Crystal structure of *trans*-bis(triphenylphospine oxide)tetrachlorotitanum(IV), $TiCl_4[(C_6H_5)_3PO]_2$

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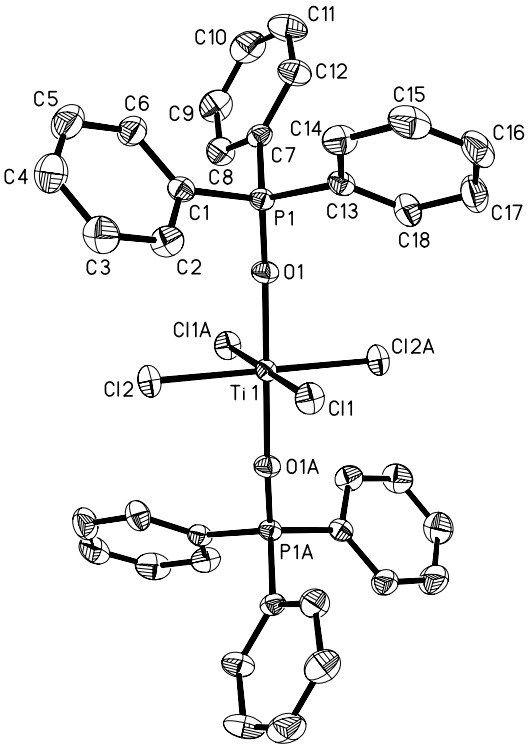

Abstract

$C_{36}H_{30}Cl_4O_2P_2Ti$, triclinic, $P\bar{1}$ (no. 2), a = 9.492(1) Å, b = 9.640(1) Å, c = 10.429(1) Å, α = 102.100(2)°, β = 108.657(2)°, γ = 92.652(2)°, V = 877.4 Å^3, Z = 1, $R_{gt}(F)$ = 0.043, $wR_{ref}(F^2)$ = 0.106, T = 273 K.

Source of material

The title compound has been prepared solvothermally. In a typical synthesis, the mixture of boric acid (0.123 g, 2 mmol), triphenylphosphine (0.130 g, 0.5 mmol), tetrabutyl titanate (0.15 mL), benzene (0.10 mL), phosphorus oxychloride (0.10 mL), and hydrochloric acid (37 %, 0.05 mL) was placed in a thick-walled glass tube. The tube was sealed under vacuum, and then kept at 110 °C for three days to give pure single crystals. The yellow block-like crystals were collected by filtration, washed with distilled water and dried at ambient conditions.

Discussion

The structural isomerism of the octahedral molecular complexes of $TiCl_nF_{4-n}L_2$ (n = 0-4) has been known for a long time, and several species of which have been structurally characterized, such as *cis*-$TiF_4(dmso)_2$, *cis*-$TiCl_2F_2(Ph_3PO)_2$, *cis*-$TiF_4(Ph_3PO)_2$, *cis*-$TiCl_4(HSR)_2$, *cis*-$TiCl_4(^tBuNC)_2$ [1-5]. Up to now, the complexes obtained are *cis*-arranged isomers. Herein, we report a compound of *trans*-$TiCl_4(Ph_3PO)_2$ with high stability in air.

In the title crystal structure, there is nearly idealized octahedral environment around the Ti atom, which is exceedingly rare to be found for such complexes. The titanium atoms are situated on inversion centers with an essentially D_{4h} local symmetry. The titanium coordination sphere contains four chlorine atoms and two Ph_3PO molecules located in *trans* positions relative to each other. The bond angles of the titanium coordination octahedron reveal nearly idealized octahedral coordination geometry, all *trans* angles are equal to 180° (∠O–Ti–O^i = 180.0°, ∠Cl1–Ti–Cl1^i = 180.0°, ∠Cl2–Ti–Cl2^i = 180.0°, i = –x+1,–y+2,–z+2) and the *cis* angles are all very close to 90° (∠O–Ti–Cl angles range from 89.90(5)° to 90.10° (av. = 90.0°), and ∠Cl–Ti–Cl from 89.88(2)° to 90.12° (av. = 90.0°)). The Ti–O–P angle (163.2(1)°) is similar to that in *cis*-$TiCl_2F_2(Ph_3PO)_2$ [167.8(2)° and 158.0(2)°]. The Ti—O bond lengths are 1.923(2) Å, and the Ti—Cl1 and Ti—Cl2 distances are 2.3283(6) Å and 2.3336(6) Å, respectively.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.15 × 0.20 × 0.22 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.71 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, φ/ω
$2\theta_{max}$:	56.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6070, 4207
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2709
$N(param)_{refined}$:	205
Programs:	SHELXS-97 [6], SHELXL-97 [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.0826	0.8984	0.8555	0.062
H(3)	2*i*	–0.1220	0.8561	0.9218	0.076
H(4)	2*i*	–0.2145	0.6251	0.9028	0.087
H(5)	2*i*	–0.1012	0.4363	0.8220	0.091
H(6)	2*i*	0.1045	0.4767	0.7562	0.066
H(8)	2*i*	0.4727	0.5741	0.8927	0.063
H(9)	2*i*	0.5627	0.3591	0.8415	0.079
H(10)	2*i*	0.4953	0.2298	0.6178	0.087
H(11)	2*i*	0.3337	0.3097	0.4390	0.092
H(12)	2*i*	0.2386	0.5242	0.4876	0.065
H(14)	2*i*	–0.0209	0.7245	0.5350	0.063
H(15)	2*i*	–0.1015	0.8061	0.3329	0.082
H(16)	2*i*	0.0666	0.9278	0.2667	0.084
H(17)	2*i*	0.3135	0.9817	0.4079	0.081
H(18)	2*i*	0.3971	0.9029	0.6101	0.065

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1)	1*d*	½	0	0	0.0282(3)	0.0329(3)	0.0266(3)	0.0072(2)	0.0072(3)	0.0083(3)
P(1)	2*i*	0.26687(7)	0.73122(7)	0.74152(6)	0.0325(3)	0.0327(3)	0.0303(3)	0.0065(3)	0.0077(3)	0.0056(3)
Cl(1)	2*i*	0.32164(7)	1.14132(7)	0.90426(7)	0.0393(4)	0.0506(4)	0.0485(4)	0.0188(3)	0.0099(3)	0.0217(3)
Cl(2)	2*i*	0.36323(7)	0.94943(7)	1.13851(7)	0.0446(4)	0.0620(5)	0.0442(4)	0.0108(3)	0.0215(3)	0.0216(3)
O(1)	2*i*	0.3909(2)	0.8357(2)	0.8557(2)	0.0392(9)	0.038(1)	0.034(1)	0.0022(8)	0.0052(8)	0.0034(8)
C(1)	2*i*	0.1137(3)	0.6926(3)	0.7980(2)	0.033(1)	0.042(2)	0.034(1)	0.005(1)	0.008(1)	0.006(1)
C(2)	2*i*	0.0455(3)	0.8051(3)	0.8483(3)	0.044(2)	0.048(2)	0.062(2)	0.011(1)	0.020(2)	0.011(2)
C(3)	2*i*	–0.0767(3)	0.7801(4)	0.8879(3)	0.048(2)	0.073(2)	0.076(2)	0.018(2)	0.032(2)	0.011(2)
C(4)	2*i*	–0.1313(4)	0.6423(4)	0.8770(4)	0.057(2)	0.085(3)	0.085(3)	–0.002(2)	0.041(2)	0.014(2)
C(5)	2*i*	–0.0638(4)	0.5293(4)	0.8283(4)	0.078(2)	0.062(2)	0.095(3)	–0.008(2)	0.048(2)	0.011(2)
C(6)	2*i*	0.0588(3)	0.5532(3)	0.7888(3)	0.060(2)	0.047(2)	0.063(2)	0.002(1)	0.031(2)	0.008(2)
C(7)	2*i*	0.3429(3)	0.5698(2)	0.6952(3)	0.037(1)	0.029(1)	0.046(2)	0.005(1)	0.017(1)	0.006(1)
C(8)	2*i*	0.4429(3)	0.5206(3)	0.8011(3)	0.058(2)	0.049(2)	0.052(2)	0.016(1)	0.016(2)	0.016(1)
C(9)	2*i*	0.4976(4)	0.3928(3)	0.7703(4)	0.067(2)	0.052(2)	0.083(3)	0.027(2)	0.021(2)	0.028(2)
C(10)	2*i*	0.4572(4)	0.3159(3)	0.6374(4)	0.078(2)	0.046(2)	0.103(3)	0.025(2)	0.041(2)	0.015(2)
C(11)	2*i*	0.3605(4)	0.3633(3)	0.5304(4)	0.091(3)	0.057(2)	0.073(2)	0.021(2)	0.033(2)	–0.013(2)
C(12)	2*i*	0.3035(3)	0.4912(3)	0.5595(3)	0.057(2)	0.049(2)	0.051(2)	0.016(1)	0.015(2)	0.002(1)
C(13)	2*i*	0.1974(3)	0.8020(3)	0.5915(2)	0.042(1)	0.037(1)	0.030(1)	0.012(1)	0.007(1)	0.007(1)
C(14)	2*i*	0.0471(3)	0.7750(3)	0.5092(3)	0.050(2)	0.046(2)	0.049(2)	0.011(1)	–0.001(1)	0.013(1)
C(15)	2*i*	–0.0009(4)	0.8239(3)	0.3882(3)	0.072(2)	0.064(2)	0.048(2)	0.026(2)	–0.011(2)	0.011(2)
C(16)	2*i*	0.0989(5)	0.8981(4)	0.3496(3)	0.112(3)	0.064(2)	0.038(2)	0.039(2)	0.017(2)	0.023(2)
C(17)	2*i*	0.2467(4)	0.9287(4)	0.4331(3)	0.089(3)	0.075(2)	0.050(2)	0.019(2)	0.030(2)	0.029(2)
C(18)	2*i*	0.2970(3)	0.8816(3)	0.5539(3)	0.054(2)	0.069(2)	0.043(2)	0.009(2)	0.016(1)	0.018(2)

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