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A formal carbene-transfer reaction from an isolated nickelacyclobutane to an isocyanide to form a ketenimine is reported. DFT calculations support a stepwise 1,1-insertion/fragmentation pathway without a carbene intermediate. This unusual reactivity suggests a potential new role as “carbene reservoir” for nickelacyclobutanes, which are typically seen as intermediates in catalytic cyclopropanation.

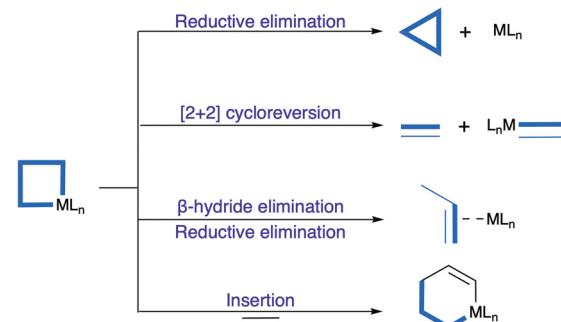
Metallacyclobutanes are often invoked as intermediates in catalytic cyclopropanation and olefin metathesis.^{1–8} Generally formed by [2+2] cycloaddition of a metal–carbene and an olefin, they are versatile intermediates that can undergo reductive elimination yielding cyclopropanes, [2+2] cycloreversion yielding a metal carbene and an olefin, and insertion of a neutral fragment yielding a metallacyclopentane (Fig. 1).^{1–8} As part of environmentally-motivated research efforts on base metal catalysis,^{9,10} Ni-catalyzed cyclopropanation has seen promising developments, where nickelacyclobutanes are proposed as key intermediates.^{5–8,11–23} To further our understanding of the reactivity of these species, we recently described the preparation of a pentacoordinated nickelacyclobutane embedded in a diphosphine pincer ligand.⁷ We found that exogenous ligands could selectively induce cyclopropanation (with the π -acceptor CO) or olefin-metathesis-like opening (with the σ -donor MeCN), in contrast with previously reported square planar nickelacyclobutanes.^{8,16,22,24}

Here we report on an unexpected reactive pathway induced by coordination of *t*-butyl isocyanide (CN^tBu , $\text{R}-\text{NC}$): a formal carbene transfer generating a ketenimine (Fig. 1) and an olefin complex. While this process could be thought of as the result of [2+2] cycloreversion followed by coupling of the resulting nickel carbene and the isocyanide,^{25–30} DFT calculations support a

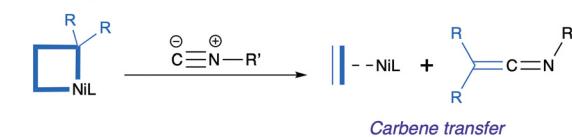
distinct mechanism involving a nickelacyclopentane intermediate formed by 1,1-insertion of CN^tBu in a Ni–C bond. It suggests that these intermediates could act as “carbene reservoirs” and undergo carbene transfer reactions without prior [2+2] cycloreversion.

Reaction of the pentacoordinate nickelacyclobutane **1** with two equiv of CN^tBu in C_6D_6 initially resulted in rapid coordination of CN^tBu in apical position to yield **1-CN**^t Bu (Scheme 1). This is evidenced by a downfield shift and sharpening of the ^1H NMR signal corresponding to the CH_2 group from δ 4.40 ppm in **1** to 4.78 ppm in **1-CN**^t Bu , and by a sharpening of the $^{31}\text{P}\{^1\text{H}\}$ NMR signal to a singlet at 27.6 ppm (ESI,† Section S3). Both observations are consistent with the displacement of the π -interacting tolyl group by an isocyanide molecule to form a symmetrical structure and parallel those made upon coordination of CO.⁷

Reactivity of metallacyclobutanes:



This work:



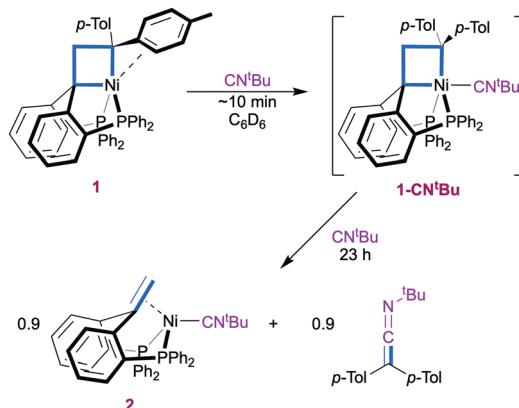
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† Electronic supplementary information (ESI) available. CCDC 2365514. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4cc04273e>

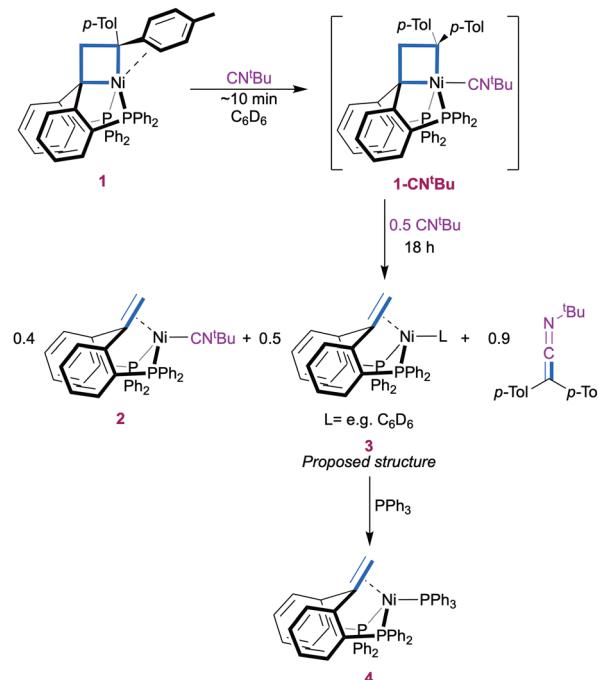
Fig. 1 Reactivity of metallacyclobutanes and present work.



Scheme 1 Carbene transfer with 2 eq. *t*-butylisocyanide.

A ^1H NMR spectrum recorded after 2 h (ESI,[†] Section S2.2) showed the appearance of the olefin complex ($^{\text{Ph}}\text{bppe}^{\text{H,H}}$)-Ni(CN^tBu) 2 and ketenimine $t\text{-BuN}=\text{C}=\text{C}(p\text{-Tol})_2$, as a result of the transfer of the $\text{C}(p\text{-Tol})_2$ carbene fragment to an isocyanide molecule. The reaction was complete after 23 h. Additionally, a small amount of 1,1-di(*p*-tolyl)ethylene was observed (~10%) suggesting [2+2] cycloreversion as a minor pathway. Complex 2 was identified by a $^{31}\text{P}\{^1\text{H}\}$ NMR singlet at $\delta(\text{C}_6\text{D}_6)$ 25.7 ppm and a characteristic ^1H NMR signal at δ 3.65 ppm ($t, J_{\text{H},\text{P}} = 2.2$ Hz, 2H), that both match those of a sample of 2 independently synthesized from $^{\text{Ph}}\text{bppe}^{\text{H,H}}$, Ni(cod)₂ and CN^tBu (ESI,[†] Section 1.3 and 3). An ATR-FTIR spectrum of the reaction mixture (ESI,[†] Section S2.2) confirms the presence of complex 2 and displays the characteristic $\text{N}=\text{C}=\text{C}$ stretching peak of $t\text{-BuN}=\text{C}=\text{C}(p\text{-Tol})_2$ as a strong signal at 2005 cm^{-1} .^{31,32} The identity of the organic product is bolstered by the presence of ketenimine peak at 183.5 ppm in the APT $^{13}\text{C}\{^1\text{H}\}$ spectrum of the reaction mixture (ESI,[†] Section S2.2).^{27,31,33} Using a large excess of CN^tBu (55 equivalents) did not result in any substantial changes in the reactivity (ESI,[†] Section S2.3). No further reaction was observed when the isolated product 2 was exposed to bis(4-tolyl) diazomethane, indicating that the CN^tBu ligand in 2 binds too strongly for catalytic turnover to be accessible with this system.

More insights into the reaction mechanism were provided by an experiment with a lower amount (1.5 equiv.) of CN^tBu (Scheme 2). A slight excess was found necessary to ensure full initial conversion to 1-CN^tBu. Monitoring the reaction over time by $^{31}\text{P}\{^1\text{H}\}$ NMR again showed gradual conversion of 1-CN^tBu ($\delta(\text{C}_6\text{D}_6)$ 27.6 ppm) to compound 2 ($\delta(\text{C}_6\text{D}_6)$ 25.7 ppm) at early stages. However, a new P-containing species (3) appeared as a slightly broad singlet at $\delta(\text{C}_6\text{D}_6)$ 18.5 ppm after 1 h and was present in a 1 : 1 ratio with 2 after 18 h when all 1-CN^tBu was consumed (ESI,[†] Section S2.1). At this time, the concentration of ketenimine was approximately equal to the sum of those of complexes 2 and 3 according ^1H NMR integration (Fig. S3, ESI[†]). As before, a small amount of 1,1-di(*p*-tolyl)ethylene (~10%) was observed. Complex 3 is proposed to be a ($^{\text{Ph}}\text{bppe}^{\text{H,H}}$)Ni(L) type Ni(0) complex (e.g. L = C₆D₆) on the basis of its NMR characteristics. Namely, a broad ^1H NMR singlet at $\delta(\text{C}_6\text{D}_6)$ 3.79 ppm is consistent with a Ni-bound

Scheme 2 Carbene transfer with 1.5 eq. *t*-butylisocyanide.

olefinic CH₂ group. ^1H - ^{31}P HMBC confirmed that the signal at $\delta(\text{C}_6\text{D}_6)$ 3.79 ppm is related to the $^{31}\text{P}\{^1\text{H}\}$ NMR peak at 18.5 ppm. The identity of complex 3 was further confirmed by quenching the reaction mixture with 1.5 equivalents of PPh₃, which resulted in full conversion of complex 3 to ($^{\text{Ph}}\text{bppe}^{\text{H,H}}$)-Ni(PPh₃) (4) while complex 2 remained unaffected (Fig. S6 and S7, ESI[†]). Complex 4 was identified by comparison with a sample independently synthesized from the $^{\text{Ph}}\text{bppe}^{\text{H,H}}$ ligand, Ni(cod)₂, and PPh₃ (ESI,[†] Section 1.3 and 3), and its molecular structure was confirmed by X-ray crystal structure determination in addition to its spectroscopic identification (ESI,[†] Section 4). These results indicate that the second equivalent of CN^tBu in Scheme 1 is not required for the carbene transfer step itself, but simplifies the final reaction mixture by capturing the formed Ni(0) fragment.

Ketenimines are versatile compounds in organic synthesis,^{29,31,34-36} which can be synthesized, amongst other, by (catalytic) coupling of a metal carbene and an isocyanide reagent.²⁵⁻³⁰ This could suggest a mechanism in which reversible [2+2] cycloreversion of the pentacoordinated nickelacyclobutane generates a carbene fragment that is intercepted by the isocyanide reagent. A similar [2+2] cycloreversion has been proposed by Miyashita to explain the reaction of the tetracoordinated nickelacyclobutane (PPh₃)₂Ni(2,2-dimethylpropano-1,3-diy) with CO or cyclohexene to generate ketene (O=C=CH₂) or the cyclopropanation product bicyclo[4.1.0]heptane, respectively.^{21,22,37} In a somewhat related report, Neely and coworkers described an iron azametallacyclobutene with a significant iron carbene resonance, which reacts with isocyanide and CO to form ketenimines and ketenes.³⁸ On the other hand, isocyanides have also been known to undergo migratory insertion with metallacyclobutanes to yield metallacyclopentanes for several



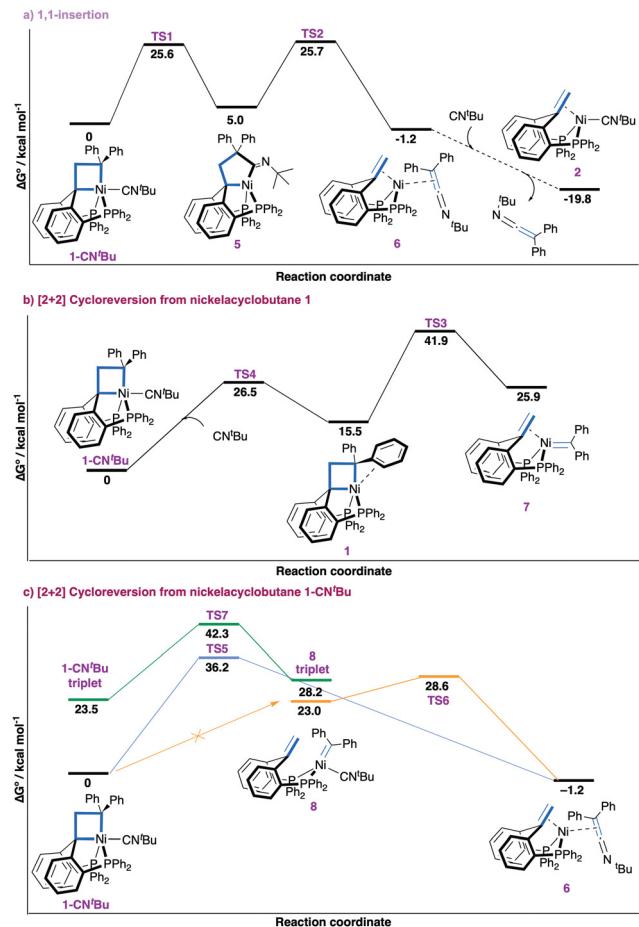


Fig. 2 ΔG° energy profiles for the reactivity of **1-CN^tBu** via 1,1-insertion (a) or [2+2] cycloreversion (b and c) mechanisms. Dashed lines connect intermediates between which no transition state was optimized.

metals.^{8,39–44} In the next section, we assess the feasibility of these different processes using DFT calculations⁴⁵ performed using a slightly truncated model with Ph groups instead of *p*-Tol.

We found the process with the lowest overall barrier to start with 1,1-insertion of the isocyanide ligand in a M–C bond of the metallacyclobutane to expand the ring (Fig. 2a). Starting from complex **1-CN^tBu**, insertion to yield nickelacyclopentane **5** (with the nitrogen lone pair opposite to nickel) is energetically accessible ($\Delta G^\ddagger = 25.6$ kcal mol⁻¹), followed by reductive fragmentation ($\Delta G^\ddagger = 25.7$ kcal mol⁻¹) forming complex **6**. Change of coordination of the ketenimine from $\eta^2(\text{C}, \text{C})$ to $\eta^1(\text{N})$ yields complex **6** a more stable isomer (-1.9 kcal mol⁻¹, ESI[†] Section S5.2). If an excess of isocyanide is available, ligand exchange to form complex **2** yields an overall free energy release of -19.8 kcal mol⁻¹. Alternative routes starting with 1,1-insertion were found to be less favorable (ESI[†] Section S5.3). The overall barrier of 25.7 kcal mol⁻¹ is at the upper bound for a slow process at room temperature and significantly lower than all other considered pathways.⁴⁶

Pathways involving a [2+2] cycloreversion process yielding a nickel carbene intermediate were calculated to be energetically

inaccessible (Fig. 2b). First, the formation of the putative carbene/olefin species **7** from the observed adduct **1-CN^tBu** after ligand dissociation is kinetically inaccessible. Initial decoordination of CN^tBu to form nickelacyclobutane **1** is endergonic by 15.5 kcal mol⁻¹ and hampered by a barrier of 26.5 kcal mol⁻¹. [2+2] Cycloreversion to **7** comes with an additional endergicity of 10.4 kcal mol⁻¹ and a prohibitively high overall barrier ($\Delta G^\ddagger = 41.9$ kcal mol⁻¹). An alternative process starting with decoordination of one phosphine arm of nickelacyclobutane **1** was discarded due to the high energy of this ligand dissociation (27.6 kcal mol⁻¹, ESI[†] Section S5.3). Second, we investigated whether the carbene fragment could be directly transferred to the CN^tBu ligand in **1-CN^tBu** (Fig. 2c). A transition state for concerted carbene transfer was located yielding complex **6** (-1.2 kcal mol⁻¹), but the associated barrier is prohibitively high ($\Delta G^\ddagger = 36.2$ kcal mol⁻¹). Third, a nickel carbene complex **8** bearing an isocyanide ligand was found to be relatively high in energy (23.0 kcal mol⁻¹). Attempts to locate a transition state for the [2+2] cycloreversion yielding **8** from **1-CN^tBu** were unsuccessful. A potential energy surface (PES) scan suggests there is actually no transition state connecting complex **8** to **1-CN^tBu** (Fig. S35, ESI[†]). Rather, the ketenimine complex **6** appears to be an intermediate in the hypothetical transformation of **1-CN^tBu** into **8**. This suggests complex **8** is not an intermediate of the process. Additionally, we disfavor complex **8** as a plausible intermediate due to the high free energy ($\Delta G^\ddagger = 28.6$ kcal mol⁻¹) of the transition state for the formation of ketenimine complex **6** from **8**. Fourth, the possibility of two-state reactivity involving the triplet state was also considered,⁴⁷ but the [2+2] cycloreversion process in triplet state was associated with a prohibitively high barrier ($\Delta G^\ddagger = 42.3$ kcal mol⁻¹). Finally, the direct carbene transfer and [2+2] cycloreversion process starting from a tetracoordinated nickelacyclobutane (**1-CN^tBu-noP**) resulting from decoordination of one phosphine arm was computed (ESI[†] Section 5.4). Both processes were found unfeasible with overall barriers of $\Delta G^\ddagger = 52.1$ kcal mol⁻¹ and $\Delta G^\ddagger = 48.3$ kcal mol⁻¹, respectively. Hence, no energetically accessible pathway for direct carbene transfer with or without a nickel carbene intermediate was identified, further supporting the sequential 1,1-insertion/reductive fragmentation as operative mechanism for the observed formal carbene transfer reaction.

The contrasting reactivity of **1-CN^tBu** (carbene transfer) and **1-CO** (cyclopropane formation)⁷ is surprising in view of the isoelectronic character of CO and isocyanides. To obtain additional insights, the different decomposition pathways were investigated computationally for both compounds (ESI[†] Sections S5.5 and S5.6). For **1-CN^tBu** the transition state for cyclopropane formation by reductive elimination was found to be prohibitively high in energy ($\Delta G^\ddagger = 33.9$ kcal mol⁻¹) in good agreement with experiment. The calculated barrier of 22.5 kcal mol⁻¹ for [2+2] cycloreversion yielding (PC_{carbeneP})-Ni(CN^tBu) is *ca.* 3 kcal mol⁻¹ lower than that for isocyanide insertion. The disparity is at odds with experimental observations but within the typical error range of DFT calculations. Additionally, the experimental observation of a small amount

of 1,1-di(*p*-tolyl)ethene alongside the carbene transfer process is consistent with a small difference between the barriers for [2+2] cycloreversion and insertion. For **1-CO**, cyclopropane formation is the favoured reaction pathway with an overall barrier of 23.8 kcal mol⁻¹ in good agreement with experiment. The [2+2] cycloreversion process is higher in energy by 4 kcal mol⁻¹ and insertion pathway is higher by 6.1 kcal mol⁻¹. These differences highlight the high sensitivity of the penta-coordinated nickelacyclobutane **1** towards the electronic nature of the exogeneous ligand in apical position, the stronger π -accepting character of CO markedly favouring reductive elimination of a cyclopropane unit.

In summary, we disclose an unusual carbene transfer reaction from a pentacoordinated nickelacyclobutane to a molecule of CN^tBu yielding a ketenimine. DFT calculations support a mechanistic pathway that does not involve a nickel carbene intermediate but instead a nickelacyclopentane resulting from 1,1-insertion of CN^tBu into a Ni-C bond. These results further highlight the importance of the coordination environment of nickelacyclobutane intermediates for selective reactions. The possibility to access carbene-like reactivity without an actual carbene intermediate (e.g. generated by [2+2] cycloreversion) suggests a possible use of metallacyclobutanes as “carbene reservoirs” to tame unstable metal carbene fragments.

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Data availability

The supplementary data of this article have been included in the ESI[†] contains synthesis and characterization of new compounds, additional experiments and computational details. CCDC number 2365514[†] contains supplementary crystallographic data that can be obtained at the Cambridge Crystallographic Data Centre.

Conflicts of interest

There are no conflicts to declare.

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