

Supporting Information: DFT methods applied to answer the question: how accurate is the Ligand Acidity Constant method for estimating the pK_a of transition metal hydride complexes $MHXL_4$ when X is varied?

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S1 Special Geometries

As mentioned in Tab. 1 of the main article there were two optimized $\text{MHX}(\text{CO})_4$ structures for which it was not possible to characterize them as either *cis* or *trans* according to the nomenclature shown in Fig. 3 of the main article. These two structures of $\text{FeHB}(\text{CH}_3)_2(\text{CO})_4$ and $\text{FeHN}(\text{CH}_3)_2(\text{CO})_4$ are shown in Fig. S1. Both structures were obtained from PBE0-D3BJ/def2-TZVP{ECP:def2-SD}+COSMO-RS(THF) structure optimizations. The structures obtained with PBE0-D3BJ/def2-QZVP{ECP:def2-SD}+DCOSMO-RS(THF) were virtually identical.

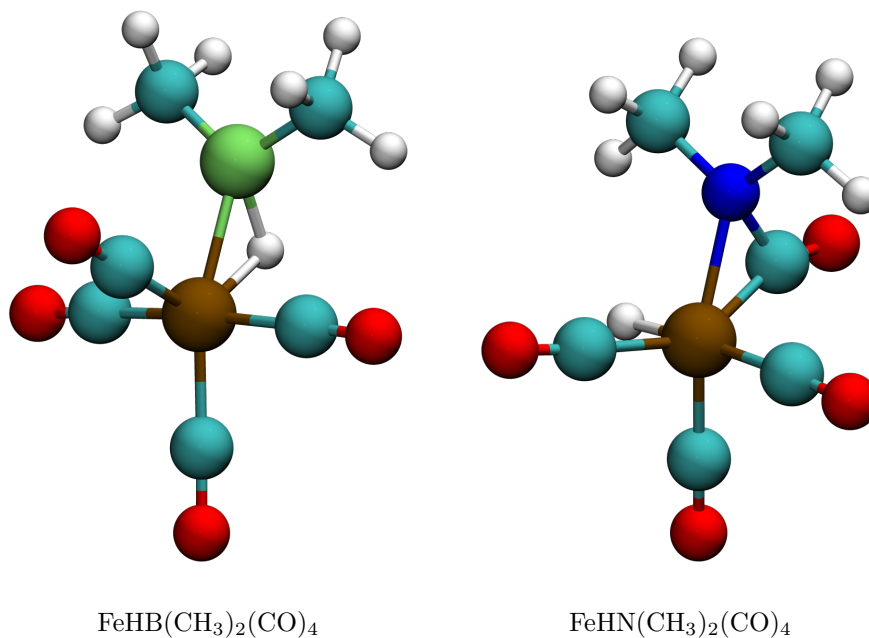


Figure S1: Geometries of $\text{FeHB}(\text{CH}_3)_2(\text{CO})_4$ and $\text{FeHN}(\text{CH}_3)_2(\text{CO})_4$ calculated PBE0-D3BJ/def2-TZVP{ECP:def2-SD}+COSMO-RS(THF)

S2 Correlation of A_L and Levers's Electrochemical Ligand Parameter E_l

When correlating the A_L values of anionic ligands with Levers's Electrochemical Ligand Parameter E_l it is possible to identify a similar trend as shown when correlating the A_L values of neutral ligands with Levers's Electrochemical Ligand Parameter. When shifting the anionic ligands by +13.116 V (difference of offsets in linear regression) a general correlation can be observed. This procedure is shown Figure S4.

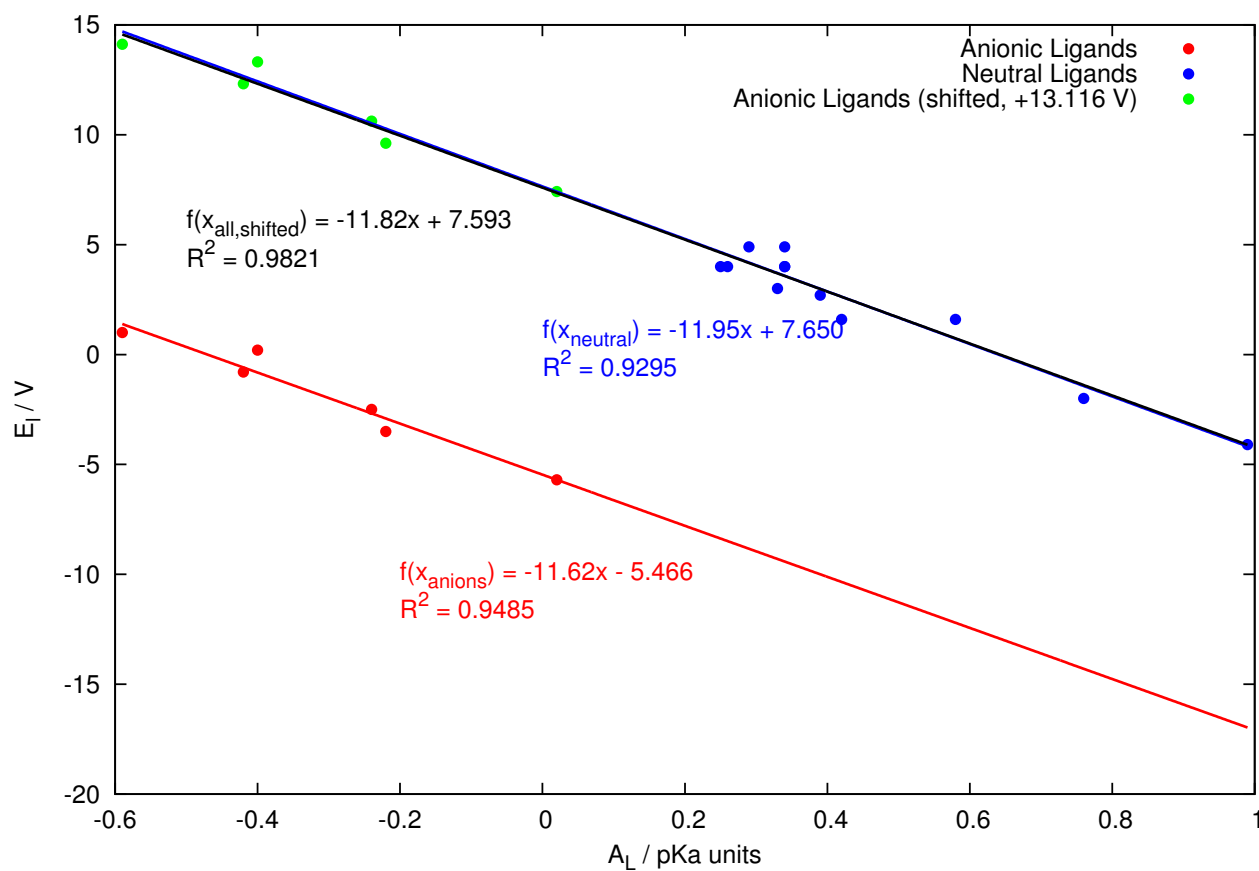


Figure S2: LAC ligand parameters A_L vs. Levers's Electrochemical Ligand Parameter E_l including linear regression.

S3 Additional Natural Charges Analysis

In addition to the simpler $[\text{Fe}(\text{CO})_4\text{XH}]$ set of complexes, where X^- can be any halide, the natural charges for the halides in $[\text{Ru}(\text{PR}_3)_4\text{XH}]$ were also calculated, and are shown in Table S1.

Table S1: Natural charges (partial charges) obtained from NPA/NBO analysis.

X^-	A_L^{DFT}	El. Neg.	Natural Charges of X^-		
			$[\text{Ru}(\text{PR}_3)_4\text{XH}]$	$[\text{Ru}(\text{PR}_3)_4\text{X}]^-$	Δ
F^-	-0.8	3.98	-0.78	-0.74	-0.03
Cl^-	-2.5	3.16	-0.66	-0.73	0.08
Br^-	-3.5	2.96	-0.62	-0.73	0.10
I^-	-4.8	2.66	-0.57	-0.72	0.15

S4 Detailed Validation Results

In order to assess the error of the methodology used for this article a large part of the structures were re-calculated using a bigger basis set and an improved implicit solvation model. The results of these calculations are shown in Tab. S2, the additional calculations for the CO ligand using the standard basis set and solvation model (def2-TZVP and COSMO-RS) are shown in Tab. S3. When comparing all results for L = CO of Tab. S2 and Tab. 1 of the main article [excluding the $X^- = H^-$ calculations which serve as references] a mean absolute difference of 0.3 pK_a units between the two data sets is calculated.

Table S2: Ligand parameters (A_L^{DFT}) in reference to H^- . Method: PBE0-D3BJ/def2-QZVP{ECP:def2-SD}+DCOSMO-RS(THF).

Ligands L Ligand X^-	(CO) ₄				(PR ₃) ₄				A_L^{DFT}	A_L^{LAC}
	Fe	Ru	Os	avg.	Fe	Ru	Os	avg.		
CH ₃ ⁻	1.5	1.6	1.9	1.7	-	-	-	-	-	-
NH ₂ ⁻	1.4	1.3	2.2	1.6	-	-	-	-	-	-
OH ⁻	-0.1	0.6	0.9	0.5	-	-	-	-	-	-
OC(CH ₃) ₃ ⁻	-1.4	-1.2	0.0	-0.9	-	-	-	-	-	-
H ⁻	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
B(OCH ₂ -) ₂ ⁻	0.2	0.6	0.5	0.5	-	-	-	-	-	-
F ⁻	-3.9	-3.2	-1.9	-3.0	-	-	-	-	-	-
OCH ₃ ⁻	-2.1	-2.6	-1.0	-1.9	-	-	-	-	-	-
SH ⁻	-3.0	-2.1	-1.5	-2.2	-	-	-	-	-	-
B(CH ₃) ₂ ⁻	†	1.2	0.7	1.0	-	-	-	-	-	-
N(CH ₃) ₂ ⁻	†	-0.3	-0.7	-0.5	-	-	-	-	-	-
Cl ⁻	-5.9	-4.7	-3.5	-4.7	-	-	-	-	-	-6.0
SCH ₃ ⁻	-2.0	-1.5	-0.8	-1.5	-	-	-	-	-	-
P(CH ₃) ₂ ⁻	-1.1	-0.8	-0.6	-0.8	-	-	-	-	-	-
Br ⁻	-6.2	-4.9	-3.8	-5.0	-	-	-	-	-	-
I ⁻	-6.4	-5.2	-4.2	-5.3	-	-	-	-	-	-
CN ⁻	-8.9	-7.2	-6.4	-7.5	-	-	-	-	-	-11.0
SiCl ₃ ⁻	-11.0	-9.1	-8.3	-9.4	-	-	-	-	-	-12.0
CO*	-3.7	-0.5	1.9	-0.8	-3.8	-2.1	-4.0 [‡]	-3.3	-2.0	-4.1

Values given, assuming $\Delta C_{charge}^ = 30$.

†Geometries discussed in Sec. S1 and shown in Fig. S1, values removed from study.

‡The geometry of $[OsH(trans-CO)(PR_3)_4]^+$ did not fully converge and had two small imaginary frequencies remaining. The optimization oscillated within less than 0.3 kJ/mol and the remaining unoptimized modes corresponded to concerted methyl rotations in the backbone. But even assuming a variation of ± 0.5 kJ/mol, the value reported for this ligand as well as the average values reported in the table above remain unchanged. Hence we decided to include this value in our statistics, in spite of the incomplete convergence.

Table S3: Ligand parameters (A_L^{DFT}) for CO, in reference to H^- . Method: PBE0-D3BJ/def2-TZVP{ECP:def2-SD}+COSMO-RS(THF).

Ligands L Ligand X^-	(CO) ₄				(PR ₃) ₄				A_L^{DFT}	A_L^{LAC}
	Fe	Ru	Os	avg.	Fe	Ru	Os	avg.		
CO*	4.4	7.9	10.9	7.7	1.8	3.1	3.0	2.6	5.2	-4.1

* Values given, assuming $\Delta C_{charge}^* = 30$.

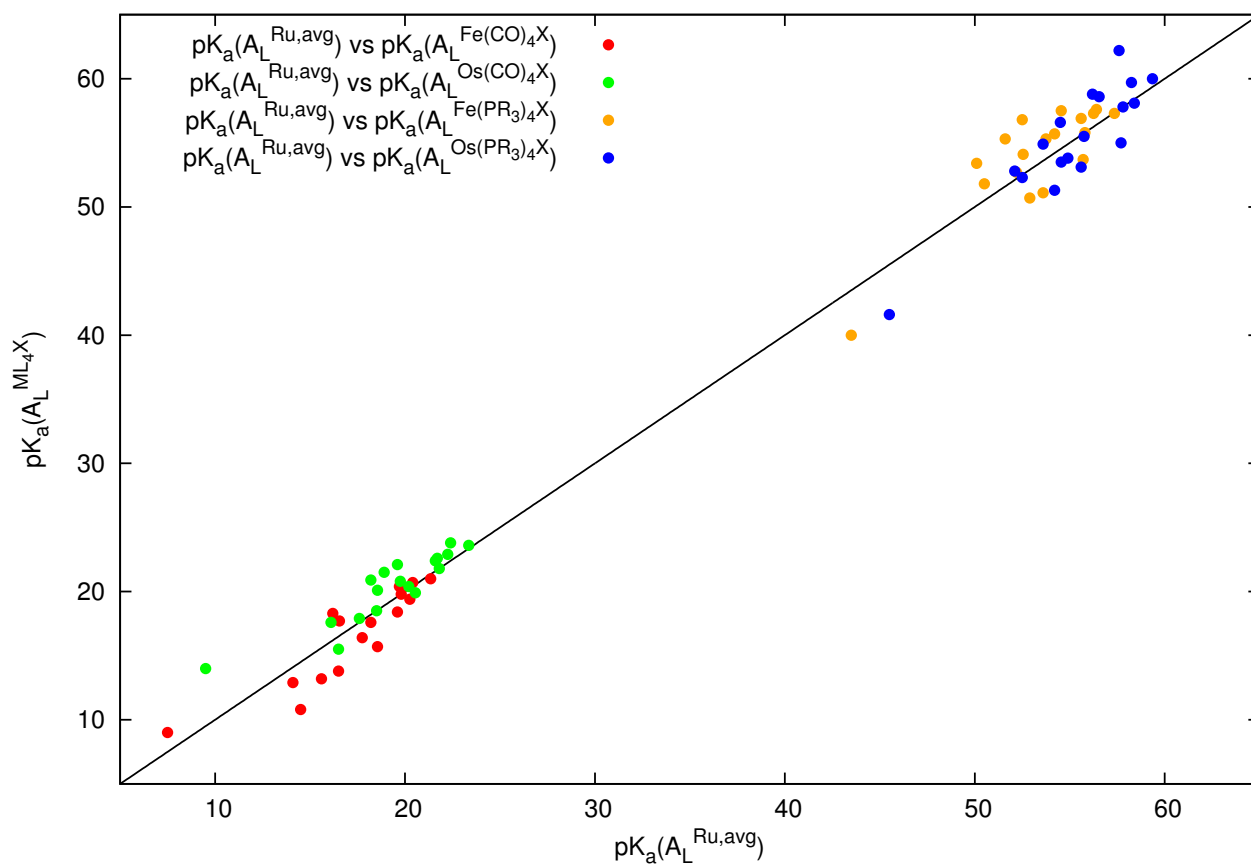


Figure S3: Correlation of $\text{p}K_a$ values calculated using an average A_L^{DFT} from all calculations of Ruthenium complexes and $\text{p}K_a$ values calculated using the A_L^{DFT} values resulting from calculations on different metals.

S5 Energies and Geometries

In addition to this document two other files are part of the SI. A file named `energies.txt` and a compressed archive `structures.tar`. The first contains a list of all Gibbs energies in solution ΔG , for all data sets used. The latter contains all optimized geometries as `.xyz` files in a sorted folder structure.