Supporting information for Estimating the acidity of transition metal hydride and dihydrogen complexes by adding ligand acidity constants

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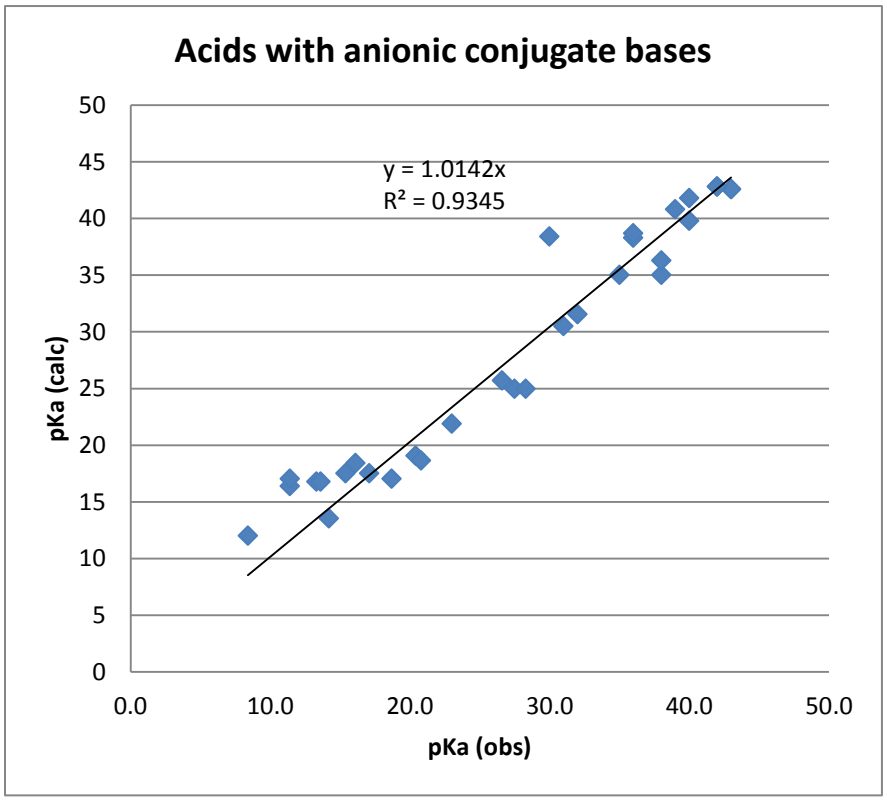
Spreadsheet.

An Excel spreadsheet with two tabs (see the bottom of the spreadsheet) is available separately that contains the data for Tables 2 and 3 as well as linked formulae, standard deviations, etc. There is one tab labelled "Ligands" for Table 2 and one tab labelled "Complexes" for Table 3.

Data for the C_{charge} = 30 for acids with anionic conjugate bases.

Entry	Acid	Base	Solvent	pK_a in solvent	Calc pK_a
1	CoH(PPh2CH2CH2PPh2)2	[Co(dppe)2]-	MeCN	38.0	35
2	CoH(CO)3(PPh3)	[Co(CO)3(PPh3)]-	MeCN (H2O)	15.4	18
3	CoH(CO)3(P(OPh)3)	[Co(CO)3(P(OPh)3)]-	MeCN (H2O)	11.4	16
5	CoH(CO)4	[Co(CO)4]-	MeCN (H2O, MeOH)	8.4	12
6	Cr(H)(Cp)(CO)3	[Cr(Cp)(CO)3]-	MeCN	13.3	17
8	Fe(Cp*)(CO)2H	K[Fe(Cp*)(CO)2]	THF	31.0	31
9	Fe(Cp)(CO)2H	[HNEt3][Fe(Cp)(CO)2]	MeCN	27.5	25
15	FeH2(CO)4	[FeH(CO)4]-	MeCN (H2O)	11.4	17
27	Ir(H)2(Cp*)(PMe3)	(Li)IrH(Cp*)(PMe3)	THF	40.0	40
28	IrH5(PCy3)2	Q+[cis-IrH4(PCy3)2]-	THF	43.0	43
29	IrH5(PiPr3)2	Q+[cis-IrH4(PiPr3)2]-	THF	43.0	43
47	MnH(CO)4(PPh3)	[HNEt3][Mn(CO)4(PPh3)]	MeCN	20.4	19
48	MnH(CO)5	[H(morpholine)][Mn(CO)5]	MeCN	14.2	14
49	Mo(H)(Cp*)(CO)3	[Mo(Cp*)(CO)3]-	MeCN	17.1	18
50	Mo(H)(Cp)(CO)3	[Mo(Cp)(CO)3]-	MeCN	13.6	17
64	Os(H2)(H)2(CO)(PiPr3)2	Z+[OsH3(CO)(PiPr3)2]-	THF	36	38
65	Os(Cp)(CO)2H	[Os(Cp)(CO)2]-	THF	32.0	32
66	OsH2(CO)4	[OsH(CO)4]-	MeCN	20.8	19
96	ReH7(PCy3)2	[ReH6(PCy3)2]-	THF	42	43
97	ReH7(PPh3)2	[ReH6(PPh3)2]-	THF	30	38
98	ReH5(PMePh2)3	[ReH4(PMePh2)3]-	THF	40	42
99	ReH2(Cp)(CO)2	[ReH(Cp)(CO)2]-	MeCN	23.0	22
109	RhH(dppb)2	[Rh(dppb)2]-	MeCN	35.0	35
120	RuH2(H2)2(PiPr3)2	Q+[RuH5(PiPr3)2]-	THF	39	41
121	RuH2(H2)(CO)(PiPr3)2	(Q+ or Z+)[RuH3(CO)(PiPr3)2]-	THF	38	36
122	RuH2(H2)(PPh3)3	Q+[RuH3(PPh3)3]-	THF	36	39

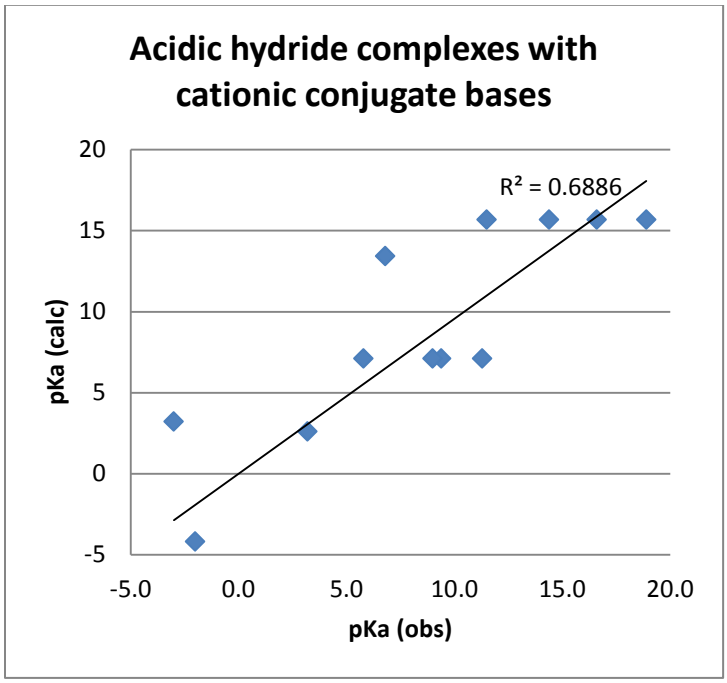
123	Ru(Cp)(CO)2H	[HNEt3][Ru(Cp)(CO)2]	MeCN	28.3	25
124	RuH2(CO)4	[RuH(CO)4]-	MeCN	18.7	17
165	[WH6(PMe2Ph)3	[WH5(PMe2Ph)3]-	THF	42	43
166	W(Cp)(CO)2(PMe3)H	K[W(Cp)(CO)2(PMe3)]	MeCN	26.6	26
167	W(H)(Cp)(CO)3	[W(Cp)(CO)3]-	MeCN (H2O, CH3OH)	16.1	18



Data for the C_{charge} = -15 for acids with cationic conjugate bases.

Entry	Acid	Base	Solvent	pK_a in solvent	Calc pK_a
4	[CoH(PPh2CH2CH2PPh2)2(CH3CN)](BF4)2	[Co(dppe)2]+	MeCN	11.3	7
87	trans-[Os(H2)(CH3CN)(PPh2CH2CH2Ph2)2]2+	trans-[OsH(CH3CN)(dppe)2]+	CH2Cl2	-3	3
95	[PtH2(EtXantphos)2] 2+	[PtH(EtXantphos)2] +	MeCN	6.8	13
111	[Rh(H)(PMe2CH2CH2PMe2)2(CH3CN)]2+	[Rh(dmpe)2]+	MeCN	18.9	16
112	[RhH(CH3CN)(PEt2CH2CH2PEt2)2]2+	[Rh(depe)2]+	MeCN	16.6	16
113	[RhH(CH3CN)(PEt2CH2CH2CH2PEt2)2]2+	[Rh(depp)2]+	MeCN	14.4	16
114	[RhH(CH3CN)(PEt2CH2C6H4CH2PEt2)2]2+	[Rh(depx)2]+	MeCN	11.5	16
115	[RhH(CH3CN)(dppb)2]2+	[Rh(dppb)2]+	MeCN	9.4	7
116	[RhH(CH3CN)(PPh2CH2CH2PPh2)2]2+	[Rh(dppe)2]+	MeCN	9.0	7
118	[RhH(CH3CN)(dppp)2]2+	[Rh(dppp)2]+	MeCN	5.8	7

159	[Ru(H2)(PPh3)2(Cn)] 2+	RuH(PPh3)2(Cn)]+	CH2Cl2	3.2	3
164	[Ru(H2)(PPh3)(CO)(Cn)] 2+	RuH(PPh3)(CO)(Cn)] +	CH2Cl2	-2	-4



Values of C_{charge} -14 or -16 give significantly larger deviations. The scatter is due to many factors including ligands with large bite angles (entries 95, 114) and approx. pKa values for a protonated ether reference (entry 87).