Synthesis and characterization of permethylpentalene titanium aryloxide and alkoxide complexes

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ABSTRACT

A series of titanium complexes containing the permethylpentalene ligand ($C_8Me_6^{2-}$; Pn*) - Pn*Ti(O-2,6-Me-C_6H_3)Cl (**1**), Pn*Ti(O-2,4-^{t}Bu-C_6H_3)Cl (**2**), Pn*Ti(O^{t}Bu)Cl (**3**), Pn*Ti(O-2,6-Me-C_6H_3)$_2$ (**4**), Pn*Ti(O^{t}Bu)$_2$ (**5**) – or the (hydro)permethylpentalene ligand ($C_8Me_6H^-$; Pn*(H)) - Pn*(H)Ti(O-2,6-Me-C_6H_3)Cl_2 (**6**) and Pn*(H)Ti(O-2,6-Me_2-C_6H_3)$_3$ (**7**) - were prepared by the reaction of [Pn*TiCl(μ-Cl)]$_2$ with the corresponding potassium salt or alcohol. All complexes have been characterized by single crystal X-ray diffraction studies and NMR spectroscopy. The (hydro)permethylpentalene complexes contain a stereocenter and planar chirality which can be described as R,R_P or S,S_P configurations.

Keywords: permethylpentalene, bonding modes, zirconium, alkoxide, aryloxide.

1. Introduction

The pentalene ligand ($C_8H_6^{2-}$; Pn) has demonstrated versatility as a supporting ligand in organometallic chemistry[1], recently highlighted by Cloke, O'Hare and co-workers[1a-1b]. Preparation of substituted pentalene derivatives has proved difficult[2a]; however, the synthesis of a permethylated organic precursor and its conversion into the a dilithium salt ($C_8Me_6^{2-}$; Pn*) has been reported by O'Hare and coworkers[2b-2c]. This has facilitated the exploration of organometallic chemistry with the class of ligand; for example, the synthesis of homoleptic permethylpentalene complexes of first row transition metals, $M_2Pn^*_2$ (M = V, Cr, Mn, Co)[2d], and f-block *bis* ligand complexes, M(Pn*)$_2$ (M = Ce or U)[2e-2f] have been reported. Recently, we have shown the synthesis of new group 4 chloride complexes[3a-3b] for solution and slurry phase ethylene polymerization[3c-3d], and (hydro)permethylpentalene complexes for lactide[4a] and slurry phase ethylene polymerization[4b].

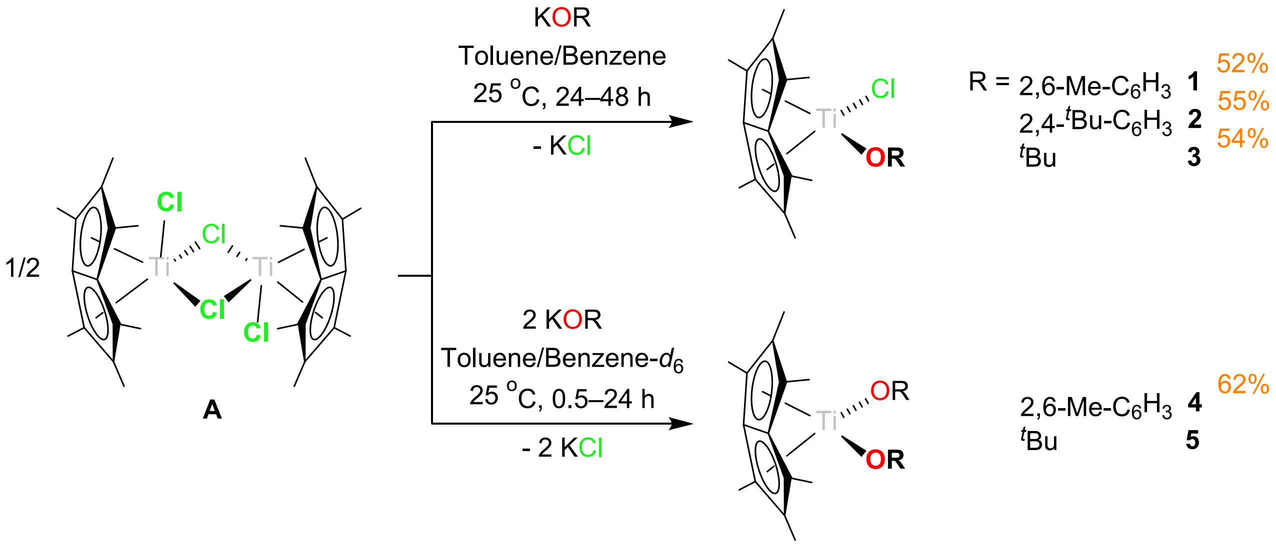
The favored binding modes of pentalene to the early and late transition metals are in stark contrast to one another. Whereas η^5- is the most common binding mode for later transition metals such as iron and cobalt[1h], it is virtually unknown in group 4 pentalene chemistry; η^5,η^5-pentalene titanium sandwich-complexes, reported by Cloke and co-workers are the only structurally characterised examples[5], whilst the 'ate' complex $Li_2[(\eta^5\text{-Pn})_2ZrMe_2]$ and $Cp(CH_3)Zr(\mu\text{-}\eta^5,\eta^5\text{-Pn})FeCp^*$ have been disclosed by Jonas and co-workers in the patent literature[6].

Here, we report the synthesis and characterization of titanium aryloxide and alkoxide complexes based on the permethylpentalene and (hydro)permethylpentalene ligands by derivatization of $[Pn^*TiCl(\mu\text{-}Cl)]_2$.

2. Result and discussion

2.1 Synthesis and characterization of permethylpentalene complexes

0.5 equivalents of $[Pn^*TiCl(\mu\text{-}Cl)]_2$ (**A**) was reacted with one or two equivalents of KOR where (R = 2,6-Me-C_6H_3, 2,4-^{t}Bu-C_6H_3 or ^{t}Bu) at room temperature in toluene, benzene or benzene-d_6 for 0.5–48 h. Upon work-up, $Pn^*Ti(O\text{-}2,6\text{-}Me\text{-}C_6H_3)Cl$ (**1**), $Pn^*Ti(O\text{-}2,4\text{-}{}^tBu\text{-}C_6H_3)Cl$ (**2**), and $Pn^*Ti(O\text{-}2,6\text{-}Me\text{-}C_6H_3)_2$ (**4**) were afforded as maroon or purple solids in moderate yields (52–54%); $Pn^*Ti(O^tBu)Cl$ (**3**) and $Pn^*Ti(O^tBu)_2$ (**5**) were highly air-sensitive (Scheme 1).



Scheme 1. Synthesis of $Pn^*TiOR_xCl_{2-x}$ (R = 2,6-Me-C_6H_3, 2,4-^{t}Bu-C_6H_3, ^{t}Bu)

Single crystals suitable for X-ray diffraction studies of maroon **1** and purple **2** were grown from room temperature toluene and benzene solutions respectively. Crystals were obtained by slow cooling to −35 °C in hexane for **3** and in toluene for **4**, and on evaporation of a benzene-d_6 solution for **5**.

Their molecular structures are depicted in Figure 1. Selected average bond lengths and angles for the complexes are collated in Table S1–S3.

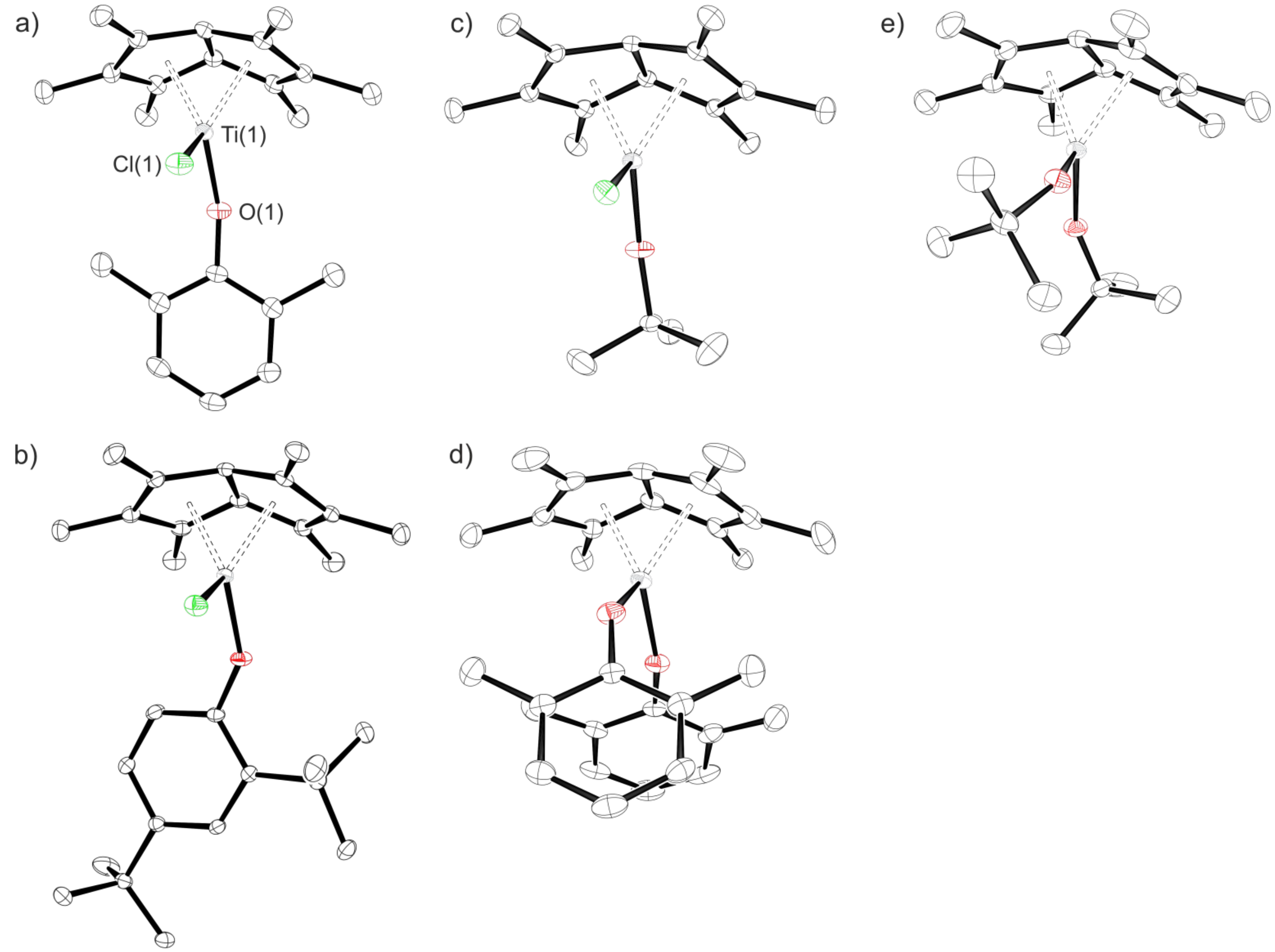


Figure 1. Molecular structures of a) Pn*Ti(O-2,6-Me-C_6H_3)Cl (**1**), b) Pn*Ti(O-2,4-^{t}Bu-C_6H_3)Cl (**2**), c) Pn*Ti(O^{t}Bu)Cl (**3**), d) Pn*Ti(O-2,6-Me-C_6H_3)$_2$ (**4**), and e) Pn*Ti(O^{t}Bu)$_2$ (**5**), with thermal ellipsoids at 50%. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°); for **1**: Ti1-O1 1.838(2), Ti1-Cl1 2.3236(9), Ti1-O1-C15 155.7(2) and O1-Ti1-Cl1 96.87(8); for **2**: Ti1-O1 1.8541(14), Ti1-Cl1 2.3377(7), Ti1-O1-C15 147.17(13) and O1-Ti1-Cl1 98.90(6); for **3**: Ti1-O1 1.7923(13), Ti1-Cl1 2.3452(5), O1-Ti1-Cl1 98.60(5); for **4**: Ti1-O1 1.8712(17), Ti1-O2 1.8890(16) and Ti1-O1-C15 159.15(16); and for **5**: Ti1-O1 1.863(3), Ti1-O2 1.843(3), and O1-Ti1-O2 104.51(8).

Solid state structural analysis shows that Pn*Ti(O-2,6-Me-C_6H_3)Cl (**1**) and Pn*Ti(O-2,4-^{t}Bu-C_6H_3)Cl (**2**) adopt a distorted tetrahedral arrangement around the titanium center, exemplified by Cl1–Ti1–O1 angles of 96.89(8)° and 98.90(6)° in **1** and **2** respectively. The angles and distances found in both molecules are similar to (η^5-Cp)(η^5-Cp^R)Ti(O-2,6-Me-C_6H_3)Cl (R=1-Me, 3-^{i}Pr) and other titanocene analogues[7,8]. The fold angles (where fold angle is defined as the angle by which the ligand is found to deviate from planarity)[1b] in both structures, 36.2(2)° in complex **1** and 35.01(12)° in complex **2** are comparable with other η^8-pentalene titanium complexes such as PnTiCp(Cl) and PnTiCp (33 and 37° respectively) synthesized by Jonas and coworkers[9].

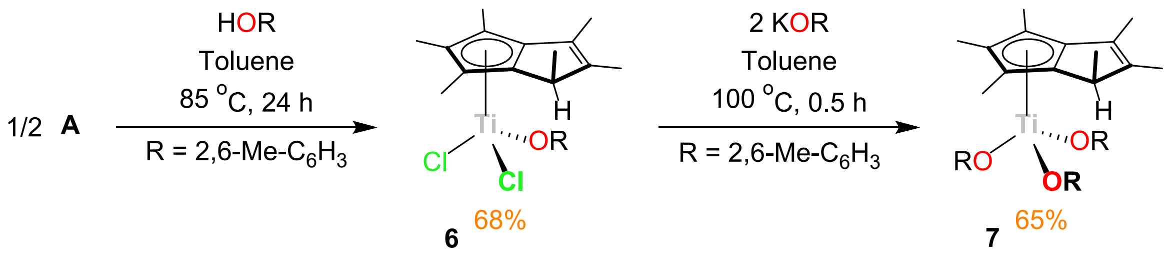
In contrast to both Pn*Ti(O-2,6-Me-C_6H_3)Cl (**1**) and Pn*Ti(O-2,4-^{t}Bu-C_6H_3)Cl (**2**), the Ti–O distance in Pn*Ti(O^{t}Bu)Cl (**3**) (1.7923(13) Å) is relatively short and, combined with the comparatively large Ti–O–C angle of 162.12(13)°, is indicative of significant Ti-O π overlap[10-12]. This phenomenon is also encountered in the metallocene analogues of Pn*Ti(O^{t}Bu)Cl[13-14]. However, it is not observed in Pn*Ti(O^{t}Bu)$_2$ (**5**).

The ^{1}H NMR spectra of complexes **1** and **2** display a 6:6:6 splitting pattern for the pentalene methyl protons, consistent with molecular C_s symmetry (Fig. S1 and S3). Upon heating a toluene-d_8 solution of complex **1**, two of the pentalene methyl resonances broaden and eventually coalesce at 115 °C. The observed fluxionality is likely a result of rotation of the permethylpentalene fragment around the titanium center ($\Delta G^\ddagger \approx$ 78.06 kJ mol^{-1}). The room temperature ^{1}H NMR spectrum of Pn*Ti(O-2,6-Me-C_6H_3)$_2$ (**4**) reveals three sharp singlets in a 12:12:6 intensity ratio between 2.13 and 1.77 ppm, suggesting that the C_{2v} symmetry in the solid state is retained in solution (Fig. S5). The singlet at 1.81 ppm corresponds to the methyl protons on the aryloxide ligand, agreeing well with titanocene derived analogues[15-16]. The ^{1}H NMR spectrum of Pn*Ti(O^{t}Bu)$_2$ (**5**) displays three singlets in the expected intensity ratio of 12:6:18 corresponding to the permethylpentalene and *tert*-butyl protons respectively (Fig. S7).

2.2 Synthesis and characterization of (hydro)permethylpentalene complexes

Two equivalents of 2,6-Me-C_6H_3OH and one equivalent of [Pn*TiCl(μ-Cl)]$_2$ (**A**) were combined in toluene and stirred at 80 °C for 2 h to afford Pn*(H)Ti(O-2,6-Me-C_6H_3)Cl_2 (**6**), isolated as a red solid in 68% yield (Scheme 2). This unusual reaction results in monoprotonation of the permethylpentadienyl anion to yield the (hydro)permethylpentalene ligand with concomitant ligand exchange of chloride for aryloxide.

Complex **6** was subsequently reacted with two equivalents of KO-2,6-Me-C_6H_3 in toluene leading to the formation of Pn*(H)Ti(O-2,6-Me$_2$-C_6H_3)$_3$ (**7**), which was isolated as an orange solid in 65% yield (Scheme 2). Complex **7** has been previously prepared by reaction of Pn*(H)TiCl_3 with three equivalents of KO-2,6-Me-C_6H_3 but was not crystallographically characterised[4a].



Scheme 2. Synthesis of Pn*(H)Ti(O-2,6-Me-C_6H_3)$_x$Cl$_{3-x}$

Slow cooling of saturated hexane solutions at −35 °C afforded red and orange crystals of Pn*(H)Ti(O-2,6-Me-C_6H_3)Cl_2 (**6**) and Pn*(H)Ti(O-2,6-Me-C_6H_3)$_3$ (**7**) respectively (Figure 2).

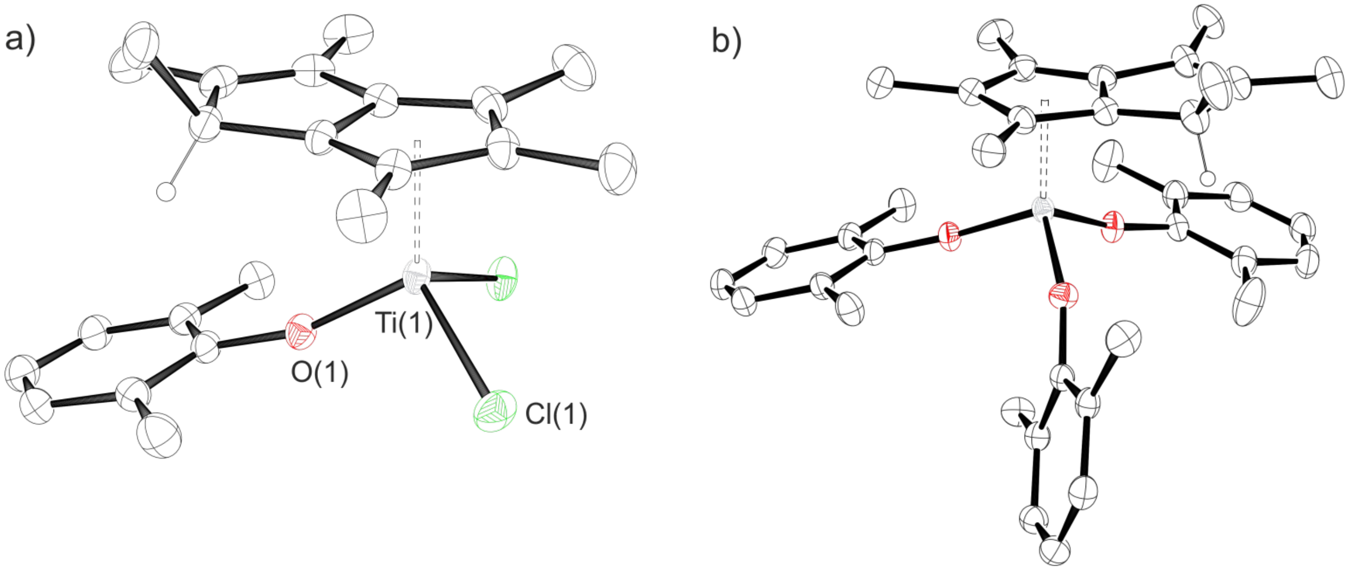


Figure 2. Molecular structures of a) Pn*(H)Ti(O-2,6-Me-C_6H_3)Cl_2 (**6**) and b) Pn*(H)Ti(O-2,6-Me-C_6H_3)$_3$ (**7**) with ellipsoids at 50% probability. Hydrogen atoms (except Pn*(H)) have been omitted for clarity. Selected bond lengths (Å) and angles (°) for **6**: Ti1-O1 1.7925(17), Ti1-Cl1 2.2761(8), Ti1-Cl2 2.2746(7), Ti1-Ct 2.0300(1); Ti1-O1-C15 163.94(16), Cl1-Ti1-O1 102.95(6); and for **7**: Ti1-O1 1.8395(18), Ti1-O2 1.8280(18), Ti1-O3 1.8538(18), Ti1-Ct 2.0647(1); Ti1-O1-C15 160.45(17), Ti1-O2-C23 164.16(18), Ti1-O3-C31 155.38(16), (Ct = ring centroid).

The complexes are monomeric with a four coordinate *pseudo*-tetrahedral titanium metal center and adopt a structure similar to that of the classic piano stool arrangement displayed by many monocyclopentadienyl complexes[17–19]. It is evident that the (hydro)permethylpentalene ligand is bound in an η^5-fashion and, with reference to our previously synthesized (hydro)permethylpentalene complexes, the methyl group attached to C1 is always oriented *anti* to the metal center which minimizes steric hindrance; this stereochemistry could be achieved by coordination of the alcohol to the titanium center followed by intramolecular protonation of the permethylpentalene ligand. These complexes contain a stereocenter at C1, which can be described using *R* and *S* descriptors in accordance with the Cahn-Ingold-Prelog rules[20], as well as planar chirality, which can be described with R_P and S_P. Both complexes crystallize in centrosymmetric space groups (**6**: $P2_1/c$; **7**: $P2_1/n$) and so the stereochemistry of the complexes can be described as R,R_P or S,S_P.

The Ti–O distances in complex **7** (1.8395(18), 1.8280(18) and 1.8538(18) Å) are longer than the distance observed in complex **6**, 1.7925(17) Å. The Ti–O distances in complex **7** are found to be similar to those of the cyclopentadienyl complex, $CpTi(O\text{-}2,6\text{-}^iPr\text{-}C_6H_3)_3$ (1.80(2), 1.79(2) and 1.80(2) Å)[21].

The ^1H NMR spectra of **6** and **7** display a diagnostic doublet and a quartet corresponding to the methyl group and proton attached to the sp^3-hybridised carbon (Fig. S9 and S11). In addition, due to the reduction in symmetry (C_s or C_{2v} to C_1), each pentalene methyl group is in a unique environment, which results in five new and distinct singlets each with a relative integral of three.

3. Material and methods

3.1 General procedure

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of dinitrogen. Where necessary, solvents were dried using an SPS drying system (hexane, pentane, toluene). Deuterated NMR solvents were dried over NaK (benzene-d_6, toluene-d_8), vacuum transferred and freeze-pump-thaw-degassed three times prior to use. Elemental analyses were conducted by Mr Stephen Boyer at the elemental analysis service at London Metropolitan University. ^1H NMR spectra were recorded at 298 K, unless otherwise stated, on Varian Mercury VX Works 300 MHz spectrometer. Two dimensional ^1H-^1H and ^{13}C-^1H correlation experiments were used, when necessary, to confirm ^1H and ^{13}C assignments. All NMR spectra were referenced internally to residual protio solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz. $KO\text{-}2,6\text{-}Me\text{-}C_6H_3$ and $KO\text{-}2,4\text{-}^tBu\text{-}C_6H_3$ were prepared with reference to published methods[22].

3.2 Complex synthesis and characterization

Synthesis of Pn*Ti(O-2,6-Me-C_6H_3)Cl (1): $[Pn^*TiCl(\mu\text{-}Cl)]_2$ (150 mg, 0.25 mmol) and $KO\text{-}2,6\text{-}Me\text{-}C_6H_3$ (78 mg, 0.50 mmol) were combined in toluene (30 mL) and left to stir for 24 h at room temperature. The resultant solution was filtered before being concentrated *in vacuo*. X-ray quality single crystals were obtained on storing the toluene concentrated solution at −35 °C for 24 h. Yield = 52%. ^1H NMR

(C_6D_6, 298 K, 300 MHz): δ 7.04 (d, 2H, $^3J_{HH}$ = 7.3 Hz, 3,5-C_6H_3), 6.82 (t, 1H, $^3J_{HH}$ = 7.4 Hz, 4-C_6H_3), 2.11, 2.06, 1.68 (s, 6H each, CH_3-Pn*), 1.61 (s, 6H, 2,6-*Me*-C_6H_3). $^{13}C\{^1H\}$ NMR (C_7D_8, 298 K, 75.1 MHz): δ 130.7, 126.2, 124.4, 123.4, 120.4 (quaternary carbons), 18.1 (2,6-*Me*-C_6H_3), 13.2 12.5 11.1 (CH_3-Pn*). The quaternary bridgehead carbon atoms were not observable and certain quaternary carbon signals were obscured by solvent resonances. Analysis calculated for $C_{22}H_{27}ClTiO$ (%): C, 67.62; H, 6.98; found: C, 67.70; H, 7.03.

Synthesis of Pn*Ti(O-2,4-^{t}Bu-C_6H_3)Cl (2): [Pn*TiCl(μ-Cl)]$_2$ (150 mg, 0.25 mmol) and KO-2,4-^{t}Bu-C_6H_3 (120 mg, 0.50 mmol) were stirred in toluene (30 mL) at room temperature for 48 h. The resultant solution was filtered and the solvent removed *in vacuo*. Subsequent dissolution in minimal hot benzene and storage at room temperature for 24 h led to the formation of single crystals suitable for an X-ray diffraction study. Yield = 55%. ^1H NMR (C_6D_6, 298 K, 300 MHz): δ 7.54 (d, 1H, $^4J_{HH}$ = 2.4 Hz, 3,5-C_6H_3), 7.18 (dd, 1H, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.4 Hz, 3,5-C_6H_3), 6.41 (d, 1H, $^3J_{HH}$ = 8.3 Hz, 2-C_6H_3), 2.07, 1.80, 1.64 (s, 6H each, CH_3-Pn*), 1.59, 1.35 (s, 9H, 2,4-C(CH_3)-C_6H_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 75.1 MHz): δ 161.2 (1-C_6H_3), 142.7, 140.8, 139.1, 136.5, 130.3, 124.6 (quaternary carbons), 123.8, 123.8 (3,5-C_6H_3) 122.8 (quaternary carbon) 121.2 (2,5-C_6H_3), 35.6, 34.6 (2,4-C(CH_3)-C_6H_3), 32.0, 30.9 (2,4-C(CH_3)-C_6H_3), 13.0, 12.5, 10.8 (CH_3-Pn*). Analysis calculated for $C_{28}H_{39}TiClO$ (%): C, 70.80; H 8.29; found: C, 70.65; H, 8.23.

Synthesis of Pn*Ti(O^{t}Bu)Cl (3): [Pn*TiCl(μ-Cl)]$_2$ (150 mg, 0.25 mmol) and K(O^{t}Bu) (53 mg, 0.50 mmol) were combined in toluene (30 mL) and left to stir for 2 h at room temperature. The resultant solution was filtered and the solvent was removed under reduced pressure. Minimal hot hexane was added and X-ray quality single crystals were obtained on cooling to room temperature and storing at −35 °C for 24 h. Yield = 54%. ^1H NMR (C_6D_6, 298 K, 300 MHz): δ 2.09, 1.90, 1.62 (s, 6H each, CH_3-Pn*), 1.31 (s, 9H, OC(CH_3)). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 75.1 MHz): δ 138.4, 136.4 (Pn*-*bridgehead*), 128.9, 122.2, 121.9 (*Pn**), 81.2 (C(CH_3)), 32.5 (C(CH_3)), 13.1, 12.9, 10.9 (CH_3-Pn*).

Synthesis of Pn*Ti(O-2,6-Me-C_6H_3)$_2$ (4): [Pn*TiCl(μ-Cl)]$_2$ (150 mg, 0.25 mmol) and KO-2,6-Me-C_6H_3 (158 mg, 1.00 mmol) were stirred in toluene (30 mL) for 24 h at 25 °C. The resultant solution was filtered and subsequently concentrated *in vacuo*. Crystals suitable for an X-ray ray diffraction study were obtained on storing a concentrated toluene solution at −35 °C for 24 h. Yield = 62%. ^1H NMR (C_6D_6, 298 K, 300 MHz): δ 6.96 (d, 4H, $^3J_{HH}$ = 7.5 Hz, 3,5-C_6H_3), 6.69 (t, 2H, $^3J_{HH}$ = 7.3 Hz, 4-C_6H_3), 2.13 (s, 12H, CH_3-Pn*), 1.81 (s, 12H, 2,6-*Me*-C_6H_3), 1.77 (s, 6H, CH_3-Pn*). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 75.1 MHz): δ 162.5 (1-C_6H_3), 139.7, 131.0, 125.2, 120.5, 118.9 (quaternary carbons), 17.7 (2,6-*Me*-C_6H_3), 11.9, 10.9 (CH_3-Pn*). The quaternary bridgehead carbon atoms were not observable. Analysis calculated for $C_{30}H_{36}TiO_2$ (%): C, 75.62; H, 7.63; Found: C, 75.48; H, 7.77.

Synthesis of Pn*Ti(O^{t}Bu)$_2$(5): [Pn*TiCl(μ-Cl)]$_2$ (20 mg, 0.035 mmol) and KO^{t}Bu (16 mg, 0.14 mmol) were combined in C_6D_6 (1 mL). The resulting dark red solution was filtered and slowly evaporated which led to the formation of crystals suitable for an X-ray diffraction study. ^{1}H NMR (C_6D_6, 298 K, 300 MHz): δ 2.08 (s, 12H, C*H*$_3$-Pn*), 1.76 (s, 6H, C*H*$_3$-Pn*), 1.31 (s, 18H, C(C*H*$_3$)). ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 75.1 MHz): 134.4, 128.7, 116.6 (*Pn**), 76.4 (*C*(CH$_3$)), 33.6 (C(C*H*$_3$)), 13.1, 10.8 (*C*H$_3$-Pn*). The quaternary bridgehead carbon atoms were not observable.

Synthesis of Pn*(H)Ti(O-2,6-Me-C$_6$H$_3$)Cl$_2$ (6): [Pn*TiCl(μ-Cl)]$_2$ (350 mg, 0.57 mmol) and H(O-2,6-Me-C_6H_3) (139 mg, 1.14 mmol) were stirred in toluene (50 mL) at 85 °C for 24 h, before being filtered and concentrated under vacuum. Single crystals suitable for an X-ray diffraction study were formed on storing the concentrated solution at −35 °C for 24 h. Yield = 68%. ^{1}H NMR (C_6D_6, 298 K, 300 MHz): δ 6.82–6.72 (overlapping m, 3H, 3,5-C$_6$*H*$_3$ and 4-C$_6$*H*$_3$), 3.19 (q, 1H, $^3J_{HH}$ = 7.3 Hz, Pn*(*H*)), 2.24 (s, 6H, 2,6-*Me*-C_6H_3), 2.23, 2.12, 2.08, 1.79, 1.44 (s, 3H each, C*H*$_3$-Pn*(H)), 0.84 (d, 3H, $^3J_{HH}$ = 7.5 Hz, 1-C*H*$_3$-Pn*(H)). ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 75.1 MHz): δ 162.7 (1-*C*$_6$H$_3$), 150.6, 147.8, 141.2, 136.9, 129.8, 129.1 (quaternary carbons), 128.1 (3,5-*C*$_6$H$_3$) 123.7 (quaternary carbons) 123.1 (4-*C*$_6$H$_3$), 44.2 (1-*Pn**(H)), 17.2 (2,6-*Me*-C_6H_3), 15.5, 14.1, 13.5, 13.2, 11.8, 11.6 (*C*H$_3$-Pn*). The quaternary bridgehead carbon atoms were not observable. Analysis calculated for $C_{22}H_{28}Cl_2TiO$ (%): C, 61.84; H, 6.62; Found: C, 61.71; H, 6.70

Synthesis of Pn*(H)Ti(O-2,6-Me-C$_6$H$_3$)$_3$ (7): A solution of Pn*(H)Ti(O-2,6-Me-C_6H_3)Cl$_2$ (50 mg, 0.12 mmol) and KO-2,6-Me-C_6H_3 (37.5 mg, 0.24 mmol) in toluene (10 mL) was stirred for 30 minutes at 100 °C. The resultant bright orange solution was filtered and the solvent removed under reduced pressure. Subsequent dissolution in minimal hot hexane followed by storage at −35 °C for 24 h led to the formation of single crystals suitable for an X-ray diffraction study. Yield = 65%. ^{1}H NMR (C_6D_6, 298 K, 300 MHz): δ 6.90 (d, 6H, $^3J_{HH}$ = 7.2 Hz, 3,5-C$_6$*H*$_3$), 6.73 (t, 3H, $^3J_{HH}$ = 7.3 Hz, 4-C$_6$*H*$_3$) 3.59 (q, 1H, $^3J_{HH}$ = 7.7 Hz, Pn*(*H*)), 2.28 (s, 18H, 2,6-*Me*-C_6H_3) 2.21, 2.14, 1.96, 1.58, 1.53 (s, 3H each, C*H*$_3$-Pn*(H)) 1.08 (d, 3H, $^3J_{HH}$ = 7.32 Hz, 1-C*H*$_3$-Pn*(H)). ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 75.1 MHz): δ 164.1 (1-*C*$_6$H$_3$), 147.3, 144.1, 138.9, 130.7 (*Pn**), 129.06 (2,3,4,5,6-*C*$_6$H$_3$), 128.93 (*Pn**), 127.41 (2,3,4,5,6-*C*$_6$H$_3$), 122.49 (*Pn**), 120.79 (2,3,4,5,6- *C*$_6$H$_3$), 116.96 (*Pn**), 44.46 (1-*Pn**(H)), 18.15 (1-*C*H$_3$-Pn*(H)), 15.3, 13.4, 12.5, 12.0, 11.8, 11.6 (*C*H$_3$-Pn*(H)).

3.3 X-ray crystallography

Crystals were mounted on glass fibers using perfluoropolyether oil, transferred to a goniometer head on the diffractometer and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems CRYOSTREAM unit[23]. Data collections were performed using an Enraf-Nonius FR590 KappaCCD diffractometer, utilizing graphite-monochromated Mo K_α X-ray radiation (λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package[24] and corrected for absorption using SORTAV[25]. Structures were solved using the direct-methods program SIR92[26] or a charge flipping algorithm (SUPERFLIP)[27], and refined using full-matrix least squares refinement on all F^2 data using the CRYSTALS[28-29] or Win-GX[30] program suite.

Pn*Ti(O-2,6-Me-C_6H_3)Cl (1): Single crystals were grown from a toluene solution at –35 °C, $C_{22}H_{27}ClOTi$, M_r = 390.81, triclinic, P–1, a = 11.2997(2) Å, b = 11.6154(2) Å, c= 15.7437(3) Å, α = 77.0104(7)°, β=89.3195(7)° γ = 85.2957(8)°, V = 2006.66(6) $Å^3$, Z = 4, T =150 K, prism, red brown, 9129 independent reflections, R(int) = 0.038, R_1 = 0.046 wR_2 = 0.133 [I >2σ(I)].

Pn*Ti(O-2,4-^{t}Bu-C_6H_3)Cl (2): Single crystals were grown from a benzene solution at -35 °C, $C_{28}H_{39}ClOTi$, M_r = 474.97, monoclinic, $P2_1/n$, a = 11.7910(1) Å, b = 9.5199(1) Å, c = 23.5743(3) Å, α = 102.4652(5)°, β=90° γ=90°, V = 2583.82(5) $Å^3$, Z = 4, T =150 K, block, purple, 5884 independent reflections, R(int) = 0.029, R_1 = 0.038 wR_2 = 0.091 [I >2σ(I)].

Pn*Ti(O^{t}Bu)Cl (3): Single crystals were grown from a hexane solution at –35 °C, $C_{18}H_{27}ClOTi$, M_r = 342.76, triclinic, P-1, a = 8.8527(1) Å, b = 10.1475(2) Å, c=10.7183(2) Å, α = 79.8812(7)°, β = 78.4070(7)° γ = 73.9368(7)°, V = 898.98(3) $Å^3$, Z = 2, T =150 K, block, dark red, 4073 independent reflections, R(int) = 0.016, R_1 = 0.0335 wR_2 = 0.0852 [I >2σ(I)].

(Pn*)Ti(O-2,6-Me-C_6H_3)$_2$ (4): Single crystals were grown from a toluene solution at –35 °C, $C_{30}H_{36}O_2Ti$, M_r = 476.51, Orthorhombic, $Pbca$, a = 9.2636(1) Å, b = 15.4563(1) Å, c = 35.7542(3) Å, V = 5119.32(8) $Å^3$, Z = 8, T =150 K, block, dark red, 5807 independent reflections, R(int) = 0.036, R_1 = 0.047 wR_2 = 0.092 [I >2σ(I)].

(Pn*)Ti(O^{t}Bu)$_2$ (5): Single crystals were grown from a benzene solution at –35 °C, $C_{22}H_{36}O_2Ti$, M_r = 380.43, monoclinic, $P2_1/n$, a = 12.7185(2) Å, b = 10.9762(1) Å, c = 15.9690(2) Å, β = 93.2853(6)°, V = 2225.62(5) $Å^3$, Z = 4, T =150 K, prism, red brown, 5062 independent reflections, R(int) = 0.022, R_1 = 0.0594 wR_2 = 0.162 [I >2σ(I)].

Pn*(H)Ti(O-2,6-Me-C_6H_3)Cl_2 (6): Single crystals were grown from hexane solution at –35 °C, $C_{22}H_{28}Cl_2TiO$, M = 427.27, monoclinic, $P2_1/c$, a = 8.5552(2) Å, b = 17.7148(5) Å, c = 14.6706(4) Å, α = γ = 90.00 °, β = 106.6445(11), V = 2130.22(10) $Å^3$, T = 150(2) K, Z = 4, 4844 independent reflections, *R*(int) = 0.019, R_1 = 0.0537 wR_2 = 0.119 [I >2σ(I)].

Pn*(H)Ti(O-2,6-Me-C_6H_3)$_3$ (7): Single crystals were grown from hexane solution at –35 °C, $C_{38}H_{46}TiO_3$, *M* = 598.68, monoclinic, *P*2_1/n, *a* = 8.9702(2) Å, *b* = 24.3863(6) Å, *c* = 14.6936(4) Å, α = γ = 90.00 °, β = 91.352(2), *V* = 3213(14) $Å^3$, *T* = 150(2) K, *Z* = 4, 6634 independent reflections, *R*(int) = 0.060, R_1 = 0.0501 wR_2 = 0.125 [I >2σ(I)].

4. Conclusions

Five η^8-permethylpentalene titanium aryloxide and alkoxide complexes have been synthesized. All have been fully characterized, including in the solid state. Furthermore, a new reaction pathway for η^8-permethylpentalene complexes was identified whereby treatment with an alcohol results in the related η^5-coordinated (hydro)permethylpentalene alkoxide complex. This offers a potential route to new homo- and heterobimetallic complexes following subsequent deprotonation of the protonated ligand.

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Appendix A. Supplementary data

The supporting information contains NMR spectroscopy and X-ray crystallography tables. CCDC 925041-925046 and 1862855 contains the supplementary crystallographic data for complexes **1**–**7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Competing interests

The authors have no competing interests to declare.

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