

Journal of Organometallic Chemistry, 414 (1991) C15–C18
 Elsevier Sequoia S.A., Lausanne
 JOM 21974PC

Preliminary communication

Preparation and molecular structure of 1,1-dibromo-2,3,4,5,6,7-hexaphenyltitanacycloheptatriene

Karel Mach^a and Sergei I. Troyanov^{*,b}

^a *The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, 182 23 Prague 8 (Czechoslovakia)*

^b *Chemistry Department of Moscow State University, Lenin Hills, 119899 Moscow (USSR)*

(Received April 10th, 1991)

Abstract

The complex $\overline{\text{CPh}(\text{CPh})_4\text{CPhTiBr}_2}$ has been obtained by reaction of the system $\text{C}_6\text{Me}_6-(\text{C}_6\text{H}_6)\text{Ti}(\text{AlBr}_4)_2-2\text{Et}_3\text{Al}$ with diphenylacetylene. The titanacycloheptatriene ring is not planar, all C–C bonds are roughly equivalent and all carbon atoms are at bonding distances to titanium. The complex is a product of catalyst deactivation in which the oxidative addition of trimeric intermediate to Ti^{II} results in a release of aluminium-containing ligands.

The mechanism of cyclotrimerization of substituted acetylenes has recently been studied using bis(tetrahaloaluminato)(arene)titanium(II) complexes, $(\text{C}_6\text{H}_6)\text{Ti}(\text{AlX}_4)_2$ (X = Cl, Br, or partly Et) [1]. In particular with diphenylacetylene (DPA), evidence was obtained for the formation of 1:1 and 2:1 DPA:Ti complexes by electronic absorption spectroscopy; the X-ray single crystal analysis of the 2:1 product for X = Br revealed that it is the tetraphenylcyclobutadiene complex of Ti^{II} , $(\text{C}_4\text{Ph}_4)\text{Ti}(\text{AlBr}_4)_2$, which retained the pyramidal structure of the bis(tetra-bromoaluminato)titanium skeleton known from (arene)titanium(II) complexes [2–6]. The absence of a *d*–*d* absorption band in the electronic absorption spectra of the 2:1 complexes indicated that *d*-electron orbitals are strongly mixed with π -orbitals of the cyclobutadiene moiety [7]. The formation of further species corresponding to 3:1 complexes was indicated by their electronic absorption spectra but isolation was precluded by the instability of these complexes, which easily released hexaphenylbenzene (HPB). The catalytic activity of (arene)titanium(II) complexes was strongly affected by addition of Et_3Al : positively when X = Cl, negatively when X = Br.

Addition of a 6-fold excess of DPA to the benzene solution of $(\text{C}_6\text{Me}_6)\text{Ti}^{\text{II}}-(\text{AlBr}_3\text{Et})_2$ prepared by mixing C_6Me_6 with $(\text{C}_6\text{H}_6)\text{Ti}(\text{AlBr}_4)_2$ and Et_3Al in the ratio known for the chloro complex [8,9] resulted in the intense blue colouration of the solution due to the formation of 1,1-dibromo-2,3,4,5,6,7-hexaphenyltitana-

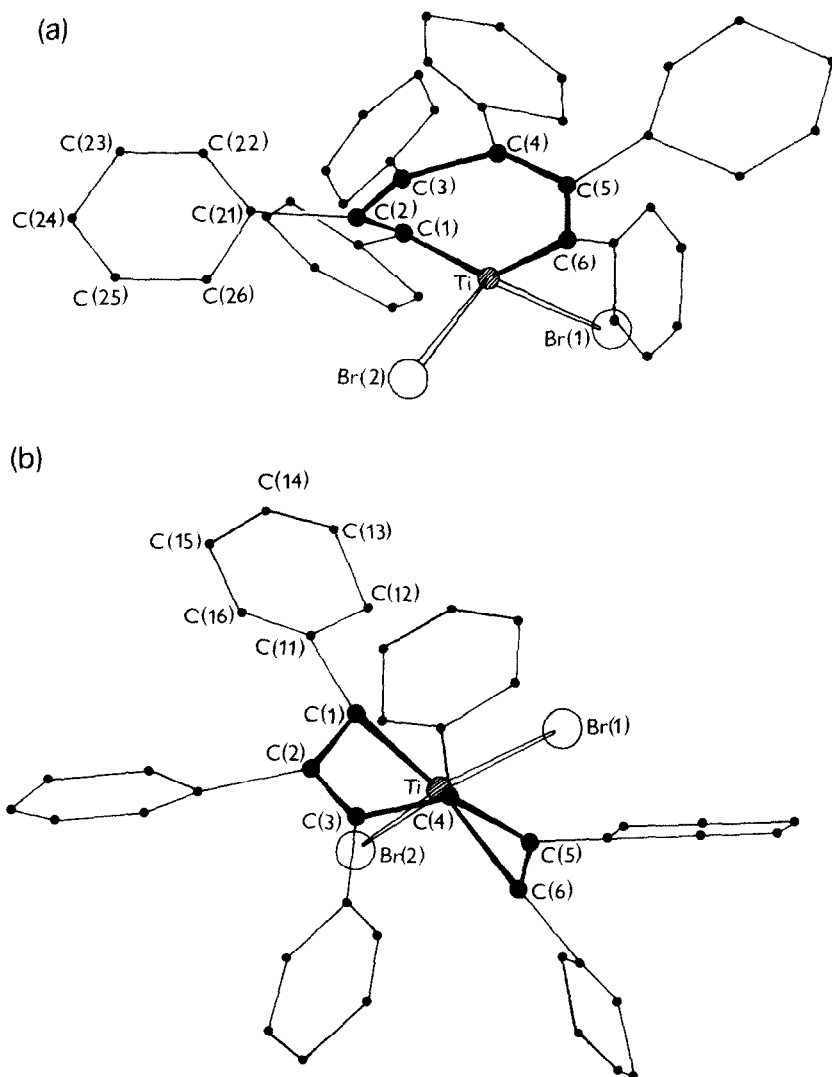


Fig. 1. The molecular structure and atom numbering scheme.

cycloheptatriene, $\overline{\text{CPh(CPh)}_4\text{CPhTiBr}_2}$ (**1**) [10*]. The conversion of the arene complex to **1** was quantitative according to measurement of the electronic absorption spectra. Single crystals of **1** (benzene solvate) were obtained from the hexane–benzene mixture by slow cooling and their structure was determined by X-ray analysis [11*].

The structure of **1** is depicted in Fig. 1; selected bond lengths and angles are listed in Table 1. The coordination around titanium is approximately tetrahedral. The Ti–C(1) and Ti–C(6) bond lengths (2.06, 2.04 Å) correspond to a strong σ -bond [12] whereas other Ti–C distances (2.37–2.51 Å) correspond to a π -bonding interac-

* Reference number with asterisk indicates a note in the list of references.

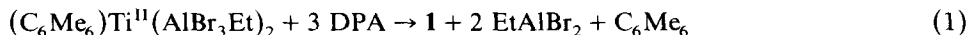
Table 1

Selected bond lengths and angles in **1** (esd's in parentheses)

<i>Bond lengths (Å)</i>			
Ti–Br(1)	2.398(3)	Ti–Br(2)	2.415(3)
Ti–C(1)	2.06(1)	C(1)–C(2)	1.43(2)
Ti–C(2)	2.47(1)	C(2)–C(3)	1.40(2)
Ti–C(3)	2.37(1)	C(3)–C(4)	1.45(2)
Ti–C(4)	2.38(1)	C(4)–C(5)	1.42(2)
Ti–C(5)	2.51(1)	C(5)–C(6)	1.36(2)
Ti–C(6)	2.04(1)	C(n)–C(n1)	av.1.47
<i>Bond angles (°)</i>			
Br(1)–Ti–Br(2)	107.3(1)	C(2)–C(3)–C(4)	114(1)
C(1)–Ti–C(6)	128.3(6)	C(3)–C(4)–C(5)	113(1)
Ti–C(1)–C(2)	88.1(9)	C(4)–C(5)–C(6)	111(1)
C(1)–C(2)–C(3)	108(1)	Ti–C(6)–C(5)	93.0(9)

tion. For example, the Ti–C distances in bis(tetrabromoaluminato)(tetraphenylcyclobutadiene)titanium, (C₄Ph₄)Ti(AlBr₄)₂ (**2**) are 2.27–2.30 Å [1]. The titanacycle is not planar as is seen from Fig. 1(b) and the carbon atoms (3) and (4) are closer to titanium than C(2) and C(5). Both these features are analogous to those found in 1,1-bis(tetrachloroaluminato)-2,3,4,5,6,7-hexaphenylzirconacycloheptatriene, CPh(CPh)₄CPhZr(AlCl₄)₂ (**3**), which has recently been prepared and its X-ray structure determined by Calderazzo et al. [13]. In contrast to the structure of **3**, the Ti–C(1) and Ti–C(6) bond lengths are shorter by 0.13 Å and the longest C–C distance is between C(3) and C(4) (1.45 Å) compared to the longest distance between C(3) and C(4) (1.49 Å) in **3**. The light asymmetry in the titanacycle (see Table 1) may be brought about by closer packing arising from smaller atom radius of Ti compared to Zr; in **3** the larger atom radius is responsible for accommodating four chlorine ligands along with the metallacycle. The asymmetry in **1** is retained in solution as the ¹³C NMR spectrum shows six different quaternary *sp*² carbon atoms in the region δ 134.05–143.71 attributable to the titanacycle. The strong absorption band of **1** in the visible region at 580 nm apparently reflects a large mixing of *d*-orbitals with *π*-orbitals, which may account for the nearly equal C–C distances in the metallacycle.

The formation of **1** from (C₆Me₆)Ti^{II}(AlBr₃Et)₂ exemplifies one deactivation mode in the cycloaddition reactions catalyzed by (arene)titanium(II) complexes [14]. The oxidative addition of an organic reaction intermediate to Ti^{II} decreases the stability of bis(aluminato)titanium(IV) skeleton, which results in a release of the aluminium components to give **1** according to eq. 1.



Acknowledgement. Kind submission of the manuscript of ref. 13 by the authors is highly appreciated.

References and notes

- 1 F. Calderazzo, F. Marchetti, G. Pampaloni, W. Hiller, H. Antropiusová and K. Mach, Chem. Ber., 122 (1989) 2229.

- 2 U. Thewalt and F. Österle, *J. Organomet. Chem.*, 172 (1979) 317.
- 3 U. Thewalt and F. Stollmaier, *J. Organomet. Chem.*, 228 (1982) 149.
- 4 S.I. Troyanov and V.B. Rybakov, *Metalloorg. Khim.*, 1 (1988) 1280.
- 5 S.I. Troyanov, M.Yu. Furkalyuk and V.B. Rybakov, *Metalloorg. Khim.*, 1 (1988) 298.
- 6 S.I. Troyanov and K. Mach, *J. Organomet. Chem.*, 389 (1990) 41.
- 7 B.E. Bursten and R.F. Fenske, *Inorg. Chem.*, 18 (1979) 1760.
- 8 K. Mach, H. Antropiusová and J. Poláček, *J. Organomet. Chem.*, 194 (1980) 285.
- 9 K. Mach, H. Antropiusová and J. Poláček, *J. Organomet. Chem.*, 385 (1990) 335.
- 10 Preparation of **1**. $(C_6H_6)Ti(AlBr_4)_2$ in benzene (0.02 M, 20 ml) was mixed with C_6Me_6 (72 mg, 0.4 mmol) and Et_3Al (1.0 M in benzene, 0.8 ml) in an evacuated ampoule and diphenylacetylene (0.4 g, 2.4 mmol) was added under shaking. An intense blue solution was separated from a white precipitate and small amount of a rusty precipitate and was diluted with hexane. Dark blue crystals were separated and recrystallized from the same solvent. Yield 0.22 g, 76%. 1H NMR (400 MHz, C_6D_6 , 25 °C): δ 6.749–6.916 mt (18H), 7.318 mt (4H), 7.463 mt (4H), 7.698 mt (4H); ^{13}C NMR (100 MHz, C_6D_6 , 25 °C): δ 127.6–132.34 (36C of Ph groups), 134.05 s, 134.60 s, 135.69 s, 138.84 s, 141.25 s, 143.71 s; UV–Vis (C_6H_6): 305–580 nm.
- 11 Crystal structure determination of **1** ($T = 296$ K; Enraf–Nonius CAD-4 four-circle diffractometer, Mo- K_α , graphite monochromator, $\theta_{max} = 23^\circ$): $C_{42}H_{30}TiBr_2 \cdot 0.5C_6H_6$, $M = 781.48$, monoclinic, space group $P2_1/c$, a 20.817(3), b 8.843(2), c 21.114(3) Å, β 93.64(3)°, V 4065 Å³, $Z = 4$, D_c 1.276 g cm⁻³, $\mu = 21.7$ cm⁻¹. Dark blue, nearly rectangular platelet approx. 0.1 × 0.3 × 0.4 mm mounted in a glass capillary under argon. 5834 row data intensity corrected for absorption, 2566 unique observed reflections with $F^2 \geq 2\sigma(F^2)$; structure solved (SHELX-86) by a combination of direct method and Fourier difference techniques and refined by full-matrix least-squares refinement with anisotropic thermal parameters for all nonhydrogen atoms of complex molecule and isotropic for C atoms of solvate benzene molecule. Positions of hydrogen atoms were calculated. The final residuals were $R = 0.075$ and $R_w = 0.081$. The atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
- 12 D. Cozak and M. Melnik, *Coord. Chem. Rev.*, 74 (1986) 53.
- 13 F. Calderazzo, G. Pampaloni, P. Pallavicini, J. Strähle and K. Wurst, *Organometallics*, submitted.
- 14 J. Poláček, H. Antropiusová, L. Petrusová and K. Mach, *J. Mol. Catal.*, 58 (1990) 53.