

2-(Diphenylphosphinoylmethyl)-pyrrole–2-(diphenylphosphinomethyl)-pyrrole (0.43/0.57) and tetrachlorido-(5-diphenylphosphinomethyl-2*H*-pyrrole- κ^2 *N,P*)titanium(IV)

Lewis M. Broomfield, Manfred Bochmann and Joseph A. Wright*

School of Chemistry, University of East Anglia, Norwich, NR4 7TJ, England
Correspondence e-mail: joseph.wright@uea.ac.uk

Received 16 December 2009

Accepted 4 February 2010

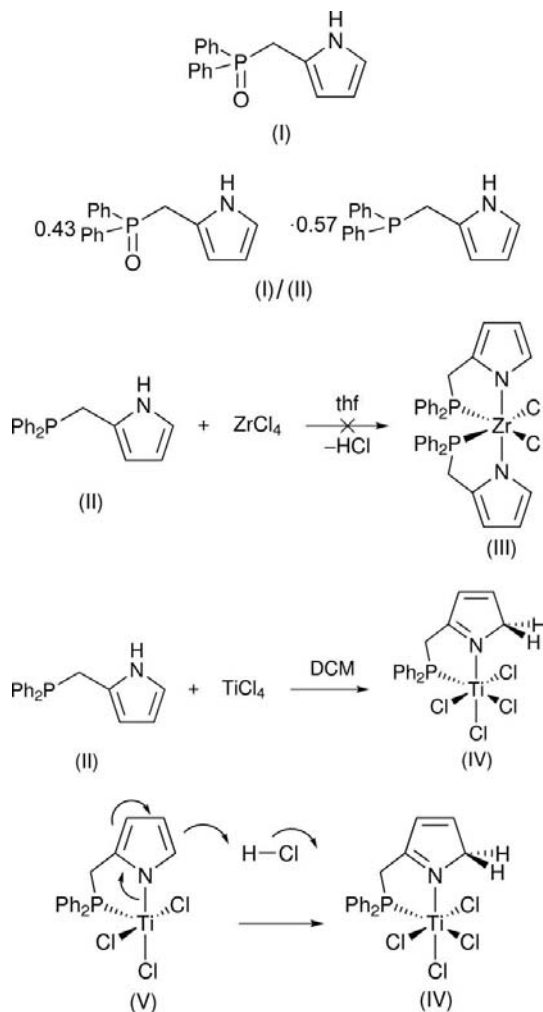
Online 24 February 2010

The title phosphine oxide–phosphine, $0.43\text{C}_{17}\text{H}_{16}\text{NOP}\cdot 0.57\text{C}_{17}\text{H}_{16}\text{NP}$, (I)/(II), was obtained as a 0.861 (6):1.139 (6) cocrystallized mixture. Hydrogen bonding between the two constituents leads to the formation of 2:2 solid-state assemblies. Instead of forming the expected simple *N,P*-chelated system *via* loss of the N-bound H atom, reaction of 2-(diphenylphosphinomethyl)pyrrole, (II), with TiCl_4 leads to the formation of the title titanium(IV) complex, $[\text{TiCl}_4(\text{C}_{17}\text{H}_{16}\text{NP})]$, (IV), containing a rearranged neutral ligand in which the N-bound H atom moves to one of the pyrrole C atoms, giving a partially unsaturated ring.

Comment

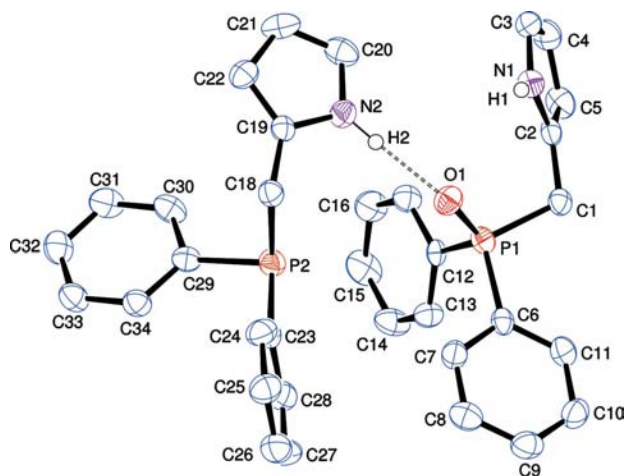
The desire to improve on existing catalytic processes and find new catalytic systems continues to drive synthetic chemists to create novel ligand systems. For example, ongoing efforts to find post-metallocene polymerization catalysts for alkenes (Gibson & Spitzmesser, 2003) have led to the introduction of a large class of salicylaldimine and pyrrolaldimine ligands (see, for example, Yoshida *et al.*, 2001; Tsurugi & Mashima, 2006; Cui *et al.*, 2003; Yang *et al.*, 2007). The combination of an anionic pyrrolate moiety with other donors is, however, less common. In an effort to explore routes to new *N,P*- and *N,O*-chelate ligands based on pyrrolates, we have recently introduced the families of pyrrole–phosphine oxide [see (I) in the scheme as an example] and pyrrole–phosphine ligands [see (II) in the scheme as an example] (Broomfield, Boschert *et al.*, 2009; Broomfield, Wright *et al.*, 2009). These ligands are attractive as the nature of the groups on the P atom [phenyl in both (I) and (II)] can be varied at a late stage of the synthesis by appropriate choice of the phosphine starting material. The introduction of other groups onto the pyrrole ring is another potential method for tuning the properties of the ligand

system. Exploring the reactivity of pyrrole–phosphine oxide ligands with early transition metals has shown that the phosphine oxide acts as a well behaved ligand with these metals. We report here on efforts to use 2-(diphenylphosphino-methyl)pyrrole, (II), with early transition metals.



Reaction of (II) with ZrCl_4 in tetrahydrofuran (THF) was carried out with the intention of forming the bis-ligand complex (III) (see scheme). However, crystallization of the reaction mixture led to the isolation of crystals with an approximately stoichiometric mixture of cocrystallized (I) and (II), denoted (I)/(II) (Fig. 1). Synthesis of (II) from (I) is complicated by the reactivity of the phosphine with oxygen, and it is possible that the metal complex is not involved in formation of the cocrystals. The occupancy of O1 was refined freely, establishing that the site is largely occupied [occupancy = 0.861 (6)].

The molecular geometry of (I) here (Table 1) is very similar to that observed when the same molecule crystallizes in the absence of (II) (Broomfield, Wright *et al.*, 2009). The geometric data observed for (I) are also in the range anticipated for this molecule. More interesting are the intermolecular interactions between (I) and (II) (Fig. 2 and Table 2). Hydrogen bonding between two molecules of (I) leads to solid-state dimer formation. This is in contrast with the

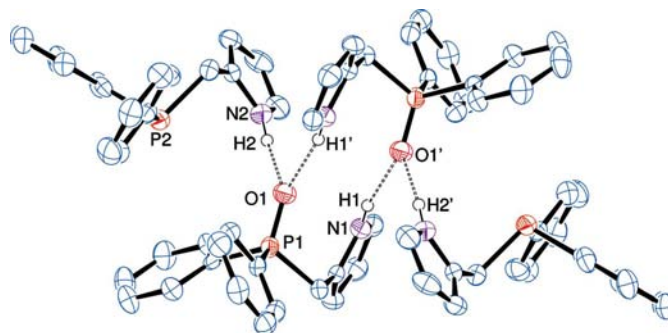

Figure 1

The structure of (I)/(II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms except H1 and H2 have been omitted for clarity. The dashed line indicates a hydrogen bond.

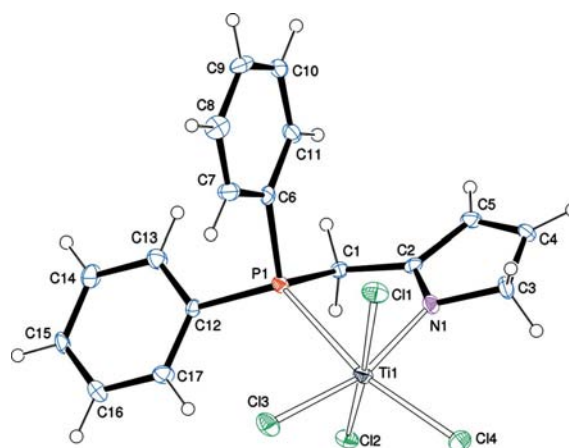
supramolecular arrangement seen in crystals of (I) alone, where infinite one-dimensional chains are formed by hydrogen bonding between adjacent molecules (Broomfield, Wright *et al.*, 2009). The $O1 \cdots N1^i$ [symmetry code: (i) $-x, -y + 1, -z$] separation observed here [2.821 (4) Å] is slightly shorter than that seen in the infinite chain arrangement [2.868 (3) Å]. In addition to this pairing hydrogen-bond interaction, each molecule of (I) also hydrogen bonds to one molecule of (II), with an $O1 \cdots N2$ distance of 2.790 (3) Å. The result of this hydrogen-bond framework is the formation of an overall zero-dimensional 2:2 supramolecular structure.

A search of the Cambridge Structural Database (CSD, Version 5.31, 20 November 2009 release; Allen, 2002) reveals five structures which consist of independent molecules of a phosphine and its oxide, *viz.* refcodes AZUDII (Atkinson *et al.*, 2004), EXUDAC (Mohamed *et al.*, 2004), QEMFAP (Chekhlov, 2000), SIXJEO (Carriedo *et al.*, 1990) and UJAPEA (Hitchcock *et al.*, 2003). All show statistical interspersion of the phosphine oxide in the structure, in marked contrast with the pattern seen here. The presence of the strongly hydrogen-bonding amine group and the resulting hydrogen-bond network may account for the greater order seen in the present structure.

In contrast with the lack of reaction between (II) and $ZrCl_4$, reaction of (II) with $TiCl_4$ did lead to the formation of a metal-containing species (see scheme). However, analysis of the difference Fourier map following data collection revealed that C3 carries two H atoms and the ligand is neutral overall, giving complex (IV) (Fig. 3). The C–C distances in the nitrogen-containing ring are fully in agreement with the locations of the H atoms (Table 3). The coordination geometry of the metal atom is approximately octahedral, with the $N1-Ti1-P1$ bite angle significantly smaller than 90° , presumably due to the constraint imposed by the ligand backbone. The mechanism for the reaction is likely to involve initial coordination of (II) to the metal, yielding (V), followed by an acid-mediated


Figure 2

The hydrogen-bond arrangement in (I)/(II). Displacement ellipsoids are drawn at the 50% probability level and dashed lines indicate hydrogen bonds. Primed atoms are generated by the symmetry operation $(-x, 1 - y, -z)$.


Figure 3

The structure of (IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

rearrangement (see scheme). This type of rearrangement has previously been reported when pyrroles are reacted in the presence of the strong Lewis base $B(C_6F_5)_3$ (Guidotti *et al.*, 2003; Focante *et al.*, 2004; Kehr *et al.*, 2001).

There are two structures in the CSD which contain a rearranged pyrrole ligand without the presence of a porphyrin ring or secondary bonding interactions, *viz.* refcodes WELTIQ (DuBois *et al.*, 1999) and XITLES (Kreckmann *et al.*, 2007). WELTIQ contains rhenium, and has an $Re-N$ bond distance of 2.171 (6) Å, while XITLES is a tungsten complex, with a $W-N$ distance of 2.136 (3) Å. The $Ti-N$ distance obtained in the current work, 2.174 (5) Å, is therefore somewhat longer than might initially be anticipated on the basis of the smaller size of the Ti centre compared with Re and W. In the case of $Ti-P$ bonds, a search of the CSD gives a range of 2.254–2.904 Å for 226 database entries, with a mean value of 2.584 (4) Å. The value observed for (IV) [2.6428 (17) Å] is above the average but is not atypical. Presumably, the chelating nature of the ligand in (IV) is responsible for the length of the bonds observed here.

In summary, whilst ligand (II) shows good promise in forming complexes with later transition metals, early metals

reveal additional ligand reactivity which may have to be modulated in order to obtain the desired complexes successfully. Efforts to control this reactivity are ongoing, for example, by blocking the 2-position on the pyrrole ring with a bulky alkyl to prevent ligand rearrangement.

Experimental

Compound (II) was obtained as described elsewhere (Broomfield, Wright *et al.*, 2009). Reaction of the free ligand with $ZrCl_4$ in THF, followed by the addition of an equal amount of hexane and cooling to 243 K, led to the formation of crystals of (I)/(II) [0.861 (6):1.139 (6)]. Reaction of $TiCl_4$ with the free ligand in dichloromethane, followed by dilution with hexane and cooling to 243 K, gave crystals of (IV) after storage for a few days.

Compound (I)/(II)

Crystal data

0.43C₁₇H₁₆NOP·0.57C₁₇H₁₆NP $V = 2941.9 (5) \text{ \AA}^3$
 $M_r = 272.18$ $Z = 8$
 Monoclinic, $P2_1/c$ Mo $K\alpha$ radiation
 $a = 9.6282 (9) \text{ \AA}$ $\mu = 0.18 \text{ mm}^{-1}$
 $b = 15.2848 (14) \text{ \AA}$ $T = 140 \text{ K}$
 $c = 20.391 (2) \text{ \AA}$ $0.32 \times 0.08 \times 0.08 \text{ mm}$
 $\beta = 101.376 (8)^\circ$

Data collection

Oxford Diffraction Xcalibur 3/CCD diffractometer 30196 measured reflections
 5167 independent reflections
 Absorption correction: multi-scan (ABSPACK; Oxford Diffraction, 2006) 3223 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.110$
 $T_{min} = 0.822$, $T_{max} = 0.986$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$ H atoms treated by a mixture of independent and constrained refinement
 $wR(F^2) = 0.095$
 $S = 1.01$
 5167 reflections $\Delta\rho_{max} = 0.26 \text{ e \AA}^{-3}$
 361 parameters $\Delta\rho_{min} = -0.31 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I)/(II).

O1—P1	1.458 (2)	P2—C23	1.842 (3)
P1—C12	1.808 (3)	P2—C29	1.848 (3)
P1—C6	1.811 (3)	P2—C18	1.871 (3)
P1—C1	1.827 (3)		
O1—P1—C12	112.83 (12)	C6—P1—C1	107.23 (13)
O1—P1—C6	112.16 (13)	C23—P2—C29	101.88 (13)
C12—P1—C6	106.31 (13)	C23—P2—C18	101.63 (13)
O1—P1—C1	111.55 (13)	C29—P2—C18	99.95 (13)
C12—P1—C1	106.36 (13)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (I)/(II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O1 ⁱ	0.86 (3)	1.99 (3)	2.821 (4)	164 (3)
N2—H2 \cdots O1	0.88 (3)	1.91 (3)	2.790 (3)	174 (3)

Symmetry code: (i) $-x, -y + 1, -z$.

Table 3

Selected geometric parameters (\AA , $^\circ$) for (IV).

Ti1—N1	2.174 (5)	C2—N1	1.303 (6)
Ti1—Cl3	2.2293 (18)	C2—C5	1.439 (7)
Ti1—Cl1	2.2663 (19)	C3—N1	1.464 (6)
Ti1—Cl4	2.2766 (17)	C3—C4	1.471 (7)
Ti1—Cl2	2.3079 (19)	C4—C5	1.320 (7)
Ti1—P1	2.6428 (17)		
N1—Ti1—Cl4	91.10 (12)	N1—Ti1—P1	71.36 (11)
Cl3—Ti1—Cl4	106.38 (7)	Cl1—Ti1—P1	89.10 (6)
Cl1—Ti1—Cl2	168.17 (7)		

Compound (IV)

Crystal data

$[TiCl_4(C_{17}H_{16}NP)]$ $\gamma = 100.588 (16)^\circ$
 $M_r = 454.98$ $V = 955.6 (3) \text{ \AA}^3$
 Triclinic, $P\bar{1}$ $Z = 2$
 $a = 8.1481 (17) \text{ \AA}$ Mo $K\alpha$ radiation
 $b = 8.6323 (16) \text{ \AA}$ $\mu = 1.09 \text{ mm}^{-1}$
 $c = 14.202 (3) \text{ \AA}$ $T = 140 \text{ K}$
 $\alpha = 98.159 (15)^\circ$ $0.14 \times 0.06 \times 0.06 \text{ mm}$
 $\beta = 98.727 (16)^\circ$

Data collection

Oxford Diffraction Xcalibur 3/CCD diffractometer 10184 measured reflections
 3347 independent reflections
 Absorption correction: multi-scan (ABSPACK; Oxford Diffraction, 2006) 1864 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.112$
 $T_{min} = 0.905$, $T_{max} = 0.937$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$ 217 parameters
 $wR(F^2) = 0.098$ H-atom parameters constrained
 $S = 0.89$ $\Delta\rho_{max} = 0.53 \text{ e \AA}^{-3}$
 3347 reflections $\Delta\rho_{min} = -0.48 \text{ e \AA}^{-3}$

All C-bound H atoms were refined using a riding model (SHELXL97; Sheldrick, 2008), and with $U_{iso}(H) = 1.2U_{eq}(C)$ for CH and CH_2 groups or $1.5U_{eq}(C)$ for methyl groups. Methyl groups were allowed additional rotational freedom. In (I)/(II), atoms H1 and H2 (bound to N) were located in a difference Fourier map, and both coordinates and U_{iso} values were freely refined. The site occupancy of the O atom in (I)/(II) (O1) was freely refined to a value of 0.861 (6).

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*, *PLATON* (Spek, 2009), *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004).

JAW thanks the EPSRC for funding. LMB thanks the University of East Anglia for funding. The authors express their gratitude to the Chemical Database Service (Fletcher *et al.*, 1996) for providing access to the Cambridge Structural Database.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3032). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst. B* **58**, 380–388.
- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Atkinson, R. C. J., Gibson, V. C., Long, N. J., White, A. J. P. & Williams, D. J. (2004). *Dalton Trans.* pp. 1823–1826.
- Broomfield, L. M., Boschert, D., Wright, J. A., Hughes, D. L. & Bochmann, M. (2009). *J. Organomet. Chem.* **694**, 4084–4089.
- Broomfield, L. M., Wright, J. A. & Bochmann, M. (2009). *Dalton Trans.* pp. 8269–8279.
- Carriedo, G. A., Rodriguez, M. L., Garcia-Granda, S. & Aguirre, A. (1990). *Inorg. Chim. Acta*, **178**, 101–106.
- Chekhlov, A. N. (2000). *Zh. Strukt. Khim.* **41**, 788–794.
- Cui, C., Shafir, A., Reeder, C. L. & Arnold, J. (2003). *Organometallics*, **22**, 3357–3359.
- DuBois, M. R., Vasquez, L. D., Peshherbe, L. & Noll, B. C. (1999). *Organometallics*, **18**, 2230–2240.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.
- Focante, F., Carmurati, I., Nanni, D., Leardini, R. & Resconi, L. (2004). *Organometallics*, **23**, 5135–5141.
- Gibson, V. C. & Spitzmesser, S. K. (2003). *Chem. Rev.* **103**, 283–316.
- Guidotti, S., Camurati, I., Focante, F., Angellini, L., Moscardi, G., Resconi, L., Leardini, R., Nanni, D., Mercandelli, P., Sironi, A., Beringhelli, T. & Maggioni, D. (2003). *J. Org. Chem.* **68**, 5445–5465.
- Hitchcock, P. B., Lee, T.-H. & Leigh, G. J. (2003). *Dalton Trans.* pp. 2276–2279.
- Kehr, G., Roesmann, R., Fröhlich, R., Holst, C. & Erker, G. (2001). *Eur. J. Inorg. Chem.* pp. 535–538.
- Kreckmann, T., Arndt, S., Schrock, R. R. & Müller, P. (2007). *Organometallics*, **26**, 5702–5711.
- Mohamed, E. M., Panchanatheswaran, K., Low, J. N. & Glidewell, C. (2004). *Acta Cryst. C* **60**, o475–o478.
- Oxford Diffraction (2006). *ABSPACK, CrysAlis CCD and CrysAlis RED*. Versions 1.171. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst. D* **65**, 148–155.
- Tsurugi, H. & Mashima, K. (2006). *Organometallics*, **25**, 5210–5212.
- Yang, Y., Li, S., Cui, D., Chen, X. & Jing, X. (2007). *Organometallics*, **26**, 671–678.
- Yoshida, Y., Matsui, S., Takagi, Y., Mitani, M., Nakano, T., Tanaka, H., Kashiwa, N. & Fujita, T. (2001). *Organometallics*, **20**, 4793–4799.