Synthesis and Reactivity of titanium 'POCOP' pincer complexes

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Abstract

The 'POCOP' pincer ligand, $[2,6-(R_2PO)_2C_6H_3]$, has been attached to titanium in both Ti(III) and Ti(IV) complexes for the first time. Using a lithium-halogen exchange route $[2.6-(R_2O)_2C_6H_3]$ Li ([^RPOCOP]Li) can be synthesised. Both the iso-propyl and tert-butyl derivatives can be made, but only the latter isolated. These can be reacted with the Ti(III) and Ti(IV) synthons to make [^{IBu}POCOP]TiCl₂ (1), [^{IBu}POCOP]TiCl₃ (2) and {[^{IPr}POCOP]TiCl₂(µ-Cl)}₂ (4). In the presence of Ti(IV), THF and [^RPOCOP]Li an unprecedented ligand rearrangement occurs. 1 can be derivatised with alkylating agents to make bis-methyl, phenyl and neopentyl complexes. The last of these can activate H₂ to make a rare example of a titanium hydride chloride, with the metal pincer fragment staying attached. This opens the door for this archetypical pincer ligand to be used with early transition metals.

Introduction

Since their initial discovery by Shaw in 1976 pincer complexes have held a privileged position in organometallic chemistry.^[1–3] Pincer complexes are widely applied in catalysis for example in iron catalysed hydrogenations,^[4–13] iridium and ruthenium catalysed alkane dehydrogenation,^[14–27] and cross-coupling reactivity.^[28–38] Pincer ligands also support interesting reactivity, for example acting as a two-electron sink to augment reactivity.^[39–54] Of the many different pincer ligands developed some of the most recognisable are those of the ^RPCP and ^RPOCOP design, where a central arene is flanked by two phosphines connected via a methylene group or an oxygen atom respectively (^RPCP = 2,6-(CH₂PR₂)₂C₆H₃), ^RPOCOP = 2,6-(OPR₂)₂C₆H₃)).

The ^RPCP ligand is the progenitor of pincer ligands. It, and its close cousin ^RPOCOP have been extensively used with late transition metals. The ease of changing the phosphine and arene substituents has resulted in these ligands being adopted in a multitude of challenging reactivity.^[55] For example Ir ^RPOCOP complexes have been used in tandem with olefin metathesis catalysts to perform alkane metathesis,^[56] and have been able to support single-

crystal to single-crystal ligand exchange.^[57] However to date there is only one report of the ^RPOCOP motif being used with early transition metals.^[58] The origin of this scarcity is that the traditional route to these complexes relies on the oxidative addition of a strong C-H bond, as well as this is disfavoured for early transition metals (both because of the relatively weak bonds formed, and the lack of suitable synthons in an N-2 oxidation state).

However early transition metal pincer complexes are enjoying a renaissance.^[59] Pioneered by Fryzuk's work on aliphatic 'PNP' pincer complexes,^[60] more recently others have taken up the baton making early transition metal pincer complexes capable of activating small molecules (e.g. N₂, CH₄) in interesting reactivity.^[61–70] An issue with these systems however is that they can be challenging to derivatise and tune the steric and electronic profile of the pincer ligand.

Herein we report the selective synthesis of a ^RPOCOP Titanium complexes. We demonstrate ligand platforms with different steric profiles and binding to the metal in different oxidation states (with divergent chemistries). We have taken one of these synthons further onwards, derivatising it to make a number or alkyl and aryl Ti(^RPOCOP) complexes. One of these complexes is reacted with dihydrogen to form a rare Ti hydride chloride, displaying the ^RPOCOP ligands' ability to support interesting reactivity from the metal centre.

Results and Discussion

Synthesis of titanium ^RPOCOP complexes was achieved via the salt metathesis reaction of the lithium salt of the ^RPOCOP ligand and either TiCl₃·3THF or TiCl₄. A similar method from the iodo-^RPOCOP compound has been described, however the lithiated material was not isolated nor characterised.^[71,72] **[^{tBu}POCOP]Li** (^RPOCOP = 2,6-(OPR₂)C₆H₃) was isolated *via* the lithium halogen exchange reaction of (^{tBu}POCOP)Br with a slight excess of ⁿBuLi (Scheme 1, yield 99%).





[t^{Bu}**POCOP]Li** can be stored at -40°C in an inert atmosphere as a colourless solid for over two months with no degradation. [t^{Bu}**POCOP]Li** is extremely moisture-sensitive and exposure to water leads to intractable contamination by (t^{Bu}POCOP)H. [t^{Bu}**POCOP]Li** is extremely soluble in hydrocarbon solvents, including aliphatic solvents. Crystals of [^{tBu}**POCOP]Li** suitable for x-ray diffraction were grown from slow evaporation of pentane (Figure 1).



Figure 1: ORTEP plot of [^{tBu}POCOP]Li. Ellipsoids at 50% probability, hydrogens omitted for clarity. ^tBu groups on phosphines only have the central carbon shown for clarity. Colour key: black (carbon); purple (phosphorus), red (oxygen), grey (lithium). Selected bond lengths (Å): Li(1)-C(1) 2.197(11), Li(1)-C(23) 2.264(11), Li(1)-O(3) 2.164(10), Li(1)-P(1) 2.614(10), Li(2)-C(1) 2.234(11), Li(2)-C(23) 2.192(11), Li(2)-O(2) 2.116(9), Li(2)-P(4) 2.544(10).

Organolithium compounds aggregate in the solution phase (and indeed in the solid and gaseous phase) to varying degrees.^[73] There are only a couple of other examples of a lithium 'PCP' complexes.^[74,75] [^{tBu}POCOP]Li has a similar structure to the related [^{Me}PCP]Li complex.^[75] The dimeric structure of [^{tBu}POCOP]Li is retained in non-donor solvents at room temperature. This is demonstrated by a quintet resonance in the ⁷Li{¹H} NMR spectrum, though some fluxionality must be present to allow the Li centres to couple equally to all four phosphorus atoms in the dimer. Such fluxionality in pincer complexes has precedence.^[75,76]

Synthesis of Titanium (III) POCOP Chloride, (1BuPOCOP)TiCl₂, 1

The synthesis of (${}^{tBu}POCOP$)TiCl₂, (**1**) in pentane (Scheme 2) yielded an electric blue solution which can be isolated as a light blue solid. Blue crystals suitable for x-ray diffraction studies can be grown from a concentrated solution of **1** in cyclopentane cooled to $-40^{\circ}C$ as blue crystals. **1** can be made on a gram scale in decent (59%) yields.

Scheme 2: Synthesis of 1.



The solid-state structure shows a five-coordinate titanium centre in near-perfect square based pyramid, with one of the chloride ligand in the axial position (figure 2). The τ^5 parameter (as defined by Addison *et al.*^[77] where 0 = square-based pyramid and 1 = trigonal bipyramid) was found to be 0.03. The titanium-phosphorus bonds were found to be 2.5825(7) Å and 2.6026(7) Å. The titanium-chloride bonds were found to be 2.2917(8) Å and 2.3178(8) Å, and the P-Ti-P bond angle was found to be 142.17(3)°. These values are in line with literature values for a titanium (III) centre.^[78-81]



Figure 2: ORTEP plot of **1**. Thermal ellipsoids at 50% probability, hydrogens omitted for clarity. Colour key: sky blue (titanium), black (carbon); purple (phosphorus), red (oxygen), green (chlorine). Selected bond lengths (Å) and bond angles (°): Ti(1)-P(1) 2.5825(7) , Ti(1)-P(2) 2.6026(7), Ti(1)-Cl(1) 2.2917(7), Ti(1)-Cl(2) 2.3177(7), Ti(1)-C(1) 2.196(2), P(1)-Ti(1)-P(2) 142.16(3)°.

Evan's NMR of **1** determined an μ_{eff} value of 1.858 μ_B , corresponding to one unpaired electron on the titanium centre, which was confirmed by the DFT-calculated spin density (see ESI). Unfortunately, due to the paramagnetic nature of the complex, only broad resonances were observed in the ¹H NMR spectrum (see supplementary information) and no resonances were observed in the ³¹P{¹H} NMR spectrum.

The presence of a titanium(III) metal centre was further confirmed by X-Band CW EPR of **1** (figure 3). The room temperature EPR signal is a triplet with a g_{iso} value of 1.9665 and isotropic hyperfine coupling value, a_0 of 2.31 mT, This is representative of a single unpaired electron centred on the titanium centre coupled to two equivalent phosphorus (I=1/2) nuclei.^[61]



Figure 3: X Band CW EPR spectra of **1** at room temperature. Black shows experimental data and red shows simulated data ($g_{iso} = 1.9665$. $a_0 = 2.31$ mT).

Synthesis of Titanium (IV) POCOP Chlorides, (^RPOCOP)TiCl₃ (2)

The reaction of (^{HBu}POCOP)Li and TiCl₄ in pentane (scheme 3) yields (^{HBu}POCOP)TiCl₃, **2**, as a red solid in 57% yield. Single crystals suitable for x-ray diffraction studies were grown from a saturated hexane solution cooled to -40° C. **2** is the Ti(IV) analogous complex of **1**.

Scheme 3: Synthesis of 2



The solid-state structure of **2** (figure 4) shows titanium in an extremely distorted octahedral geometry, with the sum of the angles around the equatorial plane (featuring the POCOP ligand and CI(2)) being 364.46(15)° but the axial CI(1)-Ti(1)-CI(3) angle being only 143.18(7)°. The origin of this distortion appears to be due to a second-order Jahn Teller effect, but a more comprehensive theoretical analysis is currently beyond the scope of this paper. Generally the Ti(1)-X bond lengths show a small increase when compared to **1**, presumably due to the increased steric encumbrance in **2**.



Figure 4: ORTEP plot of **2**. Thermal ellipsoids at 50% probability, hydrogens omitted for clarity. Colour key: sky blue (titanium), black (carbon); purple (phosphorus), red (oxygen), green (chlorine). Selected bond lengths (Å) and bond angles (°): Ti(1)-C(1) 2.206(7), Ti(1)-P(1) 2.6120(15), Ti(1)-P(2) 2.6345(17), Ti(1)-Cl(1) 2.2637(19), Ti(1)-Cl(2) 2.3818(17), Ti(1)-Cl(3) 2.3003(16); Σ equatorial angles: 364.46(15) [C(1)-Ti(1)-P(1) 71.77(14), C(1)-Ti(1)-P(2) 68.60(14), P(1)-Ti(1)-Cl(2) 79.60(5), P(2)-Ti(1)-Cl(2) 144.48(6)], Cl(1)-Ti(1)-Cl(3) 143.18(7).

The ¹H NMR spectrum shows the characteristic doublet resonance for the P^tBu₂ groups (1.41 ppm, ²J_(H-P) 13 Hz) and the ³¹P{¹H} NMR spectrum shows a single resonance at 187.6 ppm, roughly 30 ppm downfield from the free protonated ligand, (^{tBu}POCOP)H at 153.1 ppm.^[82]

Unexpectedly, targeting **2** using [^{tBu}**POCOP**]Li and a different titanium synthon, TiCl₄·2THF, instead promoted ligand rearrangement, yielding (κ^2 , *O*, *P*-(1-O-2-P^tBu₂-3(OP^tBu₂)-C₆H₃) ₂TiCl₂, **3** (scheme 4). This structure sees one of the O-P bonds cleaved and the phosphine group migrating to the original *ipso* carbon. Two rearranged ligands bind to the single titanium metal centre. This is the first example of such a rearrangement of the POCOP ligand.

Scheme 4: Synthesis of 3.



THF is required for this rearrangement to occur - conducting the reaction in toluene or diethyl ether does not produce either **2** or **3**. **2** cannot be converted to **3** despite heating in THF and excess [^{tBu}POCOP]Li. Heating [^{tBu}POCOP]Li in THF in the absence of titanium does not induce ligand rearrangement. **3** is still exclusively the only observable product even with a strict 1:1 equivalence of TiCl₄·2THF and [^{tBu}POCOP]Li. This rearrangement is curiously not seen with

TiCl₃.3THF. This appears to be an unique rearrangement in the presence of both Ti(IV) and THF.

The rearrangement is clearly seen in the ¹H and ³¹P{¹H} NMR spectra with two resonances observed corresponding to the tert-butyl protons; one ^tBu ¹H resonance still observed as a doublet at 1.10 ppm (${}^{2}J_{H-P} = 12$ Hz) whilst the other observed as a broad singlet (1.76 ppm). The ³¹P{¹H} also displays two resonances which integrate 1:1, one at 159.0 ppm, which is a similar chemical shift to the free protonated ligand,^[82] whilst the other is upfield at 78.2 ppm. These are assigned to the free and ligating phosphine respectively.

Single crystals of **3**, suitable for x-ray diffraction, could be grown by cooling a saturated hexane solution to -40° C (figure 5). The titanium adopts an approximately octahedral geometry, as demonstrated by the P(1)-Ti(1)-P(3) and Cl(1)-Ti(1)-Cl(2) angles (178.4(2)° and 95.3(2)° respectively). The deviation from ideal octahedral geometry arises due to the constraint of the P and O being 1,2-substituted on the arene ring, thus pulling the oxygen away (P(1)-Ti(1)-O(1) 71.3(4)°). This is also presumably the cause for the slight lengthening of the Ti-P bonds as compared with **2**.



Figure 5: ORTEP plot of **3**. Thermal ellipsoids at 50% probability, hydrogens omitted for clarity. Colour key: sky blue (titanium), black (carbon); purple (phosphorus), red (oxygen), green (chlorine). Selected bond lengths (Å) and bond angles (°): Ti(1)-P(1) 2.746(5), Ti(1)-P(3) 2.754(5), Ti(1)-Cl(1) 2.306(6), Ti(1)-Cl(2) 2.315(6), Ti(1)-O(1) 1.822(14), Ti(1)-O(3) 1.831(13), P(1)-Ti(1)-P(3) 178.4(2), P(1)-Ti(1)-O(1) 71.3(4), Cl(1)-Ti(1)-Cl(2) 95.3(2), O(1)-Ti(1)-O(3) 89.5(6).

Only a single stereoisomer of this product is observed, with the two phosphine groups trans to each other and the chloride and oxo groups in cis geometries. This is demonstrated by only one ligating ³¹P resonance observed in the ³¹P{¹H} NMR spectrum and no P-P coupling as the P centres are equivalent. The isomer shown in figure 5 has been determined to be the lowest energy isomer by DFT, with all possible isomers and their relative energies shown in figure 6.



Figure 6: Isomers of **3** and their relative energies.

To explore the influence of sterics within the ligand, and prove the broader applicability of this route to tuneable ligands, the iso-propyl derivative was also targeted. It was found ^tBuLi was needed to affect the lithium-halogen exchange - [^{iPr}POCOP]Li is an off-white oil, and could not be isolated. However it could be made *in-situ* and used directly onwards in reaction with TiCl₄ in pentane. This yielded dimeric {(^{iPr}POCOP)TiCl₂(μ -Cl)}₂ (**4**, scheme 5).

Scheme 5: Synthesis of 4.



Single crystals of **4** suitable for x-ray diffraction can be grown from a saturated hexane solution cooled to -40° C (figure 7). The geometry around the titanium is a near-perfect pentagonal bipyramid (Σ equatorial angles 360.89(5)°). The structural parameters are in line with similar motifs,^[83] for example the Ti-Cl distance for the terminal Cl is nearly identical to that found in **2**.



Figure 7: ORTEP plot of **4**. Thermal ellipsoids at 50% probability, hydrogens omitted for clarity. Colour key: sky blue (titanium), black (carbon); purple (phosphorus), red (oxygen), green (chlorine). Selected bond lengths (Å) and bond angles (°): Ti-Cl(1) 2.293(1), Ti(1)-Cl(2) 2.336(1), Ti(1)-Cl(3) 2.587(1), Ti(1)-P(1) 2.578(1), Ti(1)-P(2) 2.587(1), Ti(1)-C(1) 2.252(4), Ti(1)-Ti(1') 4.116(1), Σ equatorial angles 360.89(5), Cl(1)-Ti(1)-Cl(2) 174.05(5).

The origin of the structural difference between **2** and **4** arises due to the reduction of steric encumbrance due to the ligands. The dimeric structure is 15 kcal mol⁻¹ more favoured than the monomeric structure for **4**. However making the substituents 'Bu rather than 'Pr reverses this, making the monomer form 1 kcal mol⁻¹ more stable than the dimer. There is still a small steric clash in the iso-propyl derivative when compared to a simple methylated model (see supplementary information)

Derivatisations of TiCl₂(^{tBu}POCOP)

With a high-yielding synthesis of **1** devised alkylation and arylation experiments were undertaken. Attempts at alkylating **2** with Grignard and alkyl lithium reagents resulted in reduction.

Methyl

1 can be reacted with two equivalents of MeMgCl resulting in an immediate colour change from blue to teal, forming TiMe₂(^{tBu}POCOP) (**5**, Scheme 6). Teal crystals suitable for x-ray diffraction studies can be grown from concentrated pentane solution at –40 °C (Figure 8). The geometry around the titanium centre remained unchanged from the starting material as square based pyramid, with a τ_5 parameter of 0.017 and C(1) determined to be the axial ligand.^[84]

Scheme 6: Synthesis of 5.



Figure 8: ORTEP plot of **5**. Thermal ellipsoids at 50% probability, hydrogens omitted for clarity. Colour key: sky blue (titanium), black (carbon); purple (phosphorus), red (oxygen). Selected bond lengths (Å) and bond angles (°): Ti(1)-P(1) 2.6243(9), Ti(1)-P(2) 2.6180(9), Ti(1)-C(1) 2.138(4), Ti(1)-C(2) 2.143(4), Ti(1)-C(3) 2.241(3), P(1)-Ti(1)-P(2) 141.44(3), C(2)-Ti(1)-C(3) 140.53(14).

The Ti-P bond lengths are slightly elongated in **5** when compared to **1**. The Ti-Me distances are comparable to other Ti pincer dimethyl complexes.^[65,85] **5** is paramagnetic with a $\mu_{eff} = 2.03 \ \mu_{B}$ (Evan's method). Figure 9 shows the CW EPR of **5** measured at 298 K.



Figure 9: X Band CW EPR spectra of **5** at room temperature. Black shows experimental data and red shows simulated data ($g_{iso} = 1.970$, $a_0 = 2.251$ mT, 0.642 mT).

The experimental spectrum in Figure 9 can be simulated as a triplet of septets (g = 1.970; $a_0 = 2.251 \text{ mT}$, 0.642 mT). This arises due to coupling of the electron to the two ³¹P nuclei and slightly weaker coupling to the six ¹H attached to the methyl groups. This implies that the SOMO is primarily positioned on the titanium centre (implied by the g value) but has significant character on both the phosphorus and methyl ligands.

Phenyl

When **1** was reacted with PhMgCl, only the monosubstituted product was isolated, TiClPh(^{tBu}POCOP) (**6**), even if excess PhMgCl is used or the reaction is heated overnight (Scheme 7). Use of PhMgBr on one occasion resulted in halogen exchange resulting in TiBrPh(^{tBu}POCOP) (see supporting information). Single crystals of **6** suitable for x-ray diffraction studies could be grown from cooling a concentrated solution of pentane to -40 °C (Figure 10).



Scheme 7: Synthetic route of TiCIPh(^{tBu}POCOP)

Figure 10: ORTEP plot of **6**. Thermal ellipsoids at 50% probability, hydrogens omitted for clarity. Colour key: sky blue (titanium), black (carbon); purple (phosphorus), red (oxygen), green (chlorine). Selected bond lengths (Å) and bond angles (°): Ti(1)-P(1) 2.6146(7), Ti(1)-P(2) 2.6110(7), Ti(1)-C(1) 2.213(2), Ti(1)-C(23) 2.100(2), Ti(1)-Cl(1) 2.3160(7), P(1)-Ti(1)-P(2) 143.73(2), C(1)-Ti(1)-Cl(1) 144.37(6).

The geometry around the titanium centre remained unchanged from the starting material as square based pyramid, with a τ_5 parameter of 0.0108 and the phenyl ring in the axial position. The plane of the phenyl ring is perpendicular to the POCOP aryl ring. Interestingly this is only the second example of a crystallographically characterised 'TiPhCl' fragment with an unsubstituted phenyl ring.^[85]

The room temperature CW EPR spectrum (see supporting information, figure S3) consistently had signals, a major species (60%, $g_{iso} = 1.9665$, $a_0 = 2.26$ mT) and one minor (40%, $g_{iso} = 1.9720$, $a_0 = 2.24$ mT). These two species occur even if excess PhMgCl is used in the synthesis. The magnetic moment was measured by Evan's method ($\mu_{eff} = 2.08 \mu_B$). These data imply there

is a single unpaired electron that is almost entirely located on the titanium centre with some coupling to the phosphorus atoms.

Neopentyl

1 can also be derivatised using organolithiums, and the addition of 1 equivalence of neopentyl lithium yields ($^{HBu}POCOP$)TiClNp (**7**) as dark green crystals in 61% yield (Scheme 8). Similarly to **6**, substitution of two chloride ligands for neopentyl fragments does not occur, even when using excess neopentyl lithium and forcing conditions. Single crystals suitable for x-ray crystallography can be grown from a saturated pentane solution cooled to -40°C (figure 11).

Scheme 8: Synthesis of 7.



Figure 11: Two ORTEP plots of **7**. Thermal ellipsoids at 50% probability, hydrogens omitted for clarity. The phosphine tert-butyl groups are omitted from the side-on view. Colour key: sky blue (titanium), black (carbon); purple (phosphorus), red (oxygen), green (chlorine). Selected bond lengths (Å) and bond angles (°): Ti(1)-P(1) 2.6223 (17), Ti(1)-P(2) 2.6232(17), Ti(1)-C(1) 2.033(6), Ti(1)-C(6) 2.222(5), Ti(1)-Cl(1) 2.3799(14), P(1)-Ti(1)-P(2) 139.03(6), C(6)-Ti(1)-Cl(1) 140.40(15), Ti(1)-C(1)-C(2) 156.3(5).

The geometry around the titanium centre is still a square based pyramid, however significantly more distorted than **1** (τ_5 = 0.265 for **7**). The neopentyl fragment is remarkably distorted towards linerarity around C1 (Ti(1)-C(1)-C(2) = 156.3(5)°), such a distortion could arise from

some form of agostic interactions with the C-H bonds around C(1). This interaction must be somewhat fluxional however since no coupling to these protons is observed in the roomtemperature solution EPR (see supplementary information, figure S4). The single crystal x-ray data was of insufficient quality to refine the H-atom positions. The optimised geometry of 7 employing the BP86-D3 functional allows for a more detailed analysis of the interaction between the neopentyl fragment and titanium. The bond metrics associated with the crystallographic structure are reproduced very well. The computed Ti-+H(1) distance of 2.04 Å is significantly shorter than Ti...H(2) with 2.44 Å. Additionally, both C(1)-H bonds are somewhat elongated with respect to the remaining C-H bonds (1.11 Å), although distances of 1.14 Å and 1.12 Å for C(1)–H(1) and C(1)–H(2), respectively, imply that this effect is more pronounced for the former (Fig. S38). The weakening of these bonds is also reflected in their stretching frequencies which are red-shifted to $v_{C(1)H(1)} = 2689 \text{ cm}^{-1}$ and $v_{C(1)H(2)} = 2888 \text{ cm}^{-1}$, while the other C-H bonds show symmetric and antisymmetric modes at around 3087 cm⁻¹ and 2959 cm⁻¹, respectively. These data are diagnostic of α -agostic interactions between Ti and the C(1)H₂ group, where exchange of the symmetry-equivalent hydrogen atoms would imply a degree of fluxionality. This is further validated by NBO and QTAIM analyses of the computed electron density (see figures S40 and S41). For the former, several contributions to $\sigma_{CH} \rightarrow d_{Ti}$ donor/acceptor interactions can be identified, with the leading interactions stabilising the structure by ~7–13 kcal mol⁻¹, considering both α -and β -spin manifolds). The topology analysis reveals reduced QTAIM parameters associated with the bond critical points (BCPs) of C(1)–H(1) (ρ (**r**) = 0.245 au; $\nabla^2 \rho$ (**r**) = -0.734 au) and C(1)–H(2) (ρ (**r**) = 0.257 au; $\nabla^2 \rho$ (**r**) = -0.835 au), diagnostic of weakened bonds due to their interaction with the Ti centre. No BCP for the Ti...H interaction has been located, however, the complete absence of BCPs and associated bond paths in these types of systems is not uncommon and is not considered a requirement for agostic interactions.[86,87]

Similarly to **1** and **6**, **7** only displays a triplet in the EPR, indicating the unpaired electron is centred on the metal centre (major component g = 1.9665) but couples to the two ³¹P nuclei ($a_0 = 2.20 \text{ mT}$). The effective magnetic moment ($\mu_{eff} = 1.75 \mu B$) was measured using Evan's method and corresponds to a single unpaired electron.

Hydrogen Activation Studies

Having demonstrated the ability of the '(^{tBu}POCOP)Ti' platform to allow for derivatisation the possibility that these complexes could be used to activate small molecules was explored. For the 'Ti(^RPOCOP)' to be useful in reactivity it is imperative that the pincer-metal fragment

remains intact in reactive conditions. One of the most fundamental reactions is the activation of hydrogen. When a pentane solution of **7** was charged with 1 bar of dihydrogen the solution quickly changed from green to royal purple. Single crystals x-ray diffraction studies showed this product to be $[(^{tBu}POCOP)TiCl(\mu-H)]_2$ (**8**, scheme 9). The reaction can also proceed in the solid state, using crystalline **7** and charged with 1 bar of H₂ at room temperature. The green solid changes from green to purple over 10 minutes, with a loss of crystallinity.

Scheme 9: Hydrogen activation by 7 to form 8.



This is a rare example of a titanium hydride chloride, with only two others being isolated and structurally characterised (excluding those that are due to another element-hydride binding to the metal centre e.g. BH_4^{-}).^[86,89] Titanium hydride chlorides are invoked as intermediates in a range of catalytic processes but are extremely challenging to observe.^[90,91] The mechanism of the above reaction was probed by DFT calculations (see Figure S43). It traverses a σ -bond metathesis pathway that involves a typical four-membered kite-shaped transition state with an overall Free Energy activation barrier of 22.5 kcal mol⁻¹. Formation of monomeric (^{1Bu}POCOP)TiCl(H) after release of neopentane is exergonic (–9.9 kcal mol⁻¹). Subsequent dimerization of two units (^{1Bu}POCOP)TiCl(H) then forms **8** with an overall exergonicity of 20 kcal mol⁻¹.

Single crystals suitable for x-ray diffraction could be grown from a saturated SiMe₄ solution cooled to -40° C. The resultant structure is shown in figure 12. The bridging hydrides could be located on the electron density map but the data was not of sufficient quality to be able to refine their positions reliably. Interestingly these crystals were grown in a N₂ atmosphere, showing **8** to be stable in the presence of N₂. This is in contrast to previous titanium pincer hydrides.^[92]



Figure 12: ORTEP plot of **8**. Thermal ellipsoids at 50% probability, hydrogens (except for H(1) and H(2)) and *tert*-butyl methyl groups omitted for clarity. Colour key: sky blue (titanium), black (carbon); purple (phosphorus), red (oxygen), green (chlorine), white sphere (hydrogen). Selected bond lengths (Å) and bond angles (°): Ti(1)-Ti(2) 3.1708(12), Ti(1)-P(1) 2.6858(13), Ti(1)-P(2) 2.6898(13), Ti(1)-C(1) 2.212(4), Ti(2)-P(3) 2.6906(13), Ti(2)-P(4) 2.6799(13), Ti(2)-C(23) 2.221(4), Ti(1)-Cl(1) 2.3157(14), Ti(2)-Cl(2) 2.3113(14), P(1)-Ti(1)-P(2) 138.03(5), C(1)-Ti(1)-Cl(1) 129.99(14), P(3)-Ti(2)-P(4) 137.77(5), C(23)-Ti(1)-Cl(2) 129.79(13). Angle between Cl(1)-Ti(1)-Ti(2) plane and Cl(2)-Ti(2)-Ti(1): 72.25°.

The geometry of **8** is quite distorted away from the optimal octahedron. The Ti(1)-Ti(2) distance is in the region where there could be a Ti-Ti bond,^[93] however the retention of the unpaired electrons (as evidenced by the EPR spectrum, see supplementary information figure S5), implies there is no bond present. Looking down the Ti-Ti axis the bonding around the metal centres are eclipsed, however with the POCOP ligands at approximately 90° to one another, presumably this results in minimising the steric clash between the tert-butyl groups. The DFToptimised geometry of **8** is in good agreement with its experimental counterpart, although the BP86 functional somewhat underestimates the Ti-Ti separation. A survey of different functionals reveals that this trend is general for meta-GGA and GGA functionals, whilst hybrid functionals tend to give Ti-Ti distances closer to the experimental value. Nonetheless, the calculations support the assignment of two bridging hydrides in the structure of **8**, with other isomers being energetically disfavoured (see figures S44 and S45). In the computed triplet electronic ground state of **8**, stabilised relative to the antiferromagnetically coupled singlet diradical by \sim 1 kcal mol⁻¹, one unpaired electron is centred on each Ti ion.

NMR studies of the reaction mixture at 5°C showed formation of neopentane and a broad resonance at a chemical shift at -0.52 ppm from the Ti-(μ -H)-Ti environment. **8**, like **1**, **6** and **7**, gives a triplet in its CW EPR spectrum at room temperature (see supplementary information, figure S5). The principle resonance comes at a coincident g_{iso} value as the other examples measured, with coupling to two phosphorus resonances. This implies the electron is localised onto the titanium centre and there is no bonding interaction between the metal centres. The effective magnetic moment of (measured by Evan's method) is 3.37 μ_B corresponding to two unpaired electrons, as would be expected for the dimer.

Conclusion

The ^RPOCOP ligand framework has been successfully deployed onto titanium. Both (^RPOCOP)Ti(III) and (^RPOCOP)Ti(IV) complexes can be made, and different substituents on the POCOP ligand can be used. For Ti(IV), using the bulky ^{tBu}POCOP ligand results in monomeric species **2** to be formed whereas changing the ligand for the slightly smaller ^{iPr}POCOP allows for dimerization (**4**). Interestingly in the presence of THF, Ti(IV) and [^{tBu}POCOP]Li results in an unprecedented rearrangement of the POCOP ligand. Such a rearrangement does not occur when Ti(III) is used. (^{tBu}POCOP)TiCl₂, **1**, can be made on the gram-scale and can be easily derivatised with alkylating and arylating reagents. All of these species have been well-characterised including using x-ray crystallography and EPR.

The neopentyl compound (^{tBu}POCOP)TiNpCl, **7**, was reacted with H₂, demonstrating the ability of the POCOP ligand to stay attached even in reactive condition. This resulted in the formation of a rare titanium hydride chloride complex, which is remarkably stable under an inert atmosphere. Overall this opens the door to using this valuable and easily customisable ligand platform, the fundamental pincer ligand, with early transition metals.

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