Journal Name

ARTICLE

Dispersion Forces Play a Role in (Me$_2$IPr)Fe(=NAd)R$_2$ (Ad = adamantyl; R = ^{neo}Pe, 1-nor) Insertions and Fe-R Bond Dissociation Enthalpies

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Supplemental Information

Experimental

General Considerations. All manipulations were performed using either glovebox or high vacuum line techniques, unless stated otherwise. All glassware was oven dried at 180°C. THF and ether were distilled under nitrogen from purple sodium benzophenone ketyl and vacuum transferred from the same prior to use. Hydrocarbon solvents were treated in the same manner with the addition of 1-2 mL/L tetraglyme. Benzene-d_6 was dried over sodium, vacuum transferred and stored over sodium. Toluene-d_8 was dried over sodium and stored over 4 Å molecular sieves under N2 atmosphere. THF-d_8 was dried over sodium, and vacuum transferred from sodium benzophenone ketyl prior to use. Chloroform-d_1 (Cambridge Isotope Laboratories) was used as received. Complexes **1a,b**, **2a,b**, **3a,b**,[1] and [(1-nor)Li]$_4$[2,3] were prepared via literature methods.

NMR spectra were obtained using Inova 300 MHz and 400 MHz spectrometers. Chemical shifts are reported relative to benzene-d_6 (^{1}H ⍰ 7.16; ^{13}C{^{1}H} ⍰ 128.39). Solution magnetic measurements were conducted via Evans' method in C$_6$D$_6$.

Procedures. 1. (Me$_2$IPr)Fe{N(NCPh$_2$)(1-nor)}(1-nor) (4b). To a 25-mL flask charged with (Me$_2$IPr)Fe(1-nor)$_2$ (**1b**) (61 mg, 0.14 mmol) and Ph$_2$CN$_2$ (28 mg, 0.14 mmol) was added 10 mL C$_6$H$_6$ via vacuum transfer at -78°C. Warming the solution to 23°C resulted in an immediate color change to brown-orange, with no observed effervescence. After stirring the solution for 1 h, the volatiles were removed, the brown residue was washed with hexanes (3 x 10 mL), and the brown-orange solid was collected (51 mg, 57%). Crystals suitable for X-ray diffraction were obtained via cooling a concentrated ether solution to -30°C. ^{1}H NMR (C$_6$D$_6$): ⍰ -35.81 (2H), -34.26 (2H), -25.86 (4H), -9.79 (12H), -6.68 (4H), 10.26 (5H), 27.77 (4H), 32.42 (6H), 40.71 (2H), 42.58 (1H), 49.00 (2H), 58.24 (1H), 74.49 (2H). μ_{eff} (Evans) = 4.7 μ_B.

2. (Me$_3$P)$_2$Fe(1-nor)$_2$ (5b). To a 25-mL flask charged with FeCl$_2$(PMe$_3$)$_2$ (273 mg, 0.979 mmol) and (1-nor)Li (200 mg, 1.959 mmol) was added via vacuum transfer 15 mL pentane at -78°C via vacuum transfer. The solution was allowed to warm slowly with stirring for 20 h, resulting in a orange-yellow solution at 23°C. Filtration of the solution, followed by concentration and cooling it to -78°C yielded orange-yellow microcrystals (239 mg, 61%), which were collected by filtration. Crystals suitable for X-ray diffraction were obtained via slow evaporation of a concentrated pentane solution at -30°C. ^{1}H NMR (C$_6$D$_6$): δ -22.72 (4H), 10.44 (4H), 27.11 (4H), 50.70 (2H), 92.47 (18H). μ_{eff} (Evans) = 5.2 μ_B.

X-ray Crystal Structures. *Crystal data for* **4b**: C$_{38}$H$_{52}$N$_4$Fe, *M* = 620.68, monoclinic, P2$_1$/c, *a* = 10.4328(4), *b* = 20.1032(7), *c* = 17.3563(6) Å, ⍰ = 106.003(2)°, *V* = 3499.1(2) Å^3, *T* = 223(2) K, ⍰ = 0.71073 Å, *Z* = 4, R_{int} = 0.0408, 37447 reflections, 8039 independent, R_1(all data) = 0.0589, wR_2 = 0.0949, GOF = 1.012, CCDC-1583545.

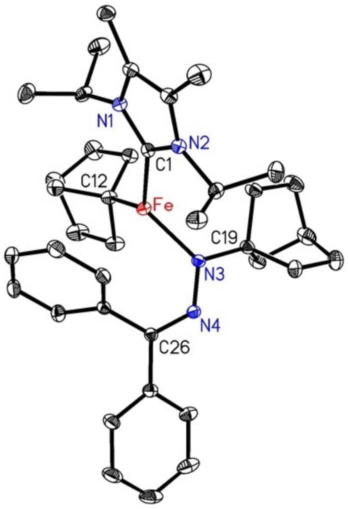

Figure S1. Molecular view of (Me$_2$IPr)Fe{N(N=CPh$_2$)(1-nor)}(1-nor) (**4b**). Interatomic distances (Å) and angles (°): Fe-N3, 2.0023(14); Fe-C1, 2.1450(16); Fe-C12, 2.0780(17); N3-N4, 1.3521(18); N4-C26, 1.305(2); N3-C19, 1.457(2); N3-Fe-C12, 113.41(6); N3-Fe-C1, 117.91(6); C1-Fe-C12, 123.96(6); Fe-N3-N4, 128.29(10); Fe-N3-C19, 119.90(10; N3-N4-C26, 121.57(14).

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Crystal data for **5b**: $C_{20}H_{40}P_2Fe$, M = 398.31, orthorhombic, Pnma, a = 18.2193(12), b = 14.0581(7), c = 9.3097(6) Å, V = 2384.5(2) Å^3, T = 223(2) K, λ = 0.71073 Å, Z = 4, R_{int} = 0.0285, 20682 reflections, 2271 independent, R_1(all data) = 0.0467, wR_2 = 0.1282, GOF = 1.082, CCDC-1583546.

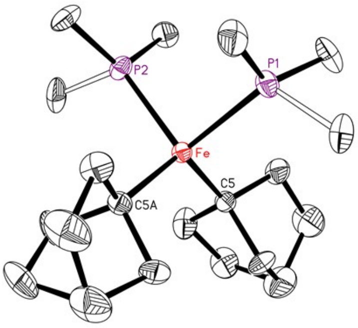

Figure S2. Molecular view of highly disordered $(Me_3P)_2Fe(1\text{-nor})_2$ (**5b**). Interatomic distances (Å) and angles (°): Fe-C5, 2.057(2); Fe-P1, 2.4127(10); Fe-P2, 2.4076(9); C5-Fe-C5A, 120.32(12); C5(C5A)-Fe-P2, 108.50(7); C5(C5A)-Fe-P1, 109.00(6); P1-Fe-P2, 99.53(4).

Crystal data for $[(1\text{-nor})Li]_4$: $C_{28}H_{44}Li_4$, M = 408.39, monoclinic, P2$_1$, a = 10.3771(2), b = 10.1982(2), c = 11.7698(2) Å, V = 1245.57(4) Å^3, T = 100.0(10) K, λ = 0.71073 Å, Z = 2, R_{int} = 0.0410, 33926 reflections, 5229 independent, R_1(all data) = 0.0428, wR_2 = 0.1123, GOF = 1.069, CCDC-1583544.

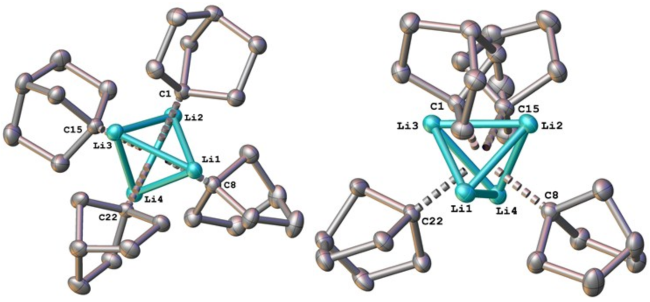

Figure S3. Two molecular views of tetrameric $[(1\text{-nor})Li]_4$. Interatomic distances (Å) and angles (°): Li1-C1, 2.213(5); Li-C8, 2.190(5); Li1-C22, 2.219(5); Li2-C1, 2.225(5); Li2-C8, 2.217(5); Li2-C15, 2.190(5); Li3-C1, 2.193(5); Li3-C15, 2.230(5); Li3-C22, 2.217(5); Li4-C8, 2.190(5); Li4-C15, 2.198(5); Li4-C22, 2.189(5); Li-Li, 2.419(17) (ave).

Computational Methods

The B3PW91[4] functional in conjunction with the GD3 and GD3BJ empirical dispersion corrections[5] was used for the optimization of geometries and vibrational frequencies. These methods were used in conjunction with the 6-311++G(d,p) all-electron basis set. Test calculations with and without counterpoise corrections suggested that the impact on energetics was ± 1 – 2 kcal/mol from basis set superposition error. All stationary points were characterized by the calculation of vibrational frequencies to ensure the correct number of imaginary frequencies appropriate to minima, i.e., zero. Reported enthalpies and free energies utilized non-scaled vibrational frequencies, and assume a temperature of 298.15 K and 1 atm. All simulations were performed with the Gaussian 09 code.[6]

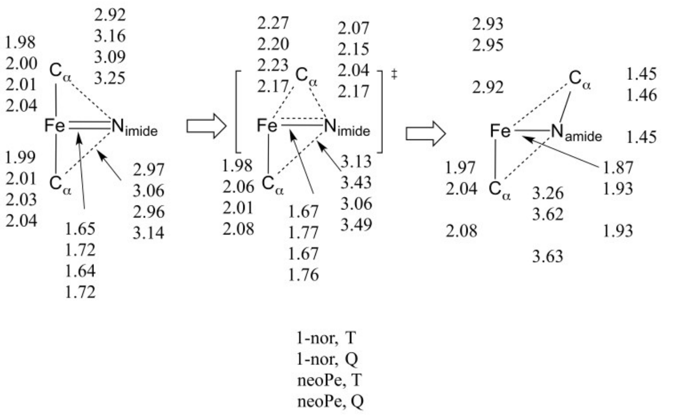

Figure S4. Calculated distances used in conjunction with enthalpies shown in Figs. 1 and 2 in the text.

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