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Research on Titanium-cyclopentadienyl Complexes with Phosphines and Arsines: the Crystal and Molecular Structure of μ-1-diphenylphosphino-μ-2-diphenylarsinoethanebis[chlorodicyclopentadienyltitanium(III)]

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The adduct between Cp_2TiCl_2 (Cp = η^5-cyclopentadienyl) and Arphos (Arphos = 1-diphenylphosphino-2-diphenylarsinoethane) was prepared by reducing Cp_2TiCl_2 with manganese powder in presence of potassium t-butylate, using diethylenglycoldimethylether as solvent and then adding the ligand. The crystals are monoclinic ($P2_1/n$) with cell parameters: a = 9.581(1), b = 14.678(2), c = 14.523(2) Å, β = 98.29(1)°, Z = 2. The structural analysis was carried out from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to an R value of 5.8%. The titanium atom is tetrahedrally surrounded by two cyclopentadienyl rings in a staggered configuration, one chlorine and one P or As atom (disordered distributed with population parameters 50%) from the centrosymmetrical ligand molecule which joins adjacent coordination polyhedra so that the resulting complex molecule is dimeric.

Introduction

During a study on the catalytic effect exerted by dinitrogen on reduction of Cp_2TiCl_2 (Cp = η^5-cyclopentadienyl) by manganese, using dialkoxyethanes as solvents, several reduction products were obtained, but the only one suitable for an X-ray single crystal characterization was the title compound. Similar compounds were obtained with other aryl-phosphines but none of them gave crystals suitable for X-ray examination. These compounds are very air-sensitive when in solution, while in solid state the rate of their oxidation by atmospheric oxygen is greatly reduced. The effects of dinitrogen on the rate of reduction of Cp_2TiCl_2 by manganese in dialkoxyethanes are discussed elsewhere [1].

The title compound was considered worthy of a crystal structure analysis not only in order to have a characterization of the reduction product confirming the supposed oxidation state III for titanium, but also because the numbers of known structures of cyclopentadienyl–Ti(III) is rather limited and, as far as the authors know, there is no structural information available on Ti–P and Ti–As bonds. Unfortunately the latter aspect was not met successfully, as it was found that the structure is disordered, the disorder involving just the phosphorus and arsenic atoms, so the structural parameters involving these atoms are not reliable.

Experimental

The complex was prepared by reducing $(\eta^5\text{-}C_5H_5)_2TiCl_2$ with manganese powder in presence of potassium t-butylate, using diethylenglycoldimethylether as solvent under purified nitrogen. After reduction the solution was filtered and an excess of the ligand (commercial product checked by mass spectrometry) was added. Some days later a small amount of green crystals of the title compound was obtained. A cube shaped crystal of dimensions 0.20 × 0.20 × 0.23 mm^3 was chosen for collection of all X-ray data and mounted in a glass capillary under N_2.

Cell parameters were determined by rotation and Weissenberg photographs and successively refined by least-squares using the θ values of 12 high-angle reflections accurately measured on a Siemens AED single crystal computer controlled diffractometer, using Mo-Kα radiation. For the X-ray data collection a triclinic cell with dimensions a = 24.23, b = 16.30, c = 22.00 Å, α = 41.8, β = 46.9, γ = 68.1° was employed, its c axis being coincident with the ϕ axis of the diffractometer. The final monoclinic cell was obtained by applying the transformation matrix: $-\frac{1}{2} -\frac{1}{2}\ \frac{1}{2}/0\ 1\ -1/\frac{1}{2}\ -\frac{1}{2}\ -\frac{1}{2}$. The resulting crystal data are: $C_{46}H_{44}AsCl_2PTi_2$, M = 869.4, monoclinic, a = 9.581(1), 14.678(2), 14.523(2) Å, β = 98.29(1)°, V = 2021.0(5) Å^3, Z = 2, d_{calcd} = 1.43 g cm^{-3}, λ(Mo-Kα) = 0.71069 Å, μ(Mo-Kα) = 14.05 cm^{-1}. Space group $P2_1/n$ (from systematic absences). Because of problems with crystal decomposition it was not possible to obtain an accurate experimental density.

Intensity data of 5565 reflections were obtained using Nb-filtered Mo-Kα radiation on the diffractometer and the ω–2θ scan technique in the range $3° \leq \theta \leq 52°$; after applying the transformation matrix, 1200 independent reflections, having $I \geq 2\sigma(I)$, were assumed as 'observed' and used in the structural analysis. The intensity of a check reflection was measured every 20 reflections: its intensity was practically constant showing no crystal decomposition. The structure amplitudes were corrected for Lorentz and polarization effects, but not for absorption (μ = 14.05 cm^{-1}). The absolute scale factor was determined first by Wilson's method then as a variable parameter in the least-squares refinement.

The structure was solved localizing first As and Ti from the analysis of the vector space, then by a successive Fourier calculation which gave the coordinates of all non-hydrogen atoms. As the molecule, which is not centrosymmetric, lies on a symmetry center, it was necessary to postulate a disordered distribution of As and P assuming an occupancy factor which turned out to be 0.5 for both atoms from the refinement. The refinement was carried out by full-matrix least squares using the SHELX system [2] of computer programs with initially isotropic and then anisotropic thermal parameters.

The hydrogen atoms were placed at the calculated positions and introduced into the final structure factor calculation: the final *R* was 5.8%. The weighting scheme, employed in the last stages of the refinement, was $w = k/((F_0)^2 + gF_0^2)$ with k = 1.1474 and g = 0.005. The atomic scattering factors used were taken from International Tables [3]. The atomic fractional coordinates are quoted in Table I and a listing of thermal parameters has been deposited with the Editor.

A list of observed and calculated structure factors is available from the authors on request.

All the calculations were performed on the CYBER 76 computer of the Centro di Calcolo

TABLE I. Fractional Atomic Coordinates $\times 10^4$.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
P, AS	1004(2)	936(1)	1218(1)	C11	–2962(16)	2202(15)	950(13)
Ti	–2306(3)	–449(2)	–2902(2)	C12	–1887(15)	1535(10)	887(11)
Cl	3222(4)	–751(2)	1967(3)	C13	171(15)	–85(9)	521(9)
C1	2098(13)	1453(8)	344(8)	C14	4628(22)	999(19)	2741(17)
C2	3295(13)	957(10)	189(10)	C15	3712(27)	1733(16)	2580(15)
C3	4023(16)	1249(13)	–529(11)	C16	3091(19)	1909(11)	3410(22)
C4	3618(19)	2040(13)	–1045(12)	C17	3680(25)	1324(16)	4087(13)
C5	2432(18)	2474(11)	–872(12)	C18	4623(20)	712(12)	3649(19)
C6	1617(16)	2222(10)	–195(10)	C19	1409(20)	–809(13)	3668(15)
C7	–497(13)	1772(10)	1192(10)	C20	402(24)	–567(17)	2892(15)
C8	–174(16)	2627(10)	1582(10)	C21	–151(22)	309(19)	3056(19)
C9	–1223(17)	3295(12)	1646(11)	C22	525(26)	619(15)	3917(19)
C10	–2618(21)	3059(12)	1319(12)	C23	1482(21)	–47(17)	4299(12)

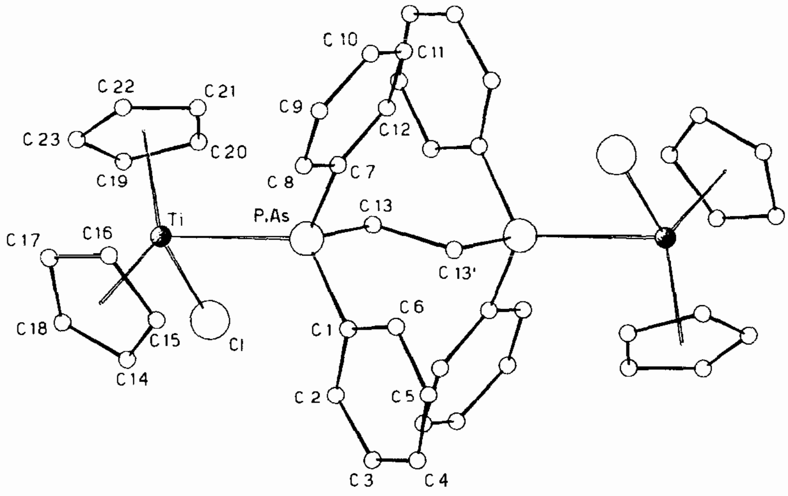

Fig. 1. View of the molecular structure of the dimer.

TABLE II. Bond Distances (Å) and Angles (°) with E.s.d.s in Parentheses (R = ring centroids).

Ti–(P, As)	2.677(3)	C(22)–C(23)	1.40(3)
Ti–Cl	2.462(5)	C(23)–C(19)	1.44(3)
Ti–R1	2.06(2)	(P, As)–Ti–Cl	81.0(1)
Ti–R2	2.07(2)	R1–Ti–R2	134.2(9)
Ti–C(14)	2.41(2)	R1–Ti–Cl	106.6(6)
Ti–C(15)	2.40(2)	R1–Ti–As, P	108.7(6)
Ti–C(16)	2.35(2)	R2–Ti–Cl	108.7(6)
Ti–C(17)	2.39(2)	R2–Ti–(As, P)	104.7(6)
Ti–C(18)	2.36(2)	(P, As)–C(1)–C(6)	121(1)
Ti–C(19)	2.38(2)	(P, As)–C(1)–C(2)	116(1)
Ti–C(20)	2.35(2)	C(1)–(P, As)–C(13)	100.7(5)
Ti–C(21)	2.41(2)	C(1)–(P, As)–C(7)	102.5(5)
Ti–C(22)	2.42(3)	C(7)–(P, As)–C(13)	103.9(5)
Ti–C(23)	2.39(2)	C(2)–C(1)–C(6)	122(1)
C(1)–C(2)	1.40(2)	C(1)–C(2)–C(3)	117(1)
C(1)–C(6)	1.41(2)	C(2)–C(3)–C(4)	121(1)
C(2)–C(3)	1.40(2)	C(3)–C(4)–C(5)	117(1)
C(3)–C(4)	1.41(2)	C(4)–C(5)–C(6)	125(1)
C(4)–C(5)	1.36(2)	C(1)–C(6)–C(5)	115(1)
C(5)–C(6)	1.39(2)	(P, As)–C(7)–C(12)	122(1)
C(7)–C(8)	1.39(2)	(P, As)–C(7)–C(8)	117(1)
C(8)–C(9)	1.42(2)	C(8)–C(7)–C(12)	120(1)
C(9)–C(10)	1.40(2)	C(7)–C(8)–C(9)	122(1)
C(10)–C(11)	1.39(2)	C(8)–C(9)–C(10)	117(1)
C(11)–C(12)	1.43(2)	C(10)–C(11)–C(12)	120(1)
(P, As)–C(1)	1.92(1)	C(7)–C(12)–C(11)	118(1)
(P, As)–C(7)	1.89(1)	(P, As)–C(13)–C(13$^{\mathrm{I}}$)	114(1)
(P, As)–C(13)	1.92(1)	C(15)–C(14)–C(18)	108(2)
C(13)–C(13$^{\mathrm{I}}$)	1.52(2)	C(14)–C(15)–C(16)	109(2)
C(14)–C(15)	1.39(3)	C(15)–C(16)–C(17)	108(2)
C(15)–C(16)	1.44(3)	C(16)–C(17)–C(18)	106(2)
C(16)–C(17)	1.36(3)	C(14)–C(18)–C(17)	108(2)
C(17)–C(18)	1.48(3)	C(20)–C(19)–C(23)	106(2)
C(18)–C(14)	1.39(3)	C(19)–C(20)–C(21)	108(2)
C(19)–C(20)	1.42(3)	C(20)–C(21)–C(22)	108(2)
C(20)–C(21)	1.42(3)	C(21)–C(22)–C(23)	108(2)
C(21)–C(22)	1.40(3)	C(22)–C(23)–C(19)	108(2)

$\mathrm{I} = \bar{x}, \bar{y}, \bar{z}$

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Results and Discussion

The complex molecule is depicted in Fig. 1: the titanium atom is penta*hapto* coordinated by two cyclopentadienyl rings and σ-bonded to one chlorine atom and one As or P atom from the ligand, so that the resulting coordination polyhedron can be considered a distorted tetrahedron. This arrangement is commonly found in Ti(III) and Ti(IV) η^5-cyclopentadienyl derivatives [4–9]. The distances between Ti and the ring centroids, 2.06(2) and 2.07(2) Å, have the expected values and the same can be said for the C–Ti distances (range 2.35(2)–2.42(3) Å), for the C–C distances (range 1.39(4)–1.48(3) Å and for the angles (range 106(2)–109(2)°) in the rings, the differences being not significative (Table II). The accuracy of the data is not enough to reveal displacements from planarity (if any) in the two cyclopentadienyl rings (Table III) which assume a staggered conformation in the complex with a Cp–Ti–Cp angle of 134.2(9)° in agreement with the values given in the literature for that conformation [5, 7, 8, 10] (Fig. 2). The other angles on titanium are close to the expected tetrahedral values except As–Ti–Cl (81.0(1)°, which is near to the Cl–Ti–Cl angles found in [(C$_5$H$_5$)$_2$TiCl]$_2$ and [(CH$_3$C$_5$H$_4$)$_2$TiCl]$_2$, 77.11(5)–79.30(6)° [7], where chlorine-bridges are present. The Ti–Cl bond distance, 2.462(5) Å, is

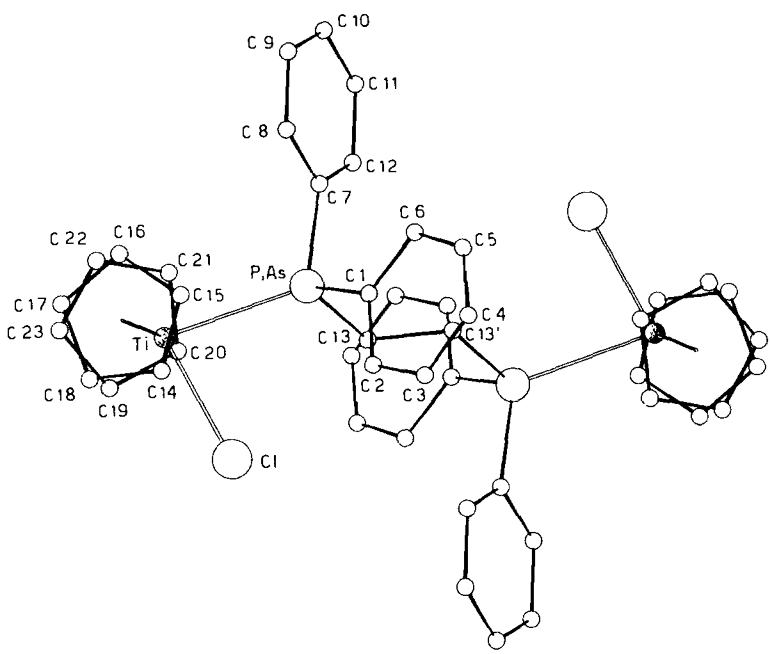

Fig. 2. Projection of the structure perpendicular to the R_1–Ti–R_2 plane (R = ring centroid).

TABLE III. Weighted Least-squares Planes for Cyclopentadienyl Rings with Displacements of Each Atom.[a]

Plane C(14) C(15) C(16) C(17) C(18)

$0.7152X + 0.6329Y + 0.2963Z = 4.8509$

C(14)	0.01(2)
C(15)	−0.01(2)
C(16)	0.02(2)
C(17)	−0.03(2)
C(18)	0.01(2)

Plane C(19) C(20) C(21) C(22) C(23)

$0.7898X + 0.4180Y - 0.4487Z = -2.3958$

C(19)	−0.01(2)
C(20)	0.01(2)
C(21)	−0.01(2)
C(22)	0.00(3)
C(23)	0.00(2)

[a] X, Y, Z are the orthogonal coordinates obtained from the fractional ones applying the matrix $\|a \; 0 \; c\cos\beta | 0 \; b \; 0 | 0 \; 0 \; c\sin\beta\|$.

TABLE IV. Some Contacts less than 3.6 Å.

(P, As)...C(15)	3.24(2)	C(12)...C(13)	3.18(2)
(P, As)...C(20)	3.39(2)	C(12)...C($13^{\rm I}$)	3.52(2)
(P, As)...C(21)	3.17(2)	C(13)...C(20)	3.49(2)
C(1)...C(8)	3.47(2)	C(16)...C(22)	3.27(3)
C(1)...C(15)	3.41(2)	C(16)...C(23)	3.58(3)
C(1)...C($13^{\rm I}$)	3.09(2)	C(17)...C(22)	3.17(3)
C(2)...C(13)	3.46(2)	C(17)...C(23)	2.96(3)
C(2)...C($13^{\rm I}$)	3.57(2)	C(18)...C(23)	3.46(3)
C(4)...C($9^{\rm III}$)	3.41(2)	C(22)...C($23^{\rm IV}$)	3.54(3)
C(6)...C(7)	3.13(2)	Cl...C(13)	3.48(1)
C(6)...C(8)	3.35(2)	Cl...C(14)	3.04(2)
C(6)...C($13^{\rm I}$)	3.57(2)	Cl...C(18)	3.38(2)
C(6)...C($17^{\rm II}$)	3.56(2)	Cl...C(19)	3.22(2)
C(7)...C($13^{\rm I}$)	3.55(2)	Cl...C(20)	3.19(2)
C(7)...C(21)	3.43(3)		

$\mathrm{I} = \bar{x}, \bar{y}, \bar{z}$
$\mathrm{II} = -\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
$\mathrm{III} = \frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
$\mathrm{IV} = \frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$

similar that found in [Ti(cp)$_2$(COCH$_3$)] [11] (2.494(6) Å), but significantly longer than the related bonds in other Ti(III) (2.292(7)–2.418(7), 2.351(4)–2.399(8) Å [12]; 2.251(3) Å [13]) and Ti(IV) compounds (2.364(3) Å av. [5], 2.263(4)–2.270(4) Å [4]), and also in comparison with the sum of the covalent radii: Ti(III)–Ti(IV) 1.36, Cl 0.99 Å [12]; however the number of structural examples of chlorides of Ti(III) is too small for a more significant comparison.

As far as the authors know there is no structural information on Ti–P and Ti–As bond distances in the literature, and unfortunately the disorder found in the crystals does not allow to attribute in this work much significance to the value 2.677(3) Å found. However it must be pointed out that this value is relevantly larger than those which can be supposed from the covalent radii (r_{cov}Ti = 1.32 Å, r_{cov}P = 1.06 Å, r_{cov}As = 1.20 Å) suggesting that the interaction is made rather weak probably by the crowding of the bulky ligands around the Ti atom.

The ligand molecule is centrosymmetric, with the center of symmetry located between their methylene carbons. Their donor atoms join two adjacent coordination polyhedra, so that the resulting complex molecule is dimeric. The centrosymmetry of the dimers is caused by the disordered distribution of the P and As atoms (population parameter 50%) and by the '*trans*' configuration of the bridge. The orientation of the phenyl rings is determined by intramolecular packing requirements which produces contacts corresponding to normal Van der Waals interactions (Table IV), the dihedral angle formed by planes of these rings being 73.3°. The (P, As)–C distances, 1.89(1)–1.92(1) Å, are intermediate between the values usually found for the C–P and C–As reported in the literature. The dimers are packed in the crystal by normal Van der Waals contacts (Table IV).

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