Journal of Organometallic Chemistry, 355 (1988) 113–119
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The preparation and crystal structure of [bis(dimethylphosphino)ethane](trichloro)-cyclopentadienyltitanium(IV) *

David L. Hughes, G. Jeffery Leigh *, and David G. Walker

AFRC IPSR Nitrogen Fixation Laboratory, The University of Sussex, Brighton, BN1 9RQ (Great Britain)

(Received May 11th, 1988)

Abstract

The compound [bis(dimethylphosphino)ethane](trichloro)cyclopentadienyltitanium(IV) is produced by the direct reaction of $[Ti(C_5H_5)Cl_3]$ with $Me_2PCH_2CH_2PMe_2$, even in the presence of $NaC_{10}H_8$. It crystallizes in a form which contains two conformers in the unit cell, which differ in the orientation of the C_5H_5 ring with respect to the chlorine and phosphorus atoms.

Introduction

We recently reported the reactions of $[Ti(C_5H_5)Cl_3]$ with a range of hydrazines or hydrazine derivatives to yield titanium(IV) hydrazido(1 −) complexes that contain the hydrazide bound side-on to the titanium [1]. In an endeavour to force the hydrazide residue to bind end-on, we decided to investigate reactions of the hydrazine reagents with titanium compounds in lower oxidation states. In view of the existence of the complexes $[Ti(C_5H_5)Cl_2(PMe_3)_2]$ [2], $[Zr(C_5H_5)Cl(dmpe)_2]$ [3], and $[TiCl_2(dmpe)_2]$ [4], it seemed entirely reasonable to attempt the preparation of $[Ti(C_5H_5)Cl_2(dmpe)]$ (dmpe = $Me_2PCH_2CH_2PMe_2$).

Results and discussion

The reaction of $[Ti(C_5H_5)Cl_3]$ with dmpe in the presence of sodium and a catalytic amount of naphthalene produced an orange-yellow solid that we at first took to be the required material. However, analyses were never entirely satisfactory, and the reaction with $NHMeNMe_2$ produced the known titanium(IV) complex $[Ti(C_5H_5)Cl_2(NMeNMe_2)]$ [5]. The identity of our product as $[Ti(C_5H_5)Cl_3(dmpe)]$

---

* Dedicated to Professor E.O. Fischer on his 70th birthday, in friendship.

0022-328X/88/$03.50

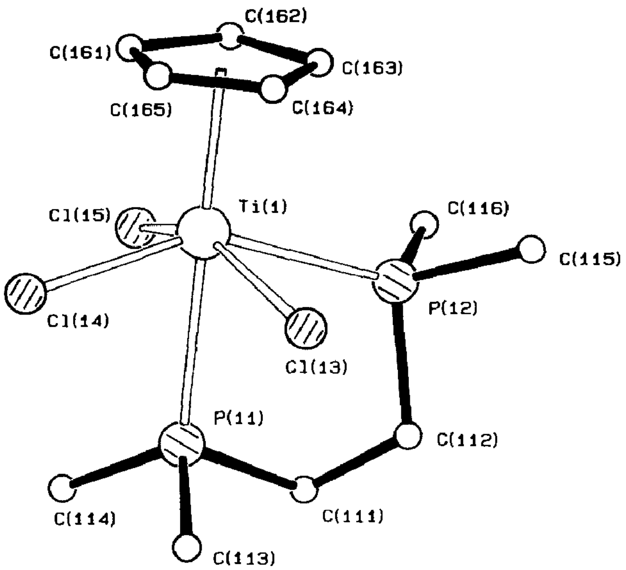

Fig. 1. View of one of the two independent molecules of [Ti(C_5H_5)Cl_3(dmpe)], showing the atomic numbering scheme.

was confirmed by X-ray structure analysis, and we were able to obtain it direct from [Ti(C_5H_5)Cl_3] and dmpe.

We do not know why no reduction occurs with naphthalenesodium. It is, however likely that the reason is kinetic. For the preparation of [Ti(C_5H_5)Cl_2(PMe_3)$_2$], the reductant was magnesium metal [2]. There is ample evidence that titanium forms titanium–magnesium bonds in appropriate reductive systems, and it is conceivable that this is involved in the actual reduction process. Naphthalene(1 −) would require a completely different mechanism. It is also clear from our results, and consistent with accumulated literature data, that tertiary phosphines are not good ligands for titanium. Dmpe is lost from [Ti(C_5H_5)Cl_3(dmpe)] upon reaction with $NMe_2NMeSiMe_3$ under very mild conditions. The description of the synthesis of [Ti(C_5H_5)Cl_2(PMe_3)$_2$] [2] suggests that orange [Ti(C_5H_5)Cl_3(PMe_3)$_2$] does exist, but it has not been isolated or characterized.

The complex [Ti(C_5H_5)Cl_3(dmpe)] crystallises in the space group *Pbca* with 16 molecules in the unit cell, which contains two crystallographically distinct molecules that have very similar dimensions. The coordination around the metal atom is roughly octahedral (Fig. 1) if the cyclopentadienyl group is assumed to occupy one coordination position. This is the arrangement exhibited by [Mo(C_5H_5)Cl_3(dppe)] [6] and [Nb(C_5H_5)X_3(dppe)] [7] (X = Cl or Br, dppe = $Ph_2PCH_2CH_2PPh_2$). Compared to those in "tetrahedral" [Ti(C_5H_5)Cl_3] [8], the mean Ti–Cp (calculated centre of C_5H_5 ring) and Ti–Cl distances are slightly elongated (2.10 compared to 2.01, and 2.40 compared to 2.22 Å, respectively); the Ti–Cl distances in [$TiCl_2$(dmpe)$_2$] [4], at 2.446(4) Å, are, as expected, slightly longer than in our complex. The Ti–P distances (ca. 2.62 Å) fall in the expected range; Ti–P separations in titanium-dmpe complexes appear to vary over a range of 2.52–2.67 Å, with no obvious pattern. There are no large *trans* influences evident from the bond lengths.

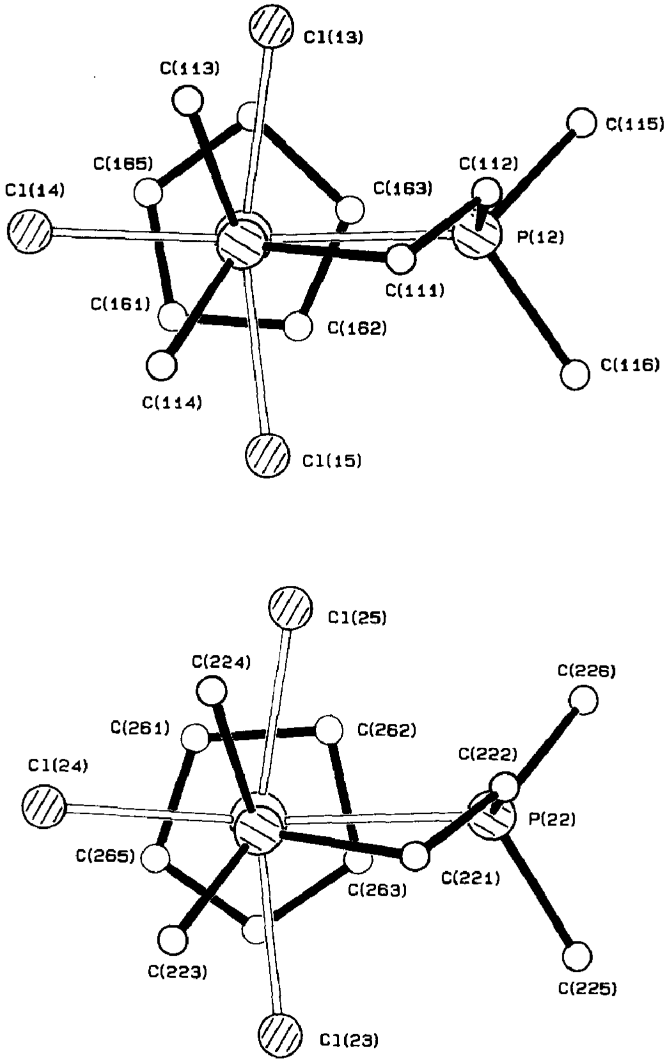

Fig. 2. Projections of the two independent molecules viewed down their Ti–Cp axes; Cp is the calculated centre of the C_5H_5 ring. (N.B. The lower molecule, that of Ti(2), is the inverse of that having the coordinates listed in Table 1).

In both independent molecules, the chlorines are bent away from the cyclopentadienyl rings and towards the two phosphorus atoms. However, the conformations of the two molecules are subtly different. Viewed in projection down the Ti–Cp axis (Fig. 2), the projection of the Ti–P equatorial bond falls close to and above a C_5H_5 ring carbon atom [C(263)] in one case or close to but below the corresponding C_5H_5 ring carbon atom [C(163)] in the other case. The Cp rings in the two molecules are almost mirror images. There are many intramolecular contacts (but no significant intermolecular contacts) less than the sums of van der Waals' radii, but they are equivalent in each form. We are thus observing two stereoisomers, in which the Cp ring occupies one of two sites, presumably produced by the ring carbon atom–chlorine atom repulsions. An analogous state of affairs is not observed in [Nb(C_5H_5)X_3(dppe)] [7] (for which there is only one molecular form in the unit cell, although the distortions from ideal 'octahedral' symmetry are similar to those found here) nor in [Mo(C_5H_5)Cl_3(dppe)] [6] (for which there are similar distortions, with two identical molecules in the asymmetric unit).

Experimental

Compounds were handled in Schlenk tubes in dioxygen-free dinitrogen. [Ti(C_5H_5)Cl_3] [9] and dmpe [10] were prepared as described elsewhere. NMR spectra were recorded on a JEOL FX-90Q spectrometer, with a pulse delay of 150 s for the ^1H spectra.

[Bis(dimethylphosphino)ethane](trichloro)cyclopentadienyltitanium(IV). A solution of (trichloro)cyclopentadienyltitanium(IV) (0.53 g, 2.4 mmol) in tetrahydro-

Table 1

Final atomic coordinates coordinates (fractional $\times 10^4$). E.s.ds are in parentheses

Atom	*x*	*y*	*z*
Ti(1)	4251(2)	2321(6)	7828(3)
Cl(13)	4867(3)	2360(9)	6966(4)
Cl(14)	4333(4)	442(8)	7978(5)
Cl(15)	3442(3)	2314(11)	8054(5)
P(11)	3893(4)	1437(9)	6660(5)
P(12)	4025(4)	3929(8)	6991(6)
C(111)	3652(10)	2462(33)	6050(16)
C(112)	3925(14)	3419(33)	6063(20)
C(113)	4301(12)	747(30)	6047(17)
C(114)	3432(10)	521(24)	6751(15)
C(115)	4415(15)	4987(36)	6782(22)
C(116)	3523(16)	4779(38)	7237(23)
C(161)	4314(15)	2463(48)	9117(19)
C(162)	4208(16)	3461(39)	8895(22)
C(163)	4559(16)	3869(42)	8481(24)
C(164)	4934(18)	3097(40)	8458(25)
C(165)	4745(16)	2284(43)	8866(22)
Ti(2)	6828(2)	2451(6)	9916(3)
Cl(23)	6691(4)	4267(7)	10337(4)
Cl(24)	6295(3)	2550(10)	8897(4)
Cl(25)	6689(3)	555(7)	10046(5)
P(21)	6009(3)	2439(10)	10521(4)
P(22)	6985(3)	2118(7)	11322(4)
C(221)	6072(8)	2466(30)	11523(12)
C(222)	6454(8)	1791(21)	11775(14)
C(223)	5594(12)	3454(27)	10362(17)
C(224)	5662(11)	1262(24)	10353(15)
C(225)	7212(10)	3257(22)	11842(15)
C(226)	7370(10)	1051(26)	11553(15)
C(261)	7377(12)	1886(27)	9036(18)
C(262)	7558(12)	1662(28)	9769(16)
C(263)	7648(8)	2754(22)	10002(14)
C(264)	7490(12)	3478(31)	9515(16)
C(265)	7309(12)	2974(29)	8926(19)

Table 2

Molecular dimensions. Bond lengths are in Å, angles in degrees. E.s.ds are in parentheses

(a) About the Ti atoms			
Ti(1)–Cl(13)	2.385(9)	Ti(2)–Cl(23)	2.426(12)
Ti(1)–Cl(14)	2.375(12)	Ti(2)–Cl(24)	2.422(8)
Ti(1)–Cl(15)	2.400(10)	Ti(2)–Cl(25)	2.413(12)
Ti(1)–P(11)	2.609(11)	Ti(2)–P(21)	2.636(9)
Ti(1)–P(12)	2.602(12)	Ti(2)–P(22)	2.624(9)
Ti(1)–C(161)	2.35(4)	Ti(2)–C(261)	2.37(3)
Ti(1)–C(162)	2.41(4)	Ti(2)–C(262)	2.37(4)
Ti(1)–C(163)	2.44(5)	Ti(2)–C(263)	2.433(25)
Ti(1)–C(164)	2.50(5)	Ti(2)–C(264)	2.43(4)
Ti(1)–C(165)	2.38(4)	Ti(2)–C(265)	2.37(3)
Ti(1)–Cp(1) [a]	2.11	Ti(2)–Cp(2) [a]	2.08
Cl(13)–Ti(1)–Cl(14)	91.1(5)	Cl(23)–Ti(2)–Cl(24)	94.9(4)
Cl(13)–Ti(1)–Cl(15)	148.9(3)	Cl(23)–Ti(2)–Cl(25)	149.1(3)
Cl(14)–Ti(1)–Cl(15)	94.4(5)	Cl(24)–Ti(2)–Cl(25)	90.9(4)
Cl(13)–Ti(1)–P(11)	77.3(3)	Cl(23)–Ti(2)–P(21)	74.0(4)
Cl(14)–Ti(1)–P(11)	73.5(4)	Cl(24)–Ti(2)–P(21)	74.5(3)
Cl(15)–Ti(1)–P(11)	75.0(4)	Cl(25)–Ti(2)–P(21)	78.5(4)
Cl(13)–Ti(1)–P(12)	78.1(4)	Cl(23)–Ti(2)–P(22)	82.6(3)
Cl(14)–Ti(1)–P(12)	148.7(4)	Cl(24)–Ti(2)–P(22)	149.5(3)
Cl(15)–Ti(1)–P(12)	81.5(4)	Cl(25)–Ti(2)–P(22)	77.2(3)
P(11)–Ti(1)–P(12)	75.5(4)	P(21)–Ti(2)–P(22)	75.7(3)
Cp(1)–Ti(1)–Cl(13)	101.8	Cp(2)–Ti(2)–Cl(23)	102.8
Cp(1)–Ti(1)–Cl(14)	106.4	Cp(2)–Ti(2)–Cl(24)	105.9
Cp(1)–Ti(1)–Cl(15)	106.0	Cp(2)–Ti(2)–Cl(25)	104.6
Cp(1)–Ti(1)–P(11)	179.0	Cp(2)–Ti(2)–P(21)	176.8
Cp(1)–Ti(1)–P(12)	104.5	Cp(2)–Ti(2)–P(22)	104.3
(b) In the ligands			
P(11)–C(111)	1.83(3)	P(21)–C(221)	1.826(22)
P(11)–C(113)	1.85(3)	P(21)–C(223)	1.78(4)
P(11)–C(114)	1.776(29)	P(21)–C(224)	1.81(3)
P(12)–C(112)	1.82(4)	P(22)–C(222)	1.801(25)
P(12)–C(115)	1.79(4)	P(22)–C(225)	1.831(27)
P(12)–C(116)	1.87(5)	P(22)–C(226)	1.79(3)
C(111)–C(112)	1.44(5)	C(221)–C(222)	1.47(3)
C(161)–C(162)	1.35(6)	C(261)–C(262)	1.46(4)
C(161)–C(165)	1.36(5)	C(261)–C(265)	1.39(4)
C(162)–C(163)	1.37(5)	C(262)–C(263)	1.45(4)
C(163)–C(164)	1.46(6)	C(263)–C(264)	1.35(4)
C(164)–C(165)	1.37(5)	C(264)–C(265)	1.35(4)
Ti(1)–P(11(–C(111)	110.4(13)	Ti(2)–P(21)–C(221)	108.8(9)
Ti(1)–P(11)–C(113)	115.2(12)	Ti(2)–P(21)–C(223)	123.3(12)
Ti(1)–P(11)–C(114)	120.1(10)	Ti(2)–P(21)–C(224)	116.3(12)
C(111)–P(11)–C(113)	102.2(16)	C(221)–P(21)–C(223)	102.6(15)
C(111)–P(11)–C(114)	102.4(15)	C(221)–P(21)–C(224)	103.8(15)
C(113)–P(11)–C(114)	104.3(16)	C(223)–P(21)–C(224)	99.8(13)
Ti(1)–P(12)–C(112)	108.1(14)	Ti(2)–P(22)–C(222)	109.2(9)
Ti(1)–P(12)–C(115)	122.1(15)	Ti(2)–P(22)–C(225)	116.2(9)
Ti(1)–P(12)–C(116)	119.9(14)	Ti(2)–P(22)–C(226)	117.0(10)
C(112)–P(12)–C(115)	99.5(18)	C(222)–P(22)–C(225)	104.7(13)

Continued

Table 2 (continued)

C(112)–P(12)–C(116)	107.1(20)	C(222)–P(22)–C(226)	105.4(13)
C(115)–P(12)–C(116)	97.6(20)	C(225)–P(22)–C(226)	103.2(13)
P(11)–C(111)–C(112)	111.0(25)	P(21)–C(221)–C(222)	112.0(20)
P(12)–C(112)–C(111)	113.3(28)	P(22)–C(222)–C(221)	112.4(19)
C(162)–C(161)–C(165)	105.5(54)	C(262)–C(261)–C(265)	111.7(35)
C(161)–C(162)–C(163)	109.6(50)	C(261)–C(262)–C(263)	98.7(29)
C(162)–C(163)–C(164)	109.4(49)	C(262)–C(263)–C(264)	112.1(27)
C(163)–C(164)–C(165)	99.9(45)	C(263)–C(264)–C(265)	110.0(33)
C(161)–C(165)–C(164)	115.6(54)	C(261)–C(265)–C(264)	106.7(37)
(c) Torsion angles in dmpe			
P(11)–C(111)–C(112)–P(12)	53(3)	P(21)–C(221)–C(222)–P(22)	−54(2)

[a] Cp is the calculated centre of the cyclopentadienyl ring.

furan (thf) (40 cm^3) was treated with dmpe (0.7 cm^3). After 15 h stirring at 20 °C, the mixture was filtered, layered with diethyl ether, (40 cm^3) and set aside to deposit crystals. Yield essentially quantitative. Repeated dissolution in thf and layering with ether gave orange crystals suitable for X-ray crystal structure analysis. Found: C, 36.5; H, 5.8. $C_{11}H_{21}Cl_3P_2Ti$ calcd.: C, 35.8; H, 5.7%. ^{1}H NMR spectrum (C_6D_6): δ 6.53, 6.56, 6.40 (C_5H_5); 1.63, 1.51, 0.90, 0.80 (CH_3); 1.42, 1.30 (CH_2) ppm. $^{31}P\{^1H\}$ (CH_2Cl_2): −115.0, −120.0 ppm (rel. $P(OMe)_3$). $^{13}C\{^1H\}$ (thf): 123.6, 120.4 (C_5H_5); 15.3, 15.1, 14.6, 14.1 (CH_3) (rel. $SiMe_4$).

X-ray crystallographic analysis of [Ti(C_5H_5)Cl_3(dmpe)]

Crystal data. $C_{11}H_{21}Cl_3P_2Ti$, $M = 369.5$. Orthorhombic, space group *Pbca* (no. 61), *a* 29.244(6), *b* 12.485(2), *c* 18.141(4) Å. *V* 6623.1 Å^3. $Z = 16$. D_c 1.48 g cm^{-3}, $F(000) = 3040$, μ(Mo-$K_{\bar{\alpha}}$) 11.7 cm^{-1}, λ(Mo-$K_{\bar{\alpha}}$) = 0.71069 Å.

An orange needle crystal, ca. 0.6 × 0.05 × 0.14 mm, sealed in a glass capillary, was mounted, after preliminary photographic examination, on an Enraf–Nonius CAD4 diffractometer. Accurate cell dimensions (from 25 reflections with θ 7–11°) and intensity data were measured using monochromated Mo-radiation. Few reflections were found with intensities significantly above background at θ 18° and the data collection was halted at this value.

In this limited data set, intensities of 2268 unique reflections were corrected for Lorentz-polarisation effects, deterioration (from the monitoring of two reflections which showed steady decay to ca. 72% of the starting intensities) and to eliminate negative intensities (by Bayesian statistics).

The twelve heavier atoms (Ti, P and Cl) of two independent molecules were identified in an E-map in SHELXS [11] and the C atoms were located in succeeding difference maps in the SHELX programme [12]. Hydrogen atoms were included in idealised positions and their parameters were set to ride on those of their bonded C atoms. Full-matrix least-squares refinement gave convergence at $R = 0.14$ and $R_w = 0.11$ [12] for 1395 reflections with $I > \sigma(I)$ and $w = \sigma(F)^{-2}$, with the heavier atoms allowed anisotropic thermal parameters and the C atoms refined isotropically. A final difference map showed major peaks close to the heavier atoms; there were no indications of any other molecules in the crystal. Scattering curves for neutral atoms were from reference [13]. Final atomic coordinates are listed in Table 1, and bond dimensions are in Table 2.

All computations were run on the VAX 11/750 machine at AFRC-IHRL (G.C.R.I., Littlehampton), using programs listed in Table 4 of reference 14.

References

1 D.L. Hughes, I.A. Latham and G.J. Leigh, J. Chem. Soc., Dalton Trans., (1986) 393, and papers cited therein.

2 A. Razavi, D.T. Mallin, R.O. Day, M.D. Rausch and H.G. Alt, J. Organomet. Chem., 333 (1987) C48.

3 S. Gambarotta and M.Y. Chiang, J. Chem. Soc., Chem. Commun., (1987) 698.

4 G.S. Girolami, G. Wilkinson, A.M.R. Galas, M. Thornton-Pett and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1985) 1339.

5 E.M.R. Kiremire, G.J. Leigh, J.R. Dilworth and R.A. Henderson, Inorg. Chim. Acta, 83 (1984) L83.

6 K. Starker and M.D. Curtis, Inorg. Chem., 24 (1985) 3006.

7 J.-C. Duran, K. Prout, A. de Cian, M.L.H. Green and N. Siganporia, J. Organomet. Chem., 136 (1977) C4.

8 L.M. Engelhardt, R.I. Papasergio, C.L. Raston and A.H. White, Organometallics, 3 (1984) 18.

9 I.A. Latham, G.J. Leigh, G. Huttner and I. Jibril, J. Chem. Soc., Dalton Trans., (1986) 385.

10 R.J. Burt, J. Chatt, W. Hussain and G.J. Leigh, J. Organomet. Chem., 182 (1979) 203.

11 Program SHELXS-86. G.M. Sheldrick in G.M. Sheldrick, C. Krüger and R. Goddard (Eds.), 'Crystallographic Computing 3', Oxford University Press, 1985, p. 175.

12 Program SHELX-76. G.M. Sheldrick, Program for Crystal Structure Determination, University of Cambridge, 1976.

13 'International Tables for X-ray Crystallography', Kynoch Press, Birmingham, 1974, Vol. 4, pp. 99 and 149.

14 S.N. Anderson, D.L. Hughes and R.L. Richards, J. Chem. Soc., Dalton Trans., (1986) 245.