Electronic Supplementary Material (ESI) for ChemComm.

Double CO_2 Activation by 14-electron η^8-Permethylpentalene Titanium Dialkyl Complexes

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Electronic Supplementary Information

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S1 Experimental Details

All organometallic manipulations were performed under an atmosphere of N_2 using standard Schlenk line techniques, on a dual vacuum-inlet gas manifold or MBraun UNIlab glovebox. Solvents used were dried by either; reflux over sodium-benzophenone diketyl (Et_2O), over 3 Å molecular sieves (1,4-dioxane), or passage through activated alumina (pentane, hexane, benzene) using a MBraun SPS-800 solvent system. Solvents were stored in dried glass ampoules over K mirrors with the exception of 1,4-dioxane which was stored on pre-dried 3 Å molecular sieves and all thoroughly degassed by passage of a stream of N_2 gas through the liquid. Toluene-d_8 and benzene-d_6 were purchased from Goss Scientific and freeze-pump-thaw degassed, dried by reflux over molten K, and purified by trap-to-trap distillation. MeMgCl (3.0 M in THF) and $PhCH_2MgCl$ (1.0 M in Et_2O) were supplied by Aldrich, CO2 (99.995%) by ARGO international and used as received. $[Pn^*TiCl(\mu\text{-}Cl)]_2$[1] was prepared according to literature procedure.

NMR spectra were recorded using Varian Mercury VX-Works (300 MHz) and Varian Mercury (300 MHz) spectrometers at 298 K unless stated otherwise. Chemical shifts, δ, are reported in parts per million (ppm) and coupling constants, J, are reported in hertz (Hz). ^1H and ^{13}C NMR chemical shifts are given relative to Me_4Si and referenced internally to the residual proton shift of the deuterated solvent employed. Oxygen or moisture sensitive samples were prepared using dried and degassed solvents under an inert atmosphere in a glovebox and were sealed in Wilmad 5mm 505-PS-7 tubes fitted with Young's type concentric stopcocks.

IR spectra were recorded on a Nicolet iS5 ThermoScientific spectrometer (range 4000 400 cm^{-1}, resolution 1 cm^{-1}) as KBr discs. Samples were prepared in the glovebox, mixed and ground with anhydrous KBr, then pressed into discs using an in-house purpose built press and holder, the spectra were recorded immediately.

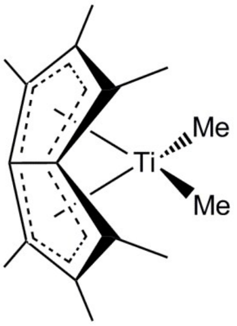
Electron Impact (EI) mass spectra were recorded by Mr Colin Sparrow of the Chemistry Research Laboratory, Oxford, using a Bruker FT-ICR-MS Apex III spectrometer. Compounds **1** and **2** failed to produce accurate mass spectra, which has been previously observed with other Pn^*TiX_2 compounds not containing a X = Cl, O bond.

Elemental microanalyses were conducted by Stephen Boyer at London Metropolitan University, London.

S2 X-ray Crystallographic Details

Single crystal X-ray diffraction data were collected and structure determinations and refinement were carried out by Dr Mark Chadwick of the Chemistry Research Laboratory, Oxford. Crystals were mounted on 0.2 mm MiTeGen MicroMounts using perfluoropolyether oil and cooled rapidly to 150 K in a stream of N_2 using an Oxford Cryosystems Cryostream unit.[2] Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoKα radiation, $\lambda = 0.71073$ Å). Intensity data were processed using the DENZO-SMN package.[3] The structure was then solved using the direct-methods program SIR92, which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[4–6]

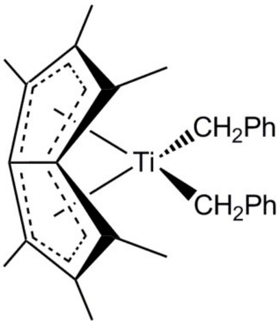
S3 Synthesis of Pn*TiMe$_2$ (1)



MeMgCl (3.0 M in THF, 0.918 ml, 2.754 mmol) was added to a slurry of [Pn*TiCl(μ-Cl)]$_2$ (0.400 g, 0.656 mmol) in Et_2O (40 ml) whist stirring at −78 °C. The mixture instantly turned green, then red and finally upon warming to room temperature purple. 1,4-dioxane (5 ml) was added to precipitate all magnesium salts,[7,8] and the resulting suspension filtered through Celite on a frit and eluted with pentane. The volatiles were removed under vacuum and subjected to a dynamic vacuum (10^{-3} mbar) for five hours. The residue was extracted with hexane and filtered *via* cannula, reduced to minimum volume and **1** precipitated as pink block shaped crystals when cooled to −78 °C (0.266 g, 1.008 mmol, 76.9%).

Analysis (%) calcd for $C_{16}H_{24}Ti$: C, 72.7; H, 9.2. Found: C, 72.6; H, 9.25. **^{1}H NMR** (C_6D_6, 300 MHz): $\delta = 0.15$ (6H, s, TiMe), 1.78 (6H, s, Me), 1.89 (12H, s, Me). **^{13}C NMR** (C_6D_6, 75 MHz): $\delta = 11.0$ (q, $^1J_{CH} = 126.8$, Me), 12.7 (q, $^1J_{CH} = 126.0$, Me), 41.1 (q, $^1J_{CH} = 114.8$, TiMe), 117.5 (s, ring-C), 129.8 (s, ring-C), 137.4 (s, ring-C). **IR** (KBr, cm^{-1}): 2944 (m), 2905 (m), 2870 (m), 1457 (br), 1378 (s), 1097 (m), 1021 (s), 870 (m), 797 (m), 764 (m), 689 (m), 668 (m).

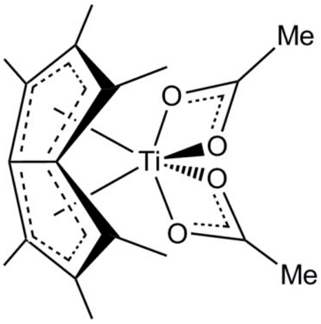
S4 Synthesis of Pn*Ti(CH_2Ph)$_2$ (2)



$PhCH_2MgCl$ (1.0 M in Et_2O, 2.754 ml, 2.754 mmol), was added to a slurry of [Pn*TiCl(μ-Cl)]$_2$ (0.400 g, 0.656 mmol) in Et_2O (40 ml) whist stirring at −78 °C. The mixture instantly turned dark brown and was allowed to stir for 20 minutes at −78 °C before warming to room temperature. 1,4-dioxane (5 ml) was added to precipitate magnesium salts,[7,8] then all volatiles were stripped under reduced pressure and subjected to a dynamic vacuum (10^{-3} mbar) for six hours. The residuum was extracted with pentane and filtered through Celite on a frit before being reduced to minimum volume and cooled to −35 °C to yield **2** as a bronze microcrystalline solid (0.423 g 1.015 mmol, 77.4%). Single crystals of **2** were obtained from a concentrated hexane solution at −35 °C.

Analysis (%) calcd for $C_{28}H_{32}Ti$: C, 80.8; H, 7.75. Found: C, 80.6; H, 7.8. **^{1}H NMR** (C_6D_6, 300 MHz): δ = 1.69 (6H, s, Me), 1.75 (12H, s, Me), 1.82 (4H, s, $TiCH_2$), 6.83 (4H, d, *o*-Ph), 6.90 (2H, t, *p*-Ph), 7.13 (4H, t, *m*-Ph). **^{13}C NMR** (C_6D_6, 75 MHz): δ = 10.9 (q, $^1J_{CH}$ = 126.7, Me), 12.5 (q, $^1J_{CH}$ = 127.8, Me), 68.1 (t, $^1J_{CH}$ = 120.9, $TiCH_2$), 117.2 (s, ring-C), 121.8 (*p*-Ph), 126.4 (*o*-Ph), 128.9 (*m*-Ph), 129.8 (s, ring-C), 136.1 (s, ring-C), 148.8 (*ipso*-Ph). **IR** (KBr, cm^{-1}): 3058 (m), 3011 (m), 2978 (m), 1590 (s), 1559 (m), 1479 (s), 1381 (m), 1208 (s), 1093 (m), 1027 (s), 936 (m), 877 (m), 801 (m), 744 (s), 693 (m), 669 (m).

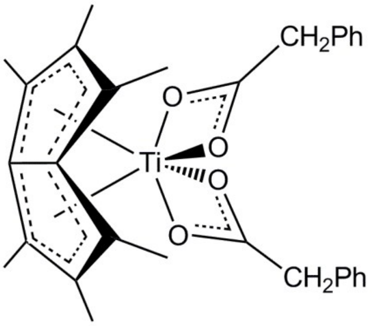
S5 Synthesis of Pn*Ti(κ^2-$O_2CMe)_2$ (3)



1 (0.058 g, 0.220 mmol) was added to a finger ampoule and dissolved in benzene (20 ml). The pink solution was degassed *via* a freeze-pump-thaw method; freezing the solution into a glass then subjecting it to a dynamic vacuum (10^{-3} mbar) for 20 minutes followed by thawing under a static vacuum. This cycle was completed twice more before CO_2 was admitted to the stirred solution, resulting in an instant colour change through a murky orange-brown to a bright orange. The reaction was allowed to stir for a further 15 hours after which solvent was removed *in vacuo* and subjected to a dynamic vacuum (10^{-3} mbar) for three hours. The residue was extracted with hexane and filtered through Celite in the glovebox before being reduced to minimum volume and slow cooled to −35 °C, affording **3** as an orange crystalline solid. The mother liquor was further concentrated and cooled to provide a second crop of crystalline solid (0.063 g, 0.180 mmol, 81.9%).

Analysis (%) calcd for $C_{18}H_{24}TiO_4$: C, 61.4; H, 6.9. Found: C, 61.4; H, 6.8. **^{1}H NMR** (C_7D_8, 300 MHz): δ = 1.72 (6H, s, Me), 1.78 (6H, s, O_2CMe), 1.80 (6H, br s, Me), 2.01 (6H, br s, Me). **^{13}C NMR** (C_7D_8, 75 MHz): δ = 10.0 (q, $^1J_{CH}$ = 127.3, Me), 11.4 (q, $^1J_{CH}$ = 125.3, Me), 22.8 (q, $^1J_{CH}$ = 127.3, $O_2C\mathit{Me}$), 119.0 (br s, ring-C), 120.9 (br s, ring-C), 133.3 (s, ring-C), 133.5 (s, ring-C), 188.5 (s, $O_2\mathit{C}Me$). **^{1}H NMR** (C_7D_8, 300 MHz, 263 K): δ = 1.72 (6H, s, Me), 1.78 (6H, s, O_2CMe), 1.78 (6H, s, Me), 2.05 (6H, s, Me). **^{13}C NMR** (C_7D_8, 75 MHz, 263 K): δ = 9.9 (q, $^1J_{CH}$ = 126.6, Me), 11.4 (q, $^1J_{CH}$ = 128.4, Me), 11.5 (q, $^1J_{CH}$ = 126.6, Me), 22.9 (q, $^1J_{CH}$ = 126.7, $O_2C\mathit{Me}$), 118.9 (s, ring-C), 120.9 (s, ring-C), 133.2 (s, ring-C), 133.3 (s, ring-C), 188.5 (s, $O_2\mathit{C}Me$). **^{1}H NMR** (C_7D_8, 300 MHz, 343 K): δ = 1.72 (6H, s, Me), 1.77 (6H, s, O_2CMe), 1.88 (12H, br s, Me). **^{13}C NMR** (C_7D_8, 75 MHz, 343 K): δ = 10.0 (q, $^1J_{CH}$ = 125.2, Me), 11.4 (q, $^1J_{CH}$ = 126.9, Me), 22.8 (q, $^1J_{CH}$ = 126.9, $O_2C\mathit{Me}$), 120.3 (br s, ring-C), 133.5 (s, ring-C), 133.8 (s, ring-C), 188.5 (s, $O_2\mathit{C}Me$). **IR** (KBr, cm^{-1}): 2991 (m), 2947 (m), 2914 (m), 2859 (w), 1541 (s, ν_{CO}), 1473 (s, ν_{CO}), 1378 (m), 1261 (m), 1101 (m), 1018 (m), 949 (s), 798 (s), 706 (m), 689 (s), 668 (m). **HRMS (EI)**: *m/z* calcd for $C_{18}H_{24}TiO_4$: 352.1154, found: 352.1150. **MS (EI)**: *m/z* 352 (M^+, 10%), 292 ($M^+{-}O_2CMe$, 100).

S6 Synthesis of $\mathbf{Pn^*Ti(\kappa^2\text{-}O_2CCH_2Ph)_2}$ (4)



CO_2 was admitted to a benzene solution (20 ml) of **2** (0.064 g, 0.154 mmol) using the same freeze-pump-thaw method described in the synthesis of **3**. The reaction was much slower taking 40 hours to run to completion as judged by ^{1}H NMR spectroscopy and resulted in a yellow solution. Crystals were precipitated from a concentrated hexane solution, at −35 °C (0.056 g, 0.112 mmol, 72.6%).

Analysis (%) calcd for $C_{30}H_{32}TiO_4$: C, 71.4; H, 6.4. Found: C, 71.3; H, 6.4. **^{1}H NMR** (C_7D_8, 300 MHz): δ = 1.59 (6H, s, Me), 1.60 (6H, br s, Me), 2.09 (6H, br s, Me), 3.37 (4H, br s, O_2CCH_2Ph), 7.04 (2H, t, *p*-Ph), 7.09 (4H, t, *m*-Ph), 7.18 (4H, d, *o*-Ph). **^{13}C NMR** (C_7D_8, 75 MHz): δ = 9.9 (q, $^1J_{CH}$ = 127.7, Me), 11.3 (q, $^1J_{CH}$ = 127.7, Me), 43.9 (t, $^1J_{CH}$ = 128.4, O_2CCH_2Ph), 119.7 (br s, ring-C), 120.9 (br s, ring-C), 126.8 (*p*-Ph), 128.4 (*m*-Ph), 129.9 (*o*-Ph), 133.4 (s, ring-C), 133.7 (s, ring-C), 135.4 (*ipso*-Ph), 188.6 (s, O_2CCH_2Ph). **^{1}H NMR** (C_7D_8, 300 MHz, 263 K): δ = 1.54 (6H, s, Me), 1.58 (6H, s, Me), 1.99 (6H, s, Me), 3.34, 3.42 (4H, ABq, $^2J_{H\text{-}H}$ = −14.1, O_2CCH_2Ph), 7.06 (2H, t, *p*-Ph), 7.10 (4H, t, *m*-Ph), 7.19 (4H, d, *o*-Ph). **^{13}C NMR** (C_7D_8, 75 MHz, 263 K): δ = 9.8 (q, $^1J_{CH}$ = 126.3, Me), 11.2 (q, $^1J_{CH}$ = 127.4, Me), 11.3 (q, $^1J_{CH}$ = 127.4, Me), 43.8 (t, $^1J_{CH}$ = 128.6, O_2CCH_2Ph), 119.5 (s, ring-C), 120.9 (s, ring-C), 126.8 (*p*-Ph), 128.1 (*o*-Ph), 128.4 (*m*-Ph), 133.4 (s, ring-C), 133.5 (s, ring-C), 135.3 (*ipso*-Ph), 188.6 (s, O_2CCH_2Ph). **^{1}H NMR** (C_7D_8, 300 MHz, 343 K): δ = 1.60 (6H, s, Me), 1.88 (12H, br s, Me), 3.36 (4H, s, O_2CCH_2Ph), 7.03 (2H, t, *p*-Ph), 7.08 (4H, t, *m*-Ph), 7.18 (4H, d, *o*-Ph). **^{13}C NMR** (C_7D_8, 75 MHz, 343 K): δ = 9.9 (q, $^1J_{CH}$ = 127.1, Me), 11.2 (q, $^1J_{CH}$ = 127.6, Me), 44.0 (t, $^1J_{CH}$ = 129.1, O_2CCH_2Ph), 120.6 (s, ring-C), 126.9 (*p*-Ph), 128.5 (*m*-Ph), 130.0 (*o*-Ph), 133.6 (s, ring-C), 134.0 (s, ring-C), 135.6 (*ipso*-Ph), 188.6 (s, O_2CCH_2Ph). **IR** (KBr, cm^{-1}): 3054 (m), 3036 (m), 2989 (m), 2908 (m), 1538 (s, ν_{CO}), 1458 (m, ν_{CO}), 1380 (m), 1280 (m), 1162 (m), 1076 (m), 946 (m), 862 (m), 797 (m), 716 (m), 669 (m). **HRMS (EI)**: *m/z* calcd for $C_{30}H_{32}TiO_4$: 504.1780, found: 504.1783. **MS (EI)**: *m/z* 504 (M^+, 20%), 368 ($M^+{-}O_2CCH_2Ph$, 100).

S7 References

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