Dispersion Forces Play a Role in (Me2IPr)Fe(=NAd)R2 (Ad = adamantyl; R = neoPe, 1-nor) Insertions and Fe-R Bond Dissociation Enthalpies

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

Thomas R. Cundari*, a Brian P. Jacobs, b Samantha N. MacMillan, b and Peter T. Wolczanski* b

Calculations show that dispersion forces in four-coordinate \((\text{Me}_2\text{IPr})\text{Fe(=NAd)(1-nor)}\) \((2b)\) contribute to greater \(\Delta D(\text{FeR})\) and slow its migratory insertion relative to the neopentyl analogue.

\[
\begin{align*}
\Delta D(\text{Fe-C(\text{neoPe})}) & = 17.3 \text{ kcal/mol} \\
\Delta D(\text{Fe-C(1-nor)}) & = 12.0 \text{ kcal/mol}
\end{align*}
\]
Introduction

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

Thomas R. Cundari$^{a,*}$, Brian P. Jacobs,$^b$ Samantha N. MacMillan,$^b$ and Peter T. Wolczanski*$^{a,b}$

The effects of dispersion on migratory insertion reactions and related iron-carbon bond dissociation energies pertaining to (Me$_2$IPr)FeR$_2$ (R = neoPe, 1-nor), and the conversion of (Me$_2$IPr)Fe(=NAd)R$_2$ to (Me$_2$IPr)Fe{N(Ad)R}R are investigated via calculations and structural comparisons. Dispersion appears to be an underappreciated, major contributor to common structure and reactivity relationships.

Dedicated to Philip P. Power, synthetic chemist extraordinaire, on the occasion of his 65th birthday.

In a recent communication,$^4$ the relative rates of a rare imide insertion into a metal-carbon bond was reported. The process, which is shown in Scheme 1, is the conversion of an intermediate (Me$_2$IPr)Fe(=NAd)R$_2$ (Ad = adamantyl; R = neoPe (2a), 1-nor (2b)), generated from the corresponding dialkyls (1a,b) and adamantyl azide, to a high spin (S = 2) iron(II) amide-alkyl, (Me$_2$IPr)Fe{N(Ad)R}R (R = neoPe (3a), 1-nor (3b)). Calculations supporting the mechanism proved less than satisfactory unless dispersion corrections were incorporated.

Power et al.$^2$ have suggested that dispersion is a crucial stabilization factor in congested, and low coordinate transition metal compounds.$^3$ For example, dispersion forces are thought to provide favorable interligand energies in M(1-nor)$_4$ (M = Fe, 45.9 kcal/mol; Co, 38.3 kcal/mol)$^4$ as inferred from calculations of 1-nor homolysis. Fürstner has attributed the modest stability of Fe(II)(Hex)$_4$ in part to similar forces. As a consequence, it is worth investigating the importance of dispersion$^{5-7}$ in bond homolysis, and related contributions to other unimolecular processes,$^8$, such as migratory insertion.

In assessing the insertion reactions illustrated in Scheme 1 via calculations, the more favorable enthalpy of converting 2a -> 3a ($\Delta H^\ddagger$ = -32.0 kcal/mol) vs. 2b -> 3b (-29.9 kcal/mol) translates into a lower barrier (17.4 vs. 20.9 kcal/mol). What is the origin of the greater driving force that leads to faster rates for R = neopentyl vs. R = 1-norbornyl?

Calculations (Table 1) on the homolysis of the iron-alkyl bonds suggested that the difference between the Fe(IV)-R and Fe(II)-R species were significantly greater for R = neoPe ($\Delta \Delta H^\ddagger$ = -17.3 kcal/mol) vs. R = 1-nor ($\Delta \Delta H^\ddagger$ = -12.0 kcal/mol). Note that the primary difference was in the Fe(IV) species, 2a vs. 2b, where the 1-norbornyl derivative was calculated to have a 7.0 kcal/mol greater bond dissociation enthalpy (BDE), whereas it was only calculated to be 1.7 kcal/mol stronger in the ferrous product, 3a vs. 3b. Herein it is suggested that dispersion plays a significant role in the BDE disparity, and other structural comparisons support the importance of dispersion.
Prior to assessing factors that address BDEs, it is important to determine whether a simple insertion reaction coordinate (RC) that has substantial iron-carbon bond breaking is reasonable. Using

\[
\text{[Fe]}{\text{N(Ad)}}{\text{[Fe]}(=\text{NAd})(1-\text{nor})}^{\text{dispersion.}}
\]

Before the transition state.

Intersystem crossing from the GS triplet of 2a to its corresponding quintet surface, prior to the transition state of insertion, is in accord with the calculation of a lower lying quintet TS. As a consequence, a straightforward RC of Fe-C(\text{neo}Pe) bond-breaking and N-C(\text{neo}Pe) bond making is deemed reasonable. The transition state is characterized by an imaginary frequency at 303 cm\(^{-1}\).

Fig. 2 illustrates the related parabolic diagram pertaining to the insertion of the 1-norbornyl derivative: (Me\text{IPr})Fe(\text{N-Ad})(1-\text{nor})\text{Pe} case can also contribute to the higher frequency relative to the 1-nor system.

**Figure 1.** Parabolic fit of metric parameters and enthalpies pertaining to the insertion reaction: (Me\text{IPr})Fe(\text{N-Ad})(\text{Ad})\text{Pe} \rightarrow (Me\text{IPr})Fe(\text{N-Ad})(\text{Ad})\text{Pe} simulation of (2a) \rightarrow (Me\text{IPr})Fe(\text{N-Ad})(1-\text{nor})\text{Pe} (3a); x-axis is d(NC) = RC as per dashed lines.

**Figure 2.** Parabolic fit of metric parameters and enthalpies pertaining to the insertion reaction: (Me\text{IPr})Fe(\text{N-Ad})(1-\text{nor})\text{Pe} \rightarrow (Me\text{IPr})Fe(\text{N-Ad})(1-\text{nor})\text{Pe} ; x-axis is d(NC) = RC as per dashed lines.

**Factors influencing insertion rates via BDEs**

Now that the reaction coordinate has been explored and is shown to be consistent with elements of Fe-C bond breaking, factors that influence the BDEs of the two systems can be analyzed. Experimental carbon-hydrogen bond energies for \text{neo}Pe-H and (1-nor)H are 100.3 (99.4 calc) and 96.7 (104.2 calc; 105.5 (G4 ab initio)) kcal/mol, respectively. The (1-nor)H BDE is somewhat higher than expected (e.g., Me\text{CCH}, BDE = 95.7 kcal/mol, 92.1 calc,
common to both insertion processes is the adamantyl group attached to the imide in (Me$_2$IPr)Fe(N=AdR)$_2$ ($R =$ neo$^{\text{npe}}$ Pe (2a), 1-nor (2b)), and the amide in (Me$_2$IPr)Fe(N=Ad)(R)R ($R =$ neo$^{\text{npe}}$ Pe (3a), 1-nor (3b)). While no other Fe(IV) imide proved stable enough to provide an experimental comparison, treatment of (Me$_2$IPr)Fe(1-nor)$_2$ with PH$_3$CN$^{14-17}$ did provide another Fe(II) amide complex, (Me$_2$IPr)Fe(N=N=CPH$_3$)(1-nor)(1-nor) (4b), 57%, according to eq 1. No

\[
\text{(Me$_2$IPr)Fe(1-nor)$_2$ + PH$_3$CN} \rightarrow \text{(Me$_2$IPr)Fe(N=N=CPH$_3$)(1-nor)(1-nor) (4b) (1)}
\]

intermediates were detected, as the solution merely darkened from light-yellow to orange-brown, consistent with transient imide formation and rapid insertion. The $\mu_{\text{eff}}$, conducted via Evans' method,$^{18}$ was 4.7 $\mu_B$, consistent with an $S =$ 2 center.

Fig. 3 illustrates a molecular view of (Me$_2$IPr)Fe(N=N=CPH$_3$)(1-nor)(1-nor)(1-nor) (4b), replete with pertinent bond distances and angles. The complex is pseudo trigonal, although the core angles only sum to 355.28°, as the iron is slightly out of the plane, and directed toward a phenyl group, with long Fe-C$_{\text{ortho}}$ and Fe-H(C$_{\text{ortho}}$) contact distances of 2.65 and 2.74 Å. The Fe-C(NHC) and Fe-C(Ad) bond distances are 2.1450(16) and 2.0780 Å, respectively, and the iron-nitrogen distance of 2.0023(14) Å is consistent with a single bond of an amide. Additional metric parameters of the amide linkage support the Fe-N(1-nor)-N=CPH$_3$ formulation.

Calculations of the iron-1-norbomyl bond dissociation energy and free energy pertaining to (Me$_2$IPr)Fe(N=N=CPH$_3$)(1-nor)(1-nor) (4b) afford slightly smaller values than that of (Me$_2$IPr)Fe(N=Ad)(1-nor)(1-nor) (3b). Differences in BDE calculated with and without dispersion ($\Delta$BDE = 19.7 kcal/mol) are essentially the same as in 3b. The system has other components that do not permit a ready comparison of adamantyl vs. Ph$_2$C=N group effects, especially since the likely imide precursor was not observed.

\[\text{(Me$_2$IPr)Fe(N=N=CPH$_3$)(1-nor)(1-nor) (4b)}\]

\[\text{Interatomic distances (Å) and angles (°): Fe-N3, 2.0023(14); Fe-C1, 2.1450(16); Fe-N3-N4, 128.29(10); Fe-N3-C19, 119.90(10; N3-N4-C26, 1.3521(18); N4-C26, 1.305(2); N3-Fe-N3, 123.96(6); Fe-N3-N4, 1.305(2); N3-Fe-N3, 123.96(6); Fe-N3-N4, 128.29(10); Fe-N3-C19, 119.90(10; N3-N4-C26, 121.57(14).} \]
ligand is less than claimed for Fe(1-nor) in the products, one for each of six (1-nor)/(1-nor) interactions on the reactant side are offset by two
stabilization in the homoleptic complexes, mostly in Fe(1-nor)4. Note that (Me3P)4Fe actually exists as (Me3P)4HFeHFe(C2H4PMe3)2, but its reactivity is akin to the iron(0) tetrakis-phosphine species, which is prepared from (1-nor)Li and Fe(II) sources in weakly donating solvents. Theopold's related studies on [Co(1-nor)Li]n (n = -1, 0, +1) helped show that disproportionation to M(IV) and M(0) is the likely path for iron and cobalt. The maximization of dispersion is a plausible factor enabling formation of the M(IV) species, but if a significant donor ligand is also present, as in the PMe3 case above, iron(II) persists as the stable form. Presumably, favoring Fe(II)4 entails both ligand donor interactions as well as, at least in the case of PMe3, additional dispersion factors.

![Figure 4. Molecular view of highly disordered (Me3P)4Fe(1-nor)4 (5b). Interatomic distances (Å) and angles (°): Fe-C5, 2.057(2); Fe-P1, 2.4127(10); Fe-P2, 2.4076(9); CS-Fe-CSA, 120.32(12); CS-CSA-Fe-P2, 108.50(7); CS-CSA-Fe-P1, 109.00(6); P1-Fe-P2, 99.53(4).](image)

Despite severe rotational disorders in the 1-norbornyl and PMe3 ligands, a reasonable structural model for (Me3P)4Fe(1-nor)4 (5b) was obtained via X-ray crystallography, and a molecular view is illustrated in Fig. 4. The C-Fe-C angle pertaining to the 1-nor groups is 120.32(12)°, while the phosphorus atoms are 99.53(4)° apart, and all remaining core angles are 108.75(29)°. The bond distances of 2.057(2) and 2.410(4) Å pertaining to d(Fe-C) and d(Fe-P), respectively, are normal for tetrahedral ferrous species.

![Figure 5. Calculated ∆H and ∆G for the comproportionation of (Me3P)4Fe + Fe(1-nor)Li to 2 (Me3P)4Fe(1-nor)Li2 (5b) with and without corrections due to dispersion.](image)

Fig. 5 shows the isodesmic reaction of Fe(1-nor)Li4 and (Me3P)4Fe comproportionating to two equiv of (Me3P)4Fe(1-nor)Li2 (5b). First, note that (Me3P)4Fe actually exists as (Me3P)4HFe(C2H4PMe3)2, but its reactivity is akin to the iron(0) tetrakis-phosphine species, and is thus considered close in energy. Depending on the levels of theory utilized, dispersion accounts for ~15 kcal/mol of enthalpic stabilization in the homoleptic complexes, mostly in Fe(1-nor)Li4. The six (1-nor)/(1-nor) interactions on the reactant side are offset by two in the products, one for each 5b. While the magnitude per 1-nor ligand is less than claimed for Fe(1-nor)Li4 alone, these results – all on known, isolable (or isomeric in the case of (Me3P)4Fe complexes – support the contention that dispersion plays a crucial role in low coordinate complexation. The lower values are undoubtedly due to the fact that dispersion via the PMe3 ligands contributes substantially, albeit at longer distances due to the d(Fe-P) being ~0.35 Å longer than the d(Fe-C).

Note that the comproportionation of Fe(0) and Fe(IV) to two equiv Fe(II) is favorable in the isodesmic calculation above, in contrast to the synthesis of Fe(1-nor)Li4 which is prepared from (1-nor)Li and Fe(II) sources in weakly donating solvents. Theopold's related studies on [Co(1-nor)Li]n (n = -1, 0, +1) helped show that disproportionation to M(IV) and M(0) is the likely path for iron and cobalt. The maximization of dispersion is a plausible factor enabling formation of the M(IV) species, but if a significant donor ligand is also present, as in the PMe3 case above, iron(II) persists as the stable form. Presumably, favoring Fe(II)4 entails both ligand donor interactions as well as, at least in the case of PMe3, additional dispersion factors.

![Figure 5. Two molecular views of tetrameric [(1-nor)Li]4. Interatomic distances (Å) and angles (°): Li1-C1, 2.213(5); Li3-C8, 2.190(5); Li1-C22, 2.219(5); Li1-C21, 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) Å (ave).](image)

Crystallization of (1-nor)Li2 from pentane solvent afforded a tetramer, whose structure is illustrated in Fig. 6. The lithium atoms are disposed in a regular tetrahedron, with d(Li-Li) = 2.419(17) Å (ave). The α-carbons of each 1-norbornyl unit are equidistant to each Lii face, with d(C(α)-Li) = 2.206(16) Å (ave). Interactions of the β-carbons with the lithium atoms range from 2.3 to 3.6 Å.
tetramerization of (1-nor)Li to tetrahedral [(1-nor)Li], calculated without and with (GD3, GD3BJ) dispersion.

Fig.7 depicts the gas phase dimerization of [(1-nor)Li]₂ and tetramerization of (1-nor)Li to tetrahedral [(1-nor)Li]₄ with associated enthalpies calculated with and without empirical dispersion. Assuming six (1-nor)/(1-nor) interactions in the tetramer, dispersion accounts for ~30-40 kcal/mol, or roughly 6-8 kcal/mol per interaction relative to 4 (1-nor)Li. The amount of dispersive energy in each aggregation is method dependent with the GD3BJ correction giving the higher values.

Since the bonding of each RLi fragment differs in the monomer and each aggregate, it is imperative to compare the [(1-nor)Li]₂ systems with one in which a significantly smaller amount of dispersion is likely. Fig. 8 illustrates the related case of MeLi aggregation, which manifests similar enthalpic changes, but less dispersion is likely. Even for the tetramerization of MeLi, dispersion contributes 6-17 kcal/mol, whereas the corresponding tetramerization of (1-nor)Li has a corresponding 32-49 kcal/mol. It is noteworthy that such corrections appear important even for small RLi.

**Conclusions**

According to the calculations herein, there is no question that dispersion is consequential to structural stability. As an enthalpic contribution, chemical reactivity and affiliated rates can also be affected. The magnitude of these effects is surprising, especially the realization that simple bond dissociation enthalpies can have a substantial dispersion component.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

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**Notes and references**

Complexes 1a,b, 2a,b, 3a,b, and [(1-nor)Li], were prepared via literature methods. Amide 4b and dialkyl 5b were prepared as described in the text. For full experimental and calculational details, see the supplementary information.

**Crystal data for 4b**: C₉₆H₁₆N₁₆Fe, M = 620.68, monoclinic, P2₁/c, a = 10.4328(4), b = 20.1032(7), c = 17.3563(6) Å, β = 106.003(2)°, V = 3499.1(2) Å³, T = 223(2) K, λ = 0.71073 Å, Z = 4, R₁ = 0.0408, 37447 reflections, 8039 independent, R₁(all data) = 0.0589, wR₂ = 0.0949, GOF = 1.012, CCDC-1583545.
Crystal data for 5b: C$_{28}$H$_{30}$P$_2$Fe, 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.

Crystal data for [(1-nor)Li], C$_{28}$H$_{30}$Li, 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.