Table S1.– Crystal data and structure refinement for **cClBzl**.

Formula	C30 H28 Cl5 N Pt S
Formula Weight	806.93
Crystal System	Monoclinic
Space group	P21 (No. 4)
a, b, c [Angstrom]	10.8180(10) 12.2240(7) 12.162(2)
alpha, beta, gamma [deg]	90 110.436(10) 90
V [Ang**3]	1507.1(3)
Z	2
D(calc) [g/cm**3]	1.778
Mu(MoKa) [/mm]	5.189
F(000)	788
Crystal Size [mm]	0.30 x 0.50 x 0.50
Data Collection	
Temperature (K)	296
Radiation [Angstrom]	MoKa 0.71073
Theta Min-Max [Deg]	1.8, 25.0
Dataset	0: 12 ; 0: 14 ; -14: 13
Tot., Uniq. Data, R(int)	2950, 2796, 0.020
Observed data [I > 2.0 sigma(I)]	2657
Refinement	
Nref, Npar	2796, 343
R, wR, S	0.0185, 0.0471, 1.11
w = 1/[\s^2^(Fo^2^)+(0.0300P)^2^+0.5090P] where P=(Fo^2^+2Fc^2^)/3	
Max. and Av. Shift/Error	0.00, 0.00
Flack x	0.00(1)
Min. and Max. Resd. Dens. [e/Ang^3]	-0.76, 0.74

Table S2.- Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms for **cClBzl**.

Atom	x	y	z	U(eq) [Ang^2]
Pt1	0.97386(2)	0.77743(2)	0.66240(1)	0.0343(1)
Cl1	1.18469(16)	0.85744(16)	0.76900(16)	0.0576(5)
Cl2	0.80489(18)	0.60368(18)	0.40345(16)	0.0671(7)
Cl3	0.5125(2)	0.5592(2)	0.32776(19)	0.0831(8)
Cl4	0.34825(18)	0.6345(2)	0.4764(2)	0.0843(8)
Cl5	0.47687(16)	0.7693(3)	0.69933(17)	0.0635(7)
S1	1.06384(15)	0.60766(13)	0.77327(15)	0.0467(5)
N1	0.8933(5)	0.8267(4)	0.7936(4)	0.0362(14)
C1	1.0484(7)	0.7452(6)	0.5296(6)	0.058(3)
C2	0.9076(7)	0.9236(5)	0.5782(6)	0.054(2)
C3	0.7848(5)	0.7233(4)	0.5872(4)	0.0317(17)
C4	0.7208(6)	0.6620(5)	0.4860(5)	0.0411(17)
C5	0.5864(6)	0.6366(5)	0.4509(5)	0.0467(17)
C6	0.5112(6)	0.6705(5)	0.5161(6)	0.046(2)
C7	0.5715(6)	0.7299(5)	0.6173(5)	0.0406(17)
C8	0.7042(5)	0.7571(4)	0.6521(5)	0.036(2)
C9	0.7697(5)	0.8142(4)	0.7600(5)	0.0378(17)
C10	0.9623(6)	0.8821(5)	0.9070(5)	0.0437(17)
C19	1.3641(8)	0.5092(8)	0.9468(7)	0.067(3)
C20	1.4436(9)	0.4313(9)	1.0195(7)	0.080(3)
C21	1.4492(9)	0.3294(8)	0.9782(8)	0.078(3)
C22	1.3752(8)	0.3031(6)	0.8682(8)	0.072(3)
C23	1.2957(7)	0.3790(7)	0.7932(7)	0.064(3)
C24	0.9631(7)	0.4893(6)	0.7160(7)	0.055(2)
C25	0.8386(6)	0.4908(5)	0.7450(6)	0.051(2)
C26	0.7269(9)	0.4390(8)	0.6616(8)	0.078(3)
C27	0.6095(9)	0.4327(9)	0.6861(12)	0.095(4)
C28	0.6093(10)	0.4821(10)	0.7887(13)	0.103(5)
C29	0.7131(11)	0.5314(9)	0.8662(12)	0.099(5)
C30	0.8283(9)	0.5333(7)	0.8432(8)	0.068(3)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor

Table S3.- Hydrogen Atom Positions and Isotropic Displacement Parameters for **cClBzl**.

Atom	x	y	z	U(iso) [Ang^2]
H1A	1.13900	0.76770	0.55430	0.0870
H1B	0.99820	0.78490	0.46030	0.0870
H1C	1.04230	0.66830	0.51290	0.0870
H2A	0.97960	0.97440	0.59640	0.0810
H2B	0.84000	0.95290	0.60400	0.0810
H2C	0.87230	0.91170	0.49500	0.0810
H9	0.72190	0.84150	0.80440	0.0450
H10A	0.90270	0.93390	0.92300	0.0530
H10B	1.03710	0.92260	0.90170	0.0530
H12	0.83660	0.78290	1.03250	0.0780
H13	0.91340	0.66050	1.18540	0.1090
H14	1.12520	0.60680	1.25060	0.1160
H15	1.27250	0.67060	1.16710	0.1090
H16	1.19960	0.79360	1.01100	0.0810
H17A	1.18900	0.54410	0.66750	0.0730
H17B	1.26560	0.63660	0.75390	0.0730
H19	1.36000	0.57890	0.97590	0.0800
H20	1.49330	0.44880	1.09680	0.0960
H21	1.50480	0.27730	1.02660	0.0940
H22	1.37750	0.23200	0.84190	0.0870
H23	1.24540	0.35950	0.71670	0.0770
H24A	0.94010	0.48700	0.63150	0.0660
H24B	1.01300	0.42380	0.74860	0.0660
H26	0.73170	0.41010	0.59250	0.0930
H27	0.53530	0.39710	0.63580	0.1140
H28	0.53120	0.48070	0.80450	0.1240
H29	0.70760	0.56330	0.93370	0.1190
H30	0.90240	0.56540	0.89780	0.0820

The Temperature Factor has the Form of Exp(-T) Where T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms

Table S4.- (An)isotropic Displacement Parameters for **cClBzl**.

Atom	U(1,1) or U	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
Pt1	0.0312(1)	0.0367(1)	0.0365(1)	0.0057(2)	0.0137(1)	0.0013(2)
Cl1	0.0405(8)	0.0645(10)	0.0663(10)	0.0028(8)	0.0168(7)	-0.0147(8)
Cl2	0.0612(11)	0.0865(14)	0.0557(10)	-0.0248(10)	0.0232(8)	0.0129(10)
Cl3	0.0678(13)	0.0929(17)	0.0729(13)	-0.0443(12)	0.0050(10)	-0.0086(11)
Cl4	0.0399(9)	0.1131(18)	0.0936(15)	-0.0315(14)	0.0152(10)	-0.0240(11)
Cl5	0.0472(7)	0.0777(16)	0.0777(9)	-0.0128(16)	0.0372(7)	-0.0058(12)
S1	0.0366(8)	0.0407(8)	0.0653(10)	0.0094(7)	0.0210(7)	0.0067(6)
N1	0.042(3)	0.032(2)	0.033(2)	0.0008(19)	0.011(2)	0.000(2)
C1	0.050(4)	0.079(6)	0.054(4)	0.004(3)	0.031(3)	0.003(3)
C2	0.057(4)	0.042(4)	0.063(4)	0.013(3)	0.022(3)	0.001(3)
C3	0.030(3)	0.032(3)	0.031(3)	0.003(2)	0.008(2)	0.008(2)
C4	0.049(3)	0.038(3)	0.035(3)	0.000(2)	0.013(3)	0.011(3)
C5	0.046(3)	0.040(3)	0.042(3)	-0.005(3)	0.000(3)	0.001(3)
C6	0.029(3)	0.050(4)	0.053(4)	-0.006(3)	0.008(3)	-0.003(3)
C7	0.035(3)	0.042(3)	0.049(3)	0.003(3)	0.020(3)	0.003(3)
C8	0.029(2)	0.038(5)	0.039(3)	0.002(2)	0.010(2)	0.004(2)
C9	0.039(3)	0.039(3)	0.039(3)	-0.002(2)	0.018(2)	0.002(2)
C10	0.045(3)	0.040(3)	0.040(3)	-0.007(3)	0.007(3)	-0.001(3)
C11	0.052(3)	0.030(5)	0.033(2)	-0.009(2)	0.005(2)	-0.002(3)
C12	0.079(5)	0.065(7)	0.049(3)	-0.006(4)	0.019(3)	-0.009(4)
C13	0.127(10)	0.084(7)	0.055(5)	0.005(5)	0.022(6)	-0.038(7)
C14	0.157(11)	0.055(5)	0.048(5)	0.006(4)	-0.003(6)	-0.009(6)
C15	0.099(8)	0.076(6)	0.063(5)	-0.006(5)	-0.014(5)	0.025(6)
C16	0.065(4)	0.071(7)	0.049(3)	0.002(5)	-0.005(3)	0.009(5)
C17	0.042(4)	0.066(5)	0.078(5)	0.024(4)	0.027(4)	0.010(3)
C18	0.033(3)	0.063(4)	0.064(4)	0.021(4)	0.019(3)	0.011(3)
C19	0.064(5)	0.074(5)	0.065(5)	-0.006(4)	0.025(4)	0.011(4)
C20	0.070(5)	0.117(8)	0.045(4)	0.008(5)	0.011(4)	0.023(5)
C21	0.080(6)	0.090(6)	0.070(5)	0.033(5)	0.032(5)	0.038(5)
C22	0.082(5)	0.051(7)	0.092(5)	0.009(4)	0.041(4)	0.015(4)
C23	0.052(4)	0.078(6)	0.062(4)	0.000(4)	0.019(3)	0.002(4)
C24	0.053(4)	0.046(4)	0.069(4)	0.005(3)	0.026(3)	0.006(3)
C25	0.037(3)	0.040(3)	0.078(5)	0.027(3)	0.024(3)	0.005(3)
C26	0.081(6)	0.068(5)	0.081(6)	0.019(5)	0.025(5)	0.006(5)
C27	0.051(5)	0.074(6)	0.148(10)	0.017(7)	0.018(6)	-0.015(4)
C28	0.060(6)	0.097(8)	0.168(12)	0.039(8)	0.060(7)	0.009(6)
C29	0.103(8)	0.084(7)	0.148(10)	0.023(7)	0.092(8)	0.004(6)
C30	0.076(5)	0.058(5)	0.083(5)	0.022(4)	0.044(5)	0.009(4)

The Temperature Factor has the Form of Exp(-T) Where T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms T = 2*(Pi**2)*Sumij(h(i)*h(j)*U(i,j)*Astar(i)*Astar(j)), for Anisotropic Atoms. Astar(i) are Reciprocal Axial Lengths and h(i) are the Reflection Indices.

Table S5 - Bond Distances (Angstrom) for **cClBz**.

Pt1	-Cl1	2.4030(19)	C17	-C18	1.518(11)
Pt1	-S1	2.4811(17)	C18	-C19	1.368(11)
Pt1	-N1	2.154(5)	C18	-C23	1.395(11)
Pt1	-C1	2.079(7)	C19	-C20	1.377(13)
Pt1	-C2	2.060(6)	C20	-C21	1.352(14)
Pt1	-C3	2.037(5)	C21	-C22	1.336(13)
Cl2	-C4	1.727(7)	C22	-C23	1.373(12)
Cl3	-C5	1.715(6)	C24	-C25	1.507(11)
Cl4	-C6	1.715(7)	C25	-C26	1.426(12)
Cl5	-C7	1.729(7)	C25	-C30	1.342(11)
S1	-C17	1.793(8)	C26	-C27	1.404(15)
S1	-C24	1.799(8)	C27	-C28	1.387(19)
N1	-C9	1.264(8)	C28	-C29	1.332(19)
N1	-C10	1.483(7)	C29	-C30	1.369(17)
C3	-C4	1.400(8)	C1	-H1A	0.9596
C3	-C8	1.426(8)	C1	-H1B	0.9598
C4	-C5	1.400(9)	C1	-H1C	0.9591
C5	-C6	1.383(9)	C2	-H2A	0.9596
C6	-C7	1.381(9)	C2	-H2B	0.9601
C7	-C8	1.388(9)	C2	-H2C	0.9597
C8	-C9	1.436(8)	C9	-H9	0.9302
C10	-C11	1.496(8)	C10	-H10A	0.9706
C11	-C12	1.385(11)	C10	-H10B	0.9698
C11	-C16	1.406(12)	C12	-H12	0.9295
C12	-C13	1.377(13)	C13	-H13	0.9300
C13	-C14	1.334(19)	C14	-H14	0.9300
C14	-C15	1.380(18)	C15	-H15	0.9307
C15	-C16	1.390(15)	C16	-H16	0.9303
C17	-H17A	0.9700	C24	-H24A	0.9697
C17	-H17B	0.9699	C24	-H24B	0.9696
C19	-H19	0.9296	C26	-H26	0.9296
C20	-H20	0.9304	C27	-H27	0.9301
C21	-H21	0.9309	C28	-H28	0.9297
C22	-H22	0.9294	C29	-H29	0.9293
C23	-H23	0.9301	C30	-H30	0.9305

Table S6.- Bond Angles (Degrees) for **cClBzl**.

Cl1	-Pt1	-S1	85.92(6)	Cl3	-C5	-C6	118.5(5)
Cl1	-Pt1	-N1	92.28(15)	C4	-C5	-C6	121.0(6)
Cl1	-Pt1	-C1	86.8(2)	Cl4	-C6	-C5	121.0(5)
Cl1	-Pt1	-C2	90.9(2)	Cl4	-C6	-C7	120.3(5)
Cl1	-Pt1	-C3	171.61(15)	C5	-C6	-C7	118.6(6)
S1	-Pt1	-N1	90.84(13)	Cl5	-C7	-C6	118.0(5)
S1	-Pt1	-C1	94.5(2)	Cl5	-C7	-C8	121.0(4)
S1	-Pt1	-C2	176.5(2)	C6	-C7	-C8	120.9(6)
S1	-Pt1	-C3	96.56(14)	C3	-C8	-C7	121.9(5)
N1	-Pt1	-C1	174.5(2)	C3	-C8	-C9	116.4(5)
N1	-Pt1	-C2	88.0(2)	C7	-C8	-C9	121.5(5)
N1	-Pt1	-C3	79.7(2)	N1	-C9	-C8	118.9(5)
C1	-Pt1	-C2	86.6(3)	N1	-C10	-C11	111.6(5)
C1	-Pt1	-C3	101.0(2)	C10	-C11	-C12	121.0(6)
C2	-Pt1	-C3	86.4(3)	C10	-C11	-C16	119.7(7)
Pt1	-S1	-C17	108.2(3)	C12	-C11	-C16	119.3(7)
Pt1	-S1	-C24	113.1(3)	C11	-C12	-C13	119.7(9)
C17	-S1	-C24	101.0(4)	C12	-C13	-C14	120.7(10)
Pt1	-N1	-C9	112.5(4)	C13	-C14	-C15	122.0(9)
Pt1	-N1	-C10	127.9(4)	C14	-C15	-C16	118.8(10)
C9	-N1	-C10	119.2(5)	C11	-C16	-C15	119.4(9)
Pt1	-C3	-C4	132.8(4)	S1	-C17	-C18	111.8(5)
Pt1	-C3	-C8	111.7(3)	C17	-C18	-C19	122.6(7)
C4	-C3	-C8	115.5(5)	C17	-C18	-C23	119.4(7)
Cl2	-C4	-C3	122.2(5)	C19	-C18	-C23	117.9(7)
Cl2	-C4	-C5	115.7(4)	C18	-C19	-C20	121.1(9)
C3	-C4	-C5	121.9(6)	C19	-C20	-C21	119.8(8)
Cl3	-C5	-C4	120.4(5)	C20	-C21	-C22	120.3(9)
C21	-C22	-C23	121.3(8)	C11	-C10	-H10B	109.31
C18	-C23	-C22	119.5(7)	H10A	-C10	-H10B	107.96
S1	-C24	-C25	111.7(5)	C11	-C12	-H12	120.05
C24	-C25	-C26	115.6(7)	C13	-C12	-H12	120.20
C24	-C25	-C30	124.9(7)	C12	-C13	-H13	119.60
C26	-C25	-C30	119.5(8)	C14	-C13	-H13	119.68
C25	-C26	-C27	118.5(9)	C13	-C14	-H14	119.02
C26	-C27	-C28	116.9(11)	C15	-C14	-H14	119.03
C27	-C28	-C29	124.6(12)	C14	-C15	-H15	120.55
C28	-C29	-C30	117.8(12)	C16	-C15	-H15	120.63
C25	-C30	-C29	122.6(9)	C11	-C16	-H16	120.33
Pt1	-C1	-H1A	109.47	C15	-C16	-H16	120.25
Pt1	-C1	-H1B	109.41	S1	-C17	-H17A	109.31
Pt1	-C1	-H1C	109.48	S1	-C17	-H17B	109.24
H1A	-C1	-H1B	109.44	C18	-C17	-H17A	109.19
H1A	-C1	-H1C	109.54	C18	-C17	-H17B	109.23
H1B	-C1	-H1C	109.49	H17A	-C17	-H17B	107.94
Pt1	-C2	-H2A	109.46	C18	-C19	-H19	119.50
Pt1	-C2	-H2B	109.49	C20	-C19	-H19	119.43
Pt1	-C2	-H2C	109.51	C19	-C20	-H20	120.04
H2A	-C2	-H2B	109.43	C21	-C20	-H20	120.14

H2A	-C2	-H2C	109.47	C20	-C21	-H21	119.88
H2B	-C2	-H2C	109.45	C22	-C21	-H21	119.82
N1	-C9	-H9	120.59	C21	-C22	-H22	119.39
C8	-C9	-H9	120.53	C23	-C22	-H22	119.28
N1	-C10	-H10A	109.30	C18	-C23	-H23	120.27
N1	-C10	-H10B	109.39	C22	-C23	-H23	120.23
C11	-C10	-H10A	109.23	S1	-C24	-H24A	109.28
S1	-C24	-H24B	109.29	C28	-C27	-H27	121.56
C25	-C24	-H24A	109.20	C27	-C28	-H28	117.71
C25	-C24	-H24B	109.26	C29	-C28	-H28	117.68
H24A	-C24	-H24B	108.04	C28	-C29	-H29	121.12
C25	-C26	-H26	120.71	C30	-C29	-H29	121.12
C27	-C26	-H26	120.74	C25	-C30	-H30	118.67
C26	-C27	-H27	121.53	C29	-C30	-H30	118.69

Table S7.- Summary of the combined $\{(k_1/k_{-1})k_2\}$ kinetic (extrapolated from Eyring plots at 298 K) and activation parameters derived from the rate law indicated in equation 3 for the systems studied and literature data.

Complex	Entering ligand	Solvent	$\{(k_1/k_{-1})k_2\}^{298}$ /s^{-1}	$\Delta H_{1,2}^{\ddagger}$ /kJ mol^{-1}	$\Delta S_{1,2}^{\ddagger}$ /J K^{-1}mol^{-1}
aFMe	ϕ	Acetone	0.0098	92±10	23±33
	ϕ	Toluene	0.011	81±10	-12±35
aFBzl	χ	Acetone	0.40	77±11	4±36
	χ	Toluene	0.70	73±9	-3±32
bBrMe	α	Acetone	0.042	91±7	32±22
	χ	Acetone	0.025	90±7	23±24
bFMe	χ	Acetone	0.035	88±3	20±11
	ϵ	Acetone	0.030	83±11	3±36
	χ	Toluene	0.025[a]	--	--
cClMe [b]	χ	Acetone	0.048	85±5	16±17
	ϵ	Acetone	0.040	95±4	44±12
	χ	Chloroform	0.048	88±8	24±29
	ϵ	Chloroform	0.032	83±9	4±31
cClEt	χ	Acetone	0.37	89±5	44±16
	ϵ	Acetone	0.26	94±5	58±17
	χ	Toluene	0.46	74±8	-5±28
cClBzl	χ	Acetone	0.60	71±6	-13±19
	χ	Chloroform	0.49	91±2	51±5
	χ	Toluene	0.53	91±1	52±4
	ϵ	Toluene	0.14[c]	--	--
cFMe	χ	Acetone	0.035	90±4	26±15
	χ	Toluene	0.042	79±3	-9±12
	ϵ	Toluene	0.0094[c]	--	--
dFMe	α	Acetone	0.13	105±13	85±43
	χ	Acetone	0.038	84±12	7±39
	χ	Toluene	0.10[c]	--	--

[a] Only runs at 25 and 35 °C have been carried out

[b] From reference 5a

[d] At 288 K, only runs at 15 and 35 °C have been carried out

Table S8.– Values of k_{obs} determined as a function of platinum compound, solvent, temperature, and entering (P) and leaving (S) ligand concentrations.

Compound	Phosphine	Solvent	T/°C	10^3×[P] /M	10^3×[S] /M	$10^3 \times k_{obs}$ /s^{-1}
aFMe	α	Acetone	10	2.5	-	61
				6.3	-	120
				8.5	-	180
				10	-	180
				13	-	240
				17	-	280
				21	-	470
			20	2.5	-	120
				6.3	-	290
				10	-	450
				13	-	580
				15	-	730
			30	2.5	-	130
				6.3	-	430
				10	-	720
				13	-	940
				15	-	1000
			40	2.5	-	210
				6.3	-	560
				10	-	930
				13	-	1100
				15	-	1600
	χ	Acetone	10	2.5	50	5.0
				7.5	110	14
				13	130	18
				18	75	28
				23	23	41
				23	25	42
			15	2.5	-	7.4
				2.5	5.0	5.5
				2.5	20	7.0
				5.0	-	14
				7.5	5.0	22
				7.5	20	25

		10	-	23
		13	5.0	36
		13	20	34
		15	-	37
		18	5.0	40
		18	20	45
		20	-	55
		23	-	59
		23	5.0	60
		23	20	58
	20	2.5	25	11
		2.5	38	9.2
		2.5	50	9.3
		7.5	110	22
		7.5	150	19
		18	75	48
		23	23	68
		23	2.5	71
	30	2.5	50	15
		7.5	110	34
		13	130	55
		18	75	84
		23	23	98
	40	2.5	50	26
		7.5	110	75
		13	130	110
		18	75	150
		23	23	190
		23	2.5	200
Toluene	10	7.5	110	24
		7.5	150	23
		13	130	37
		18	75	54
		23	2.5	64
		23	23	65
	20	7.5	110	30
		7.5	150	30
		13	130	66
		18	75	86

			23	2.5	110
			23	23	90
		30	7.5	110	57
			7.5	150	57
			13	130	98
			18	75	150
			23	2.5	200
			23	23	200
		40	7.5	110	110
			7.5	150	120
			13	130	200
			18	75	290
			23	2.5	340
			23	23	350
ϵ	Acetone	10	7.5	110	12
			7.5	150	12
			13	130	18
			18	75	27
			23	2.5	37
			23	23	34
		20	7.5	110	22
			7.5	150	22
			13	130	30
			18	75	50
			23	2.5	59
			23	23	60
		30	7.5	110	31
			7.5	150	32
			13	130	54
			18	75	66
			23	2.5	110
			23	23	100
		40	7.5	110	70
			7.5	150	52
			13	130	120
			18	75	150
			23	2.5	200
			23	23	170
	Toluene	10	7.5	110	25

			7.5	150	18
			13	130	30
			18	75	45
			23	2.5	59
			23	23	54
		20	7.5	110	50
			7.5	150	41
			13	130	64
			18	75	91
			23	2.5	120
			23	23	110
		30	7.5	110	120
			7.5	150	96
			13	130	140
			18	75	210
			23	2.5	260
			23	23	230
		40	7.5	110	190
			7.5	150	120
			13	130	270
			18	75	360
			23	2.5	360
			23	23	400
δ	Acetone	10	7.5	110	27
			7.5	150	24
			13	130	31
			18	75	52
			23	2.5	67
			23	23	68
		20	7.5	110	36
			7.5	150	38
			13	130	68
			18	75	90
			23	2.5	100
			23	23	120
		30	7.5	110	52
			7.5	150	50
			13	130	84
			18	75	130

	Toluene	10	7.5	110	34
			7.5	150	30
			13	130	56
			18	75	80
			23	2.5	93
			23	23	95
		20	7.5	110	59
			7.5	150	60
			13	130	92
			18	75	120
			23	2.5	190
			23	23	170
		30	7.5	110	140
			7.5	150	140
			13	130	220
			18	75	290
			23	2.5	380
			23	23	330
ϕ	Acetone	10	3.0	7.5	0.46
			5.0	5.0	0.69
			5.0	50	0.24
			6.0	30	0.24
			8.0	60	0.17
			18	75	0.33
			23	2.5	2.0
		20	3.0	7.5	0.98
			5.0	5.0	1.6
			5.0	50	0.39
			6.0	30	0.75
			8.0	60	0.48
			12	25	2.2
			18	25	2.6
			23	25	3.0
			25	2.5	8.9
		30	2.5	50	1.2
			3.0	7.5	6.5
			5.0	5.0	13
			5.0	50	2.3
			6.0	30	3.9

		7.5	110	1.6
		8.0	60	2.7
		13	130	2.2
		18	75	4.5
		23	2.5	3.2
		23	23	13
		25	2.5	26
	40	3.0	7.5	15
		5.0	5.0	25
		5.0	50	4.9
		6.0	30	8.5
		7.5	25	13
		8.0	60	6.0
		13	25	16
		18	25	20
		23	25	25
		25	2.5	44
		28	25	30
Toluene	10	3.0	7.5	0.50
		5.0	5.0	1.2
		5.0	50	0.17
		6.0	30	0.26
		8.0	60	0.22
		25	2.5	2.1
		100	2.5	4.1
		180	2.5	5.1
		250	2.5	5.3
	20	3.0	7.5	1.5
		5.0	5.0	3.4
		5.0	50	0.54
		6.0	30	0.95
		8.0	60	0.80
		25	2.5	9.3
		100	2.5	19
		180	2.5	20
		250	2.5	24
	30	3.0	7.5	6.4
		5.0	5.0	19
		5.0	50	2.5

				6.0	30	4.0
				8.0	60	3.5
				25	2.5	33
				180	2.5	31
				250	2.5	32
			40	3.0	7.5	15
				5.0	5.0	21
				5.0	50	3.8
				6.0	30	9.5
				8.0	60	5.7
				25	2.5	36
				100	2.5	72
				180	2.5	100
				250	2.5	120
aFBzl	χ	Acetone	10	3.0	7.5	20
				5.0	5.0	30
				5.0	5.0	25
				5.0	50	6.6
				6.0	30	13
				8.0	60	9.2
				15	15	28
				25	2.5	37
				25	25	29
				35	35	32
				45	45	32
				63	63	32
			20	2.5	5.0	45
				5.0	2.5	87
				5.0	5.0	56
				5.0	7.5	47
				5.0	13	35
				5.0	18	33
				5.0	23	30
				7.5	5.0	64
				13	5.0	88
				15	15	73
				18	5.0	80
				25	25	81
				35	35	78

		45	45	80
		63	63	82
	30	3.0	7.5	140
		5.0	5.0	180
		5.0	5.0	220
		5.0	50	73
		6.0	30	96
		8.0	60	77
		15	15	220
		25	2.5	270
		25	25	230
		35	35	230
		45	45	260
	40	3.0	7.5	250
		5.0	5.0	310
		5.0	5.0	300
		5.0	50	120
		6.0	30	200
		8.0	60	130
		15	15	330
		25	2.5	400
		25	25	350
		35	35	350
		45	45	380
Toluene	10	3.0	7.5	25
		5.0	5.0	36
		6.0	30	18
		8.0	60	15
		25	2.5	66
	20	3.0	7.5	58
		5.0	5.0	95
		5.0	50	28
		6.0	30	38
		8.0	60	32
		25	2.5	130
	30	3.0	7.5	220
		5.0	5.0	290
		5.0	50	110
		6.0	30	160

				8.0	60	130
				25	2.5	340
			40	3.0	7.5	420
				5.0	5.0	520
				5.0	50	190
				6.0	30	310
				8.0	60	240
				25	2.5	640
bBrMe	α	Acetone	10	3.0	7.5	1.5
				5.0	5.0	2.6
				6.0	30	0.84
				8.0	60	0.61
				25	2.5	6.2
			20	2.5	5.0	9.0
				5.0	2.5	19
				5.0	7.5	9.6
				5.0	13	7.7
				5.0	18	5.8
				5.0	23	5.0
				7.5	5.0	16
				13	5.0	21
				18	5.0	25
			30	3.0	7.5	25
				5.0	5.0	49
				5.0	5.0	46
				5.0	50	8.0
				6.0	30	15
				8.0	60	11
				15	15	48
				25	2.5	110
				25	25	47
				35	35	47
				45	45	48
				65	65	47
			40	3.0	7.5	61
				5.0	5.0	110
				5.0	50	20
				6.0	30	37
				8.0	60	26

				25	2.5	370
	χ	Acetone	10	3.0	7.5	1.1
				5.0	5.0	2.2
				5.0	50	0.36
				6.0	30	0.63
				8.0	60	0.46
				25	2.5	5.9
			20	2.5	5.0	4.5
				5.0	2.5	12
				5.0	7.5	6.1
				5.0	13	3.9
				5.0	18	2.7
				5.0	23	2.2
				7.5	5.0	8.6
				13	5.0	12
				18	5.0	14
			30	3.0	7.5	18
				5.0	5.0	33
				5.0	5.0	32
				5.0	50	5.2
				6.0	30	10
				8.0	60	7.3
				15	15	32
				25	2.5	89
				25	25	33
				35	35	32
				45	45	31
				65	65	33
			40	3.0	7.5	44
				5.0	5.0	86
				5.0	50	13
				6.0	30	26
				8.0	60	18
				25	2.5	320
bFMe	χ	Acetone	10	3.0	7.5	1.4
				5.0	5.0	2.2
				5.0	50	0.44
				6.0	30	0.77
				8.0	60	0.55

		25	2.5	4.5
	20	2.5	5.0	7.2
		5.0	2.5	12
		5.0	7.5	7.7
		5.0	13	5.7
		5.0	18	4.3
		5.0	23	3.7
		7.5	5.0	11
		13	5.0	13
		18	5.0	15
	30	3.0	7.5	18
		5.0	5.0	31
		5.0	5.0	31
		5.0	50	6.1
		6.0	30	10
		8.0	60	7.2
		15	15	30
		25	2.5	63
		25	25	30
		35	35	29
		45	45	31
		65	65	31
	40	3.0	7.5	51
		5.0	5.0	76
		5.0	50	17
		6.0	30	29
		8.0	60	23
		25	2.5	170
Toluene	25	3.0	7.5	6.8
		5.0	5.0	14
		5.0	50	23
		6.0	30	42
		8.0	60	29
		25	2.5	33
	35	3.0	7.5	26
		5.0	5.0	46
		5.0	50	9.3
		6.0	30	17
		8.0	60	12

				25	2.5	89
	ϵ		10	3.0	7.5	1.2
				5.0	5.0	2.0
				5.0	50	0.36
				6.0	30	0.67
				8.0	60	0.46
				25	2.5	4.3
			20	3.0	7.5	5.2
				5.0	5.0	10
				5.0	50	1.8
				6.0	30	3.1
				8.0	60	2.3
				25	2.5	19
			30	3.0	7.5	17
				5.0	5.0	27
				5.0	50	5.8
				6.0	30	11
				8.0	60	7.6
				25	2.5	49
			40	3.0	7.5	39
				5.0	5.0	62
				5.0	50	11
				6.0	30	22
				8.0	60	16
				25	2.5	130
cClEt	χ	Acetone	10	3.0	7.5	17
				5.0	5.0	31
				6.0	30	12
				8.0	60	7.3
				25	2.5	75
			15	3.0	7.5	26
				5.0	5.0	40
				5.0	50	8.0
				6.0	30	14
				8.0	60	11
				25	2.5	98
			20	3.0	7.5	42
				5.0	5.0	82
				5.0	50	16

			6.0	30	27
			8.0	60	20
			25	2.5	150
		30	3.0	7.5	120
			5.0	5.0	200
			5.0	50	51
			6.0	30	81
			8.0	60	63
			25	2.5	330
		40	3.0	7.5	340
			5.0	5.0	600
			5.0	50	170
			6.0	30	270
			8.0	60	210
	Toluene	10	3.0	7.5	30
			5.0	5.0	52
			5.0	50	10
			6.0	30	17
			8.0	60	14
		20	3.0	7.5	63
			5.0	5.0	110
			5.0	50	20
			6.0	30	36
			8.0	60	24
			25	2.5	240
		30	3.0	7.5	210
			5.0	5.0	390
			5.0	50	68
			6.0	30	130
			8.0	60	85
			25	2.5	890
		40	3.0	7.5	680
			5.0	5.0	1500
			5.0	50	210
			6.0	30	410
			8.0	60	280
			25	2.5	2400
ϵ	Acetone	11	3.0	7.5	12

				5.0	5.0	25
				5.0	50	3.7
				6.0	30	6.9
				8.0	60	5.4
				25	2.5	57
			15	3.0	7.5	19
				5.0	5.0	40
				5.0	50	6.5
				6.0	30	13
				8.0	60	8.5
				25	2.5	100
			20	3.0	7.5	43
				5.0	5.0	91
				5.0	50	14
				6.0	30	25
				8.0	60	21
				25	2.5	160
			30	3.0	7.5	110
				5.0	5.0	210
				5.0	50	41
				6.0	30	71
				8.0	60	57
				25	2.5	270
			40	3.0	7.5	320
				5.0	5.0	620
				5.0	50	130
				6.0	30	230
				8.0	60	280
				25	2.5	2400
cClBzl	χ	Acetone	10	3.0	7.5	41
				5.0	5.0	67
				5.0	50	12
				6.0	30	24
				8.0	60	15
				25	2.5	130
			20	2.5	5.0	130
				5.0	2.5	240
				5.0	7.5	150
				5.0	13	110

		5.0	18	84
		5.0	23	71
		7.5	5.0	210
		13	5.0	250
		18	5.0	300
	30	3.0	7.5	220
		5.0	5.0	420
		6.0	30	120
		8.0	60	97
		25	2.5	610
	40	3.0	7.5	650
		5.0	5.0	1200
		5.0	50	240
		6.0	30	390
		8.0	60	310
Toluene	10	3.0	7.5	27
		5.0	5.0	52
		5.0	50	7.2
		6.0	30	14
		8.0	60	9.5
		25	2.5	120
	20	3.0	7.5	96
		5.0	5.0	180
		5.0	50	27
		6.0	30	52
		8.0	60	34
		25	2.5	410
	30	3.0	7.5	300
		5.0	5.0	620
		5.0	50	91
		6.0	30	170
		8.0	60	120
		25	2.5	1500
	40	3.0	7.5	900
		5.0	5.0	2200
		5.0	50	310
		6.0	30	560
		8.0	60	400
		25	2.5	3900

		Chloroform	10	3.0	7.5	24
				5.0	5.0	54
				5.0	50	6.6
				6.0	30	12
				8.0	60	8.6
				25	2.5	110
			20	3.0	7.5	76
				5.0	5.0	150
				5.0	50	25
				6.0	30	45
				8.0	60	32
				25	2.5	300
			30	3.0	7.5	230
				5.0	5.0	520
				5.0	50	90
				6.0	30	150
				8.0	60	110
				25	2.5	960
			40	3.0	7.5	650
				5.0	5.0	1100
				5.0	50	250
				6.0	30	410
				8.0	60	320
				25	2.5	2100
	ϵ	Toluene	15	3.0	7.5	46
				5.0	5.0	88
				5.0	50	13
				6.0	30	26
				8.0	60	17
				25	2.5	200
			35	3.0	7.5	490
				5.0	5.0	880
				5.0	50	140
				6.0	30	280
				8.0	60	190
				25	2.5	2100
cFMe	χ	Acetone	10	3.0	7.5	1.2
				5.0	5.0	1.9
				5.0	50	0.41

			6.0	30	0.69
			8.0	60	0.51
			25	2.5	3.8
		20	2.5	5.0	6.2
			5.0	2.5	11
			5.0	7.5	6.5
			5.0	13	4.6
			5.0	18	3.6
			5.0	23	3.1
			7.5	5.0	10
			13	5.0	12
			18	5.0	13
		30	3.0	7.5	18
			5.0	5.0	29
			5.0	5.0	29
			5.0	50	6.2
			6.0	30	11
			8.0	60	7.8
			15	15	29
			25	2.5	39
			25	25	27
			35	35	28
			45	45	28
			65	65	29
		40	3.0	7.5	45
			5.0	5.0	75
			5.0	50	16
			6.0	30	26
			8.0	60	20
			25	2.5	110
χ	Toluene	10	3.0	7.5	1.7
			5.0	5.0	3.2
			5.0	50	0.62
			6.0	30	1.1
			8.0	60	0.81
			25	2.5	6.5
		20	3.0	7.5	7.1
			5.0	5.0	12
			5.0	50	2.4

				6.0	30	4.4
				8.0	60	3.1
				25	2.5	19
			30	3.0	7.5	21
				5.0	5.0	33
				5.0	50	6.3
				6.0	30	11
				8.0	60	9.1
				25	2.5	55
			40	3.0	7.5	46
				5.0	5.0	92
				5.0	50	18
				6.0	30	28
				8.0	60	20
				25	2.5	260
	ϵ	Toluene	15	3.0	7.5	2.2
				5.0	5.0	4.2
				5.0	50	0.85
				6.0	30	1.5
				8.0	60	1.1
				25	2.5	12
			35	3.0	7.5	24
				5.0	5.0	43
				5.0	50	9.6
				6.0	30	16
				8.0	60	12
				25	2.5	110
dFMe	α	Acetone	10	3.0	7.5	1.9
				5.0	5.0	4.0
				5.0	50	0.71
				6.0	30	1.2
				8.0	60	0.97
				25	2.5	11
			20	2.5	5.0	15
				5.0	2.5	24
				5.0	7.5	17
				5.0	13	13
				5.0	18	12
				5.0	23	9.2

			7.5	5.0	22
		30	3.0	7.5	43
			5.0	5.0	61
			5.0	5.0	61
			5.0	50	21
			6.0	30	33
			8.0	60	23
			15	15	62
			25	2.5	85
			25	25	63
			35	35	57
			45	45	59
			65	65	62
		40	3.0	7.5	78
			5.0	5.0	130
			5.0	50	41
			6.0	30	70
			8.0	60	54
χ	Acetone	10	3.0	7.5	1.5
			5.0	5.0	2.5
			5.0	50	0.45
			6.0	30	0.90
			8.0	60	0.61
			25	2.5	7.4
		20	2.5	5.0	9.5
			5.0	2.5	19
			5.0	7.5	10
			5.0	13	5.9
			5.0	18	5.0
			5.0	23	4.2
			7.5	5.0	20
			13	5.0	29
			18	5.0	34
		30	3.0	7.5	21
			5.0	5.0	36
			5.0	5.0	39
			5.0	50	7.7
			6.0	30	13
			8.0	60	9.5

		15	15	38
		25	2.5	60
		25	25	37
		35	35	36
		45	45	35
		65	65	34
	40	3.0	7.5	44
		5.0	5.0	75
		5.0	50	14
		6.0	30	22
		8.0	60	19
		25	2.5	140
Toluene	15	3.0	7.5	2.8
		5.0	5.0	5.1
		5.0	50	0.95
		6.0	30	1.8
		8.0	60	1.2
		25	2.5	14
	35	3.0	7.5	28
		5.0	5.0	45
		5.0	50	10
		6.0	30	18
		8.0	60	13
		25	2.5	79

Table S9.– Relevant characterization data for the complexes studied in acetone-d_6 solution, δ in ppm (references: $SiMe_4$ for ^1H, 85% H_3PO_4 for ^{31}P and $H_2[PtCl_6]$ for ^{195}Pt), J in Hz. F_x indicates the fluoro ligand, F_Z indicates the *ortho* fluoro substituent on the ^{arom}C.

Complex	$\delta(Me_a)$ (^2J(PtH)) [^3J(PH)]	$\delta(Me_b)$ (^2J(PtH)) [^3J(PH)]	$\delta(CH_2)$ (^2J(HH))	δ(CHN) (^2J(HH))	$\delta(SR_2)$ (^3J(PtH))	δ(Pt)	δ(P) (J(PPt))
aFMe[a]	0.89 (67) $^3J(F_XH)$ = 7.2	1.54 (64) $^3J(F_XH)$ = 9.3 $^5J(F_ZH)$ = 7.2	5.15, 5.23 (7.8)	9.18 (47)	2.02 (12)	-2144	
aFBzl	0.95 (68) $^3J(F_XH)$ = 7.4	1.64 (63) $^3J(F_XH)$ = 9.4 $^5J(F_ZH)$ = 7.4	5.18, 5.26 (13)	9.08 (48)	3.67, 3.83 (9.2, 7.6) $^2J(H_aH_b)$ = 14		
aFα	0.64 (56) [7.8] $^3J(F_XH)$ = 7.8	Obscured by phosphine protons	4.47, 5.02 (15)	8.64 (48)			-15.88 (1074) $^2J(PF_X)$ = 31
aFχ	0.73 (58) [7.9] $^3J(F_XH)$ = 7.9	1.67 (62) [8.0] $^3J(F_XH)$ = 8.0 $^5J(F_ZH)$ = 8.0	4.33, 4.96 (15)	8.70 (50)			-2.30 (1002) $^2J(PF_X)$ = 32
aFδ	0.70 (57) [7.7] $^3J(F_XH)$ = 7.7	1.66 (64) [7.9] $^3J(F_XH)$ = 7.9 $^5J(F_ZH)$ = 7.9	4.37, 5.00 (15)	8.64 (50)			3.68 (1026) $^2J(PF_X)$ = 30
aFϵ	0.72 (58) [7.7] $^3J(F_XH)$ = 7.7	1.68 (64) [8.1] $^3J(F_XH)$ = 8.1 $^5J(F_ZH)$ = 8.1	4.37, 4.99 (15)	8.70 (53)			-2.67 (1004) $^2J(PF_X)$ = 32
aFϕ	0.56 (55) [7.4] $^3J(F_XH)$ = 7.4	Obscured by phosphine protons	5.15, 5.47 (14)	8.96 (49)			2.79 (1018) $^2J(PF_X)$ = 34
bBrMe	1.13 (70)	1.77 (67) $^5J(F_ZH)$ = 7.2	5.29, 5.50 (14)	8.79 (46)	2.13 (14)	-2744	
bBrα	0.97 (58) [8.0]	1.81 (69) [7.9] $^5J(F_ZH)$ = 7.9	4.44, 5.41 (15)	8.33 (48)			-21.03 (1082)
bBrχ	1.08 (59) [8.0]	1.97 (67) [8.2] $^5J(F_ZH)$ = 8.2	5.43, 5.53 (16)	8.31 (49)			-7.88 (992)

bFMe	0.88 (68) $^3J(F_XH)$ = 7.2	1.52 (63) $^3J(F_XH)$ = 9.2 $^5J(F_ZH)$ = 7.0	5.06, 5.15 (16)	8.92 (47)	2.01 (12)	-2153 $J(PtF_X)$ = 107	
bBFχ	0.79 (55) [7.5] $^3J(F_XH)$ = 7.5	1.71 (64) [8.5] $^3J(F_XH)$ = 8.5 $^5J(F_ZH)$ = 6.6	4.14, 4.96 (15)	8.47 (51)			-1.49 (1002) $^2J(PF_X)$ = 31
bFϵ	0.77 (57) [7.7] $^3J(F_XH)$ = 7.7	1.70 (64) [9.2] $^3J(F_XH)$ = 9.2 $^5J(F_ZH)$ = 6.9	4.15, 4.97 (15)	8.46 (50)			-1.63 (1011) $^2J(PF_X)$ = 31
cClMe[a]	1.06 (69)	1.75 (67)	5.31, 5.51 (14)	9.29 (44)	2.14 (13)	-2521	
cClEt	1.08 (69)	1.78 (67)	5.37, 5.49 (14)	9.32 (44)	1.07 t (7.5) 2.57 m	-2493	
cClBzl	1.10 (70)	1.84 (67)	5.39, 5.56 (13)	9.13 (42)	3.79, 3.94 (11.3, 7.8) $^2J(H_aH_b)$ = 14	-2537	
cClχ[a]	1.04 (60) [7.9]	1.93 (67) [8.4]	4.71, 5.54 (15)	8.81 (43)			−9.85 (961)
cClϵ[a]	0.91 (60) [8.0]	1.83 (66) [8.4]	4.72, 5.45 (19)	8.78 (47)			−8.23 (969)
cFMe	0.95 (69) $^3J(F_XH)$ = 7.0	1.64 (62) $^3J(F_XH)$ = 10	5.16, 5.28 (13)	9.43 (45)	2.06 (12)	-2025 $J(PtF_X)$ = 137	
dFMe	0.97 (69) $^3J(F_XH)$ = 7.5	1.14 (66) $^3J(F_XH)$ = 7.5	5.09, 5.17 (13)	8.79 (48)	1.90 (12)	-2270 $J(PtF_X)$ = 94	
cFχ	0.89 (56) [7.7] $^3J(F_XH)$ = 7.7	1.79 (62) [9.7] $^3J(F_XH)$ = 9.7	4.46, 5.15 (14)	8.90 (46)			-0.72 (969) $^2J(PF_X)$ = 32
dFα	0.62 (57) [8.3] $^3J(F_XH)$ = 8.3	1.16 (67) [8.8] $^3J(F_XH)$ = 6.7	4.26, 4.96 (14)	8.13 (50)			-15.95 (1092) $^2J(PF_X)$ = 30
dFχ	0.65 (59) [7.9] $^3J(F_XH)$ = 7.8	1.25 (67) [8.0] $^3J(F_XH)$ = 6.6	4.17, 4.95 (15)	8.28 (49)			-1.77 (1013) $^2J(PF_X)$ = 31

[a] Bernhardt, P.V.; Gallego, C.; Martinez, M. *Organometallics*, **2000**, *19*, 4862.

FIGURE S1.- Combined Eyring plot for the substitution reactions studied on compound **bFMe** with different phosphines and in different solvents.

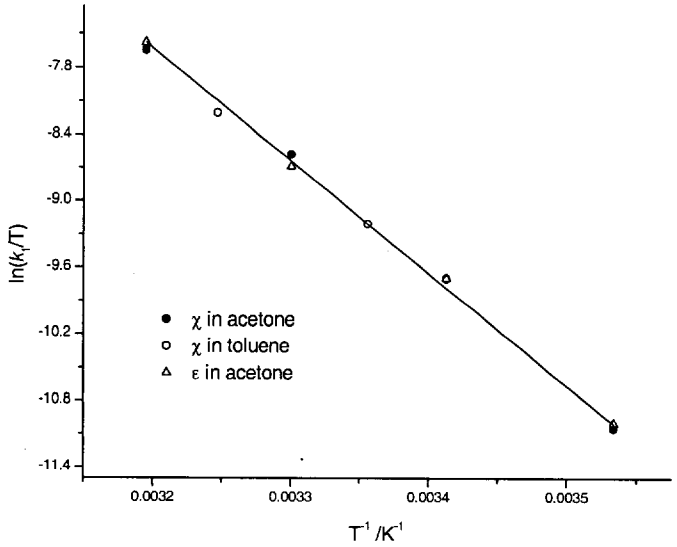

FIGURE S2.- Eyring plots for the **cClEt** (acetone solution) and **cClBzl** systems (acetone and chloroform solutions).