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A Dinickel Catalyzed Cyclopropanation without the Formation of a Metal Carbene Intermediate

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Abstract: (NDI)Ni₂ catalysts (NDI = naphthyridine–diimine) promote cyclopropanation reactions of 1,3-dienes using (Me₃Si)CHN₂. Mechanistic studies reveal that a metal carbene intermediate is not part of the catalytic cycle. The (NDI)Ni₂(CHSiMe₃) complex was independently synthesized and found to be unreactive toward dienes. Based on DFT models, we propose an alternative mechanism that begins with a Ni₂-mediated coupling of (Me₃Si)CHN₂ and the diene. N₂ extrusion followed by radical C–C bond formation generates the cyclopropane product. This model reproduces the experimentally observed regioselectivity and diastereoselectivity of the reaction.

Introduction

Most transition metal catalyzed cyclopropanation reactions diazoalkanes as carbene precursors.^[1] Mechanistic use proposals for these reactions generally invoke the formation of a metal carbene complex by catalyst-induced N₂ extrusion (Figure 1). It should be noted however that for a majority of catalysts, the key M=CR₂ intermediate cannot be directly observed, let alone structurally characterized.^[2] Therefore, alternative cyclopropanation pathways that do not involve M=CR₂ species warrant consideration. Additionally, identifying such pathways may provide new avenues to develop cyclopropanation reactions with substrate scopes or selectivity properties that are complementary to existing methods.

Catalytic cyclopropanations are mechanistically related to oxygen-atom transfer reactions. For example, the active oxidant in a cytochrome P450 catalyzed oxidation is a ferryl porphyrin radical cation (compound I), generated from the activation of O₂.^[3] Abiological variants of this process have also been developed, often using iodosylarenes or peroxycarboxylic acids as O-atom sources.^[4] Collman and Brauman demonstrated that the selectivites observed in (TPP)Mn catalyzed alkane C-H hydroxylations are dependent on the identity of the oxidant.^[5] This observation indicates that the O-atom donor is present in the selectivity-determining step, effectively ruling out a common M=O intermediate. In related work, Nam investigated a (TMC)Fe catalyzed epoxidation and observed that chiral peroxycarboxylic acid and iodosylarene reagents can induce high levels of enantioselectivity.^[6] Taken together, these and several other studies^[7] show that high-valent M=O species may not always be true catalytic intermediates, even in cases where they have been synthesized and characterized. Similar observations have been made for nitrene transfer reactions using organoazides and iminoiodinanes ${}^{\scriptscriptstyle[8]}$





Figure 1. Metal carbenes are key intermediates in several catalytic cyclopropanation reactions using diazoalkanes. Dinickel complexes catalyze regioselective cyclopropanations of 1,3-dienes without generating a Ni₂(μ -CR₂) intermediate.

Here, we present a diazoalkane-based cyclopropanation reaction that does not involve the formation of a metal-bound carbene intermediate (Figure 1). The reaction being investigated is a (NDI)Ni₂ catalyzed (NDI = naphthyridine–diimine) cyclopropanation of 1,3-dienes using (Me₃Si)CHN₂. The putative (NDI)Ni₂(CHSiMe₃) intermediate in this reaction is an isolable molecule but is unreactive toward 1,3-dienes. On the basis of DFT

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modeling studies, we instead propose a mechanism in which the Ni_2 (diazoalkane) adduct reacts with the 1,3-diene to generate a metallacycle. Subsequent N_2 elimination and diradical cyclization yields the cyclopropane product.

Results and Discussion

Catalytic Regioselective Cyclopropanation of 1,3-Dienes

Transition metal catalyzed cyclopropanation reactions of unsymmetrical 1,3-dienes have previously been investigated, but they have limited synthetic utility because of their poor regioselectivity.^[9] For example, additions of ethyl diazoacetate to myrcene (**2**) yield mixtures of monocyclopropane regioisomers (ranging from 1.2:1 to 3.1:1) using common cyclopropanation catalysts such as Rh₂(OAc)₄, Cu(OTf)₂, and Pd(OAc)₂.^[10] Presumably, this lack of selectivity reflects the inability of the metal carbene intermediate to adequately discriminate between the two double bonds on the basis of subtle differences in their steric and electronic properties.

In light of this precedent, we were surprised to find that (^{i-Pr}NDI)Ni₂(C₆H₆) (1) catalyzes the cyclopropropanation of myrcene (2) using (Me₃Si)CHN₂ (3) to afford 4 as a single regioisomer within the limits of ¹H NMR detection (Figure 2). After a reaction time of 6 h at 22 °C, product 4 is obtained in 92% yield as a 10:1 ratio of diastereomers. The (NDI)Ni₂ catalyst appears to be uniquely active in this transformation relative to other nickel catalysts. For example, complexes bearing structurally related nitrogen-based chelating ligands (5–7) provided no yield of cyclopropanes under the same set of reaction conditions.



Figure 2. Ni₂-catalyzed cyclopropanation of myrcene (2) using (Me₃Si)CHN₂ (3). Reaction conditions: 2 (0.05 mmol), 3 (0.06 mmol), catalyst (5 mol%), 22 °C, 12 h, C₆D₆. Yields and *trans/cis* ratios were determined by ¹H NMR integration.

The scope of 2-substituted 1,3-dienes is summarized in Figure 3. Common polar and non-polar functional groups are tolerated. The regioselectivity is uniformly high regardless of the substituent at the 2-position. On the other hand, the diastereoselectivity is variable and does not display any straightforward correlation to the steric or electronic properties of the substituent. Larger silyl groups lead to improvements in diastereoselectivity (**15** vs. **13**). The relative stereochemistry of the major diastereomer was assigned using NOESY experiments, and product **14** proved to be a crystalline solid whose structure

could be determined by XRD analysis. Isolated alkenes are catalyst unreactive using 1, allowing for the monocyclopropanation of a triene to form product 11 in 80% yield. 2,3-Disubstituted dienes and terminally substituted dienes do not undergo cyclopropanation. Finally, the vinylcyclopropane products of this reaction are viable substrates for Ni-catalyzed 1,3-rearrangements to form trimethylsilylcyclopentenes.^[11] The rearrangement of 8 exhibits a modest selectivity for activation of the C–C bond bearing the TMS group, consistent with an α-silicon effect.^[12] An inspection of the crystal structure of 14 reveals that the C-C(TMS) bond is 0.04 Å longer than the C-C bond that leads to the minor regioisomer.



Figure 3. Substrate scope studies. Reaction conditions: 1,3-diene (0.2 mmol), (Me₃Si)CHN₂ (0.22 mmol), 1 (5 mol%), 22 °C, 6 h, C₆H₆. For 15, (PhMe₂Si)CHN₂ was used instead of (Me₃Si)CHN₂. Isolated yields and dr values were determined following purification by column chromatography.

Synthesis of Ni2 Diazoalkane, Carbene, and Diene Complexes

In order to gain insight into the cyclopropanation mechanism and the origin of the regioselectivity, we targeted the synthesis of plausible catalytic intermediates. (Me₃Si)CHN₂ (**3**) reacts stoichiometrically with (^{*i*-P}rNDI)Ni₂(C₆H₆) (**1**) to yield a dark brown crystalline solid that was determined to be the μ - η^2 : η^1 diazoalkane adduct (**18**) by XRD analysis (Figure 4b). The N1–N2 distance of the bound diazo ligand is elongated (1.29(2) Å) relative to the expected distance for a free diazoalkane (e.g., 1.146(2) Å for bis(4-dibromophenyl)diazomethane).^[13] The C1–N2–N1 angle is also bent (133(1)°), indicating a reduction in the N1–N2 bond

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order. The ¹H NMR spectrum for **18** displays a well-defined set of paramagnetically shifted signals spanning a broad chemical shift window of –79 to +120 ppm. The effective magnetic moment was calculated to be $2.80\mu_{\rm B}$, consistent with an *S* = 1 ground state (Evans method, THF- d_8 , 298 K).



Figure 4. (a) Conversion of ($^{i-P_T}ND$)Ni₂(N₂CHSiMe₃) complex (18) to ($^{i-P_T}ND$)Ni₂(CHSiMe₃) (19). (b) Solid-state structure of 18. Selected bond distances and angles: Ni1–Ni2, 2.627(1) Å; Ni1–N1, 1.74(2) Å; Ni2–N2, 1.80(1) Å; Ni2–N1 1.90(3) Å; N1–N2, 1.29(2) Å; C1–N2, 1.30(1) Å; C1–N2–N1 133(1)^e. (c) Solid-state structure of 19. Selected bond distances: Ni1–Ni2 2.354(4) Å; Ni1–C1 1.897(4) Å; Ni2–C1 1.901(5) Å. (d) Solid-state structure of 20. Selected bond distances: Ni1–Ni2 2.5778(5) Å; Ni1–C1 1.970(2) Å; Ni1–C2 2.062(2) Å; Ni2–C3 1.982(2) Å; Ni2–C4 1.992(2) Å; C1–C2 1.384(4) Å; C2–C3 1.456(3) Å; C3–C4 1.368(4) Å.

The diazoalkane adduct **18** is stable in THF solution for >24 h at room temperature. However, upon warming to 60 °C, it undergoes N₂ extrusion to yield the dark purple (^{*i*} P'NDI)Ni₂(CHSiMe₃) complex (**19**) (Figure 4a).^[14] We^[15] and Hillhouse^[16] previously characterized Ni₂(µ-CPh₂) complexes that display unsymmetrical structures due to a π-interaction between one Ni and the Ph substituent. By comparison, **19** lacks this feature and is pseudo-C_s symmetric in the solid state (Figure 4c). The number of ¹H NMR signals in THF-d₈ suggests that this symmetry is maintained in solution. Like the diazo precursor **18**, **19** exhibits an *S* = 1 ground state, assigned on the basis of its effective magnetic moment (2.79µ_B; Evans method, 298 K). DFT models corroborate this spin state assignment and show one unpaired electron residing in the NDI π-system and the other in a Ni₂-based orbital.

We next examined the interaction between the Ni₂ catalyst and the 1,3-diene component of the reaction. Upon heating a 1:1 mixture of (^{*P*P}NDI)Ni₂(C₆H₆) (1) and phthalimide-substituted diene **21** at 60 °C in THF for 12 h, quantitative ligand substitution was observed to form the green diamagnetic diene adduct **20**. In the solid state, the bound diene resides in an *s*-cis geometry and binds in a μ - η^2 : η^2 fashion across the two Ni centers (Figure 4d). The C1–C2 and C3–C4 distances are elongated (1.384(4) Å and 1.368(4) Å, respectively), indicating a significant degree of backbonding from the Ni–Ni bond. In solution, the ¹H NMR spectrum for **20** shows no evidence of line broadening, and the number of signals corresponds to a *C*₁-symmetric species, suggesting that there are no fluxional processes that interconvert other possible binding modes of the diene.

Mechanistic Studies of Cyclopropanation

The successful isolation of Ni₂ diazoalkane, carbene, and diene complexes provided us with a unique opportunity to assess their relevance to the mechanism of the catalytic cyclopropanation. To determine the primary catalyst resting states under standard turnover conditions, a reaction between **2** and **3** was monitored by ¹H NMR spectroscopy. At 73% conversion of the diene, (^{*i*-Pr}NDI)Ni₂(N₂CHSiMe₃) (**18**) accounted for 40% of the total catalyst loading. Isolated complexes **18** and **20** could be used as catalysts in the place of (^{*i*-Pr}NDI)Ni₂(C₆H₆) (**1**) and provided **4** in similar yields and diastereoselectivities, verifying that they are both catalytically competent (Table 1, entries 1 and 2).

Table 1. Evaluating the catalytic activity of (NDI)Ni2 complexes.[a]



entry	catalyst	trans:cis	Yield 4
1	(^{i.Pr} NDI)Ni ₂ (N ₂ CHSiMe ₃) (18)	10:1	92%
2	(^{i-Pr} NDI)Ni ₂ (diene) (20)	10:1	87%
3	(^{i-Pr} NDI)Ni ₂ (CHSiMe ₃) (19)	-	0%



A stoichiometric reaction between the isolated (^{i-Pr}NDI)Ni₂(N₂CHSiMe₃) complex (**18**) and diene **21** (1.0 equiv) yielded cyclopropane **13** in 60% yield (7:1 dr) after 12 h at room temperature (Figure 5a). As the reaction progresses, the unreacted diene coordinates to the free (NDI)Ni₂ that is being generated, preventing full conversion from being reached. Similarly, (^{i-Pr}NDI)Ni₂(diene) (**20**) also reacts with (Me₃Si)CHN₂ (**3**) (1.0 equiv) to form a mixture of cyclopropane **13** (30% yield), unreacted **20** (70% yield), and the (^{i-Pr}NDI)Ni₂(C₆D₆) (**1**) (30% yield) (Figure 5b). Nearly quantitative yield of cyclopropane **13** was achieved, when the equivalency of (Me₃Si)CHN₂ (**3**) was increased to 3.0 equiv. Thus, experiments under both catalytic

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and stoichiometric conditions are consistent with **18** and **20** either lying on the catalytic cycle or being in an off-cycle equilibrium.

We reasoned that (^{*i*-P^T}NDI)Ni₂(CHSiMe₃) (**19**) was unlikely to be an intermediate in the catalytic cyclopropanation, because it is only generated from the diazoalkane precursor **18** at elevated temperatures. The catalytic cyclopropanation, by contrast, reaches full conversion within hours at room temperature. As further evidence that **19** is not a catalytic intermediate, it does not react stoichiometrically with diene **21** even after heating at 80 °C for 12 h (Figure 5c). (^{*i*-P^T}NDI)Ni₂(CHSiMe₃) (**19**) is also not competent as a catalyst for the reaction between **3** and **2** (Table 1, entry 3). Interestingly, when **19** was treated with a less hindered diene (**22**), there was still no formation of cyclopropanated products, but the [4 + 1]-cycloaddition product **16** was obtained in 20% yield. Notably, there are no detectable [4 + 1]-cycloaddition products formed in any of the catalytic reactions shown in Figure 3.



Figure 5. Stoichiometric cyclopropanation reactions with (a) 18, (b) 20, and (c) 19. Yields and dr values were determined by ¹H NMR integration.

DFT Models for the Ni₂-Catalyzed Cyclopropanation

The experimental results described above indicate that there is a viable cyclopropanation mechanism that proceeds from the diazoalkane and does not involve the formation of a Ni₂

carbene complex. To identify such a mechanism, DFT calculations were carried out with the constraint that any reasonable model would need to rationalize the unusual regioselectivity observed in the reaction. First, the diazoalkane and diene adducts were calculated at the BP86/6-311G(d,p) level of theory (Figure 6). The optimized structures (**S1** and **S2**) were found to closely reproduce the structures observed experimentally by XRD (**18** and **20**). Additionally, the calculations accurately determined an S = 1 ground state for the diazoalkane complex and an S = 0 ground state for the diene complex.

A (NDI)Ni₂ complex containing both the diazoalkane and the diene bound to the active site was located **(S3)**. The diazoalkane lies in the (NDI)Ni₂ plane and maintains its μ - η^2 ; η^1 coordination mode. The diene binds in an η^2 -fashion through the less hindered double bond. The Ni–Ni distance is significantly elongated to 3.103 Å, suggesting the absence of a direct metal-to-metal covalent bond. The 1-position of the diene is located in close proximity to the diazoalkane carbon, and a transition state **(S4)** for the coupling could be successfully optimized with an activation barrier of +16.3 kcal/mol. ^[17] The resulting metallacycle **(S5)** is nearly isoenergetic with **S3**.

From here, we explored several possible concerted pathways for cyclopropanation where C-C bond-formation occurs in concert with N₂ expulsion. While several such transition states could be located, they were all found to be prohibitively high in energy. Instead, an energetically viable stepwise mechanism was identified. Homolytic cleavage of the C-N bond (S6) has a calculated activation barrier of +18.0 kcal/mol. The resulting diradical intermediate (S7) was modeled as an open-shell singlet with a C-centered α-TMS radical. The other unpaired electron (anti-parallel spin) is delocalized in the π -system of the NDI ligand. The triplet spin state for S7 was also considered and found to be 0.6 kcal/mol lower in energy. Given this small energy difference, any barrier to spin flipping would likely make the open-shell singlet pathway more favorable. From S7, the final cyclopropane product is generated from a low-barrier attack of the C-centered radical on the Ni-bound allyl ligand (+1.0 kcal/mol).

In the calculated reaction pathway, the initial coupling step (S4) is reversible, and the N₂ expulsion step (S6) is ratedetermining and irreversible. Therefore, the regioselectivity of the cyclopropanation is determined by the relative energies of the S6 transition states. Gratifyingly, the transition state leading to the alternative regioisomer (S6') is 5.9 kcal/mol higher in energy. In S6', the metallacycle is rotated in order to alleviate an unfavorable steric interaction between the benzyl group and an *i*-Pr substituent of the catalyst (Figure 6).

Because C–N bond cleavage in **S6** forms of a planar radical intermediate, the diastereoselectivity of the cyclopropanation is not determined in this step but rather in the later recombination step **S8**. From **S7**, single bond rotation would allow for the C–C bond formation to occur on either face of the radical. The transition state leading to the alternative diastereomer was calculated to be 1.1 kcal/mol higher in energy, which is consistent with the dr determined experimentally for this substrate combination (6:1 dr; $\Delta\Delta G^{\ddagger} = +1.1$ kcal/mol).

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Conclusion

In summary, (NDI)Ni₂ catalysts promote cyclopropanation reactions of 1,3-dienes using (Me₃Si)CHN₂. Mechanistic studies rule out (NDI)Ni₂(CHSiMe₃) (**19**) as a catalytic intermediate. Complex **19** is only generated from the diazoalkane adduct **18** when heated for an extended period of time at 60 °C. By contrast, the catalytic cyclopropanation reaches full conversion within hours at room temperature. Furthermore, isolated **19** does not react stoichiometrically with dienes nor does it function as a cyclopropanation catalyst.

An alternative mechanism was identified using DFT models. An initial coupling of the bound diazoalkane and the 1,3-diene forms a metallacyclic intermediate. Homolytic C–N bond cleavage expels N₂ and generates a diradical intermediate that undergoes rapid recombination to form the cyclopropane product. Notably, this calculated pathway reproduces the experimentally observed regioselectivity and diastereoselectivity of the reaction. It also provides a rationale for the observation that monoalkenes, unlike 1,3-dienes, do not undergo cyclopropanation. Together, these results show that diazoalkanes can participate in catalytic cyclopropanation reactions without the generation of a metal carbene intermediate. The unusual selectivity properties of the Ni₂ catalyzed reaction arise from avoiding a direct [2 + 1]cycloaddition of a $M=CR_2$ and an alkene, the most common mechanism proposed for other classes of catalysts.

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Keywords: nickel • carbenes • metal-metal interactions • cyclopropane • homogeneous catalysis

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Entry for the Table of Contents



Dinickel complexes catalyze regioselective cyclopropanations of unsymmetrical 1,3-dienes using TMSCHN₂. Mechanistic studies suggest that the reaction proceeds by a diazoalkane–diene coupling mechanism and does not require the formation of a dinickel carbene intermediate.

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