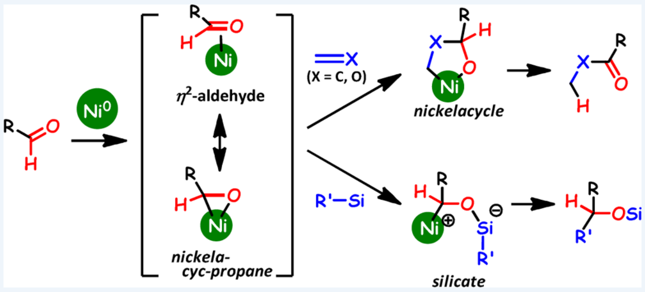
ACCOUNTS
of chemical research

Catalytic Transformation of Aldehydes with Nickel Complexes through η^2 Coordination and Oxidative Cyclization

Published as part of the Accounts of Chemical Research special issue "Earth Abundant Metals in Homogeneous Catalysis".

Yoichi Hoshimoto,[†,‡] Masato Ohashi,[†] and Sensuke Ogoshi*[,†,§]

[†]Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan
[‡]Frontier Research Base for Global Young Researchers, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan
[§]ACT-C, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan



CONSPECTUS: Chemists no longer doubt the importance of a methodology that could activate and utilize aldehydes in organic syntheses since many products prepared from them support our daily life. Tremendous effort has been devoted to the development of these methods using main-group elements and transition metals. Thus, many organic chemists have used an activator−(aldehyde oxygen) interaction, namely, η^1 coordination, whereby a Lewis or Brønsted acid activates an aldehyde. In the field of coordination chemistry, η^2 coordination of aldehydes to transition metals by coordination of a carbon−oxygen double bond has been well-studied; this activation mode, however, is rarely found in transition-metal catalysis. In view of the distinctive reactivity of an η^2-aldehyde complex, unprecedented reactions via this intermediate are a distinct possibility.

In this Account, we summarize our recent results dealing with nickel(0)-catalyzed transformations of aldehydes via η^2-aldehyde nickel and oxanickelacycle intermediates. The combination of electron-rich nickel(0) and strong electron-donating N-heterocyclic carbene (NHC) ligands adequately form η^2-aldehyde complexes in which the aldehyde is highly activated by back-bonding. With Ni(0)/NHC catalysts, processes involving intramolecular hydroacylation of alkenes and homo/cross-dimerization of aldehydes (the Tishchenko reaction) have been developed, and both proceed via the simultaneous η^2 coordination of aldehydes and other π components (alkenes or aldehydes). The results of the mechanistic studies are consistent with a reaction pathway that proceeds via an oxanickelacycle intermediate generated by the oxidative cyclization with a nickel(0) complex. In addition, we have used the η^2-aldehyde nickel complex as an effective activator for an organosilane in order to generate a silicate reactant. These reactions show 100% atom efficiency, generate no wastes, and are conducted under mild conditions.

1. INTRODUCTION

Aldehydes are among the most important carbonyl compounds. They are frequently used as a key component in organic synthesis via activation of the formyl group.[1] A number of methods have been developed whereby aldehydes are activated via coordination to typical and transition metals. An η^1 coordination of the formyl oxygen to Lewis acidic metals is accepted as a particularly important method.[1] The electrophilicity at the formyl carbon is enhanced via this η^1 coordination, which promotes the addition of a variety of nucleophiles to aldehydes. The oxidative addition of the C−H bond of a carbonyl group to a metal center is a key step for some catalytic transformations of aldehydes, and η^1 coordination has often been proposed as the preliminary step.[2] The η^2 coordination of aldehydes is rarely found in homogeneous transition-metal catalysis,[3−5] however, even though many examples of η^2-aldehyde complexes have been reported in the field of coordination chemistry.[1d,e,6] Both the formyl oxygen and carbon demonstrate nucleophilic reactivity with the contribution of an oxametallacyclopropane resonance form,[4a,b,7] which has enhanced interest in the reactivity of η^2-aldehyde complexes.

In order to generate a η^2-aldehyde complex as an intermediate in transition-metal catalysis, the choice of a catalyst is critical since strong back-donation from the catalyst metal center to the η^2-aldehyde ligand is essential in stabilizing such an intermediate. On the basis of this aspect, the combination of an electron-rich transition metal and a strong electron-donating ligand would be ideal to generate an η^2-aldehyde intermediate in transition-metal catalysis. Nickel(0) is a promising candidate since several reports on the isolation of (η^2-aldehyde)Ni(PR$_3$)$_2$ complexes[6] and on the nickel(0)-catalyzed intermolecular addition of organometallic reagents to aldehydes via η^2-aldehyde nickel(0) intermediates have been reported.[3a−f] In addition, aldehydes

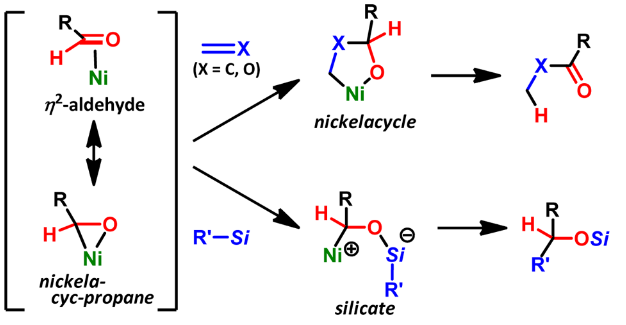
Received: February 3, 2015
Published: May 8, 2015

DOI: 10.1021/acs.accounts.5b00061
Acc. Chem. Res. 2015, 48, 1746−1755

and unsaturated compounds such as alkenes, alkynes, dienes, and allenes are known to simultaneously coordinate to nickel(0).[4,5] Oxidative cyclization then takes place to provide an oxanickelacycle with the formation of C−C, C−Ni, and O−Ni bonds. Oxanickelacycles have often been proposed as key intermediates in nickel(0)-catalyzed multicomponent coupling reactions.[5a,d] These oxanickelacycles possess a β-hydrogen that is derived from the aldehyde. Thus, we envisioned the development of the catalytic transformation of aldehydes via β-hydrogen elimination from the oxanickelacycle intermediates.[4g,8]

In this Account, we summarize our recent results dealing with nickel(0)-catalyzed transformations of aldehydes via η^2-aldehyde nickel and oxanickelacycle intermediates (Scheme 1). All of these reactions can be carried out with 100% atom efficiency under conditions that are milder than those for previously developed catalytic systems using 4d and 5d metals. The results of mechanistic studies that include stoichiometric reactions and kinetic studies will be presented as well.

Scheme 1. Catalytic Transformations of Aldehydes via η^2-Aldehyde Nickel (or Nickelacyclopropane) and Nickelacycle Intermediates Described in this Account



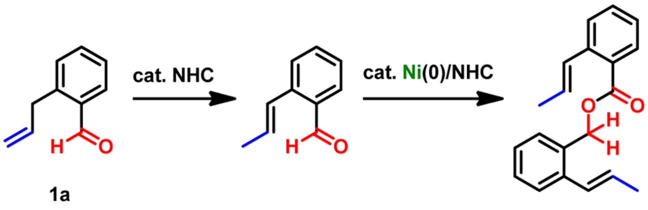
2. INITIAL FINDINGS

In 2004, we reported the stoichiometric reaction of *o*-allylbenzaldehyde (**1a**) with $Ni(cod)_2$ and PCy_3 to give (η^2:η^2-$CH_2{=}CHCH_2C_6H_4CHO)Ni(PCy_3)$ followed by the formation of a dimeric oxanickelacycle complex.[4a] This was the first direct observation of the oxidative cyclization of η^2-aldehyde and η^2-alkene ligands on Ni(0). Thermolysis of this nickelacycle complex at 130 °C proceeded to completion for 24 h, giving a complicated mixture including 2-methylindanone (**2a**) in 35% yield. These results convinced us that we could develop a nickel-catalyzed intramolecular hydroacylation proceeding via an oxanickelacycle intermediate.

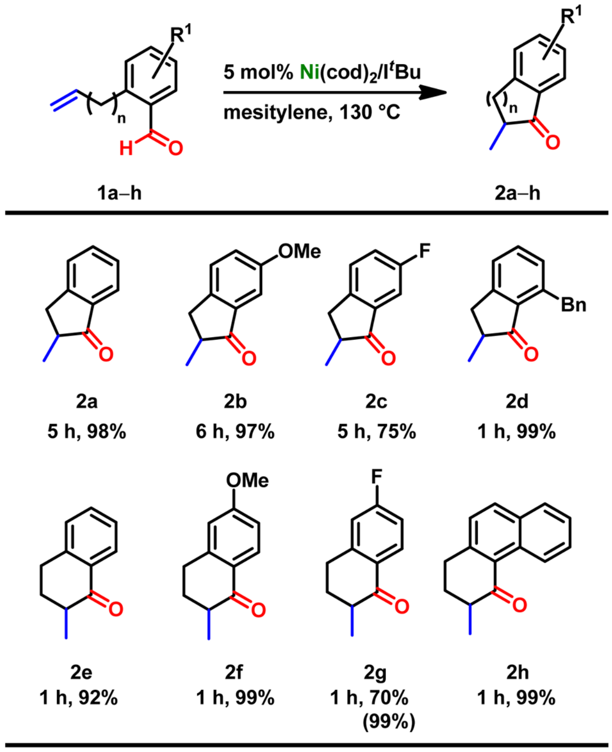
3. NI(0)-CATALYZED INTRAMOLECULAR ALKENE HYDROACYLATION

There would be obvious merits of developing a novel hydroacylation system that proceeds via an oxanickelacycle intermediate. First, unfavorable decarbonylation from an acylmetal intermediate, which could be generated via oxidative addition of a formyl group to the catalyst,[2b,9] can be avoided since the target Ni system would proceed without the generation of an acylnickel intermediate.[10] Decarbonylation is an inevitable side reaction in most of the reported catalyst systems with Pd and Rh,[11] which causes a decrease in atom efficiency and deactivation of the catalyst via a coordination with carbon monoxide. Second, the nickel-catalyzed synthesis of benzocyclic ketones, the structural motifs of which appear in the synthetic intermediates of numerous biologically active natural products and medicinal agents, represents a highly environmentally favorable route (100% atom efficiency, neutral conditions, and no waste). Thus, we began optimizing the reaction conditions for the nickel(0)-catalyzed intramolecular hydroacylation; however, despite the almost total consumption of **1a** when a variety of tertiary phosphine ligands and *N*-aryl-substituted N-heterocyclic carbenes (NHCs) were employed, complicated mixtures including a slight amount of **2a** (∼30%) were obtained.[4c] Major problems for the Ni(0)/*N*-aryl-NHC systems included an NHC-catalyzed 1,3-hydride shift followed by the dimerization of aldehydes, giving a benzyl ester (Scheme 2). Fortunately, these observations gave us an opportunity to develop the nickel-catalyzed dimerization of aldehydes—the Tishchenko reaction (vide infra).[4e] Employing *N*-alkyl-substituted NHCs was effective in suppressing the 1,3-hydride shift, and **2a** was finally formed in 98% isolated yield in the presence of 5 mol % $Ni(cod)_2$/1,3-di-*tert*-butylimidazol-2-ylidene (I^tBu) in mesitylene (130 °C, 5 h). Under these conditions, a variety of 1-indanone derivatives **2a−d** were prepared in excellent yields (Scheme 3). Furthermore, this

Scheme 2. NHC-Catalyzed Isomerization of 5-Enal to 4-Enal Followed by Dimerization to Give a Benzyl Ester



Scheme 3. Ni(0)-Catalyzed Intramolecular Alkene Hydroacylation[a]

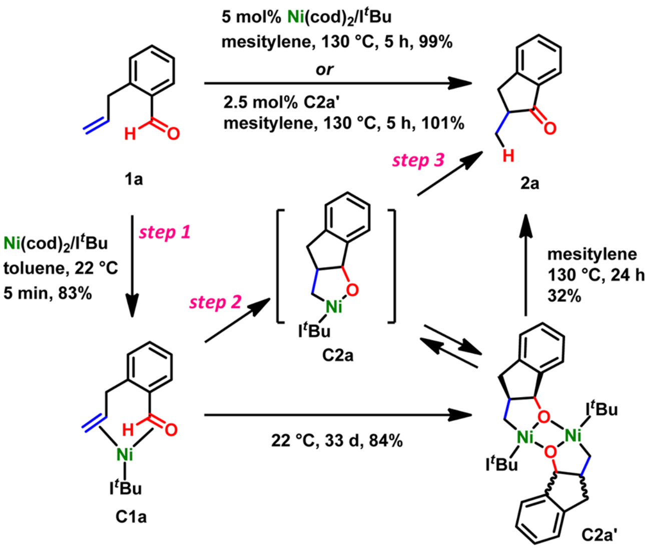


[a] Isolated yields are given. The GC yield of **2g** is given in parentheses.

nickel-catalyzed system could be applied to the synthesis of 1-tetralone derivatives **2e−h**, which were difficult to prepare in the reported transition-metal-catalyzed alkene hydroacylation without introducing chelation assistance.[12] Decarbonylation was not observed in any of the reactions shown in Scheme 3.

Stoichiometric reactions were conducted in order to gain deeper insight into the reaction mechanism (Scheme 4). The reaction of **1a** with Ni(cod)$_2$ and I^{t}Bu in toluene at 22 °C gave $(\eta^2{:}\eta^2\text{-CH}_2{=}\text{CHCH}_2\text{C}_6\text{H}_4\text{CHO})\text{Ni}(\text{I}^t\text{Bu})$ (**C1a**) quantitatively within 5 min, and **C1a** was isolated in 83% yield. The dimeric oxanickelacycle **C2a′** was obtained in 84% isolated yield from **C1a**, probably through dimerization of the monomeric complex **C2a**, which was not observed by NMR spectroscopy. The structure of **C2a′** in solution was unambiguously identified by NMR spectroscopy as a mixture of two isomers, **C2a′-*syn*** and **C2a′-*anti***. The molecular structure of **C2a′-*anti*** was unambiguously confirmed by X-ray analysis (Figure 1). Thermolysis of **C2a′** at 130 °C for 24 h resulted in the production of **2a** in 32% yield (32% conversion). In addition, in the presence of 2.5 mol % **C2a′**, **2a** was obtained in 101% yield from both **1a** and **C2a′** (the maximal yield of **2a** was 105%) within 5 h. On the basis of these results, the dimerization of **C2a** has no significant influence on the catalytic efficiency under the catalytic reaction conditions.

Scheme 4. Stoichiometric Reactions with 1a and Proposed Reaction Pathways



A plausible reaction mechanism is as follows (Scheme 4). Coordination of **1** to Ni(0)/I^{t}Bu gives rise to (η^2:η^2-enal)nickel complex **C1** (step 1), and then oxidative cyclization takes place to yield the monomeric nickelacycle intermediate **C2** (step 2). Next, β-hydride elimination and reductive elimination occur to give cyclic ketone **2** with regeneration of the catalyst (step 3).

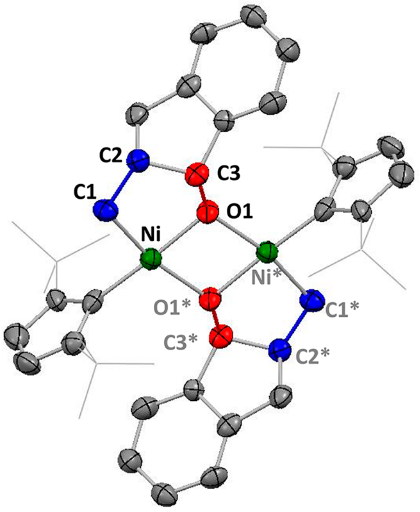


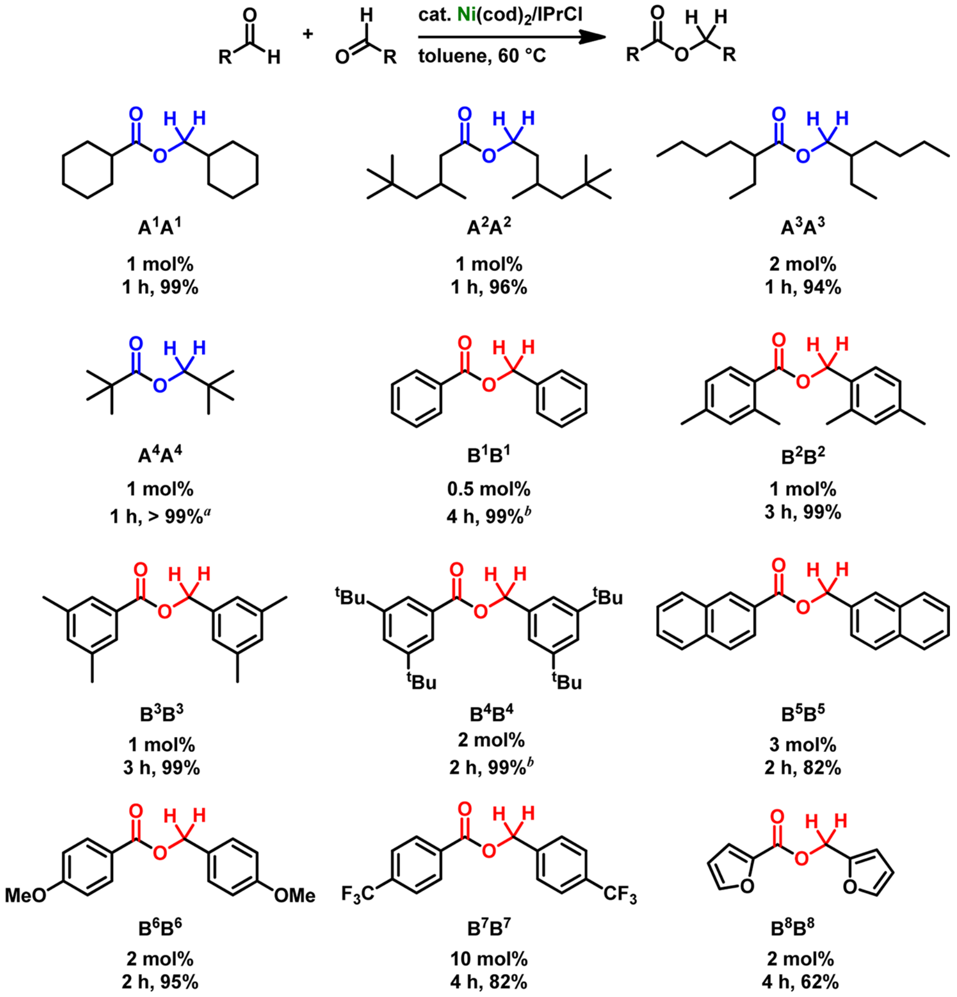
Figure 1. Molecular structure of **C2a′-*anti*** (CCDC 892817) with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ni−O1 1.883(6), Ni−C1 1.918(6), C2−C10 1.883(6). Selected bond angles (deg): C1−Ni−O1 87.6(3), O1*−Ni−C11 103.1(3), C1−Ni−C11 89.6 (4), O1−Ni−O1* 79.7(2).

4. NI(0)-CATALYZED HOMODIMERIZATION OF ALDEHYDES TO GIVE ESTERS (THE TISHCHENKO REACTION)

During the course of our study of nickel-catalyzed alkene hydroacylation, we found that a Ni(0)/NHC complex could efficiently catalyze the dimerization of aldehydes to give esters. The synthesis of esters via the dimerization of aldehydes is known as the Tishchenko reaction.[13] Because of its high atom-efficiency and environmentally favorable reaction conditions (neutral and mild), the Tishchenko reaction is among the most important methods to prepare esters; however, unsolved challenges remain. For example, there are few catalysts applicable to the Tishchenko reaction of both aliphatic and aromatic aldehydes.[13b,14] When this work was begun, we noticed a difference between the reaction mechanisms of the reported systems and our nickel systems. The reported systems are classified into two categories on the basis of the reaction mechanism: (i) Lewis acid-catalyzed reactions via η^1-aldehyde metal complexes and (ii) late-transition-metal-catalyzed hydroacylation of aldehydes via C−H bond activation.[13a,b,15] In these mechanisms, two aldehydes react with the catalyst in a *step-by-step* manner. By contrast, the mechanism of the nickel(0)-catalyzed reaction is supposed to involve two aldehyde molecules that *simultaneously* react with the catalyst, i.e., the reaction proceeds via a bis(η^2-aldehyde)nickel intermediate, the formation of which was eventually confirmed by NMR analysis (vide infra).[16] Thus, we envisioned that the reactivity of the bis(η^2-aldehyde)nickel intermediate would be quite sensitive to the environment surrounding the formyl group of the aldehyde. In fact, the catalyst Ni(0)/1,3-bis(2,6-diisopropylphenyl)-4,5-dichloroimidazol-2-ylidene (IPrCl) was applied to the Tishchenko reaction of various aliphatic (**A**) and aromatic (**B**) aldehydes to give the corresponding esters (**AA** and **BB**) in excellent yields (Scheme 5). Again, decarbonylation was not observed in the presented reactions, while the reported transition-metal-catalyzed Tishchenko reaction, which took place via acylmetal intermediates, suffered from decarbonylation.[15]

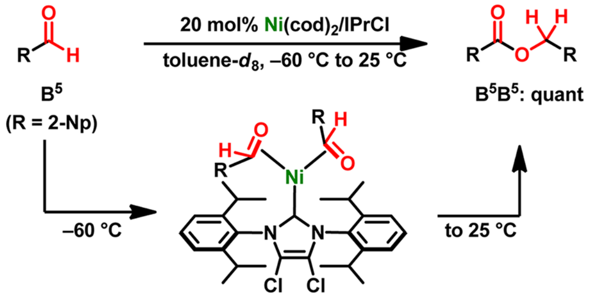
In the presence of Ni(cod)$_2$/IPrCl (20 mol %), the Tishchenko reaction of **B**^{5} was monitored by NMR spectroscopy (Scheme 6). At −60 °C, the resonances of the formyl hydrogen and carbon ligated to nickel(0) were observed at δ_H 4.7 in the ^{1}H NMR spectrum and δ_C 109.3 in the ^{13}C NMR spectrum, respectively, which shows that **B**^{5} coordinates to the nickel(0) center in the η^2 mode. The ratio of the integrations of the formyl hydrogen and the isopropyl group of IPrCl indicates that two aldehyde molecules coordinate to the nickel(0) center. The

Scheme 5. Ni(0)-Catalyzed Tishchenko Reaction



Isolated yields are shown, unless otherwise noted. [a]GC yield. [b]The reaction was run at 80 °C.

Scheme 6. Formation of Bis(η^2-B^5)Ni(IPrCl) As Confirmed by NMR Analysis



reaction mixture was allowed to warm to 25 °C to quantitatively give the corresponding ester.

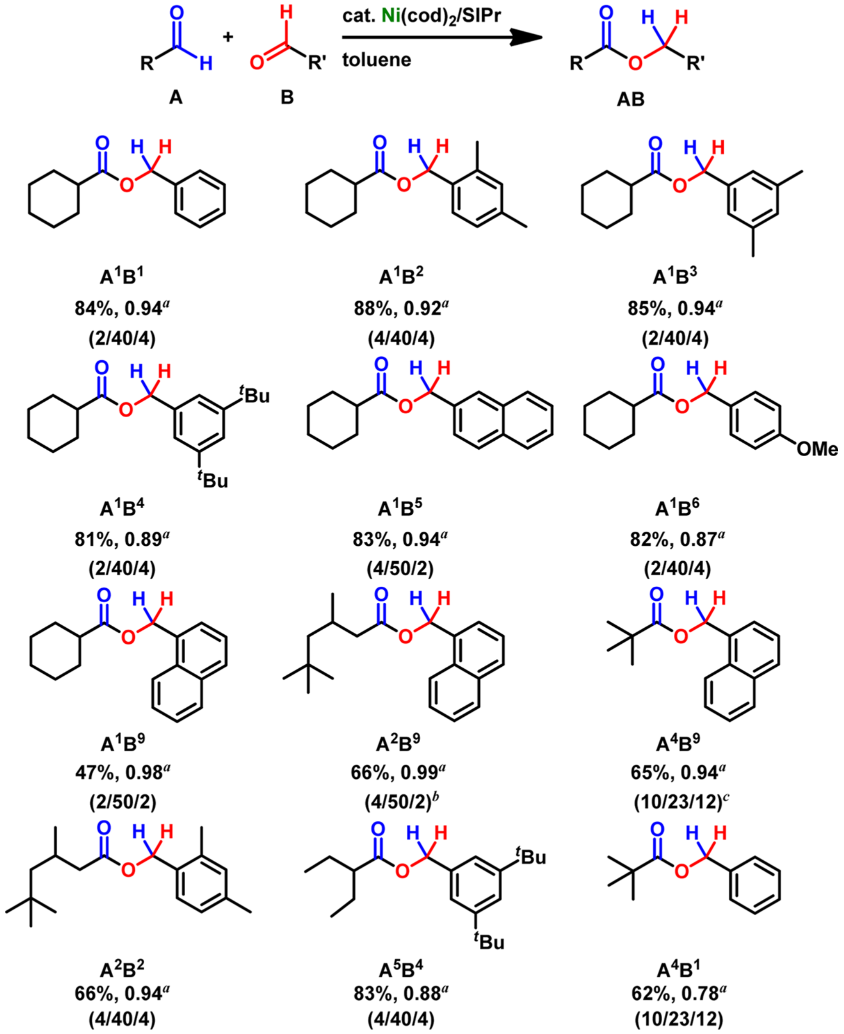
5. NI(0)-CATALYZED CROSS-DIMERIZATION OF AROMATIC AND ALIPHATIC ALDEHYDES TO GIVE BENZYL ESTERS (THE CROSSED TISHCHENKO REACTION)

Why has the Tishchenko reaction not been regarded as a common method to prepare esters despite a successful history of more than 120 years? One answer may involve the versatility of the reaction: before 2010, the reported catalyst was difficult to apply in the selective crossed Tishchenko reaction of two different aldehydes (**A** and **B**) to prepare a single cross-coupled ester selectively from among the four possible esters: two cross-coupled products (**AB** and **BA**) and two homocoupled products (**AA** and **BB**).[13c,17] Since the Tishchenko reaction is an ideal method for ester synthesis, the development of a new catalyst that can discriminate between two different aldehydes has been a long-term goal in the development of a selective crossed Tishchenko reaction.[18−20]

To our delight, we achieved the first selective crossed Tishchenko reaction of aliphatic and aromatic aldehydes using a Ni(0)/1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (SIPr) catalyst system.[4d] In the presence of a catalytic amount of $Ni(cod)_2$ and SIPr, the crossed Tishchenko reaction of an aliphatic aldehyde **A** with an equimolar amount of an aromatic aldehyde **B** proceeded in a highly selective manner to yield the cross-coupled ester **AB** as almost a single product (Scheme 7), as shown by the values of the selectivity, defined as **AB**/(**AB** + **BA** + **AA** + **BB**). This reaction can be applied to a variety of aliphatic aldehyde (1°, 2°, and *cyc*-2°) and aromatic aldehyde combinations. In particular, the reaction with naphthaldehyde derivatives (B^5 and B^9) produced excellent selectivity (>0.94). In some cases using B^9, the ligand was changed to 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) or 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes). A significant de-

DOI: 10.1021/acs.accounts.5b00061
Acc. Chem. Res. 2015, 48, 1746−1755

Scheme 7. Ni(0)-Catalyzed Crossed Tishchenko Reaction of Aliphatic Aldehydes (A) with Aromatic Aldehydes (B)



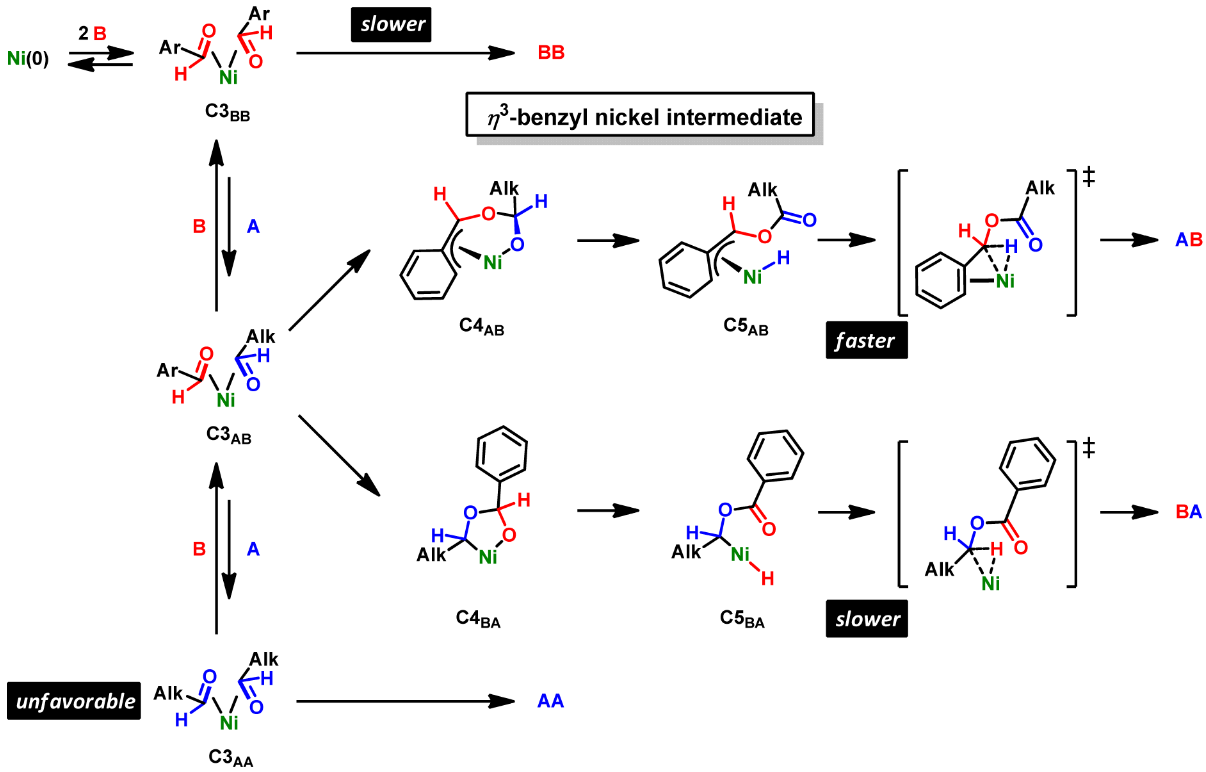
Isolated yields are given. Reaction conditions in the following order are shown in parentheses: catalyst loading (mol %)/temperature (°C)/time (h). ^{a}Selectivity = **AB**/(**AB** + **BA** + **AA** + **BB**). ^{b}IPr was used. ^{c}IMes was used.

crease in selectivity was observed in the reaction of **A^4** with benzaldehyde derivatives, while **A^{4}B^9** was obtained selectively. The reaction of two different aliphatic or two different aromatic aldehydes was examined; however, it was difficult to prepare a single cross-coupled ester selectively under the presented reaction conditions.[19] It is noteworthy that the aliphatic aldehyde **A** tends to become the carboxylic acid part of the ester while the aromatic aldehyde **B** becomes the alcohol part.[17] The advantage of this catalyst system is its simplicity in the isolation of the cross-coupled ester **AB**. In most cases, **AB** can be isolated from the reaction mixture by simple distillation.

Plausible reaction pathways for the production of the four esters are shown in Scheme 8. This proposal was based on the following experimental results: (i) the reaction exhibits a zeroth-order dependence upon both the aliphatic and aromatic aldehydes and a first-order dependence upon the Ni(0)/SIPr catalyst; (ii) a primary kinetic isotope effect (KIE) was observed for the aliphatic aldehyde and a normal secondary KIE for the aromatic aldehyde; (iii) the formation of the bis(η^2-aromatic aldehyde)nickel(SIPr) complex, **C3$_{\mathbf{BB}}$**, was observed at −60 °C by NMR analysis under the crossed Tishchenko conditions; (iv) the homodimerization reaction of aliphatic aldehydes was much faster than that of the aromatic aldehydes under Ni(0)/SIPr catalysis; and (v) decarbonylation was not observed. On the basis of these results, we surmised that the reaction proceeds via a nickelacycle intermediate and that reductive elimination would be involved in the rate-limiting step. For the predominant formation of **AB** over **BA**, the coordination of an aryl group to nickel could play a key role, which would stabilize **C4$_{\mathbf{AB}}$** and **C5$_{\mathbf{AB}}$** compared with **C4$_{\mathbf{BA}}$** and **C5$_{\mathbf{BA}}$** by forming an η^3-benzylnickel complex. The effective formation of an η^3-benzylnickel complex was reported by employing **B^9**,[4b] which rationalized that the crossed Tishchenko reaction with **B^9** exhibited a significantly high degree of selectivity (Scheme 6). We cannot exclude the possibility that the reaction proceeds via an acylnickel intermediate, which was proposed as a more favorable pathway by density functional theory (DFT) calculations using simplified models.[21]

After our report, a highly selective thiolate-catalyzed crossed Tishchenko reaction of two aromatic aldehydes was reported in 2012 by Connon et al.,[19] which also promoted the development of the crossed Tishchenko reaction. Further studies should establish a waste-free route to a variety of ester compounds via the Tishchenko reaction.

Scheme 8. Plausible Mechanism for the Ni(0)-Catalyzed Crossed Tishchenko Reaction



6. NI(0)-CATALYZED SYNTHESIS OF BENZOXASILOLES

In a communication published in 2004 (see section 2),[4a] we also reported the seeds of our later work, i.e., the electrophilic addition of Me_3SiOTf to (η^2-PhCHO)Ni(PCy_3)$_2$ to give (η^1:η^1-$Me_3SiOCH(Ph)$)Ni(PCy_3)OTf. This result showed that η^2-aldehyde nickel complexes are sufficiently reactive toward organosilicon compounds. Thus, we envisioned the generation of a reactive silicate that could be triggered by the activation of an aldehyde via back-donation from an electron-rich nickel(0) complex, and we believed that this could be applied to organic synthesis. Very recently, this was successfully applied to the highly efficient syntheses of 3-aryl-, 3-vinyl-, and 3-alkynyl-2,1-benzoxasiloles (**4a**−**l**) from benzaldehydes with aryl-, vinyl-, and alkynylsilyl groups, respectively, at the ortho position (**3a**−**l**) (Scheme 9).[4h] For the synthesis of 3-aryl-2,1-benzoxasiloles **4a**−**h**, a 1:1 mixture of Ni(cod)$_2$ and IPr was effective, while production of the corresponding vinylbenzoxasiloles (**4i**−**k**) was totally hampered under the same conditions as a result of the qunatitative formation of (η^2:η^2-$CH_2{=}CHSi(Me)_2C_6H_4CHO$)-Ni(IPr). After optimization of the reaction conditions, **4i**−**k** were obtained in high yields by employing 2 mol % Ni(cod)$_2$ and 4 mol % IPr in THF at 60 °C (Scheme 9). In addition, 3-alkynyl-2,1-benzoxasilole **4l** was also obtained in 95% yield under the same reaction conditions. To the best of our knowledge, this is the first report of the synthesis of 3-vinyl- and 3-alkynyl-2,1-benzoxasiloles.

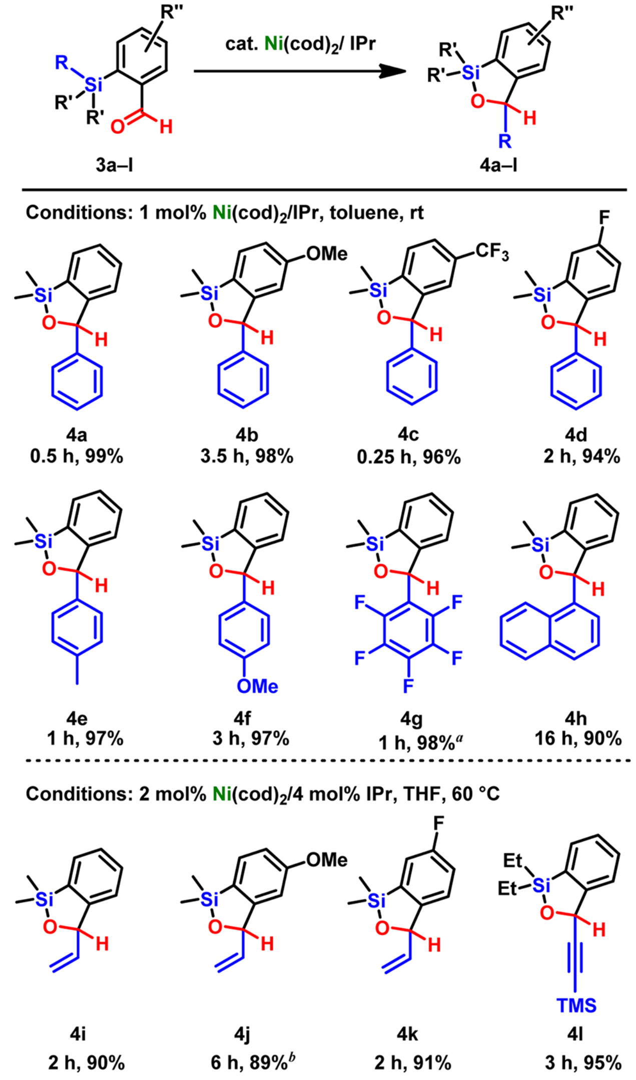
The reaction mechanism remains unclear, but the following steps would be involved. Coodination of an aldehyde moiety to Ni(0) gives rise to the formation of an η^2-aldehyde nickel intermediate. As its resonance form, the contribution of an oxanickelacycle complex should be considered. This coordination activates the aldehyde as a nucleophile that continuously activates the silicon via an intramolecular addition reaction, giving a silicate intermediate. Then an intermolecular aryl transfer takes place to give the product. The following results support this proposal. First, the stoichiometric reaction of **3b** and (η^6-toluene)Ni(IPr) in toluene-d_8 at −50 °C afforded the oxanickelacyclopropane complex **C6** in 74% yield (Scheme 10a), where (η^6-toluene)Ni(IPr) was prepared from Ni(cod)$_2$ and IPr in the presence of H_2 in toluene.[22] The formation of **C6** was confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR analyses. In the ^{1}H and ^{13}C NMR spectra, the resonances of the carbonyl hydrogen and carbon were observed at δ_H 5.90 and δ_C 86.1, respectively, both of which are shifted upfield compared with those of **3b** (δ_H 9.60 and δ_C 192.4). In addition, the methyl groups on Si in **C6** were observed as two diastereotopic peaks because of the formation of a chiral carbon center ligated to the nickel (**C6**: δ_H 0.52 (s, 3H), 0.46 (s, 3H); δ_C −0.1, −0.5. **3b**: δ_H 0.59 (s, 6H); δ_C −1.2). In the ^{29}Si NMR spectrum, the resonance of **C6** was observed at −8.8 ppm, which was slightly shifted from the peak at −7.6 ppm for **3b**. Second, a crossover experiment using **3b** and **3f** gave four benzoxasiloles in similar yields: **4b**, **4f**, and the two crossover products **4a** and **4m** (Scheme 10b). An exchange of the aryl groups between **3b** and **3f** was not observed during the reaction. In addition, no aryl exchange reaction between **4b** and **4f** was observed when the isolated **4b** and **4f** were subjected to the reaction conditions. These results would support the proposal that an intermolecular aryl transfer process is involved in this reaction.

We are now conducting detailed mechanistic studies of this nickel catalysis along with the expansion of the reaction to asymmetric variants. These results will be reported in the near future.

7. CONCLUSIONS

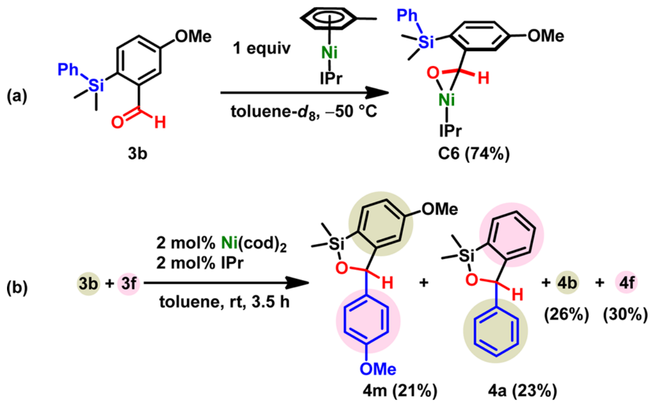
We have described recent achievements in the catalytic transformation of aldehydes via η^2 coordination to nickel(0).

Scheme 9. Ni(0)-Catalyzed Synthesis of Benzoxasiloles



Isolated yields are given. ^{a}4 mol % Ni(cod)$_2$/IPr was used. ^{b}1 mol % Ni(cod)$_2$ and 2 mol % IPr were used.

Scheme 10. (a) Stoichiometric Reaction of 3b with (η^6-Toluene)Ni(IPr); (b) Crossover Experiment with 3b and 3f



The choice of a catalyst was a key. The combination of electron-rich nickel(0) and strong electron-donating NHC ligands was adequate because the aldehydes are highly activated by the strong back-bonding from the Ni(0)/NHC catalyst. This activated aldehyde moiety in the η^2-aldehyde nickel complex was utilized as an effective activator for an organosilane in order to generate a silicate reactant.

By the use of the Ni(0)/NHC catalyst, the intramolecular hydroacylation of alkenes and the homo/cross-dimerization of aldehydes were developed for the first time. These reactions proceed via (η^2-aldehyde)(η^2-alkene)nickel(0) or bis(η^2-aldehyde)nickel(0) complexes, respectively, which was unambiguously confirmed by stoichiometric and kinetic experiments. Furthermore, the results of the mechanistic studies were consistent with reaction pathways involving the nickelacycle complexes.

All of these reactions feature 100% atom efficiency, generate no wastes, and can be conducted under neutral conditions. Thus, these reactions would be regarded as environmentally favorable methods to transform aldehydes. We are hopeful that the presented reactions will help introduce new strategies for the catalytic transformation of aldehydes and contribute to further progress in this field of chemistry.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ogoshi@chem.eng.osaka-u.ac.jp.

Notes

The authors declare no competing financial interest.

Biographies

Yoichi Hoshimoto received his M.Sc. and Ph.D. from Osaka University under the supervision of Professor Sensuke Ogoshi in 2013. He then joined the Frontier Research Base for Global Young Researchers at Osaka University as a tenure-track assistant professor. His recent research interests include homogeneous catalysis with organometallic complexes and Lewis acid−base chemistry.

Masato Ohashi received his Ph.D. from Tokyo Institute of Technology under the supervision of Professor Hiroharu Suzuki in 2003. After joining the research group of Kazushi Mashima at Osaka University as a JST Postdoctoral Fellow, he moved to Aachen in 2006, where he was a Humboldt Research Follow with Jun Okuda (RWTH-Aachen). In 2007, he joined the Ogoshi group at Osaka University as an assistant professor. In 2012, he was appointed as an associate professor at Osaka University. His current research interests include transition-metal-catalyzed transformation reactions of organofluorine compounds as well as their mechanistic investigation.

Sensuke Ogoshi studied at Osaka University and received his Ph.D. under the supervision of Professor Shinji Murai in 1993. In that year he joined the faculty at Osaka University as an assistant professor. He was promoted to associate professor in 1999 and has been a full professor since 2007. In the meantime, he also pursued his academic career at the University of Alberta during 1996−1997, where he joined the research group of Professor Jeffrey M. Stryker (JSPS Fellowships for Research Abroad). His research is directed toward the discovery of new transition-metal complexes that can act as key reaction intermediates in new transformation reactions of unsaturated compounds. In addition, he has been focusing on the correlation between structure and reactivity of organotransition-metal complexes.

■ ACKNOWLEDGMENTS

We are indebted to our colleagues whose experimental and intellectual contributions constitute the work described in this Account. These works were supported by MEXT, ACT-C, and the Frontier Research Base for Global Young Researchers at Osaka University.

■ REFERENCES

(1) (a) Shambayati, S.; Schreiber. S. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. *1*, Chapter 1. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley-Interscience: New York, 2003. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition-Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. Also see: (d) Huang, Y.-H.; Gladysz, J. A. Aldehyde and Ketone Ligands in Organometallic Complexes and Catalysis. *J. Chem. Educ.* **1988**, *65*, 298−303. (e) Schuster, D. M.; White, P. S.; Templeton, J. L. *p*-Anisaldehyde as a Ligand in Molybdenum and Tungsten Complexes: σ or π? *Organometallics* **1996**, *15*, 5467−5469 and references therein.

(2) (a) Garralda, M. A. Aldehyde C−H activation with late transition metal organometallic compounds. Formation and reactivity of acyl hydrido complexes. *Dalton Trans.* **2009**, 3635−3645. (b) Fristrup, P.; Kreis, M.; Palmelund, A.; Norrby, P.-O.; Madsen, R. The Mechanism for the Rhodium-Catalyzed Decarbonylation of Aldehydes: A Combined Experimental and Theoretical Study. *J. Am. Chem. Soc.* **2008**, *130*, 5206−5215. Also see references cited in ref 11.

(3) For selected examples of Ni catalysis, see: (a) Takahashi, G.; Shirakawa, E.; Tsuchimoto, T.; Kawakami, Y. Alkynes as activators in the nickel-catalysed addition of organoboronates to aldehydes. *Chem. Commun.* **2005**, 1459−1461. (b) Hirano, K.; Yorimitsu, H.; Oshima, K. Nickel-catalysed reactions with trialkylboranes and silacyclobutanes. *Chem. Commun.* **2008**, 3234−3241. (c) Arao, T.; Kondo, K.; Aoyama, T. Nickel-catalyzed 1,2-addition of arylboroxines to aromatic aldehydes. *Tetrahedron Lett.* **2007**, *48*, 4115−4117. (d) Bouffard, J.; Itami, K. A Nickel Catalyst for the Addition of Organoboronate Esters to Ketones and Aldehydes. *Org. Lett.* **2009**, *11*, 4410−4413. (e) Sakurai, F.; Kondo, K.; Aoyama, T. Et-duphos-nickel-catalyzed asymmetric arylation of benzaldehyde derivatives bearing an *ortho*-Me_2PhSi group with potassium aryltriolborates. *Tetrahedron Lett.* **2009**, *50*, 6001−6003. (f) Biswas, K.; Prieto, O.; Goldsmith, P. J.; Woodward, S. Remarkably Stable $(Me_3Al)_2 \cdot$DABCO and Stereoselective Nickel-Catalyzed AlR_3 (R = Me, Et) Additions to Aldehydes. *Angew. Chem., Int. Ed.* **2005**, *44*, 2232−2234. For recent examples of Cu catalysis and related works, see: (g) Kubota, K.; Yamamoto, E.; Ito, H. Copper(I)-Catalyzed Enantioselective Nucleophilic Borylation of Aldehydes: An Efficient Route to Enantiomerically Enriched α-Alkoxyorganoboronate Esters. *J. Am. Chem. Soc.* **2015**, *137*, 420−424. (h) Bertz, S. H.; Hardin, R. A.; Ogle, C. A. Aldehydes and Ketones Form Intermediate π Complexes with the Gilman Reagent, Me_2CuLi, at Low Temperatures in Tetrahydrofuran. *J. Am. Chem. Soc.* **2013**, *135*, 9656−9658. (i) Zhao, H.; Dang, L.; Marder, T. B.; Lin, Z. DFT Studies on the Mechanism of the Diboration of Aldehydes Catalyzed by Copper(I) Boryl Complexes. *J. Am. Chem. Soc.* **2008**, *130*, 5586−5594.

(4) For selected examples of our contributions in this field, see: (a) Ogoshi, S.; Oka, M.-A.; Kurosawa, H. Direct Observation of Oxidative Cyclization of η^2-Alkene and η^2-Aldehyde on Ni(0) Center. Significant Acceleration by Addition of Me_3SiOTf. *J. Am. Chem. Soc.* **2004**, *126*, 11802−11803. (b) Ogoshi, S.; Kamada, H.; Kurosawa, H. Reaction of (η^2-arylaldehyde)nickel(0) complexes with Me_3SiX (X=OTf, Cl). Application to catalytic reductive homocoupling reaction of arylaldehyde. *Tetrahedron* **2006**, *62*, 7583−7588. (c) 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. *Angew. Chem., Int. Ed.* **2012**, *51*, 10812−10815. (d) Hoshimoto, Y.; Ohashi, M.; Ogoshi, S. Nickel-Catalyzed Selective Conversion of Two Different Aldehydes to Cross-Coupled Esters. *J. Am. Chem. Soc.* **2011**, *133*, 4668−4671. (e) Ogoshi, S.; Hoshimoto, Y.; Ohashi, M. Nickel-catalyzed Tishchenko reaction *via* hetero-nickelacycles by oxidative cyclization of aldehydes with nickel(0) complex. *Chem. Commun.* **2010**, *46*, 3354−3356. (f) Ohashi, M.; Saijo, H.; Arai, T.; Ogoshi, S. Nickel(0)-Catalyzed Formation of Oxaaluminacyclopentenes via an Oxanickelacyclopentene Key Intermediate: Me_2AlOTf-Assisted Oxidative Cyclization of an Aldehyde and an Alkyne with Nickel(0). *Organometallics* **2010**, *29*, 6534−6540. (g) Ogoshi, S.; Arai, T.; Ohashi, M.; Kurosawa, H. Nickeladihydrofuran. Key intermediate for nickel-catalyzed reaction of alkyne and aldehyde. *Chem. Commun.* **2008**, 1347−1349. (h) Hoshimoto, Y.; Yabuki, H.; Kumar, R.; Suzuki, H.; Ohashi, M.; Ogoshi, S. Highly Efficient Activation of Organosilanes with η^2-Aldehyde Nickel Complexes: Key for Catalytic Syntheses of Aryl-, Vinyl-, and Alkynyl-Benzoxasiloles. *J. Am. Chem. Soc.* **2014**, *136*, 16752−16755.

(5) Ni-catalyzed reactions via simultaneous η^2 coordination of aldehydes and other π components have been reported. For reviews, see: (a) Montgomery, J. Nickel-Catalyzed Reductive Cyclizations and Couplings. *Angew. Chem., Int. Ed.* **2004**, *43*, 3890−3908. (b) Ng, S.-S.; Ho, C.-Y.; Schleicher, K. D.; Jamison, T. F. Nickel-catalyzed coupling reactions of alkenes. *Pure Appl. Chem.* **2008**, *80*, 929−939. (c) Moslin, R. M.; Miller-Moslin, K.; Jamison, T. F. Regioselectivity and enantioselectivity in nickel-catalysed reductive coupling reactions of alkynes. *Chem. Commun.* **2007**, 4441−4449. (d) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. Recent advances in homogeneous nickel catalysis. *Nature* **2014**, *509*, 299−309. For selected examples in addition to the above reviews, see: (e) Jackson, E. P.; Montgomery, J. Regiocontrol in Catalytic Reductive Couplings through Alterations of Silane Rate Dependence. *J. Am. Chem. Soc.* **2015**, *137*, 958−963. (f) Whittaker, A. M.; Dong, V. M. Nickel-Catalyzed Dehydrogenative Cross-Coupling: Direct Transformation of Aldehydes into Esters and Amides. *Angew. Chem., Int. Ed.* **2015**, *54*, 1312−1315. (g) Haynes, M. T., II; Liu, P.; Baxter, R. D.; Nett, A. J.; Houk, K. N.; Montgomery, J. Dimer Involvement and Origin of Crossover in Nickel-Catalyzed Aldehyde−Alkyne Reductive Couplings. *J. Am. Chem. Soc.* **2014**, *136*, 17495−17504. (h) Partridge, K. M.; Bader, S. J.; Buchan, Z. A.; Taylor, C. E.; Montgomery, A. Streamlined Strategy for Aglycone Assembly and Glycosylation. *Angew. Chem., Int. Ed.* **2013**, *52*, 13647−13650. (i) Shareef, A.-R.; Sherman, D. H.; Montgomery, J. Nickel-catalyzed regiodivergent approach to macrolide motifs. *Chem. Sci.* **2012**, *3*, 892−895. (j) Ogata, K.; Atsuumi, Y.; Shimada, D.; Fukuzawa, S.-I. Nickel-Catalyzed Three-Component Coupling between Aryl Aldehydes, Norbornenes, and Silanes Leading to Indanols through Aromatic C−H Bond Activation of Aryl Aldehydes. *Angew. Chem., Int. Ed.* **2011**, *50*, 5896−5899. (k) Malik, H. A.; Sormunen, G. J.; Montgomery, J. A General Strategy for Regiocontrol in Nickel-Catalyzed Reductive Couplings of Aldehydes and Alkynes. *J. Am. Chem. Soc.* **2010**, *132*, 6304−6305. (l) Liu, P.; McCarren, P.; Cheong, P. H.-Y.; Jamison, T. F.; Houk, K. N. Origins of Regioselectivity and Alkene-Directing Effects in Nickel-Catalyzed Reductive Couplings of Alkynes and Aldehydes. *J. Am. Chem. Soc.* **2010**, *132*, 2050−2057. (m) Saito, N.; Kobayashi, A.; Sato, Y. Nickel-Catalyzed Enantio- and Diastereoselective Three-Component Coupling of 1,3-Dienes, Aldehydes, and a Silaborane Leading to α-Chiral Allylsilanes. *Angew. Chem., Int. Ed.* **2012**, *51*, 1228−1231. (n) Saito, N.; Katayama, T.; Sato, Y. Nickel-Catalyzed Highly Regioselective Multicomponent Coupling of Ynamides, Aldehydes, and Silane: A New Access to Functionalized Enamides. *Org. Lett.* **2008**, *10*, 3829−3832. (o) Sato, Y.; Hinata, Y.; Seki, R.; Oonishi, Y.; Saito, N. Nickel-Catalyzed Enantio- and Diastereoselective Three-Component Coupling of 1,3-Dienes, Aldehydes, and Silanes Using Chiral N-Heterocyclic Carbenes as Ligands. *Org. Lett.* **2007**, *9*, 5597−5599. (p) Kimura, M.; Ezoe, A.; Mori, M.; Iwata, K.; Tamaru, Y. Regio- and Stereoselective Nickel-Catalyzed Homoallylation of Aldehydes with 1,3-Dienes. *J. Am. Chem. Soc.* **2006**, *128*, 8559−8568.

(6) For selected examples for Ni complexes, see: (a) Walther, D. Reaktionen von Heteroolefinen an Zentralmetallen in Niedrigen Oxidationsstufen: Stable Aldehydkompleze des Nickel(0) und Verwandte Verbindungen. *J. Organomet. Chem.* **1980**, *190*, 393−401. (b) Kaiser, J.; Sieler, J.; Walther, D.; Dinjus, E.; Golić, L. Benzaldehydebis(tricyclohexylphosphine)nickel(0). *Acta Crystallogr.* **1982**, *B38*, 1584−1586. For theoretical studies, see: (c) Sakaki, S.; Kitaura, K.; Morokuma, K.; Ohkubo, K. Ab Initio MO Study of Nickel(0) Complexes: Stereochemistry of $Ni(PH_3)_2L$ (L = H_2CO or $(CO)_2$) and Comparison of Coordinate Bonds of Various Ligands.

Inorg. Chem. **1983**, *22*, 104−108. (d) Delbecq, F.; Sautet, P. η^2 versus η^1 Coordination of Aldehydes and Ketones in Organometallic Complexes. A Semiempirical Theoretical Study. *J. Am. Chem. Soc.* **1992**, *114*, 2446−2455. Also see the following examples of the reactivity of η^2-aldehyde nickel complexes in catalytic transformations: (e) Cornella, J.; Gómez-Bengoa, E.; Martin, R. Combined Experimental and Theoretical Study on the Reductive Cleavage of Inert C−O Bonds with Silanes: Ruling out a Classical Ni(0)/Ni(II) Catalytic Couple and Evidence for Ni(I) Intermediates. *J. Am. Chem. Soc.* **2013**, *135*, 1997−2009. (f) Kelley, P.; Lin, S.; Edouard, G.; Day, M. W.; Agapie, T. Nickel-Mediated Hydrogenolysis of C−O Bonds of Aryl Ethers: What Is the Source of the Hydrogen? *J. Am. Chem. Soc.* **2012**, *134*, 5480−5483. For examples using other transition metals, see ref 4h and references therein.

(7) Thiyagarajan, B.; Kerr, M. E.; Bollinger, J. C.; Young, V. G., Jr.; Bruno, J. W. Electrophilic Attack on the Carbon Terminus of a Niobium-Bound Formaldehyde Ligand. *Organometallics* **1997**, *16*, 1331−1334.

(8) (a) Han, R.; Hillhouse, G. L. Carbon−Oxygen Reductive-Elimination from Nickel(II) Oxametallacycles and Factors That Control Formation of Ether, Aldehyde, Alcohol, or Ester Products. *J. Am. Chem. Soc.* **1997**, *119*, 8135−8136. (b) Bausch, C. C.; Patman, R. L.; Breit, B.; Krische, M. J. Divergent Regioselectivity in the Synthesis of Trisubstituted Allylic Alcohols by Nickel- and Ruthenium-Catalyzed Alkyne Hydrohydroxymethylation with Formaldehyde. *Angew. Chem., Int. Ed.* **2011**, *50*, 5687−5690.

(9) Tsuji, J.; Ohno, K. Organic Synthesis by Means of Noble Metal Compounds XXI. Decarbonylation of Aldehydes Using Rhodium Complex. *Tetrahedron Lett.* **1965**, *6*, 3969−3971.

(10) For Ni(0)/PR_3-catalyzed hydroacylation that was proposed to proceed via an acylnickel intermediate, see: (a) Tsuda, T.; Kiyoi, T.; Saegusa, T. Nickel(0)-Catalyzed Hydroacylation of Alkynes with Aldehydes to α,β-Enones. *J. Org. Chem.* **1990**, *55*, 2554−2558. (b) Taniguchi, H.; Ohmura, T.; Suginome, M. Nickel-Catalyzed Ring-Opening Hydroacylation of Methylenecyclopropanes: Synthesis of γ,δ-Unsaturated Ketones from Aldehydes. *J. Am. Chem. Soc.* **2009**, *131*, 11298−11299. (c) Yang, F.; Jin, T.; Yamamoto, Y. Synthesis of 2,3-dihydro-1*H*-inden-1-one derivatives via Ni-catalyzed intramolecular hydroacylation. *Tetrahedron* **2012**, *68*, 5223−5228. For a theoretical study, see: (d) Meng, Q.; Shen, W.; He, R.; Li, M. Theoretical investigation of $Ni(PMe_3)_4$-catalyzed intermolecular hydroacylation of alkynes with benzaldehydes. *Transition Met. Chem.* **2011**, *36*, 793−799.

(11) (a) Willis, M. C. Transition Metal Catalyzed Alkene and Alkyne Hydroacylation. *Chem. Rev.* **2010**, *110*, 725−748. (b) Leung, J. C.; Krische, M. J. Catalytic intermolecular hydroacylation of C−C π-bonds in the absence of chelation assistance. *Chem. Sci.* **2012**, *3*, 2202−2209. (c) Kakiuchi, F.; Murai, S. Activation of C−H Bonds: Catalytic Reactions. *Top. Organomet. Chem.* **1999**, *3*, 47−79.

(12) For selected examples of chelation-assisted intramolecular alkene hydroacylations, see: (a) Lenges, C. P.; Brookhart, M. Co(I)-Catalyzed Inter- and Intramolecular Hydroacylation of Olefins with Aromatic Aldehydes. *J. Am. Chem. Soc.* **1997**, *119*, 3165−3166. (b) Bendorf, H. D.; Colella, C. M.; Dixon, E. C.; Marchetti, M.; Matukonis, A. N.; Musselman, J. D.; Tiley, T. A. Chelation-assisted intramolecular hydroacylation: synthesis of medium ring sulfur heterocycles. *Tetrahedron Lett.* **2002**, *43*, 7031−7034. (c) Shen, Z.; Dornan, P. K.; Khan, H. A.; Woo, T. K.; Dong, V. M. Mechanistic Insights into the Rhodium-Catalyzed Intramolecular Ketone Hydroacylation. *J. Am. Chem. Soc.* **2009**, *131*, 1077−1091. (d) Bendorf, H. D.; Ruhl, K. E.; Shurer, A. J.; Shaffer, J. B.; Duffin, T. O.; LaBarte, T. L.; Maddock, M. L.; Wheeler, O. W. Amine-directed intramolecular hydroacylation of alkenes and alkynes. *Tetrahedron Lett.* **2012**, *53*, 1275−1277.

(13) (a) Törmäkangas, O. P.; Koskinen, A. M. P. The Tishchenko reaction and its modifications in organic synthesis. *Recent Res. Dev. Org. Chem.* **2001**, *5*, 225−255. (b) Seki, T.; Nakajo, T.; Onaka, M. The Tishchenko Reaction: A Classic and Practical Tool for Ester Synthesis. *Chem. Lett.* **2006**, *35*, 824−829. (c) Dzik, W. I.; Gooβen, L. J. Selective Crossed-Tishchenko Reaction—A Waste-Free Synthesis of Benzyl Esters. *Angew. Chem., Int. Ed.* **2011**, *50*, 11047−11049.

(14) A limited number of catalysts can catalyze the Tishchenko reaction of enolizable aldehydes. See: Ooi, T.; Ohmatsu, K.; Sasaki, K.; Miura, T.; Maruoka, K. Isopropoxyaluminum 1,1′-biphenyl-2-oxy-2′-perfluorooctanesulfonamide as a catalyst for Tishchenko reaction. *Tetrahedron Lett.* **2003**, *44*, 3191−3193.

(15) For examples, see: (a) Murahashi, S.-I.; Naota, T.; Ito, K.; Maeda, Y.; Taki, H. Ruthenium-Catalyzed Oxidative Transformation of Alcohols and Aldehydes to Esters and Lactones. *J. Org. Chem.* **1987**, *52*, 4319−4327. (b) Bernard, K. A.; Atwood, J. D. Evidence for C−O Bond Formation, Aldehyde Decarbonylation, and Dimerization by Reaction of Formaldehyde and Acetaldehyde with *trans*-ROIr(CO)-$(PPh_3)_2$. *Organometallics* **1988**, *7*, 235−236. (c) Bergens, S. H.; Fairlie, D. P.; Bosnich, B. Homogeneous Catalysis: Catalytic Intramolecular Conversion of 1,4-Dialdehydes to γ-Lactones. *Organometallics* **1990**, *9*, 566−571. (d) Barrio, P.; Esteruelas, M. A.; Oñate, E. Reactions of a Hexahydride-Osmium Complex with Aldehydes: Double C−H_α Activation−Decarbonylation and Single C−H_α Activation−Hydroxylation Tandem Processes and Catalytic Tishchenko Reactions. *Organometallics* **2004**, *23*, 1340−1348. (e) Tejel, C.; Ciriano, M. A.; Passarelli, V. Rhodium(III)-Catalyzed Dimerization of Aldehydes to Esters. *Chem.—Eur. J.* **2011**, *17*, 91−95.

(16) For the isolation of a bis(η^2-aldehyde) tungsten complex, see: Yeh, W.-Y.; Lin, C.-S. Syntheses and Structures of Tungsten *o*-(Diphenylphosphino)benzaldehyde Complexes Bearing π-Bonded Aldehyde Groups. *Organometallics* **2004**, *23*, 917−920.

(17) For selected examples of the crossed Tishchenko reaction of two different aldehydes, see: (a) Lin, I.; Day, A. R. A Study of the Mixed Tischtschenko Reaction. *J. Am. Chem. Soc.* **1952**, *74*, 5133−5135. (b) Morita, K.-I.; Nishiyama, Y.; Ishii, Y. Selective Dimerization of Aldehydes to Esters Catalyzed by Zirconocene and Hafnocene Complexes. *Organometallics* **1993**, *12*, 3748−3752.

(18) For highly selective crossed Tishchenko reactions of aldehydes with α-keto esters or ketones, see: (a) Chan, A.; Scheidt, K. A. Hydroacylation of Activated Ketones Catalyzed by N-Heterocyclic Carbenes. *J. Am. Chem. Soc.* **2006**, *128*, 4558−4559. (b) Cronin, L.; Manoni, F.; O'Connor, C. J.; Connon, S. J. Tunable Bromomagnesium Thiolate Tishchenko Reaction Catalysts: Intermolecular Aldehyde−Trifluoromethylketone Coupling. *Angew. Chem., Int. Ed.* **2010**, *49*, 3045−3048. (c) O'Connor, C. J.; Manoni, F.; Curran, S. P.; Connon, S. J. Microwave-assisted efficient thiolate-catalysed homo- and crossed intermolecular Tishchenko reactions. *New J. Chem.* **2011**, *35*, 551−553. (d) Mascarenhas, C. M.; Miller, S. P.; White, P. S.; Morken, J. P. First Catalytic Asymmetric Aldol-Tishchenko Reaction—Insight into the Catalyst Structure and Reaction Mechanism. *Angew. Chem., Int. Ed.* **2001**, *40*, 601−603. (e) Mlynarski, J. Direct Asymmetric Aldol-Tishchenko Reaction. *Eur. J. Org. Chem.* **2006**, 4779−4786.

(19) For a highly selective thiolate-catalyzed crossed Tishchenko reaction of two aromatic aldehydes, see: Curran, S. P.; Connon, S. J. The Thiolate-Catalyzed Intermolecular Crossed Tishchenko Reaction: Highly Chemoselective Coupling of Two Different Aromatic Aldehydes. *Angew. Chem., Int. Ed.* **2012**, *51*, 10866−10870.

(20) Transition-metal-catalyzed hydroacylations of ketones that are analogous to the Tishchenko reaction have been reported. See: (a) Hsu, J.-L.; Fang, J.-M. Stereoselective Synthesis of δ-Lactones from 5-Oxoalkanals via One-Pot Sequential Acetalization, Tishchenko Reaction, and Lactonization by Cooperative Catalysis of Samarium Ion and Mercaptan. *J. Org. Chem.* **2001**, *66*, 8573−8584. (b) Shen, Z.; Khan, H. A.; Dong, V. M. Rh-Catalyzed Carbonyl Hydroacylation: An Enantioselective Approach to Lactones. *J. Am. Chem. Soc.* **2008**, *130*, 2916−2917. (c) Phan, D. H. T.; Kim, B.; Dong, V. M. Phthalides by Rhodium-Catalyzed Ketone Hydroacylation. *J. Am. Chem. Soc.* **2009**, *131*, 15608−15609. (d) Omura, S.; Fukuyama, T.; Murakami, Y.; Okamoto, H.; Ryu, I. Hydroruthenation triggered catalytic conversion of dialdehydes and keto aldehydes to lactones. *Chem. Commun.* **2009**, 6741−6743.

(21) Chinese chemists reported DFT calculations on nickel-catalyzed homo and crossed Tishchenko reactions. This was very informative, but their calculations did not fully agree with our experimental results (e.g., the reaction of $\mathbf{A}^4$ with benzaldehyde derivatives). See: Yu, H.; Fu, Y.

Mechanistic Origin of Cross-Coupling Selectivity in Ni-Catalyzed Tishchenko Reactions. *Chem.—Eur. J.* **2012**, *18*, 16765−16773.

(22) Hoshimoto, Y.; Hayashi, Y.; Suzuki, H.; Ohashi, M.; Ogoshi, S. One-Pot, Single-Step, and Gram-Scale Synthesis of Mononuclear [(η^6-arene)Ni(N-heterocyclic carbene)] Complexes: Useful Precursors of the Ni^0−NHC Unit. *Organometallics* **2014**, *33*, 1276−1282.