Reactivity of Titanium(II) Arene Derivatives with Substituted Alkynes. Cyclooligomerization Reactions and Crystal and Molecular Structure of $[\eta^4\text{-}C_4(C_6H_5)_4]Ti[(\mu\text{-}Br)_2(AlBr_2)]_2$ *)

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By treating $Ti(\eta^6\text{-toluene})[(\mu\text{-}X)_2(AlX_2)]_2$ (X = Cl: **1a**, X = Br **1b**) with C_2R_2 (R = Me, Ph) tetraorganylcyclobutadiene complexes of formula $Ti(\eta^4\text{-}C_4R_4)[(\mu\text{-}X)_2(AlX_2)]_2$ (R = Ph, X = Cl: **2a**, X = Br: **2b**; R = Me, X = Br: **3b**) have been obtained in good yields. Compound **2b** has been studied by X-ray diffraction methods. The titanium atom possesses an approximate square pyramidal coordination, the apical position being occupied by the symmetrically bonded tetraphenylcyclobutadiene ring, the four bridging bromides to the two $AlBr_2$ groups forming the base of the pyramid, 0.99 Å away from the titanium atom. The tetrabromoaluminato moiety of **2b** can be substituted by carbocyclic anionic ligands, such as Cp and COT, and the corresponding complexes **4** and $Ti(\eta^4\text{-}C_4Ph_4)(COT)$ were obtained. The spectroscopic study of the $Ti(\eta^6\text{-benzene})[(\mu\text{-}X)_2(AlX_2)]_2$/diphenylacetylene (DPA) system (X = Cl: **5a**, X = Br: **5b**) has revealed the existence of three products, corresponding to the 1:1, 1:2, and 1:3 molar ratios. The possible role of the known $AlX_3 \cdot C_4R_4$ complexes in this reaction is discussed. The cyclotrimerization reactions of substituted acetylenes in the presence of η^6-arene titanium(II) complexes as precursors have been studied. In toluene or methylcyclohexane $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$ was found to catalyze the formation of alkyl-substituted aromatic hydrocarbons from 2-butyne, phenylacetylene, and 1-hexyne at about 80°C over 15 h with turnovers (moles of converted alkyne per mole of titanium) of about 520, 900, and 990, respectively. The cyclooligomerization of DPA in the presence of $Ti(\eta^6\text{-benzene})[(\mu\text{-}X)_2(AlX_2)]_2$ (X = Cl, Br) was studied in detail. The activity of the chloro derivative **5a** is higher than that of the bromide catalytic precursor **5b**. In addition to hexaphenylbenzene and octaphenylcyclooctatetraene, other oligomerization by-products (triphenylethylene, 1,1,2,2-tetraphenylethane, 1,2,3-triphenylnaphthalene, and 1,2,3-triphenylazulene) were observed, whose formation was drastically reduced in the presence of alkyl aluminium halides.

Reaktivität von Titan(II)-Aren-Derivaten mit substituierten Alkinen. Cyclooligomerisations-Reaktionen und Kristall- und Molekülstruktur von $[\eta^4\text{-}C_4(C_6H_5)_4]Ti[(\mu\text{-}Br)_2(AlBr_2)]_2$

Durch Umsetzung von $Ti(\eta^6\text{-toluol})[(\mu\text{-}X)_2(AlX_2)]_2$, (X = Cl: **1a**, X = Br: **1b**) mit C_2R_2 (R = Me, Ph) wurden Tetraorganylcyclobutadien-Komplexe der Zusammensetzung $Ti(\eta^4\text{-}C_4R_4)[(\mu\text{-}X)_2(AlX_2)]_2$ (R = Ph, X = Cl: **2a**, Br: **2b**; R = Me, X = Br: **3**) in guten Ausbeuten erhalten. Verbindung **2b** wurde mit Röntgenbeugungsmethoden untersucht. Das Titan-Atom ist näherungsweise quadratisch-pyramidal koordiniert, wobei die apikale Position von dem symmetrisch gebundenen Tetraphenylcyclobutadien-Ring eingenommen wird und die vier zu den $AlBr_2$-Gruppen verbrückenden Brom-Atome die 0.99 Å vom Titan-Atom entfernte Basisfläche der Pyramide bilden. Die Tetrabromoaluminat-Gruppe in **2b** kann durch carbocyclische anionische Liganden wie Cp und COT ersetzt werden, wobei die entsprechenden Komplexe **4** und $Ti(\eta^4\text{-}C_4Ph_4)(COT)$ erhalten wurden. Die spektroskopische Untersuchung des Systems $Ti(\eta^6\text{-benzol})[(\mu\text{-}X)_2(AlX_2)]_2$/diphenylacetylen (DPA) (X = Cl: **5a**, X = Br: **5b**) erbrachte den Nachweis dreier den molaren Verhältnissen von 1:1, 1:2 und 1:3 entsprechender Produkte. Die mögliche Rolle des $AlX_3 \cdot C_4R_4$-Komplexes in dieser Reaktion wird diskutiert. Die Cyclotrimerisierungsreaktionen von substituiertem Acetylen in Gegenwart von η^6-Aren-Titan(II)-Komplexen als Vorstufen wurden untersucht. Es zeigte sich, daß $Ti(\eta^6\text{-toluol})[(\mu\text{-}Br)_2(AlBr_2)]_2$ in Toluol oder Methylcyclohexan bei ca. 80°C im Verlaufe von 15 h die Bildung von Alkyl-substituierten aromatischen Kohlenwasserstoffen aus 2-Butin, Phenylacetylen und 1-Hexin mit einem Umsatz (mol abreagierendes Alkin pro mol Titan) von 600, 900 bzw. 990 katalysiert. Die Cyclooligomerisierung von DPA in Gegenwart von $Ti(\eta^6\text{-benzol})[(\mu\text{-}X)_2(AlX_2)]_2$ (X = Cl, Br) wurde ausführlich untersucht. Die Aktivität des Chloro-Derivats **5a** übersteigt die der Bromo-Katalysator-Vorstufe **5b**. Außer Hexaphenylbenzol und Octaphenylcyclooctatetraen wurden weitere Nebenprodukte der Oligomerisierung beobachtet (Triphenylethen, 1,1,2,2-tetraphenylethan, 1,2,3-Triphenylnaphthalin und 1,2,3-Triphenylazulen), deren Bildung in Gegenwart von Alkylaluminiumhalogeniden deutlich verringert war.

In 1959, Natta and co-workers reported[1)] that the reaction of $TiCl_4$ with the $Al/AlCl_3$/benzene system yields a derivative containing both titanium and aluminium. Later, this compound was rec-

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ognized to be a π-arene derivative of titanium(II)[2], the synthesis was extended to other methyl-substituted aromatic hydrocarbons as ligands, and the chemistry of these compounds was extensively studied especially as far as the chloro derivatives were concerned[3].

These complexes, containing titanium in the relatively uncommon oxidation state II (d^2 configuration) of general formula $Ti(\eta^6\text{-arene})[(\mu\text{-}X)_2(AlX_2)]_2$, show a moderate catalytic activity in the polymerization of ethylene, propylene[1,2a], a high catalytic activity and selectivity in the cyclotrimerization of butadiene[4], and they readily undergo the arene exchange reaction[3a]. Moreover, it has been shown by ESR spectra[5] that these compounds undergo oxidation with cyclopentadiene to the corresponding cyclopentadienyl titanium(III) species.

In a preliminary communication[6a] and in an earlier paper[6b], some of us have reported the isolation of the bromo and the iodo derivatives, which are usually more easily handled, probably due to their lower tendency to undergo hydrolysis in the presence of adventitious moisture. The reaction of the toluene derivative with diphenylacetylene (DPA) was reported[6a] to give a compound to which the structure of a tetraphenylcyclobutadiene complex was assigned on the basis of spectroscopic and chemical evidence. On the other hand, 2-butyne, over prolonged reaction times, was reported[4b,6] to yield the η^6-hexamethylbenzene titanium(II) compound, starting from $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$, thus showing that the titanium(II) derivatives of this class containing the less methyl-substituted arene could promote the cyclooligomerization of substituted acetylenes.

Cyclotrimerization of DPA and other substituted acetylenes is an interesting problem. Most transition metals catalyze this reaction[7], and tetraphenylcyclobutadiene or metallacyclopentadiene complexes were often suggested as catalytic intermediates. In the case of the titanium-based catalysts, the cyclotrimerization of DPA was accomplished with the $TiCl_4/AlR_3$[8,9] Ziegler-Natta system. Drefahl and co-workers[10] noticed that a low amount of a tetramer was obtained in addition to hexaphenylbenzene (HPB) with the $TiCl_4/AlR_3$ system at the nearly optimum molar ratio Ti:Al of 1:1. The DPA/Ti turnover was, however, only about 10. Bis(cyclopentadienyl)titanacyclopentadienes were obtained in the reduction of dichlorobis(cyclopentadienyl)titanium(IV), Cp_2TiCl_2, with magnesium in THF in the presence of DPA[11], and larger titanacycles were formed with phenylacetylene or 3-hexyne[12]. The reduction of $TiCl_3$ with magnesium in THF in the presence of an excess of DPA yielded the cyclobutadiene complex $[Mg_2Cl_3(THF)_6][Ti(\eta^4\text{-}C_4Ph_4)Cl_3]$[13], whereas in the additional presence of COT the complex $Ti(\eta^4\text{-}C_4Ph_4)(COT)$ was obtained[14b]. The catalytic activity of these complexes was either low[12] or substantially absent[13].

In this paper, the detailed preparative work concerning the tetraorganylcyclobutadiene complexes of titanium, $Ti(\eta^4\text{-}C_4R_4)[(\mu\text{-}X)_2(AlX_2)]_2$, is reported, together with the crystal and molecular structure of the bromo/phenyl derivative. Besides, several reactions of the $\pi\text{-}C_4Ph_4$ titanium complexes are reported, and the catalytic properties of the π-arene and π-cyclobutadiene derivatives in the oligomerization of substituted acetylenes are examined by both product analysis and UV/VIS spectroscopy.

Synthesis of the Tetraorganylcyclobutadiene Complexes of Titanium and X-ray Structure Determination of the Tetraphenyl Derivative

The reaction of $Ti(\eta^6\text{-toluene})[(\mu\text{-}X)_2(AlX_2)]_2$ (**1**) with two equivalents of DPA or 2-butyne in toluene at room temperature or below (0°C) afforded the tetraorganylcyclobutadiene derivatives **2** and **3** [eq. (1)]. The reaction is very fast and the products are obtained as diamagnetic solids, extremely reactive towards oxygen, moisture, and Lewis bases.

$$\mathbf{1} + 2\,\mathrm{DPA} \longrightarrow (\eta^4\text{-}C_4Ph_4)Ti[(\mu\text{-}X)_2(AlX_2)]_2 + \text{toluene} \qquad (1)$$
$$R = Ph, X = Cl: \mathbf{2a}; R = Ph, X = Br: \mathbf{2b};$$
$$R = Me, X = Br: \mathbf{3b}^{15)}$$

The reaction according to eq. (1) was usually carried out with crude solutions of **1** obtained by treating TiX_4 with Al and AlX_3 in toluene followed by filtration of unreacted aluminium. Although the stoichiometric amount of AlX_3 [see eq. (1) of ref.[6b]] was used to prepare the solutions of the η^6-arene titanium(II) complex, the presence of AlX_3 in these solutions cannot be excluded. However, the same products were obtained when solid preformed compound **1** was treated with the disubstituted acetylenes. In view of the fact that small equilibrium concentrations of AlX_3 may be present by dissociation of **1** and in connection with the spectroscopic study of this reaction discussed below (*vide infra*), it is believed that the presence of AlX_3 is essential for the dimerization of C_2R_2 to give the tetraorganylcyclobutadiene ligand.

In the case of DPA, although a transient green colour was observed during the addition of the η^6-arene complex in toluene solution to the toluene solution of the alkyne (intractable oils were obtained in the reverse order of addition), compounds different from **2** have never been isolated. By operating with a Ti/alkyne molar ratio of 1:1, correspondingly low yields of **2** were obtained.

The presence of the tetraphenylcyclobutadiene ring in **2** was suggested by the infrared spectrum of **2b** showing, beyond the absorptions typical of the aromatic ring, a strong absorption at 1393 cm^{-1} assigned[16] to the C–C stretching vibration of the metal-coordinated four-membered ring.

Compound **2b** is not affected by CO at atmospheric pressure, but it reacts with two equivalents of TlCp in toluene to give the titanatetraphenylcyclopentadiene derivative **4**[14a] in practically quantitative yields [eq. (2)] and with solvent-free K_2COT to give the known $Ti(\eta^4\text{-}C_4Ph_4)(COT)$[14b] [eq. (3)].

$$\mathbf{2b} \xrightarrow{TlCp} Cp_2Ti\overline{C(Ph)=C(Ph)C(Ph)=C}(Ph) \qquad (2)$$

4

$$\mathbf{2b} \xrightarrow{K_2COT} Ti(\eta^4\text{-}C_4Ph_4)(COT) \qquad (3)$$

In order to conclusively establish the structure of the compound obtained by the reaction of **1** and in view of the still limited number of crystallographically studied titanium organometallic derivatives with carbocyclic ligands, it was decided to study the more easily crystallizable bromo derivative by X-ray diffraction methods.

The structure (Figures 1 and 2) consists of a tetraphenylcyclobutadiene ligand symmetrically (the titanium–carbon bond distances to the carbocyclic ligand are identical within the experimental error, see Table 1) bonded to titanium, which is surrounded by four bridging bromides to the $AlBr_2$ fragments, thus completing the idealized square pyramidal geometry.

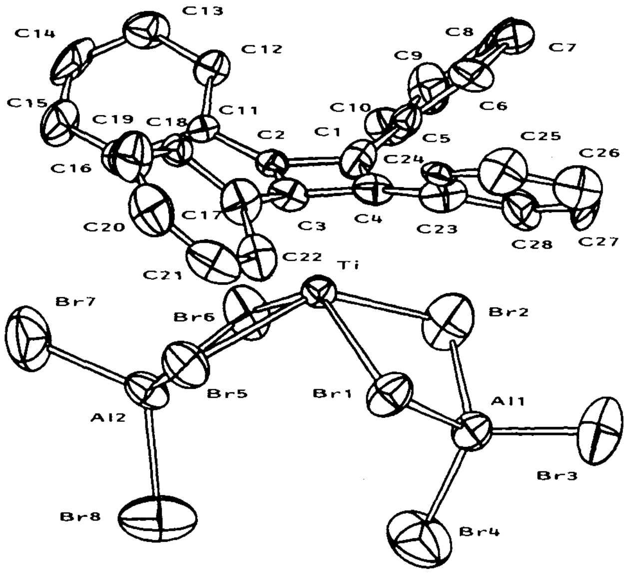

Figure 1. Perspective view of $Ti(\eta^4\text{-}C_4(C_6H_5)_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ (thermal ellipsoids are drawn at 50% probability level)

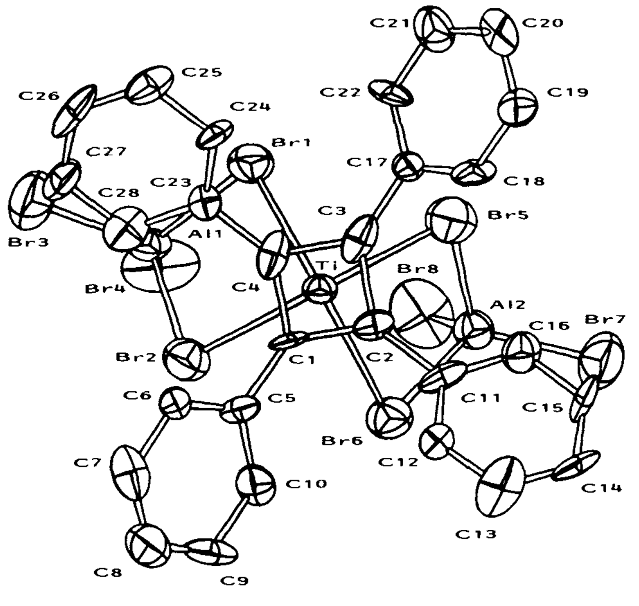

Figure 2. ORTEP projection of $Ti(\eta^4\text{-}C_4(C_6H_5)_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ in the $C_4(C_6H_5)_4-Ti$ direction

Table 1. Selected interatomic distances [Å] and angles [°] in $Ti(\eta^4\text{-}C_4(C_6H_5)_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ (estimated standard deviations in parentheses refer to the last significant digit)

Ti-Br1	2.682(4)	Ti-Br5	2.665(4)
Ti-Br2	2.673(4)	Ti-Br6	2.652(4)
Ti-C1	2.27(2)	Ti-C3	2.30(2)
Ti-C2	2.30(2)	Ti-C4	2.27(3)
Br1-Al1	2.351(6)	Br5-Al2	2.295(7)
Br2-Al1	2.337(7)	Br6-Al2	2.361(6)
Br3-Al1	2.218(8)	Br7-Al2	2.211(7)
Br4-Al1	2.214(7)	Br8-Al2	2.220(7)
C1-C2	1.45(3)	C1-C5	1.42(2)
C1-C4	1.47(3)	C2-C11	1.47(3)
C2-C3	1.48(3)	C3-C17	1.48(2)
C3-C4	1.47(3)	C4-C23	1.49(3)
Br1-Ti-Br2	81.4(1)	Br2-Ti-Br5	140.6(2)
Br1-Ti-Br5	81.9(1)	Br2-Ti-Br6	83.7(1)
Br1-Ti-Br6	132.0(2)	Br5-Ti-Br6	81.6(1)
Br1-Ti-C1	125.3(5)	Br5-Ti-C1	133.0(5)
Br1-Ti-C2	138.9(5)	Br5-Ti-C2	96.4(4)
Br1-Ti-C3	101.9(5)	Br5-Ti-C3	85.2(5)
Br1-Ti-C4	91.6(5)	Br5-Ti-C4	119.7(4)
Br2-Ti-C1	85.2(4)	Br6-Ti-C1	98.2(5)
Br2-Ti-C2	119.3(4)	Br6-Ti-C2	87.7(5)
Br2-Ti-C3	133.2(6)	Br6-Ti-C3	121.1(5)
Br2-Ti-C4	96.2(5)	Br6-Ti-C4	135.3(5)
C1-Ti-C2	37.1(6)	C2-Ti-C3	37.5(7)
C1-Ti-C3	54.6(6)	C2-Ti-C4	53.5(8)
C1-Ti-C4	37.7(6)	C3-Ti-C4	37.6(7)
Ti-Br1-Al1	90.4(2)	Ti-Br5-Al2	89.0(2)
Ti-Br2-Al1	90.9(2)	Ti-Br6-Al2	88.0(2)
Br1-Al1-Br2	96.2(2)	Br5-Al2-Br6	96.5(3)
Br1-Al1-Br3	109.4(3)	Br5-Al2-Br7	107.5(3)
Br1-Al1-Br4	113.8(3)	Br5-Al2-Br8	110.1(4)
Br2-Al1-Br3	111.8(3)	Br6-Al2-Br7	113.0(3)
Br2-Al1-Br4	109.6(3)	Br6-Al2-Br8	107.7(2)
Br3-Al1-Br4	114.6(4)	Br7-Al2-Br8	119.5(3)
C2-C1-C4	89(1)	C2-C3-C4	88(1)
C2-C1-C5	134(2)	C2-C3-C17	137(2)
C4-C1-C5	134(2)	C4-C3-C17	134(2)
C1-C2-C3	91(1)	C1-C4-C3	91(2)
C1-C2-C11	133(2)	C1-C4-C23	136(2)
C3-C2-C11	135(2)	C3-C4-C23	131(2)

As a matter of fact, the structure is similar to that of the π-arene derivatives reported by Thewalt and co-workers[2c,d], the apical position of the idealized square pyramid being occupied by the carbocyclic ligand in both cases. The closest approach to our structure is that reported by the Liefde-Meijer and co-workers[13] for the anionic tetraphenylcyclobutadiene complex $[(C_4Ph_4)TiCl_3]^{\ominus}$. The C–C bond distances within the carbocyclic ligand in our compound average 1.47(3) Å, which is virtually the same as the 1.45(6) Å distance found by de Liefde-Meijer and co-workers for their compound. In our compound, the titanium atom is 0.99 Å away from the best plane passing through the bridging bromides, and the titanium–carbon distance from the centroid of the carbocyclic ligand is 2.03 Å, the analogous distances reported by Thewalt and co-workers for $Ti(\eta^6\text{-}C_6Me_6)[(\mu\text{-}Cl)_2(AlCl_2)]_2$[2c] and $Ti(\eta^6\text{-benzene})[(\mu\text{-}Cl)_2(AlCl_2)]_2$[2d] being 1.19, 2.06, and 1.11, 2.07 Å, respectively. Recently, the structure of $Ti(\eta^6\text{-benzene})[(\mu\text{-}X)_2(AlX_2)]_2$ (X = Br, I)[17], has been reported, and a titanium–carbon distance from the centroid of the carbocyclic ligand of 2.07 Å has been measured.

The titanium–bromine bond distance of 2.66 Å in **2b** compares quite well with the values of 2.728(7), 2.769(7), 2.722(2), and 2.705(3) Å found in $Ti(\eta^6\text{-benzene})[(\mu\text{-}Br)_2(AlBr_2)]_2$[17] and in $(CH_3C_5H_4)_2Ti(\mu\text{-}Br)_2Ti(CH_3C_5H_4)_2$[18], respectively. Concerning the aluminum–bromine bond distances, the longer (average, 2.34 Å) and the shorter (average, 2.22 Å) values are very similar to those reported by Troyanov and Rybakov (average 2.33 and 2.24 Å)[17] and compare well with the bridging (2.41 Å) and the terminal (2.22 Å) Al – Br bond distances, respectively, in Al_2Br_6[19]. Finally, the phenyl rings are rotated around the C – C bond connecting them to the cyclobutadiene moiety, the angles of tilt ranging from 29 to 39°. Moreover, the same C – C bonds are bent away from titanium, the deviations from the coplanarity with the best plane of the C_4 ring ranging from 9 to 13°. Both features, probably necessary in order to minimize the steric hindrance, are frequently encountered, to a greater or smaller extent, in other tetraphenylcyclobutadiene metal complexes, namely those of manganese[20], cobalt[21], rhodium[22], nickel[23], molybdenum[24], and ruthenium[25].

The tetraphenylcyclobutadiene complex **2b** is characterized by an intense absorption in the electronic spectrum at 486 nm (both in benzene and toluene). It is not possible to give a reliable value of the molar extinction coefficient in view of the prompt decomposition of the compound in the presence of adventitious moisture or air; however, ε should be around 20000 M^{-1} cm^{-1} for this band. The high intensity of this unique band suggests that we are dealing with a charge-transfer type of electronic transition. It is therefore tempting to suggest that our tetraorganyl complexes should be better regarded as titanium(IV) derivatives of the $[C_4Ph_4]^{2-}$ anion. In this connection, it is interesting to note that the electronic spectra of the η^6-arene complexes show three main absorptions[3c,6b] in the 10000 – 30000 cm^{-1} region, as expected for a titanium(II) species of d^2 configuration. Although the tetraphenylcyclobutadiene dianion has not been explicitly considered to be involved in bonding to transition elements, the concept of metallo-aromaticity introduced by Bursten and Fenske[26] for the cyclobutadiene complex $C_4H_4Fe(CO)_3$, could probably be extended to our titanium system with similar bonding considerations. On the other hand, alkali metal derivatives of the tetraphenylcyclobutadiene dianion are stable at room temperature[27,28].

Spectroscopic Studies of the Reaction of η^6-Arene Titanium(II) Complexes with Diphenylacetylene

The reaction of DPA with the η^6-benzene complexes **5a,b** in different molar ratios was monitored by electronic absorption spectroscopy. It was possible to show that three types of complexes are formed as a function of the DPA/Ti molar ratio used and other experimental conditions. The complexes are here denoted as **Ia, Ib, IIa, IIb, IIIa, IIIb** (**a**: chloro, **b**: bromo derivatives), and they are formed at DPA/Ti molar ratios of 1:1, 2:1, and 3:1, respectively. Their absorption spectra are shown in Figure 3, and the absorption bands are given in Table 2; all the chloro and the bromo complexes behave in the same way, and where experiments gave the same results for **a** and **b** complexes, the derivatives are denoted as **I, II,** and **III**. The complex denoted as **II**, was found to be identical to that isolated from the reaction of Ti(η^6-toluene)[(μ-X)$_2$(AlX$_2$)]$_2$ and 2 equivalents of DPA (compound **2a** or **2b**) on the basis of its UV/VIS spectrum in benzene or toluene as solvent.

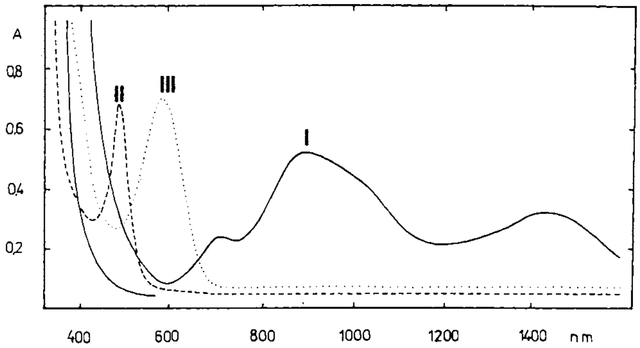

Figure 3. Electronic absorption spectra (benzene solutions) of: **I** (full line) obtained from Ti(η^6-benzene)[(μ-Br)$_2$(AlBr$_2$)]$_2$ + $AlEt_2Br$ (0.1 equivalent) + C_2Ph_2 (1.0 equivalent); **II** (dashed line) obtained from Ti(η^6-benzene)[(μ-Br)$_2$(AlBr$_2$)]$_2$ + C_2Ph_2 (2.0 equivalents); **III** (dotted line) obtained from Ti(η^6-benzene)[(μ-Br)$_2$(AlBr$_2$)]$_2$ + C_2Ph_2 (24 equivalents), 60°C/5 min

Table 2. Electronic absorption spectra of the complexes present in solution in the Ti(η^6-arene)$_4$)[(μ-X)$_2$(AlX$_2$)]$_2$/C_2Ph_2 system[a]

Compound	λ [nm]
5a	396, 554, 820[b]
5b	402, 576, 870[b]
I	700 – 710 w, 870 – 890 w, 1400 – 1430 w
II	486 vs
III	580 – 585 vs

[a] The spectra of the chloro and bromo complexes **I – III** and of their mono- and diethylated complexes do not differ within the accuracy of wavelength determination. These spectra were also invariant with respect to solvent (benzene or toluene). – [b] H. Antropiusová, K. Mach, J. Zelinka, *Trans. Met. Chem.* **3** (1978) 127.

The formation of complexes **II** by mixing the η^6-benzene titanium complex **5** with 2 equivalents of DPA both in benzene and in toluene solutions was accompanied by minor amounts of **I**, see Figure 3. On the other hand, complexes **I** could not be prepared by reaction of **5** with 1 equivalent of DPA; the complexes **II** were always formed as the main soluble products, **I** being present as a minor product. The unreacted **5a** or **5b** could not be observed due to the fact that their CT band near 400 nm was overshadowed by a strong absorption of **II** and **I** in this region. Subsequent addition of 1 equivalent of DPA led to the transient partial formation of **III**; however, upon ageing, **II** was obtained nearly quantitatively. The reaction between equimolar amounts of the η^6-benzene complex **5** and **II** did not yield **I**, but a poorly soluble product absorbing at 515 nm. Addition of 2 equivalents of DPA to these systems followed by warming at 60°C yielded **II** again (in admixture with **I**). With 3 or more equivalents of DPA, simultaneous formation of **II** and **I** was observed followed by their slow conversion to **III**. The formation of **III** was enhanced by warming to 60°C, while oligomers of DPA separated from the solution, see spectrum III of Figure 3.

The rapid formation of **II** and the occurrence of products of the cationic conversion of DPA (*vide infra*) led us to suggest that the cyclobutadiene ligand formation in **II** is catalyzed by small amounts of aluminium halides present in the system. We believe that the fast formation of the tetramethylcyclobutadiene$-AlX_3$ (X = Cl, Br) complexes reported in the literature[29a,b] and verified in the present work through their isolation (*vide infra*) may preceed the formation of **2**. It is possible to suggest that a $C_4R_4-AlX_3$ complex may be formed as an intermediate, and that ligand exchange may further occur with the η^6-arene titanium compound still present in solution. In this connection, an important observation is that by Hoberg and co-workers: according to these authors, a transfer of the tetramethylcyclobutadiene ligand occurs from its $AlCl_3$ complex to nickel(II)[29c] and to palladium(II)[29d].

The complexes **I, II,** and **III** were found to be EPR-inactive both at 77 K and at room temperature. This is in agreement with the structure of **II**; as far as the structures of **I** and **III** are concerned, the absence of EPR signals implies that they probably contain either titanium(II) or titanium (IV) (the formation of dimers or clusters containing titanium(III) with paired spins seems to be improbable because both compounds are well soluble in benzene). The low intensity absorption bands of **I** in the visible and near infrared region (Table 2) are consistent with the presence of titanium(II) in this compound[30]: thus, it can be suggested to contain coordinated DPA instead of, or in addition to, an arene group. The strong absorption band near 600 nm in the spectrum of **III**, which is attributable to a charge-transfer band, may overlap to a possible low-intensity d-d absorption of a titanium(II) complex. In any case, complex **III** does not contain HPB or octaphenyl-COT (OPCOT) coordinated to the bis(tetrahaloaluminato) fragment, since the spectrum of **III** was not obtained upon addition of HPB or OPCOT to **1** or **5**.

Cyclooligomerization of Substituted Acetylenes

As mentioned above, oligomerization of substituted acetylenes in the presence of preformed tetraorganylcyclobutadiene complexes of titanium has been found[13,14b] to be a rather inefficient process. On the other hand, we find that the (η^6-toluene)titanium complex reacts with the stoichiometric amount of 2-butyne to give the (η^4-C_4Me_4)titanium derivative **3b** *in toluene as solvent*, thus showing that the aromatic used as reaction medium is not capable to compete with the coordinated tetramethylcyclobutadiene ligand within the coordination sphere of titanium. On the other hand, treatment of the (η^6-toluene)titanium complex with three equivalents of 2-butyne led to the formation of the (η^6-hexamethylbenzene)titanium derivative, and yet the solvent was toluene in this experiment too. This shows that the (η^4-C_4Me_4)titanium derivative is not stable towards further addition of 2-butyne, and the resulting fully methyl-substituted η^6-arene complex undergoes a very slow, if any, substitution by the aromatic hydrocarbon constituting the medium, due to stabilization by methyl substitution, a fact which is well established in π-arene complexes of transition metals[3a,31].

The obvious question was now whether these systems were able to cyclooligomerize substituted acetylenes. As shown in Table 3, by using the preformed η^6-toluene complex in methylcyclohexane[32] as medium, 2-butyne was found to be cyclotrimerized to hexamethylbenzene at 80°C for 15 h with a turnover (moles of 2-butyne converted *per* mole of titanium) of about 520. This result should be compared with the recent one obtained by Rosenthal and co-workers[33] for the trimerization of, among others, 1,4-dimethoxy-2-butyne, in the presence of the 2-ethylhexanoatonickel(II)/$P(C_6H_{11})_3$/$NaBH_4$ system[33c], for which turnovers of about 3 orders of magnitude higher than ours have been obtained at 82.5°C over 120 h. On the other hand, when the preformed (η^4-tetramethylcyclobutadiene)titanium complex **3b** was used in methylcyclohexane as solvent, 2-butyne was still converted to hexamethylbenzene, even at room temperature, with a turnover of about 8 (Run 4, Table 3). The comparison of experiments 1 and 2 of Table 3 shows that the aromatic solvent does not play an important role in this catalytic reaction.

The titanium(η^6-arene) and -(η^4-cyclobutadiene) complexes contain two tetrahaloaluminato groups per titanium: as such, the presence in solution of small amounts of aluminum trihalides and their intervention in the cyclotrimerization process had to be taken into consideration. As a matter of fact, 2-butyne is known[34] to cyclotrimerize to hexamethyl Dewar benzene in the presence of $AlCl_3$ as catalyst at temperatures comprised between 35 and 40°C, while at

Table 3. Cyclotrimerization of alkynes in the presence of $Ti(L)[(\mu\text{-}Br)_2(AlBr_2)]_2$[a]

Run	L	Alkyne	Solvent	Temp. [°C]	Product	Turnover[b]
1	η^6-toluene	2-butyne	toluene	25	HMB	13
2	η^6-toluene	2-butyne	$Me\text{-}C_6H_{11}$	25	HMB	12
3	η^6-toluene	2-butyne	$Me\text{-}C_6H_{11}$	80	HMB	520
4	η^4-C_4Me_4	2-butyne	$Me\text{-}C_6H_{11}$	25	HMB	8.5
5	η^6-toluene	phenylacetylene	toluene	25	1,3,5-triphenylbenzene[c]	18
6	η^6-toluene	phenylacetylene	toluene	80	1,3,5-triphenylbenzene[c]	930
7	η^6-toluene	1-hexyne	toluene	25	1,2,4- (53%) + 1,3,5-tris(*n*-butyl)benzene (47%)	49
8	η^6-toluene	1-hexyne	toluene	80	1,2,4- (53%) + 1,3,5-tri(*n*-butyl)benzene (47%)	990

[a] Reaction time is 15 h. Replacing the titanium catalytic precursor with $AlBr_3$ led to the following results in methylcyclohexane (reaction temp. [°C], product, turnover): 25, HMB, ≪ 1; 80, HMB, 11. Trace amounts of hexamethyl Dewar benzene were found in both experiments. — [b] Turnover = mole of reacted alkyne/mole of titanium. — [c] The 1,3,5 isomer was usually contaminated by small amounts of the 1,2,4 isomer (IR spectrum in nujol).

temperatures around 50 °C hexamethylbenzene is obtained prevalently. Moreover, it is known[29a,b,35] that 2-butyne and AlX_3 give a 1:1 tetramethylcyclobutadiene σ complex (dark-red for X = Cl) whose molecular structure was established by X-ray diffraction methods[29a]. The corresponding $AlBr_3$ adduct does not appear to have been isolated, but its reactivity in solution has been studied[35e,f]. Although the literature[36a] mentions the use of $AlBr_3$ for the cyclotrimerization of 2-butyne to hexamethyl Dewar benzene in benzene as solvent, we have not been able to find anything but traces of hexamethyl Dewar benzene when $AlBr_3$ and 2-butyne were mixed in methylcyclohexane as solvent at 25 °C for a time (15 h) comparable to that used with our titanium catalytic systems. On the other hand, at 80 °C, the turnover for the cyclotrimerization to HMB (only traces of hexamethyl Dewar benzene have been observed) was about 11. Moreover, we have observed that $AlBr_3$ is much less effective than $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$ in the cyclotrimerization of 1-hexyne, the turnover being 3 under substantially comparable conditions. Phenylacetylene has been reported to be decomposed by $AlBr_3$[36b]. In conclusion, the titanium centre does appear to be essential for the cyclotrimerization of acetylenes.

The cyclooligomerization products of DPA were studied by using the $Ti(\eta^6\text{-benzene})[(\mu\text{-}X)_2(AlX_2)]_2$ (X = Cl: **5a**, X = Br: **5b**) systems as catalytic precursors. It follows from the results reported in Table 4 that both complexes produce large amounts of by-products besides HPB and OPCOT, probably induced by the presence of equilibrium concentrations of AlX_3. The by-products contained variable amounts of triphenylethene and 1,1,2,2-tetraphenylethane, deriving from the Friedel-Crafts addition of DPA to benzene, and 1,2,3-triphenylnaphthalene and 1,2,3-triphenylazulene, products of cationic dimerization of DPA[37]. These compounds were also formed by interaction of $AlCl_3$ or $AlBr_3$ with DPA in benzene, whereas no HPB or OPCOT were obtained. The formation of the cited by-products was substantially suppressed by addition of $AlEt_2X$ or $AlEt_3$ to the (η^6-benzene)titanium(II) complexes.

Table 4. Oligomerization of DPA to HPB and OPCOT catalyzed by $Ti(\eta^6\text{-benzene})[(\mu\text{-}X)_2(AlX_2)]_2$ in the presence of aluminium alkyls[a], X = Cl: **5a**; Br: **5b**

Run	Catalytic System (molar ratio)	DPA [g]	HPB and OPCOT [g]	HPB (%)	OPCOT (%)	Turnover[b]	By-products[c]
1	**5a**	2	1.0	92	8	140	+ + +
2	**5a**/$AlEt_2Cl$ (1/1)	2	1.35	76	24	190	+ +
3	**5a**/$AlEt_2Cl$ (1/2)	2	1.77	56	44	249	---
4	**5a**/$AlEt_2Cl$ (1/3)	2	1.20	83	17	160	---
5	**5a**/$AlEt_3$ (1/0.5)	2	1.22	79	21	171	+ +
6	**5a**/$AlEt_3$ (1/0.7)	2	1.62	61	39	228	---
7	**5a**/$AlEt_3$ (1/1)	2	1.18	88	12	166	---
8	**5b**	2	0.24	95	5	34	+ +
9	**5b**/$AlEt_3$ (1/0.5)	2	0.19	93	7	27	+
10	**5b**/$AlEt_3$ (1/1)	1	0.06	70	30	8	---
11	**5a**/$AlEt_2Cl$ (1/1)	1	0.83	25	75	[g]	n.d.[d]
12	**5a**/$AlEt_2Cl$ (1/1)[e]	1.0	0.85	59	41	[g]	n.d.[d]
13	**5a**/$AlEt_2Cl$ (1/1)[f]	1	0.92	32	68	[g]	n.d.[d]
14	**5a**/$AlEt_2Cl$ (1/1)	0.5	0.44	13	87	[g]	n.d.[d]

[a] Reaction conditions: Ti−X: 0.04 mmol; solvent: benzene (8 ml); T = 60 °C; t = 8 h. — [b] For the definition of turnover, see Table 2. — [c] The presence of by-products (generally triphenylethene > 1,1,2,2-tetraphenylethane > 1,2,3-triphenylnaphthalene > 1,2,3-triphenylazulene) is indicated by one or more + labels. — [d] n.d. = not determined. — [e] 20−30 °C/72 h. — [f] 75 °C/6 h. — [g] Complete consumption of DPA.

The catalytic behaviour of (η^6-benzene)titanium(II) complexes with respect to DPA is analogous to their behaviour in the cyclotrimerization of butadiene to (*Z,E,E*)-1,5,9-cyclododecatriene[4c,38]. The chloro complex **5a** is more active than **5b**, and addition of ethylaluminum compounds increases the activity of the former while decreases the activity of the latter (Table 4). This may be explained[4c,38] by considering both the lower electronegativity of the bromide ligand compared to chloride and the electron-donating effect of ethyl groups introduced into the terminal positions of the (η^6-arene)titanium(II) derivatives[38]. As a result of both effects, higher rates of cycloaddition are achieved together with a faster deactivation of the catalytic species. Both the kinetic study of butadiene consumption reported in ref.[38] and the results reported in this paper show that the optimum catalytic activity is achieved by using $AlEt_2Cl$/**5a** = 1:1 or 2:1 or, alternatively, $AlEt_3$/**5a** = 0.5:1.0 or 0.7:1.0 molar ratios (Runs 2, 3 and 5, 6, respectively, of Table 4).

The products obtained by oligomerization of DPA, namely HPB and OPCOT, have probably little influence on the oligomerization reaction, because both of them are easily displaced from the coordination sphere of titanium due to both steric hindrance or absence of conjugation[39]. The present study has no licence to decide between the cycloaddition to a cyclobutadiene moiety or the insertion into a titanacyclopentadiene complex[40]; however, the results reported in this paper strongly suggest that η^4-tetraphenylcyclobutadiene complexes **2a** or **2b** may be catalytic intermediates or else they may participate in an equilibrium together with a catalytic titanacyclopentadiene species. The role of the AlX_3−(σ-cyclobutadiene) complexes, as commented earlier, in the ligand-transfer process is also to be considered.

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Experimental

Unless otherwise stated, all operations were carried out in an atmosphere of prepurified argon. The reaction vessels were oven-dried before use. Solvents were carefully dried by conventional methods.

Infrared spectra were recorded with Perkin-Elmer 283 and UR 75 (Zeiss, Jena) instruments equipped with grating on solutions, nujol mulls, or KBr pellets of the compounds prepared under rigorous exclusion of moisture and oxygen. ^1H-NMR and ^{13}C-NMR spectra were measured with Jeol PS-100 and Varian VXR-400 instruments, respectively. Mass spectra were obtained with a Jeol D-100 spectrometer at 75 eV using a direct inlet. Electronic absorption spectra in the range 300 – 2000 nm were measured with a Varian Cary 17 D spectrometer using all-sealed quartz cuvettes (Hellma, d = 0.1 and 1.0 cm) attached to the reaction vessel. The typical concentration of $Ti(\eta^6\text{-arene})[(\mu\text{-}X)_2(AlX_2)]_2$ complexes (X = Cl, Br) in benzene or toluene solution was 10^{-2} M.

Gaschromatographic analyses were performed with a Dani 8400 instrument and with a Perkin-Elmer F 21 preparative gaschromatograph equipped with a Carbowax 20 M column.

$AlBr_3$, $AlEt_2Cl$, and $AlEt_3$ were commercial products sublimed or distilled *in vacuo* prior to use. TlCp[41)] and $Ti(\eta^6\text{-arene})[(\mu\text{-}X)_2(AlX_2)]_2$ (arene = benzene, toluene; X = Cl, Br) were prepared according to literature[1,2a,3,6b)]. K_2COT, free from potassium-coordinated THF, was obtained from K and COT in THF, followed by evaporation of the solvent *in vacuo* and drying the residue at 80°C/10^{-2} Torr.

Reaction of $Ti(\eta^6\text{-toluene})[(\mu\text{-}X)_2AlX_2]_2$ with Diphenylacetylene (DPA)

a) *X = Cl: Synthesis of $Ti(\eta^4\text{-}C_4Ph_4)[(\mu\text{-}Cl)_2(AlCl_2)]_2$* (**2a**): A 0.12 M toluene solution[6b)] of $Ti(\eta^6\text{-toluene})[(\mu\text{-}Cl)_2(AlCl_2)]_2$ (25 ml, 3 mmol of titanium) was added dropwise to a solution of DPA (1.07 g, 6.0 mmol) in toluene (25 ml). Rapidly, the colour of the solution turned brown, green, and finally red-brown with precipitation of dark-brown crystals. After 15 h of stirring at room temp., the product was filtered, washed with toluene (2 × 5 ml) and dried *in vacuo* yielding 1.37 g of $Ti(\eta^4\text{-}C_4Ph_4)[(\mu\text{-}Cl)_2(AlCl_2)]_2$ as oxygen- and moisture-sensitive dark-brown crystals. The filtrate, on cooling to −30°C, gave another crop of product (0.32 g), total yield 76%.

$C_{28}H_{20}Al_2Cl_8Ti$ (741.9) Calcd. Al 7.3 Cl 38.2 Ti 6.5
Found Al 7.3 Cl 37.8 Ti 6.5

b) *X = Br: Synthesis of $Ti(\eta^4\text{-}C_4Ph_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$* (**2b**): A 0.09 M toluene solution[6b)] of $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$ (75 ml, 6.7 mmol of Ti) was added dropwise at room temp. to a solution of DPA (2.51 g, 14.1 mmol) in toluene (30 ml). Rapidly, the colour of the solution turned brown, green, and finally red-brown with precipitation of dark-brown crystals. After 2 h of stirring at room temp., the microcrystalline substance was filtered, washed with toluene (2 × 5 ml) and dried *in vacuo* yielding 4.71 g (64%) of $Ti(\eta^4\text{-}C_4Ph_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ as oxygen- and moixture-sensitive dark-brown crystals. χ_M^{corr} (18°C): -353×10^{-6} cgsu; diamagnetic correction: -349×10^{-6} cgsu. – IR (nujol/polychlorotrifluoroethylene): $\tilde{\nu}$ = 3070 cm^{-1} vw, 1590 m, 1578 w, 1495 s, 1448 m, 1393 vs, 1280 w, 1185 w, 1075 m-w, 1025 w, 1001 vw, 920 vw, 780 vs, 782 m, 778 m, 739 m, 702 vs, 685 m, 540 m-s, 475 m-s, 460 m-s, 425 m-s.

$C_{28}H_{20}Al_2Br_8Ti$ (1097.6) Calcd. Al 4.9 Br 58.2 Ti 4.4
Found Al 4.8 Br 58.6 Ti 4.2

$Ti(\eta^4\text{-}C_4Ph_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$: X-ray Data and Refinement[42)]: Dark brown crystals of $Ti(\eta^4\text{-}C_4Ph_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$, obtained by crystallization from toluene, were sealed in glass capillaries under argon and studied by Weissemberg methods. Systematic absences and symmetries in diffraction patterns univocally indicated the monoclinic $P2_1/c$ space group as the possible choice. The crystal which showed the most sharp spots was used for the subsequent analysis.

Crystal data: $Ti[\eta^4\text{-}C_4(C_6H_5)_4][(\mu\text{-}Br)_2(AlBr_2)]_2$, $C_{28}H_{20}Al_2Br_8Ti$; M = 1097.6; specimen size: 0.4 × 0.2 × 0.2 mm; a = 14.634(4), b = 11.704(3), c = 20.709(4) Å; β = 103.62°; V = 3447.2 Å^3 (by least-squares refinement of the diffraction geometry of 25 reflections); Mo-K_α radiation (λ = 0.71069 Å); Z = 4; $D_{calcd.}$ = 2.115 g cm^{-3}; μ(Mo-K_α) = 95.025 cm^{-1}; $F(000)$ = 2064; T = 293 K.

Data collection and processing: CAD4 diffractometer, $2\Theta/\Theta$ scan, graphite monochromatized Mo-K_α radiation; 11270 reflections measured (3° < Θ < 24°), 3434 unique (merging to R = 0.031 after empirical absorption correction; max., min., average absorption corrections: 1.417, 0.659, 0.969); 2318 reflections with $I > 3\sigma(I)$. Standard reflections ($00\bar{8}$, 540, $\bar{3}35$) showed no significant deviation in the intensity during data collection.

Structure analysis and refinement: Structure solution by direct methods[43)]. H atoms in calculated idealized positions. Full-matrix least-squares refinement (on F) with anisotropic thermal parameters for all non-H atoms. H positions included only in structure factors calculations. In the last cycle, 353 parameters were refined, the largest shift/error ratio being 0.01. The final R and R_w values were 0.056 and 0.066, respectively. Calculations were performed with the VAXSDP[44)] program system on a DEC MicroVAXII computer. Atomic coordinates are listed in Table 5.

Reaction of $Ti(\eta^4\text{-}C_4Ph_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ with TlCp: A solution of $Ti(\eta^4\text{-}C_4Ph_4)[\mu\text{-}Br)_2(AlBr_2)]_2$ (0.85 g, 0.77 mmol) in toluene

Table 5. Fractional atomic coordinates of $Ti(\eta^4\text{-}C_4(C_6H_5)_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ with estimated standard deviations in parentheses

Atom	x	y	z
Ti	0.7599(2)	0.2475(3)	0.0504(2)
Br1	0.8651(2)	0.0611(2)	0.0464(1)
Br2	0.6776(2)	0.1758(2)	-0.0721(1)
Br3	0.8486(2)	-0.0165(3)	-0.1306(1)
Br4	0.6717(2)	-0.1386(3)	-0.0465(2)
Br5	0.7844(2)	0.1845(3)	0.1770(1)
Br6	0.5843(2)	0.2730(2)	0.0617(1)
Br7	0.5818(2)	0.2442(3)	0.2447(1)
Br8	0.5841(3)	-0.0166(3)	0.1335(2)
Al1	0.7650(5)	0.0067(5)	-0.0552(3)
Al2	0.6246(5)	0.1633(5)	0.1599(3)
C1	0.775(1)	0.417(2)	0.0009(9)
C2	0.780(1)	0.440(1)	0.0705(8)
C3	0.872(1)	0.383(1)	0.0905(9)
C4	0.868(1)	0.362(2)	0.0198(9)
C5	0.721(1)	0.461(2)	-0.0602(9)
C6	0.764(1)	0.498(2)	-0.1101(8)
C7	0.707(2)	0.546(2)	-0.170(1)
C8	0.613(2)	0.559(2)	-0.180(1)
C9	0.570(1)	0.521(2)	-0.132(1)
C10	0.623(2)	0.474(2)	-0.0737(9)
C11	0.724(1)	0.513(2)	0.104(1)
C12	0.683(1)	0.605(1)	0.0747(8)
C13	0.636(2)	0.680(2)	0.105(1)
C14	0.635(1)	0.665(2)	0.171(1)
C15	0.680(1)	0.573(2)	0.2039(9)
C16	0.725(1)	0.497(2)	0.1735(9)
C17	0.949(1)	0.375(2)	0.1518(8)
C18	0.961(1)	0.467(2)	0.196(1)
C19	1.031(1)	0.466(2)	0.251(1)
C20	1.097(1)	0.380(2)	0.2647(9)
C21	1.080(2)	0.285(2)	0.220(1)
C22	1.010(1)	0.285(2)	0.1664(9)
C23	0.942(1)	0.326(1)	-0.0144(8)
C24	1.032(1)	0.339(2)	0.0141(9)
C25	1.104(1)	0.313(2)	-0.019(1)
C26	1.075(1)	0.270(2)	-0.083(1)
C27	0.984(1)	0.256(2)	-0.114(1)
C28	0.913(1)	0.287(2)	-0.082(1)

(50 ml) was treated with TlCp (0.44 g, 1.60 mmol). A green suspension was obtained within the time of mixing the reagents. The suspension was filtered, and the colourless solid was identified as $TlAlBr_4$ (0.64 g) from its bromide analysis. The green solution was concentrated to 10 ml; addition of *n*-heptane (30 ml) caused the separation of a green solid which was filtered, dried in vacuo (0.40 g, 97% yield) and identified as $Cp_2\overline{TiC(Ph)=C(Ph)C(Ph)=C}(Ph)$ [14a], from its analytical (C,H) and IR data.

Reaction of $Ti(\eta^4\text{-}C_4Ph_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ *with* K_2COT: $Ti(\eta^4\text{-}C_4Ph_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ (0.54 g, 0.49 mmol) was added to a well stirred suspension of K_2COT (0.11 g, 0.77 mmol) in toluene (50 ml). Formation of a green solution together with precipitation of a solid was observed within the time of mixing the reagents. After 6 h stirring at room temp., the suspension was filtered, and the volume of the solution was reduced to 5 ml. Addition of *n*-heptane (30 ml) caused the separation of a green solid which was filtered, dried in vacuo at room temp. (0.15 g, 60% yield), and identified as $Ti(\eta^4\text{-}C_4Ph_4)(COT)$ [14b] from its analytical (C,H) and IR data.

Reaction of $Ti(\eta^6\text{-}toluene)[(\mu\text{-}Br)_2(AlBr_2)]_2$ *with 2-Butyne*

a) *Synthesis of* $Ti(\eta^4\text{-}C_4Me_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ (**3b**): 2-Butyne (0.55 g, 10.2 mmol) in toluene (25 ml) was treated at −20°C with a 0.1 M solution[6b] of $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$ (50 ml, 5.0 mmol of Ti). The violet colour of the solution turned green and finally yellow-green with precipitation of a microcrystalline solid. After 1 h of stirring at room temp., the dark-green, oxygen- and moisture-sensitive $Ti(\eta^4\text{-}C_4Me_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ was recovered by filtration, washing with toluene (2 × 25 ml), and drying in vacuo (2.89 g, 68% yield).

$C_8H_{12}Al_2Br_8Ti$ (849.3)	Calcd.	Al 6.3	Br 75.3	Ti 5.6
	Found	Al 6.2	Br 74.6	Ti 5.5

b) *Synthesis of* $Ti(\eta^6\text{-}C_6Me_6)[(\mu\text{-}Br)_2(AlBr_2)]_2$: A solution of 2-butyne (1.38 g, 25.5 mmol) in toluene (25 ml) was treated at −20°C with a 0.09 M solution[6b] of $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$ (75 ml, 6.7 mmol of Ti). Immediate formation of a black oil was observed which crystallized after 48 h of stirring at room temp. to a violet solid. Filtration, washing with toluene (5 × 5 ml) and drying in vacuo afforded 5.80 g (96% yield) of the violet $Ti(\eta^6\text{-}C_6Me_6)[(\mu\text{-}Br)_2(AlBr_2)]_2$, being very sensitive to oxygen and moisture.

$C_{12}H_{18}Al_2Br_8Ti$ (903.4)	Calcd.	Al 6.0	Br 70.8	Ti 5.3
	Found	Al 6.0	Br 70.9	Ti 5.3

Reaction of $Ti(\eta^4\text{-}C_4Me_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ *with 2-Butyne:* A solution of $Ti(\eta^4\text{-}C_4Me_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ (0.86 g, 1.01 mmol) in toluene (50 ml) was treated at room temp. with 2-butyne (0.24 g, 4.0 mmol). Immediate formation of a violet solid was observed which was filtered and dried in vacuo affording 0.73 g (80% yield) of $Ti(\eta^6\text{-}C_6Me_6)[(\mu\text{-}Br)_2(AlBr_2)]_2$ identified from its analytical (Al, Br, Ti) and IR data.

Cyclotrimerization of Alkynes in the Presence of $Ti(L)[(\mu\text{-}Br)_2(AlBr_2)]_2$

a) $L = \eta^6$*-toluene, Alkyne = 2-Butyne:* Only the detailed description of Run 3, Table 3 is reported, Runs 1 and 2 being performed in a similar way. A suspension of $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$ (0.09 g, 0.1 mmol) in methylcyclohexane (25 ml) was treated at room temp. with 2-butyne (4.89 g, 89 mmol). The orange suspension was stirred at 80°C for 15 h (reflux condenser cooled to about −40°C). The reaction mixture was cooled to room temp. which caused the formation of large crystals of hexamethylbenzene (HMB): a TLC analysis [eluant: *n*-hexane/CH_2Cl_2 (1:1)] of the solution showed the presence of unreacted 2-butyne and HMB. The suspension was treated with ice under argon. After addition of Et_2O, the organic layer was separated from the aqueous solution which was extracted several times with Et_2O: the collected diethyl ether extracts were dried with $MgSO_4$, filtered, and dried in vacuo at room temp. The residue was sublimed at 50°C/10^{-2} Torr affording 3.10 g of HMB (IR and ^1H NMR) corresponding to a turnover of 520.

b) $L = \eta^4\text{-}C_4Me_4$, *Alkyne = 2-Butyne* (Run 4, Table 3): A suspension of $Ti(\eta^4\text{-}C_4Me_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ (0.22 g, 0.26 mmol) in methylcyclohexane (10 ml) was treated with 2-butyne (1.38 g, 25.5 mmol). By operating at room temp. for 15 h, 0.12 g of HMB were obtained corresponding to a turnover of 8.5.

c) $L = \eta^6$*-toluene, Alkyne = Phenylacetylene* (Run 5, Table 3): A 0.077 M toluene solution[6b] of $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$ (25 ml, 1.9 mmol) was treated dropwise at room temp. with a 1.5 M toluene solution of phenylacetylene (30 ml, 45 mmol) within 1 h. An exothermic reaction with formation of an oily product and a red solution was observed. After 15 h stirring at room temp., the solvent was removed in vacuo, and the residue was hydrolyzed at 0°C under an argon atmosphere. The aqueous suspension was extracted several times with diehtyl ether, and the collected ether extracts were dried with $MgSO_4$. The ether was then removed, and the residue was dissolved in boiling *n*-heptane to afford an orange solid on cooling to 0°C. This solid was dissolved in a toluene/*n*-heptane (1:1) mixture. On partial evaporation of the solvent, a cream-coloured solid separated which was filtered, dried in vacuo (3.43 g, turnover = 18), and identified as a mixture of 1,2,4- and 1,3,5-triphenylbenzene from its elemental analysis (C,H) and IR data (in nujol)[9].

In another run, the mixture of triphenylbenzenes was passed through a SiO_2 column by using *n*-hexane as eluant, the solvent was removed *in vacuo* and the residue recrystallized from hexane to give 1,2,4- and 1,3,5-triphenylbenzene, the 1,2,4-isomer being more soluble.

d) $L = \eta^6$*-toluene, Alkyne = 1-Hexyne* (Run 7, Table 3): A solution[6b] of $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2(AlBr_2)]_2$ (0.18 g, 0.22 mmol) in toluene (25 ml) was treated dropwise with a solution of 1-hexyne (1.60 g, 19.5 mmol) in toluene (25 ml). A strongly exothermic reaction with formation of an orange suspension was observed. After 3 h, a gaschromatographic analysis of the solution showed that a mixture of 1,2,4- and 1,3,5-tris(*n*-butyl)benzene was present as the only species in addition to unreacted 1-hexyne. No significant change in the composition of the solution was observed after 15 h of stirring at room temp. The solid was filtered off, and the toluene was removed by distillation at atmospheric pressure. The dark-brown residue was distilled at 120–125°C/10^{-1} Torr to give 0.89 g (turnover = 49) of a mixture of 1,2,4- and 1,3,5-tris(*n*-butyl)benzene (53:47 ratio, purity > 99% according to GC analysis).

Experiments c) and d) were carried out also at about 80°C (Runs 6 and 8, Table 3), the corresponding turnovers being 930 and 990, respectively.

Cyclotrimerization of 1-Hexyne in the Presence of $AlBr_3$: A solution of $AlBr_3$ (0.52 g, 1.9 mmol) in toluene (25 ml) was treated dropwise with 17.2 mmol of 1-hexyne. An exothermic reaction took place with formation of a red-brown solution. After 15 h of stirring at room temp., a gaschromatographic analysis of the solution showed that 2.3 mmol of a mixture of 1,2,4- and 1,3,5-tris(*n*-butyl)benzene (44:57 ratio) was formed, corresponding to a reacted 1-hexyne/aluminum molar ratio of 4:1.

Reaction of AlX_3 *with 2-Butyne*

a) $X = Cl$: The compound $C_4Me_4 \cdot AlCl_3$ was isolated by a modification of the published procedure[29a,b]. A suspension of $AlCl_3$ (3.87 g, 29 mmol) in CH_2Cl_2 (25 ml) was treated dropwise at −10°C with 2-butyne (3.46 g, 64 mmol). Immediate reaction with formation of a red-orange solution was observed. After warming to room temp., the solution was treated with *n*-heptane (50 ml) which caused the precipitation of a heavy orange solid which was filtered, washed with *n*-heptane (2 × 10 ml) and dried *in vacuo* affording 5.62 g (80% yield) of $C_4Me_4 \cdot AlCl_3$. – IR (nujol): $\tilde{\nu}$ = 1640 cm^{-1} w, 1280 w, 1180 w, 1105 w, 1045 vw, 1005 w, 875 m-w, 790 vw, 740 w, 680 w, 580 w, 535 w, 490 vs-br., 410 m. – UV/VIS (CH_2Cl_2, 25°C): λ_{max} (lg ε) = 368 nm (2.672), 404 (2.362). – ^1H NMR (CD_2Cl_2/TMS, 25°C): δ = 1.37 (s, 3H), 2.4 (s, 9H).

$C_8H_{12}AlCl_3$ (241.5) Calcd. Al 11.2 Cl 44.0
Found Al 11.0 Cl 44.1

b) *X = Br:* A solution of $AlBr_3$ (2.54 g, 9.5 mmol) in methylcyclohexane (50 ml) was treated at 0°C with 2-butyne (3.24 g, 60 mmol). Immediate precipitation of a yellow solid was observed within the time of mixing the reagents. The suspension was stirred at 25°C for 15 h. The solid was filtered, washed with methylcyclohexane (2 × 5 ml), and dried in vacuo at room temp. affording $C_4Me_4 \cdot AlBr_3$ (3.46 g, 97% yield) of a moisture-sensitive yellow solid. – IR (nujol/polychlorotrifluoroethylene): $\tilde{\nu}$ = 2960 cm^{-1} w, 2910 w, 1640 w, 1460 s, 1420 m, 1380 s, 1350 w, 1280 w, 1105 w, 1005 w, 875 w, 740 w, 600 w, 580 w, 535 w, 510 m, 490 m, 450 w, 410 vs, 380 m. – UV/VIS (CH_2Cl_2, 25°C): λ_{max} (lg ε) = 340 nm (2.544), 390 (2.255). – ^1H NMR (CD_2Cl_2/TMS): δ = 1.35 (s, 3H), 2.36 (s, 9H) at 25°C; 1.35 (s, 3H), 2.27 (s, 3H), 2.35 (s, 6H) at −40°C.

$C_8H_{12}AlBr_3$ (374.9) Calcd. Al 7.2 Br 63.9
Found Al 7.1 Br 63.3

The solution contained unreacted 2-butyne and only traces of hexamethyl Dewar benzene [TLC on silica gel, eluant: hexane/CH_2Cl_2 (10:1)]. On hydrolysis at 0°C the solid afforded hexamethyl Dewar benzene, HMB and at least two other unidentified compounds[36a].

The experiment was carried out also at about 80°C in methylcyclohexane; HMB was formed with a turnover of 11 after 15 h.

Spectroscopic Monitoring of the Reaction between $Ti(\eta^6\text{-arene})[(\mu\text{-}X)_2(AlX_2)]_2$ (arene = benzene, toluene; X = Cl, Br) with Stoichiometric Amounts of DPA: Weighed amounts of DPA corresponding to 1, 2, 3, or more equivalents of DPA with respect to the titanium complex were placed in an all-glass reactor equipped with a couple of all-sealed quartz cells (0.1 and 1 cm) and evacuated on a vacuum line with an oil diffusion pump. Benzene was condensed over DPA from a storage vessel; the titanium complex, dissolved in benzene, was rapidly poured into the DPA solution and the mixture was vigorously stirred: the final concentration of titanium in this mixture was about 5×10^{-3} M. When the reaction was carried out in the presence of an ethylaluminum compound, this was added directly to the DPA solution, or it was previously mixed with the titanium derivative, the nature of the reaction products being independent of the addition procedure.

Oligomerization of DPA in the Presence of $Ti(\eta^6\text{-benzene})[(\mu\text{-}X)_2(AlX_2)]_2$ (X = Cl, Br) and an Alkylating Agent: A reaction vessel containing DPA and attached to a vacuum line was evacuated, and benzene was added to DPA by condensation. Solutions of $Ti(\eta^6\text{-benzene})[(\mu\text{-}X)_2(AlX_2)]_2$ and $AlEt_2X$ or $AlEt_3$ were introduced from the attached ampoule by means of breakable seals. After mixing the catalytic system at room temp., the reaction vessel was immersed in a thermostat and stirred. Reaction conditions are reported in Table 4. After reaction, the vessel was opened in air, and EtOH was added in order to decompose the organotitanium complexes. After evaporation of benzene and EtOH in a rotary evaporator, EtOH was added (50 ml), and the mixture was boiled for 10 min. After cooling to room temp., the insoluble product was filtered and dried in air. The filtered solution was evaporated to a small volume in vacuo. The solid product, which was recovered by filtration, consisted of a mixture of HPB and octaphenyl-COT (OPCOT). Yields and conversions are reported in Table 4. The filtrate contained triphenylethene, 1,1,2,2-tetraphenylethane, 1,2,3-triphenylnaphthalene, and 1,2,3-triphenylazulene (traces); see Table 4. The individual products were isolated by column chromatography (SiO_2, *n*-hexane) and identified by a combination of IR, ^1H- and ^{13}C-NMR, and mass spectra.

Pure HPB[45] was separated by extraction with $CHCl_3$ from the reaction products consisting mainly of HPB and OPCOT. Its ^{13}C-NMR spectrum in CCl_4 corresponded to the published spectrum[46]. – IR (KBr): $\tilde{\nu}$ = 3104 cm^{-1} w, 3081 m, 3058 m, 3027 m, 2997 w, 1964 w, 1944 w, 1893 w, 1873 w, 1822 w-sh, 1802 w, 1753 w, 1600 s, 1578 m, 1498 s, 1440 s, 1403 s, 1332 w, 1280 w, 1180 w, 1160 m, 1146 m, 1076 s, 1031 s, 1004 m, 922 m, 912 m, 837 w, 824 m, 786 s, 732 vs, 701 vs, 687 s, 673 w, 556 vs. – MS: *m/z* (%) = 534 (100) [$M^{+\bullet}$].

The residue from the $CHCl_3$ extraction was dissolved in diphenyl ether at 250°C in a sealed ampoule and slowly cooled at room temp. The colourless crystals were separated, washed with benzene and ethanol, and dried in vacuo. This compound was identified as OPCOT having a "tub-shaped" structure[39] by single crystal X-ray analysis[47]. – IR (KBr): $\tilde{\nu}$ = 3098 cm^{-1} vw, 3080 m, 3061 br.-m, 3027 br.-m, 2997 vw, 1950 br.-w, 1889 br.-w, 1805 w, 1762 vw, 1599 s, 1573 m, 1488 vs, 1440 s, 1334 vw, 1313 vw, 1281 w, 1268 w, 1182 m, 1156 m, 1089 m, 1066 s, 1030 s, 1002 w, 991 vw, 970 vw, 918 m, 887 w, 862 w, 840 w, 788 s, 780 s, 771 vs, 760 s, 773 vs, 705 vs, 655 m, 619 w, 588 m, 556 m, 535 m, 513 m, 480 w, 448 w. – MS: *m/z* (%) = 714 (16.4), 713 (61.8), 712 (100) [M^+], 635 (9.2), 621 (8.0), 557 (11.6), 545 (20.2), 480 (6.9), 479 (8.0), 467 (19.7), 402 (5.8), 389 (7.0), 367 (18.4), 365 (6.3), 356 (5.0), 343 (21.4), 291 (10.4), 289 (9.2), 277 (15.0), 275 (18.5), 239 (25.0), 238 (12.7), 232 (9.2), 200 (15.6), 178 (10.5), 167 (34.7), 165 (21.0), 149 (6.5), 131 (7.0), 119 (6.0), 115 (5.5), 91 (14.0).

The composition of DPA oligomer mixtures (see Table 4) was studied by infrared analysis by using the absorptions at 1403 and 556 cm^{-1} for HPB and those at 588, 556, and 535 cm^{-1} for OPCOT.

CAS Registry Numbers

1a: 56214-53-0 / **1b**: 113809-49-7 / **2a**: 113809-74-8 / **2b**: 113809-75-9 / **3b**: 113809-76-0 / **4**: 1317-21-1 / **5a**: 12312-06-0 / **5b**: 12287-30-8 / DPA: 501-65-5 / HMP: 87-85-4 / HPB: 992-04-1 / OPCOT: 2041-08-9 / TlCp: 34822-90-7 / K_2COT: 59391-85-4 / $Ti(\eta^4\text{-}C_4Ph_4)(COT)$: 39475-28-0 / $Ti(\eta^6\text{-}C_6Me_6)[(\mu\text{-}Br)_2(AlBr_2)]_2$: 67634-86-0 / $AlEt_2Cl$: 96-10-6 / $AlEt_3$: 97-93-8 / $AlBr_3$: 7727-15-3 / $AlEt_2Br$: 760-19-0 / $C_4Me_4 \cdot AlCl_3$: 31886-99-4 / $C_4Me_4 \cdot AlBr_3$: 70492-15-8 / $AlCl_3$: 7446-70-0 / 2-butyne: 503-17-3 / phenylacetylene: 536-74-3 / 1-hexyne: 693-02-7 / 1,2,4-triphenylbenzene: 1165-53-3 / 1,3,5-triphenylbenzene: 612-71-5 / 1,2,4-tri(*n*-butyl)benzene: 14800-16-9 / 1,3,5-tri(*n*-butyl)benzene: 841-07-6 / triphenylethene: 58-72-0 / 1,1,2,2-tetraphenylethane: 632-50-8 / 1,2,3-triphenylnaphthalene: 1942-39-8 / 1,2,3-triphenylazulene: 1055-26-1

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[1] G. Natta, G. Mazzanti, G. Pregaglia, *Gazz. Chim. Ital.* **89** (1959) 2065.

[2] [2a] H. Martin, F. Vohwinkel, *Chem. Ber.* **94** (1961) 2416. – [2b] H. de Vries, *Recl. Trav. Chim. Pays-Bas* **81** (1962) 359. – [2c] U. Thewalt, F. Österle, *J. Organomet. Chem.* **172** (1979) 317. – [2d] U. Thewalt, F. Stollmaier, *J. Organomet. Chem.* **228** (1982) 149.

[3] [3a] S. Pasynkiewicz, R. Giezynski, S. Dzierzgowski, *J. Organomet. Chem.* **54** (1973) 203. – [3b] R. Giezynski, S. Dzierzgowski, S. Pasynkiewicz, *J. Organomet. Chem.* **87** (1975) 295. – [3c] H. Antropiusová, K. Mach, J. Zelinka, *Trans. Met. Chem.* **3** (1978) 127.

[4] [4a] F. Vohwinkel, *Trans. N. Y. Acad. Sci.* **26** (1964) 446. — [4b] S. Dzierzgowski, R. Giezinski, S. Pasynkiewicz, *J. Mol. Cat.* **2** (1977) 243. — [4c] J. Poláček, H. Antropiusová, V. Hanuš, L. Petrusová, K. Mach, *J. Mol. Cat.* **29** (1985) 165.

[5] K. Mach, H. Antropiusová, J. Poláček, *Trans. Met. Chem.* **4** (1979) 312; K. Mach, H. Antropiusová, J. Poláček, *J. Organomet. Chem.* **172** (1979) 325.

[6] [6a] P. Biagini, F. Calderazzo, G. Pampaloni, *J. Chem. Soc., Chem. Commun.* **1987**, 1015. — [6b] idem, *J. Organomet. Chem.* **355** (1988) 99.

[7] A. Nakamura, *Mem. Inst. Sci. Ind. Res. Osaka Univ.* **19** (1962) 81, *Chem. Abstr.* **59** (1963) 8786e; P. M. Maitlis, *Adv. Organomet. Chem.* **4** (1966) 95; A. Efraty, *Chem. Rev.* **77** (1977) 691.

[8] E. F. Lutz, *J. Am. Chem. Soc.* **83** (1961) 2551.

[9] A. Furlani Donda, E. Cervone, M. A. Biancifiori, *Recl. Trav. Chim. Pays-Bas* **81** (1962) 585, and references therein.

[10] G. Drefahl, H. H. Hörhold, H. Bretschneider, *J. Prakt. Chem.* **25** (1964) 113 [*Chem. Abstr.* **62** (1965) 463a].

[11] V. B. Shur, V. V. Burlakov, M. E. Vol'pin, *J. Organomet. Chem.* **347** (1988) 77, and references therein.

[12] M. F. Farona, S. Thanedar, A. Famili, *J. Pol. Sci. A: Polymer Chem.* **24** (1986) 3529.

[13] M. E. E. Meijer-Veldman, J. L. de Boer, H. J. de Liefde Meijer, A. M. M. Schreurs, J. Kroon, A. L. Spek, *J. Organomet. Chem.* **269** (1984) 255.

[14] [14a] K. Sonogashira, N. Hagihara, *Bull. Chem. Soc. Jpn.* **39** (1966) 1178. — [14b] H. O. van Oven, *J. Organomet. Chem.* **55** (1973) 309.

[15] Throughout this paper compounds **a** and **b** are chloro and bromo derivatives, respectively.

[16] H. P. Fritz, *Z. Naturforsch., Teil B,* **16** (1961) 415.

[17] S. I. Troyanov, V. B. Rybakov, *Metalloorg. Khim.* **1** (1988) 1280.

[18] R. Jungst, D. Sekutowski, J. Davis, M. Luly, G. Stucky, *Inorg. Chem.* **16** (1977) 1645.

[19] A. F. Wells, *Structural Inorganic Chemistry,* 5th Edition, p. 444, Clarendon Press, Oxford, 1984.

[20] M. D. Rausch, B. H. Edwards, J. L. Atwood, R. D. Rogers, *Organometallics* **1** (1982) 1567.

[21] M. D. Rausch, G. F. Westover, E. Mintz, G. M. Reisner, I. Bernal, A. Clearfield, J. M. Troup, *Inorg. Chem.* **18** (1979) 2605.

[22] G. G. Cash, J. F. Helling, M. Mathew, G. J. Palenik, *J. Organomet. Chem.* **50** (1973) 277.

[23] J. J. Eisch, A. M. Piotrowski, A. A. Aradi, C. Krüger, M. J. Romao, *Z. Naturforsch., Teil B,* **40** (1985) 624.

[24] [24a] A. Efraty, J. A. Potenza, L. Zyontz, J. Daily, M. H. A. Huang, B. Toby, *J. Organomet. Chem.* **145** (1978) 315. — [24b] M. Mathew, G. J. Palenik, *J. Organomet. Chem.* **61** (1973) 301.

[25] M. Crocker, M. Green, A. G. Orpen, D. M. Thomas, *J. Chem. Soc., Chem. Comm.* **1984**, 1141.

[26] B. E. Bursten, R. F. Fenske, *Inorg. Chem.* **18** (1979) 1760.

[27] G. Boche, H. Etzrodt, M. Marsch, W. Thiel, *Angew. Chem.* **94** (1982) 141; *Angew. Chem. Int. Ed. Engl.* **21** (1982) 133.

[28] G. Boche, H. Etzrodt, *Tetrahedron Lett.* **24** (1983) 5477.

[29] [29a] C. Krüger, P. J. Roberts, Y. H. Tsay, J. B. Koster, *J. Organomet. Chem.* **78** (1974) 69. — [29b] P. B. J. Driessen, H. Hogeveen, *J. Organomet. Chem.* **156** (1978) 265. — [29c] H. Hoberg, H. J. Riegel, *J. Organomet. Chem.* **229** (1982) 85. — [29d] H. Hoberg, H. J. Riegel, K. Seevogel, *J. Organomet. Chem.* **229** (1982) 281.

[30] H. A. Øye, D. M. Gruen, *Inorg. Chem.* **3** (1964) 836.

[31] [31a] V. S. Leong, N. J. Cooper, *Organometallics* **7** (1988) 2058. — [31b] E. L. Muetterties, J. R. Bleeke, A. C. Sievert, *J. Organomet. Chem.* **178** (1978) 197. — [31c] E. L. Muetterties, J. R. Bleeke, J. R. Wucherer, T. A. Albright, *Chem. Rev.* **82** (1982) 499, and references therein.

[32] Methylcyclohexane was used to minimize the effect of the solvent on the cyclotrimerization process.

[33] [33a] W. Schulz, U. Rosenthal, *Z. Chem.* **26** (1986) 176. — [33b] W. Schulz, U. Rosenthal, D. Walther, *Z. Chem.* **27** (1987) 264. — [33c] U. Rosenthal, W. Schulz, *J. Organomet. Chem.* **321** (1987) 103.

[34] W. Schäfer, *Angew. Chem.* **78** (1966) 716; *Angew. Chem. Int. Ed. Engl.* **5** (1966) 669.

[35] [35a] H. Hogeveen, H. Jorristma, P. A. Wade, P. van Rantwijk, J. B. Koster, J. J. Prooi, A. Sinnema, H. van Bekkum, *Tetrahedron Lett.* **1974**, 3915. — [35b] D. S. B. Grace, H. Hogeveen, P. A. Wade, *Tetrahedron Lett.* **1976**, 123. — [35c] P. B. J. Driessen, H. Hogeveen, *J. Organomet. Chem.* **156** (1978) 265. — [35d] P. B. J. Driessen, H. Hogeveen, *J. Am. Chem. Soc.* **100** (1978) 1193. — [35e] P. B. J. Driessen, H. Hogeveen, *Tetrahedron Lett.* **1979**, 271. — [35f] H. Hogeveen, D. M. Kok, *Tetrahedron Lett.* **21** (1980) 659.

[36] [36a] W. Schäfer, H. Hellmann, *Angew. Chem.* **79** (1967) 566; *Angew. Chem. Int. Ed. Engl.* **6** (1967) 518. — [36b] H. Hogeveen, R. F. Kingma, D. M. Kok, *J. Org. Chem.* **47** (1982) 989.

[37] C. J. Cooksey, J. L. Courtneidge, A. G. Davies, P. S. Gregory, *J. Chem. Soc., Perkin Trans. 2,* **1988**, 807.

[38] J. Poláček, H. Antropiusová, L. Petrusová, K. Mach, *J. Mol. Cat.*, in press.

[39] G. S. Pawley, W. N. Lipscomb, H. H. Freedman, *J. Am. Chem. Soc.* **86** (1964) 4725.

[40] G. M. Whitesides, W. J. Ehmann, *J. Am. Chem. Soc.* **91** (1969) 3800; H. Papermans, R. Willem, M. Gielen, C. Hoogzand, *Bull. Soc. Chim. Belg.* **97** (1988) 115.

[41] H. Meister, *Angew. Chem.* **69** (1957) 533.

[42] Further details of the crystal structure investigation are available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, West Germany, on quoting the depository number CSD-53885, the names of the authors, and the journal citation.

[43] G. M. Sheldrick, *Crystallographic Computing,* vol. 3, pp. 175 and 184, Oxford University Press, 1985.

[44] B. A. Frenz, "The ENRAF-NONIUS CAD4 SDP: a Real-Time System for Concurrent X-Ray Data Collection and Crystal Structure Determination", in *Computing in Crystallography* (H. Schenck, R. Olthof-Hazekamp, H. von Koningsveld, G. C. Bassi, Eds.) pp. 64–71, Delft University Press, 1978.

[45] W. Dilthey, G. Hurtig, *Ber. Dtsch. Chem. Ges.* **67** (1934) 2004.

[46] W. Storek, J. Sauer, R. Sosser, *Z. Naturforsch., Teil A,* **34** (1979) 1334.

[47] U. Thewalt, University of Ulm, personal communication to K. Mach.

[165/89]