Crystal and Molecular Structure of Triscyclopentadienyltitanium: the Cyclopentadienyl Group as a Two-centre Three-electron Ligand

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Summary The molecular structure determination of triscyclopentadienyltitanium shows one cyclopentadienyl ligand is bonded to the metal by only two carbons and an M.O. description in terms of a three-centre, four-electron bonding model is suggested.

THE cyclopentadienyl radical commonly bonds to transition metals either as a 1-electron (1e) σ- or 5-electron (5e) sandwich bonded π-cyclopentadienyl system. We have determined the crystal and molecular structure of the neutral paramagnetic molecule triscyclopentadienyltitanium first described by Fischer.[1]

Crystal data: $C_{15}H_{15}Ti$, $M = 243{\cdot}2$, orthorhombic, $a = 13{\cdot}47$, $b = 10{\cdot}23$, $c = 17{\cdot}18$ Å, space group *Pbca*, $Z = 8$, Cu-K_α radiation, $\mu = 60$ cm^{-1}; four-circle diffractometer data, 1461 independent reflections. The structure, determined by the heavy-atom method, is being refined by full-matrix least-squares. Hydrogen atoms have been located. R is presently 0·065.

The crystals are built up from discrete monomeric $(C_5H_5)_3Ti$ molecules with two 5e-π-cyclopentadienyl groups each forming five equivalent bonded metal–carbon contacts and one unusual π-cyclopentadienyl group with only two (adjacent) carbon atoms at bonded distances from the titanium. In Figure 1 the molecule is shown in projection on to the plane defined by the metal atom and the centroids of the two normal π-cyclopentadienyl groups. All three rings are essentially perpendicular to this plane and themselves planar within experimental error. The eight shorter non-bonded carbon–carbon contacts between the three π-cyclopentadienyl groups are approximately equivalent (in the range 3·07—3·27 Å). The geometry of the (5e-π-$C_5H_5)_2Ti$ portion is that commonly found in other bent 5e-π-cyclopentadienyltitanium systems, *e.g.* $(C_5H_5)_4Ti$,

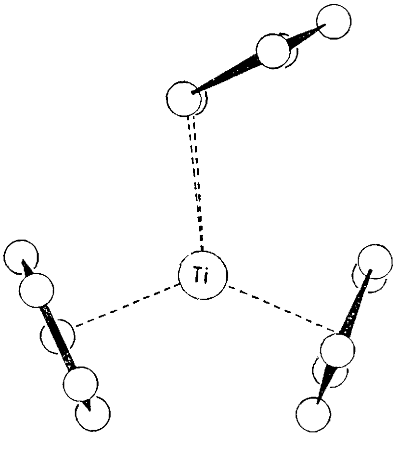

FIGURE 1. $(C_5H_5)_3Ti$ *projected on to the plane containing the metal atom and the centroids of the two normal π-cyclopentadienyl groups.*

$(C_5H_5)_2Ti(S_2C_6H_4)$,[3] and $(C_5H_5)_2Ti(\mu\text{-SMe})_2Mo(CO)_4$,[4] with a staggered configuration and the titanium atom 2·04 and 2·06 Å, respectively, along the normals to the π-cyclopentadienyl rings. The ring normals are inclined at an angle of 133°, the Ti–C distances are in the range 2·34—2·41 Å and the bonded C–C distances within the rings in the range 1·38—1·44 Å.

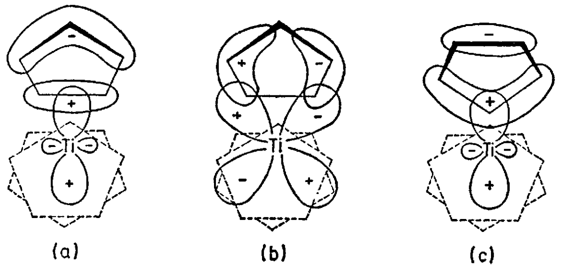
(a) (b) (c)

FIGURE 2. (a) *The σ-symmetry interaction between ψ_B and ψ_{-1}.* (b) *The π-symmetry interaction between $\psi_C(d_{xy})$ and ψ_{+1}.* (c) *The ψ_B — ψ_{-1} interaction for the inverted conformation where ψ_B and ψ_C are the titanium orbitals and ψ_{+1} and ψ_{-1} those of the cyclopentadienyl group. For ψ_{+1} and ψ_{-1} only the part on the same side of the ligand as the titanium atom is shown.*

The Ti–C bond lengths to the atoms of the remaining C_5H_5 ring are, cyclically, 2·42, 2·48, 3·36, 3·78, and 3·31 Å; there is no significant variation in the C–C bonded distances (1·42—1·44 Å) around the ring. The mean plane of this ring makes an angle of 112° with that defined by its two titanium–carbon atom bonds which itself is inclined at an angle of 93° to the plane of the titanium and the 5e-π-ring centroids.

It is suggested that the unusual cyclopentadienyl radical is acting as a 3-electron ligand, so that the titanium adopts a 17-electron configuration. On this basis the bonding may be simply described in terms of the model recently suggested for bent bis-(π-cyclopentadienyl) compounds.[5] Orbital symmetry permits non-zero overlap between ψ_0 and ψ_{-1} on the ring and ψ_B on the metal (σ-symmetry), and between ψ_{+1} on the ring and ψ_C on the metal (π-symmetry), Figure 2(a) and (b).

The suggestion is, therefore, that one of the molecular orbitals arising from the former interaction will be localised mainly on the ligand. This could well look very like ψ_0, possibly accounting for the near equality of C–C bonds around the ring, in which case the interaction could be regarded simply as one between ψ_{-1} and ψ_B. The resulting bonding M.O., together with that from ψ_{+1} and ψ_C, then permits the formation of the postulated 3-centre, 4-electron bond. This description of the bonding is essentially the same as that for a hypothetical compound where the unusual cyclopentadienyl group is inverted [see Figure 2(c)]. However, in this case the bonding would mainly involve three carbons of the cyclopentadienyl group, in an allylic type system. If, as would be expected, the three metal–carbon distances were about the same and the C_5-ring remained essentially planar then it necessarily follows[6] that all the metal–carbon distances would be the same, as they are in a metal–5e-π-cyclopentadienyl system. Such a model with pseudo-equivalent π-cyclopentadienyl groups would lead to a grossly overcrowded structure if the present bonded titanium carbon contacts were maintained and it seems that the observed structure is preferred because it leads to lower molecular overcrowding.

The configuration adopted by the 3e-π-cyclopentadienyl group may serve as a model for the intermediate state in the 1,2-shift mechanism[7] in fluctional π-cyclopentadienyl metal systems.

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