Supporting information

Enthalpy of Ligand Substitution in *cis* Organopalladium Complexes with Monodentate Ligands

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Table SI1. Experimental values of heat released in substitution experiments in the following reaction:

(a) *cis*-[$PdRf_2(solv)_2$] + 2L(soln) $\xrightarrow[273.1\ K]{THF}$ *cis*-[$PdRf_2L_2$] + 2solv

Ligand	$-\Delta H_r$ (kJ·mol^{-1})	Media (kJ·mol^{-1}) (standard deviation)
$SbPh_3$	57.60 58.95 63.43	59.99 (3.1)
$AsPh_3$	71.15 69.73 73.81	71.57 (2.1)
$AsMePh_2$	94.34 98.25 93.83	95.47 (2.4)
PPh_3	108.09 113.41 106.07	109.19 (3.8)
$PCyPh_2$	129.49 129.36 119.65	129.36 (5.6)
$PMePh_2$	154.80 157.77 165.99	159.52 (5.8)
PMe_3	187.36 184.83 188.17	186.79 (1.7)
dppf	143.88 142.20 142.53	142.87 (0.9)
dppe	154.13 154.60 151.80	153.51 (1.5)

Table SI2. Experimental values of heat released in substitution experiments in the following reaction:

(b) *cis*-[$PdRf_2(OH_2)_2$] + 2L(soln) $\xrightarrow[273.1\ K]{THF}$ *cis*-[$PdRf_2L_2$] + 2 OH_2

PPh_3	96.02 90.90 92.62	93 (3)

Table SI3. Experimental data for the calculation of the first and second substitution enthalpies in substitution experiments in the following reaction:

cis-[$PdRf_2(solv)_2$] + L(soln) $\xrightarrow[273.1\ K]{THF}$ *cis*-[$PdRf_2Lsolv$] + *cis*-[$PdRf_2L_2$] + solv.

To a solution of *cis*- [$PdRf_2(THF)_2$] (29.67 µmol) in THF (2 mL) was added the ligand dissolved in 2 mL of THF.

Ligand added (mmol)	Q_i (J)	n_{1i} (µmol)	n_{2i} (µmol)
PPh_3 (29.74)	1.709	29.67	0.07
PPh_3 (36.98)	2.023	29.67	7.31
PPh_3 (44.61)	2.507	29.67	14.94
PPh_3 (297)	3.240	29.67	29.67
$PCyPh_2$ (35.03)	2.499	29.67	5.36
$PCyPh_2$ (44.72)	2.993	29.67	15.05
$PCyPh_2$ (55.15)	3.483	29.67	25.48
$PCyPh_2$ (300)	3.743	29.67	29.67

Table SI4. ^{19}F NMR chemical shift (ppm) of the complexes of total and partial substitution observed in THF solution at T = 271.3 K.

L = PPh_3			L = $PCyPh_2$	
Complex	F_{orto}	F_{para}	F_{orto}	F_{para}
***cis*-[$PdRf_2L(THF)$]**	-88.6, -90.1	-119.0, -121.3	-87.4, -89.8	-119.1, -120.8
***cis*-[$PdRf_2L(OH_2)$]**	-88.5, -89.2	-120.1, -122.2	-89.4, -90.9	-120.2, -121.9
***cis*-[$PdRf_2L_2$]**	-89.1	-120.9	-87.6	-120.3

Table SI5. Crystal data and structure refinement for *cis*-[$PdRf_2(PMePh_2)_2$] (CCDC 732755).

Empirical formula	$C_{38}H_{26}Cl_4F_6P_2Pd$	
Formula weight	906.73	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.330(3) Å	α = 70.502(5)°
	b = 12.578(4) Å	β = 85.855(5)°
	c = 15.373(5) Å	γ = 64.014(5)°
Volume	1849.4(9) $Å^3$	
Z	2	
Density (calculated)	1.628 Mg/m^3	
Absorption coefficient	0.936 mm^{-1}	
F(000)	904	
Crystal size	0.328 x 0.111 x 0.060 mm^3	
Theta range for data collection	1.91 to 23.30°	
Index ranges	-12<=h<=12, -9<=k<=13, -17<=l<=17	
Reflections collected	8767	
Independent reflections	5293 [R(int) = 0.0186]	
Completeness to theta = 23.30°	99.1 %	
Absorption correction	SADABS	
Max. and min. transmission	1 and 0.808042	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5293 / 0 / 462	
Goodness-of-fit on F^2	1.028	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0251, wR2 = 0.0647	
R indices (all data)	R1 = 0.0285, wR2 = 0.0676	
Largest diff. peak and hole	0.321 and -0.318 e.$Å^{-3}$	

Table SI6. Crystal data and structure refinement for [PdRf$_2$(dppe)] (CCDC 732756).

Empirical formula	$C_{38}H_{24}Cl_4F_6P_2Pd$	
Formula weight	904.71	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.1928(11) Å	α = 90°
	b = 19.654(2) Å	β = 93.943(3)°
	c = 18.569(2) Å	g = 90°
Volume	3711.0(7) Å^3	
Z	4	
Density (calculated)	1.619 Mg/m^3	
Absorption coefficient	0.933 mm^{-1}	
F(000)	1800	
Crystal size	0.129 x 0.07 x 0.036 mm^3	
Theta range for data collection	1.51 to 23.27°	
Index ranges	-11<=h<=10, -17<=k<=21, -18<=l<=20	
Reflections collected	17548	
Independent reflections	5347 [R(int) = 0.1449]	
Completeness to theta = 23.27°	99.9 %	
Absorption correction	SADABS	
Max. and min. transmission	1 and 0.541294	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5347 / 0 / 460	
Goodness-of-fit on F^2	0.963	
Final R indices [I > 2σ(I)]	R1 = 0.0544, wR2 = 0.0876	
R indices (all data)	R1 = 0.1559, wR2 = 0.1193	
Largest diff. peak and hole	0.467 and -0.414 e.Å^{-3}	

Table SI7. Crystal data and structure refinement for [PdRf$_2$(dppf)] (CCDC 732757).

Empirical formula	C46 H28 Cl4 F6 Fe P2 Pd	
Formula weight	1060.67	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 16.707(4) Å	α= 90∞.
	b = 14.682(4) Å	β= 113.402(4)∞.
	c = 18.509(5) Å	γ = 90∞.
Volume	4166.7(18) Å^3	
Z	4	
Density (calculated)	1.691 Mg/m^3	
Absorption coefficient	1.175 mm^{-1}	
F(000)	2112	
Crystal size	0.26 x 0.22 x 0.14 mm^3	
Theta range for data collection	1.83 to 28.33°.	
Index ranges	-22<=h<=22, -19<=k<=19, -24<=l<=24	
Reflections collected	41333	
Independent reflections	10379 [R(int) = 0.0310]	
Completeness to theta = 28.33∞	99.8 %	
Absorption correction	SADABS	
Max. and min. transmission	1 and 0.821621	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10379 / 0 / 541	
Goodness-of-fit on F^2	1.091	
Final R indices [I>2sigma(I)]	R1 = 0.0303, wR2 = 0.0714	
R indices (all data)	R1 = 0.0498, wR2 = 0.0848	
Largest diff. peak and hole	0.658 and -0.343 e.Å^{-3}	