Electronic Supplementary Information

CO_2 activation by permethylpentalene amido complexes

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Table of Contents

1. General details

All organometallic syntheses were performed under an inert atmosphere of nitrogen gas, using standard Schlenk techniques on a dual vacuum-inert gas manifold or in a MBraun UNIlab glovebox.[1] All glassware was placed in an oven at 180 °C for prior to use. Where necessary, solvents were distilled from the desiccant under a flow of nitrogen and transferred using a siphoning technique via steel cannulae. Molecular sieves (3 Å, 8-12 mesh) were supplied from Acros Organics and were baked at 140 °C under vacuum ($<10^{-1}$ mbar) for at least six hours before use.

Single crystal X-ray diffraction studies. Dr. Alexander Kilpatrick and Dr. Zoë Turner (University of Oxford) carried out the data collection and structure determination. Crystals were mounted on glass fibres (MiTeGen Micromounts) using perfluoropolyether oil (Fomblin YR1800, Alfa Aesar) and transferred to a goniometer head on the diffractometer. They were cooled rapidly to 150 K under a stream of cold nitrogen using the Oxford Cryosystems CRYOSTREAM unit.[2] An Enraf-Nonius FR590 KappaCCD diffractometer was used for data collection using graphite-monochromatic Mo K_α X-ray radiation ($\lambda = 0.71073$ Å). The intensity data was then processed using the DENZO-SMN package[3] and corrected for absorption using SORTAV.[4] Intensity data were collected using a multi-scan method with SCALEPACK (within DENZO-SMN). The structures were solved utilising the direct-methods program Superflip[5] with refinement using full-matrix least squares refinement on all F^2 data using the WIN-GX[6] and OLEX-2[7] program suites. In general, distances were calculated using the full variance/co-variance matrix. Dihedral angles were calculated with CCDC's Mercury[8] or using PLATON.[9] Illustrations of the solid-state molecular structures were created using ORTEP.[10]

Solution phase nuclear magnetic resonance (NMR) spectroscopy. Air-sensitive compounds were prepared in a glovebox under a nitrogen atmosphere and NMR tubes were sealed with

5 mm Young's taps. Spectra were recorded on a Bruker Avance III HD nanobay 400 MHz or Bruker Avance III 500 MHz NMR spectrometers. NMR spectra were referenced internally to the residual protio-solvent (^{1}H) or the signals of the solvent (^{13}C). ^{7}Li and ^{27}Al spectra were referenced externally relative to LiCl (9.7 M in D_2O) and $Al(NO_3)_3$ (1.1 M in D_2O) respectively. Solid state NMR was recorded on a Bruker Avance III HD 400MHz Solid state NMR spectrometer.

Fourier Transform Infrared (FTIR) spectroscopy. Air-sensitive samples were prepared in the glovebox as a thin film on NaCl plates and packed into an airtight cell. IR spectra were recorded on a Nicolet iS5 ThermoScientific spectrometer (range 400-4000 cm^{-1}, resolution 1 cm^{-1}) in transmission mode. Spectral data were analysed in Bruker OPUS software and treated with a baseline correction.

Electron impact mass spectrometry (EI-MS). EI-MS samples were run with the data collected by Mr. Colin Sparrow (University of Oxford) and Dr. Alaa Abdul-Sada (University of Sussex).

Elemental analysis. EA samples were prepared in the glovebox and packed into vials stored under nitrogen. Samples were then tested by Mr. Stephen Boyer (London Metropolitan University).

Starting materials. All reagents were used as received, unless specified otherwise. Solvents were supplied by Rathburn, Fisher scientific or Sigma Aldrich. Pentane, hexane, CH_2Cl_2, $CHCl_3$, benzene and toluene were dried on an MBraun SPS-800 solvent purification system. THF and Et_2O tetrahydrofuran was distilled from purple Na/benzophenone ketyl radical. Pentane, hexane, CH_2Cl_2, $CHCl_3$ and THF were stored over pre-activated 3 Å molecular sieves. Benzene, toluene and Et_2O were stored over a potassium mirror and these solvents were all degassed prior to use. Dry solvents were stored in oven-dried ampoules under a N_2 atmosphere, sealed with either Rotoflo or Young's taps and degassed prior to use.

Deuterated solvents used in the NMR analysis of air sensitive compounds were dried over NaK (C_6D_6, C_7D_8) or CaH_2 (C_5D_6N, $CDCl_3$), vacuum transferred and freeze-pump-thaw degassed three times prior to use. C_6D_6, C_5D_6N and $CDCl_3$ were stored over pre-activated 3 Å molecular sieves. C_6D_6 was purchased from Sigma Aldrich, and C_5D_6N and $CDCl_3$ from Goss scientific and $C_6D_4Cl_2$ from Cambridge Isotope Laboratories (minimum 99.5 at.%D).

The following were supplied by Sigma Aldrich: Activated charcoal, Br_2, $^{i}Bu_2AlCl$, $^{n}BuLi$ (1.6 M in hexane), CaH_2, Celite, $(CH_3)_3Al$, $CH_3COOC_2H_5$, $(CHO)_2$, $CO(CH_2COOCH_3)_2$, DiBACl, HCl, KH, L-Selectride (1.0 M in THF), $LiAlH_4$, $LiNCy_2$, $LiNMe_2$, $LiN(SiMe_3)_2$, LiTMP, $KN(SiMe_3)_2$, MeI, Mg, $MgSO_4$, $NaHCO_3$, NaOH, Na_2CO_3, Na_2SO_4, $Na_2S_2O_3$, $NHCy_2$, $NH_2{}^{t}Bu$, $NH_2\{C_6H_3(CH_3)_2\}$, NH_4Cl, $NHMe_2$, $NHPh_2$, $NH^{i}Pr_2$ and TiBA. TMP(H) was supplied by Cambridge Isotope Laboratories, Me_3SnCl by Tokyo Chemical Industry, TMEDA by BDH Chemicals and $CeCl_3$ by Alfa Chemicals. MeLi, LiCp, KC_8, $LiN^{i}Pr_2$, polymethylaluminoxane (sMAO), NaCp and $ZrCl_4{\cdot}2THF$ were kindly donated by the O'Hare group. Ethylene was supplied by BOC gases and passed through a high pressure drying column made of potassium wool. CO and CO_2 were supplied by Argo. The following species were prepared according to the published literature procedures: $Li_2Pn^*[TMEDA]_{0.194}$,[11,12] $[Pn^*Zr(\mu\text{-}Cl_{3/2})]_2(\mu\text{-}Cl_2){\cdot}LiTHF_{1.96}$,[13] $Pn^*ZrCpCl$[14] and $KNPh_2{\cdot}THF_{0.27}$.[15]

2. Experimental details

*2.1 Synthesis and characterisation of Pn*ZrCp(NMe_2) (**1**)*

An ampoule was charged with Pn*ZrCpCl (100 mg, 0.27 mmol) and $LiNMe_2$ (19 mg, 0.37 mmol), and benzene (20 mL) was added at room temperature. The resultant yellow solution was stirred for 3 days, filtered and the yellow filtrate was frozen at -78 °C and the solvent was sublimed under vacuum for 5 h. A spectroscopically pure yellow solid of **1** was isolated. Yield: 83%. Crystals of **1** suitable for a single crystal X-ray diffraction study were grown from a saturated C_6D_6 solution at room temperature. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ 5.73 (5H, s, Cp-*H*), 2.41 (6H, s, N-*Me*), 2.10 (6H, s, Pn*-*Me* WT), 1.90, 1.83 (6H, s, Pn*-*Me* NWT). **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6, 298 K): δ 126.8, 119.4 (Pn*-*bridgehead*), 125.1 (Pn*-*ring* WT), 112.4, 104.0 (Pn*-*ring* NWT), 107.9 (Cp-*ring*), 48.1 (N-*Me*), 13.7 (Pn*-*Me* WT), 12.1, 11.1 (Pn*-*Me* NWT). **EI-MS**: *m/z* = 385 (25%, $[M]^+$), 342 (100%, $[M - NMe_2]^+$). Despite repeated attempts, as in all similar instances, satisfactory elemental analysis (EA) results could not be obtained for samples of **1**. Representative data are reported. **EA** (calculated for $C_{21}H_{29}NZr$): C, 58.74 (65.23); H, 5.73 (7.56); N, 1.48 (3.62).

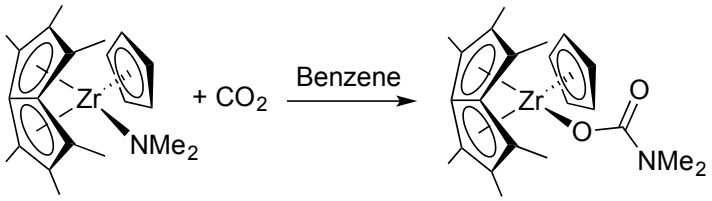
*2.2 Synthesis and characterisation of Pn*ZrCp(NPh_2) (**2**)*

An ampoule was charged with Pn*ZrCpCl (100 mg, 0.27 mmol) and $KNPh_2 \cdot THF_{0.27}$ (70 mg, 0.31 mmol), and pre-cooled THF (20 mL) was added at -78°C. The resultant yellow solution was allowed to warm to room temperature, stirred for 16 h then filtered and dried under vacuum. The yellow solid was redissolved in a pentane (20 mL) and toluene (10 mL) mixture, then filtered. The filtrate was reduced to minimum volume and stored at -80 °C for 3 days. The resultant yellow crystalline solid was isolated by filtration and dried *in vacuo* to give **2** as a spectroscopically pure solid. Yield: 60%. Crystals of **2** suitable for a single crystal X-ray diffraction study were grown at room temperature from a saturated solution of C_6D_6. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ 7.14 (4H, d, $^3J_{HH}$ = 7.8 Hz, Ph-*H*), 6.72 (4H, dd, $^3J_{HH}$ = 7.8 Hz, Ph-*H*), 6.67 (2H, t, $^3J_{HH}$ = 7.7 Hz, Ph-*H*), 5.52 (5H, s, Cp-*H*), 1.81 (6H, s, Pn*-*Me* WT), 1.87, 1.67 (6H, s, Pn*-*Me* NWT). **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6, 298 K): δ 158.8 (Ph-*ipso*), 143.6, 129.2, 123.9, 118.2, 117.9 (Ph-*C*), 129.5, 118.1 (Pn*-*bridgehead*), 127.2 (Pn*-*ring* WT), 112.0, 105.5 (Pn*-*ring* NWT), 110.8 (Cp-*ring*), 13.7, 11.2 (Pn*-*Me* NWT), 11.5 (Pn*-*Me* WT). **EI-MS**: *m/z* = 509 (30%, $[M]^+$), 341 (100%, $[M - NPh_2]^+$). **EA** (calculated for $C_{38}H_{38}N_2Zr$): C, 72.75 (72.89); H, 6.40 (6.51); N, 2.80 (2.74).

*2.3 Synthesis and characterisation of Pn*Zr(NPh$_2$)$_2$ (**3**)*

An ampoule was charged with [Pn*Zr(μ-Cl$_{3/2}$)]$_2$(μ-Cl$_2$)·LiTHF$_{1.96}$ (120 mg, 0.14 mmol) and KNPh$_2$·THF$_{0.27}$ (140 mg, 0.62 mmol), and THF (20 mL) was added at room temperature. The resultant yellow-orange solution was stirred for 16 h then stripped to dryness and partially redissolved in pentane (4 × 20 mL). The filtrate was reduced to minimum volume then stored at -80 °C for 3 days. The resultant yellow solid was isolated by filtration and dried for 3 h to yield 93 mg of spectroscopically pure **3**. A second crop of **3** (30 mg) was obtained by washing the remaining solid with toluene (10 mL). The resultant filtrate was dried to afford a spectroscopically pure yellow solid. Overall yield: 75%. Crystals of **3** suitable for a single crystal X-ray diffraction study were grown at room temperature from a saturated solution of C$_6$D$_6$. **^{1}H NMR** (400 MHz, C$_6$D$_6$, 298 K): δ 7.09 (8H, dd, $^3J_{HH}$ = 7.8 Hz, Ph-*H*), 6.80 (4H, t, $^3J_{HH}$ = 7.9 Hz, Ph-*H*), 6.66 (8H, d, $^3J_{HH}$ = 7.8 Hz, Ph-*H*), 1.87 (6H, s, Pn*-*Me* WT), 1.77 (12H, s, Pn*-*Me* NWT). **^{13}C{^{1}H} NMR** (100 MHz, C$_6$D$_6$, 298 K): δ 151.4 (Ph-*ipso*), 129.7, 122.3, 121.3 (Ph-*C*), 131.3 (Pn*-*ring* NWT), 130.2 (Pn*-*bridgehead*), 110.1 (Pn*-*ring* WT), 11.7 (Pn*-*Me* WT), 11.4 (Pn*-*Me* NWT). **EI-MS**: *m/z* = 613 (20%, [M]$^+$), 445 (100%, [M − NPh$_2$]$^+$). **EA** (calculated for C$_{38}$H$_{38}$N$_2$Zr): C, 74.17 (74.34); H, 6.60 (6.24); N, 4.65 (4.56).

*2.4 Synthesis and characterisation of Pn*Zr(η^1-O$_2$CNMe$_2$) (**4**)*

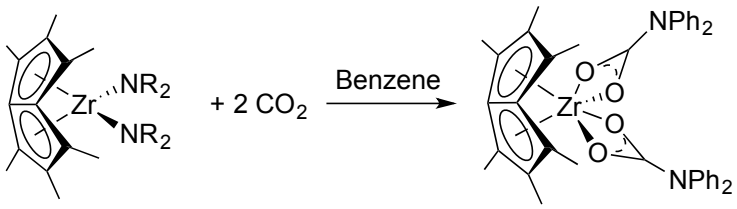


Eq. S1. Formation of Pn*ZrCp(η^1-O$_2$CNMe$_2$) (**4**).

An NMR tube containing **1** (10 mg, 0.025 mmol) in C$_6$D$_6$ was frozen at -78 °C, evacuated under dynamic vacuum and exposed to a 1 bar overpressure of CO$_2$. The mixture thawed to afford a spectroscopically pure yellow solution of **4**. This solution was frozen at -78 °C, exposed to dynamic vacuum, then removed from the cold bath to allow the C$_6$D$_6$ to sublime overnight. The residual solid was washed with pentane (3 × 1 mL) and dried *in vacuo* giving the product as a yellow powder. Yield: 88%. The carboxylation reaction of **1** was more difficult to control on larger scales and resulted in the formation of undesired side products. Pure **4** was obtained most reliably on an NMR scale. The reported yield is from four combined NMR tubes.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 5.81 (5H, s, Cp-*H*), 2.52 (6H, s, N-*Me*), 2.09, 1.98 (6H, s, Pn*-*Me* NWT), 1.88 (6H, s, Pn*-*Me* WT). **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6, 298 K): δ 166.7 (*C*(O)O), 138.3, 121.22 (Pn*-*bridgehead*), 130.6 (Pn*-*ring* WT), 107.9 (Cp-*H*), 106.9, 104.7 (Pn*-*ring* NWT), 34.6 (N-*Me*), 13.2, 11.1 (Pn*-*Me* NWT), 11.1 (Pn*-*Me* WT). **EI-MS**: *m/z* = 429 (85%, $[M]^+$), 341 (15%, $[M - CO_2NMe_2]^+$). **EA** (calculated for $C_{17}H_{24}NO_2Zr$): C, 55.66 (55.85), H, 6.04 (6.62), N, 3.07 (3.83).

*2.5 Synthesis and characterisation of Pn*Zr(κ^2-O$_2$CNPh$_2$)$_2$ (**5**).*



Eq. S2. Formation of Pn*Zr(κ^2-O$_2$CNPh$_2$)$_2$ (**5**).

An ampoule was charged with **3** (40 mg, 0.27 mmol) in benzene (20 mL) and the yellow solution was frozen at -78 °C. The headspace was evacuated under dynamic vacuum then exposed to a 1 bar overpressure of CO_2. The reaction mixture was allowed to warm to room temperature and gave a white suspension. After 16 h stirring, the reaction mixture was filtered, frozen at -78 °C and dried *in vacuo* for 5 h, to yield a spectroscopically pure white solid of **5**. Yield: 44 %. Crystals of **5** suitable for a single crystal X-ray diffraction study were grown at room temperature from a saturated solution of C_6D_6. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ 7.21 (8H, d, $^3J_{HH}$ = 7.9 Hz, Ph-*H*), 7.00 (8H, dd, $^3J_{HH}$ = 7.2 Hz, Ph-*H*), 6.89 (4H, t, $^3J_{HH}$ = 7.2 Hz, Ph-*H*), 2.08, 1.92 (6H, s, Pn*-*Me* NWT), 2.03 (12H, s, Pn*-*Me* WT). **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6, 298 K): δ 167.6 (*C*(O)O), 143.6 (Ph-*ipso*), 129.5, 127.3, 124.8, 121.1, 118.2 (Ph-*ring*), 128.9, 109.2 (Pn*-*ring* NWT), 109.7 (Pn*-*bridgehead*), 132.9 (Pn*-*ring* WT), 11.3, 11.1 (Pn*-*Me* NWT), 10.6 (Pn*-*Me* WT). **EI-MS**: *m/z* = 700 (100%, $[M]^+$), 444 (95%, $[Pn*ZrNPh_2]^+$). **EA** (calculated for $C_{40}H_{38}N_2O_4Zr$): C, 66.10 (68.44); H, 4.76 (5.46); N, 5.13 (3.99).

3. NMR and IR spectroscopy

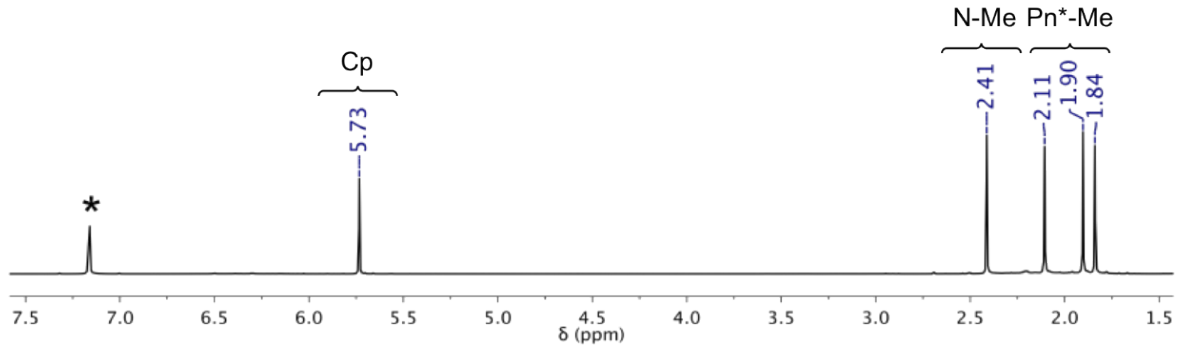


Fig. S1. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) of Pn*ZrCp(NMe_2) (**1**). * denotes residual protio solvent.

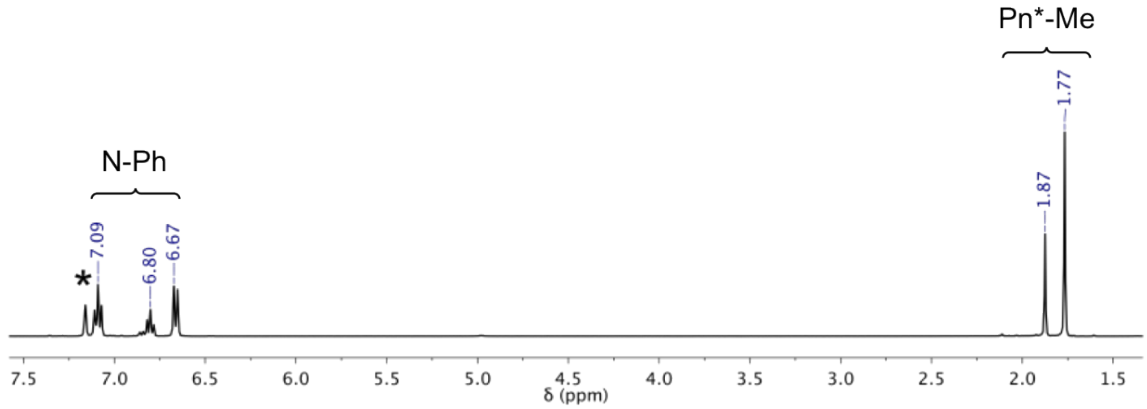


Fig. S2. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) of Pn*Zr(NPh_2)$_2$ (**3**). * denotes residual protio solvent.

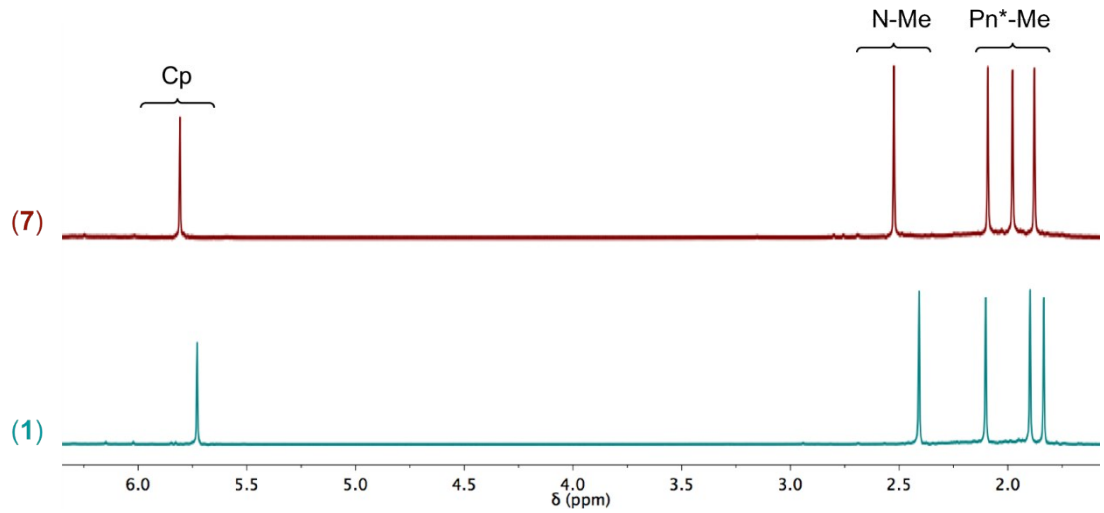


Fig. S3. Overlay of ^{1}H NMR spectra (400 MHz, C_6D_6, 298 K) of Pn*ZrCp(NMe_2) (**1**) and Pn*ZrCp(η^1-O_2CNMe_2) (**4**).

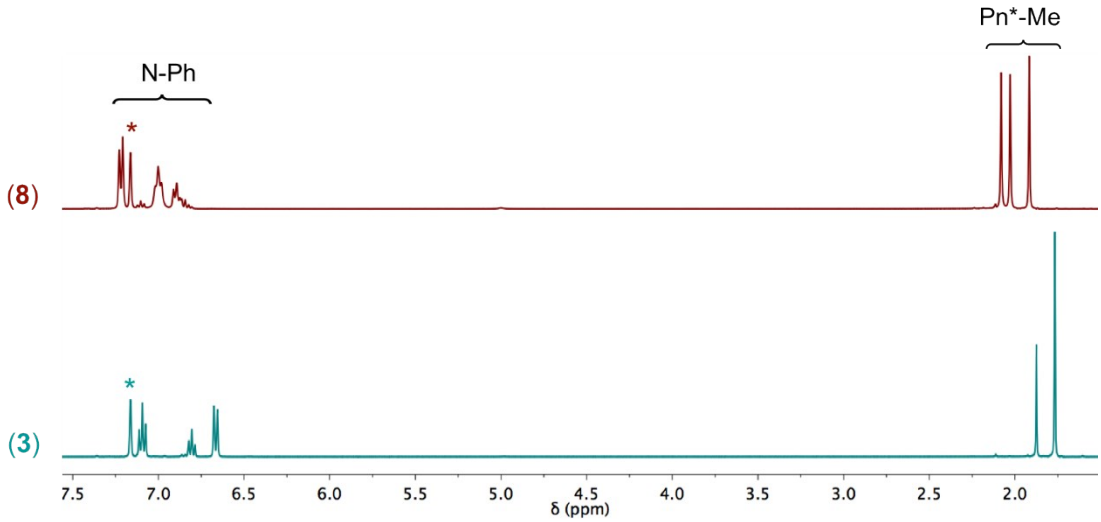


Fig. S4. Overlay of ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) of Pn*Zr(NPh_2)$_2$ (**3**) and Pn*Zr(κ^2-O_2CNPh_2)$_2$ (**5**). * denotes residual protio solvent peak.

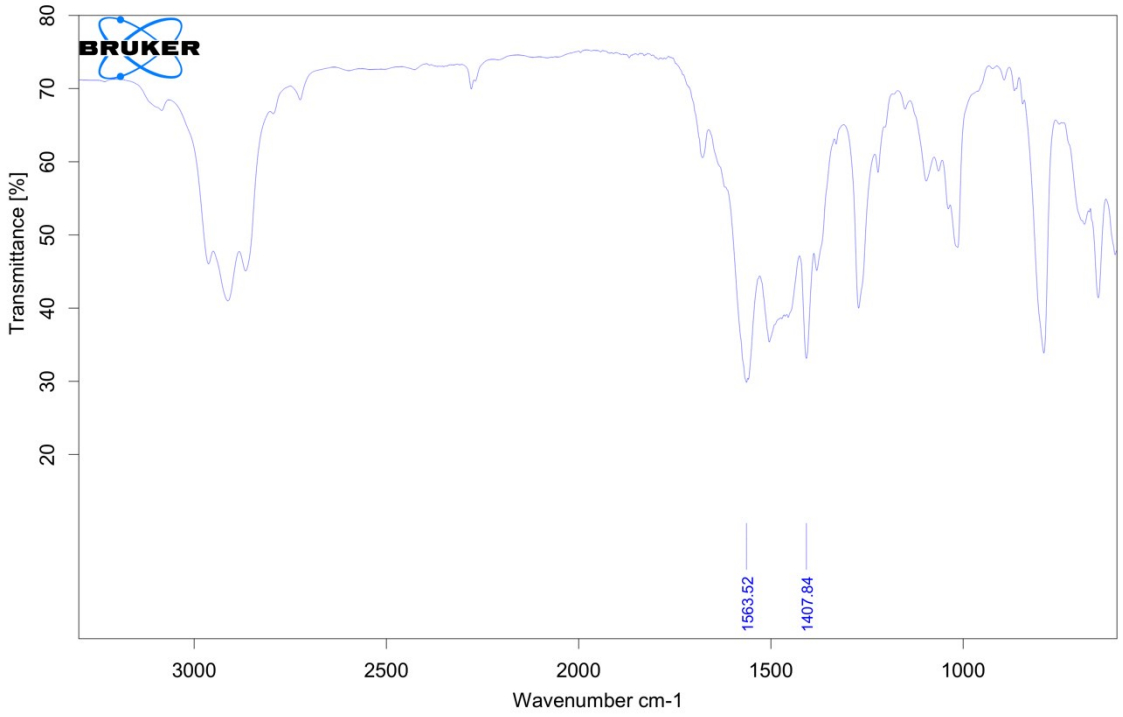


Fig. S5. IR spectrum of **4**, with the bands assigned to the η^1-carbamate ligand highlighted.

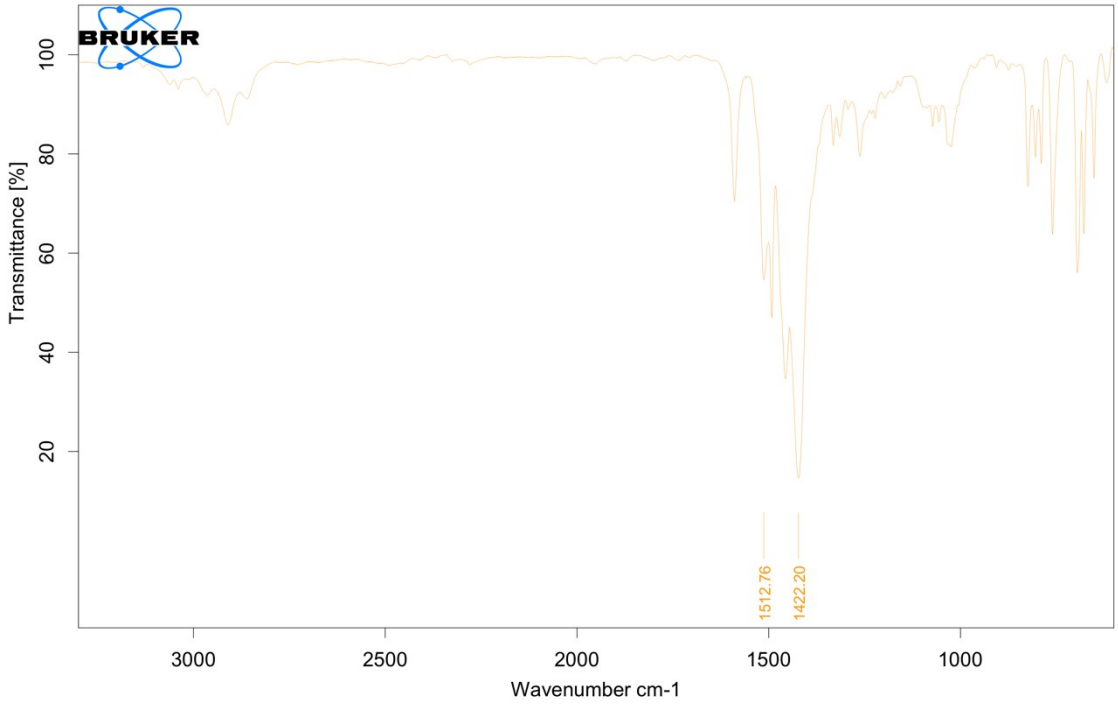


Fig. S6. IR spectrum of **5**, with the bands assigned to the κ^2-carbamate ligands highlighted.

4. X-ray crystallography

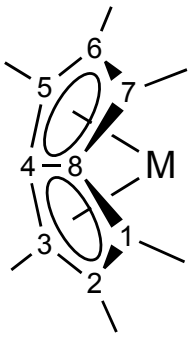


Chart S1. Numbering scheme for the X-ray assignment of η^8-Pn* complexes.

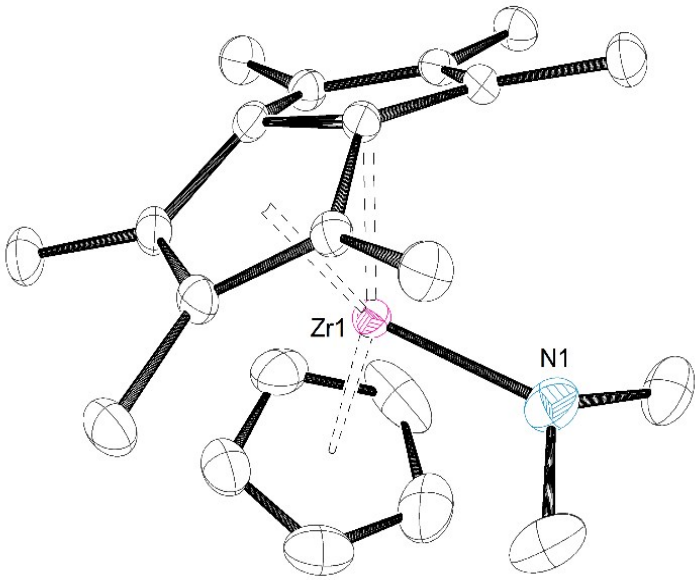


Fig. S7. Solid-state molecular structure of Pn*ZrCp(NMe_2) (**1**). H atoms are omitted for clarity and thermal ellipsoids are set at 50% probability.

Table S1. Selected distances (Å), angles (°) and parameters for **5** and comparable complexes.

Parameter	5	$Zr(\kappa^2\text{-}O_2CNEt_2)_4$	$CpZr(\kappa^2\text{-}O_2CNEt_2)_3$	$Pn^*Ti(\kappa^2\text{-}O_2CMe)_2$
M – O[a]	2.239(4)	2.201(2)	2.226	2.143
M – O[b]	2.223(3)–2.258(4)	2.194(3)–2.276(3)	2.180–2.276	2.139–2.149
C – O[a]	1.276	1.282(4)	1.283	1.269
C – O[b]	1.270(7)–1.282(7)	1.278(4)–1.297(4)	1.278–1.297	1.265–1.272
O – C – O/N[a]	120	120	120	119
C – N[a]	1.376(8)	1.340(5)	1.349	–
C – N – C[a]	120	120	120	–

[a] Average value (*ca.* 0.1 Å). [b] Range.

5. References.

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