

European Journal of Inorganic Chemistry

Supporting Information

Cooperative Dinitrogen Activation: Identifying the Push-Pull Effects of Transition Metals and Lewis Acids in Molecular Orbital Diagrams

Frederico F. Martins and Vera Krewald*

Contents

Additional structures of Lewis acids	p. 2
Lewis acidity	p. 3
FIA/HIA Calculations	p. 5
Table S1. Data required for the fluoride affinity calculation	
Table S2. Data required for the hydride affinity calculation	
Correlations with HIAs	p. 7
Thermochemistry of adduct formation	p. 8
Table S3. Thermochemistry of adduct formation	
Description of the N-N bond in Metal-N ₂ -LA adducts	p. 6
Table S4. Mayer Bond Orders and N-N stretching frequencies	
Table S5. NBO analysis of three LA adducts	
Frontier orbitals	p. 11
Table S6. Relative energies of the competitive binding of the LA	
Electrochemistry	p. 12
Table S7. Calculated Gibbs energies for the anchor complex S1	
Table S8. Mulliken spin populations on the rhenium ion for the Lewis acid adducts studied in different oxidation states.	

Additional supporting data is provided at the ioChem-BD database with the DOI: [10.19061/iochem-bd-4-56](https://doi.org/10.19061/iochem-bd-4-56)

Additional structures of Lewis acids

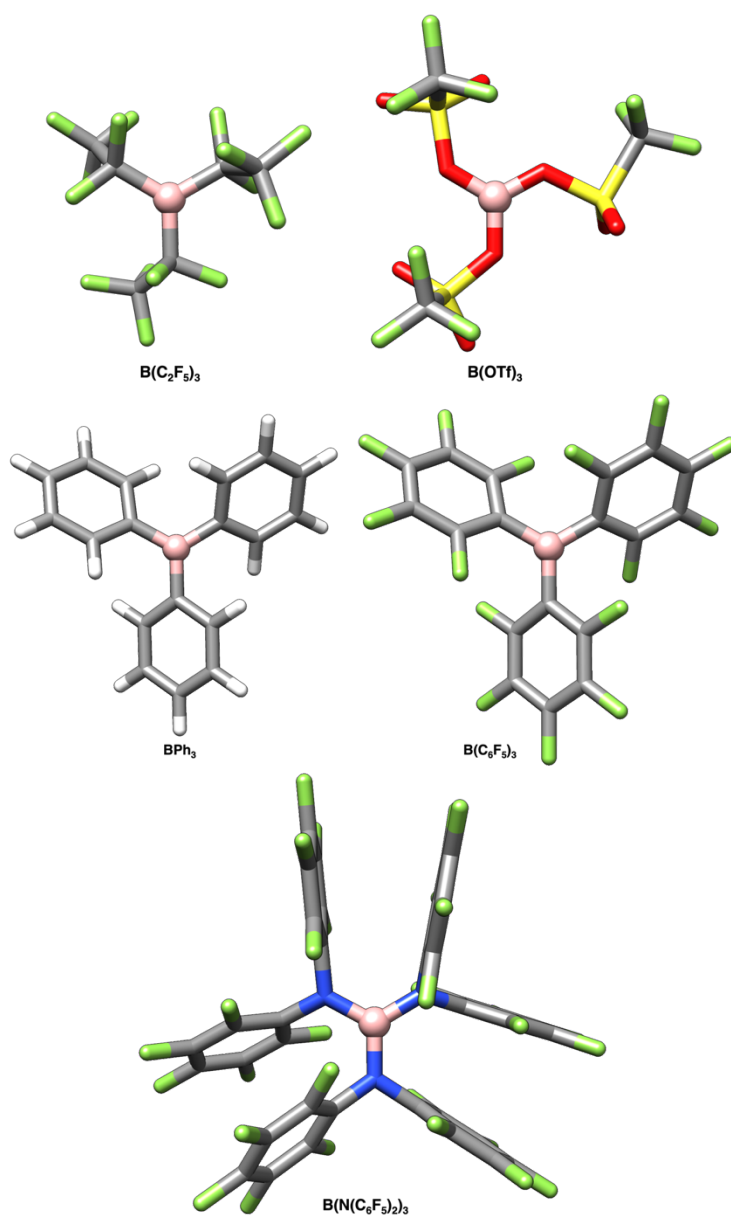


Figure S1. Three dimensional structures of the bulkier Lewis acids not shown in the main text.

Lewis Acidity

Experimental attempts to devise a Lewis acidity scale have relied on measuring the change of a physical property, such as luminescence, NMR shifts or IR bands, when binding the same molecular entity to different Lewis acids (LAs).¹⁻⁵ Computational efforts have followed a similar approach by calculating the relative thermodynamic stability of binding the same electron donor, usually the fluoride or the hydride anion, to a range of LAs. These are known as the fluoride ion affinity (FIA)^{6,7} and the hydride ion affinity (HIA)⁸ and the accuracy of these calculations has improved over the years.^{6, 9, 10} The fluoride ion is a good proxy of a nonpolarizable base and the hydride of a polarizable base, such as a transition metal complex.¹¹ However, the literature on the latter is limited with a focus on hydrocarbon-based LAs.¹²⁻¹⁵

One of the latest contributions to this field were FIA calculations by Greb and coworkers¹⁶ who applied coupled cluster and its domain-based local pair natural orbital variant¹⁷⁻¹⁹ to a series of LAs containing halide, carbon and oxygen-based groups with group 13-15 central atoms. Although the accuracy of such a high-level method is remarkable, we have used it here to benchmark a computationally less demanding Density Functional Theory (DFT) approach to predict the FIA for several boranes, see Figure S2. As expected, DFT with a generalized gradient functional does not achieve coupled cluster accuracy, but it is suitable to obtain an equally sensible Lewis acidity scale. We note that a higher accuracy of the electronic energies may be achieved with a hybrid functional, but since vibrational frequencies will be employed for further analyses, the choice fell on BP86 as the density functional.

We find a generally good qualitative agreement between the FIAs calculated with a simple BP86/def2-TZVP approach and those reported by Greb and coworkers, see Figure S2. There is a shift in the absolute FIA values predicted at the DFT level with respect to the DLPNO coupled cluster calculations, so that relative values should be analyzed instead. Two outliers are BH₃ and B(N(C₆F₅)₂)₃, which have maximum errors of 59 and -87 kJ mol⁻¹, respectively, corresponding to relative errors of less than 12%. Overall, we find the correlation of sufficient quality to evaluate the influence of LAs in potential push-pull systems for dinitrogen activation. Since the Lewis acidity depends on the Lewis base used as a reference,²⁰⁻²³ we report calculated hydride ion affinities (HIA) for the same set of LAs below.¹³ As shown in Figure S2 (bottom), the results are qualitatively the same.

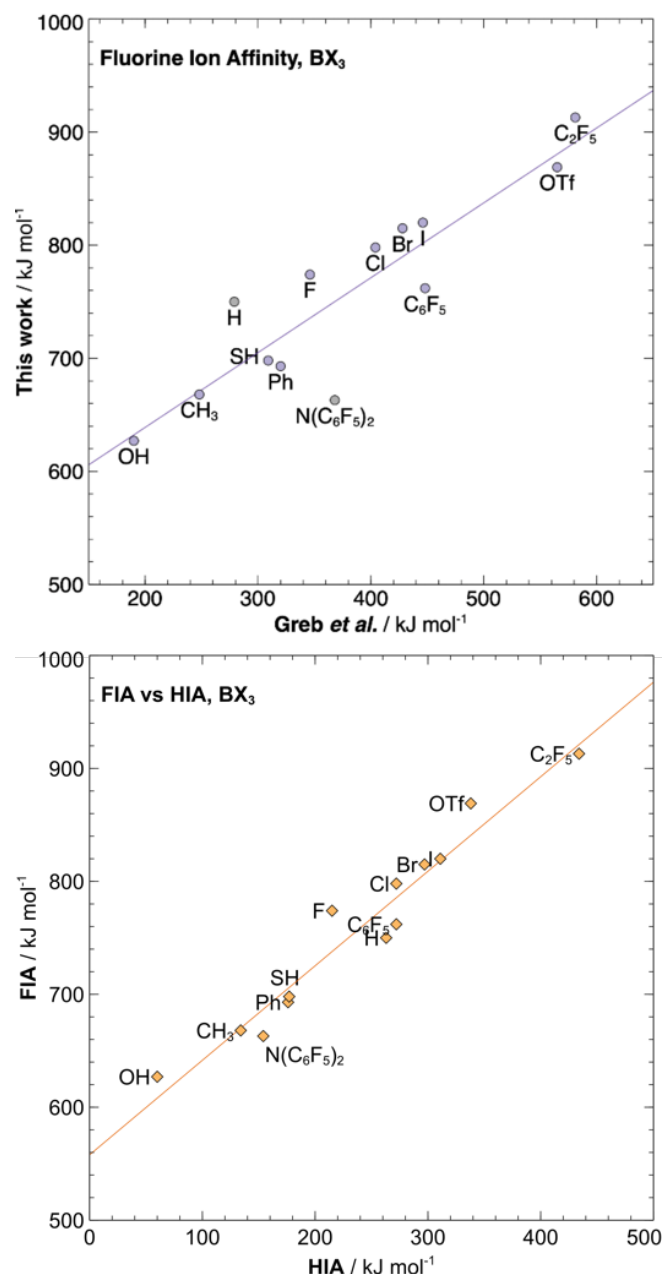


Figure S2. Top: Fluorine ion affinity calculation of BX_3 boranes, X =data label, using DFT (BP86/def2-TZVP) vs. the data from Greb and coworkers¹⁶; linear fit parameters: $y = 0.6621x + 506.47$, $R^2 = 0.8029$ (blue line), excluding the outliers BH_3 and $B(N(C_6F_5)_2)_3$ results in linear fit with $y = 0.6934x + 496.77$, $R^2 = 0.9234$. Bottom: calculated FIAs vs. calculated HIAs at the same level of theory; linear fit parameters: $y = 0.8368x + 557.9$, $R^2 = 0.9436$ (orange line).

FIA/HIA Calculations

Fluoride Ion Affinities were calculated using an adaptation of the method described by Greb and coworkers.¹⁶

The enthalpy for the following reaction (ΔH_1) is first calculated, with the density functional approximation of the present work (BP86/def2-TZVP):



It is then anchored to the high-level theory CCSD(T)/CBS value reported by Greb *et al.* (952.5 kJ mol⁻¹) for the following reaction:



The difference between the enthalpies of both reactions provides a reliable approximation of the fluoride ion affinity for the said Lewis acid.

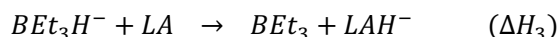


Table S1. Data required for the fluoride affinity calculation.

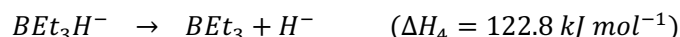
LA	$\Delta H_{\text{LA}} / \text{Ha}$	$\Delta H_{\text{SiMe}_3\text{F}} / \text{Ha}$	$\Delta H_{\text{LA-F}} / \text{Ha}$	$\Delta H_{\text{SiMe}_3^+} / \text{Ha}$	$\Delta H_1 / \text{Ha}$	$\Delta H_1 / \text{kJ}$	FIA / kJ
B(OH)₃	-252.569		-352.614		0.1251	325.37	627
BPh₃	-719.841		-819.911		0.0999	259.63	693
BF₃	-324.690		-424.791		0.0688	178.81	774
BCl₃	-1405.750		-1505.860		0.0595	154.70	798
B(OTf)₃	-2910.343		-3010.480		0.0320	83.23	869
B(C₂F₅)₃	-1751.830	-509.204	-1851.980	-409.034	0.0152	39.51	913
B(C₆F₅)₃	-2209.150		-2309.250		0.0735	190.99	762
B(CH₃)₃	-144.540		-244.601		0.1095	284.68	668
BI₃	-918.486		-1018.600		0.0511	132.83	820
BBr₃	-7748.250		-7848.370		0.0529	137.61	815
B(SH)₃	-1221.470		-1321.540		0.0978	254.27	698
BH₃	-26.578		-126.670		0.0777	202.12	750
B(N(C₆F₅)₂)₃	-4557.810		-4657.87		0.1113	289.40	663

Hydride Ion Affinities were calculated using a similar method, albeit using a different reference molecule due to the nature of the hydride anion.¹³

The enthalpy for the following reaction (ΔH_3) is first calculated, with the density functional approximation of the present work (BP86/def2-TZVP):



In this case, we have calculated the anchor at the same level of theory (BP86/def2-TZVP) as better data was not available:



The difference between the enthalpies of both reactions provides a reliable approximation of the hydride ion affinity for the said Lewis acid.

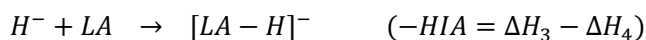


Table S2. Data required for the hydride affinity calculation.

LA	$\Delta H_{LA} / \text{Ha}$	$\Delta H_{\text{BEt}_3\text{H}} / \text{Ha}$	$\Delta H_{LA-H} / \text{Ha}$	$\Delta H_{\text{BEt}_3} / \text{Ha}$	$\Delta H_1 / \text{Ha}$	$\Delta H_1 / \text{kJ}$	HIA / kJ
B(OH)₃	-252.569		-253.235		0.0242	62.89	60
BPh₃	-719.841		-720.551		-0.0205	-53.23	176
BF₃	-324.690		-325.415		-0.0353	-91.69	215
BCl₃	-1405.750		-1406.497		-0.0575	-149.49	272
B(OTf)₃	-2910.343		-2911.116		-0.0826	-214.76	338
B(C₂F₅)₃	-1751.827	-263.117	-1752.636	-262.427	-0.1197	-311.10	434
B(C₆F₅)₃	-2209.154		-2209.901		-0.0572	-148.74	272
B(CH₃)₃	-144.540		-145.234		-0.0041	-10.67	134
BI₃	-918.486		-919.248		-0.0724	-188.24	311
BBr₃	-7748.250		-7749.007		-0.0671	-174.34	297
B(SH)₃	-1221.472		-1222.183		-0.0209	-54.45	177
BH₃	-26.578		-27.322		-0.0541	-140.64	263
B(N(C₆F₅)₂)₃	-4557.812		-4558.514		-0.0121	-31.49	154

Correlations with HIAs

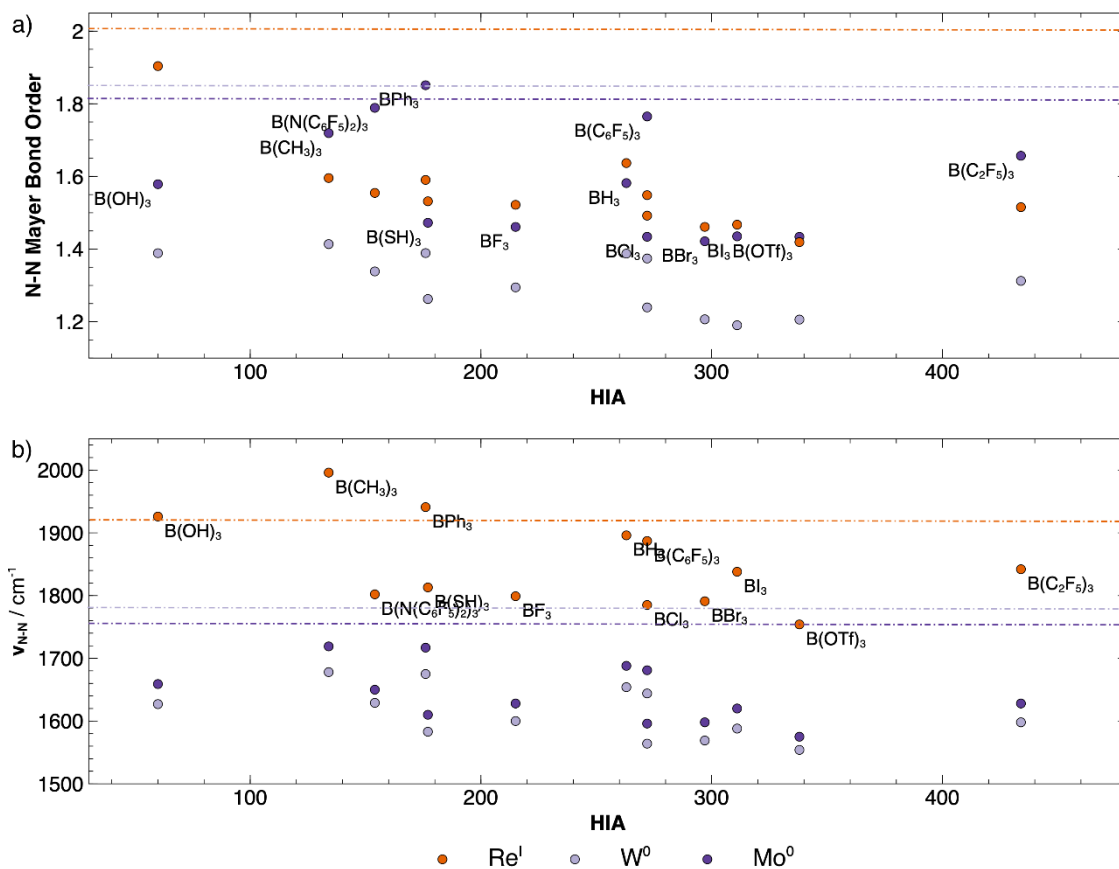


Figure S3. a) N-N Mayer bond orders and b) N-N vibrational frequency vs calculated HIA. Points represent different metal ion-LA adducts: Re^I (orange), W⁰ (dark blue) and Mo⁰ (light blue). Dashed lines represent the values of the bare complexes.

Thermochemistry of adduct formation

Table S3. Thermochemistry of adduct formation; all values given are ΔG for the chemical entity specified in Hartrees or kcal/mol as indicated.

Metal-N ₂	Lewis Acid	chemical entity			ΔE	
		LA / Ha	M+LA / Ha	Adduct / Ha	/ Ha	/ kcal mol ⁻¹
Re(I)	B(OH) ₃	-252.60103	-3512.7005	-3512.69	0.0121	7.60
	BPh ₃	-719.899	-3979.9984	-3980.01	-0.0068	-4.25
	BF ₃	-324.721	-3584.8205	-3584.83	-0.0125	-7.87
	BCl ₃	-1405.7844	-4665.8839	-4665.91	-0.0275	-17.28
	B(OTf) ₃	-2910.42	-6170.524	-6170.57	-0.0442	-27.75
	B(C ₂ F ₅) ₃	-1751.8978	-5011.9974	-5012.05	-0.0533	-33.42
	B(C ₆ F ₅) ₃	-2209.2413	-5469.3409	-5469.35	-0.0078	-4.90
	B(CH ₃) ₃	-144.578	-3404.6773	-3404.67	0.0074	4.62
	BI ₃	-918.527	-4178.6268	-4178.67	-0.0439	-27.56
	BBr ₃	-7748.29	-11008.388	-11008.4	-0.0360	-22.59
	B(SH) ₃	-1221.51	-4481.6094	-4481.61	0.0031	1.93
	BH ₃	-26.6004	-3286.7	-3286.73	-0.0323	-20.26
B(N(C ₆ F ₅) ₂) ₃	-4557.96	-7818.0591	-7817.97	0.0848	53.18	
W(0)	B(OH) ₃	-252.60103	-3501.5471	-3501.54	0.0086	5.40
	BPh ₃	-719.899	-3968.845	-3968.87	-0.0269	-16.90
	BF ₃	-324.721	-3573.6671	-3573.71	-0.0423	-26.51
	BCl ₃	-1405.7844	-4654.7305	-4654.8	-0.0664	-41.66
	B(OTf) ₃	-2910.42	-6159.3706	-6159.46	-0.0904	-56.74
	B(C ₂ F ₅) ₃	-1751.8978	-5000.844	-5000.94	-0.0916	-57.50
	B(C ₆ F ₅) ₃	-2209.2413	-5458.1875	-5458.22	-0.0365	-22.90
	B(CH ₃) ₃	-144.578	-3393.5239	-3393.53	-0.0092	-5.80
	BI ₃	-918.527	-4167.4734	-4167.56	-0.0899	-56.40
	BBr ₃	-7748.29	-10997.235	-10997.3	-0.0786	-49.33
	B(SH) ₃	-1221.51	-4470.456	-4470.49	-0.0302	-18.94
	BH ₃	-26.6004	-3275.5466	-3275.6	-0.0526	-32.99
B(N(C ₆ F ₅) ₂) ₃	-4557.96	-7806.9057	-7806.86	0.0491	30.78	
Mo(0)	B(OH) ₃	-252.60103	-3502.6511	-3502.64	0.0127	7.94
	BPh ₃	-719.899	-3969.949	-3969.97	-0.0215	-13.51
	BF ₃	-324.721	-3574.7711	-3574.81	-0.0369	-23.17
	BCl ₃	-1405.7844	-4655.8345	-4655.89	-0.0593	-37.19
	B(OTf) ₃	-2910.42	-6160.4745	-6160.56	-0.0822	-51.57
	B(C ₂ F ₅) ₃	-1751.8978	-5001.9479	-5002.03	-0.0850	-53.32
	B(C ₆ F ₅) ₃	-2209.2413	-5459.2914	-5459.32	-0.0310	-19.47
	B(CH ₃) ₃	-144.578	-3394.6279	-3394.63	-0.0058	-3.63
	BI ₃	-918.527	-4168.5774	-4168.66	-0.0812	-50.97
	BBr ₃	-7748.29	-10998.339	-10998.4	-0.0705	-44.23
	B(SH) ₃	-1221.51	-4471.56	-4471.58	-0.0236	-14.80
	BH ₃	-26.6004	-3276.6505	-3276.70	-0.0482	-30.24
B(N(C ₆ F ₅) ₂) ₃	-4557.96	-7808.0097	-7807.95	0.0556	34.88	

Description of the N-N bond in Metal-N₂-LA adducts

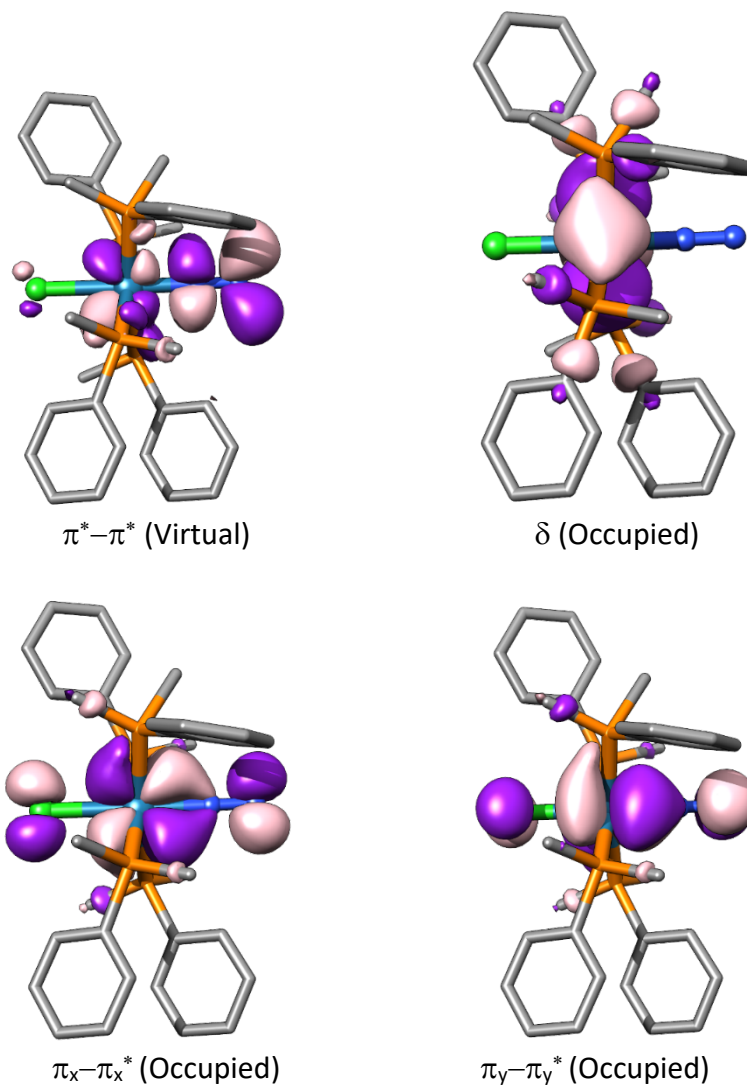
Table S4. Mayer Bond Orders and N-N stretching frequencies for the Lewis acid adducts in the present work.

Metal-N ₂	Lewis Acid	N-N	
		Mayer BO	$\nu_{N-N} / \text{cm}^{-1}$
Re(I)	B(OH) ₃	1.9038	1926
	BPh ₃	1.5904	1941
	BF ₃	1.5218	1799
	BCl ₃	1.4920	1785
	B(OTf) ₃	1.4191	1754
	B(C ₂ F ₅) ₃	1.5154	1842
	B(C ₆ F ₅) ₃	1.5485	1887
	B(CH ₃) ₃	1.5956	1996
	BI ₃	1.4672	1838
	BBr ₃	1.4611	1791
	B(SH) ₃	1.5316	1813
	BH ₃	1.6368	1896
	B(N(C ₆ F ₅) ₂) ₃	1.5546	1802
	W(0)	B(OH) ₃	1.3888
BPh ₃		1.3890	1675
BF ₃		1.2946	1600
BCl ₃		1.2394	1564
B(OTf) ₃		1.2059	1554
B(C ₂ F ₅) ₃		1.3124	1598
B(C ₆ F ₅) ₃		1.3741	1644
B(CH ₃) ₃		1.4137	1678
BI ₃		1.1903	1588
BBr ₃		1.2066	1569
B(SH) ₃		1.2625	1583
BH ₃		1.3875	1654
B(N(C ₆ F ₅) ₂) ₃		1.3385	1629
Mo(0)		B(OH) ₃	1.5787
	BPh ₃	1.8511	1717
	BF ₃	1.4610	1628
	BCl ₃	1.4339	1596
	B(OTf) ₃	1.4338	1575
	B(C ₂ F ₅) ₃	1.6569	1628
	B(C ₆ F ₅) ₃	1.7651	1681
	B(CH ₃) ₃	1.7193	1719
	BI ₃	1.4351	1620
	BBr ₃	1.4215	1598
	B(SH) ₃	1.4725	1610
	BH ₃	1.5817	1688
	B(N(C ₆ F ₅) ₂) ₃	1.7888	1650

Table S5. NBO analysis of three LA adducts calculated with the PBE0 functional and otherwise identical settings: relevant bonding orbitals (and lone pair), respective occupations and atomic contributions. Final column shows the sum of N-N occupations.

LA	Bond	Occ	%Atom ₁	%Atom ₂	N-N Occ
BPh₃	N-B	1.96695	76.29	23.71	5.95
	N-N	1.99229	49.79	50.21	
	N-N	1.98050	45.62	54.38	
	N-N	1.97755	45.12	54.88	
	Re-N	1.95295	21.83	78.17	
B(C₂F₅)₃	Re-N	1.95714	22.12	77.88	5.93
	N-N	1.99259	38.29	61.71	
	N-N	1.97091	42.15	57.85	
	N-N	1.96785	41.28	58.72	
	N-B	1.97487	73.28	26.72	
B(OTf)₃	Lone Pair (N)	1.62468	-		3.94
	Re-N	1.95900	23.08	76.92	
	Re-N	1.93062	52.56	47.44	
	N-N	1.99162	50.08	49.92	
	N-N	1.95254	41.80	58.20	
	N-B	1.82419	75.55	24.45	

Frontier orbitals



Scheme S4. Depiction of the frontier orbitals along the Cl-Re-N-N axis. Contour value: 0.034.

Table S6. Relative electronic energies (kcal mol⁻¹) of the competitive binding of the LA to the nitrogen ligand (X-M-N-N-LA) or the halogen (LA-X-M-N-N) and resulting Boltzmann ratios at 298 K.

LA / $E_{\text{electronic}}$ / kcal mol ⁻¹	X-M-N-N-LA	LA-X-M-N-N	ΔE (N _{bound} - Cl _{bound})	N-LA / LA-X ratio (298 K)
B(Ph) ₃	-3980.86	-3980.84	-0.02	1.03
B(C ₂ F ₅) ₃	-5012.71	-5012.67	-0.04	1.07
B(OTf) ₃	-6171.23	-6171.19	-0.04	1.07

Electrochemistry

Redox potentials were calculated using an adaptation of the method reported by Miller, Siewert, Schneider and coworkers.²⁴

The potential was calculated using the Nernst equation

$$E_{redox} = \frac{\Delta G_{ox} - \Delta G_{red}}{F}$$

It was then anchored to a known experimental value (in this case, vs SCE). The anchor chosen was the first (reversible) oxidation of mer-[ReCl(N₂)(PPhCPh=CPh)(PMe₂Ph)₃] (S1).²⁵

$$E_{anchor} = \frac{\Delta G_{ox(anchor)} - \Delta G_{red(anchor)}}{F} + E_{exp. measurement}$$

$$Potential_{SCE} = E_{redox} - E_{anchor}$$

Finally, we added a correction factor to move from the SCE scale to SHE:

$$Potential_{SHE} = Potential_{SCE} + 0.241 V$$

Table S7. DFT calculated Gibbs energies for the anchor complex S1 and experimentally measured oxidation potential.

	S1	S1 ⁺
$\Delta G / \text{Ha}$	-3719.8409	-3719.6696
Oxidation potential vs SCE ²⁵	0.19 V	

Table S8. Mulliken spin populations on the rhenium ion for the Lewis acid adducts studied in different oxidation states.

LA	Re ⁰	Re ^I	Re ^{II}	Re ^{III}
-	0.018	0.00	0.721	0.00
BPh ₃	0.021	0.00	0.675	0.00
BH ₃	0.027	0.00	0.661	0.00
B(C ₂ F ₅) ₃	0.325	0.00	1.045	0.00
BCl ₃	0.358	0.00	0.744	0.00
B(OTf) ₃	0.429	0.00	0.952	0.00

References

1. Gaffen, J. R.; Bentley, J. N.; Torres, L. C.; Chu, C.; Baumgartner, T.; Caputo, C. B., A Simple and Effective Method of Determining Lewis Acidity by Using Fluorescence. *Chem* **2019**, *5* (6), 1567-1583.
2. Willcox, D.; Melen, R. L., Illuminating Lewis Acidity Strength. *Chem* **2019**, *5* (6), 1362-1363.
3. Mayer, U.; Gutmann, V.; Gerger, W., The acceptor number — A quantitative empirical parameter for the electrophilic properties of solvents. *Monatshefte für Chemie / Chemical Monthly* **1975**, *106* (6), 1235-1257.
4. Pelmeshnikov, A. G.; van Santen, R. A.; Janchen, J.; Meijer, E., Acetonitrile-d₃ as a probe of Lewis and Brønsted acidity of zeolites. *The Journal of Physical Chemistry* **1993**, *97* (42), 11071-11074.
5. Fenwick, J. T. F.; Wilson, J. W., Thermochemical investigation into the Lewis acidity of the boron atom in some triaryloxyboranes. *Inorganic Chemistry* **1975**, *14* (7), 1602-1604.
6. Christe, K. O.; Dixon, D. A.; McLemore, D.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A., On a quantitative scale for Lewis acidity and recent progress in polynitrogen chemistry. *Journal of Fluorine Chemistry* **2000**, *101* (2), 151-153.
7. Haartz, J. C.; McDaniel, D. H., Fluoride ion affinity of some Lewis acids. *Journal of the American Chemical Society* **1973**, *95* (26), 8562-8565.
8. Yatsimirskii, K. B., Hydride affinity as a measure of acidity (electrophilicity). *Theoretical and Experimental Chemistry* **1981**, *17* (1), 75-79.
9. Böhler, H.; Trapp, N.; Himmel, D.; Schleep, M.; Krossing, I., From unsuccessful H₂-activation with FLPs containing B(Ohfp)₃ to a systematic evaluation of the Lewis acidity of 33 Lewis acids based on fluoride, chloride, hydride and methyl ion affinities. *Dalton Transactions* **2015**, *44* (16), 7489-7499.
10. Krespan, C. G.; Dixon, D. A., Fluoroolefin condensation catalyzed by aluminum chlorofluoride. *Journal of Fluorine Chemistry* **1996**, *77* (2), 117-126.
11. Pearson, R. G., Hard and Soft Acids and Bases. *Journal of the American Chemical Society* **1963**, *85* (22), 3533-3539.
12. Campodónico, P. R.; Aizman, A.; Contreras, R., Electrophilicity of quinones and its relationship with hydride affinity. *Chemical Physics Letters* **2009**, *471* (1), 168-173.
13. Clark, E. R.; Del Grosso, A.; Ingleson, M. J., The Hydride-Ion Affinity of Borenum Cations and Their Propensity to Activate H₂ in Frustrated Lewis Pairs. *Chemistry – A European Journal* **2013**, *19* (7), 2462-2466.
14. Saeidian, H.; Malekian, H.; Vessally, E., Density functional estimation of hydride and proton affinities of substituted allenes and heteroallenes. *Journal of Physical Organic Chemistry* **2021**, *34* (10), e4251.
15. Vianello, R.; Peran, N.; Maksić, Z. B., Hydride Affinities of Some Substituted Alkynes: Prediction by DFT Calculations and Rationalization by Triadic Formula. *The Journal of Physical Chemistry A* **2006**, *110* (47), 12870-12881.
16. Erdmann, P.; Leitner, J.; Schwarz, J.; Greb, L., An Extensive Set of Accurate Fluoride Ion Affinities for p-Block Element Lewis Acids and Basic Design Principles for Strong Fluoride Ion Acceptors. *ChemPhysChem* **2020**, *21* (10), 987-994.
17. Neese, F.; Hansen, A.; Liakos, D. G., Efficient and accurate approximations to the local coupled cluster singles doubles method using a truncated pair natural orbital basis. *The Journal of Chemical Physics* **2009**, *131* (6).

18. Neese, F.; Wennmohs, F.; Hansen, A., Efficient and accurate local approximations to coupled-electron pair approaches: An attempt to revive the pair natural orbital method. *The Journal of Chemical Physics* **2009**, *130* (11).
19. Riplinger, C.; Neese, F., An efficient and near linear scaling pair natural orbital based local coupled cluster method. *The Journal of Chemical Physics* **2013**, *138* (3).
20. Erdmann, P.; Greb, L., Multidimensional Lewis Acidity: A Consistent Data Set of Chloride, Hydride, Methide, Water and Ammonia Affinities for 183 p-Block Element Lewis Acids. *ChemPhysChem* **2021**, *22* (10), 935-943.
21. Laurence, C.; Graton, J.; Gal, J.-F., An Overview of Lewis Basicity and Affinity Scales. *Journal of Chemical Education* **2011**, *88* (12), 1651-1657.
22. Mayer, R. J.; Hampel, N.; Ofial, A. R., Lewis Acidic Boranes, Lewis Bases, and Equilibrium Constants: A Reliable Scaffold for a Quantitative Lewis Acidity/Basicity Scale. *Chemistry – A European Journal* **2021**, *27* (12), 4070-4080.
23. Greb, L., Lewis Superacids: Classifications, Candidates, and Applications. *Chemistry – A European Journal* **2018**, *24* (68), 17881-17896.
24. Lindley, B. M.; van Alten, R. S.; Finger, M.; Schendzielorz, F.; Würtele, C.; Miller, A. J. M.; Siewert, I.; Schneider, S., Mechanism of Chemical and Electrochemical N₂ Splitting by a Rhenium Pincer Complex. *Journal of the American Chemical Society* **2018**, *140* (25), 7922-7935.
25. J. L. Pombeiro, A.; Teresa A. R. S. Costa, M.; Wang, Y.; F. Nixon, J., Syntheses and redox properties of the first phosphirene–dinitrogen and phosphirene–diazene complexes. *Journal of the Chemical Society, Dalton Transactions* **1999**, (21), 3755-3758.