Statistical Modeling of a Ligand Knowledge Base

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Supporting Information

Table S1: Values of Tolman's Electronic Parameter, $A_1 \nu(\text{CO})$ in $[(\text{CO})_3\text{NiL}]$, for LKB; Ligand Weightings in Robust Models

No.	Ligand	TEP (cm^{-1})	From substituent contributions?	Weights in RLM1	Weights in RLM2
1	PH_3	2083.2		0.9992	0.9954
2	PMe_3	2064.1		0.9966	0.9889
3	PEt_3	2061.7		0.9839	0.9975
4	PPr_3				
5	P^iPr_3	2059.2		0.9947	0.9887
6	PBu_3	2060.3		0.9892	0.9545
7	P^tBu_3	2056.1		0.9463	0.9926
8	$\text{P}(\text{CF}_3)_3$	2114.9	✓	0	0.9976
9	PCy_3	2056.4		0.9638	0.8922
10	PBz_3	2066.4		0	0.9727
11	PF_3	2110.8		0.9863	0.9753
12	PCl_3	2097.0		0.8572	0.8998
13	$\text{P}(\text{OMe})_3$	2079.5		0.9639	0.8957
14	$\text{P}(\text{OEt})_3$	2076.3		0.9994	0.6348
15	$\text{P}(\text{OPh})_3$	2085.3		0.8860	0.9494
16	$\text{P}(\text{NH}_2)_3$				
17	$\text{P}(\text{NMe}_2)_3$	2061.9		0.8780	0
18	PPyr_3				
19	$\text{P}(\text{NC}_4\text{H}_8)_3$				
20	PPip_3	2062.1	✓	0.9884	0
21	$\text{P}(\text{CHCH}_2)_3$	2069.5		0.9998	0.9536
22	PPh_3	2068.9		0.9223	0.9297
23	$\text{P}(\text{C}_6\text{F}_5)_3$	2090.9		0.8792	0.9310
24	$\text{P}(\text{o-Me-Ph})_3$	2066.6		0.9969	0.9761
25	$\text{P}(\text{m-Me-Ph})_3$	2067.2		0.9903	0.9790
26	$\text{P}(\text{p-Me-Ph})_3$	2066.7		0.9414	0.6049
27	$\text{P}(\text{o-MeO-Ph})_3$	2058.3		0.9839	0.9577
28	$\text{P}(\text{p-MeO-Ph})_3$	2066.1		0.8070	0.2423
29	$\text{P}(3,5\text{-(CF}_3)_2\text{-Ph})_3$				
30	$\text{P}(\text{p-F}_3\text{C-Ph})_3$				
31	$\text{P}(\text{p-F-Ph})_3$	2071.3			0.9559
32	$\text{P}(\text{p-Cl-Ph})_3$	2072.8			0.9954
33	$\text{P}(\text{p-Me}_2\text{N-Ph})_3$				
34	PHF_2	2100.8	✓	0.6095	0.9341
35	PFH_2	2090.9	✓	0.9640	0.9132
36	PHCl_2	2094.0	✓	0.9186	0.9333
37	PCIH_2	2087.5	✓	0.9575	0.9685
38	PMeF_2	2095.1	✓	0.8246	0.7916
39	PFMe_2	2079.5	✓	0.7160	0.9988
40	PMeCl_2	2088.3	✓	0.9183	0.7530
41	PClMe_2	2076.1	✓	0.9504	0.9969
42	$\text{PMe}(\text{CF}_3)_2$	2097.9	✓	0	0.6639
43	$\text{P}(\text{CF}_3)\text{Me}_2$	2080.9		0.6743	0.8758

Table S1 (Cont'd)

No.	Ligand	TEP (cm ⁻¹)	From substituent contributions?	Weights in RLM1	Weights in RLM2
44	PMe ^t Bu ₂	2058.7	✓	0.9999	0.8634
45	P ⁱ BuMe ₂	2061.3	✓	0.9821	0.9806
46	PMePh ₂	2067.0		0.9596	0
47	PPhMe ₂	2065.3		0.9708	0.9772
48	PEtPh ₂	2066.7		0.8646	0.9607
49	PPhEt ₂	2063.7		0.9974	0.9963
50	PCyPh ₂	2064.8	✓	0.8455	0.9885
51	PPhCy ₂	2060.5	✓	0.9742	0.7346
52	PPyrPh ₂				
53	PPhPyr ₂				
54	P(o-Me-Ph)Ph ₂	2068.2	✓	0.9958	0.9840
55	PPh(o-Me-Ph) ₂	2067.4	✓	0.9975	0.9990
56	P(o-MeO-Ph)Ph ₂	2066.1		0.9910	0.9959
57	PPh(o-MeO-Ph) ₂	2062.2	✓	0.9870	0.9981
58		2087.3		0.7472	0.9979
59
60	.				
61	.				

Table S2: Descriptor Coefficients for TEP Models (OLS, RLM, LASSO, LAR)

Descriptor	Coefficient
<i>Model: OLS</i>	
(Intercept)	2555.28
PA	-0.52
LP s-character	-0.65
Q(Pt fragm.)	-47.79
$\Delta A-P-A(Pd)$	-2.18
P-B	253.16
P-Pt	-350.17
<i>Model: RLM1</i>	
(Intercept)	3263.42
PA	-0.39
LP s-character	-0.64
Q(Pt fragm.)	41.06
BE(Pd)	-0.24
$\Delta A-P-A(Pd)$	-1.73
P-Pd	-68.74
P-Pt	-174.22
He ₈ _steric	0.34
Pd-Cl trans	-209.44
<i>Model: RLM2</i>	
(Intercept)	2605.61
E _{HOMO}	-215.36
Q(Pt fragm.)	-9.98
$\Delta P-A(B)$	528.37
$\Delta A-P-A(Pt)$	-0.94
P-Pt	-243.71
He ₈ _steric	0.16
<i>Model: LASSO</i>	
PA	-6.33
E _{HOMO}	-2.78
LP s-character	-2.73
BE(B)	-0.73
BE(Pd)	-0.05
$\Delta P-A(B)$	1.86
$\Delta P-A(Pt)$	-1.26
$\Delta A-P-A(B)$	-0.25
$\Delta A-P-A(Pd)$	-1.72
$\Delta A-P-A(Pt)$	-0.17
P-B	0.52
P-Pt	-10.04
He ₈ _steric	1.78
$<(H_3P)Pt(PH_3)$	-0.20

Table S2: Cont'd

Descriptor	Coefficient
<i>Model: LAR</i>	
PA	-1.86
EHOMO	-4.95
ΔP -A(B)	1.46
ΔA -P-A(B)	-0.86
ΔA -P-A(Pd)	-0.31
P-Pt	-6.46
Pd-Cl trans	-1.09

Figure S1: Diagnostic Plot for OLS Model.

Figure S2: Cont'd, b) RLM2

Figure S3: Diagnostic Plots for LASSO and LAR

a) LASSO, i) Plot of 10-fold Crossvalidation Values against Tuning Parameter

ii) Cross-validation Estimates of Prediction Error

Figure S3: Cont'd

b) LAR, i) Plot of 10-fold Crossvalidation Values against Tuning Parameter

ii) Cross-validation Estimates of Prediction Error

Figure S4: Diagnostic Plots for PCR Model.
i) Cross-validation Estimates of Prediction Error

ii) Residuals vs. Fitted

Figure S5: Diagnostic Plot for PLS Model
i) Cross-validation Estimates of Prediction Error

ii) Residuals vs. Fitted