Supplementary information:

Experimental Section

General methods: The syntheses of **2** and **3** were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under nitrogen over molecular sieves (4 Å). Routine ^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a FT Bruker AVANCE 300 (^{1}H: 300.1 MHz, ^{13}C: 75.5 MHz, ^{19}F: 282.4 MHz, ^{31}P: 121.5 MHz) instrument at 25°C. ^{1}H NMR spectral data were referenced to residual $CHCl_3$ [7.26 ppm], ^{13}C chemical shifts are reported relative to $CDCl_3$ [77.0 ppm], and the ^{31}P NMR data are given relative to external H_3PO_4. The ^{19}F spectra were measured relative to neat $CFCl_3$. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (CNRS), Strasbourg. The diphosphite **L** (having *S,S* stereochemistry) and complex **1** were prepared according to reported procedures.[15] For convenience, spectroscopic data for **1** are also given below.

(η^3-allyl)-c*is*-*P,P'*-{[(*S,S*)-5,11,17,23-tetra-*tert*-butyl-25,27-dipropyloxy-26,28-bis(1,1'-binaphthyl-2,2'-dioxyphosphanyloxy)calix[4]arene]}palladium(II) tetrafluoroborate dimer, 2: A solution of (*S,S*)-5,11,17,23-tetra-*tert*-butyl-25,27-dipropyloxy-26,28-bis(1,1'-binaphthyl-2,2'-dioxyphosphanyloxy)calix[4]arene (0.110 g, 0.08 mmol) in acetone (30 mL) was slowly added to a suspension of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (0.014 g, 0.04 mmol) and NH_4BF_4 (0.009 g, 0.09 mmol) in acetone (30 mL) at 0°C. The reaction mixture was stirred for 1 h at room temperature, then filtered through Celite. The solvent was evaporated and the residue was washed with hexane (10 mL) to afford the product as a pale yellow solid. Recrystallisation from CH_2Cl_2-hexane afforded colourless crystals (0.099 g, 78%). The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are essentially identical to those reported earlier for complex **1** (and given below). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 128.74 and 126.67 (AB spin system, $J_{PP'}$ = 108.4 Hz, $OP(OAr)_2$). $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$): δ –153.87 (s, BF_4). Found: C 67.63, H 6.01%. Calc. For $C_{93}H_{95}BF_4O_8P_2Pd\cdot 1CH_2Cl_2$ (M_r = 1594.56 + 84.93): C 67.17, H 5.82%. Crystals (colourless) suitable for X-ray diffraction were obtained by slow diffusion of heptane into a CH_2Cl_2 solution of the complex.

Bis{(η^3-allyl)-c*is-P,P'*-{[(*S*,*S*)-5,11,17,23-tetra-*tert*-butyl-25,27-dipropyloxy-26,28-bis(1,1'-binaphthyl-2,2'-dioxyphosphanyloxy)calix[4]arene]}palladium(II)} 1.0 hexafluorophos phate, 1.0 tetrafluoroborate, 3: Colourless crystals of the product, suitable for X-ray diffraction, were obtained by slow diffusion of petroleum ether into a CH_2Cl_2 solution of a stoichiometric amount of (η^3-allyl)-c*is-P,P'*-{[(*S*,*S*)-5,11,17,23-tetra-*tert*-butyl-25,27-dipropyloxy-26,28-bis(1,1'-binaphthyl-2,2'-dioxyphosphanyloxy)calix[4]arene]}palladium(II) hexafluorophosphate (0.100 g, 0.06 mmol) and (η^3-allyl)-c*is-P,P'*-{[(*S*,*S*)-5,11,17,23-tetra-*tert*-butyl-25,27-dipropyloxy-26,28-bis(1,1'-binaphthyl-2,2'-dioxy-phosphanyloxy)calix[4]are ne]}palladium(II) tetrafluoroborate (0.096 g, 0.06 mmol). The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were identical to those of complex **1**. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 128.70 and 126.62 (AB spin system, $J_{PP'}$ = 108.4 Hz, $OP(OAr)_2$), –144.38 (sept, J_{PF} = 712.8 Hz, PF_6). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ –73.60 (d, J_{FP} = 712.8 Hz, PF_6), –153.91 (s, BF_4). Found: C 68.66, H 5.81%. Calc. For $C_{186}H_{190}F_{10}O_{16}P_5BPd_2$ (M_r = 1654.08): C 68.74, H 5.89%. The 1:1 BF_4 / PF_6 ratio was verified on a crystalline sample of **3**.

X-ray crystallographic data of 3: $C_{186}H_{190}BF_{10}O_{16}P_5Pd_2 \bullet 3CH_2Cl_2 \bullet 1C_5H_{12}$, M_r = 3576.76, monoclinic, $P2_1$, a = 21.7830(7), b = 19.1953(6), c = 23.4584(8)Å, β = 94.962(2), V = 9771.9(6) Å^3, Z = 2, D_c = 1.216 Mg m^{-3}, λ(MoK$_\alpha$) = 0.71073Å, μ = 0.373 cm^{-1}, F(000) = 3728, T = 293(2) K. Single crystals were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of the complex. A sample was studied on a Bruker AXS X8-APEX II with graphite-monochromated MoK$_\alpha$ radiation. The data collection ($2\theta_{max}$ = 56°, distance detector = 60mm, ϕ scan frames via 0.7° ϕ rotation and 20 s per frame, range HKL : H -28,28 K -25,15 L -30,30) gave 75013 reflections. These led to 30297 independent reflections, for which 15086 had $I > 2.0\ \sigma(I)$. The structure was solved with SIR-97,[19] which revealed the non hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found from the Fourier difference map. The whole structure was refined with SHELXL97[20] by the full-matrix least-square techniques (use of $|F^2|$; x, y, z, β_{ij} for Pd, P, Cl, C and O atoms, x, y, z in riding mode for H atoms; 2127 variables and 15086 observations with $I > 2.0\ \sigma(I)$; calc $w = 1/[\sigma^2(Fo^2) + (0.0642P)^2]$ where $P = (F_o^2 + 2\ F_c^2)/3$ with the resulting R = 0.0537, R_W = 0.1189 and S_W = 0.834, $\Delta\rho < 0.650$ eÅ^{-3}. Flack parameter: 0.02 (2). The molecule crystallises

with three molecules of dichloromethane and one molecule of pentane. The full crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif by citing CCDC 292540.

NMR data for monomer 1: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (d, 1H, C*H* arom, ^{3}J = 8.9 Hz), 8.13 (d, 1H, C*H* arom, ^{3}J = 8.9 Hz), 8.04 (d, 1H, C*H* arom, ^{3}J = 8.2 Hz), 7.97 (d, 1H, C*H* arom, ^{3}J = 8.1 Hz), 7.82-7.02 (m, 21H, C*H* arom and *m*-ArH), 7.00 (d, 1H, *m*-ArH, ^{4}J = 2.1 Hz), 6.74 (d, 1H, *m*-ArH, ^{4}J = 2.2 Hz), 6.70 (d, 1H, *m*-ArH, ^{4}J = 2.2 Hz), 6.50 (d, 1H, *m*-ArH, ^{4}J = 2.4 Hz), 6.42 (d, 1H, *m*-ArH, ^{4}J = 2.0 Hz), 6.37 (d, 1H, *m*-ArH, ^{4}J = 2.2 Hz), 6.31 (d, 1H, *m*-ArH, ^{4}J = 2.1 Hz), 5.16 and 3.57 (AB system, 2H, ArCH_2Ar, ^{2}J = 13.1 Hz), 5.12 and 3.47 (AB system, 2H, ArCH_2Ar, ^{2}J = 13.2 Hz), 5.06 and 3.10 (AB system, 2H, ArCH_2Ar, ^{2}J = 13.2 Hz), 5.14-4.99 (m, 1H, central allyl), 4.93 and 3.00 (AB system, 2H, ArCH_2Ar, ^{2}J = 13.2 Hz), 4.35-4.25 (m, 1H, OCH_2), 4.25-4.14 (m, 1H, OCH_2), 4.03-3.89 (m, 2H, OCH_2), 2.79-2.56 (m, 2H, terminal allyl), 2.35-2.12 (m, 2H, terminal allyl), 2.12-1.82 (4H, CH_2CH$_3$), 1.17-1.01 (6H, CH$_2$CH_3), 1.14 (s, 9H, C(CH_3)$_3$), 1.08 (s, 9H, C(CH_3)$_3$), 0.81 (s, 9H, C(CH_3)$_3$), 0.78 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 151.43-119.88 (arom C and central allyl *C*H), 78.02 (s, OCH$_2$), 77.87 (s, OCH$_2$), 77.23 (s, terminal allyl *C*H$_2$), 34.00 (s, *C*(CH$_3$)$_3$), 33.93 (s, *C*(CH$_3$)$_3$), 33.66 (s, *C*(CH$_3$)$_3$), 33.61 (s, *C*(CH$_3$)$_3$), 33.27 (s, ArCH$_2$Ar), 33.19 (s, ArCH$_2$Ar), 33.13 (s, ArCH$_2$Ar), 33.06 (s, ArCH$_2$Ar), 31.23 (s, C(*C*H$_3$)$_3$), 31.17 (s, C(*C*H$_3$)$_3$), 30.93 (s, C(*C*H$_3$)$_3$), 24.15 (s, *C*H$_2$CH$_3$), 23.47 (s, *C*H$_2$CH$_3$), 10.07 (s, CH$_2$*C*H$_3$), 10.01 (s, CH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 128.51 and 126.36 (AB spin system, $J_{PP'}$ = 107.7 Hz, OP(OAr)$_2$), –144.38 (sept, J_{PF} = 712.8 Hz, PF_6). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ –73.6 (d, J_{FP} = 713.0 Hz, PF_6). Found: C 65.09, H 5.51%. Calc. For $C_{93}H_{95}F_6O_8P_3Pd{\cdot}1CH_2Cl_2$ (M_r = 1654.08 + 84.93): C 64.92, H 5.62%. MS (ESI TOF): m/z 1507.57 [M^+, expected isotopic profile].