Journal of Organometallic Chemistry, 132 (1977) 367—375
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THE CRYSTAL STRUCTURE OF DICARBONYLDICYCLOPENTADIENYLTITANIUM(II), $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$

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(Received November 15th, 1976)

Summary

The crystal structure of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ has been determined from single-crystal X-ray diffraction data collected by counter methods. Dicarbonyldicyclopentadienyltitanium(II) crystallizes in the orthorhombic space group *Pnma* with lattice constants $a = 7.837(9)$, $b = 11.475(8)$, $c = 12.232(8)$ Å, and $\rho_c = 1.41$ g cm^{-3} for $Z = 4$. Least-squares refinement gave a final conventional R value of 0.086 for 648 independent observed reflections. The molecule, which resides on a crystallographic mirror plane that passes through the cyclopentadienyl groups, possesses almost exact C_{2v} point symmetry. The Ti—C(carbonyl) bond length is 2.030(11) Å, while the average Ti—C(η^5) distance is 2.347(13) Å. The C—Ti—C bond angle is 87.6(6)°, and the ring center—Ti—ring center angle is 138.6°.

Introduction

The determination of the structure of carbonyl compounds of the transition metals has been an enduring problem. Numerous investigations by both electron and X-ray diffraction techniques have followed the initial study [1] of $Ni(CO)_4$ in 1935. The necessity of producing accurate bond lengths and angles has often required even more effort than the original determination. Thus, although the structure of $Fe(CO)_5$ was first obtained [2] in 1939, at least seven papers on the subject were reported [3—9] in the 1960's.

Because of the high current interest in metal carbonyls from the standpoint of catalysis, synthesis and unique bonding features, a wealth of well-determined structural parameters are now available for most transition metal carbonyls. In marked contrast, however, no such structural information has ever been obtained for carbonyl derivatives of the group IVB metals, even though synthetic breakthroughs and chemical studies on this unique class of organometallic compounds are expanding rapidly at the present time [10—17]. We have previously communicated the preliminary results [18] of the X-ray crystallographic study of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$, we now present a full discussion of the structure together with a comparison of the metal—carbon bond lengths in first-row transition metal—carbonyl complexes.

Experimental

Dicarbonyldicyclopentadienyltitanium(II) was prepared by the literature method [12] and recrystallized from toluene Single crystals of the compound were sealed in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of the angular settings of 12 reflections (2θ > 20°) accurately centered on an Enraf—Nonius CAD-4 diffractometer are given in Table 1. Because of problems with crystal decomposition it was not possible to obtain an accurate experimental density The space group was determined as *Pnma* or $Pn2_1a$ from systematic absences $0kl$, $k + l = 2n + 1$ and $hk0$, $h = 2n - 1$ Solution and refinement of the structure showed the correct choice to be the centric *Pnma*

Data were collected on the diffractometer with graphite crystal monochromated Mo-K_α radiation The diffracted intensities were collected by the $\omega - 2\theta$ scan technique with a take-off angle of 3 5° The scan rate was variable and was determined by a fast 20° min^{-1} prescan Calculated speeds for the slow scan (based on the net intensity gathered in the prescan) ranged from 7 to 0 2° min^{-1} Other diffractometer parameters and the method of estimation of standard deviations have been previously described [19] As a check on the stability of the instrument and crystal, three reflections were measured after every 30 reflections, no significant variation was noted

One independent octant of data was measured out to $2\theta = 52°$, a slow scan was performed on a total of 648 unique reflections Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 15 was obtained in the prescan Based on these considerations, the data set of 648 reflections (used in the subsequent structure determination and refinement) was considered observed, and consisted in the main of those for

TABLE 1

CRYSTAL DATA

Mol formula	$(C_5H_5)_2Ti(CO)_2$
Mol wt	234 11
Linear abs coeff μ	7 82 cm^{-1}
Calc density	1 41 g cm^{-3}
Max crystal dimensions	0 20 X 0 30 X 0 54 mm
Space group	orthorhombic *Pnma*
Molecules/unit cell	4
Cell constants [a]	a = 7 837(9) b = 11 475(8) c = 12 232(8) Å
Cell volume	1100 0 $Å^3$

[a] Mo-K_α radiation λ = 0 71069 Å Ambient temperature of 23 ± 1°C

which $I > 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects, but not for absorption (μ = 7.82 cm^{-1}), since the estimated minimum and maximum transmission factors are 0.75 and 0.84, respectively.

The function $w(|F_o| - |F_c|)^2$ was minimized [20]. No corrections were made for extinction. Neutral atom scattering factors were taken from the compilations of Cromer and Waber [21] for Ti, O, and C, those for H were from "International Tables for X-ray Crystallography" [22]. The scattering by Ti was corrected for the real and imaginary components of anomalous dispersion using Cromer's table [23].

Structure solution and refinement

The existence of four molecules per unit cell in the space group *Pnma* demanded that the molecule reside on either a mirror plane or a center of inversion: chemical intuition clearly ruled out the latter possibility. Interpretation of a Patterson map gave the position of the titanium atom, and a subsequent difference Fourier afforded the coordinates of the remaining non-hydrogen atoms. Least-squares refinement with isotopic temperature factors yielded $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ = 0.15. Conversion to anisotropic thermal parameters and further refinement gave R_1 = 0.090. The placement of the six symmetry-independent hydrogen atoms in calculated positions, and more cycles of least-squares refinement led to final values of R_1 = 0.086 and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$ = 0.082. The weighting scheme was based on unit weights, and unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviation. The estimated standard deviation of an observation of unit weight was 0.60. The final values of the positional and thermal parameters are given in Table 2 *.

Discussion

The molecular structure and atom numbering scheme of dicarbonyldicyclopentadienyltitanium(II) is given as Fig. 1, while the important bond distances and angles are listed in Table 3. The molecule, which resides on a crystallographic mirror plane that passes through the cyclopentadienyl groups, possesses almost exact C_{2v} point symmetry.

There are two features of the structure of primary importance: the metal—carbonyl and the metal—cyclopentadienyl interactions. In order to interpret the Ti—C(carbonyl) bond length of 2.030(11) Å, it is illustrative to draw a comparison across the first transition series. However, difficulties arise immediately because there are hundreds of structures of carbonyl compounds from which to choose. For our purposes it would be best to have bond distance data for compounds which are closely related to $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$. Since structural

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[*] The table of structure factors has been deposited as NAPS Document No. 02976 (7 pages). Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $ 5 for photocopies or $ 3 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 2

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS[a] FOR DICARBONYLDICYCLOPENTADIENYLTITANIUM(II)

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti	0.3418(3)	0.2500	0.0046(2)	0.0113(3)	0.0062(2)	0.0050(1)	0.0000	0.0002(2)	0.0000
O	0.1757(14)	0.0585(7)	0.1591(7)	0.0586(33)	0.0092(8)	0.0151(9)	−0.0069(14)	0.0132(15)	0.0026(7)
C(1)	0.0712(21)	0.2500	−0.0741(16)	0.0131(31)	0.0251(33)	0.0128(18)	0.0000	−0.0038(20)	0.0000
C(2)	0.1569(17)	0.1484(11)	−0.1153(12)	0.0227(26)	0.0137(14)	0.0170(15)	−0.0069(19)	−0.0096(19)	0.0021(13)
C(3)	0.2853(18)	0.1897(10)	−0.1741(10)	0.0363(35)	0.0131(13)	0.0099(10)	−0.0010(17)	−0.0068(15)	−0.0017(9)
C(4)	0.5584(25)	0.2500	0.1381(13)	0.0345(50)	0.0151(20)	0.0094(15)	0.0000	−0.0102(22)	0.0000
C(5)	0.5929(15)	0.1497(10)	0.0703(10)	0.0236(25)	0.0091(10)	0.0121(11)	0.0005(14)	−0.0074(14)	0.0014(9)
C(6)	0.6198(12)	0.1885(9)	−0.0349(10)	0.0134(21)	0.0108(11)	0.0138(12)	0.0018(11)	−0.0010(11)	−0.0020(9)
C(7)	0.2358(15)	0.1272(9)	0.1028(9)	0.0278(26)	0.0067(9)	0.0106(10)	−0.0006(13)	0.0018(13)	0.0003(8)
H(1)	−0.035	0.250	−0.023[b]						
H(2)	0.123	0.063	−0.101						
H(3)	0.374	0.177	−0.214						
H(4)	0.526	0.250	0.219						
H(5)	0.575	0.065	0.096						
H(6)	0.643	0.136	-0.103						

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ [b] Hydrogen atoms placed in calculated positions (1.00 Å from the bonded carbon atom) with $B = 6.0$ Å^2

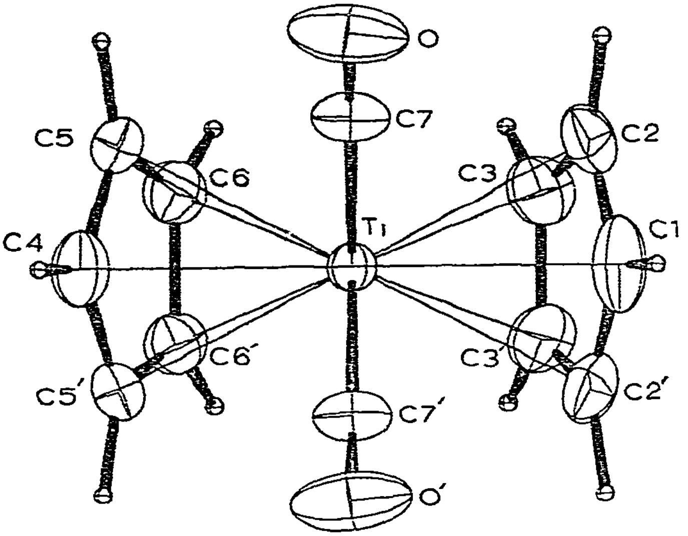

Fig 1 Structure of dicarbonyldicyclopentadienyltitanium(II) with the atoms displayed as their 50% probability ellipsoids for thermal motion

data on such analogues do not in general exist, Table 4 contains a reasonable alternative. for each metal an average of several metal—carbon(carbonyl) bond lengths taken from recent crystal structure determinations is listed. In this manner the trend in bond lengths is clearly shown The metal—carbon separations agree well with those predicted from metallic radii data [24] with only a slight bond length increase noted in the early transition metal complexes This means that the dearth of *d*-electrons in (η^5-C_5H_5)$_2$Ti(CO)$_2$ does not cause a marked elongation of the Ti—C(carbonyl) bond over that which would be suggested by metallic radii considerations

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR (η^5-C_5H_5)$_2$Ti(CO)$_2$

Ti—C(1)	2 328(16)	Ti—C(4)	2 356(16)
Ti—C(2)	2 368(12)	Ti—C(5)	2 354(11)
Ti—C(3)	2 336(11)	Ti—C(6)	2 340(10)
Ti—C(7)	2 030(11)		
Ti—Cent1 [a]	2 032	Ti—Cent2	2 018
C(1)—C(2)	1 44(2)	C(4)—C(5)	1 43(1)
C(2)—C(3)	1 32(2)	C(5)—C(6)	1 39(1)
C(3)—C(3) [b]	1 38(2)	C(6)—C(6)	1 41(1)
C(7)—O	1 15(1)		
C(7)—Ti—Cent1	104 1	C(7)—Ti—Cent2	105 4
C(7)—Ti—C(7)	87 9(6)	Cent1—Ti—Cent2	138 6
Ti—C(7)—O	179 4(9)		
C(2)—C(1)—C(2)	108(1)	C(5)—C(4)—C(5)	107(1)
C(1)—C(2)—C(3)	105(1)	C(4)—C(5)—C(6)	108(1)
C(2)—C(3)—C(3)	111(1)	C(4)—C(6)—C(6)'	109(1)

[a] Cent1 is the centroid of the cyclopentadienyl ring which contains C(1) C(2) and C(3) Cent2 is that of C(4) C(5) and C(6) [b] Primed atoms are related to those given in Table 2 by (x $\frac{1}{2}-y$ z)

TABLE 4

SUMMARY OF METAL—CARBON(CARBONYL) BOND LENGTHS ACROSS THE FIRST TRANSITION METAL SERIES

Metal (M)	M—C(carbonyl) [a] (Å)	R [b]	Δ(Ti—M)		Compound	Ref
			M—C	R		
Ti	2.03	1.47			$(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$	This work
V	1.93	1.34	0.10	0.13	$[\{(C_6H_5)_3P\}_2N][V(CO)_6]$	45
Cr	1.86	1.28	0.17	0.19	$(\eta^5\text{-}C_{13}H_9)Cr(CO)_2(NO)$	46
Mn	1.80	1.27	0.23	0.20	$(CO)_3MnB_9H_{12}\cdot THF$	47
Fe	1.77	1.26	0.26	0.21	$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(SO_2)$	48
Co	1.76	1.25	0.27	0.22	$Co_3(CO)_7As_2F_4C_{10}H_{15}$	49
Ni	1.80	1.24	0.23	0.23	$Ni_2[(CF_3)_2PSP(CF_3)_2(CO)_3$	50
Cu	1.76	1.28	0.27	0.19	$[HB(C_3N_2H_3)_3]Cu(CO)$	51

[a] The M—C distance is the average from several recent determinations and the compound given is an example of one which possesses the average distance. [b] Ref. 24.

The nature of the interaction of the cyclopentadienyl group with early transition metal atoms has recently been extensively investigated. The original model for the bonding in $(\eta^5\text{-}C_5H_5)_2ML_2$ complexes was supplied by Ballhausen and Dahl [25] in 1961. An alternative explanation was given by Alcock [26] in 1967, and features of both were incorporated in the modification proposed by Green, Green and Prout [27] in 1972. Important experimental substantiation came in the form of a large body of structural data [28]. It was seen that the important parameter was the L—M—L bond angle: metals with d^2 electronic configurations were found to exhibit values from 76 → 82°, whereas d^1 gave 85 → 88°, and d^0, 94 → 97°. Lauher and Hoffmann [29] have subsequently reported calculated values for the L—M—L angles of ~85° for d^1, and 110° for d^0.

The data given in Table 5 show additional variables superimposed on this general trend. Thus, the d^0 complexes exhibit angles mainly in the range 86 → 95°, and the d^1 moieties, from 76 → 82°. However, the diversity of ligand systems employed causes noteworthy discrepancies. The metallocyclic ring systems with first row elements, exemplified by $(\eta^5\text{-}C_5H_5)_2Ti(bipy)$ [30], $[(\eta^5\text{-}C_5H_5)_2Ti\cdot DME]_2[Zn_2Cl_6]\cdot C_6H_6$ [31], $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_4$ [32], and $(\eta^5\text{-}C_5H_5)_2TiC_8H_4\text{-}(C_6F_5)_2$ [33], show a narrow range of L—Ti—L angles (76.1 → 80.3°) due to the constraints of the heteroatom rings.

In assessing the meaning of the L—Ti—L bond angle, another important consideration is the Ti—L bond length. For $(\eta^5\text{-}C_5H_5)_2TiCl_2$ [34], the Ti—Cl distance is 2.364(2) Å, while in $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$, the Ti—C separation is 2.030(11) Å. This causes a comparatively greater steric interaction between carbonyl carbon atoms, and may be the origin of the large C—Ti—C bond angle, 87.9(6)°.

The one parameter which seems to be relatively unaffected by the choice of the L group is the distance of the titanium atom to the center of the cyclopentadienyl ring. For d^0 the average of the eight determinations [32—39] given in Table 5 is 2.068(8) Å, while for d^1 the average of the eight values [31,40—44] is 2.045(11) Å. Because of crystallographic problems there is a large uncertainty associated with the 2.11 Å distance listed for $(\eta^5\text{-}C_5H_5)_2Ti(bipy)$ [30]. The most accurate value for the d^2 case is that given for $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$,

TABLE 5

COMPARISON OF STRUCTURAL PROPERTIES OF COMPOUNDS OF THE GENERAL FORMULA $(\eta^5\text{-}C_5H_5)_2TiL_2$

Compound	Electronic configuration of titanium	L—Ti—L Angle (°)	Distance of Ti from cyclopentadienyl ring centroid (Å)	Ref
$(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$	d^2	87 9(6)	2 025	This wo
$(\eta^5\text{-}C_5H_5)_2Ti(bipy)$ [a]	d^2	76 1(4)	2 11	30
$(\eta^5\text{-}C_5H_5)_2Ti[C_6H_3(CH_3)_2]$	d^1		2 030	40
$(\eta^5\text{-}C_5H_5)_2Ti(BH_4)$	d^1		2 03	42
$[(\eta^5\text{-}C_5H_5)_2Ti\ \ DME]_2[Zn_2Cl_6]\ \ C_6H_6$ [b]	d^1	76 6(2)	2 04	31
$[(\eta^5\text{-}C_5H_5)_2TiCl]_2ZnCl_2\ \ 2C_6H_6$	d^1	82 09(6)	2 04	31
$[(\eta^5\text{-}C_5H_5)_2TiCl]_2$	d^1	78 42(7)	2 05	43
$(\eta^5\text{-}C_5H_5)_2Ti(\eta^2\text{-}C_5H_5)$	d^1		2 05	41
$[(\eta^5\text{-}C_5H_4CH_3)_2TiCl]_2$	d^1	79 26(6)	2 06	43
$[(\eta^5\text{-}C_5H_5)_2TiCl]_2MnCl_2 \cdot 2THF$ [c]	d^1	81 31(6)	2 06	44
$(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6F_5)_2$ [d]	d^0	78 3(4)	2 049	33
$(\eta^5\text{-}C_5H_5)_2Ti(NCO)_2$	d^0	94 7(2)	2 056	35
$(\eta^5\text{-}C_5H_5)_2TiCl_2$	d^0	94 53(6)	2 059	34
$(CH_2)_3(\eta^5\text{-}C_5H_4)_2TiCl_2$	d^0	93 69(5)	2 061	36
$(\eta^5\text{-}C_5H_5)_2TiS_5$	d^0	94 6	2 064	37
$(\eta^5\text{-}C_5H_5)_2TiC_4(C_6H_5)_4$	d^0	80 3(2)	2 065	32
$(\eta^5\text{-}C_5H_5)_2Ti(Cl)OCCo_3(CO)_9$	d^0	92 0	2 07	38
$(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}C_5H_5)_2$	d^0	86 3	2 078	39

[a] Here and elsewhere in the manuscript bipy is used as an abbreviation for the bipyridyl ligand [b] DME is dimethoxyethane [c] THF is tetrahydrofuran [d] TiC_8 is the titanaindene group

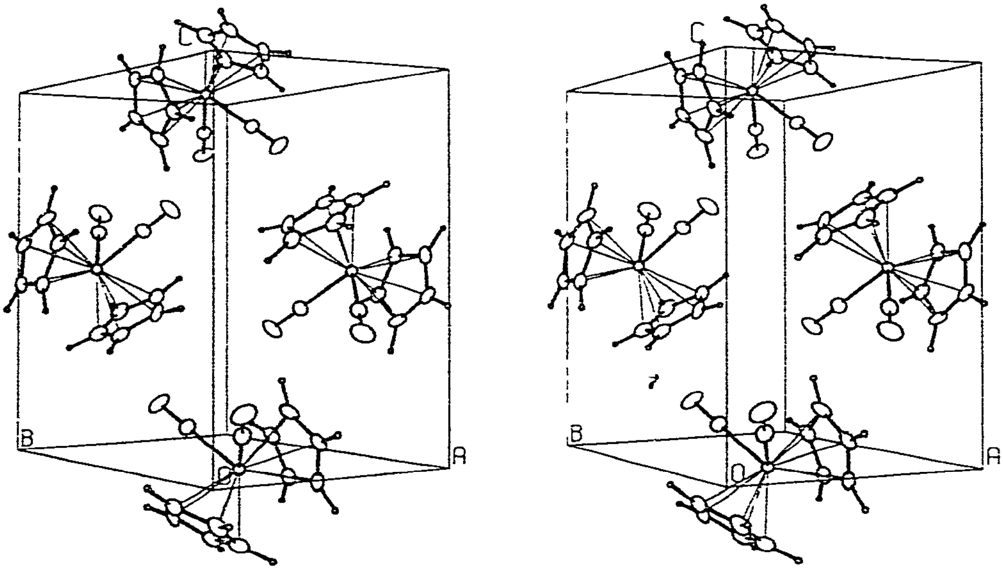

Fig. 2 Stereoscopic view of the unit cell packing for $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$

2.025 Å. Although there is a rather large spread in the values given in Table 5, the differences among the averages are undoubtedly real because of the large number of determinations involved Thus, with the addition of d electrons there is a decrease in the Ti—ring center distance (or a decrease in the Ti—C(η^5) bond length). Therefore, it appears that the d electrons reside in an orbital which is at least slightly bonding with respect to the titanium—cyclopentadienyl interaction.

It is interesting to note that the cyclopentadienyl rings exist in an eclipsed configuration (Fig. 1) A consequence of this is the abnormally high centroid—Ti—centroid angle, 138 6°. In molecules with the staggered arrangement, the value ranges from 130.97° in $(\eta^5\text{-}C_5H_5)_2TiCl_2$ [34] up to 134 8(3)° in $(\eta^5\text{-}C_5H_5)_2TiC_4(C_6H_5)_4$ [32]. An eclipsed configuration is also found in $(CH_2)_3(\eta^5\text{-}C_5H_4)_2TiCl_2$, but here apparently the constraint placed by the three-carbon atom bridge reduces the centroid—Ti—centroid angle to 132.64°

The carbonyl group bonds to the titanium atom in a strictly linear fashion· the Ti—C—O angle is 179.4(9)° The C—O bond length of 1 15(1) Å is well within accepted values for the ligand [45].

The unit cell packing, shown in Fig. 2, is typical of a molecular compound of this type

Acknowledgements

The authors are grateful to the National Science Foundation for a grant to M D R. in support of this research program, to the Research Grants Committee of the University of Alabama for a grant to J L A., and to the Deutsche Akademischer Austauschdienst, Bonn/Bad Godesberg, Germany, for a fellowship for H A.

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