Electronic Supplementary Information for Dalton Transactions

A Ligand Knowledge Base for Carbenes (LKB-C): Maps of Ligand Space

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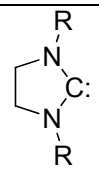
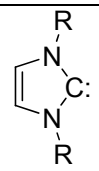
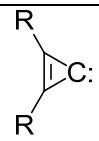
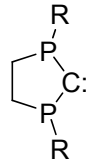
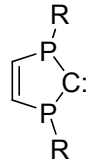
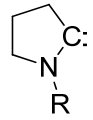
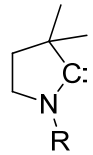
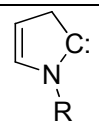
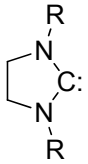
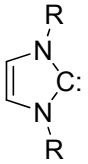
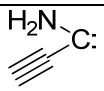
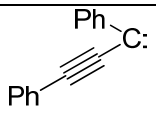
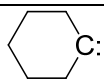
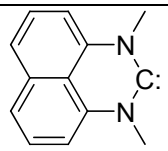
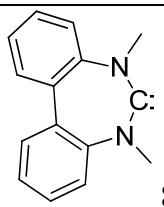
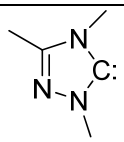
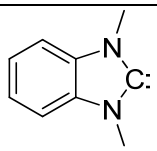
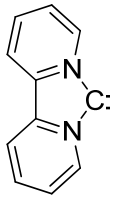
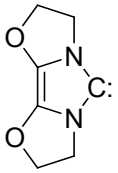
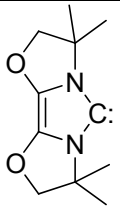
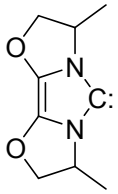
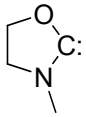
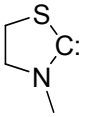
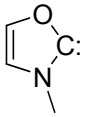
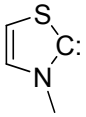
Supporting Information

Table S1: Ligands in LKB-C.

a) symmetrical, R=	H	Me	Ph
:CR_2	1	2	3
	4	5	6
	7	8	9
	10	11	12
	13	14	15
	16	17	18
b) asymmetrical, R=	H	Me	Ph
:CMe(OR)	19	20	21
:CPh(OR)	22	23	24
:CHR	(1)	25	26
:CMeR	(25)	(2)	27
	28	29	30
	31	32	33
	34	35	36
:CR(CH=CH_2)	37	38	39

:CH(CH=C(H)R)	(37)	40	41
:CR($P(NMe_2)_2$)	42	43	44
:C(NMe_2)(PR_2)	45	46	47

c) other species			
	R=cyclohexyl 48 R=^{t}butyl 49 R=adamantyl (Ad) 50 R=2,4,6-Me_3-C_6H_2 (Mes) 51 R=2,6-iPr_2-C_6H_3 52		R=Cy 53 R=^{t}Bu 54 R=Ad 55 R=Mes 56 R=2,6-iPr_2-C_6H_3 57
:C(OMe)($CH=CH_2$) 58	:C(OMe)(CH=C(H)Me) 59	:C($CH=C(H)Me)_2$ 60	:CMe(NH_2) 61
:CMe(NMe_2) 62	:CPh(NMe_2) 63	 64	 65
 66	 67	:$C(CN)_2$ 68	:CMe(CN) 69
:CPh(CN) 70	:CF_2 71	:CCl_2 72	:CBr_2 73
:CI_2 74	:$C(CF_3)_2$ 75	:CMe(CF_3) 76	:CMeCl 77
:C(OMe)(NMe_2) 78	:C(OPh)(NMe_2) 79	:C(SMe)(NMe_2) 80	:C(SPh)(NMe_2) 81
 82	 83	 84	 85
 86	 87	 88	 89
 90	 91	 92	 93
 94	 95	 96	 97

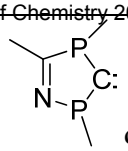
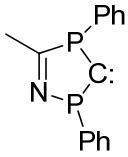
 98	 99	 100	CO 101
CS 102	$C=CH_2$ 103	$C=CMe_2$ 104	$C=CPh_2$ 105
$C=C=CH_2$ 106	$C=C=CMe_2$ 107	$C=C=CPh_2$ 108	$C=C=C=CH_2$ 109
$C=C=C=CMe_2$ 110	$C=C=C=CPh_2$ 111	C≡N-H 112	C≡N-Me 113
C≡N-Ph 114			

Table S2: Descriptor loadings for principal component analysis on carbene ligands.

	PC1	**PC2**	**PC3**	**PC4**
% of variance explained	*41.4*	*16.9*	*12.2*	*7.4*
$E_{HOMO(s)}$	0.201	0.065	0.361	-0.191
$E_{LUMO(s)}$	0.281	0.016	-0.040	0.022
$E_{t\text{-}s}$	0.236	0.035	-0.298	0.072
He_8_steric	0.172	-0.209	-0.014	0.114
PA	0.228	-0.020	0.309	0.035
Q(Au fragm.)	-0.297	-0.040	-0.028	0.040
BE(Au)	-0.055	0.279	0.369	-0.168
Au-Cl	0.237	-0.083	0.296	0.084
Au-C	0.265	-0.176	0.006	0.034
Δ C-A (Au)	-0.013	-0.337	0.258	0.104
Δ A-C-B (Au)	0.039	0.365	-0.022	0.411
Q(Pd fragm.)	-0.268	-0.084	0.010	0.158
BE (Pd)	-0.171	0.242	0.257	-0.158
Pd-Cl *trans*	0.163	0.048	0.425	-0.009
Pd-C	0.199	-0.102	-0.046	0.126
Δ C-A (Pd)	-0.072	-0.304	0.228	0.187
Δ A-C-B (Pd)	0.053	0.342	0.080	0.425
Q(Ru fragm.)	-0.261	-0.107	0.054	0.110
BE (Ru)	-0.246	0.178	0.185	-0.160
Ru-C	0.259	-0.076	-0.041	0.007
Ru-Cl	0.280	0.079	-0.091	-0.102
Ru-P	-0.248	-0.200	0.052	0.170
Δ C-A (Ru)	0.009	-0.220	0.152	0.272
Δ A-C-B (Ru)	0.016	0.325	0.023	0.479
< Cl-Ru-Cl	0.114	0.177	-0.085	-0.219
< P-Ru-P	-0.019	0.134	-0.067	-0.128

Table S3: Descriptor loadings for principal component analysis on all C-donor ligands.

	PC1	PC2	PC3	PC4
% of variance explained	47.7	16.0	13.6	5.9
$E_{HOMO(s)}$	0.218	-0.228	0.265	0.040
$E_{LUMO(s)}$	0.272	0.112	-0.030	-0.053
$E_{t\text{-}s}$	0.163	0.372	-0.167	-0.036
He_8_steric	0.182	-0.063	-0.209	0.525
PA	0.225	-0.224	0.157	0.090
Q(Au fragm.)	-0.294	-0.038	-0.061	0.054
BE(Au)	-0.032	-0.189	0.491	0.135
Au-Cl	0.254	-0.240	-0.058	0.051
Au-C	0.273	-0.120	-0.092	0.020
Δ C-A (Au)	0.042	-0.372	-0.237	-0.193
Q(Pd fragm.)	-0.268	-0.038	-0.099	-0.013
BE (Pd)	-0.156	-0.142	0.397	0.011
Pd-Cl *trans*	0.206	-0.277	0.193	-0.035
Pd-C	0.231	-0.097	-0.080	-0.040
Δ C-A (Pd)	-0.018	-0.367	-0.251	-0.239
Q(Ru fragm.)	-0.260	-0.132	-0.097	0.091
BE (Ru)	-0.239	-0.110	0.293	-0.134
Ru-C	0.269	-0.035	-0.034	0.177
Ru-Cl	0.271	0.168	0.058	-0.079
Ru-P	-0.228	-0.218	-0.218	0.062
Δ C-A (Ru)	0.047	-0.244	-0.238	-0.255
< Cl-Ru-Cl	0.112	0.196	0.170	-0.638
< P-Ru-P	-0.101	0.200	0.110	0.210

Table S4: Descriptor coefficients for regression models 1-3, for prediction of calculated bond energy for dissociation of *trans*-CO in $[Cr(CO)_5L]$ (kcal/mol)

Descriptors	**Coefficients**
Model 1	
Intercept	-22.4479
$E_{t\text{-}s}$	0.0578
Q(Au fragm.)	-15.9614
Ru-C	34.2148
He_8_steric	-0.0473
Model 2	
Intercept	-26.3109
$E_{t\text{-}s}$	0.0581
PA	0.0269
Q(Au fragm.)	-9.2826
BE (Pd)	-0.0688
Ru-C	35.2689
He_8_steric	-0.0662
Model 3	
Intercept	305.2383
E_{HOMO}	-46.7534
$E_{t\text{-}s}$	0.0257
P_A	0.0620
BE (Au)	0.1323
Au-Cl	-55.9431
Au-C	63.1273
BE (Ru)	-0.1231
Ru-P	-119.1609
He_8_steric	-0.0780

Table S5: Calculated response data and model predictions for calculated bond energy for dissociation of *trans*-CO in $[Cr(CO)_5L]$ (kcal/mol)

No.	Calc. BE (trans CO)	Model 1, predicted	Model 1, residual	Model 2, predicted	Model 2, residual	Model 3, predicted	Model 3, residual
1	39.13	39.62	-0.49	37.72	1.41	38.89	0.24
2	41.80	42.86	-1.06	42.33	-0.53	42.08	-0.28
3	43.01	43.97	-0.96	44.38	-1.37	43.74	-0.73
4	50.99	53.38	-2.39	52.83	-1.84	51.98	-0.99
5	52.34	52.25	0.09	52.27	0.07	52.09	0.25
6	50.38	50.00	0.38	50.49	-0.11	50.53	-0.15
7	51.91	52.92	-1.01	52.25	-0.34	52.36	-0.45
8	52.81	53.69	-0.88	53.68	-0.87	52.61	0.20
9	51.54	51.58	-0.04	51.94	-0.40	51.64	-0.10
10	48.08	47.37	0.71	47.42	0.66	47.76	0.32
11	49.30	48.15	1.15	48.26	1.04	48.67	0.63
12	49.61	47.80	1.81	48.13	1.48	49.09	0.52
13	45.20	43.79	1.41	44.40	0.80	45.02	0.18
14	47.33	45.48	1.85	46.13	1.20	45.95	1.38
15	46.45	45.21	1.24	46.20	0.25	45.67	0.78
16	44.84	43.87	0.97	44.49	0.35	45.05	-0.21
17	48.46	45.78	2.68	46.45	2.01	46.48	1.98
18	47.67	45.75	1.92	46.69	0.98	46.39	1.28
19	44.39	45.09	-0.70	45.13	-0.74	44.45	-0.06
20	45.50	46.77	-1.27	45.90	-0.40	46.24	-0.74
21	44.29	44.97	-0.68	44.77	-0.48	44.42	-0.13
22	44.57	47.08	-2.51	46.12	-1.55	46.14	-1.57
23	45.26	46.47	-1.21	46.06	-0.80	46.38	-1.12
24	43.74	44.27	-0.53	44.64	-0.90	45.21	-1.47
25	41.13	41.29	-0.16	40.21	0.92	39.74	1.39
26	42.56	42.87	-0.31	42.79	-0.23	42.81	-0.25
27	41.42	43.18	-1.76	43.14	-1.72	43.40	-1.98
28	48.65	49.21	-0.56	48.78	-0.13	48.72	-0.07
29	49.87	49.58	0.29	49.44	0.43	48.79	1.08
30	48.52	48.58	-0.06	48.87	-0.35	49.10	-0.58
31	49.12	50.00	-0.88	49.76	-0.64	48.88	0.24
32	49.57	49.57	0.00	49.28	0.29	48.50	1.07
33	48.78	48.42	0.36	48.52	0.26	48.12	0.66
34	48.46	48.45	0.01	47.94	0.52	48.81	-0.35
35	49.14	49.27	-0.13	49.16	-0.02	48.98	0.16
36	48.48	48.17	0.31	48.42	0.06	49.13	-0.65
37	41.44	41.90	-0.46	41.22	0.22	41.46	-0.02
38	42.77	43.34	-0.57	42.99	-0.22	42.98	-0.21
39	42.41	44.06	-1.65	44.39	-1.98	44.27	-1.86
40	42.43	42.69	-0.26	42.21	0.22	42.53	-0.10
41	43.11	43.20	-0.09	43.01	0.10	43.45	-0.34
42	40.21	44.29	-4.08	45.58	-5.37	44.25	-4.04
43	45.09	43.22	1.87	43.62	1.47	41.87	3.22

No.	Calc. BE (trans CO)	Model 1, predicted	Model 1, residual	Model 2, predicted	Model 2, residual	Model 3, predicted	Model 3, residual
45	49.45	47.97	1.48	48.03	1.42	48.07	1.38
46	46.19	47.43	-1.24	47.15	-0.96	47.12	-0.93
47	45.42	47.46	-2.04	48.01	-2.59	46.89	-1.47
48	52.60	52.42	0.18	52.16	0.44	52.05	0.55
49	50.52	49.04	1.48	48.68	1.84	48.96	1.56
50	49.35	50.92	-1.57	50.57	-1.22	50.26	-0.91
51	51.72	50.06	1.66	50.49	1.23	51.17	0.55
52	51.46	49.35	2.11	49.87	1.59	51.00	0.46
53	53.74	53.68	0.06	53.55	0.19	53.10	0.64
54	51.54	51.92	-0.38	51.70	-0.16	52.16	-0.62
55	51.20	53.10	-1.90	52.85	-1.65	52.52	-1.32
56	52.43	50.65	1.78	51.07	1.36	52.44	-0.01
57	52.23	52.18	0.05	52.78	-0.55	53.68	-1.45
58	46.06	46.27	-0.21	45.57	0.49	45.78	0.28
59	45.70	46.41	-0.71	45.80	-0.10	45.97	-0.27
60	40.28	43.13	-2.85	43.21	-2.93	43.24	-2.96
61	47.92	48.73	-0.81	48.13	-0.21	48.57	-0.65
62	49.44	49.06	0.38	49.00	0.44	48.56	0.88
63	48.01	48.00	0.01	48.28	-0.27	48.30	-0.29
64	43.25	44.88	-1.63	43.88	-0.63	44.16	-0.91
65	47.12	46.84	0.28	46.92	0.20	47.16	-0.04
66	43.61	43.11	0.50	43.91	-0.30	43.07	0.54
67	44.53	44.02	0.51	44.96	-0.43	44.36	0.17
68	38.41	38.64	-0.23	38.51	-0.10	38.33	0.08
69	40.69	40.27	0.42	39.95	0.74	39.54	1.15
70	42.04	42.01	0.03	42.44	-0.40	42.06	-0.02
71	43.36	44.44	-1.08	43.60	-0.24	43.47	-0.11
72	40.49	40.82	-0.33	41.14	-0.65	41.70	-1.21
73	40.38	39.58	0.80	40.33	0.05	40.19	0.19
74	38.08	39.39	-1.31	40.34	-2.26	39.73	-1.65
75	38.20	38.32	-0.12	38.69	-0.49	38.03	0.17
76	39.98	40.51	-0.53	39.25	0.73	40.24	-0.26
77	41.83	41.37	0.46	41.16	0.67	41.25	0.58
78	50.99	50.46	0.53	49.99	1.00	50.44	0.55
79	49.95	48.69	1.26	48.62	1.33	49.84	0.11
80	50.80	47.84	2.96	47.67	3.13	48.37	2.43
81	49.52	47.35	2.17	47.62	1.90	48.47	1.05
82	42.32	43.33	-1.01	42.89	-0.57	41.73	0.59
83	41.22	41.84	-0.62	41.02	0.20	40.79	0.43
84	42.39	43.23	-0.84	42.80	-0.41	42.60	-0.21
85	41.52	43.18	-1.66	42.21	-0.69	41.92	-0.40
86	51.65	50.93	0.72	50.75	0.90	51.68	-0.03
87	48.26	49.29	-1.03	49.10	-0.84	49.56	-1.30
88	52.38	53.41	-1.03	53.27	-0.89	52.29	0.09
89	52.50	52.25	0.25	52.25	0.25	52.38	0.12

No.	Calc. BE (trans CO)	Model 1, predicted	Model 1, residual	Model 2, predicted	Model 2, residual	Model 3, predicted	Model 3, residual
90	52.76	51.09	1.67	52.17	0.59	50.92	1.84
91	52.70	52.43	0.27	52.36	0.34	52.50	0.20
92	51.62	52.94	-1.32	52.61	-0.99	52.04	-0.42
93	52.46	52.71	-0.25	52.67	-0.21	52.20	0.26
94	51.68	50.33	1.35	50.55	1.13	50.53	1.15
95	50.27	49.21	1.06	49.64	0.63	49.78	0.49
96	50.94	51.04	-0.10	51.31	-0.37	51.39	-0.45
97	50.62	50.50	0.12	50.98	-0.36	51.04	-0.42
98	45.37	46.05	-0.68	46.06	-0.69	45.32	0.05
99	48.18	45.47	2.71	46.05	2.13	46.24	1.94
100	47.28	45.43	1.85	46.26	1.02	46.21	1.07
101	44.58	47.60	-3.02	46.57	-1.99	45.83	-1.25
102	40.61	42.19	-1.58	41.84	-1.23	41.26	-0.65
103	41.26	41.25	0.01	40.63	0.63	39.99	1.27
104	42.61	41.92	0.69	42.22	0.39	42.45	0.16
105	41.57	40.93	0.64	41.49	0.08	41.28	0.29
106	42.79	41.20	1.59	41.20	1.59	42.39	0.40
107	44.57	42.95	1.62	43.34	1.23	44.11	0.46
108	44.97	43.77	1.20	44.56	0.41	45.52	-0.55
109	42.16	41.22	0.94	41.32	0.84	41.41	0.75
110	41.57	41.55	0.02	41.96	-0.39	42.01	-0.44
111	42.37	40.92	1.45	41.40	0.97	41.45	0.92
112	47.22	47.53	-0.31	47.47	-0.25	47.92	-0.70
113	48.42	48.63	-0.21	48.85	-0.43	49.48	-1.06
114	47.62	46.64	0.98	46.98	0.64	47.60	0.02

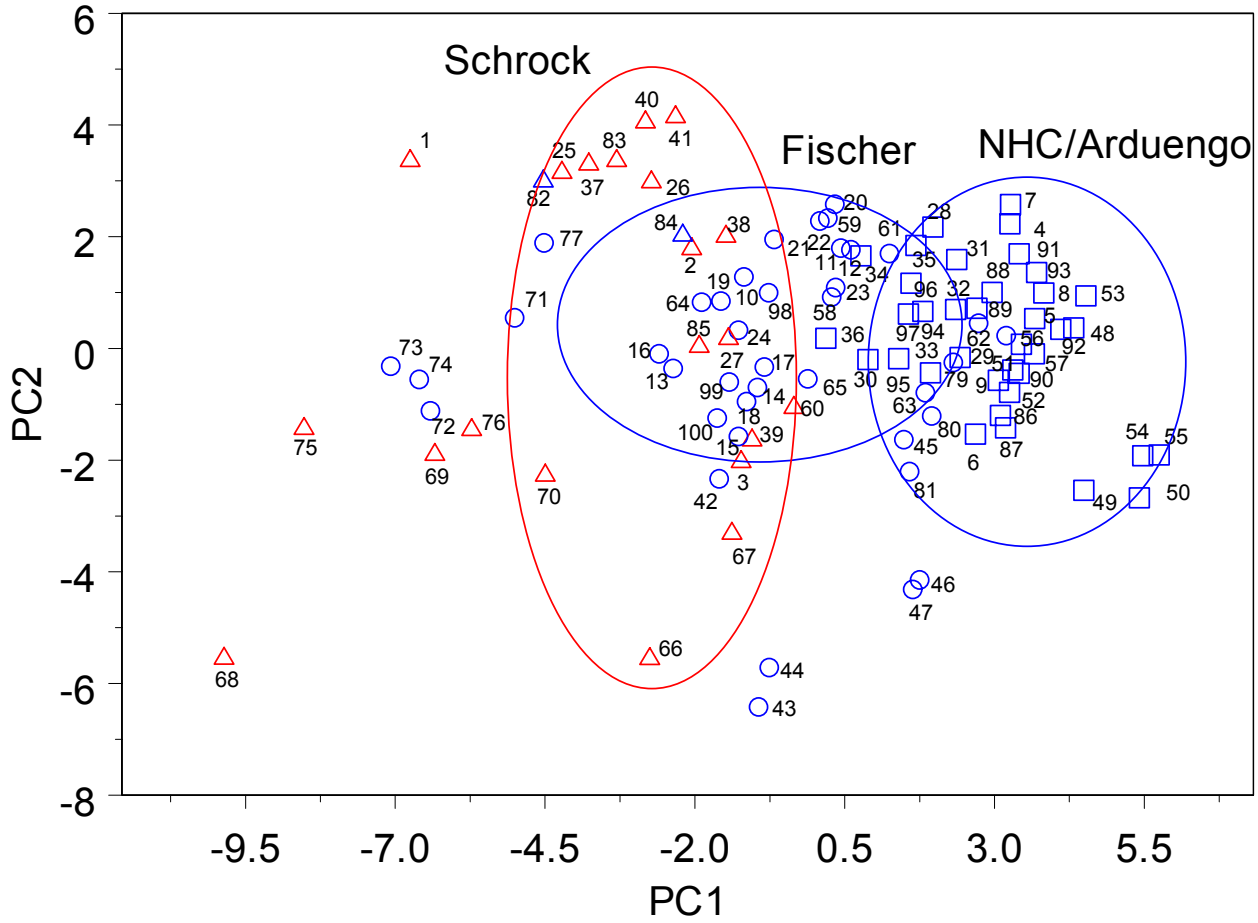


Fig. S1: Principal component score plot (PC1 and PC2) for carbene ligands in LKB-C. Colours distinguish ground state electron configuration of free ligand (red = triplet, blue = singlet), shapes relate to substitution pattern, where triangle, Δ = Schrock-type, circle, ○ = Fischer type, square, □ = NHC/Arduengo.

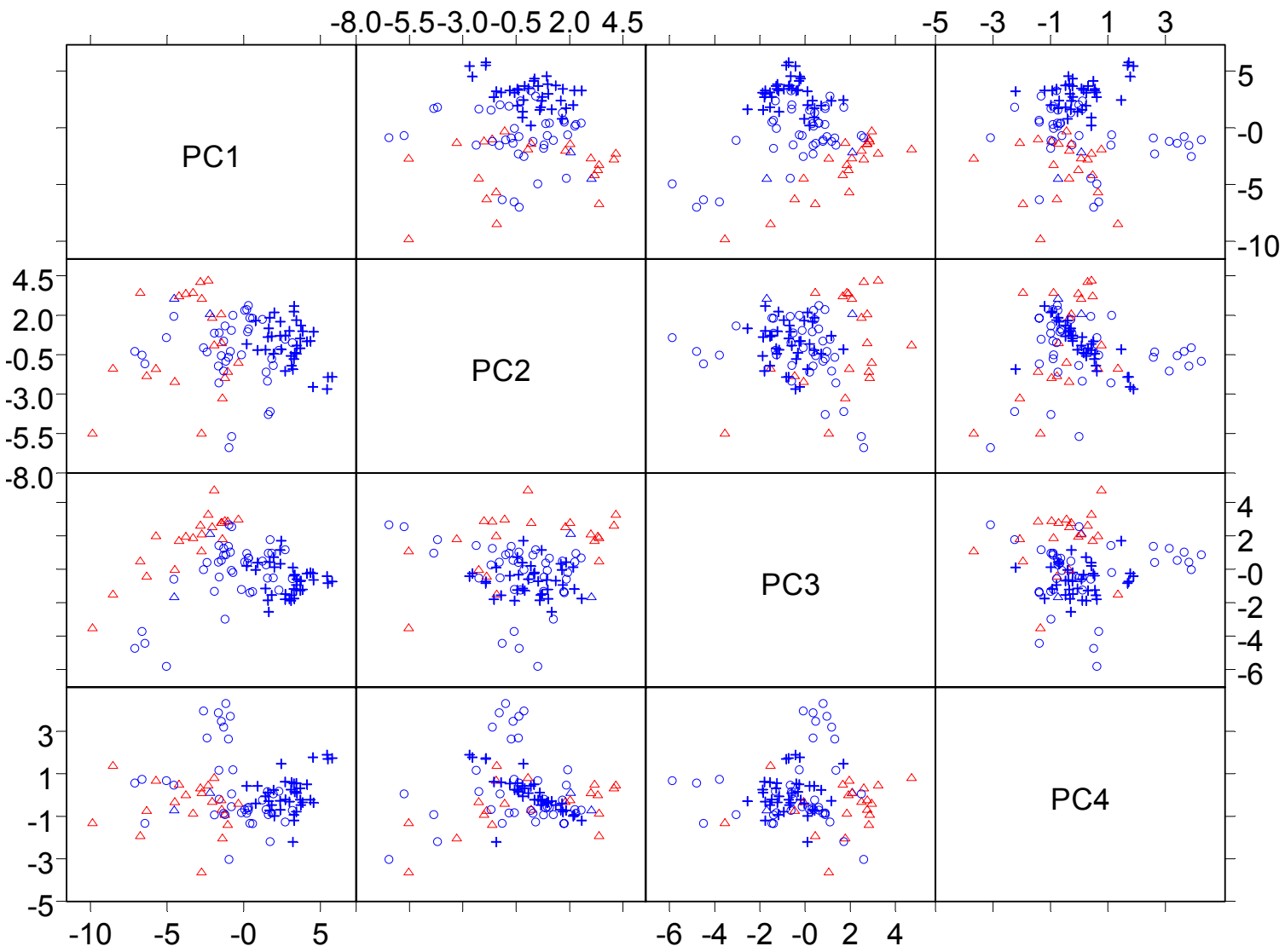


Fig. S2: Matrix plot of PCs 1-4 for principal component analysis of carbene ligands.

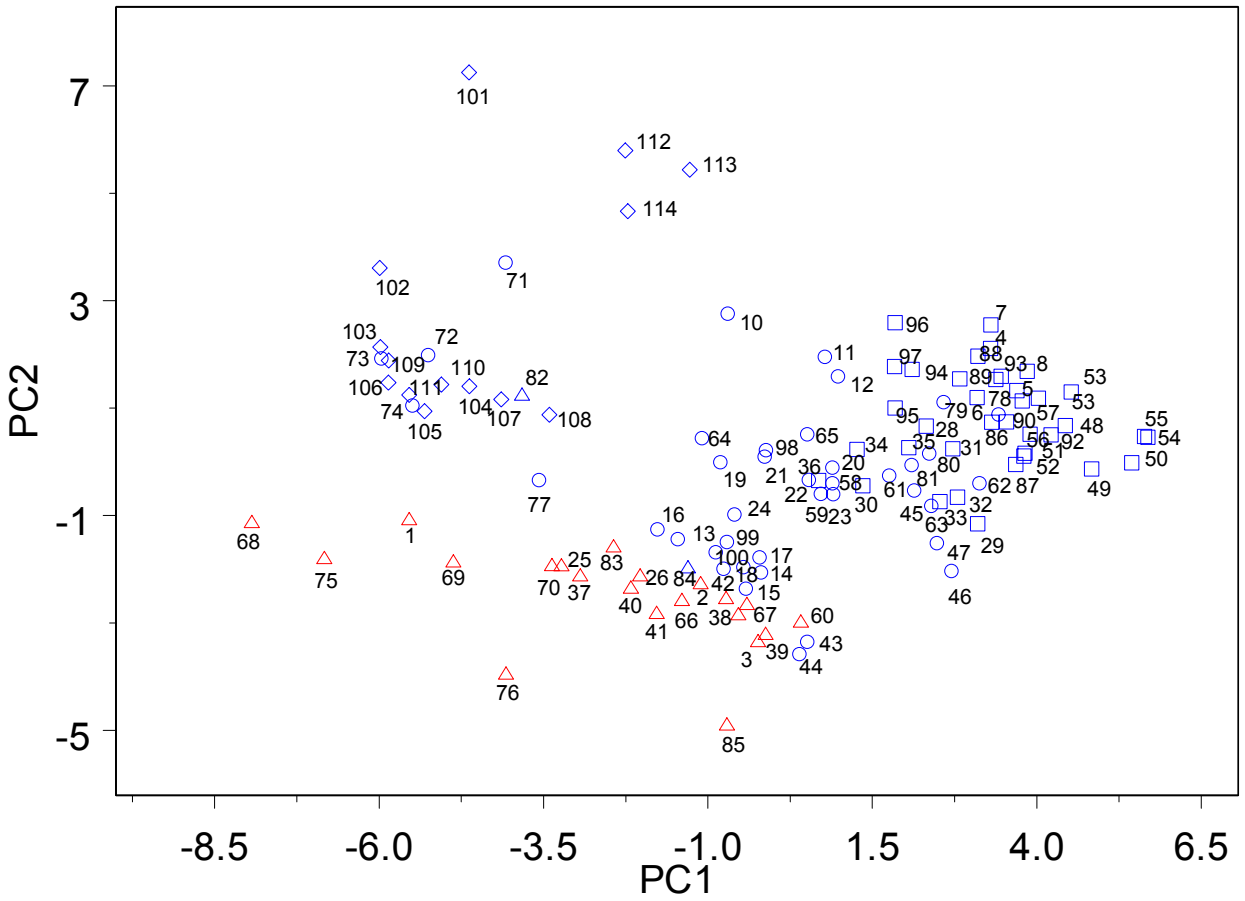


Fig. S3: Principal component score plot (PC1 and PC2) for all ligands in LKB-C. Colours distinguish ground state electron configuration of free ligand (red = triplet, blue = singlet), shapes relate to substitution pattern, where triangle, Δ = Schrock-type, circle, ○ = Fischer type, square, □ = NHC/Arduengo, diamond, ◊ = other ligands.

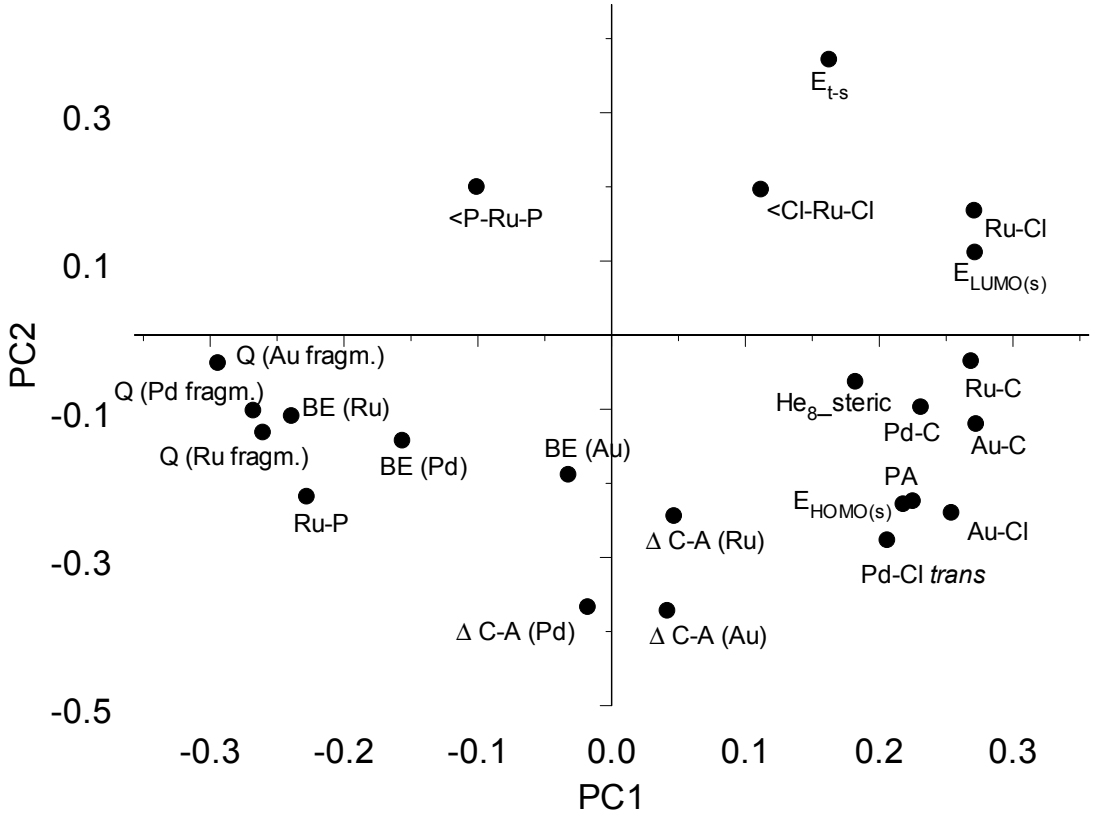


Fig. S4: Principal component loadings (PC1 and PC2) for analysis on all ligands.

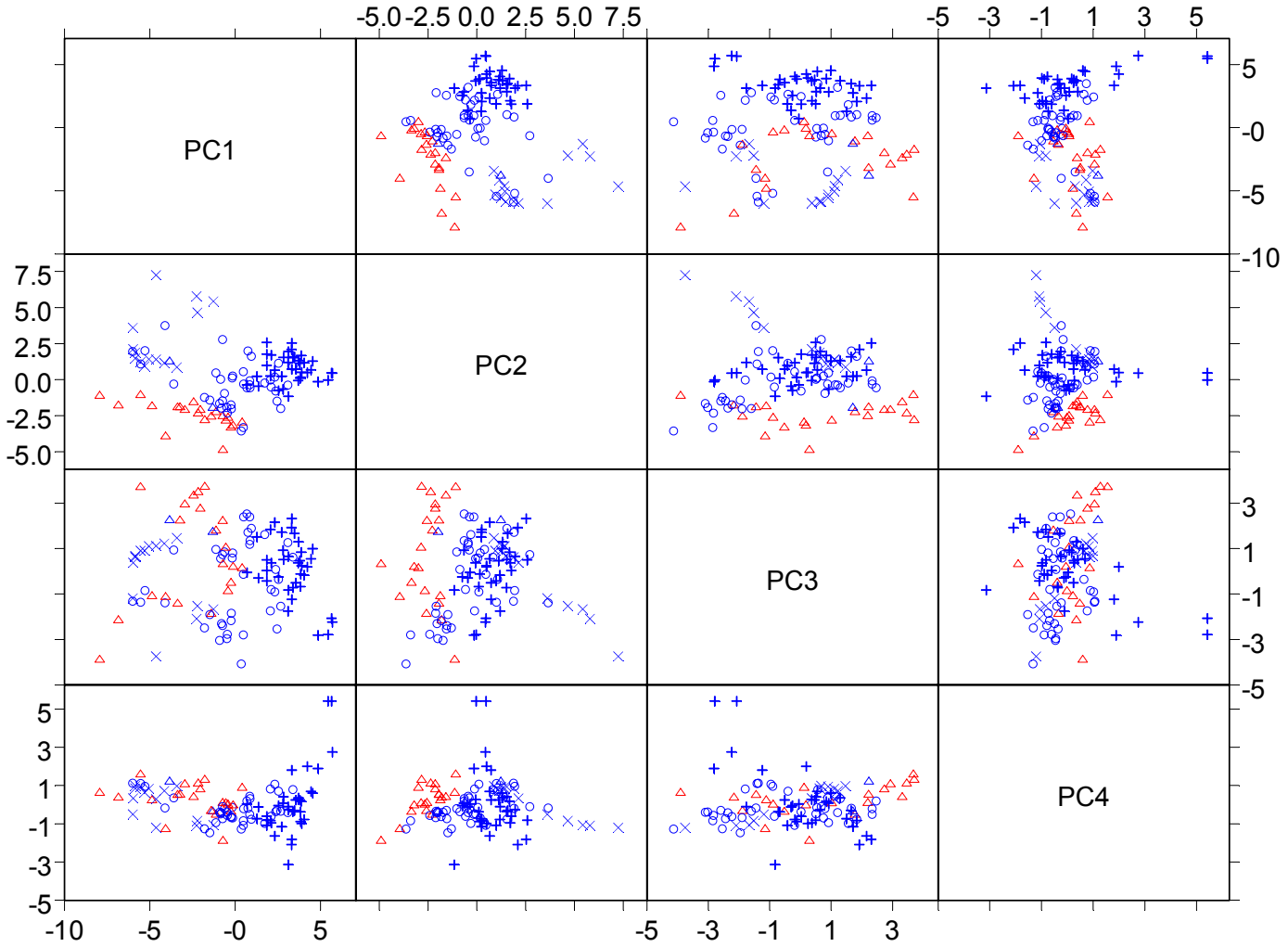


Fig. S4: Matrix plot of PCs 1-4 for principal component analysis of all ligands in LKB-C.