

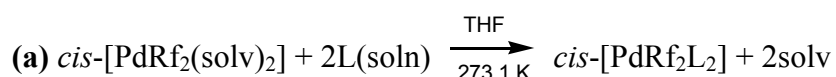
Supporting information

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

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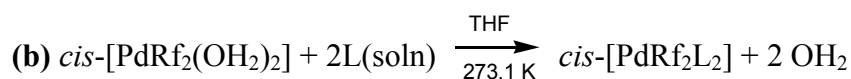
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Table SI1. Experimental values of heat released in substitution experiments in the following reaction:



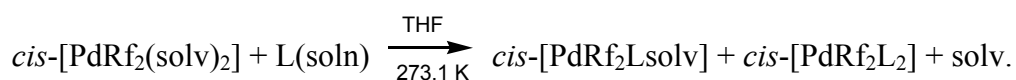
Ligand	$-\Delta H_r$ (kJ·mol ⁻¹)	Media (kJ·mol ⁻¹) (standard deviation)
SbPh ₃	57.60	59.99 (3.1)
	58.95	
	63.43	
AsPh ₃	71.15	71.57 (2.1)
	69.73	
	73.81	
AsMePh ₂	94.34	95.47 (2.4)
	98.25	
	93.83	
PPh ₃	108.09	109.19 (3.8)
	113.41	
	106.07	
PCyPh ₂	129.49	129.36 (5.6)
	129.36	
	119.65	
PMePh ₂	154.80	159.52 (5.8)
	157.77	
	165.99	
PMe ₃	187.36	186.79 (1.7)
	184.83	
	188.17	
dppf	143.88	142.87 (0.9)
	142.20	
	142.53	
dppe	154.13	153.51 (1.5)
	154.60	
	151.80	

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



PPh₃	96.02	93 (3)
	90.90	
	92.62	

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



To a solution of *cis*- [PdRf₂(THF)₂] (29.67 μmol) in THF (2 mL) was added the ligand dissolved in 2 mL of THF.

Ligand added (mmol)	<i>Q_i</i> (J)	<i>n_{1i}</i> (μmol)	<i>n_{2i}</i> (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 $T = 271.3\text{ K}$.

L = PPh₃			L = PCyPh₂	
Complex	F_{orto}	F_{para}	F_{orto}	F_{para}
<i>cis</i>-[PdRf₂L(THF)]	-88.6,	-119.0,	-87.4,	-119.1,
	-90.1	-121.3	-89.8	-120.8
<i>cis</i>-[PdRf₂L(OH₂)]	-88.5,	-120.1,	-89.4,	-120.2,
	-89.2	-122.2	-90.9	-121.9
<i>cis</i>-[PdRf₂L₂]	-89.1	-120.9	-87.6	-120.3

Table S15. Crystal data and structure refinement for *cis*-[PdRf₂(PMePh₂)₂] (CCDC 732755).

Empirical formula	C ₃₈ H ₂₆ Cl ₄ F ₆ P ₂ Pd	
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 > 2σ(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 [PdRf₂(dppe)] (CCDC 732756).

Empirical formula	C ₃₈ H ₂₄ Cl ₄ F ₆ P ₂ Pd	
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	γ = 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 [PdRf₂(dppf)] (CCDC 732757).

Empirical formula	C ₄₆ H ₂₈ Cl ₄ F ₆ Fe P ₂ 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 > 2σ(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	