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Preliminary communication

CRYSTAL AND MOLECULAR STRUCTURE OF TITANOCENE DICARBONYL, $(h^5\text{-}C_5H_5)_2Ti(CO)_2$

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Summary

The first X-ray structural determination of a complex with a Ti—carbonyl linkage is reported. The Ti—C(carbonyl) bond length is 2.030(11) Å, and the average Ti—C(cyclopentadienyl) distance is 2.347(9) Å.

Although titanocene dicarbonyl (dicarbonyldicyclopentadienyltitanium(II)) was first obtained by Murray in 1958 [1], the chemistry of this unique metal carbonyl has been little developed, due primarily to the considerable experimental difficulties and low yields incurred in its preparation by the original literature method. Very recently, however, several greatly improved methods for the synthesis of titanocene dicarbonyl have been reported [2-4], and a variety of reactions involving displacement of the carbonyl ligands by acetylenes, 2,2′-bipyridine, alkyl halides, acyl halides, iodine, 9,10-phenanthroquinone, etc., have been described [2,4-8].

In view of the high current interest in titanocene dicarbonyl and the fact that no detailed structural information is available on any carbonyl derivative of a Group VIB metal, it was of interest to undertake an X-ray crystallographic investigation of this molecule. Our results are reported in the present communication, together with a comparison of structural parameters with iron carbonyls.

The dark reddish-brown air-sensitive compound cystallizes in the orthorhombic space group *Pnma* with unit cell parameters $a = 7.837(9)$, $b = 11.475(8)$, $c = 12.232(8)$ Å, and $Z = 4$. Full matrix least-squares refinement of 648 observed reflections measured on an Enraf-Nonius CAD-4 diffractometer has given a final R value of 0.086. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in calculated positions.

The molecule, shown in Fig. 1, resides on a crystallographic mirror plane, which bisects each of the cyclopentadienyl groups. The configuration of the rings is eclipsed, and the centroid—metal—centroid angle in 138.6°. This is much larger than the value for $(C_5H_5)_2TiCl_2$ (131.0°) [9], where the rings are staggered, or for $(CH_2)_3(C_5H_4)_2TiCl_2$ (132.6°) [10], where the rings are eclipsed, but bridged together. The C(carbonyl)—Ti—C(carbonyl) angle is 87.9(6)°.

An important structural feature is the Ti—C(carbonyl) bond distance: 2.030(11) Å. In order to examine the meaning of this length, a comparison with iron is made in Table 1. The Fe—C(carbonyl) bond lengths reported in the literature cover a wide range, but the recent structure determination of the Fe^{II} complex $(C_5H_5)Fe(CO)_2(C{\equiv}CC_6H_5)$ [11] presents a molecule geometrically similar to $(C_5H_5)_2Ti(CO)_2$. From Table 1, it is seen that the Ti—C-(carbonyl) bond is longer than one might predict. It is possible that this observation could be due to the smaller number of *d*-electrons available for titanium, or to the higher energy of the titanium *d*-orbitals [13].

In view of the renewed theoretical interest in molecules of the type $M(\eta^5\text{-}C_5H_5)_2L_2$ [14,15], it is worthwhile to note the effect of the oxidation state of the titanium atom on the Ti—C(cyclopentadienyl) bond lengths. For several well-determined structures of Ti^{IV} complexes [10,16-18], the

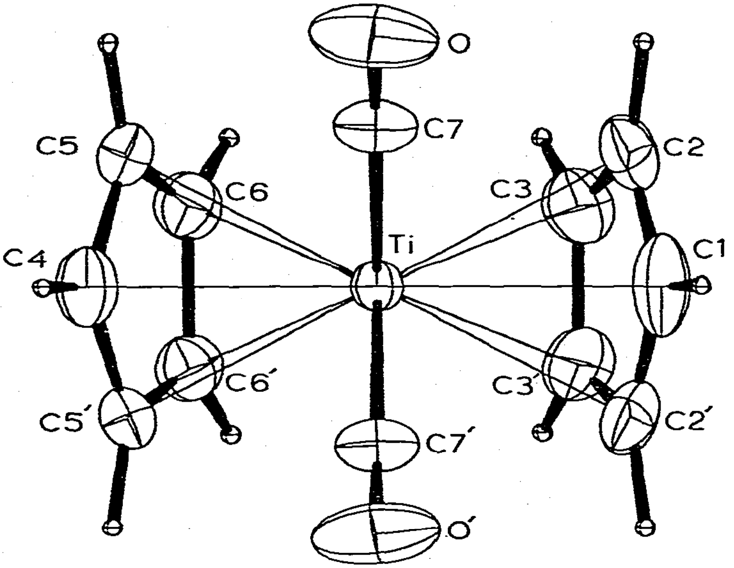

Fig. 1. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$.

TABLE 1

COMPARISON OF TITANIUM— AND IRON—CARBONYL BOND LENGTHS WITH METALLIC [a] RADII

	M—C (carbonyl)	R
Ti	2.030(11)	1.47
Fe	1.754(4)	1.26
Δ (Ti—Fe)	0.28	0.21

[a] Metallic radii with legancy = 12 as given by ref. 12.

average Ti—C separation is 2.379 Å. The Ti—C lengths for Ti^{III} complexes [19-21] average ~2.36 Å, and the value from the $(C_5H_5)_2Ti(CO)_2$ structure is 2.347 Å*. The trend is therefore the reverse of what simple ionic radii would predict. This result is consitent with a model in which the *d*-electrons occupy a molecular orbital which is bonding with respect to the metal—ring interaction. The effect of the decrease in the metal ion radius in going from $(C_5H_5)_2Ti^{II}$ to $(C_5H_5)_2Ti^{IV}$ is thus offset by a weakening of the metal—ring bonding.

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References

1 J.G. Murray, J. Amer. Chem. Soc., 81 (1959) 752; 83 (1961) 1287.
2 G. Fachinetti and C. Floriani, J. Chem. Soc. Chem. Commun., (1972) 654.
3 H. Alt and M.D. Rausch, J. Amer. Chem. Soc., 96 (1974) 5936.
4 P.C. Wailes, R.S.P. Coutts and H. Weigold, Organometallic Chemistry of Titanium, Zirconium and Hafnium, Academic Press, New York, 1974, p. 239ff.
5 K. Sonogashira and N. Hagihara, Bull. Chem. Soc. Jap., 39 (1966) 1178.
6 E.O. Fischer and R. Amtmann, J. Organometal. Chem., 9 (1967) P15.
7 C. Floriani and G. Fachinetti, J. Chem. Soc. Chem. Commun., (1972) 790.
8 G. Fachinetti and C. Floriani, J. Chem. Soc. Chem. Commun., (1974) 66.
9 A. Clearfield, D.K. Warner, C.H. Saldarriaga-Molina, R. Ropal and I. Bernal, personal communication.
10 B.R. Davis and I. Bernal, J. Organometal. Chem., 30 (1971) 75; E.F. Epstein and I. Bernal, Inorg. Chim. Acta, 7 (1973) 211.
11 R. Goddard, J. Howard and P. Woodward, J. Chem. Soc. Dalton, (1974) 2025.
12 L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, N.Y., 1960, p. 403.
13 E. Clementi, J. Chem. Phys., 41 (1964) 295.
14 J.L. Petersen and L.F. Dahl, J. Amer. Chem. Soc., 96 (1974).
15 J.C. Green, M.L.H. Green and C.K. Prout, J. Chem. Soc. Chem. Commun., (1972) 421.
16 J.L. Atwood, W.E. Hunter, H. Alt and M.D. Rausch, unpublished results.
17 E.F. Epstein, I. Bernal and H. Köpf, J. Organometal. Chem., 26 (1971) 229.
18 J.L. Calderon, F.A. Cotton, B.G. DeBoer and J. Takats, J. Amer. Chem. Soc., 93 (1971) 3592.
19 P.A. Kroon and R.B. Helmholdt, J. Organometal. Chem., 25 (1970) 451.
20 K.M. Melmed, D. Coucouvanis and S.J. Lippard, Inorg. Chem., 12 (1973) 232.
21 C.R. Lucas, M. Green, R.A. Forder and K. Prout, J. Chem. Soc., Chem. Commun., (1973) 97.
22 G.D. Stucky and A.M. PcPherson, personal communication.

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*The Ti—C bond lengths average 2.42 Å in dicyclopentadienylpyridyltitanium(II), but due to the range (2.356 → 2.507 Å), and to crystallographic disorder, they are not included in thus comparison [22].