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Synthesis and Reactivity of Six-Membered Oxa-Nickelacycles: A Ring-Opening Reaction of Cyclopropyl Ketones

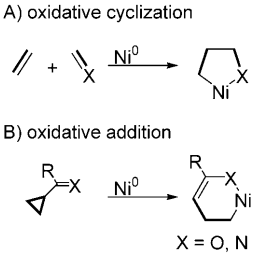
Takashi Tamaki, Midue Nagata, Masato Ohashi, and Sensuke Ogoshi*[a]

Abstract: Cyclopropanecarboxaldehyde (**1a**), cyclopropyl methyl ketone (**1b**), and cyclopropyl phenyl ketone (**1c**) were reacted with $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) and PBu_3 at 100 °C to give η^2-enonenickel complexes (**2a–c**). In the presence of PCy_3 (Cy = cyclohexyl), **1a** and **1b** reacted with $[Ni(cod)_2]$ to give the corresponding μ-η^2:η^1-enonenickel complexes (**3a**, **3b**). However, the reaction of **1c** under the same reaction conditions gave a mixture of **3c** and cyclopentane derivatives (**4c**, **4c′**), that is, a [3+2] cycloaddition product of **1c** with (*E*)-1-phenylbut-2-en-1-one, an isomer of **1c**. In the presence of a catalytic amount of $[Ni(cod)_2]$ and PCy_3, [3+2] homo-cycloaddition proceeded to give a mixture of **4c** (76%) and **4c′** (17%). At room temperature, a possible intermediate, **6c**, was observed and isolated by reprecipitation at −20 °C. In the presence of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), both **1a** and **1c** rapidly underwent oxidative addition to nickel(0) to give the corresponding six-membered oxa-nickelacycles (**6ai**, **6ci**). On the other hand, **1b** reacted with nickel(0) to give the corresponding μ-η^2:η^1-enonenickel complex (**3bi**). The molecular structures of **6ai** and **6ci** were confirmed by X-ray crystallography. The molecular structure of **6ai** shows a dimeric η^1-nickelenolate structure. However, the molecular structure of **6ci** shows a monomeric η^1-nickelenolate structure, and the nickel(II) 14-electron center is regarded as having "an unusual T-shaped planar" coordination geometry. The insertion of enones into monomeric η^1-nickelenolate complexes **6c** and **6ci** occurred at room temperature to generate η^3-oxa-allylnickel complexes (**8**, **9**), whereas insertion into dimeric η^1-nickelenolate complex **6ai** did not take place. The diastereoselectivity of the insertion of an enone into **6c** having PCy_3 as a ligand differs from that into **6ci** having IPr as a ligand. In addition, the stereochemistry of η^3-oxa-allylnickel complexes having IPr as a ligand is retained during reductive elimination to yield the corresponding [3+2] cycloaddition product, which is consistent with the diastereoselectivity observed in Ni^0/IPr-catalyzed [3+2] cycloaddition reactions of cyclopropyl ketones with enones. In contrast, reductive elimination from the η^3-oxa-allylnickel having PCy_3 as a ligand proceeds with inversion of stereochemistry. This is probably due to rapid isomerization between *syn* and *anti* isomers prior to reductive elimination.

Keywords: cycloaddition · cyclopropanes · enolates · enones · nickel

Introduction

Many nickel-catalyzed transformations by means of a hetero-nickelacycle have been reported, in which two different key reaction steps to generate a hetero-nickelacycle from nickel(0) species have been proposed. One proposed reaction is the oxidative cyclization of two π components with a nickel(0) complex to give five-membered hetero-nickelacycles (Scheme 1A). Earlier studies of hetero-nickelacycles, reported by Hoberg et al., focused on oxidative cyclization, including carbon dioxide or isocyanate as a π component.[1] We recently reported oxidative cyclization reactions of carbon–carbon unsaturated compounds and aldehyde, ketone, or imine with nickel(0).[2] These reactions have been proposed as an important key step in multicomponent coupling reactions[3] as



Scheme 1. Formation of hetero-nickelacycles from nickel(0).

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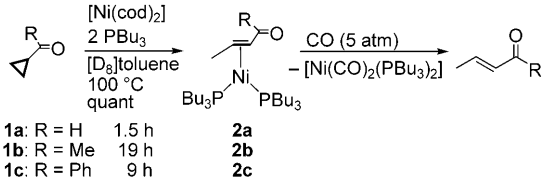
well as [2+2+2] cycloaddition reactions.[4,5] Formation of cyclic nickelenolates by a similar oxidative cyclization was also observed by Montgomery and Schlegel et al.[6]

The other type of reaction to generate a hetero-nickelacycle is the oxidative addition of cyclopropyl ketones and cyclopropyl imines to give six-membered hetero-nickelacycles (Scheme 1B), which has also been proposed as an important key step in nickel-catalyzed [3+2] cycloaddition reactions to give cyclopentane derivatives. As a stoichiometric reaction, ring-opening reactions by oxidative addition of cyclopropanes to a transition metal have been reported.[7] However, catalytic applications have been limited due to the poor coordination ability of cyclopropanes.[8] Therefore, cyclopropyl compounds with an unsaturated bond that can coordinate to a low valent transition metal, such as methylenecyclopropanes,[9] vinylcyclopropanes,[10] cyclopropyl ketones,[11] cyclopropyl imines,[12] and allenylcyclopropanes[13] have been employed as substrates in transition-metal-catalyzed transformations that include ring-opening reactions of the cyclopropyl ring as a key reaction step.

The nickel-catalyzed [3+2] cycloaddition reaction was simultaneously reported for the first time by our group and by Montgomery and Liu.[14] Our prior work focused on the catalytic homo-dimerization of cyclopropyl ketones using phosphine ligands and observation of key intermediates in the pathway. The complementary studies of Montgomery and co-workers demonstrated this catalytic reaction using *N*-heterocyclic carbene ligands as well as the crossed reactions of cyclopropyl ketones or cyclopropyl imines with enones. We have recently focused on providing insights into the mechanism and origin of diastereoselectivity of these reactions, and therefore, we have also addressed the formation of six-membered hetero-nickelacycles by oxidative addition of cyclopropanes attached to a carbon–oxygen double bond. In this paper, we report on the synthesis and structure of six-membered oxa-nickelacycles generated by oxidative addition of cyclopropyl ketones to nickel(0) in the presence of PR_3 and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr).[15] These oxa-nickelacycles reacted with enones to give new nickelacycles with η^3-enolate structures. We also discuss a possible reaction mechanism of [3+2] cycloaddition reaction of cyclopropyl ketones with enones.

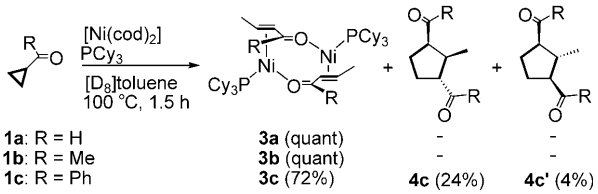
Results and Discussion

Reaction of cyclopropyl ketones with nickel(0): The reaction of cyclopropanecarboxaldehyde (**1a**), cyclopropyl methyl ketone (**1b**), or cyclopropyl phenyl ketone (**1c**) with [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) and PBu_3 at 100 °C in [D_8]toluene gave an η^2-enonenickel complex (**2a–c**) quantitatively (Scheme 2). This result indicates that the ring-opening reaction of the cyclopropyl ring attached to the carbonyl group occurred at the proximal position toward the carbonyl group. The treatment of **2a**, **2b**, and **2c** with carbon monoxide (5 atm) led to dissociation of the coordinated enones, (*E*)-crotonaldehyde, (*E*)-3-penten-2-one, and (*E*)-1-phenylbut-2-en-1-one, respectively.[16] Thus, if dissociation of the coordinated enones from nickel(0) can occur, this isomerization reaction might proceed catalytically. However, in the presence of 10 mol% of [Ni(cod)$_2$] and 20 mol% of PBu_3, no catalytic isomerization reaction of **1c** occurred at 100 °C for 48 h. This finding might be due to strong coordination of the enone to nickel(0) in **2c**.



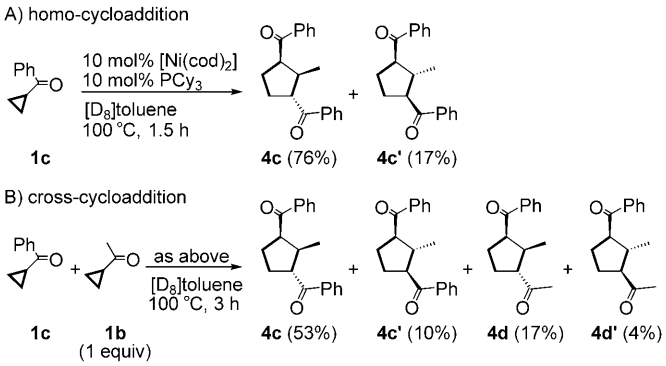
Scheme 2. Reaction of cyclopropyl ketone with nickel(0) and PBu_3.

In the presence of PCy_3 (Cy = cyclohexyl), the ring-opening reaction of **1a** and **1b** occurred to give μ-η^2:η^1-enone-nickel dimer complexes (**3a**, **3b**) quantitatively (Scheme 3).



Scheme 3. Reaction of cyclopropyl ketone with nickel(0) and PCy_3.

The molecular structure of **3b** was confirmed by X-ray crystallography.[14a] Under the same reaction conditions, the reaction of **1c** gave a mixture of the corresponding μ-η^2:η^1-enonenickel complex (**3c**) and unexpected cyclopentane products (**4c**, **4c′**). In contrast to the reaction in the presence of PBu_3, **3a**, **3b**, and **3c** were generated even in the presence of two equivalents of PCy_3. The cycloaddition reaction proceeded catalytically to give a mixture of **4c** and **4c′** in 93% yield (Scheme 4A). At the end of the reaction, the formation of **3c** (76% based on [Ni(cod)$_2$]) was observed. Although cyclopropyl methyl ketone did not undergo the homo-cycloaddition reaction under the reaction conditions

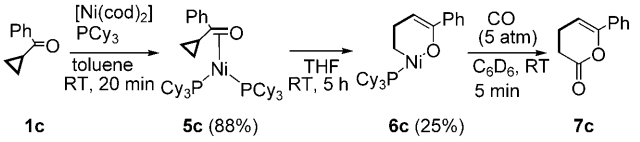


Scheme 4. Catalytic reaction of cyclopropyl ketone.

in Scheme 4A, the cross-cycloaddition with cyclopropyl phenyl ketone competed with the homo-cycloaddition of cyclopropyl phenyl ketone to give a mixture of **4c**, **4c′**, **4d**, and **4d′** (Scheme 4B). These results suggest that there might be an intermediate in the reaction that can supply cyclopropyl ketone as a three-carbon unit for this cycloaddition, that is, six-membered oxa-nickelacycle (Scheme 1B with X = O). Therefore, a stoichiometric reaction at a lower temperature was carried out to observe the formation of a key reaction intermediate.

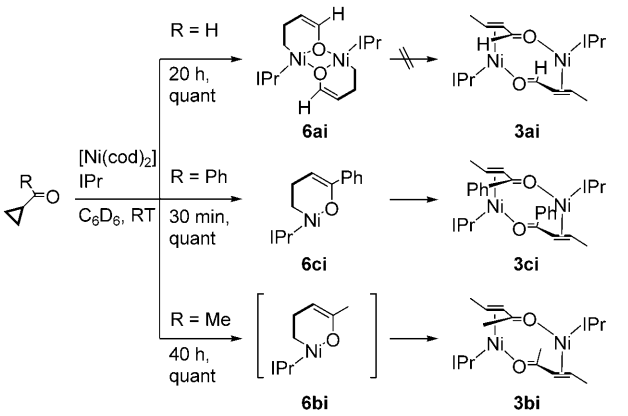
The reaction of **1c** (2 equiv) with [Ni(cod)$_2$] (1 equiv) and PCy_3 (1 equiv) in C_6D_6 at 40 °C was followed by ^{1}H and ^{31}P NMR spectroscopy. The rapid formation of an η^2-ketone-nickel complex (**5c**, 32% based on Ni) was observed in 5 min. Then, **5c** decreased gradually and a new complex (**6c**) with a resonance at $\delta = 5.21$ ppm in the ^{1}H NMR spectrum was generated (40%). After 48 h, **6c** disappeared and **3c** (60%) and a mixture of **4c** and **4c′** (40% as a mixture) were generated with cyclopropyl phenyl ketone (1 equiv) and 40% of [Ni(cod)$_2$] and PCy_3 remaining intact (Figure 1). The reaction of **1a** with [Ni(cod)$_2$] and PCy_3 in C_6D_6 also generated the expected new complex (**6a**), with resonances at $\delta = 4.77$ and 6.51 ppm attributed to two vinyl hydrogen atoms, as an inseparable mixture with **3a** at room temperature. The reaction of **1b** with [Ni(cod)$_2$] and PCy_3 in C_6D_6 at room temperature generated the corresponding η^2-ketone-nickel complex (**5b**) in poor yield, and no oxidative addition proceeded for at least 48 h. However, at 40 °C, only enone dimer complex **3b** was observed as a reaction product. Only **6c** seemed to be an isolable key intermediate.

The reaction of **1c** with [Ni(cod)$_2$] and PCy_3 in toluene gave **5c** in 88% isolated yield (Scheme 5). In THF at room temperature for 5 h, **5c** underwent oxidative addition to nickel(0) to generate **6c** in 60% yield. THF and COD were removed completely under reduced pressure. The residue was dissolved in a minimum amount of toluene, and reprecipitation at −20 °C gave **6c** as a pale orange solid in 25% isolated yield. Elemental analysis is consistent with the expected composition. The ^{13}C NMR spectroscopic resonance of the methylene carbon attached to nickel is coupled with phosphorus. The ^{1}H and ^{13}C chemical shifts of the nickelenolate moiety (-NiOC(Ph)=CH-) are in the range of those for reported nickelenolates.[6] The treatment of **6c** with carbon monoxide (5 atm) led to the formation of the expected lactone (**7c**) quantitatively,[16,17] which is consistent with the structure of **6c** depicted in Scheme 5. Its monomeric structure is inferred from the molecular structure of **6ci**, an analogue of **6c** (vide infra). The decomposition of **6c** at room temperature for 36 h gave a mixture of **3c** (68%) and a trace amount of **4c**.



Scheme 5. Isolation of **6c**.

In contrast to the reactions in the presence of PCy_3 or PBu_3, IPr promoted the ring-opening reaction much faster, even at room temperature (Scheme 6). In the presence of IPr, both **1a** and **1c** underwent oxidative addition to give the expected six-membered oxa-nickelacycles (**6ai**, **6ci**). The treatment of **6ai** and **6ci** with carbon monoxide gave the corresponding lactones (**7a**, **7c**), respectively.[16] Both **6ai** and **6ci** were isolated; however, **6ci** gradually isomerized into the corresponding η^2-enonenickel dimer complex (**3ci**) at room temperature, as observed for **6c**. The reaction of **1b** under the same reaction conditions gave an η^2-enonenickel dimer complex (**3bi**) quantitatively, and no corresponding six-membered oxa-nickelacycle (**6bi**) was observed, which suggests that **6bi** is a transient intermediate. On the other hand, **6ai** did not undergo isomerization and was stable enough to obtain a single crystal, suitable for X-ray crystallography, by recrystallization at room temperature.



Scheme 6. Ni^0/IPr-promoted ring-opening reaction.

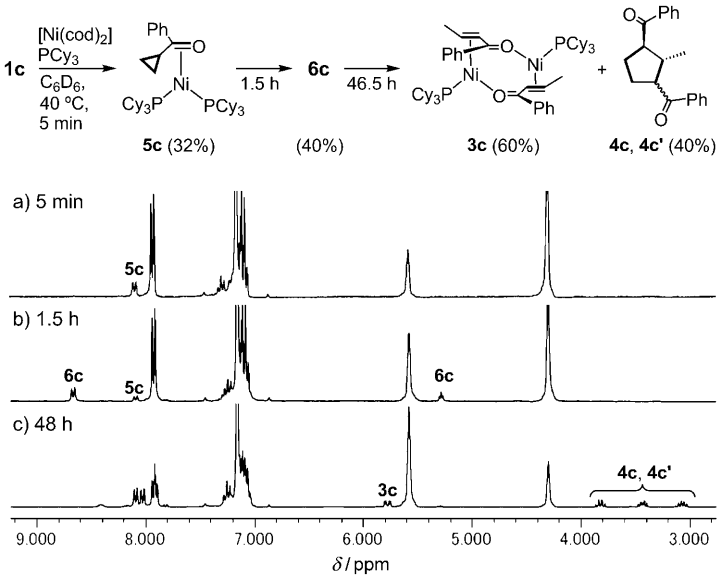


Figure 1. Monitoring the formation of **6c** at 40 °C.

The molecular structure of **6ai** shows a dimeric η^1-nickelenolate structure (Figure 2). The sum of the bond angles around nickel along the C1, O1, O2, and C5 is 359.96°.

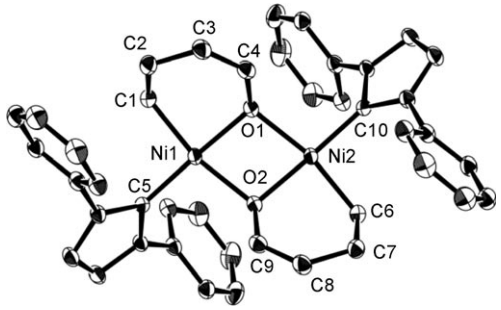


Figure 2. Molecular structure of **6ai**. Hydrogen atoms and *i*Pr groups are omitted for clarity.

Thus, Ni, C1, O1, O2, and C5 are on the same plane and **6ai** is a typical square-planar nickel(II) 16-electron complex. Bond lengths C3–C4 (1.328(2) Å) and C4–O1 (1.336(2) Å) are in the range of a normal carbon–carbon double-bond length and a carbon–oxygen single-bond length, respectively. A single crystal of **6ci** was obtained by recrystallization at −20 °C. The molecular structure of **6ci** is an unexpected monomeric η^1-nickelenolate structure (Figure 3A). The sum of the bond angles around nickel along the C1, O1, and C5 is 359.87°. Thus, Ni, C1, O1, and C5 are on the same plane and **6ci** is "an unusual T-shaped square-planar" nickel(II) 14-electron complex. Bond lengths C3–C4 (1.334(3) Å) and C4–O1 (1.334(2) Å) are also in the range of a normal carbon–carbon double-bond length and a carbon–oxygen single-bond length, respectively. A space-filling model of **6ci** clearly indicates that such geometry is mostly due to the bulkiness caused by the phenyl ring on the C4 atom together with the bulky IPr ligand, which prevents other donor molecules from approaching the fourth coordination site of the square planar (Figure 3B). The ^{1}H and ^{13}C NMR spectra of both **6ai** and **6ci** in C_6D_6 are consistent with an η^1-nickelenolate structure, which suggests that both complexes might have an η^1-nickelenolate structure in solution. As mentioned above, **6ai** did not isomerize into the corresponding η^2-enonenickel dimer complex (**3ai**) at room temperature, although **6ci** slowly underwent isomerization into **3ci**. This result might be explained by the dimeric structure of **6ai**. The dimeric structure of **6ai** might be too stable to disaggregate into a monomer, which is required to generate a vacant site to undergo β-hydrogen elimination as the initial step in isomerization to **3ai**.

Reaction of oxa-nickelacycles with enones: At room temperature, **6c** reacted with (*E*)-3-penten-2-one to give the expected nickelacycle complex (*anti*-**8c**) (Scheme 7). This reaction proceeded somewhat slowly due to its poor solubility. Employing (*E*)-1-phenylbut-2-en-1-one instead of (*E*)-3-penten-2-one afforded the corresponding η^3-oxa-allylnickel

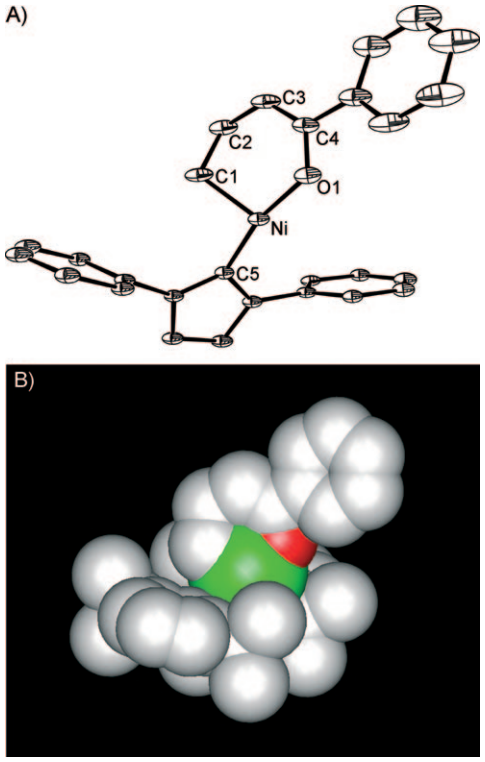
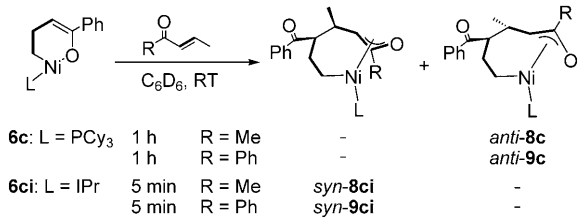


Figure 3. A) Molecular structure of **6ci**. Hydrogen atoms and *i*Pr groups are omitted for clarity. B) Space-filling model of **6ci** represented from the front perspective of six-membered oxa-nickelacycle (the color of atoms: Ni green, O red, C gray).



Scheme 7. Insertion of enones into an oxa-nickelacycle.

complex (*anti*-**9c**). The stereochemistry of both *anti*-**8c** and *anti*-**9c** is regarded as depicted in Scheme 7 on the basis of NOE correlations among hydrogen atoms attached to C3, C5, and C6.

The reaction of **6ci** with (*E*)-3-penten-2-one and (*E*)-1-phenylbut-2-en-1-one gave *syn*-**8ci** and *syn*-**9ci**, respectively, in which the diastereomeric relationship between the benzoyl group and the methyl group is different from that of *anti*-**9c** (Scheme 7). Both the molecular structures of *syn*-**8ci** and *syn*-**9ci** were determined by X-ray crystallography (Figures 4 and 5). The NOESY measurements of *syn*-**9ci** in C_6D_6 showed that the hydrogen atom attached to C6 has an NOE contact with that of C4, whereas NOE correlation between *H*–C4 and *H*–C3 is not detected at all, thereby indicating that the stereochemistry observed in the solid state is maintained even in solution. On the other hand, **6ai** did not react

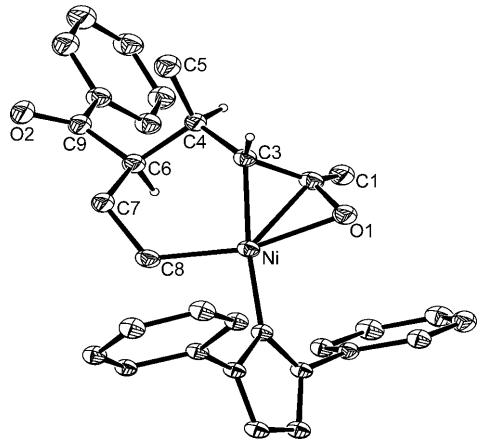


Figure 4. Molecular structure of *syn*-**8ci**. Hydrogen atoms except for those attached to C3, C4, and C6 atoms and *i*Pr groups are omitted for clarity.

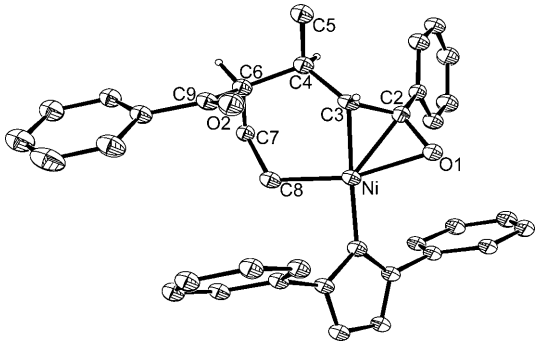
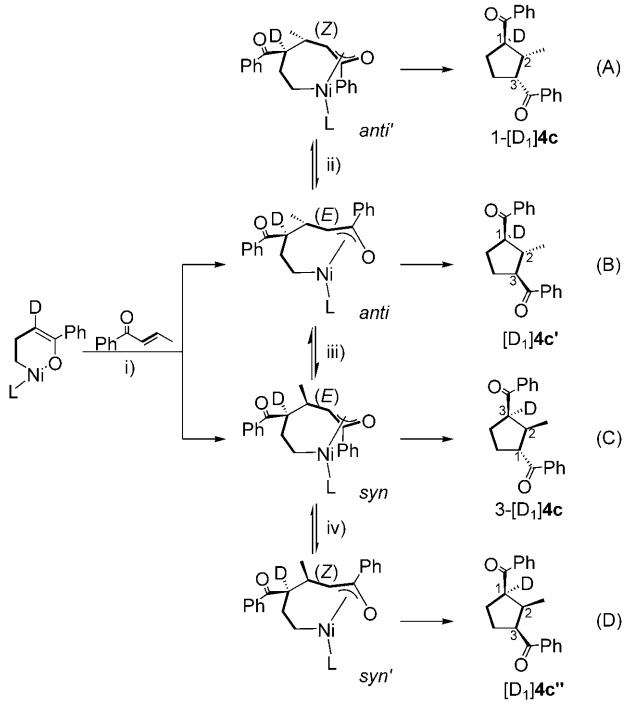


Figure 5. Molecular structure of *syn*-**9ci**. Hydrogen atoms except for those attached to C3, C4, and C6 atoms and *i*Pr groups are omitted for clarity.

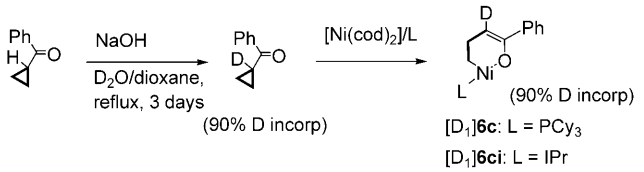
with (*E*)-3-penten-2-one and (*E*)-1-phenylbut-2-en-1-one at room temperature. This result indicates that the nickelenolate complex was stabilized by its dimeric structure.

As above, the diastereoselectivity of the η^3-oxa-allylnickel complex differs from ligand to ligand. In addition, η^3-oxa-allylnickel complexes *anti*-**9c** (with PCy_3) and *syn*-**9ci** (with IPr) had been assumed as a key intermediate in homo-dimerization reactions of **1c** by using Ni^0/PCy_3 (by our group) and Ni^0/IPr (by Montgomery's group) catalytic systems.[14a,b] We wondered, nevertheless, why the same major product **4c** was obtained from the two catalytic reactions. Given that reductive elimination of cyclopentane derivative from η^3-oxa-allylnickel complexes progressed with the retention of stereochemistry, the prospective stereochemistry observed in the reaction products can be accounted for by the processes A–D shown in Scheme 8; paths A–D are interchanged by equilibria that involve insertion/reinsertion of enones (iii) and flipping of the η^3-oxa-allyl moiety (ii and iv). In addition, the introduction of a deuterium atom into the nickelenolate complex enabled us to distinguish between two products along path A (from *anti'*) and along path C (from *syn*).



Scheme 8. Prospective diastereomeric relationship between η^3-oxa-allylnickel complexes and reductive elimination products.

The deuterium-labeled cyclopropyl phenyl ketone ([D_1]**1c**) was prepared according to the reported procedure[18] and 90% of deuterium was incorporated regioselectively at the α position of the carbonyl group as revealed by ^1H and ^2H NMR spectroscopy. When preparation of nickelenolates **6c** and **6ci** was applied by using [D_1]**1c** instead of **1c**, the reaction products [D_1]**6c** and [D_1]**6ci** incorporated deuterium at the γ position regioselectively (Scheme 9).

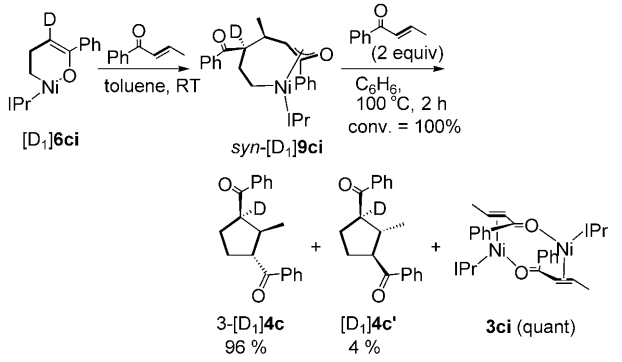


Scheme 9. Synthesis of [D_1]**6c** and [D_1]**6ci**.

Treatment of deuterio-nickelenolates with (*E*)-1-phenylbut-2-en-1-one resulted in formation of the corresponding γ-deuterio-η^3-oxa-allylnickel complexes. During the successive process for preparation of labeled complexes, no degradation of deuterium ratio was observed (see the Supporting Information).

When a solution of the isolated *syn*-[D_1]**9ci** in benzene was heated at 100 °C for 2 h in the presence of two equivalents of (*E*)-1-phenylbut-2-en-1-one, *syn*-[D_1]**9ci** was consumed completely to result in the formation of the reductive elimination products (3-[D_1]**4c**, [D_1]**4c′**) in quantitative yield

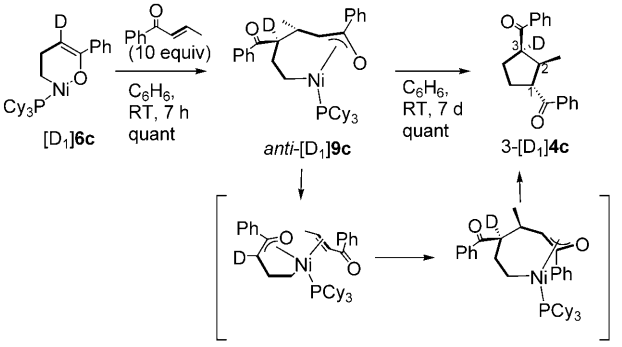
with excellent *syn* diastereoselectivity (96:4; Scheme 10).[19] This result clearly indicates that the diastereomeric relationship in *syn*-**9ci** is retained during the reductive elimination



Scheme 10. Reductive elimination of cyclopentanes from *syn*-[D_1]**9ci**.

step and hence the relationship is reflected in that of the cyclopentane derivative **4c**. Furthermore, the observed diastereoselectivity in the reductive elimination of **4c** from *syn*-**9ci** is strongly consistent with that of Ni^0/IPr-catalyzed homo-dimerization of cyclopropyl phenyl ketone.

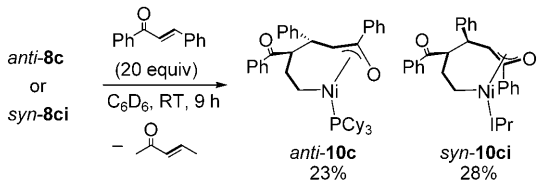
On the other hand, reductive elimination from the PCy_3-ligated analogue *anti*-[D_1]**9c** was found to progress with an *inversion* of the stereochemistry (Scheme 11). The deuterio-



Scheme 11. Reductive elimination of cyclopentanes from *anti*-[D_1]**9c**.

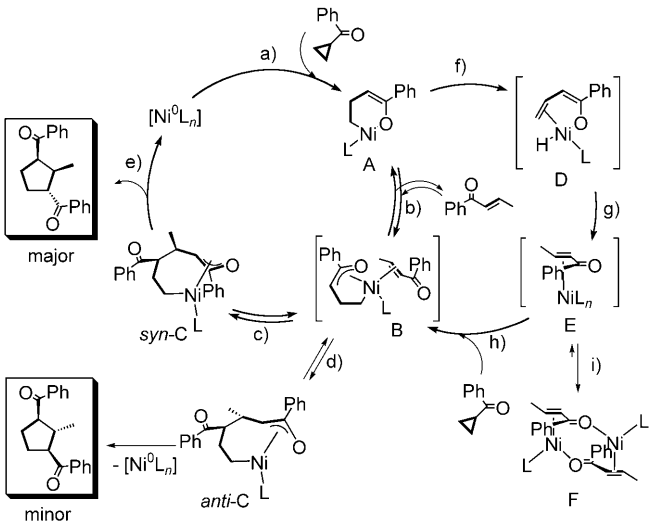
η^3-oxa-allylnickel complex *anti*-[D_1]**9c**, which was prepared in situ by treating [D_1]**6c** with (*E*)-1-phenylbut-2-en-1-one, underwent gradual reductive elimination at room temperature to give the same product (3-[D_1]**4c**) as observed in Scheme 10. The formation of [D_1]**4c′**, the anticipated product from *anti*-[D_1]**9c** with retention of stereochemistry, was not observed at all. This labeling experiment revealed that rapid isomerization between *syn* and *anti* isomers (equilibrium (iii) in Scheme 8) occurs prior to reductive elimination, and that the reductive elimination product is derived not from the kinetically controlled *anti* isomer (along path B in Scheme 8) but from its *syn* isomer (along path C in Scheme 8).

The occurrence of carbon–carbon bond cleavage and the dissociation of the enone was confirmed by addition of an excess amount of *trans*-chalcone to a solution of *anti*-**8c** and *syn*-**8ci** (Scheme 12). The replacement of (*E*)-3-pentene-2-one with *trans*-chalcone to give *anti*-**10c** and *syn*-**10ci**, respectively, was observed.[20]



Scheme 12. Exchange of enone.

Reaction path for nickel-catalyzed [3+2] cycloaddition: The nickel-catalyzed [3+2] cycloaddition of cyclopropyl ketones with enones might proceed as follows (Scheme 13). The oxi-



Scheme 13. Plausible reaction mechanism for [3+2] cycloaddition.

dative addition of cyclopropyl ketone to Ni^0 generates an oxa-nickelacycle (**A**). The insertion of an enone into **A** leads to the formation of an η^3-oxa-allylnickel intermediate (**C**). Reductive elimination from *anti*-**C** and *syn*-**C** gives the corresponding cyclopentane derivatives and regenerates the nickel(0) species. Lability of coordinated enone in a key intermediate (**B**) is caused not only rapid isomerization between *anti*-**C** and *syn*-**C** but insertion/reinsertion equilibrium of enones (paths b, c, and d). This reversible insertion/reinsertion process is also supported by Scheme 12. In homo-cycloaddition, the isomerization of cyclopropyl ketone to the corresponding enone (along paths f, g, and h) might occur to supply an isomeric enone to the nickel-catalyzed [3+2] cycloaddition.

There are notable differences in the diastereoselectivity of the insertion of an enone into oxa-nickelacycles with different ligands (one with PCy_3 and the other with IPr). The stoichiometric reaction of the oxa-nickelacycle with IPr as a ligand with an enone gave a single isomer of the η^3-oxa-allylnickel species with *syn* stereochemistry. However, the η^3-oxa-allylnickel complex with *anti* stereochemistry was selectively obtained under the same reaction conditions by using PCy_3 as a ligand (Scheme 7). Nevertheless, labeling experiments clearly revealed that reductive elimination from either η^3-oxa-allylnickel complex, *anti*-[D_1]**9c** and *syn*-[D_1]**9ci**, gives the same product (3-[D_1]**4c**) (Scheme 10 and 11). These observations could be rationalized based on the results mentioned above. The diastereomeric relationship in *syn*-**9ci** is retained during the reductive elimination step. In contrast, thermal isomerization of *anti*-**9c** with PCy_3 would take place prior to reductive elimination and, as a result, its *syn* diastereoisomer predominantly undergoes reductive elimination to give the same product as observed in that derived from *syn*-**9ci**. Reversible isomerization between *anti*-**C** and *syn*-**C** can also account for the formation of a minor product that is derived from the η^3-oxa-allylnickel intermediate (*anti*-**C**). It should be mentioned that mechanisms involving direct isomerization between major and minor products can be excluded since neither **3ci** nor **3c**, observed in situ after the homo-dimerization reactions of **1c**, catalyzed the isomerization between major and minor products in the catalytic reactions (see the Supporting Information).

Conclusion

We demonstrated for the first time the formation of six-membered oxa-nickelacycles by oxidative addition of cyclopropyl ketones to nickel(0) complexes. IPr is a better ligand than PCy_3 for the generation of six-membered hetero-nickelacycles. Molecular structures of oxa-nickelacycle with IPr were determined by X-ray crystallography, in which dimeric and monomeric η^1-nickelenolate structures exist. In the molecular structure for monomeric complexes, the nickel(II) 14-electron center is regarded as having "an unusual T-shaped planar" coordination geometry. The insertion of enones into a monomeric η^1-nickelenolate complex took place at room temperature to generate η^3-oxa-allylnickel complexes, whereas the insertion into a dimeric η^1-nickelenolate complex did not occur. We also confirmed that the insertion of enones into oxa-nickelacycles is reversible. Differing diastereoselectivity was observed when enones were inserted into oxa-nickelacycles with different ligands (one with PCy_3 and the other with IPr). Labeled experiments revealed that the stereochemistry of IPr-ligated η^3-oxa-allylnickel complexes was retained during reductive elimination, thereby giving corresponding [3+2] cycloaddition products. This finding is strongly consistent with the diastereoselectivity observed in Ni^0/IPr-catalyzed [3+2] cycloaddition reactions of cyclopropyl ketones with enones. In contrast, because of rapid isomerization between *syn* and *anti* isomers prior to reductive elimination, the reductive elimination from the η^3-oxa-allylnickel with PCy_3 as a ligand took place with a simultaneous inversion of the stereochemistry. These observations provide deep insights into the nickel-catalyzed [3+2] cycloaddition reactions of cyclopropyl ketones.

Experimental Section

General: All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or dry box techniques. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded using JEOL GSX-270S, JEOL AL-400, Bruker DPX 400, and Varian UNITY INOVA600 spectrometers at room temperature unless otherwise stated. The chemical shifts in ^1H NMR spectra were recorded relative to Me_4Si or residual protiated solvent (C_6D_5H (δ = 7.16 ppm) or C_7D_7H (δ = 7.02 or 7.13 ppm)). The chemical shifts in the ^{13}C NMR spectra were recorded relative to Me_4Si. The chemical shifts in the ^{31}P NMR spectra were recorded using 85% H_3PO_4 as external standard. Assignment of the resonances in ^1H and ^{13}C NMR spectra was based on ^1H–^1H COSY, HMQC, and HMBC experiments. Elemental analyses were performed at the Instrumental Analysis Center, Faculty of Engineering, Osaka University. For some compounds, accurate elemental analysis were precluded by extreme air or thermal sensitivity and/or systematic problems with elemental analysis of organometallic compounds. X-ray crystallographic data were collected using a Rigaku RAXIS-RAPID Imaging Plate diffractometer.

Isolation of 6ai: Cyclopropanecarboxaldehyde (37.1 mg, 0.53 mmol) was added to a solution of [Ni(cod)$_2$] (111.8 mg, 0.40 mmol) and IPr (155.1 mg, 0.40 mmol) in toluene (3 mL). The reaction mixture was stirred at room temperature for 4 h. The solution changed from red to yellow. The solution was concentrated in vacuo. The residue was dissolved in toluene, and the solution was concentrated in vacuo again. The residue was washed with hexane to give **6ai** (203.2 mg, a yellow solid, 98%). A single crystal for X-ray diffraction analysis was prepared by recrystallization from toluene/hexane at −20 °C. ^1H NMR (400 MHz, C_6D_6): δ = 7.38 (t, J = 7.2 Hz, 4H; IPr), 7.34 (d, J = 7.2 Hz, 4H; IPr), 7.24 (d, J = 7.2 Hz, 4H; IPr), 6.43 (s, 4H; N(C***H***)$_2$N), 5.26 (d, J = 6.0 Hz, 2H; -NiOC***H***CH-), 4.05 (td, J = 4.4 Hz, 6.0 Hz, 2H; -NiOCHC***H***-), 3.55 (t, J = 6.4 Hz, 4H; IPr), 2.83 (t, J = 6.4 Hz, 4H; IPr), 1.89 (d, J = 6.4 Hz, 12H; IPr), 1.36 (d, J = 6.4 Hz, 12H; IPr), 1.09 (d, J = 6.4 Hz, 12H; IPr), 0.99 (d, J = 6.4 Hz, 12H; IPr), 0.47 (d, J = 4.4 Hz, 4H; -NiCH$_2$C***H***$_2$-), −0.09 ppm (t, J = 6.0 Hz, 4H; -NiC***H***$_2$CH$_2$-); ^{13}C NMR (100 MHz, C_6D_6): δ = 188.2 (s; N***C***N), 147.5 (s; -NiO***C***HCH-), 146.3 (s; IPr), 146.0 (s; IPr), 137.1 (s; IPr), 129.5 (s; IPr), 124.7 (s; IPr), 124.1 (s; IPr), 123.5 (s; N(***C***H)$_2$N), 99.2 (s; -NiOCH***C***H-), 28.7 (s; IPr), 28.6 (s; IPr), 26.2 (s; IPr), 24.5 (s; IPr), 23.1 (s; IPr), 21.2 (s; -NiCH$_2$***C***H$_2$-), 2.0 ppm (s; -Ni***C***H$_2$CH$_2$-); elemental analysis calcd (%) for $C_{62}H_{84}N_4Ni_2O_2$: C 71.97, H 8.18, N 5.41; found: C 72.14, H 8.25, N 5.28. X-ray data for **6ai**: M_r = 517.39 (monomer); yellow; monoclinic; $C2/c$ (no. 15); a = 21.712(15), b = 11.938(8), c = 22.976(16) Å; β = 108.666(6)°; V = 5642.1(68) Å^3; Z = 8; ρ_{calcd} = 1.218 g cm^{-3}; T = −150.0 °C; R (R_w) = 0.0379 (0.0955).

Isolation of 6ci: Cyclopropyl phenyl ketone (150.0 mg, 1.03 mmol) was added to a solution of [Ni(cod)$_2$] (277.1 mg, 1.01 mmol) and IPr (393.1 mg, 1.01 mmol) in cold toluene (7 mL, −20 °C). The reaction mixture was stirred for 2 min, and the solution changed from red to purple. The solution was concentrated in vacuo. The residue was dissolved in cold toluene (−20 °C), and the solution was concentrated in vacuo again. The residue was washed with hexane to give **6ci** (587.4 mg, a purple solid, 92%). A single crystal for X-ray diffraction analysis was prepared by recrystallization from toluene/hexane at −20 °C. ^1H NMR (270 MHz, C_6D_6): δ = 7.84 (d, J = 7.6 Hz, 2H; Ph), 7.03–7.29 (m, 9H; IPr, Ph), 6.29 (s, 2H; N(C***H***)$_2$N), 5.14 (t, J = 4.2 Hz, 1H; -NiOC(Ph)C***H***-), 2.79 (quintet, J = 6.8 Hz, 4H; IPr), 1.60 (d, J = 6.8 Hz, 12H; IPr), 1.53 (2H; -NiC***H***$_2$CH$_2$-, obscured by IPr peak), 1.06 (d, J = 6.8 Hz, 12H; IPr), 0.61 ppm (td, J = 4.2 Hz, 6.0 Hz, 2H; -NiCH$_2$C***H***$_2$-); ^{13}C NMR (100 MHz, [D_8]toluene, −80 °C): δ = 180.2 (s; N***C***N), 156.6 (s; -NiO***C***(Ph)CH-), 145.1 (s; IPr), 141.0 (s; Ph), 137.3 (s; IPr), 130.1 (s; IPr), 127.1 (s; Ph), 125.0 (s;

Ph), 124.7 (s; Ph), 124.0 (s; IPr), 123.0 (s; N(*C*H)$_2$N), 93.2 (s; -NiOC(Ph)*C*H-), 28.6 (s; IPr), 25.6 (s; -NiCH$_2$*C*H$_2$-), 24.1 (s; IPr), 8.5 ppm (s; -Ni*C*H$_2$CH$_2$-); elemental analysis calcd (%) for $C_{37}H_{46}N_2NiO$: C 74.88, H 7.81, N 4.72; found: C 74.58, H 7.81, N 4.65. X-ray data for **6ci**·0.5(C_6H_{14}): M_r = 636.57; purple; monoclinic; *C*2/*c* (no. 15); a = 22.586(5), b = 14.833(3), c = 23.912(5) Å; β = 116.078(3)°; V = 7195.5(24) Å^3; Z = 8; ρ_{calcd} = 1.175 g cm^{-3}; T = −150.0 °C; R (R_w) = 0.0519 (0.1109).

Generation of [Ni{μ-η^1,η^3-CH$_2$CH$_2$CH(COPh)CH(CH$_3$)CH=C(Ph)O}-(PCy$_3$)] (*anti*-9c): (*E*)-1-Phenyl-2-buten-1-one (14.6 mg, 0.1 mmol) was added to a solution of **6c** (0.01 mmol, 4.9 mg) in C_6D_6 (0.5 mL) at room temperature. The reaction was followed by ^{1}H and ^{31}P NMR spectra. After 7 h, the solution changed from orange to deep orange, and the orange precipitation disappeared. Compound *anti*-**9c** was generated quantitatively. ^{1}H NMR (270 MHz, C_6D_6): δ = 7.03–7.99 (m, 10H; Ph), 5.51 (dd, J = 9.9, 1.3 Hz, 1H; -C*H*=(CPh)ONi-), 3.27–3.32 (m, 1H; -C*H*-(COPh)CHCH$_3$-), 2.31–2.50 (m, 1H; -CH(COPh)C*H*CH$_3$-), 1.06–2.14 (m, 35H; including 2H of -NiCH$_2$C*H*$_2$- at δ = 1.00 and 1.57 ppm), 0.42–0.54 (m, 1H; -NiC*H*$_2$CH$_2$-), 0.22–0.33 ppm (m, 1H; -NiC*H*$_2$CH$_2$-); ^{31}P NMR (109 MHz, C_6D_6): δ = 34.03 ppm (s).

Isolation of [Ni{μ-η^1,η^3-CH$_2$CH$_2$CH(COPh)CH(CH$_3$)CH=C(Ph)O}(IPr)] (*syn*-9ci): Cyclopropyl phenyl ketone (65.0 mg, 0.44 mmol) was added to a solution of [Ni(cod)$_2$] (111.1 mg, 0.40 mmol) and IPr (162.3 mg, 0.42 mmol) in toluene (6 mL). The reaction mixture was stirred at ambient temperature for 5 min. Then (*E*)-1-phenyl-2-buten-1-one (60.6 mg, 0.41 mmol) was added at room temperature. The solution changed from purple to dark brown. The reaction mixture was stirred for 20 min, followed by concentration in vacuo. The residue was dissolved in toluene, and the solution was concentrated in vacuo again. The residue was washed with hexane to give *syn*-**9ci** (252.1 mg, a yellow solid) in 85% yield. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.38–7.51 (d, J = 7.6 Hz, 6H; Ph, IPr), 6.95–7.19 (m, 10H; Ph, IPr), 6.60 (s, 2H; N(C*H*)$_2$N), 4.73 (d, J = 9.6 Hz, 1H; -C*H*=C(Ph)ONi-), 3.46 (t, J = 6,4 Hz, 2H; IPr), 2.93 (m, 1H; -C*H*(COPh)CH(CH$_3$)-), 2.75 (quintet, J = 6.8 Hz, 2H; IPr), 1.95 (m, 1H; -CH(COPh)C*H*(CH$_3$)-), 1.53 (d, J = 6.8 Hz, 6H; IPr), 1.32 (d, J = 6.8 Hz, 3H; -CH(COPh)CH(C*H*$_3$)-), 1.23 (m, 1H; -NiCH$_2$C*H*$_2$-), 1.19 (d, J = 7.2 Hz, 6H; IPr), 1.07 (d, J = 7.2 Hz, 6H; IPr), 1.05 (d, J = 7.2 Hz, 6H; IPr), 0.60 (t, J = 3.8 Hz, 12.0 Hz, 1H; -NiCH$_2$C*H*$_2$-), 0.21 (m, 1H; -NiC*H*$_2$CH$_2$-), −0.16 ppm (td, J = 12.0 Hz 1H; -NiC*H*$_2$CH$_2$-); ^{13}C NMR (100 MHz, C_6D_6): δ = 201.1 (s; -CH(*C*OPh)CH(CH$_3$)-), 192.2 (s; N*C*N), 155.1 (s; Ph), 146.8 (s; IPr), 146.7 (s; IPr), 141.0 (s; Ph), 138.5 (s; Ph), 136.9 (s; IPr), 131.4 (s; Ph), 130.0 (s; IPr), 128.7 (s; Ph), 128.5 (s; Ph), 128.1 (s; Ph), 127.9 (s; Ph), 124.4 (s; IPr), 124.2 (s; Ph), 75.0 (s; -*C*H=C(Ph)ONi-), 54.2 (s; -*C*H(COPh)CH(CH$_3$)-), 33.5 (s; -CH(COPh)*C*H-(CH$_3$)-), 29.4 (s; -NiCH$_2$*C*H$_2$-), 29.0 (s; IPr), 28.9 (s; IPr), 26.4 (s; IPr), 25.5 (s; IPr), 23.2 (s; IPr), 22.7 (s; IPr), 20.1 (s; -CH(COPh)CH(*C*H$_3$)-), 0.98 ppm (s; -Ni*C*H$_2$CH$_2$-); elemental analysis calcd (%) for $C_{47}H_{56}N_2NiO_2$: C 76.02, H 7.63, N 3.79; found: C 76.32, H 7.67, N 3.83. X-ray data for *syn*-**9ci**: M_r = 739.67; yellow; monoclinic; $P2_1/a$ (no. 14); a = 14.9301(5), b = 15.8322(6), c = 18.3235(7) Å; β = 111.6129(11)°; V = 4026.7(3) Å^3; Z = 4; ρ_{calcd} = 1.220 g cm^{-3}; T = −150.0 °C; R (R_w) = 0.0956 (0.3224).

Reaction of *syn*-[D$_1$]9ci with (*E*)-1-phenyl-2-buten-1-one: (*E*)-1-Phenyl-2-buten-1-one (4.2 mg, 0.028 mmol) was added to a solution of *syn*-[D$_1$]**9ci** (10.6 mg, 0.014 mmol) in C_6H_6 (0.5 mL). The reaction mixture was heated at 100 °C for 2 h. The solution changed from yellow to brown. All of the starting material were converted to generate a mixture of 3-[D$_1$]**4c** and [D$_1$]**4c′**. NMR spectroscopic analysis of 3-[D$_1$]**4c** revealed a selective incorporation of deuterium at the 3-position.

Reaction of *anti*-[D$_1$]9c with (*E*)-1-phenyl-2-buten-1-one: (*E*)-1-Phenyl-2-buten-1-one (15.7 mg, 0.11 mmol) was added to a solution of *anti*-[D$_1$]**9c** (0.01 mmol, generated in situ from the procedure mentioned above) in C_6H_6 (0.5 mL). The reaction mixture was monitored at room temperature for 7 d. After 7 d, the solution changed from yellow to brown. The complex *anti*-[D$_1$]**9c** was completely consumed to generate 3-[D$_1$]**4c** quantitatively. NMR spectroscopic analysis of 3-[D$_1$]**4c** revealed a selective incorporation of deuterium at the 3-position.

CCDC 726581 (**6ai**), 726582 (**6ci**·0.5(C_6H_{14})), 726583 ((*syn*-**8ci**)·0.5(C_7H_8)), 726584 (*syn*-**9ci**) and 726585 (*syn*-**10ci**·0.5(C_7H_8)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[16] The treatment of nickel compounds with carbon monoxide can yield $[Ni(CO)_4]$ (extremely toxic) due to the addition of insufficient amounts of PR_3 or IPr, careless handling, or an accident. The reaction mixture must be handled in a well-ventilated fume hood.

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[20] The complex *syn*-**10ai** was alternatively synthesized by the reaction of **6ci** with *trans*-chalcone, and its molecular structure was confirmed by X-ray diffraction study (see also the Supporting Information).

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