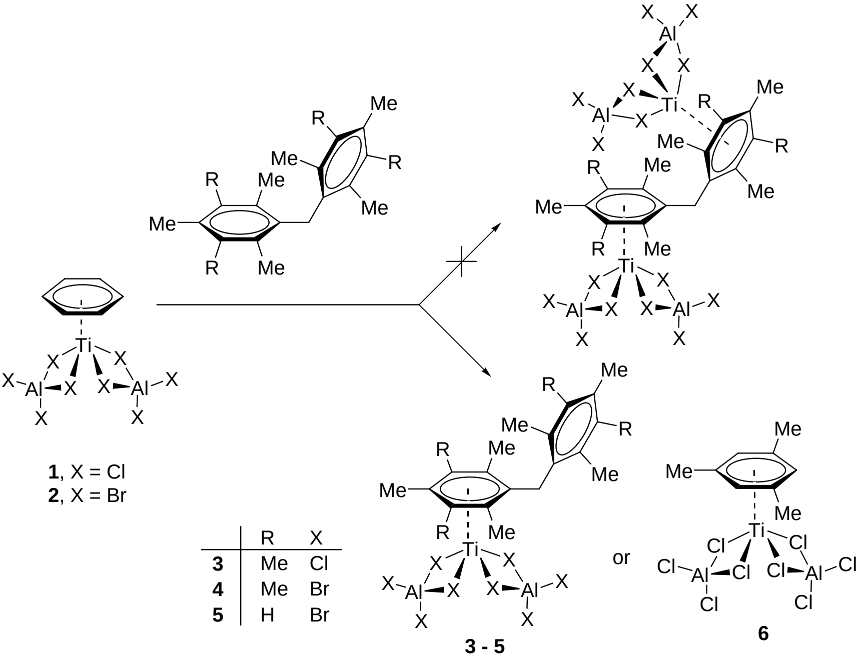
TABLE I
Crystal data and measurement parameters of compounds **3**, **4**, **5**, and **6**

Parameter	Compound			
	3	**4**	**5**	**6**
Formula	$C_{23}H_{32}Al_2Cl_8Ti$	$C_{23}H_{32}Al_2Br_8Ti$	$C_{19}H_{24}Al_2Br_8Ti$	$C_9H_{12}Al_2Cl_8Ti$
M	693.9	1 049.6	993.5	505.6
Crystal colour, habit	violet, prism	blue, prism	blue, prism	violet, prism
Crystal size, mm	0.5 × 0.4 × 0.3	0.4 × 0.4 × 0.3	0.4 × 0.3 × 0.3	0.5 × 0.5 × 0.4
System	monoclinic	monoclinic	monoclinic	orthorhombic
Space group Z	$P2_1/n$	$P2_1/n$	$P2_1/n$	$Pbca$
Z	4	4	4	8
a, Å	15.654(6)	15.876(4)	10.497(3)	8.574(2)
b, Å	12.862(3)	12.953(3)	24.624(6)	13.571(2)
c, Å	16.219(6)	16.748(4)	11.891(4)	35.743(7)
β, °	103.04(2)	103.04(2)	99.97(3)	
U, Å^3	3 156(2)	3 355.4(14)	3 027(2)	4 951(2)
D_{calc}, g cm^{-3}	1.461	2.078	2.180	1.615
μ(MoKα), mm^{-1}	1.017	9.847	10.908	1.510
θ range for data collected, °	2.60–28.27	2.01–24.16	1.56–24.10	2.28–24.13
Reflection collected	39 316	28 196	25 938	30 974
Independent reflections/R_{int}	7 648/0.0710	5 271/0.1168	4 714/0.1461	3 287/0.0646
Refined parameters	308	307	281	187
GooF on F^2	0.948	0.897	0.858	1.073
R_1/wR_2 [$I > 2\sigma(I)$], %	6.44/16.18	4.79/9.21	4.34/7.70	4.85/12.42
R_1/wR_2 (all data), %	11.63/19.49	10.61/10.56	9.81/8.83	6.53/13.13
Extinction coefficient	0.0161(14)	0.0161(14)	0	0
E_{max}, E_{min}, e Å^{-3}	0.507, –0.471	0.66, –0.690	0.640, –0.470	0.445, –0.334

using a riding model. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-134041 (**3**), CCDC-134042 (**4**), CCDC-134043 (**5**), and CCDC-134044 (**6**). Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk. (ORTEP plots of **3**, **5** and **6** see Figs 1–3).

RESULTS AND DISCUSSION

Complexes **1** and **2** reacted with bis(pentamethylphenyl)methane and complex **2** with dimesitylmethane in a unique way (Scheme 1) affording (π-arene)-titanium(II) complexes **3**, **4**, and **5** in high yields.



	R	X
3	Me	Cl
4	Me	Br
5	H	Br

SCHEME 1

A two-fold molar excess of **1** or **2** with respect to the diarylmethanes did not give complexes $CH_2[(\eta^6\text{-arene})Ti\{(\mu\text{-}X)_2AlX_2\}_2]_2$ containing 2 Ti atoms per diarylmethane, but the excess complexes **1** and **2** remained unreacted and were removed with the mother liquors. Surprisingly, the reaction between **1** and dimesitylmethane ran in a different way, yielding $(\eta^6\text{-mesitylene})Ti\{(\mu\text{-}Cl)_2AlCl_2\}_2$ (**6**) as the only titanium complex isolated from the reaction mixture. A high yield of **6** (85%) indicates that the cleavage of dimesitylmethane was followed by a specific hydrogen transfer to the aro-

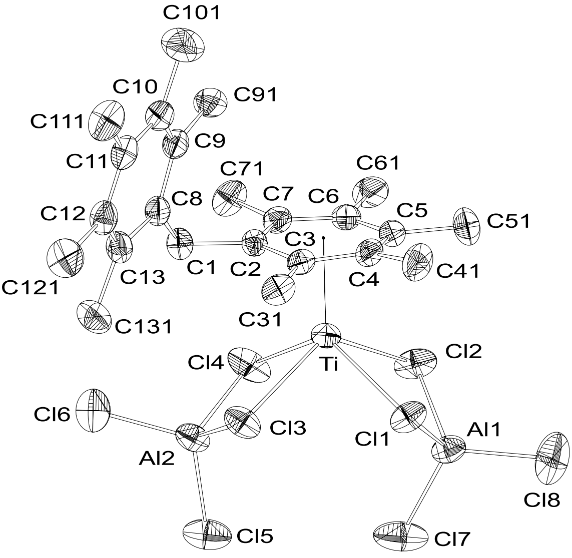


FIG. 1
ORTEP plot of **3** with thermal ellipsoids drawn at the 50% probability level

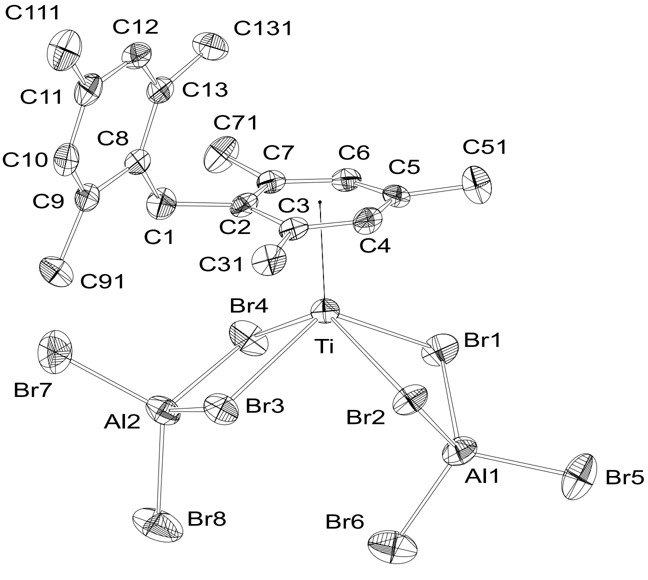


FIG. 2
ORTEP plot of **5** with thermal ellipsoids drawn at the 50% probability level

matic radical or cation. The other organic products of this apparent Friedel–Crafts cracking were not studied. Nonetheless, this negative result shows that complexes **3**–**5** could hardly be obtained from the Fischer–Hafner synthesis, with benzene solutions of the diarylmethanes refluxed in the presence of a large amount of $AlCl_3$. The formation of mesitylene from dimesitylmethane is in line with the results of Tsuge *et al.*[13] who studied reactions of diarylmethanes in the presence of strong Lewis acids like $AlCl_3$ and, for methyl substituted diphenylmethanes, they found mesitylene among other products.

The (π-arene)titanium(II) complexes are extremely sensitive to air and moisture that cause evolution of $AlCl_3$ exhibiting strong Lewis acidity. It was shown that the (π-arene)titanium(II) complexes react with the hydroxyl groups which are inherently present in glass[6c]. It is therefore difficult to generalise the above results, although all the experiments were repeated twice. The compounds obtained were characterised by UV-VIS spectra, showing a sharp and very intense charge transfer band at 400 nm; however, this is little sensitive to the number of methyl substituents on the coordinated aromatic rings[6d,8,14]. The infrared spectra of samples in KBr pellets have not been assigned yet. There is a danger that the KBr matrix may react with tetrahaloaluminate ligands to give species like $[K(AlBrCl_3)]$. Thus, in addition to a semiquantitative elemental analysis by EDAX, the main information on the composition and structure of the obtained complexes **3**–**6** is drawn from the X-ray crystal study.

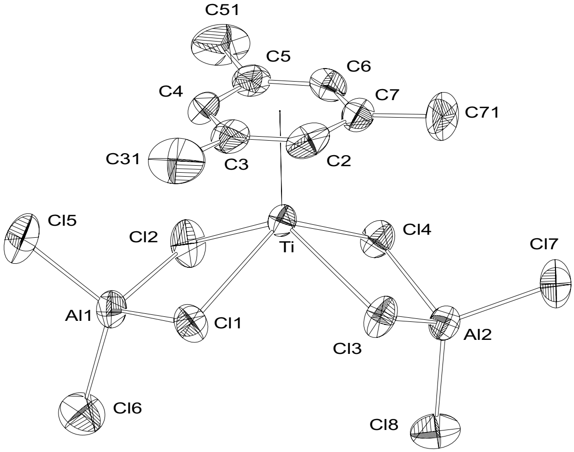


FIG. 3
ORTEP plot of **6** with thermal ellipsoids drawn at the 50% probability level

Compound **6** is isotypic to the analogous π-mesitylene complex $(\eta^6\text{-}C_6H_3Me_3)Ti\{(\mu\text{-}Br)_2AlBr_2\}_2$ (compound **7**)[4b] showing nearly the same lattice constants and position of the titanium in the cell (values of **7** in brackets): a = 8.574 Å, b = 13.571 Å, and c = 35.743 Å (9.988, 13.884, and 37.196 Å); x, y, z for Ti: 0.0645, –0.1605, and –0.1227 (0.062, –0.138, and –0.121). The slightly larger cell parameters are apparently due to a larger radius of bromine.

Compounds **3** and **4** exhibit nearly the same lattice constants, the bromo compound **4** possessing a slightly larger cell volume. Differences, however, are found in some geometrical values (*vide infra*). The similarity of the investigated structures is further demonstrated by very similar average distances of the Ti–C, Ti–(μ-X), Al–(μ-X), and $Al\text{–}X_{terminal}$ bonds (Table II), as well as by similar valence angles (μ-X)–Ti–(μ-X) (range: 76.10(5) to 80.24(5)°) and Ti–(μ-X)–Al (range: 86.32(7) to 93.02(7)°). Rather similar molecular structures were also established for other titanium π-arene chloroaluminate complexes containing hexamethylbenzene[4c] or benzene[15] as ligand.

The dominant structural feature for all these compounds is the pentacoordinate titanium atom with the four (μ-X) atoms forming the base of a

TABLE II
Selected bond distances (in Å) of compounds **3**, **4**, **5**, and **6**

Distance	Compound			
	3	**4**	**5**	**6**
Ti–CE[a]	2.053(4)	2.065(9)	2.082(8)	2.053(4)
$(Ti\text{–}C)_{av}$	2.49(3)	2.50(3)	2.50(6)	2.51(2)
$(Ti\text{–}X)_{av}$	2.616(6)	2.78(2)	2.77(2)	2.60(1)
$(Al\text{–}(\mu\text{-}X))_{av}$	2.163(3)	2.321(6)	2.337(7)	2.173(3)
$(Al\text{–}X_{term})_{av}$	2.080(7)	2.244(5)	2.24(1)	2.079(7)
$(C\text{–}C)_{ring}$[b]	1.408(5)	1.41(1)	1.40(1)	1.378(5)
$C\text{–}CH_3$[b]	1.513(7)	1.51(1)	1.51(1)	1.504(7)
$(C\text{–}C)_{ring}$[c]	1.399(5)	1.40(2)	1.39(2)	–
$C\text{–}CH_3$[c]	1.506(3)	1.515(3)	1.50(2)	–
$(C\text{–}C)_{bridge}$	1.52(1)	1.53(1)	1.529(9)	–

[a] CE, centre of the coordinated phenyl ring. [b] Coordinated ring. [c] Non-coordinated ring.

tetragonal pyramid and with the π-bonded arene ligand at its apex. The bridging halogen atoms lie nearly in one plane, forming a distorted trapezoid with almost similar side lengths and angles close to 90° (**3**: 3.29 ± 0.05 Å, 90.0 ± 0.3°; **4**: 3.51 ± 0.03 Å, 90 ± 1°; **5**: 3.54 ± 0.02 Å, 90 ± 3°; **6**: 3.29 ± 0.05 Å, 90 ± 1°). The least-square planes formed by the terminal halogen and aluminium atoms are in all cases perpendicular to the planes formed by the bridging halogen and aluminium atoms. The least-square planes of the coordinated arene ring and that of the bridging halogen atoms are nearly parallel. Differences in the structures are found in the orientation of the diphenylmethane ligand towards the inorganic framework. This is expressed by the angle between the Al–Al and the C2–C5 vectors (**3**: 14.1°; **4**: 20.1°; **5**: 27.7°). Another difference lies in the bending of the four-membered rings (μ-X)–Al–(μ-X)–Ti. In all cases, one is rather planar whereas the other is bent around the (μ-X)–(μ-X) vector (**3**: 3.8 and 25.9°; **4**: 5.4 and 39.5°; **5**: 7.5 and 34.7°; **6**: 4.3 and 17.0°; **7**: 2.4 and 18°). It is evident that in the isotypic compounds **6** and **7** only slight differences occur, as expected, whereas the values for **3** and **4** differ by 1.6 and 13.6°, respectively. In the compounds **3**, **4**, and **5**, the non-coordinated part of the ligand is situated in the direction opposite to the bent $AlCl_4$ group and, hence, an intramolecular interaction as a reason can be excluded. Since no special intermolecular contacts are observed for the investigated compounds, packing effects should be responsible for the variations in the described geometric parameters.

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