

Electronic Supporting Information (ESI)

Metal phosphine aldehyde complexes and their application in Cu-free Sonogashira and Suzuki–Miyaura cross-coupling reactions

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1. NMR Data

3-(Diphenylphosphino)propanal (**PCHO**)

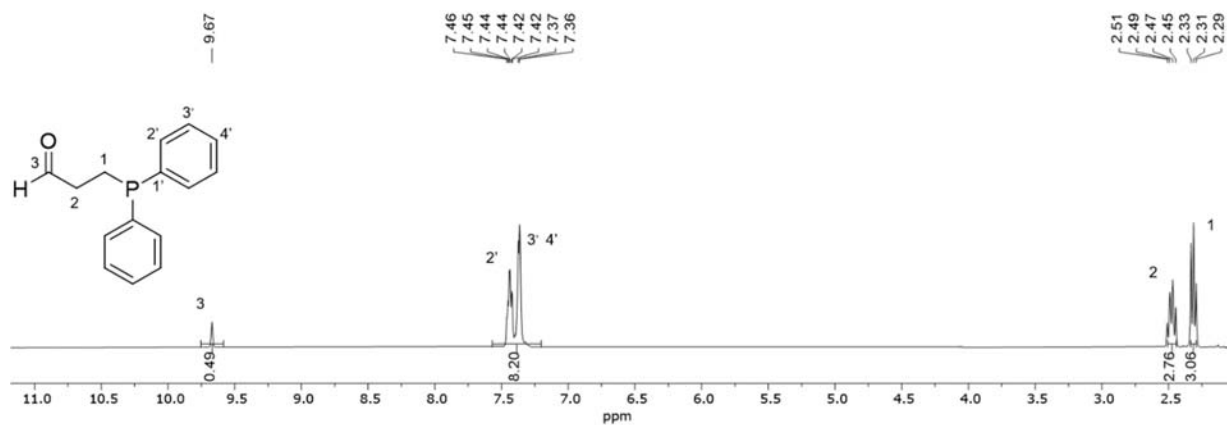


Figure S1. ¹H NMR spectrum of **PCHO** in CD₃CN at 25 °C.

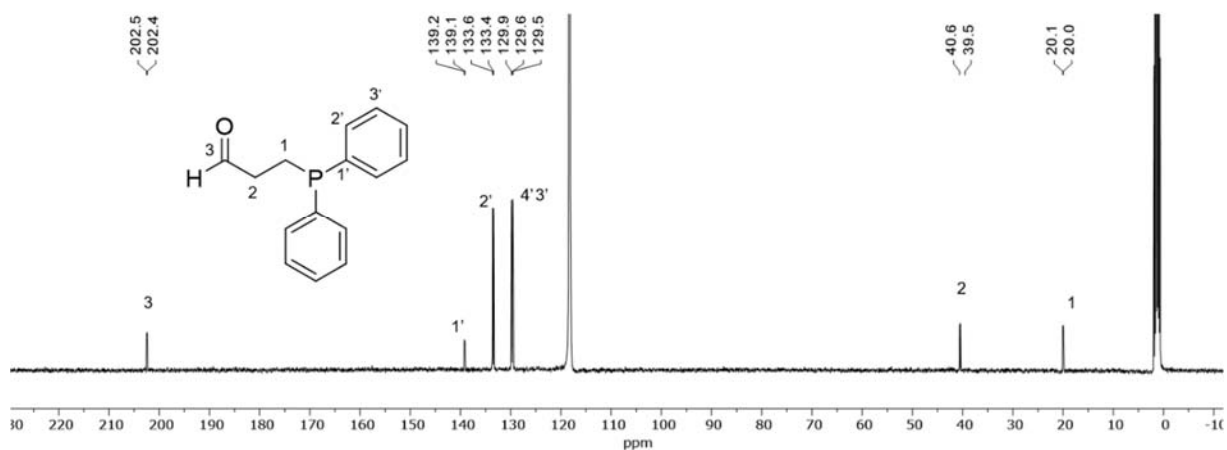


Figure S2. ¹³C{¹H} NMR spectrum of **PCHO** in CD₃CN at 25 °C.

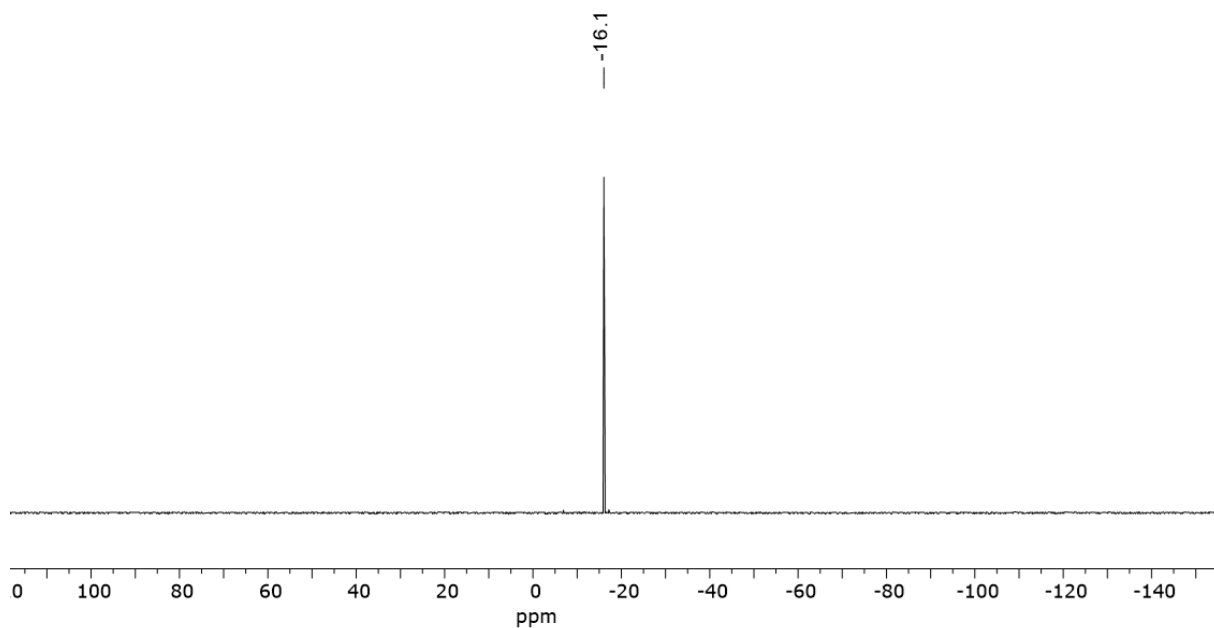


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **PCHO** in CD_3CN at 25 °C.

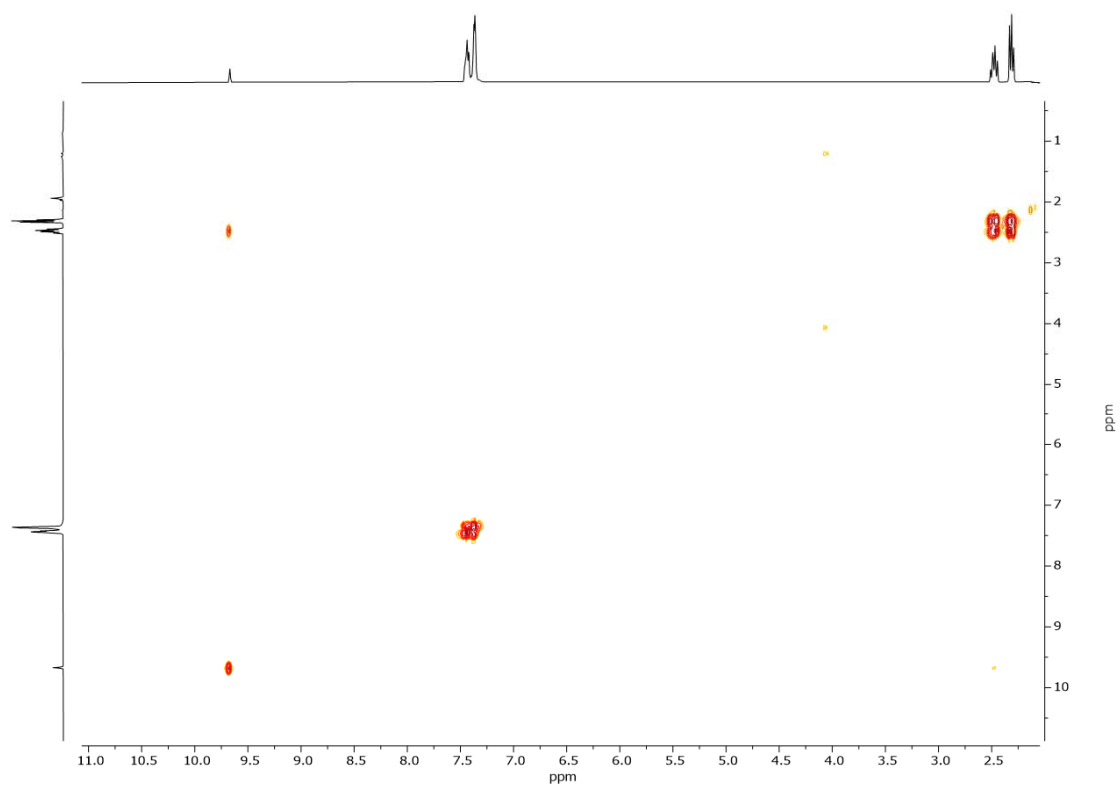


Figure S4. ^1H - ^1H COSY spectrum of **PCHO** in CD_3CN at 25 °C.

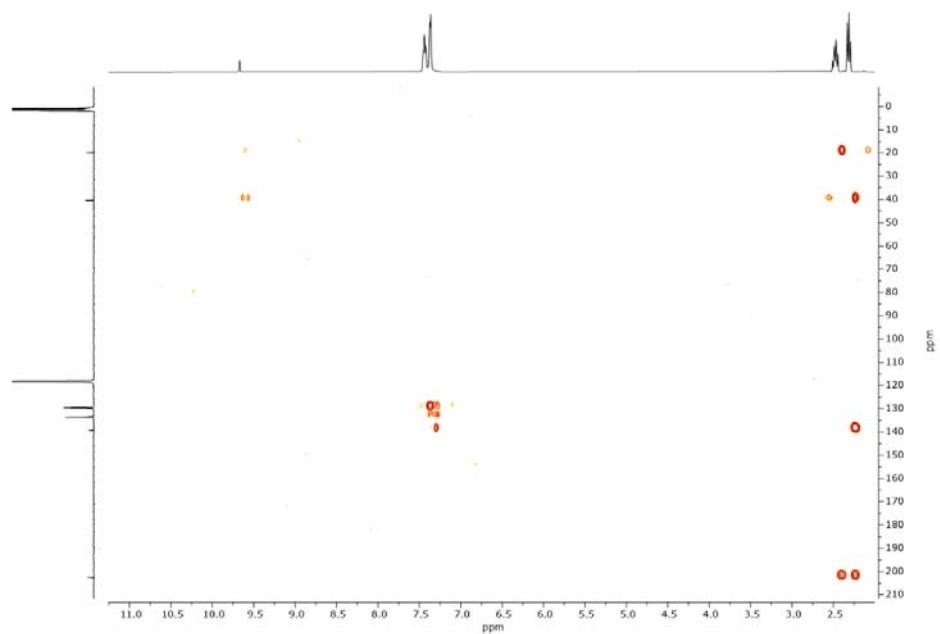


Figure S5. ^1H - ^{13}C HMBC spectrum of **PCHO** in CD_3CN at 25 $^\circ\text{C}$.

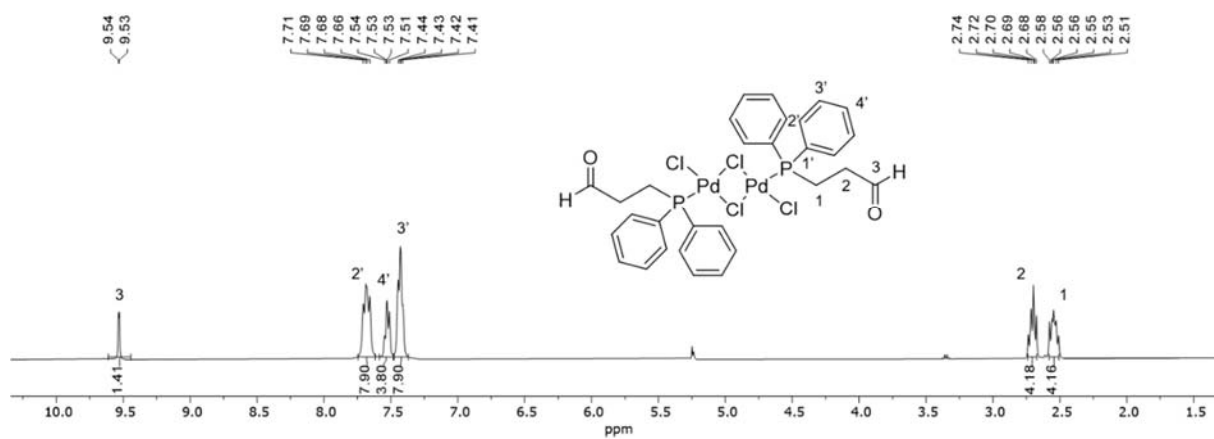


Figure S6. ^1H NMR spectrum of $\mathbf{1}$ in CD_2Cl_2 at $25\text{ }^\circ\text{C}$.

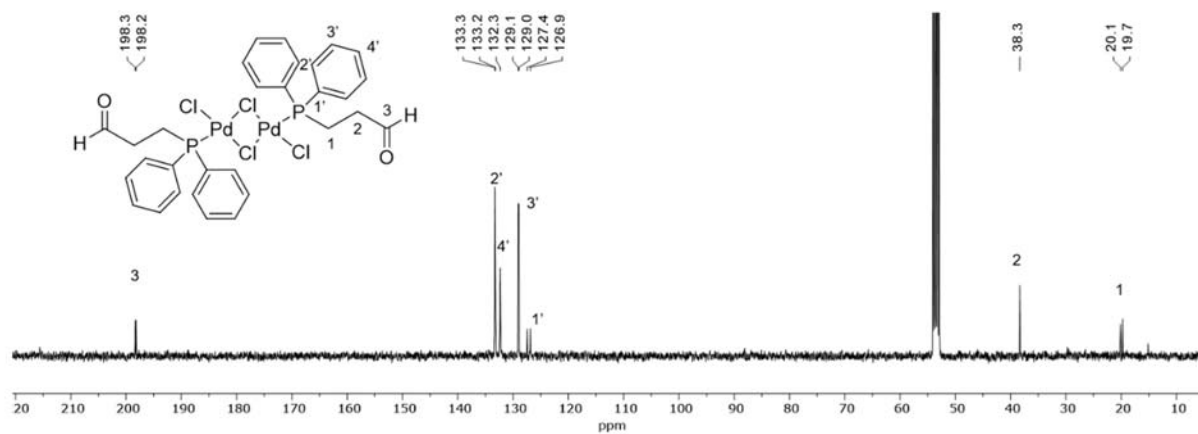


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\mathbf{1}$ in CD_2Cl_2 at $25\text{ }^\circ\text{C}$.

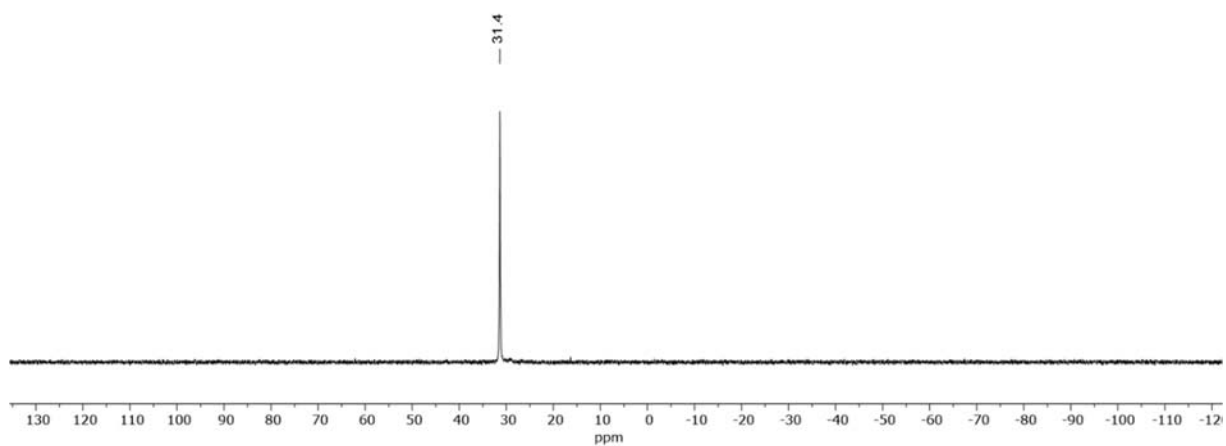


Figure S8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in CD_2Cl_2 at 25 °C.

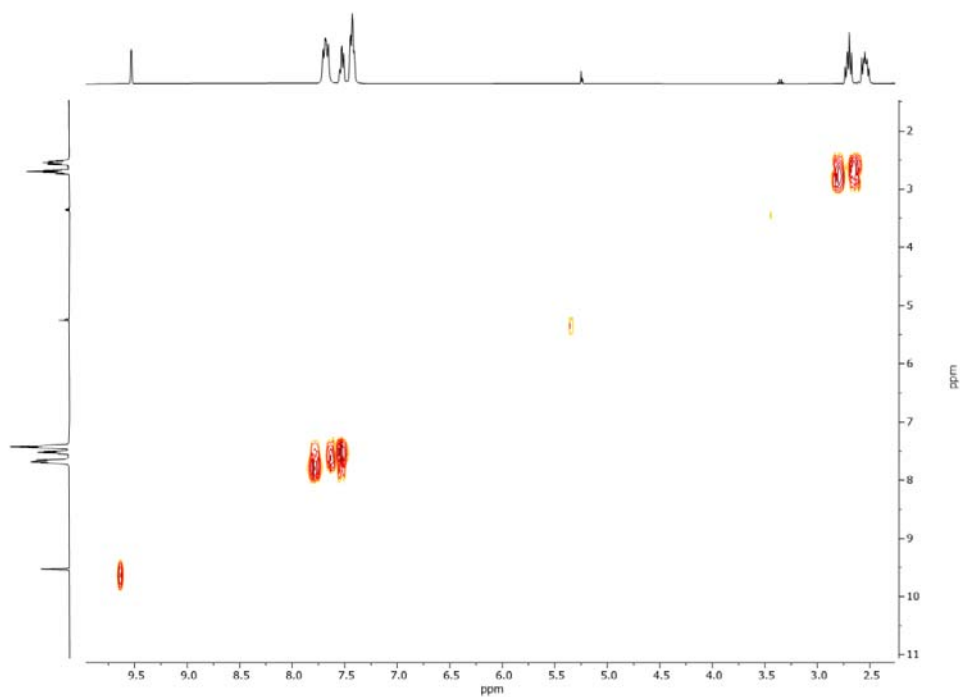


Figure S9. ^1H - ^1H COSY spectrum of **1** in CD_2Cl_2 at 25 °C.

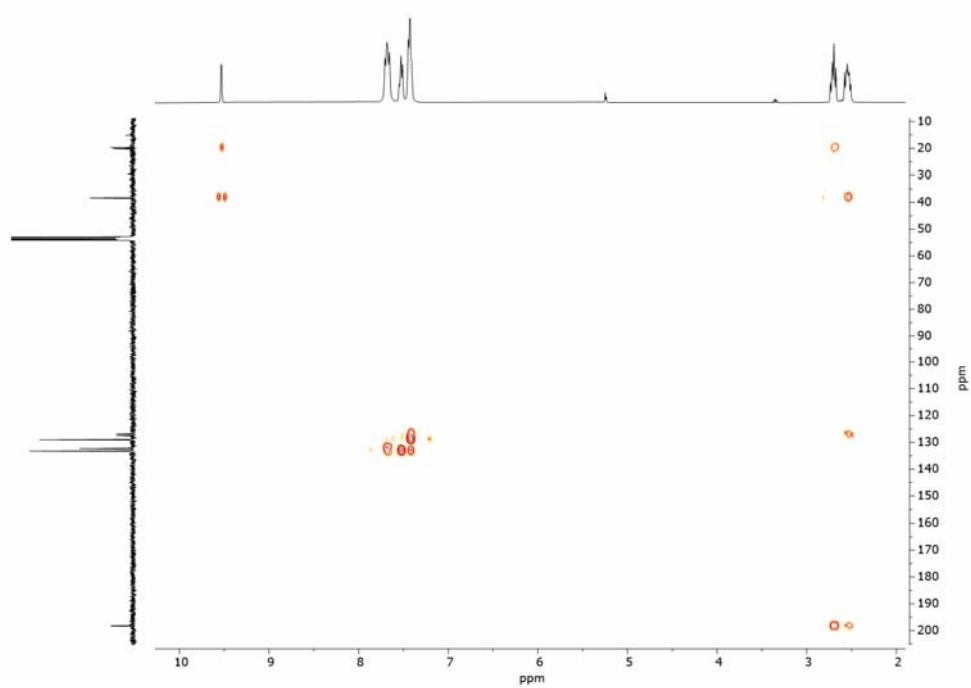


Figure S10. ^1H - ^{13}C HMBC spectrum of **1** in CD_2Cl_2 at 25 °C.

trans-[PdCl₂(PCHO-κP)₂] (**2**)

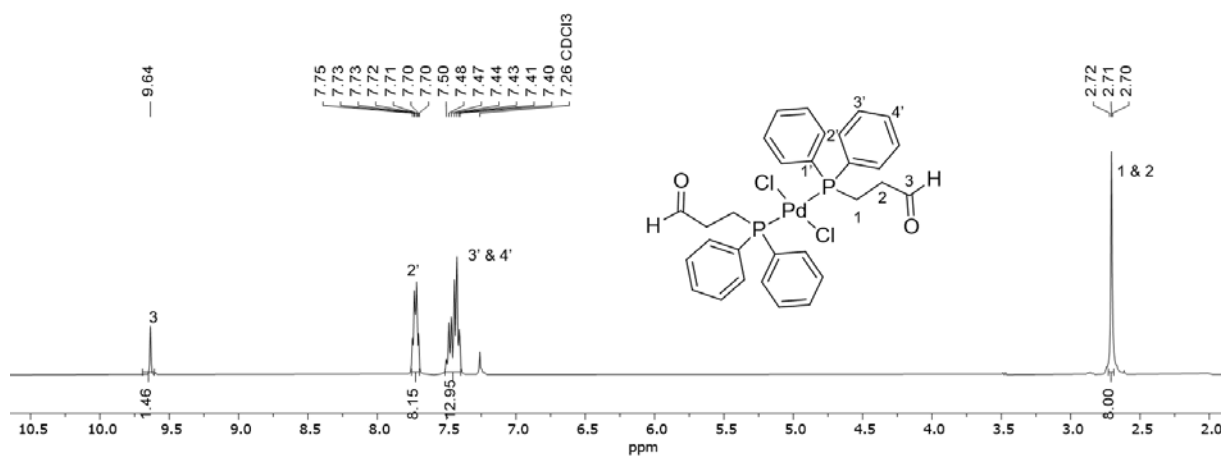


Figure S11. ¹H NMR spectrum of **2** in CDCl₃ at 25 °C.

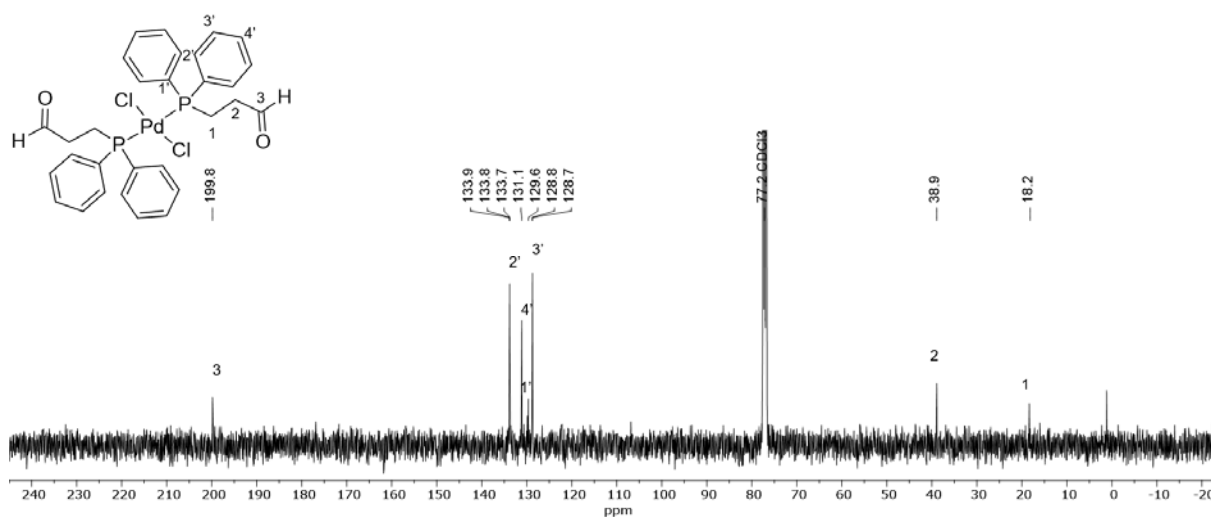


Figure S12. ¹³C{¹H} NMR spectrum of **2** in CDCl₃ at 25 °C.

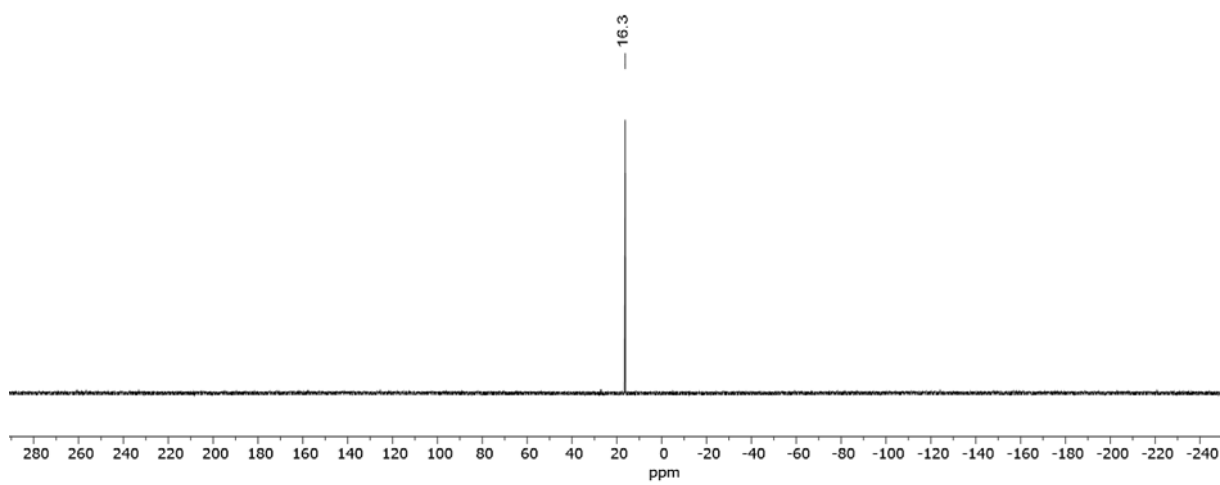


Figure S13. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in CDCl_3 at 25 °C

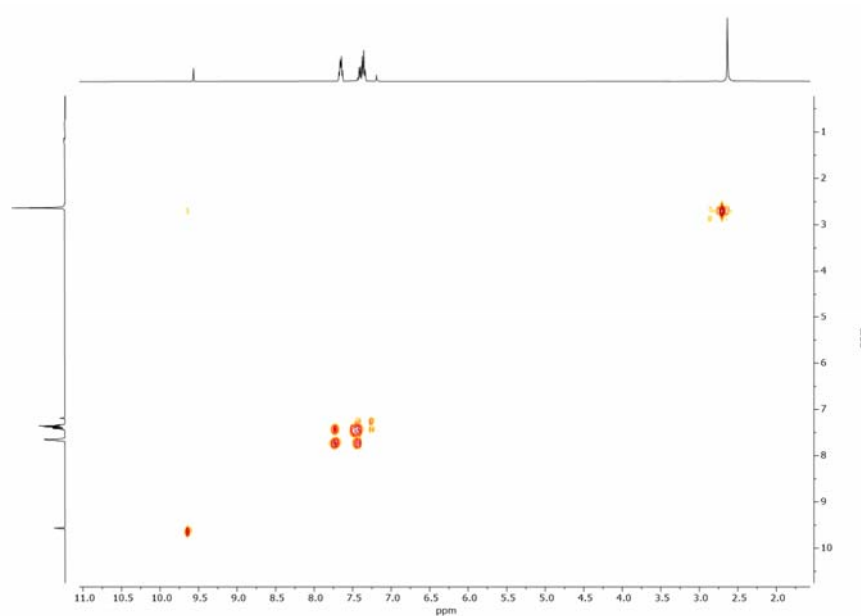


Figure S14. ^1H - ^1H COSY spectrum of **2** in CDCl_3 at 25 °C.

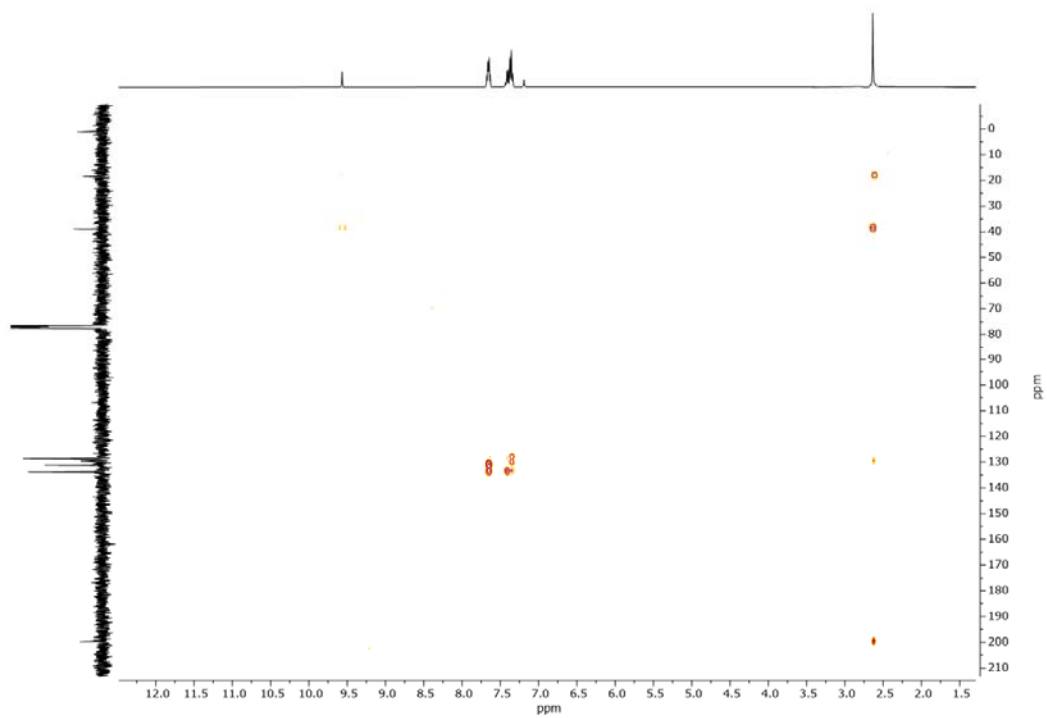


Figure S15. ^1H - ^{13}C HMBC spectrum of **2** in CDCl_3 at 25 °C.

trans-[PtCl₂(PCHO-κP)₂] (**3**)

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 9.65 – 9.64 (m, 1H), 7.77 – 7.72 (m, 4H), 7.50 – 7.71 (m, 6H), 2.80 – 2.72 (m, 4H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm) = 199.9 – 199.8 (m, C3), 133.9 – 133.7 (m, C2'), 131.1 (C4'), 129.5 – 129.2 (C1'), 128.7 – 128.6 (m, C2'), 38.7 (C2), 17.0 (C1). ³¹P{¹H} NMR (162 MHz, CDCl₃) δ (ppm) = 12.4 (s + Pt satellites, ¹J_{P,Pt} = 2564 Hz).

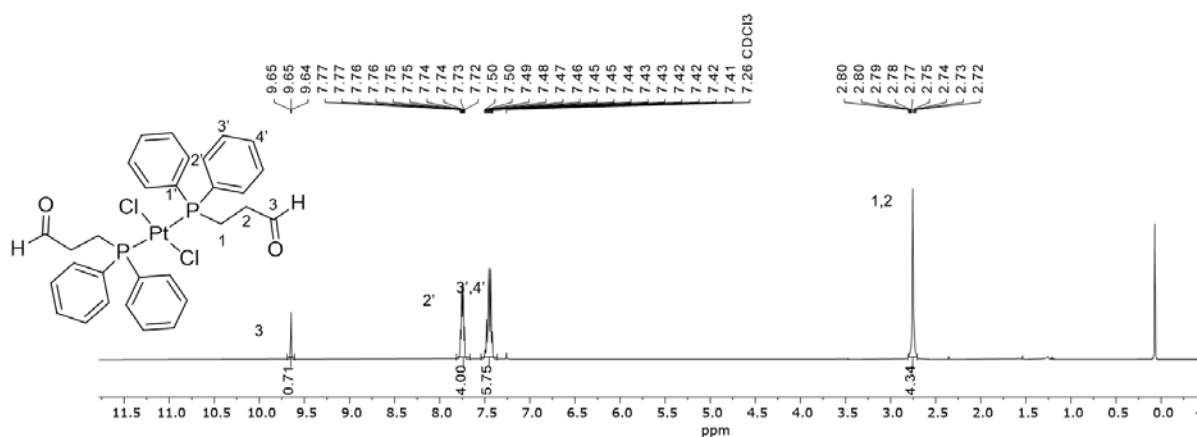


Figure S16. ¹H NMR spectrum of **3** in CDCl₃ at 25 °C.

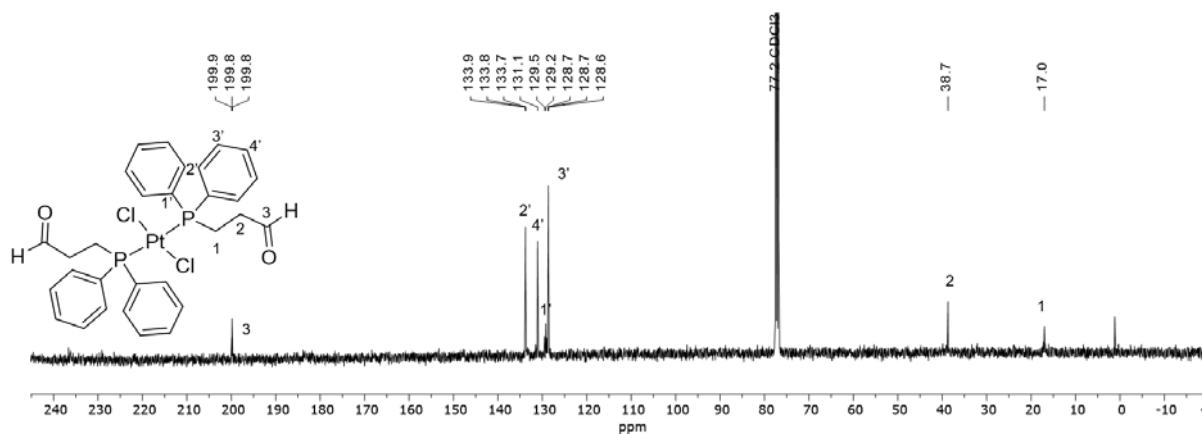


Figure S17. ¹³C{¹H} NMR spectrum of **3** in CDCl₃ at 25 °C.

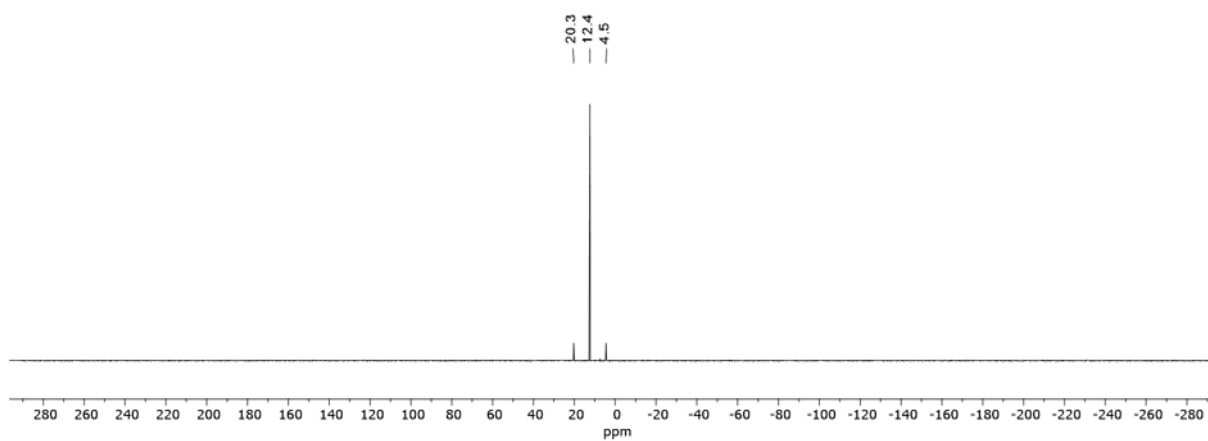


Figure S18. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** in CDCl_3 at 25 °C.

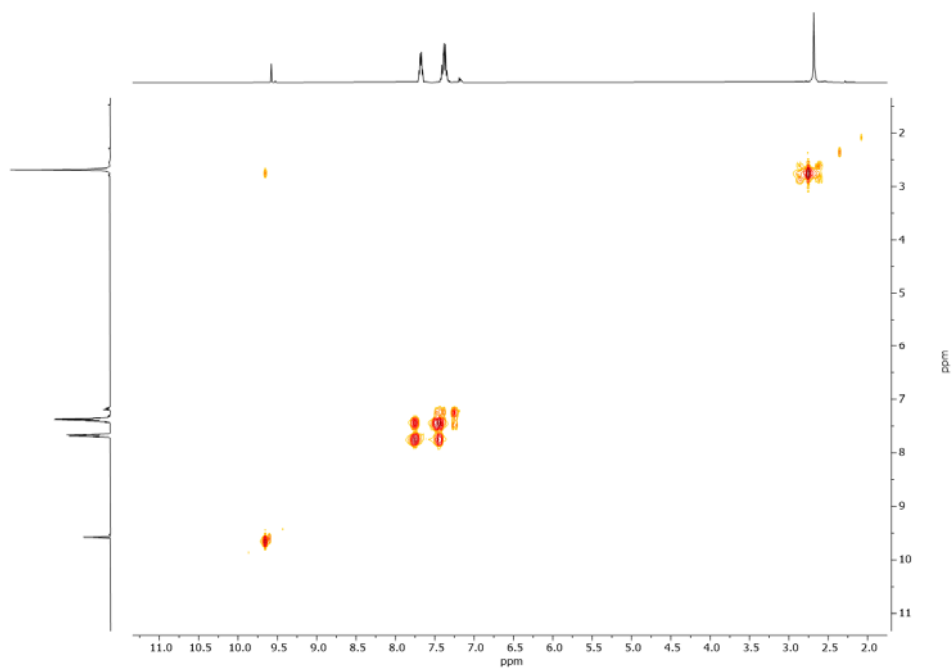


Figure S19. ^1H - ^1H COSY spectrum of **3** in CDCl_3 at 25 °C.

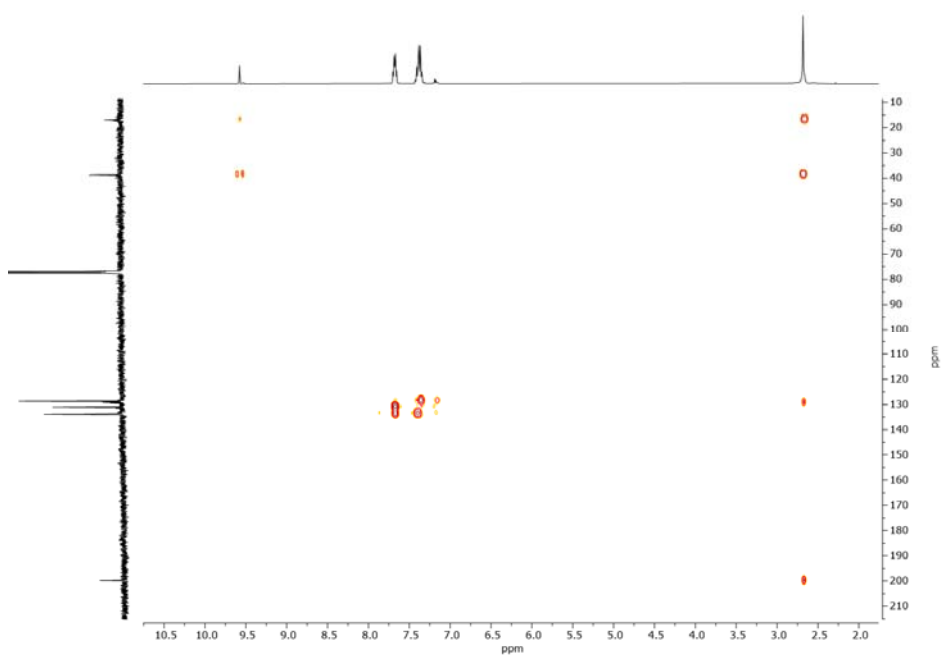


Figure S20. ^1H - ^{13}C HMBC spectrum of **3** in CDCl_3 at 25 °C.

cis-[PtCl₂(PCHO-κP)₂] (**4**)

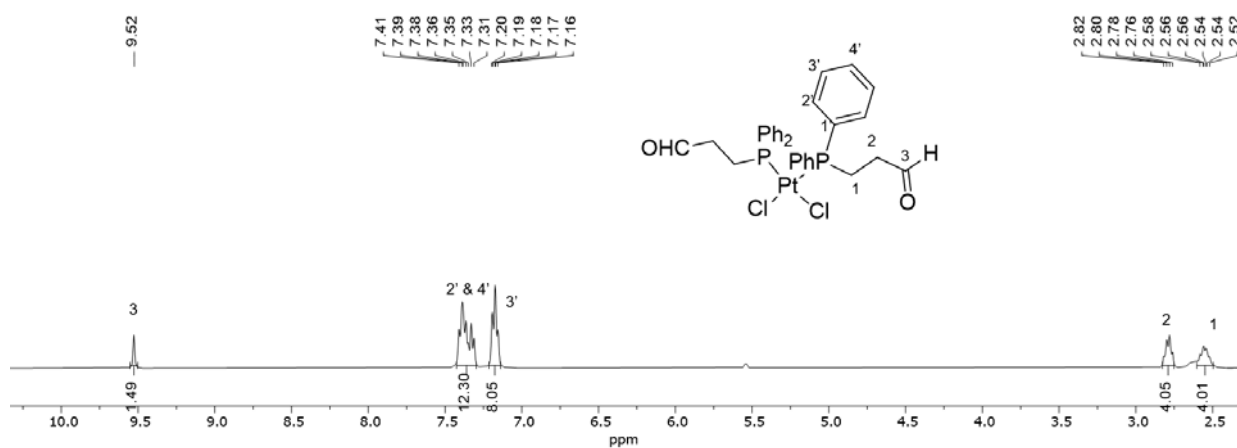


Figure S21. ¹H NMR spectrum of **4** in CDCl₃ at 25 °C.

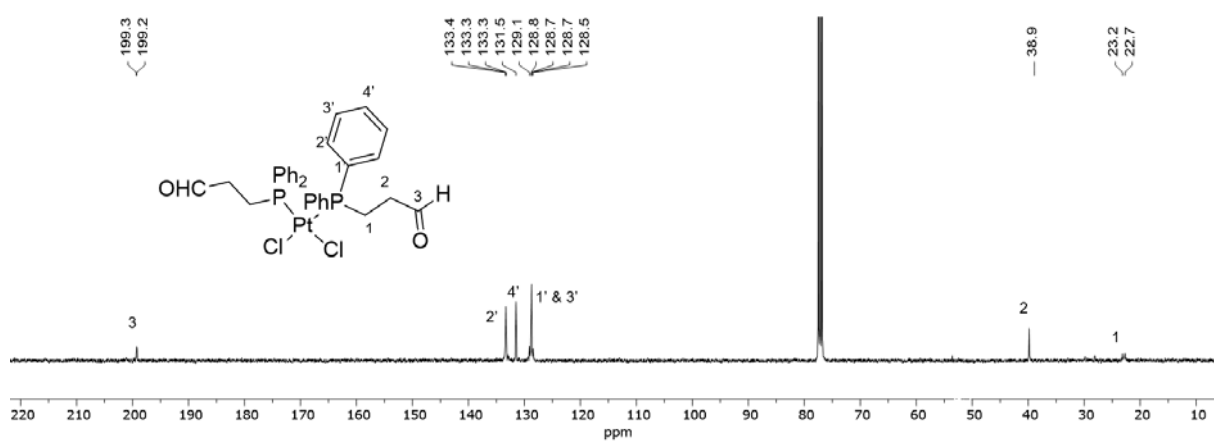


Figure S22. ¹³C{¹H} NMR spectrum of **4** in CDCl₃ at 25 °C.

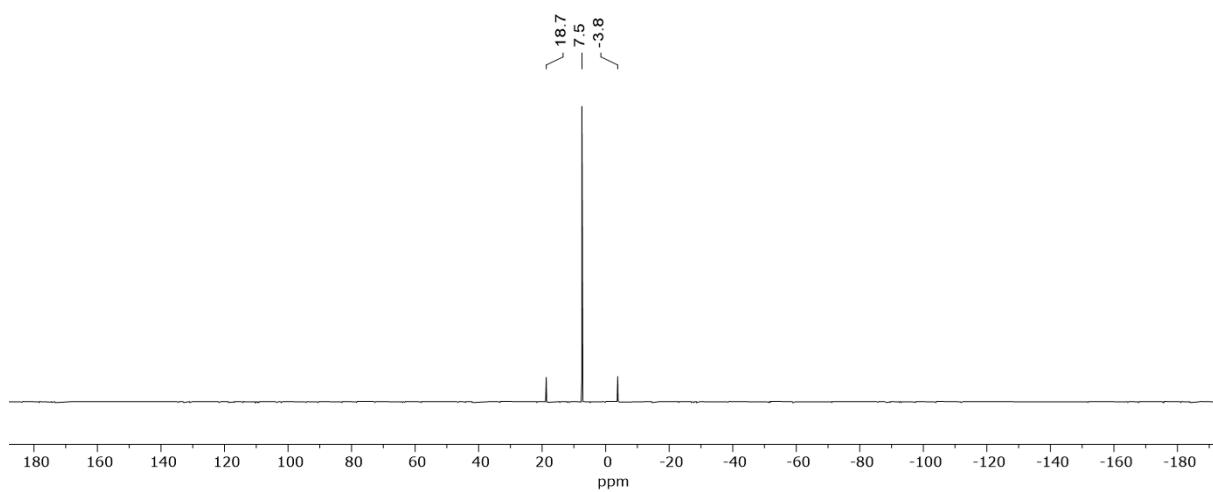


Figure S23. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** in CDCl_3 at 25 °C.

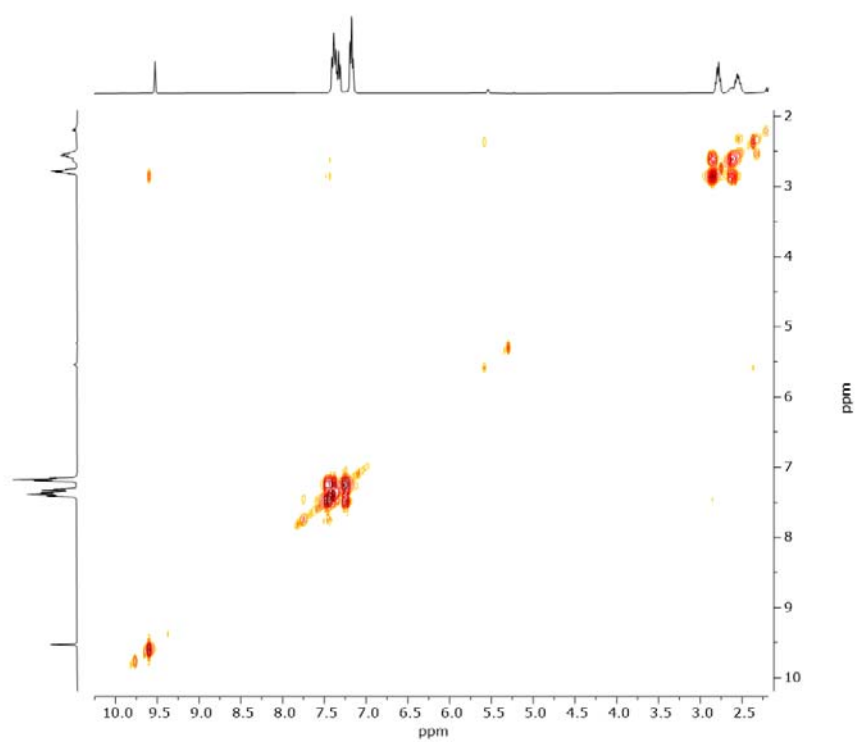


Figure S24. ^1H - ^1H COSY spectrum of **4** in CDCl_3 at 25 °C.

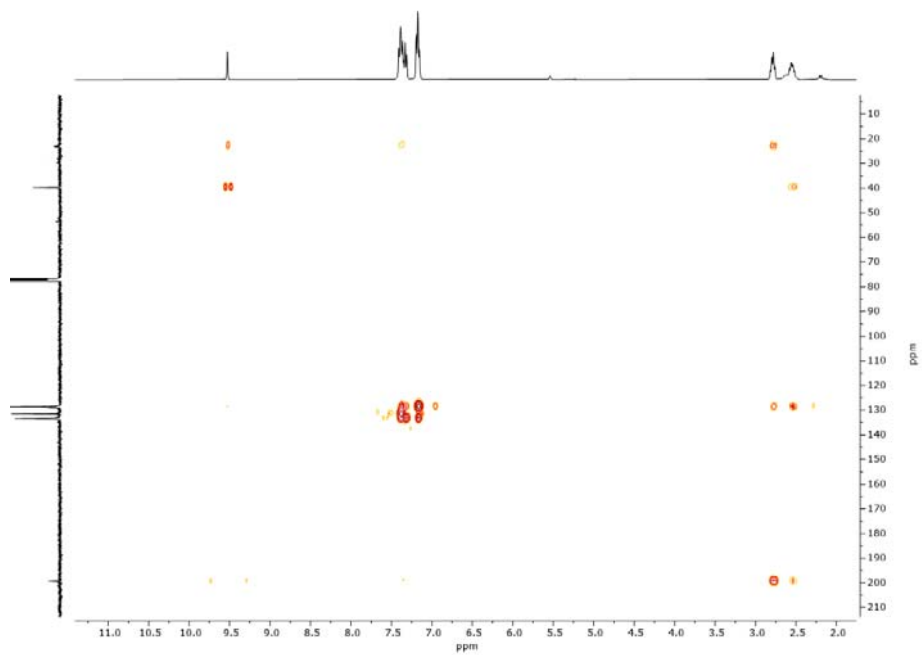


Figure S25. ^1H - ^{13}C HMBC spectrum of **4** in CDCl_3 at 25 °C.

2. X-Ray Diffraction Analyses

Table S1. Data collection and structure refinement data of complexes **1-4**.

Compound	1	2	3	4
Empirical formula	C ₃₀ H ₃₀ Cl ₄ O ₂ P ₂ Pd ₂	C ₃₀ H ₃₀ Cl ₂ O ₂ P ₂ Pd	C ₃₀ H ₃₀ Cl ₂ O ₂ P ₂ Pt	C ₃₀ H ₃₀ Cl ₂ O ₂ P ₂ Pt
Formula weight	839.08	661.78	750.47	750.47
Temperature [K]	130(2)	130(2)	130(2)	130(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pbca</i>
Unit cell dimensions				
a [pm]	731.84(1)	737.86(3)	736.69(2)	1819.64(3)
b [pm]	1225.50(2)	1012.92(2)	1015.36(2)	1724.11(3)
c [pm]	1768.33(3)	1045.43(3)	1042.53(3)	3613.85(6)
α [deg]	90	104.828(2)	104.886(2)	90
β [deg]	90.789(1)	104.879(3)	104.784(2)	90
γ [deg]	90	96.825(2)	96.938(2)	90
Volume [nm ³]	1.58581(4)	0.71562(4)	0.71406(3)	11.3376(3)
Z	2	1	1	16
ρ (calc.) [Mg/m ³]	1.757	1.536	1.745	1.759
μ [mm ⁻¹]	1.599	0.973	5.238	5.279
F(000)	832	336	368	5888
Crystal size [mm ³]	0.40 · 0.20 · 0.20	0.40 · 0.30 · 0.20	0.15 · 0.10 · 0.04	0.70 · 0.05 · 0.01
Θ_{\min} - Θ_{\max} [deg]	2.022 / 35.771	2.112 / 34.755	2.118 / 32.467	1.979 / 27.099
Index ranges	-11 ≤ h ≤ 11 -19 ≤ k ≤ 20 -28 ≤ l ≤ 28	-11 ≤ h ≤ 11 -16 ≤ k ≤ 15 -16 ≤ l ≤ 15	-11 ≤ h ≤ 10 -15 ≤ k ≤ 15 -15 ≤ l ≤ 15	-22 ≤ h ≤ 21 -20 ≤ k ≤ 22 -45 ≤ l ≤ 44
Reflections collected	30772	17006	16489	100227
Independent reflections [<i>R</i> _(int)]	7047 [0.0375]	5761 [0.0244]	4762 [0.0573]	11678 [0.0700]
Completeness (Θ [deg])	100.0 % (34.34)	100.0 % (33.14)	100.0 % (30.51)	100.0 % (25.350)
<i>T</i> _{Min} / <i>T</i> _{Max}	1.00000 / 0.89776	1.00000 / 0.99129	1.00000 / 0.94180	1.00000 / 0.69745
Restraints/parameters	0 / 181	0 / 229	0 / 229	0 / 667
Goof [on F ²]	1.072	1.053	1.025	1.100
R1 / wR2 [<i>I</i> > 2σ(<i>I</i>)]	0.0343 / 0.0795	0.0258 / 0.0587	0.0294 / 0.0632	0.0384 / 0.0733
R1 / wR2 (all data)	0.0429 / 0.0854	0.0291 / 0.0605	0.0296 / 0.0635	0.0520 / 0.0779
Residual electron density [e·Å ⁻³]	1.251 / -1.253	0.574 / -0.891	2.252 / -1.998	0.974 / -1.445
Comments	-	compounds 2 and 3 are isotypic		
CCDC deposition number	2233898	2233899	2233900	2240480

CCDC deposition numbers given in Table S1 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://summary.ccdc.cam.ac.uk/structure-summary-form> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Molecular structures

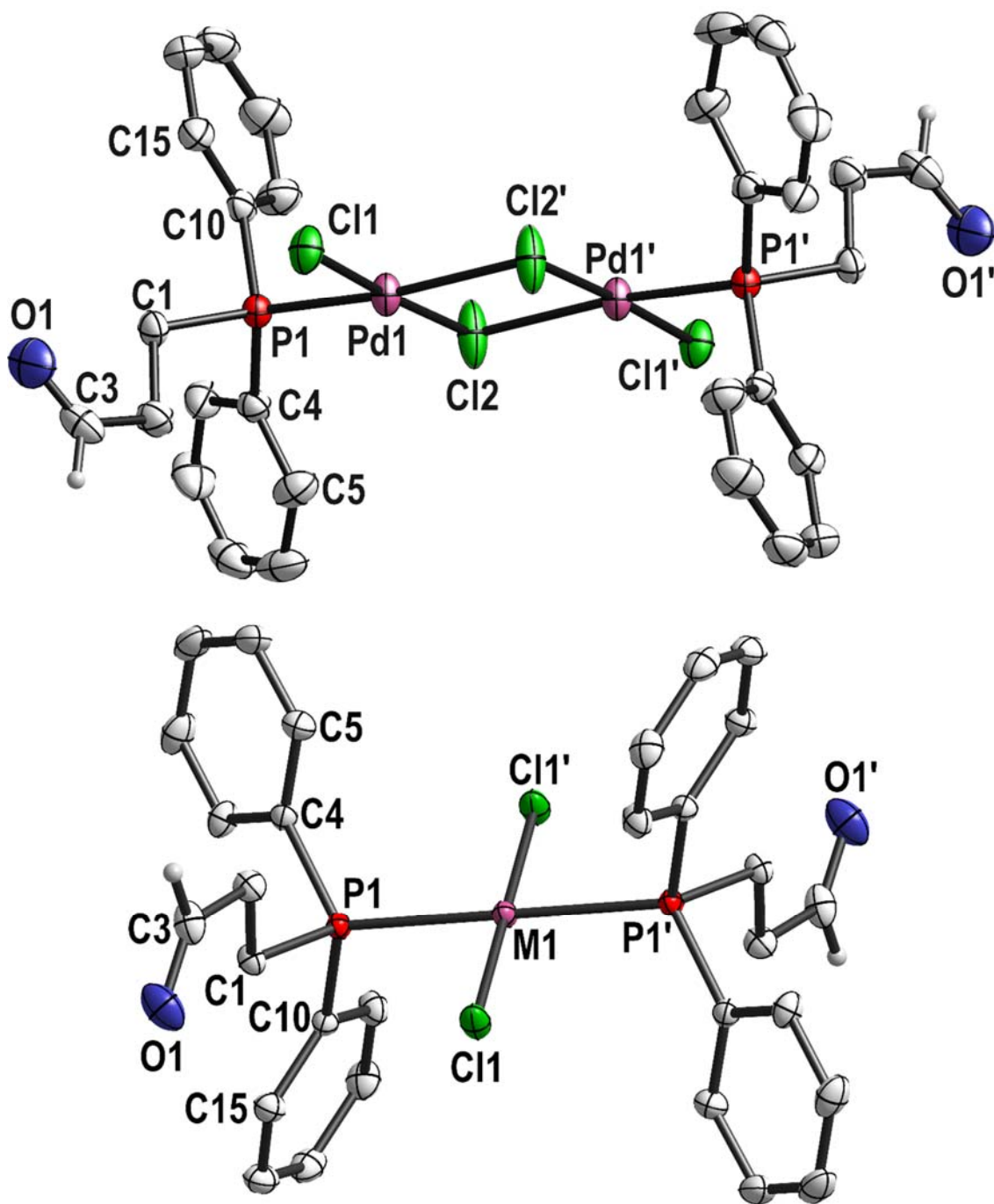


Figure S26-a. Molecular structures and labelling schemes of $trans\text{-}[\text{PdCl}(\mu\text{-Cl})(\text{PCHO-}\kappa\text{P})_2]$ (**1**; top) and $trans\text{-}[\text{MCl}_2(\text{PCHO-}\kappa\text{P})_2]$ (**2** and **3**; M = Pd, Pt; bottom). Hydrogen atoms, except CHO, are omitted for clarity; displacement ellipsoids are set at the 50% probability level.

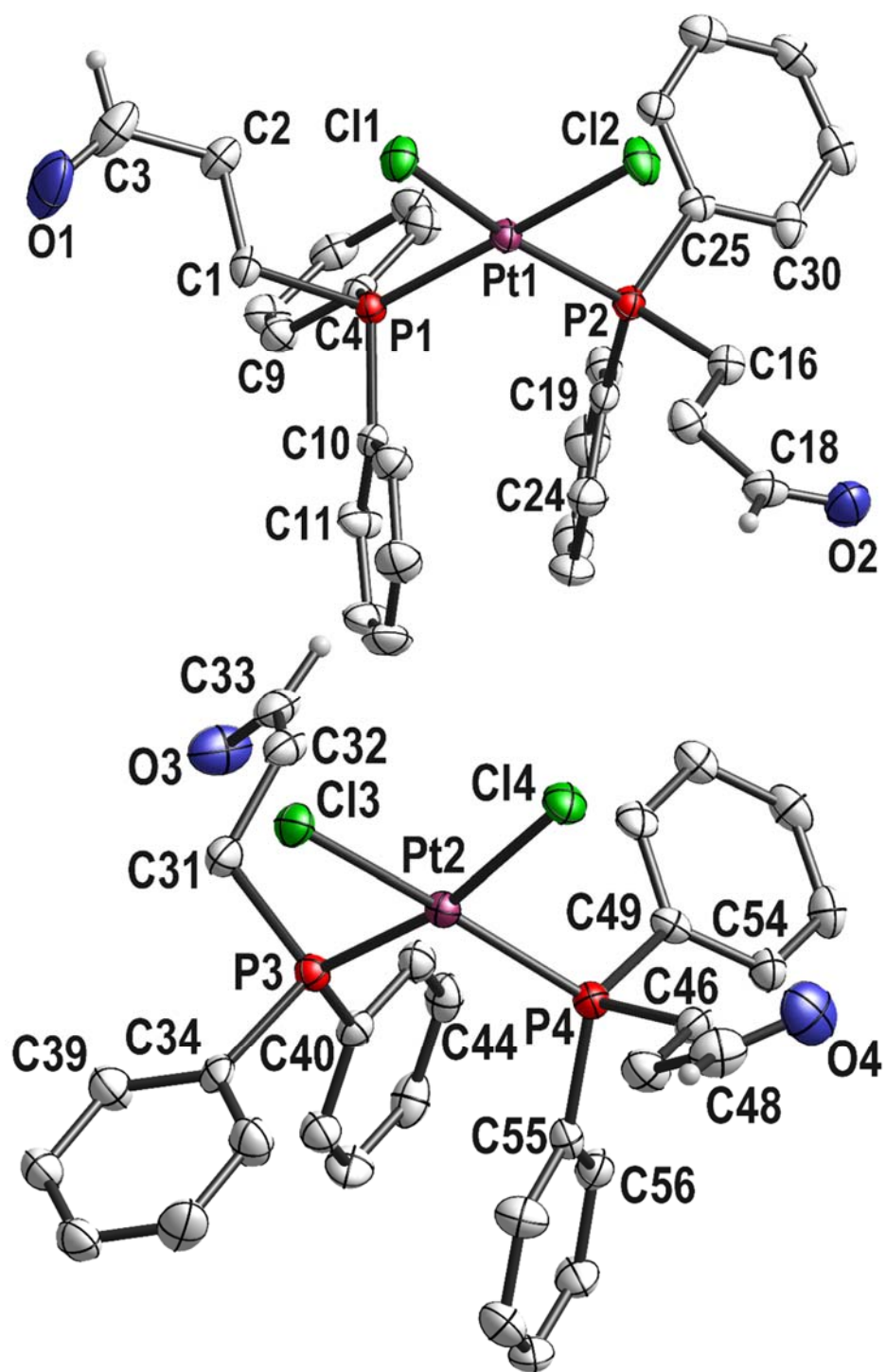


Figure S26-b. Molecular structures and labelling schemes of *cis*-[PtCl₂(PCHO- κ P)₂] (**4**). Hydrogen atoms, except CHO, are omitted for clarity; displacement ellipsoids are set at the 50% probability level; two independent molecules in the asymmetric unit.

Selected bond lengths and bond angles

Table S2. Selected Bond Lengths [pm] and Angles [°] for *trans*-[PdCl(μ -Cl)(PCHO- κ P)]₂ (**1**).

Pd(1)-P(1)	221.80(4)
Pd(1)-Cl(1)	228.23(5)
Pd(1)-Cl(2)	232.21(5)
Pd(1)-Cl(2')	243.15(5)
P(1)-C(10)	180.8(2)
P(1)-C(4)	181.3(2)
P(1)-C(1)	182.3(2)
O(1)-C(3)	119.3(3)
P(1)-Pd(1)-Cl(1)	90.55(2)
P(1)-Pd(1)-Cl(2)	91.38(2)
Cl(1)-Pd(1)-Cl(2)	177.26(2)
P(1)-Pd(1)-Cl(2')	172.48(2)
Cl(1)-Pd(1)-Cl(2')	91.39(2)
Cl(2)-Pd(1)-Cl(2')	86.45(2)
Pd(1)-Cl(2)-Pd(1')	93.55(2)
C(10)-P(1)-C(4)	108.10(8)
C(10)-P(1)-C(1)	107.10(8)
C(4)-P(1)-C(1)	102.63(8)
C(10)-P(1)-Pd(1)	105.98(6)
C(4)-P(1)-Pd(1)	115.55(6)
C(1)-P(1)-Pd(1)	117.01(6)
C(2)-C(1)-P(1)	111.7(1)

Table S3. Selected Bond Lengths [pm] and Angles [°] for *trans*-[PdCl₂(PCHO-κP)₂] (**2**).

Pd(1)-Cl(1)	229.95(3)
Pd(1)-P(1)	233.21(3)
P(1)-C(10)	181.2(1)
P(1)-C(4)	181.7(1)
P(1)-C(1)	182.7(1)
O(1)-C(3)	119.9(2)
Cl(1)-Pd(1)-Cl(1')	180.00(2)
Cl(1)-Pd(1)-P(1')	89.84(1)
Cl(1)-Pd(1)-P(1)	90.16(1)
Cl(1')-Pd(1)-P(1)	89.84(1)
P(1')-Pd(1)-P(1)	180.0
C(10)-P(1)-C(4)	105.08(6)
C(10)-P(1)-C(1)	105.13(6)
C(4)-P(1)-C(1)	103.44(6)
C(10)-P(1)-Pd(1)	109.83(4)
C(4)-P(1)-Pd(1)	116.62(4)
C(1)-P(1)-Pd(1)	115.62(4)
C(2)-C(1)-P(1)	113.13(9)
C(2)-C(1)-H(1A)	111.(1)
P(1)-C(1)-H(1A)	108(1)
C(2)-C(1)-H(1B)	110(1)
P(1)-C(1)-H(1B)	104(1)

Table S4. Selected Bond Lengths [pm] and Angles [°] for *trans*-[PtCl₂(**PCHO-κP**)₂] (**3**).

Pt(1)-Cl(1)#1	230.71(7)
Pt(1)-Cl(1)	230.71(7)
Pt(1)-P(1)#1	231.61(7)
Pt(1)-P(1)	231.61(7)
P(1)-C(10)	181.2(3)
P(1)-C(4)	181.5(3)
P(1)-C(1)	182.3(3)
O(1)-C(3)	119.8(4)

Cl(1)#1-Pt(1)-Cl(1)	180.0
Cl(1)#1-Pt(1)-P(1)#1	90.23(2)
Cl(1)-Pt(1)-P(1)#1	89.77(2)
Cl(1)#1-Pt(1)-P(1)	89.77(2)
Cl(1)-Pt(1)-P(1)	90.23(2)
P(1)#1-Pt(1)-P(1)	180.0
C(10)-P(1)-C(4)	105.0(1)
C(10)-P(1)-C(1)	105.0(1)
C(4)-P(1)-C(1)	103.2(1)
C(10)-P(1)-Pt(1)	110.84(9)
C(4)-P(1)-Pt(1)	116.07(9)
C(1)-P(1)-Pt(1)	115.54(9)
C(2)-C(1)-P(1)	113.1(2)
C(2)-C(1)-H(1A)	109(2)
P(1)-C(1)-H(1A)	106(2)
C(2)-C(1)-H(1B)	108(2)
P(1)-C(1)-H(1B)	107(2)

Table S5. Selected Bond Lengths [pm] and Angles [°] for *cis*-[PtCl₂(**PCHO-κP**)₂] (**4**).

Pt(1)-P(1)	225.1(1)
Pt(1)-P(2)	225.2(1)
Pt(1)-Cl(1)	233.4(1)
Pt(1)-Cl(2)	235.8(1)
P(1)-C(4)	181.1(5)
P(1)-C(10)	181.9(5)
P(1)-C(1)	182.9(5)
P(2)-C(25)	181.9(5)
P(2)-C(19)	182.5(5)
P(2)-C(16)	183.3(5)
O(1)-C(3)	118.8(8)
O(2)-C(18)	119.4(6)
Pt(2)-P(3)	224.7(1)
Pt(2)-P(4)	224.9(1)
Pt(2)-Cl(3)	235.6(1)
Pt(2)-Cl(4)	235.9(1)
P(3)-C(34)	181.9(5)
P(3)-C(40)	182.3(5)
P(3)-C(31)	182.9(5)
P(4)-C(49)	180.8(5)
P(4)-C(55)	183.1(5)
P(4)-C(46)	183.3(5)
O(3)-C(33)	119.7(6)
O(4)-C(48)	119.3(7)
P(1)-Pt(1)-P(2)	98.71(5)
P(1)-Pt(1)-Cl(1)	90.22(5)
P(2)-Pt(1)-Cl(1)	170.72(5)
P(1)-Pt(1)-Cl(2)	176.32(5)
P(2)-Pt(1)-Cl(2)	84.26(5)
Cl(1)-Pt(1)-Cl(2)	86.73(5)
C(4)-P(1)-C(10)	110.7(2)
C(4)-P(1)-C(1)	100.9(2)
C(10)-P(1)-C(1)	103.1(2)

C(4)-P(1)-Pt(1)	116.9(2)
C(10)-P(1)-Pt(1)	107.3(2)
C(1)-P(1)-Pt(1)	117.0(2)
C(25)-P(2)-C(19)	103.0(2)
C(25)-P(2)-C(16)	104.3(2)
C(19)-P(2)-C(16)	102.3(2)
C(25)-P(2)-Pt(1)	110.5(2)
C(19)-P(2)-Pt(1)	123.1(2)
C(16)-P(2)-Pt(1)	111.8(2)
P(3)-Pt(2)-P(4)	99.66(5)
P(3)-Pt(2)-Cl(3)	85.40(5)
P(4)-Pt(2)-Cl(3)	171.44(5)
P(3)-Pt(2)-Cl(4)	167.30(5)
P(4)-Pt(2)-Cl(4)	88.31(5)
Cl(3)-Pt(2)-Cl(4)	87.97(5)
C(34)-P(3)-C(40)	105.4(2)
C(34)-P(3)-C(31)	104.7(2)
C(40)-P(3)-C(31)	101.6(2)
C(34)-P(3)-Pt(2)	115.7(2)
C(40)-P(3)-Pt(2)	118.9(2)
C(31)-P(3)-Pt(2)	108.8(2)
C(49)-P(4)-C(55)	107.2(2)
C(49)-P(4)-C(46)	102.2(2)
C(55)-P(4)-C(46)	102.9(2)
C(49)-P(4)-Pt(2)	115.0(2)
C(55)-P(4)-Pt(2)	116.9(2)
C(46)-P(4)-Pt(2)	111.2(2)

3. Isolation Experiments

Procedure for Sonogashira cross-coupling reaction

A mixture of bromobenzene (65.4 μ L, 0.625 mmol, 1.0 equiv.), phenylacetylene (75.5 μ L, 0.687 mmol, 1.1 equiv.), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (75.5 μ L, 0.781 mmol, 1.25 equiv.), **2** (20.6 mg, 0.031 mmol, 5 mol%) and dry degassed 1,4-dioxane (5.0 mL) was heated at 100 °C under a nitrogen atmosphere for 4h. The reaction mixture was passed over celite and washed with DCM (3 x 10 mL). The crude reaction mixture was purified using a Biotage Isolera (25 g SNAP Ultra cartridge, cyclohexane) to afford diphenylacetylene as a white solid (102.6 mg, 0.57 mmol, 92%). ^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.52 (m, 4H), 7.41 – 7.33 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 131.7, 128.5, 128.4, 123.4, 89.5. Data are in accordance with the literature.¹

Procedure for Suzuki–Miyaura cross-coupling reaction

A mixture of bromobenzene (65.4 μ L, 0.625 mmol, 1.0 equiv.), *p*-tolylboronic acid (127.5 mg, 0.937 mmol, 1.5 equiv.), 1,1,3,3-tetramethylguanidine (TMG) (98.0 μ L, 0.781 mmol, 1.25 equiv.), **2** (20.6 mg, 0.031 mmol, 5 mol%) and dry degassed toluene (5.0 mL) was heated at 100 °C under a nitrogen atmosphere for 5 h. The reaction mixture was passed over celite and washed with DCM (3 x 10 mL). The crude reaction mixture was purified using a Biotage Isolera (25 g SNAP Ultra cartridge, *n*-hexane) to afford 4-methyl-1,1'-biphenyl as a white solid (83.0 mg, 0.49 mmol, 79%). ^1H NMR (400 MHz, CDCl_3) δ 7.61 – 7.56 (m, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.36 – 7.29 (m, 1H), 7.25 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 141.3, 138.5, 137.2, 129.6, 128.9, 127.1, 127.1, 127.1, 21.2. Data are in accordance with the literature.²

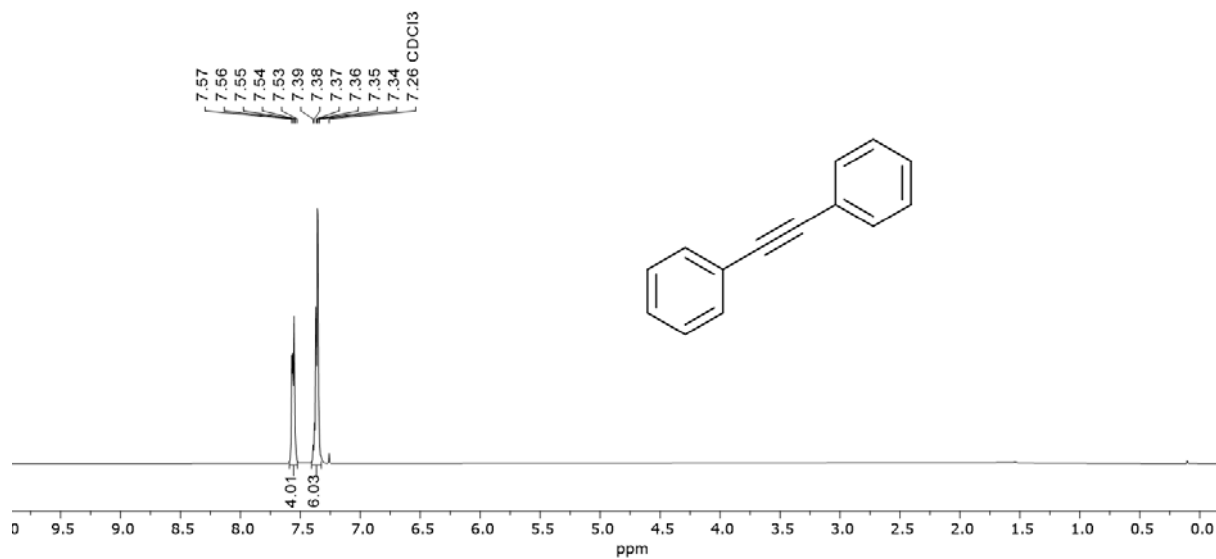


Figure S27. ¹H NMR spectrum of diphenylacetylene in CDCl₃ at 25 °C

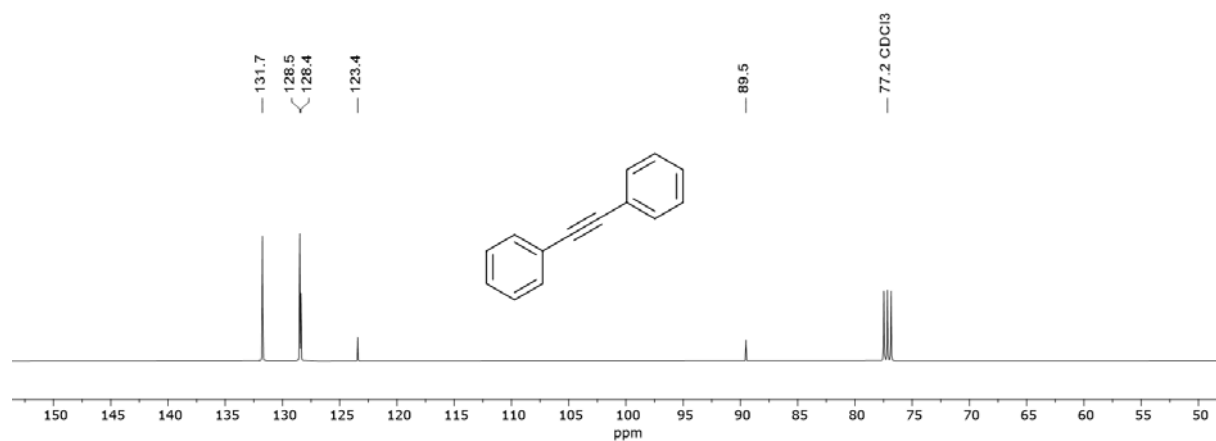


Figure S28. ¹³C{¹H} NMR spectrum of diphenylacetylene in CDCl₃ at 25 °C

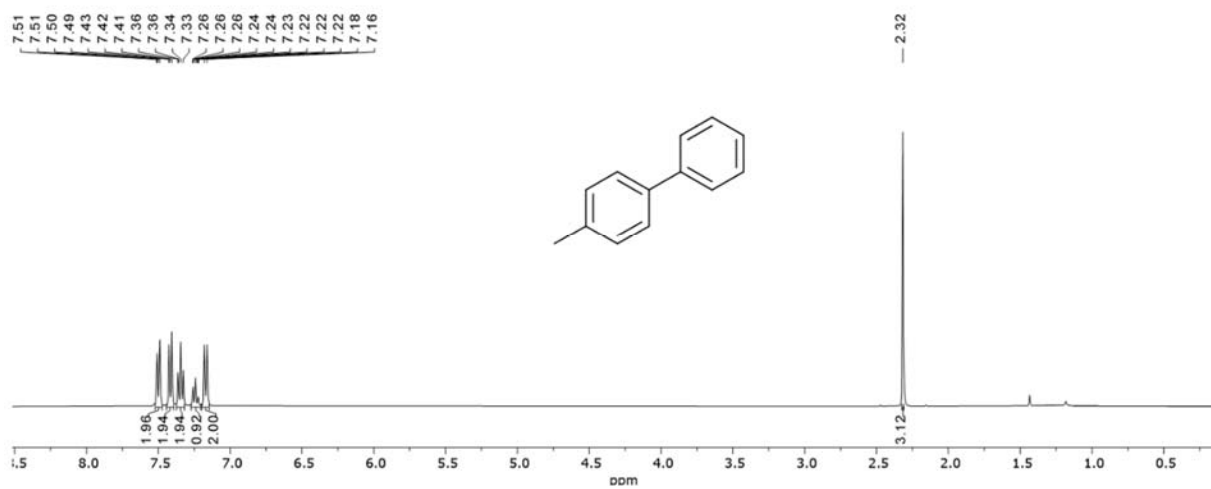


Figure S29. ¹H NMR spectrum of 4-methyl-1,1'-biphenyl in CDCl₃ at 25 °C

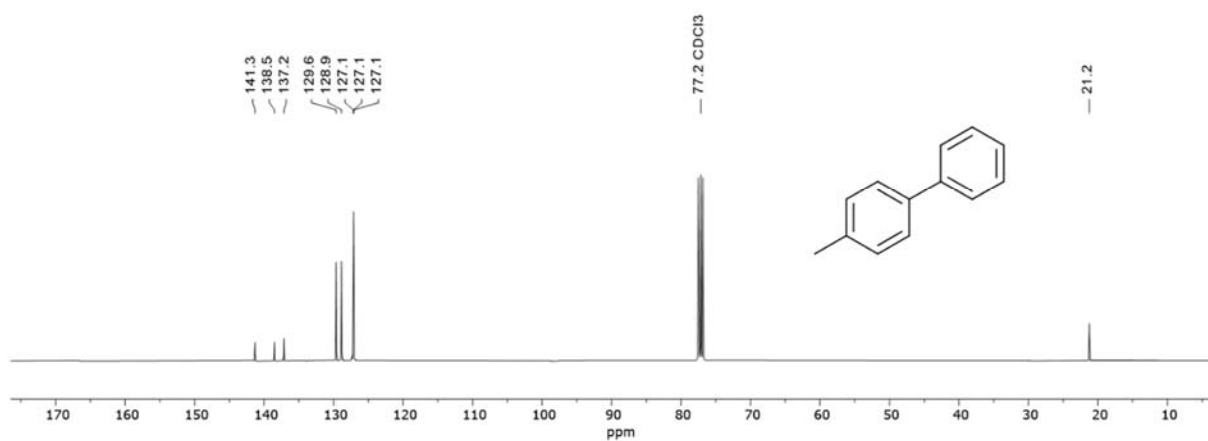


Figure S30. ¹³C{¹H} NMR spectrum of 4-methyl-1,1'-biphenyl in CDCl₃ at 25 °C

4. Tests for the homogeneous/heterogeneous nature of the catalyst

To find out the nature of the catalyst, firstly a mercury test was performed. The addition of mercury led to a loss of catalytic activity. For the Sonogashira reaction, the yield of the reaction after the addition of mercury was 11% and for the Suzuki–Miyaura cross-coupling reaction 7%. This would imply that the reaction is catalysed by Pd nanoparticles which will form an amalgam with Hg and the catalysis will be inhibited. However, the reliability of the mercury test is questionable for complexes of the type $[\text{PdCl}_2(\text{PR}_3)_2]$.³ Therefore, the stability of the pre-catalyst was studied by heating **2** with mercury in deuterated toluene. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed the formation of multiple products which implies that **2** is not stable in the presence of Hg and the test is a false positive (Figure S31).

Secondly, Crabtree's test⁴ was performed for both reactions. Dibenzo[a,e]cyclooctatetraene (DCT) acts as a poison for homogeneous catalysts as it can act as a strong ligand. For Sonogashira and Suzuki–Miyaura cross-coupling reactions performed with the addition of DCT, yields of 57% and 75% were observed on completion. Though there is a loss of catalytic activity, the catalysis is not completely inhibited. It was found that **2** does not react with DCT at 100 °C in deuterated toluene, and therefore Crabtree's test is also not suitable (Figure S32).

Maitlis' test⁵ was performed by passing the hot reaction mixture after half the completion time over a tightly packed column of celite. If the catalysis is heterogeneous, the Pd nanoparticles would stay on the column and the filtrate would be catalytically inactive. Therefore, fresh substrates and base were added to the clear yellow filtrate, and the reaction mixture was heated at 100 °C for 4 hours for the Sonogashira reaction and 5 hours for the Suzuki–Miyaura cross-coupling reaction. The solution was still catalytically active and yields increased by 98% and 62% for Sonogashira and Suzuki–Miyaura cross-coupling reactions, respectively, in comparison to the half-time yields.

Procedure for mercury test and Crabtree's test for the Sonogashira cross-coupling reaction

In two separate Schlenk flasks, a mixture of bromobenzene (13.1 μL , 0.125 mmol, 1.0 equiv.), phenylacetylene (15.1 μL , 0.137 mmol, 1.1 equiv.), DBU (23.3 μL , 0.156 mmol, 1.25 eq.), **2** (4.1 mg, 0.006 mmol, 5 mol%) and 1,4-dioxane (1.0 mL) was heated under a nitrogen atmosphere for 30 minutes. After 30 minutes, for the mercury test, mercury (14 μL , 0.937 mmol, 1500 mol%) and for Crabtree's test, DCT (6.4 mg, 0.031 mmol, 25 mol%) were added and the reaction mixture was stirred for 3.5 hours. The yields were determined by GC-MS using naphthalene as an internal standard (10 μL of the reaction solution were diluted with 1.000 mL of a naphthalene stock solution in acetone).

Procedure for mercury test and Crabtree's test for the Suzuki-Miyaura cross-coupling reaction

In two separate Schlenk flasks, a mixture of bromobenzene (13.1 μL , 0.125 mmol, 1.0 equiv.), *p*-tolylboronic acid (25.5 mg, 0.187 mmol, 1.5 equiv.), TMG (19.6 μL , 0.156 mmol, 1.25 equiv.), **2** (4.1 mg, 0.006 mmol, 5 mol%) and toluene (1.0 mL) were heated under a nitrogen atmosphere for 30 minutes. After 30 minutes, for the mercury test, mercury (14 μL , 0.937 mmol, 1500 mol%) and for Crabtree's test, DCT (6.4 mg, 0.031 mmol, 25 mol%) were added and the reaction mixture was stirred for 3.5 hours. The yields were determined by GC-MS using naphthalene as an internal standard (10 μL of the reaction solution were diluted with 1.000 mL of a naphthalene stock solution in acetone).

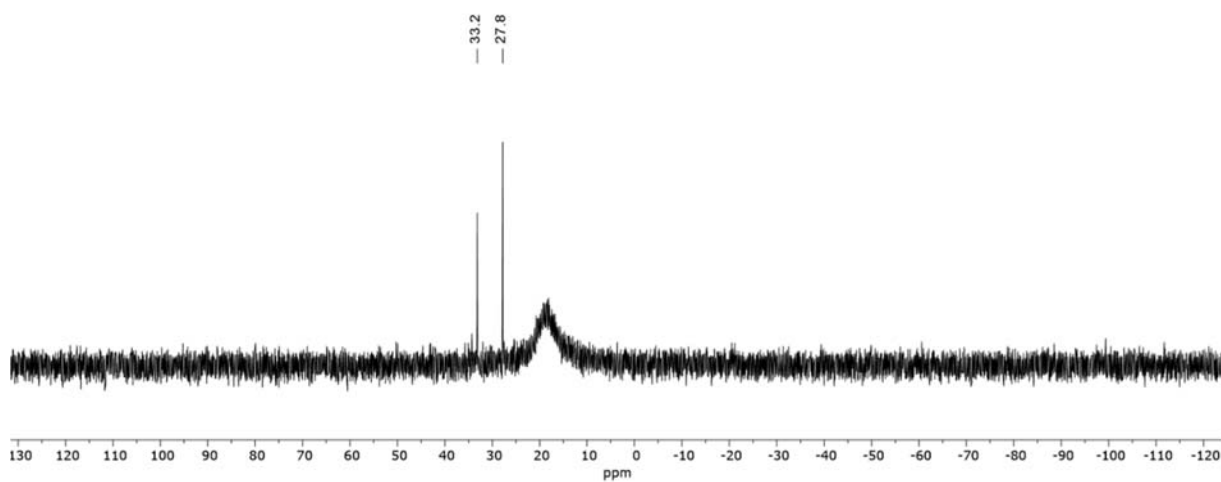


Figure S31. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for **2** reacting with Hg in toluene- d_8 at 25 °C

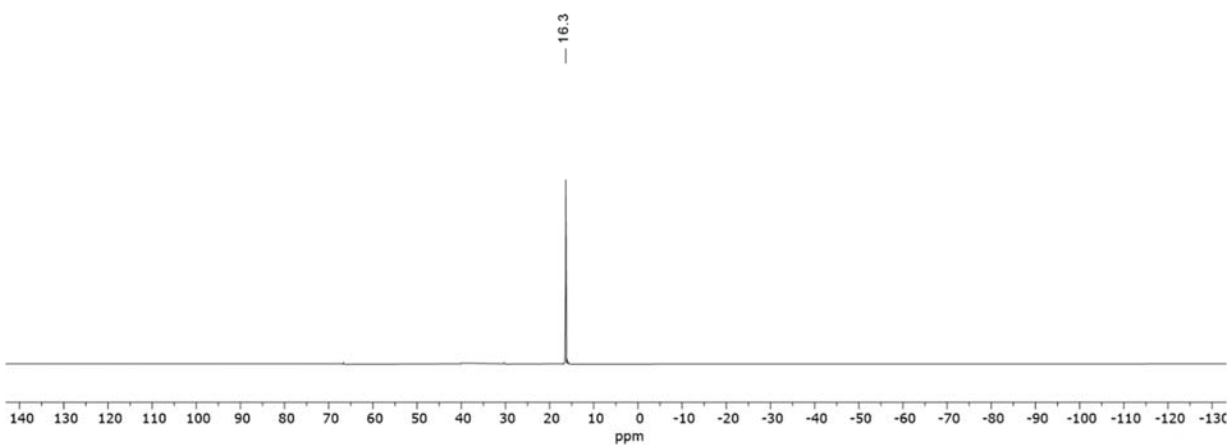


Figure S32. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for **2** not reacting with DCT in toluene- d_8 at 25 °C

5. DFT Calculations for *cis*- and *trans*-[MCl₂(PCHO-κP)₂] (M = Pd, Pt)

Method

In order to estimate the relative stability of *cis*- and *trans*-[MCl₂(PCHO-κP)₂] (M = Pd, Pt), the single point energies of these structures were calculated. For this purpose we optimised the geometry of the X-ray crystal structures using density functional theory (DFT)⁶ in ORCA 5.0 package.⁷ The hybrid functional PBE0 has been chosen based on the results of benchmark studies for a set of the transition metal complexes.⁸ In order to stabilise the optimised geometry via non-covalent interactions Becke-Johnson dispersion corrections of third order (D3BJ) were included in the functional.⁹ The density fitting technique resolution-of-identity approximation (RI-J) and chain-of-sphere approximation (COSX)¹⁰ in the geometry optimisation were applied in order to speed up the calculations. The polarised basis set def2-TZVPP¹¹ for all non-transition metals and with the additional zeroth order regular approximation (ZORA)¹² for the transition metal platinum was used for better convergence of the energies. The Conductor-like Polarizable Continuum Model (CPCM) was incorporated in this calculation in order to reproduce the stabilising effect of the solvent (toluene).¹³

The energy of *cis*- and *trans*-[PtCl₂(PCHO-κP)₂] were calculated as -13780284.4 kcal/mol (-21960.2764 E_h) and -13780278.3 kcal/mol (-21960.2667 E_h), respectively. The energy gap between *cis*- and *trans*-isomers is only 6.1 kcal/mol, indicating the preferable formation of the *cis*-configuration.

The energies of *cis*- and *trans*-[PdCl₂(PCHO-κP)₂] were calculated as -5035789.197 kcal/mol (-8025.1237 E_h) and -5035797.041 kcal/mol (-8025.1362 E_h), respectively. The energy gap is 7.8 kcal/mol indicating that the *trans* configuration of the Pd complex is more stable than the *cis* isomer.

Table S6. Selected experimental and calculated bond lengths and angles of *cis*-[PtCl₂(PCHO-κP)₂].

Bond	Bond lengths [pm] and angles	Bond lengths [pm] and angles
	[°] (exp)	[°] (calc)
P2-Pt	225.2(1)	225.1
P1-Pt	225.1(1)	224.8
Cl2-Pt	235.8(1)	235.9
Cl1-Pt	233.4(1)	234.0
P1-C10	181.9(5)	181.5
P2-C19	182.5(5)	182.0
P1-C1	182.9(5)	182.8
P2-C16	183.3(5)	182.9
Cl2-Pt-Cl1	86.73(5)	87.1
P2-Pt-P1	98.71(5)	97.2
P2-Pt-Cl2	84.26(5)	84.4
P1-Pt-Cl1	90.22(5)	91.4

Table S7. Coordinates of the atoms of the optimised structure of *cis*-[PtCl₂(PCHO-κP)₂].

Atom	X	Y	Z
Pt	5.80253	6.80537	7.72212
Cl1	3.89543	7.25457	6.44201
Cl2	6.22722	9.12519	7.68744
P1	5.38378	4.60714	7.67132
P2	7.55914	6.72709	9.12770
O1	1.94756	2.90275	5.09949
O2	6.62169	9.39360	12.79265
C1	3.90019	4.04339	6.76434
H1	3.73716	3.00950	7.07869
H2	3.05722	4.63079	7.12952
C2	4.00204	4.12742	5.25795
H3	4.05228	5.16822	4.92232

H4	4.91318	3.65150	4.87514
C3	2.85633	3.47630	4.55581
H5	2.89182	3.54887	3.45047
C4	6.68200	3.61715	6.88439
C5	7.72258	4.26977	6.23126
H6	7.76977	5.35118	6.26343
C6	8.68863	3.54915	5.54637
H7	9.49474	4.07292	5.04728
C7	8.61903	2.16504	5.50486
H8	9.37493	1.59803	4.97508
C8	7.56738	1.50614	6.12894
H9	7.49783	0.42621	6.08147
C9	6.59616	2.22649	6.80479
H10	5.76671	1.69956	7.25953
C10	5.01901	3.94559	9.32190
C11	5.56919	2.78708	9.85448
H11	6.34018	2.24876	9.32161
C12	5.15885	2.33175	11.09864
H12	5.60142	1.43242	11.50917
C13	4.20438	3.03008	11.82075
H13	3.88808	2.67120	12.79272
C14	3.66044	4.19629	11.29859
H14	2.91786	4.75096	11.85928
C15	4.06598	4.65346	10.05614
H15	3.64423	5.56728	9.65108
C16	7.30717	7.92114	10.49003
H16	8.00359	7.67672	11.29356
H17	7.59834	8.88903	10.08351
C17	5.87939	7.99593	10.99316
H18	5.22141	8.40848	10.21976
H19	5.44480	7.01669	11.22734
C18	5.72128	8.84440	12.21223

H20	4.67741	8.94382	12.57133
C19	8.02492	5.19605	9.99514
C20	8.83946	4.25945	9.36134
H21	9.18482	4.43682	8.35231
C21	9.23921	3.11115	10.02446
H22	9.87529	2.39551	9.51777
C22	8.84348	2.89100	11.33620
H23	9.16488	1.99818	11.85890
C23	8.04084	3.82196	11.97704
H24	7.72686	3.65954	13.00067
C24	7.63022	4.96527	11.31065
H25	7.00243	5.67371	11.83301
C25	9.13390	7.22367	8.37679
C26	9.20597	7.60014	7.04033
H27	8.30645	7.61504	6.43830
C27	10.42005	7.98419	6.49022
H28	10.46726	8.27663	5.44835
C28	11.56381	8.00348	7.27374
H29	12.51030	8.30871	6.84396
C29	11.49567	7.63450	8.61117
H30	12.38649	7.65102	9.22707
C30	10.28725	7.24095	9.16036
H31	10.24340	6.94026	10.20068

Table S8. Selected experimental and calculated bond lengths and angles of *trans*-[PtCl₂(PCHO-κP)₂].

Bond	Bond lengths [pm] and angles	Bond lengths [pm] and angles
	[°] (exp)	[°] (calc)
P2-Pt	231.61(7)	231.2
P1-Pt	231.61(7)	231.2
Cl2-Pt	230.71(7)	230.7
Cl1-Pt	230.71(7)	230.7
P1-C10	181.2(3)	181.0
P2-C19	181.5(3)	181.2
P1-C1	182.3(3)	182.0
P2-C16	182.3(3)	182.0
Cl2-Pt-Cl1	180.0	180.0
P2-Pt-P1	89.77(2)	89.5
P2-Pt-Cl2	89.77(2)	89.5
P1-Pt-Cl1	90.23(2)	90.5

Table S9. Coordinates of the atoms of the optimised structure of *trans*-[PtCl₂(PCHO-κP)₂].

Atom	X	Y	Z
Pt	1.12650	8.56810	4.80919
Cl1	0.54477	7.31649	6.66438
P1	0.28547	6.93281	3.41648
O1	-3.06962	4.47799	5.42211
C1	-0.92986	5.80490	4.16603
C2	-2.17778	6.54327	4.59969
C3	-3.19132	5.66349	5.25420
C4	-0.57443	7.48269	1.91973
C5	-1.26240	8.69277	1.92482
C6	-2.01683	9.06749	0.82379
C7	-2.08260	8.24081	-0.28892

C8	-1.39545	7.03478	-0.29934
C9	-0.64474	6.65439	0.80200
C10	1.63095	5.87208	2.83385
C11	2.56972	6.41190	1.95371
C12	3.63934	5.64579	1.52427
C13	3.78955	4.34001	1.97547
C14	2.86496	3.80379	2.85779
C15	1.78673	4.56541	3.28688
H1	-1.16581	5.02863	3.43523
H2	-0.46518	5.33432	5.03251
H3	-2.67853	7.04289	3.76180
H4	-1.93520	7.34066	5.31218
H5	-4.10673	6.18766	5.59381
H6	-1.19232	9.34501	2.78646
H7	-2.54649	10.01219	0.83222
H8	-2.66666	8.53856	-1.15150
H9	-1.44247	6.38845	-1.16756
H10	-0.10816	5.71298	0.78914
H11	2.46057	7.43515	1.61336
H12	4.36126	6.07004	0.83706
H13	4.62912	3.74315	1.63972
H14	2.97802	2.78730	3.21525
H15	1.07364	4.13145	3.97535
Cl2	1.70725	9.81946	2.95362
P2	1.96928	10.20403	6.20028
O2	5.33706	12.64302	4.19659
C16	3.18945	11.32591	5.44972
C17	4.43377	10.58133	5.01596
C18	5.45252	11.45656	4.36325
C19	2.82428	9.65513	7.70018
C20	3.51038	8.44399	7.69897
C21	4.25983	8.06916	8.80334

C22	4.32251	8.89683	9.91548
C23	3.63744	10.10403	9.92192
C24	2.89153	10.48445	8.81732
C25	0.62604	11.26999	6.77837
C26	-0.32121	10.73007	7.64937
C27	-1.38924	11.49949	8.07677
C28	-1.52963	12.80865	7.63224
C29	-0.59654	13.34509	6.75905
C30	0.48039	12.58017	6.33235
H16	3.42973	12.10167	6.17974
H17	2.72610	11.79786	4.58322
H18	4.93154	10.07821	5.85360
H19	4.18724	9.78590	4.30254
H20	6.36514	10.92778	4.02275
H21	3.44236	7.79082	6.83792
H22	4.78766	7.12346	8.79805
H23	4.90248	8.59890	10.78076
H24	3.68195	10.75105	10.78975
H25	2.35606	11.42650	8.82733
H26	-0.21976	9.70416	7.98413
H27	-2.11786	11.07506	8.75681
H28	-2.36826	13.40803	7.96591
H29	-0.70198	14.36418	6.40676
H30	1.20023	13.01438	5.65108

Table S10. Selected experimental and calculated bond lengths and angles of *trans*-[PdCl₂(PCHO-κP)₂].

Bond	Bond lengths [pm] and angles	Bond lengths [pm] and angles
	[°] (exp)	[°] (calc)
P2-Pd	233.21(3)	232.9
P1-Pd	233.21(3)	232.9
Cl2-Pd	229.95(3)	230.1
Cl1-Pd	229.95(3)	230.1
P1-C3	181.7(1)	181.1
P2-C5	181.1(1)	180.8
P1-C1	182.7(1)	182.1
P2-C4	182.7(1)	182.1
Cl2-Pd-Cl1	180.0	180.0
P2-Pd-P1	179.99(1)	179.9
P2-Pd-Cl2	89.84(1)	89.4
P1-Pd-Cl1	89.84(1)	89.4

Table S11. Coordinates of the atoms of the optimised structure of *trans*-[PdCl₂(PCHO-κP)₂].

Atom	X	Y	Z
Pd	1.74657	3.51988	4.82152
Cl1	1.15969	2.26605	6.67150
Cl2	2.33343	4.77363	2.97145
P1	2.61221	5.14762	6.23026
P2	0.87883	1.89329	3.41283
C1	3.82431	6.28205	5.48272
C2	1.25812	6.19776	6.80748
C3	3.47266	4.59591	7.72556
C4	-0.33385	0.75958	4.16050
C5	2.23192	0.84223	2.83487
C6	0.01841	2.44633	1.91803

C7	5.07097	5.54502	5.04293
H1	3.35619	6.75160	4.61765
H2	4.06093	7.05772	6.21421
C8	0.34894	5.67207	7.72689
C9	1.06214	7.48138	6.30539
C10	4.14265	3.37590	7.72430
C11	3.56073	5.43000	8.83791
C12	-1.57970	1.49743	4.60123
H3	0.13438	0.28943	5.02519
H4	-0.57144	-0.01568	3.42890
C13	3.14168	1.36771	1.91592
C14	2.42665	-0.44195	3.33601
C15	-0.65053	3.66693	1.92025
C16	-0.07084	1.61297	0.80526
C17	6.08960	6.42943	4.40217
H5	4.82607	4.75853	4.31896
H6	5.56858	5.03283	5.87523
C18	-0.73036	6.43003	8.14661
H7	0.48813	4.66591	8.10426
C19	-0.02502	8.23437	6.72597
H8	1.75063	7.90313	5.58491
C20	4.89865	2.99721	8.82302
H9	4.05708	2.71839	6.86824
C21	4.31194	5.04519	9.93721
H10	3.03800	6.37925	8.84758
C22	-2.59896	0.61347	5.24162
H11	-1.33386	2.28341	5.32539
H12	-2.07729	2.01035	3.76933
C23	4.22023	0.60900	1.49564
H13	3.00352	2.37430	1.53932
C24	3.51308	-1.19569	2.91491
H14	1.73776	-0.86360	4.05617

C25	-1.40662	4.04694	0.82206
H15	-0.56406	4.32387	2.77666
C26	-0.82211	1.99910	-0.29356
H16	0.45100	0.66324	0.79487
O1	5.97310	7.61766	4.25039
H17	7.00306	5.90595	4.05586
C27	-0.91983	7.71273	7.64736
H18	-1.42884	6.01698	8.86430
H19	-0.16882	9.23286	6.33123
C28	4.98227	3.82944	9.93008
H20	5.41468	2.04489	8.81741
H21	4.37306	5.69581	10.80121
O2	-2.48367	-0.57503	5.39215
H22	-3.51152	1.13765	5.58925
C29	4.40843	-0.67427	1.99392
H23	4.91914	1.02192	0.77828
H24	3.65589	-2.19461	3.30893
C30	-1.49135	3.21543	-0.28547
H25	-1.92182	4.99970	0.82841
H26	-0.88413	1.34904	-1.15792
H27	-1.76655	8.30320	7.97620
H28	5.56712	3.52866	10.79107
H29	5.25458	-1.26531	1.66466
H30	-2.07624	3.51723	-1.14608

Table S12. Coordinates of the atoms of the optimised structure of *cis*-[PdCl₂(**PCHO**-κ*P*)₂] (no experimental data are available for *cis*-[PdCl₂(**PCHO**-κ*P*)₂]).

Atom	X	Y	Z
Pd	5.82084	6.83967	7.72710
Cl1	3.90000	7.28962	6.47677
Cl2	6.30390	9.14255	7.75756
P1	5.35349	4.63007	7.67833
P2	7.60777	6.71558	9.13294
O1	1.98603	2.95550	5.00620
O2	6.51868	9.20137	12.87772
C1	3.89052	4.07593	6.73181
H1	3.72152	3.03909	7.03417
H2	3.03818	4.66319	7.07339
C2	4.03762	4.17347	5.23057
H3	4.09797	5.21857	4.90923
H4	4.95844	3.69920	4.86934
C3	2.90990	3.53151	4.49151
H5	2.97500	3.61343	3.38829
C4	6.65012	3.59750	6.95120
C5	7.65892	4.21364	6.21731
H6	7.69211	5.29520	6.16389
C6	8.61624	3.45494	5.56191
H7	9.39822	3.94769	4.99726
C7	8.57049	2.07109	5.63531
H8	9.32167	1.47532	5.13101
C8	7.55009	1.44763	6.34222
H9	7.50050	0.36642	6.38540
C9	6.58550	2.20449	6.98653
H10	5.78030	1.70551	7.51116
C10	4.92378	4.02150	9.33096
C11	5.55025	2.96507	9.97895

H11	6.40601	2.47593	9.53391
C12	5.10070	2.55000	11.22425
H12	5.59933	1.72797	11.72307
C13	4.03603	3.19230	11.83495
H13	3.68936	2.86557	12.80787
C14	3.41874	4.26302	11.19983
H14	2.59097	4.77568	11.67445
C15	3.85973	4.67742	9.95517
H15	3.37882	5.51727	9.46409
C16	7.30958	7.84330	10.53925
H16	8.00559	7.59458	11.34160
H17	7.56126	8.83763	10.17302
C17	5.87265	7.83081	11.02243
H18	5.20602	8.23387	10.25091
H19	5.48610	6.82354	11.22132
C18	5.65383	8.63161	12.26431
H20	4.60062	8.67202	12.60679
C19	8.12909	5.16939	9.94160
C20	8.93586	4.26876	9.24699
H21	9.24135	4.48761	8.23345
C21	9.37635	3.10467	9.85277
H22	10.00203	2.41697	9.29698
C22	9.03372	2.83288	11.17062
H23	9.38803	1.92810	11.64958
C23	8.24522	3.72967	11.87376
H24	7.97541	3.52908	12.90327
C24	7.78842	4.88676	11.26187
H25	7.16648	5.56422	11.83071
C25	9.16062	7.26541	8.37693
C26	9.22487	7.59713	7.02855
H26	8.32713	7.56649	6.42452
C27	10.42833	7.99807	6.46787

H27	10.47013	8.25580	5.41669
C28	11.56785	8.08119	7.25353
H28	12.50562	8.40166	6.81587
C29	11.50682	7.75732	8.60289
H29	12.39437	7.82413	9.22010
C30	10.30989	7.34343	9.16240
H30	10.27237	7.07566	10.21195

6. *trans*-[PdCl₂(PPh₂*n*Bu)₂]

Synthesis:¹⁴ PPh₂*n*Bu (168.1 mg, 0.69 mmol) in chloroform (5 mL) was added to a suspension of [PdCl₂(CH₃CN)₂] (90.0 mg, 0.34 mmol) in chloroform (5 mL) under a nitrogen atmosphere. The reaction mixture was stirred for 3 h. The solvent was completely removed and the yellow residue was dissolved in toluene (1 mL). Addition of *n*-hexane (6 mL) led to formation of fine yellow crystals within a few minutes. The mixture was cooled in an ice bath, filtered, the solid washed with cold *n*-hexane (3 × 5 mL) and dried in vacuum. Yield: 168 mg, 74%. ¹H NMR (400 MHz, C₆D₆) δ = 7.87 – 7.78 (m, 4H), 7.03 (m, 6H), 2.51 (m, 2H), 1.59 (m, 2H), 1.27 (m, 2H), 0.73 (t, 3H, *J* = 7.3 Hz). ³¹P{¹H} NMR (162 MHz, C₆D₆) δ = -16.4.

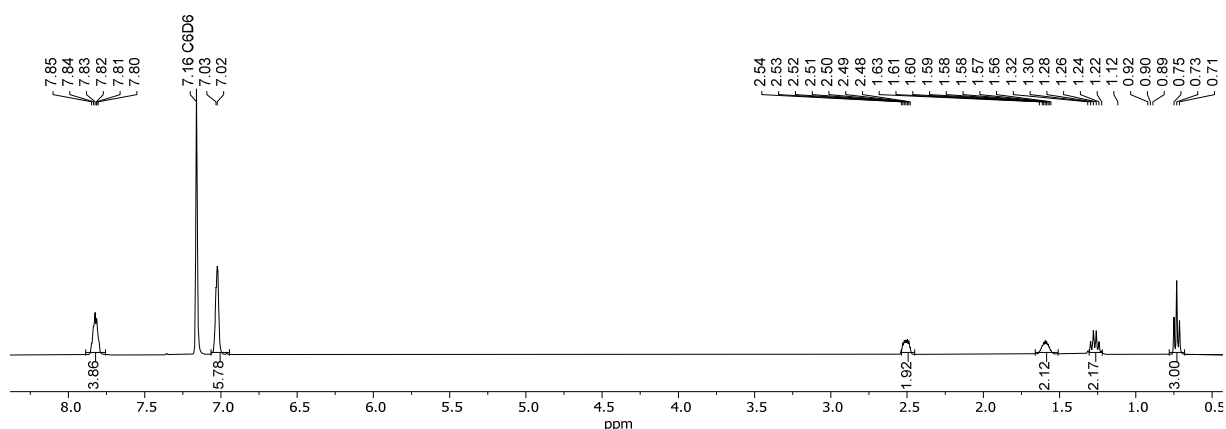


Figure S33. ¹H NMR spectrum of *trans*-[PdCl₂(PPh₂*n*Bu)₂] in C₆D₆ at 25 °C

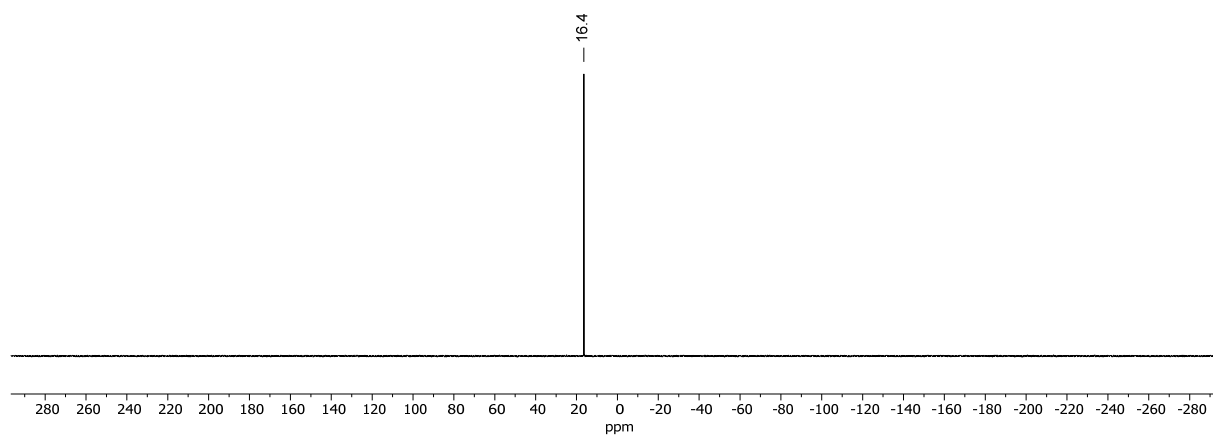


Figure S34. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of *trans*-[PdCl₂(PPh₂*n*Bu)₂] in C₆D₆ at 25 °C

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