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Mechanistic Studies on the Nickel-Catalyzed Cyclopropanation with Lithiomethyltrimethylammonium Triflate.

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ABSTRACT: We report here our mechanistic study of the previously published nickel-catalyzed cyclopropanation reaction using lithiomethyltrimethylammonium triflate as methylene donor. The cyclopropane yield is highly dependent on the olefin substrate and correlates well with the binding affinity of the olefin to Ni(o) as established elsewhere. Based on this observation we developed a simplified mechanistic model that can explain several odd observation we found in our initial report. Most importantly, a binding equilibrium between olefin substrate and phosphine ligand appears to govern the ratio between product formation and unproductive ylide decomposition in a side-reaction.

1. Introduction

Only a few methods are known for transferring methylene to electron-rich alkenes to form cyclopropanes. For large scale production, the Simmons-Smith and related metal carbenoid-based reactions are preferred, though they often suffer from the generation of large amounts of waste.¹ Transition metal-catalyzed cyclopropanation using diazo-methane is a well-studied and very versatile method, but, due to the inherent instability and toxicity of the reagent itself, or its precursors, the reaction is limited to small-scale reactions.²

To circumvent these drawbacks, extensive research had focused on the *in situ* generation of diazomethane from more stable precursors, in order to circumvent the need for isolation or the design of new reagents as methylene donors.³

Recently, we took the alternative approach of non-diazo methylene donors and reported on the nickel-catalyzed cyclopropanation of several electron-rich, alkyl substituted alkenes using lithiomethyltrimethylammonium triflate as methylene donor, generated *in situ* from tetramethylammonium triflate and BuLi (Scheme 1).⁴

In that report, we also noted a peculiar behavior with respect to the catalyst loading. The highest yield of cyclopropanation of cyclooctene (COE) was obtained with a catalyst loading in the range of 0.5 to 1.0 mol%. At lower or higher loadings, a decreased yield was obtained, resulting in a bell-shaped curve for catalyst loading versus yield. We observed polyethylene and small amounts of cyclopropane (C₃H₆) as side-products, presumably stemming from initial formation of ethene via homocoupling of two nickel carbenes.

We proposed an explanation based on two competing processes with the same intermediate species, i.e., a nickel carbene that can undergo either cyclopropanation with an alkene to afford the cyclopropane product or homocoupling

with another nickel carbene molecule to afford ethene. The initially formed ethene could then react further, to afford the observed side products. Overall, this would lead to an unproductive decomposition of the reagent. We predicted the product formation to be kinetically 1st order in catalyst and the homocoupling to be 2nd order (assuming the homocoupling step to be rate-limiting, rather than nickel carbene formation) or at least bimolecular with respect to the proposed nickel carbene. Overlaying these two competing reactions could then explain the observed behavior, where the homocoupling kinetically outcompetes product formation at high catalyst loadings, at least for the reported case of catalyst loadings above the optimum 0.5 to 1 mol% with (Ph₃P)₂NiBr₂ as precatalyst and COE as substrate.

Additionally, we observed that the yield was influenced by whether the flask was open or closed to an argon Schlenk line, when using COE as substrate.⁵ Based on these and other experimental observations, and in analogy to literature precedent of isolated nickel species, we postulated a possible catalytic cycle with a nickel carbene as an important intermediate.⁶

Herein, we report mechanistic studies, including extensive kinetic and computational investigations, which support the involvement of a reactive nickel carbene intermediate, and reveal the intricate balance between ligand and alkene binding that explains the observed substrate-dependence of the cyclopropanation yield.

The rationale for this work is formulated as the following series of questions, which we seek to address herein.

Firstly, what is the possible resting state of the catalyst? What are the ligands bound to the nickel?

Secondly, what is the cause of the substrate dependence that we noticed earlier? How does the substrate dependence relate to the catalyst resting state?

Thirdly, what causes the effect of the catalyst loading on the cyclopropanation yield?

Fourthly, why is there a difference between running the reaction open or closed to the argon Schlenk line?

The findings we report here help us to formulate an answer as to what might be the catalyst resting state and how this relates to the π -acidity and formation constant of the π -complex of the substrate with the catalyst. The resultant model we propose, albeit rather simple, offers an explanation to the aforementioned effect on catalyst loading. Alkene competition experiments within this model framework offer insights regarding the reactivity and stability of the resting state.

Scheme 1. Previously Reported Cyclopropanation using Tetramethylammonium Triflate as Methylene Donor and a Proposed Simplified Catalytic Cycle.⁴

a) General reaction scheme

b) Simplified catalytic cycle

2. Experimental Methods

Kinetic measurements were conducted by quenching aliquots under protic conditions. Product formation was measured by GC-FID using a previously added internal standard and k_{obs} was determined using initial rates. The consumption of ylide was measured indirectly by determining the relative amount of remaining $[\text{NMe}_4]^+$ by ^1H NMR against a previously added internal standard. An exponential fit over the entire reaction profile was used to determine k_{obs} .

We used two different Methods, A and B, that differ in the generation of the ammonium ylide reagent, either *in situ* (A) or preformed (B) (see Scheme 2).

For method A, $[\text{NMe}_4]\text{OTf}$ (1.1 equiv), alkene and catalyst were mixed together, cooled to 0 °C, then BuLi (1 equiv) was added to form the ylide *in situ*.

For method B, the ammonium salt was deprotonated first (in the presence or absence of alkene) before the catalyst

was added to the preformed ylide to initiate the cyclopropanation/ylide decomposition.

Scheme 2. Two Different Methods Employed to Generate the Active Reagent $[\text{LiCH}_2\text{NMe}_3]\text{OTf}$, either after (A) or before (B) Addition of Catalyst.

(Method A / in situ)

(Method B / preformed)

Computations.

All calculations were performed using Gaussian 09 Revision D.⁷ All geometries were optimized and frequencies calculations were performed to ensure real minima for the intermediates (i.e., $N_{\text{imag}} = 0$) and 1st order saddle points for the transition states (i.e., $N_{\text{imag}} = 1$). The energies reported are zero-point corrected energies. We first performed a benchmarking procedure, in which we compared crystal structures of literature-reported compounds that are analogous to the intermediates in our system to computationally optimized structures (19 different combinations of density functionals and basis sets were tested, Table S20 summarizing the results is provided in the Supporting Information). Following this procedure, we settled on the functional/basis-set combination Mo6L/def2-SVP, and these results are presented in the text. In addition, we performed calculations at the same level with an implicit solvent model, which yielded similar results.

For the Kinetic Isotope Effect calculations, we employed the ISOEFF software, which calculates isotope effects based on the Bigeleisen equation, using input from a quantum mechanical calculation (i.e., the Hessian matrix obtained from Gaussian).⁸

3. Results

Our earlier published work reported yields for cyclopropanation over a limited range of conditions and substrates. In the present report, we extend the experimental data with measurements of rates for cyclopropanation or homocoupling.

3.1 Kinetic Orders

The limited scope and most of the unusual features observed for the reaction, had been explained by means of the catalytic cycle depicted in Scheme 1, in particular *via* the competition between a productive cyclopropanation that would be kinetically 1st-order in nickel carbene and an unproductive homocoupling that would be 2nd-order in the same carbene. Addition of NMe_3 (up to 1 equiv with respect to ylide) as reported earlier (to test for reversible nickel

carbene formation),⁴ as well as NMe₂Bn (10 equiv, this report) paradoxically did not improve the cyclopropanation yield or produce a rearrangement product from a putative NMe₂Bn derived ylide (Schemes S17 and S18).⁹ This motivated us to execute kinetic experiments—measuring rates as opposed to yields—to confirm or call into question the putative catalytic cycle in Scheme 1.

We used three different methods for preparation of the active Ni(o) species: a) reduction of Ni(II) *in situ* prior to ylide formation, b) reduction of Ni(II) *in situ* with the ylide, and c) initiation with a Ni(o) catalyst. The plot of k_{obs} for cyclopropanation of norbornene (the best substrate) versus catalyst loading between 0.25 and 1.0 mol% shows kinetic orders between 0.80 ± 0.02 and 1.17 ± 0.08 , as depicted in Figure 1.

Figure 1. Plot of k_{obs} versus [catalyst] using $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ and Method A (squares) or Method B (circles) as precatalyst or $\text{Ni}(\text{PPh}_3)_4$ (Method A, triangles) with NBE. The red curves depict a fit to the function $y = ax^b$ to establish the order in [Ni] as follows: $b = 1.17 \pm 0.08$ (squares), $b = 0.80 \pm 0.02$ (circles), $b = 1.0 \pm 0.1$ (triangles).

We attribute the non-overlapping lines for the three initiation methods to slightly different initiation efficiencies, but we note that all methods deliver close to 1st-order dependence of cyclopropanation rate on Ni concentration. The initiation method with $\text{Ni}(\text{PPh}_3)_4$, the Ni(o) source, gave the cleanest 1st-order kinetics, as well as the highest absolute rates, implying the most efficient activation. Thus, we used the $\text{Ni}(\text{PPh}_3)_4$ catalyst for the determination of the kinetic order of homocoupling with respect to Ni concentration. For this latter experiment, the consumption of ylide, determined by quenching of aliquots taken of a reaction set up substrate-free, but otherwise identical to the cyclopropanation runs with preformed ylide (method B), was performed by tracking tetramethylammonium disappearance by ¹H NMR, as described in the SI. The plot of k_{obs} , shown in Figure 2, covering the range of catalyst concentration from 0.5 to 2.0 mol%, gave an order of $1.34 \pm .001$ in catalyst, which is closer to 1st than it is to the 2nd-order behavior that we had expected.

Figure 2. Plot of $[\text{Ni}(\text{PPh}_3)_4]$ versus k_{obs} for the consumption of ylide in the absence of alkene. The red curve depicts a fit to the function $y = ax^b$ to establish the order in [Ni], $b = 1.341 \pm 0.001$.

The unexpected results with excess trimethylamine⁴ and, particularly, the unexpected kinetic order for homocoupling in the absence of substrate, motivated us to determine the kinetic order of the reaction with respect to substrate and phosphine, namely, norbornene and triphenylphosphine. The plots of k_{obs} for cyclopropanation of norbornene versus concentration of either norbornene or triphenylphosphine, shown in Figures 3 and 4, show orders of 0.18 ± 0.02 and 0.17 ± 0.05 , respectively, over an approximately one order-of-magnitude range of concentrations. While the proposed catalytic cycle in Scheme 1 could afford a variety of kinetic orders, depending on which step is rate-limiting, the close to zero-order kinetics with respect to both substrate and phosphine were nevertheless surprising.

Figure 3. Plot of k_{obs} versus [NBE] using 0.5 mol% $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ (Method A). The red curve depicts a fit to the

function $y = ax^b$ to establish the order in norbornene, $b = 0.18 \pm 0.02$.

Figure 4. Plot of k_{obs} versus $[\text{PPh}_3]$ using 0.5 mol% $\text{Ni}(\text{acac})_2$ (Method A). The red curve depicts a fit to the function $y = ax^b$ to establish the order in PPh_3 , $b = 0.17 \pm 0.05$.

The order in ylide shows a more complex behavior and appears to be 0 or 1 depending on the exact reaction conditions and conversion. An additional discussion about the order in ylide can be found in the Supporting Information (Figure S11).

3.2 Kinetic Isotope Effect

While not entirely foolproof, kinetic isotope effects generally deliver information on the rate-limiting transition state, which makes them appropriate for the present situation. Switching to the perdeuterated ammonium salt $[\text{N}(\text{CD}_3)_4]\text{OTf}$ under otherwise identical conditions (using method A) yielded a large secondary kinetic isotope effect of 2.1 (Scheme 3). This is consistent with sp^3 - to sp^2 -rehybridization in the rate-limiting transition state, which suggests that the transition state from the Ni-coordinated ylide to the Ni carbene is rate-limiting.

Scheme 3. Determination of a Secondary KIE using Perdeuterated Tetramethylammonium Triflate.

Having the measured $k_{\text{H}}/k_{\text{D}}$ of 2.1, we computationally investigated a number of catalytic cycles to see whether other elementary steps, other than the carbene formation, could plausibly be consistent with the KIE. For each step in a composite catalytic cycle, shown in the SI (Figure S78), we employed the ISOEFF software, which calculates isotope effects based on the Bigeleisen equation, using input from

a quantum mechanical calculation (i.e., the Hessian matrix obtained from Gaussian), and found a predicted kinetic isotope effect of $k_{\text{H}}/k_{\text{D}} = 2.50$ for the carbene formation step. No other elementary step gives a KIE even close to compatible with that which we observed experimentally (Table S24).

3.3 Relative Rates of Cyclopropanation for Different Substrates

Figure 5. Plot of mole fraction of alkene 1, X_1 , versus product ratio, $[\text{P}_1]/[\text{P}_2]$, derived from alkene 1 and alkene 2, respectively, with the following pairs of alkenes. 1: norbornene, 2: cyclooctene (squares); 1: norbornene, 2: 1-octene (circles); 1: 1-octene, 2: 1-nonene (triangles). 0.5 mol% $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ was used as precatalyst. The red curves depict a fit to the function $y = aX_1/(1-X_1)$ (see eq (1) and Discussion). $a = 6.2 \pm 0.2$ (squares), $a = 3.7 \pm 0.1$ (circles), $a = 0.96 \pm 0.01$ (triangles).

Given that norbornene provides significantly higher yields, and, accordingly, better mass balances, than the other olefinic substrates tested, we opted, for the determination of rate constants for the cyclopropanation of cyclooctene and 1-octene, for example, for a competition experiment. Binary mixtures of norbornene with the other olefins were cyclopropanated, and the ratio of product cyclopropanes determined by GC-FID of quenched aliquots, giving the results shown in Figure 5. Adjusting the product ratios for the ratio of the substrates, we obtained the relative rate constants for cyclopropanation of the cyclooctene and 1-octene, relative to that for norbornene, shown in Table 1 (see Discussion).

3.4 Further Yields and Job Plots

We extended the range of yield measurements considerably, as compared to those in our previous report, concentrating on variations in the catalyst loading, variation of the catalyst itself, the Ni:phosphine ratio, and addition of an excess of PPh_3 . These results are given in tabular form in

the SI, and appear in Figures 9-10 in the Discussion, where they will be used as the test set (see below) to assess the adequacy of the our newly proposed catalytic cycle and the minimal kinetic model derived from that catalytic cycle.

4. Discussion

In the following, we discuss the results of our mechanistic studies and how they change and strengthen our understanding of the reaction mechanism at hand.

Mirroring the general structure of the Results section, we look first at the kinetic orders to establish the resting state of the catalyst and discuss the KIE, in order to infer the rate-limiting step. Based on this data we then propose a catalytic cycle. At its heart is a pre-equilibrium between the phosphine ligand(s) and the alkene substrate coordinated to nickel(o) that leads us to propose a Curtin-Hammett-like scenario.

Depending on which side the pre-equilibrium lies, one branch leads to cyclopropanation and the other consumes the ylide in an unproductive side-reaction. We develop this scenario into a very simple mathematical model. In order to do so, we first look at the special case of the alkene competition experiments (Figure 5), ignoring the side-reaction. Then, we generalize the mathematical formalisms to a single alkene in competition with homocoupling using only one fit parameter.

Finally, we apply this model to our data to shed light on the anomalous observations we made initially.

4.1 Resting State of Catalyst

In our originally proposed catalytic cycle, we assumed that a competition exists between product formation, which is 1st order in catalyst, and a background reaction that decomposes the ylide unproductively in a bimolecular homocoupling reaction. This bimolecular homocoupling would be 2nd order in catalyst, assuming the homocoupling step, whatever its exact nature, to be the rate-limiting step (see below, discussion about KIE).

Contrary to these initial assumptions, we observed the reaction to be approximately 1st order in catalyst for the reaction with norbornene, as well as in the absence of any added alkene at all, i.e., when we look at the homocoupling reaction in isolation. Using norbornene as substrate, we observed approximately 0th order in olefinic substrate, indicative of saturation behavior in alkene. We also observed a 0th order in PPh₃ when tracking product formation. Considering these three kinetic orders together, we propose that the resting state is a nickel(o) species with the alkene and/or PPh₃ already coordinated, meaning that substrate coordination has already taken place before the rate-limiting step. Additionally, we argue that the homocoupling reaction has the same resting state manifold and the actual homocoupling step itself is *not* rate-limiting. Thus, product formation and homocoupling intersect *via* the same resting state manifold of Ni(o) species.

4.2 Rate-Limiting Step

The normal secondary KIE of 2.1 suggests a sp³- to sp²-rehybridization in the rate-limiting transition state. This result is most consistent with nickel carbene formation being

rate-limiting. Going from the tetrahedral sp³-hybridized nickel ylide adduct to the planar sp²-hybridized carbon in the nickel carbene is the only such step in our proposed mechanism.¹⁰ In order to corroborate this finding, we performed DFT calculations on a model system and obtained the KIEs for all relevant steps in our proposed catalytic cycle (Table S24). Indeed, not only is the calculated KIE for the carbene formation in satisfactory agreement with our experimental value, all other KIEs are close to one or inverse. This corroboration strongly indicates that we correctly identified the turnover-limiting transition state. Additionally, this makes an alternative mechanism, a nucleophilic attack on the nickel-bound alkene by the ylide, followed by ring-closure, unlikely.¹¹ None of the steps in the alternative mechanism involves a change in hybridization of the appropriate carbon and thus no (large) KIE would be expected.

Furthermore, the carbene formation by extrusion of NMe₃ can be seen (formally) as an oxidative process, where the niccolate(o) is oxidized to a nickel(II) carbene.¹² This is in agreement with the description of Hillhouse's isolated carbene complexes and selectivities for polar olefins with diazomethane as observed by Ibers.^{2c} This picture is corroborated by our calculations, which show that the barrier for NMe₃ extrusion is lowered in a system with more strongly σ -donating ligands, e.g. two PH₃ ligands, than in a system with a less electron-rich nickel center ligated by one phosphine and one ethene (9 versus 15 kcal mol⁻¹, Tables S21 and S25).

4.3 Proposed Catalytic Cycle

Combining the insights presented above regarding the resting state and the rate-limiting step we propose the catalytic cycle presented in Figure 6. The aforementioned pre-equilibrium in which PPh₃ and alkene compete for nickel(o) is denoted with the equilibrium constant K in Figure 6 in the colored block in the center of the diagram. This mechanistic conclusion led us to Tolman's work on the binding affinity of alkenes to nickel(o), specifically nickel(o)-tri-*o*-tolyl phosphite complexes, in which norbornene ($K = 4.4$) was shown to bind significantly more strongly to nickel(o) than, e.g., cyclooctene ($K = 0.062$) (Scheme 4).¹³ We had observed that more strongly bound alkenes (based on Tolman's equilibrium constants) resulted in higher yields for the cyclopropanation, which is consistent with the proposed mechanism.^{14,15}

Scheme 4. Tolman's Alkene Equilibrium Constants.^{13a}

Alkene	K ^a
Norbornene	4.4

1-Hexene ^b	5.0 × 10 ⁻¹
Cyclooctene	6.2 × 10 ⁻²
Cyclohexene	3.5 × 10 ⁻⁴

^aTaken from ref. 13a. ^bAlso used for other 1-alkenes.

The analogous mechanistic scenario was proposed for the (ligandless) Pd-catalyzed cyclopropanation with diazomethane. In a DFT study by Straub, the extrusion of N₂ from diazomethane by an alkene-ligated Pd(o) complex to form a Pd carbene was identified as the most likely rate-determining step, followed by facile intramolecular cyclopropanation of the η²-bound alkene.¹⁶ Indeed, the improved yields with diazo compounds or α-lithiated sulfones for

more π-acidic alkenes were noted previously.^{2c,ub,17} After adduct formation of the ammonium ylide with the active catalyst, extrusion of NMe₃ in the rate-limiting step leads to a nickel carbene species. Once the nickel carbene is formed, the bound alkene can undergo intramolecular [2+2]-addition to the nickelacyclobutane. This is followed by rapid reductive elimination to give the product. The viability of these kinetically invisible steps has been confirmed by our calculations and has been observed for analogous systems as pointed out earlier.⁴

If on the other hand no alkene is coordinated at the time the nickel carbene is formed, it can undergo unproductive homocoupling.

Figure 6. Proposed catalytic cycle. Central to the reaction is the highlighted equilibrium between ligand and alkene binding.

4.4 Derivation of a Minimal Model

As discussed above, we derive our model first for the specific case of two competing alkenes (Scheme 5 and Figure 5).

Scheme 5. Simplified Mechanistic Scenario with an Alkene Exchange Equilibrium before Cyclopropanation.

Assuming a Curtin-Hammett scenario, the two alkenes exchange rapidly in a pre-equilibrium (K) before the rate-limiting nickel carbene formation (k_1 , k_2).¹⁸ This is followed by a fast, irreversible [2+2]-cycloaddition once the nickel carbene is formed (i.e., bimolecular alkene exchange is expected to be much slower for the nickel carbene complex compared to unimolecular nickelacyclobutane formation). This simplified mechanistic scenario leads to the following equation for the product ratio derived from alkene 1 and 2, respectively,

$$\frac{[P_1]}{[P_2]} = \frac{k_1 K_1}{k_2 K_2} \frac{X_1}{(1 - X_1)} \quad (1)$$

where k_i is the rate constant for the cyclopropane formation from the respective nickel alkene complex, K_i is corresponding to Tolman's equilibrium constant for alkene i , and X_i is the mole fraction of alkene 1 (see Supporting Information for full derivation).¹⁹

Comparing the fit function from Figure 5, $y = aX_1/(1 - X_1)$, with eq (1) gives $a = k_1 K_1/(k_2 K_2)$. We then arrive at a relative order of rate constants k_{rel} as seen in Table 1. The competition experiment between 1-octene and 1-nonene serves as an internal validation. The obtained value of $a = 0.96$ is very close to the expected value of 1, indicating that both alkenes behave identically, or at least very similarly (Figure 5).^{13a}

Table 1. Determination of Relative Rate Constants from Competition Experiments.

Alkene	K^a	k_{rel}
Norbornene	4.4	1 ^c
1-Octene	$5.0 \times 10^{-1}{}^b$	2.4
Cyclooctene	6.2×10^{-2}	11.4

^aValues for K are taken from ref. 13a. See also discussion in ref. 14. ^bValue for 1-hexene in ref. 13a. ^c k_{rel} for NBE set to 1.

This model reveals that weakly binding/weaker π -acidic substrates react faster (i.e., k_i/k_{rel} is larger, less ground state stabilization), but less of the corresponding nickel(o) alkene species is present in solution (K_i is smaller) because they stabilize nickel(o) less.²⁰ This is logically consistent with an oxidative process (nickel carbene formation) being slower at a less electron-rich metal.

We can now proceed to the more general case in which a single alkene is in a pre-equilibrium with PPh_3 . The observed 1st order kinetics in catalyst for the ylide consumption *in the absence of added alkene* indicates that the nickel carbene formation is also the rate-determining step in the substrate-free case, with an analogous resting state being before that transition state. With this idea in mind, we extend the aforementioned mechanistic model with rapid alkene/alkene exchange before the rate-determining nickel

carbene formation, to the general case for the cyclopropanation reaction. This leads to the following mechanistic sketch shown in Scheme 6.

Both pathways, cyclopropanation and unproductive ylide decomposition/homocoupling, share the same resting state manifold, i.e., a nickel(o) species with alkene (NiA) and phosphine ligands (NiP) in equilibrium. If a nickel(o) species with an alkene ligand reacts with an ylide to form the nickel carbene, it will follow the pathway of cyclopropanation (k_{CP}). If, on the other hand, there is no bound alkene but only phosphine ligands on the nickel, it will react unproductively once the nickel carbene is formed (k_H). Both pathways have the same dependence on ylide concentration, (approximately) 1st order, as evidenced by the reaction profile of ylide consumption (Figure S12).

This regime leads again to a Curtin-Hammett scenario, where the yield is determined by the competition between the two rates, $k_{CP}[ylide][NiA]$ and $k_H[ylide][NiP]$, with the pre-equilibrium between NiA and NiP controlled by relative concentrations and binding affinities of alkene versus phosphine.

Scheme 6. Simplified Mechanistic Scenario with an Alkene Exchange Equilibrium before Cyclopropanation.

Standard mathematical treatment of this scenario yields the following equation (see Supporting Information for full derivation).

$$\% \text{ yield} = 100 \cdot \frac{\frac{k_{CP}}{k_H} ([Ni]_{tot} - [NiP])}{\frac{k_{CP}}{k_H} [Ni]_{tot} + \left(1 - \frac{k_{CP}}{k_H}\right) [NiP]} \quad (2)$$

where $[NiP]$ is a function of the total concentrations of Ni, phosphine, and alkene, $[Ni]_{tot}$, $[P]_{tot}$, and $[A]_{tot}$, respectively, as well as the equilibrium constant K . The yield is

thus dependent on these three concentrations, as well as on the alkene binding constant K and on the ratio of the rate constants k_{CP}/k_H (Scheme 6).

This model can also be applied to the rate of cyclopropanation to give eq. (3). In this case, $k_{obs,rel}$ is normalized against an arbitrarily chosen reference k_{obs} of a given series of experimental data (usually the lowest concentration of $[Ni]_{tot}$).

$$k_{obs} = k_{CP}[NiA] = k_{CP}([Ni]_{tot} - [NiP]) \quad (3)$$

$$k_{obs,rel,n} = \frac{k_{CP}([Ni]_{tot,n} - [NiP]_n)}{k_{CP}([Ni]_{tot,1} - [NiP]_1)} = \frac{[NiA]_n}{[NiA]_1} \quad (4)$$

At this point we refrain from making any assumptions about what the possible species NiP and NiA might look like, except that NiA is a species with *at least one alkene coordinated*, whereas NiP is a species in which one alkene has been replaced by a phosphine ligand (PPh_3 in this case), most likely however an alkene-free *tris*-phosphine nickel complex.

4.5 Fit of Model to Data

Next, we apply this mechanistic model to our data to see if it agrees with our observations, at least qualitatively.

Figure 7. Plot of K (from Tolman,¹³ log scale) versus the experimental yield (black symbols, 1.0 mol% $(Ph_3P)_2NiBr_2$) and the predicted yield (red line) based on our mechanistic model for the cyclopropanation of cyclohexene (diamond, data from ref. 4), COE (square), 1-octene (circle), and NBE (triangle). The ratio k_{CP}/k_H was used as a parameter to fit the experimental data according to eq (2) to give $k_{CP}/k_H = 0.014$. $[Ni]_{tot} = 0.5$ mM, $[P]_{tot} = 1$ mM, $[A]_{tot} = 250$.

Using the model described above, we used the ratio k_{CP}/k_H as the *sole* parameter to fit eq (2) to the cyclopropanation yields with different alkenes (Figure 7) at *one* representative set of concentrations (see Figure S20 for other catalyst concentrations). This gives a ratio of rate constants k_{CP}/k_H of 0.014. That is, the rate *constant* of homocoupling (k_H) is larger than that for cyclopropanation (k_{CP}). Note that k_{CP} is therefore an *average* value over all alkenes. Because the al-

kene is necessarily involved in the rate-limiting step (according to our model), k_{CP} should vary with the nature of the alkene and thus k_{CP} is not independent of K .

We already gleaned this interdependence of k_{CP} and K in the alkene competition experiments (as k_{rel} in Table 1), but we chose to use the admittedly extreme simplification of a single k_{CP}/k_H ratio, and compare the numerical results to experiment.

4.6 Comparison of Model to Data

The extracted parameter k_{CP}/k_H (Figure 7) is the *sole fit* to our mechanistic data; accordingly, all further predictions are based thereupon.

Figure 8. Plot of COE concentration versus the measured yield (squares) and predicted yield (red curve) based on our model (eq (2)) for cyclopropanation of COE using 1.0 mol% $(Ph_3P)_2NiBr_2$. $k_{CP}/k_H = 0.014$, $[Ni]_{tot} = 0.5$ mM, $[P]_{tot} = 1$ mM with no further adjustment of parameters. Data from ref. 4.

Figure 8, in which the computed yield for cyclopropanation of cyclooctene over a broad range of substrate concentrations matches the experiment well, despite the fit of k_{CP}/k_H at a single concentration, gives a first indication that this rather bold approximation provides a better-than-qualitative description of the reaction.

In agreement with our rate data above, the model reasonably reproduces the orders in NBE, PPh_3 and catalyst (Figures S24, S25, and S26), as would be expected.

Figure 9. Plot of mole fraction of nickel X_{Ni} (using $Ni(acac)_2$) versus the measured rate (squares) and predicted rate (red solid curve) (approximated as initial yield after 30 min) based on our model (eq (4)) for the cyclopropanation of NBE, all with no further adjustment of parameters. $k_{CP}/k_H = 0.014$, $[Ni]_{tot} + [P]_{tot} = 0.5$ mM, $[A]_{tot} = 250$ mM.

The model also predicts that for NBE as substrate, the rate of cyclopropanation might change significantly but the yield does not vary noticeably, despite there being an exchange of phosphine and olefin in the resting state, as seen in Figure 9.

At higher X_{Ni} , the experimental yields and rates deviate downwards from those predicted by our model. A reasonable explanation for this behavior is a less stable catalyst under the very low concentration of phosphine ligand (Figure 9).

Figure 10. Plot of catalyst concentration versus yield for COE (squares), 1-octene (circles) and norbornene (triangles). The black curves depict the predicted yield based on our model (eq (2)), with no further adjustment of parameters. $k_{CP}/k_H = 0.014$, $[P]_{tot} = 2[Ni]_{tot}$, $[A]_{tot} = 250$ mM.

One key initial finding, as mentioned in the Introduction and for which we sought an explanation, was that at higher catalyst loading the yield of cyclopropanation is suppressed using COE as substrate. This has been shown here also for norbornene (and 1-octene) as substrate, but only if a $Ni(II)$ precatalyst is used, and only to a small extent in

the NBE case. When an already reduced precatalyst, $Ni(PPh_3)_4$, was used the same effect was observed for cyclooctene but not for norbornene (Figure 10). This shows, on the one hand, that the reduction of $Ni(II)$ to $Ni(o)$, as we propose, is an issue and does lead to partial catalyst deactivation. This can also be gleaned from the data in Figure 1.

On the other hand, with the model in hand, this catalyst loading effect can be explained by the specific interplay between K for the alkene and the catalyst concentration employed. With increasing precatalyst loading, there is a simultaneous increased concentration of phosphine ligand (P_{tot}) in the system, while the concentration of alkene (A_{tot}) is kept constant. Based on the value of K , it is possible for the phosphine ligand to replace the alkene binding to the catalyst, i.e. $[NiP]$ increases and more ylide decomposes unproductively in a parasitic side reaction. Thus, the observed decrease in yield is not present for a strongly binding alkene (NBE) but is observable for a weakly binding alkene (COE) (Figure 10). In accordance with this model, addition of an excess of PPh_3 under otherwise standard conditions for COE led to a strongly suppressed or even completely inhibited cyclopropanation reaction (see Supporting Information). This also explains why chelating bisphosphine or strongly binding monophosphine ligands have proven to be worse ligands than PPh_3 in terms of yield. The alkene cannot compete for a coordination site on the metal, leaving the ylide to decompose unproductively. The binding of phosphines to $Ni(o)$ has been shown to be dominated by steric effects.²¹ The initial rise in cyclopropanation yield as the Ni concentration is increased is likely explained by outcompeting catalyst decomposition and uncatalyzed ylide decomposition relative to the slow rate of cyclopropanation at low catalyst loadings.

4.7 Implication for Ligand Design

Thus far, we have only looked at the influence of the alkene substrate on the proposed pre-equilibrium. To make the reaction catalyst-controlled, guided by our mechanistic insight, a catalyst/ligand system is needed that does not inhibit, or even promotes, binding of the substrate, yet still has an ancillary ligand to stabilize $Ni(o)$. We took inspiration from a recent report by Wu and Doyle regarding the influence of remote steric effects.²² A small buried volume $\%V_{Bur}$ of a phosphine ligand would allow for substrate coordination. A large cone angle with substituents pointing away from the immediate coordination sphere of Ni would nevertheless result in a large steric profile with respect to coordination of more than one phosphine.

With this rationale in mind, we synthesized two new triaryl phosphine ligands with differing numbers of 3,5-di-*tert*-butylphenyl groups on phosphorous, either one or two. Indeed, both ligands gave improved yields over the standard ligand PPh_3 for the cyclopropanation of COE, 32 % and 48 %, respectively (Figure 11 and Table S18).

To test our hypothesis of the remote steric effect, we generated a steric-only regression model using five different phosphines ranging from the sterically small $PPhMe_2$ to our new, larger ligands (as well as spanning the largest

range of yields presently possible for the substrate COE).²³ We generated for the ligand set two steric parameters, buried volume %V_{Bur} and exact ligand solid cone angle Θ° .²⁴

Figure 11. Plot of measured yield versus predicted yield using a steric-only regression model with buried volume %V_{Bur} and exact solid cone angles Θ° . Ar = (3,5-di-*t*BuPh).

Already a good correlation between predicted and measured yields for our small ligand set can be achieved using only these two steric parameters, displaying the merit of harnessing remote steric effects on the ligand design. Additionally, the applicability of our rationale is reflected in the coefficients extracted from the regression model (Figure 11), i.e., the larger the cone angle with concomitantly small buried volume, the higher the predicted yield.

To further assess the veracity of the implicated pre-equilibrium binding, we measured the binding constants *K* for cyclooctene in the presence of the ligands in Figure 11 (see Supporting Information). Indeed, the *K* correlates well with the cyclopropanation yield. Figure 7 has been reproduced in the Supporting Information with the additional data (Figure S76).

5. Conclusion

In summary, our mechanistic studies lead us to propose a kinetic model that explains (most) experimental observations, at least qualitatively, and gave us initial guidelines for an improved, and partially verified, rational ligand design.

- 1) The active nickel catalyst with at least one alkene bound, NiA, is the resting state of the catalytic (cyclopropanation) cycle. The concentration of NiA, in turn, depends on the equilibrium constant *K*; for NBE the concentration of NiA is higher than for COE. This species can undergo nickel carbene formation with the ammonium ylide present in solution, followed by rapid product formation, most likely via a nickelacyclobutane.
- 2) Depending on the binding constant *K* of the alkene substrate, a significant amount of the nickel catalyst can exist as an alkene-free nickel species (NiP) that can also undergo nickel carbene formation in the rate-determining step to engage in rapid homocoupling (and, potentially, further

side reactions)(highlighted equilibrium in Figure 6). We propose NiP to be the resting state of this side-reaction cycle.

- 3) Carbene formation is faster for NiP than NiA ($k_H > k_{CP}$, Figure 7). Thus, NiP competes for the ylide in a parasitic cycle. This explains the pronounced substrate-dependence of the yield that we noted earlier. Unless the substrate binds well enough to drive the equilibrium to the alkene-ligated nickel species, and, therefore, cyclopropanation, the phosphine-ligated species will dominate and engage in the faster and unproductive background reaction, i.e. homocoupling (Figure 6).
- 4) Additionally, competition experiments indicate that there is an inverse relationship between the equilibrium constant *K* and the rate constant k_{CP} for cyclopropanation (i.e. k_{rel} in Table 1). Together with the larger rate constant for homocoupling k_H over the (average) rate constant for cyclopropanation k_{CP} (Figure 7) one can see that the higher the π -acidity of the ligand is (NBE > PPh₃), the smaller the rate constant becomes.
- 5) The product of the homocoupling, ethene, is also itself an outstanding ligand.¹³ A headspace analysis of the reaction showed that cyclopropane is a side-product of the reaction. Leaving the flask open to the Schlenk line likely allows the ethene to escape and thus might be the reason for the effect of an open versus a closed reaction flask.
- 6) Our mechanistic studies have afforded us with a blueprint for an improved ligand design. The pre-equilibrium binding can be influenced by employing ligands with remote steric hindrance, expressed as a small buried volume and a large cone angle, thus discouraging saturation of the catalyst with phosphine ligands, i.e., resulting in a larger *K*. Our measured binding constants for several phosphines give credence to this hypothesis.

The above-outlined mechanism and the resulting blueprint for an improved ligand design will serve as a highly valuable basis for the rational design of new ligands with above-mentioned features. Our initial results showcase a promising way forward. These mechanism-driven efforts, including an enlarged and more detailed ligand parametrization set, are currently ongoing and will be reported in due course.

ASSOCIATED CONTENT

This material is available free of charge via the Internet at <http://pubs.acs.org>.

Experimental details, characterizations, and geometries for all computed structures.

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Notes

The authors declare no competing financial interest.

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Supporting Information:

Mechanistic Studies on the Nickel-Catalyzed Cyclopropanation with Lithiomethyltrimethylammonium Triflate

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1. General methods

Note: All flasks and glass-coated stir bars (self-made or commercially available) used for cyclopropanation reactions were cleaned consecutively in a KOH/*i*-PrOH base bath, *aqua regia* and dried overnight in an oven at 150 °C. As noted previously, the lithiomethyl trimethylammonium reagent is prone to decomposition even when low concentrations of undesired trace metals are present in the reaction mixture.^{1,2} Additionally, all cyclopropanation reactions were conducted in a closed Schlenk flask to allow no gas exchange, unless noted otherwise.

All reactions were conducted in a glove box with N₂-atmosphere or using standard Schlenk techniques under Ar if not noted otherwise.

Concentration of solutions was conducted using a rotary evaporator at 40 °C. ¹H, ¹³C, ³¹P and ¹⁹F NMR spectra were recorded at 300 or 400 MHz (Bruker AV300 or AVIII400 spectrometers).

Chemical shifts were determined relative to the residual solvent peaks. The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC-FID analysis was performed on a Finnigan Focus CG with a Zebtron ZB-5MS, 30m*0.25 mm column. Headspace analysis was performed on a Thermo Scientific Trace1300 GC/ISQ Single Quad MS with a Phenomenex Zebtron ZB-1MS (60 m) column using an isothermal temperature program at 40 °C by Daniel Zindel (LPC, ETH Zürich). UV-Vis measurements were performed on a Hitachi U-2010 spectrophotometer. Elemental analyses and high resolution mass spectrometry were performed by the Molecular and Biomolecular Analysis Service MoBiAS, ETH Zürich.

Anhydrous THF was distilled from Na/benzophenone under N₂ prior to use.

Dibromobis(triphenylphosphine)nickel(II) (99%) was purchased from Sigma-Aldrich, stored in the glove box and used as received. *n*-BuLi (2.0 M in cyclohexane) was purchased from Sigma-Aldrich and used as received. Cyclooctene was purchased from Sigma-Aldrich (95%) or TCI (>95%), distilled from Na under Ar and degassed by freeze-pump-thaw cycles prior to use. Cyclohexene was purchased from Sigma-Aldrich (≥99%), distilled from Na under Ar and degassed by freeze-pump-thaw cycles prior to use. Norbornene (99%) was purchased from Sigma-Aldrich, stored in the glove box and used as received. Cyclooctane was purchased from TCI and used as received. *n*-Undecane (≥ 99.8%, analytical standard) was purchased from Fluka and used as received. Tetramethylammonium chloride (≥ 98%) was purchased from Sigma-Aldrich, dried under vacuum and stored in the glove box. Tetramethyl-d₁₂-ammonium chloride was purchased from Cambridge Isotope Laboratories (98%) or Sigma-Aldrich (98 atom % D), dried under vacuum, and used immediately or stored in the glove box. Silver(I) trifluoromethanesulphonate was purchased from ABCR (99%) or TCI (>98.0%) and used as received. PBNPh₂ (99%) was purchased from Strem, stored in the glove box and used as received.

All other chemicals were purchased from commercial suppliers and used as received.

Authentic products, exo-tricyclo[3.2.1.0^{2,4}]octane, bicyclo[6.1.0]nonane, bicyclo[4.1.0]heptane, and hexylcyclopropane, were prepared following reported procedures and matched reported data.^{2,3,4}

Augustin A. S. W. Tchawou (Chen group) is thanked for the preparation of authentic heptylcyclopropane and its GC calibration curve.⁵

Tetramethylammonium triflate was prepared as reported previously, dried under vacuum and stored in the glove box.^{1,2}

All data was analyzed with Microsoft Excel 2016 and/or OriginLab OriginPro 2016 or 2019.

2. In Situ and Preformation of Lithiomethyltrimethylammonium Triflate for Kinetic Measurements

Scheme S1. Two Different Methods Employed to Generate the Active Reagent [LiCH₂NMe₃]⁺OTf⁻, either after (A) or before (B) Addition of Catalyst.

Method A / in situ

Method B / preformed

We used two different Methods, A and B, that differ in the generation of the ammonium ylide reagent, either in situ (A) or preformed (B).

For method A, $[\text{NMe}_4]\text{OTf}$ (1.1 equiv), alkene and catalyst were mixed together, cooled to 0 °C, then BuLi (1 equiv) was added to form the ylide in situ. Under these conditions, a small induction phase was observed, most likely due to a non-instantaneous deprotonation of the not fully soluble ammonium salt in THF.

For method B, the ammonium salt was deprotonated first (in the *presence or absence of alkene*) before the catalyst was added to the preformed ylide to initiate the cyclopropanation/ylide decomposition. In this case, no induction phase was observed.

In general, we had opted to use method A due to the more convenient reaction set up. In cases where we studied the consumption of ylide, method B was used to simplify the kinetics by having the maximum concentration of ylide present upon addition of catalyst.

We have only observed two significant differences between method A and B. For method A, we observe a small induction phase due to the deprotonation as mentioned above. Method B appears to form a smaller amount of active catalyst, likely due to the reduction with the ylide itself instead of BuLi. A more detailed discussion of the tetramethylammonium deprotonation can be found in Section 23.

3. Kinetic Measurements of Norbornene Cyclopropanation with $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ – Method A (Direct Deprotonation)

Scheme S2. Reaction Scheme for the Determination of the Order in Catalyst using Method A.

Inside the glove box, an oven-dried 50 mL Schlenk flask equipped with a J. Young inlet valve, glass stopper, screw cap with septum and a glass-coated stir bar was charged with $[\text{NMe}_4]\text{OTf}$ (245.5 mg, 1.1 mmol, 1.1 equiv), $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ in THF (prepared as stock solution, added dropwise by difference with a 2.5 mL gastight Hamilton syringe (previously dried at 50 °C in a vacuum oven)) and norbornene (471 mg, 5.0 mmol, 5 equiv). The flask was removed from the glove box and attached to a Schlenk line. Dry THF ($x \text{ mL} + (\text{catalyst in THF}) \text{ mL} = 19.5 \text{ mL THF}$) was added via syringe. Undecane (50 μL) was added via a 50 μL micro syringe as internal standard. The flask was immersed in an ice bath and the reaction allowed to equilibrate (over ca. 20 min).

Then, an aliquot (ca. 0.2 mL) was taken with a disposable 1 mL plastic syringe (flushed several times with Ar) and immediately quenched by injection into 2 mL H_2O / 2 mL pentane ($t = 0 \text{ min}$).

BuLi (500 μL , 1 mmol, 1 equiv; 2 M in cyclohexane) was added dropwise over ca. 30 s via a 1 mL gastight Hamilton syringe (by difference; previously dried at 50 °C in a vacuum oven) ($t = 0 \text{ min}$ with first drop).

After the addition was completed, the flask was sealed/closed to the Schlenk line again and only opened when an aliquot was taken.

After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO_4 and analyzed by GC-FID. The yield was determined by the integral ratio of the product versus undecane as internal standard using a previously determined calibration curve.

Figure S1. Plot of time versus product concentration for four different catalyst concentrations of $(\text{Ph}_3\text{P})_2\text{NiBr}_2$. The black lines depict an initial rate fit with omission of the first few data points of the induction phase (lightly shaded) to obtain k_{obs} .

Figure S2. Plot of the catalyst concentration $[\text{Ni}]$ of $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ versus k_{obs} for product formation with in situ deprotonation (Method A). The red curve depicts a fit to the function $y = ax^b$ to establish the order in $[\text{Ni}]$, $b = 1.17 \pm 0.08$.

4. Kinetic Measurements of Norbornene Cyclopropanation with $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ – Method B (Preformed Ylide)

Scheme S3. Reaction Scheme for the Determination of the Order in Catalyst using Method B.

Inside the glove box, an oven-dried 50 mL Schlenk flask equipped with a J. Young inlet valve, glass stopper, screw cap with septum and a glass-coated stir bar was charged with $[\text{NMe}_4]\text{OTf}$ (245.5 mg, 1.1 mmol, 1.1 equiv) and norbornene (471 mg, 5.0 mmol, 5 equiv). The flask was removed from the glove box and attached to a Schlenk line. Dry THF (x mL + (catalyst in THF) mL = 19.5 mL THF) was added via syringe. Undecane (50 μL) was added via a 50 μL micro syringe as internal standard. The flask was immersed in an ice bath and the reaction allowed to equilibrate (over ca. 20 min).

BuLi (500 μL , 1 mmol, 1 equiv; 2 M in cyclohexane) was added dropwise over ca. 30 s via a 1 mL gastight Hamilton syringe (by difference; previously dried at 50 $^\circ\text{C}$ in a vacuum oven). The flask was sealed/closed to the Schlenk line unless reagents were added or aliquots collected.

After 15 min, an aliquot (ca. 0.2 mL) was taken with a disposable 1 mL plastic syringe (flushed several times with Ar) and immediately quenched by injection into 2 mL H_2O / 2 mL pentane ($t = 0$ min).

Then, $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ (x mol%) in THF (prepared as stock solution inside the glove box) was added dropwise by difference with a 2.5 mL gastight Hamilton syringe (previously dried at 50 $^\circ\text{C}$ in a vacuum oven) over ca. 30 s ($t = 0$ min with first drop). After the addition was completed, the flask was sealed/closed to the Schlenk line again and only opened when an aliquot was taken.

After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO_4 and analyzed by GC-FID. The yield was determined by the integral ratio of the product versus undecane as internal standard using a previously determined calibration curve.

Figure S3. Plot of time versus product concentration for four different catalyst concentrations of $(\text{Ph}_3\text{P})_2\text{NiBr}_2$. The black lines depict an initial rate fit with omission of the first few data points of the induction phase (lightly shaded) to obtain k_{obs} .

Figure S4. Plot of the catalyst concentration [Ni] of (Ph₃P)₂NiBr₂ versus k_{obs} for product formation using the preformed ylide (Method B). The red curve depicts a fit to the function $y = ax^b$ to establish the order in [Ni], $b = 0.80 \pm 0.02$.

5. Determination of Secondary KIE with [N(CD₃)₄]OTf – Method A

Scheme S4. Reaction Scheme for the Determination of a Secondary KIE Using [N(CD₃)₄]OTf.

Inside the glove box, an oven-dried 50 mL Schlenk flask equipped with a J. Young inlet valve, glass stopper, screw cap with septum and a glass-coated stir bar was charged with [N(CD₃)₄]OTf (258.8 mg, 1.1 mmol, 1.1 equiv), (Ph₃P)₂NiBr₂ in THF (0.5 mol%, prepared as stock solution, added dropwise by difference with a 2.5 mL gastight Hamilton syringe (previously dried at 50 °C in a vacuum oven)) and norbornene (471 mg, 5.0 mmol, 5 equiv). The flask was removed from the glove box and attached to a Schlenk line. Dry THF (x mL + (catalyst in THF) mL = 19.5 mL THF) was added via syringe. Undecane (50 μL) was added via a 50 μL micro syringe as internal standard. The flask was immersed in an ice bath and the reaction allowed to equilibrate (over ca. 20 min).

Then, an aliquot (ca. 0.2 mL) was taken with a disposable 1 mL plastic syringe (flushed several times with Ar) and immediately quenched by injection into 2 mL H₂O / 2 mL pentane (t = 0 min).

BuLi (500 μL, 1 mmol, 1 equiv; 2 M in cyclohexane) was added dropwise over ca. 30 s via a 1 mL gastight Hamilton syringe (by difference; previously dried at 50 °C in a vacuum oven) (t = 0 min with first drop).

After the addition was completed, the flask was sealed/closed to the Schlenk line again and only opened when an aliquot was taken.

After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO₄ and analyzed by GC-FID. The yield was determined by the integral ratio of the product versus undecane as internal standard using a previously determined calibration curve. The same response factor for the product-d₂ was assumed.

Figure S5. Plot of time versus product concentration using tetramethylammonium triflate or tetramethylammonium-d₁₂ triflate to probe a possible secondary KIE. The red lines depict an initial rate fit with omission of the first few data points of the induction phase (lightly shaded) to obtain k_{obs} , i. e. k_{H} and k_{D} , for the protiated and deuterated tetramethylammonium reagent, respectively.

Table S1. Determination of the Secondary KIE using Tetramethylammonium-d₁₂ Triflate.

$k_{\text{H}} / \text{mM min}^{-1}$	$k_{\text{D}} / \text{mM min}^{-1}$	$k_{\text{H}}/k_{\text{D}}$
(0.57 ± 0.04)	(0.27 ± 0.01)	(2.1 ± 0.3)

6. Kinetic Measurements of Norbornene Cyclopropanation with (Ph₃P)₂NiBr₂ – Order in NBE

Scheme S5. Reaction Scheme for the Determination of the Order in Norbornene.

Inside the glove box, an oven-dried 50 mL Schlenk flask equipped with a J. Young inlet valve, glass stopper, screw cap with septum and a glass-coated stir bar was charged with [NMe₄]OTf (245.5 mg, 1.1 mmol, 1.1 equiv), (Ph₃P)₂NiBr₂ in THF (0.5 mol%, prepared as stock solution, added by difference with a 2.5 mL gastight Hamilton syringe (previously dried at 50 °C in a vacuum oven)) and norbornene (x equiv). The flask was removed from the glove box and attached to a Schlenk line. Dry THF (x mL + (catalyst in THF) mL = 19.5 mL THF) was added via syringe. Undecane (50 μL) was added via a 50 μL micro syringe as internal standard. The flask was immersed in an ice bath and the reaction allowed to equilibrate (over ca. 20 min). Then, an aliquot (ca. 0.2 mL) was taken with a disposable 1 mL plastic syringe (flushed several times with Ar) and immediately quenched by injection into 2 mL H₂O / 2 mL pentane (t = 0 min).

BuLi (500 μL, 1 mmol, 1 equiv; 2 M in cyclohexane) was added dropwise over ca. 30 s via a 1 mL gastight Hamilton syringe (by difference; previously dried at 50 °C in a vacuum oven) (t = 0 min with first drop).

After the addition was completed, the flask was sealed/closed to the Schlenk line again and only opened when an aliquot was taken.

After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO₄ and analyzed by GC-FID. The yield was determined by the integral ratio of the product versus undecane as internal standard using a previously determined calibration curve.

Figure S6. Plot of time versus product concentration for four different norbornene (NBE) concentrations. The black lines depict an initial rate fit with omission of the first few data points of the induction phase (lightly shaded) to obtain k_{obs} .

Figure S7. Plot of the norbornene concentration [NBE] versus k_{obs} for product formation. The red curve depicts a fit to the function $y = ax^b$ to establish the order in [NBE], $b = 0.18 \pm 0.02$.

7. Kinetic Measurements of Norbornene Cyclopropanation with Ni(acac)₂/PPh₃ – Order in PPh₃

Scheme S6. Reaction Scheme for the Determination of the Order in PPh₃.

Inside the glove box, an oven-dried 50 mL Schlenk flask equipped with a J. Young inlet valve, glass stopper, screw cap with septum and a glass-coated stir bar was charged with [NMe₄]OTf (245.5 mg, 1.1 mmol, 1.1 equiv), Ni(acac)₂ in THF (0.5 mol%, prepared as stock solution, added by difference with a 2.5 mL gastight Hamilton syringe (previously dried at 50 °C in a vacuum oven)), PPh₃ in THF (prepared as stock solution, added by difference with a 2.5 mL gastight Hamilton syringe (previously dried at 50 °C in a vacuum oven)), and norbornene (471 mg, 5.0 mmol, 5 equiv). The flask was removed from the glove box and attached to a Schlenk line. Dry THF (x mL + (catalyst in THF) mL = 19.5 mL THF) was added via syringe. Undecane (50 μL) was added via a 50 μL micro syringe as internal standard. The flask was immersed in an ice bath and the reaction allowed to equilibrate (over ca. 20 min).

Then, an aliquot (ca. 0.2 mL) was taken with a disposable 1 mL plastic syringe (flushed several times with Ar) and immediately quenched by injection into 2 mL H₂O / 2 mL pentane (t = 0 min).

BuLi (500 μL, 1 mmol, 1 equiv; 2 M in cyclohexane) was added dropwise over ca. 30 s via a 1 mL gastight Hamilton syringe (by difference; previously dried at 50 °C in a vacuum oven) (t = 0 min with first drop).

After the addition was completed, the flask was sealed/closed to the Schlenk line again and only opened when an aliquot was taken.

After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO₄ and analyzed by GC-FID. The yield was determined by the integral ratio of the product versus undecane as internal standard using a previously determined calibration curve.

Figure S8. Plot of time versus product concentration for four different triphenylphosphine concentrations with constant nickel concentration. The black lines depict an initial rate fit with omission of the first few data points of the induction phase (lightly shaded) to obtain k_{obs} .

Figure S9. Plot of the triphenylphosphine concentration $[PPh_3]$ versus k_{obs} for product formation. The red curve depicts a fit to the function $y = ax^b$ to establish the order in $[PPh_3]$, $b = 0.17 \pm 0.05$.

8. Kinetic Measurements of Norbornene Cyclopropanation with $(Ph_3P)_2NiBr_2$ – Method B (Preformed Ylide) – Order in Ylide

Scheme S7. Reaction Scheme for the Determination of the Order in Ylide using Method B.

Inside the glove box, an oven-dried 50 mL Schlenk flask equipped with a J. Young inlet valve, glass stopper, screw cap with septum and a glass-coated stir bar was charged with $[NMe_4]OTf$ ($(x+0.1)$ mmol, $(x+0.1)$ equiv) and norbornene (471 mg, 5.0 mmol, 5 equiv). The flask was removed from the glove box and attached to a Schlenk line. Dry THF (x mL + (catalyst in THF) mL = 19.5 mL THF) was added via syringe. Undecane (50 μ L) was added via a 50 μ L micro syringe as internal standard. The flask was immersed in an ice bath and the reaction allowed to equilibrate (over ca. 20 min).

BuLi (x mmol, x equiv; 2 M in cyclohexane) was added dropwise over ca. 30 s via a 1 mL gastight Hamilton syringe (by difference; previously dried at 50 °C in a vacuum oven). The flask was sealed/closed to the Schlenk line unless reagents were added or aliquots collected.

After 15 min, an aliquot (ca. 0.2 mL) was taken with a disposable 1 mL plastic syringe (flushed several times with Ar) and immediately quenched by injection into 2 mL H_2O / 2 mL pentane ($t = 0$ min).

Then, $(Ph_3P)_2NiBr_2$ (0.5 mol%) in THF (prepared as stock solution inside the glove box) was added dropwise by difference with a 2.5 mL gastight Hamilton syringe (previously dried at 50 °C in a vacuum oven) over ca. 30 s ($t = 0$ min with first drop). After the addition was completed, the flask was sealed/closed to the Schlenk line again and only opened when an aliquot was taken.

After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of $MgSO_4$ and analyzed by GC-FID. The yield was determined by the integral ratio of the product versus undecane as internal standard using a previously determined calibration curve.

Figure S10. Plot of time versus product concentration for three different ammonium ylide concentrations with 0.5 mol $(\text{Ph}_3\text{P})_2\text{NiBr}_2$. The black lines depict an initial rate fit with omission of the first few data points of the induction phase (lightly shaded) to obtain k_{obs} .

Figure S11. Plot of ylide concentration [ylide] versus k_{obs} for product formation. The black curves depict a fit to the function $y = ax^b$ to establish the order in [ylide] at high and at low concentration, $b = 1.23$ and -0.08 , respectively.

The order in ylide shows a complex behavior. Pörschke et al. have detailed the Lewis acidic nature of $\text{Ni}(0)$.⁶ The binding of a carbanion to $\text{Ni}(0)$ can be imagined as a push-pull-system, i.e., the binding is determined by the σ -donor strength of the carbanion and the (π)-acceptor strength of the ligands on $\text{Ni}(0)$ in a temperature-dependent equilibrium. The qualitative order was given as $\text{LiCH}_3 > [\text{Me}_3\text{PCH}_2] > [\text{Ph}_3\text{PCH}_2] > [\text{Me}_2(\text{O})\text{SCH}_2]$ for the carbanion and as $\text{Ni}(\text{CO})_3 > \text{Ni}(\text{C}_2\text{H}_4)_2 > \text{Ni}(\text{CDT})$ for the $\text{Ni}(0)$ fragment (CDT = *all-trans*-1,5,9-Cyclododecatriene) in ref. S6.

Thus, one can conclude that the nature and concentration of the alkene in solution (or *absence* thereof) will also affect the additional equilibrium of ylide binding (without changing the turnover-limiting transition state).

One sees this behavior by comparing reaction profiles for the reaction in *presence* and *absence* of a substrate. The reaction profile for the consumption of ylide in the *absence* of substrate displays a well-behaved 1st order decay (**Figure S12**). This is consistent with a weak acceptor fragment Ni(0)(PPh₃)₂ and the ylide not coordinated in the resting state. In the case of norbornene as substrate, a relatively good π -acceptor, the reaction profile for product formation displays a much longer initial phase of linearity than one would expect for a simple 1st order dependence on ylide (see, e.g., **Figure S17**). This is consistent with a concentration dependent switch from 0th to 1st order in ylide at high conversion. Although there is insufficient data in **Figure S11**, the general behavior shown therein is also consistent with our mechanistic model.

9. Kinetic Measurements of Ylide decomposition / Homocoupling with Ni(PPh₃)₄ in the Absence of Alkene

Scheme S8. Reaction Scheme for the Determination of the Order in Catalyst in the Absence of Added Alkene.

Inside the glove box, an oven-dried 50 mL Schlenk flask equipped with a J. Young inlet valve, glass stopper, screw cap with septum and a glass-coated stir bar was charged with [NMe₄]OTf (245.5 mg, 1.1 mmol, 1.1 equiv). The flask was removed from the glove box and attached to a Schlenk line. Dry THF (x mL + (catalyst in THF) mL = 19.5 mL THF) was added via syringe. Cyclooctane (100 μ L) was added via a 100 μ L micro syringe as internal standard. The flask was immersed in an ice bath and the reaction allowed to equilibrate (over ca. 20 min).

BuLi (500 μ L, 1 mmol, 1 equiv; 2 M in cyclohexane) was added dropwise over ca. 30 s via a 1 mL gastight Hamilton syringe (by difference; previously dried at 50 $^\circ$ C in a vacuum oven). The flask was sealed/closed to the Schlenk line unless reagents were added or aliquots collected.

After 15 min, an aliquot (ca. 0.2 mL) was taken with a disposable 1 mL plastic syringe (flushed several times with Ar) and immediately quenched by injection into 0.2 mL 1 M TFA in DCM (t = 0 min).

Then, Ni(PPh₃)₄ (x mol%) in THF (prepared as stock solution inside the glove box) was added dropwise by difference with a 2.5 mL gastight Hamilton syringe (previously dried at 50 $^\circ$ C in a vacuum oven) over ca. 30 s (t = 0 min with first drop). After the addition was completed, the flask was sealed/closed to the Schlenk line again and only opened when an aliquot was taken.

Aliquots were diluted with 0.3 mL CD₃OD and analyzed by ¹H NMR. Spectra were subsequently analyzed with MestReNova. The integrated 'Full Auto (Bernstein Polynomials)' baseline correction was applied. The spectrum was referenced to the residual solvent peak of CD₃OD (δ = 3.31). Signals of cyclooctane (δ = 1.55, s) and trimethylammonium (δ = 2.90, s) were integrated using the peak integration function. The signal of tetramethylammonium (δ = 3.20, t) was integrated using the sum function.

The integral ratio of tetramethylammonium to cyclooctane at t = 0 min was set to 55 mM and all other integral ratios at later time points were referenced to that value.

The integral ratio of trimethylammonium to cyclooctane was also referenced to the integral ratio of tetramethylammonium to cyclooctane at t = 0 min and scaled by 4/3 to account for the number of protons.

Figure S12. Plot of time versus tetramethylammonium concentration for three different catalyst concentrations. The red curves depict a fit to the function $y = a e^{-kt} + b$ to obtain k_{obs} .

Figure S13. Plot of the catalyst concentration $[\text{Ni}]$ of $\text{Ni}(\text{PPh}_3)_4$ versus k_{obs} for tetramethylammonium disappearance. The red curve depicts a fit to the function $y = ax^b$ to establish the order in $[\text{Ni}]$, $b = 1.341 \pm 0.002$.

Figure S14. Plot of time versus tetramethylammonium concentration for three different $\text{Ni}(\text{PPh}_3)_4$ concentrations and one $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ concentration as comparison. The red curves depict a fit to the function $y = a e^{-kt} + b$ to obtain k_{obs} .

Figure S15. Plot of time versus trimethylammonium concentration after an acidic quench for three different catalyst concentrations. The red curves depict a fit to the function $y = a(1 - e^{-kt})$ to obtain k_{obs} for the formation of trimethylamine.

Figure S16. Plot of the catalyst concentration [Ni] of $\text{Ni}(\text{PPh}_3)_4$ versus k_{obs} for trimethylammonium formation after an acidic quench. The red curve depicts a fit to the function $y = ax^b$ to establish the order in [Ni], $b = 1.4 \pm 0.1$.

10. Kinetic Measurements of Norbornene Cyclopropanation with $\text{Ni}(\text{PPh}_3)_4$

Scheme S9. Reaction Scheme for the Determination of the Order in Catalyst using $\text{Ni}(\text{PPh}_3)_4$.

Inside the glove box, an oven-dried 50 mL Schlenk flask equipped with a J. Young inlet valve, glass stopper, screw cap with septum and a glass-coated stir bar was charged with $[\text{NMe}_4]\text{OTf}$ (245.5 mg, 1.1 mmol, 1.1 equiv), and norbornene (471 mg, 5.0 mmol, 5 equiv). The flask was removed from the glove box and attached to a Schlenk line. Dry THF (x mL + (catalyst in THF) mL = 19.5 mL THF) was added via syringe. Undecane (50 μL) was added via a 50 μL micro syringe as internal standard. The flask was immersed in an ice bath and the reaction allowed to equilibrate (over ca. 20 min).

$\text{Ni}(\text{PPh}_3)_4$ (x mol%) in THF (prepared as stock solution inside the glove box) was added dropwise by difference with a 2.5 mL gastight Hamilton syringe (previously dried at 50 $^\circ\text{C}$ in a vacuum oven) over ca. 30 s ($t = 0$ min with first drop). Then, an aliquot (ca. 0.2 mL) was taken with a disposable 1 mL plastic syringe (flushed several times with Ar) and immediately quenched by injection into 2 mL H_2O / 2 mL pentane ($t = 0$ min).

BuLi (500 μL , 1 mmol, 1 equiv; 2 M in cyclohexane) was added dropwise over ca. 30 s via a 1 mL gastight Hamilton syringe (by difference; previously dried at 50 $^\circ\text{C}$ in a vacuum oven) ($t = 0$ min with first drop).

After the addition was completed, the flask was sealed/closed to the Schlenk line again and only opened when an aliquot was taken.

After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO_4 and analyzed by GC-FID. The yield was determined by the integral ratio of the product versus undecane as internal standard using a previously determined calibration curve.

Figure S17. Plot of time versus product concentration for four different catalyst concentrations. The black lines depict an initial rate fit with omission of the first few data points of the induction phase and the later data points at high conversions (lightly shaded) to obtain k_{obs} .

Figure S18. Plot of the catalyst concentration [Ni] of Ni(PPh₃)₄ versus k_{obs} for product formation. The red curve depicts a fit to the function $y = ax^b$ to establish the order in [Ni], $b = 1.0 \pm 0.1$.

11. Influence of Catalyst Loading on the Cyclopropanation of Different Alkenes

Scheme S10. Influence of Different Precatalysts and Loading on Product Formation.

Inside the glove box, an oven-dried 5 mL Schlenk flask equipped with a Teflon and a glass-coated stir bar was charged with [NMe₄]OTf (22.3 mg, 0.1 mmol, 1 equiv), alkene (0.5 mmol, 5 equiv, as stock solution (NBE) or neat (cyclooctene, 1-octene)), catalyst in THF (prepared as stock solution), and THF (tot. vol. THF: 2 mL, 0.05 M). The flask was removed from the glove box, cooled to 0 °C in an ice/water bath, and BuLi (2 M in cyclohexane; 53 µL, 0.105 mmol, 1.05 equiv) was added dropwise via micro syringe under a counterflow of Ar. The flask was sealed (no gas exchange). After 16 h, undecane (10 µL; internal standard) was added and an aliquot (ca. 0.2 mL) was partitioned between 2 mL pentane and 2 mL water. After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO₄ and analyzed by GC-FID. The yield was determined by the integral ratio of the product versus undecane as internal standard using a previously determined calibration curve.

Figure S19. Plot of catalyst concentration [Ni]_{tot} versus % yield of product for three different alkenes, cyclooctene (COE, squares), 1-octene (1Oct, circles), and norbornene (NBE, triangles), and three different catalysts, (Ph₃P)₂NiBr₂ (green), Ni(PPh₃)₄ (red), and Ni(cod)₂ (yellow).

Table S2. Influence of Catalyst Loading on the Cyclopropanation of Different Alkenes.

Entry	Alkene	Precatalyst	[Ni] / mM	Yield / %
1	Norbornene	Ni(PPh ₃) ₄	0.5	85.4
2			1.5	90.2
3			2.5	91.9
4		Ni(cod) ₂	0.5	76.2
5			1.5	75.8
6			2.5	75.3
7		(Ph ₃ P) ₂ NiBr ₂	0.25	86.3
8			0.5	83.1
9			1.0	84.5
10			1.5	79.9
11			2.0	78.4
12			2.5	67.5
13	1-Octene	(Ph ₃ P) ₂ NiBr ₂	0.25	64.4
14			0.5	61.9
15			1.0	52.0
16			1.5	40.7
17			2.0	27.5
18			2.5	16.3
19	Cyclooctene	Ni(PPh ₃) ₄	0.5	17.2
20			1.5	4.6
21			2.5	1.0
22		(Ph ₃ P) ₂ NiBr ₂	0.5	25.1

23	1.0	15.4
24	1.5	7.8
25	2.0	2.8
26	2.5	0.8

12. Fit for k_{CP}/k_H for Different Catalyst Loadings

Data was taken from section 11 using $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ as catalyst and norbornene ($K = 4.4$), 1-octene ($K = 0.5$), or cyclooctene ($K = 0.062$) as the substrate.⁷ The experimental data was fit to equation (S33) using k_{CP}/k_H as parameter for each catalyst concentration separately (see **Scheme S15** and equations (S16) and (S17)).

Figure S20. a)-e) Plots of K (log scale) versus the experimental yield and the predicted yield based on equation (S33) for different concentrations of $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ as catalyst.⁷ f) Plot of k_{CP}/k_H versus catalyst concentration $[\text{Ni}]_{\text{tot}}$.

13. Method of Continuous Variation – Alkene Competition

Scheme S11. MCV Competition Experiment between Two Alkenes.

Inside the glove box, an oven-dried 5 mL Schlenk flask equipped with a Teflon tap and a glass-coated stir bar was charged with [NMe₄]OTf (22.3 mg, 0.1 mmol, 1 equiv), (Ph₃P)₂NiBr₂ in 0.1 mL THF (0.5 mol%, prepared as stock solution), alkene 1 in THF (prepared as stock solution, 500 mM), alkene 2 in THF (prepared as stock solution, 500 mM) and 0.9 mL THF (tot. vol. THF: 2 mL, 0.05 M). The flask was removed from the glove box, cooled to 0 °C in an ice/water bath, and BuLi (2 M in cyclohexane; 53 µL, 0.105 mmol, 1.05 equiv) was added dropwise via micro syringe under a counterflow of Ar. The flask was sealed (no gas exchange).

After 6 h, the reaction was worked up (NBE/1Oct).

After 30 min, the reaction was quenched with 0.1 mL H₂O (NBE/COE and 1Oct/1Non).

Undecane (10 µL; internal standard) was added and an aliquot (ca. 0.2 mL) was partitioned between 2 mL pentane and 2 mL water. After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO₄ and analyzed by GC-FID. The yield was determined by the integral ratio of the products versus undecane as internal standard using a previously determined calibration curve.

The total concentration of added alkene 1 and alkene 2 was kept constant, [A1]_{tot} + [A2]_{tot} = 250 mM.

Table S3. MCV Alkene Competition Experiment with Norbornene and Cyclooctene.

X _{NBE}	[NBE] _{tot} / mM	V _{NBEstock} / mL	[COE] _{tot} / mM	V _{COEstock} / mL	[P _{NBE}]/[P _{COE}]
0.1	25	0.1	225	0.9	1.464770072
0.2	50	0.2	200	0.8	2.485806392
0.3	75	0.3	175	0.7	3.716750536
0.4	100	0.4	150	0.6	5.382796308
0.5	125	0.5	125	0.5	7.202673907
0.6	150	0.6	100	0.4	12.87358766
0.7	175	0.7	75	0.3	17.697543
0.8	200	0.8	50	0.2	26.31536905
0.9	225	0.9	25	0.1	53.71648742

Table S4. MCV Alkene Competition Experiment with Norbornene and 1-Octene.

X _{NBE}	[NBE] _{tot} / mM	V _{NBEstock} / mL	[1Oct] _{tot} / mM	V _{1Octstock} / mL	[P _{NBE}]/[P _{1Oct}]
0.1	25	0.1	225	0.9	0.25236
0.2	50	0.2	200	0.8	0.576194
0.3	75	0.3	175	0.7	0.91573
0.4	100	0.4	150	0.6	1.550245
0.5	125	0.5	125	0.5	2.096557
0.6	150	0.6	100	0.4	4.033734
0.7	175	0.7	75	0.3	7.189614
0.8	200	0.8	50	0.2	14.03366
0.9	225	0.9	25	0.1	34.18419

Table S5. MCV Alkene Competition Experiment with 1-Octene and 1-Nonene.

X _{1Oct}	[1Oct] _{tot} / mM	V _{1Octstock} / mL	[1Non] _{tot} / mM	V _{1Nonstock} / mL	[P _{1Oct}]/[P _{1Non}]
0.1	25	0.1	225	0.9	0.114310346
0.2	50	0.2	200	0.8	0.257989186
0.3	75	0.3	175	0.7	0.435932707
0.4	100	0.4	150	0.6	0.679684628
0.5	125	0.5	125	0.5	1.021350891
0.6	150	0.6	100	0.4	1.533079553
0.7	175	0.7	75	0.3	2.403979384
0.8	200	0.8	50	0.2	4.036792419
0.9	225	0.9	25	0.1	8.462446599

Figure S21. Plot of mole fraction of alkene 1 X_1 versus product ratio $[P_1]/[P_2]$ derived from alkene 1 and alkene 2. Numeration is as follows: 1: Norbornene (NBE), 2: Cyclooctene (COE) (squares); 1: Norbornene, 2: 1-Octene (1Oct) (circles); 1: 1-Octene, 2: 1-Nonene (1Non) (triangles). The red curves depict a fit to the function $y = aX_1/(1-X_1)$ (equation (S15)).

The fit parameter a from **Figure S21** is defined as (see equation (S15))

$$a = \frac{k_1 K_1}{k_2 K_2} \quad (\text{S1})$$

Setting $k(\text{NBE}) \equiv k_{\text{rel}}(\text{NBE}) = 1$, one can obtain relative rate constants k_{rel} with respect to norbornene for the alkenes using the fit parameter a as follows

$$k_{\text{rel},2} = \frac{k_{\text{rel,NBE}} K_{\text{NBE}}}{a K_2} = \frac{K_{\text{NBE}}}{a K_2} \quad (\text{S2})$$

Table S6. Relative Rate Constants k_{rel} for Several Alkenes.

Alkene	K^a	a^b	k_{rel}
Norbornene	4.4	-	1
1-Octene	0.5	3.7	2.4
Cyclooctene	0.062	6.2	11.4

^aTaken from ref. S7. ^bFit parameter a taken from **Figure S21**.

14. Kinetic Measurements of Cyclopropanation with Norbornene and Cyclooctene – Competition Experiment

Scheme S12. Competition Experiment between Norbornene and Cyclooctene.

Inside the glove box, an oven-dried 50 mL Schlenk flask equipped with a J. Young inlet valve, glass stopper, screw cap with septum and a glass-coated stir bar was charged with $[\text{NMe}_4]\text{OTf}$ (245.5 mg, 1.1 mmol, 1.1 equiv), $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ in THF (0.5 mol%, prepared as stock solution, added by difference with a 2.5 mL gastight Hamilton syringe (previously dried at 50 °C in a vacuum oven)), cyclooctene (650 μL , 5.0 mmol, 5 equiv), and norbornene (471 mg, 5.0 mmol, 5 equiv). The flask was removed

from the glove box and attached to a Schlenk line. Dry THF (x mL + (catalyst in THF) mL = 19.5 mL THF) was added via syringe. Undecane (50 μ L) was added via a 50 μ L micro syringe as internal standard. The flask was immersed in an ice bath and the reaction allowed to equilibrate (over ca. 20 min).

Then, an aliquot (ca. 0.2 mL) was taken with a disposable 1 mL plastic syringe (flushed several times with Ar) and immediately quenched by injection into 2 mL H₂O / 2 mL pentane (t = 0 min).

BuLi (500 μ L, 1 mmol, 1 equiv; 2 M in cyclohexane) was added dropwise over ca. 30 s via a 1 mL gastight Hamilton syringe (by difference; previously dried at 50 °C in a vacuum oven) (t = 0 min with first drop).

After the addition was completed, the flask was sealed/closed to the Schlenk line again and only opened when an aliquot was taken.

After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO₄ and analyzed by GC-FID. The yield was determined by the integral ratio of the product versus undecane as internal standard using a previously determined calibration curve.

Figure S22. Left axis: Plot of time versus product concentration using norbornene (1) and cyclooctene (2) as substrates in a competition experiment. The black lines depict an initial rate fit with omission of the first few data points of the induction phase and the later data points at high conversions (lightly shaded) to obtain k_{obs} . The products are tricyclo[3.2.1.0^{2,4}]octane (blue circles) and bicyclo[6.1.0]nonane (red squares). Right axis: Plot of time versus product ratio $[P_1]/[P_2]$ (black triangles).

The values from **Figure S22** can be compared to the results from **Figure S21** and **Table S3** from section 13. Both have $X_{\text{NBE}} = 0.5$, albeit with a different total concentration of alkenes (500 mM versus 250 mM). $[P_1]/[P_2] = 7.7$ after 240 min compared to 7.2 (**Table S3**).

Using equation (S15) and inserting $X_1 = 0.5$ we arrive at the following approximation

$$\frac{k_{\text{obs},1}}{k_{\text{obs},2}} \approx \frac{k_1 K_1}{k_2 K_2} \quad (\text{S3})$$

Setting k for NBE again as 1 ($k_{\text{rel},1} = 1$) as in section 13 and taking k_{obs} from the initial rate fit from **Figure S22**, we obtained $k_{\text{rel},2}$ for COE

$$k_{\text{rel},2} = \frac{K_1 k_{\text{obs},2}}{K_2 k_{\text{obs},1}} k_{\text{rel},1} = 7.5 \quad (\text{S4})$$

This can again be compared to the result from section 13 for COE: $k_{\text{rel}} = 11.4$.

15. Method of Continuous Variation – Ni/PPh₃

Scheme S13. MCV Experiment with Varying Ratio of Ni to PPh₃.

Inside the glove box, an oven-dried 5 mL Schlenk flask equipped with a Teflon tap and a glass-coated stir bar was charged with [NMe₄]OTf (22.3 mg, 0.1 mmol, 1 equiv), norbornene (47 mg, 0.5 mmol, 5 equiv), Ni(acac)₂ in THF (prepared as stock solution, 5 mM), PPh₃ in THF (prepared as stock solution, 5 mM), and 1.8 mL THF (tot. vol. THF: 2 mL, 0.05 M). The flask was removed from the glove box, cooled to 0 °C in an ice/water bath, and BuLi (2 M in cyclohexane; 53 µL, 0.105 mmol, 1.05 equiv) was added dropwise via micro syringe under a counterflow of Ar. The flask was sealed (no gas exchange). After 30 min, the reaction was quenched with 0.1 mL H₂O. Undecane (10 µL; internal standard) was added and an aliquot (ca. 0.2 mL) was partitioned between 2 mL pentane and 2 mL water.

After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO₄ and analyzed by GC-FID. The yield was determined by the integral ratio of the products versus undecane as internal standard using a previously determined calibration curve.

The total concentration of added Ni and PPh₃ was kept constant, [Ni]_{tot} + [PPh₃]_{tot} = 0.5 mM.

Table S7. MCV Ni/PPh₃

X_{Ni}	[Ni] _{tot} / mM	V_{Nistock} / mL	[PPh ₃] _{tot} / mM	V_{Pstock} / mL	% yield 30 min	% yield 16 h
0.1	0.05	0.02	0.45	0.18	6.768188684	90.733705
0.2	0.1	0.04	0.4	0.16	14.63634768	92.883315
0.3	0.15	0.06	0.35	0.14	22.08597692	85.754546
0.4	0.2	0.08	0.3	0.12	27.66665363	85.441463
0.5	0.25	0.1	0.25	0.1	31.13132601	83.052698
0.6	0.3	0.12	0.2	0.08	38.3908584	
0.7	0.35	0.14	0.15	0.06	39.92518041	83.611353
0.8	0.4	0.16	0.1	0.04	43.74514148	
0.9	0.45	0.18	0.05	0.02	43.4492871

Figure S23. Plot of mole fraction of nickel X_{Ni} (using Ni(acac)₂) versus the measured rate (squares) and predicted rate (red solid curve) (approximated as initial yield after 30 min) based on our model (eqs (S33) and (S35)) and the measured (triangles) and predicted yield (red dashed curve) (after 16 h) for the cyclo-propanation of NBE, all with no further adjustment of parameters. $k_{\text{CP}}/k_{\text{H}} = 0.014$, $[\text{Ni}]_{\text{tot}} + [\text{P}]_{\text{tot}} = 0.5 \text{ mM}$, $[\text{A}]_{\text{tot}} = 250 \text{ mM}$.

16. Derivation for Alkene Competition Equation

Scheme S14. Simplified Mechanistic Scenario with an Alkene Exchange Equilibrium Before Cyclopropanation.

Assuming that alkene *i* is already coordinated in the resting state of the catalyst, NiAi, the rate of cyclopropanation to give the product *Pi* is given by

where [Y] is the concentration of ylide.

The product ratio [P1]/[P2] for two competing alkenes A1 and A2 is then given by

$$\frac{[P_1]}{[P_2]} = \frac{k_1[NiA1][Y]}{k_2[NiA2][Y]} = \frac{k_1[NiA1]}{k_2[NiA2]} \quad (S6)$$

Before the turnover-limiting transition state (nickel carbene formation), an equilibrium establishes in which A1 and A2 are competing for Ni ([A1], [A2] >> [Ni]), i.e. a Curtin-Hammett scenario.

The unknown equilibrium constant K in equation (S7) can be redefined using the values determined by Tolman via a hypothetical displacement of the alkene with the ligand P to give NiP (defined by Tolman as alkene displacing ligand P)

$$K_1 = \frac{[\text{NiA1}][\text{P}][\text{A2}]}{[\text{NiP}][\text{A1}][\text{A2}]} = \frac{[\text{NiA1}][\text{P}]}{[\text{NiP}][\text{A1}]} \quad (\text{S8})$$

$$K_2 = \frac{[\text{NiA2}][\text{P}][\text{A1}]}{[\text{NiP}][\text{A2}][\text{A1}]} = \frac{[\text{NiA2}][\text{P}]}{[\text{NiP}][\text{A2}]} \quad (\text{S9})$$

Going from the left hand side of the equilibrium to the right hand side as defined above gives

$$K = \frac{K_1}{K_2} = \frac{[\text{NiA1}][\text{P}][\text{NiP}][\text{A2}]}{[\text{NiP}][\text{A1}][\text{NiA2}][\text{P}]} = \frac{[\text{NiA1}][\text{A2}]}{[\text{A1}][\text{NiA2}]} \quad (\text{S10})$$

$$[\text{NiA2}] = \frac{K_2}{K_1} \frac{[\text{NiA1}][\text{A2}]}{[\text{A1}]} \quad (\text{S11})$$

Inserting equation (S11) into the equation (S6) gives

r

$$\frac{[\text{P}_1]}{[\text{P}_2]} = \frac{k_1[\text{NiA1}]}{k_2[\text{NiA2}]} = \frac{k_1 K_1 [\text{NiA1}][\text{A1}]}{k_2 K_2 [\text{NiA1}][\text{A2}]} = \frac{k_1 K_1 [\text{A1}]}{k_2 K_2 [\text{A2}]} \quad (\text{S12})$$

For the Job plot the total alkene concentration is kept constant, $[\text{A}]_{\text{tot}} = [\text{A1}] + [\text{A2}] = \text{const.}$, and we can define the molar fraction X of alkene 1 and 2, respectively,

$$X_1 = \frac{[\text{A1}]}{[\text{A}]_{\text{tot}}} \quad (\text{S13})$$

$$X_2 = \frac{[\text{A2}]}{[\text{A}]_{\text{tot}}} = 1 - X_1 \quad (\text{S14})$$

and insert equations (S13) and (S14) in equation (S12) to give

$$\frac{[\text{P}_1]}{[\text{P}_2]} = \frac{k_1 K_1 [\text{A1}]}{k_2 K_2 [\text{A2}]} = \frac{k_1 K_1 X_1 [\text{A}]_{\text{tot}}}{k_2 K_2 X_2 [\text{A}]_{\text{tot}}} = \frac{k_1 K_1 X_1}{k_2 K_2 X_2} = \frac{k_1 K_1 X_1}{k_2 K_2 (1 - X_1)} \quad (\text{S15})$$

17. Derivation for Alkene-Ligand Competition Equation

Scheme S15. Simplified Mechanistic Scenario with an Alkene-Phosphine Exchange Equilibrium Before Cyclopropanation.

where NiA is the alkene-ligated resting state before turnover-limiting nickel carbene formation.

On the other hand, all side-products resulting from homocoupling we term P_H and the rate of formation is given as

$$\frac{d[P_H]}{dt} = k_H[NiP][Y] \quad (S17)$$

where NiP is the non-alkene-ligated resting state before turnover-limiting nickel carbene formation that does not engage in cyclopropanation.

Before the turnover-limiting transition state (nickel carbene formation), an equilibrium is established in which alkene A and ligand P are competing for Ni, i.e., a Curtin-Hammett scenario.

In addition the following boundary conditions with the known concentrations $[Ni]_{tot}$, $[P]_{tot}$, and $[A]_{tot}$ apply :

- The total amount of nickel $[Ni]_{tot}$ (added as precatalyst) is distributed among the possible resting states NiA and NiP

$$[Ni]_{tot} = [NiA] + [NiP] \quad (S19)$$

$$\rightarrow [NiA] = [Ni]_{tot} - [NiP] \quad (S20)$$

- The total amount of ligand $[P]_{tot}$ is either free or bound to nickel

$$[P]_{tot} = [P] + [NiP] \quad (S21)$$

$$\rightarrow [P] = [P]_{tot} - [NiP] \quad (S22)$$

- The total amount of alkene $[A]_{\text{tot}}$ is either free or bound to nickel and approximately constant over the reaction (excess alkene)

$$[A]_{\text{tot}} = [A] + [\text{NiA}] \quad (\text{S23})$$

$$\rightarrow [A] = [A]_{\text{tot}} - [\text{NiA}] = [A]_{\text{tot}} - [\text{Ni}]_{\text{tot}} + [\text{NiP}] \quad (\text{S24})$$

Inserting the above three boundary conditions (S20), (S22), and (S24) into the equation (S18) one gets

$$K = \frac{[P][\text{NiA}]}{[A][\text{NiP}]} \xrightarrow{\text{boundary cond.}} K = \frac{([P]_{\text{tot}} - [\text{NiP}])([\text{Ni}]_{\text{tot}} - [\text{NiP}])}{([A]_{\text{tot}} - [\text{Ni}]_{\text{tot}} + [\text{NiP}])([\text{NiP}])} = \frac{[P]_{\text{tot}}[\text{Ni}]_{\text{tot}} - ([P]_{\text{tot}} + [\text{Ni}]_{\text{tot}})[\text{NiP}] + [\text{NiP}]^2}{([A]_{\text{tot}} - [\text{Ni}]_{\text{tot}})[\text{NiP}] + [\text{NiP}]^2} \quad (\text{S25})$$

Further rearranging leads to the quadratic equation (S26) in $[\text{NiP}]$

$$\begin{aligned} \Rightarrow K([A]_{\text{tot}} - [\text{Ni}]_{\text{tot}})[\text{NiP}] + K[\text{NiP}]^2 &= [P]_{\text{tot}}[\text{Ni}]_{\text{tot}} - ([P]_{\text{tot}} + [\text{Ni}]_{\text{tot}})[\text{NiP}] + [\text{NiP}]^2 \\ \Rightarrow 0 &= [P]_{\text{tot}}[\text{Ni}]_{\text{tot}} - ([P]_{\text{tot}} + [\text{Ni}]_{\text{tot}})[\text{NiP}] - K([A]_{\text{tot}} - [\text{Ni}]_{\text{tot}})[\text{NiP}] + [\text{NiP}]^2 - K[\text{NiP}]^2 \\ \Rightarrow 0 &= [P]_{\text{tot}}[\text{Ni}]_{\text{tot}} - ([P]_{\text{tot}} + [\text{Ni}]_{\text{tot}}) + K([A]_{\text{tot}} - [\text{Ni}]_{\text{tot}})[\text{NiP}] + (1 - K)[\text{NiP}]^2 \\ \Rightarrow 0 &= [P]_{\text{tot}}[\text{Ni}]_{\text{tot}} - ([P]_{\text{tot}} + [\text{Ni}]_{\text{tot}} + K[A]_{\text{tot}} - K[\text{Ni}]_{\text{tot}})[\text{NiP}] + (1 - K)[\text{NiP}]^2 \\ \Rightarrow 0 &= [P]_{\text{tot}}[\text{Ni}]_{\text{tot}} - ([P]_{\text{tot}} + K[A]_{\text{tot}} + (1 - K)[\text{Ni}]_{\text{tot}})[\text{NiP}] + (1 - K)[\text{NiP}]^2 \text{ quadratic eq. in } [\text{NiP}] \end{aligned}$$

$$[\text{NiP}] = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (\text{S26})$$

$a = (1 - K), b = -([P]_{\text{tot}} + K[A]_{\text{tot}} + (1 - K)[\text{Ni}]_{\text{tot}}), c = [P]_{\text{tot}}[\text{Ni}]_{\text{tot}}$

Solving for $[\text{NiP}]$ and checking for the physically meaningful (-) solution one arrives at equation (S27)

$$[\text{NiP}] = \frac{([P]_{\text{tot}} + K[A]_{\text{tot}} + (1 - K)[\text{Ni}]_{\text{tot}}) - \sqrt{([P]_{\text{tot}} + K[A]_{\text{tot}} + (1 - K)[\text{Ni}]_{\text{tot}})^2 - 4(1 - K)[P]_{\text{tot}}[\text{Ni}]_{\text{tot}}}}{2(1 - K)} \quad (\text{S27})$$

The same can be done for $[\text{NiA}]$ to give equation (S28)

$$[\text{NiA}] = \frac{-([P]_{\text{tot}} + K[A]_{\text{tot}} + (K - 1)[\text{Ni}]_{\text{tot}}) + \sqrt{([P]_{\text{tot}} + K[A]_{\text{tot}} + (K - 1)[\text{Ni}]_{\text{tot}})^2 + 4K(1 - K)[A]_{\text{tot}}[\text{Ni}]_{\text{tot}}}}{2(1 - K)} \quad (\text{S28})$$

We can define the ratio of cyclopropanation product P_{CP} to all side-products deriving from homocoupling P_{H} using equations (S16) and (S17) and simplify by inserting equation (S19)

$$\frac{[P_{\text{CP}}]}{[P_{\text{H}}]} = \frac{k_{\text{CP}}[\text{NiA}][Y]}{k_{\text{H}}[\text{NiP}][Y]} = \frac{k_{\text{CP}}[\text{NiA}]}{k_{\text{H}}[\text{NiP}]} = \frac{k_{\text{CP}}([\text{Ni}]_{\text{tot}} - [\text{NiP}])}{k_{\text{H}}[\text{NiP}]} = f(x) \rightarrow [P_{\text{H}}] = \frac{[P_{\text{CP}}]}{f(x)} \quad (\text{S29})$$

Assuming that we have full conversion, i.e., all ylide is consumed, and that all ylide reacts via our proposed reaction scheme, i.e., either cyclopropanation or homocoupling-derived side-products, the yield of the reaction is given by

$$\frac{\% \text{ yield}}{100} = \frac{[P_{\text{CP}}]}{[P_{\text{CP}}] + [P_{\text{H}}]} \quad (\text{S30})$$

Using the rearranged equation (S29) and inserting into equation (S30) one arrives at

$$\frac{\% \text{ yield}}{100} = \frac{[P_{CP}]}{[P_{CP}] + [P_H]} = \frac{[P_{CP}]}{[P_{CP}] + \frac{[P_{CP}]}{f(x)}} = \frac{[P_{CP}]}{[P_{CP}] + \frac{[P_{CP}]}{f(x)}} \frac{f(x)}{f(x)} = \frac{[P_{CP}]}{[P_{CP}](1 + \frac{1}{f(x)})} \frac{f(x)}{f(x)} = \frac{[P_{CP}]f(x)}{[P_{CP}](f(x) + \frac{f(x)}{f(x)})} = \frac{f(x)}{f(x) + 1} \quad (S31)$$

Resubstituting $f(x)$ from equation (S29) into equation (S31) and rearranging gives equation (S32)

$$\begin{aligned} \frac{\% \text{ yield}}{100} &= \frac{f(x)}{f(x) + 1} = \frac{\frac{k_{CP}}{k_H} \frac{([Ni]_{tot} - [NiP])}{[NiP]}}{\frac{k_{CP}}{k_H} \frac{([Ni]_{tot} - [NiP])}{[NiP]} + 1} \frac{[NiP]}{[NiP]} = \frac{\frac{k_{CP}}{k_H} ([Ni]_{tot} - [NiP])}{\frac{k_{CP}}{k_H} ([Ni]_{tot} - [NiP]) + [NiP]} = \frac{\frac{k_{CP}}{k_H} ([Ni]_{tot} - [NiP])}{\frac{k_{CP}}{k_H} [Ni]_{tot} - \frac{k_{CP}}{k_H} [NiP] + [NiP]} \\ &= \frac{\frac{k_{CP}}{k_H} ([Ni]_{tot} - [NiP])}{\frac{k_{CP}}{k_H} [Ni]_{tot} + (1 - \frac{k_{CP}}{k_H}) [NiP]} \end{aligned} \quad (S32)$$

Finally, one can insert equation (S27) into equation (S32) to arrive at the final equation (S33)

$$\frac{\% \text{ yield}}{100} = \frac{\frac{k_{CP}}{k_H} ([Ni]_{tot}) - \frac{([P]_{tot} + K[A]_{tot} + (1 - K)[Ni]_{tot}) - \sqrt{([P]_{tot} + K[A]_{tot} + (1 - K)[Ni]_{tot})^2 - 4(1 - K)[P]_{tot}[Ni]_{tot}}}{2(1 - K)}}{\frac{k_{CP}}{k_H} [Ni]_{tot} + (1 - \frac{k_{CP}}{k_H}) \frac{([P]_{tot} + K[A]_{tot} + (1 - K)[Ni]_{tot}) - \sqrt{([P]_{tot} + K[A]_{tot} + (1 - K)[Ni]_{tot})^2 - 4(1 - K)[P]_{tot}[Ni]_{tot}}}{2(1 - K)}} \quad (S33)$$

With our simplified model and assumptions we made, equation (S33) predicts the yield for cyclopropanation based on the known concentration $[Ni]_{tot}$ and $[P]_{tot}$ (added amounts of the precatalyst), and $[A]_{tot}$ (in large excess, 5 equiv, approx. constant).

By analogy to equation (S16), the initial rate constant of cyclopropanation k_{obs} is given as

$$k_{obs} = k_{CP}[NiA] \quad (S34)$$

With the general equation (S34) in hand, we can define a relative rate constant k_{rel} normalized to the first k_{obs} (e.g. lowest $[Ni]_{tot}$) in a series of measurements as

$$k_{rel,n} = \frac{k_{obs,n}}{k_{obs,1}} = \frac{k_{CP}[NiA]_n}{k_{CP}[NiA]_1} = \frac{[NiA]_n}{[NiA]_1} \quad (S35)$$

18. Comparison of Rate Data to Model Prediction

Figure S24. Plot of NBE concentration versus the normalized measured rate (squares) and predicted rate (red curve) based on our

model (eq (S35)) for cyclopropanation with no further adjustment of parameters. $k_{CP}/k_H = 0.014$, $[Ni]_{tot} = 0.25$ mM, $[P]_{tot} = 0.5$ mM.

Figure S25. Plot of ligand (PPh₃) concentration versus the normalized measured rate (squares) and predicted rate (red curve) based on our model (eq (S35)) for the cyclopropanation of NBE with no further adjustment of parameters. $k_{CP}/k_H = 0.014$, $[Ni]_{tot} = 0.25$ mM, $[A]_{tot} = 250$ mM.

Figure S26. Plot of catalyst, (Ph₃P)₂NiBr₂, concentration versus the measured rate (squares) using method A and predicted rate (red curve) based on our model (eq (S35)), with no further adjustment of parameters. $k_{CP}/k_H = 0.014$, $[P]_{tot} = 2[Ni]_{tot}$, $[A]_{tot} = 250$ mM.

19. Headspace Analysis

Scheme S16. Headspace Analysis in the Absence of Added Alkene.

Inside the glove box, an oven-dried 50 mL Schlenk flask equipped with a J. Young inlet valve, glass stopper, screw cap with septum and a glass-coated stir bar was charged with $[\text{NMe}_4]\text{OTf}$ (245.5 mg, 1.1 mmol, 1.1 equiv). The flask was removed from the glove box and attached to a Schlenk line. Dry THF (18.5 mL) was added via syringe. Cyclooctane (100 μL) was added via a 100 μL micro syringe as internal standard. The flask was immersed in an ice bath and the reaction allowed to equilibrate (over ca. 20 min).

BuLi (500 μL , 1 mmol, 1 equiv; 2 M in cyclohexane) was added dropwise over ca. 30 s via a 1 mL gastight Hamilton syringe (by difference; previously dried at 50 $^{\circ}\text{C}$ in a vacuum oven). The flask was sealed/closed to the Schlenk line unless reagents were added or aliquots collected.

After 15 min, an aliquot (ca. 0.2 mL) was taken with a disposable 1 mL plastic syringe (flushed several times with Ar) and immediately quenched by injection into 0.2 mL 1 M TFA in DCM ($t = 0$ min).

Then, $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ (1 mol%, 0.01 mmol) in 1 mL THF (prepared as stock solution inside the glove box) was added dropwise by difference with a 2.5 mL gastight Hamilton syringe (previously dried at 50 $^{\circ}\text{C}$ in a vacuum oven) over ca. 30 s ($t = 0$ min with first drop). After the addition was completed, the flask was sealed/closed to the Schlenk line again until *after* the headspace aliquot was taken.

After 60 min, the headspace was sampled with a 2.5 mL gastight Hamilton syringe (previously dried at 50 $^{\circ}\text{C}$ in a vacuum oven). Another aliquot ($t = 60$ min) was then taken as described above.

The headspace sample (ca. 1 mL gas volume) was then analyzed by GC-MS.

Aliquots were diluted with 0.3 mL CD_3OD and analyzed by NMR.

An analogous reaction was conducted with $[\text{N}(\text{CD}_3)_4]\text{OTf}$ (258.8 mg, 1.1 mmol, 1.1 equiv).

RT: 0.00 - 18.59

Figure S27. Top: GC-MS chromatogram of a headspace sample after 60 min as described above with $[N(CH_3)_4]OTf$. Peaks at $t = 7.05$ and 7.11 min are THF. Peak at $t = 8.50$ min is cyclohexane. Double peaks are due to detector overload (air (inset) and

THF). Top, inset: Magnified chromatogram between 4 and 5 min with labeled peaks. Bottom: Mass spectra of selected compounds and their assigned structures with mass.

RT: 0.00 - 9.13

Figure S28. Top: GC-MS chromatogram of a headspace sample after 60 min as described above with $[N(CD_3)_4]OTf$. Peaks at $t = 7.01$ and 7.06 min are THF. Peak at $t = 8.45$ min is cyclohexane. Double peaks are due to detector overload (air (inset) and

THF). Top, inset: Magnified chromatogram between 4 and 5 min with analogous peak assignment as in **Figure S27**. Bottom: Mass spectra of selected compounds and their assigned structures with mass.

Figure S29. Overlaid ¹H NMR spectra of aliquots taken after 0 min (red, before addition of catalyst) and 60 min (see above for detailed description) using [N(CH₃)₄]OTf. Inset: Enlarged regions show disappearance of [N(CH₃)₄]⁺, formation of [HN(CH₃)₃]⁺, and formation of cyclopropane C₃H₆ (assignment based on GC-MS and D-labelling).

Figure S30. Overlaid ^1H NMR spectra of aliquots taken after 0 min (red, before addition of catalyst) and 60 min (see above for detailed description) using $[\text{N}(\text{CD}_3)_4]\text{OTf}$. Inset: Enlarged regions show disappearance of $[\text{N}(\text{CD}_3)_3(\text{CHD}_2)]^+$ (from H^+ quench) and formation of cyclopropane C_3HD_5 (assignment based on GC-MS and D-labelling).

20. Trapping Experiments with BnNMe_2

Scheme S17. Attempted Cyclopropanation of Norbornene with Methyltriphenylphosphonium Triflate in the Presence of N,N -Dimethylbenzylamine.

Inside the glove box, an oven-dried 5 mL Schlenk flask equipped with a Teflon tap and a glass-coated stir bar was charged with $[\text{NMe}_4]\text{OTf}$ (22.3 mg, 0.1 mmol, 1 equiv), $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ in 0.2 mL THF (1 mol%, prepared as stock solution), norbornene (47 mg, 0.5 mmol, 5 equiv), and 1.8 mL THF (tot. vol. THF: 2 mL, 0.05 M). The flask was removed from the glove box, cooled to 0 °C in an ice/water bath. BnNMe_2 (150 μL , 1.0 mmol, 10 equiv) and BuLi (2 M in cyclohexane; 53 μL , 0.105 mmol, 1.05 equiv) were added dropwise via micro syringe under a counterflow of Ar. The flask was sealed (no gas exchange). The flask was removed from the cooling bath and stirred at room temperature for 2 h. An aliquot was taken and showed no product formation by GC.

The reaction was heated to 50 °C for an additional 14 h. Another aliquot was analyzed by GC and showed no product formation.

Aliquots (ca. 0.2 mL) were partitioned between 2 mL pentane and 2 mL water. After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO_4 and analyzed by GC-FID.

The reaction was repeated in the absence of norbornene.

In both cases no rearrangement product stemming from carbene trapping and formation of *N,N,N*-trimethylbenzylammonium ylide was observed, namely *N,N*-dimethyl-1-(*o*-tolyl)methanamine and/or *N,N*-dimethyl-1-phenylethan-1-amine.

Scheme S18. Cyclopropanation of Norbornene in the Presence of *N,N*-Dimethylbenzylamine.

Inside the glove box, an oven-dried 5 mL Schlenk flask equipped with a Teflon tap and a glass-coated stir bar was charged with $[\text{NMe}_4]\text{OTf}$ (22.3 mg, 0.1 mmol, 1 equiv), norbornene (47 mg, 0.5 mmol, 5 equiv), and 1.8 mL THF (tot. vol. THF: 2 mL, 0.05 M). The flask was removed from the glove box, cooled to 0 °C in an ice/water bath. BuLi (2 M in cyclohexane; 53 μL , 0.105 mmol, 1.05 equiv) was added dropwise via micro syringe under a counterflow of Ar. The flask was sealed (no gas exchange). After 10 min, BnNMe_2 (150 μL , 1.0 mmol, 10 equiv) was added, followed immediately by $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ in 0.2 mL THF (1 mol%, prepared as stock solution). The reaction was allowed to warm to RT inside the ice/water bath overnight. Undecane (10 μL ; internal standard) was added and an aliquot (ca. 0.2 mL) was partitioned between 2 mL pentane and 2 mL water. After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO_4 and analyzed by GC-FID. The yield was determined by the integral ratio of the cyclopropane product versus undecane as internal standard using a previously determined calibration curve.

The reaction was repeated in the absence of norbornene.

In both cases no rearrangement product stemming from carbene trapping and formation of *N,N,N*-trimethylbenzylammonium ylide was observed, namely *N,N*-dimethyl-1-(*o*-tolyl)methanamine and/or *N,N*-dimethyl-1-phenylethan-1-amine.

Scheme S19. Rearrangement of *N,N,N*-Trimethylbenzylammonium Ylide.

Inside the glove box, an oven-dried 5 mL Schlenk flask equipped with a Teflon tap and a glass-coated stir bar was charged with $[\text{BnNMe}_3]\text{OTf}$ (29.9 mg, 0.1 mmol, 1 equiv) and 2 mL THF. The flask was removed from the glove box, cooled to 0 °C in an ice/water bath. BuLi (2 M in cyclohexane; 50 μL , 0.1 mmol, 1.0 equiv) was added dropwise via micro syringe under a counterflow of Ar. The flask was sealed (no gas exchange).

After 45 min, the reaction was quenched with a few drops of CD_3OD . An aliquot (ca. 0.2 mL) was partitioned between 2 mL Et_2O and 2 mL water. After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO_4 and analyzed by GC-MS. The remaining mixture was evaporated to dryness and analyzed by NMR.

The products were identified by GC-MS and by comparison to literature NMR data.⁸

Figure S31. Left: GC-MS chromatogram of the *N,N,N*-trimethylbenzylammonium ylide rearrangement after 45 min. Right: Mass spectra of the rearrangement products.

21. Addition of Excess PPh_3

Scheme S20. Cyclopropanation of Cyclooctene in the Presence of Excess PPh_3 .

Inside the glove box, an oven-dried 5 mL Schlenk flask equipped with a Teflon and a glass-coated stir bar was charged with $[\text{NMe}_4]\text{OTf}$ (22.3 mg, 0.1 mmol, 1 equiv), PPh_3 (A: 7.2 mg, 0.027 mmol, 27 mol% or B: 26.6 mg, 0.101 mmol, 101 mol%), COE (65 μL , 0.5 mmol, 5 equiv), $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ in THF (0.001 mmol, 0.01 equiv, prepared as stock solution), and THF (tot. vol. THF: 2 mL, 0.05 M). The flask was removed from the glove box, cooled to 0°C in an ice/water bath, and BuLi (2 M in cyclohexane; 53 μL , 0.105 mmol, 1.05 equiv) was added dropwise via micro syringe under a counterflow of Ar. The flask was sealed (no gas exchange) and the reaction was allowed to warm to RT inside the ice/water bath. After 16 h, the reaction was quenched with 0.1 mL CD_3OD . Undecane (10 μL ; internal standard) was added and an aliquot (ca. 0.2 mL) was partitioned between 2 mL pentane and 2 mL water. After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO_4 and analyzed by GC-MS.

The remaining reaction mixture was evaporated to dryness on the Schlenk line. The solid residue was dissolved in $\text{CD}_3\text{OD}/\text{CDCl}_3$ (0.35 mL/0.35 mL) and analyzed by NMR. (Some solid remained undissolved, most likely polyethylene. Solubility tests showed $[\text{PMePh}_3]\text{Br}$, $[\text{NMe}_4]\text{OTf}$, and PPh_3 to be soluble in this solvent mixture at comparable concentrations).

Mixtures of authentic samples of $[\text{PMePh}_3]\text{Br}/\text{PPh}_3$, $\text{PPh}_2\text{Ph}/\text{PPh}_3$, and $[\text{NMe}_4]\text{OTf}/\text{PPh}_3$ were prepared in the same solvent mixture at comparable concentration (ca. 0.1 mmol / 0.7 mL per compound) and analyzed by NMR.

Addition of an excess of PPh_3 resulted in a strongly or even completely suppressed cyclopropanation of COE. A small amount of PBnPh_2 ($>10:1$ $\text{PPh}_3:\text{PBnPh}_2$ by ^{31}P NMR) had formed (**Figure S32**), likely via a Ni(0) -promoted/catalyzed phospho-Stevens rearrangement of a small amount of in situ formed $\text{Ph}_3\text{P}=\text{CH}_2$.⁹

Figure S32. Stacked $^{31}\text{P}\{^1\text{H}\}$ spectra plot for a mixture of authentic PPh_3 and PBnPh_2 (Spectrum 4), reaction A with additional 27 mol% PPh_3 (Spectrum 3), reaction B with additional 101 mol% PPh_3 (Spectrum 2), and a mixture of authentic PPh_3 and $[\text{PMePh}_3]^+\text{Br}^-$ (Spectrum 1). Left inset: Expansion of the $[\text{PMePh}_3]^+$ region. Right inset: Expansion of the $\text{PPh}_3/\text{PBnPh}_2$ region.

SAK-967_A.2.fid
 Sample SAK-967_A_31P
 Instrument AV-NEO 400 MHz
 Group chen
 162 MHz 31P Spectrum with 1H decoupling
 31P-HDEC.ETH MeOD /opt/v ckunzi 1

Figure S33. $^{31}\text{P}\{^1\text{H}\}$ spectrum for reaction A with additional 27 mol% PPh_3 .

Figure S34. $^{31}\text{P}\{^1\text{H}\}$ spectrum for reaction B with additional 101 mol% PPh_3 .

Figure S35. Stacked ^1H spectra plot for a mixture of authentic PPh_3 and PBnPh_2 (Spectrum 5), reaction A with additional 27 mol% PPh_3 (Spectrum 4), reaction B with additional 101 mol% PPh_3 (Spectrum 3), a mixture of authentic PPh_3 and $[\text{NMe}_4]\text{OTf}$ (Spectrum 2), and a mixture of authentic PPh_3 and $[\text{PMePPh}_3]\text{Br}$ (Spectrum 1). Right inset: Expansion of the $\text{P}(\text{CH}_2\text{Ph})\text{Ph}_2$, $[\text{PPh}_3(\text{CH}_3)]^+$, $[\text{N}(\text{CH}_3)_4]^+$ region.

Figure S36. GC-MS chromatogram and mass spectra for reaction A with additional 27 mol% PPh₃. Note: Cyclooctane is an impurity in cyclooctene.

Figure S37. Enlarged GC-MS chromatogram for reaction A with additional 27 mol% PPh_3 for the product region. Note: Cyclooctane is an impurity in cyclooctene.

Figure S38. Enlarged GC-MS chromatogram for reaction A with additional 27 mol% PPh_3 for the phosphine region.

Figure S39. Enlarged GC-MS chromatogram and mass spectrum for reaction A with additional 27 mol% PPh_3 for the product region (bottom) and an authentic sample of the cyclopropanation product (top).

Figure S40. GC-MS chromatogram and mass spectra for reaction B with additional 101 mol% PPh₃. Note: Cyclooctane is an impurity in cyclooctene.

Figure S41. Enlarged GC-MS chromatogram for reaction B with additional 101 mol% PPh_3 for the product region. No cyclopropanation of COE occurred. Note: Cyclooctane is an impurity in cyclooctene.

Figure S42. Enlarged GC-MS chromatogram for reaction B with additional 101 mol% PPh_3 for the phosphine region.

22. Synthesis of $[\text{N}(\text{CD}_3)_4]\text{OTf}$

Tetramethylammonium- d_{12} triflate was prepared in analogy to the protiated compound as reported previously, dried under vacuum and stored in the glove box.^{1,2}

The elemental analysis values for C, H are outside the tolerance, most likely due to the level of deuteration. All other analysis techniques confirmed the purity.

Elemental analysis: Found: C, 25.02; H, 4.61; N, 6.05. Calc. for $\text{C}_5\text{D}_{12}\text{F}_3\text{NO}_3\text{S}$: C, 25.52; D, 10.27; N, 5.95; O, 20.40; F, 24.22; S, 13.63. D determined as H: H, 5.42.

^1H NMR (400 MHz, CD_3OD): δ 3.15 (m, small amount of $[\text{N}(\text{CD}_3)_3(\text{CD}_2\text{H})]^+$).

^1H NMR (600 MHz, D_2O): δ 3.16 (m, small amount of $[\text{N}(\text{CD}_3)_3(\text{CD}_2\text{H})]^+$).

^2H NMR (92 MHz, D_2O): δ 3.04 (s).

^{13}C NMR (101 MHz, CD_3OD): δ 121.8 (q, $^1J_{\text{C-F}} = 319$ Hz), 54.7 (m).

^{13}C NMR (150 MHz, D_2O): δ 119.6 (q, $^1J_{\text{C-F}} = 317$ Hz), 54.1 (m).

^{19}F NMR (376 MHz, CD_3OD): δ -80.1.

^{19}F NMR (470 MHz, D_2O): δ -78.8.

HRMS (ESI, M^+ , $[\text{N}(\text{CD}_3)_4]^+$): m/z calcd for $\text{C}_4\text{D}_{12}\text{N}$ 86.1717; Found 86.1716 (100%), 85.1655 (2.7%, $[\text{N}(\text{CD}_3)_3(\text{CD}_2\text{H})]^+$).

Figure S43. ^1H NMR (400 MHz, CD_3OD) spectrum of $[\text{N}(\text{CD}_3)_4]\text{OTf}$.

H3429.1.fid
 Stefan Kuenzi/Chien SAK-845 OPR:SB
 600 MHz 1H NMR

Figure S44. ^1H NMR (600 MHz, D_2O) spectrum of $[\text{N}(\text{CD}_3)_4]\text{OTf}$.

H3429.7.fid
 Stefan Kuenzi/Chen SAK-845 OPR:SB
 92 MHz 2H spectrum without 1H decoupling
 o1p=5.5 sw= 12

Figure S45. 2H NMR (92 MHz, D_2O) spectrum of $[N(CD_3)_4]OTf$.

Figure S46. ^{13}C NMR (101 MHz, CD_3OD) spectrum of $[\text{N}(\text{CD}_3)_4]\text{OTf}$.

Figure S47. ¹³C NMR (150 MHz, D₂O) spectrum of [N(CD₃)₄]OTf.

SAK-845_02052018.2.fid
 Sample SAK-845_02052018_19F
 Instrument AV-NEO 400 MHz
 Group chen
 400 MHz 1H Spectrum
 19F-HDEC.ETH MeOD /opt/v/ ckunzi 19

Figure S48. ^{19}F NMR (376 MHz, CD_3OD) spectrum of $[N(CD_3)_4]OTf$.

F2239.2.fid
 Stefan Kuenzi/Chien SAK-845 OPR:SB
 19F NMR spectrum

Figure S49. ^{19}F NMR (470 MHz, D_2O) spectrum of $[\text{N}(\text{CD}_3)_4]\text{OTf}$.

23. Deprotonation Kinetics of $[\text{N}(\text{CH}_3)_4]\text{OTf}$ and $[\text{N}(\text{CD}_3)_4]\text{OTf}$

Scheme S21. Deprotonation and Deuterium Quench with Subsequent Analysis by ESI-MS.¹

Inside the glove box, an oven-dried 50 mL Schlenk flask equipped with a J. Young inlet valve, glass stopper, screw cap with septum and a glass-coated stir bar was charged with $[\text{NMe}_4]\text{OTf}$ (245.5 mg, 1.1 mmol, 1.1 equiv). The flask was removed from the glove box and attached to a Schlenk line. Dry THF (19.5 mL) was added via syringe. The flask was immersed in an ice bath and the reaction allowed to equilibrate (over ca. 20 min).

BuLi (500 μL , 1 mmol, 1 equiv; 2 M in cyclohexane) was added dropwise over ca. 30 s via a 1 mL gastight Hamilton syringe (by difference; previously dried at 50 $^\circ\text{C}$ in a vacuum oven) ($t = 0$ min with the first drop). The flask was sealed/closed to the Schlenk line unless reagents were added or aliquots collected.

Aliquots (ca. 0.2 mL) were taken with a disposable 1 mL plastic syringe (flushed several times with Ar) and immediately quenched by injection into 0.5 mL D_2O .

Aliquots were diluted with MeOH and analyzed by ESI-MS.

Assuming that all ammonium ylide is quenched by deuterium incorporation from D_2O , then the ratio of the peak areas at $m/z = 75$ to 74, A_{75}/A_{74} can be taken as extent of deprotonation and is proportional to the ylide concentration in solution.¹

$$\text{ratio} = \frac{A_{75} - 0.043 A_{74}}{A_{74}} \quad (\text{S36})$$

The peak area for $m/z = 75$ has to be corrected for the natural abundance of ^{13}C for $[\text{N}(\text{CH}_3)_4]^+$ at $m/z = 74$ (4.3%). At natural abundance before deprotonation and deuterium labelling the ratio should be 0.043.

Figure S50. Plot of time versus the peak ratio as defined in eq (S36). The red circle denotes the theoretical value at $t = 0$ min. A maximal ratio is achieved after 10 to 15 min and the ratio stays approximately constant until the last time point at 45 min.

Figure S50 indicates that the deprotonation is finished after 10 to 15 min and that the ylide is stable in solution for at least 45 min under these conditions.

Scheme S22. Deprotonation and Deuterium Quench with Subsequent Analysis by ^1H NMR.

Inside the glove box, an oven-dried 50 mL Schlenk flask equipped with a J. Young inlet valve, glass stopper, screw cap with septum and a glass-coated stir bar was charged with $[\text{NMe}_4]\text{OTf}$ (245.5 mg, 1.1 mmol, 1.1 equiv). The flask was removed from the glove box and attached to a Schlenk line. Dry THF (19.5 mL) was added via syringe. The flask was immersed in an ice bath and the reaction allowed to equilibrate (over ca. 20 min).

An aliquot (ca. 0.2 mL) was taken and immediately quenched by injection into 0.2 mL 1 M DCl / D_2O ($t = 0$ min).

BuLi (500 μL , 1 mmol, 1 equiv; 2 M in cyclohexane) was added dropwise over ca. 30 s via a 1 mL gastight Hamilton syringe (by difference; previously dried at 50°C in a vacuum oven) ($t = 0$ min with the first drop). The flask was sealed/closed to the Schlenk line unless aliquots collected.

Aliquots (ca. 0.2 mL) were taken with a disposable 1 mL plastic syringe (flushed several times with Ar) and immediately quenched by injection into 0.2 mL 1 M DCl / D_2O ($t = 0$ min).

Aliquots were diluted with 0.3 mL CD_3OD and analyzed by ^1H NMR. Spectra were subsequently analyzed with MestReNova. The integrated 'Full Auto (Bernstein Polynomials)' baseline correction was applied. The spectrum was referenced to the residual solvent peak of CD_3OD ($\delta = 3.31$). Signals of cyclooctane ($\delta = 1.55$, s) and the signal of $[\text{N}(\text{CH}_3)_4]^+$ ($\delta = 3.24$, t) (overlap with $[\text{N}(\text{CH}_3)_3(\text{CH}_2\text{D})]^+$ and $[\text{N}(\text{CH}_3)_3(\text{CH}_2\text{D})]^+$ ($\delta = 3.23$, br m) were integrated using the sum function.

Figure S51. Plot of time versus integral ratio of ammonium species $[A]^+$ to COA (cyclooctane, internal standard) with the following integral areas of ammonium species: $[N(CH_3)_3(CH_2D)]^+$ (black squares), $[N(CH_3)_4]^+$ plus $[N(CH_3)_3(CH_2D)]^+$ (blue circles), sum of both species, $[N(CH_3)_4]^+$ plus $[N(CH_3)_3(CH_2D)]^+$ (orange triangles).

Figure S52. 1H NMR spectrum expanded from 3.35 ppm to 3.10 ppm after 0 min (left, before BuLi addition), after 2 min (middle), and after (15 min). Residual solvent signal of CD_3OD at 3.31 ppm, $[N(CH_3)_4]^+$ at 3.24 ppm overlapping with $[N(CH_3)_3(CH_2D)]^+$, and $[N(CH_3)_3(CH_2D)]^+$ at 3.23 ppm.

Scheme S23. Deprotonation of Tetramethylammonium- d_{12} and Proton Quench with Subsequent Analysis by 1H NMR.

Inside the glove box, an oven-dried 50 mL Schlenk flask equipped with a J. Young inlet valve, glass stopper, screw cap with septum and a glass-coated stir bar was charged with $[N(\text{CD}_3)_4]\text{OTf}$ (258.8 mg, 1.1 mmol, 1.1 equiv). The flask was removed from the glove box and attached to a Schlenk line. Dry THF (19.5 mL) was added via syringe. The flask was immersed in an ice bath and the reaction allowed to equilibrate (over ca. 20 min).

An aliquot (ca. 0.2 mL) was taken and immediately quenched by injection into 0.2 mL 1 M TFA in DCM ($t = 0$ min).

BuLi (500 μL , 1 mmol, 1 equiv; 2 M in cyclohexane) was added dropwise over ca. 30 s via a 1 mL gastight Hamilton syringe (by difference; previously dried at 50 $^\circ\text{C}$ in a vacuum oven) ($t = 0$ min with the first drop). The flask was sealed/closed to the Schlenk line unless aliquots collected.

Aliquots (ca. 0.2 mL) were taken with a disposable 1 mL plastic syringe (flushed several times with Ar) and immediately quenched by injection into 0.2 mL 1 M TFA in DCM.

Aliquots were diluted with 0.3 mL CD_3OD and analyzed by 1H NMR. Spectra were subsequently analyzed with MestReNova. The integrated 'Full Auto (Bernstein Polynomials)' baseline correction was applied. The spectrum was referenced to the

residual solvent peak of CD₃OD (δ = 3.31). Signals of cyclooctane (δ = 1.55, s) and the signal of tetramethylammonium-d₁₁ [N(CD₃)₃(CD₂H)]⁺ (δ = 3.16, m) were integrated using the sum function.

The integral ratio of [N(CD₃)₃(CD₂H)]⁺ to COA (cyclooctane, internal standard) is taken as the extent of deprotonation.

Figure S53. Plot of time versus integral ratio of [N(CD₃)₃(CD₂H)]⁺ to COA (cyclooctane, internal standard).

Figure S54. ¹H NMR spectrum expanded from 3.35 ppm to 3.10 ppm after 0 min (left, before BuLi addition), after 2 min (middle), and after (15 min). Residual solvent signal of CD₃OD at 3.31 ppm and [N(CD₃)₃(CD₂H)]⁺ at 3.16 ppm.

For all deprotonation experiments (**Figure S50**, **Figure S51**, and **Figure S53**) one can see that the ylide-derived species after quenching, either [N(CH₃)₃(CH₂D)]⁺ or [N(CD₃)₃(CD₂H)]⁺, reaches its maximum concentration after about 10 to 15 min. After that time, the concentration is approximately constants at least up to 45 min. There is no apparent difference in the deprotonation rate between the perprotiated and the perdeuterated tetramethylammonium salt. Thus, there is no (large) primary KIE for the deprotonation and the rate appears to be dictated by the limited solubility of the ammonium reagent in THF.

24. UV-Vis Alkene Binding Titrations

Inside the glove box, a vacuum-oven dried quartz cuvette (10 mm path length) with septum screw cap was charged with phosphine (ca. 10 mM, 20 equiv relative to Ni, see below) and 1.8 mL THF. To this solution was added Ni(cod)₂ in 0.2 mL (prepared as stock solution, ca. 4.1 mg in 3 mL THF, ca. 0.5 mM, see below). A separate oven-dried 4 mL vial with septum screw cap was charged with alkene, either neat or as stock solution in THF. The cuvette and vial were removed from the glove box and wrapped with parafilm. The vial containing the alkene was placed under an N₂-atmosphere using a needle inlet. The first measurement was taken without any added alkene and denoted as '0 μ L alkene'. Then, alkene was added (by difference) using a gastight 25 μ L Hamilton microsyringe and the cuvette was agitated for several seconds to mix. Measurements were taken at room temperature.

The data was analyzed by measuring the absorbance at a specific wavelength as indicated (see below), converting this value to [NiP], the phosphine-only ligated Ni species, using [NiP]₀ (no alkene added) = [Ni(cod)₂]. The resulting plot of [alkene] versus

[NiP] is fitted to equation (S27) in Excel using a least square method with the binding constant K as fit parameter. ($[\text{Ni}]_{\text{tot}} = [\text{Ni}(\text{cod})_2]$, $[\text{A}]_{\text{tot}} = [\text{alkene}]$, $[\text{P}]_{\text{tot}} = [\text{phosphine}]$). The volume increase by adding alkene was neglected for the concentration.

Table S8. Binding Constants K for Different Alkenes and Phosphines

Phosphine	K_{COE}	$K_{1\text{-Octene}}$	K_{NBE}
PPh_3	0.081	0.95	33
$\text{P}(\text{O-}o\text{-tolyl})_3$ (Tolman) ^a	0.062	0.5	4.4
$\text{P}(\text{O-}o\text{-tolyl})_3$	0.071	-	-
PPhMe_2	0.0014	-	-
PPh_2Me	0.0013	-	-
$\text{P}(3,5\text{-di}^i\text{BuPh})\text{Ph}_2$	0.11 ^b	-	-
$\text{P}(3,5\text{-di}^i\text{BuPh})_2\text{Ph}$	0.090	-	-

^a Values are taken from ref. S7 (in benzene). ^b Average of two independent runs.

Table S9. UV-Vis Binding Titration for COE in the Presence of PPh_3

	$V_{\text{COE}} / \mu\text{L}$	$[\text{COE}] / \text{mM}$	$\text{Abs}(500 \text{ nm}) / \text{a.u.}$	$[\text{NiP}] / \text{mM}$
$[\text{Ni}]_{\text{tot}} / \text{mM}$	0	0	2.469	0.54535539
0.54535539	5	19.23949542	2.137	0.472022871
	10	38.47899083	1.863	0.411501455
$[\text{PPh}_3] / \text{mM}$	15	57.71848625	1.658	0.366220833
9.912692058	20	76.95798167	1.488	0.328671049
	30	115.4369725	1.249	0.275880471
K	40	153.9159633	1.07	0.236342757
0.081278083	50	192.3949542	0.944	0.208511741
	60	230.873945	0.842	0.185981871
	70	269.3529358	0.765	0.168974027
	80	307.8319267	0.702	0.155058519

Figure S55. Left: Plot of UV-Vis spectra at different concentrations of COE and constant $[\text{PPh}_3]$. Right: Absorbance at 500 nm transformed to $[\text{NiP}]$ and plotted against $[\text{COE}]$. The red curve depicts a fit to equation (S27) using the binding constant K as fit parameter.

Table S10. UV-Vis Binding Titration for 1-Octene in the Presence of PPh_3

	$V_{1\text{Oct}} / \mu\text{L}$	$[1\text{Oct}] / \text{mM}$	$\text{Abs}(500 \text{ nm}) / \text{a.u.}$	$[\text{NiP}] / \text{mM}$
$[\text{Ni}]_{\text{tot}} / \text{mM}$	0	0	2.469	0.54535539
0.54535539	5	15.92995277	0.94	0.207628216
	10	31.85990553	0.577	0.127448384
$[\text{PPh}_3] / \text{mM}$	15	47.7898583	0.423	0.093432697
9.912692058	20	63.71981107	0.34	0.075099568
	30	95.5797166	0.262	0.057870843
K	40	127.4396221	0.227	0.050140005
0.952027012	50	159.2995277	0.209	0.046164146
	60	191.1594332	0.197	0.043513573

	70	223.0193387	0.186	0.041083881
	80	254.8792443	0.175	0.038654189

Figure S56. Left: Plot of UV-Vis spectra at different concentrations of 1-octene (1Oct) and constant $[PPh_3]$. Right: Absorbance at 500 nm transformed to $[NiP]$ and plotted against $[1Oct]$. The red curve depicts a fit to equation (S27) using the binding constant K as fit parameter.

Table S11. UV-Vis Binding Titration for NBE in the Presence of PPh_3

	$V_{NBE} / \mu L$	$[NBE] / mM$	Abs(500 nm) / a.u.	$[NiP] / mM$
$[Ni]_{tot} / mM$	0	0	2.31	0.484760347
0.484760347	5	0.503451938	1.288	0.270290618
	10	1.006903877	0.79	0.165783841
$[PPh_3] / mM$	15	1.510355815	0.559	0.117307807
12.77212246	20	2.013807754	0.439	0.092125451
	30	3.02071163	0.312	0.065474125
NBE stock sol. / mM	40	4.027615507	0.253	0.0530928
201.3807754	50	5.034519384	0.217	0.045538093
	60	6.041423261	0.192	0.040291769
K	70	7.048327138	0.175	0.036724269
32.85322907	80	8.055231014	0.162	0.03399618

Figure S57. Left: Plot of UV-Vis spectra at different concentrations of NBE and constant $[PPh_3]$. Right: Absorbance at 500 nm transformed to $[NiP]$ and plotted against $[NBE]$. The red curve depicts a fit to equation (S27) using the binding constant K as fit parameter.

Table S12. UV-Vis Binding Titration for COE in the Presence of $P(O-o-tolyl)_3$

	$V_{COE} / \mu L$	$[COE] / mM$	Abs(450 nm) / a.u.	$[NiP] / mM$
$[Ni]_{tot} / mM$	0	0	0.974	0.508998364
0.508998364	5	19.23949542	0.829	0.433223453
	10	38.47899083	0.743	0.388281093
$[P(O-o-tolyl)_3] / mM$	15	57.71848625	0.677	0.353790444

11.35202634	20	76.95798167	0.627	0.327661164
	25	96.19747709	0.588	0.307280326
K	30	115.4369725	0.549	0.286899489
0.070991781	40	153.9159633	0.493	0.257634696
	50	192.3949542	0.451	0.235686101
	60	230.873945	0.42	0.219485947
	70	269.3529358	0.394	0.205898722
	80	307.8319267	0.372	0.194401839

Figure S58. Left: Plot of UV-Vis spectra at different concentrations of COE and constant $[P(O\text{-}o\text{-tolyl})_3]$. Right: Absorbance at 450 nm transformed to $[NiP]$ and plotted against $[COE]$. The red curve depicts a fit to equation (S27) using the binding constant K as fit parameter.

Table S13. UV-Vis Binding Titration for COE in the Presence of $PPhMe_2$

	$V_{COE} / \mu L$	$[COE] / mM$	Abs(460 nm) / a.u.	$[NiP] / mM$
$[Ni]_{tot} / mM$	0	0	1.09	0.508998364
0.508998364	5	19.23949542	1.093	0.510399277
	10	38.47899083	1.087	0.507597451
$[PPhMe_2] / mM$	15	57.71848625	1.084	0.506196538
11.22050094	20	76.95798167	1.081	0.504795625
	30	115.4369725	1.075	0.501993799
K	40	153.9159633	1.069	0.499191973
0.001442832	50	192.3949542	1.063	0.496390148
	60	230.873945	1.055	0.49265438
	70	269.3529358	1.053	0.491720438
	80	307.8319267	1.044	0.487517699

Figure S59. Left: Plot of UV-Vis spectra at different concentrations of COE and constant $[PPhMe_2]$. Right: Absorbance at 460 nm transformed to $[NiP]$ and plotted against $[COE]$. The red curve depicts a fit to equation (S27) using the binding constant K as fit parameter.

Table S14. UV-Vis Binding Titration for COE in the Presence of PPh₂Me

	$V_{\text{COE}} / \mu\text{L}$	$[\text{COE}] / \text{mM}$	$\text{Abs}(460 \text{ nm}) / \text{a.u.}$	$[\text{NiP}] / \text{mM}$
$[\text{Ni}]_{\text{tot}} / \text{mM}$	0	0	1.987	0.508998364
0.508998364	5	19.23949542	1.959	0.501825765
	10	38.47899083	1.959	0.501825765
$[\text{PPh}_2\text{Me}] / \text{mM}$	15	57.71848625	1.959	0.501825765
9.989511013	20	76.95798167	1.971	0.504899736
	30	115.4369725	1.959	0.501825765
K	40	153.9159633	1.951	0.499776451
0.001314885	50	192.3949542	1.939	0.49670248
	60	230.873945	1.921	0.492091523
	70	269.3529358	1.921	0.492091523
	80	307.8319267	1.903	0.487480567

Figure S60. Left: Plot of UV-Vis spectra at different concentrations of COE and constant [PPh₂Me]. Right: Absorbance at 460 nm transformed to [NiP] and plotted against [COE]. The red curve depicts a fit to equation (S27) using the binding constant K as fit parameter.**Table S15.** UV-Vis Binding Titration for COE in the Presence of P(3,5-di^tBuPh)Ph₂ (run 1).

	$V_{\text{COE}} / \mu\text{L}$	$[\text{COE}] / \text{mM}$	$\text{Abs}(500 \text{ nm}) / \text{a.u.}$	$[\text{NiP}] / \text{mM}$
$[\text{Ni}]_{\text{tot}} / \text{mM}$	0	0	2.538	0.496879355
0.496879355	5	19.23949542	2.119	0.414849233
	10	38.47899083	1.827	0.357682656
$[\text{P}(3,5\text{-di}^t\text{BuPh})\text{Ph}_2] / \text{mM}$	15	57.71848625	1.607	0.314611948
11.88219273	20	76.95798167	1.437	0.281330037
	30	115.4369725	1.192	0.23336493
K	40	153.9159633	1.025	0.200670346
0.113042717	50	192.3949542	0.898	0.175806801
	60	230.873945	0.802	0.15701231
	70	269.3529358	0.727	0.142329114
	80	307.8319267	0.666	0.130386781

Figure S61. Left: Plot of UV-Vis spectra at different concentrations of COE and constant [P(3,5-di^tBuPh)Ph₂] (run 1). Right: Absorbance at 500 nm transformed to [NiP] and plotted against [COE]. The red curve depicts a fit to equation (S27) using the binding constant K as fit parameter.

Table S16. UV-Vis Binding Titration for COE in the Presence of P(3,5-di^tBuPh)Ph₂ (run 2).

	V _{COE} / μ L	[COE] / mM	Abs(500 nm) / a.u.	[NiP] / mM
[Ni] _{tot} / mM	0	0	2.469	0.496879355
0.496879355	5	19.23949542	2.137	0.430065282
	10	38.47899083	1.873	0.37693602
[P(3,5-di ^t BuPh)Ph ₂] / mM	15	57.71848625	1.688	0.339705286
14.01831727	20	76.95798167	1.533	0.308511969
	30	115.4369725	1.29	0.259608898
K	40	153.9159633	1.118	0.224994378
0.108069763	50	192.3949542	0.99	0.199234735
	60	230.873945	0.892	0.179512509
	70	269.3529358	0.811	0.163211485
	80	307.8319267	0.743	0.149526675

Figure S62. Left: Plot of UV-Vis spectra at different concentrations of COE and constant [P(3,5-di^tBuPh)Ph₂] (run 2). Right: Absorbance at 500 nm transformed to [NiP] and plotted against [COE]. The red curve depicts a fit to equation (S27) using the binding constant K as fit parameter.

Table S17. UV-Vis Binding Titration for COE in the Presence of P(3,5-di^tBuPh)₂Ph

	V _{COE} / μ L	[COE] / mM	Abs(500 nm) / a.u.	[NiP] / mM
[Ni] _{tot} / mM	0	0	2.432	0.508998364
0.508998364	5	19.23949542	2.229	0.46651207
	10	38.47899083	1.959	0.410003205
[P(3,5-di ^t BuPh) ₂ Ph] / mM	15	57.71848625	1.714	0.358726643
10.88921762	20	76.95798167	1.466	0.306822205
	30	115.4369725	1.241	0.259731484
K	40	153.9159633	1.061	0.222058908
0.090263004	50	192.3949542	0.899	0.188153589
	60	230.873945	0.766	0.160317741
	70	269.3529358	0.653	0.136667735
	80	307.8319267	0.565	0.118250031

Figure S63. Left: Plot of UV-Vis spectra at different concentrations of COE and constant $[P(3,5\text{-di}^t\text{BuPh})_2\text{Ph}]$. Right: Absorbance at 500 nm transformed to $[\text{NiP}]$ and plotted against $[\text{COE}]$. The red curve depicts a fit to equation (S27) using the binding constant K as fit parameter.

25. Synthesis and Evaluation of New Ligands

(3,5-Di-*tert*-butylphenyl)diphenylphosphane. A flame-dried 50 mL Schlenk flask with rubber septum was charged with 1-bromo-3,5-di-*tert*-butylbenzene (424 mg, 1.58 mmol, 1.05 equiv), evacuated and refilled with Ar (3x). Dry THF (15 mL) was added via syringe and the reaction was cooled to $-78\text{ }^{\circ}\text{C}$ before BuLi (0.75 mL, 2 M in cyclohexane, 1.5 mmol, 1 equiv) was added dropwise via syringe over ca. 2 min. The solution became slightly turbid.

The reaction was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h, then Ph_2PCl (277 μL , 1.5 mmol, 1 equiv) was added dropwise via syringe over ca. 2 min.

The reaction was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h, removed from the cooling bath and stirred at RT for an additional 30 min.

Silica (3 g) was added and all volatiles were removed under vacuum. The residue was loaded on a short column (SiO_2 , length: 5 cm, diameter: 2 cm), and eluted with hexane (3x10 mL), then toluene (3x10 mL) using vacuum. The combined toluene fractions were evaporated to dryness and further dried under vacuum to give a colorless, viscous oil (503 mg, 1.34 mmol, 90 %). (The oil is prone to oxidation.)

^1H NMR (400 MHz, CDCl_3): δ 7.40 (t, $J = 1.8$ Hz, 1H), 7.36 – 7.30 (m, 10H), 7.17 (dd, $J = 8.5, 1.8$ Hz, 2H), 1.25 (s, 18H).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ -3.89.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 150.77 (d, $J = 6.9$ Hz), 138.01 (d, $J = 10.9$ Hz), 135.67 (d, $J = 8.8$ Hz), 133.80 (d, $J = 19.1$ Hz), 128.64 (s), 128.47 (d, $J = 6.8$ Hz), 128.37 (d, $J = 20.2$ Hz), 122.89 (s), 35.07 (s), 31.52 (s).

HRMS (ESI, $[\text{M}+\text{H}]^+$): m/z calcd for $\text{C}_{26}\text{H}_{32}\text{P}$ 375.2236; Found 375.2235.

Elemental analysis: Calc. for $\text{C}_{26}\text{H}_{31}\text{P}$: C, 83.39; H, 8.34, P, 8.27. Found: C, 83.49; H, 8.40.

SAK-958_tofrac.11.fid
 Sample SAK-958_tofrac_31P
 group chen
 Instrument Bruker AV III HD 400 MHz (D 309)
 31P-HDEC CDCl₃ /opt/v dkunzi 20

Figure S65. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) spectrum of (3,5-di-*tert*-butylphenyl)diphenylphosphane.

Figure S66. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of (3,5-di-*tert*-butylphenyl)diphenylphosphane.

Bis(3,5-di-*tert*-butylphenyl)(phenyl)phosphane. A flame-dried 50 mL Schlenk flask with rubber septum was charged with 1-bromo-3,5-di-*tert*-butylbenzene (848 mg, 3.15 mmol, 2.1 equiv), evacuated and refilled with Ar (3x). Dry THF (15 mL) was added via syringe and the reaction was cooled to -78 °C before BuLi (1.5 mL, 2 M in cyclohexane, 3.0 mmol, 2 equiv) was added dropwise via syringe over ca. 5 min. Within several minutes a white precipitate formed.

After 70 min at -78 °C, PhPCl₂ (102 μL , 1.5 mmol, 1 equiv) was added dropwise via syringe. (The precipitate dissolved again within 30 min).

The reaction was stirred at -78 °C for 1 h, then removed from the cooling bath and stirred at room temperature for 30 min. Silica (4 g) was added and all volatiles were removed under vacuum. The residue was loaded on a short column (SiO_2 , length:

ca. 5 cm, diameter: 2 cm), eluted with hexane (3x10 mL), then toluene (3x10 mL). The combined toluene fractions were evaporated to give the product as colorless oil that solidified to a white solid upon drying under vacuum (550 mg, 1.13 mmol, 75 %).

¹H NMR (400 MHz, CDCl₃): δ 7.41 (td, *J* = 1.9, 0.6 Hz, 2H), 7.36 – 7.33 (m, 5H), 7.18 (dd, *J* = 8.3, 1.9 Hz, 4H), 1.27 (s, 36H).

³¹P{¹H} NMR (162 MHz, CDCl₃): δ -3.11 (s).

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 150.62 (d, *J* = 6.8 Hz), 138.67 (d, *J* = 11.1 Hz), 136.34 (d, *J* = 9.0 Hz), 133.65 (d, *J* = 18.8 Hz), 128.42 (s), 128.30 (d, *J* = 6.7 Hz), 128.26 (d, *J* = 19.8 Hz), 122.65 (s), 35.03 (s), 31.53 (s).

HRMS (ESI, [M+H]⁺): *m/z* calcd for C₃₄H₄₈P 487.3488; Found 487.3486.

Elemental analysis: Calc. for C₃₄H₄₇P: C, 83.90; H, 9.73, P, 6.36. Found: C, 84.15; H, 9.73.

Figure S67. ¹H NMR (400 MHz, CDCl₃) spectrum of bis(3,5-di-*tert*-butylphenyl)(phenyl)phosphane.

SAK-953_Ar2PPh_2.fid
 Sample SAK-953_Ar2PPh_31P
 Instrument AV-NEO 400 MHz
 Group chen
 162 MHz 31P Spectrum with 1H decoupling
 31P-HDEC.ETH CDCl₃ /opt/v ckunzi 51

Figure S68. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) spectrum of bis(3,5-di-*tert*-butylphenyl)(phenyl)phosphane.

Figure S69. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of bis(3,5-di-*tert*-butylphenyl)(phenyl)phosphane.

Scheme S24. Evaluation of New Ligands.

Inside the glove box, an oven-dried 5 mL Schlenk flask equipped with a Teflon and a glass-coated stir bar was charged with $[\text{NMe}_4]\text{OTf}$ (22.3 mg, 0.1 mmol, 1 equiv), COE (65 μL , 0.5 mmol, 5 equiv), (dme) NiBr_2 in THF (0.001 mmol, 0.01 equiv, prepared as stock solution), ligand in THF (0.002 mmol, 0.02 equiv, prepared as stock solution), and THF (tot. vol. THF: 2 mL, 0.05 M). The flask was removed from the glove box, cooled to 0 $^\circ\text{C}$ in an ice/water bath, and BuLi (2 M in cyclohexane; 53 μL , 0.105 mmol, 1.05 equiv) was added dropwise via micro syringe under a counterflow of Ar. The flask was sealed (no gas exchange) and the reaction was allowed to warm to RT overnight. After 16 h, undecane (10 μL ; internal standard) was added and an aliquot (ca. 0.2 mL) was partitioned between 2 mL pentane and 2 mL water. After vigorous mixing of the aliquot with a vortex mixer, the organic phase was filtered through a plug of MgSO_4 and analyzed by GC-FID. The yield was determined by the integral ratio of the product versus undecane as internal standard using a previously determined calibration curve.

Table S18. Evaluation of New Ligands.

Entry	Ligand	Yield / % ^a
1	P(3,5-di ^t BuPh)Ph ₂	32
2	P(3,5-di ^t BuPh) ₂ Ph	48

^a Average of two independent runs.

26. Ligand Parametrization Model

The steric parameter were taken from section 27.6 (**Table S27**) for the DFT-optimized (C₂H₄)₂NiPR₃ complexes. Multivariate ligand parametrization models were generated using the *Multiple Linear Regression* fit as implemented in the OriginPro software package.

Table S19. Steric Parameters, Binding Constants and Yields with COE for Several Phosphines

Phosphine	Exact cone angle θ°	Exact solid cone angle Θ°	%V _{Bur}	K	% Yield
PPhMe ₂	138.947	122.863	26.5	0.0014	3 ^a
PPh ₂ Me	155.594	129.365	28.6	0.0013	0.3 ^a
PPh ₃	168.196	135.023	30.4	0.081	25
P(3,5-di ^t BuPh)Ph ₂	188.849	142.79	31.2	0.11	32
P(3,5-di ^t BuPh) ₂ Ph	195.345	148.329	31.1	0.090	48

^a Data from ref. S2.

Figure S70. Plot of exact cone angle θ° versus % yield for the cyclopropanation of COE with different phosphine ligands. Ar = (3,5-di^tBuPh).

Figure S71. Plot of exact solid cone angle Θ° versus % yield for the cyclopropanation of COE with different phosphine ligands. Ar = (3,5-di^tBuPh).

Figure S72. Plot of buried volume $\%V_{\text{Bur}}$ versus % yield for the cyclopropanation of COE with different phosphine ligands. Ar = (3,5-di^tBuPh).

Figure S73. Plot of binding constant K_{COE} versus % yield for the cyclopropanation of COE with different phosphine ligands. Ar = (3,5-di^tBuPh).

Figure S74. Plot of measured yield versus predicted yield for a ligand parametrization model using exact solid cone angle Θ° , buried volume $\%V_{\text{Bur}}$, and binding constant K_{COE} . Ar = (3,5-di^tBuPh).

Figure S75. Plot of measured yield versus predicted yield for a ligand parametrization model using exact solid cone angle Θ° and buried volume $\%V_{\text{Bur}}$. Ar = (3,5-diⁱBuPh).

Figure S76. Plot of binding constant K (log scale) versus measured yields for the cyclopropanation for selected ligands and alkenes. Black circles represent yields of alkenes as indicated with PPh_3 as ligand and K from Tolman (see ref. S7) and the corresponding fit to our model as red curve. Green diamonds represent yields of COE with different phosphine ligands as indicated and K from **Table S8**. Ar = (3,5-diⁱBuPh), CHE = Cyclohexene, COE = Cyclooctene, 1Oct = 1-Octene, NBE = Norbornene.

27. Computational Details

All calculations were performed using Gaussian 09 Revision D.¹⁰ All geometries were optimized and frequencies calculations were performed to ensure real minima for the intermediates (i.e., $N_{\text{imag}} = 0$) and first-order saddle points for the transition states (i.e., $N_{\text{imag}} = 1$). The energies reported are zero-point corrected energies. We first performed a benchmarking procedure, in which we compared crystal structures of literature-reported compounds that are analogous to the intermediates in our system to computationally optimized structures (19 different combinations of density functionals and basis sets were tested, a table summarizing the results is provided in Section 27.1). Following this procedure, we settled on the functional/basis-set combination M06L/def2-SVP, and these results are presented in the text. In addition, we performed calculations at the same level with an implicit solvent model, which yielded similar results.

All geometries can be found in the accompanying .xyz file.

For the Kinetic Isotope Effect calculations, we employed the ISOEFF software, which calculates isotope effects based on the Bigeleisen equation, using input from a quantum mechanical calculation (i.e., the Hessian matrix obtained from Gaussian).¹¹

27.1. Results of Benchmarking Procedure

To choose the best density functional for this work, we first performed a benchmarking procedure, whereby we computationally optimized the geometries of three structures and compared them to literature-reported crystal structures. The three structures chosen were the Pörschke nickel-lithium complex, and the two Hillhouse nickel carbenes.¹² The structures and their respective CCDC identifiers are given in **Figure S77**.

Figure S77. Structures and their respective CCDC identifiers that have been used as benchmark compounds in this study.

The root mean squared deviation (RMSD) was calculated for each optimized geometry against the respective crystal structure (except for some cases in which the geometry did not converge). The method of choice (highlighted in **Table S20**) is the one that consistently provided the best fit, coupled with a reasonable amount of computational resources and ease of convergence.

Table S20. Root Mean Squared Deviation (RMSD) for Optimized Geometries.

Functional	Basis Set	Pörschke	Hillhouse1	Hillhouse2
BP86	def2tzvp		0.0653	0.0940
PBE1PBE	6-31g*	0.0787	0.1839	0.0811
B3LYP	6-311g**	0.0718	0.2413	0.0860
B3LYP	LANL2DZ	0.0627	0.2323	0.0963
B3LYP	LANL2DZ/6-31g*	0.0617	--	0.0881
B3LYP	LANL2TZf/6-311+g**	0.0607	--	--
TPSSTPSS	6-31g*	0.0964	0.2487	0.0732
B97D	def2SVP	0.1199	0.0535	0.1055
M06L	6-31g*	0.1110	0.0622	0.1416
wB97XD	def2SVP	0.0792	0.0398	--
M06	6-31g*	0.0957	0.0860	0.1343
PBEPBE	def2SVP	0.1030	0.0485	0.0795
TPSSTPSS	def2SVP	0.1133	0.1295	0.0845
B97D3	def2SVP	0.1037	0.0597	0.0849
M06L	def2SVP	0.1087	0.0676	0.0953
PBEPBE	def2TZVP	0.0753	0.0927	0.0691
TPSSTPSS	def2TZVP	0.0851	0.0512	0.3123
B97D3	def2TZVP	0.0757	0.0859	0.0681
M06L	def2TZVP	0.0941	0.1616	0.0748

27.2. Energies of Structures for Ni-Phosphine-Alkene Cycle (NiPA) and KIEs

All structures were optimized at the M06L/def2-SVP level of theory. Frequencies analysis was performed for all optimized structures to ensure that intermediates are real minima and transition states are first-order saddle points.

The product "1 + 7" refers to a complex of the NiPA system and cyclopropane, which is obtained following the reductive elimination. The separated products lie at a slightly higher energy.

The product "1* + 7" refers to the sum of the energies of the separated products.

Figure S78. Left: Proposed catalytic cycles for the model system with one phosphine and one alkene. Right: Energy profile for the catalytic system with one phosphine ligand and one alkene.

Table S21. Computed Energies for the Blue Pathway for the catalytic system with one phosphine ligand and one alkene.

Chemical Transformation			Energy / kcal mol ⁻¹
1+2	to	3	-42.78
3	to	TS3-4	15.02
TS3-4	to	4 + Me ₃ N*LiOTf	-12.37
4	to	TS4-5	9.47
TS4-5	to	5	-19.22
5 + ethylene	to	6	-29.23
6	to	TS6-7	3.81
TS6-7	to	7 + 1 (complex)	-9.54

Table S22. Computed Energies for the Red Pathway for the catalytic system with one phosphine ligand and one alkene.

Chemical Transformation			Energy / kcal mol ⁻¹
1+2	to	3	-42.78
3	to	TS3-4	15.02
TS3-4	to	4 + Me ₃ N*LiOTf	-12.37
4	to	TS4-5	9.47
TS4-5	to	5	-19.22
5 + ethylene	to	6	-29.23
6 + ethylene	to	6*	9.47
6*	to	TS6*-7	1.06
TS6*-7	to	7 + 1*	-26.63

Table S23. Computed Energies for the Green Pathway for the catalytic system with one phosphine ligand and one alkene.

Chemical Transformation			Energy / kcal mol ⁻¹
1+2	to	3	-42.78
3	to	TS3-4	15.02
TS3-4	to	4 + Me ₃ N ⁺ LiOTf	-12.37
4 + ethylene	to	4'	-9.44
4'	to	TS4'-6	5.48
TS4'-6	to	6	-35.03
6	to	TS6-7	3.81
TS6-7	to	7 + 1 (complex)	-9.54

Table S24. Computed KIEs for the catalytic system with one phosphine ligand and one alkene with perdeuterated reagent [LiCD₂N(CD₃)₃]OTf.

Chemical Transformation			KIE
3	to	4	2.50
4	to	5	0.63
6	to	1	1.11

27.3. Energies of Structures for Ni-Phosphine₂ Cycle (NiP₂)

All structures were optimized at the M06L/def2-SVP level of theory. Frequencies analysis was performed for all optimized structures to ensure that intermediates are real minima and transition states are first-order saddle points. The product "1P₂ + 7" refers to a complex of the NiP₂ system and cyclopropane, which is obtained following the reductive elimination. The separated products lie at a slightly higher energy.

Figure S79. Left: Catalytic cycle for the model system with two phosphine ligands. Right: Energy profile for the catalytic system with two phosphine ligands.

Table S25. Computed Energies for the Blue Pathway for the catalytic system with two phosphine ligands.

Chemical Transformation			Energy / kcal mol ⁻¹
1P ₂ +2	to	3P ₂	-44.96
3P ₂	to	TS3P ₂ -4P ₂	8.97
TS3P ₂ -4P ₂	to	4P ₂ + Me ₃ N ⁺ LiOTf	-20.63
4P ₂ + ethylene	to	5P ₂	-16.13
5P ₂	to	TS5P ₂ -6P ₂	4.43
TS5P ₂ -6P ₂	to	6P ₂	-35.87
6P ₂	to	TS6P ₂ -7	14.81
TS6P ₂ -7	to	7 + 1P ₂ (complex)	-7.74

27.4. Energies of Structures for Ni-Alkene₂ Cycle (NiA₂)

All structures were optimized at the M06L/def2-SVP level of theory. Frequencies analysis was performed for all optimized structures to ensure that intermediates are real minima and transition states are first-order saddle points.

As can be seen in the scheme below, when two alkene ligands were placed on Ni, the overall pathway undergoes two significant changes. Firstly, the rate determining step (**3**→**4** in previous cases) does not afford the nickel carbene; rather, the nickelacyclobutane is formed concurrently with the cleavage of the C-N bond, affording intermediate **5** directly. Secondly, the complexation of a second alkene to the **5** does not afford a stable system (**6** in previous cases). Instead, the complexation triggers the reductive elimination, which results in an intermediate that is a complex of the NiA₂ and cyclopropane (the energy of this intermediate is the energy used to produce the plot below). We could not locate a transition state for the complexation of the alkene to **5** and the subsequent immediate formation of the cyclopropane.

Figure S80. Left: Proposed catalytic cycle for the model system with two alkene ligands. Right: Energy profile for the catalytic system with two alkene ligands.

Table S26. Computed Energies for the pathway for the catalytic system with two alkene ligands.

Chemical Transformation			Energy / kcal mol ⁻¹
1A ₂ +2	to	3A ₂	-32.31
3A ₂	to	TS3A ₂ -5A ₂	13.76
TS3A ₂ -5A ₂	to	5A ₂ + Me ₃ N [⊕] LiOTf [⊖]	-19.50
5A ₂ + ethylene	to	7 + 1A ₂ (complexed)	-47.74

27.5. Observations regarding the Reductive Elimination Transition State

In the course of our computational investigation, we observed that during the reductive elimination step for each of the types of catalysts proposed (Ni-Phosphine-Alkene, Ni-Phosphine₂, and Ni-Alkene₂), the nickelacyclobutane undergoes a twisting. The cyclopropane group leaves the complex only after having twisted 90° from its orientation in the preceding intermediate.

We show below images from the three cases, comparing the relative orientation of the leaving cyclopropane group to the two remaining ligands, at the starting point and at the transition state of the reductive elimination. In each case, we have selected two perspectives: the top image positions the nickelacyclobutane in the plane perpendicular to the page; the bottom image positions the nickelacyclobutane in the plane of the page.

The rotation is probably clearest in the case of Ni-Phosphine-Alkene. It appears less pronounced in the case of Ni-Phosphine₂, however this is because the cyclopropane continues to rotate after the transition state (see third column). For the Ni-Alkene₂, interestingly, the relative positions of the groups on nickel remain the same, but the alkene ligands themselves rotate.

a) Ni-Phosphine-Alkene

b) Ni-Phosphine₂

c) Ni-Alkene₂

27.6. Optimization of Model Compounds and Parameter Calculation for Ligands

We studied five compounds differing in their ligands to calculate the (steric) properties of the phosphines. The bis-alkene complexes were chosen because they represent possible intermediates in the catalytic cycle and simplify the calculations

without restricting the phosphine geometry too severely by the $\text{Ni}(\text{C}_2\text{H}_4)_2$ fragment. The exact ligand cone angles θ° and the exact ligand solid cone angles Θ° were calculated and visualized using the freely available *Mathematica* packages, FindConeAngle and FindSolidAngle, respectively.¹³ For both packages the Bondi radii were used as implemented. The buried volume $\%V_{\text{Bur}}$ was calculated and visualized using the Web tool SambVca 2.¹⁴ For the $\%V_{\text{Bur}}$ calculation the following settings were employed as implemented in the Web tool: Bondi radii scaled by 1.17, a sphere radius of 3.5 Å, a mesh spacing of 0.1 Å, and H atoms were excluded from the calculations.

All structures were optimized at the M06L/def2-SVP level of theory. Frequencies analysis was performed for all optimized structures to ensure that the geometries are real minima.

Figure S81. Structures evaluated to generate ligand parameters.

Table S27. Steric Parameters for Several Phosphines

Phosphine	Exact cone angle θ°	Exact solid cone angle Θ°	$\%V_{\text{Bur}}$
PPhMe ₂	138.947	122.863	26.5
PPh ₂ Me	155.594	129.365	28.6
PPh ₃	168.196	135.023	30.4
P(3,5-di ^t BuPh)Ph ₂	188.849	142.79	31.2
P(3,5-di ^t BuPh) ₂ Ph	195.345	148.329	31.1

^a -

Figure S82. Left: Steric map of PPhMe₂. Middle: Cone around PPhMe₂. Right: 3D plot of the solid angle of PPhMe₂.

Figure S83. Left: Steric map of PPh₂Me. Middle: Cone around PPh₂Me. Right: 3D plot of the solid angle of PPh₂Me.

Figure S84. Left: Steric map of PPh_3 . Middle: Cone around PPh_3 . Right: 3D plot of the solid angle of PPh_3 .

Figure S85. Left: Steric map of $\text{P(3,5-di'BuPh)Ph}_2$. Middle: Cone around $\text{P(3,5-di'BuPh)Ph}_2$. Right: 3D plot of the solid angle of $\text{P(3,5-di'BuPh)Ph}_2$.

Figure S86. Left: Steric map of $\text{P(3,5-di'BuPh)}_2\text{Ph}$. Middle: Cone around $\text{P(3,5-di'BuPh)}_2\text{Ph}$. Right: 3D plot of the solid angle of $\text{P(3,5-di'BuPh)}_2\text{Ph}$.

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