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Catalytic Tuning of Phosphinoethane Ligand. An Improved Catalyst for Hydrocarbon Functionalization.

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1. Introduction

More than two decades have passed since the first demonstration of hydrocarbon C-H bond activation by well-characterized organometallics complexes. However, the selective catalytic functionalization of unactivated hydrocarbons under mild conditions via C-H bond activation pathways remains a subject of considerable research interest and importance [1]. Organometallic systems that are capable of effecting the catalytic functionalization of hydrocarbons remain rare [2]. Substantial experimental and computational research has focused on the delineation of different mechanisms by which organometallic complexes effect carbon-hydrogen bond scission including π -bond metathesis, oxidative addition, oxidative hydrogen migration, electrophilic substitution, acid/base and radical pathways. From the foregoing research a wealth of information has been deduced about the chemical factors that control and delineate the various activation mechanisms [1].

In a minimalist sense a useful catalytic cycle to hydrocarbon functionalization would include (a) generation of the catalyst or catalyst precursor (L_nM , where L_n and M represent generic ligand and metal moieties, respectively), (b) activation of the carbon-hydrogen bond (*e.g.*, $L_nM + R-H \rightarrow L_nM(R)(H)$), (c) insertion of a chemical moiety (E) into the carbon-hydrogen bond (*e.g.*, $L_nM(R)(H) + XE \rightarrow L_nM(ER)(H) + X$ or $L_nM(R)(H) + XE \rightarrow L_nM(R)(EH) + X$) where XE represents a transfer reagent such as organic azides (RN_3) for nitrene transfer or O_2 for oxygen atom transfer, (d) generation of the functionalized REH product (*e.g.*, $L_nM(ER)(H) + RH \rightarrow L_nM(R)(H) + REH$ or $L_nM(ER)(H) \rightarrow L_nM(EH)$). In the latter scenario an additional requirement would be

the removal of the REH organic product from the L_nM inner coordination sphere and regeneration of the active species. What has emerged from numerous experimental and computational studies is that certain metals tend to be competent for one or perhaps more of these steps, but that the identification of metal complexes that are competent for the full range of catalytic steps is quite difficult. For example, the early metal (Group 4 and 5) imido complexes ($L_nM=N-Si^tBu_3$) of Wolczanski are spectacular in their avidity for C-H bond activation via a $[2_\sigma+2_\pi]$ mechanism [3] but that the resultant amide complexes ($L_nM(R)(N(H)Si^tBu_3)$) are "too stable," being unable to, for example, generate amine ($RN(H)Si^tBu_3$) product via reductive elimination.

Late transition metal (*i.e.*, Group 8 and beyond in the present context) nitrene complexes represent a profitable target for the development of novel hydrocarbon functionalization catalysts for several reasons. First and foremost, the development of new supporting ligation such as β -diketiminates [4] (also denoted as *nacnac* ligands) and bulky, chelating *bis*-phosphines [5] have lead to the synthesis and structural characterization of late transition metal nitrenes. Notable examples included first row transition metal nitrenes of Fe [6], Co [7] and Ni [5a,b,f,8] to augment earlier examples incorporating the heavier metals, *e.g.*, $Cp^*Ir=N^tBu$ [9] and $(Cumene)Os=N^tBu$ [10]. Second, the isovalent nature of the nitrene (NR) and oxo (O) moieties immediately suggests useful synthetic analogies - both in a structural and mechanistic sense - from the biological realm, in particular for the metals iron (see, for example, the recent report by Que and coworkers [11]) and copper [12]. Third, the ready synthesis of late metal nitrene complexes via group transfer reagents such as organic azides suggest that the generation and regeneration of nitrene active species within a catalytic cycle is quite feasible in both a kinetic and thermodynamic sense [6-8]. Fourth, nitrene transfer chemistry to organic substrates like olefins and CO has been effectively demonstrated by late transition metal nitrenes of the 3d metals [5-8].

While nitrene transfer to a C-H bond (amination) is as yet very rare, the report of copper-catalyzed alkane functionalization via a tandem pathway (dehydrogenation followed by aziridination of the resulting olefin) by Vedernikov and Caulton must be regarded as a very exciting breakthrough [13]. While amination catalysis by late metal catalysts (most notably palladium [14] and copper [15]) is well established in organic synthesis, such processes involve an initial functionalization of a hydrocarbon to produce a more reactive surrogate (*e.g.*, an organic chloride). Direct amination of hydrocarbons is thus more desirable from an atom economical point of view.

Computational chemistry methods have greatly aided the understanding of the mechanisms of carbon-hydrogen bond activation from the classic studies of Hoffmann and coworkers [16,17] utilizing extended Hückel techniques to more recent works by Goddard, Oxgaard and coworkers [18] (to mention just one from among many possible excellent examples). What have been less studied from a computational perspective are the subsequent steps that close the appropriate catalytic cycles for hydrocarbon functionalization. Furthermore, computational chemistry has been more reactive in terms of explaining and rationalizing experimental results as opposed to proactive by isolating novel systems that might warrant serious experimental consideration for catalytic hydrocarbon functionalization. Such steps are essential to the eventual realization of long-cherished aims such as computer-aided catalyst design. To this end, we have undertaken a study of catalytic amination by nickel nitrene complexes ($L_nNi(NR)$).

2. Computational Methods

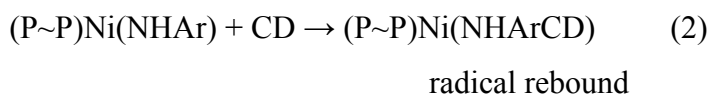
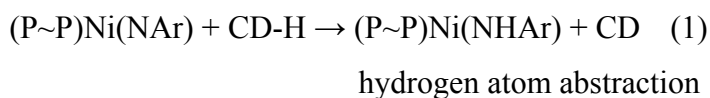
The Gaussian 03 package [19] was used for all calculations described herein. Specifically, a hybrid quantum/molecular mechanical approach, within the ONIOM [20] methodology, were employed to study as realistic as possible chemical systems. The B3LYP hybrid density functional in conjunction with the 6-31G(d) all-electron basis set was used for the quantum region, which comprised the metal, ligating atoms, the CH_2CH_2 backbone atoms of the *bis*-phosphine supporting ligands, the six carbons of the Ar (2,6-diisopropyl-phenyl) nitrene substituent and the three hydrogen atoms directly attached to these aromatic carbons. Any remaining atoms were modeled using the Universal Force Field (UFF [21]) force field. For model complexes employing the dtbpe (dtbpe = *bis*(di-*tert*-butyl-phosphino)ethane) ligand, the *tert*-butyl groups were included in the MM region, and thus modeled with the UFF force field. To produce a more faithful modeling of the electron-withdrawing nature of the trifluoromethyl group, it was decided to model the CF_3 groups within the QM region in our dfmpe (*bis*(di-trifluoromethyl-phosphino)ethane) model of the fluorinated *bis*-phosphine ligands reported by Roddick and coworkers [22]. The CD-H substrate was calculated quantum mechanically (B3LYP/6-31G(d)).

All stationary points were singlets and fully geometry optimized using gradient methods without symmetry constraint. The calculated energy Hessian confirmed the

stationary points as a minima (no imaginary frequency) or transition state (one imaginary frequency). The thermochemistry of the reaction was determined at 1 atm and 298.15 K using unscaled ONIOM(B3LYP/6-31G(d):UFF) frequencies. Intrinsic reaction coordinates were followed from transition states to confirm the nature of the reactants and products connected by these transition states. Solvent effects were neglected.

3. Results and Discussion

The overall nickel-catalyzed reaction sequence studied for hydrocarbon functionalization is shown in equations 1 and 2 (P~P denotes a chelating *bis*-phosphine coligand). In our initial thermodynamic analysis a two-step mechanism (*i.e.*, hydrogen atom abstraction from a hydrocarbon followed by rebound of the hydrocarbonyl radical onto the nitrogen of the erstwhile nitrene) was assumed for several reasons. First, our joint theory-experiment study of hydrocarbon C-H bond activation of iron-nitrene complex with the Holland group [6a] implicates activation by a hydrogen atom abstraction (HAA) pathway. In that case, no "rebound" of the hydrocarbonyl radical onto the amide nitrogen to produce a ligated amine was observed, although there is ample precedence for HAA/rebound by ferryl (FeO) intermediates in hydroxylation mechanisms for cytochromes P-450 and their mimics [23]. Our other motivation for analyzing a two-step mechanism is the utility this affords in delineating the various thermodynamic consequences upon the conversion of the nickel-nitrogen bond from a multiple bond (nitrene active species) to a formally single bond (the nickel-amide complex formed via HAA) and then from the amide's formal single bond to the dative Ni←N bond of the amine formed in the rebound step. In our previous studies of ruthenium-X (X = amide) complexes in collaboration with the Gunnoe group [24], the thermodynamic consequences of diminution of the metal-nitrogen bond strength upon carbon-hydrogen addition was found to be an important factor in determining the feasibility of C-H bond activation.



3.1. Amination of 1,4-Cyclohexadiene by (dtbpe)Ni(NAr)

The amination of 1,4-cyclohexadiene (CD-H) by a full model of the nitrene complex (*viz* (dtbpe)Ni(NAr)) reported by Hillhouse and coworkers [5a] was studied using hybrid ONIOM(B3LYP/6-31G(d):UFF) methods. The choice of CD-H as an initial substrate was motivated by previous experimental reports that imply that late metal nitrenes are thermodynamically limited to the activation of weak carbon-hydrogen bonds such as the *bis*-allylic C-H bond of 1,4-cyclohexadiene [6a,8]. Holland's group has also shown that steric factors cannot be discounted in C-H bond activation by late metal nitrenes. For example, their (β -diketiminate)Fe(NAd)(4^tBuPy) complex (Ad = 1-adamantyl) can activate CD-H and the fused-ring analogue, indene, but not the three-ring congener, 9,10-dihydroanthracene, despite all three systems having comparable C-H bond strengths [6a].

Overall, the amination of 1,4-cyclohexadiene by (dtbpe)Ni(NAr) to form the three-coordinate, Ni⁰-ligated product (dtbpe)Ni(NHArCD) is significantly endothermic ($\Delta H_{\text{am}} = +19.0$ kcal/mol) and thus is, of course, expected to be very endergonic given the reduction in molecularity inherent in nitrene insertion into the *bis*-allylic C-H bond of CD-H. The computed result is not surprising as one would have expected this reaction, if feasible, to have been reported by Hillhouse and coworkers in their extensive mechanistic studies of the reactivity of (dtbpe)Ni(NAr) and related multiply bonded nickel complexes [5].

Despite the thermodynamic unfavorability of CD-H amination by (dtbpe)Ni(NAr) it is instructive to look at the different steps in a hypothetical two-step functionalization: HAA of CD-H followed by rebound of the CD radical. The HAA step to form the Ni^I-amide complex (which is a doublet spin state), (dtbpe)Ni(NHAr), is calculated to be thermodynamically reasonable, $\Delta H_{\text{HAA}}(\text{dtbpe}) = -1.3$ kcal/mol. This result is implicitly reasonable in that there is a rough balance in the bond strengths of the N-H bond being formed (QM/MM calculations indicate a value of 79.1 kcal/mol for NAr + H \rightarrow NHAr using the same ONIOM methods being applied here to the nickel complexes) and the C-H bond being cleaved (experimentally CD-H \rightarrow CD + H is quoted as 76 ± 1 kcal/mol and calculated as 71.2 kcal/mol using B3LYP/6-31G(d) methods) [25]. Thus, the primary factor in the thermodynamics of equation 1 (HAA) is

expected to be the π -bond energy of the nickel-nitrene active species, assuming a formal reduction in the NiN bond order from two (nitrene) to one (amide), see Figure 1.

Model calculations were performed to quantify the change in nickel-nitrogen bond energy upon conversion of the nitrene to the amide. The nickel-nitrene bond dissociation enthalpy was calculated from the reaction, $((\text{dtbpe})\text{Ni}(\text{NAr}) \rightarrow (\text{dtbpe})\text{Ni} + \text{NAr})$ and a value of 93.2 kcal/mol obtained. The aryl-nitrene was calculated in its triplet ground state [26]; the $(\text{dtbpe})\text{Ni}$ fragment was determined to be a singlet ground state with the triplet being 3.4 kcal/mol higher in energy. The nickel-amide bond dissociation enthalpy of 86.7 kcal/mol was estimated in an analogous fashion $((\text{dtbpe})\text{Ni}(\text{NHAr}) \rightarrow (\text{dtbpe})\text{Ni} + \text{NHAr})$. For this reaction the NHAr product and amide reactant are both doublets.

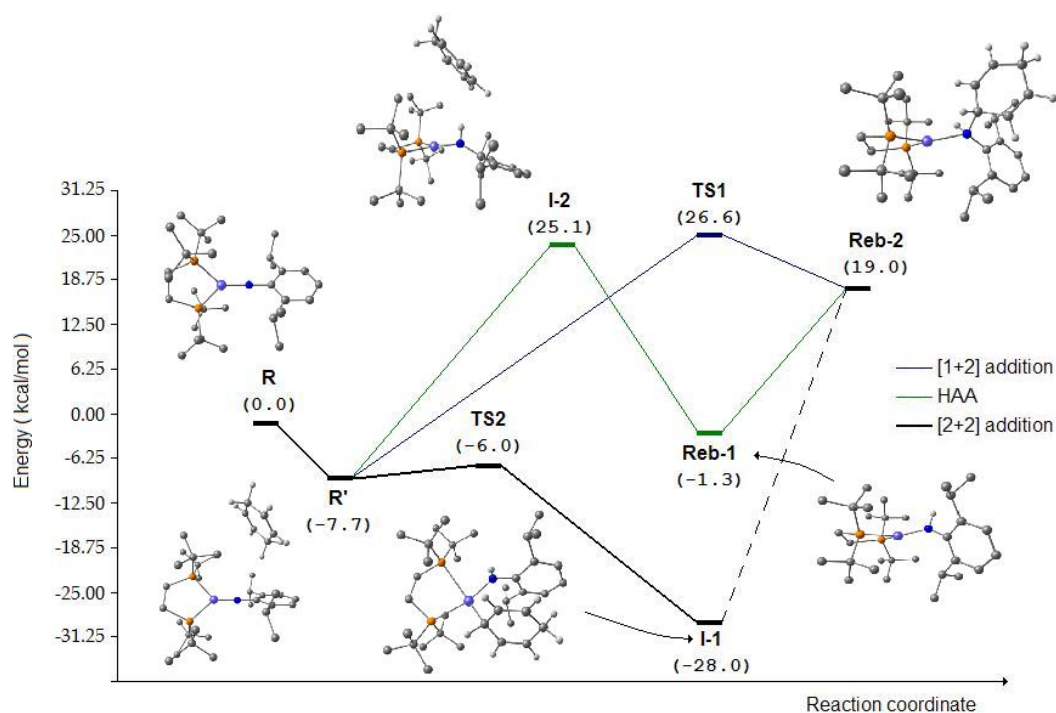


Figure 1. Potential energy surface (enthalpy diagram) of the amination of 1,4-Cyclohexadiene by $(\text{dtbpe})\text{Ni}(\text{NAr})$. Numbers in parenthesis are relative energies (in kcal/mol) with respect to the reactant (**R**) molecule.

The calculated difference in the nickel-nitrene and nickel-amide bond dissociation enthalpies can be used as a simple estimate of the nickel-nitrogen π -bond energy. The present QM/MM calculations imply a rough nickel-nitrene π -bond energy for (dtbpe)Ni(NAr) of ($\Pi_{\text{NiN}} \sim \Delta H_{\text{HAA}} + \text{BE}_{\text{NH}} - \text{BE}_{\text{CD-H}} \sim \Delta H_{\text{HAA}} + 7.9 \sim 1.4 + 7.9$) 6.5 kcal/mol. Such a low estimate is expected for a multiply bonded complex with a relatively high d-electron count (d^{10} in the present case if we assume a neutral nitrene moiety; d^8 even if an imide description is utilized for the NAr^{2-} ligand), and are consistent with the known chemistry of these complexes, for example, their high reactivity with olefin complexes [5].

Our thermochemical analysis thus indicates that the thermoneutrality of the HAA step is due to the coupling of a small difference in the X-H bonds formed ($X = \text{N}$) and broken ($X = \text{C}$) combined with a very small nickel-nitrogen π -bond energy. Thus, we turn our attention to the second step of our mechanism, radical rebound, which is found to be both highly endothermic ($\Delta H_{\text{reb}}(\text{dtbpe}) = +20.3$ kcal/mol). As with the HAA step, we attempted to understand the thermodynamics in terms of the underlying bonds being broken and formed. The rebound step entails the formation of a nitrogen-carbon bond for our amine product, NArCD . At the metal center, radical rebound causes a further reduction in the nickel-nitrogen bond order from a formal single bond (amide complex) to a dative bond (amine complex). The nitrogen-carbon bond is calculated to be very weak for this bulky amine; a bond enthalpy of 39.0 kcal/mol is obtained (Figure 2).

As alluded to above, the loss in metal-ligand bond strength upon the addition of a methane C-H bond to a ruthenium-amide ((PCP)Ru(CO)(NH₂)) to give an amine product ((PCP)Ru(CO)(CH₃)(NH₃)), PCP = 2,6-(CH₂P^tBu₂)₂C₆H₃, was found to be an important factor in thwarting the C-H bond activating ability of this complex [24]. Hence, it was assumed that such would also be the case in the present Ni-based catalysts. Combining the previously calculated Ni-amide bond enthalpy of 86.7 kcal/mol with the corresponding Ni-amine bond enthalpy at the same QM/MM level of theory (*i.e.*, 22.6 kcal/mol) immediately implicates the loss of metal-ligand bond enthalpy as a key factor in the thermodynamic unfavorability of the rebound step for the (dtbpe)Ni system. *The 64.1 kcal/mol loss in nickel-nitrogen bond enthalpy upon radical rebound is not compensated by the weak C-N bond formed.* While less bulky hydrocarbyl radicals might have an enhanced C-N bond enthalpy it is likely that such

substrates will entail stronger C-H bond energies, which would then unfavorably impact the hydrogen atom abstraction step.

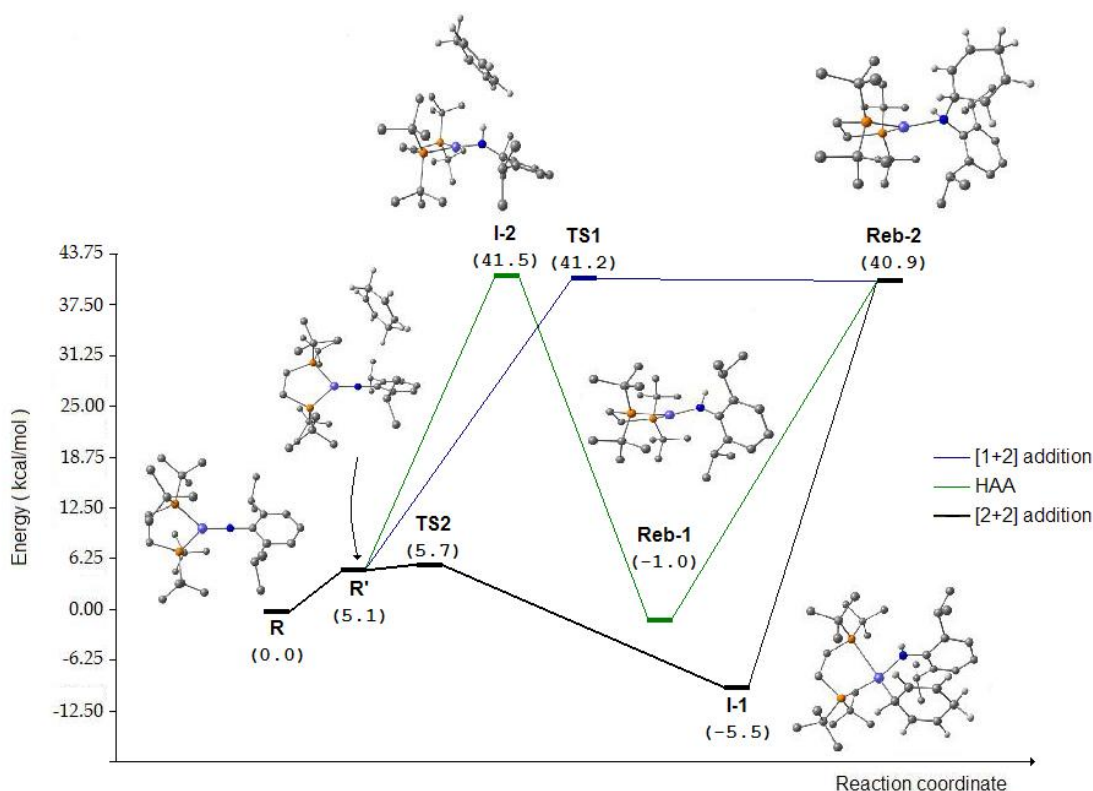


Figure 2. Free-energy surface of the amination of 1,4-cyclohexadiene by (dtbpe)Ni(NAr). Numbers in parenthesis are relative energies (in kcal/mol) with respect to the reactant (**R**) molecule.

The present results, although not indicative of a potent hydrocarbon functionalization catalyst based on a (dtbpe)Ni functionality, are instructive. *The calculations, when combined with our previous studies of Ru complexes [24], indicate that a possible route to thermodynamic feasibility lies in the identification of a ligand modification that would enhance the metal-amine bond strength while diminishing the metal-amide bond strength.* Such a situation could also benefit the HAA step by providing more thermodynamic driving force, assuming the nickel-nitrene bond energy remains unchanged upon this chemical modification. Such bond enthalpy changes are, however, hard to predict *a priori* and hence further QM/MM simulations were carried out to address these hypotheses.

3.2. Amination of 1,4-Cyclohexadiene by (dfmpe)Ni(NAr)

In our search for a synthetically feasible, *bis*-phosphine nickel-nitrene that might affect catalytic hydrocarbon functionalization, two main criteria were employed to ensure maximum experimental relevance. First, it was assumed that the phosphine must be a chelating *bis*(phosphino)ethane given the prevalence of chelating supporting ligation (*e.g.*, β -diketiminates, dtbpe, tris(phosphino)borates, and tris(pyrazolyl)borates) [5-8] in the experimental literature of late transition metal nitrenes that are stable enough to be structurally characterized. Such a criterion also helps maintain sufficiently close similarity to the Hillhouse-type complexes [5] with their demonstrated nitrene transfer chemistry. Second, the modification must have plausible (*i.e.*, experimentally characterized examples existed in the literature) synthetic precursors, preferably those that contain nickel in a formally zero-valent state. Such a requirement implies L_nNi-LL synthons in which LL is a prototypical labile ligand such as COD (η^2, η^2 -1,5-cyclooctadiene) or 2,2'-bipyridine. Such labile ligands (LL) would presumably be readily displaced by available organic azides (*e.g.*, AdN_3 or ArN_3) to form the required nickel-nitrene starting materials.

Using the above criteria, plus the implication derived from the dtbpe simulations that enhanced nickel-amine bond enthalpy was needed to drive the rebound step (and hence the formation of functionalized amine product), a survey of the literature and the Cambridge Structural Database [27] was conducted for plausible targets. This examination suggested the dfepe ($(R_f)_2PCH_2CH_2P(R_f)_2$, $R_f = C_2F_5$) ligand as an intriguing target. Roddick and coworkers have extensively studied this highly electron-deficient *bis*-phosphine for a host of intriguing platinum chemistry [22]. However, this same group has also published the experimental characterization of a variety of Ni^0 complexes of dfepe, including $(dfepe)Ni(CO)_2$, $(dfepe)Ni(bpy)$ and $(dfepe)Ni(COD)$ [22]. The latter complex was structurally characterized, while the carbonyl complex was studied by analysis of the CO stretching frequencies, which highlighted the extreme electron-deficient nature of this chelating *bis*-phosphine, a property deemed to be potentially very beneficial in enhancing the nickel-amine bond enthalpy. To maintain the greatest degree of electronic and steric fidelity to the dfepe ligand, while minimizing the conformational complexity that would arise from the introduction of perfluoroethyl

substituents, we replaced the C_2F_5 groups of dfpe with CF_3 to yield the dfmpe model ligand, $((\text{CF}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CF}_3)_2)$ [28].

The amination of CD-H by (dfmpe)Ni(NAr) was calculated using analogous QM/MM methods employed above for the dtbpe-substituted systems. *It was found that overall the enthalpy change for the formation of the metal-bound amine product is now exothermic and mildly endergonic!* The calculated amination enthalpy (ΔH_{am}) for the dfmpe-based complex is -17.3 kcal/mol, with a corresponding free energy change of +3.9 kcal/mol.

As before, we dissected the overall thermodynamic changes into two steps: hydrogen atom abstraction and radical rebound. Interestingly, the HAA step changed relatively little in energetics upon the dtbpe to dfmpe modification: $\Delta H_{\text{HAA}}(\text{dtbpe}) = 6.4$ kcal/mol; $\Delta H_{\text{HAA}}(\text{dfmpe}) = -5.2$ kcal/mol. *However, there is a more profound energetic change in the rebound step upon going from the dtbpe ligand to the fluorinated dfmpe.* $\Delta H_{\text{reb}}(\text{dtbpe}) = 20.3$ kcal/mol; $\Delta H_{\text{reb}}(\text{dfmpe}) = -2.6$ kcal/mol. Thus, replacement of dtbpe with dfmpe leads to a nickel-nitrene for which both HAA and rebound are now thermodynamically feasible. Kinetic factors will be discussed below.

The great change in the thermodynamics of amination upon replacement of dtbpe with dfmpe must presumably have both steric (dfmpe is less sterically constrained than dtbpe) and electronic (dfmpe is more electron-deficient than dtbpe) components. The less bulky substituents of dfmpe are expected to enhance addition of chemical groups at the nitrene nitrogen. It was expected from simple acid-base arguments that the nickel-amine bond energy would be enhanced by making the nickel a stronger Lewis acid in Ni(dfmpe) than in Ni(dtbpe). The overall effect of introducing a more electron-deficient phosphine on the nickel-amide bond strength was, however, unclear. Hence, this was addressed quantitatively by QM/MM calculations.

As expected, dfmpe enhances nickel-amine bond energy; the bond is increased from 22.6 to 36.5 kcal/mol, a 13.9 kcal/mol enhancement. More surprisingly, the nickel-amide bond is reduced upon introduction of the dfmpe ligand. The Ni-amide bond enthalpy of 86.7 kcal/mol for (dtbpe)Ni-NHAr is reduced to 67.7 kcal/mol for the corresponding nickel-amide bond energy of (dfmpe)Ni-NHAr, a 19.0 kcal/mol reduction in nickel-amide bond strength. This lessening on Ni-amide bond is driven entirely by electronic effects: the σ^* orbital (donation) becomes less stabilized with the

dfmpe ligand as the retrodonation diminishes from dtbpe to dfmpe. However, this condition is not achieved for the Ni-amine bond; methyl groups in the dtbpe ligand provoke the pyramidalization in the N-CD bond be more distorted and unfavour the overlap between x^2-y^2 orbital of Ni and the p_x orbital of amine group. Even methyl groups in dtbpe ligand are sterically more demanding, the dfmpe ligand favors this bonding interaction pointing towards the cyclohexadiene in a less stressing Ni-amine coordination. *Combining the two effects, the dtbpe to dfmpe substitution realizes 33 kcal/mol more driving force for the radical rebound step for the nickel complex with the latter ligand.* As a result, the rebound step that was previously so energetically forbidding is now enthalpically favorable, -2.6 kcal/mol! Even with the unfavorable TΔS term for radical rebound, the free energy change is expected to be close to thermoneutral (~1.0 kcal/mol). *Hence, from a thermodynamic viewpoint (dfmpe)Ni(NAr) appears a feasible candidate for further investigation as a hydrocarbon amination catalyst.* Presumably, the steric and electronic differences between our dfmpe model and Roddick's dfepe ligand are small enough to also warrant consideration of (dfepe)Ni(NAr) in this regard [29].

3.3. Closure of the Catalytic Cycle

While the thermodynamic feasibility of amination of CD-H by (dfmpe)Ni(NAr) is an exciting and necessary first step in catalyst development, other issues must be addressed. These include the following: First, it must be possible to synthesize (dfmpe)Ni(NAr) utilizing synthetic approaches common in the literature for late transition metal nitrenos [6-8], most specifically nitrene transfer from an organic azide with displacement of a labile ligand; Second, it must be thermodynamically feasible to displace the amine product (NHArCD in our exercise) by reaction with a group transfer reagent (*i.e.*, ArN_3) to regenerate the active nitrene species; Third, kinetic factors must be reasonable so as to permit a suitable reaction rate. Assessment of these issues from the computational chemistry perspective will entail the isolation of transition states for the processes just discussed. In this section, we consider each one of these in turn for (dfmpe)Ni(NAr).

a. Product Displacement by Reaction with ArN_3

The calculations above discussed indicate that the formation of metal-bound amine product, NHArCD , from nitrene and substrate is feasible in a thermodynamic sense. However, for a useful catalytic system, the amine product must be removed from the inner coordination sphere of the nickel complex, and the nitrene active species regenerated. We note that the original communication of the structural characterization of $(\text{dtbpe})\text{Ni}(\text{NAr})$ involved a multi-step synthesis from $(\text{dtbpe})\text{NiCl}_2$ starting materials [5a]. However, a recent report [30] describes the synthesis of cationic nickel nitrenes with dtbpe supporting ligation via reactions of nickel starting materials with ArN_3 and AdN_3 . As the amine is a neutral, labile (see the calculated nickel-amine bond enthalpies given above) ligand and the nickel in $(\text{dfmpe})\text{Ni}(\text{NHArCD})$ is formally zero-valent, the displacement of amine by a group transfer reagent such as ArN_3 is immediately suggested by literature precedent from the successful syntheses reported by several groups [6-8].

A QM/MM calculation of the energetics of amine product displacement with regeneration of the nickel-nitrene active species was thus performed equation 3.



Regeneration of the nitrene active species is calculated to be highly exothermic, $\Delta H_{\text{reg}} = -36.7 \text{ kcal/mol}$. The free energy change is expected to be even more negative given the increase in molecularity of the reaction. Hence, the catalyst regeneration step is indicated by the computations to be very favorable. We have assumed [6-8] that for this (and the following) requirement, these nitrene-transfer reactions will be kinetically facile given their substantial thermodynamic driving force. Mechanistic studies of metal-mediated organic azide decomposition are rare [31] and further research in this direction would be welcome and is ongoing in our laboratory [32].

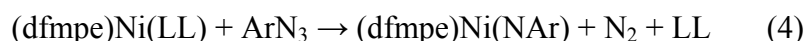
b. Initial Generation of the $(\text{dfmpe})\text{Ni}(\text{NAr})$ Active Species

Two main synthetic routes to the generation of late transition metal nitrenes have been employed: displacement of a labile ligand by reaction with an organic azide [6-8], and a more concerned route employed by Hillhouse and coworkers [5a] involving

reactions with alkali metal reagents (C_8K and LiNHAr), chemical oxidation (with a tropylium salt), and then deprotonation by a sodium-*bis*(silyl)amide reagent. Although the latter is used in the synthesis of (P~P)Ni(nitrene) complexes [5a], we have focused our initial research efforts on the more straightforward organic azide syntheses [6-8]. A modeling study of the multi-step Hillhouse synthesis for (dfmpe)Ni(NAr) is underway; gas-phase studies indicate that the individual steps, and the addition mechanism, are exothermic, but the involvement of charged species implying careful consideration of solvent effects is required.

Returning to our modeling of the synthesis of (dfmpe)Ni(NAr) by reaction of a (dfmpe)Ni(LL) starting material, LL = labile ligand, with ArN_3 , we identified three plausible candidates for LL from the work of Roddick *et al.* [22] These include the complexes (dfmpe)Ni(CO)₂, (dfmpe)Ni(COD) and (dfmpe)Ni(bpy), all of which are models of experimentally characterized dfepe complexes [22]. It should be pointed out that these three LL candidates are only a very small subset of the possibilities suggested by a survey of the CSD [27] for low-coordinate Ni^0 complexes; other possibilities include LL = dihapto-coordinated olefins, alkynes, ketones, arenes, benzyne, naphthalene, C_6F_6 , ArNCO , and carbodiimides.

ONIOM(B3LYP/6-31G(d):UFF) calculations were carried out for equation 4 to model the synthesis of the (dfmpe)Ni(NAr) active species, LL = (CO)₂, COD, and bpy; the latter two complexes are bidentate ligands.



The extreme electron-deficient nature of dfmpe is insufficient to ameliorate the strength of the Ni-CO interactions as indicated by the QM/MM calculated endothermicity of equation 4 for LL = CO. Even with the favorable entropic factors gained from displacement of two equivalents of CO, the reaction still remains close to thermoneutral ($\Delta H_4 = +19.6$ kcal/mol; $\Delta G_4 = -0.3$ kcal/mol). *However, the other two Roddick-inspired candidates, (dfmpe)Ni(COD) and (dfmpe)Ni(bpy), give displacement reactions for equation 4 that are calculated to be significantly exergonic: $\Delta G_4(\text{COD}) = -21.1$ kcal/mol and $\Delta G_4(\text{bpy}) = -22.6$ kcal/mol.*

c. Transition States for C-H Bond Activation

Analysis of the literature [1,3,6a,8] for C-H bond activation by multiply bonded metal complexes suggests three plausible mechanisms for carbon-hydrogen bond scission by (dfmpe)Ni(NAr): (a) direct [1+2] insertion; (b) a two-step mechanism involving [2+2] addition to yield a four-coordinate, Ni^{II}-amide intermediate, (dfmpe)Ni(NHAr)(CD), which is then followed by reductive elimination to give the desired product; and (c) hydrogen-atom abstraction to yield a three-coordinate, Ni^I-amide complex, (dfpme)Ni(NHAr), followed by radical rebound to give the metal-bond amine product, (dfmpe)Ni(NHArCD). Proposed mechanism (a) is supported by the extensive study of C-H bond insertion by late metal carbenoid species, including the well-known Simmons-Smith (zinc) reagents [33]. Proposed mechanism (b) is an alkane analogue of the mechanism proposed by Hillhouse *et al.* on the basis of their mechanistic studies of the reaction of (dtbpe)Ni(E), E = nitrene, carbene, phosphinides, with olefin substrates [5]; small models of these reaction (replacing *tert*-butyl groups of dtbpe with hydrogen atoms; NAr replaced by NH; ethylene substrate) have been reported by our group [34]. Furthermore, there is an ample precedent for both mechanism steps, including 1,2-addition across metal-element multiple bonds (albeit for early transition metals [3]) and reductive elimination by nickel(II) complexes [35]. The proposal (c) is inspired by the studies of Holland *et al.* [6a] and Warren *et al.* [8] on CD-H bond activation by Fe-nitrenes and Ni-nitrenes, respectively, although both of those nitrene complexes are open-shell (paramagnetic) entities. However, Mayer and coworkers have published substantially on the ability of closed-shell (diamagnetic) multiply bonded complexes to perform HAA for hydrocarbon substrates [36]. Finally, it must be noted that a three-coordinate, Ni^I-amide complex has been characterized by Hillhouse *et al.* [5a], and indeed is a synthetic precursor to their Ni-nitrene complex.

Initial studies were carried out with small model substrates (methane) and ligands (dhpe = H₂PCH₂CH₂PH₂) to compare the [1+2], [2+2] and HAA/rebound mechanisms [37]. Our studies for the small nitrene model, (dhpe)Ni(NH), indicates that a single-step [1+2] (*i.e.*, insertion) mechanism has a lower barrier than a two-step (*i.e.*, [2+2] addition then reductive elimination) process [38]. *Constructing appropriate transition states from the [1+2] and [2+2] small models, plus isolation of the HAA transition state for full chemical models, indicates that hydrogen atom abstraction is the*

preferred pathway to C-H activation of 1,4-cyclohexadiene by (dfmpe)Ni(NAr). Starting geometry optimizations from [1+2] and [2+2] transition states for activation of CD-H by the full (dfmpe)Ni(NAr) complex indicates, despite the investigation of multiple starting conformations, that all searches collapse to an HAA transition state. The single imaginary frequency of this HAA transition state is characterized by movement of the hydrogen atom of the C-H bond being activated from the CD-H substrate to the nitrene nitrogen, Figure 3.

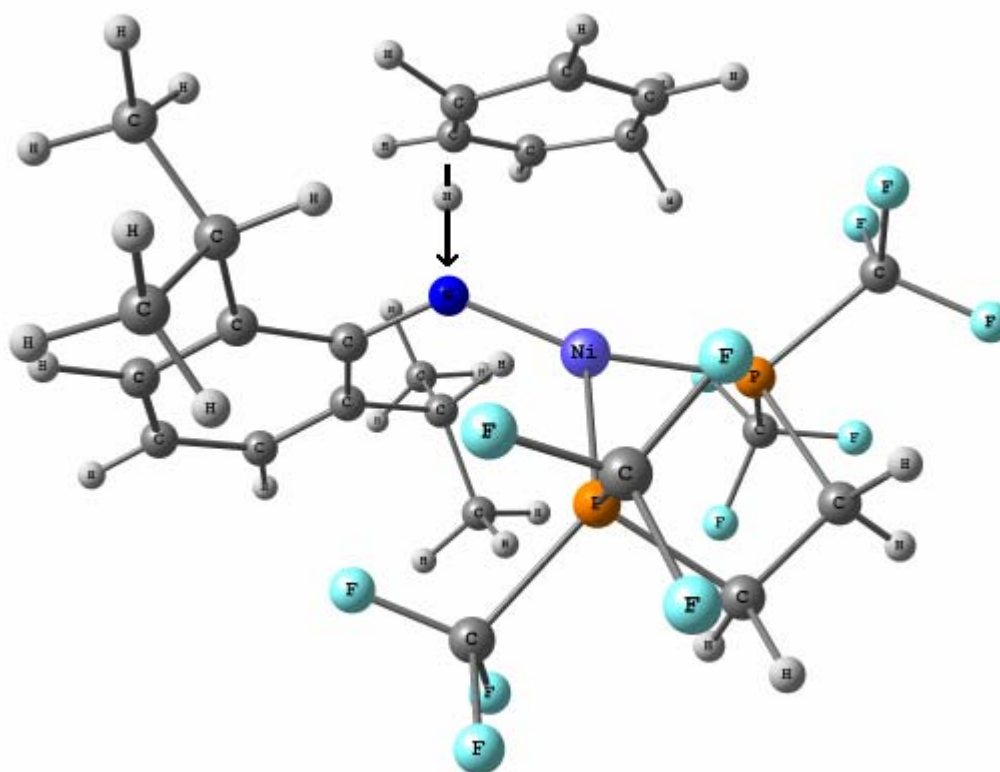


Figure 3. Transition state structure found for the Hydrogen Atom Abstraction (HAA) reaction mechanism at $1148i\text{ cm}^{-1}$. The bold arrow points out the reaction coordinate followed for this pathway.

The calculated transition state is only 19.6 kcal/mol (enthalpy) above the separated reactants, (dfmpe)Ni(NAr) and CD-H. Calculation of the intrinsic reaction coordinate (IRC) leads to a nominally bound adduct of the two reactants, which is bound by -9.5 kcal/mol relative to separated reactants. *The calculated enthalpic barrier of $(19.6 - 9.5 =) 10.1\text{ kcal/mol}$ is thus quite reasonable.*

The calculated IRC from the HAA transition state to the product side indicates that the products are indeed the radical pair, (dfmpe)Ni(NHAr) and CD, and neither an inserted amine product, (dfmpe)Ni(NHArCD), nor a square-planar complex, (dfmpe)Ni(NHAr)(CD). The radical pair is calculated by the QM/MM methods to be 4.8 kcal/mol (enthalpy) less stable than the separated reactants, (dfmpe)Ni(NAr) and CD-H. The square-planar complex, (dfmpe)Ni(NHAr)(CD), was generated independently and found to be -14.7 kcal/mol more stable than separated reactants and hence, 9.9 kcal/mol more stable than the radical pair (Figure 4).

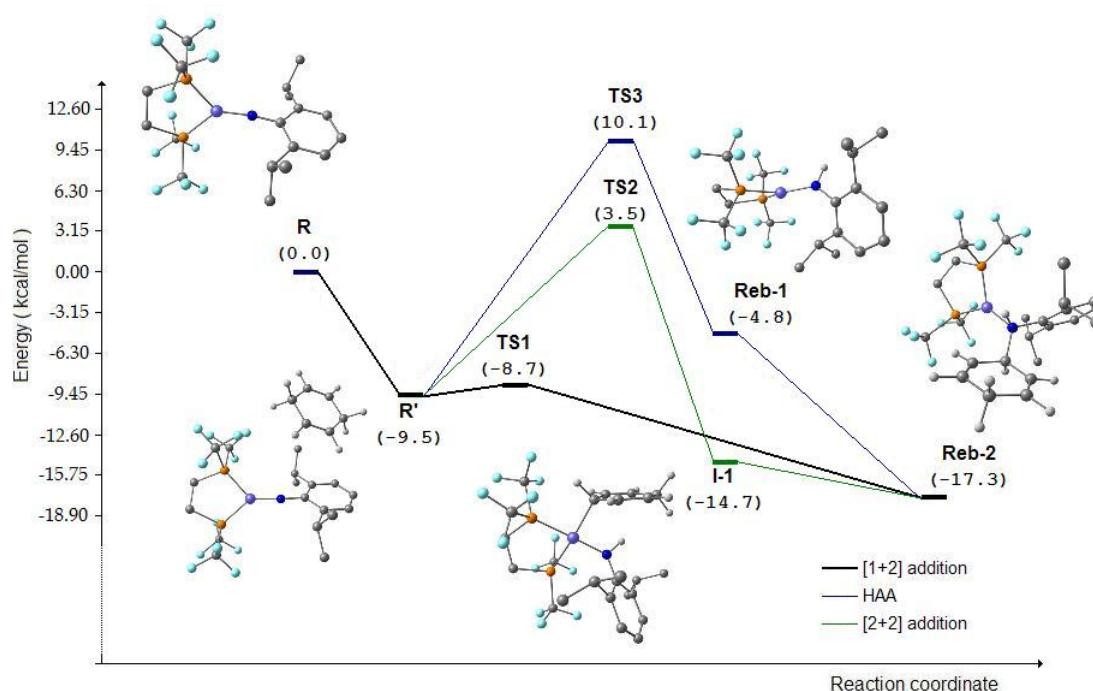


Figure 4. Potential energy surface (enthalpy diagram) of amination of 1,4-cyclohexadiene by (dfmpe)Ni(NAr). Numbers in parenthesis are relative energies (in kcal/mol) with respect to the reactant (**R**) molecule.

Given that the IRC indicates that the course of the reaction follows the pathway nitrene + CD-H \rightarrow amide + CD, two subsequent routes from amide intermediate to amine product seem plausible. The first possibility is the formation of a nickel-carbon bond to yield (dfmpe)Ni(NHAr)(CD), which would then undergo reductive elimination to produce the final metal-bound product, (dfmpe)Ni(NHArCD). The second possibility

entertained was direct formation of a nitrogen-carbon bond by radical rebound. From our calculations, the metal-bound product is the most stable entity within the catalytic cycle we have modeled; this complex lies -17.3 kcal/mol in energy relative to separate reactants. Thus, formation of (dfmpe)Ni(NHArCD) is exothermic by 12.6 kcal/mol from the radical pair and exothermic by 2.7 kcal/mol from (dfmpe)Ni(NHAr)(CD), see Figure 5. Although we were unable to isolate a reductive elimination transition state connecting (dfmpe)Ni(NHAr)(CD) and (dfmpe)Ni(NHArCD), several observations are germane. First, one would expect steric factors to favor the rebound mechanism over the "metal rebound" mechanism as the former would entail the formation of less crowded three-coordinate, Ni^0 -amine product rather than a four-coordinate, Ni^{II} intermediate. Second, our model calculations suggest that reductive elimination from four-coordinate, Ni^{II} intermediates is facile, and even if formed, is thus not expected to present an insurmountable kinetic impediment.

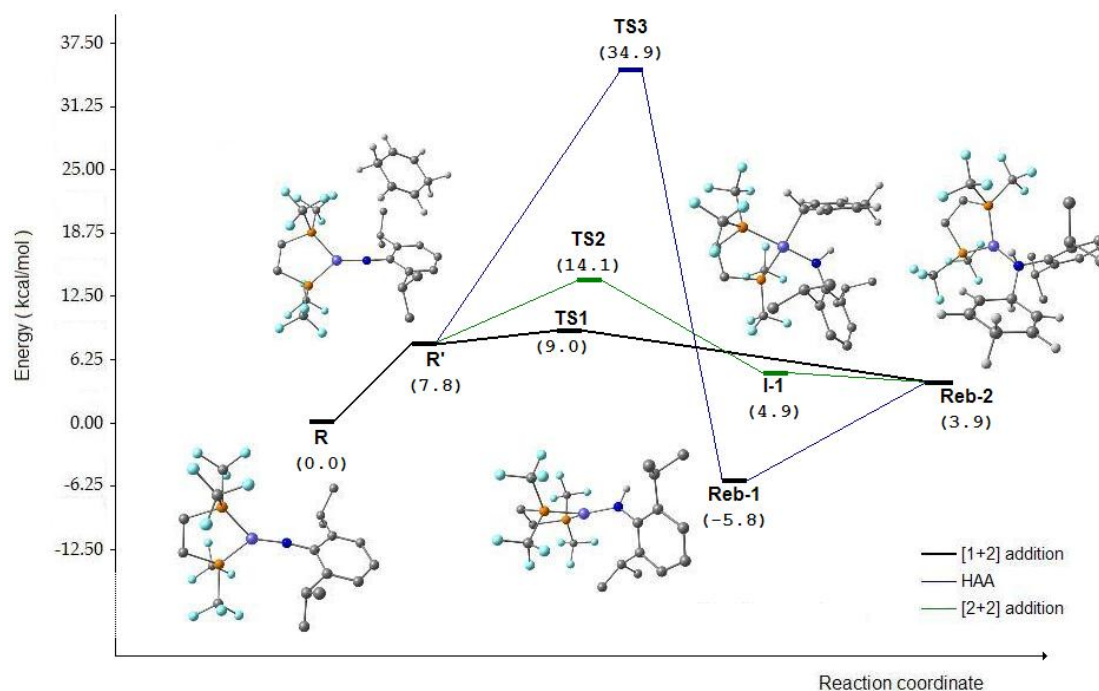


Figure 5. Free-energy surface of the amination of 1,4-cyclohexadiene by (dfmpe)Ni(NAr). Numbers in parenthesis are relative energies (in kcal/mol) with respect to the reactant (**R**) molecule.

4. Conclusions

A computational chemistry study of a catalytic cycle for amination of a hydrocarbon has been studied in order to identify novel and promising systems for experimental study. A nickel-nitrene active species was chosen on the basis of the growing body of experimental research on this and similar late transition metal multiply bonded complexes, although to our knowledge, no bona fide examples of C-H bond functionalization have been yet reported. An existing system reported by the Hillhouse group was modified using a variety of criteria designed to maintain maximum overlap with experimentally reported nitrene complexes and feasible synthons thereof. Several intriguing results emanated from this first generation catalyst-design research. Our calculations indicate that introducing a more electron-deficient ligand might enhance the metal-amine bond strength meanwhile the metal-amide bond strength is diminished. Moreover, the overall enthalpy change for the formation of the metal-bound amine product becomes significantly more favorable when the dtbpe ligand is exchanged by the dfmpe ligand. Hence, from a thermodynamic point of view $(dfmpe)Ni(NAr)$ complex seems to be a feasible candidate to be analyzed experimentally as a hydrocarbon amination catalyst.

The amination of 1,4-cyclohexadiene produces a square-planar complex, $(dtbpe)Ni(NHAr)(CD)$, when the bulkier dtbpe ligand is employed, which is thermodynamically favored instead of the expected $(dtbpe)Ni(NHArCD)$ amine product by 47.09 kcal/mol. Whereas the amination of CD-H by $(dfmpe)Ni(NAr)$ change significantly the course of the reaction increasing the feasibility of the direct C-H bond activation producing the Ni-amine product by radical rebound. We have discussed above the kinetics factors involved in these catalytic amination reactions. Furthermore, the catalyst regeneration step was predicted to be very favorable for the reported mechanisms here. We believe such systems deserve serious experimental considerations for catalytic hydrocarbon functionalization.

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Reactivity of TpRu(L)(NCMe)R ($\text{L} = \text{CO}, \text{PMe}_3$; $\text{R} = \text{Me}, \text{Ph}$) Systems with Isonitriles

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