



**Double CO₂ Activation by 14-electron η^8 -
Permethylpentalene Titanium Dialkyl Complexes**

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Double CO₂ Activation by 14-electron η⁸-Permethylpentalene Titanium Dialkyl Complexes

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The novel 14 electron species η⁸-Pn*TiR₂ (Pn* = C₈Me₆; R = Me, CH₂Ph) have been synthesised and spectroscopically and structurally characterised. Subsequent reaction with CO₂ leads to the activation and double insertion of CO₂ into both Ti-alkyl bonds to form the electronically saturated η⁸-Pn*Ti(κ²-O₂CR)₂ (R = Me, CH₂Ph) complexes.

Transformation of simple abundant chemical feedstocks such as CO₂ to more industrially relevant compounds is arguably one of the paramount objectives of modern chemistry.^{1–3} It has long been recognised that metal centres play an important role in providing low energy reaction pathways through binding and activation of these small molecules.¹ This is especially pertinent for CO₂, due to it being highly thermodynamically stable and kinetically inert.⁴ Examples of CO₂ insertion into Ti-C bonds are relatively rare^{5–13} (especially Ti-C σ-bonds),^{11–14} even though it was first observed over 40 years ago, with the first examples documented by Vol'pin, trapping the thermal decomposition product of Cp₂TiPh₂,¹⁵ and Zucchini's work with Ti(CH₂Ph)₄.¹⁴

Pentalene (Pn = C₈H₆) has a diverse yet poorly developed organometallic chemistry in comparison with the related *bis*(cyclopentadienyl)metal analogues. One of the many attractions to the versatile pentalene dianion (Pn²⁻) in organometallic synthesis is its flexibility, offering a wide variety of multihaptic coordination modes.¹⁶ The most recently discovered and most fascinating is the η⁸-mode,^{17–19} whereby all eight carbon atoms coordinate to a single metal centre, concomitant with strong folding about its bridgehead bond, essentially capping off an entire face of a metal's coordination sphere. Previous work by O'Hare *et al.* using the permethylated analogue (Pn* = C₈Me₆),^{20,21} concluded that the high yielding synthesis of η⁸-Pn* complexes necessitates the use of cis-

Pn* starting materials. It was discovered that isomeric control could be imparted on the Pn* synthon used and subsequently transferred to an organometallic complex, which led to a series of group 4 η⁸-Pn*M dichloride complexes.²² Subsequent salt metathesis reactions with this series produced a family of mixed sandwich complexes [Pn*MCp_{2-x}Cl_x (M = Ti, Zr, Hf; x = 0, 1)], that demonstrated very high activity for the polymerisation of ethylene (up to 6993 kg mol⁻¹ h⁻¹ bar⁻¹).²³ Due to the incipient nature of pentalene titanium chemistry, Cp remains the only carbon based ligand to be incorporated into any "PnTi"-fragment.¹⁹ Similarly, literature examples documenting the reaction of Pn metal complexes with small molecules are relatively scarce.^{24–26} However, Cloke *et al.* have recently reported the elegant reductive deoxygenation of CO₂, with the Ti double sandwich compound (μ-η⁵:η⁵-Pn^R)₂Ti [R = 1,4-(SiⁱPr₃)₂].^{27,28} Herein we report the synthesis and characterisation of the first Pn*Ti dialkyl complexes and investigate their subsequent reactivity with CO₂.

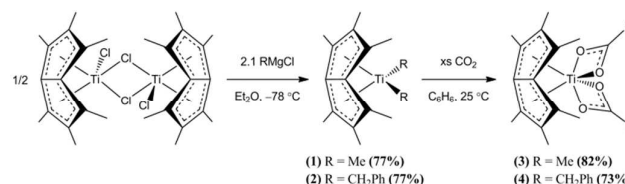
The complexes Pn*TiR₂ [R = Me (**1**), CH₂Ph (**2**)], were synthesised by salt metathesis reactions between [Pn*TiCl(μ-Cl)]₂²² and the appropriate Grignard reagent (Scheme 1).[†] Subsequent work-up yielded **1** and **2** as microcrystalline solids, both in high yield. **1** and **2** have been characterised by ¹H and ¹³C NMR spectroscopy, elemental analysis, and X-ray crystallography; the structures are shown in Fig. 1 and 2.[‡] The ligands in both compounds are coordinated in a pseudo tetrahedral arrangement around Ti as exemplified by the R-Ti-R angle 104.84(9)° (**1**) and 107.49(9)° (**2**). These angles are considerably larger than seen for the analogous bis-Cp species, Cp₂TiR₂ [91.3(1), 91.0(2)°; R = Me, CH₂Ph],^{29,30} which indicates the η⁸-Pn* moiety is less sterically demanding than two Cp units, allowing the R-Ti-R angle to widen and approach the idealised tetrahedral angle (109.47°). Similarly, the average Ti-R bond lengths

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‡ Electronic Supplementary Information (ESI) available: General and synthetic methods, instrumentation and characterising data of compounds of **1-4**. CCDC 1063831-1063834. [§] For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x



Scheme 1. Synthetic routes (and yields) to **1-4**

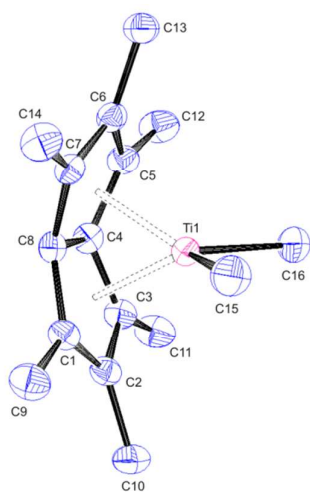


Fig. 1 Molecular structure of **1**. Ellipsoids shown at 50% probability, H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°). Ti1-C15 = 2.139(2), Ti1-C16 = 2.132(2), Ti1-Ct1 = 1.932(2), Ti1-Ct2 = 1.930(2), C15-Ti1-C16 = 104.84(9), fold angle = 35.66(3). Ct1 and Ct2 are the two η^5 -centroids of the Pn* ring.

of **1** and **2** (2.136, 2.172 Å) are shorter than for Cp_2TiR_2 [2.176, 2.225 Å; R = Me, CH_2Ph], which is rationalised by the relatively electron deficient nature of the Ti centres in **1** and **2**, forming a stronger Ti-R interaction. This is due to Pn* formally containing two fewer electrons than two Cp moieties,³¹ giving a total electron count of 14 for **1** and **2**, compared to 16 for Cp_2TiR_2 . As expected, upon exchange of two Me groups for the more sterically demanding CH_2Ph ligands, the fold angle (defined as the angle by which the ligand is found to deviate from planarity)¹⁶ of **2** (33.1°) is smaller than that of **1** (35.7°). It is well documented that electron deficient benzyl complexes of the early transition metals may distort in order to relieve electronic unsaturation *via* methylene C-H agostic and/or C_6H_5 π -system interactions with the metal centre.^{32–35} On inspection, the two benzyl ligands in **2** are bound in an asymmetric manner and inequivalent, as demonstrated by their markedly different Ti- CH_2 -C_{ipso} angles [101.94(15) and 115.23(15)°] and Ti-C_{ipso} distances [2.886(2) and 3.085(2) Å]. Although these values are

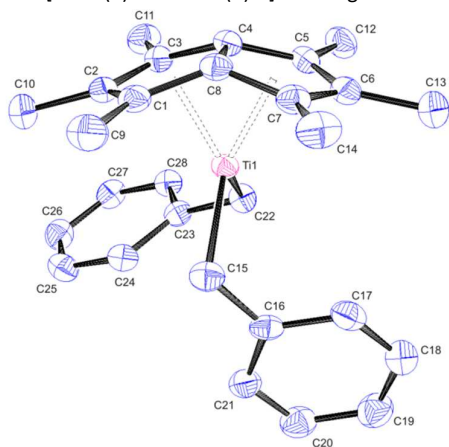


Fig. 2 Molecular structure of **2**. Ellipsoids shown at 50% probability, H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°). Ti1-C15 = 2.191(2), Ti1-C22 = 2.152(2), Ti1-Ct1 = 1.961(2), Ti1-Ct2 = 1.942(2), C15-Ti1-C22 = 107.49(9), fold angle = 33.14(3). Ct1 and Ct2 are the two η^5 -centroids of the Pn* ring.

borderline in the region for such interactions, a comparison with formal η^2 -bonding,³⁴ results in this bonding mode being discounted for **2**. This and NMR analysis (*vide infra*), results in assignment of two η^1 - CH_2Ph ligands with their solid state inequivalence attributed to crystal packing forces or a very weak Ti- π interaction. Owing to the thermal instability of the 16-electron species Cp_2TiMe_2 ,³⁶ it was somewhat surprising to find that both **1** and **2** are stable indefinitely at room temperature in both the solution and solid state. Indeed, **1** was found to be stable in solution at elevated temperatures (≤ 60 °C) for several days; full decomposition was only observed after heating above 100 °C (24 hours), producing no identifiable organometallic species. There is no spectroscopic evidence for the formation of a carbene species, analogous to the proposed reactive intermediate in the thermolysis of Cp_2TiMe_2 ,³⁷ nor a Pn* equivalent of the finally observed tuck-in structure. The latter is unsurprising as this would lead to a large deformation of the Pn* ring system.

The ¹H NMR spectra of **1** and **2** are consistent with the structures observed in the solid state and are of C_{2v} symmetry, resulting in two Pn* resonances in a 12:6 intensity ratio, which fall within their usual chemical shift range.^{22,23} The remaining upfield resonance in **1** corresponds to the terminal methyl group ($\delta = 0.15$ ppm). The ¹H/¹³C/¹J_{C-H} values for the methylene group in **2** (1.82, 68.1 ppm and 120.9 Hz) agree well with $\text{Cp}_2\text{Ti}(\text{CH}_2\text{Ph})_2$ (1.87, 74.1 ppm and 124.3 Hz) and are distinctly different to the values indicative of η^n -benzyl ($n \neq 1$) bonding.^{32,38} The remaining Pn* and Ph chemical shifts fall within their usual range and are unremarkable.

Due to the electron deficient and coordinatively unsaturated nature of **1** and **2**, these 14 electron monomeric species reactivity towards small molecules, in particular CO_2 , was investigated. Exposure of **1** and **2** to a CO_2 atmosphere[†] led to the smooth formation of Pn*Ti(κ^2 - O_2CR)₂ [R = Me (**3**), CH_2Ph (**4**)], in 82 and 73% yields respectively. The formation of **3** proceeded appreciably quicker than **4** (as judged by ¹H NMR spectroscopy), which may be attributed to the reduced steric bulk around the Ti centre (Me vs. CH_2Ph). **3** and **4** have been characterised by ¹H and ¹³C NMR spectroscopy, elemental analysis, high resolution MS (EI), and X-ray crystallography.¹⁵ Their structures are shown in Fig. 3 and 4. A CO_2 moiety has inserted into both Ti-R bonds in **3** and **4**. They are coordinated in a symmetrical bidentate manner, resulting in a distorted octahedral arrangement of ligands around the titanium centres and two 18 electron species. The molecules possess C_2 symmetry – the principal axis intersects the mid-point of the Pn* bridgehead bond and the Ti atom. The double insertion is in contrast to reactivity observed for the related Cp_2TiMe_2 , which only inserts CO_2 into one Ti-Me bond, either photochemically¹³ or at elevated temperature.³⁹ **4** is the first example of CO_2 insertion into any M- CH_2Ph bond (M = transition metal), to be fully characterised in both solution and the solid state. Indeed, the double insertion is very rare and there are only two documented examples where the M-(κ^2 - $\text{O}_2\text{CCH}_2\text{Ph}$)₂ motif has been structurally characterised, both for 1D coordination polymers incorporating Cd.^{40,41} The two four membered metallocycles of **4** are bound in a highly symmetrical fashion and are essentially planar, with no atom deviating from the mean Ti-O-C-O plane by more than 0.046 Å. The same is observed

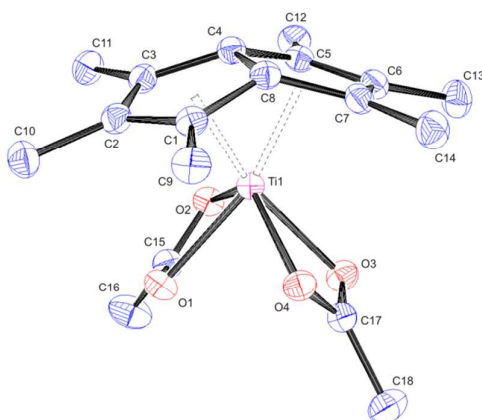


Fig. 3 Molecular structure of **3**. Ellipsoids shown at 50% probability, H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°). Ti1-O1 = 2.1393(14), Ti1-O2 = 2.1489(14), Ti1-O3 = 2.1426(14), Ti1-O4 = 2.1406(14), C15-O1 = 1.267(2), C15-O2 = 1.271(2), C17-O3 = 1.270(2), C17-O4 = 1.263(2), Ti1-Ct1 = 1.958(2), Ti1-Ct2 = 1.955(2), O1-Ti1-O2 = 62.20(5), O3-Ti1-O4 = 61.22(5), O1-C15-O2 = 118.64(18), O3-C17-O4 = 118.87(17), fold angle = 32.37(3). Ct1 and Ct2 are the two η^5 -centroids of the Pn* ring.

for **3** and both possess nearly identical C-O and Ti-O distances, within each metallocycle. The average Ti-O bond length for **4** is slightly smaller than **3** (2.1386 vs. 2.1429 Å) but the corresponding range is marginally larger (2.1196-2.1610 and 2.1393-2.1489 Å respectively). **3** has a slightly shorter average Ti-O distance than the analogous isoelectronic CpTi(O₂CMe)₃ (2.154 Å).⁴² However, there are two distinct distances in each acetate moiety, indicating an asymmetric bonding motif. IR spectroscopy has proven an insightful technique in the coordination of metal-carboxylate species.⁴³ Data indicates a bidentate, κ^2 -O-O'-bonding mode for **3** and **4**, further substantiating the observed solid state structure.

The ¹H NMR spectra of **3** consists of four resonances in a 6:6:6:6 intensity ratio, indicative of C₂ symmetry. The reduced symmetry of the molecule, results in three Pn* resonances (cf. **1** and **2**), inclusive

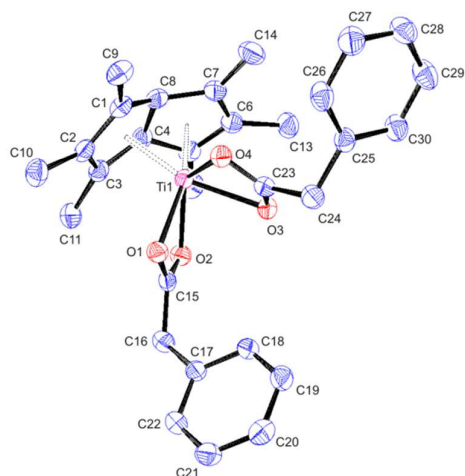


Fig. 4 Molecular structure of **4**. Ellipsoids shown at 50% probability, H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°). Ti1-O1 = 2.1421(13), Ti1-O2 = 2.1318(14), Ti1-O3 = 2.1610(14), Ti1-O4 = 2.1196(14), C15-O1 = 1.265(2), C15-O2 = 1.272(2), C23-O3 = 1.271(2), C23-O4 = 1.272(2), Ti1-Ct1 = 1.959(2), Ti1-Ct2 = 1.958(2), O1-Ti1-O2 = 61.31(5), O3-Ti1-O4 = 62.20(5), O1-C15-O2 = 118.42(17), O3-C23-O4 = 117.97(18), fold angle = 31.92(3). Ct1 and Ct2 are the two η^5 -centroids of the Pn* ring.

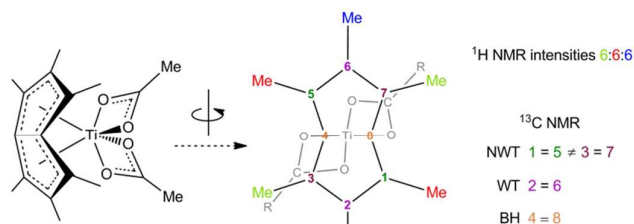


Fig. 5 ¹H/¹³C NMR splittings for static, C₂ symmetric complexes **3** and **4** (NWT = Non-wingtip, WT = Wingtip, BH = Bridgehead).

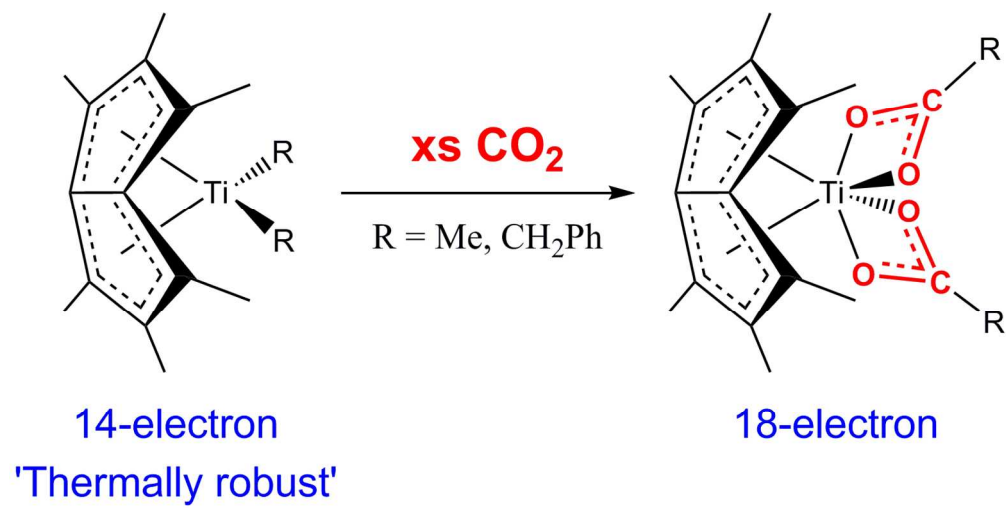
of two pairs of broad independent NWT-Me protons ($\nu_{1/2}$ = 80.7 and 108.0 Hz; Fig. 5). Variable temperature ¹H NMR studies reveal a change in symmetry from a static C₂ system at -10 °C, to a C_{2v} system above 30 °C, with equivalent NWT-Me groups. The nature of this fluxionality is postulated to be the rotation of the Pn* fragment around the Ti centre, analogous to the phenomenon of ring-whizzing, regularly observed in complexes incorporating Cp and Cp* fragments. Modelling this process (C₂→C_{2v}) results in a Gibbs free energy of activation of $\Delta G^\ddagger \approx 61.26$ kJ mol⁻¹.^{44,45} This is very close to that calculated for **4** ($\Delta G^\ddagger \approx 60.94$ kJ mol⁻¹), which shows analogous behaviour over the temperature range. The carboxylate carbon shift of **3** is in excellent agreement with that observed in CpTi(O₂CMe)₃ and almost identical to **4** (δ = 188.5, 189.2 and 188.6 ppm respectively).⁴² The methylene proton resonance in **4** is a broad singlet (δ = 3.37 ppm; $\nu_{1/2}$ = 6.7 Hz), which transforms to an AB quartet (J_{H-H} = -14.1 Hz) at -10 °C, due to the static C₂ symmetric system possessing diastereotopic CH₂ groups.

In summary, we have reported the first examples of pentalene Ti-dialkyl complexes, including the first examples of any PnTi fragment possessing a Ti-C σ -bond. Exposure to CO₂ leads to double insertion, providing the first fully characterised example of CO₂ activation by a M-CH₂Ph bond (M = transition metal). We are currently exploring the reactivity of **1** and **2** towards other small molecules, including CO and H₂.

Notes and references

§ Crystal data for (**1**): C₁₆H₂₄Ti, Monoclinic (P2₁/n), $a = 9.5686(2)$ Å, $b = 10.0906(2)$ Å, $c = 15.5541(3)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 97.1528(8)^\circ$, volume = 3741.0(9) Å³, $Z = 4$, $\lambda = 0.71073$ Å, $T = 150(2)$ K, $\mu = 0.553$ mm⁻¹, $D_{\text{calc}} = 1.178$ Mg m⁻³, 3388 independent reflections [R(int) = 0.018]; $R_1 = 0.0388$, $wR_2 = 0.0986$ [$I > 2\sigma(I)$]. CCDC 1063831. Crystal data for (**2**): C₂₈H₃₂Ti, Triclinic (P-1), $a = 9.4641(2)$ Å, $b = 10.4852(2)$ Å, $c = 13.1120(3)$ Å, $\alpha = 72.542(1)^\circ$, $\beta = 79.030(1)^\circ$, $\gamma = 64.773(1)^\circ$, volume = 1119.89(4) Å³, $Z = 2$, $\lambda = 0.71073$ Å, $T = 150(2)$ K, $\mu = 0.393$ mm⁻¹, $D_{\text{calc}} = 1.235$ Mg m⁻³, 5000 independent reflections [R(int) = 0.031]; $R_1 = 0.0415$, $wR_2 = 0.0939$ [$I > 2\sigma(I)$]. CCDC 1063832. Crystal data for (**3**): C₁₈H₂₄TiO₄, Triclinic (P-1), $a = 8.0338(2)$ Å, $b = 9.4658(2)$ Å, $c = 11.9668(3)$ Å, $\alpha = 78.479(1)^\circ$, $\beta = 88.724(1)^\circ$, $\gamma = 75.332(1)^\circ$, volume = 862.25(4) Å³, $Z = 2$, $\lambda = 0.71073$ Å, $T = 150(2)$ K, $\mu = 0.513$ mm⁻¹, $D_{\text{calc}} = 1.357$ Mg m⁻³, 3922 independent reflections [R(int) = 0.019]; $R_1 = 0.0428$, $wR_2 = 0.1070$ [$I > 2\sigma(I)$]. CCDC 1063833. Crystal data for (**4**): C₃₀H₃₂TiO₄, Monoclinic (C2/c), $a = 34.4240(6)$ Å, $b = 8.8424(2)$ Å, $c = 19.0704(4)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 119.2628(9)^\circ$, volume = 5064.08(18) Å³, $Z = 8$, $\lambda = 0.71073$ Å, $T = 150(2)$ K, $\mu = 0.372$ mm⁻¹, $D_{\text{calc}} = 1.323$ Mg m⁻³, 5734 independent reflections [R(int) = 0.025]; $R_1 = 0.0420$, $wR_2 = 0.1005$ [$I > 2\sigma(I)$]. CCDC 1063834.

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136x69mm (300 x 300 DPI)

The synthesis of new 14-electron permethylpentalene complexes and their subsequent activation of CO₂