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On the crystal structures of bis(cyclopentylcyclopentadienyl)titanium dichloride and bis(cyclohexylcyclopentadienyl)titanium dichloride

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Abstract

The space groups of two crystal structures reported in recently (Q. Huang, Y. Qian, Y. Tang and S. Chen, J. Organomet. Chem., 340 (1988) 179) should be revised. The structures were described in space groups $P2_1$ and $P1$; the revised space groups are $P2_1/m$ and $C2$, respectively. The first change involves the addition of a center of symmetry, the second only a change in Laue symmetry (from $\bar{1}$ to $2/m$). Least squares refinements in the revised space groups have not been carried out since F values could not be obtained.

Results and discussion

(1) Bis(cyclopentylcyclopentadienyl)titanium dichloride

The structure was described [1] in space group $P2_1$ ($a = 6.584(2)$, $b = 24.011(7)$, $c = 6.713(1)$ Å, $\beta = 118.70(2)°$, $Z = 2$) and refined to $R_f = 0.034$ ($R_w = 0.036$) for 1191 reflections with $I > 1.96\sigma(I)$. Significant differences, up to 0.094(7) Å between equivalent Ti–C bonds and 0.19(1) Å between equivalent C–C bonds, were observed. The structure should be described in space group $P2_1/m$. Approximate coordinates in $P2_1/m$ are obtained by placing the titanium and chlorine atoms on the mirror and by averaging the coordinates of the other atoms related, in pairs, by the mirror (Table 1).

The $P2_1/m$ parameters of Table 1 lead, of course, to bond lengths and angles that are essentially the averages of the values previously reported, and are considerably more reasonable than the individual values. The differences between equivalent bonds previously reported were undoubtedly the result of problems associated with refining a centrosymmetric structure in a non-centrosymmetric space group.

(2) Bis(cyclohexylcyclopentadienyl)titanium dichloride

The structure [1] was described in space group $P1$ ($a = 6.679(3)$, $b = 6.743(4)$, $c = 13.772(8)$ Å, $\alpha = 81.76(5)$, $\beta = 76.24(4)$, $\gamma = 60.15(4)°$, $Z = 1$) and refined to

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Table 1

Coordinates ($\times 10^4$) in space group $P2_1/m$. Numbers in square brackets are shifts from the $P2_1$ coordinates necessary to achieve the $P2_1/m$ symmetry

Atom	x	y	z
Ti	8879	2500	12856
C11	5921	2500[4]	3897
C12	1838	2500[4]	6696
C(1,11)	8938[50]	1488[0]	3257[47]
C(2,12)	6940[56]	1641[7]	1232[36]
C(3,13)	7632[37]	1892[6]	−230[31]
C(4,14)	10037[188]	1888[2]	873[146]
C(5,15)	10876[102]	1652[5]	3029[63]
C(6,16)	8993[93]	1212[29]	5287[36]
C(7,17)	11105[54]	867[35]	6697[71]
C(8,18)	10485[178]	509[1]	8171[32]
C(9,19)	7887[196]	460[19]	6950[202]
C(10,20)	7074[120]	807[25]	4785[189]

Table 2

Coordinates ($\times 10^4$) for Ti and Cl and ($\times 10^3$) for the C atoms. The values on the left are obtained by transforming the coordinates in Table 3 of ref. 1, as described in the text; values on the right are derived by symmetrizing and averaging according to C2

Atom	x'	y'	z'	x'	y'	z'
Ti	0	0	0	0	0	0
C11	−1463(3)	−2408(7)	23(2)			
C121	1459(3)	−2423(7)	−25(3)	1461	−2415	−24
C1	−116(1)	−28(3)	−183(1)			
C21	115(1)	−25(2)	184(1)	116	−26	184
C2	−179(1)	96(3)	−146(1)			
C22	181(3)	106(3)	146(1)	180	101	146
C3	−107(2)	269(3)	−104(1)			
C23	108(1)	271(3)	105(1)	107	270	104
C4	11(1)	239(2)	−111(1)			
C24	−11(1)	240(3)	113(1)	−11	240	112
C5	3(1)	67(2)	−159(1)			
C25	1(1)	64(4)	162(1)	2	65	160
C6	−161(1)	−221(3)	−238(1)			
C26	162(1)	−223(3)	239(1)	162	−222	238
C7	−302(2)	−220(4)	−301(2)			
C27	305(1)	−223(4)	302(1)	303	−222	302
C8	−345(2)	−427(5)	−351(2)			
C28	349(2)	−427(4)	354(2)	347	−425	353
C9	−286(1)	−463(4)	−424(1)			
C29	288(2)	−468(4)	424(1)	287	−466	424
C10	−146(2)	−477(5)	−358(2)			
C30	147(2)	−471(4)	363(1)	146	−474	360
C11	−96(2)	−267(4)	−306(1)			
C31	94(2)	−282(3)	305(1)	95	−275	305

$R_f = 0.082$ ($R_w = 0.087$) for 1481 reflections with $I > 2.50\sigma(I)$. Space group $C2$ is to be preferred. The lattice vectors [1$\bar{2}$0], [100] and [$\bar{1}$11] define a C centered cell (a' 11.697, b' 6.679, c' 14.759 Å, α 90.20, β 115.04, γ 90.16°, $Z = 2$) and the corresponding transformation: $x' = \frac{1}{2}(\bar{y} + z)$, $y' = x + \frac{1}{2}(y + z)$, $z' = z$ leads to coordinates that are compatible with space group $C2$ within the reported esd's (left hand columns of Table 2). When these coordinates are symmetrized and averaged so as to correspond to space group $C2$, the values in the right-hand columns of Table 2 result. The change in space group requires that the molecule has an exact two-fold axis with the Ti atom located on the axis. Since the space group revision involves only a change in Laue group (from $\bar{1}$ to $2/m$) there are no significant changes in the geometry of the molecule [2].

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