Computational assessment on the Tolman cone angles for P-ligands

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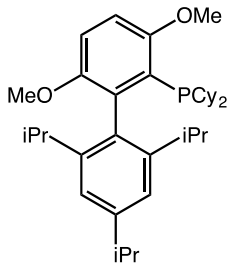
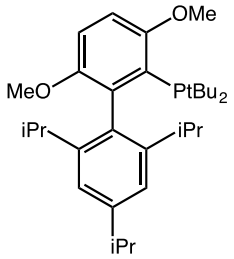
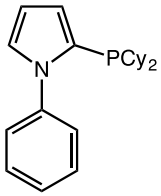
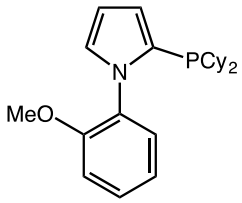
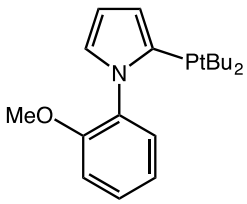
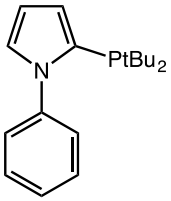
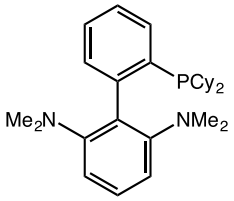
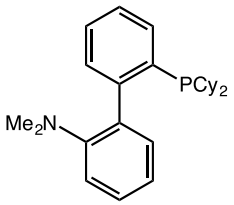
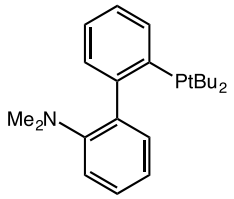
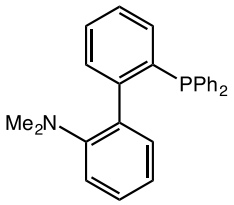
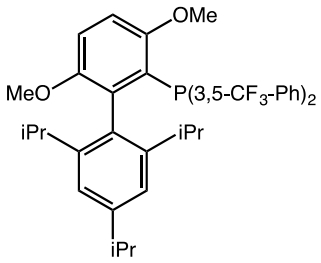
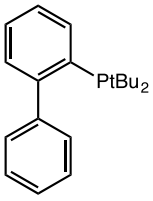
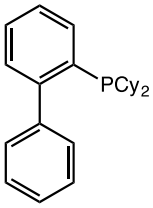
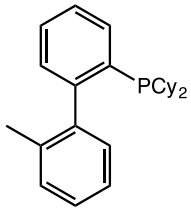
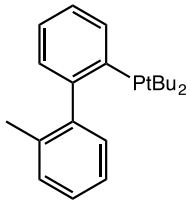
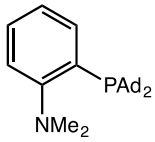
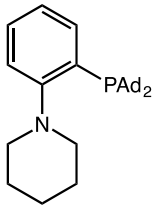
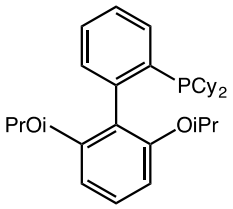
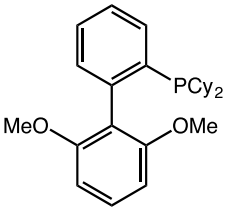
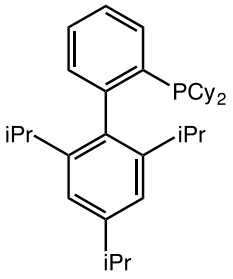
Table S1. Schematic representation of Buchwald and other bulky biaryl P-ligands.

#	**Ligand**	**Structure**
36	BrettPhos	
37	*t*BuBrettPhos	
38	CataCxium-PCy	
39	CataCxium-POMeCy	
40	CataCxium-POMetB	
41	CataCxium-PtB	

42	CPhos	
43	DavePhos	
44	*t*BuDavePhos	
45	PhDavePhos	
46	JackiePhos	
47	JohnPhos	
48	CyJohnPhos	

49	MePhos	
50	*t*BuMePhos	
51	MeDalPhos	
52	MorDalPhos	
53	RuPhos	
54	SPhos	
55	XPhos	

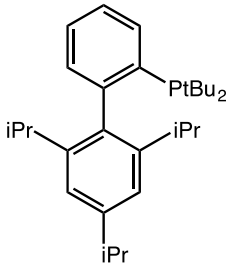
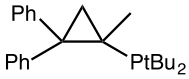
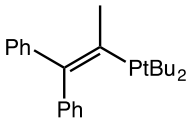
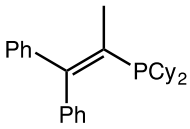
56	*t*BuXPhos	
57	cBridP	
58	CycBridP	
59	vBridP	
60	CyvBridP	

Table S2. Linear cone angle values (θ_L) for biaryl ligands in their open and close conformations, and energy difference between both structures.

#	Ligand	θ_L close	θ_L open	E_{REL}*
36	BrettPhos	251.3	202.4	7.8
37	*t*BuBrettPhos	250.9	218.6	9.6
38	CataCxium-PCy	216.6	178.9	6.2
39	CataCxium-POMeCy	221.2	178.7	4.7
40	CataCxium-POMetB	224.0	188.7	10.3
41	CataCxium-PtB	225.2	188.7	8.3
42	CPhos	214.7	174.2	12.3
43	DavePhos	211.2	177.3	5.9
44	*t*BuDavePhos	228.1	195.0	9.7
45	PhDavePhos	206.9	163.8	7.7
46	JackiePhos	236.2	209.5	3.8
47	JohnPhos	228.9	190.9	7.0
48	CyJohnPhos	208.0	180.2	3.9
49	MePhos	208.9	199.5	2.5
50	*t*BuMePhos	228.9	191.7	10.6
51	MeDalPhos	214.7	191.5	5.0
52	MorDalPhos	231.2	192.6	6.1
53	RuPhos	231.5	219.9	5.4
54	SPhos	227.4	218.3	1.0
55	XPhos	238.7	174.7	9.4
56	*t*BuXPhos	250.6	185.7	15.7
57	cBridP	226.0	186.6	10.0
58	CycBridP	224.3	185.0	6.0
59	vBridP	227.4	188.5	6.6
60	CyvBridP	211.1	181.8	4.1

* EREL corresponds to the relative energy computed between the open and close conformations: E_{REL} = E(θ_L open) - E(θ_L close)

Table S3. List of steric descriptors of the studied ligands, form literature: solid angle (Θ),[1] LKB-P He_8,[2] angular symmetric deformation coordinate (S_4'),[3] and computed $\%V_{bur}$ parameter[4] for linear ($\%V_{bur-L}$), tetrahedral ($\%V_{bur-T}$) and octahedral ($\%V_{bur-O}$) coordination environments.

#	Ligand	Θ(°)	He_8 (kcal mol^{-1})	S4' (°)	$\%V_{bur-L}$	$\%V_{bur-T}$	$\%V_{bur-O}$
1	PH_3		2.3	66.9	18.2	18.3	17.8
2	PMe_3	124	3.0	39.4	23.3	23.3	22.6
3	PEt_3	143	6.0	39.0	28.6	28.9	24.8
4	PPr_3		6.1	39.2	27.0	27.0	24.7
5	P*i*Pr_3	163	12.2	28.4	31.6	30.5	27.4
6	PBu_3	148	6.1	40.2	25.5	25.4	24.0
7	P*t*Bu_3	182	23.4	7.4	37.0	35.6	30.7
8	PNp_3		31.3	48.6	39.0	35.9	30.0
9	$PCyp_3$		9.2	33.3	33.1	31.4	29.3
10	PCy_3		16.7	28.6	32.9	31.9	28.2
11	PPh_3	129	8.0	32.6	29.8	29.5	27.0
12	P(*o*-Tol)$_3$	142	30.1	31.0	35.0	33.7	30.1
13	P(*o*-ClC_6H_4)$_3$		23.6	28.4	40.5	38.5	30.9
14	P(*p*-Tol)$_3$	135	6.6	33.6	29.8	29.4	27.0
15	P(*p*-ClC_6H_4)$_3$	129	8.2	33.7	29.9	29.6	27.0
16	P(3,5-$Me_2C_6H_3$)$_3$				29.8	29.4	27.1
17	P(3,5-$Cl_2C_6H_3$)$_3$				29.8	29.8	27.0
18	P(naph)$_3$		23.5	21.9	35.5	34.0	30.4
19	PBn_3	163	12.7	38.1	33.9	29.1	25.8
20	PF_3		1.5	62.0	20.9	21.6	20.4
21	PCl_3		2.2	48.3	23.8	24.5	22.7
22	PBr_3		3.1	45.1	24.7	25.2	23.3
23	PI_3		4.1	37.9	26.0	26.4	24.1
24	P(CF_3)$_3$		3.0	52.2	28.6	29.1	26.3
25	P(CCl_3)$_3$		20.7	28.7	38.3	38.3	31.8

26	$P(C_2F_5)_3$	9.9	39.9	37.0	37.1	31.0
27	$P(C_6F_5)_3$	11.6	35.7	36.3	35.5	30.8
28	$P(OMe)_3$	4.2	40.2	26.3	29.0	25.9
29	$P(OEt)_3$	3.0	45.9	31.6	30.2	26.4
30	$P(OPr)_3$			33.7	30.7	25.5
31	$P(O\textit{i}Pr)_3$	4.4	47.9	32.5	31.5	25.4
32	$P(OBu)_3$	7.1	49.4	33.1	29.0	26.0
33	$P(O\textit{t}Bu)_3$	9.4	46.4	33.6	33.4	27.5
34	$P(ONp)_3$	4.3	49.7	33.8	27.3	24.5
35	$P(OPh)_3$	5.9	48.9	32.6	27.7	22.2
36	BrettPhos			55.0	35.0	30.5
37	*t*BuBrettPhos			58.5	36.5	31.7
38	CataCxium-PCy	19.9	28.4	43.4	31.9	30.4
39	CataCxium-POMeCy	22.3		48.3	32.5	28.6
40	CataCxium-POMetB			51.4	34.6	30.6
41	CataCxium-PtB	37.4		48.7	34.7	30.6
42	CPhos	31.7	36.5	51.3	32.9	28.2
43	DavePhos	26.1	37.9	49.6	31.4	28.3
44	*t*BuDavePhos	43.7	14.2	51.4	36.1	31.2
45	PhDavePhos			47.9	30.5	27.5
46	JackiePhos			54.1	34.3	30.9
47	JohnPhos	45.9	19.0	50.4	34.9	30.7
48	CyJohnPhos			47.7	31.6	28.5
49	MePhos	23.5	32.2	43.6	31.4	28.3
50	*t*BuMePhos	43.0	19.7	51.0	34.9	30.1
51	MeDalPhos			44.9	35.1	30.4
52	MorDalPhos			47.6	35.3	30.8
53	RuPhos	18.0	36.3	54.0	35.1	32.7
54	SPhos	24.1	26.0	48.8	35.4	32.0

55	XPhos		22.2	28.6	52.4	31.9	29.9
56	*t*BuXPhos		34.6	10.6	53.8	33.8	30.4
57	cBridP		44.9	14.7	50.6	44.1	34.4
58	CycBridP				46.8	39.5	30.7
59	vBridP				50.2	43.6	34.1
60	CyvBridP				43.1	35.9	31.0
61	PH_2Me				19.4	19.5	18.9
62	PH_2Et				20.6	20.6	19.7
63	PH_2*i*Pr				21.7	21.6	20.9
64	PH_2*t*Bu				21.9	21.8	21.1
65	PH_2Np				19.5	19.5	19.0
66	PH_2Ph				21.1	21.1	19.7
67	$PHMe_2$		2.6	45.2	21.1	21.2	20.7
68	$PHEt_2$				23.3	23.2	21.8
69	PH*i*Pr_2				24.6	24.3	23.0
70	PH*t*Bu_2				29.8	28.9	26.0
71	$PHNp_2$				26.0	26.6	23.8
72	$PHAd_2$		11.3	31.4	29.9	28.9	26.1
73	$PHPh_2$	112			24.9	24.7	23.3
74	PMe_2Et	133	3.6	38.4	25.1	25.1	23.6
75	PMe_2Pr		3.9	38.8	25.1	25.1	23.7
76	PMe_2*i*Pr		3.9	31.4	25.6	25.6	23.9
77	PMe_2*t*Bu	144	4.7	31.6	27.7	27.9	25.9
78	PMe_2Np				24.0	24.0	23.0
79	$PMeAd_2$				33.0	31.9	28.6
80	PMe_2Ph	126	3.2	36.1	26.0	25.9	24.0
81	PMe_2Bn		4.6	39.3	27.8	23.5	22.7
82	$PMeEt_2$	138	4.3	39.4	25.1	25.1	23.7
83	$PMePr_2$				25.1	25.1	23.7

84	PMe*i*Pr_2	151	5.4	20.9	29.0	28.5	26.2
85	PMe*t*Bu_2	163	15.0	20.3	32.8	31.8	28.6
86	$PMeNp_2$				31.4	30.3	26.3
87	$PMePh_2$	124	4.8	34.6	27.8	27.1	25.5
88	$PMeBn_2$				28.5	31.6	25.3
89	PMeEtPr				25.1	25.1	23.7
90	PEt_2Pr				27.1	25.5	23.9
91	PEt_2Ph	137	7.3	36.4	28.0	26.5	24.9
92	PEt_2Bn				32.1	27.5	25.1
93	$PEtPr_2$				27.0	27.0	24.6
94	$PEtPh_2$	140	5.4	34.3	29.8	28.4	26.4
95	$PEtBn_2$				30.4	29.9	25.4
96	P*i*Pr_2Cy				33.0	31.9	28.5
97	P*i*PrCy_2				32.9	32.0	28.2
98	P*i*PrAd_2				35.5	33.8	29.7
99	P*i*Pr_2Ph		10.5	28.4	31.8	30.7	27.9
100	P*i*PrPh_2	139	9.4	33.8	31.9	31.0	27.6
101	P*i*Pr_2Bn				33.8	32.6	29.0
102	P*i*PrBn_2				31.9	30.8	27.1
103	PAd_2Bu (CataCxium-A)		19.3	17.6	34.3	32.8	29.5
104	P*t*Bu_2Cy		22.9	5.3	35.3	33.8	29.9
105	P*t*Bu_2Ph	168	22.9	13.1	36.1	34.5	29.9
106	P*t*Bu_2Bn		22.6	21.2	38.1	35.3	30.6
107	P*t*BuCy_2		18.5	21.9	34.4	33.1	28.7
108	P*t*BuAd_2		32.2	5.9	37.3	35.7	30.4
109	P*t*BuPh_2	149	9.2	20.8	32.3	31.1	28.2
110	P*t*BuBn_2		15.4	19.1	36.9	32.8	29.2
111	PNp_2Ph				33.4	31.6	27.4
112	PNp_2Bn				37.9	35.2	30.3

113	$PNpPh_2$				34.3	27.7	26.1
114	$PNpBn_2$				38.4	34.1	26.4
115	PCy_2Ph		12.5	21.1	31.7	30.6	27.9
116	$PCyPh_2$		10.9	33.2	31.9	30.9	27.7
117	PAd_2Bn (CataCxium-Abn)		26.4	21.6	38.5	35.0	29.3
118	PPh_2Bn	139	6.8	36.6	32.6	30.7	27.9
119	PBn_2Ph		9.3	28.9	32.0	26.9	26.4

Table S4. Predicted P-ligand dissociation (ΔH_R) from open titanocene [Ti(2,4-$C_7H_{11})_2(PR_3)$] complexes. ΔH_R is computed as: $\Delta H_R = -0.145\theta_O + 32.389$

#	Ligand	θ_O	ΔH_R (kcal mol^{-1})
1	PH_3	101.0	17.7
2	PMe_3	122.1	14.7
3	PEt_3	157.8	9.5
4	PPr_3	157.7	9.5
5	P*i*Pr_3	163.1	8.7
6	PBu_3	160.6	9.1
7	P*t*Bu_3	167.1	8.2
8	PNp_3	155.0	9.9
9	$PCyp_3$	161.5	9.0
10	PCy_3	164.9	8.5
11	PPh_3	152.0	10.4
12	P(*o*-Tol)$_3$	175.6	6.9
13	P(*o*-$ClC_6H_4)_3$	173.7	7.2
14	P(*p*-Tol)$_3$	152.1	10.3
15	P(*p*-$ClC_6H_4)_3$	152.0	10.4
16	P(3,5-$Me_2C_6H_3)_3$	164.9	8.5
17	P(3,5-$Cl_2C_6H_3)_3$	160.6	9.1
18	P(naph)$_3$	173.1	7.3
19	PBn_3	153.3	10.2
20	PF_3	104.7	17.2
21	PCl_3	116.4	15.5
22	PBr_3	120.7	14.9
23	PI_3	125.7	14.2
24	$P(CF_3)_3$	139.1	12.2
25	$P(CCl_3)_3$	159.3	9.3
26	$P(C_2F_5)_3$	165.3	8.4

27	$P(C_6F_5)_3$	159.3	9.3
28	$P(OMe)_3$	153.0	10.2
29	$P(OEt)_3$	152.6	10.3
30	$P(OPr)_3$	155.1	9.9
31	$P(O\textit{i}Pr)_3$	146.0	11.2
32	$P(OBu)_3$	153.4	10.2
33	$P(O\textit{t}Bu)_3$	157.7	9.5
34	$P(ONp)_3$	147.7	11.0
35	$P(OPh)_3$	130.5	13.5
36	BrettPhos	181.6	6.1
37	*t*BuBrettPhos	182.3	6.0
38	CataCxium-PCy	179.7	6.3
39	CataCxium-POMeCy	163.2	8.7
40	CataCxium-POMetB	168.1	8.0
41	CataCxium-PtB	168.0	8.0
42	CPhos	164.2	8.6
43	DavePhos	164.4	8.6
44	*t*BuDavePhos	172.7	7.3
45	PhDavePhos	155.6	9.8
46	JackiePhos	193.6	4.3
47	JohnPhos	166.7	8.2
48	CyJohnPhos	164.8	8.5
49	MePhos	165.3	8.4
50	*t*BuMePhos	160.8	9.1
51	MeDalPhos	170.4	7.7
52	MorDalPhos	173.4	7.3
53	RuPhos	212.7	1.6
54	SPhos	201.7	3.1
55	XPhos	172.2	7.4

56	*t*BuXPhos	178.9	6.5
57	cBridP	198.3	3.6
58	CycBridP	194.1	4.2
59	vBridP	201.3	3.2
60	CyvBridP	174.6	7.1
61	PH_2Me	110.0	16.4
62	PH_2Et	126.0	14.1
63	PH_2*i*Pr	128.7	13.7
64	PH_2*t*Bu	128.9	13.7
65	PH_2Np	114.0	15.9
66	PH_2Ph	120.7	14.9
67	$PHMe_2$	120.8	14.9
68	$PHEt_2$	141.7	11.8
69	PH*i*Pr_2	130.6	13.4
70	PH*t*Bu_2	162.8	8.8
71	$PHNp_2$	152.8	10.2
72	$PHAd_2$	164.2	8.6
73	$PHPh_2$	139.2	12.2
74	PMe_2Et	138.5	12.3
75	PMe_2Pr	138.3	12.3
76	PMe_2*i*Pr	140.6	12.0
77	PMe_2*t*Bu	143.2	11.6
78	PMe_2Np	129.7	13.6
79	$PMeAd_2$	165.7	8.4
80	PMe_2Ph	133.2	13.1
81	PMe_2Bn	123.9	14.4
82	$PMeEt_2$	137.5	12.5
83	$PMePr_2$	137.1	12.5
84	PMe*i*Pr_2	160.1	9.2

85	PMe*t*Bu$_2$	165.2	8.4
86	PMeNp$_2$	151.0	10.5
87	PMePh$_2$	142.3	11.8
88	PMeBn$_2$	145.2	11.3
89	PMeEtPr	137.3	12.5
90	PEt$_2$Pr	140.0	12.1
91	PEt$_2$Ph	139.4	12.2
92	PEt$_2$Bn	145.8	11.2
93	PEtPr$_2$	142.2	11.8
94	PEtPh$_2$	148.2	10.9
95	PEtBn$_2$	154.4	10.0
96	P*i*Pr$_2$Cy	164.5	8.5
97	P*i*PrCy$_2$	164.2	8.6
98	P*i*PrAd$_2$	169.2	7.9
99	P*i*Pr$_2$Ph	162.4	8.8
100	P*i*PrPh$_2$	156.6	9.7
101	P*i*Pr$_2$Bn	172.7	7.3
102	P*i*PrBn$_2$	171.0	7.6
103	PAd$_2$Bu (CataCxium-A)	169.2	7.9
104	P*t*Bu$_2$Cy	168.6	7.9
105	P*t*Bu$_2$Ph	167.7	8.1
106	P*t*Bu$_2$Bn	177.4	6.7
107	P*t*BuCy$_2$	169.4	7.8
108	P*t*BuAd$_2$	173.0	7.3
109	P*t*BuPh$_2$	155.6	9.8
110	P*t*BuBn$_2$	166.3	8.3
111	PNp$_2$Ph	171.7	7.5
112	PNp$_2$Bn	173.0	7.3
113	PNpPh$_2$	146.4	11.2

114	$PNpBn_2$	159.8	9.2
115	PCy_2Ph	162.2	8.9
116	$PCyPh_2$	158.2	9.4
117	PAd_2Bn (CataCxium-Abn)	165.2	8.4
118	PPh_2Bn	165.5	8.4
119	PBn_2Ph	171.3	7.6

Table S5. Computed reaction barriers (in kcal mol^{-1}) and ligand descriptors for the Suzuki-Miyaura reaction between bromobenzene and [Pd-PR_3] catalyst.

		PMe_3	$PtBu_3$	PPh_3	$P(CF_3)_3$
Barrier (kcal mol^{-1})	Oxidative addition	3.9	3.2	4.3	11.0
	Transmetalation	18.3	19.8	16.4	14.4
	Reductive elimination	4.7	3.2	3.9	1.7
Descriptors	HOMO (Hartree)	-0.190	-0.173	-0.187	-0.277
	LUMO (Hartree)	0.033	0.028	-0.051	-0.058

Table S6. Standardized ligand descriptors and predicted reaction barriers (OA = oxidative addition, TM = transmetalation, RE = Reductive Elimination, in kcal mol^{-1}) for the Suzuki-Miyaura reaction between bromobenzene and [Pd-PR_3] catalyst. The reaction barriers are computed as:

$OA = 0.012\theta_T - 78.600E_{HOMO} - 12.478$

$TM = 0.033\theta_T - 44.353E_{LUMO} + 12.771$

$RE = -0.029\theta_T + 27.906E_{HOMO} + 13.595$

#	Ligand	θ_T	E_{HOMO}	E_{LUMO}	OA	TM	RE
1	PH_3	-1.946	-0.957	0.280	8.2	16.2	3.6
2	PMe_3	-1.354	0.398	1.058	3.9	18.2	4.8
3	PEt_3	0.671	0.476	0.896	4.2	19.4	3.5
4	PPr_3	0.677	0.465	0.884	4.3	19.4	3.4
5	P*i*Pr_3	0.721	0.663	0.855	3.7	19.4	3.6
6	PBu_3	0.777	0.493	0.933	4.2	19.6	3.4
7	P*t*Bu_3	1.287	0.829	0.936	3.3	20.0	3.4
8	PNp_3	0.721	0.569	0.735	4.0	19.2	3.5
9	$PCyp_3$	0.515	0.624	0.752	3.7	19.0	3.7
10	PCy_3	0.913	0.729	0.898	3.5	19.6	3.6
11	PPh_3	0.539	0.483	-0.906	4.2	15.9	3.6
12	P(*o*-Tol)$_3$	1.276	0.610	-0.861	4.0	16.6	3.2
13	P(*o*-ClC_6H_4)$_3$	1.331	0.261	-1.226	5.1	16.0	2.7
14	P(*p*-Tol)$_3$	0.535	0.641	-0.931	3.7	15.9	3.7
15	P(*p*-ClC_6H_4)$_3$	0.546	0.139	-1.364	5.3	15.1	3.2
18	P(naph)$_3$	1.307	0.683	-1.440	3.8	15.5	3.3
19	PBn_3	0.543	0.259	-0.613	4.9	16.5	3.3
20	PF_3	-1.590	-1.817	-0.548	11.0	15.0	2.4
21	PCl_3	-1.419	-1.578	-2.275	10.3	11.8	2.5
22	PBr_3	-1.227	-1.471	-3.260	10.0	10.1	2.5
23	PI_3	-0.996	-1.028	-3.618	8.7	9.6	2.9
24	P(CF_3)$_3$	-0.471	-1.709	-1.088	11.0	14.8	1.7
25	P(CCl_3)$_3$	0.784	-1.438	-2.369	10.5	13.4	1.2

26	$P(C_2F_5)_3$	0.861	-1.580	-1.379	11.0	15.3	1.0
28	$P(OMe)_3$	0.161	-0.013	0.280	5.7	17.9	3.2
29	$P(OEt)_3$	0.744	-0.159	0.377	6.3	18.5	2.7
31	$P(O\textit{i}Pr)_3$	0.818	0.232	0.382	5.1	18.6	3.1
32	$P(OBu)_3$	1.107	0.113	0.386	5.5	18.8	2.7
33	$P(O\textit{t}Bu)_3$	0.965	0.406	0.433	4.6	18.8	3.2
34	$P(ONp)_3$	0.551	0.028	0.299	5.7	18.2	3.0
35	$P(OPh)_3$	0.001	0.140	-0.823	5.1	15.7	3.5
38	CataCxium-PCy	0.956	0.811	-0.729	3.2	16.6	3.6
41	CataCxium-PtB	1.274	0.746	-0.726	3.5	16.9	3.3
42	CPhos	1.031	1.121	-0.771	2.3	16.6	3.9
43	DavePhos	0.850	1.051	-0.903	2.4	16.2	4.0
44	*t*BuDavePhos	1.490	0.872	-0.886	3.2	16.7	3.3
47	JohnPhos	1.305	0.833	-0.936	3.3	16.5	3.4
48	CyJohnPhos	0.983	0.690	-0.945	3.6	16.2	3.5
49	MePhos	0.898	0.651	-0.835	3.7	16.4	3.5
50	*t*BuMePhos	1.292	0.845	-0.882	3.2	16.6	3.4
53	RuPhos	2.199	0.816	-0.835	3.6	17.4	2.8
54	SPhos	2.152	0.905	-0.613	3.3	17.8	2.9
55	XPhos	0.852	0.632	-0.898	3.8	16.2	3.5
56	*t*BuXPhos	1.073	0.750	-0.917	3.5	16.3	3.5
57	cBridP	2.389	0.862	-0.674	3.5	17.8	2.7
67	$PHMe_2$	-1.419	0.079	0.745	4.9	17.5	4.5
72	PAd_2H	0.770	0.477	0.375	4.3	18.5	3.4
74	PMe_2Et	-0.430	0.431	0.961	4.1	18.7	4.2
75	PMe_2Pr	-0.425	0.445	0.912	4.0	18.6	4.2
76	$PMe_2\textit{i}Pr$	-0.259	0.523	0.987	3.8	18.9	4.2
77	$PMe_2\textit{t}Bu$	-0.293	0.533	1.030	3.8	18.9	4.2
80	$PPhMe_2$	-0.215	0.448	-0.641	4.1	15.9	4.0

81	PMe_2Bn	0.277	0.353	-0.488	4.5	16.5	3.6
82	$PMeEt_2$	-0.476	0.455	0.912	4.0	18.6	4.2
84	PMe*i*Pr_2	0.563	0.646	0.820	3.7	19.2	3.7
85	PMe*t*Bu_2	0.712	0.680	0.818	3.6	19.3	3.7
87	PPh_2Me	-0.231	0.433	-0.836	4.1	15.5	4.0
91	$PPhEt_2$	0.118	0.344	-0.811	4.5	15.8	3.7
94	PPh_2Et	-0.003	0.456	-0.839	4.1	15.6	3.9
99	PPh*i*Pr_2	0.679	0.506	-0.759	4.2	16.3	3.5
100	PPh_2*i*Pr	0.747	0.397	-0.910	4.5	16.1	3.3
103	PAd_2Bu (CataCxium-A)	0.979	0.818	0.735	3.2	19.4	3.6
104	PCy*t*Bu_2	1.026	0.828	0.900	3.2	19.7	3.6
105	PPh*t*Bu_2	1.247	0.738	-0.630	3.6	17.0	3.4
106	P*t*Bu_2Bn	1.506	0.599	-0.427	4.1	17.6	3.0
107	PCy_2*t*Bu	1.064	0.821	0.865	3.2	19.7	3.6
108	PAd_2*t*Bu	1.324	0.918	0.773	3.0	19.7	3.5
118	PPh_2Bn	0.697	0.431	-0.870	4.4	16.1	3.4

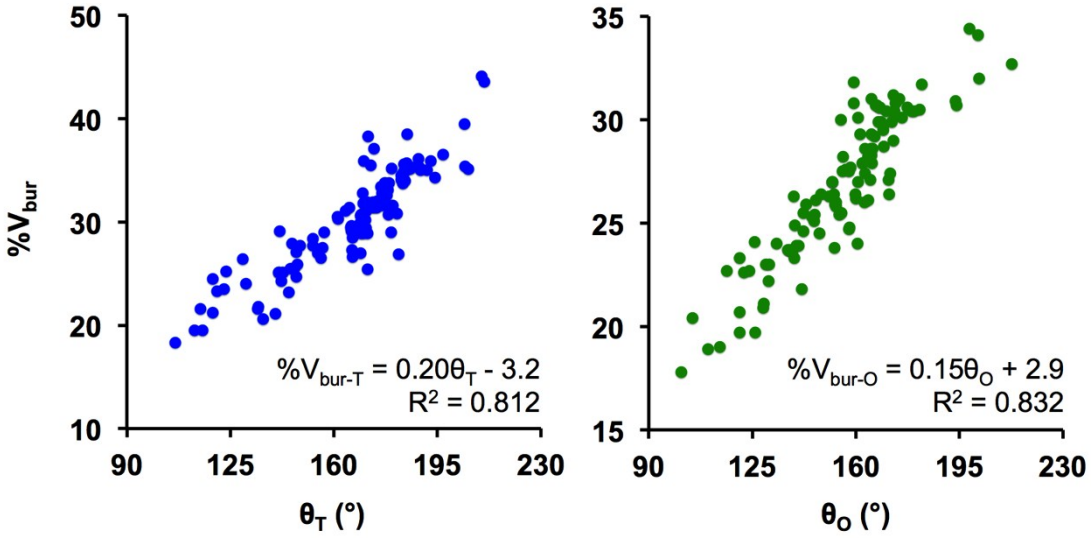


Figure S1. Correlation between the computed tetrahedral (θ_T) and octahedral (θ_O) cone angles and their corresponding $\%V_{Bur}$ descriptors.

Table S7. Force Field parameters used in the MM conformational search

All parameters where taken from the Generalized Amber Force Field (GAFF)[5] except the metal related ones, that have been parameterized using a scan along the corresponding coordinate.

	k(kcal·mol^{-1})	r_{eq}/Å
Au-P	372.999	2.3483
Au-Cl	241.617	2.4435

	k(kcal·mol^{-1})	α_{eq}/º
Au-P-C	153.271	114.5268
Cl-Au-P	53.184	179.941

Van der Waals (Au): Lennard- Jones ε=2.41700, σ=0.2000

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