Cine-Substitution of Enolates: Enolate Dance/Coupling of Cycloalkenyl Pivalates by Nickel Catalysis

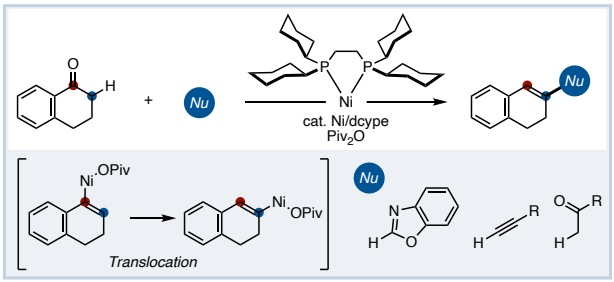
Eito Moriya,[a] Kei Muto,[b] and Junichiro Yamaguchi*[a]

[a] Department of Applied Chemistry, Waseda University, 513 Wasedatsurumakicho, Shinjuku, Tokyo 162-0041, Japan.

[b] Waseda Institute for Advanced Study, Waseda University, 513 Wasedatsurumakicho, Shinjuku, Tokyo 162-0041, Japan.

Supporting Information Placeholder

ABSTRACT: This manuscript describes the development of Ni/dcype-catalyzed enolate dance/coupling reaction of alkenyl pivalates with nucleophiles, resulting in *cine*-substitution. Pivalates derived 1-tetralone undergo this reaction, to produce C2-functionalized dihydronaphthalenes. The direct utilization of 1-tetralone is also feasible, employing Piv_2O to generate the corresponding enol pivalate *in situ*. Mechanistic investigations including stoichiometric experiments, suggest that the reaction proceeds via C–O oxidative addition, nickel 1,2-translocation, and subsequent coupling with a nucleophile.



The synthesis of functionalized cyclic alkenes is central focus in organic chemistry due to their extensive applications for both bioactive compounds and valuable synthetic intermediates. Cyclic ketones serve as a readily accessible platform for synthesizing substituted cyclic alkenes (Figure 1A). Classic reactions such as Wittig and Horner–Wadsworth–Emmons olefinations can convert a carbonyl into an *exo*-cyclic alkene,[1] we categorize as "type-1". Conversely, the synthesis of α-functionalized *endo*-cyclic alkenes is defined as "type-2". Beyond typical 1,2-addition, followed by dehydration protocols, various transition-metal-catalyzed reactions have been developed, rendering type-2 synthesis milder and reducing the number of synthetic steps.[2]

In this context, β-functionalized cyclic alkenes can also be synthesized from ketones (*i.e.* a sequence involving carbonyl α-functionalization, reduction, and subsequent dehydration can yield β-functionalized cyclic alkenes). Compared to the above mentioned types, this type-3 alkene synthesis is relatively elusive. To access type-3 olefins in a shorter-step, a catalytic *cine*-substitution[3,4] of enolates (alkenyl–OR species) offers a potential solution. Very recently, two elegant examples have emerged using palladium catalysis (Figure 1B). Encompassing a Catellani-process, the Dong group has successfully achieved a palladium/norbornene-catalyzed *cine*-substitution of cycloalkenyl triflates with carbamoyl chlorides.[5] In another notable example, by harnessing a deoxygenative Mizoroki–Heck process, the Krische group demonstrated that Pd(I)species can catalyze a *cine*-substitution of cycloalkenyl triflates with aryl iodides.[6] Despite their uniqueness, these reactions have been primarily limited in carbamoylation and arylation. Furthermore, they require the use of expensive palladium as a catalyst.

Inspiration for the development of a conceptually distinct *cine*-substitution of cyclic alkenes originated from our previous work on the ester dance (translocation)/coupling reaction of aromatic esters (Figure 1C).[7,8] For example, under the influence of Pd/dcypt catalyst, phenyl 1-naphthoate and a nucleophilic counterpart undergo a sequential esterdance/decarbonylative coupling,[9] furnishing 2-functionalized naphthalene. This reaction is thought to proceed through the intramolecular *ortho*-deprotonation of an aryl–Pd–OPh intermediate. Extending this reaction approach to cyclic alkene substrates could open opportunities for developing a *cine*-substitution of cyclic alkenes. To explore this, we revisited our previous work on a Ni/dcype-catalyzed C–H/C–O coupling of 1,3-azoles and alkenyl pivalates that yielded alkenyl–azoles.[10,11] Considering the similarity in catalyst structure between dcypt and dcype, and the growing understanding on the concerted-metalation deprotonation ability of pivalate,[12] we postulated the following mechanistic scenario: First, an oxidative addition of alkenyl–OPiv to Ni/dcype catalyst forms an alkenyl–Ni–OPiv species. If the pivalate-assisted-deprotonation of a neighboring C–H bond takes place, we anticipated that nickel could translocate across the alkene. Subsequently, a reaction with a nucleophile could then complete the *cine*-substitution. Based on this mechanistic blueprint, we herein report our findings on nickel-catalyzed enolate dance/coupling reaction of cyclic alkenyl pivalates with various nucleophiles. Moreover, we

unveiled that the present catalysis allows for the direct use of tetralones in the presence of Piv_2O, involving *in-situ* formation of alkenyl–OPiv.

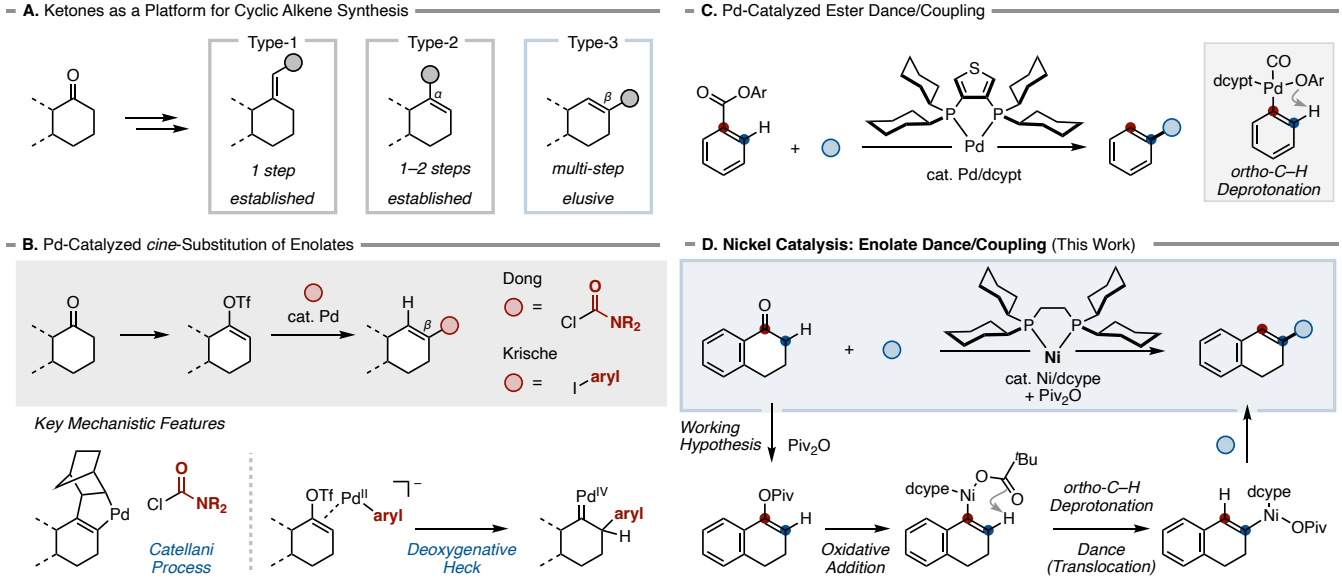
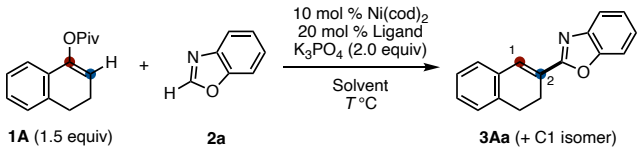


Figure 1. (A) Cycloalkene synthesis from cyclic ketones. (B) Pd-catalyzed *cine*-substitution of cycloalkenyl triflates. (C) Pd-catalyzed ester dance/coupling of aromatic esters. (D) Ni-catalyzed *cine*-substitution of cycloalkenyl pivalates.

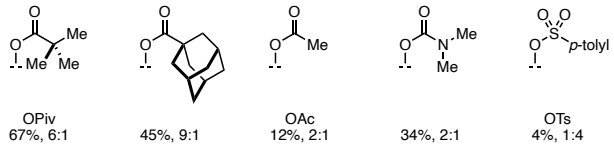
We initially tested various alkenyl pivalates under our previously established Ni/dcype catalytic conditions ($Ni(cod)_2$, dcype, K_3PO_4, in 1,4-dioxane at 135 °C) in the presence of benzoxazole (**2a**) (Table 1).[10] To our delight, 3,4-dihydronaphthalen-1-yl pivalate (**1A**), prepared from 1-tetralone, underwent the desired *cine*-substitution, yielding 2-azolated dihydronaphthalene **3Aa** in 16% yield alongside 5% yield of the C1-isomer (Table 1, entry 1).

Table 1. Conditions screening



Entry	Ligand	Solvent	*T*/ °C	**3Aa**/ %[a]	C2:C1
1	dcype	1,4-dioxane	135	16	3:1
2	dcype	1,4-dioxane	150	55	6:1
3	dcype	*t*-AmylOH	150	0	1:>99
4	dcype	THF	150	45	6:1
5	dcype	*m*-xylene	150	67	6:1
6	dcypt	*m*-xylene	150	50	4:1
7	dppe	*m*-xylene	150	0	–
8	PCy_3 [b]	*m*-xylene	150	0	–

*Effect of Leaving Group of **1** (conditions for entry 5)*



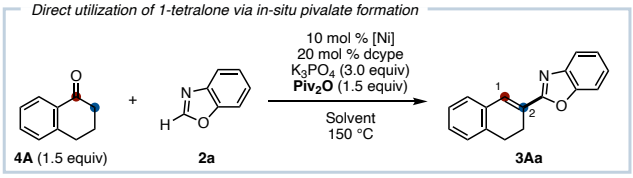
Conditions: **1A** (0.60 mmol), **2a** (0.40 mmol), $Ni(cod)_2$ (10 mol %), ligand (20 mol %), K_3PO_4 (2.0 equiv), solvent (1.5 mL), 135–150 °C, 24 h. [a] Yield was determined by ^1H NMR analysis. [b] Ligand (40 mol %).

Increasing temperature to 150 °C improved the yield of **3Aa** to 55% (Table 1, entry 2). Interestingly, replacement of 1,4-dioxane with *t*-amyl alcohol altered the regioselectivity, favoring the C1 isomer at a 36% yield (Table 1, entry 3). The use of other solvent such as THF and *m*-xylene increased the yield of **3Aa**, with *m*-xylene delivering the best results (Table 1, entries 4 and 5). Switching the ligand from dcype to structural relevant dcypt preserved the catalytic activity, albeit with a slightly diminished yield of **3Aa** (Table 1, entry 6). Other bidentate phosphine like dppe, proved ineffective, resulting in no reaction (Table 1, entry 7). Inspired by Martin's recent report of a pivalate translocation reaction using a stoichiometric amount of Ni/PCy_3 complex, we tested PCy_3, which unfortunately did not yield the desired product (Table 1, entry 8).[13] This suggests that our reaction may proceed via a different pathway from the Martin's report. Incidentally, we also attempted the reaction using a palladium catalyst instead of nickel, but only recovered the starting material **1A**.[2g–2i] Using the conditions in entry 5, we evaluated the effect of leaving group. A bulky carboxylate, 1-adamantane carboxylate gave **3Aa** in 45% yield with increased regioselectivity (9:1), whereas a less bulky acetate resulted in poor yield and regioselectivity. Carbamate also yielded **3Aa**, albeit with low regioselectivity, while tosylate showed

reverse regioselectivity. Overall, we identified optimal conditions using $Ni(cod)_2$/dcype catalyst and K_3PO_4 in *m*-xylene at 150 °C for reacting pivalate **1A** and **2a**.

Building on the success of the *cine*-substitution with pivalate **1A**, we next envisaged the direct utilization of 1-tetralone (**4A**) in this enolate dance/coupling reaction in the presence of Piv_2O (Scheme 1). Conducting the reaction of **4A** with **2a** under the optimized conditions yielded **3Aa** in 15% with moderate regioselectivity. Delightfully, switching the solvent to THF drastically improved both the yield of **3Aa** to 55% and the regioselectivity to 14:1, which was attributed for the first *in-situ* formation of pivalate **1A** (See the SI for details). Additionally, we established a glovebox-free protocol using air stable $Ni(dcype)(CO)_2$[14] achieving slightly better yield than $Ni(cod)_2$. Reducing the amount of this nickel complex to 5.0 mol %, maintaining both yield and regioselectivity.

Scheme 1. Direct utilization of 1-tetralone through *in-situ* pivalate formation

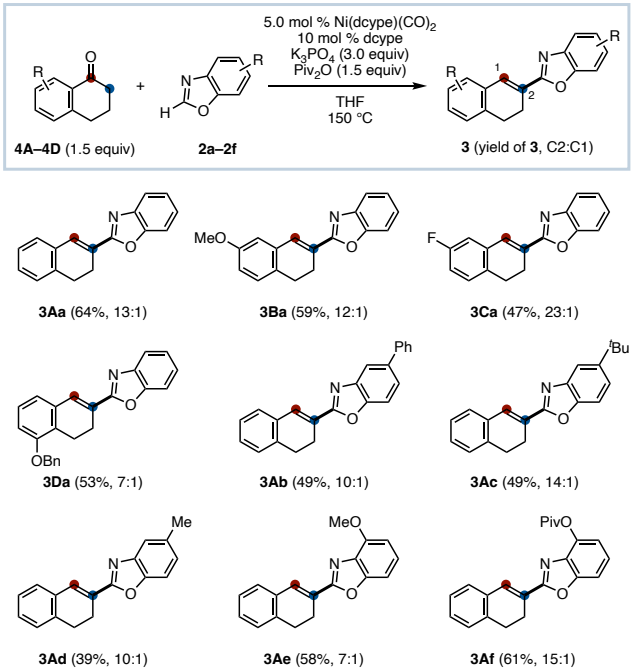


[Ni]	Solvent	Yield of **3Aa**, (C2:C1)[a]
$Ni(cod)_2$	*m*-xylene	15% (5:1)
$Ni(cod)_2$	THF	55% (14:1)
$Ni(dcype)(CO)_2$	THF	64% (13:1)
$Ni(dcype)(CO)_2$[a]	THF	64% (13:1)

Conditions: **4** (0.60 mmol), **2** (0.40 mmol), [Ni] (10 mol %), dcype (20 mol %), K_3PO_4 (3.0 equiv), Piv_2O (1.5 equiv), solvent (1.5 mL), 150 °C, 24 h. [a] Yield was determined by ^1H NMR analysis.

With the optimal reaction conditions in hands, we further explored the substrate scope of this reaction using 1-tetralones **4** (Scheme 2). In addition to **3Aa**, this reaction allowed to synthesize 7-methoxy substituted compound **3Ba** in 59% yield with good regioselectivity. Fluorine-substituted **3Ca** was also generated in a moderate yield and maintained good regioselectivity. 5-Benzyloxydihydronaphthalen-2-yl benzoxazole **3Da** was synthesized with a 53% yield. These results indicated that electronic and positional variations on the aromatic ring on tetralone **4** did not significantly affect this reaction progress. We then assessed of this reaction with various benzoxazoles. Both 5-phenyl- and 5-alkyl-substituted benzoxazoles underwent this reaction, giving the corresponding enloate dance/coupling products in moderate yields (**3Ab**, **3Ac**, and **3Ad**). Furthermore, 4-methoxybenzoxazole was incorporated at the C2 position, furnishing **3Ae** in 58% yield with moderate regioselectivity. Notably, the potentially competitive 4-pivaloxy substituted benzoxazole **2f** reacted smoothly under the present conditions, resulting in **3Af** with a 61% yield and moderate regioselectivity. This finding demonstrates that the *in-situ* generated alkenyl pivalate exhibits higher reactivity toward Ni/dcype catalyst than the aryl–OPiv moiety. Unfortunately, other 1,3-azoles such as oxazole, benzothiazoles, and benzimidazoles were not applicable to these reaction conditions, leading to poor yields of products or no reaction (See the SI for details). Despite extensively investigations, other cyclic alkenes have not yet proven suitable for this reaction.

Scheme 2. Substrate scope



Conditions: **4** (0.60 mmol), **2** (0.40 mmol), $Ni(dcype)(CO)_2$ (5.0 mol %), dcype (10 mol %), K_3PO_4 (3.0 equiv), Piv_2O (1.5 equiv), THF (1.5 mL), 150 °C, 48 h.

To gain mechanistic insights, we next conducted several control experiments. First, 1-tetralone (**4A**) was subjected to the optimized conditions without any nucleophilic counterparts, resulting in the formation of dihydronaphthalen-2-yl pivalate (**5**) in a 35% yield along with its isomer **1A** in a 52% yield. Moreover, conducting the reaction without nickel catalyst led to the formation of pivaloyl enolate **1A** quantitatively. These results would indicate that the present *cine*-substitution reaction indeed proceeds through **1A** as an intermediate, which then reacts with nickel catalyst in an enolate dance reaction resulting in translocation of the pivalate group. To directly assess this mechanism, a stoichiometric reaction was conducted. First, $Ni(cod)_2$/dcype and pivalate **1A** were reacted in the presence of benzonitrile,[15] confirming the C–O oxidative addition (Figure 2B). This reaction proceeded smoothly even at 60 °C in the presence of PivOH, giving desired oxidatively added nickel complex **A**. The structure of complex **A** was ambiguously confirmed by X-ray crystallographic analysis. It is of note that this is the first example directly proving oxidative addition of alkenyl C–OPiv to nickel. Strikingly, we successfully confirmed that complex **A** undergoes a translocation reaction upon heating at 100 °C, generating 3,4-dihydronaphthalen-2-yl nickel complex **B** (Figure 2C). This type of nickel translocation is hitherto unknown, and the stoichiometric experiments strongly suggest that the mechanism of the present system is distinct from the recent ring-walking of aryl pivalates mediated by dinuclear nickel species reported by Martin.[13] Further experiments involved reacting **1A**, $Ni(cod)_2$, and dcype at 100 °C leading to the formation of complex **B** through the intermediacy of complex **A** (Figure 2D).

Monitoring this reaction that within first 60 min, the concentration of **A** reached at a short plateau, followed by a gradual increase in the concentration of **B** while the concentration of **A** decreased. Although the detailed mechanism on this nickel translocation remains unclear, we hypothesize that it may involve a nickel–cyclic alkyne complex intermediate.[16,17]

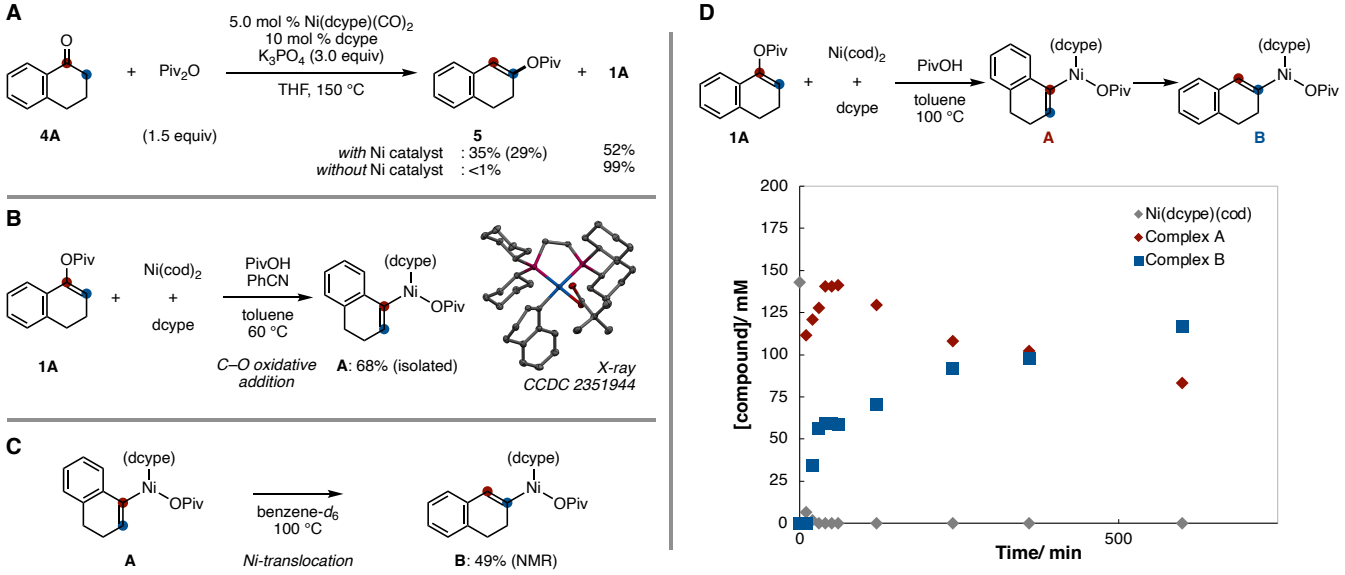
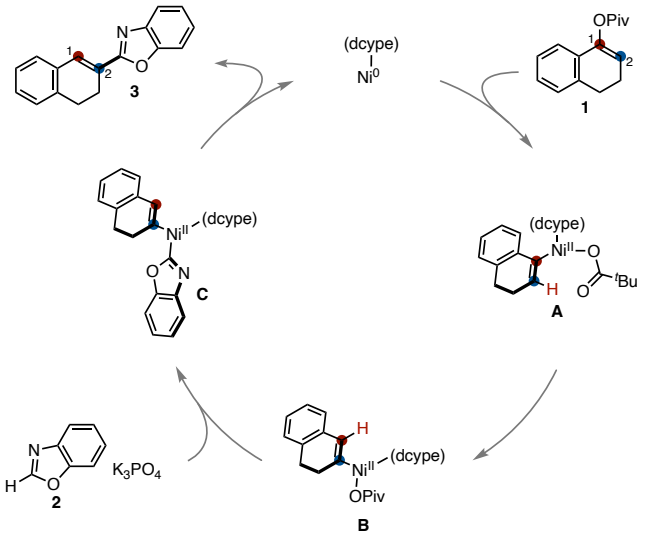


Figure 2. (A) Control experiments conducted without nucleophiles. (B) Oxidative addition of **1A** to Ni/dcype complex and the X-ray structure of complex **A**. (C) Isomerization of the 1-alkenyl–Ni complex **A** to the 2-alkenyl–Ni complex **B**. (D) Sequential oxidative addition and isomerization reaction of **1A**, including a time-course plot of the reaction.

Based on these mechanistic studies and our previous results,[10,18–20] a proposed catalytic cycle is illustrated in Scheme 3. The cycle commences with the oxidative addition of **1** to the Ni(0)/dcype complex, producing the 1-nickelated dihydronaphthalene intermediate **A**. This intermediate **A** is subsequently isomerized to form positional isomer **B**. Isomer **B** then undergoes reaction with benzoxazole **2**, facilitated by K_3PO_4, leading to the formation of the azole–Ni species **C**. The cycle completes with the reductive elimination, yielding product **3** and regenerating the Ni(0) species.

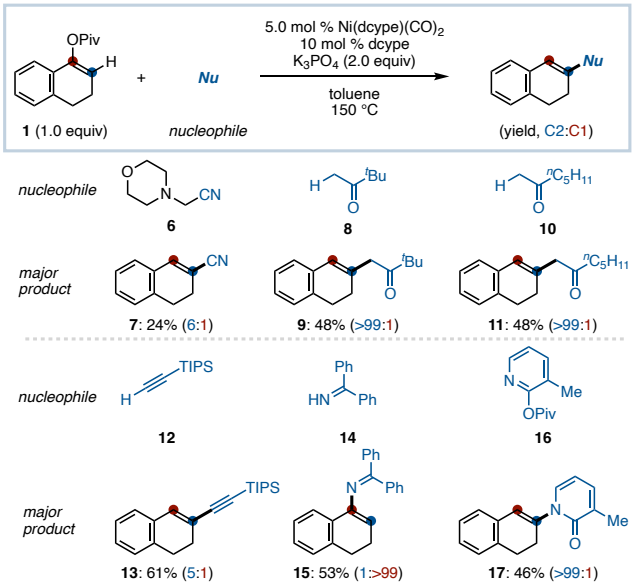
Scheme 3. Proposed reaction mechanism.



Given that this reaction proceeds through the translocation/coupling manner, it offers the opportunity to employ a variety of nucleophilic counterparts beyond benzoxazole **2**.

To demonstrate this, we conducted reactions of **1A** with various nucleophiles based on our knowledge of Ni/dcype chemistry (Scheme 4). Based on our previous success in C–O bond cyanation,[21] we used aminoacetonitrile **6** under the present reaction conditions, achieving alkenyl cyanide **7**, albeit in a 24% yield. Next, we tested α-alkenylation of ketones.[22] Using pinacolone (**8**), the reaction yielded ketone **9** with remarkable regioselectivity. Similarly, 2-heptanone (**10**) produced the coupling product **11** in 48% yield with excellent regioselectivity. Hypothesizing a nucleophile with a p*K*a similar to ketones might react, we next conducted the reaction using terminal alkyne **12**. Delightfully, TIPS-acetylene proved to be a feasible nucleophile in our protocol, furnishing enyne **13** in a 61% yield with moderate regioselectivity. Finally, we attempted utilizing heteroatom nucleophiles. According to Rueping's report, we employed ketimine **14** for amination,[23] which selectively afforded 1-iminated dihydronaphthalene **15**. Considering that imine **14** might rapidly react with nickel intermediate **A** before the translocation, we used **16** as a masked-nucleophilic nitrogen source. Interestingly, this approach yielded the C2 aminated product **17** in a 46% yield with excellent regioselectivity. These studies on substrate scope not only showcased the broad applicability of nucleophiles in this *cine*-substitution, but also highlighted that one of the key mechanistic features of this *cine*-substitution is the use of nucleophile that reacts with the nickel(II) species slower than the nickel translocation (the process from **A** to **B**).

Scheme 4. Reaction using other nucleophiles



Conditions: **1A** (0.40 mmol), nucleophiles (1.0–2.0 equiv), Ni(dcype)(CO)$_2$ (5.0 mol %), dcype (10 mol %), K_3PO_4 (2.0 equiv), toluene (1.5 mL), 150 °C, 24 h. For details, see the SI.

In summary, we have developed a Ni-catalyzed *cine*-substitution of alkenyl pivalates with various nucleophiles, a process that provides a conceptually novel substituted for synthesizing cyclic alkenes from ketones. Mechanistic studies strongly suggest that this reaction involves a unique nickel-translocation on alkenyl–nickel species. We are currently undergoing further studies to overcome the substrate limitations of alkenyl pivalates, aiming to generalize this transformation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the website.

Experimental procedures and spectroscopic data for compounds including ^{1}H-, ^{13}C-, ^{19}F-, and ^{31}P-NMR spectra and crystallographic data (PDF).

AUTHOR INFORMATION

Corresponding Author

Junichiro Yamaguchi – Department of Applied Chemistry, Waseda University, 513 Wasedatsurumakicho, Shinjuku, Tokyo 162-0041, Japan; orcid.org/0000-0002-3896-5882; Email: junyamaguchi@waseda.jp

Author Information

Eito Moriya – Department of Applied Chemistry, Waseda University, 513 Wasedatsurumakicho, Shinjuku, Tokyo 162-0041, Japan.

Kei Muto – Waseda Institute for Advanced Study, Waseda University, Shinjuku, Tokyo 162-0041, Japan; orcid.org/0000-0001-8301-4384

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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