Reaction of Carbon Dioxide with Diphenyltitanocene and *X*-Ray Crystal Structure of the Product

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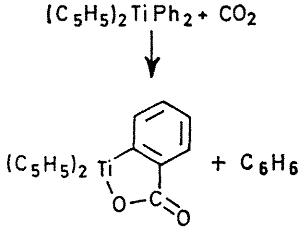
Summary The reaction of carbon dioxide with dicyclopentadienyldiphenyltitanium leads to carboxylation of the phenyl ring and to metallocycle formation; the molecular structure of the compound has been determined by an *X*-ray study.

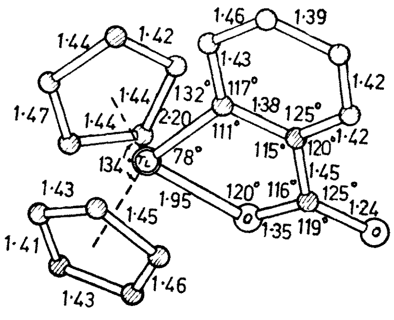
CARBON DIOXIDE is known to react with transition metal compounds (excluding carbonate formation) either with the formation of complexes[1,2] or with insertion of CO_2 into the metal–hydrogen bond.[3,4] We have now investigated the reaction of bis-(π-cyclopentadienyl)diphenyltitanium with carbon dioxide (80—90°; CO_2 bubbled through a solution in xylene), which gave diamagnetic, air-stable, red crystals, m.p. 192—195° (decomp.), (35%) soluble in acetone and benzene, but insoluble in ether or light petroleum. The i.r. spectrum shows Ph and C_5H_5 absorptions and also bands at 880m, 1130s, 1280vs, 1620s, and 1660vs cm^{-1}; ^1H n.m.r. spectrum: δ 6·5—7·55 (phenyl) and 6·45 (C_5H_5) p.p.m. (relative areas 4 : 10).

Heating of the compound with dilute H_2SO_4 (1 : 1) gives benzoic acid and the action of BF_3 in methanol (100°; 3 h) gives methylbenzoate (70%). Pyrolysis at 200° gives CO_2, benzene, and cyclopentadiene. These data, together with elemental analyses, its molecular weight, and its mass spectrum support the formulation as structure (I).



(I)

We carried out an *X*-ray study to investigate the mode of CO_2 co-ordination. Crystals of (I) are orthorhombic. *Crystal data*: $a = 13{\cdot}744(2)$, $b = 14{\cdot}410(2)$, $c = 13{\cdot}774(2)$ Å; $D_m = 1{\cdot}46$, $D_c = 1{\cdot}46$ g cm^{-3} for $Z = 8$, space group *Pbca*. The structure was determined by the heavy atom method and refined by least-squares (full-matrix, isotropic temperature factors). At the present stage of refinement $R = 0{\cdot}13$ for *ca.* 800 independent reflexions. The molecular structure (Figure) is in full agreement with the formulation (I). Standard deviations are in the range 0·01–0·03 Å for bond lengths and of 1—3° for bond angles depending upon atomic numbers. All ten Ti–C(cyclopentadienyl) distances are practically equivalent (2·39 Å) and agree well with those found in other titanocene derivatives.[5–8] Average C–C bond lengths in the π-cyclopentadienyl (1·44 Å) and σ-phenyl (1·41 Å) rings are normal. The titanium atom has a distorted tetrahedral co-ordination (assuming that each cyclopentadienyl ligand occupies one co-ordination site). The dihedral angle between π-cyclopentadienyl ring planes (46°) is similar to that for other titanocene derivatives.

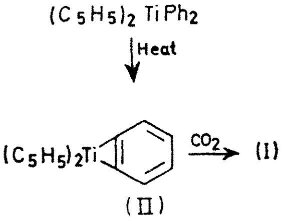


FIGURE

The Ti–C(Ph) σ-bond is significantly shorter (2·20 Å) than the sum (2·30 Å) of the single-bonded covalent radii of Ti (1·56 Å) and C (0·74 Å) and also than the Ti–C σ-bond length (2·32 Å) in π-$(C_5H_5)_2Ti(\sigma$-$C_6H_5)_2$.[5] The Ti–O distance (1·95 Å) is close to those in, *e.g.*, $[TiCl(\pi$-$C_5H_5)(C_9H_6NO)_2]$ (1·954 and 1·987 Å).[9] The C–O (1·35 Å) and C=O (1·24 Å) distances in the carboxy-group are close to normal (1·36 and 1·23 Å[10]) and the C(Ph)–C(carboxylate) bond length (1·45 Å) is close to twice the covalent radius of

C(sp^2) (1·48 Å). The five-membered metallocycle is strictly planar and makes an angle of only 3° with the plane of the phenyl ring.

The formation of (I) can be visualized as occurring *via* insertion of CO_2 into a Ti–C bond of the phenylene titanium complex (II). It has been suggested recently[11] that the latter is an intermediate in the thermal decomposition of $(C_5H_5)_2$ $TiPh_2$. A similar insertion of diphenylacetylene into (II) gives 1,1-di-(π-cyclopentadienyl)-2,3-diphenyl-1-titanaindene.[12]



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