Supporting Information for B613865A

Structurally Characterized Intermediates in the Stepwise Insertion of CO/Ethylene or CO/Methyl Acrylate into the Metal-Carbon Bond of Pd(II) Complexes Stabilised by (Phosphinomethyl)Oxazoline Ligands

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1. Experimental

General considerations

All manipulations were carried out under inert dinitrogen atmosphere, using standard Schlenk-line conditions and dried and freshly distilled solvents. The ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra were recorded unless otherwise stated on a Bruker Avance 300 instrument at 300.13, 75.48, 121.49 and 282.38 MHz, respectively, using TMS, or H_3PO_4 (85% in D_2O) as external standards with downfield shifts reported as positive. All NMR spectra were measured at 25 ºC, unless otherwise specified. The assignment of the chemical shifts and coupling constants of the complex spin systems formed by the $CHCH_2$ protons in complexes **7a**,**b** was made by $^{1}H,^{1}H$-COSY and $^{1}H,^{13}C$-HMQC, decoupled ^{31}P and dept135 NMR experiments. IR spectra in the range 4000–400 cm^{-1} were recorded on a Bruker IFS66FT and a Perkin Elmer 1600 Series FTIR. Elemental analyses were preformed by the "Service de Microanalyse, Université Louis Pasteur (Strasbourg, France)". [PdMeCl(COD)] and [$PdCl_2$(COD)] (COD is 1,5-cyclooctadiene, C_8H_{12}) were prepared according to literature procedures,[1, 2] as were ligands **1a**,**b**, complexes **2a**,**b** and **3a**,**b**.[3]

Preparation and Spectroscopic Data for 4a

A solution of **2a** (0.31 g, 0.73 mmol) in CH_2Cl_2 (50 mL) was stirred under 1 atm CO at room temperature over 1 h. After removal of the solvent under vacuum, the residue was washed with pentane (20 mL) and dried in vacuum, to afford **4a** as a yellow powder (0.30 g, 91% yield). IR (KBr): ν_{CO} = 1684 s, ν_{CN} = 1642 s cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 2.20 [d, $^{4}J_{HP}$ = 1.4 Hz, 3H, $C(O)CH_3$], 3.28 (dt, $^{2}J_{HP}$ = 10.1 Hz, $^{5}J_{HH}$ = 1.9 Hz, 2H, PCH_2), 3.94 (tt, $^{3}J_{HH}$ = 9.7

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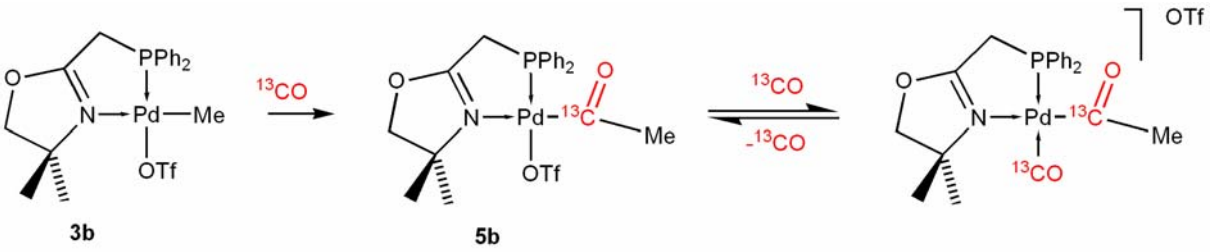
Hz, $^{5}J_{HH}$ = 1.9 Hz, 2H, NCH_2), 4.55 (t, $^{3}J_{HH}$ = 9.7 Hz, 2H, OCH_2), 7.45-7.55 (complex m, 6H), 7.66-7.74 (m, 4H); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 18.2 (s); Anal. Calcd for $C_{18}H_{19}ClNO_2PPd$: C 47.60, H 4.22, N 3.08, Found: C 47.51; H 4.11; N 2.90.

Preparation and Spectroscopic Data for 4b

Complex **4b** was obtained in a similar manner to **4a** from **2b** (0.25g, 0.55 mmol). Yellow powder (0.25 g, 95% yield). IR (KBr): ν_{CO} = 1685 s, ν_{CN} = 1632 s cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.54 [s, 6H, $NC(CH_3)_2$], 2.17 [d, $^{4}J_{HP}$ = 1.6 Hz, 3H, $C(O)CH_3$], 3.28 (d, $^{2}J_{HP}$ = 10.4 Hz, 2H, CH_2P), 4.12 (s, 2H, OCH_2), 7.45-7.55 (complex m, 6H), 7.67-7.75 (complex m, 4H); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 18.0 (s); Anal. Calcd for $C_{20}H_{23}ClNO_2PPd$: C 49.81, H 4.81, N 2.90, Found: C 51.10; H 4.90; N 2.60.

Variable temperature NMR measurements with 3b

A solution of **3b** (*ca* 0.020 g, 3.5 × 10^{-2} mmol) in CD_2Cl_2 (*ca* 0.6 mL) in a NMR tube with Teflon seal was exposed to an atmosphere of ^{13}CO.



Complex **5b** was identified by its NMR spectra at room temperature. Selected data: ^{1}H NMR (CD_2Cl_2): δ = 1.38 [s, 6H, $NC(CH_3)_2$], 2.09 [dd, $^{4}J_{HP}$ = 2.0 Hz, $^{2}J_{HC}$ = 6.0 Hz, 3H, $C(O)CH_3$], 3.37 (d, $^{2}J_{HP}$ = 11.2 Hz, 2H, CH_2P), 4.18 (s, 2H, OCH_2); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 21.6 (d, $^{2}J_{PC}$ = 9.7 Hz); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 222.7 [d, $^{2}J_{PC}$ = 9.7 Hz, *C*$(O)CH_3$].

At -100 ºC, the equilibrium between **5b** and the palladium acyl carbonyl complex [Pd{C(O)Me}(CO)(P,N)]OTf (P,N = **1b**) is completely shifted towards the latter as shown by NMR spectroscopy. Selected data: ^{1}H NMR (CD_2Cl_2, -100 ºC): δ = 1.27 [s, 6H, $NC(CH_3)_2$], 2.00 [d, $^{2}J_{HC}$ = 5.0 Hz, 3H, $C(O)CH_3$], 3.71 (d, $^{2}J_{HP}$ = 9.7 Hz, 2H, CH_2P), 4.29 (s, 2H, OCH_2); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, -100 ºC): δ 18.3 (dd, $^{2}J_{PCtrans}$ = 83.8 Hz, $^{2}J_{PCcis}$ = 4.1 Hz); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, -100 ºC): δ 223.1 [d, $^{2}J_{PC}$ = 4.1 Hz, *C*$(O)CH_3$], 175.3 [d, $^{2}J_{PC}$ = 83.8 Hz, PdC(O)].

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Figure S-1 $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, -100 ºC) spectrum of complex [Pd{C(O)Me}(CO)(P,N)]OTf (P,N = **1b**).

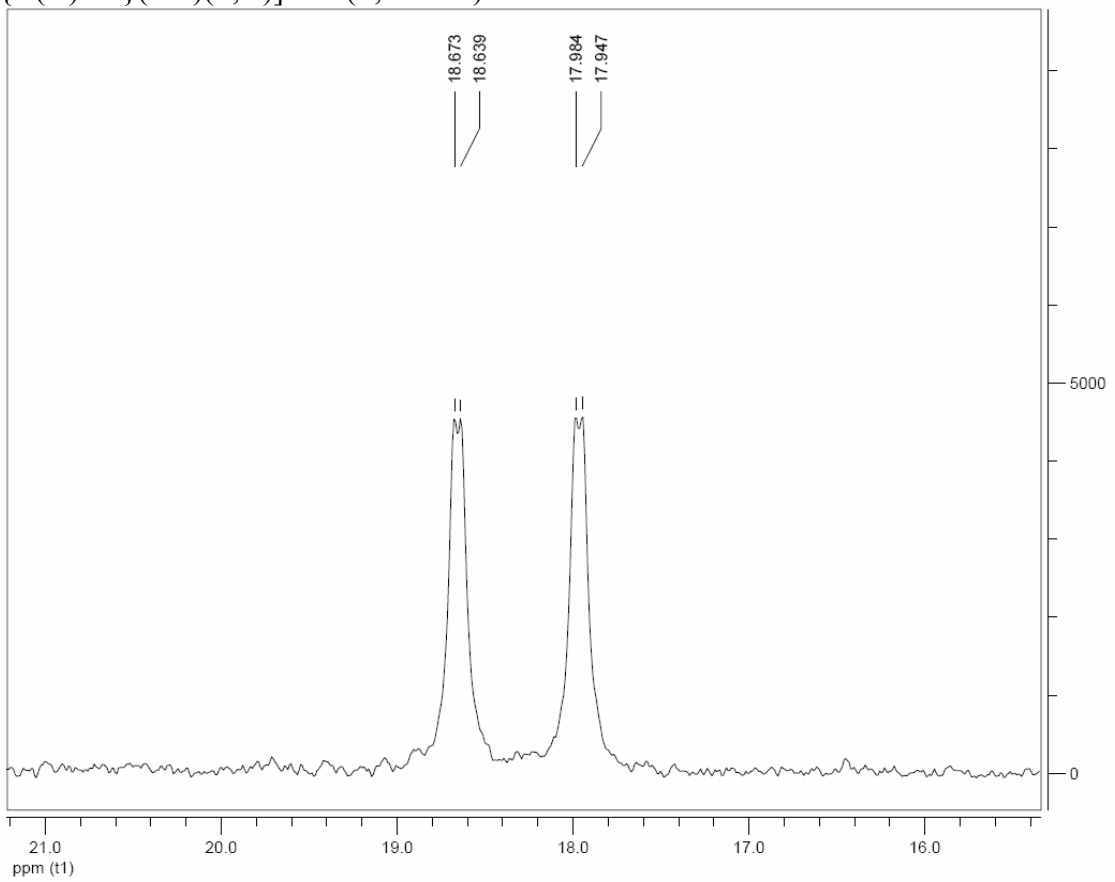
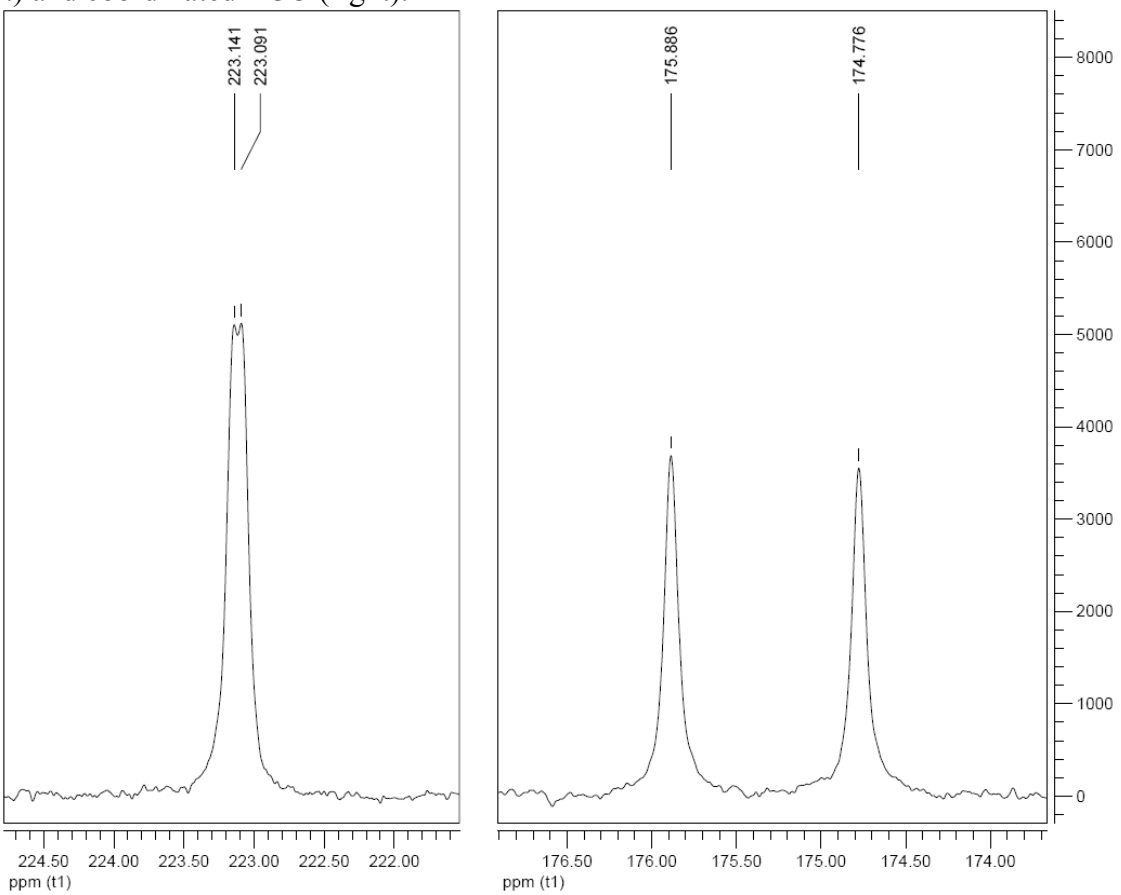


Figure S-2: Portion of the $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, -100 ºC) spectrum of complex [Pd{C(O)Me}(CO)(P,N)]OTf (P,N = **1b**) showing the peaks corresponding to the acyl carbon (left) and coordinated ^{13}CO (right).



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Preparation and Spectroscopic Data for 6a

A solution of **3a** (0.48 g, 0.89 mmol) in CH_2Cl_2 (50 mL) was stirred under 1 atm CO at room temperature for 1 h, which was then replaced by 1 atm ethylene and the solution was further stirred for 1 h. After filtration and removal of the volatiles under vacuum, the residue was washed with diethylether (20 mL) and pentane (2 × 20 mL) and dried under vacuum, to afford **6a** as yellow powder (0.46 g, 87% yield). IR (KBr): $\nu_{CO/CN}$ = 1634 s cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.65 (td, $^3J_{HH}$ = 6.1, $^3J_{HP}$ = 1.9 Hz, 2H, $PdCH_2$), 2.45 [s, 3H, $C(O)CH_3$], 3.08 (brt, $^3J_{HH}$ = 6.1 Hz, 2H, $PdCH_2CH_2$), 3.55 (dt, $^2J_{HP}$ = 10.8 Hz, $^5J_{HH}$ = 1.8 Hz, 2H, CH_2P), 4.05 (tt, $^3J_{HH}$ = 9.6 Hz, $^5J_{HH}$ = 1.8 Hz, 2H, NCH_2), 4.74 (t, $^3J_{HH}$ = 9.6 Hz, 2H, OCH_2), 7.51-7.59 (complex m, 6H), 7.64-7.73 (m, 4H); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.4 (s); $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ -78.6 (s); Anal. Calcd for $C_{21}H_{23}F_3NO_5PPdS$: C 42.33, H 3.89, N 2.35, Found: C 42.51; H 4.01; N 2.28.

Preparation and Spectroscopic Data for 6b

Complex **6b** was obtained in a similar manner to **6a** from **3b** (0.37 g, 0.65 mmol). White pale powder (0.37 g, 91% yield). IR (KBr): $\nu_{CO/CN}$ = 1629 s cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.47 [s, 6H, $NC(CH_3)_2$], 1.67 (td, $^3J_{HH}$ = 6.2, $^3J_{HP}$ = 1.9 Hz, 2H, $PdCH_2$), 2.49 [s, 3H, $C(O)CH_3$], 3.12 (brt, $^3J_{HH}$ = 6.2 Hz, 2H, $PdCH_2CH_2$), 3.58 (d, $^2J_{HP}$ = 11.0 Hz, 2H, CH_2P), 4.36 (s, 2H, OCH_2), 7.52-7.60 (complex m, 6H), 7.65-7.73 (m, 4H); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.7 (s); $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ -78.5 (s); Anal. Calcd for $C_{23}H_{27}F_3NO_5PPdS$: C 44.28, H 4.36, N 2.24, Found: C 44.45; H 4.40; N 2.05.

Preparation and Spectroscopic Data for 7a

A solution of **3a** (0.96 g, 1.78 mmol) and methyl acrylate (160 μL, 1equiv.) in CH_2Cl_2 (50 mL) was stirred under 1 atm CO at room temperature for 1 h. The workup as described for **6a**, afforded **7a** as a yellow powder (1.09 g, 93.6% yield). IR (KBr): $\nu_{C(O)OMe}$ = 1683 m, $\nu_{CO/CN}$ = 1633 s cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$): spin system for $PdCH_aCH_bH_c$: δ = 2.46 (appearance of dt, $^3J_{HaHb}$ = 1.2, $^3J_{HaHc}$ = 6.2, $^3J_{HaP}$ = 1.5 Hz, 1H, H_a), 2.90 (brd, $^2J_{HbHc}$ = 18.7 Hz, 1H, H_b), 3.26 (brdd, $^3J_{HaHc}$ = 6.2, $^2J_{HbHc}$ = 18.7 Hz, 1H, H_c, partial overlap with $C(O)OCH_3$), 2.52 [s, 3H, $C(O)CH_3$], ABMNX spin system (A = B = M = N = H, X = P, δ_A 3.15, δ_B 4.14, $^2J_{AB}$ = 17.6, $^2J_{AX}$ = 12.7, $^2J_{BX}$ = 9.2, $^5J_{AH}$ = 1.0, $^5J_{AH}$ = 1.6, $^5J_{BH}$ = 1.9, $^5J_{BH}$ = 2.2, Hz, 2H, CH_2P, δ_B partial overlap with NCH*H*) 3.24 [s, 3H, $C(O)OCH_3$], 3.90 (m, 1H, NC*H*H), 4.19 (m, 1H, NCH*H*) ABMN spin system (A = B = M = N = H, δ_A 4.62, δ_B 4.81, $^2J_{AB}$ = 10.8, $^3J_{AH}$ = 8.3, $^3J_{BH}$ = 8.6 Hz, 2H, OCH_2), 7.52-7.67 (complex m, 6H), 7.79-7.91 (m, 4H); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.8 (s); $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ -78.6 (s); Anal. Calcd for $C_{23}H_{25}F_3NO_7PPdS$: C 42.25, H 3.85, N 2.14, Found: C 42.22; H 3.99; N 2.00.

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Preparation and Spectroscopic Data for 7b

Complex **7a** was obtained in a similar manner to **7a** from **3b** (0.54 g, 0.95 mmol) and methyl acrylate (85.6 μL, 1 equiv.). Yellow powder (0.53 g, 82% yield). IR (KBr): $\nu_{C(O)OMe}$ = 1684 m, $\nu_{CO/CN}$ = 1629 s cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$): δ = 1.45 [s, 3H, NC(C*H*$_3$)(CH$_3$)], 1.51 [s, 3H, NC(CH$_3$)(C*H*$_3$)], spin system for $PdCH_aCH_bH_c$: 2.46 (appearance of dt, $^3J_{HaHb}$ = 1.4, $^3J_{HaHc}$ = 6.3, $^3J_{HaP}$ = 1.8 Hz, 1H, H_a), 2.87 (brd, $^2J_{HbHc}$ = 18.7 Hz, 1H, H_b), 3.27 (brdd, $^3J_{HaHc}$ = 6.3, $^2J_{HbHc}$ = 18.7 Hz, 1H, H_c), 2.55 [s, 3H, C(O)CH$_3$], ABX spin system (A = B = H, X = P, δ_A 3.08, δ_B 4.38, $^2J_{AB}$ = 17.6, $^2J_{AX}$ = 13.6, $^2J_{BX}$ = 9.6 Hz, 2H, CH_2P, δ_B partially overlapping with OCH_2), 3.22 [s, 3H, C(O)OCH$_3$], AB spin system (A = B = H, δ_A 4.2, δ_B 4.4, $^2J_{AB}$ = 8.5 Hz, 2H, OCH_2), 7.54-7.67 (complex m, 6H), 7.81-7.94 (m, 4H); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.3 (s); $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ -78.6 (s); Anal. Calcd for $C_{25}H_{29}F_3NO_7PPdS$: C 44.03, H 4.29, N 2.05, Found: C 44.28; H 4.44; N 1.80.

Complexes **2a,b**, **4a,b**, and **7a,b** can be stored for several months in a Schlenk flask under N_2 atmosphere, whereas complexes **3a,b** and **6a,b** start to show signs of decomposition into palladium black after 3-4 weeks.

2. Crystal Structure Determinations

Crystals suitable for X-ray determination were obtained for of **2a** (Figure S-3), **2b** (Figure S-4), **3a** (Figure S-5), **3b** (Figure S-6), **4b** (Figure S-7) and **6b** (Figure S-8) by slow diffusion of hexane into a CH_2Cl_2 solution of the respective complex at 5 ºC, and for **7a** (Figure S-9) and **7b** (Figure S-10) by slow diffusion of pentane into a THF solution of the respective complex also at 5 ºC. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) (Tables S-1 and S-2). Data were collected using phi-scans and the structures were solved by direct methods using the SHELX 97 software,[4, 5] and the refinement was by full-matrix least squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{C\text{-}H}$ = 0.95 Å, U_{11} = 0.04). Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication n° CCDC ******. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Complex **2a** crystallized with two independent molecules in the asymmetric unit (Figure S-3). A comparison between the bond lengths and angles (Table S-3) of the independent molecules reveals that they present approximately the same conformation around the metal centre.

Complex **2b** crystallized in a chiral space group ($P2_12_12_1$), however, in solution the complex is not chiral.

The structure of **3a** (Figure S-5) contains three independent molecules in the asymmetric unit with approximately the same conformation around the metal centre (Table S-3).

Insertion products **6b** and **7a** crystallized with two independent cations and two triflate anions in the asymmetric unit (Figures S-8 and S-9 respectively). In the structure of **6b** the two independent cations have very similar bonding parameters (Table S-4), however the comparison between these 2 cations (Figure S-8 b)) reveals that the ellipsoids of the cation containing Pd2 are larger than those of the cation containing Pd1. This is probably due to a less efficient stabilization by the neighbouring triflate anions thus leading to higher thermal parameters in the Pd2 than in the Pd1 cation. In **7a** the two slightly different cations found in the asymmetric unit also have very similar bonding parameters (Table S-4), but present stereogenic centres of opposite chirality. This is confirmed by their opposite torsion-angle values [O2-Pd1-C17-C21 = 87.2 (3)] and [O6-Pd2-C39-C43 = -87.2 (3)]. The symmetry-equivalent asymmetric units contain enantiomers of these cations.

Figure S-3 ORTEP view of the molecular structure of compound **2a** (H atoms omitted for clarity). Thermal ellipsoids include 50% of the electron density

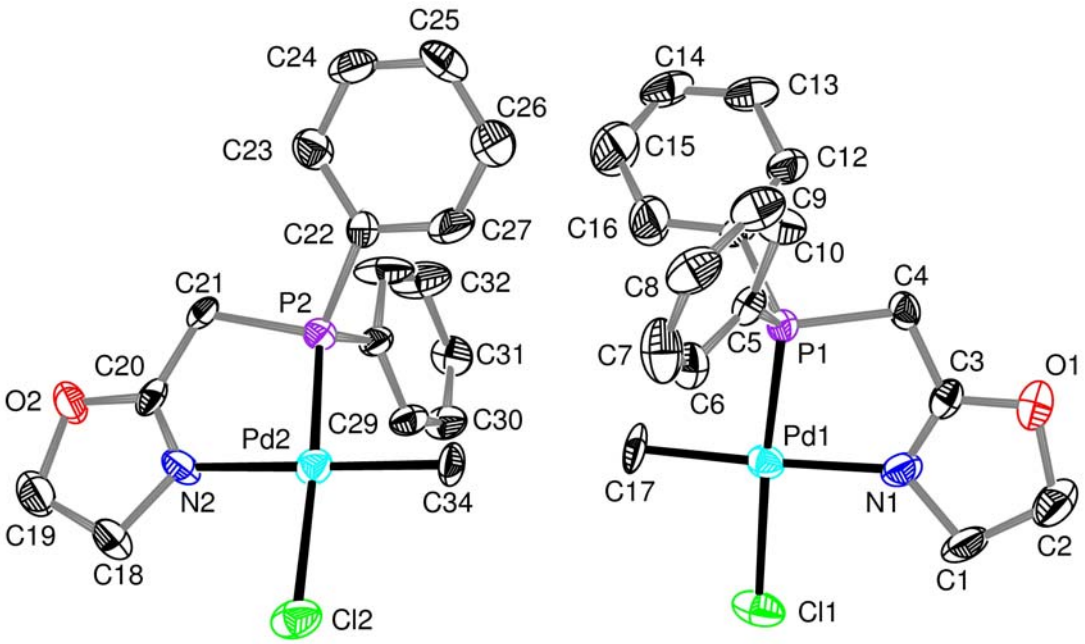

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Figure S-4 ORTEP view of the molecular structure of compound **2b** (H atoms omitted for clarity). Thermal ellipsoids include 50% of the electron density

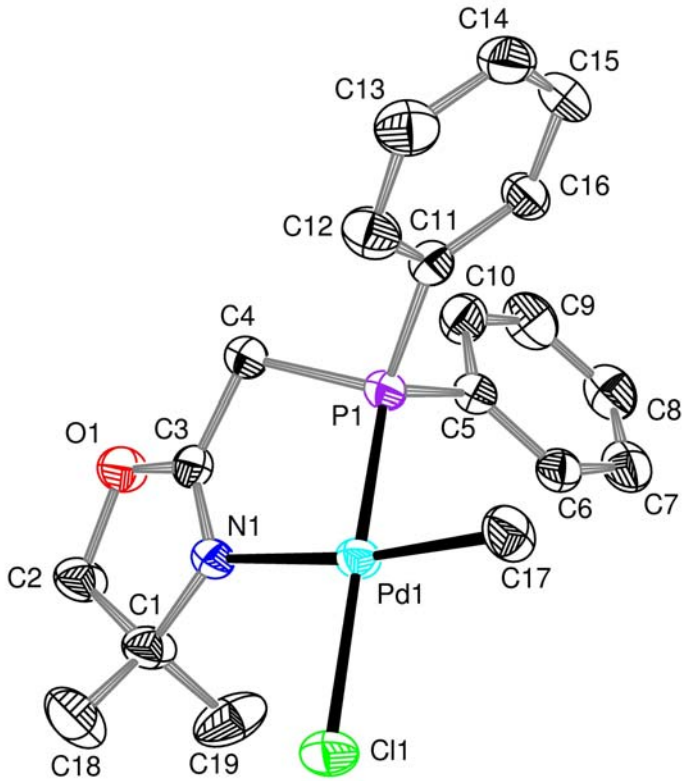

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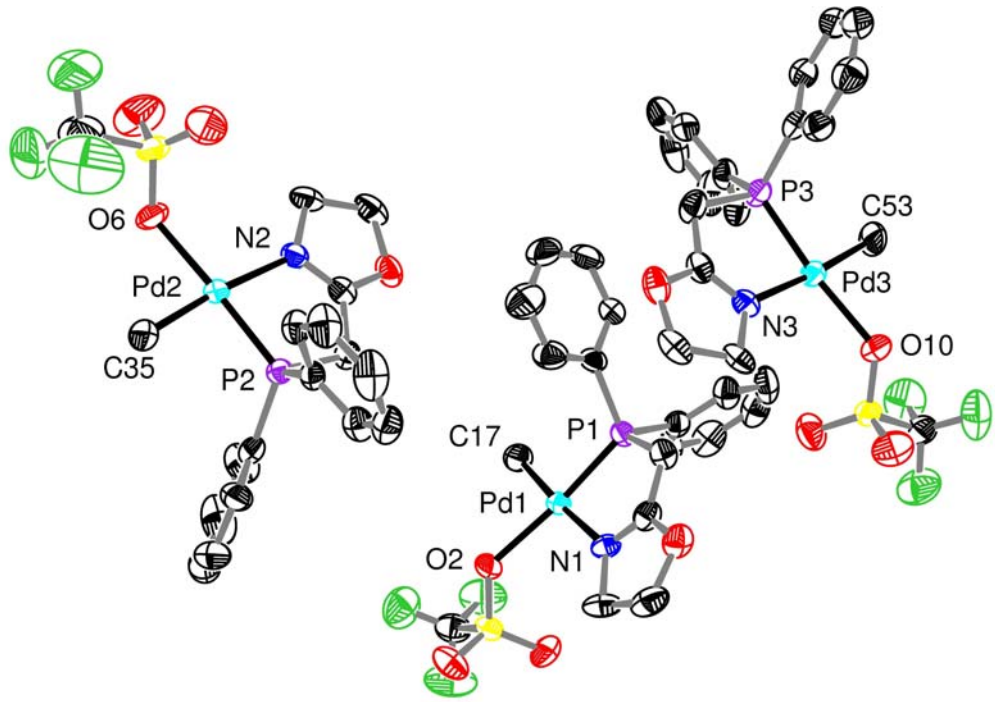
Figure S-5: a) ORTEP view of the molecular structure of compound **3a**; **b)** Comparative views of the three different molecules in **3a** (H atoms omitted for clarity). Thermal ellipsoids include 50% of the electron density.

a)



b)

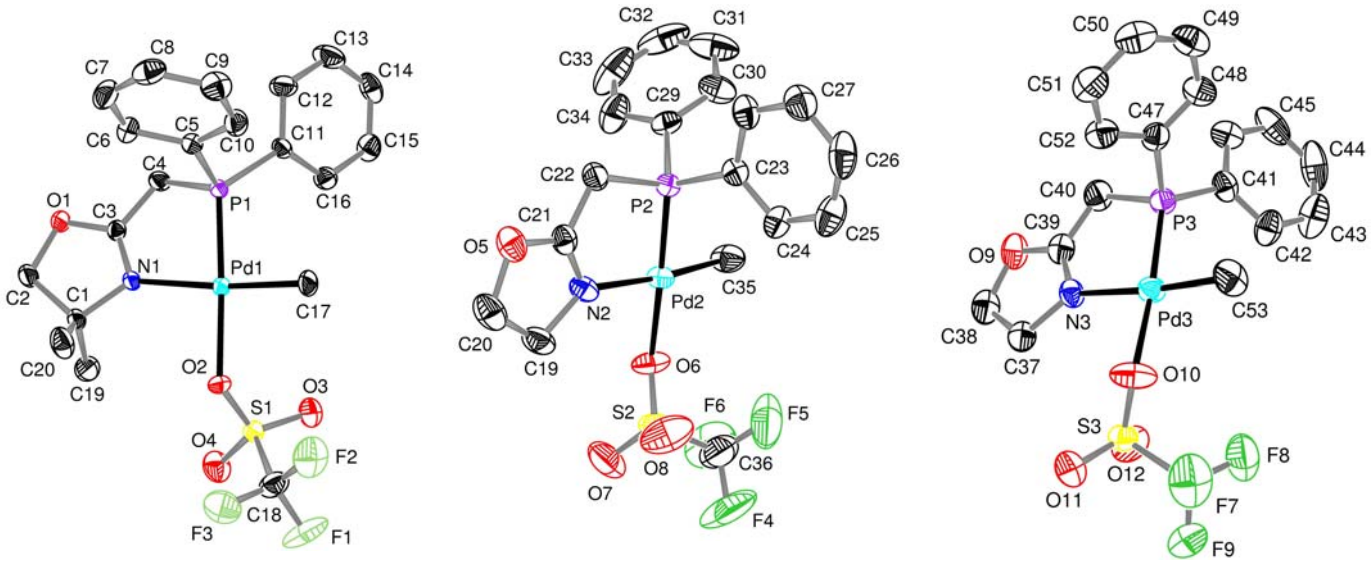


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Figure S-6: ORTEP view of the molecular structure of compound **3b** (H atoms omitted for clarity). Thermal ellipsoids include 50% of the electron density

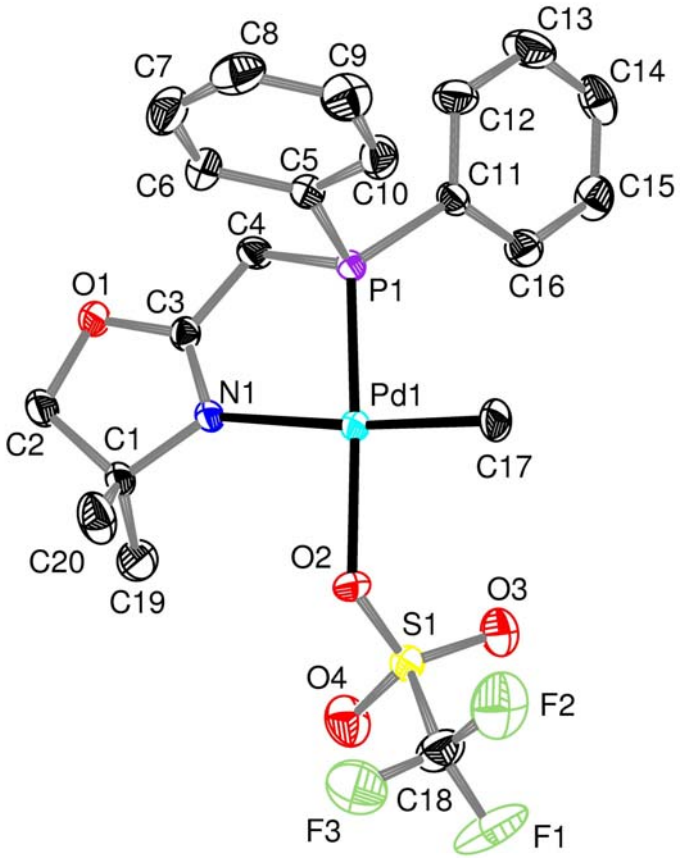

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Figure S-7: ORTEP view of the molecular structure of compound **4b** (H atoms omitted for clarity). Thermal ellipsoids include 50% of the electron density

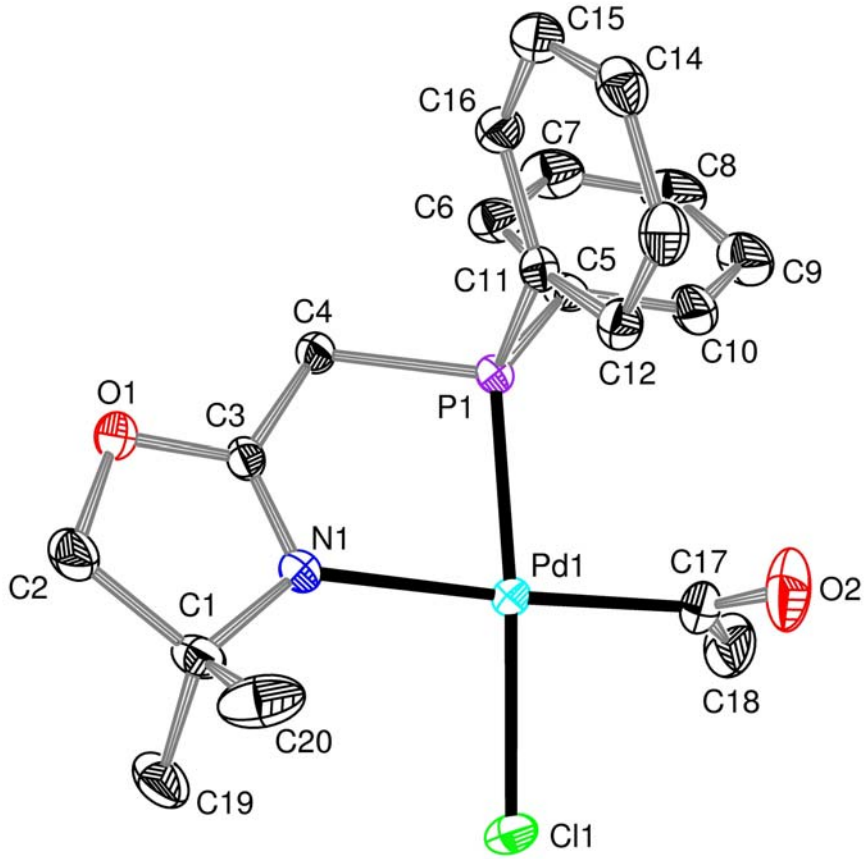

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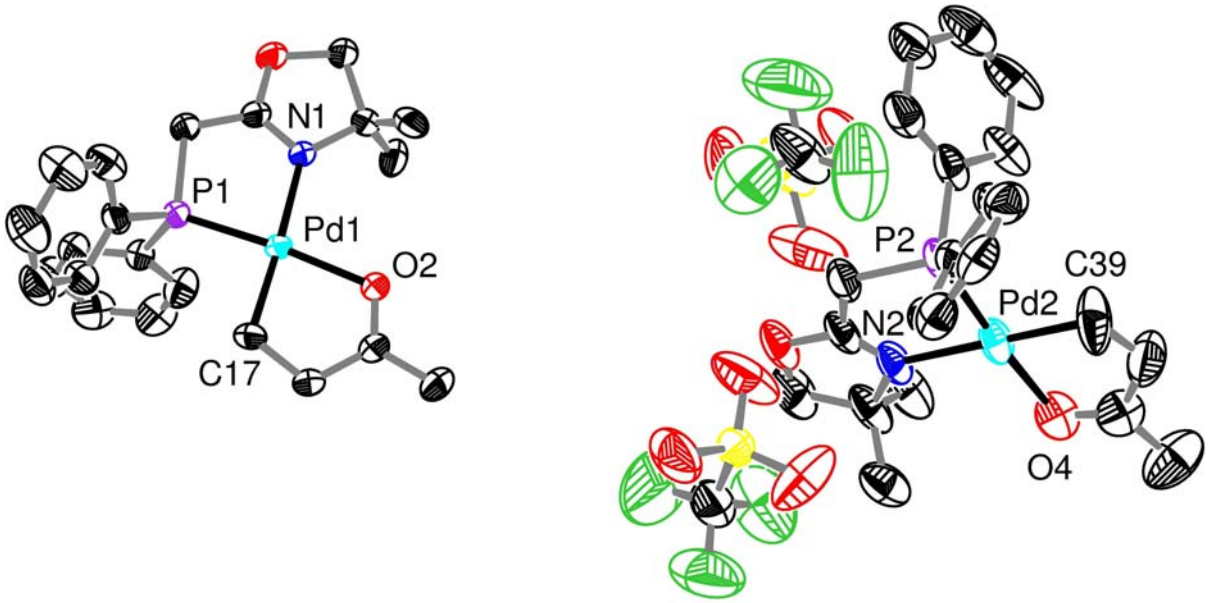
Figure S-8: a) ORTEP view of the molecular structure of compound **6b**; **b)** Comparative view of the two different cations in **6b** (H atoms omitted for clarity). Thermal ellipsoids include 50% of the electron density

a)



b)

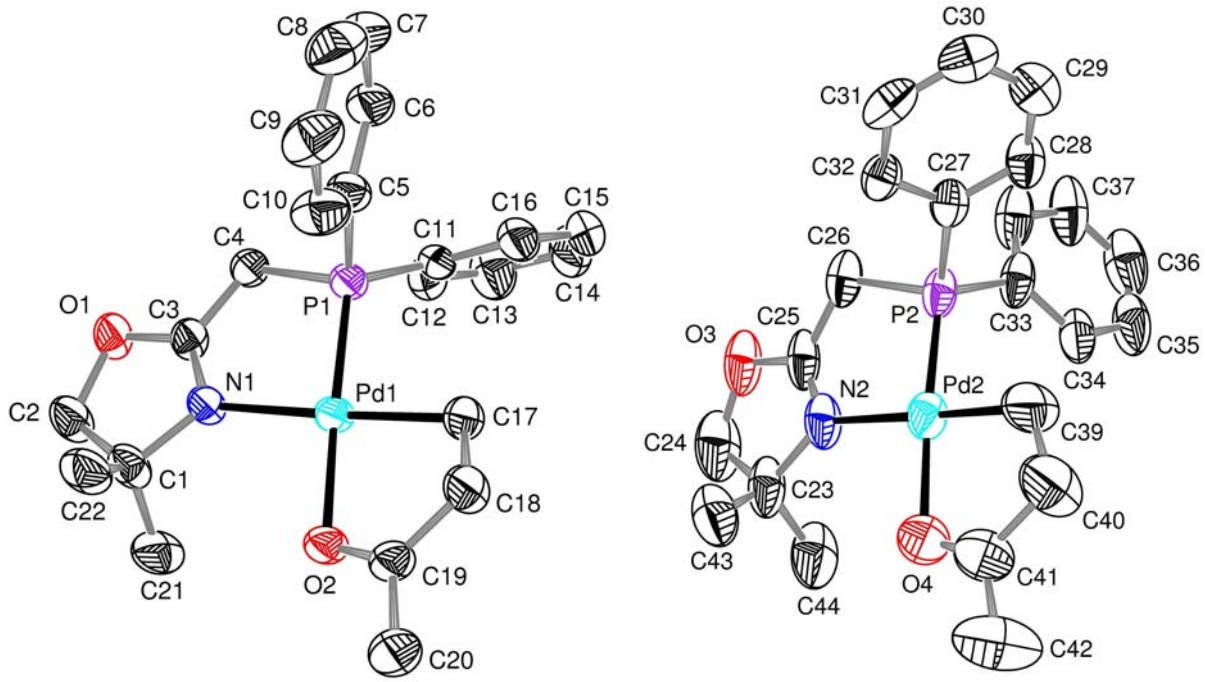


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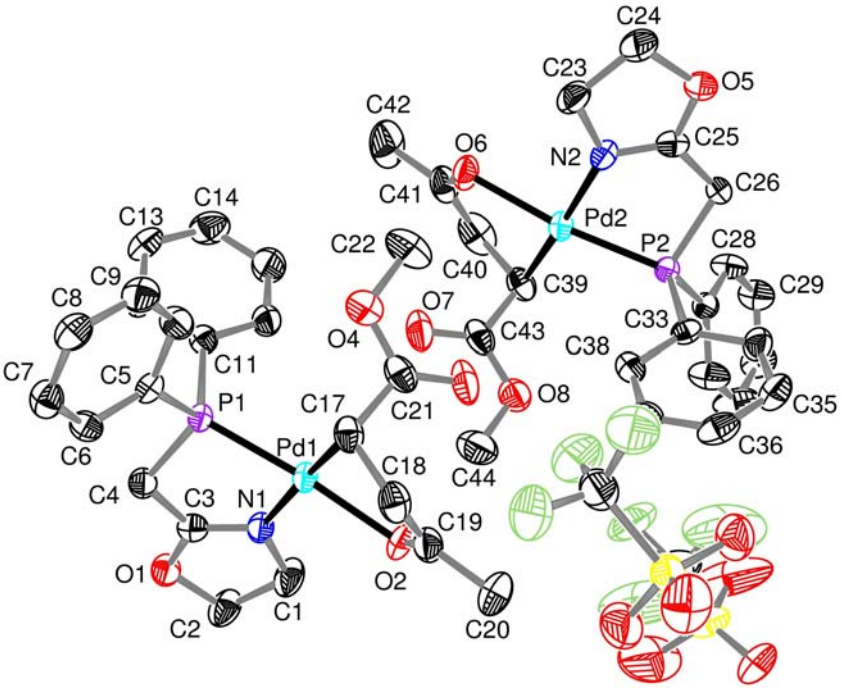
Figure S-9: ORTEP view of the molecular structure of compound **7a**; **b)** Comparative view of the two different cations in **7a** (on the left cation with stereogenic centre of configuration S and on the right of configuration R) (H atoms omitted for clarity). Thermal ellipsoids include 50% of the electron density.

a)



b)

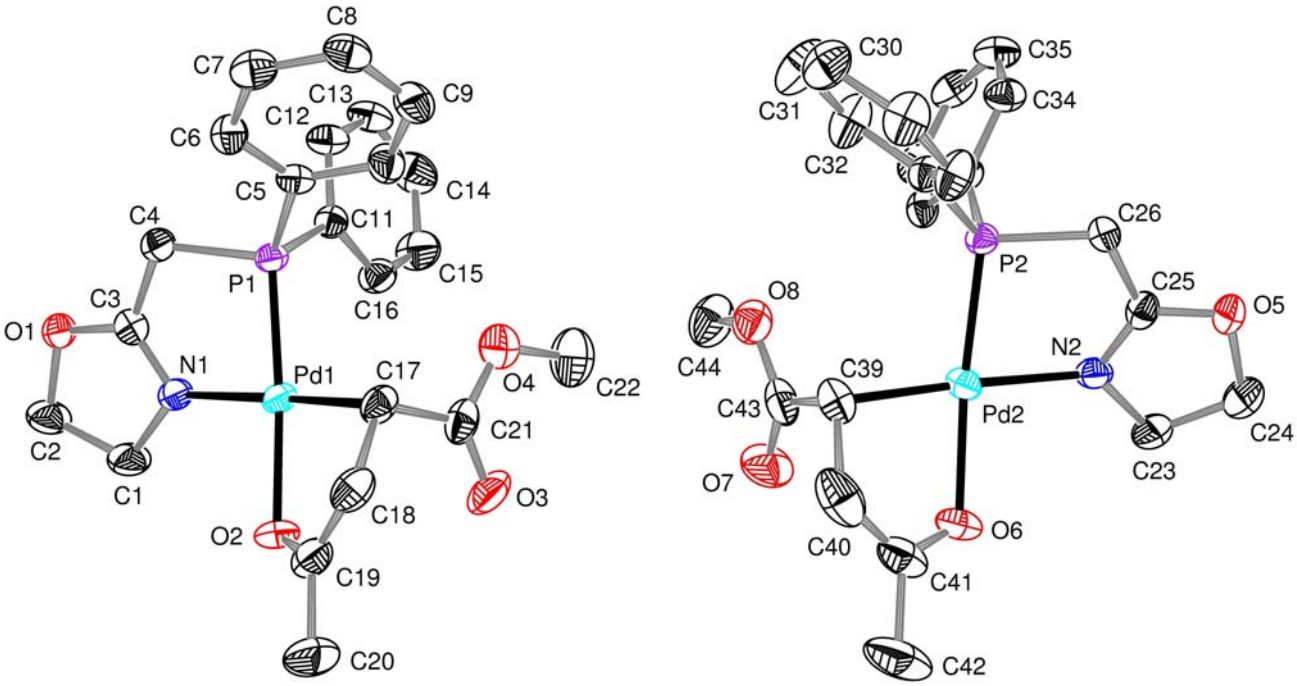


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Figure S-10: ORTEP view of the molecular structure of the cation in complex **7b** (H atoms omitted for clarity). Thermal ellipsoids include 50% of the electron density

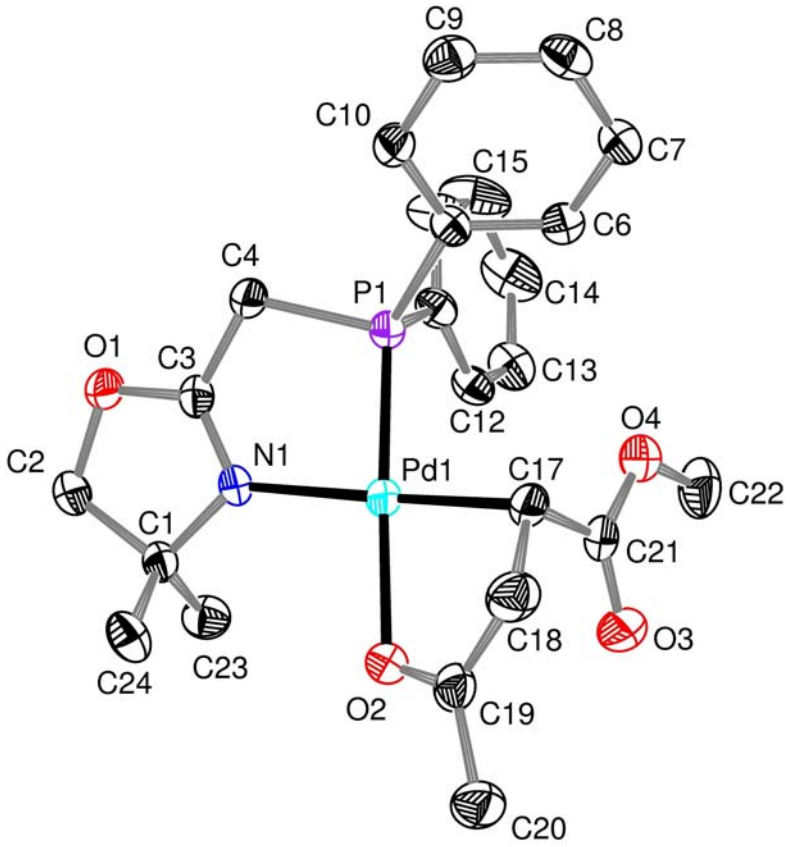

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Table S-1 Crystal data and details of the structure determination for the complexes **2a**,**b**, and **3a**,**b**.

	2a	**2b**	**3a**	**3b**
Formula	$2[C_{17}H_{19}ClNOPPd]$	$C_{19}H_{23}ClNOPPd$	$3[C_{17}H_{19}NOPPd{\cdot}CF_3SO_3]$	$C_{19}H_{23}NOPPd{\cdot}CF_3SO_3$
M_r	426.15	454.20	539.77	567.82
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$
a [Å]	8.5550 (4)	7.7310 (10)	17.4710 (2)	8.3330 (10)
b [Å]	8.8270 (5)	11.711 (2)	13.1780 (2)	9.827 (2)
c [Å]	22.6280 (9)	21.589 (4)	29.3020 (3)	14.261 (3)
α [º]	82.744 (4)			92.55 (5)
β [º]	83.051 (4)		107.1200 (6)	100.18 (5)
γ [º]	86.4320 (16)			98.93 (5)
V [Å^3]	1680.70 (14)	1954.6 (6)	6447.36 (14)	1132.4 (4)
Z	4	4	12	2
D_x [Mg m^{-3}]	1.684	1.543	1.668	1.665
μ [mm^{-1}]	1.358	1.173	1.084	1.033
T [K]	173 (2)	173 (2)	173 (2)	173 (2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
θ_{max} [º]	27.46	30.04	30.03	30.05
data set [h; k; l]	-7/11; -9/11; -25/25	-10/10; -16/16; -30/30	-24/24; -18/17; -41/41	-11/11; -13/11; -13/20
tot., unique data, R(int)	8059, 6429, 0.0480	5650, 5650	33223, 18821, 0.0835	8568, 6592, 0.0173
observed data [$I > 2\sigma(I)$]	4199	4464	9279	5724
No. reflns, No. params	6429, 397	5650, 217	18821, 784	6592, 280
R_1, wR_2, GOF	0.0956, 0.2694, 1.105	0.0397, 0.1272, 0.863	0.0548, 0.1518, 0.948	0.0303, 0.0714, 1.054
Flack parameter		−0.04 (4)		

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Table S-2 Crystal data and details of the structure determination for the complexes **4b**, **6b**, and **7a**,**b**.

	4b	**6b**	**7a**	**7b**
Formula	$C_{20}H_{23}ClNO_2PPd$	$2[C_{22}H_{27}NO_2PPd{\cdot}CF_3SO_3]$	$2[C_{22}H_{25}NO_4PPd{\cdot}CF_3SO_3]$	$C_{24}H_{29}NO_4PPd{\cdot}CF_3SO_3$
M_r	482.21	623.89	1307.74	681.92
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	8.962 (5)	11.4740 (5)	11.2740 (5)	8.927 (5)
b [Å]	10.100 (5)	13.9030 (7)	14.8270 (5)	12.268 (5)
c [Å]	12.534 (5)	18.0810 (10)	17.4450 (9)	13.682 (5)
α [º]	82.414 (5)	92.4860 (15)	73.4310 (16)	76.667 (5)
β [º]	80.486 (5)	96.7650 (15)	85.1550 (15)	87.664 (5)
γ [º]	64.312 (5)	112.951 (3)	73.2490 (14)	75.302 (5)
V [Å^3]	1006.0 (9)	2624.9 (2)	2676.4 (2)	1410.1 (11)
Z	2	4	2	2
D_x [Mg m^{-3}]	1006.0 (9)	1.579	1.623	1.606
μ [mm^{-1}]	1.148	0.902	0.894	0.852
T [K]	173 (2)	173 (2)	173 (2)	173 (2)
λ [Å]	0.71069	0.71073	0.71073	0.71069
θ_{max} [º]	35.00	30.07	29.16	27.46
data set [h; k; l]	-14/14; -16/16; 0/20	-16/14; -18/19; -25/25	-15/15; -20/20; -23/23	-11/11; -15/15; 0/17
tot., unique data, R(int)	8736, 8735, 0.0000	24511, 15294, 0.0395	23205, 14401, 0.0464	6394, 6394,
observed data [$I > 2\sigma(I)$]	8240	8608	8027	5427
No. reflns, No. params	8735, 235	15294, 625	14401, 667	6394, 352
R_1, wR_2, GOF	0.0226, 0.0635, 1.046	0.0724, 0.2146, 1.079	0.0511, 0.1375, 0.961	0.0542, 0.1722, 1.075

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Table S-3 Comparison of the bond lengths [Å] and angles [º] for the different molecules in the structures of **2a** and **3a**.

2a		**2a'**		**3a**		**3a'**		**3a''**	
Pd1-N1	2.103 (12)	Pd2-N2	2.098 (11)	Pd1-N1	2.131 (4)	Pd2-N2	2.124 (4)	Pd3-N3	2.139 (4)
Pd1-P1	2.212 (4)	Pd2-P2	2.230 (3)	Pd1-P1	2.1699 (12)	Pd2-P2	2.1716 (12)	Pd3-P3	2.1741 (13)
Pd1-C17	2.057 (13)	Pd2-C34	2.087 (12)	Pd1-C17	2.026 (5)	Pd2-C35	2.017 (5)	Pd3-C53	2.032 (5)
				Pd1-O2	2.156 (3)	Pd2-O6	2.151 (3)	Pd3-O10	2.175 (3)
Pd1-Cl1	2.383 (4)	Pd2-Cl2	2.376 (4)						
N1-C3	1.291 (18)	N2-C20	1.284 (17)	N1-C3	1.281 (6)	N2-C21	1.288 (6)	N3-C39	1.284 (6)
C3-C4	1.468 (19)	C20-C21	1.49 (2)	C3-C4	1.476 (6)	C21-C22	1.483 (6)	C39-C40	1.487 (7)
C4-P1	1.847 (13)	C21-P2	1.851 (13)	C4-P1	1.839 (5)	C22-P2	1.846 (5)	C40-P3	1.858 (5)
N1-Pd1-P1	82.2 (3)	N2-Pd2-P2	82.8 (3)	N1-Pd1-P1	84.85 (11)	N2-Pd2-P2	84.63 (11)	N3-Pd3-P3	84.93 (11)
N1-Pd1-C17	176.4 (5)	N2-Pd2-C34	176.9 (5)	N1-Pd1-C17	174.97 (17)	N2-Pd2-C35	174.38 (17)	N3-Pd3-C53	174.96 (18)
				N1-Pd1-O2	95.14 (14)	N2-Pd2-O6	95.97 (14)	N3-Pd3-O10	95.54 (15)
N1-Pd1-Cl1	93.2 (3)	N2-Pd2-Cl2	92.3 (3)						
				P1-Pd1-O2	172.64 (9)	P2-Pd2-O6	176.65 (9)	P3-Pd3-O10	171.95 (10)
P1-Pd1-C17	94.5 (4)	P2-Pd2-C34	95.3 (4)	P1-Pd1-C17	90.68 (15)	P2-Pd2-C35	90.08 (15)	P3-Pd3-C53	90.44 (16)
P1-Pd1-Cl1	174.66 (15)	P2-Pd2-Cl2	174.38 (14)						
				C17-Pd1-O2	89.00 (18)	C35-Pd2-O6	89.19 (18)	C53-Pd3-O10	88.77 (19)
C17-Pd1-Cl1	90.1 (5)	C34-Pd2-Cl2	89.5 (4)						

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Table S-4 Comparison of the bond lengths [Å] and angles [º] for the different cations in the structures of **6a** and **7a**.

6b		**6b'**		**7a**		**7a'**	
Pd1-N1	2.104 (4)	Pd2-N2	2.127 (5)	Pd1-N1	2.082 (3)	Pd2-N2	2.088 (3)
Pd1-P1	2.1878 (14)	Pd2-P2	2.1992 (19)	Pd1-P1	2.2051 (10)	Pd2-P2	2.2022 (10)
Pd1-C17	2.030 (5)	Pd2-C39	2.012 (7)	Pd1-C17	2.046 (4)	Pd2-C39	2.046 (4)
Pd1-O2	2.125 (4)	Pd2-O4	2.145 (5)	Pd1-O2	2.112 (2)	Pd2-O6	2.120 (3)
N1-C3	1.270 (6)	N2-C25	1.249 (9)	N1-C3	1.285 (5)	N2-C25	1.295 (5)
C3-C4	1.480 (7)	C25-C26	1.523 (10)	C3-C4	1.496 (5)	C25-C26	1.487 (5)
C4-P1	1.841 (5)	C26-P2	1.855 (6)	C4-P1	1.837 (4)	C26-P2	1.843 (4)
C17-C18	1.527 (8)	C39-C40	1.383 (12)	C17-C18	1.545 (6)	C39-C40	1.543 (7)
C18-C19	1.485 (8)	C40-C41	1.485 (11)	C18-C19	1.472 (6)	C40-C41	1.472 (7)
C19-O2	1.248 (6)	C41-O4	1.223 (9)	C19-O2	1.220 (5)	C41-O6	1.237 (6)
N1-Pd1-P1	83.91 (12)	N2-Pd2-P2	83.88 (18)	N1-Pd1-P1	82.13 (9)	N2-Pd2-P2	81.72 (9)
N1-Pd1-C17	177.1 (2)	N2-Pd2-C39	178.7 (3)	N1-Pd1-C17	174.17 (15)	N2-Pd2-C39	174.28 (15)
N1-Pd1-O2	100.03 (14)	N2-Pd2-O4	100.6 (2)	N1-Pd1-O2	96.10 (12)	N2-Pd2-O6	95.33 (12)
P1-Pd1-O2	174.72 (10)	P2-Pd2-O4	175.56 (13)	P1-Pd1-O2	175.29 (8)	P2-Pd2-O6	172.10 (8)
P1-Pd1-C17	93.30 (16)	P2-Pd2-C39	95.5 (3)	P1-Pd1-C17	99.24 (11)	P2-Pd2-C39	99.99 (12)
C17-Pd1-O2	82.80 (18)	C39-Pd2-O4	80.1 (3)	C17-Pd1-O2	82.10 (14)	C39-Pd2-O6	82.26 (15)

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3. References

1. R. E. Rulke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen and K. Vrieze, *Inorg. Chem.*, 1993, **32**, 5769-5778.
2. F. T. Ladipo and G. K. Anderson, *Organometallics*, 1994, **13**, 303-306.
3. P. Braunstein, M. D. Fryzuk, M. L. Dall, F. Naud, S. J. Rettig and F. Speiser, *J. Chem. Soc., Dalton Trans.*, 2000, 1067-1074.
4. *Kappa CCD Operation Manual; Nonius BV*, (1997), Kappa CCD Operation Manual; Nonius BV, Delft, The Nederlands.
5. G. M. Sheldrick, *SHELXL97*, (1997), SHELXL97, Program for the refinement of crystal structures, University of Göttingen, Germany.

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