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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.**

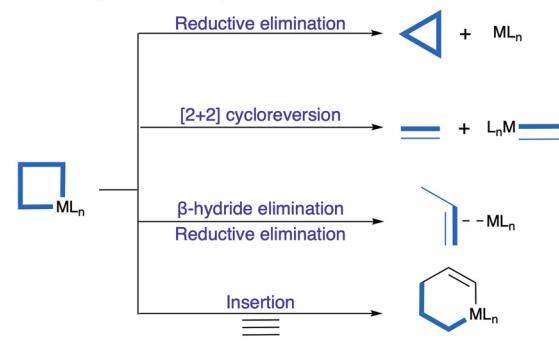
Metallacyclobutanes are often invoked as intermediates in catalytic cyclopropanation and olefin metathesis.<sup>1–8</sup> Generally formed by [2+2] cycloaddition of a metal–carbene and an olefin, they are versatile intermediates that can undergo reductive elimination yielding cyclopropanes, [2+2] cycloreversion yielding a metal carbene and an olefin, and insertion of a neutral fragment yielding a metallacyclopentane (Fig. 1).<sup>1–8</sup> As part of environmentally-motivated research efforts on base metal catalysis,<sup>9,10</sup> Ni-catalyzed cyclopropanation has seen promising developments, where nickelacyclobutanes are proposed as key intermediates.<sup>5–8,11–23</sup> 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.<sup>7</sup> We found that exogenous ligands could selectively induce cyclopropanation (with the  $\pi$ -acceptor CO) or olefin-metathesis-like opening (with the  $\sigma$ -donor MeCN), in contrast with previously reported square planar nickelacyclobutanes.<sup>8,16,22,24</sup>

Here we report on an unexpected reactive pathway induced by coordination of *t*-butyl isocyanide ( $\text{CN}^t\text{Bu}$ ,  $\text{R}-\text{NC}$ ): 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,<sup>25–30</sup> DFT calculations support a

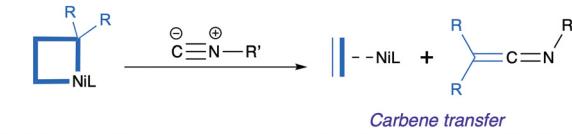
distinct mechanism involving a nickelacyclopentane intermediate formed by 1,1-insertion of  $\text{CN}^t\text{Bu}$  in a Ni–C bond. It suggests that these intermediates could act as “carbene reservoirs” and undergo carbene transfer reactions without prior [2+2] cycloreversion.

Reaction of the pentacoordinate nickelacyclobutane **1** with two equiv of  $\text{CN}^t\text{Bu}$  in  $\text{C}_6\text{D}_6$  initially resulted in rapid coordination of  $\text{CN}^t\text{Bu}$  in apical position to yield **1-CN**<sup>t</sup> $\text{Bu}$  (Scheme 1). This is evidenced by a downfield shift and sharpening of the  $^1\text{H}$  NMR signal corresponding to the  $\text{CH}_2$  group from  $\delta$  4.40 ppm in **1** to 4.78 ppm in **1-CN**<sup>t</sup> $\text{Bu}$ , 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  $\pi$ -interacting tolyl group by an isocyanide molecule to form a symmetrical structure and parallel those made upon coordination of CO.<sup>7</sup>

#### Reactivity of metallacyclobutanes:



#### This work:



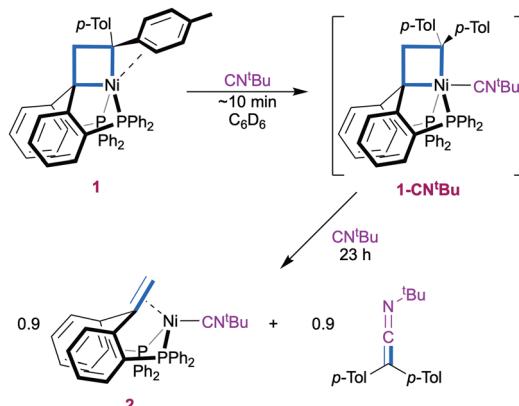
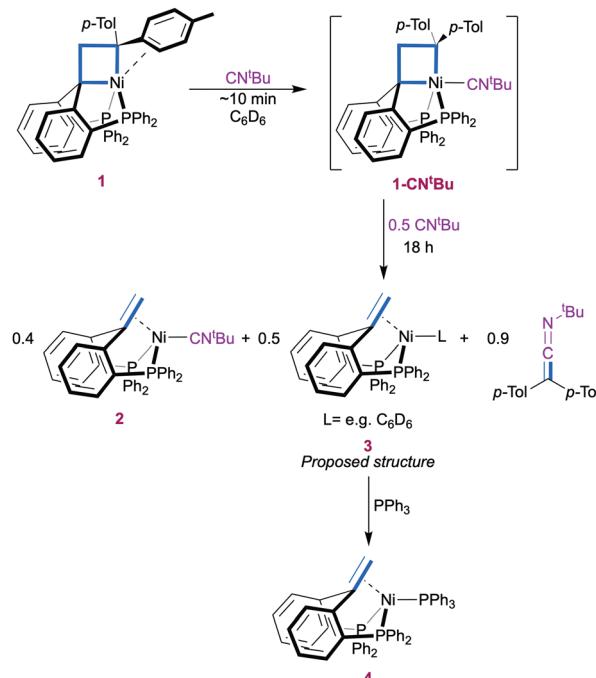
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Fig. 1 Reactivity of metallacyclobutanes and present work.



Scheme 1 Carbene transfer with 2 eq. *t*-butylisocyanide.Scheme 2 Carbene transfer with 1.5 eq. *t*-butylisocyanide.

A  $^1\text{H}$  NMR spectrum recorded after 2 h (ESI,<sup>†</sup> Section S2.2) showed the appearance of the olefin complex ( $^{\text{Ph}}\text{bppe}^{\text{H,H}}$ )-Ni(CN<sup>t</sup>Bu) 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 ( $\sim 10\%$ ) 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  $^1\text{H}$  NMR signal at  $\delta$  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)<sub>2</sub> and CN<sup>t</sup>Bu (ESI,<sup>†</sup> Section 1.3 and 3). An ATR-FTIR spectrum of the reaction mixture (ESI,<sup>†</sup> 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  $\text{cm}^{-1}$ .<sup>31,32</sup> 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,<sup>†</sup> Section S2.2).<sup>27,31,33</sup> Using a large excess of CN<sup>t</sup>Bu (55 equivalents) did not result in any substantial changes in the reactivity (ESI,<sup>†</sup> Section S2.3). No further reaction was observed when the isolated product 2 was exposed to bis(4-tolyl) diazomethane, indicating that the CN<sup>t</sup>Bu 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<sup>t</sup>Bu (Scheme 2). A slight excess was found necessary to ensure full initial conversion to 1-CN<sup>t</sup>Bu. Monitoring the reaction over time by  $^{31}\text{P}\{^1\text{H}\}$  NMR again showed gradual conversion of 1-CN<sup>t</sup>Bu ( $\delta(\text{C}_6\text{D}_6)$  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<sup>t</sup>Bu was consumed (ESI,<sup>†</sup> Section S2.1). At this time, the concentration of ketenimine was approximately equal to the sum of those of complexes 2 and 3 according  $^1\text{H}$  NMR integration (Fig. S3, ESI<sup>†</sup>). As before, a small amount of 1,1-di(*p*-tolyl)ethylene ( $\sim 10\%$ ) 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 = C<sub>6</sub>D<sub>6</sub>) on the basis of its NMR characteristics. Namely, a broad  $^1\text{H}$  NMR singlet at  $\delta(\text{C}_6\text{D}_6)$  3.79 ppm is consistent with a Ni-bound

olefinic CH<sub>2</sub> group.  $^1\text{H}$ - $^{31}\text{P}$  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 PPh<sub>3</sub>, which resulted in full conversion of complex 3 to ( $^{\text{Ph}}\text{bppe}^{\text{H,H}}$ )-Ni(PPh<sub>3</sub>) (4) while complex 2 remained unaffected (Fig. S6 and S7, ESI<sup>†</sup>). Complex 4 was identified by comparison with a sample independently synthesized from the  $^{\text{Ph}}\text{bppe}^{\text{H,H}}$  ligand, Ni(cod)<sub>2</sub>, and PPh<sub>3</sub> (ESI,<sup>†</sup> Section 1.3 and 3), and its molecular structure was confirmed by X-ray crystal structure determination in addition to its spectroscopic identification (ESI,<sup>†</sup> Section 4). These results indicate that the second equivalent of CN<sup>t</sup>Bu 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,<sup>29,31,34–36</sup> which can be synthesized, amongst other, by (catalytic) coupling of a metal carbene and an isocyanide reagent.<sup>25–30</sup> 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 (PPh<sub>3</sub>)<sub>2</sub>Ni(2,2-dimethylpropano-1,3-diy) with CO or cyclohexene to generate ketene (O=C=CH<sub>2</sub>) or the cyclopropanation product bicyclo[4.1.0]heptane, respectively.<sup>21,22,37</sup> 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.<sup>38</sup> On the other hand, isocyanides have also been known to undergo migratory insertion with metallacyclobutanes to yield metallacyclopentanes for several



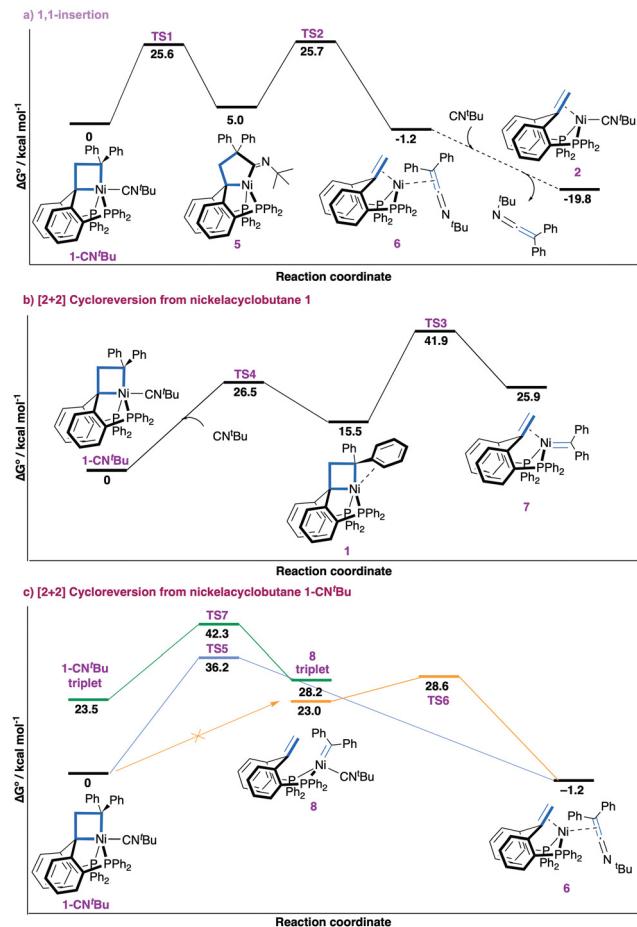


Fig. 2  $\Delta G^\circ$  energy profiles for the reactivity of **1-CN<sup>t</sup>Bu** via 1,1-insertion (a) or [2+2] cycloreversion (b and c) mechanisms. Dashed lines connect intermediates between which no transition state was optimized.

metals.<sup>8,39–44</sup> In the next section, we assess the feasibility of these different processes using DFT calculations<sup>45</sup> 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<sup>t</sup>Bu**, insertion to yield nickelacyclopentane **5** (with the nitrogen lone pair opposite to nickel) is energetically accessible ( $\Delta G^\ddagger = 25.6$  kcal mol<sup>-1</sup>), followed by reductive fragmentation ( $\Delta G^\ddagger = 25.7$  kcal mol<sup>-1</sup>) 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 ( $-1.2$  kcal mol<sup>-1</sup>, ESI<sup>†</sup> 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<sup>-1</sup>. Alternative routes starting with 1,1-insertion were found to be less favorable (ESI<sup>†</sup> Section S5.3). The overall barrier of 25.7 kcal mol<sup>-1</sup> is at the upper bound for a slow process at room temperature and significantly lower than all other considered pathways.<sup>46</sup>

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<sup>t</sup>Bu** after ligand dissociation is kinetically inaccessible. Initial decoordination of CN<sup>t</sup>Bu to form nickelacyclobutane **1** is endergonic by 15.5 kcal mol<sup>-1</sup> and hampered by a barrier of 26.5 kcal mol<sup>-1</sup>. [2+2] Cycloreversion to **7** comes with an additional endergicity of 10.4 kcal mol<sup>-1</sup> and a prohibitively high overall barrier ( $\Delta G^\ddagger = 41.9$  kcal mol<sup>-1</sup>). 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<sup>-1</sup>, ESI<sup>†</sup> Section S5.3). Second, we investigated whether the carbene fragment could be directly transferred to the CN<sup>t</sup>Bu ligand in **1-CN<sup>t</sup>Bu** (Fig. 2c). A transition state for concerted carbene transfer was located yielding complex **6** ( $-1.2$  kcal mol<sup>-1</sup>), but the associated barrier is prohibitively high ( $\Delta G^\ddagger = 36.2$  kcal mol<sup>-1</sup>). Third, a nickel carbene complex **8** bearing an isocyanide ligand was found to be relatively high in energy (23.0 kcal mol<sup>-1</sup>). Attempts to locate a transition state for the [2+2] cycloreversion yielding **8** from **1-CN<sup>t</sup>Bu** were unsuccessful. A potential energy surface (PES) scan suggests there is actually no transition state connecting complex **8** to **1-CN<sup>t</sup>Bu** (Fig. S35, ESI<sup>†</sup>). Rather, the ketenimine complex **6** appears to be an intermediate in the hypothetical transformation of **1-CN<sup>t</sup>Bu** 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<sup>-1</sup>) 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,<sup>47</sup> but the [2+2] cycloreversion process in triplet state was associated with a prohibitively high barrier ( $\Delta G^\ddagger = 42.3$  kcal mol<sup>-1</sup>). Finally, the direct carbene transfer and [2+2] cycloreversion process starting from a tetracoordinated nickelacyclobutane (**1-CN<sup>t</sup>Bu-noP**) resulting from decoordination of one phosphine arm was computed (ESI<sup>†</sup> Section 5.4). Both processes were found unfeasible with overall barriers of  $\Delta G^\ddagger = 52.1$  kcal mol<sup>-1</sup> and  $\Delta G^\ddagger = 48.3$  kcal mol<sup>-1</sup>, 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<sup>t</sup>Bu** (carbene transfer) and **1-CO** (cyclopropane formation)<sup>7</sup> 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<sup>†</sup> Sections S5.5 and S5.6). For **1-CN<sup>t</sup>Bu** the transition state for cyclopropane formation by reductive elimination was found to be prohibitively high in energy ( $\Delta G^\ddagger = 33.9$  kcal mol<sup>-1</sup>) in good agreement with experiment. The calculated barrier of 22.5 kcal mol<sup>-1</sup> for [2+2] cycloreversion yielding (PC<sub>carbeneP</sub>)-Ni(CN<sup>t</sup>Bu) is *ca.* 3 kcal mol<sup>-1</sup> 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<sup>-1</sup> in good agreement with experiment. The [2+2] cycloreversion process is higher in energy by 4 kcal mol<sup>-1</sup> and insertion pathway is higher by 6.1 kcal mol<sup>-1</sup>. 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  $\pi$ -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<sup>t</sup>Bu 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<sup>t</sup>Bu 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<sup>†</sup> contains synthesis and characterization of new compounds, additional experiments and computational details. CCDC number 2365514<sup>†</sup> 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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