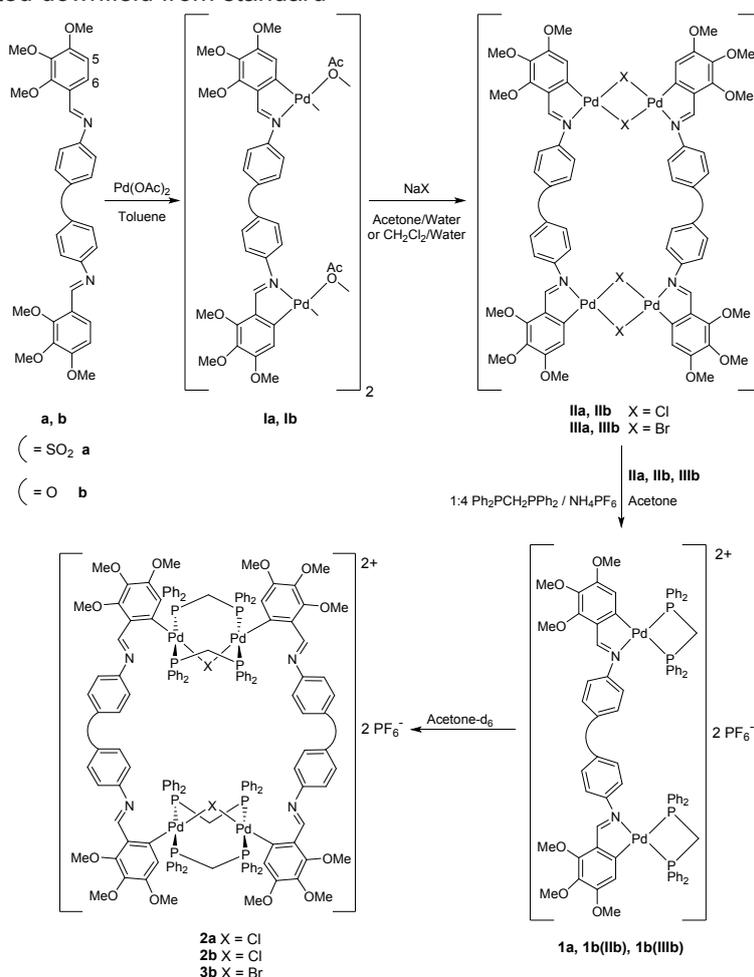


ESI

Synthetic Details

General Procedures. Solvents were purified by standard methods.¹ Palladium(II) acetate, (*p*-NH₂C₆H₄)₂SO₂, 2,3,4-(MeO)₃C₆H₂CHO, (*p*-NH₂C₆H₄)₂O and the phosphine Ph₂PCH₂PPh₂ (dppm) were purchased from Sigma-Aldrich. All preparations were carried out under dry dinitrogen. Elemental analyses were performed with a Fisons elemental analyzer, Model 1108. IR spectra were recorded as Nujol mulls or polythene discs on Perking-Elmer 1330, Mattson Model Cygnus-100, and Bruker Model IFS-66V spectrophotometers. ¹H NMR spectra in solution were recorded in CDCl₃, DMSO-d₆ or Acetone-d₆ at room temperature on Bruker DPX 250 and Varian Mercury 300 spectrometer operating at 250.13MHz and 300.14 MHz respectively using 5 mm o.d. tubes; chemical shifts, in ppm, are reported downfield relative to TMS using the solvent signal (CDCl₃, δ¹H = 7.26 ppm; DMSO-d₆, δ¹H = 2.46ppm; MeCOMe-d₆ δ¹H = 2.05ppm) as reference. ³¹P NMR spectra were recorded at 161.91 MHz and 202.46 MHz on a Varian Inova 400 and Bruker AMX 500 spectrometer respectively using 5 mm o.d. tubes and are reported in ppm relative to external H₃PO₄ (85%). Coupling constants are reported in Hz. All chemical shifts are reported downfield from standard



Scheme 1 ESI Reaction sequence leading to the synthesis of the double A-frame complexes.

Synthesis of [2,3,4-(MeO)₃C₆H₂(CH)=NC₆H₄]₂SO₂ (**a**)

¹ Perrin, D.D., Armarego, W.L.F. *Purification of Laboratory Chemicals*, Butterworth-Heinemann, London, 4th ed., 1996

A 1:2 mixture of (*p*-NH₂C₆H₄)₂SO₂ (2.57 g, 10.33 mmol) and 2,3,4-(MeO)₃C₆H₂CHO (4.0 g, 20.39 mmol) in chloroform (50 cm³) was refluxed for 3 h. After cooling to room temperature, the solvent was removed under reduced pressure to give a yellow oil. Addition of diethyl ether and stirring for 24 h gave a pale-yellow solid, which was filtered and dried under vacuum. Yield: 4.891 g, 80%. Anal. Found: C: 63.4, H: 5.2, N: 4.6, S: 5.3 %; C₃₂H₃₂N₂O₈S (604.67 g/mol); requires C: 63.6, H: 5.3, N: 4.6, S: 5.3 %. IR(cm⁻¹): ν(C=N) 1621. ¹H NMR (DMSO-d₆, δ/ppm, J/Hz): 8.58 (s, 2H, HC=N), 7.94 (d, 4H, H7H8, N = 8.2), 7.74 (d, 2H, H6, ³JH6H5 = 8.9), 7.33 (d, 4H, H9H10, N = 8.2), 6.94 (d, 2H, H5, ³JH5H6 = 8.9), 3.90 (s, 6H, MeO), 3.84 (s, 6H, MeO), 3.74 (s, 6H, MeO).

Synthesis of [{Pd{2,3,4-(MeO)₃C₆H(CH)=NC₆H₄}(μ₂-O₂CMe)}₂SO₂]₂ (**Ia**)

The ligand **a** (0.475 g, 0.785 mmol) and palladium(II) acetate (0.355 g, 1.580 mmol) were added in toluene (50 cm³) and the resulting mixture was stirred at 60° C for 24 h under argon. After cooling to r. t. the orange-brown solid formed was filtered off and dried under vacuum, to afford the final product as a dark orange solid. Yield: 0.70 g, 98%. Anal. Found: C 46.4, H 4.2, N 3.2, S 3.3 %; C₇₂H₇₂N₄O₂₄Pd₄S₂ (1867.16 g/mol) requires C 46.3, H 3.9, N 3.0, S 3.4%. IR(cm⁻¹): ν(C=N) 1566. ¹H NMR (DMSO-d₆, δ ppm, J Hz): 8.26 (s, 4H, HC=N), 7.94 (m, 8H, H7H8), 7.52 (m, 8H, H9H10), 6.16 (s, 4H, H5), 3.83 (s, 12H, MeO), 3.77 (s, 12H, MeO), 3.65 (s, 12H, MeO), 1.91 (s, 12H, MeCO₂).

Synthesis of [{Pd{2,3,4-(MeO)₃C₆H(CH)=NC₆H₄}(μ₂-Cl)}₂SO₂]₂ (**Ila**)

A solution of **Ia** (0.407 g, 0.218 mmol) in 20 cm³ of acetone was treated with a saturated solution of NaCl in ca. 20 cm³ of water. The yellow precipitate formed was filtered off, washed with water and dried under vacuum. Yield: 393 mg, 88%. Anal. Found: C, 43.5, H, 3.2, N, 3.2, S 3.4 %; C₆₄H₆₀Cl₄N₄O₁₆Pd₄S₂ (1772.80 g/mol) requires C, 43.4, H, 3.4, N, 3.2, S, 3.6%. IR(cm⁻¹): ν(C=N) 1570, ν(Pd-Cl) 309, 284. ¹H NMR (DMSO-d₆, δ ppm, J Hz): 8.28 (s, 4H, HC=N), 7.96 (m, 8H, H7H8, N = 8.5), 7.54 (m, 8H, H9H10, N = 8.4), 6.16 (s, 4H, H5), 3.85 (s, 12H, MeO), 3.79 (s, 12H, MeO), 3.67 (s, 12H, MeO).

Synthesis of [{Pd{2,3,4-(MeO)₃C₆H(CH)=NC₆H₄}(μ₂-Br)}₂SO₂]₂ (**Illa**)

A solution of **Ia** (0.224 g, 0.120 mmol) in 20 cm³ of acetone was treated with a saturated solution of LiBr in ca. 20 cm³ of water. The yellow precipitate formed was filtered off, washed with water and dried under vacuum. Yield: 350 mg, 95.6%. Anal. Found: C, 39.4, H, 3.2, N, 3.0, S, 3.1 %; C₆₄H₆₀Br₄N₄O₁₆Pd₄S₂ (1950.61 g/mol) requires C, 39.4, H, 3.1, N, 2.9, S, 3.3%. IR(cm⁻¹): ν(C=N) 1621. ¹H NMR (DMSO-d₆, δ ppm, J Hz): 8.52 (m, 8H, H7H8, N = 8.5), 8.28 (s, 4H, HC=N), 7.95 (m, 8H, H9H10, N = 8.4), 7.38 (s, 4H, H5), 3.83 (s, 12H, MeO), 3.78 (s, 12H, MeO), 3.65 (s, 12H, MeO).

Synthesis of [Pd{2,3,4-(MeO)₃C₆H(CH)=NC₆H₄}(Ph₂PCH₂PPh₂-*P,P*)]₂SO₂ · 2PF₆ (**1a**)

Ph₂PCH₂PPh₂ (0.029 g, 0.075 mmol) was added to a suspension of **Ila** (0.033 g, 0.019 mmol) in acetone (10 cm³). The mixture was stirred for 30 min, after which an excess of ammonium hexafluorophosphate was added. The mixture was stirred for a further 1 h, the complex precipitated out by addition of water, filtered off and dried *in vacuo*. IR(cm⁻¹): νC=N: 1568. ¹H NMR (MeCOMe-d₆, δ ppm, J Hz): 8.53 (d, 2H, HC=N, ⁴JHP_{trans} = 5.9), 6.04 (dd, 2H, H5, ⁴JH5P = 10.5, ⁴JH5P = 7.9), 4.65 (m, 4H, PCH₂P), 3.98 (s, 6H, MeO), 3.71 (s, 6H, MeO), 3.20 (s, 6H, MeO). ³¹P-{¹H} NMR (MeCOMe-d₆, δ ppm, J Hz): -37.2 (d, P_{trans}C, ²JPP = 72.1), -12.9 (d, P_{trans}N, ²JPP = 72.1), -149.9 (sept, PF₆, ¹JPF = 709.5).

Synthesis of $\{[\text{Pd}\{2,3,4\text{-(MeO)}_3\text{C}_6\text{H}(\text{CH})=\text{NC}_6\text{H}_4\}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2\text{-}P,P)]_2(\mu\text{-Cl})\text{SO}_2\}_2 \cdot 2\text{PF}_6$ (**2a**)

$\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (8.5 mg, 0.022 mmol) and ammonium hexafluorophosphate (0.004 g, 0.024 mmol) were added to a solution of **Ila** (8.5 mg, 0.005 mmol) in acetone- d_6 (0.6 cm^3) and left to stand until complete conversion. Yield: 16 mg, 93% related to **Ila**. Anal. Found: %, C, 55.3, H, 4.4, N, 1.6, S, 1.8 %; $\text{C}_{164}\text{H}_{148}\text{Cl}_2\text{F}_{12}\text{N}_4\text{O}_{16}\text{P}_{10}\text{Pd}_4\text{S}_2$ (3529.42 g/mol) requires C, 55.8, H, 4.2, N, 1.6, S, 1.8 % IR(cm^{-1}): $\nu_{\text{C}=\text{N}}$: 1597, $\nu_{\text{Pd}-\text{Cl}}$: 280m. ^1H NMR (MeCOMe- d_6 , δ ppm, J Hz): 8.10 (s, 4H, HC=N), 7.02 (m, 4H, H5), 4.25 (s, 12H, MeO), 3.58 (s, 12H, MeO), 3.48 (s, 12H, MeO). $^{31}\text{P}\{-^1\text{H}\}$ NMR (MeCOMe- d_6 , δ ppm): 1.48 (s), -150.0 (sept, PF_6 , ^1JPF 707.7).

Synthesis of $[2,3,4\text{-(MeO)}_3\text{C}_6\text{H}_2(\text{CH})=\text{NC}_6\text{H}_4]_2\text{O}$ (**b**)

A 1:2 mixture of ($p\text{-NH}_2\text{C}_6\text{H}_4$) $_2\text{O}$ (1.0 g, 4.99 mmol) and 2,3,4-(MeO) $_3\text{C}_6\text{H}_2\text{CHO}$ (2.0 g, 9.98 mmol) in ethanol (50 cm^3) was stirred at room temperature for 24 h. The white precipitate formed was filtered off, washed with water and dried under vacuum. Yield: 2.273 g, 82%. Anal. Found: C: 68.8, H: 5.9, N: 5.1 %; $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_7$ (556.61 g/mol) requires C: 69.0, H: 5.8, N: 5.0 %. IR(cm^{-1}): $\nu_{\text{C}=\text{N}}$ 1609. ^1H NMR (DMSO- d_6 , δ /ppm, J /Hz): 8.64 (s, 2H, HC=N); 7.75 (d, 2H, H6, $^3\text{JH6H5} = 8.7$); 7.25 (d, 4H, H9H10, $N = 8.3$); 7.03 (d, 4H, H7H8, $N = 8.3$); 6.93 (d, 2H, H5, $^3\text{JH5H6} = 8.7$); 3.86 (s, 6H, MeO); 3.84 (s, 6H, MeO); 3.75 (s, 6H, MeO).

Synthesis of $\{[\text{Pd}\{2,3,4\text{-(MeO)}_3\text{C}_6\text{H}(\text{CH})=\text{NC}_6\text{H}_4\}(\mu\text{-O}_2\text{CMe})]_2\text{O}\}_2$ (**Ib**)

The ligand **b** (0.500 g, 0.898 mmol) and palladium(II) acetate (0.403 g, 1.795 mmol) were added in toluene (30 cm^3) and the resulting mixture was stirred at 55° C for 24 h. After cooling to r. t. the red oil formed was separated, to afford the final product as a red solid. Yield: 300 mg, 40%. Anal. Found: C 48.6, H 4.2, N 3.3 %; $\text{C}_{72}\text{H}_{72}\text{N}_4\text{O}_{22}\text{Pd}_4$ (1771.04 g/mol) requires C 48.8, H 4.1, N 3.2 %. IR(cm^{-1}): $\nu_{\text{C}=\text{N}}$ 1564. ^1H NMR (DMSO- d_6 , δ ppm, J Hz): 8.02 (s, 4H, HC=N), 6.97 (d, 8H, H9H10, $N = 8.3$); 6.76 (d, 8H, H7H8, $N = 8.3$), 5.92 (s, 4H, H5), 3.74 (s, 12H, MeO), 3.65 (s, 12H, MeO), 3.57 (s, 12H, MeO), 2.17 (s, 6H, MeCO $_2$), 1.48 (s, 6H, MeCO $_2$).

Synthesis of $\{[\text{Pd}\{2,3,4\text{-(MeO)}_3\text{C}_6\text{H}(\text{CH})=\text{NC}_6\text{H}_4\}(\mu_2\text{-Cl})]_2\text{O}\}_2$ (**Iib**)

A solution of **Ib** (0.472 g, 0.266 mmol) in 25 cm^3 of dichloromethane was treated with a 0.05M solution of NaCl in ca. 35 cm^3 of water. The organic part was separated and the solvent was removed under reduced pressure. Later the residue was recrystallized on a mixture of dichloromethane-hexane giving a yellow solid. Yield: 312.8 mg, 70%. Anal. Found: C, 46.2, H, 3.7, N, 3.2 % $\text{C}_{64}\text{H}_{60}\text{Cl}_4\text{N}_4\text{O}_{14}\text{Pd}_4$ (1676.67 g/mol) requires C, 45.9, H, 3.6, N, 3.3 %. IR(cm^{-1}): $\nu_{\text{C}=\text{N}}$: 1572, $\nu_{\text{Pd}-\text{Cl}}$: 310, $\nu_{\text{Pd}-\text{Cl}}$: 294. ^1H NMR (CDCl_3 , δ ppm, J Hz): 8.08 (s, 4H, HC=N), 7.24 (d, 8H, -O-Ph, $N = 8.7$), 6.91 (d, 8H, -O-Ph, $N = 8.7$), 6.74 (s, 4H, H5), 3.97 (s, 12H, MeO), 3.94 (s, 12H, MeO), 3.79 (s, 12H, MeO).

Synthesis of $\{[\text{Pd}\{2,3,4\text{-(MeO)}_3\text{C}_6\text{H}(\text{CH})=\text{NC}_6\text{H}_4\}(\mu_2\text{-Br})]_2\text{O}\}_2$ (**Iiib**)

A solution of **Ib** (0.100 g, 0.056 mmol) in 10 cm^3 of dichloromethane was treated with a 0.05M solution of NaBr in ca. 8 cm^3 of water. The organic part was separated and the solvent was removed under reduced pressure. Later the residue was recrystallized on a mixture of dichloromethane-hexane giving a red solid. Yield: 35.5 mg, 34%. Anal. Found: C, 41.2, H, 3.2, N, 3.1 %; $\text{C}_{64}\text{H}_{60}\text{Br}_4\text{N}_4\text{O}_{14}\text{Pd}_4$ (1854.48 g/mol) requires C, 41.5, H, 3.3, N, 3.0 %. IR(cm^{-1}): $\nu_{\text{C}=\text{N}}$: 1570. ^1H NMR (CDCl_3 , δ ppm, J Hz): 8.12 (s, 4H, HC=N), 7.24 (d, 8H, -O-Ph, $N = 9.3$), 6.93 (d, 8H, -O-Ph, $N = 9.3$), 6.91 (s, 4H, H5), 3.96 (s, 12H, MeO), 3.95 (s, 12H, MeO), 3.79 (s, 12H, MeO). ^1H NMR (DMSO- d_6 , δ ppm, J Hz): 8.20 (s, 4H, HC=N), 7.30 (m, 8H, -O-Ph, $N = 7.5$), 7.30 (s, 4H, H5), 6.99 (m, 8H, -O-Ph, $N = 7.5$), 3.83 (s, 12H, MeO), 3.75 (s, 12H, MeO), 3.64 (s, 12H, MeO).

Synthesis of $[\text{Pd}\{2,3,4\text{-(MeO)}_3\text{C}_6\text{H}(\text{CH})=\text{NC}_6\text{H}_4\}(\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{-}P,P)]_2\text{O} \cdot 2\text{PF}_6$ (**1b**)

$\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (8.5 mg, 0.022 mmol) and ammonium hexafluorophosphate (0.004 g, 0.024 mmol) were added to a solution of **IIb** (8.5 mg, 0.005 mmol) or **IIIb** (0.093 g, 0.005 mmol) in acetone (0.6 cm³). ¹H NMR (MeCOMe-d₆, δ ppm, J Hz): 8.50 (d, 2H, HC=N, ⁴JHP_{trans} 6.8), 7.25 (d, 4H, H9H10, N = 8.5), 6.55 (d, 4H, H7H8, N = 8.5), 6.01 (m, 2H, H5), 4.60 (m, 4H, PCH₂P, N = 19.6), 3.97 (s, 6H, MeO), 3.69 (s, 6H, MeO), 3.15 (s, 6H, MeO). ³¹P-¹H NMR (MeCOMe-d₆, δ ppm, J Hz): -36.0 (d, ²JPP 63.0), -12.2 (d, ²JPP 63.0), -150.0 (sept, PF₆, ¹JPF 707.7).

Synthesis of $\{[\text{Pd}\{2,3,4\text{-(MeO)}_3\text{C}_6\text{H}(\text{CH})=\text{NC}_6\text{H}_4\}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2\text{-}P,P)]_2(\mu\text{-Cl})\text{O}\}_2 \cdot 2\text{PF}_6$ (**2b**)

$\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (8.5 mg, 0.022 mmol) and ammonium hexafluorophosphate (0.004 g, 0.024 mmol) were added to a solution of **IIb** (8.5 mg, 0.005 mmol) in acetone-d₆ (0.6 cm³) and left to stand until complete conversion. Yield: 16 mg, 95% related to **IIb**. Anal. Found: C, 57.2, H, 4.5, N, 1.7 %; C₁₆₄H₁₄₈Cl₂F₁₂N₄O₁₄P₁₀Pd₄ (3433.25 g/mol) requires C, 57.4, H, 4.4, N, 1.6 %. IR(cm⁻¹): νC=N: 1594, νPd-Cl: 279m. ¹H NMR (MeCOMe-d₆, δ ppm, J Hz): 8.12 (s, 4H, HC=N), 7.00 (m, 4H, H5), 6.57 (d, 8H, H7H8, N = 8.7), 4.38 (m, 8H, PCH₂P), 4.23 (s, 12H, MeO), 3.55 (s, 12H, MeO), 3.42 (s, 12H, MeO). ³¹P-¹H NMR (MeCOMe-d₆, δ ppm): 1.5 (s, 1P), -150.0 (sept, ¹JPF 707.7).

Synthesis of $\{[\text{Pd}\{2,3,4\text{-(MeO)}_3\text{C}_6\text{H}(\text{CH})=\text{NC}_6\text{H}_4\}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2\text{-}P,P)]_2(\mu\text{-Br})\text{O}\}_2 \cdot 2\text{PF}_6$ (**3b**)

$\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (7.1 mg, 0.018 mmol) and ammonium hexafluorophosphate (0.003 g, 0.018 mmol) were added to a solution of **IIIb** (8.5 mg, 0.0046 mmol) in acetone-d₆ (0.6 cm³) and left to stand until complete conversion. Yield: 14 mg, 90% related to **IIIb**. Anal. Found: C, 55.9; H, 4.2; N, 1.6 %; C₁₆₄H₁₄₈Br₂F₁₂N₄O₁₄P₁₀Pd₄ (3522.21 g/mol) requires C, 55.9; H, 4.2; N, 1.6 %. IR(cm⁻¹): νC=N: 1590. ¹H NMR (MeCOMe-d₆, δ ppm, J Hz): 8.16 (s, 4H, HC=N), 7.05 (m, 4H, H5), 4.60 (m, 8H, PCH₂P), 4.23 (s, 12H, MeO), 3.55 (s, 12H, MeO), 3.43 (s, 12H, MeO). ³¹P-¹H NMR (MeCOMe-d₆, δ ppm): 0.66 (s, 1P), -150.0 (sept, ¹JPF 707.7).

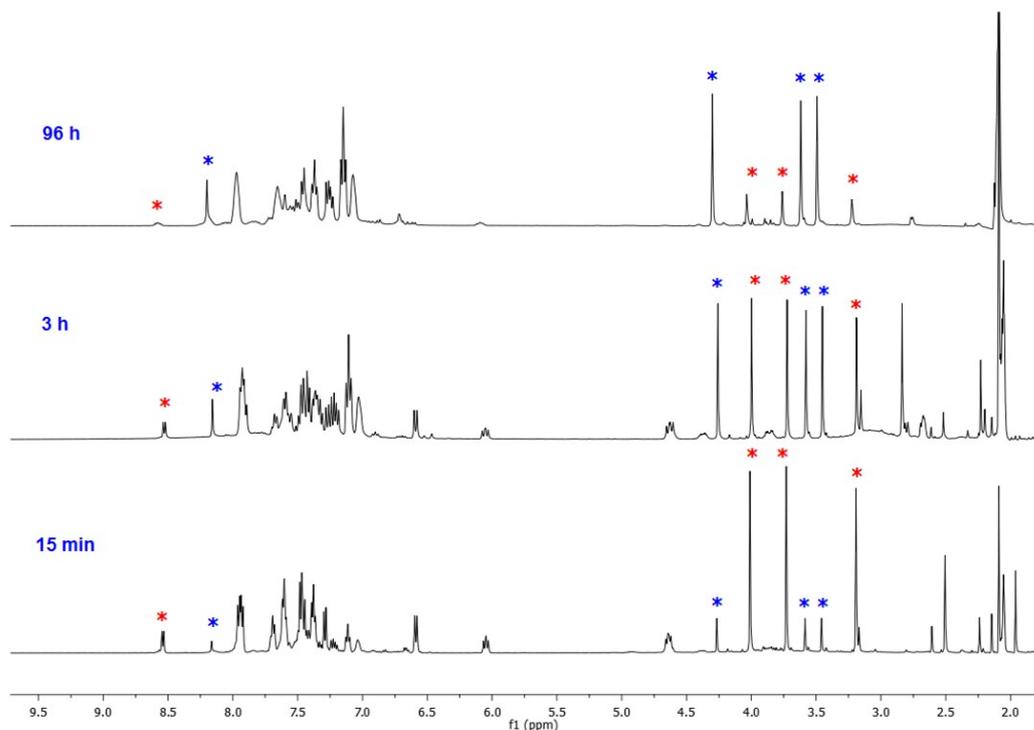


Figure 1ESI. Time-dependent ¹H NMR plot for the **1a** → **2a** shift at r.t. Compound **1a**,*. Compound **2a**,*.

Crystal Structure Analysis

Three-dimensional, X-ray data were collected on a Bruker Kappa-APEX II; Siemens Smart CCD diffractometer by the ω scan method using graphite-monochromated Mo-K α radiation. All the measured reflections were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full matrix least squares on F^2 . Hydrogen atoms were included in calculated positions. Refinement converged at a final R1 = 0.0773 and wR2 = 0.1950 (compound **2a**), R1 = 0.0442, wR2 = 0.1292 (compound **2b**), R1 = 0.0437 and wR2 = 0.1252 (compound **3b**) with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out using the program package SHELX-97.

Table 1 Crystal data and structure refinement for **2a**.

Identification code	2a
Empirical formula	C ₁₇₃ H ₁₆₃ Cl ₈ F ₁₂ N ₄ O ₁₈ P ₁₀ Pd ₄ S ₂
Formula weight	3897.09
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	a = 14.8431(11) Å $\alpha = 90^\circ$. b = 26.413(2) Å $\beta =$ 93.090(6)°. c = 22.3504(19) Å $\gamma = 90^\circ$.
Volume	8749.8(12) Å ³
Z	2
Density (calculated)	1.479 Mg/m ³
Absorption coefficient	0.718 mm ⁻¹
F(000)	3966
Crystal size	0.19 x 0.18 x 0.08 mm ³
Theta range for data collection	1.58 to 24.43°.
Index ranges	-17 ≤ h ≤ 16, -30 ≤ k ≤ 30, - 24 ≤ l ≤ 25
Reflections collected	87544
Independent reflections	14410 [R(int) = 0.2121]
Completeness to theta = 24.43°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.928 and 0.865
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	14410 / 42 / 1074
Goodness-of-fit on F2	0.992
Final R indices [I > 2σ(I)]	R1 = 0.0773, wR2 = 0.1950
R indices (all data)	R1 = 0.1533, wR2 = 0.2570
Largest diff. peak and hole	2.323 and -0.890 e.Å ⁻³

Table 2 Selected bond lengths [Å] for **2a**

Pd(1)-C(1)	1.996(9)	C(30)-	1.863(9)
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Pd(1)-P(1)	2.334(3)	P(1) C(30)-	1.833(9)
Pd(1)-P(3)	2.342(3)	P(2) C(31)-	1.816(9)
Pd(1)- Cl(1)	2.452(2)	P(3) C(31)-	1.859(9)
Pd(2)- C(17)	2.002(1)	P(4) C(7)-N(1)	1.284(1)
Pd(2)-P(2)	2.299(3)	C(23)- N(2)	1.266(1)
Pd(2)-P(4)	2.326(3)	C(11)- S(1)	1.754(9)
Pd(2)- Cl(1)	2.416(2)	C(28)- S(1)	1.761(1)
Pd(1)- Pd(2)	3.253(1)		0)

Table 3 Selected angles [°] for **2a**

C(1)-Pd(1)-P(1)	88.9(3)	P(4)-Pd(2)- Cl(1)	95.75(9)
C(1)-Pd(1)-P(3)	87.8(3)	Pd(2)-Cl(1)- Pd(1)	83.87(8)
P(1)-Pd(1)-P(3)	168.20(9)	P(2)-C(30)-P(1)	116.6(5)
C(1)-Pd(1)- Cl(1)	175.6(3)	P(3)-C(31)-P(4)	116.8(5)
P(1)-Pd(1)- Cl(1)	92.60(9)	O(7)-S(1)-O(8)	118.2(5)
P(3)-Pd(1)- Cl(1)	91.54(9)	O(7)-S(1)- C(11)	108.7(5)
C(17)-Pd(2)- P(2)	88.7(3)	O(8)-S(1)- C(11)	108.3(5)
C(17)-Pd(2)- P(4)	86.5(3)	O(7)-S(1)- C(28)	108.1(5)
P(2)-Pd(2)-P(4)	173.61(1)	O(8)-S(1)- C(28)	107.3(5)
C(17)-Pd(2)- Cl(1)	171.8(3)	C(11)-S(1)- C(28)	105.6(4)
P(2)-Pd(2)- Cl(1)	88.41(9)		

Table 4 Crystal data and structure refinement for **2b**

Identification code	2b	
Empirical formula	C ₁₇₆ H ₁₇₂ Cl ₂ F ₁₂ N ₄ O ₂₀ P ₁₀ Pd ₄	
Formula weight	3697.37	
Temperature	97(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 16.4987(6) Å	α = 82.897(2)°.
	b = 16.5332(6) Å	β = 71.882(2)°.
	c = 17.1548(5) Å	γ = 75.240(2)°.
Volume	4295.6(3) Å ³	

Z	1
Density (calculated)	1.429 Mg/m ³
Absorption coefficient	0.614 mm ⁻¹
F(000)	1892
Crystal size	0.250 x 0.220 x 0.160 mm ³
Theta range for data collection	1.275 to 25.000°
Index ranges	-19<=h<=19, -19<=k<=19, -20<=l<=20
Reflections collected	140354
Independent reflections	15101 [R(int) = 0.0442]
Completeness to theta = 25.000°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9010 and 0.8216
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	15101 / 774 / 1046
Goodness-of-fit on F ²	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1292
R indices (all data)	R1 = 0.0515, wR2 = 0.1339
Largest diff. peak and hole	2.151 and -0.969 e.Å ⁻³

Table 5 Selected bond lengths [Å] for **2b**

Pd(1)-C(1)	1.997(4)	P(1)-C(81)	1.844(3)
Pd(1)-P(2)	2.3228(8)	P(2)-C(81)	1.834(3)
Pd(1)-P(4)	2.3331(9)	P(3)-C(26)	1.832(4)
Pd(1)-Cl(1)	2.4328(8)	P(4)-C(26)	1.831(4)
Pd(1)-Pd(2)	3.1735(4)	N(1)-C(7)	1.271(5)
Pd(2)-C(82)	1.994(4)	N(2)-C(20)#1	1.278(5)
Pd(2)-P(3)	2.3168(9)	O(7)-C(11)	1.388(5)
Pd(2)-P(1)	2.3569(9)	O(7)-C(14)	1.400(5)
Pd(2)-Cl(1)	2.4607(9)	Pd(1)-Pd(2)	3.173(4)

Table 6 Selected angles [°] for **2b**

C(1)-Pd(1)-P(2)	84.98(10)	P(3)-Pd(2)-P(1)	168.01(3)
C(1)-Pd(1)-P(4)	85.96(10)	C(82)-Pd(2)-Cl(1)	176.62(1)
P(2)-Pd(1)-P(4)	168.62(3)	P(3)-Pd(2)-Cl(1)	91.27(3)
C(1)-Pd(1)-Cl(1)	171.66(1)	P(1)-Pd(2)-Cl(1)	96.33(3)
P(2)-Pd(1)-Cl(1)	93.40(3)	Pd(1)-Cl(1)-	80.85(3)

Cl(1)		Pd(2)	
P(4)-Pd(1)-	94.58(3)	P(4)-C(26)-P(3)	117.2(2)
Cl(1)			
C(82)-Pd(2)-	85.79(10)	P(2)-C(81)-P(1)	115.01(17)
P(3)			
C(82)-Pd(2)-	86.30(10)	C(11)-O(7)-	117.9(3)
P(1)		C(14)	

Table 7 Crystal data and structure refinement for **3b**.

Identification code	3b
Empirical formula	C ₈₅ H ₈₀ Br F ₆ N ₂ O ₈ P ₅ Pd ₂
Formula weight	1819.07
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
	a = 16.4980(17) Å α = 83.263(7)°.
Unit cell dimensions	b = 16.5610(16) Å β = 71.977(7)°.
	c = 17.1294(19) Å γ = 75.228(7)°.
Volume	4299.7(8) Å ³
Z	2
Density (calculated)	1.405 Mg/m ³
Absorption coefficient	1.042 mm ⁻¹
F(000)	1848
Crystal size	0.160 x 0.150 x 0.090 mm ³
Theta range for data collection	1.273 to 25.000°.
Index ranges	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20
Reflections collected	122609
Independent reflections	15141 [R(int) = 0.0595]
Completeness to theta = 25.000°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.912 and 0.851
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	15141 / 0 / 962
Goodness-of-fit on F ²	1.265
Final R indices [I > 2σ(I)]	R1 = 0.0437, wR2 = 0.1252
R indices (all data)	R1 = 0.0547, wR2 = 0.1301
Largest diff. peak and hole	2.036 and -0.918 e.Å ⁻³

Table 8 Selected bond lengths [Å] for **3b**

Pd(1)-	2.006(4)	P(2)-	1.831(4)
C(20)		C(55)	
Pd(1)-P(2)	2.3237(10)	P(3)-	1.847(4)
		C(55)	

Pd(1)-P(5)	2.3338(11)	P(4)-C(30)	1.828(4)
Pd(1)-Br(3)	2.5459(5)	P(5)-C(30)	1.835(4)
Pd(2)-C(1)	1.995(4)	N(1)-C(7)	1.281(5)
Pd(2)-P(4)	2.3168(11)	N(2)-C(26)	1.276(5)
Pd(2)-P(3)	2.3557(11)	O(1)-C(15)	1.388(5)
Pd(2)-Br(3)	2.5722(6)	O(1)-C(11)	1.404(5)
Pd(1)-Pd(2)	3.222(5)		

Table 9 Selected angles [°] for **3b**

C(20)-Pd(1)-P(2)	85.06(11)	P(4)-Pd(2)-P(3)	167.17(4)
C(20)-Pd(1)-P(5)	85.55(11)	C(1)-Pd(2)-Br(3)	176.49(1)
P(2)-Pd(1)-P(5)	167.79(4)	P(4)-Pd(2)-Br(3)	91.19(3)
C(20)-Pd(1)-Br(3)	171.50(1)	P(3)-Pd(2)-Br(3)	96.77(3)
P(2)-Pd(1)-Br(3)	93.90(3)	Pd(1)-Br(3)-Pd(2)	78.039(1)
P(5)-Pd(1)-Br(3)	94.24(3)	P(2)-C(55)-P(3)	115.8(2)
C(1)-Pd(2)-P(4)	85.70(11)	P(4)-C(30)-P(5)	118.2(2)
C(1)-Pd(2)-P(3)	86.02(12)	C(15)-O(1)-C(11)	117.9(3)

Table 10 Interactions between the dpdm and the aromatic rings of the ditopic linkers for:

2a

$\pi \cdots \pi$ interactions	Cg \cdots Cg	α	β	γ
Cg(1) \cdots Cg(2)	3.612 Å	20.0°	18.7°	23.7°
Cg(1) \cdots Cg(3)	3.587 Å	18.5°	12.5°	14.9°

Cg rings (1): C(1)-C(6); (2): C(32)-C(37); (3): C(56)-C(61)

2b

$\pi \cdots \pi$ interactions	Cg \cdots Cg	α	β	γ
Cg(1) \cdots Cg(2)	3.668 Å	23.3°	11.3°	18.9°
Cg(1) \cdots Cg(3)	3.657 Å	17.2°	21.6 °	26.4

Cg rings (1): C(1)-C(6); (2): C(45)-C(50); (3): C(69)-C(74)

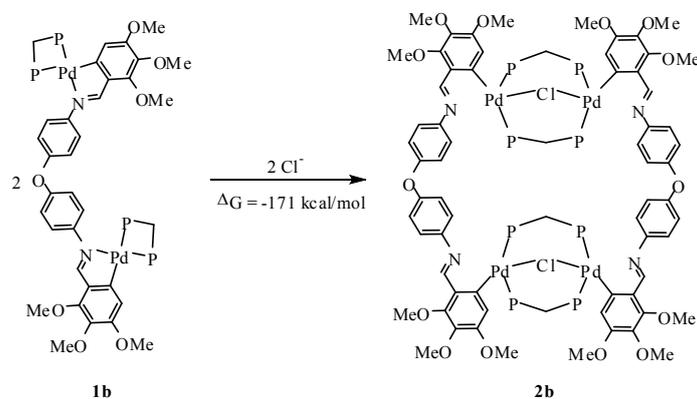
3b

$\pi \cdots \pi$ interactions	Cg \cdots Cg	α	β	γ
Cg(1) \cdots Cg(2)	3.881 Å	29.0°	14.4°	26.3°
Cg(1) \cdots Cg(3)	3.592 Å	21.7°	2.2°	19.7°

Cg rings (1): C(1)-C(6); (2): C(49)-C(54); (3): C(74)-C(79)

DFT report A-frame

Reaction studied



Scheme 2ESI: P = PPh₂.

In this case, both structures **1b** and **2b**, have been optimised using the package of programs g09² and to the B3LYP/LANL2DZ-ECP³/6-31-G(d) level of theory, frequency calculations were also performed giving not imaginary frequencies and thus confirming the stationary point in each case. For compound **1b** two conformers were found according to the rotation of the COC angle of the ether link between the cyclometalated moieties (**1b1** and **1b2**); these belong to the structure with the cyclometalated moieties pointing to the same side (**1b1**) and to different sides (**1b2**). To the purpose of this reaction calculation the ion Cl⁻ has also been computed at the same level as the others. The aim of this study is to determine which of the molecules is more stable from a thermodynamic point of view (**1b** or **2b**). The following equation has been used to calculate ΔG for the formation of **2b**:

$$\Delta G_{\text{reaction}} = \Delta G_{2b} - 2 \times (\Delta G_{1b} + \Delta G_{\text{Cl}^-})$$

The experimental part shows that, besides both compounds are formed during the reaction process (see NMR data), the A-frame complex (**2b**) shows higher thermodynamic stability being

² M. J. Frisch *et al.* *Gaussian 09*, Revision D.01; Gaussian, Inc., Wallingford CT, **2013**.

³ P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270-283.

always the only one that crystallises and this is also corroborated by the DFT calculations which determine that the ΔG of the reaction is equal to -171Kcal/mol.

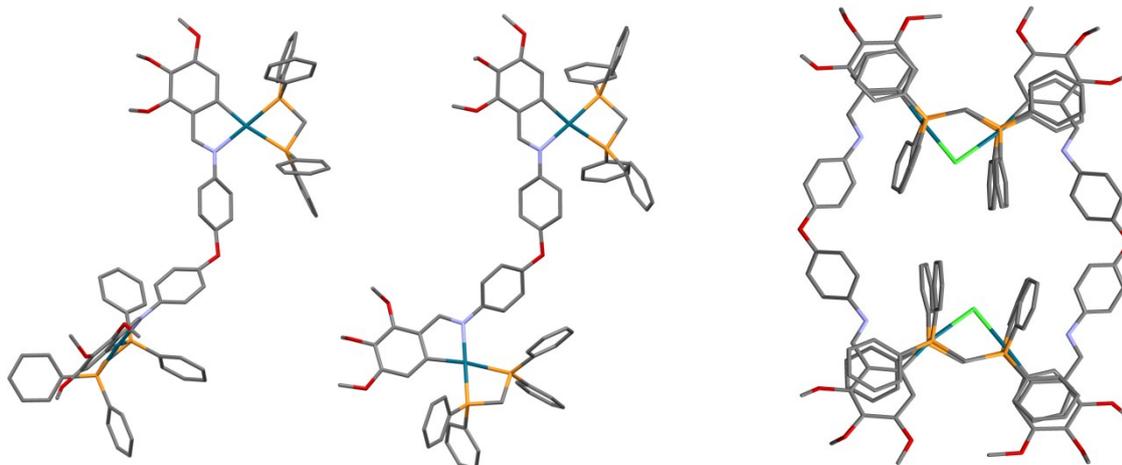


Figure 2ESI. Structures optimised in this paper. From left to the right **1b1**, **1b2** and **2b**.

The difference between **1b1** and **1b2** is 0.65 kcal/mol, so they are almost isoenergetic, which means that the $C\hat{O}C$ angle has free rotation and not major steric hindrance is present.

In the tables below a compilation of the distances and angles that suffer changes during the reaction of formation of **2b** is shown, together with the calculated structures of the compounds **1b1** and **1b2** and A-frame (Scheme 2ESI)

Table 7 Comparison of the main angles in $^{\circ}$. Here it can be noticed that the $CC=N$ and PCH_2P are bigger in the A-frame compound giving less constricted cycles, thus more stable.

Angle	2b	1b1	1b2
	123.2307		
	1		
	123.1937	119.3110	119.3277
	3	5	9
CC=N	123.1929	119.1926	119.3560
	4	4	4
	123.1630		
	5		
	115.0105		
	0		
	117.1924		
PCH₂	9	99.38091	99.29091
P	117.1924	99.28186	98.88648
	9		
	114.9866		
	9		
COC	118.3220	121.0051	121.5760
	118.3430		