Supporting Information for:

[Pd(C^N)(X)(PPh_3)] palladacycles react with 2,4,6-trifluorophenyl boronic acid to give stable transmetallation products of the type [Pd(C^N)(2,4,6-$F_3C_6H_2$)(PPh_3)]

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Contents

1.0 General Experimental Procedures

C, H, and N analyses were carried out with a Carlo Erba instrument. IR spectra were recorded on a Perkin-Elmer spectrophotometer 16F PC FT-IR, using Nujol mulls between polyethylene sheets. NMR spectroscopic data of complexes (^{1}H, ^{31}P and ^{19}F) were recorded on Bruker Avance 300 spectrometer. ESI-MS Accurate mass TOF analyses were performed on an Agilent VL mass spectrometer. The ionization mechanism used was electrospray in positive and negative ion full scan mode using acetonitrile as solvent and nitrogen gas for desolvation.

2.0 X-ray Data Collection, Structure Solution, and Refinement for (2) [Pd(Phbz)(2,4,6-$F_3C_6H_2$)(PPh_3)], (3) [Pd(Phazb)(2,4,6-$F_3C_6H_2$)(PPh_3)], (4) [Pd_2(2,4,6-$C_6F_3H_2$)$_2$(PPh_3)$_2$(μ-OH)(μ-OAc)] and (5) *trans*-[PdCl(2,4,6-$F_3C_6H_2$)(PPh_3)]

Data collection for were obtained at 100(2) K on a Bruker Smart CCD diffractometer with a nominal crystal to detector distance of 4.5 cm. Diffraction data were collected based on a ω scan run. A total of 2524 frames were collected at 0.3º intervals and 10 s per frame. The diffraction frames were integrated using the SAINT package[1] and corrected for absorption with SADABS.[2] The structures were solved by direct methods and refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-H atoms (Table 1).

3.0 Materials and methods

The cyclometallated starting materials [Pd(Phbz)(AcO)(PPh_3)], [Pd(Phbz)(succinimidate)(PPh_3)] and [Pd(Phbz)(maleimidate)(PPh_3)] were synthesized following a reported method[3] The commercially available chemicals were purchased from Aldrich Chemical Co. and were used without further purification, and all the solvents were dried by standard methods before use.

3.1 Characterization of [Pd(Phbz)(AcO)(PPh$_3$)] (0.092 g, 75%). Anal. Found: C, 65.3; H, 4.7; N, 2.5. Calc. for $C_{33}H_{28}NO_2PPd$: C, 65.2; H, 4.6; N, 2.3%. IR (cm^{-1}): ν(C=O) 1594vs, ν(Phbz) 1546s, ν(PPh$_3$) 532, 517. ESI-MS (positive mode) m/z: 548 M$^+$-AcO. ^{1}H NMR. δ_H (300 MHz, CDCl$_3$): 8.19 (d, 1H; N=CH, *J*=6.3Hz); 7.80 (m, 6H; PPh$_3$); 7.42 (m, 14H; 9H PPh$_3$ + 5H aromatics); 7.25 (d, 1H; H^6 Phbz, *J*=7.4Hz); 6.92(m, 1H; H^5 Phbz); 6.58 (m, 1H; H^4 Phbz); 6.48 (m, 1H; H^3 Phbz); 1.71 (m, 3H CH$_3$COO). ^{31}P NMR (300MHz, CDCl$_3$): 41.80.

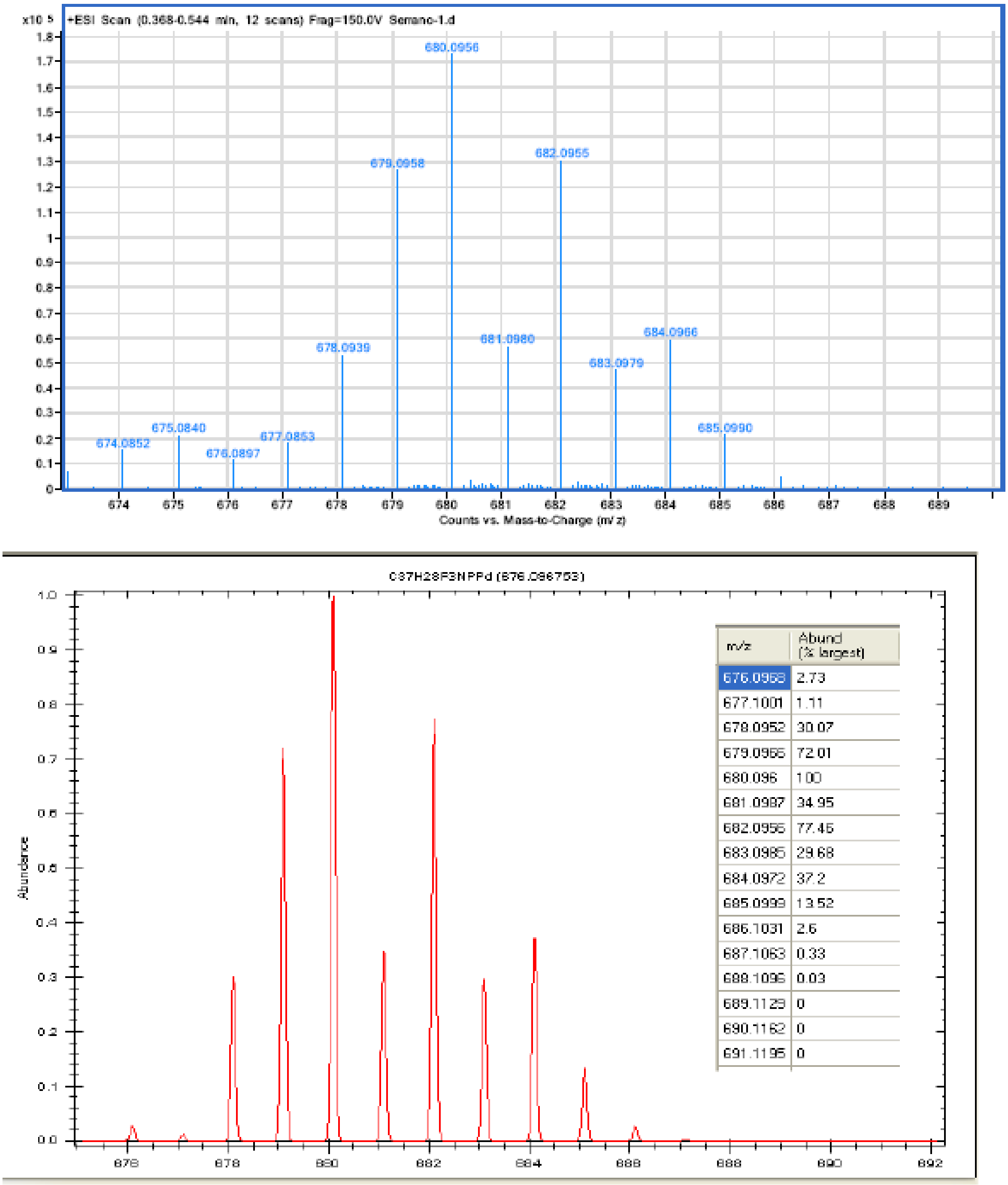
3.2 Representative procedure for the synthesis of [Pd(Phbz)(2,4,6-F$_3$C$_6$H$_2$)(PPh$_3$)] (2)

To a stirred white suspension in tetrahydrofurane (6 mL) of [Pd(Phbz)(AcO)(PPh$_3$)] (0.07 g; 0.115 mmol) was added excess of 2,4,6-trifluorophenylboronic acid (0.121 g; 0.691 mmol; 1:6 ratio) and 3 ml extra of tetrahydrofurane. A pale yellow solution was observed after 30 minutes stirring; It was then concentrated until *ca.* one fifth of the initial volume and slow addition of hexane caused the precipitation of a white solid, , that was filtered off, washed with hexane and air dried.

A pure sample of [Pd(phbz)(2,4,6-F$_3$C$_6$H$_2$)(PPh$_3$)] was also obtained when a 1:2 ratio was employed in this reaction, whilst 1:1 ratio yielded the new compound mixed with starting material [Pd(Phbz)(AcO)(PPh$_3$)] easily identified by ^{1}H and ^{31}P-NMR spectroscopy.

The desired complex [Pd(phbz)(2,4,6-F$_3$C$_6$H$_2$)(PPh$_3$)] can also be prepared using the same procedure (1:6 ratio) and imidate analogues [Pd(Phbz)(succinimidate)(PPh$_3$)] or [Pd(Phbz)(maleimidate)(PPh$_3$)] as starting materials.

(2) [Pd(Phbz)(2,4,6-F$_3$C$_6$H$_2$)(PPh$_3$)] (0.055 g, 70%). Anal. Found: C, 65.4; H, 4.2; N, 2.2. Calc. for $C_{37}H_{27}F_3NPPd$: C, 65.3; H, 4.0; N, 2.1%. IR (cm^{-1}): ν(2,4,6-F$_3$C$_6$H$_2$) 1594s, 1405s, 1100s, 990s; ν(Phbz) 1545s, ν(PPh$_3$) 528, 515. ESI-MS (positive mode) m/z: 680 M$^+$+1, 548 M$^+$-2,4,6-F$_3$C$_6$H$_2$; 499 547 M$^+$-Phbz. δ_H (300 MHz, CDCl$_3$): 8.10 (s, 1H; N=CH); 7.55 (m, 16H; 15H PPh$_3$ + 1H Phpz); 7.06 (m, 2H; Phbz); 6.78(m, 1H; Phbz); 6.69 (m, 3H; Phbz); 6.50 (d, 2H; *J*=7.5Hz, Phbz); 6.14 (dd, 2H, *J*=9.5 Hz, *J*=5.4 Hz C$_6$H$_2$F$_3$). δ_P (121.5 MHz, CDCl$_3$): 19.86. δ_F (282.3 MHz, CDCl$_3$): -84.50 (m, 2F), -120.30 (m, 1F). Spectroscopic characterization was completed by Accurate Mass LC/MS TOF, where the abundance of the experimental signals around the parent ion is consistent with the natural isotopic abundances as shown in Figure 1. As can be seen, small differences between calculated and experimental mass were found, with a relative error in mass of < 5ppm.



m/z	Abund (% largest)
676.0968	2.73
677.1001	1.11
678.0952	30.07
679.0966	72.01
680.096	100
681.0987	34.95
682.0956	77.46
683.0985	29.68
684.0972	37.2
685.0999	13.52
686.1031	2.6
687.1063	0.33
688.1096	0.03
689.1129	0
690.1162	0
691.1195	0

Figure 1. Comparison between experimental (up) and calculated (below) isotopic pattern for the peak at m/z: 680 corresponding to M^{+}+1 of (2).

Single crystals able to X-ray diffraction analysis were grown from slow diffusion of CH_2Cl_2/Hexane solution. The structure is displayed in Figure 2; bond lenghts and angles are presented in Table 2. The structure around the palladium atom can be described as nearly planar, and its deviation from the planar coordination has been quantified by measures of improper torsion angles: w_1 = 0.00 and w_2 = -2.88º, which means C(1)-N(1)-Pd(1)-C(14) defining a plane and P(1) slightly above that plane.[4] We have developed methods for the conformational classification of rings.[5] From this perspective the Pd(1)-C(1)-C(6)-C(7)-N(1) ring displays HC = 0.5140 and E = 0.4860 for σ = 10. Following the classification of Dance and Scudder for PPh_3 based on measures of torsion angles M-P-C_{ipso}-C, the conformation of PdP(phenyl)$_3$ group is described as a *no rotor* for this complex.[6]

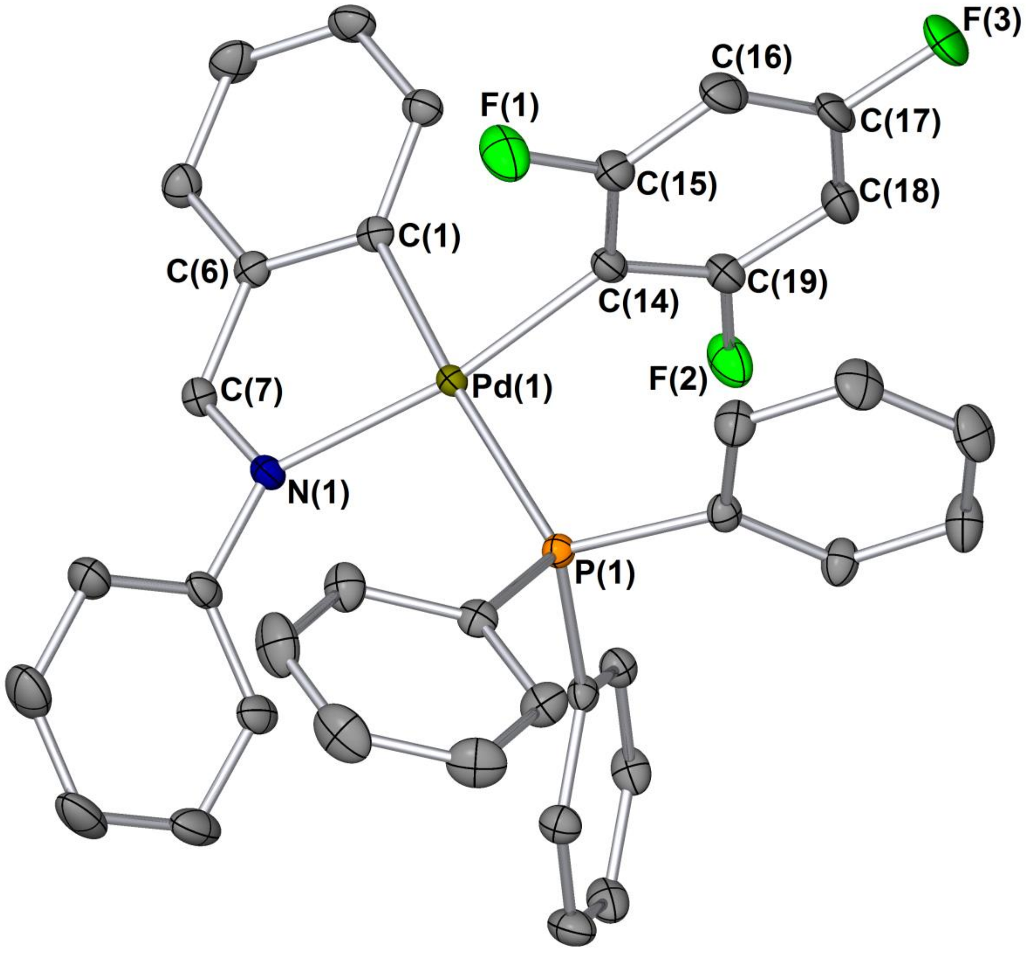


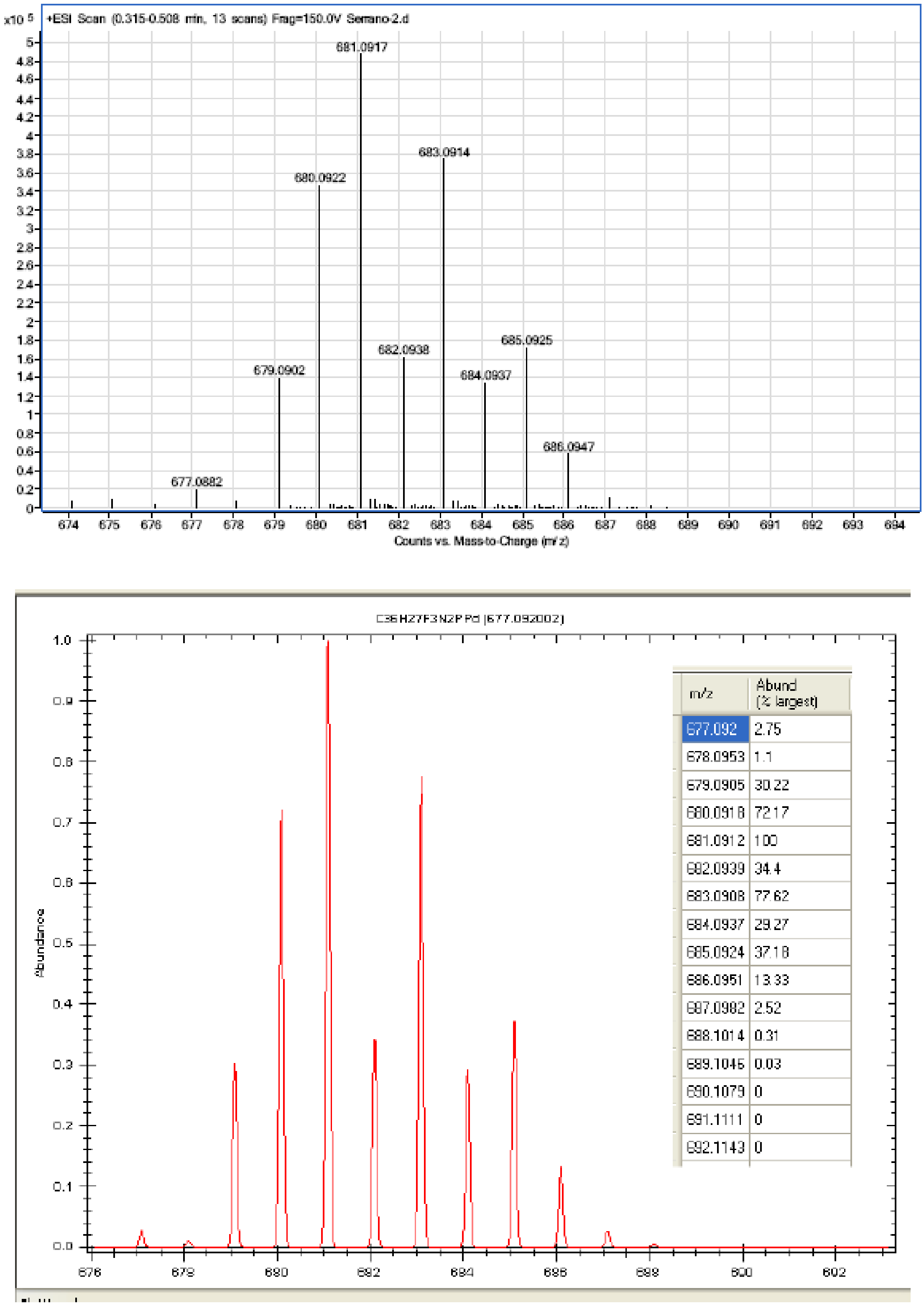
Figure 2. X-ray structure of [Pd(phbz)(2,4,6-$F_3C_6H_2$)(PPh_3)]

3.3 Representative procedure for the synthesis of [Pd(phazb)(2,4,6-$F_3C_6H_2$)(PPh_3)] (3)

To a stirred orange solution in tetrahydrofurane (6 mL) of [Pd(Phazb)(AcO)(PPh$_3$)] (0.07 g; 0.115 mmol) was added excess of 2,4,6-trifluorophenylboronic acid (0.121 g; 0.691 mmol; 1:6 ratio). The solution was allowed to stir for 30 minutes and then it was concentrated until *ca.* one fifth of the initial volume. Slow addition of hexane caused the precipitation of an orange solid that was filtered off, washed with hexane and air dried.

(3) [Pd(Phazb)(2,4,6-F$_3$C$_6$H$_2$)(PPh$_3$)] (0.053 g, 68%). Anal. Found: C, 63.7; H, 4.0; N, 4.2. Calc. for $C_{36}H_{26}F_3N_2PPd$: C, 63.5; H, 3.8; N, 4.1%. IR (cm^{-1}): ν(2,4,6-F$_3$C$_6$H$_2$) 1591s, 1402s, 1108s, 994s; ν(Phazb) 1573m, ν(PPh$_3$) 524, 512. ESI-MS (positive mode) m/z: 681 M$^+$+1, 549 M$^+$-2,4,6-F$_3$C$_6$H$_2$; 499 547 M$^+$-Phbz. δ_H (300 MHz, CDCl$_3$): 8.19 (d, 1H; Phazb, *J*=6.3Hz); 7.50 (m, 16H; 15H PPh$_3$ + 1H Phazb); 6.98 (m, 3H; Phazb); 6.79 (m, 2H; Phazb); 6.66 (m, 1H; Phazb); 6.15 (m, 2H, C$_6$H$_2$F$_3$). δ_P (121.5 MHz, CDCl$_3$): 19.85. δ_F (282.3 MHz, CDCl$_3$): -84.52 (m, 2F), -119.53 (m, 1F).

Spectroscopic characterization was completed by Accurate Mass LC/MS TOF, where the abundance of the experimental signals around the parent ion is consistent with the natural isotopic abundances as shown in Figure 3. As can be seen, small differences between calculated and experimental mass were found, with a relative error in mass of < 5ppm.



m/z	Abund (% largest)
677.092	2.75
678.0953	1.1
679.0905	30.22
680.0918	72.17
681.0912	100
682.0939	34.4
683.0908	77.62
684.0937	29.27
685.0924	37.18
686.0951	13.33
687.0982	2.52
688.1014	0.31
689.1046	0.03
690.1079	0
691.1111	0
692.1143	0

Figure 3. Comparison between experimental (up) and calculated (below) isotopic pattern for the peak at m/z: 681 corresponding to M^{+}+1 of (3).

Single crystals able to X-ray diffraction analysis were grown from slow diffusion of CH_2Cl_2/Hexane solution. The structure is displayed in Figure 4; bond lengths and angles are presented in Table 2. The coordination geometry around the palladium atom may be described as planar and their deviation from the planar coordination has been quantified by measures of improper torsion angles, with values of w_1 = -6.56º and w_2 = -2.54º.[4] These values correspond to a tetrahedral distortion from the ideal square-plane. We have developed methods for the conformational classification of rings.[5] From this perspective the Pd(1)-C(1)-C(6)-N(2)-N(1) ring displays HC = 0.5151 and E = 0.4849 for σ = 10. Following the classification of Dance and Scudder for PPh_3 based on measures of torsion angles M-P-C_{ipso}-C, the conformation of PdP(phenyl)$_3$ group is described as *no rotor* for this complex.[6]

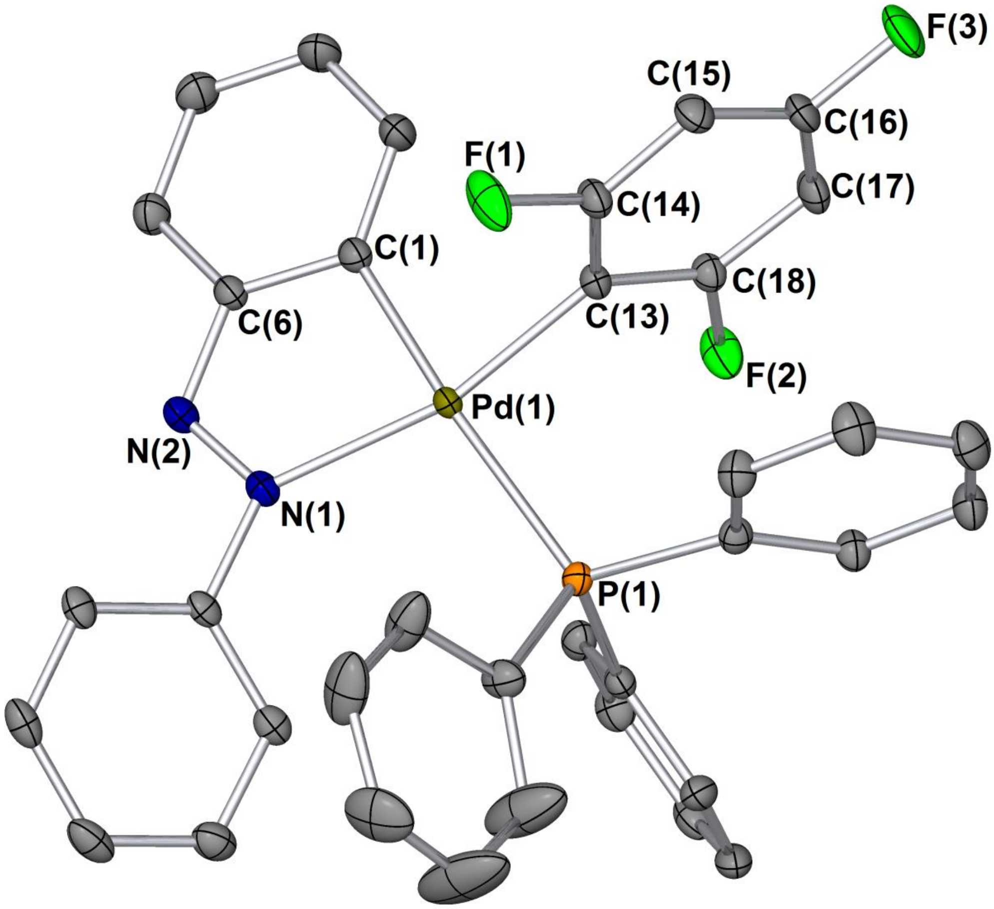


Figure 4. X-ray structure of [Pd(phazb)(2,4,6-$F_3C_6H_2$)(PPh_3)]

3.4 Representative data for [$Pd_2(2,4,6\text{-}C_6F_3H_2)_2(PPh_3)_2(\mu\text{-}OH)(\mu\text{-}OAc)$] (4)

From reactions of [Pd(phbz)(AcO)(PPh_3)] with 2,4,6-trifluorophenylboronic acid left for prolonged periods (*ca.* 16-24 h), other minor phosphorus signals were also observed in the $^{31}P/^{19}F$ NMR spectra of the crude reaction mixture. In one particular case, we observed the formation of a different set of crystals that turned out to be dimeric complex (4). Its NMR data are shown below. δ_H (300 MHz, $CDCl_3$): 7.80 (d, 12H; PPh_3, *J*=6.3Hz); 7.53 (m, 6H; PPh_3); 7.30 (m, 12H; PPh_3); 0.79 (s, 3H; CH_3COO); -1.52 (s, 1H, OH). δ_P (121.5 MHz, $CDCl_3$): 24.26. δ_F (282.3 MHz, $CDCl_3$): -87.30 (m, 2F), -119.26 (m, 1F).

Single crystals able to X-ray diffraction analysis were grown from slow diffusion of CH_2Cl_2/Hexane solution. The structure is displayed in Figure 5; bond lengths and angles are presented in Table 2. The coordination geometry around the Pd atoms may be described as planar and their deviation from the planar coordination has been quantified by measures of improper torsion angles, with values of w_1 = 1.28º and w_2 = -1.36º for Pd(1) and w_1 = 2.46º and w_2 = -2.84º for Pd(2). These values correspond respectively to a pyramidal square and tetrahedral distortion from the ideal square-plane.[4] We have developed methods for the conformational classification of rings.[5] From this perspective the Pd(1)-O(1)-Pd(2)-O(3)-C(25)-O(2) ring displays a *screw-boat* conformation distorted by 15º (SB = 0.9728; E = 0.0247; HC = 0.0025) for σ = 10. Following the classification of Dance and Scudder for PPh_3 based on measures of torsion angles M-P-C_{ipso}-C, the conformation of PdP$(\text{phenyl})_3$ groups are described as a *good rotor* for this complex.[6]

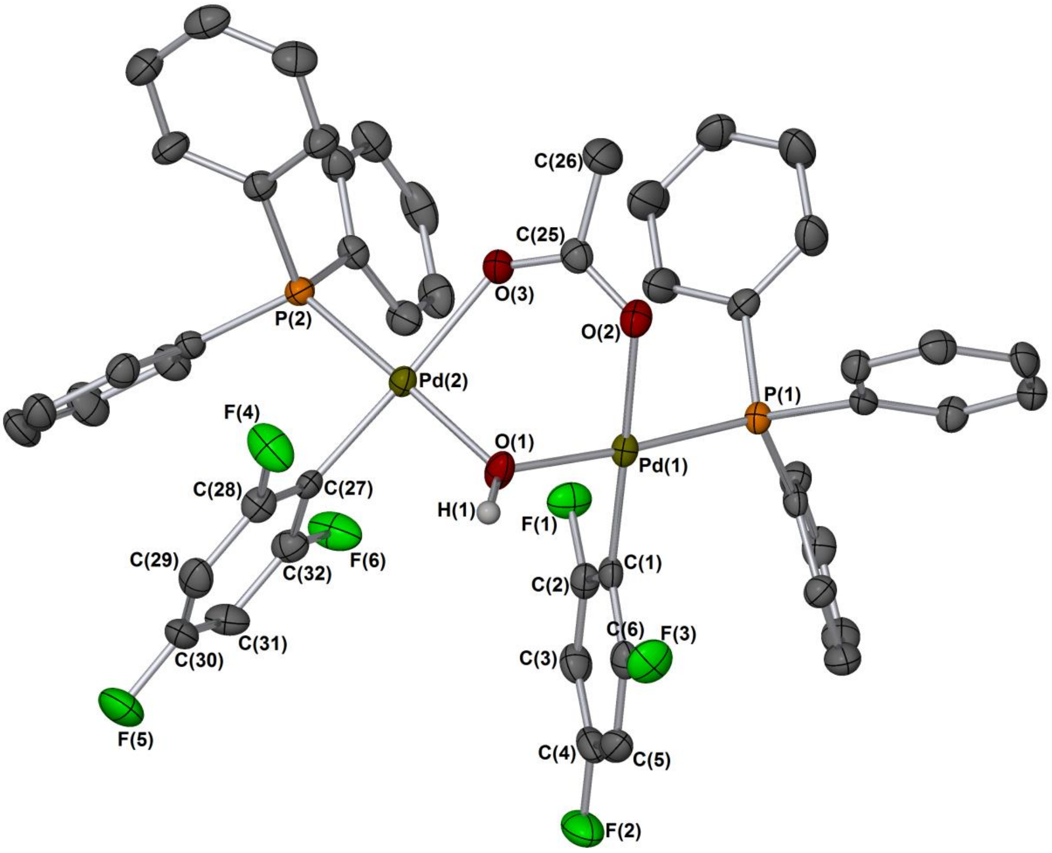


Figure 5. X-ray structure of (4) [$Pd_2(2,4,6\text{-}C_6F_3H_2)_2(PPh_3)_2(\mu\text{-}OH)(\mu\text{-}OAc)$]

3.5 Crystal structure of *trans*-[$PdCl(2,4,6\text{-}F_3C_6H_2)(PPh_3)$] (5)

In three separate instances involving the crystallisation of [$Pd(phbz)(2,4,6\text{-}F_3C_6H_2)(PPh_3)$] or [$Pd(phazb)(2,4,6\text{-}F_3C_6H_2)(PPh_3)$] from CH_2Cl_2, crystals of *trans*-[$PdCl(2,4,6\text{-}F_3C_6H_2)(PPh_3)$] were formed, the structure of which was confirmed by single crystal X-ray diffraction (Figure 6). This is adequately explained by adventitious HCl promoting the decomposition of [$Pd(phbz)(2,4,6\text{-}F_3C_6H_2)(PPh_3)$].

Bond lengths and angles are presented in Table 2. The coordination geometry around the palladium atom may be described as planar and their deviation from the planar coordination has been quantified by measures of improper torsion angles, with values of $w_1 = 1.09^\circ$ and $w_2 = 0.21^\circ$. These values correspond to a tetrahedral distortion from the ideal square-plane.[4] Following the classification of Dance and Scudder for PPh$_3$ based on measures of torsion angles M-P-C$_{ipso}$-C, the conformation of PdP(phenyl)$_3$ groups are described as *no rotor* for P(1) and *good rotor* for P(2) in this complex.[6]

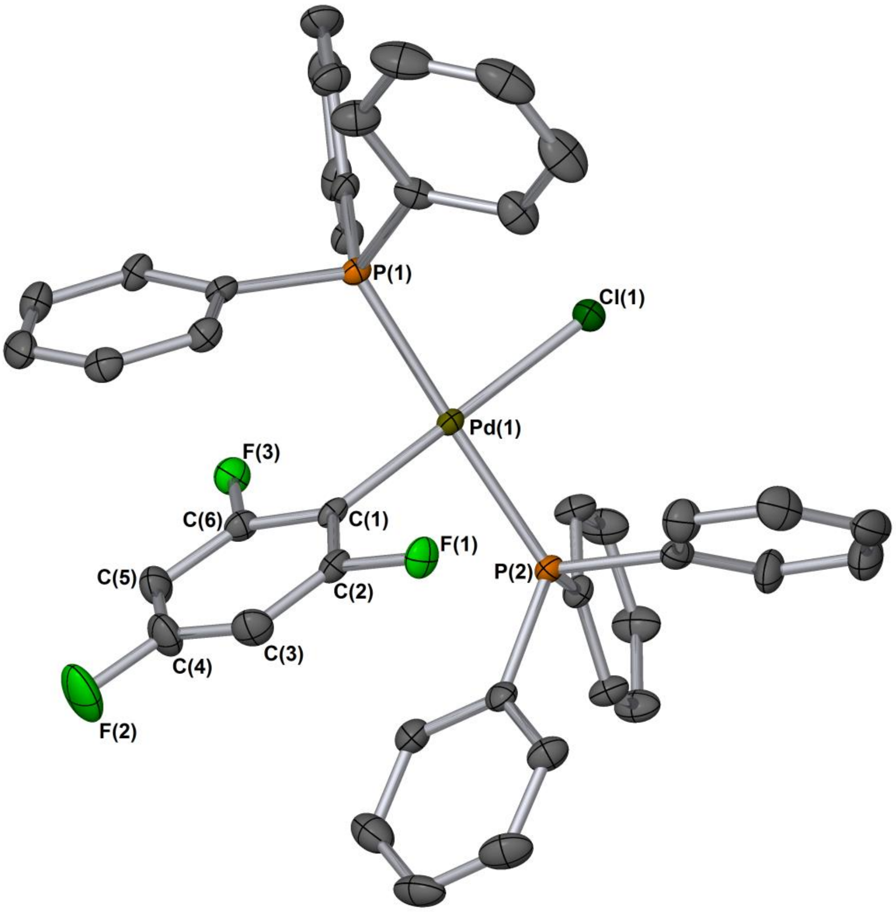


Figure 4. X-ray structure of *trans*-[PdCl(2,4,6-$F_3C_6H_2$)(PPh_3)] (5)

4.0 Collated X-ray diffraction data (including CCDC numbers)

Table 1 Crystal data and structure refinement for complexes **2**, **3**, **4** and **5**.

Compound	**2**	**3**	**4**	**5**
CCDC number	CCDC 1005721	CCDC 1005722	CCDC 1005723	CCDC 1005724
Empirical formula	$C_{37}H_{27}F_3NPPd$	$C_{36}H_{26}F_3N_2PPd$	$C_{50}H_{38}F_6O_3P_2Pd_2$	$C_{42}H_{32}ClF_3P_2Pd$
M	679.97	680.96	1075.54	797.47
T/K	100(2)	100(2)	100(2)	100(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic	orthorhombic
Space group	P21/n	P-1	P-1	Pbca
Unit cell dimensions				
a/Å	18.5049(9)	9.9041(6)	11.9714(5)	12.1168(9)
b/Å	8.9306(4)	12.3289(7)	12.3041(5)	23.2879(19)
c/Å	19.6878(10)	13.1446(8)	16.0441(7)	24.9924(19)
α/º	90	92.202(2)	67.9750(10)	90
β/º	111.881(2)	110.621(2)	88.8630(10)	90
γ/º	90	102.448(2)	86.9690(10)	90
V/Å^3	3019.2(3)	1455.37(15)	2187.72(16)	7052.2(9)
Z	4	2	2	8
D_{calcd}/Mg m^{-3}	1.496	1.554	1.633	1.502
μ/mm^{-1}	0.714	0.741	0.964	0.739
F(000)	1376	688	1076	3232
θ range for data collection (º)	2.23 to 30.58º	2.23 to 30.63º	1.37 to 28.23º	2.06 to 30.59º
Reflections collected	77364	48365	25529	121306
Independent reflections	9264	8958	9820	10820
Data/parameters/restrains	9264/0/388	8958/0/388	9820/0/572	10820/0/442
Goodness-of-fit on F^2	1.014	1.011	1.122	1.086
Final R indices [I > 2sigma(I)]	$R_1 = 0.0245$; $\omega R_2 = 0.0562$	$R_1 = 0.0366$; $\omega R_2 = 0.0952$	$R_1 = 0.0465$; $\omega R_2 = 0.1053$	$R_1 = 0.0582$; $\omega R_2 = 0.1406$
R indices (all data)	$R_1 = 0.0329$ $\omega R_2 = 0.0593$	$R_1 = 0.0409$ $\omega R_2 = 0.0982$	$R_1 = 0.0577$ $\omega R_2 = 0.1137$	$R_1 = 0.0862$; $\omega R_2 = 0.1533$
Max/min $\Delta\rho/e$Å^{-3}	0.457 and –0.412	3.451 and –1.271	1.209 and –0.585	1.576 and –1.285

Table 2. Selected bond lengths (Å) and angles (º) of complexes **2**, **3, 4** and **5**.

	2	**3**	**4**		**5**
			Pd1	Pd2	
Pd1-C1	2.0377(14)	2.020(2)	1.996(4)	1.984(4)	2.003(4)
Pd1-C14*	1.9945(13)	2.005(2)			
Pd1-N1	2.1534(11)	2.1427(17)			
Pd1-P1	2.3756(4)	2.3746(6)	2.2303(10)	2.2417(10)	2.3215(10)
Pd1-O1			2.058(3)	2.072(3)	
Pd1-O2			2.087(3)	2.124(3)	
Pd1-P2					2.3083(10)
Pd1-Cl1					2.3702(10)
C1-Pd1-C14*	88.49(6)	89.38(8)			
C1-Pd1-N1**	80.40(5)	78.02(8)			
C1-Pd1-P1	175.05(4)	170.65(6)	92.40(10)	90.99(10)	91.12(11)
C14*-Pd1-N1	168.86(5)	165.92(8)			
C14*-Pd1-P1	88.55(4)	88.78(6)			
N1-Pd1-P1	102.58(3)	104.66(5)			
C1-Pd1-O1			91.10(14)	88.24(13)	
C1-Pd1-O2			178.02(13)	176.02(9)	
O1-Pd1-O2			88.55(12)	92.76(11)	
O1-Pd1-P1			176.06(9)	175.64(8)	
O2-Pd1-P1			87.88(8)	88.25(7)	
C1-Pd1-P2					90.23(11)
C1-Pd1-Cl1					179.66(12)
P1-Pd1-P2					177.96(4)
P1-Pd1-Cl1					88.99(4)
P2-Pd1-Cl1					89.67(4)

*C13 in **3**

5.0 References

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