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Reactions of $Zr(\eta^6\text{-benzene})(AlCl_4)_2$ with Alkynes: Cyclooligomerization Reactions and Crystal and Molecular Structure of the Seven-Membered Metallacycle $[ZrCPh(CPh)_4CPh][(\mu\text{-}Cl)_2AlCl_2]_2$[†]

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Benzene solutions of the Zr(II) complex $Zr(\eta^6\text{-benzene})(AlCl_4)_2$ (1) catalyze the cyclotrimerization of 2-butyne to hexamethyl Dewar benzene (HMDB) and hexamethylbenzene (HMB) at room temperature. HMDB is the predominant initial product, followed by its isomerization to HMB. When diphenylacetylene was reacted with the (arene)zirconium(II) complex, the title metallacycle derivative was obtained, whose crystal and molecular structure was studied by X-ray diffraction methods. For $[ZrCPh(CPh)_4CPh][(\mu\text{-}Cl)_2AlCl_2]_2$, $C_{42}H_{30}Al_2Cl_8Zr\cdot 0.5C_7H_{16}$, $M_r = 1013.6$, monoclinic, space group $P2_1/n$, $a = 14.784$ (2) Å, $b = 16.390$ (2) Å, $c = 22.984$ (2) Å, $\beta = 107.17$ (1)°, $Z = 4$, $V = 5321$ (14) Å^3, $D_{calc} = 1.265$ g cm^{-3}, average transmission factor 0.989, and $\mu = 60.5$ cm^{-1}. The structure consists of a seven-membered cycle including zirconium, the coordination sphere of the latter being completed by four chlorine atoms from the two $AlCl_4$ groups.

Introduction

Acetylene derivatives, in combination with inorganic or organometallic compounds of transition metals, constitute well-known precursors to a large variety of organic materials such as substituted pyridines,[1] cyclopolyene derivatives,[2] and quinones.[3] In particular, acetylenes can undergo linear polymerization or cyclotrimerization to aromatic hydrocarbons in the presence of Ziegler–Natta catalysts[4] or cyclopentadienyl derivatives of titanium, zirconium, or hafnium.[5] Recently, some of us reported that η^6-arene derivatives of titanium(II), $Ti(\eta^6\text{-arene})[(\mu\text{-}X)_2(AlX_2)]_2$ (X = Cl, Br) catalyze the cyclotrimerization of terminal or internal acetylenes to the corresponding substituted benzene compounds;[6] moreover, the tetraphenylcyclobutadiene complex $Ti(\eta^4\text{-}C_4Ph_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ was structurally characterized. It has also been observed that the zirconium(II)–η^6-benzene complex[7] $Zr(\eta^6\text{-benzene})(AlCl_4)_2$ can be converted to the η^6-hexamethylbenzene homologue by reaction with 2-butyne in benzene as solvent.

In this paper we report that hexamethylbicyclo[2.2.0]hexa-2,5-diene (hexamethyl Dewar benzene, HMDB) is the predominant initial product of the cyclotrimerization reaction of 2-butyne catalyzed by $Zr(\eta^6\text{-benzene})(AlCl_4)_2$[7] and that the valence isomerization of HMDB to hexamethylbenzene, HMB, occurs in the presence of the zirconium(II) arene derivative. Moreover, we describe the crystal and molecular structure of the seven-membered metallacycle $[ZrCPh(CPh)_4CPh][(\mu\text{-}Cl)_2AlCl_2]_2$ (2) obtained in the reaction of $Zr(\eta^6\text{-benzene})(AlCl_4)_2$ with diphenylacetylene. In addition we report a comparative study, in the cyclotrimerization of 2-butyne, of the catalytic behavior of the zirconium(II) complex with respect to the corresponding titanium(II) system and to $AlCl_3$.

Experimental Section

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified nitrogen or argon. Solvents were carefully dried by conventional methods prior to use. IR spectra were measured with a Perkin-Elmer Model 283 instrument equipped with a grating. Gas chromatographic analyses were performed with a Dani Model 8400 gas chromatograph equipped with a Carbowax 20 M column.

Cyclotrimerization of 2-Butyne Catalyzed by $Zr(\eta^6\text{-benzene})(AlCl_4)_2$. (a) A 0.02 M benzene solution of 1 (20 mL, 0.4 mmol of Zr) was treated at 0 °C with 2-butyne (1.76 g, 32.5 mmol). Immediate reaction with formation of a violet solution (brown after a few minutes) was observed. The reaction mixture was stirred at room temperature for 120 h, during which time periodic sampling of 0.5 mL of the solution was performed; the sample was hydrolyzed and the organic phase was analyzed by gas chromatography. After 120 h of stirring at room temperature, 97% of the starting 2-butyne was consumed, corresponding to a reacted 2-butyne/Zr molar ratio of 79 (see Figure 1a).

(b) The cyclotrimerization reaction was studied also at the reflux temperature of benzene. A 0.02 M benzene solution of 1 (5 mL, 0.1 mmol of Zr) was treated at 0 °C with 2-butyne (0.83 g, 15.3 mmol). After 18 h at the reflux temperature (reflux condenser cooled at about −40 °C), the mixture was cooled at room temperature and a gas chromatographic analysis of the supernatant solution showed that hexamethylbenzene (HMB) was the major

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product; some unreacted 2-butyne and a negligible amount of HMDB were present. After hydrolysis, the organic layer was dried over $MgSO_4$. After filtration, the solvent was evaporated in vacuo, affording 0.38 g of HMB corresponding to a reacted 2-butyne/Zr molar ratio of 70.

When Zr(η^6-benzene)($AlBr_4$)$_2$ was used as catalyst, a reacted 2-butyne/Zr molar ratio of 25 was observed after 120 h under substantially identical experimental conditions.

(c) In an experiment aimed at studying the time dependence of the cyclotrimer formation (see Figures 1a and 2a), a suspension of Zr(η^6-benzene)($AlCl_4$)$_2$ (0.39 g; 0.65 mmol) in benzene (30 mL) was treated at 19.8 ± 0.1 °C with 2-butyne (2.62 g; 48.4 mmol). Immediate reaction with formation of a brown oily suspension was observed. The reaction mixture was stirred for 142 h at 19.8 ± 0.1 °C, during which time periodic sampling was performed, followed by gas chromatographic analysis as reported in section a. After 142 h at 19.8 ± 0.1 °C, 94% of the starting 2-butyne was consumed, corresponding to a reacted 2-butyne/Zr molar ratio of 70.

Isomerization of HMDB to HMB Catalyzed by Zr(η^6-benzene)($AlCl_4$)$_2$. A 0.02 M benzene solution of 1 (20 mL, 0.4 mmol of Zr) was treated at room temperature with HMDB (0.80 g, 4.9 mmol). A brown oil immediately formed. A gas chromatographic control of the reaction (0.5 mL of the solution was hydrolyzed and the organic phase was analyzed) showed that, after 5 min, some HMB was already present. The HMDB to HMB isomerization was complete in about 30 min.

No HMDB/HMB isomerization was observed in the absence of the arene derivative of Zr, even after 2.5 h at the reflux temperature of benzene.

Cyclotrimerization of 2-Butyne Catalyzed by $AlCl_3$. 2-Butyne (1.24 g, 22.9 mmol) was added to a suspension of $AlCl_3$ (0.07 g, 0.52 mmol) in benzene (30 mL). Immediate formation of a yellow-orange suspension was observed. Periodic sampling of 0.5 mL of the solution was performed, the sample being hydrolyzed and the organic phase analyzed by gas chromatography. After 120 h of stirring at 19.8 ± 0.1 °C, 12 mmol of butyne was consumed, corresponding to a molar ratio of 23 between reacted 2-butyne and $AlCl_3$ to give HMDB and HMB (see Figures 1b and 2b).

Similar results (reacted 2-butyne/$AlBr_3$ molar ratio of 17.5) were obtained when $AlBr_3$ was used as a catalyst, the other experimental conditions being substantially the same.

HMDB (4.4 mmol) was found to be isomerized to HMB in 1 h at 19.8 ± 0.1 °C in the presence of $AlCl_3$ (0.7 mmol) in benzene (35 mL).

Cyclotrimerization of 2-Butyne Catalyzed by $AlCl_3 \cdot C_4Me_4$. 2-Butyne (0.62 g, 11.5 mmol) was added to a yellow-orange suspension of $AlCl_3 \cdot C_4Me_4$ (0.042 g, 0.17 mmol) in benzene (10 mL). The reaction mixture was stirred for 142 h at 19.8 ± 0.1 °C, during which time periodic sampling was performed, followed by gas chromatographic analysis, as reported in the previous paragraphs. After 119 h at 19.8 ± 0.1 °C, 63% of the starting 2-butyne was consumed, corresponding to a reacted 2-butyne/Al molar ratio of 42, to give HMDB and HMB (see Figures 1c and 2c).

HMDB (2.5 mmol) was found to be slowly isomerized to HMB at 19.8 ± 0.1 °C in the presence of $AlCl_3 \cdot C_4Me_4$ (0.073 g, 0.3 mmol) in benzene (20 mL). After 55 h, 75% of the starting HMDB was converted to HMB.

Cyclotrimerization of 2-Butyne Catalyzed by Ti(η^6-benzene)[(μ-Cl)$_2$($AlCl_2$)]$_2$. 2-Butyne (2.3 g, 42.5 mmol) was added to a violet suspension of Ti(η^6-benzene)[(μ-Cl)$_2$($AlCl_2$)]$_2$ (0.22 g, 0.47 mmol) in benzene (25 mL). Immediate formation of a brown suspension was observed. Periodic sampling of 0.5 mL of the solution was performed, the sample being hydrolyzed and the organic phase analyzed by gas chromatography. After 115 h of stirring at 19.8 ± 0.1 °C, butyne was consumed according to a molar ratio of 90 between reacted 2-butyne and Ti to give mainly HMB (see Figures 1d and 2d).

HMDB (3.5 mmol) was found to be isomerized to HMB in 1 h at 19.8 ± 0.1 °C in the presence of Ti(η^6-benzene)[(μ-Cl)$_2$($AlCl_2$)]$_2$ (0.5 mmol) in benzene (25 mL).

Reaction of Zr(η^6-benzene)($AlCl_4$)$_2$ with Diphenylacetylene. A solution of diphenylacetylene (3.02 g, 16.9 mmol) in benzene (50 mL) was added dropwise (1 h) to a well-stirred, 0.02 M benzene solution of 1 (280 mL, 5.6 mmol) at room temperature. After addition of 25 mL of the alkyne solution, a green solution with a bright green solid was formed, and at the end of the addition a violet solution was present. After 30 min of stirring at room temperature, the mixture was filtered and the solid was washed with benzene (2 × 5 mL) and *n*-heptane (2 × 5 mL) and dried in vacuo, affording 0.26 g (7% yield) of a microcrystalline green solid to which the composition Zr(benzene)(diphenylacetylene)($AlCl_4$)$_2$ was assigned on the basis of the analytical data (Anal. Found: Al, 7.8; Cl, 41.4; Zr, 13.2. Calcd for $C_{20}H_{16}Al_2Cl_8Zr$: Al, 7.9; Cl, 41.4; Zr, 13.3.). The solid is substantially insoluble in hydrocarbons and decomposes in THF, DME, acetonitrile, acetone, and halogenated solvents. The volume of the clear violet solution was reduced to 20 mL in vacuo at room temperature, and *n*-heptane (100 mL) was added. After this mixture was cooled at +4 °C for several days, compound 2 (2.95 g, 52% yield) separated out as a crystalline dark violet solid sensitive to moisture and oxygen, which was filtered and dried in vacuo at room temperature. Anal. Found: Al, 5.5; Cl, 29.0; Zr, 9.2. Calcd for $C_{42}H_{30}Al_2Cl_8Zr$: Al, 5.6; Cl, 29.4; Zr, 9.5. IR spectrum (Nujol mull): 3090 vw, 3070 vw, 3030 vw, 1590 m, 1580 w, 1495 m, 1490 m, 1400 m, 1350 m, 1310 w, 1285 m-w, 1075 m-w, 1025 m-w, 1000 w, 780 m, 760 m-s, 690 s, 680 m-s, 560 m-s, 540 m, 500 s cm^{-1}. The compound is substantially diamagnetic. When the reaction was repeated with a 1/1 diphenylacetylene/Zr molar ratio, both compounds were obtained in low yields. In a run performed with a 1/2 diphenylacetylene/Zr molar ratio, the compounds reported above were obtained in 26 and 34% yields, respectively.

Thermal treatment of compound 2 in refluxing decalin for 6 h gave a 60% yield of hexaphenylbenzene (IR). In contrast, irradiation of 2 with a mercury lamp for 5 h at 20 °C in *n*-heptane as solvent left the compound substantially unchanged.

X-ray Diffractometric Study of 2. A crystal obtained as reported in the preceding paragraph, of approximate dimensions (mm) 0.55 × 0.25 × 0.20, was sealed in a glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer and examined with graphite-monochromatized Cu Kα radiation (λ = 1.5418 Å). Crystal data: $C_{42}H_{30}Al_2Cl_8Zr \cdot 0.5C_7H_{16}$, M_r = 1013.6, monoclinic, a = 14.784 (2) Å, b = 16.390 (2) Å, c = 22.984 (2) Å, β = 107.17 (1)° (by a least-squares fit of 25 reflections in the θ range 23–33°); space group $P2_1/n$, Z = 4, V = 5321 (14) Å^3, D_{calc} = 1.265 g cm^{-3}, average transmission factor 0.989; μ = 60.5 cm^{-1}, $F(000)$ = 2036; 293 K.

Data collection and processing; ω-scan technique with $12 < \theta < 65°$; 8790 reflections measured; after Lorentz and polarization correction, 4886 reflections having $I > 3\sigma(I)$ were retained as observed, and 4690 symmetrically independent observations remained after merging.

The zirconium atom was located in a Patterson map, and the positions of the remaining non-hydrogen atoms (Table I) were obtained through the usual combination of full-matrix least-squares refinements and difference Fourier syntheses;[8] refinement with isotropic thermal parameters for all non-hydrogen atoms converged to R = 0.103. At this stage the unmerged data set was used to apply an empirical absorption correction.[9] After merging, the refinement with isotropic thermal parameters converged to R = 0.091. Hydrogen atoms in fixed positions (C–H distance 0.95 Å) were included in structure factor calculations. The refinement with anisotropic parameters for all non-hydrogen atoms converged to R = 0.055. A solvent molecule, *n*-heptane, was located by four peaks from the difference Fourier map; *n*-heptane is generated by an inversion center, and the terminal carbon atom is disordered and refined with a multiplicity of 0.5. The last refinement, with isotropic thermal parameters for the carbon atoms of *n*-heptane and anisotropic thermal parameters for the other non-hydrogen atoms, converged to R = 0.048 and R_w = 0.053, with 4690 reflections for 494 parameters.

A final difference Fourier synthesis generated an electron density map with no peaks higher than 0.53 e Å^{-3}.

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Table I. Fractional Atomic Coordinates for Compound 2[a]

atom	x/a	y/b	z/c	B, Å²
Zr	0.00735 (4)	0.08943 (4)	0.21173 (3)	3.48 (1)
Cl11	−0.0718 (1)	0.2289 (1)	0.23081 (8)	4.82 (4)
Cl12	−0.1388 (1)	0.1216 (1)	0.10707 (8)	5.17 (5)
Cl13	−0.3069 (1)	0.2516 (2)	0.1412 (1)	6.98 (6)
Cl14	−0.1257 (2)	0.3328 (1)	0.0888 (1)	6.70 (6)
Cl21	0.0674 (1)	−0.0019 (1)	0.13569 (8)	4.80 (4)
Cl22	0.1006 (1)	0.1919 (1)	0.15262 (8)	5.12 (4)
Cl23	0.2526 (2)	0.0797 (2)	0.0884 (1)	8.50 (7)
Cl24	0.0196 (2)	0.1209 (2)	0.0023 (1)	7.39 (6)
Al1	−0.1680 (2)	0.2413 (2)	0.1373 (1)	4.72 (5)
Al2	0.1131 (2)	0.0987 (2)	0.0877 (1)	5.04 (5)
C1	−0.0860 (4)	−0.0122 (4)	0.2174 (3)	3.9 (2)
C6	0.1284 (4)	0.1213 (4)	0.2893 (3)	3.7 (2)
C2	−0.0897 (4)	0.0202 (4)	0.2733 (3)	3.7 (1)
C3	0.0020 (5)	0.0377 (4)	0.3115 (3)	3.9 (2)
C4	0.0748 (4)	−0.0102 (4)	0.2928 (3)	3.8 (2)
C5	0.1536 (4)	0.0381 (4)	0.2928 (3)	3.8 (2)
C11	−0.1448 (5)	−0.0761 (4)	0.1832 (3)	4.0 (2)
C12	−0.1554 (6)	−0.0904 (5)	0.1218 (3)	5.7 (2)
C13	−0.2063 (7)	−0.1567 (6)	0.0916 (4)	7.2 (2)
C14	−0.2454 (7)	−0.2114 (6)	0.1234 (4)	7.7 (3)
C15	−0.2340 (6)	−0.2010 (6)	0.1835 (4)	6.9 (2)
C16	−0.1857 (6)	−0.1332 (5)	0.2134 (3)	5.5 (2)
C21	−0.1786 (5)	0.0354 (4)	0.2890 (3)	4.0 (2)
C22	−0.2545 (5)	0.0721 (5)	0.2470 (3)	5.0 (2)
C23	−0.3383 (5)	0.0871 (6)	0.2608 (4)	6.3 (2)
C24	−0.3465 (6)	0.0660 (6)	0.3162 (4)	6.9 (2)
C25	−0.2727 (6)	0.0261 (7)	0.3577 (4)	7.6 (3)
C26	−0.1873 (5)	0.0113 (6)	0.3446 (3)	5.7 (2)
C31	0.0252 (5)	0.0781 (5)	0.3718 (3)	4.5 (2)
C32	−0.0229 (6)	0.1480 (6)	0.3806 (3)	5.7 (2)
C33	−0.0013 (7)	0.1838 (7)	0.4385 (4)	8.1 (3)
C34	0.0703 (8)	0.1498 (8)	0.4867 (4)	9.9 (3)
C35	0.1181 (8)	0.0828 (9)	0.4770 (4)	9.5 (3)
C36	0.0975 (6)	0.0469 (6)	0.4205 (4)	6.4 (2)
C41	0.0717 (4)	−0.1022 (4)	0.2917 (3)	4.1 (2)
C42	0.0384 (5)	−0.1410 (5)	0.3354 (4)	5.8 (2)
C43	0.0409 (6)	−0.2255 (6)	0.3387 (5)	7.4 (3)
C44	0.0765 (6)	−0.2694 (5)	0.2991 (5)	7.7 (3)
C45	0.1078 (6)	−0.2317 (5)	0.2554 (4)	6.6 (2)
C46	0.1063 (5)	−0.1471 (5)	0.2530 (4)	5.0 (2)
C51	0.2495 (5)	0.0070 (4)	0.2950 (3)	4.0 (2)
C52	0.2997 (5)	0.0423 (5)	0.2590 (3)	4.7 (2)
C53	0.3887 (5)	0.0137 (5)	0.2606 (4)	5.9 (2)
C54	0.4290 (5)	−0.0496 (5)	0.3000 (4)	6.0 (2)
C55	0.3814 (5)	−0.0839 (5)	0.3363 (4)	5.5 (2)
C56	0.2914 (5)	−0.0569 (5)	0.3340 (4)	5.1 (2)
C61	0.1894 (5)	0.1875 (5)	0.3210 (3)	4.5 (2)
C62	0.1701 (5)	0.2691 (5)	0.3025 (3)	4.9 (2)
C63	0.2212 (6)	0.3329 (5)	0.3374 (4)	6.0 (2)
C64	0.2917 (1)	0.3162 (6)	0.3902 (4)	7.2 (3)
C65	0.3116 (7)	0.2357 (6)	0.4089 (4)	7.2 (3)
C66	0.2627 (6)	0.1717 (5)	0.3745 (4)	5.8 (2)
C70	0.507 (1)	0.043 (1)	0.4890 (8)	15.5 (6)[b]
C71	0.611 (2)	0.051 (1)	0.491 (1)	20.1 (8)[b]
C72	0.617 (2)	0.149 (2)	0.477 (1)	22.8 (9)[b]
C73	0.204 (3)	0.345 (3)	0.011 (2)	18 (1)[b]

[a] Estimated standard deviations (in parentheses) refer to the least significant digit. Hydrogen atoms were not refined but included in the structure factor calculations. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [b] Isotropically refined atoms.

Results and Discussion

Catalytic (with 2-Butyne) and Stoichiometric (with Diphenylacetylene) Cyclotrimerization of Acetylenes Promoted by Zirconium(II). Benzene solutions of the Zr(II) complex $Zr(\eta^6\text{-benzene})(AlCl_4)_2$ catalyze the cyclotrimerization of 2-butyne. In a typical run, about 80 mol of 2-butyne/mol of 1 was converted to HMDB and HMB in 120 h, at room temperature. Hexamethyl Dewar benzene was the main product, at least in the initial stages of the reaction (see Figures 1a and 2a). We have proved that $Zr(\eta^6\text{-benzene})(AlCl_4)_2$, in the absence of 2-butyne, acts as an effective catalyst in the thermal[10] isomerization of HMDB to HMB (see eq 1); it may therefore be suggested

$$Zr(\eta^6\text{-benzene})(AlCl_4)_2 + n\text{HMDB} \xrightarrow{\text{benzene, 25 °C}} Zr(\eta^6\text{-HMB})(AlCl_4)_2 + (n-1)\text{HMB} + \text{benzene} \quad (1)$$

that coordination of 2-butyne to the zirconium catalytically active species to give HMDB is faster than the isomerization of HMDB to HMB. These observations are in agreement with the HMDB to HMB isomerization process becoming predominant at high 2-butyne conversions. This is shown again in Figures 1a and 2a, where, over long reaction times, the concentration of HMDB tends to de-

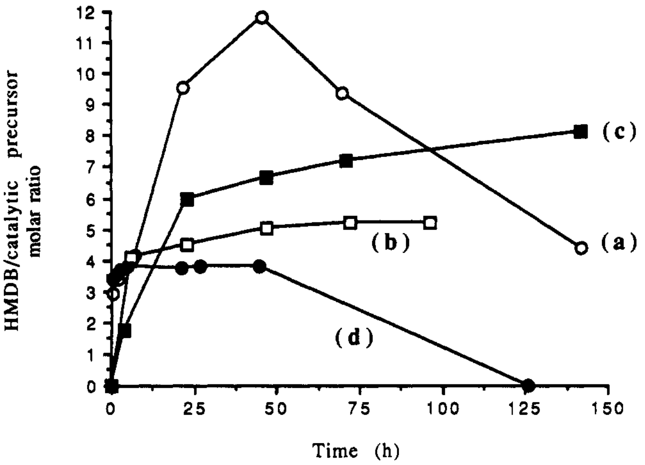

Figure 1. Time dependence of hexamethyl Dewar benzene (HMDB) formation from 2-butyne, expressed as the molar ratio between HMDB and the catalyst precursor, in the presence of (a, ○), $Zr(\eta^6\text{-benzene})(AlCl_4)_2$, 0.02 M nominal concentration, 2-butyne/Zr molar ratio 74, (b, □) $AlCl_3$, 0.017 M nominal concentration, 2-butyne/Al molar ratio 44, (c, ■) $AlCl_3\cdot C_4Me_4$, 0.017 M nominal concentration, 2-butyne/Al molar ratio 68, and (d, ●) $Ti(\eta^6\text{-benzene})[(\mu\text{-Cl})_2(AlCl_2)]_2$, 0.019 M nominal concentration, 2-butyne/Ti molar ratio 90. All experiments were carried out at 19.8 ± 0.1 °C in benzene as solvent.

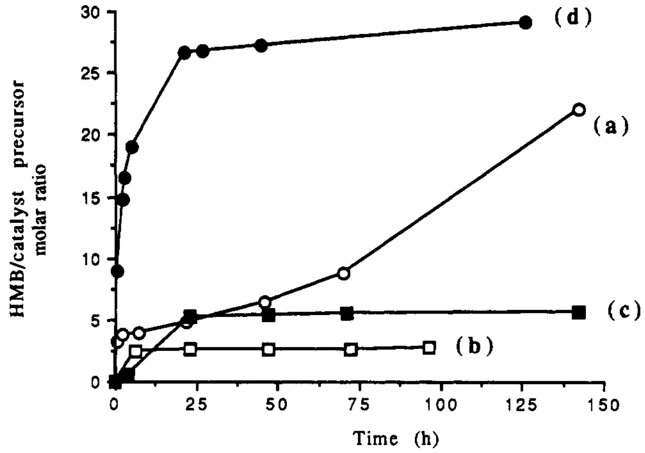

Figure 2. Time dependence of hexamethylbenzene (HMB) formation from 2-butyne, expressed as the molar ratio between HMDB and the catalyst precursor. For reaction conditions, see the caption to Figure 1.

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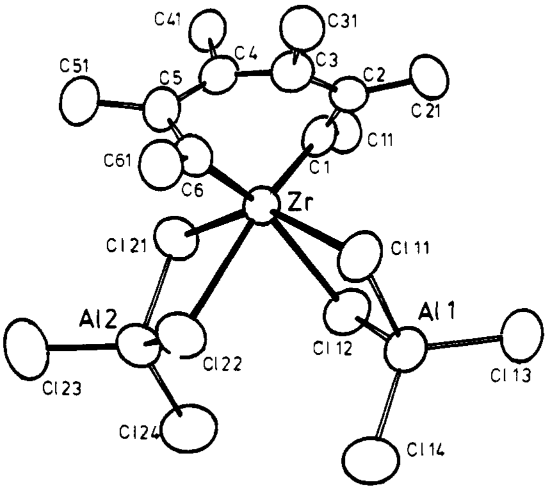

Figure 3. Molecular structure of 2. Phenyl rings are partially omitted for clarity.

Table II. Selected Bond Distances (Å) in Compound 2[a]

Zr–Cl11	2.662 (3)	Cl24–Al2	2.072 (3)
Zr–Cl12	2.768 (2)	C1–C2	1.40 (1)
Zr–Cl21	2.646 (3)	C1–C11	1.438 (9)
Zr–Cl22	2.770 (2)	C2–C3	1.410 (8)
Zr–C1	2.192 (8)	C2–C21	1.48 (2)
Zr–C6	2.184 (6)	C3–C4	1.49 (2)
Cl11–Al1	2.208 (3)	C3–C31	1.481 (9)
Cl12–Al1	2.167 (3)	C4–C5	1.41 (1)
Cl13–Al1	2.088 (3)	C4–C41	1.51 (1)
Cl14–Al1	2.073 (4)	C5–C6	1.41 (1)
Cl21–Al2	2.198 (3)	C5–C51	1.49 (1)
Cl22–Al2	2.180 (3)	C6–C61	1.460 (9)
Cl23–Al2	2.082 (3)		

[a] Estimated standard deviations (in parentheses) refer to the least significant digit.

crease and that of HMB to increase respectively.

In connection with these experiments it is important to realize that AlCl$_3$ was shown earlier to (a) catalyze the cyclotrimerization of 2-butyne[10e] and (b) rapidly isomerize HMDB to HMB[10f] *in the absence of 2-butyne*. Although no experimental details are available yet about point b, the similarities between our zirconium(II)-based system and AlCl$_3$ itself are striking.[11] This point will be discussed in a subsequent part, in comparison with the titanium(II)-based system.

When diphenylacetylene (DPA) was used instead of 2-butyne in the reaction with the zirconium(II)–η^6-benzene–tetrachloroaluminato complex, a completely different reaction pattern was observed. No hexaphenylbenzene was found in the reaction mixture at room temperature; rather, the readily soluble metallacycle $[\overline{\text{ZrCPh(CPh)}_4\text{CPh}}][(\mu\text{-Cl})_2\text{AlCl}_2]_2$ (2) was isolated in 52% yield. Evidence exists that the formation of the dark violet 2 is preceded by that of a green compound of analytical composition Zr(C$_6$H$_6$)(C$_2$Ph$_2$)(AlCl$_4$)$_2$, to which the ionic structure $\{\text{Zr}(\eta^6\text{-C}_6\text{H}_6)(\text{C}_2\text{Ph}_2)[(\mu\text{-Cl})_2(\text{AlCl}_2)]\}^+\text{AlCl}_4^-$ is tentatively assigned to account for its scarce solubility in aromatic hydrocarbons.

The solid-state structure of 2 was established by single-crystal X-ray diffraction methods. The molecule (Figure 3) consists of a seven-membered cycle containing zirconium, the latter being further bonded to two AlCl$_4$ units. Bond distances and angles are listed in Tables II and III. As far as the metallacycle is concerned, it has

Table III. Selected Bond Angles (deg) in Compound 2[a]

Cl11–Zr–Cl12	73.21 (6)	Zr–C6–C5	87.4 (4)
Cl11–Zr–Cl21	147.58 (7)	Zr–C6–C61	145.2 (5)
Cl11–Zr–Cl22	82.36 (6)	C5–C6–C61	125.2 (5)
Cl11–Zr–C1	109.1 (2)	C1–C2–C3	111.0 (6)
Cl11–Zr–C6	87.4 (2)	C1–C2–C21	124.3 (5)
Cl12–Zr–Cl21	82.06 (6)	C3–C2–C21	124.8 (6)
Cl12–Zr–Cl22	80.34 (6)	C2–C3–C4	110.9 (6)
Cl12–Zr–C1	81.5 (2)	C2–C3–C31	126.1 (7)
Cl12–Zr–C6	154.8 (2)	C4–C3–C31	121.1 (5)
Cl21–Zr–Cl22	72.93 (6)	C3–C4–C5	111.8 (6)
Cl21–Zr–C1	87.1 (2)	C3–C4–C41	120.6 (6)
Cl21–Zr–C6	108.7 (2)	C5–C4–C41	125.7 (6)
Cl22–Zr–C1	154.6 (2)	C6–C5–C4	109.8 (6)
Cl22–Zr–C6	81.3 (2)	C6–C5–C51	124.4 (6)
C1–Zr–C6	120.8 (2)	C4–C5–C51	125.8 (6)
Zr–Cl11–Al1	96.17 (9)	C1–C11–C12	123.1 (7)
Zr–Cl12–Al1	94.13 (9)	C1–C11–C16	119.6 (6)
Zr–Cl21–Al2	96.9 (1)	C12–C11–C16	116.9 (7)
Zr–Cl22–Al2	93.8 (1)	C11–C12–C13	121.5 (9)
Cl11–Al1–Cl12	95.5 (2)	C12–C13–C14	119.4 (9)
Cl11–Al1–Cl13	109.0 (1)	C13–C14–C15	120.7 (8)
Cl11–Al1–Cl14	112.4 (1)	C14–C15–C16	119.8 (9)
Cl12–Al1–Cl13	112.2 (1)	C11–C16–C15	121.5 (8)
Cl12–Al1–Cl14	111.3 (1)	C2–C21–C22	119.8 (6)
Cl13–Al1–Cl14	114.9 (1)	C2–C21–C26	120.7 (6)
Cl21–Al2–Cl22	94.7 (1)	C22–C21–C26	119.5 (8)
Cl21–Al2–Cl23	109.5 (1)	Cl23–Al2–Cl24	114.6 (2)
Cl21–Al2–Cl24	112.9 (1)	Zr–C1–C2	87.9 (4)
Cl22–Al2–Cl23	112.5 (1)	Zr–C1–C11	144.1 (5)
Cl22–Al2–Cl24	111.0 (1)	C2–C1–C11	126.6 (7)

[a] Estimated standard deviations (in parentheses) refer to the least significant digit.

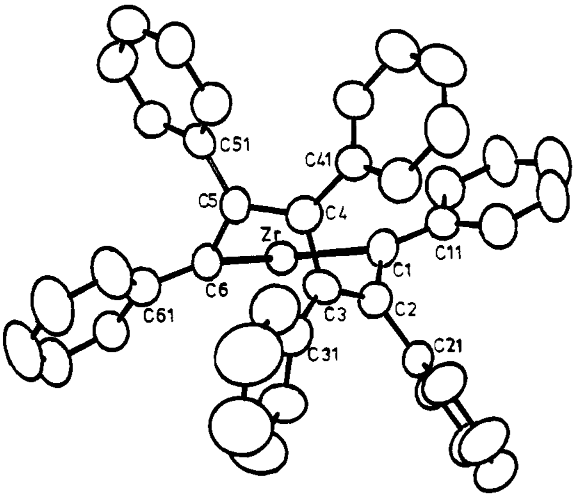

Figure 4. Molecular structure of 2. Tetrachloroaluminato groups are omitted for clarity.

to be noted that the distances between the carbon atoms forming the ring are similar (their values are between 1.40 (2) and 1.41 (1) Å) with the exception of the C3–C4 distance, which is 1.49 (2) Å. Moreover, the metallacycle is not planar (Figure 4), the C3 and C4 carbon atoms being in the closest nonbonding approach to zirconium (2.469 and 2.457 Å, respectively). The mean Zr–C bond distance is 2.188 (7) Å. Due to the particular findings concerning the C–C bond distances in the metallacycle, this compound should not be regarded as a zirconacycloheptatriene derivative, for which alternate long–short carbon–carbon distances within the ring should be expected.[12] The alternative description as a bis(carbene) derivative of zir-

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(11) We could confirm that HMDB rapidly isomerizes to HMB in the presence of AlCl$_3$ (see Experimental Section).

(12) Browning, J.; Green, M.; Penfold, B. R.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 31. Browning, J.; Green, M.; Laguna, A.; Smart, L. E.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1975**, 723.

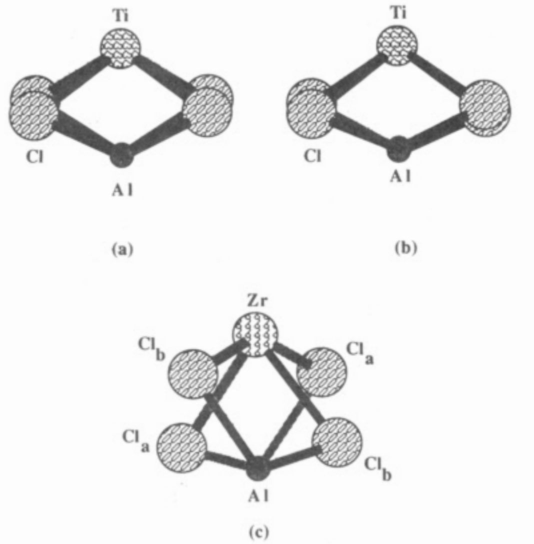


Figure 5. $M(AlCl_4)_2$ units of (a) Ti(η^6-benzene)[(μ-Cl)$_2$($AlCl_2$)]$_2$, (b) Ti(η^6-HMB)[(μ-Cl)$_2$($AlCl_2$)]$_2$, and (c) compound **2**, shown in lateral views along the Al–Al vector (terminal chloride ions have been omitted for clarity).

conium(II) might be more appropriate, although the detailed bonding parameters around zirconium and in the cycle do not satisfy any specific model completely. It will be noted that, on the basis of the carbon–carbon distances, two quasi-allyl systems may be recognized involving the C4–C5–C6 and the C1–C2–C3 sequences. It is interesting to note (see Figure 4) that the overall geometry of the six-carbon-atom sequence within the ring is similar to that suggested[13] for the six-membered cycle resulting from a quasi-conrotatory distortion of Dewar benzene in its thermal isomerization to benzene.

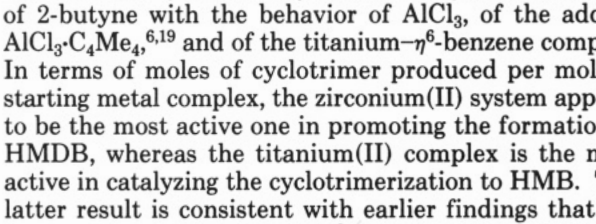
The main feature of the $Zr(AlCl_4)_2$ moiety is that the two $[AlCl_4]^-$ units are not eclipsed (Figure 5) as in the previously structurally characterized titanium(II) derivatives of this class[14] (see Figure 5a,b). In the case of our zirconium compound the dihedral angle between the planes containing Cl11, Cl12, Cl22 and Cl12, Cl21, Cl22 is 57.09 (7)° (Figure 5c). The Zr–Cl bond distances are significantly different (Zr–Cl11 = 2.662 (3) Å, Zr–Cl12 = 2.768 (2) Å, Zr–Cl21 = 2.646 (3) Å, Zr–Cl22 = 2.770 (1) Å). As far as the Al–Cl bond distances are concerned, the longer (average 2.19 Å) and the shorter (average 2.08 Å) values are very similar to those reported by Thewalt[14a,b] and Troyanov[14c,d] and their co-workers (average 2.17 and 2.07 Å, respectively) in Ti(η^6-arene)[(μ-Cl)$_2$($AlCl_2$)]$_2$ (arene = benzene, HMB) and compare well with the bridging (2.25 Å) and the terminal (2.07 Å) Al–Cl bond distances, respectively, in Al_2Cl_6.[15]

The isolation of the zirconium seven-membered cyclic derivative is important at least for two main reasons. Although some structural details are unique, the inorganic moiety of the molecule is similar to that encountered in some titanium(II)–η^6-arene derivatives.[14] There is therefore little doubt that the zirconium(II)–η^6-arene derivatives reported earlier[7] and the corresponding titanium(II) complexes should have similar solid-state and solution structures. Moreover, the formation of the seven-membered ring from the zirconium(II)–η^6-arene complexes and diphenylacetylene may have some relevance to the problem of 2-butyne trimerization of HMDB to HMB, promoted by zirconium and titanium organometallics.

Catalytic Cyclotrimerization. The cyclotrimerization of acetylenes to aromatic derivatives is a well-known reaction, extensively reviewed in the literature.[10f,16] However, to the best of our knowledge the cyclotrimerization of 2-butyne to HMDB is a rather rare process and, before this work, $AlCl_3$[10e,f] was the only efficient catalytic precursor known to carry out the highly exothermic[16d] conversion to the kinetically (at room temperature) inert HMDB. A few reports have mentioned the formation of hexaphenyl Dewar benzene from diphenylacetylene, for example by using palladium or iron complexes[17] or Mo(CO)$_3$(η^6-toluene)[18] as catalytic precursors. However, the catalytic turnover was 1 or lower[17] or it was not specified.[18]

As the presence of small amounts of $AlCl_3$ in the benzene solutions of **1** could not be excluded, arising from an equilibrium of the type shown in eq 2, the reaction of $AlCl_3$ with excess 2-butyne was studied in some detail, under experimental conditions similar to those used for the zirconium-promoted cyclotrimerization. Moreover, the titanium-promoted cyclotrimerization was investigated for comparison as well. It is also to be noted that a contribution to the cyclotrimerization may arise, for both zirconium and titanium, from a coordination site on aluminum becoming available through an equilibrium of the type shown in eq 3.

$$Zr(\eta^6\text{-benzene})(AlCl_4)_2 \rightleftarrows Zr(\eta^6\text{-benzene})(AlCl_4)Cl + AlCl_3 \quad (2)$$



(3)

Figures 1b–d and 2b–d compare the behavior of the zirconium(II)–η^6-benzene system in the cyclotrimerization of 2-butyne with the behavior of $AlCl_3$, of the adduct $AlCl_3 \cdot C_4Me_4$,[6,19] and of the titanium–η^6-benzene complex. In terms of moles of cyclotrimer produced per mole of starting metal complex, the zirconium(II) system appears to be the most active one in promoting the formation of HMDB, whereas the titanium(II) complex is the most active in catalyzing the cyclotrimerization to HMB. The latter result is consistent with earlier findings that the bromo–aluminato complex[6] of titanium(II) Ti(η^6-toluene)[(μ-Br)$_2$($AlBr_2$)]$_2$ is a more effective catalyst than $AlBr_3$ in promoting the cyclotrimerization of 2-butyne to

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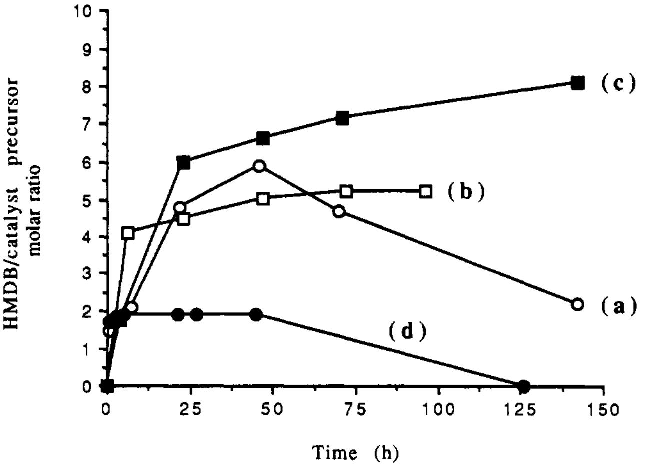

Figure 6. Time dependence of hexamethyl Dewar benzene (HMDB) formation from 2-butyne, expressed as the molar ratio between HMDB and the moles of aluminum present in the catalyst precursor. Reaction conditions are the same as in Figure 1.

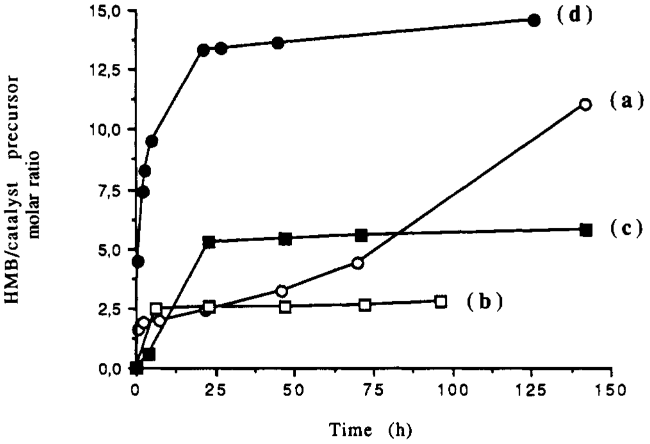

Figure 7. Time dependence of hexamethylbenzene (HMB) formation from 2-butyne, expressed as the molar ratio between HMB and the moles of aluminum present in the catalyst precursor. Reaction conditions are the same as in Figure 1.

HMB at both 25 and 80 °C and that the titanium–tetramethylcyclobutadiene complex[6] $Ti(\eta^4\text{-}C_4Me_4)[(\mu\text{-}Br)_2(AlBr_2)]_2$ is a catalytically active precursor in the cyclotrimerization of 2-butyne to HMB.

Figures 6 and 7 show the plots of the molar ratios between HMDB and HMB formed, respectively, and the chemically bonded $AlCl_3$ present in the system. This corresponds to attributing the observed catalytic activity to aluminum exclusively and to neglecting any contribution from the group 4 element and also amounts to saying that eq 2 is completely shifted to the right, a clearly unrealistic proposition. As a matter of fact, no other system, except the tetrachloroaluminato anion, was found to stabilize the titanium(II)– and the zirconium(II)–η^6-arene complexes, and all attempts to reduce the tetrachlorides MX_4 with systems other than Al/AlX_3 failed.[20] Besides being chemically unreasonable, the proposition that the zirconium– and titanium–tetrachloroaluminato complexes act as mere $AlCl_3$ carriers in our catalytic systems is not consistent with the data of Figures 6 and 7. In fact, while for reaction times up to about 50 h the behavior of $AlCl_3$, $AlCl_3{\cdot}C_4Me_4$, and $Zr(\eta^6\text{-benzene})(AlCl_4)_2$ is similar (the small differences may be attributed to the slightly different concentrations of 2-butyne used in the experiments), the effect of zirconium is clearly indicated by its tendency to isomerize HMDB to HMB to a greater extent than both $AlCl_3$ and $AlCl_3{\cdot}C_4Me_4$, even in the presence of unreacted 2-butyne. Finally, the greatly different behavior of the zirconium- and the titanium-based systems clearly indicates a specific role of the group 4 element in the catalytic cycle.

Presumably, the most appropriate interpretation of the results is that an equilibrium of the type shown in eq 3 is operating in solution and that the cyclotrimerization of 2-butyne to HMDB is actually occurring on the zirconium-modified aluminum chloride moiety of the molecule.

In conclusion, the data suggest that the aromatic product of the cyclotrimerization reaction grows predominantly on the group 4 element. The formation of HMDB should follow a different route, and we have no direct evidence of any plausible mechanism different from those already discussed in the literature, namely a cycloaddition to a metallacyclopentadiene intermediate.[16c]

We believe that the hexaphenyl-substituted complex isolated in this work is a good model to explain the formation of HMB from 2-butyne on the group 4 metal; in fact, elimination of the carbocyclic ligand from such an intermediate resulting from 2-butyne should lead to HMB directly. The sterically demanding phenyl groups allow the formation of the tetraphenylcyclobutadiene complex of titanium;[6] the larger zirconium atom induces enough stability in the seven-membered ring, and the corresponding compound becomes isolable.

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Supplementary Material Available: Listings of calculated hydrogen coordinates and anisotropic thermal parameters (U_{ij}, B_{ij}) and complete lists of bond lengths and angles (9 pages); a list of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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