

Theoretical study of group transfer from multiply-bonded nickel complexes to ethylene

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Abstract

The results of density functional theory (DFT) calculations are analyzed to investigate the thermodynamic and kinetic feasibility of nickel-mediated group transfer ($E = \text{CH}_2, \text{NH}, \text{PH}$) to ethylene to form three-membered ring products. From the results of DFT geometry optimizations it is concluded that the $(\text{dhpe})\text{Ni}=\text{O}$ congener is unstable, $\text{dhpe} = 1,2\text{-bis}(\text{-dihydrophosphino})\text{ethane}$, rearranging to a phosphine oxide. With respect to the calculated enthalpies of the individual reaction steps, as well as their enthalpic barriers, the $(\text{dhpe})\text{Ni}$ system is a potent system for heterogroup transfer to olefins to synthesize cyclic organics, i.e., aziridines, cyclopropanes and phosphiranes. The individual mechanistic steps and overall reaction are calculated to be highly exothermic for all transfer groups investigated: nitrene, carbene and phosphinidene. Furthermore, the calculated $[2_\pi + 2_\pi]$ transition states entail the dissociation of one of the Ni–P bonds of dhpe ; when the $[2 + 2]$ products are subsequently formed, dhpe reverts to η^2 coordination. The calculated results suggest that reductive elimination from the four-membered metallaheterobutane intermediate is the rate-determining step of the group transfer mechanism for all E . The greater kinetic barrier for $E\text{-C}$ reductive elimination relative to $[2_\pi + 2_\pi]$ addition correlates with the greater thermodynamic driving force for the latter.

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1. Introduction

The formation of carbon–carbon and carbon–heteroatom bonds is a fundamental purpose in synthetic organic chemistry [1]. Atom and group transfer reactions are central to the chemistry of transition metal complexes with multiply bonded ligands [2]. Such processes are finding relevance in the field of catalysis, and also have been widely proposed in catalytic processes that occur in metalloprotein active sites. For example, biological oxygen atom transfer reactions to organic substrates, catalyzed by metalloenzymes as well as biomimetics, are well known [2e].

Due to the presence of filled $d\pi$ orbital, examples of multiply bonded complexes of the late transition metals such as cobalt, nickel and copper are rare [3]. Examples of multiply bonded transition metal complexes are typically limited to metals from the early to middle transition series in high formal oxidation states [4]. The majority of terminal oxo complexes have d^{0-2} configurations [5], which therefore does not result in occupation of metal–ligand π^* orbitals for the most common octahedral and square pyramidal coordination geometries. Multiply-bonded nickel complexes with phosphinidene [6], nitrene [7], and carbene [8] ligands by Hillhouse and his group are rare examples of stable, multiply bonded complexes of the late transition metals. Furthermore, these Hillhouse complexes have been used for organic synthetic transformations, specifically group transfer to olefins to form three-membered ring products [6–8].

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Aziridines serve as important intermediates for functional group modifications and ligands in asymmetric catalysis. Their synthesis has thus been the subject of considerable interest. Evans [9] and Jacobsen [10], among others, have done important work on transition metal-catalyzed aziridination. For example, they reported that Cu(I) and Cu(II) salts form competent precatalysts and indicated that a common oxidation state is reached in both cases [9,10]. Brandt et al. performed a combination of hybrid density functional (B3LYP) calculations and kinetic experiments [11] on Cu(I) and Cu(III) complexes. These researchers proposed a catalytic cycle to rationalize the catalytic inactivity of the higher oxidation state of Cu for aziridination. Recent preparations of metastable Ni–nitrene complexes by Hillhouse et al. [7] have allowed their aziridination reactivity to be assessed; stoichiometric transfer of nitrene groups to ethylene result in the formation of aziridines [7].

Cyclopropanes are also an important class of molecules. The strain associated with the three-membered ring allows cyclopropanes to undergo useful ring-opening reactions in organic synthesis. The Simmons–Smith reaction, which employs a zinc-based catalyst and for which a carbenoid intermediate is proposed, is a classic method for the synthesis of cyclopropanes from olefins [12].

The chemistry of phosphorus-containing, three-membered ring compounds – phosphiranes – has not been studied as extensively as their oxygen, nitrogen, or carbon congeners [13]. Beyond early studies of phosphiranes by Wagner [14] and Chan [15], phosphiranes were little studied until Mathey and coworkers developed improved synthetic methods via Cr-triad complexes [16,17]. Monocyclic phosphiranes can form metallaphosphetanes with electron-rich metals via an insertion of the metal center into a σ_{PC} bond [18–20]. Phosphiranes have several interesting properties, e.g., increased resistance to oxidation as compared to normal phosphines. Phosphiranes may act as better π -acceptors versus acyclic phosphines, because the pyramidalization of the phosphorus coordination sphere decreases the energy of acceptor orbitals that are σ_{PC}^* in character. A previous computational study [21] of phosphiranes indicated that they have interesting stereoelectronic properties as compared to traditional acyclic phosphines used in organometallic catalysis, and thus pathways to their synthesis are important in this regard.

Recent preparation of stable nitrene [7], phosphinidene [6], and carbene [8] complexes with (dtbpe)Ni (dtpbe = 1,2-bis(di-tert-butylphosphino)ethane) has expanded the scope of reactivity studies of late transition metal multiply bonded complexes. The kinetics and thermodynamics of the proposed mechanism for the reaction of ethylene with (dhpe)Ni=E, (dhpe = 1,2-bis(dihydrophosphino)ethane), have been studied in the present research.

2. Computational methods

The Gaussian 03 package was employed for all calculations described in this research. In conjunction with the

B3LYP hybrid functional [22,23], the effective core potentials (ECPs) and valence basis sets of Stephens, Basch and Krauss [24] (CEP-31G) were utilized to describe nickel and main group elements. Basis sets were augmented with a d-polarization function for main group elements (exponent of 0.8 for C and N; 0.55 for P). The -31G basis set was employed for hydrogen. This level of theory has been shown to be reliable in previous studies for the prediction of transition metal geometries and energetics when used in conjunction with a suitable wavefunction or density functional theory technique [25].

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). Intrinsic reaction coordinate (IRC) calculations were carried out to confirm that calculated transition states connected the indicated reactants and products. The thermochemistry of the reactions was determined at 1 atm and 298.15 K using unscaled B3LYP/CEP-31G(d) calculated vibrational frequencies.

3. Results and discussion

The process studied is the reaction between (dhpe)Ni=E (E = CH₂, NH, PH) and two equivalents of ethylene to give cyclic organic and Ni(0)–ethylene products as shown in the following equation. Fig. 1 shows the two-step reaction sequence proposed for the above reaction [6–8].

The first phase of the mechanism, Fig. 1, is the interaction of the Ni=E complex with an equivalent of ethylene to give a four-membered ring product through a $[2\pi + 2\pi]$ mechanism. The second phase of the reaction is conversion of a metallaheterobutane through a C–E reductive elimination transition state to yield a three-membered ring product; the latter is then dissociated from the nickel by coordination of a second molecule of ethylene, Fig. 1, to give an ethylene adduct, which is the final nickel-based product characterized by Hillhouse and coworkers [6–8].

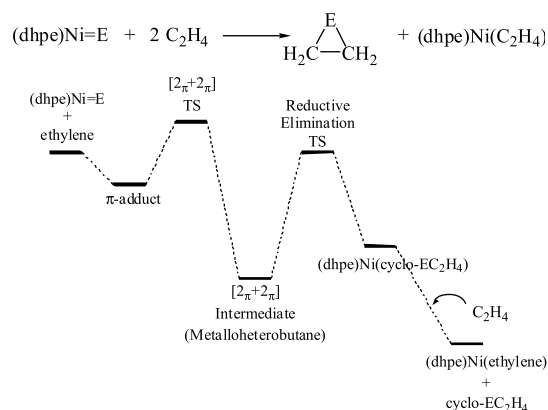


Fig. 1. Mechanism investigated for the reaction of ethylene and (dhpe)Ni=E.

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