# Nickel-Catalyzed Double Bond Transposition under Kinetic Control

Eduardo José de Carvalho-Junior and Caio C. Oliveira\*

**ABSTRACT:** Taming the reactivity of nickel catalysts is a never-ending inspiration to discover new complexes, ligands, and reaction protocols. Here, we report that a simple combination of Ni(COD)<sub>2</sub> and Lewis acids allows activation of allylic C–H bonds. Their synergism eases oxidative addition and



1,3-hydrogen atom relocation to yield unprecedented double bond monotransposition. Unique features of this work include polar inner-sphere mechanism, kinetically favored double bond transposition, ligand-controlled stereoselective *E* or *Z* isomer distribution, mechanistic insights by control experiments and NMR monitoring.

In 1897, Sabatier and Senderens described the heterogeneous nickel-catalyzed hydrogenation of ethylene to ethane, setting a milestone in chemistry.<sup>1</sup> Almost sixty years later, another landmark: Ziegler described that nickel traces in the reaction of ethylene with AlMe<sub>3</sub> led to 1-butene, instead of polyenes.<sup>2</sup> This "nickel effect" boosted the interest for the organonickel chemistry, inspiring the efforts to produce well-defined homogeneous catalysts.<sup>3</sup> Although this transition confirmed that nickel(0) complexes were highly reactive, but annoyingly unstable, it did not prevent them from finding widespread applications for the production of commodities and fine chemicals.<sup>4,5</sup>

Homogeneous reactions with Ni(0) or Ni(II) complexes can proceed through polar or radicalar modes due to the readily available Ni(I) and Ni(III) oxidative states.<sup>4</sup> Although those pathways have potential to produce complex transformations, poor selectivity is common when they occur simultaneously. Efforts to circumvent this issue led to beautiful advances in organometallic chemistry, ligand design and reaction setup. Thus, 125 years after Sabatier refers to nickel as a "spirited horse", chemists have tamed its reactivity, but they are only scratching the surface of how its catalysis can impact chemical sciences.<sup>4,6</sup>



Scheme 1. Overview on nickel catalyzed transposition of olefins

Understanding the role of homogeneous nickel species uncovered a variety of selective catalytic reactions.<sup>7</sup> For example, transformations involving one electron (radicalar) step, once believed to be difficult to handle, it is now a commonplace tool in cross-coupling reactions,<sup>8,9</sup> hydrofunctionalizations<sup>10-14</sup> and photochemical reactions.<sup>15</sup> Interestingly, since Ni(0) precursors are difficult to handle, most reactions start with Ni(II) salts in the presence of a reductant, such as manganese, zinc or Grignard reagents.<sup>16-21</sup> Examples of bench-stable Ni(0) complexes were presented recently by the groups of Cornella and Engle, taking advantage of its electron-rich low-valent nature and strong affinity to electron deficient olefines (**Scheme 1c**).<sup>22-24</sup> The former group synthesized 16-electron Ni(0) complexes with stilbene derivatives as ligands **1**.<sup>22</sup> The latter synthesized 18-electron ones using cyclooctadiene (COD)

and duroquinone **2**.<sup>24</sup> Besides the obvious contribution to enable operationally simple reactions setups, we questioned whether we could take advantage of the strong interaction between nickel(0) and electron deficient olefins to activate new catalytic transformations.

Among them, transposition of double bonds is a relevant transformation to add value to readily available terminal olefins and previous results in this area show a prevalence of noble metal catalysts (Scheme 1a).<sup>25–29</sup> However, recent catalytic advances brought nonprecious metals, such as nickel, to an unprecedented prominence (Scheme 1d).<sup>30–32</sup> For example, *i*) Iwamoto and Ogoshi reported the isomerization of allylarenes using Ni(COD)<sub>2</sub> and PAd<sub>2</sub>(*n*-Bu) [Ad=adamantyl].<sup>33</sup> Although labeling experiments indicates no proton transference from the solvent to the product, the reaction only worked in methanol; *ii*) Schoenebeck described a radicalar-based olefin transposition using a well-defined dimeric (NHC)Ni(I) complex;<sup>34</sup> *iii*) Cook took advantage of the combination of (NHC)Ni/Silanes to produce nickel-hydride capable of isomerizing a variety of terminal and 1,1-disubstituted alkenes.<sup>35</sup> Although those three elegant examples highlight distinct initiation modes, they share the same thermodynamically-driven energy profile.<sup>36</sup> Namely, the transposition finishes when the more stable isomer is reached, typically a styrene derivatives or tri- or tetrasubstituted double bond. Conversely, achieving kinetic control implies in processes where the activation barrier for the first isomerization is much lower than the next, yielding a monotransposition process.<sup>37</sup>

Considering the aforementioned affinity between Ni(0) and electron deficient double bonds, we raise the hypothesis that Lewis acids could ease their  $\pi$ -complexes formation (**Scheme 1e**). Thus, allowing its further insertion into C–H allylic bonds to yield nucleophilic allylnickel-hydride intermediates.<sup>38,39</sup> Ideally, the latter could be stabilized by the Lewis acid, enabling unprecedented allylic activation in non-activated terminal double bonds. Thereby, the success of this strategy would shed light to a pathway to transpose terminal double without adding any source of external hydride or protic solvent and this would avoid reaction initiation by migratory insertion of metal-hydride complexes to the double bond, a widespread strategy in olefin isomerization protocols.<sup>40,41</sup>

Herein, we report a complementary approach where the transposition only occurs in a stereocontrolled one-fold migration where *E* isomers are favored with wide-bite bisphosphines and the *Z* isomers are favored when small-bite 1,2-bisphosphines. This method fills a gap in nickel catalysis, opening the doors for its applications in the route to complex olefins and sustainable chemical processes. Specifically, the combination of Ni(COD)<sub>2</sub> and Lewis acids allows the activation of allylic C–H and further stereoselective monoisomerization of olefins, regardless of the addition of any external hydride source.

We rationalize a stereoelectronic preference for Ni(0) to terminal double bonds, instead of the electron richer internal ones, thus, disfavoring further oxidative additions (**Scheme 1e**).

To validate our hypotheses, a mixture of the allylbenzene **3a**, Ni(COD)<sub>2</sub> (10 mol%), Y(OTf)<sub>3</sub> (40 mol%) and PPh<sub>3</sub> (10 mol%) was heated in acetonitrile at 40 °C. After 24h, the methyl isoeugenol (**4a**) was obtained in 100% conversion, 99% yield and *E:Z* ratio >20:1. Removal of the nickel source or triphenylphosphine led to complete recovery of the starting material and removal of the Lewis acid led to only 9% conversion (**Scheme 2a**). Reactions with deuterium labeled derivatives at benzylic position **5** indicate a 1,3-hydrogen transposition and small incorporation at vinylic position. Furthermore, isomerization of **7**, labeled at vinylic position, yields 6 and 7% of deuterium incorporation at C1 and C3, respectively (**Scheme 2b**). Herein we observed the same findings of Iwamoto and Ogoshi:<sup>33</sup> a vinylic hydrogen/deuterium scrambling explained through the insertion of the allylnickel hydride **9** (blue arrow pathway) into an unreacted **7**, followed by  $\beta$ -elimination with H or D in **12**, leading to the scrambling products **3a** and **13** (**Scheme 2c**). The former will provide the product **4**, without deuterium incorporation, while the latter will provide **14** after reductive elimination. Finally, the presence of deuterium at all carbons from the allylic system indicates some extension of reversible **1**,3-hydrogen migration in this activated substrate.

Mechanistic insights about this synergistic Ni(0)-Lewis acid catalysis were obtained after carrying out key control experiments: a) The *cis*-diphenylcyclopropenyl olefin **15**, a known substrate for radical clocking experiments was submitted to our reaction and had its stereochemistry integrity preserved (**Scheme 3a**). Interestingly, the formation of the diene **16** indicates the occurrence of a ring open/elimination process and we can neglect the radical pathway; b) Competitive reaction between **3a** and **3g**, led to full conversion of the former to **4a** and full recovery of the latter. This indicated either a preference for the activation of more acidic C-H bonds or an apparent formation of a strong interaction between **4a** and Ni(0) species (**Scheme 2e**). c) Removal of allylic C-H bond implies in an absence of isomerization processes (**Scheme 2f**). For example, *cis*-stilbene (**19**) was fully recovered after 24h under our standard reaction condition. However, when *Z*-**4r** (*E:Z* 1:5.6) was submitted to the same reaction conditions, we obtained the *E* isomer as the major component in 3:1 ratio (**Scheme 2f**).

With these promising results, we expand our protocol to other allylbenzene derivatives that furnished the desired *E*-products regardless of the presence of groups at *ortho* position **4a-d** (**Scheme 2**). Interestingly, a chromene derivative **4e** was obtained under standard isomerization condition, indicating that our method was not limited to substrates bearing C-H benzylic bonds. Next, we moved to challenging substrates bearing bulky vicinal substituents to the allylic C-H bond **4f-h**. Although the

activation of these lesser acidic bonds, would lead to non-stabilized anionic-like allylnickel-hydride intermediates, it occurs effortlessly in the presence of Y(OTf)<sub>3</sub>, yielding unprecedented transposition of non-activated olefins catalyzed by Ni(0) favoring the *E* products. Since the isomerizations reactions do not improve molecular weight, volatile starting materials led to lower yield reactions, as can be seen for the aldehyde **4h**. Furthermore, acid sensitive carbamate group (**4f**) or aldehydes and formamides (**4g-h**), known substrates in Ni(0)-catalyzed C-H functionalizations were tolerated.<sup>42–44</sup> Once again, all products were obtained with stereoselectivities higher than 20:1 in favor of *E* isomers.



Scheme 2. Isomerization of allyl-benzene derivatives and control experiments.

Despite the confirmation that terminal non-activated allylic groups were suitable to our olefin transposition protocol, concerns about the positional distribution in substrates with more than one methylene group, arose during our experiments with substrates **4i-t**. Thus, the next goal was to control the monoisomerization in substrates in which additional migrations would lead to conjugated double bonds to heteroatoms (**4i-p**) or carbonyl groups (**4q-s**), commonly obtained in thermodynamically-

driven processes.<sup>26,34,45-47</sup> Despite these concerns, starting materials prone to two or three possible migrations, yielded monoisomerization with up to 6.5:1 *E:Z* ratio. Indeed, two-fold transpositions were scarcely observed, except for **4t** where the second migration occurred in 8%. For those delicate substrates, we found that the wide-bite angle ligand DPEPhos yielded the products with higher stereoselectivities than PPh<sub>3</sub>, enabling the synthesis of *E*-1,2-disubstituted double bonds, under kinetic control and unprecedented levels of stereoselection in nickel catalysis.<sup>48–50</sup> Furthermore, the bulkiness of the ligand should make it difficult for further  $\pi$ -complexes with the more substituted double bond, favoring the monotransposition.

Reaction monitoring for the olefin transposition in **3q** by <sup>1</sup>H-NMR at 26.5 mmol/L [1 spectrum/5 minutes (282 total)] indicated distinct profiles using PPh<sub>3</sub> and DPEPhos ligands. Although both ligands provide the *Z* isomer in higher formation rate, followed by its isomerization into the *E* product, the transposition and isomerization are faster with DPEPhos. These data indicate that the *E*/*Z* distribution is ruled by their equilibrium concentrations, in an unusual example of 1,3-hydrogen shift protocol with geometrical isomerization, instead of an inherent ligand control. It is worth pointing out that theoretical mechanistic investigations in other olefin isomerization protocols indicate a preferential formation of the *E* product, in contrast to our findings.<sup>34,45,51</sup>



#### Scheme 3. Kinetically controlled Ni(0)-Catalyzed transposition of olefins.

The beneficial influence of the DPEPhos inspired us to search for a ligand able to provide the Zproduct as the major stereoisomer (Scheme 4). Unlike DPEPhos, we rationalize that the new ligand would be bulkier, with smaller bite angle 1,2-bisphosphines, and this would decrease the rate of Z to Eisomerization. Despite the modest conversion, dppe (20) was able to invert the stereochemistry preference, yielding E:Z ratios of 1/2 and 1/1.5. Higher conversions were achieved with dcpe (21) (54%), dpp-ethene (22) (44%) and DuanPhos (23) (80%). The former provided E:Z ratio of 1/2, and the others, 1/3 in favor of the Z isomer. Since DuanPhos provided the highest conversion among the evaluated phosphines (80%), we choose to continue the reaction optimization. Gratifyingly, we found an acceptable balance of conversion and stereoselection for this challenging transformation, carrying out the olefin transposition in acetonitrile, at 60°C, 40 mol% of  $Y(OTf)_3$  and 10 mol% of both Ni(COD)<sub>2</sub> and DuanPhos. The products were obtained in *E:Z* ratios up to 1/5.6 and conversions up to 90%. To the best of our knowledge, they represent the first report of Z-selective monotransposition of double bonds catalyzed by nickel, opening the doors for the development of new ligand and catalyst design to expand the scope of this valuable transformation. Finally, <sup>1</sup>H-NMR monitoring for the olefin transposition indicated that this transposition is much slower than those performed with PPh<sub>3</sub> or DPEPhos. Interestingly, the reaction profile indicates that the ligand DuanPhos allows the preferential formation of the Z isomer, keeping the concentration of the E very small during the 24h of monitoring (E:Z 1:23). Additional acquisition of the same sample after 120 hours indicated the same level of conversion (40%) and E:Z ratio of 1:13.3, consistent with a slower isomerization scenario. It is important to note that the NMR samples were  $\sim 10$  times lesser concentrated than the reaction condition, contributing to the decrease of the consumption rate of **3q** in comparison with the standard reaction condition.



Scheme 4. Z-selective double bond transposition.

In conclusion, we developed an efficient catalytic monotransposition of double bonds under kinetic control. This transformation was achieved by a unique combination of Ni(0) and Lewis acids to activate weak allylic C–H bonds. This new strategy allows the stereodivergent synthesis of *E* or *Z* products according to the ligand choice. Mechanistic insights by control experiments and <sup>1</sup>H-NMR suggest a polar, inner-sphere mechanism. These unique features open the doors to new developments in Ni-catalyzed transformations and an in-depth mechanism investigation is ongoing. This methodology has the potential to expand the realm of selective metal-catalyzed reactions and sustainable industrial procesess taking advantage of this new mode to activate C-H bonds.

# ASSOCIATED CONTENT

Experimental details, materials, methods, spectral and characterization data are included in the Supporting Information.

# AUTHOR INFORMATION

## **Corresponding Author**

\*Caio C. Oliveira – Institute of Chemistry, Universidade Estadual de Campinas (Unicamp), Campinas, São Paulo 13083-970, Brazil <u>caio.oliveira@unicamp.br</u>

orcid.org/0000-0002-2277-8003

## Author

Eduardo José de Carvalho-Junior – Institute of Chemistry, Universidade Estadual de Campinas (Unicamp), Campinas, São Paulo 13083-970, Brazil orcid.org/0000-0002-3278-6058

## **Author Contributions**

E.J.C-J. synthesized and characterized the materials and designed the experiments. C.C.O. conceived the idea, conceptualized the work, and supervised the project. All the authors revised the paper.

#### **Funding Sources**

The authors gratefully acknowledge support from FAPESP (São Paulo Research Foundation, Grant Numbers 2018/01669-5; 2019/00080-0; 2014/25770-6). This work was supported by the Serrapilheira Institute (grant number Serra-1709-22464).

#### Acknowledgments

The authors thank MSc Nicola Leone for providing very helpful details regarding NMR experimental setup. We dedicate this article with respect and admiration to Prof. Ronaldo Aloise Pilli (UNICAMP).

### References

- (1) Sabatier, P.; Senderens, J.-B. Action du nickel sur l'éthylène. Synthèse de l'éthane. *C. R. Acad. Sci. Paris* **1897**, *124*, 1358–1360.
- (2) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. Das Mülheimer Normaldruck-Polyäthylen-Verfahren. Angewandte Chemie 1955, 67 (19–20), 541–547. https://doi.org/10.1002/ange.19550671902.

- (3) Fischer, K.; Jonas, K.; Misbach, P.; Stabba, R.; Wilke, G. The "Nickel Effect." *Angewandte Chemie International Edition in English* **1973**, *12* (12), 943–953. https://doi.org/10.1002/anie.197309431.
- (4) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. Recent Advances in Homogeneous Nickel Catalysis. *Nature* **2014**, *509* (7500), 299–309. https://doi.org/10.1038/nature13274.
- (5) Keim, W. Nickel: An Element with Wide Application in Industrial Homogeneous Catalysis. *Angewandte Chemie International Edition in English* **1990**, *29* (3), 235–244. https://doi.org/10.1002/anie.199002351.
- (6) Ananikov, V. P. Nickel: The "Spirited Horse" of Transition Metal Catalysis. ACS Catal. 2015, 5 (3), 1964–1971. https://doi.org/10.1021/acscatal.5b00072.
- Chernyshev, V. M.; Ananikov, V. P. Nickel and Palladium Catalysis: Stronger Demand than Ever. ACS Catal.
  2022, 12 (2), 1180–1200. https://doi.org/10.1021/acscatal.1c04705.
- (8) Phapale, V. B.; Cárdenas, D. J. Nickel-Catalysed Negishi Cross-Coupling Reactions: Scope and Mechanisms. Chem. Soc. Rev. 2009, 38 (6), 1598–1607. https://doi.org/10.1039/B805648J.
- Hu, X. Nickel-Catalyzed Cross Coupling of Non-Activated Alkyl Halides: A Mechanistic Perspective. Chem. Sci. 2011, 2 (10), 1867–1886. https://doi.org/10.1039/C1SC00368B.
- (10) Zhang, Z.; Bera, S.; Fan, C.; Hu, X. Streamlined Alkylation via Nickel-Hydride-Catalyzed Hydrocarbonation of Alkenes. J. Am. Chem. Soc. 2022, 144 (16), 7015–7029. https://doi.org/10.1021/jacs.1c13482.
- (11) Buendia, M. B.; Higginson, B.; Kegnæs, S.; Kramer, S.; Martin, R. Redox-Neutral Ni-Catalyzed Sp3 C–H Alkylation of α-Olefins with Unactivated Alkyl Bromides. ACS Catal. 2022, 12 (7), 3815–3820. https://doi.org/10.1021/acscatal.2c01057.
- (12) Gaydou, M.; Moragas, T.; Juliá-Hernández, F.; Martin, R. Site-Selective Catalytic Carboxylation of Unsaturated Hydrocarbons with CO2 and Water. J. Am. Chem. Soc. 2017, 139 (35), 12161–12164. https://doi.org/10.1021/jacs.7b07637.
- (13) Lv, X.-Y.; Abrams, R.; Martin, R. Dihydroquinazolinones as Adaptative C(Sp3) Handles in Arylations and Alkylations via Dual Catalytic C–C Bond-Functionalization. *Nat Commun* **2022**, *13* (1), 2394. https://doi.org/10.1038/s41467-022-29984-0.
- (14) Qian, D.; Bera, S.; Hu, X. Chiral Alkyl Amine Synthesis via Catalytic Enantioselective Hydroalkylation of Enecarbamates. J. Am. Chem. Soc. 2021, 143 (4), 1959–1967. https://doi.org/10.1021/jacs.0c11630.
- (15) Wenger, O. S. Photoactive Nickel Complexes in Cross-Coupling Catalysis. Chemistry A European Journal 2021, 27 (7), 2270–2278. https://doi.org/10.1002/chem.202003974.
- (16) Balakrishnan, V.; Murugesan, V.; Chindan, B.; Rasappan, R. Attenuation of Ni(0) Decomposition: Mechanistic Insights into AgF-Assisted Nickel-Mediated Silylation. *Inorg. Chem.* 2022, 61 (3), 1438–1446. https://doi.org/10.1021/acs.inorgchem.1c03108.
- (17) Dander, J. E.; Weires, N. A.; Garg, N. K. Benchtop Delivery of Ni(Cod)2 Using Paraffin Capsules. Org. Lett. 2016, 18 (15), 3934–3936. https://doi.org/10.1021/acs.orglett.6b01758.
- (18) Weber, F.; Ballmann, M.; Kohlmeyer, C.; Hilt, G. Nickel-Catalyzed Double Bond Transposition of Alkenyl Boronates for in Situ Syn-Selective Allylboration Reactions. *Org. Lett.* **2016**, *18* (3), 548–551. https://doi.org/10.1021/acs.orglett.5b03585.
- (19) Lee, W.-C.; Wang, C.-H.; Lin, Y.-H.; Shih, W.-C.; Ong, T.-G. Tandem Isomerization and C–H Activation: Regioselective Hydroheteroarylation of Allylarenes. Org. Lett. 2013, 15 (20), 5358–5361. https://doi.org/10.1021/ol402644y.
- (20) Wang, L.; Liu, C.; Bai, R.; Pan, Y.; Lei, A. Easy Access to Enamides: A Mild Nickel-Catalysed Alkene Isomerization of Allylamides. *Chem. Commun.* **2013**, *49* (72), 7923–7925. https://doi.org/10.1039/C3CC43875A.
- (21) Frauenrath, H.; Brethauer, D.; Reim, S.; Maurer, M.; Raabe, G. Highly Enantioselective Isomerization of 4,7-Dihydro-1,3-Dioxepins Catalyzed by Me-DuPHOS-Modified Dihalogenonickel Complexes and Determination of the Absolute Configuration of the Isomerization Products. *Angewandte Chemie International Edition* 2001, 40 (1), 177–179. https://doi.org/10.1002/1521-3773(20010105)40:1<177::AID-ANIE177>3.0.CO;2-X.
- (22) Nattmann, L.; Saeb, R.; Nöthling, N.; Cornella, J. An Air-Stable Binary Ni(0)–Olefin Catalyst. *Nat Catal* **2020**, *3* (1), 6–13. https://doi.org/10.1038/s41929-019-0392-6.
- (23) Nattmann, L.; Cornella, J. Ni(4-TBustb)3: A Robust 16-Electron Ni(0) Olefin Complex for Catalysis. Organometallics 2020, 39 (18), 3295–3300. https://doi.org/10.1021/acs.organomet.0c00485.
- (24) Tran, V. T.; Li, Z.-Q.; Apolinar, O.; Derosa, J.; Joannou, M. V.; Wisniewski, S. R.; Eastgate, M. D.; Engle, K. M. Ni(COD)(DQ): An Air-Stable 18-Electron Nickel(0)–Olefin Precatalyst. Angewandte Chemie International Edition 2020, 59 (19), 7409–7413. https://doi.org/10.1002/anie.202000124.
- (25) Vasseur, A.; Bruffaerts, J.; Marek, I. Remote Functionalization through Alkene Isomerization. *Nature Chem* **2016**, *8* (3), 209–219. https://doi.org/10.1038/nchem.2445.
- (26) Sommer, H.; Juliá-Hernández, F.; Martin, R.; Marek, I. Walking Metals for Remote Functionalization. ACS Cent. Sci. 2018, 4 (2), 153–165. https://doi.org/10.1021/acscentsci.8b00005.
- (27) Farquhar, A. H.; Gardner, K. E.; Acosta-Calle, S.; Camp, A. M.; Chen, C.-H.; Miller, A. J. M. Cation-Controlled Olefin Isomerization Catalysis with Palladium Pincer Complexes. *Organometallics* 2022. https://doi.org/10.1021/acs.organomet.2c00315.
- (28) Massad, I.; Marek, I. Alkene Isomerization Revitalizes the Coates–Claisen Rearrangement. *Angewandte Chemie International Edition* **2021**, *60* (34), 18509–18513. https://doi.org/10.1002/anie.202105834.

- (29) Wille, A.; Tomm, S.; Frauenrath, H. A Highly Z-Selective Isomerization (Double-Bond Migration) Procedure for Allyl Acetals and Allyl Ethers Mediated by Nickel Complexes. *Synthesis* **1998**, *1998* (03), 305–308. https://doi.org/10.1055/s-1998-2028.
- (30) Occhialini, G.; Palani, V.; Wendlandt, A. E. Catalytic, Contra-Thermodynamic Positional Alkene Isomerization. *J. Am. Chem. Soc.* **2022**, *144* (1), 145–152. https://doi.org/10.1021/jacs.1c12043.
- (31) Zhao, K.; Knowles, R. R. Contra-Thermodynamic Positional Isomerization of Olefins. J. Am. Chem. Soc. 2022, 144 (1), 137–144. https://doi.org/10.1021/jacs.1c11681.
- (32) Tricoire, M.; Wang, D.; Rajeshkumar, T.; Maron, L.; Danoun, G.; Nocton, G. Electron Shuttle in N-Heteroaromatic Ni Catalysts for Alkene Isomerization. JACS Au 2022, 2 (8), 1881–1888. https://doi.org/10.1021/jacsau.2c00251.
- (33) Iwamoto, H.; Tsuruta, T.; Ogoshi, S. Development and Mechanistic Studies of (E)-Selective Isomerization/Tandem Hydroarylation Reactions of Alkenes with a Nickel(0)/Phosphine Catalyst. ACS Catal. 2021, 11 (11), 6741–6749. https://doi.org/10.1021/acscatal.1c00908.
- (34) Kapat, A.; Sperger, T.; Guven, S.; Schoenebeck, F. E-Olefins through Intramolecular Radical Relocation. *Science* **2019**, *363* (6425), 391–396. https://doi.org/10.1126/science.aav1610.
- (35) Kawamura, K. E.; Chang, A. S.; Martin, D. J.; Smith, H. M.; Morris, P. T.; Cook, A. K. Modular Ni(0)/Silane Catalytic System for the Isomerization of Alkenes. *Organometallics* **2022**, *41* (4), 486–496. https://doi.org/10.1021/acs.organomet.2c00010.
- (36) Liu, C.-F.; Wang, H.; Martin, R. T.; Zhao, H.; Gutierrez, O.; Koh, M. J. Olefin Functionalization/Isomerization Enables Stereoselective Alkene Synthesis. *Nat Catal* **2021**, *4* (8), 674–683. https://doi.org/10.1038/s41929-021-00658-2.
- (37) Liu, X.; Zhang, W.; Wang, Y.; Zhang, Z.-X.; Jiao, L.; Liu, Q. Cobalt-Catalyzed Regioselective Olefin Isomerization Under Kinetic Control. *J. Am. Chem. Soc.* **2018**, *140* (22), 6873–6882. https://doi.org/10.1021/jacs.8b01815.
- (38) Hegedus, L. S.; Varaprath, S. Unsaturated (.Pi.-Allyl)Nickel Halide Complexes. Reactions to Produce Dienes. Organometallics 1982, 1 (2), 259–263. https://doi.org/10.1021/om00062a006.
- (39) Hegedus, L. S.; Evans, B. R.; Korte, D. E.; Waterman, E. L.; Sjoberg, K. Reactions of .Pi.-Allylnickel Bromide Complexes with Quinones. Synthesis of Isoprenoid Quinones. J. Am. Chem. Soc. 1976, 98 (13), 3901–3909. https://doi.org/10.1021/ja00429a028.
- (40) Crossley, S. W. M.; Barabé, F.; Shenvi, R. A. Simple, Chemoselective, Catalytic Olefin Isomerization. J. Am. Chem. Soc. 2014, 136 (48), 16788–16791. https://doi.org/10.1021/ja5105602.
- (41) Zhang, S.; Bedi, D.; Cheng, L.; Unruh, D. K.; Li, G.; Findlater, M. Cobalt(II)-Catalyzed Stereoselective Olefin Isomerization: Facile Access to Acyclic Trisubstituted Alkenes. J. Am. Chem. Soc. 2020, 142 (19), 8910–8917. https://doi.org/10.1021/jacs.0c02101.
- (42) Donets, P. A.; Cramer, N. Diaminophosphine Oxide Ligand Enabled Asymmetric Nickel-Catalyzed Hydrocarbamoylations of Alkenes. *J. Am. Chem. Soc.* **2013**, *135* (32), 11772–11775. https://doi.org/10.1021/ja406730t.
- (43) Hoshimoto, Y.; Hayashi, Y.; Suzuki, H.; Ohashi, M.; Ogoshi, S. Synthesis of Five- and Six-Membered Benzocyclic Ketones through Intramolecular Alkene Hydroacylation Catalyzed by Nickel(0)/N-Heterocyclic Carbenes. Angewandte Chemie International Edition 2012, 51 (43), 10812–10815. https://doi.org/10.1002/anie.201206186.
- (44) Xiao, L.-J.; Fu, X.-N.; Zhou, M.-J.; Xie, J.-H.; Wang, L.-X.; Xu, X.-F.; Zhou, Q.-L. Nickel-Catalyzed Hydroacylation of Styrenes with Simple Aldehydes: Reaction Development and Mechanistic Insights. J. Am. Chem. Soc. 2016, 138 (9), 2957–2960. https://doi.org/10.1021/jacs.6b00024.
- (45) Guven, S.; Kundu, G.; Weßels, A.; Ward, J. S.; Rissanen, K.; Schoenebeck, F. Selective Synthesis of Z-Silyl Enol Ethers via Ni-Catalyzed Remote Functionalization of Ketones. J. Am. Chem. Soc. 2021, 143 (22), 8375–8380. https://doi.org/10.1021/jacs.1c01797.
- (46) Fiorito, D.; Scaringi, S.; Mazet, C. Transition Metal-Catalyzed Alkene Isomerization as an Enabling Technology in Tandem, Sequential and Domino Processes. *Chemical Society Reviews* **2021**, *50* (2), 1391–1406. https://doi.org/10.1039/D0CS00449A.
- (47) Larionov, E.; Li, H.; Mazet, C. Well-Defined Transition Metal Hydrides in Catalytic Isomerizations. *Chem. Commun.* **2014**, *50* (69), 9816–9826. https://doi.org/10.1039/C4CC02399D.
- (48) Gensow), M.-N. B. (née; Freixa, Z.; Leeuwen, P. W. N. M. van. Bite Angle Effects of Diphosphines in C–C and C–X Bond Forming Cross Coupling Reactions. *Chem. Soc. Rev.* 2009, 38 (4), 1099–1118. https://doi.org/10.1039/B806211K.
- (49) Marcone, J. E.; Moloy, K. G. Kinetic Study of Reductive Elimination from the Complexes (Diphosphine)Pd(R)(CN). J. Am. Chem. Soc. **1998**, 120 (33), 8527–8528. https://doi.org/10.1021/ja980762i.
- (50) Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. Wide Bite Angle Diphosphines: Xantphos Ligands in Transition Metal Complexes and Catalysis. Acc. Chem. Res. 2001, 34 (11), 895–904. https://doi.org/10.1021/ar000060+.
- (51) Garhwal, S.; Kaushansky, A.; Fridman, N.; de Ruiter, G. Part per Million Levels of an Anionic Iron Hydride Complex Catalyzes Selective Alkene Isomerization via Two-State Reactivity. *Chem Catalysis* 2021, 1 (3), 631– 647. https://doi.org/10.1016/j.checat.2021.05.002.