Supplementary Material for Faraday Discussions
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SUPPORTING INFORMATION

Experimental Details

Solvents: Solvents were obtained from an *Anhydrous Engineering* alumina column based drying system with the exception of THF which was distilled from Na and benzophenone under an inert $N_{2(g)}$ atmosphere prior to use. Solvents were degassed where necessary by three freeze-thaw cycles. [$^2H_2$]-Dichloromethane for NMR analyses was purchased from *Cambridge Isotopes Limited* and distilled from pre-dried 3 Å molecular sieves under an inert atmosphere of $N_{2(g)}$ prior to use. [$^2H_8$]-Tetrahydrofuran for NMR analyses was purchased from *Cambridge Isotopes Limited* and distilled from sodium-benzophenone under an inert atmosphere of $N_{2(g)}$ prior to use.

Materials: The preparation of the oligomeric forms of all of the complexes reported on herein, has been described in detail elsewhere.[11] Monomers are obtained by appropriate dilution.

Techniques: All air-sensitive manipulations were conducted under an inert $N_{2(g)}$ atmosphere using standard Schlenk-line techniques. NMR samples were prepared in 5 mm diameter NMR tubes, sealed by means of a Young-valve.

Instrumentation: NMR spectra were acquired on *JEOL, ECP300*, *ECP400 and Varian 500 NMR* instruments utilising the ^{2}H-signal from the solvent as the frequency lock. Optical rotations were run on a *Bellingham and Stanley ADP220 Polarimeter*; concentrations, c, are reported in g/100 mL. HPLC samples were analysed on a *Dionex Ultimate 3000 Series* instrument using a Chiralpak (25 x 4.6 cm) AD-H column eluting with heptane: 2-propanol at a flow rate 0.5 ml/min, detecting at 254 nM. UV spectra were run on an Ocean Optics spectrophotometer with Spectrasuite software.

^{31}P NMR dilution studies (*R,R*)-[**5**]$^{+}$ [BAr'F]$^{-}$ (44 mg, 25 x 10^{-3} mmol) was dissolved in 0.5 cm^{3} CD_2Cl_2 to give a final [Pd] of 50 mM. Dilution of the NMR sample was performed by withdrawal of a portion of the sample followed by the addition of CD_2Cl_2 to restore the total volume to 0.5 cm^{3}. Spectra were collected at 300 MHz employing a 200 ppm spectral width, 0 ppm offset and between 1024 scans.

Confirmation of oligomeric non-chelate coordination modes [$^{2}H_{10}$]-(*R,R*)-[**5**]$^{+}$ [BAr'F]$^{-}$ (35 mg, 20 x 10^{-3} mmol) was placed in a 5 mm diameter NMR tube fitted with a Young's valve then dissolved in 0.5 cm^{3} [$^{2}H_8$]-THF or [$^{2}H_2$]-CD_2Cl_2 under and atmosphere of $N_{2(g)}$ to give a final $[Pd]_{TOT}$ of 40 mM. ^{31}P^{31}PCOSY analysis was conducted at 300 MHz employing a standard ^{1}H^{1}HCOSY pulse sequence adapted for heteronuclear analysis

with a 100 ppm spectra width, 0 ppm x-offset, 2048 x-points, 512 y-points and 52 scans per y-increment.

Confirmation of homochiral lower-order oligomer. $[^2H_{20}]$-(*R,R*)-[**5**]$^+$ [BAr'F]$^-$ (14 mg, 8 x 10^{-3} mmol) and $[^2H_0]$-(*S,S*)-[**5**]$^+$ [BAr'F]$^-$ (14 mg, 8 x 10^{-3} mmol) were placed in a 5 mm diameter NMR tube fitted with a Young's valve then dissolved in 0.5 cm^3 $[^2H_8]$-THF under and atmosphere of $N_{2(g)}$ to give a final $[Pd]_{TOT}$ of 32 mM. $^{31}P^{31}P$COSY analysis was conducted at 300 MHz employing a standard $^1H^1H$COSY pulse sequence adapted for heteronuclear analysis with a 100 ppm spectra width, 0 ppm x-offset, 2048 x-points, 512 y-points and 52 scans per y-increment.

Monomer-oligomer variation with enantiomeric excess Separate stock solutions of (*R,R*)-[**5**]$^+$ [BAr'F]$^-$ and (*S,S*)-[**5**]$^+$ [BAr'F]$^-$ with $[Pd]_{TOT}$ of 20 mM in CD_2Cl_2 were generated and volumes of the samples were withdrawn and mixed in a 5 mm NMR tube to give NMR samples with a total 0.5 cm^3 volume, $[Pd]_{TOT}$ of 20 mM and varying ee. Spectra were collected at 300 MHz employing a 200 ppm spectral width, 0 ppm offset and between 1024 scans.

Pseudoenantiomer titration $[^2H_{20}]$-(*R,R*)-[**5**]$^+$ [BAr'F]$^-$ (14 mg, 8 x 10^{-3} mmol) and $[^2H_0]$-(*S,S*)-[**5**]$^+$ [BAr'F]$^-$ (14 mg, 8 x 10^{-3} mmol) were placed in a 5 mm diameter NMR tube fitted with a Young's valve then dissolved in

0.5 cm^3 [$^2H_8$]-THF under and atomosphere of $N_{2(g)}$ to give a final $[Pd]_{TOT}$ of 32 mM. The ratio of [$^2H_{20}$]-(*R,R*)-[**5**]$^+$ [BAr'F]$^-$ and [$^2H_0$]-(*S,S*)-[**5**]$^+$ [BAr'F]$^-$ was adapted by addition of a solid sample of [$^2H_0$]-(*S,S*)-[**5**]$^+$ [BAr'F]$^-$ to the NMR sample. ^{31}P NMR spectra were collected at 500 MHz employing a 200 ppm spectral width, 0 ppm offset and between 3072 and 8192 scans to achieve reasonable signal/noise ratio in monomeric chelate.

Polarimetry Separate stock solutions of (*R,R*)-[**5**]$^+$ [BAr'F]$^-$ and (*S,S*)-[**5**]$^+$ [BAr'F]$^-$ with $[Pd]_{TOT}$ of 10 mM in THF were generated and volumes of the samples were withdrawn and mixed in a polarimetry cell with a total 2.0 cm^3 volume, [Pd] of 10 mM and varying ee. Sample dilution was performed by withdrawal of a portion of the sample followed by the addition of THF resulting in a total volume of 2.0 cm^3. Five measurements were taken and averaged at each concentration and enantiomeric excess.

UV Analysis. Typical procedure: (*R,R*)-[**5**]$^+$ [BAr'F]$^-$ (31.3 mg, 1.8 x 10^{-3} mmol) was dissolved in 0.2 cm^3 CH_2Cl_2 to give a final $[Pd]_{TOT}$ of 281 nm. 1.5 μL was withdrawn and dropped into a cuvette containing rapidly stirring 3 cm^3 CH_2Cl_2 at 294 K to give a final $[Pd]_{TOT}$ of 0.046 mM. Equilibration of the sample was analysed by monitoring absorbance at 281 nm.

Stoichiometric alkylation of [5]$^+$ Standard procedure: [**5**]$^+$ X^- (0.027 mmol, 1 mM, 1 eq) was dissolved in THF (11.5 cm^3). After stirring for 20 min, M^+

$^{-}CH(CO_2CH_2C_6H_5)_2$ (0.055 mmol, 2.0 eq) in THF was added and the solution turned a dark yellow colour. The reaction was stirred for a further 30 min after which saturated aqueous NH_4Cl (20 cm^3) and Et_2O (20 cm^3) was added. The organic and aqueous phases were separated. The organic fraction was dried over $MgSO_{4(s)}$, filtered and the volatiles removed *in vacuo*. The resulting yellow residue was dissolved Et_2O (2 cm^3) and filtered through a plug of silica which was repeated until the filtrate became colourless. Determination of ee was conducted through HPLC analysis on a Chiralpak AD-H column, eluting with 90:10 n-heptane:2-propanol at a flow rate 0.5 ml/min. Retention time: (*S*)-**6**: 19.5 min, (*R*)-**6**: 21.7 min.

Experiments performed in the presence of NaBAr'F were conducted as above but with the addition of solid NaBAr'F to the complex and stirring for 10 min before the addition of the nucleophile.

Catalytic Alkylation Standard procedure: Phenanthrene (42 mg, 0.24 mmol, 1 eq, Internal standard) was dissolved in THF (0.8 cm^3) followed by the addition of $[\mathbf{5}]^+X^-$ (0.006 mmol, 2.5 mol %) in THF (1 cm^3) and subsequently *rac*-cyclohexenyl acetate **4** (36 mg, 0.24 mmol, 1 eq) in THF (1 cm^3). The reaction was stirred for 20 min before the addition of $M(HC(CH_2CO_2Bn)_2)$ (0.48 mmol, 0.150 M, 2 eq) in THF (3.2 cm^3). The reaction was sampled by withdrawing 0.20 cm^3 aliquots and quenching into a biphasic mixture of saturated aqueous NH_4Cl (0.8 cm^3) and Et_2O (0.8 cm^3)

at regular time intervals. The organic phase was removed and filtered through a plug of silica. The sample was then analysed by GC-FID to monitor reaction conversion (analysis against control sample withdrawn before nucleophile addition, t = 0 min). Determination of ee: as for stoichiometric alkyklation.

Modeling details Molecular modeling of (η^3-alkenyl)Pd complexes was performed using a modified[34] and validated[11] MM3* force field in MacroModel.[35] A dielectric constant of 9 was used as a very rough solvent representation.[11] Re-optimization of MM conformers of monomeric complexes using DFT methods indicate that the conformational energies from the modified force field are accurate to within 5-10 kJ mol^{-1}.[11] Conformational searches employed the combined Monte Carlo[36]/Low Mode[37] search implemented in MacroModel, with 50% of the steps using each method. Torsions in small rings were excluded from the Monte Carlo steps; from previous experience with similar systems,[11] we know that all backbone cyclohexanes adopt a chair conformation with both substituents in equatorial positions, and that the η^3-cyclohexenyl moiety prefers a boat conformation.

Single Crystal X-ray Diffraction. A single crystal of $[Pd_4(\eta^3\text{-}C_3H_5)_4(\mathbf{2})_4][OTf]_4\cdot(C_2H_2Cl_4)_{4.5}$, measuring 0.7 × 0.4 × 0.4 mm, was rapidly

removed from the solvent ($C_2H_2Cl_4$) and placed under a stream of nitrogen (T = 173 K) on a Bruker Siemens SMART CCD area-detector three circle diffractometer, with Mo-K_α radiation (λ = 0.71073 Å). Intensities were integrated[38] from several series of exposures, each covering 0.3° in ω, and the total data set being a hemisphere. Absorption corrections were applied, based on multiple and symmetry equivalent measurements.[39] The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections. With the exception of four carbon atoms in a disordered allyl fragment on the complex cation and a $C_2H_2Cl_4$ solvate, all non-hydrogen atoms were refined with unrestrained anisotropic displacement parameters. Hydrogens were placed in calculated positions and refined with riding constraints. Due to highly diffuse $C_2H_2Cl_4$ solvent, the position of only one ordered solvent molecule could be satisfactorily refined. Additional solvent molecules were identified, but attempts at modeling these were unsuccessful and so their scattering contributions were removed using the SQUEEZE routine in PLATON.[40] The total number of solvent molecules expressed in the complex formula (4.5) is consistent with a residual electron density count of 422 electron per unit cell. The asymmetric unit, a $Pd_2(\eta^3\text{-}C_3H_5)_2\{(R,R)\text{-}\mathbf{2}\}_2$ fragment, is related to the rest of the molecule by inversion symmetry, giving a *meso* cyclic tetramer with a uniform disc-like appearance. Two distinct conformations of **2**, in which the amide oxygens are disposed either *cis*- or *trans*- (with respect to the cyclohexane mean plane), alternate around the cyclic system, facilitating

the assembly of a compact structure with minimal void space in the centre of the tetrameric ring. Further elimination of voids within the molecule is achieved by directing two allyl groups and two phenyl rings towards the inversion centre. The remaining allyl groups are oriented away from the plane encompassing the four Pd centres and consequently occupy unhindered regions of the molecule, being disordered over two possible positions. Of particular interest are short O(amide)···Pd contacts, ranging from 2.979(7) Å to 3.157(7) Å, which suggest that formation of a formal Pd-O bond would exert minimal strain on ligand **2**. The underlying significance of this arises in the suspected mechanism of de-oligomerisation in solution whereby an amide oxygen competitively coordinates to Pd, promoting dissociation of the Pd-P bond. The observation of hydrogen bonding between triflate counter-ions and amide hydrogens, with N(H)···O donor-acceptor separations ranging from 2.92(1) Å to 3.12(1) Å, further give an indication of the potential non-spectator role played by the counter-ion in oligomer assembly, providing such interactions are maintained in solution. These interactions are also a key factor in the crystal packing, with each molecule being linked to its four nearest neighbours by four such bridging, hydrogen-bonded, triflate anions.

Table 1. Crystal data and structure refinement for $[Pd_4(\eta^3\text{-}C_3H_5)_4(\mathbf{2})_4][OTf]_4\cdot(C_2H_2Cl_4)_{4.5}$

Empirical formula	C201 H189 Cl18 F12 N8 O20 P8 Pd4 S4	
Formula weight	4704.30	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 21.659(13) Å	α = 90°
	b = 23.210(19) Å	β = 100.67(5)°
	c = 26.022(14) Å	γ = 90°
Volume	12855(15) $Å^3$	
Z (Z')	2 (0.5)	
Density (calculated)	1.215 Mg/m^3	
Absorption coefficient	0.605 mm^{-1}	
F(000)	4786	
Crystal size	0.7 x 0.4 x 0.4 mm	
θ range for data collection	1.82 to 25.00°	
Index ranges	-22<=h<=25, -27<=k<=26, -30<=l<=30	
Reflections collected	66164	
Independent reflections	22372 [R_{int} = 0.0487]	
Completeness to θ = 25.00°	98.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22372 / 11 / 1179	
Goodness-of-fit on F^2	S = 0.960	
R indices [for 14235 reflections with I>2σ(I)]	R_1 = 0.0824, wR_2 = 0.2369	
R indices (for all 22380 data)	R_1 = 0.1076, wR_2 = 0.2667	
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$,	
	where $P = [\max(F_o^2, 0) + 2F_c^2]/3$	
	a = 2.00, b = 0.00	
Largest diff. peak and hole	3.100 and -1.189 $eÅ^{-3}$	

Small Angle Neutron Scattering (SANS) experiments were carried out on the time-of-flight LOQ instrument at ISIS, UK where incident wavelengths are $2.2 \leq \lambda \leq 10$ Å, resulting in an effective Q (= $(4\pi/\lambda)\sin(\theta/2)$, θ scattering angle < 10°) range of 0.009–0.249 $Å^{-1}$. Appropriate detector masking was used to remove data affected by detector element imperfections. Fully deuterated solvent (>99% d_8-THF) was employed to provide contrast against the non-deuterated ligand **2**. Samples were held in 2-mm path-length Hellma cuvettes, thermostatted at 25°C. The revived signals were corrected for transmission, empty cell and solvent background. Then, absolute intensities (±5%) for I(Q) (cm^{-1}) were determined by calibrating against a known partially deuterated polymer standard.[29]

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