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# Novel $\eta^3$-allyl complexes of titanium

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Dedicated to Professor Fausto Calderazzo.

## Abstract

Treatment of $TiCl_4(dmpe)$ (**1a**) and $TiCl_4(depe)$ (**1b**) with two equivalents of $C_3H_5MgCl$ in toluene at −30°C affords two novel allyl–titanium complexes: a dinuclear mixed-valent $Ti_2^{5+}$ species $Ti_2(\mu\text{-}Cl)_2Cl_2(dmpe)_2(\mu^2\text{-}\eta^3\text{-}C_3H_5)$ (**2**) and a mononuclear $Ti^{III}$ complex, $TiCl(depe)(\eta^3\text{-}C_3H_5)_2$ (**3**). Syntheses and crystal structures of **1b**, **2** and **3** are presented. In complex **2**, in addition to two bridging chloride ligands a $\eta^3$-allyl group spans two titanium atoms with a Ti...Ti separation of 2.908(1) Å. The allyl bridge is symmetrical with each terminal carbon atom having a Ti–C distance of 2.154(6) Å, while the central carbon atom is equidistant from the titanium atoms, $Ti\text{–}C_{cent}$, 2.430(6) Å. Each Ti atom in **2** is further coordinated by a chelating dmpe ligand and a chloride ion. In the mononuclear complex **3** two $\eta^3$-allyl groups are bound to the $Ti^{III}$ center and the coordination is completed by a chelating diphosphine ligand and one chloride ion. The Ti–C distances in **3** vary from 2.286(3) to 2.478(3) Å. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Titanium complexes; Allyl ligands; Crystal structures

## 1. Introduction

We have found [1] that treatment of $TiCl_4(dmpe)$ with one and two equivalents of $PhCH_2MgCl$ afforded mono- and di-substituted $Ti^{IV}$ products: $TiCl_3(PhCH_2)(dmpe)$ and $TiCl_2(PhCH_2)_2(dmpe)$, respectively. In contrast, analogous reactions of $TiCl_4(dmpe)$ with one and two equivalents of $Bu^tMgCl$ resulted in reduction products: a $Ti^{III}$ dinuclear complex $Ti_2(\mu\text{-}Cl)_2Cl_4(dmpe)_2$ and a $Ti^{II}$ trinuclear cluster $[Ti(\mu\text{-}Cl)Cl(dmpe)]_3$.

Here we extend this work and present a study of the reactions of $TiCl_4(PP)$ (PP = dmpe, depe) with the allyl reagent, $C_3H_5MgCl$. Systematic synthesis of mono- and dinuclear late transition metal allyl complexes has established them as an important and interesting class of organometallic compounds with different coordination modes of the allyl ligands [2]. In contrast, there are relatively few examples of early transition metal complexes which contain an allyl group (Ti [3a–c], V [3b], Cr [3d–f]). To our knowledge, there have been no reports of the structurally characterized titanium–allyl compounds. In this paper, we present syntheses and crystal structures of two novel complexes with $C_3H_5^-$ ligands coordinated to titanium.

## 2. Experimental

### 2.1. General procedures

Manipulations during the preparation of all compounds were carried out under an atmosphere of argon using standard Schlenk techniques. Chemicals were purchased from the following commercial sources and used as received: $TiCl_4$ and $C_3H_5MgCl$ (Aldrich); dmpe ($Me_2PC_2H_4PMe_2$) and depe ($Et_2PC_2H_4PEt_2$) (Strem Chemicals), $C_6D_6$ (Cambridge Isotope Laboratories).

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All solvents used were freshly distilled under $N_2$ from suitable drying agents. NMR spectra were recorded at room temperature (r.t.) on a UNITY-plus 300 multinuclear spectrometer operated at 300 MHz for $^1H$, and at 121.4 MHz for $^{31}P$ (using 85% $H_3PO_4$ as an external standard). X-band ESR spectra of toluene glasses were recorded at 10 K with a frequency of 9.4 GHz on a Bruker ESR 300 spectrometer. Elemental analyses were done on all compounds by Canadian Microanalytical Services, and were satisfactory.

### 2.2. Synthesis of compounds

#### 2.2.1. $TiCl_4$(depe) (**1b**)

This followed the preparation of $TiCl_4$(dmpe) [1]. A solution of 1 ml of $TiCl_4$ (9 mmol) in 20 ml of hexane was cooled to −30°C; then a stoichiometric amount of depe (2 ml, 9 mmol) was added. An orange solid started to precipitate upon mixing. The mixture was warmed to r.t., and stirring was continued over 1 h. The precipitate was isolated by filtration, washed thoroughly with hexane (2 × 20 ml) and dried under vacuum. Yield: 3.186 g (89.4%).

Crystals suitable for X-ray crystallography were obtained by slow crystallization from toluene solution upon layering with hexane. $^{31}P\{^1H\}$-NMR ($C_6D_6$, 20°C): $\delta = 40.93$. $^1H$-NMR ($C_6D_6$, 20°C): $\delta = 1.85$ (m, 4H, $CH_2$), 1.62 (m, 4H, $CH_2$), 1.12 (d, 4H, $CH_2$), 0.87 (m, 12 H, $CH_3$).

#### 2.2.2. $Ti_2(\mu\text{-}Cl)_2Cl_2(dmpe)_2(\mu^2\text{-}\eta^3\text{-}C_3H_5)$ (**2**)

$TiCl_4$(dmpe) (0.509 g, 1.5 mmol), prepared according to reference [1], was suspended in 15 ml of toluene. The orange suspension was cooled to −78°C and 1.6 ml (3.2 mmol) of a 2 M solution of $C_3H_5MgCl$ in THF was then added. The color immediately turned dark-brown. Stirring was continued for 2 h keeping the temperature below −30°C. Then the mixture was quickly filtered, and the brown filtrate was placed in the freezer.

Dark-brown crystals of **2** appeared in a few days. Yield: 0.130 g (29.9%). ESR ($C_7H_8$, 10 K): centered at 3428 G, $g = 1.96$.

#### 2.2.3. $TiCl(depe)(\eta^3\text{-}C_3H_5)_2$ (**3**)

To a cooled suspension (−78°C) containing 0.590 g (1.5 mmol) of $TiCl_4$(depe) in 20 ml of toluene were added 1.6 ml of a 2 M solution (3.2 mmol) of $C_3H_5MgCl$ in THF. The color of the suspension turned dark-brown immediately. The mixture was stirred for 2 h while maintaining the temperature below −30°C. It was then filtered and the brown filtrate was placed in the freezer. Brown crystals of **3** appeared in 1 day. Yield: 0.192 g (34.5%). ESR ($C_7H_8$, 10 K): centered at 3433 G, $g = 1.96$.

### 2.3. X-ray crystallographic procedures

Single crystals of **1**–**3** were obtained as described above. In each case, a crystal of suitable quality was affixed to the end of a quartz fiber with grease, and then placed in a cold nitrogen stream (−60°C) on a Nonius Fast diffractometer equipped with an area detector and monochromated Mo–$K_\alpha$ radiation ($\lambda = 0.71073$ Å). Unit cell determinations and data collections followed routine procedures and practices of this laboratory [4]. Oscillation photographs of principal axes were taken to confirm Laue class and axial lengths. All data were corrected for Lorentz and polarization effects.

All calculations were performed on a DEC Alpha running VMS. The coordinates of the titanium atoms for all of the structures were found in direct methods E-maps using the structure solution program SHELXTL [5]. The positions of the remaining atoms were located by the use of a combination of least-squares refinement and difference Fourier maps in the SHELXL-93 program [6]. All hydrogen atoms of allyl groups in **2** and **3** (and some hydrogen atoms of phosphine ligands) were found in a difference Fourier map and further refined. The rest of hydrogen atoms were included at idealized positions for the structure factor calculations but not refined. Details of data collection and structure refinement for **1b**, **2** and **3** are reported in Table 1.

## 3. Results and discussion

### 3.1. Description of structures

#### 3.1.1. $TiCl_4$(depe) (**1b**)

This compound crystallizes in the monoclinic $C2/c$ space group with four molecules per unit cell. A perspective view of the molecule is presented in Fig. 1; the structural data are listed in Table 2. Each molecule consists of four chlorine (two of them are structurally independent) and two phosphorus (with one being independent) atoms bound to the $Ti^{IV}$ center with average Ti–Cl distances of 2.2904(8) Å and Ti–P distances of 2.5981(9) Å. The polyhedron around the titanium atom(IV) is a distorted octahedron with bond angles ranging from 76.71(4) to 111.03(5)°.

#### 3.1.2. $Ti_2(\mu\text{-}Cl)_2Cl_2(dmpe)_2(\mu^2\text{-}\eta^3\text{-}C_3H_5)$ (**2**)

Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. A perspective view of the molecular structure is shown in Fig. 2. Selected bond distances and angles are listed in Table 3. The complex consists of discrete dinuclear titanium units bridged by two chloride ligands (average Ti–$Cl_{br}$ distances are 2.468(2) Å) and by an allyl group.

Table 1
Crystallographic data for $TiCl_4$(depe) (**1b**), $Ti_2(\mu\text{-}Cl)_2Cl_2(dmpe)_2(\mu^2\text{-}\eta^3\text{-}C_3H_5)$ (**2**) and $TiCl(depe)(\eta^3\text{-}C_3H_5)_2$ (**3**)

| | **1b** | **2** | **3** |
|---|---|---|---|
| Empirical formula | $TiCl_4P_2C_{10}H_{24}$ | $Ti_2Cl_4P_4C_{15}H_{37}$ | $TiClP_2C_{16}H_{34}$ |
| Formula weight (g mol$^{-1}$) | 395.93 | 578.93 | 371.72 |
| Crystal size (mm) | 0.30 × 0.28 × 0.23 | 0.28 × 0.12 × 0.08 | 0.90 × 0.30 × 0.05 |
| Temperature (°C) | −60 | −60 | −60 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $C2/c$ (no. 15) | $P2_1/n$ (no. 14) | $P2_1/c$ (no. 14) |
| $a$ (Å) | 9.2317(5) | 11.509(1) | 7.6228(4) |
| $b$ (Å) | 12.0115(5) | 16.115(4) | 14.085(2) |
| $c$ (Å) | 17.1318(7) | 14.630(3) | 18.919(2) |
| $\beta$ (°) | 104.951(4) | 95.36(4) | 100.739(9) |
| $V$ (Å$^3$) | 1835.4(2) | 2701.5(9) | 1995.7(4) |
| $Z$ | 4 | 4 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.433 | 1.423 | 1.237 |
| Absorption coefficient ($\mu$) (mm$^{-1}$) | 1.203 | 1.224 | 0.714 |
| Radiation ($\lambda$) (Å) | Mo–$K_\alpha$ (0.71073) | Mo–$K_\alpha$ (0.71073) | Mo–$K_\alpha$ (0.71073) |
| Data/observed/parameters | 1185/1126/126 | 3235/2922/254 | 2592/2427/221 |
| $R_1$ [a] ($wR_2$ [b]) [$I>2\sigma(I)$] | 0.0376/0.0956 | 0.0475/0.1025 | 0.0326/0.0785 |
| $R_1$ [a] ($wR_2$ [b]) (all data) | 0.0390/0.0972 | 0.0624/0.1120 | 0.0351/0.0817 |
| Goodness-of-fit | 1.117 | 1.085 | 1.073 |

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Two titanium atoms are crystallographically independent with a Ti(1)···Ti(2) separation of 2.908(1) Å. Each has a chelating diphosphine ligand (average Ti–P distances are 2.595(2) Å) and one terminal chloride ion (Ti–$Cl_{term}$ is 2.389(2) Å).

The distances to the terminal carbon atoms of the allyl group, Ti(1)–C(3) and Ti(2)–C(1) are: 2.155(6) and 2.153(6) Å, respectively. The distances from both titanium atoms to the central carbon, C(2) are both equal to 2.430(6) Å. The allyl C–C bond lengths are 1.434(8) Å; the C–C–C angle is 122.4(6)°.

### 3.1.3. TiCl(depe)($\eta^3$-$C_3H_5$)$_2$ (**3**)

Crystals of **3** conform to the monoclinic space group $P2_1/c$ with four molecules per unit cell. A perspective view of the molecular structure is shown in Fig. 3. Selected bond distances and angles are listed in Table 4.

In the molecule of **3** a titanium(III) center is coordinated by a chelating diphosphine ligand with Ti–P(1) and Ti–P(2) distances of 2.6333(7) and 2.5795(8) Å, respectively; by one terminal chloride (Ti–Cl(1) is 2.452(8) Å) and two allyl groups.

In the crystal structure the two allyl ligands have slightly different dimensions: the shortest titanium–carbon distances for two different $C_3H_5^-$ groups are Ti–C(6) and Ti–C(1) (2.286(3) and 2.314(3) Å, respectively). The distances from the $Ti^{III}$ to the central carbon atoms of the two allyl ligands are about the same: 2.369(2) versus 2.373(3) Å. While the distances from the titanium center to the peripheral C(3) and C(4) atoms are much longer: 2.434(3) and 2.478(3) Å. In both allyl groups the C–C–C angles are the same, 125.1(3)°. The carbon–carbon distances within the allyl group are nonequivalent; with C(1)–C(2) of 1.386(4) and C(5)–C(6) of 1.397(4) Å being a bit longer than C(2)–C(3) of 1.369(5) and C(4)–C(5) of 1.362(4) Å.

### 3.2. Synthetic and structural considerations

Monoadducts of titanium tetrachloride with diphosphines, $TiCl_4$(PP) (PP = dmpe, **1a**; depe, **1b**), used as starting materials in the synthesis of the titanium–allyl

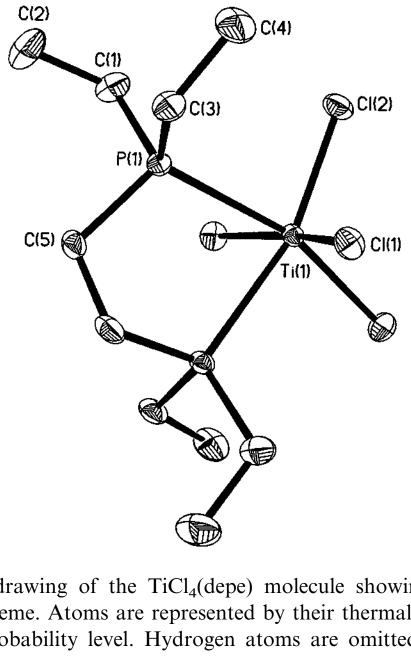

Fig. 1. A drawing of the $TiCl_4$(depe) molecule showing the atom labeling scheme. Atoms are represented by their thermal ellipsoids at the 40% probability level. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) in **1b**

| | | | |
|---|---|---|---|
| Ti(1)–Cl(1) | 2.3050(7) | | |
| Ti(1)–Cl(2) | 2.2758(8) | | |
| Ti(1)–P(1) | 2.5981(9) | | |
| P(1)–Ti(1)–P(1)′ | 76.71(4) | | |
| Cl(1)–Ti(1)–Cl(2) | 93.11(4) | Cl(1)–Ti(1)–P(1) | 84.98(3) |
| Cl(1)′–Ti(1)–Cl(2) | 95.69(3) | Cl(1)–Ti(1)–P(1)′ | 82.80(3) |
| Cl(1)–Ti(1)–Cl(1)′ | 164.41(5) | Cl(2)–Ti(1)–P(1) | 86.13(3) |
| Cl(2)–Ti(1)–Cl(2)′ | 111.03(5) | Cl(2)–Ti(1)–P(1)′ | 162.84(4) |

Table 3
Selected bond distances (Å) and angles (°) in **2**

| | | | |
|---|---|---|---|
| Ti(1)···Ti(2) | 2.9078(13) | | |
| Ti(1)–C(2) | 2.430(6) | Ti(2)–C(2) | 2.430(5) |
| Ti(1)–C(3) | 2.155(6) | Ti(2)–C(1) | 2.153(6) |
| Ti(1)–P(1) | 2.564(2) | Ti(2)–P(3) | 2.564(2) |
| Ti(1)–P(2) | 2.629(2) | Ti(2)–P(4) | 2.623(2) |
| Ti(1)–Cl(1) | 2.457(2) | Ti(2)–Cl(1) | 2.466(2) |
| Ti(1)–Cl(2) | 2.471(2) | Ti(2)–Cl(2) | 2.478(2) |
| Ti(1)–Cl(3) | 2.389(2) | Ti(2)–Cl(4) | 2.389(2) |
| P(1)–Ti(1)–P(2) | 74.56(6) | | |
| Cl(1)–Ti(1)–Cl(2) | 85.60(6) | Cl(1)–Ti(2)–Cl(2) | 85.25(5) |
| Cl(1)–Ti(1)–Cl(3) | 174.19(6) | Cl(1)–Ti(2)–Cl(4) | 176.41(6) |
| Cl(2)–Ti(1)–Cl(3) | 90.10(6) | Cl(2)–Ti(2)–Cl(4) | 92.36(6) |
| P(1)–Ti(1)–Cl(1) | 89.19(5) | P(3)–Ti(2)–Cl(1) | 88.32(6) |
| P(1)–Ti(1)–Cl(2) | 154.17(6) | P(3)–Ti(2)–Cl(2) | 153.62(6) |
| P(1)–Ti(1)–Cl(3) | 93.02(6) | P(3)–Ti(2)–Cl(4) | 92.67(6) |
| P(2)–Ti(1)–Cl(1) | 90.47(6) | P(4)–Ti(2)–Cl(1) | 94.42(5) |
| P(2)–Ti(1)–Cl(2) | 80.20(5) | P(4)–Ti(2)–Cl(2) | 80.49(6) |
| P(2)–Ti(1)–Cl(3) | 84.96(6) | P(4)–Ti(2)–Cl(4) | 82.52(6) |
| C(1)–C(2) | 1.434(8) | C(1)–C(2)–C(3) | 122.4(6) |
| C(2)–C(3) | 1.433(8) | | |

compounds, are easily prepared by stoichiometric addition of the appropriate phosphine to the solutions of $TiCl_4$ in hexane. Compounds **1a** and **1b** can be isolated in high yields (85–90%); they are thermally stable crystalline orange solids soluble in aromatic solvents. The structure of **1a** has been reported recently [1], while the structure of **1b** is presented here. The structures of the two $TiCl_4(PP)$ molecules are essentially the same with slight differences in average Ti–Cl (2.289(2) in **1a** vs 2.2904(8) Å in **1b**) and Ti–P distances (2.581(2) in **1a** versus 2.5981(9) Å in **1b**).

Treatment of **1a** and **1b** with two equivalents of $C_3H_5MgCl$ in toluene under similar reaction conditions at temperatures below −30°C resulted in quite different products: a dinuclear mixed-valence $Ti_2^{5+}$ complex $Ti_2(\mu\text{-Cl})_2Cl_2(dmpe)_2(\mu^2\text{-}\eta^3\text{-}C_3H_5)$ (**2**) and a mononuclear $Ti^{III}$ compound $TiCl(depe)(\eta^3\text{-}C_3H_5)_2$ (**3**), respectively. In contrast to our previous work [1] both reduction and substitution processes proceed at the same time in the $C_3H_5MgCl–TiCl_4(PP)$ systems. The difference in the products isolated under similar experimental conditions for two starting materials, $TiCl_4(dmpe)$ and $TiCl_4(depe)$, could only be attributed to the different steric bulk of the two phosphine ligands. Recently we have observed how bulkiness of diphosphines can influence the structural parameters of the same type of complexes, $Ti_2(\mu\text{-Cl})_2Cl_4(PP)_2$ for PP = dmpe, depe, and dippe [1].

These new titanium–allyl complexes, which appear to be extremely air-sensitive, are readily soluble in aromatic solvents such as benzene and toluene, but solutions of **2** decompose at r.t. very fast. The X-band ESR spectra of toluene glasses at 10 K confirm the paramagnetism of these complexes. In the case of **2**, a complex pattern is observed centered at 3428 G with a *g* value of 1.96. The spectrum of **3** is centered at 3433 G, giving a *g* value of 1.96. Complexes **2** and **3** are the first two titanium–allyl compounds for which structural data are available, so a few words may be added

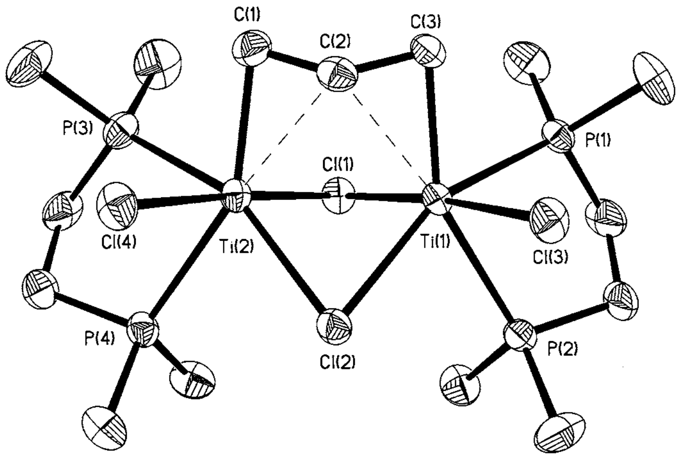

Fig. 2. Perspective drawing of the $Ti_2(\mu\text{-Cl})_2Cl_2(dmpe)_2(\mu^2\text{-}\eta^3\text{-}C_3H_5)$ molecule showing the atom labeling scheme. Atoms are represented by their thermal ellipsoids at the 40% probability level. Hydrogen atoms are omitted for clarity.

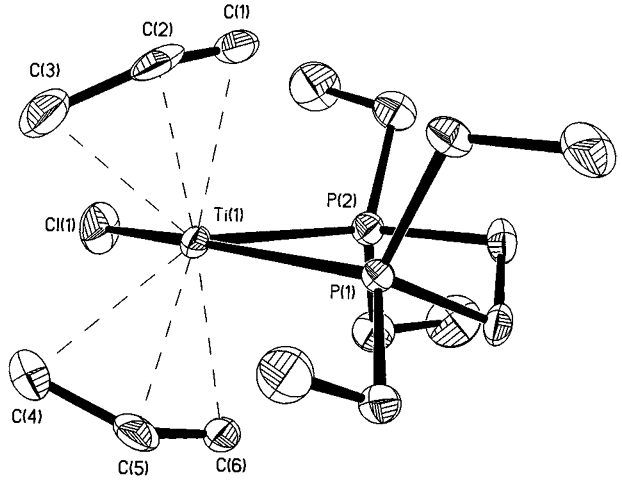

Fig. 3. A drawing of the $TiCl(depe)(\eta^3\text{-}C_3H_5)_2$ molecule showing the atom labeling scheme. Atoms are represented by their thermal ellipsoids at the 40% probability level. Hydrogen atoms are omitted for clarity.

Table 4
Selected bond distances (Å) and angles (°) in **3**

| | | | |
|---|---|---|---|
| Ti(1)–C(1) | 2.314(3) | Ti(1)–C(6) | 2.286(3) |
| Ti(1)–C(2) | 2.369(2) | Ti(1)–C(5) | 2.373(3) |
| Ti(1)–C(3) | 2.434(3) | Ti(1)–C(4) | 2.478(3) |
| Ti(1)–Cl(1) | 2.4521(8) | | |
| Ti(1)–P(1) | 2.6633(7) | | |
| Ti(1)–P(2) | 2.5795(8) | | |
| P(1)–Ti(1)–P(2) | 76.22(2) | | |
| P(1)–Ti(1)–Cl(1) | 161.05(3) | | |
| Cl(1)–Ti(1)–P(2) | 85.54(3) | | |
| C(1)–C(2) | 1.386(4) | C(1)–C(2)–C(3) | 125.0(3) |
| C(2)–C(3) | 1.369(5) | C(4)–C(5)–C(6) | 125.2(3) |
| C(4)–C(5) | 1.362(4) | | |
| C(5)–C(6) | 1.397(4) | | |

concerning their structures, coordination modes and dimensions of the allyl groups in these molecules.

It is known [2b] that allyl ligands are capable of acting as one-electron donors (σ-allyl) or as three-electron donors (π-allyl). In the latter mode of bonding, the π-allyl can coordinate to a single metal atom (complex **3**) or may bridge two metal atoms (complex **2**).

The most interesting feature of the dinuclear molecule **2** is the presence of the bridging allyl group. The allyl bridge is highly symmetrical with C(1) and C(3) being equidistant from Ti(1) and Ti(2), (Ti–C, 2.154(6) Å), while the central carbon atom, C(2), is significantly further but equidistant from the two titanium atoms (2.430(6) Å). The C–C–C angle of 122.4(6)° in the allyl group is quite normal. There is a little increase in carbon–carbon bond distances within the allyl ligand upon coordination: the average C–C bond length is 1.434(8) Å. This can be compared to the quite long C–C bond distances of 1.47(1) Å in the $W_2(\mu^2\text{-}C_3H_5)_2(NMe_2)_4$ explained by a significant reduction of the allyl ligands and by a corresponding oxidation of the $W_2^{6+}$ moiety [2b]. The characteristics of the allyl group in **2** also indicate a considerable electronic delocalization over the $Ti_2(C_3H_5)$ moiety.

In addition to the allyl group, the two titanium centers are bridged by two chloride ligands, the dihedral angles between the Ti(1)–C(2)–Ti(2) plane and two planes containing μ-Cl: Ti(1)–Cl(1)–Ti(2) and Ti(1)–Cl(2)–Ti(2) are 63.34 and 50.82°, respectively. This results in the Ti···Ti separation of 2.908(1) Å, and each titanium atom can be described as seven-coordinate.

Concerning $Ti^{II}$–$Ti^{III}$ species, a search revealed just two more mixed-valent titanium species. One of these is an indenyl complex with two hydride bridges and quite short Ti···Ti distance of 2.745 Å [7]. The second example is a dinuclear species in which two titanium fragments are attached through a cyclopentadienyl $C_5H_4$-group, and the Ti···Ti separation is more than 3.33 Å [8]. Therefore, useful speculation on the Ti–Ti bonding tendencies for the mixed $Ti_2^{5+}$ species cannot be made using these three completely different molecules.

In the mononuclear $Ti^{III}$ compound **3**, two allyl ligands are coordinated by one titanium center. The polyhedron around $Ti^{III}$ consists of two phosphorus atoms, one chloride ion and six carbon atoms of allyl groups (with Ti–C distances ranging from 2.286(3) to 2.478(3) Å). This affords unusual coordination around the $Ti^{III}$ center, which is known to be octahedral in most of its compounds.

When the characteristics of the allyl groups in complexes **2** and **3** are compared, we can see the essential difference, although in both cases $C_3H_5$ ligands are exhibiting an $\eta^3$-bonding mode. In contrast to **2**, which has a highly symmetric $C_3H_5$-bridge, the two allyl groups in **3** are nonequivalent and each is slightly asymmetric: the difference in C–C bond length is 0.017 Å for the $C_1$–$C_2$–$C_3$ group and 0.035 Å for the $C_4$–$C_5$–$C_6$ group. In addition, the average C–C distances in **3** are significantly shorter than that displayed in complex **2** (1.378(4) Å vs 1.434(8) Å). While the average Ti–C distances are elongated in **3** compared to **2** (2.376(3) Å vs 2.246(6) Å).

In conclusion, compounds **2** and **3** are the first titanium complexes containing allyl ($C_3H_5^-$) ligands. Complex **2** is a unique compound with an allyl ligand coordinated to the dinuclear $d^2$–$d^1$ system and a rare example of a crystallographically characterized mixed-valent $Ti_2^{5+}$ species.

## 4. Supplementary material

Crystallographic data for the structural analysis of compounds **1b**, **2** and **3** can be obtained from the authors.

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