

Divergent Behaviour on the Cyclopalladation of Phosphorus Ylides and Iminophosphoranes

David Aguilar, Miguel Angel Aragüés, Raquel Bielsa, Elena Serrano, Rafael Navarro, and Esteban P.Urriolabeitia*.

Departamento de Compuestos Organometálicos, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza (Spain).

E-mail: esteban@unizar.es

Dr. Esteban P. Urriolabeitia (corresponding author): Universidad de Zaragoza-C.S.I.C., Plaza de San Francisco s/n, E-50009 Zaragoza (Spain). Fax: (+34) 976761187. E-mail: esteban@unizar.es

SUPPORTING INFORMATION

Complete Experimental Section

Safety note: *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and they should be handled with great caution. See *J. Chem. Ed.* **1973**, *50*, A335-A337.

General Methods. Solvents were dried and distilled under argon using standard procedures before use. Elemental analyses were carried out on a Perkin-Elmer 2400-B microanalyser. Infrared spectra ($4000\text{-}200\text{ cm}^{-1}$) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from nujol mulls between polyethylene sheets. The ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded in CDCl_3 , CD_2Cl_2 or dmso-d_6 solutions at $25\text{ }^\circ\text{C}$ (other temperatures were specified) on Bruker ARX-300, Avance-400 and Avance-500 spectrometers (δ , ppm; J , Hz); ^1H and $^{13}\text{C}\{^1\text{H}\}$ were referenced using the solvent signal as internal standard while $^{31}\text{P}\{^1\text{H}\}$ was externally referenced to H_3PO_4 (85%). The ^1H SELNO-1D and SELRO-1D NMR experiments were performed with optimized mixing times (D8/P15), depending of the irradiated signal. ESI/APCI mass spectra were recorded using an Esquire 3000 ion – trap mass spectrometer (Bruker Daltonic GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas. Helium served as a cooling gas for the ion trap and collision gas for MS^n experiments. Other mass spectra (positive ion FAB) were recorded from CH_2Cl_2 solutions on a V. G. Autospec spectrometer. The starting compounds **1a**, **1d**, **1f¹** and **8a²** were prepared according to reported methods.

Synthesis of Iminophosphoranes. Compounds **1b**, **1c** and **1e** were prepared following the method reported by Pomerantz *et al.*¹ Here we described the synthesis of **1b** as a representative example. To a cooled ($0\text{ }^\circ\text{C}$) solution of $4\text{-MeOC}_6\text{H}_4\text{C(O)NH}_2$ (0.502 g,

3.32 mmol) and PPh₃ (0.871 g, 3.32 mmol) in freshly distilled THF (20 mL) under Ar, a solution of DAD (0.765 g, 3.32 mmol) in THF (5 mL) was added dropwise. The resulting solution was allowed to reach r. t. and then stirred for additional 12 h. After the reaction time, the solvent was removed to dryness and the oily residue was treated with dry Et₂O (20 mL), giving **1b** as a yellow solid. Yield: 1.34 g (98.2 %). Anal. Calc. for C₂₆H₂₂NO₂P (411.44): C, 75.90; H, 5.39; N, 3.40. Found: C, 75.95; H, 5.50; N, 3.42. MS (FAB+): m/z (%) = 412 [M⁺, 25%]. IR (ν , cm⁻¹): 1617 (ν_{CO}), 1339 (ν_{NP}). ¹H NMR (CDCl₃): δ = 3.78 (s, 3H, OMe), 6.83 (dd, 2H, H₃+H₅, ³J_{HH} = 8.8, ⁴J_{HH} = 1.8), 7.38-7.43 (m, 6H, H_m, PPh₃), 7.46-7.50 (m, 3H, H_p, PPh₃), 7.74-7.79 (m, 6H, H_o, PPh₃), 8.23 (dd, 2H, H₂+H₆). ¹³C{¹H} NMR (CDCl₃): δ = 54.28 (OMe), 111.77 (C₃), 127.48 (d, ¹J_{P-C} = 99.5, C_i, PPh₃), 127.61 (d, ³J_{P-C} = 12.3, C_m, PPh₃), 130.33 (d, ⁴J_{P-C} = 2.1, C_p, PPh₃), 130.48 (C₁), 131.12 (d, ⁴J_{P-C} = 2.8, C₂), 132.11 (d, ²J_{P-C} = 9.8, C_o, PPh₃), 160.75 (C₄), 175.00 (d, ¹J_{P-C} = 7.9, CO). ³¹P{¹H} NMR (CDCl₃): δ = 20.35.

Synthesis of 1c. 3-MeOC₆H₄C(O)NH₂ (0.500 g, 3.31 mmol) was reacted with PPh₃ (0.870 g, 3.31 mmol) and DAD (0.760 g, 3.31 mmol) to give **1c** as a pale yellow solid. Yield: 0.541g (39.8 %). Anal. Calcd. for C₂₆H₂₂NO₂P (411.44): C, 75.90; H, 5.39; N, 3.40; found: C, 76.06; H, 5.55; N, 3.41. MS (FAB+): m/z (%) = 412 [M⁺, 30%]. IR (ν , cm⁻¹): 1595 (ν_{CO}), 1329 (ν_{NP}). ¹H NMR (CD₂Cl₂): δ = 3.76 (s, 3H, OMe), 6.91 (dd, 1H, H₄, ³J_{HH} = 8.0, ⁴J_{HH} = 2.7), 7.22 (t, 1H, H₅, ³J_{HH} = 8.0), 7.39-7.45 (m, 6H, H_m, PPh₃), 7.50-7.54 (m, 3H, H_p, PPh₃), 7.71-7.76 (m, 7H, H₂ + H_o(PPh₃)), 7.82 (d, 1H, H₆). ¹³C{¹H} NMR (CDCl₃): δ = 55.38 (OMe), 113.79 (d, ⁴J_{P-C} = 2.7, C₂), 117.39 (C₄), 122.29 (d, ⁴J_{P-C} = 2.1, C₆), 128.31 (d, ¹J_{P-C} = 97.1, C_i, PPh₃), 128.67 (C₅), 128.75 (d, ³J_{P-C} = 2.3, C_m, PPh₃), 132.30 (d, ⁴J_{P-C} = 2.8, C_p, PPh₃), 133.18 (d, ²J_{P-C} = 9.9, C_o, PPh₃),

140.24 (d, $^3J_{P-C} = 20.6$, C₁), 159.29 (C₃), 176.10 (d, $^2J_{P-C} = 7.9$, CO). $^{31}P\{^1H\}$ NMR (CD₂Cl₂): $\delta = 20.79$.

Synthesis of 1e. 3-MeC₆H₄C(O)NH₂ (0.516 g, 3.82 mmol) was reacted with PPh₃ (1.00 g, 3.82 mmol) and DAD (0.88 g, 3.82 mmol) to give **1e** as a white solid. Yield: 0.887 g, (58.7 %). Anal. Calc. for C₂₆H₂₂NOP (395.44): C, 78.96; H, 5.61; N, 3.54; found: C, 78.91; H, 4.98; N 3.95. MS (FAB+): m/z (%) = 396 [M⁺, 22%]. IR(ν , cm⁻¹): 1596 (ν_{CO}), 1326 (ν_{NP}). 1H NMR (CD₂Cl₂): $\delta = 2.31$ (s, 3H, Me), 7.17-7.19 (m, 2H, C₆H₄), 7.38-7.43 (m, 6H, H_m, PPh₃), 7.48-7.52 (m, 3H, H_p, PPh₃), 7.71-7.76 (m, 6H, H_o, PPh₃), 7.97-8.01 (m, 2H, C₆H₄). $^{13}C\{^1H\}$ NMR (CDCl₃): $\delta = 21.42$ (Me), 126.77 (C₆H₄), 127.62 (C₆H₄), 128.69 (d, $^3J_{P-C} = 12.2$, C_m, PPh₃), 129.87 (d, $^1J_{P-C} = 98.1$, C_i, PPh₃), 130.09 (C₆H₄), 131.49 (C₆H₄), 132.23 (C_p, PPh₃), 133.21 (d, $^2J_{P-C} = 9.9$, C_o, PPh₃), 137.23 (C₃, C₆H₄), 138.20 (d, $^3J_{P-C} = 17.3$, C₁, C₆H₄), 179.58 (d, $^2J_{P-C} = 6.4$, CO). $^{31}P\{^1H\}$ NMR (CD₂Cl₂): $\delta = 20.70$.

Synthesis of 2a. To a solution of Pd(OAc)₂ (0.500 g, 1.31 mmol) in CH₂Cl₂ (20 mL), **1a** (0.294 g, 1.31 mmol) was added and the resulting solution was refluxed for 2 h. At this point some decomposition is evident. After cooling, the black suspension was filtered over Celite, giving an orange solution. This clear solution was evaporated to dryness and the oily residue was redissolved in MeOH (20 mL). To this solution an excess of anhydrous LiCl (0.222 g, 5.24 mmol) was added, and the stirring was prolonged at r.t. for 20 h. During this time a yellow solid (**2a**) precipitated, which was filtered, washed with additional MeOH (10 mL) and Et₂O (40 mL) and dried by suction. Yield: 0.205 g (30.0 %). Anal. Calc. for C₅₀H₃₈Cl₂N₂O₂P₂Pd₂ (1044.55): C, 57.49; H, 3.67; N, 2.68; found: C, 57.37; H, 4.01; N, 2.58. MS (FAB+): m/z (%) = 487 [(M/2-Cl)⁺, 28%]. IR (ν , cm⁻¹): 1654 (ν_{CO}), 1284 (ν_{NP}). 1H NMR (CDCl₃): $\delta = 6.77$ -6.80 (m,

2H, H₅, H₆), 6.90 (t, 1H, H₄, ³J_{HH} = 7.5), 7.15 (d, 1H, H₃, ³J_{HH} = 7.5), 7.33-7.38 (m, 6H, H_m, PPh₃), 7.43-7.46 (m, 3H, H_p, PPh₃), 7.89-7.94 (m, 6H, H_o, PPh₃). ³¹P{¹H} NMR (CDCl₃): δ = 30.20.

Synthesis of 2b. Compound **2b** was prepared following the same synthetic method than that reported for **2a**. Thus, Pd(OAc)₂ (0.273 g, 1.21 mmol) was reacted with **1b** (0.500 g, 1.21 mmol) and LiCl (0.206 g, 4.86 mmol) to give **2b** as a yellow solid. Yield: 0.116 g, (17.3 %). Anal. Calc. for C₅₂H₄₂Cl₂N₂O₄P₂Pd₂ (1104.57): C, 56.54; H, 3.83; N, 2.54; found: C, 55.93; H, 3.30; N, 2.70. MS (FAB+): m/z (%) = 516 [(M/2- Cl)⁺, 30%]. IR (v, cm⁻¹): 1649 (ν_{CO}), 1310 (ν_{NP}). ¹H NMR (CDCl₃): δ = 3.51 (s, 3H, OMe), 6.32 (s, 1H, H₆), 6.48 (dd, 1H, H₄, ³J_{HH} = 8.3, ⁴J_{HH} = 2.3), 7.11 (d, 1H, H₃, ³J_{HH} = 8.3), 7.31-7.36 (m, 6H, H_m, PPh₃), 7.42-7.46 (m, 3H, H_p, PPh₃), 7.87-7.92 (m, 6H, H_o, PPh₃). ³¹P{¹H} NMR (CDCl₃): δ = 30.20.

Synthesis of 2c. Compound **2c** was prepared following the same synthetic method than that reported for **2a**. Thus, Pd(OAc)₂ (0.160 g, 0.73 mmol) was reacted with **1c** (0.301 g, 0.73 mmol) and LiCl (0.124 g, 2.93 mmol) to give **2c** as a yellow solid. Yield: 0.395 g, (97.8 %). Anal. Calc. for C₅₂H₄₂Cl₂N₂O₄P₂Pd₂ (1104.57): C, 56.54; H, 3.83; N, 2.54; found: C, 56.64; H, 3.90; N, 2.50. MS (FAB+): m/z (%) = 516 [(M/2- Cl)⁺, 20%]. IR (v, cm⁻¹): 1643 (ν_{CO}), 1310 (ν_{NP}). ¹H NMR (CDCl₃): δ = 3.05 (s, 3H, OMe), 6.45 (d, 1H, H₆, ³J_{HH} = 8.0), 6.62 (d, 1H, H₅, ³J_{HH} = 8.0), 6.77 (d, 1H, H₃, ⁴J_{HH} = 2.5), 7.37-7.40 (m, 6H, H_m, PPh₃), 7.44-7.48 (m, 3H, H_p, PPh₃), 7.90-7.95 (m, 6H, H_o, PPh₃). ³¹P{¹H} NMR (CDCl₃): δ = 29.97.

Synthesis of 2d. Compound **2d** was prepared following the same synthetic method than that reported for **2a**. Thus, Pd(OAc)₂ (0.280 g, 1.26 mmol) was reacted with **1d** (0.500 g, 1.26 mmol) and LiCl (0.210 g, 5.06 mmol) to give **2d** as a yellow solid. Yield: 0.224

g, (33.0 %). Anal. Calc. for $C_{52}H_{42}Cl_2N_2O_2P_2Pd_2$ (1072.60): C, 58.23; H, 3.95; N, 2.61; found: C, 58.40; H, 4.07; N, 2.56. MS (FAB+): m/z (%) = 500 [(M/2- Cl)⁺, 22 %]. IR (ν , cm⁻¹): 1646 (ν_{CO}), 1307 (ν_{NP}). ¹H NMR (CDCl₃): δ = 2.20 (s, 3H, Me), 6.65-6.80 (m, 3H, H₄,H₅,H₆), 7.33-7.36 (m, 6H, H_m, PPh₃), 7.41-7.45 (m, 3H, H_p, PPh₃), 7.88-7.93 (m, 6H, H_o, PPh₃). ¹³C{¹H} NMR (CDCl₃): δ = 19.52 (Me), 125.80 (d, ¹J_{P-C} = 101.7, C_i, PPh₃), 127.75, (C₆H₄), 128.55 (C₆H₄), 129.02 (d, ³J_{P-C} = 12.9, C_m, PPh₃), 131.60 (C₆H₄), 133.14 (d, ⁴J_{P-C} = 2.2, C_p, PPh₃), 134.06 (d, ²J_{P-C} = 10.1, C_o, PPh₃), 136.07 (d, ³J_{P-C} = 13.0, C₂, C₆H₄), 140.02 (d, ⁴J_{P-C} = 2.7, C₃, C₆H₄), 145.09 (C₁, C₆H₄), 181.65 (d, ²J_{P-C} = 6.9, CO). ³¹P{¹H} NMR (CDCl₃): δ = 31.31.

Synthesis of 2e. Compound **2e** was prepared following the same synthetic method than that reported for **2a**. Thus, Pd(OAc)₂ (0.140 g, 0.63 mmol) was reacted with **1e** (0.250 g, 0.63 mmol) and LiCl (0.107 g, 2.53 mmol) to give **2e** as a yellow solid. Yield: 0.149 g, (44.0 %). Anal. Calc. for $C_{52}H_{42}Cl_2N_2O_2P_2Pd_2$ (1072.60): C, 58.23; H, 3.95; N, 2.61; found: C, 58.07; H, 3.88; N, 2.43. MS (FAB+): m/z (%) = 500 [(M/2- Cl)⁺, 25%] IR (ν , cm⁻¹): 1647 (ν_{CO}), 1290 (ν_{NP}). ¹H NMR (CD₂Cl₂): δ = 2.15 (s, 3H, Me), 6.53 (d, 1H, H₅, ³J_{HH} = 6.7), 6.63 (d, 1H, H₆, ³J_{HH} = 6.2), 6.89 (s, 1H, H₃), 7.36-7.41 (m, 6H, H_m, PPh₃), 7.48-7.52 (m, 3H, H_p, PPh₃), 7.89-7.93 (m, 6H, H_o, PPh₃). ¹³C{¹H} NMR (CDCl₃): δ = 20.62 (Me), 125.29 (d, ¹J_{P-C} = 101.7, C_i, PPh₃), 128.35 (d, ⁴J_{P-C} = 3.0, C₃, C₆H₃), 128.65 (d, ³J_{P-C} = 12.9, C_m, PPh₃), 130.91 (C₆H₃), 132.82 (C_p, PPh₃), 133.20 (C₆H₃), 133.29 (C₆H₃), 133.79 (d, ²J_{P-C} = 10.2, C_o, PPh₃), 138.94 (d, ³J_{P-C} = 13.9, C₂, C₆H₃), 139.46 (C₁, C₆H₃), 181.04 (d, ²J_{P-C} = 5.4, CO). ³¹P{¹H} NMR (CD₂Cl₂): δ = 29.92.

Synthesis of 3c. To a solution of **2c** (0.295 g, 0.270 mmol) in CH₂Cl₂ (20 mL), Tl(acac) (0.162 g, 0.530 mmol) was added, resulting in the immediate precipitation of TlCl. This

suspension was stirred for 1h at 25 °C and then filtered over Celite. The clear yellow solution was evaporated to dryness and the residue treated with cold *n*-pentane (10 mL), to give **3c** as a yellow solid. Yield: 0.192 g (58.4%). Anal. Calc. for C₃₁H₂₈NO₄PPd (615.94): C, 60.45; H, 4.58; N, 2.27; found: C, 59.95; H, 4.29; N, 1.97. IR (ν , cm⁻¹): 1650 (ν_{CO}), 1582, 1513 (ν_{CO} , acac) 1267 (ν_{NP}). ¹H NMR (CDCl₃): δ = 0.98 (s, 3H, Me, acac), 1.88 (s, 3H, Me, acac), 3.65 (s, 3H, OMe), 4.93 (s, 1H, CH, acac), 6.79 (dd, 1H, H₅, C₆H₄, ³J_{HH} = 8.3, ⁴J_{HH} = 2.9), 6.87 (d, 1H, H₃, C₆H₄, ⁴J_{HH} = 2.9), 7.40-7.45 (m, 7H, H₆ + H_m, PPh₃), 7.49-7.53 (m, 3H, H_p, PPh₃), 7.93-7.97 (m, 6H, H_o, PPh₃). ³¹P{¹H} NMR (CDCl₃): δ = 28.04.

Synthesis of 4c. To a solution of **2c** (0.301 g, 0.27 mmol) in CH₂Cl₂ (10 mL) an excess of py (87.56 μ L, 1.08 mmol) was added, and the resulting yellow solution was stirred for 30 min at r. t. After the reaction time, the solvent was evaporated to dryness and the residue treated with cold *n*-hexane (15 mL) to give **4c** as a yellow solid. Yield: 0.199 g (57.8%). Anal. Calc. for C₃₁H₂₆ClN₂O₂PPd (631.39): C, 58.97; H, 4.15; N, 4.44; found: C, 59.45; H, 4.34; N, 4.56. MS (FAB+): m/z (%) = 595 (100%) [(M-Cl)⁺]. IR (ν , cm⁻¹): 1644 (ν_{CO}), 1582, 1513 (ν_{CO} , acac), 1273 (ν_{NP}). ¹H NMR (CDCl₃): δ = 3.65 (s, 3H, OMe), 6.10 (d, 1H, H₆, ³J_{HH} = 8.4), 6.56 (dd, 1H, H₅, ³J_{HH} = 8.4, ⁴J_{HH} = 3.0), 6.94 (d, 1H, H₃, ⁴J_{HH} = 3.0), 7.23-7.26 (m, 2H, H_m, py), 7.43-7.47 (m, 6H, H_m, PPh₃), 7.49-7.52 (m, 3H, H_p, PPh₃), 7.65-7.70 (m, 1H, H_p, py), 8.01-8.06 (m, 6H, H_o, PPh₃), 8.78 (dd, 2H, H_o, py, ³J_{HH} = 6.2, ⁴J_{HH} = 1.2). ³¹P{¹H} NMR (CDCl₃): δ = 30.82.

Synthesis of 5c. To a suspension of **2c** (0.300 g, 0.27 mmol) in dry acetone (15 mL), AgClO₄ (0.113 g, 0.54 mmol) was added, the resulting grey suspension was stirred at r. t. with exclusion of light for 20 min, and then filtered over Celite. To the freshly prepared yellow solution of the bis – solvate derivative dppe (0.216 g, 0.54 mmol) was

added, the resulting solution further stirred for 4 h and then the solvent evaporated to dryness in vacuo. The treatment of the residue with Et₂O (25 mL) gives **5c** as an orange solid. Yield: 0.398 g (80.1%). Anal. Calc. for C₅₂H₄₅ClNO₆P₃Pd (1014.71): C, 61.55; H, 4.47; N, 1.38; found: C, 61.57; H, 4.79; N, 1.30. MS (FAB+): m/z (%) = 914 (100%) [(M-ClO₄)⁺]. IR (ν , cm⁻¹): 1709 (ν_{CO}), 1285 (ν_{NP}). ¹H NMR (CDCl₃): δ = 2.21-2.31 (m, 2H, CH₂), 2.44-2.56 (m, 2H, CH₂), 3.72 (s, 3H, OMe), 6.84-6.91 (m, 2H, C₆H₄), 6.84-7.78 (m, 36H, 20H (PPh₂) + 15H (PPh₃) + 1H (C₆H₄)). ³¹P{¹H} NMR (CDCl₃): δ = 21.09 (PPh₃), 39.96 (d, dppe, ²J_{PP} = 29.0), 61.90 (d, dppe, ²J_{PP} = 29.0).

Synthesis of 6c. Compound **6c** was prepared following the same synthetic method than that reported for **5c**. Thus, **2c** (0.308 g, 0.28 mmol) was reacted with AgClO₄ (0.116 g, 0.56 mmol) and 2,2'-bipy (0.087 g, 0.56 mmol) to give **6c** as a yellow solid. Yield: 0.291 (77.5%). Anal. Calc. for C₃₆H₂₉ClN₃O₆PPd (772.47): C, 55.97; H, 3.78; N, 5.44; found: C, 55.73; H, 3.99; N, 5.49. MS (FAB+): m/z (%) = 672 (40%) [(M-ClO₄)⁺]. IR (ν , cm⁻¹): 1711 (ν_{CO}), 1281 (ν_{NP}). ¹H NMR (dmso-d₆): δ = 3.83 (s, 3H, OMe), 7.06 (dd, 1H, H₅, ³J_{HH} = 8.5, ⁴J_{HH} = 2.9), 7.39 (d, 1H, H₆), 7.42 (d, 1H, H₃), 7.66-7.94 (m, 21H, PPh₃ (15H) + bipy (6H)), 8.29 (t, 1H, bipy, ³J_{HH} = 8.1), 8.56 (d, 1H, bipy, ³J_{HH} = 8.1). ³¹P{¹H} NMR (dmso-d₆): δ = 22.98.

Synthesis of 7c. Compound **7c** was prepared following the same synthetic method than that reported for **5c**. Thus, **2c** (0.291 g, 0.26 mmol) was reacted with AgClO₄ (0.109 g, 0.52 mmol) and phen (0.095 g, 0.52 mmol) to give **7c** as a yellow solid. Yield: 0.283 g (77.1%). Complex **7c** was recrystallized from CH₂Cl₂/n – hexane to give yellow crystals of **7c**·0.5CH₂Cl₂. The amount of CH₂Cl₂ was quoted by ¹H NMR. Anal. Calc. for [C₃₈H₂₉ClN₃O₆PPd]·0.5CH₂Cl₂ (838.96): C, 55.19; H, 3.60; N, 5.00; found: C, 55.53; H, 4.07; N, 5.11. MS (FAB+): m/z (%) = 696 (100%) [(M-ClO₄)⁺]. IR (ν , cm⁻¹): 1644

(ν_{CO}), 1282 (ν_{NP}). 1H NMR ($CDCl_3$): δ = 3.85 (s, 3H, OMe), 7.01 (dd, 1H, H_5 , $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 3.0), 7.23 (d, 1H, H_6 , $^3J_{HH}$ = 8.5), 7.33 (d, 1H, $H\alpha'$, phen, $^3J_{HH}$ = 4.3), 7.40 (d, 1H, H_3 , $^4J_{HH}$ = 3.0), 7.57-7.62 (m, 6H, H_m , PPh_3), 7.67-7.71 (m, 4H, $H\beta'$ (phen) + H_p , PPh_3), 7.75-7.80 (m, 8H, $H\delta$ + $H\delta'$ (phen) + H_o , PPh_3), 7.84 (dd, 1H, $H\beta$, $^3J_{HH}$ = 5.0, $^3J_{HH}$ = 8.0), 8.45 (d, 1H, $H\gamma$, $^3J_{HH}$ = 8.0), 8.49 (d, 1H, $H\gamma'$, $^3J_{HH}$ = 8.0), 9.02 (d, 1H, $H\alpha$, $^3J_{HH}$ = 5.0). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 22.91.

Synthesis of 8b. Compound **8b** was prepared following the method reported by Ramírez with minor changes.² PPh_3 (0.23 g, 0.873 mmol) was reacted with $BrCH_2C(O)C_6H_4-3-OMe$ (0.20 g, 0.87 mmol) in dry THF (10 mL) to give $[Ph_3PCH_2C(O)C_6H_4-3-OMe]Br$ in 75 % yield. Selected spectroscopic data of the phosphonium salt. IR (ν , cm^{-1}): 1670 (ν_{CO}). 1H NMR ($CDCl_3$): δ = 3.84 (s, 3H, OMe), 6.03 (d, 2H, CH_2P , $^2J_{P-H}$ = 12.1), 7.06 (dd, 1H, H_4 , $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 2.0), 7.30 (t, 1H, H_5 , $^3J_{HH} \cong ^4J_{HH}$ = 8.1), 7.57 (td, 6H, H_m , PPh_3 , $^3J_{HH}$ = 7.8, $^4J_{PH}$ = 3.5), 7.71- 7.66 (m, 4H, H_2 + H_p - PPh_3), 7.59-7.83 (m, 7H, H_6 + H_o - PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 38.96 (d, CH_2P , $^1J_{PC}$ = 61.5), 56.36 (OMe), 112.80 (C_2 , C_6H_4), 118.92 (d, C_{ipso} , PPh_3 , $^1J_{PC}$ = 89.4), 122.56 (C_4 , C_6H_4), 122.78 (C_6 , C_6H_4), 130.01 (C_5 , C_6H_4), 130.15 (d, C_m , PPh_3 , $^3J_{PC}$ = 13.1), 134.03 (d, C_o , PPh_3 , $^2J_{PC}$ = 10.7), 134.73 (d, C_p , PPh_3 , $^4J_{PC}$ = 3.0), 136.60 (d, C_1 , C_6H_4 , $^3J_{PC}$ = 5.7), 159.98 (C_3 , C_6H_4), 192.12 (d, $C=O$, $^2J_{PC}$ = 6.0). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 21.96. In a second step, a methanolic solution (5 mL) of the phosphonium salt (0.23 g, 0.47 mmol) was reacted with a solution of Na_2CO_3 (0.075 g, 0.70 mmol) in water (10 mL), giving the instantaneous formation of a white suspension. This suspension was further diluted with H_2O (40 mL) and stirred for 30 min, giving **8b** as a white solid. Yield: 0.10 g (50 %). Anal. Calc. for $C_{27}H_{23}O_2P$ (410.48 g/mol): C, 79.00; H, 5.65; found: C, 78.63; H, 5.41. Selected spectroscopic data of **8b**: IR (ν , cm^{-1}): 1516

(ν_{CO}) 1H NMR ($CDCl_3$): $\delta = 3.75$ (s, 3H, OMe), 4.36 (d, 1H, CHP, $^2J_{PH} = 24.4$), 6.84 (d, 1H, H₄, $^3J_{HH} = 7.1$), 7.15 - 7.19 (m, 1H, H₅), 7.38 - 7.42 (m, 6H, H_m, PPh₃), 7.47 - 7.50 (m, 5H, H₂ + H₆ + H_p-PPh₃), 7.65 (m, 6H, H_o-PPh₃). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta = 51.05$ (d, CHP, $^1J_{PC} = 112.0$), 55.39 (OMe), 111.32 (C₂), 116.08 (C₄), 119.58 (C₆), 118.92 (d, C_{ipso}, PPh₃, $^1J_{PC} = 91.2$), 128.64 (C₅), 128.92 (d, C_m, PPh₃, $^3J_{PC} = 12.3$), 132.10 (d, C_p, PPh₃, $^4J_{PC} = 2.8$), 133.18 (d, C_o, PPh₃, $^2J_{PC} = 10.2$), 142.94 (d, C₁, $^3J_{PC} = 14.7$), 159.46 (C₃), 184.18 (d, C=O, $^2J_{PC} = 3.3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 16.66$.

Synthesis of 8c. Compound **8c** was prepared following the method reported by Ramírez with minor changes.² PPh₃ (1.03 g, 3.94 mmol) was reacted with BrCH₂C(O)C₆H₃-2,5-(OMe)₂ (0.25 g, 0.98 mmol) in refluxing CHCl₃ to give [Ph₃PCH₂C(O)C₆H₃-2,5-(OMe)₂]Br in 58% yield. Selected spectroscopic data of the phosphonium salt. IR (ν , cm⁻¹): 1651 (ν_{CO}). 1H NMR ($CDCl_3$): $\delta = 3.68$ (s, 3H, OMe), 3.92 (s, 3H, OMe), 6.07 (d, 2H, CH₂P, $^2J_{PH} = 11.2$), 6.88 (d, 1H, H₃, $^3J_{HH} = 8.8$), 7.04 (dd, 1H, H₄, $^4J_{HH} = 3.2$), 7.16 (d, 1H, H₆), 7.57-7.61 (m, 6H, H_m, PPh₃), 7.68 (m, 3H, H_p, PPh₃), 7.83 (m, 6H, H_o, PPh₃). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.52$. In a second step, a methanolic solution (10 mL) of the phosphonium salt (0.30 g, 0.58 mmol) was reacted with a solution of Na₂CO₃ (0.061 g, 0.58 mmol) in water (10 mL), giving the instantaneous formation of a white suspension. This suspension was further diluted with MeOH (40 mL) and stirred for additional 30 min, giving **8c** as a white solid. Yield: 0.18 g (72.1%). Anal. Calc. for C₂₈H₂₅O₃P (440.21 g/mol): C, 76.35; H, 5.72; found: C, 76.77; H, 5.75. Selected spectroscopic data of **8c**: MS (MALDI) [m/z, (%)]: 441 (80%) [M + H]⁺. IR (ν , cm⁻¹): 1508 (ν_{CO}) 1H NMR ($CDCl_3$): $\delta = 3.81$ (s, 3H, OMe), 3.87 (s, 3H, OMe), 4.75 (d, 1H, CHP, $^3J_{PH} = 28.2$), 6.86 (dd, 1H, H₄, $^3J_{HH} = 8.9$, $^4J_{HH} = 3.0$), 6.89 (d, 1H, H₃), 7.47-7.52 (m, 7H, H₆ + H_m-PPh₃), 7.57 (m, 3H, H_p, PPh₃), 7.78 (dd, 6H, H_o, PPh₃). $^{13}C\{^1H\}$ NMR

(CDCl₃) (the C₁ of the benzoyl group was not observed): δ = 55.46 (d, CHP, ¹J_{PC} = 107.9), 55.89 (OMe), 57.14 (OMe), 113.94 (C₆), 113.98 (C₃), 116.22 (C₄), 127.32 (d, C_{ipso}, PPh₃, ¹J_{PC} = 91.0), 128.82 (d, C_m, PPh₃, ³J_{PC} = 12.2), 131.92 (d, C_p, PPh₃, ⁴J_{PC} = 2.7), 133.23 (d, C_o, PPh₃, ²J_{PC} = 10.1), 152.05 (C₂), 153.66 (C₅), 191.46 (d, C=O, ²J_{PC} = 3.0). ³¹P{¹H} NMR (CDCl₃): δ = 15.27.

Synthesis of 9a. To a solution of **8a** (1.00 g, 2.63 mmol) in CH₂Cl₂ (10 mL), Pd(OAc)₂ (0.59 g, 2.63 mmol) was added, and the resulting brown solution was refluxed for 4 h. Then the solvent was evaporated to dryness, and the yellow residue was redissolved in MeOH (15 mL), treated with an excess of LiCl (0.44 g, 10.52 mmol) and further stirred for 30 min at r.t. During this time **9a** precipitated as a yellow solid, which was filtered, washed with additional MeOH (5 mL) and Et₂O (20 mL) and dried by suction. Yield: 0.61 g, (45%). The NMR characterization of **9a** showed that it was a mixture of two diastereoisomers in 2.5:1 molar ratio. Anal. Calc. for C₅₂H₄₀Cl₂O₂P₂Pd₂ (1042.60): C, 59.91; H, 3.87; found: C, 58.97; H, 4.02. MS (MALDI) [m/z, (%)]: 485.1 (30%) [M/2 – Cl]⁺. IR (ν, cm⁻¹): 1625 (ν_{CO}). ¹H NMR (dmso-d₆): δ = 5.13 (s, CHP, major), 5.41 (s, CHP, minor) 7.13-7.25 (m, C₆H₄), 7.37-7.42 (m, H_m, PhCO minor + C₆H₄), 7.46-7.49 (m, H_m, PhCO major), 7.51-7.91 (m, PPh₂+C₆H₄), 7.94-7.98 (m, PPh₂), 8.04 (d, H_o, PhCO major, ³J_{HH} = 7.2), 8.17 (d, H_o, PhCO minor, ³J_{HH} = 7.6). ³¹P{¹H} NMR (dmso-d₆): δ = 17.71 (major), 19.53 (minor).

Synthesis of 9b: Compound **9b** was prepared following the same synthetic method than that reported for **9a**. Thus, **8b** (0.070 g, 0.17 mmol) was reacted with Pd(OAc)₂ (0.038 g, 0.17 mmol) in CH₂Cl₂ and with LiCl (0.029 g, 0.68 mmol) in MeOH (15 ml) to give **9b** as a yellow solid. Yield: 0.085 g (91%). **9b** was characterized by NMR as a mixture of diastereoisomers in 1.3:1 molar ratio. Anal. Calc. for C₅₄H₄₄Cl₂O₄P₂Pd₂ (1102.6): C,

58.82; H, 4.02; found: C, 59.32; H, 4.03. MS (MALDI) [m/z, (%)]: 1066.2 (8 %) [M-Cl-H]⁺; IR (ν , cm⁻¹): 1627 (ν_{CO}). ¹H NMR (CDCl₃): δ = 3.57 (s, OMe, major), 3.60 (s, OMe, minor), 4.74 (s, CHP, minor), 4.83 (d, CHP, major, ²J_{PH} = 2.3), 6.72-7.93 (m, Ph, major + minor). ³¹P{¹H} NMR (CDCl₃): δ = 17.92 (s, major), 19.50 (s, minor).

Synthesis of 9c. Compound **9c** was prepared following the same synthetic method than that reported for **9a**. Thus, **8c** (0.16 g, 0.36 mmol) was reacted with Pd(OAc)₂ (0.082 g, 0.36 mmol) in CH₂Cl₂ and with LiCl (0.061 g, 1.44 mmol) in MeOH (15 ml) to give **9c** as a yellow solid. Yield: 0.165 g (77%). **9c** was characterized by NMR as a mixture of diastereoisomers in 1.25:1 molar ratio. Anal. Calc. for C₅₆H₄₈Cl₂O₆P₂Pd₂ (1162.65): C, 57.85; H, 4.16; found: C, 58.03; H, 4.26. MS (MALDI) [m/z, (%)]: 1127 (11 %) [M-Cl]⁺. IR (ν , cm⁻¹): 1626 (ν_{CO}). ¹H NMR (CDCl₃): δ = 3.47 (s, OMe, minor), 3.53 (s, OMe, major), 3.61 (s, OMe, major), 3.75 (m, OMe, minor), 5.10 (d, CHP, major, ²J_{P-H} = 4.0), 5.29 (s, CHP, minor), 6.69-6.80 (m, H₃ + H₄, C₆H₄, major + minor), 6.97-7.47 (m, H₆, major + minor, Ph+C₆H₄, major + minor), 7.84-7.85 (m, H_o, PPh₂, major + minor). ³¹P{¹H} NMR (CDCl₃): δ = 21.38 (minor), 21.90 (major).

Synthesis of 9d. To a suspension of **8a** (0.300 g, 0.788 mmol) in NCMe (25 mL) PtCl₂ (0.210 g, 0.788 mmol) was added, and the resulting mixture was refluxed for 24 h. During the first steps of the reaction the initial brown suspension dissolved (25 min), giving a yellow solution. After the reaction time, the resulting solution was evaporated to dryness, and the residue treated with Et₂O (15 mL), giving 0.447 g of a yellow solid. The characterization of this solid showed to be a mixture of **9d** and the phosphonium salt [Ph₃PCH₂C(O)Ph]Cl. Exhaustive treatment of this mixture with water allows the isolation of pure **9d**. Yield: 0.338 g (35.2%). **9d** was characterized spectroscopically as the mixture (3:2.4:1.4:1 molar ratios) of the four isomers cis (*RR/SS* and *RS/SR*) and

trans (*RR/SS* and *RS/SR*). This compound has already been described by Burmeister.³ Only relevant spectroscopic data will be given here. MS (FAB+) [m/z, (%)]: 1184.1 (74%) [M – Cl]⁺. IR (v, cm⁻¹): 1625 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ = 4.88 (s, CHP, min.), 4.90 (s, CHP, min.), 5.00 (s, CHP, min.), 5.04 (s, CHP, maj.), 6.94 – 7.98 (m, Ph). ³¹P{¹H} NMR (CD₂Cl₂): δ = 26.32 (s, C₆H₄-2-PPh₂, maj.), 27.38 (s, C₆H₄-2-PPh₂, min.), 27.41 (s, C₆H₄-2-PPh₂, maj.), 27.60 (s, C₆H₄-2-PPh₂, min.).

Synthesis of 10a: Compound **10a** was prepared following the same synthetic method than that reported for **3c**. Thus, **9a** (0.200 g, 0.190 mmol) was reacted with Tl(acac) (0.120 g, 0.38 mmol) in CH₂Cl₂ to give **10a** as a yellow solid. Yield: 0.101 g (46.4%). Anal. Calc. for C₃₁H₂₇O₃PPd (584.95): C, 63.65; H, 4.65; found: C, 64.24; H, 4.48. MS (MALDI) [m/z, (%)]: 485 (100%) [(M-acac)⁺]. IR (v, cm⁻¹): 1625 (ν_{CO}), 1564, 1514 (ν_{CO}, acac). ¹H NMR (CDCl₃): δ = 1.70 (s, 3H, CH₃, acac), 1.89 (s, 3H, CH₃, acac), 4.80 (d, 1H, CHP, ²J_{PH} = 3.3), 5.11 (s, 1H, CH, acac), 7.04-7.12 (m, 1H, C₆H₄), 7.12-7.18 (m, 1H, C₆H₄), 7.20-7.22 (m, 1H, C₆H₄), 7.25-7.31 (m, 2H, H_m, PhCO), 7.33-7.42 (m, 3H, H_p (PhCO) + H_m (PPh₂)), 7.42-7.51 (m, 2H, H_m, PPh₂), 7.50-7.57 (m, 2H, H_p (PPh₂)), 7.63-7.68 (m, 1H, C₆H₄), 7.89-7.96 (m, 4H, H_o, PPh₂), 8.15 (d, 2H, H_o, PhCO, ³J_{HH} = 9.6). ³¹P{¹H} NMR (CDCl₃): δ = 21.20.

Synthesis of 10b: Compound **10b** was prepared following the same synthetic method than that reported for **3c**. Thus, **9b** (0.06 g, 0.054 mmol) was reacted with Tl(acac) (0.033 g, 0.109 mmol) in CH₂Cl₂ to give **10b** as a yellow solid. Yield: 0.031 g (46.3%). Anal. Calc. for C₃₂H₂₉O₄PPd (614.95): C, 62.50; H, 4.75; found: C, 62.00; H, 4.75. MS (MALDI) [m/z, (%)]: 515.0 (67%) [(M-acac)⁺]. IR (v, cm⁻¹): 1618 (ν_{CO}), 1564, 1515 (ν_{CO}, acac). ¹H NMR (CDCl₃): δ = 1.73 (s, 3H, CH₃, acac), 1.88 (s, 3H, CH₃, acac), 3.72 (s, 3H, OMe), 4.78 (d, 1H, CHP, ²J_{PH} = 3.6), 5.11 (s, 1H, CH, acac), 6.91 (dd, 1H,

H_4 , $\text{C}_6\text{H}_4\text{O}$, $^3\text{J}_{\text{HH}} = 9.0$, $^4\text{J}_{\text{HH}} = 2.0$), 7.07 (m, 1H, H_5 , C_6H_4), 7.15-7.23 (m, 3H, H_5 ($\text{C}_6\text{H}_4\text{O}$) + H_3 , H_4 (C_6H_4)), 7.38 (m, 2H, H_m , PPh_2), 7.43-7.54 (m, 4H, H_m (PPh_2) + H_p (PPh_2)), 7.64-7.67 (m, 2H, H_2 + H_6 , $\text{C}_6\text{H}_4\text{O} + \text{C}_6\text{H}_4$), 7.77-7.82 (m, 3H, H_o (PPh_2) + H_6 ($\text{C}_6\text{H}_4\text{O}$)), 7.89 (m, 2H, H_o , PPh_2). $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3): 27.81 (CH_3 , acac), 27.96 (CH_3 , acac), 35.50 (d, CHP, $^1\text{J}_{\text{PC}} = 65.6$), 55.44 (OMe), 99.46 (s, CH-acac), 113.07 (d, C_2 , $\text{C}_6\text{H}_4\text{O}$, $^4\text{J}_{\text{PC}} = 1.5$), 118.23 (C_4 , $\text{C}_6\text{H}_4\text{O}$), 121.82 (d, C_6 , $\text{C}_6\text{H}_4\text{O}$, $^4\text{J}_{\text{PC}} = 1.1$), 124.57 (d, C_5 , C_6H_4 , $^4\text{J}_{\text{PC}} = 13.3$), 126.13 (d, C_ipso , PPh_2 , $^1\text{J}_{\text{PC}} = 70.0$), 127.47 (d, C_ipso , PPh_2 , $^1\text{J}_{\text{PC}} = 57.56$), 125.49 (C_5 , $\text{C}_6\text{H}_4\text{O}$), 128.55 (d, C_m , PPh_2 , $^3\text{J}_{\text{PC}} = 11.4$), 128.67 (d, C_m , PPh_2 , $^3\text{J}_{\text{PC}} = 11.7$), 129.56 (d, C_3 , C_6H_4 , $^2\text{J}_{\text{PC}} = 15.7$), 130.12 (d, C_4 , C_6H_4 , $^3\text{J}_{\text{PC}} = 3.5$), 132.38 (d, C_p , PPh_2 , $^4\text{J}_{\text{PC}} = 2.7$), 132.50 (d, C_p , PPh_2 , $^4\text{J}_{\text{PC}} = 2.8$), 132.95 (d, C_o , PPh_2 , $^2\text{J}_{\text{PC}} = 8.9$), 133.67 (d, C_6 , C_6H_4 , $^3\text{J}_{\text{PC}} = 15.4$), 134.49 (d, C_o , PPh_2 , $^2\text{J}_{\text{PC}} = 9.9$), 138.03 (d, C_2 , C_6H_4 , $^1\text{J}_{\text{PC}} = 117.53$), 139.94 (d, C_1 , $\text{C}_6\text{H}_4\text{O}$, $^3\text{J}_{\text{PC}} = 8.8$), 159.28 (C_3 , $\text{C}_6\text{H}_4\text{O}$), 159.32 (d, C_1 , C_6H_4 , $^2\text{J}_{\text{PC}} = 21.1$), 186.20 (CO, acac), 186.84 (CO, acac), 194.9 (d, $\text{C}=\text{O}$, $^2\text{J}_{\text{PC}} = 3.7$). $^{31}\text{P}\{\text{H}\}$ NMR (CDCl_3): $\delta = 20.86$.

Synthesis of 10c: Compound **10c** was prepared following the same synthetic method than that reported for **3c**. Thus, **9c** (0.037 g, 0.033 mmol) was reacted with Tl(acac) (0.019 g, 0.066 mmol) in CH_2Cl_2 to give **10c** as a yellow solid. Yield: 0.04 g (92.0%). Complex **10c** was recrystallized from $\text{CH}_2\text{Cl}_2/n$ – hexane to give yellow crystals of **10c**·0.5 CH_2Cl_2 , which were used for analytic and spectroscopic measurements. The amount of CH_2Cl_2 was quoted by ^1H NMR. Anal. Calc. for $[\text{C}_{33}\text{H}_{31}\text{O}_5\text{PPd}] \cdot 0.5\text{CH}_2\text{Cl}_2$ (687.45): C, 58.53; H, 4.69; found: C, 58.85; H, 4.31. MS (MALDI) [m/z, (%)]: 544.9 (100%) $[(\text{M}-\text{acac})^+]$. IR (ν , cm^{-1}): 1623 (ν_{CO}), 1563, 1510 (ν_{CO} , acac). ^1H NMR (CDCl_3): $\delta = 1.51$ (s, 3H, CH_3 , acac), 2.01 (s, 3H, CH_3 , acac), 3.78 (s, 3H, OMe), 3.80 (s, 3H, OMe), 5.13 (d, 1H, CHP, $^2\text{J}_{\text{PH}} = 5.0$), 5.15 (s, 1H, CH, acac), 6.82 (d, 1H, H_3 ,

$^3J_{HH} = 9.0$), 6.87 (dd, 1H, H_{4'}, $^4J_{HH} = 3.0$), 7.15-7.18 (m, 1H, H₄, C₆H₄), 7.25-7.30 (m, 2H, H₅, H₃, C₆H₄), 7.34 (d, 1H, H_{6'}), 7.50-7.56 (m, 4H, H' _m + H'' _m, PPh₂), 7.58-7.63 (m, 2H, H' _p + H'' _p, PPh₂), 7.83 (d, 1H, H₆, C₆H₄, $^3J_{HH} = 8.0$), 7.89-7.93 (m, 2H, H'' _o, PPh₂), 7.96-7.99 (m, 2H, H' _o, PPh₂). ¹³C{¹H} NMR (CDCl₃): δ = 27.15 (CH₃, acac), 27.93 (CH₃, acac), 36.05 (OMe), 36.53 (OMe), 56.30 (d, CHP, $^1J_{PC} = 88.7$), 99.3, (CH, acac), 113.14 (C₃), 114.22 (C₆), 117.53 (C₄), 124.50 (d, C₅, C₆H₄, $^4J_{PC} = 13.0$), 126.00 (d, C_{ipso}, Ph, $^1J_{PC} = 72.0$), 127.28 (d, C_{ipso}, Ph, $^1J_{PC} = 85.3$), 128.63 (d, C_m, Ph, $^3J_{PC} = 11.6$), 129.22 (d, C_m, Ph, $^3J_{PC} = 11.6$), 129.75 (d, C₃, C₆H₄, $^2J_{C-P} = 15.7$), 130.16 (d, C₄, C₆H₄, $^3J_{C-P} = 3.4$), 132.13 (d, C_p, Ph, $^4J_{PC} = 2.6$), 132.39 (d, C_p, Ph, $^4J_{PC} = 2.8$), 132.74 (d, C₁, $^3J_{PC} = 9.0$), 132.87 (d, C_o, Ph, $^2J_{PC} = 9.0$), 133.82 (d, C₆, C₆H₄, $^3J_{PC} = 15.5$) 134.47 (d, C_o, Ph, $^2J_{PC} = 10.0$), 137.95 (d, C₂, C₆H₄, $^1J_{PC} = 116.95$), 151.50 (C₂), 153.51 (C₅), 159.28 (d, C₁, C₆H₄, $^2J_{PC} = 22.5$), 185.83 (CO, acac), 186.95 (CO, acac), 197.10 (d, C=O, $^2J_{PC} = 4.0$). ³¹P{¹H} NMR (CDCl₃): δ = 23.39.

Synthesis of 10d. Compound **10d** was prepared following the same synthetic method than that reported for **3c**. Thus, **9d** (0.151 g, 0.124 mmol) was reacted with Tl(acac) (0.074 g, 0.248 mmol) in CH₂Cl₂ to give **10d** as a yellow solid. Yield: 0.068 g (40.7%). Anal. Calc. for C₃₁H₂₇O₃PPt (673.62): C, 55.27; H, 4.04; found: C, 55.03; H, 4.41. MS (MALDI) [m/z, (%)]: 574.3 (42%) [(M-acac)⁺]. IR (ν , cm⁻¹): 1634 (ν_{CO}), 1564, 1519 (ν_{CO} , acac). ¹H NMR (CDCl₃): δ = 1.65 (s, 3H, CH₃, acac), 1.77 (s, 3H, CH₃, acac), 5.14 (s, 1H, CHP, $^2J_{PtH} = 60.0$), 5.18 (s, 1H, CH, acac), 7.02-7.07 (m, 1H, C₆H₄), 7.13-7.19 (m, 1H, C₆H₄), 7.21-7.28 (m, 3H, C₆H₄ + H_m (PhCO)), 7.32-7.49 (m, 7H, H_p (PhCO) + H_m + H_p (PPh₂)), 7.56-7.62 (m, 1H, C₆H₄), 7.79 (m, 4H, H_o, PPh₂), 8.15 (dd, 2H, H_o, PhCO, $^3J_{HH} = 8.6$, $^4J_{HH} = 1.4$). ³¹P{¹H} NMR (CDCl₃): δ = 28.35.

Synthesis of 11a: To a suspension of **9a** (0.20 g, 0.19 mmol) in CH₂Cl₂ (15 mL), PPh₃ (0.10 g, 0.38 mmol) was added. The initial yellow suspension gradually dissolved and, after 30 min stirring at r. t. the resulting solution was filtered over a Celite pad in order to remove any residual insoluble solid. The clear solution was evaporated to dryness, and the treatment of the oily residue with Et₂O (30 mL) gave **11a** as a yellow solid. Yield: 0.250 g, (81.3 %). Anal. Calc. for C₄₄H₃₅ClO₂Pd (783.60): C, 67.44; H, 4.50; found: C, 67.30; H, 4.84. MS (FAB+) [m/z, (%)]: 747 (15 %) [M - Cl]⁺. IR (v, cm⁻¹): 1610 (ν_{CO}). ¹H NMR (CDCl₃): δ = 5.43 (s, 1H, CHP), 6.45 (s, 2H, C₆H₄), 6.79-6.84 (m, 1H, C₆H₄), 7.07-7.11 (m, 6H, H_m, PPh₃), 7.15 (m, 1H, C₆H₄), 7.18-7.25 (m, 9H, H_o+H_p, PPh₃), 7.27-7.38 (m, 5H, H_m, PPh₂, H_m+H_p, (PhCO)), 7.43-7.60 (m, 4H, H_m+H_p+H_p, PPh₂), 7.78 (m, 2H, H_o, PPh₂), 7.96-7.80 (m, 2H, H_o, PPh₂), 8.36 (d, 2H, H_o, PhCO, ³J_{HH} = 7.2). ³¹P{¹H} NMR (CDCl₃): δ = 14.57 (d, 1P, C₆H₄-2-PPh₂, ³J_{PP} = 17.7), 31.45 (d, 1P, Pd-PPh₃).

Synthesis of 12a: To a suspension of **9a** (0.20 g, 0.19 mmol) in THF (20 mL), AgClO₄ (0.08 g, 0.38 mmol) was added. The resulting mixture was stirred for 30 min at 25 °C with exclusion of light, and then filtered over Celite. To the freshly prepared solution of the bis-solvate, dppm (0.15 g, 0.38 mmol) was added, and the resulting solution was stirred at 25 °C for 4 h. After the reaction time, the solvent was evaporated to dryness and the residue treated with Et₂O (25 mL) to give **12a** as an orange solid. Yield: 0.240 g (63.2 %). Anal. Calc. for C₅₁H₄₂ClO₆P₃Pd (985.76): C, 62.10; H, 4.30; found: C, 62.20; H, 4.24. MS (FAB+) [m/z, (%)]: 886 (45 %) [M-ClO₄]⁺. IR (v, cm⁻¹): 1614 (ν_{CO}). ¹H NMR (CDCl₃): δ = 3.45-3.54 (m, 1H, CH₂, dppm), 3.60-3.69 (m, 1H, CH₂, dppm), 5.33 (dd, 1H, CHP, ³J_{PH} = 8.0, ²J_{PH} = 3.2), 6.63-6.71 (m, 2H, C₆H₄), 6.98 (m, 1H, C₆H₄), 7.08-7.43 (m, 25H, PhCO + PPh₂ + C₆H₄), 7.48-7.58 (m, 4H, H_m(PPh₂) + H_p(PPh₂) +

$\text{H}_\text{p}(\text{PhCO}))$, 7.68 (t, 1H, H_p , PPh_2 , $^3J_{\text{HH}} = 7.6$), 7.74 (m, 2H, H_o , PPh_2), 7.93 (m, 2H, H_o , PPh_2), 8.30 (d, 2H, H_o , PhCO , $^3J_{\text{HH}} = 7.2$). $^{31}\text{P}\{\text{H}\}$ NMR (CDCl_3): $\delta = 15.32$ (d, 1P, $\text{C}_6\text{H}_4\text{PPh}_2$, $^3J_{\text{PP}} = 19.6$), 24.95 (dd, 1P, PdPPh_2 , dppm), 58.20 (d, 1P, $\text{Ph}_2\text{P}=\text{O}$, dppm, $^2J_{\text{PP}} = 25.1$).

Synthesis of 13a: Complex **13a** was prepared following the same experimental method as that reported for **12a**. Thus, **9a** (0.20 g, 0.19 mmol) was reacted, in THF, with AgClO_4 (0.080g, 0.38 mmol) and dppe (0.15 g, 0.38 mmol) to give **13a** as a white solid. Yield: 0.210 g (55.7 %). Anal. Calc. for $\text{C}_{52}\text{H}_{44}\text{ClO}_5\text{P}_3\text{Pd}$ (983.79): C, 63.49; H, 4.51; found: C, 63.51; H, 4.48. MS (FAB+) [m/z, (%)]: 884 (25 %) [$\text{M} - \text{ClO}_4$]⁺. IR (ν , cm^{-1}): 1636 (ν_{CO}). ^1H NMR (CDCl_3): $\delta = 1.84$ (m, 1H, CH_2 , dppe), 2.05 (m, 1H, CH_2 , dppe), 2.45 (m, 2H, CH_2 , dppe), 4.84 (s, 1H, CHP), 6.89-7.66 (m, 39H, Ph, C_6H_4). $^{31}\text{P}\{\text{H}\}$ NMR (CDCl_3): $\delta = 24.12$ (dd, 1P, C_6H_4 -2-PPh₂, $^3J_{\text{PP}} = 23.7$, $^3J_{\text{PP}} = 19$), 43.78 (dd, 1P, P *trans*-C_{ylide}, $^3J_{\text{PP}} = 28.0$, $^3J_{\text{PP}} = 23.7$), 52.21 (pseudot, 1P, P *cis*-C_{ylide}).

Synthesis of 14a: Complex **14a** was prepared following the same experimental method as that reported for **12a**. Thus, **9a** (0.20 g, 0.19 mmol) was reacted, in THF, with AgClO_4 (0.080g, 0.38 mmol) and 1,10-phen (0.076 g, 0.38 mmol) to give **14a** as a yellow solid. Yield: 0.190 g (65.2 %). Anal. Calc. for $\text{C}_{38}\text{H}_{28}\text{ClN}_2\text{O}_5\text{PPd}$ (765.51): C, 59.62; H, 3.89; N, 3.66; found: C, 59.61; H, 3.32; N, 3.82. MS (FAB+) [m/z, (%)]: 665 (100 %) [$\text{M} - \text{ClO}_4$]⁺. IR (ν , cm^{-1}): 1634 (ν_{CO}). ^1H NMR (CD_2Cl_2): $\delta = 5.13$ (s, 1H, CHP), 7.25-7.37 (m, 5H, H_3 , H_4 , H_5 (C_6H_4) + H_m (PhCO)), 7.41-7.62 (m, 9H, H_β , H_δ , H_δ (phen) + H_6 (C_6H_4) + H_p (PhCO) + H_m (PPh_2)), 7.81-7.92 (m, 9H, H_β (phen) + H_o (PhCO) + H_o , H_p (PPh_2)), 8.34 (dd, 1H, H_γ , phen, $^3J_{\text{HH}} = 8.4$, $^4J_{\text{HH}} = 1.2$), 8.52 (dd, 1H, H_γ , phen, $^3J_{\text{HH}} = 8.0$, $^4J_{\text{HH}} = 1.2$), 8.69 (d, 1H, H_α , phen, $^3J_{\text{HH}} = 4.4$), 8.95 (dd, 1H, H_α , phen, $^3J_{\text{HH}} = 4.8$). $^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2): $\delta = 19.43$.

Synthesis of 15a: Complex **15a** was prepared following the same experimental method as that reported for **12a**. Thus, **9a** (0.20 g, 0.19 mmol) was reacted, in THF, with AgClO₄ (0.080g, 0.38 mmol) and 2,2'-bipy (0.060 g, 0.38 mmol) to give **15a** as a yellow solid. Yield: 0.22 g (77.9 %). Anal. Calc. for C₃₆H₂₈ClN₂O₅PPd (741.47): C, 58.32; H, 3.81; N, 3.79; found: C, 57.58; H, 3.95; N, 3.92. MS (FAB+) [m/z, (%)]: 641 (100 %) [M – ClO₄]⁺. IR (ν , cm⁻¹): 1638 (ν_{CO}). ¹H NMR (dmso-d₆): δ = 5.54 (s, 1H, CHP), 7.33-7.38 (m, 2H, H_m, PhCO), 7.41-7.54 (m, 5H, H_p (PhCO) + C₆H₄), 7.56-7.77 (m, 10H, H_δ, H_{δ'}, (bipy) + H_m, H_p, H_o (PPh₂)), 7.78-7.86 (m, 2H, H_o, PPh₂), 7.88 (d, 2H, H_o, PhCO, ³J_{HH} = 7.1), 8.11-8.18 (m, 2H, H_γ, H_{γ'}, bipy), 8.20-8.28 (m, 2H, H_β, H_{β'}, bipy), 8.54 (d, 2H, H_α, H_{α'}, bipy, ³J_{HH} = 7.0). ³¹P{¹H} NMR (dmso-d₆): δ = 20.15.

Synthesis of 16. Compound **16** was prepared following the same synthetic method than that reported for **8b** or **8c**. Thus, PPh₃ (1.062 g, 4.05 mmol) was reacted with BrCH₂C(O)C₆H₃-2,4-(OMe)₂ (0.350 g, 1.35 mmol) in refluxing CH₂Cl₂ (24 h) to give the corresponding phosphonium salt in 95.3 % yield. IR (ν , cm⁻¹): 1644 (ν_{CO}) cm⁻¹. ¹H NMR (CDCl₃): δ = 3.79 (s, 3H, OMe), 4.00 (s, 3H, OMe), 5.91 (d, 2H, CH₂P, ²J_{PH} = 10.8), 6.40 (d, 1H, H₃, ⁴J_{HH} = 2), 6.44 (dd, 1H, H₅, ³J_{HH} = 8.8), 7.56-7.61 (m, 6H, H_m, PPh₃), 7.68 (t, 3H, H_p, PPh₃, ³J_{HH} = 7.6), 7.76 (d, 1H, H₆), 7.82 (dd, 6H, H_o, PPh₃, ³J_{PH} = 12.8, ³J_{HH} = 8.0). ³¹P{¹H} NMR (CDCl₃): δ = 21.59. ¹³C{¹H} NMR (CDCl₃): δ = 41.54 (d, CH₂P, ¹J_{PC} = 60.0), 55.83 (OMe), 56.82 (OMe), 98.32 (C₃), 106.46 (C₅), 118.55 (d, C₁, ³J_{PC} = 4.3), 119.42 (d, C_i, PPh₃, ¹J_{PC} = 89.0), 123.24 (C₄), 130.12 (d, C_m, PPh₃, ³J_{PC} = 13.0), 133.64 (C₆), 134.0 (d, C_o, PPh₃, ²J_{PC} = 10.5), 134.5 (d, C_p, PPh₃, ⁴J_{PC} = 3.0), 162.36 (C₄), 166.57 (C₂), 189.16 (d, C=O, ²J_{PC} = 6.6). Anal. Calc. for C₂₈H₂₆BrO₃P (521.12): C, 64.50; H, 5.03; found: C, 64.40 H, 5.47. In a second step, the phosphonium salt (0.200 g, 0.384 mmol) was reacted with KOH (0.032 g, 0.576 mmol) in methanol /

water (10 mL / 10 mL) to give **8c** as a white solid. Yield: 0.067 g (39.4 %). Anal. Calc. for C₂₈H₂₅O₃P (440.21): C, 76.34; H, 5.72; found: C, 76.85 H, 5.73. IR (ν , cm⁻¹): 1517 (ν_{CO}). ¹H NMR (CDCl₃): δ = 3.74 (s, 3H, OMe), 3.79 (s, 3H, OMe), 4.65 (d, 1H, CHP, $J_{PH} = 29.2$), 6.40 (s, br, 1H, H₃), 6.43 (dd, 1H, H₅, $J_{HH} = 8.8$, $J_{PH} = 2.4$), 7.40-7.36 (m, 6H, H_m, PPh₃), 7.46 (t, 3H, H_p, PPh₃, $J_{HH} = 6.8$), 7.67 (dd, 6H, H_o, PPh₃, $J_{PH} = 12.4$, $J_{HH} = 7.2$). 7.86 (d, 1H, H₆, $J_{HH} = 8.4$), ³¹P{¹H} NMR (CDCl₃): δ = 15.32. ¹³C{¹H} NMR (CDCl₃): δ = 54.74 (d, CHP, $J_{PC} = 108.1$), 55.38 (OMe), 55.82 (OMe), 98.87 (C₃), 104.10 (C₅), 124.15 (d, C₁, $J_{PC} = 13.8$), 127.66 (d, C_i, PPh₃, $J_{PC} = 90.8$), 128.74 (d, C_m, PPh₃, $J_{PC} = 12.2$), 131.43 (C₆), 131.77 (d, C_p, PPh₃, $J_{PC} = 2.7$), 133.21 (d, C_o, PPh₃, $J_{PC} = 10.0$), 159.10 (C₄), 161.41 (C₂), 182.56 (d, C=O, $J_{PC} = 2.2$).

Synthesis of 17. A solution of **16** (0.100 g, 0.227 mmol) and Pd(OAc)₂ (0.102 g, 0.454 mmol) in CH₂Cl₂ (20 mL) was refluxed under Ar for 5 h. After the reaction time, the cold solution was filtered over Celite in order to remove some black Pd⁰ formed. The clear yellow solution was evaporated to dryness, the residue redissolved in 15 mL of MeOH and treated with excess of anhydrous LiCl (0.077 g, 1.8 mmol). Subsequent stirring at room temperature gives complex **17** as a yellow precipitate, which was filtered, washed with cold MeOH (2 mL) and Et₂O (10 mL), and air dried. Yield: 0.151 g (83.2 %). Anal. Calc. for [C₂₈H₂₃Cl₂O₃PPd₂]_n (722.17)_n: C, 46.57; H, 3.21; found: C, 46.58; H, 3.74. IR (ν , cm⁻¹): 1637 (ν_{CO}). This polymeric compound was not adequately soluble in the usual organic solvents, preventing accurate NMR measurements. Instead, it was characterized through its reactivity.

Synthesis of 18. To a suspension of **17** (0.067 g, 0.194 mmol) in 15 mL of CH₂Cl₂ Tl(acac) (0.056 g, 0.187 mmol) was added, resulting in an immediate change of the color of the suspension (yellow to gray). The resulting mixture was stirred at room

temperature for 30 min, then filtered over Celite. The pale yellow solution was evaporated to dryness. The treatment of the yellow residue with cold *n* – hexane (5 mL) gave **18** as a pale yellow solid. Yield: 0.067 g (85.2 %). Anal. Calc. for C₃₈H₃₇O₇PPd₂ (849.56): C, 53.73; H, 4.39; found: C, 53.60; H, 4.21. MS (MALDI+) [m/z, (%)]: 750 (10 %) [M-acac]⁺. IR (ν , cm⁻¹): 1586 (ν_{CO}), 1568, 1514 (ν_{CO} , acac). ¹H NMR (CDCl₃): δ = 1.46 (s, 3H, CH₃, acac), 1.99 (s, 3H, CH₃, acac), 2.01 (s, 3H, CH₃, acac), 2.04 (s, 3H, CH₃, acac), 3.88 (s, 3H, OMe), 3.93 (s, 3H, OMe), 5.16 (s, 1H, CH, acac), 5.29 (s, 1H, CH, acac), 5.45 (d, 1H, CHP, ²J_{PH} = 5.0), 6.10 (d, 1H, H₆, C₆H₂, ⁴J_{HH} = 2.5), 6.49 (d, 1H, H₄, C₆H₂), 6.99 (t, 1H, H₃, C₆H₄, ³J_{PH} = ³J_{HH} = 7.5), 7.10 (tdd, 1H, H₄, C₆H₄, ³J_{HH} = ³J_{HH} = 7.5, ⁴J_{PH} = 4.5, ⁴J_{HH} = 1.0), 7.30 (m, 1H, H₅, C₆H₄), 7.48 (td, 2H, H_m, PPh₂, ³J_{HH} = 8, ⁴J_{PH} = 3.5), 7.56-7.59 (m, 3H, H_m + H_p, PPh₂), 7.66 (td, 1H, H_p, PPh₂, ³J_{HH} = 7.0, ⁵J_{PH} = 2.0), 7.76 (dd, 2H, H_o, PPh₂, ³J_{PH} = 12), 7.91 (d, 1H, H₆, C₆H₄, ³J_{HH} = 7.8), 8.03 (dd, 2H, H_o, PPh₂, ³J_{PH} = 13). ¹³C{¹H} NMR (CDCl₃) (the signals due to the carbon atoms C₂ (C₆H₂ group) and one CO (acac group) were not observed): 27.41 (CH₃, acac), 27.46 (CH₃, acac), 27.81 (CH₃, acac), 27.90 (CH₃, acac), 31.73 (d, CHP, ¹J_{PC} = 60.8), 55.42 (OMe), 55.65 (OMe), 95.17 (C₄, C₆H₂) 99.08 (CH, acac), 100.12 (CH, acac), 105.73 (C₆, C₆H₂), 124.46 (d, 1H, C₄, C₆H₄, ³J_{PC} = 12.8), 126.10 (d, C_i, PPh₂, ¹J_{PC} = 90.4), 126.40 (d, C_i, PPh₂, ¹J_{PC} = 69.6), 128.20 (d, C_m, PPh₂, ³J_{PC} = 12.9), 128.32 (d, C_m, PPh₂, ³J_{PC} = 11.5), 129.32 (d, C₃, C₆H₄, ²J_{PC} = 11.5), 129.86 (d, C₅, C₆H₄, ⁴J_{PC} = 3.1), 132.26 (d, C_p, PPh₂, ⁴J_{PC} = 3.2), 132.72 (d, C_p, PPh₂, ⁴J_{PC} = 2.7), 132.82 (d, C_o, PPh₂, ²J_{PC} = 9.7), 133.87 (d, C₆, C₆H₄, ³J_{PC} = 15.2), 136.16 (d, C₂, C₆H₄, ¹J_{PC} = 113.2), 136.35 (d, C_o, PPh₂, ²J_{PC} = 10.7), 158.24 (d, C₁, C₆H₄, ²J_{PC} = 20.1), 160.78 (C₅, C₆H₂), 161.92 (C₁, C₆H₂), 162.49 (C₃, C₆H₂), 185.07 (CO, acac), 187.03

(CO, acac), 188.18 (CO, acac), 213.00 (d, C=O, $^2J_{PC} = 4.9$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.04$.

Synthesis of 19. To a suspension of **17** (0.100 g, 0.138 mmol) in 15 mL of CH_2Cl_2 , PPh_3 (0.073 g, 0.277 mmol) was added. The initial yellow suspension gradually dissolved, and in few minutes a pale yellow solution was obtained. This solution was stirred at room temperature for additional 30 min, and then filtered over Celite to remove any trace of insoluble materials. The clear yellow solution thus obtained was evaporated to dryness. Treatment of the yellow residue with cold *n* – hexane (5 mL) and further stirring gave **19** as a pale yellow solid. Yield: 0.146 g (84.6 %). Complex **19** was recrystallized from CH_2Cl_2/n – hexane to give pale yellow crystals of **19** \cdot 0.5 CH_2Cl_2 , which were used for analytic and spectroscopic measurements. The amount of CH_2Cl_2 was quoted by 1H NMR. Anal. Calc. for $[C_{64}H_{53}Cl_2O_3P_3Pd_2] \cdot 0.5CH_2Cl_2$ (1289.22): C, 60.09; H, 4.22; found: C, 59.92; H, 4.18. MS (MALDI+) [m/z, (%)]: 1211.0 (25%) [$M-Cl$] $^+$. IR (ν , cm^{-1}): 1584 (ν_{CO}). 1H NMR ($CDCl_3$): $\delta = 2.74$ (s, 3H, OMe), 3.80 (s, 3H, OMe), 5.46 (br, 2H, CHP + H_3 , C_6H_2), 5.83 (s, 1H, H_5 , C_6H_2), 6.43 (t, 1H, H_3 , C_6H_4 , $^3J_{PH} = ^3J_{HH} = 7.4$), 7.10 (m, 1H, H_4 , C_6H_4), 6.95 (t, 1H, H_5 , C_6H_4 , $^3J_{HH} = 8.0$), 7.10-7.64 (m, 39H, $H_6(C_6H_4)$ + Ph), 8.41 (br, 2H, H_o , Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 15.9$ (d, 1P, C_6H_4 -2-PPh₂, $^3J_{PP} = 12.9$), 32.91 (s, br, 1P, Pd-PPh₃), 46.55 (s, br, 1P, Pd-PPh₃).

Crystal Structure Determination and Data Collection of 2d and 9b \cdot 2CHCl₃. Crystals of **2d** of adequate quality for X-ray measurements were grown by vapour diffusion of Et₂O into a CH_2Cl_2 solution of **2d** at 25 °C, while crystals of **9b** \cdot 2CHCl₃ were obtained by cooling a CHCl₃ solution of **9b** at low temperature (-18 °C) and standing for several days. All crystals readily loose solvent, thus they were always handled in the mother liquor. A single crystal of each compound was very quickly

mounted at the end of a quartz fiber in a random orientation, covered with magic oil and placed under the cold stream of nitrogen. Data collection was performed at 100 K on an Oxford Diffraction Xcalibur2 diffractometer using graphite-monocromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). An hemisphere of data was collected based on three ω -scan or ϕ -scan runs. The diffraction frames were integrated using the program CrysAlis RED⁴ and the integrated intensities were corrected for absorption with SADABS.⁵

Structure Solution and Refinement. The structures were solved and developed by Patterson and Fourier methods.⁶ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at idealized positions and treated as riding atoms. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The structures were refined to F_{o}^2 , and all reflections were used in the least-squares calculations.⁷

References corresponding to the Experimental Section

- (1) Bittner, S.; Assaf, Y.; Krief, P.; Pomerantz, M.; Ziemnicka, B. T.; Smith, C. G. *J. Org. Chem.* **1985**, *50*, 1712.
- (2) Ramírez, F.; Dershowitz, S. *J. Org. Chem.* **1957**, *22*, 41.
- (3) Teagle, J. A.; Burmeister, J. L. *Inorg. Chim. Acta* **1986**, *118*, 65.
- (4) CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.27p8, 2005.
- (5) Sheldrick, G. M. SADABS: Empirical absorption correction program, Göttingen University, **1996**.
- (6) Sheldrick, G.M. SHELXS-86, *Acta Crystallogr.* **1990**, *A46*, 467.
- (7) Sheldrick, G.M. SHELXL-97: FORTRAN program for the refinement of crystal structures from diffraction data. Göttingen University, **1997**. Molecular graphics were

done using the commercial package SHELXTL-PLUS, Release 5.05/V: © 1996, Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin.

Table S1. Crystal data and structure refinement for **2d**.

Empirical formula	C52 H42 Cl2 N2 O2 P2 Pd2		
Formula weight	1072.52		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2(1)/c		
Unit cell dimensions	$a = 14.5611(4)$ Å	$\alpha = 90^\circ$.	
	$b = 9.8108(2)$ Å	$\beta = 108.644(3)^\circ$.	
	$c = 16.4092(4)$ Å	$\gamma = 90^\circ$.	
Volume	2221.14(9) Å ³		
Z	2		
Density (calculated)	1.604 Mg/m ³		
Absorption coefficient	1.047 mm ⁻¹		
F(000)	1080		
Crystal size	0.39 x 0.16 x 0.02 mm ³		
Theta range for data collection	2.62 to 28.87°.		
Index ranges	-18<=h<=18, -13<=k<=9, -20<=l<=22		
Reflections collected	16269		
Independent reflections	4495 [R(int) = 0.0425]		
Completeness to theta = 28.87°	77.2 %		
Max. and min. transmission	0.9794 and 0.6856		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	4495 / 0 / 281		
Goodness-of-fit on F ²	0.931		
Final R indices [I>2sigma(I)]	R1 = 0.0277, wR2 = 0.0582		
R indices (all data)	R1 = 0.0486, wR2 = 0.0613		
Largest diff. peak and hole	0.744 and -0.606 e.Å ⁻³		

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2d**.
 U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	1265(1)	110(1)	429(1)	11(1)
P(1)	2515(1)	2159(1)	-461(1)	11(1)
Cl(1)	75(1)	-1278(1)	658(1)	17(1)
N(1)	2397(2)	1254(2)	331(2)	11(1)
O(1)	3690(2)	2344(2)	1307(1)	20(1)
C(1)	2313(2)	-659(3)	1391(2)	12(1)
C(2)	2304(2)	-1897(3)	1797(2)	16(1)
C(3)	3101(2)	-2274(3)	2473(2)	18(1)
C(4)	3886(2)	-1411(3)	2782(2)	18(1)
C(5)	3121(2)	197(3)	1689(2)	13(1)
C(6)	3910(2)	-151(3)	2416(2)	16(1)
C(7)	4770(2)	767(3)	2791(2)	26(1)
C(8)	3114(2)	1391(3)	1127(2)	15(1)
C(9)	3744(2)	2119(3)	-500(2)	12(1)
C(10)	4016(2)	1041(3)	-920(2)	20(1)
C(11)	4972(2)	923(3)	-900(2)	23(1)
C(12)	5643(2)	1888(3)	-483(2)	22(1)
C(13)	5370(2)	2968(3)	-75(2)	20(1)
C(14)	4412(2)	3082(3)	-87(2)	17(1)
C(15)	2155(2)	3901(3)	-434(2)	12(1)
C(16)	2387(2)	4901(3)	-940(2)	15(1)
C(17)	2072(2)	6222(3)	-910(2)	17(1)
C(18)	1537(2)	6556(3)	-385(2)	18(1)
C(19)	1302(2)	5575(3)	110(2)	19(1)
C(20)	1610(2)	4242(3)	90(2)	17(1)
C(21)	1757(2)	1392(3)	-1432(2)	13(1)
C(22)	1627(2)	-20(3)	-1482(2)	15(1)
C(23)	1035(2)	-610(3)	-2225(2)	18(1)
C(24)	566(2)	179(3)	-2934(2)	21(1)
C(25)	717(2)	1581(3)	-2899(2)	23(1)
C(26)	1303(2)	2185(3)	-2152(2)	17(1)

Table S3. Bond lengths [\AA] and angles [$^\circ$] for **2d**.

Pd(1)-C(1)	1.962(3)
Pd(1)-N(1)	2.043(2)
Pd(1)-Cl(1)	2.3270(6)
Pd(1)-Cl(1)#1	2.4646(8)
P(1)-N(1)	1.629(2)
P(1)-C(21)	1.788(3)
P(1)-C(15)	1.793(3)
P(1)-C(9)	1.812(3)
Cl(1)-Pd(1)#1	2.4646(8)
N(1)-C(8)	1.393(4)
O(1)-C(8)	1.228(3)
C(1)-C(2)	1.387(4)
C(1)-C(5)	1.400(4)
C(2)-C(3)	1.376(4)
C(3)-C(4)	1.382(4)
C(4)-C(6)	1.380(4)
C(5)-C(6)	1.408(4)
C(5)-C(8)	1.489(4)
C(6)-C(7)	1.504(4)
C(9)-C(14)	1.370(4)
C(9)-C(10)	1.387(4)
C(10)-C(11)	1.386(4)
C(11)-C(12)	1.376(4)
C(12)-C(13)	1.378(4)
C(13)-C(14)	1.393(4)
C(15)-C(20)	1.383(3)
C(15)-C(16)	1.395(4)
C(16)-C(17)	1.381(4)
C(17)-C(18)	1.372(4)
C(18)-C(19)	1.372(4)
C(19)-C(20)	1.386(4)
C(21)-C(26)	1.392(4)
C(21)-C(22)	1.397(4)
C(22)-C(23)	1.376(4)
C(23)-C(24)	1.382(4)
C(24)-C(25)	1.391(4)
C(25)-C(26)	1.383(4)
C(1)-Pd(1)-N(1)	80.44(10)
C(1)-Pd(1)-Cl(1)	94.20(8)
N(1)-Pd(1)-Cl(1)	174.61(7)
C(1)-Pd(1)-Cl(1)#1	173.24(8)
N(1)-Pd(1)-Cl(1)#1	99.18(7)
Cl(1)-Pd(1)-Cl(1)#1	86.06(2)
N(1)-P(1)-C(21)	106.85(12)
N(1)-P(1)-C(15)	113.19(12)
C(21)-P(1)-C(15)	108.77(13)
N(1)-P(1)-C(9)	111.92(12)
C(21)-P(1)-C(9)	107.14(12)
C(15)-P(1)-C(9)	108.76(12)
Pd(1)-Cl(1)-Pd(1)#1	93.94(2)
C(8)-N(1)-P(1)	117.20(17)
C(8)-N(1)-Pd(1)	111.19(16)
P(1)-N(1)-Pd(1)	130.98(14)
C(2)-C(1)-C(5)	119.6(3)
C(2)-C(1)-Pd(1)	126.7(2)

C(5)-C(1)-Pd(1)	113.7(2)
C(3)-C(2)-C(1)	119.2(3)
C(2)-C(3)-C(4)	121.2(3)
C(6)-C(4)-C(3)	121.4(3)
C(1)-C(5)-C(6)	121.2(3)
C(1)-C(5)-C(8)	114.6(3)
C(6)-C(5)-C(8)	123.9(2)
C(4)-C(6)-C(5)	117.3(3)
C(4)-C(6)-C(7)	119.4(3)
C(5)-C(6)-C(7)	123.3(3)
O(1)-C(8)-N(1)	123.3(3)
O(1)-C(8)-C(5)	125.5(3)
N(1)-C(8)-C(5)	111.1(2)
C(14)-C(9)-C(10)	120.1(2)
C(14)-C(9)-P(1)	121.4(2)
C(10)-C(9)-P(1)	118.4(2)
C(11)-C(10)-C(9)	119.7(3)
C(12)-C(11)-C(10)	120.1(3)
C(11)-C(12)-C(13)	120.1(3)
C(12)-C(13)-C(14)	119.9(3)
C(9)-C(14)-C(13)	120.0(3)
C(20)-C(15)-C(16)	119.7(2)
C(20)-C(15)-P(1)	118.4(2)
C(16)-C(15)-P(1)	121.79(19)
C(17)-C(16)-C(15)	119.4(2)
C(18)-C(17)-C(16)	120.5(3)
C(17)-C(18)-C(19)	120.2(3)
C(18)-C(19)-C(20)	120.2(3)
C(15)-C(20)-C(19)	119.8(3)
C(26)-C(21)-C(22)	119.0(3)
C(26)-C(21)-P(1)	120.8(2)
C(22)-C(21)-P(1)	120.2(2)
C(23)-C(22)-C(21)	120.3(3)
C(22)-C(23)-C(24)	120.7(3)
C(23)-C(24)-C(25)	119.4(3)
C(26)-C(25)-C(24)	120.3(3)
C(25)-C(26)-C(21)	120.3(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	7(1)	12(1)	14(1)	2(1)	3(1)	0(1)
P(1)	8(1)	10(1)	14(1)	1(1)	3(1)	0(1)
Cl(1)	9(1)	18(1)	24(1)	8(1)	5(1)	1(1)
N(1)	7(1)	13(1)	11(1)	1(1)	1(1)	-1(1)
O(1)	20(1)	18(1)	18(1)	-2(1)	3(1)	-8(1)
C(1)	9(2)	15(1)	12(2)	1(1)	5(2)	2(1)
C(2)	12(2)	15(2)	22(2)	3(1)	6(2)	0(1)
C(3)	18(2)	17(2)	19(2)	7(1)	6(2)	4(1)
C(4)	14(2)	25(2)	12(2)	3(1)	-1(2)	7(1)
C(5)	13(2)	13(1)	15(2)	-2(1)	6(2)	2(1)
C(6)	13(2)	21(2)	13(2)	-2(1)	3(2)	2(1)
C(7)	20(2)	31(2)	19(2)	-1(2)	-6(2)	-3(2)
C(8)	12(2)	14(1)	22(2)	0(1)	10(2)	1(1)
C(9)	9(1)	15(1)	13(2)	4(1)	2(2)	1(1)
C(10)	18(2)	16(2)	27(2)	-2(1)	10(2)	-3(1)
C(11)	20(2)	21(2)	32(2)	1(1)	12(2)	4(1)
C(12)	9(2)	31(2)	27(2)	7(1)	7(2)	3(1)
C(13)	11(2)	27(2)	18(2)	1(1)	2(2)	-7(1)
C(14)	13(2)	18(2)	18(2)	-1(1)	5(2)	-1(1)
C(15)	6(2)	13(1)	12(2)	-1(1)	-4(2)	0(1)
C(16)	11(2)	18(2)	17(2)	-2(1)	3(2)	-1(1)
C(17)	14(2)	12(1)	21(2)	3(1)	1(2)	-3(1)
C(18)	14(2)	13(2)	25(2)	-3(1)	2(2)	1(1)
C(19)	18(2)	19(2)	23(2)	-4(1)	9(2)	1(1)
C(20)	15(2)	14(1)	20(2)	1(1)	5(2)	-1(1)
C(21)	10(2)	16(1)	15(2)	-1(1)	5(2)	0(1)
C(22)	12(1)	14(1)	19(2)	2(1)	5(2)	2(1)
C(23)	16(2)	15(2)	24(2)	-7(1)	6(2)	-1(1)
C(24)	12(2)	30(2)	18(2)	-10(1)	0(2)	-1(1)
C(25)	21(2)	28(2)	17(2)	1(1)	1(2)	6(2)
C(26)	15(2)	15(2)	21(2)	1(1)	4(2)	-1(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2d**.

	x	y	z	U(eq)
H(2A)	1753	-2477	1610	20
H(3A)	3112	-3142	2732	21
H(4A)	4421	-1691	3258	21
H(7A)	5253	294	3263	39
H(7B)	4561	1600	3010	39
H(7C)	5057	1003	2344	39
H(10A)	3549	387	-1220	23
H(11A)	5164	173	-1175	28
H(12A)	6296	1810	-476	27
H(13A)	5834	3634	213	23
H(14A)	4222	3829	192	20
H(16A)	2759	4675	-1303	18
H(17A)	2226	6905	-1256	20
H(18A)	1330	7470	-365	22
H(19A)	927	5810	469	23
H(20A)	1448	3565	434	20
H(22A)	1948	-575	-1001	18
H(23A)	947	-1570	-2252	22
H(24A)	146	-232	-3440	25
H(25A)	415	2126	-3390	28
H(26A)	1395	3144	-2130	21

Table S6. Crystal data and structure refinement for **9b2CHCl₃**.

Empirical formula	C56 H46 Cl8 O4 P2 Pd2	
Formula weight	1341.27	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.010(4) Å	α = 93.230(13)°.
	b = 9.1801(6) Å	β = 103.86(3)°.
	c = 17.024(4) Å	γ = 99.287(18)°.
Volume	1342.6(7) Å ³	
Z	1	
Density (calculated)	1.659 Mg/m ³	
Absorption coefficient	1.174 mm ⁻¹	
F(000)	672	
Crystal size	0.19 x 0.11 x 0.02 mm ³	
Theta range for data collection	2.68 to 25.00°.	
Index ranges	-10<=h<=10, -10<=k<=10, -20<=l<=20	
Reflections collected	8974	
Independent reflections	4332 [R(int) = 0.0408]	
Completeness to theta = 25.00°	91.5 %	
Absorption correction	None	
Max. and min. transmission	0.9769 and 0.8077	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4332 / 0 / 326	
Goodness-of-fit on F ²	0.960	
Final R indices [I>2sigma(I)]	R1 = 0.0324, wR2 = 0.0479	
R indices (all data)	R1 = 0.0591, wR2 = 0.0503	
Largest diff. peak and hole	0.578 and -0.604 e.Å ⁻³	

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9b·2CHCl₃**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	488(1)	-52(1)	1065(1)	14(1)
Cl(1)	1767(1)	-174(1)	-46(1)	19(1)
P(1)	1728(1)	-1617(1)	2476(1)	14(1)
C(1)	-658(4)	-300(4)	1918(2)	14(1)
C(2)	-2052(4)	172(4)	1921(2)	18(1)
C(3)	-2838(4)	-216(4)	2510(2)	22(1)
C(4)	-2290(4)	-1106(4)	3098(2)	20(1)
C(5)	-904(4)	-1595(4)	3105(2)	18(1)
C(6)	-89(4)	-1173(4)	2539(2)	14(1)
C(7)	2893(4)	-1880(4)	3466(2)	14(1)
C(8)	4017(4)	-2774(4)	3500(2)	17(1)
C(9)	4952(4)	-2978(4)	4244(2)	22(1)
C(10)	4765(5)	-2313(4)	4953(2)	24(1)
C(11)	3641(5)	-1439(4)	4924(2)	21(1)
C(12)	2732(4)	-1200(4)	4176(2)	16(1)
C(13)	1441(4)	-3355(4)	1864(2)	14(1)
C(14)	1980(4)	-3481(4)	1182(2)	20(1)
C(15)	1733(5)	-4860(4)	727(2)	24(1)
C(16)	948(5)	-6080(4)	977(2)	24(1)
C(17)	404(5)	-5967(4)	1655(2)	24(1)
C(18)	645(5)	-4602(4)	2106(2)	24(1)
C(19)	2501(4)	-171(4)	1956(2)	12(1)
C(20)	3065(4)	1270(4)	2470(2)	14(1)
O(1)	2662(3)	1487(3)	3104(1)	19(1)
C(21)	4158(4)	2484(4)	2217(2)	15(1)
C(22)	4895(4)	3671(4)	2795(2)	20(1)
C(23)	5939(5)	4790(4)	2607(2)	22(1)
C(24)	6234(4)	4780(4)	1852(2)	22(1)
C(25)	5470(5)	3603(4)	1271(2)	20(1)
O(2)	5789(3)	3696(3)	529(2)	32(1)
C(26)	4457(4)	2447(4)	1462(2)	17(1)
C(27)	4835(5)	2681(4)	-134(2)	34(1)
C(28)	562(4)	2937(4)	3997(2)	23(1)
Cl(3)	539(1)	1765(1)	4778(1)	29(1)
Cl(4)	-1297(1)	3329(1)	3592(1)	31(1)
Cl(5)	1890(1)	4586(1)	4364(1)	52(1)

Table S8. Bond lengths [\AA] and angles [$^\circ$] for **9b·2CHCl₃**.

Pd(1)-C(1)	1.977(4)
Pd(1)-C(19)	2.090(3)
Pd(1)-Cl(1)#1	2.3804(14)
Pd(1)-Cl(1)	2.4443(13)
Pd(1)-P(1)	2.9511(12)
Cl(1)-Pd(1)#1	2.3804(14)
P(1)-C(6)	1.775(4)
P(1)-C(19)	1.777(4)
P(1)-C(13)	1.802(4)
P(1)-C(7)	1.811(4)
C(1)-C(2)	1.395(5)
C(1)-C(6)	1.411(4)
C(2)-C(3)	1.391(5)
C(3)-C(4)	1.377(5)
C(4)-C(5)	1.392(5)
C(5)-C(6)	1.381(5)
C(7)-C(12)	1.378(5)
C(7)-C(8)	1.396(5)
C(8)-C(9)	1.384(4)
C(9)-C(10)	1.379(5)
C(10)-C(11)	1.384(5)
C(11)-C(12)	1.390(4)
C(13)-C(14)	1.367(5)
C(13)-C(18)	1.387(5)
C(14)-C(15)	1.402(5)
C(15)-C(16)	1.370(5)
C(16)-C(17)	1.363(6)
C(17)-C(18)	1.390(5)
C(19)-C(20)	1.488(4)
C(20)-O(1)	1.233(4)
C(20)-C(21)	1.517(5)
C(21)-C(26)	1.374(5)
C(21)-C(22)	1.389(5)
C(22)-C(23)	1.383(5)
C(23)-C(24)	1.374(5)
C(24)-C(25)	1.390(5)
C(25)-O(2)	1.364(4)
C(25)-C(26)	1.391(5)
O(2)-C(27)	1.428(4)
C(28)-Cl(5)	1.750(4)
C(28)-Cl(4)	1.756(4)
C(28)-Cl(3)	1.758(4)
C(1)-Pd(1)-C(19)	87.52(15)
C(1)-Pd(1)-Cl(1)#1	93.31(11)
C(19)-Pd(1)-Cl(1)#1	177.94(10)
C(1)-Pd(1)-Cl(1)	170.81(10)
C(19)-Pd(1)-Cl(1)	93.51(11)
Cl(1)#1-Pd(1)-Cl(1)	85.97(5)
C(1)-Pd(1)-P(1)	61.09(11)
C(19)-Pd(1)-P(1)	36.49(10)
Cl(1)#1-Pd(1)-P(1)	145.37(4)
Cl(1)-Pd(1)-P(1)	115.46(4)
Pd(1)#1-Cl(1)-Pd(1)	94.03(5)
C(6)-P(1)-C(19)	103.58(17)
C(6)-P(1)-C(13)	110.31(17)

C(19)-P(1)-C(13)	108.63(18)
C(6)-P(1)-C(7)	111.37(18)
C(19)-P(1)-C(7)	117.30(16)
C(13)-P(1)-C(7)	105.61(16)
C(6)-P(1)-Pd(1)	70.56(12)
C(19)-P(1)-Pd(1)	44.37(11)
C(13)-P(1)-Pd(1)	93.08(11)
C(7)-P(1)-Pd(1)	158.44(12)
C(2)-C(1)-C(6)	117.0(4)
C(2)-C(1)-Pd(1)	126.3(3)
C(6)-C(1)-Pd(1)	116.3(3)
C(3)-C(2)-C(1)	120.9(4)
C(4)-C(3)-C(2)	121.4(4)
C(3)-C(4)-C(5)	118.8(4)
C(6)-C(5)-C(4)	120.2(4)
C(5)-C(6)-C(1)	121.7(4)
C(5)-C(6)-P(1)	126.9(3)
C(1)-C(6)-P(1)	111.5(3)
C(12)-C(7)-C(8)	119.5(3)
C(12)-C(7)-P(1)	122.3(3)
C(8)-C(7)-P(1)	118.2(3)
C(9)-C(8)-C(7)	119.9(4)
C(10)-C(9)-C(8)	120.2(4)
C(9)-C(10)-C(11)	120.2(4)
C(10)-C(11)-C(12)	119.5(4)
C(7)-C(12)-C(11)	120.6(4)
C(14)-C(13)-C(18)	119.6(3)
C(14)-C(13)-P(1)	122.6(3)
C(18)-C(13)-P(1)	117.8(3)
C(13)-C(14)-C(15)	120.5(4)
C(16)-C(15)-C(14)	119.0(4)
C(17)-C(16)-C(15)	121.0(4)
C(16)-C(17)-C(18)	120.0(4)
C(13)-C(18)-C(17)	119.8(4)
C(20)-C(19)-P(1)	113.1(3)
C(20)-C(19)-Pd(1)	109.8(2)
P(1)-C(19)-Pd(1)	99.14(17)
O(1)-C(20)-C(19)	120.8(4)
O(1)-C(20)-C(21)	119.5(3)
C(19)-C(20)-C(21)	119.7(3)
C(26)-C(21)-C(22)	119.7(4)
C(26)-C(21)-C(20)	123.5(3)
C(22)-C(21)-C(20)	116.8(4)
C(23)-C(22)-C(21)	119.4(4)
C(24)-C(23)-C(22)	121.5(4)
C(23)-C(24)-C(25)	118.7(4)
O(2)-C(25)-C(24)	115.2(4)
O(2)-C(25)-C(26)	124.6(4)
C(24)-C(25)-C(26)	120.2(4)
C(25)-O(2)-C(27)	117.9(3)
C(21)-C(26)-C(25)	120.3(4)
Cl(5)-C(28)-Cl(4)	110.1(2)
Cl(5)-C(28)-Cl(3)	110.2(2)
Cl(4)-C(28)-Cl(3)	110.8(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z

Table S9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9b·2CHCl₃**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^{*} b^{*} U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	14(1)	15(1)	13(1)	3(1)	2(1)	2(1)
Cl(1)	16(1)	28(1)	14(1)	6(1)	1(1)	4(1)
P(1)	15(1)	14(1)	11(1)	3(1)	2(1)	1(1)
C(1)	10(2)	11(2)	14(2)	-1(2)	-5(2)	-2(2)
C(2)	16(2)	17(2)	17(2)	0(2)	-3(2)	1(2)
C(3)	14(2)	22(2)	25(2)	-5(2)	0(2)	4(2)
C(4)	22(2)	23(2)	16(2)	3(2)	10(2)	-1(2)
C(5)	21(3)	14(2)	15(2)	2(2)	-2(2)	-1(2)
C(6)	14(2)	15(2)	10(2)	-1(2)	-2(2)	-1(2)
C(7)	17(2)	12(2)	13(2)	5(2)	5(2)	0(2)
C(8)	16(2)	17(2)	16(2)	1(2)	3(2)	0(2)
C(9)	14(2)	26(3)	23(2)	6(2)	-2(2)	3(2)
C(10)	18(3)	24(3)	21(2)	10(2)	-6(2)	-5(2)
C(11)	25(3)	18(2)	14(2)	0(2)	0(2)	-5(2)
C(12)	16(2)	17(2)	15(2)	5(2)	3(2)	1(2)
C(13)	16(2)	13(2)	11(2)	5(2)	-3(2)	4(2)
C(14)	25(3)	10(2)	20(2)	1(2)	3(2)	-4(2)
C(15)	30(3)	21(2)	20(2)	-2(2)	7(2)	7(2)
C(16)	25(3)	11(2)	31(3)	-1(2)	-5(2)	6(2)
C(17)	24(3)	14(2)	30(3)	4(2)	2(2)	-4(2)
C(18)	31(3)	21(2)	19(2)	1(2)	3(2)	3(2)
C(19)	16(2)	12(2)	6(2)	1(2)	2(2)	2(2)
C(20)	9(2)	15(2)	14(2)	4(2)	-5(2)	6(2)
O(1)	24(2)	19(2)	15(2)	0(1)	6(1)	4(1)
C(21)	12(2)	14(2)	20(2)	4(2)	2(2)	7(2)
C(22)	17(2)	21(2)	20(2)	3(2)	0(2)	5(2)
C(23)	20(3)	14(2)	29(3)	2(2)	0(2)	2(2)
C(24)	14(2)	18(2)	33(3)	6(2)	4(2)	1(2)
C(25)	15(2)	25(3)	23(2)	10(2)	6(2)	4(2)
O(2)	31(2)	36(2)	29(2)	5(2)	12(2)	-7(2)
C(26)	11(2)	13(2)	22(2)	3(2)	-2(2)	0(2)
C(27)	44(3)	36(3)	23(3)	7(2)	16(3)	2(2)
C(28)	22(2)	23(2)	25(2)	8(2)	4(2)	6(2)
Cl(3)	37(1)	25(1)	29(1)	13(1)	13(1)	7(1)
Cl(4)	23(1)	34(1)	35(1)	8(1)	3(1)	7(1)
Cl(5)	35(1)	40(1)	67(1)	30(1)	-9(1)	-11(1)

Table S10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9b²CHCl₃**.

	x	y	z	U(eq)
H(2A)	-2471	767	1515	22
H(3A)	-3772	141	2508	26
H(4A)	-2849	-1381	3490	24
H(5A)	-517	-2222	3501	22
H(8A)	4141	-3241	3013	20
H(9A)	5724	-3578	4267	26
H(10A)	5410	-2456	5462	28
H(11A)	3491	-1005	5413	25
H(12A)	1994	-562	4153	19
H(14A)	2526	-2629	1016	24
H(15A)	2104	-4946	253	28
H(16A)	781	-7018	674	29
H(17A)	-141	-6823	1819	29
H(18A)	266	-4523	2578	29
H(19A)	3324	-464	1709	14
H(22A)	4684	3713	3316	24
H(23A)	6464	5585	3010	27
H(24A)	6947	5561	1729	27
H(26A)	3970	1627	1069	20
H(27A)	5084	2959	-641	50
H(27B)	3739	2712	-170	50
H(27C)	5027	1675	-46	50
H(28A)	898	2421	3554	28