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Synthesis and study of the stability of phosphane palladacycles †

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Abstract: The chemistry of phosphane palladacycles[1] has been amply developed in last years. This kind of chemistry results interesting due to their applications in numerous fields such as organic synthesis[2], catalysis[3] or as potential biologically active materials[4]. Palladacycles bearing the diphosphine *dppm* have been described before[5] and we now report a new behavior shown by palladacycles of the type $[Pd_2(Ph_2PCH_2PPh_2–P,P)_2(C,N:C,N)]$.
In this case the coordination of *dppm* spontaneously shifts from chelate to bridging mode in solution giving a core A-frame conformation with two palladium atoms with a chlorido or bromido ligand between them.

Keywords: Palladacycles, Cyclometallated compounds, dppm

1. Introduction

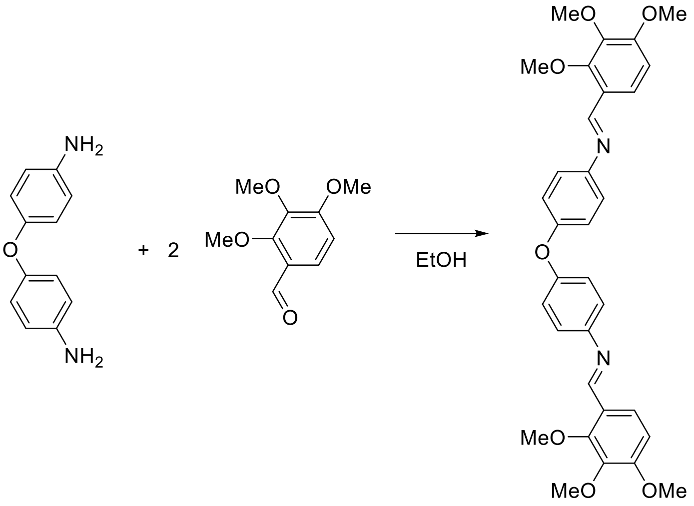
Palladium cyclometallated compounds and their derivatives have been widely studied in past years. There are many studies related to cyclometallated compounds derived from a wide variety of ligands and metals. In this work, a Schiff base was used as ligand for metallation; specifically the tetradentate [(C,N:C,N)] ligand derived from the condensation between 2,3,4-trimethoxybenzaldehyde and 4,4′-oxydianiline were chosen.

Diphosphines such as $Ph_2PCH_2PPh_2$ (dppm) present different coordination modes towads metal centers. It usually acts as chelate due to the thermodynamic stability related to coordination rings but nevertheless it may also appear bridging two metal centers. This behavior depends on the relative stability between both conformations.

In this work we report a gradual shift from a chelating to a bridging mode of this diphosphine when the metal center is palladium.

2. Materials and methods

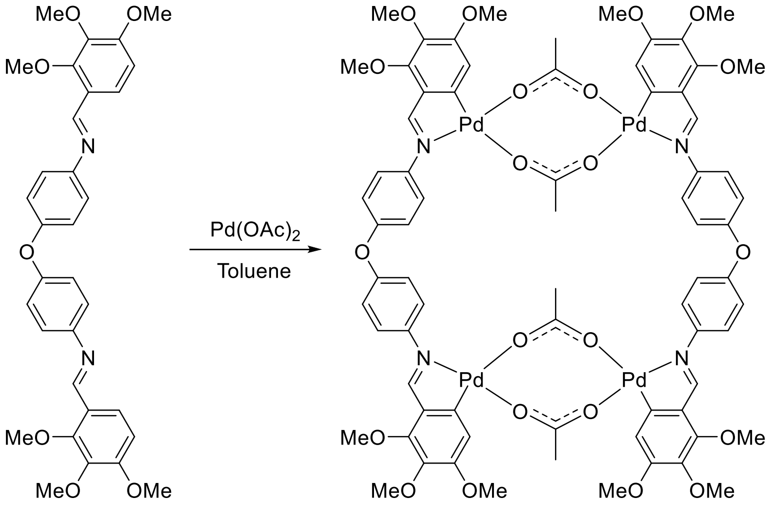
2.1. Synthesis of the ligand



Scheme 1. Synthesis reaction of the ligand

In a round bottom flask a 1:2 mixture of (p-$NH_2C_6H_4)_2O$ and 2,3,4–$(MeO)_3C_6H_2CHO$ in ethanol (50 cm^3) was stirred at room temperature during 24 h. A white precipitate was formed, which was filtered off, washed with water and dried under vacuum.

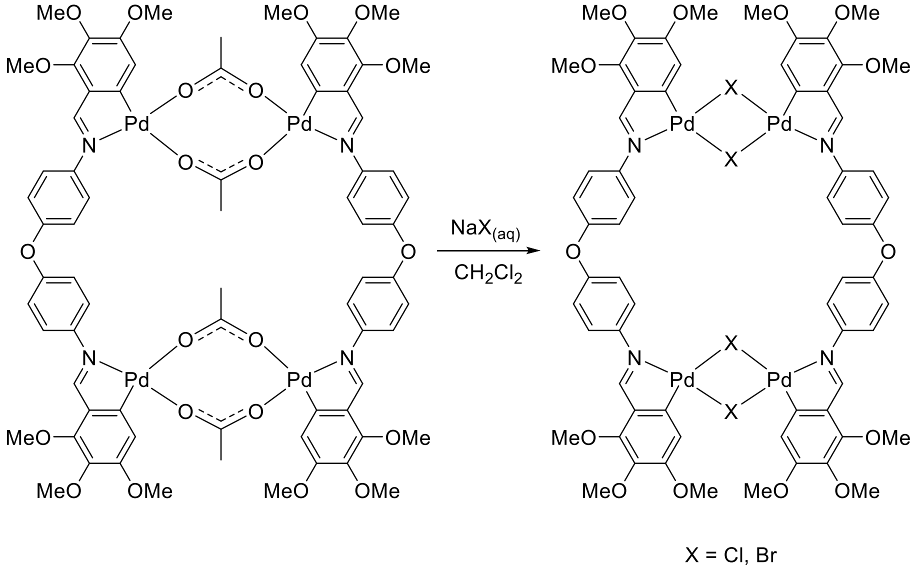
2.2. Synthesis of the cyclometallated compound



Scheme 2. Synthesis reaction of the cyclometallated compound

In a round bottom flask the ligand (0.500 g) was dissolved in toluene (30 cm^3). Then, palladium(II) acetate (2 eq.) was added and the resulting mixture was stirred at 55° C for 24 h. After cooling to r. t. the red oil formed was separated, to afford the final product as a red solid.

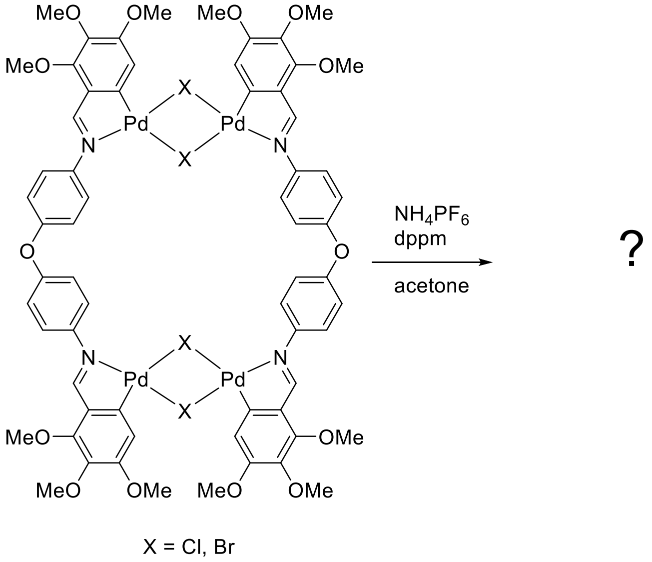
2.3. Synthesis of the halide bridging compound



Scheme 3. Synthesis reaction of the halide derivatives

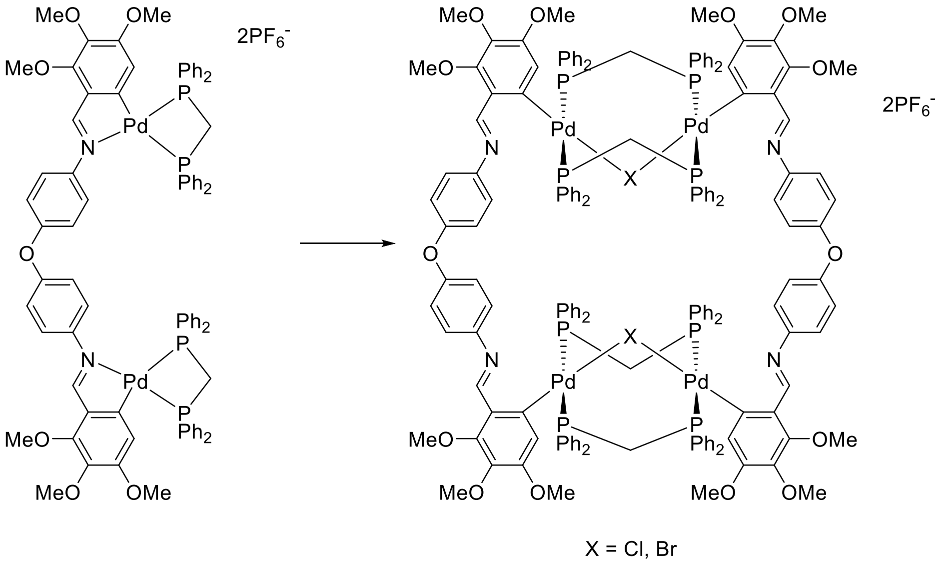
In a round bottom flask a solution of the cyclometallated precursor (0.450 g) in 25 cm^3 of dichloromethane was treated with 35 cm^3 of an aqueous solution of NaX (0.05M) and the mixture was stirred at room temperature. After eight hours the organic layer was isolated and the solvent was removed under reduced pressure. Later, the residue was recrystallized ofrom a mixture of dichloromethane-hexane to give a yellow solid.

2.1. Synthesis of the phosphane palladacycles



Scheme 4. Synthesis reaction of the final products

$Ph_2PCH_2PPh_2$ (0.020 mmol) and ammonium hexafluorophosphate (0.024 mmol) were added to a solution of the cyclometallated compound (8.5 mg, 0.005 mmol) in acetone-d_6 (0.6 cm^3) and left to stand until complete conversion.



Scheme 5. Solution shift

The resulting product shifts from chelate to a bridging coordination. The core consists of two Palladium atoms, two bridging dppm units and one bridging chlorido ligand.

3. Results

All the compounds were characterized by CHNS elemental analysis, proton and phosphorous nuclear magnetic resonance (NMR) in solution and single-crystal X-ray diffraction for the final products.

3.1. Elemental analysis

Elemental analyses were performed with a Fisons elemental analyzer, Model 1108; the results obtained are shown in **Table 1.**

Table 1. Results of the CHNS elemental analysis

Compound	% C (Found/Calcd.)	% H (Found/Calcd.)	% N (Found/Calcd.)
Ligand	68.8/69.0	5.9/5.8	5.1/5.0
Cyclometallated	48.6/48.8	4.2/4.1	3.3/3.2
Chlorido bridge	46.2/45.9	3.2/3.3	3.1/3.0
Bromido bridge	41.2/41.5	3.2/3.3	3.1/3.0

The results are consistent with the proposed structures.

3.2. Nuclear magnetic resonance

The NMR is a very useful technique for organic and inorganic chemistry. For this analysis it was used a Varian Inova 400 MHz spectrometer.

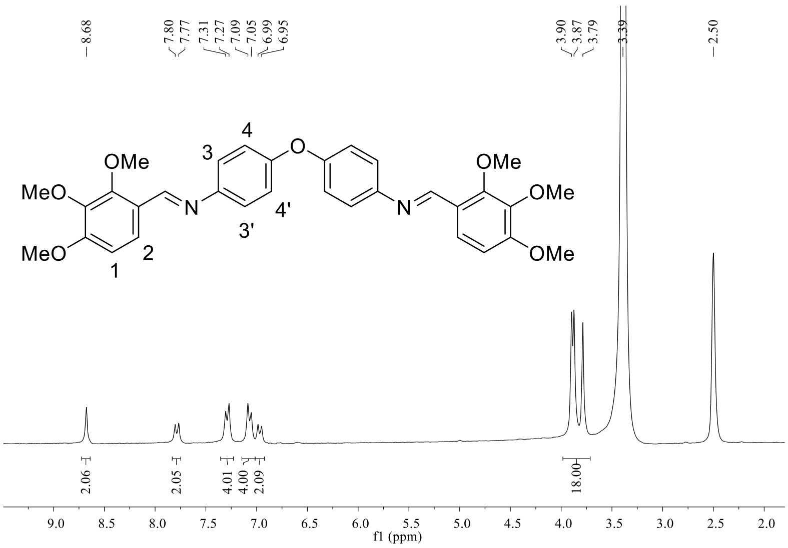


Figure 1. ^{1}H-NMR from the ligand in dmso-d$_6$

^{1}H NMR (DMSO-d$_6$, δ/ppm, J/Hz): 8.68 (s, 2H, HC=N); 7.78 (d, 2H, H2, ^{3}JH2H1 = 8.7); 7.28 (d, 4H, H3H3′, N = 8.3); 7.07 (d, 4H, H4H4′, N = 8.3); 6.97 (d, 2H, H1, ^{3}JH1H2 = 8.7); 3.90 (s, 6H, MeO); 3.87 (s, 6H, MeO); 3.79 (s, 6H, MeO).

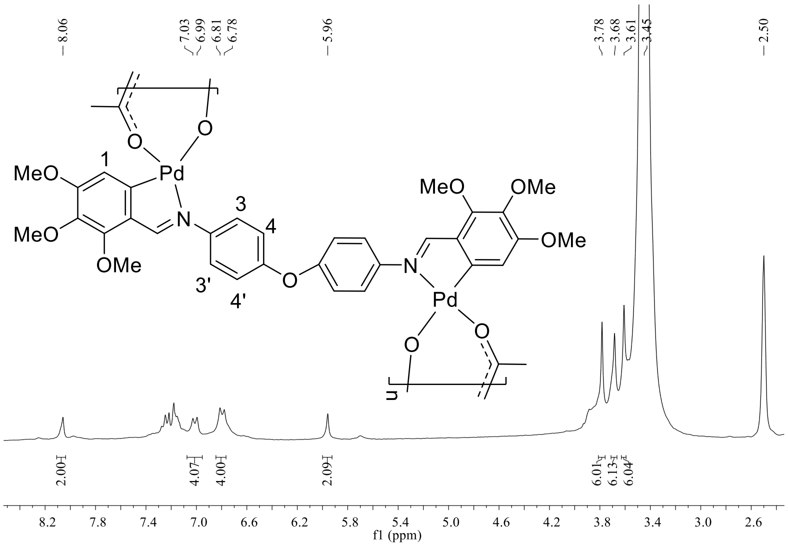


Figure 2. ^{1}H-NMR from the cyclometallated compound in dmso-d$_6$

^{1}H NMR (DMSO–d$_6$, δ ppm, J Hz): 8.06 (s, 2H, HC=N), 7.01 (d, 4H, H3H3′, N = 8.3); 6.79 (d, 4H, H4H4′, N = 8.3), 5.96 (s, 2H, H1), 3.78 (s, 6H, MeO), 3.68 (s, 6H, MeO), 3.61 (s, 6H, MeO), 2.17 (s, 3H, MeCO2), 1.48 (s, 3H, MeCO2).

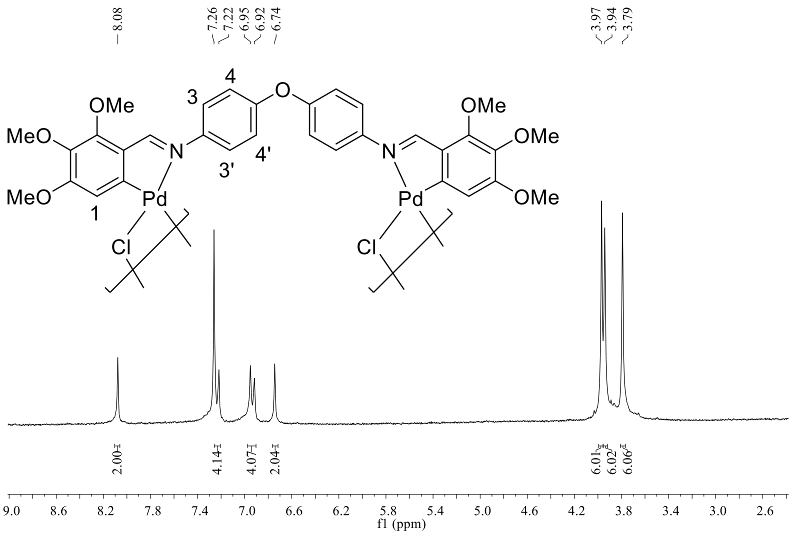


Figure 3. ^{1}H-NMR from the chlorido bridging compound in cdcl$_3$

^{1}H-NMR ($CDCl_3$, δ ppm, J Hz): 8.08 (s, 2H, HC=N), 7.23 (d, 4H, H3H3′, N = 8.7), 6.93 (d, 4H, H4H4′, N = 8.7), 6.74 (s, 2H, H1), 3.97 (s, 6H, MeO), 3.94 (s, 6H, MeO), 3.79 (s, 6H, MeO).

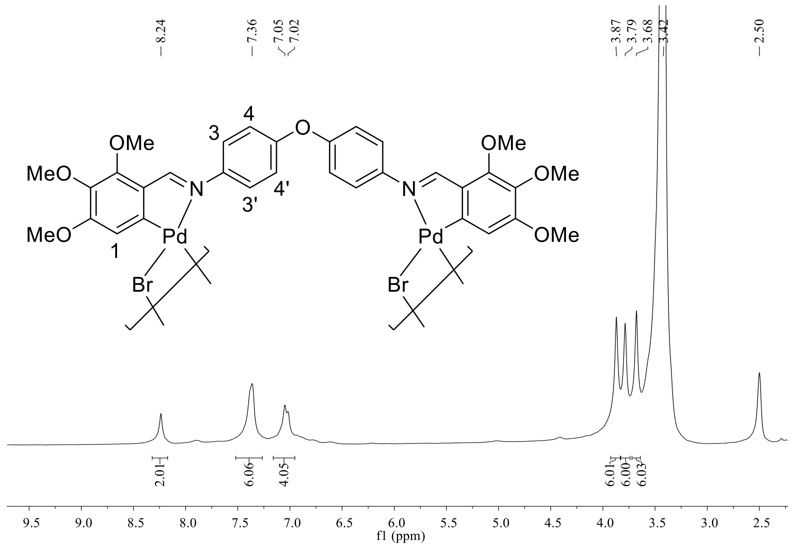


Figure 4. ^{1}H-NMR from the bromido bridging compound in dmso-d$_6$

^{1}H-NMR (DMSO–d$_6$, δ ppm, J Hz): 8.24 (s, 2H, HC=N), 7.36 (m, 4H, H3H3′), 7.36 (m, 2H, H1), 6.99 (m, 4H, H4H4′), 3.83 (s, 6H, MeO), 3.75 (s, 6H, MeO), 3.64 (s, 6H, MeO).

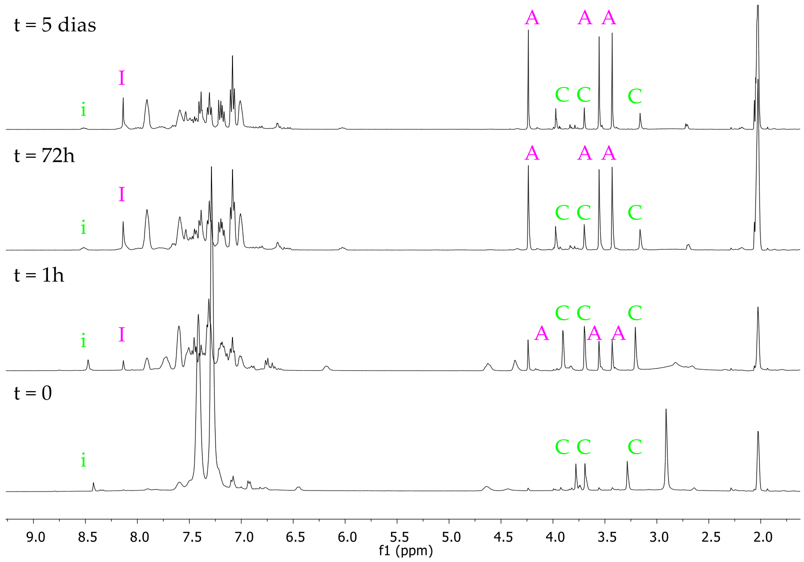
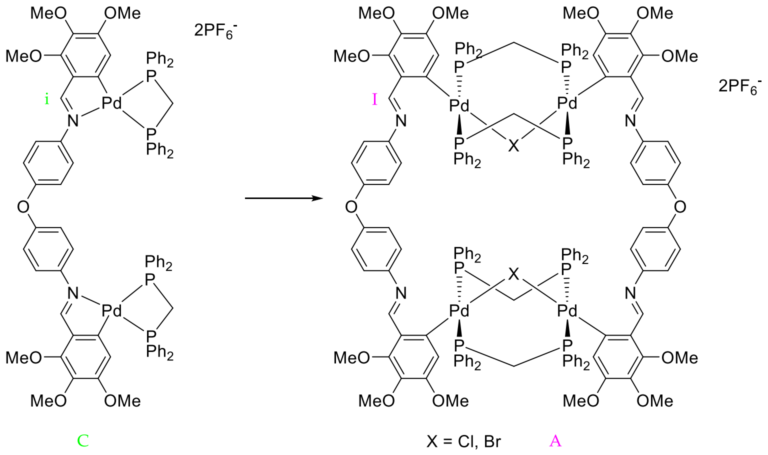


Figure 5. Shift of the phosphane palladacycle observed by ^{1}H-NMR in acetone-d$_6$



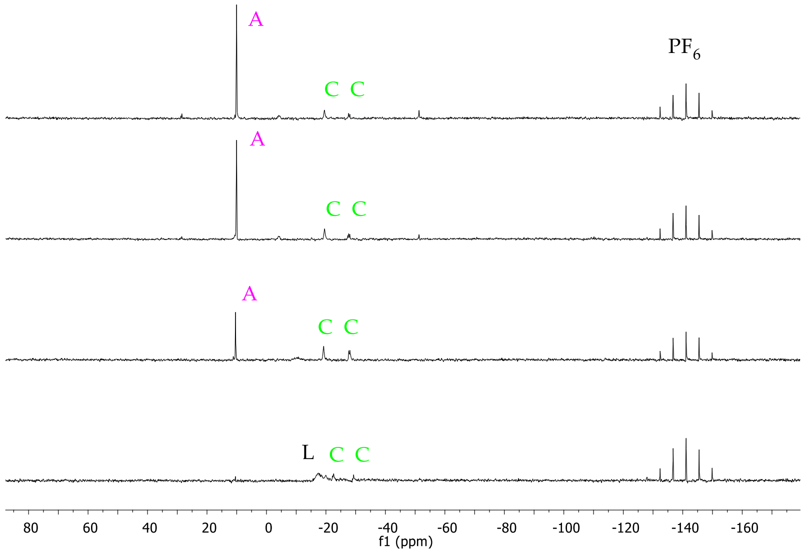


Figure 6. Shift of the phosphane palladacycle observed by ^{31}P-{^{1}H}-NMR in acetone-d$_6$.

L = *dppm*

The time-dependent shift can be easely followed by close inspection of the ^{1}H and ^{31}P NMR spectra.

3.3. *Single-crystal X-ray*

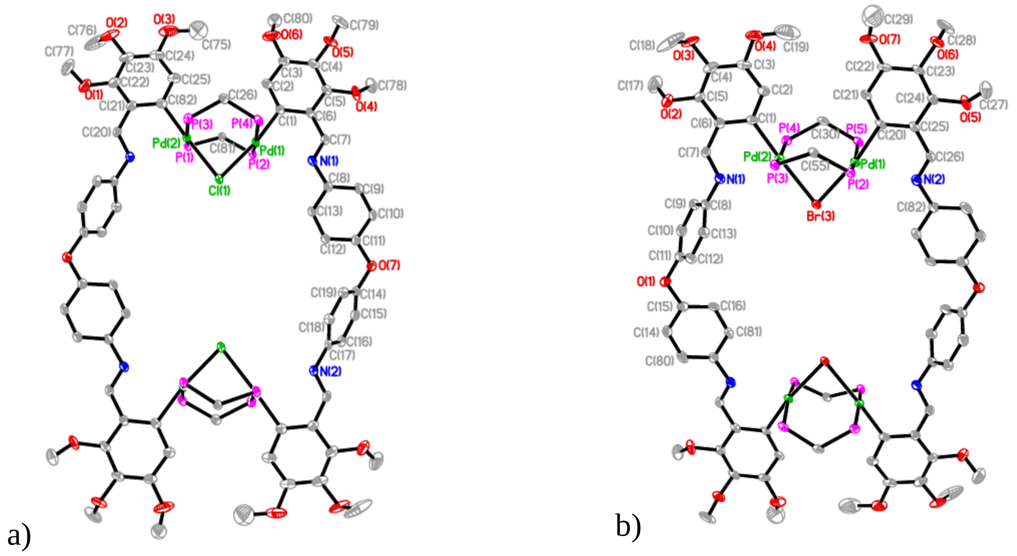


Figure 7. a) Thermal ellipsoid plot with chlorido for the asymmetric unit. Solvent molecules, hydrogen atoms and phosphane phenyls have been omitted for clarity. b) Thermal ellipsoid plot with bromido for the asymmetric unit. Solvent molecules, hydrogen atoms and phosphane phenyls have been omitted for clarity.

Table 2. Crystal data and structure refinement

Compound	**a)**	**b)**
Identification code	**2b**	**3b**
Empirical formula	$C_{176}H_{172}Cl_2F_{12}N_4O_{20}P_{10}Pd_4$	$C_{85}H_{80}BrF_6N_2O_8P_5Pd_2$
Formula weight	3697.37	1819.07
Temperature	97(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions	a = 16.4987(6) Å; α = 82.897(2)°.	a = 16.4980(17) Å; α = 83.263(7)°.
	b = 16.5332(6) Å; β = 71.882(2)°.	b = 16.5610(16) Å; β = 71.977(7)°.
	c = 17.1548(5) Å; γ = 75.240(2)°.	c = 17.1294(19) Å; γ = 75.228(7)°.
Volume	4295.6(3) Å^3	4299.7(8) Å^3
Z	1	2
Density (calculated)	1.429 Mg/m^3	1.405 Mg/m^3
Absorption coefficient	0.614 mm^{-1}	1.042 mm^{-1}
F(000)	1892	1848
Crystal size	0.250 x 0.220 x 0.160 mm^3	0.160 x 0.150 x 0.090 mm^3
Theta range for data collection	1.275 to 25.000°.	1.273 to 25.000°.
Index ranges	-19<=h<=19, -19<=k<=19, -20<=l<=20	-19<=h<=19, -19<=k<=19, -20<=l<=20

Reflections collected	140354	122609
Independent reflections	15101 [R(int) = 0.0442]	15141 [R(int) = 0.0595]
Completeness to theta = 25.000°	99.8 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9010 and 0.8216	0.912 and 0.851
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	15101 / 774 / 1046	15141 / 0 / 962
Goodness-of-fit on F^2	1.091	1.265
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1292	R1 = 0.0437, wR2 = 0.1252
R indices (all data)	R1 = 0.0515, wR2 = 0.1339	R1 = 0.0547, wR2 = 0.1301
Largest diff. peak and hole	2.151 and -0.969 e.Å^{-3}	2.036 and -0.918 e.Å^{-3}

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Conflicts of Interest: “The authors declare no conflict of interest.”

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