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Reversible Carbon−Carbon Bond Formation between 1,3-Dienes and Aldehyde or Ketone on Nickel(0)

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Abstract: The reversible oxidative cyclization of dienes and aldehydes with nickel(0) proceeded to give η^3:η^1-allylalkoxynickel complexes. The treatment of these complexes with carbon monoxide led to the formation of the corresponding lactone and/or the regeneration of a butadiene and an aldehyde concomitant with the formation of $Ni(CO)_3(PCy_3)$. The scission of the nickel−oxygen bond of the allylalkoxy complexes with $ZnMe_2$ leading to η^3-allyl(methyl)nickel was very efficient to suppress the reverse reaction of the oxidative cyclization. The methylated η^3-allylnickel compound underwent the reductive elimination. The carbonylative coupling reaction of the η^3-allyl(methyl)nickel proceeded as well under a carbon monoxide atmosphere. Similarly, the addition of Me_3SiCl to η^3:η^1-allylalkoxynickel complexes was also efficient for the inhibition of the reverse reaction. The resulting η^3-1-siloxyethylallylnickel complex was treated with carbon monoxides followed by the addition of MeOH to give the expected hydroxyester. This method is efficient as well even for the η^3:η^1-allyl(alkoxy)nickel complex containing acetone as a component, which was so prone to undergo the reverse reaction hampering its isolation. The isolation of the η^3:η^1-allylalkoxynickel complex containing ketone as a component was made easier by the use of heavier butadiene and ketone, such as 2,3-dibenzyl-1,3-butadiene and benzophenone or by the use of cyclobutanone. The reaction with styrene oxide gave the η^3:η^1-allylalkoxynickel containing phenylacetoaldehyde, an isomer of styrene oxide.

Introduction

The oligomerizations, co-oligomerizations, or polymerizations of 1,3-dienes catalyzed by nickel(0) complexes and their reaction mechanisms had been studied well.[1] Most of these studies were on the reaction of 1,3-butadienes with carbon−carbon double or triple bonds. However, there have been only a limited number of examples of the carbon−carbon formation between the 1,3-butadiene and carbon−oxygen double bond. The stoichiometric reaction of 1,3-butadiene with carbon dioxide gave the corresponding η^3:η^1-allylcarboxynickel complexes by the oxidative cyclization of C═C and C═O on nickel(0), of which structure was determined by X-ray diffraction analysis.[2] Similarly stoichiometric reactions of 1,3-butadiene with aldehydes or ketones have been reported, in which only organic compounds have been isolated as reaction products.[3] On the other hand, the formation of a carbon−carbon bond between aldehydes or ketones and 1,3-butadienes in the presence of nickel(0) catalyst and alkylating or reducing reagents has been achieved in the past decade,[4] in which the oxidative cyclization of dienes and carbonyl units on nickel(0) is proposed for a possible key step to form the carbon−carbon bond.[4b]

Recently, we made the direct observation of the oxidative cyclization of η^2-alkene and η^2-aldehyde or η^2-ketone on nickel to give nickeladihydrofurans.[5,6] If the reaction of 1,3-butadienes with aldehydes or ketones on nickel(0) proceeds via the oxidative cyclization, the formation of an η^3:η^1-allylalkoxy complex is expected. However, this step might compete with the formation of η^3:η^1-allylalkylnickel complexes arising from extremely facile diene dimerization on nickel(0) under catalytic reaction conditions.[7] In fact, in the presence of a catalytic amount of Ni(0), the reaction of a diene with aldehyde or ketone proceeded to give alcohols containing a diene and a carbonyl compound in the ratio of 2:1, in which an η^3:η^1-allylalkylnickel was proposed as a key intermediate.[8] On the other hand, only

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(4) (a) Takimoto, M.; Hiraga, Y.; Sato, Y.; Mori, M. *Tetrahedron Lett.* **1998**, 4543−4546. (b) Kimura, M.; Ezoe, A.; Shibata, K.; Tamaru, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4033−4034. (c) Kimura, M.; Fujimatsu, H.; Ezoe, A.; Shibata, K.; Shimizu, M.; Matsumoto, S.; Tamaru, Y. *Angew. Chem, Int. Ed*. **1999**, *38*, 397−400. (d) Kimura, M.; Matuo, S.; Shibata, K.; Tamaru, Y. *Angew. Chem, Int. Ed*. **1999**, *38*, 3386−3388. (e) *Modern Organonickel Chemistry*; Tamaru, Y., Eds.; Wiley−VCH: Weinheim, 2005.
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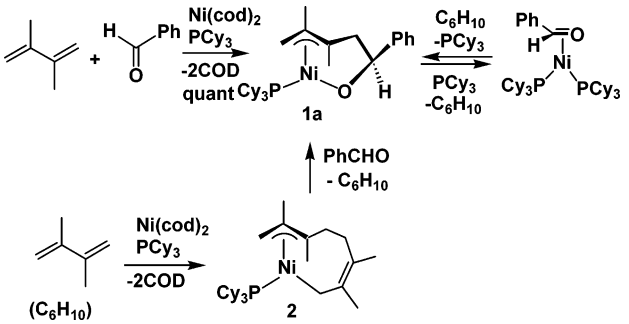
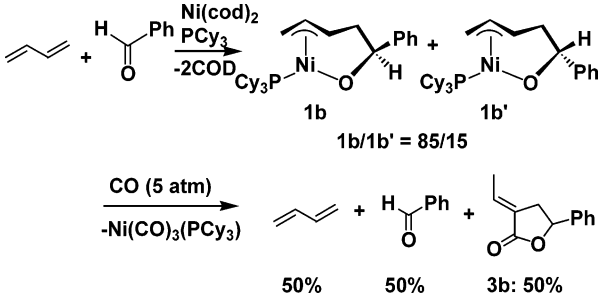
Scheme 1. Formation of η^3:η^1-Allylalkoxynickel Complex **1a**



Scheme 2. Formation of η^3:η^1-Allylalkoxynickel Complex **1b** and **1b′**



a few reaction products via η^3:η^1-allylalkylnickel had been reported in the presence of alkyl metals.[4d] Thus, it seems of particular interest to gain deep insight into the behavior of dienes, carbonyl compounds, and alkyl metals on nickel, which might be complementary to the missing part of the nickel−butadiene chemistry. Here, we report the formation and the structure of η^3:η^1-allylalkoxynickel complexes by the reaction of an aldehyde or a ketone with dienes in the presence of nickel(0) for the first time and their feasible reverse reaction accompanying the carbon−carbon cleavage. Moreover, the role of the third component, such as $ZnMe_2$ and Me_3SiCl, to suppress the reverse reaction is also discussed.

Results and Discussion

Reaction of Diene with Aldehyde. The addition of 5 equiv of 2,3-dimethyl-1,3-butadiene to a solution of benzaldehyde, PCy_3, and $Ni(cod)_2$ gave the corresponding η^3:η^1-allylalkoxynickel complex (**1a**) (Scheme 1) as a sole product. The molecular structure of **1a** was also confirmed by the X-ray diffraction analysis (Figure 1), which is consistent with that in a solution determined by the NOE measurement between an Me group bound to C3 and the hydrogen on C5. Furthermore, the stereochemistry of the only product in the nickel-catalyzed homoallylation of PhCHO with 2,3-dimethyl-1,3-butadiene in the presence of Et_3B was consistent with that assumed to be derived from an intermediate corresponding to **1a**.[1b] Both the order of the addition of substrates and the ratio of nickel and phosphine are important for the efficient formation of the η^3:η^1-allylalkoxynickel complex. Although **1a** was generated quantitatively in 10 min by the addition of 2,3-dimethyl-1,3-butadiene (5 equiv) to the solution of benzaldehyde, PCy_3, and $Ni(cod)_2$ in C_6D_6, the addition of 2,3-dimethyl-1,3-butadiene 5 min prior to benzaldehyde led to an incomplete formation of **1a** (80%) after 16 h with a homocoupling product η^3:η^1-allylalkylnickel (**2**, 20%) present. This might be due to the rapid formation of **2** and the slow transformation from **2** to **1a**. In fact, the isolated **2** reacted with benzaldehyde slowly to give **1a** (80%, 48 h) and 2,3-dimethyl-1,3-butadiene. Such a carbon−carbon bond cleavage had been also observed in the reaction of **2** with PPh_3.[7] On the other hand, the formation of **1a** by the reaction of (η^2-PhCHO)$Ni(PCy_3)_2$[9] with 2,3-dimethyl-1,3-butadiene was faster (2 h, 75%), although the reaction did not proceed completely due to the reverse reaction accompanying the carbon−carbon bond cleavage to give an equilibrium mixture. This might be caused by the presence of an excess amount of PCy_3 in solution. In fact, the addition of PCy_3 (1 equiv) to a solution of **1a** in C_6D_6 led to the formation of an equilibrium mixture with the regeneration of (η^2-PhCHO)Ni-$(PCy_3)_2$ and 2,3-dimethyl-1,3-butadiene (25% each), which is consistent with the observation mentioned above.

Similarly, the addition of 5 equiv of 1,3-butadiene to a solution of benzaldehyde, PCy_3 and $Ni(cod)_2$ led to the formation of the η^3:η^1-allylalkoxynickel complex as a mixture of two isomers (**1b**/**1b′** = 85/15) (Scheme 2). The molecular structure of **1b** was confirmed by X-ray diffraction analysis (Figure 2). The complex shows a slightly different η^3-allyl structure from that of the normal η^3-allyl ligand. The bond length between C2−C3 (1.37(2) Å) is significantly shorter than C1−C2 (1.45(2) Å). This observation suggests a larger contribution of sp^2 hybridization on C3 than C1, although Ni−C1 (2.00(1) Å) and Ni−C3 (2.01(1) Å) are comparable. The ^{13}C NMR spectra show the consistent trend; the resonance of C3 (δ 97.4) in **1b** appears at a much lower magnetic field than that of C1 (δ 31.3). A similar NMR trend was also reported in η^3-allylpalladium complexes.[10]

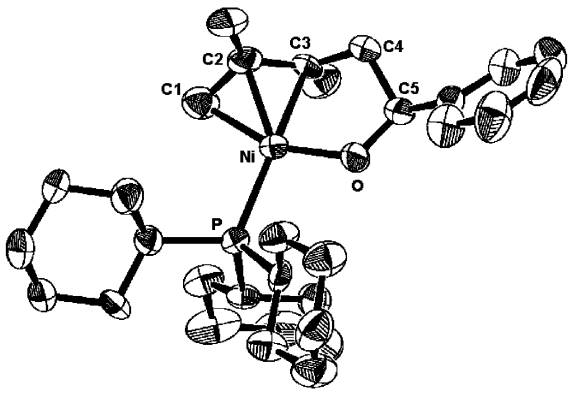


Figure 1. Molecular structure **1a**.

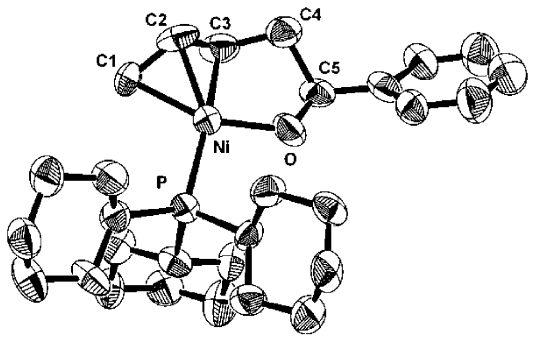
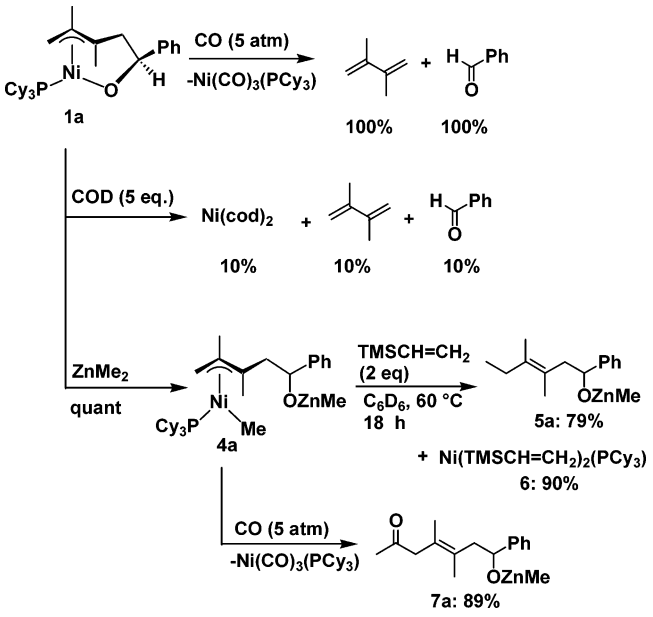


Figure 2. Molecular structure **1b**.

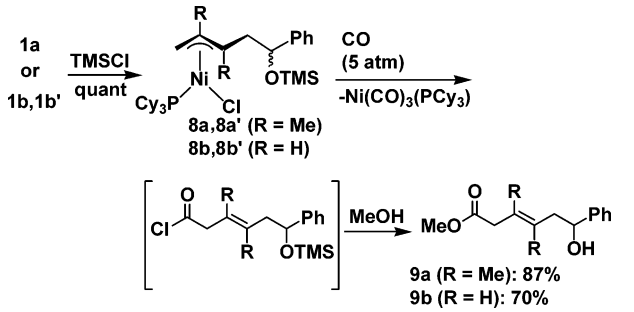
Scheme 3. Reaction of η^3:η^1-Allylalkoxynickel Complex **1a** To Form **7a**



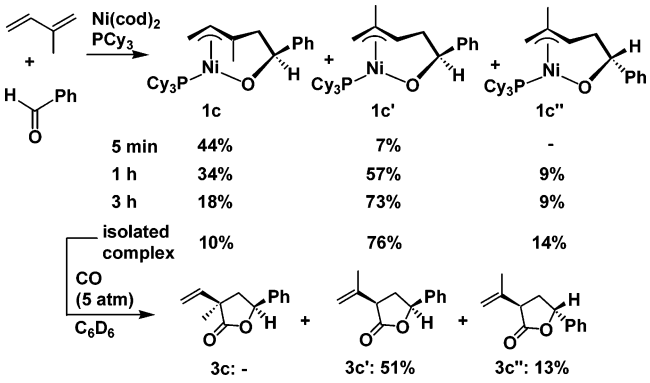
The treatment of a mixture of **1b** and **1b** with carbon monoxide (5 atm) gave a carbonylated compound, 3-(*E*)-ethylidene-5-phenyl-dihydrofuran-2(3*H*)-one (**3b**) generated by the isomerization of initial carbonylation product, 5-phenyl-3-vinyl-dihydrofuran-2(3*H*)-one, in 50% yield, as well as 1,3-butadiene and benzaldehyde concomitant with the formation of $Ni(CO)_3(PCy_3)$ (Scheme 2). However, **1a** gave no carbonylated compound, but only quantitative regeneration of 2,3-dimethyl-butadiene and benzaldehyde was observed under the same condition. Moreover, the addition of 5 equiv of COD to the solution of **1a** in C_6D_6 also led to the regeneration of $Ni(cod)_2$, PCy_3, 2,3-dimethyl-1,3-butadiene, and benzaldehyde in 10% yield for each, with 90% of **1a** remaining intact. Thus, the carbon−carbon bond cleavage to regenerate diene and aldehyde might occur very easily in the presence of suitable ligands, such as PCy_3, carbon monoxide, and COD, which can stabilize a nickel(0) species generated in situ.

We were interested in confirming if dialkylzinc compounds can generate a nickel−alkyl bond and oxygen−zinc bond by the reaction with **1a**, since the multicomponent coupling reactions proceeded in the presence of alkylmetal compounds, such as dialkylzinc.[4c,d,11] In fact, $ZnMe_2$ reacted with **1a** very rapidly to give η^3-(allyl)Ni(Me)(PCy_3) (**4a**) (Scheme 3), although the reaction of $ZnMe_2$ with **2** did not occur at all under the same reaction conditions. This result, together with the reversibility of formation of **2**, rationalizes why the dimerization of dienes does not inhibit the catalytic multicomponent reaction. Unfortunately **4a** could not be isolated in pure form due to the decomposition during concentration under reduced pressure. The ^{1}H NMR and ^{31}P NMR spectra indicate that **4a** is a mixture of isomers, which might be caused by the difference of the aggregation of the −OZnMe moiety. Thus, the formation

Scheme 4. Reaction of η^3:η^1-Allylalkoxynickel Complex **1a** or **1b**,**1b′** To Form **9a**,**9b**



Scheme 5. Reaction of Isoprene with PhCHO



of **4a** was confirmed by the transformation into organic compounds. In the presence of 2 equiv of $TMSCH{=}CH_2$, **4a** underwent the reductive elimination at 60 °C to give the corresponding organozinc compound (**5a**) and $Ni(TMSCH{=}CH_2)_2(PCy_3)$ (**6**).[12] Moreover, although the treatment of **1a** with carbon monoxide regenerated diene and PhCHO quantitatively, the reaction of **4a** with carbon monoxide under the same condition occurred to give the acylated compound (**7a**) via the insertion of carbon monoxide followed by the reductive elimination.

The treatment **1a** with Me_3SiCl is also efficient for the carbonylation of **1a** without the occurrence of the carbon−carbon bond cleavage. The η^3-1-siloxyethylallylnickel (**8a**) prepared from **1a** and Me_3SiCl reacted with carbon monoxide to give an acid chloride determined as its methyl ester in 87% yield (Scheme 4).[13] The mixture of **1b** and **1b′** also gave the corresponding methyl ester in 70% yield as well. These results suggest that the cleavage of the nickel−oxygen bond would be a key role of the reducing or alkylating reagent having Lewis acidic character, promoting the catalytic reaction by preventing the nicklacycle from undergoing the backward carbon−carbon bond cleavage.

The reaction of isoprene and PhCHO with $Ni(cod)_2$ and PCy_3 proceeded very rapidly to give a mixture of three isomers (Scheme 5). As the reaction proceeded, the ratio of isomers changed from **1c**/**1c′**/**1c″** = 87/13/0 to 18/73/9, which suggests that the kinetic compound **1c** isomerizes to **1c′** and **1c″** to give an equilibrium mixture of these three complexes. In the nickel-catalyzed reaction of the three component coupling reaction of

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(11) Calculation for the role of $ZnMe_2$ in nickel(0)-catalyzed couping reaction of enone, alkyne with $ZnMe_2$: Hratchian, H. P.; Chowdhury, S. K.; Gutiérrez-García, V. M.; Amarasinghe, K. K. D.; Heeg, M. J.; Schlegel, H. B.; Montgomery, J. *Organometallics* **2004**, *23*, 4636−4646.
(12) Olefin-promoted reductive elimination of η^3-allylnickel(II): Kurosawa, H.; Ohnishi, H.; Emoto, M.; Chatani, N.; Kawasaki, Y.; Murai, S.; Ikeda, I. *Organometallics* **1990**, *9*, 3038−3042.
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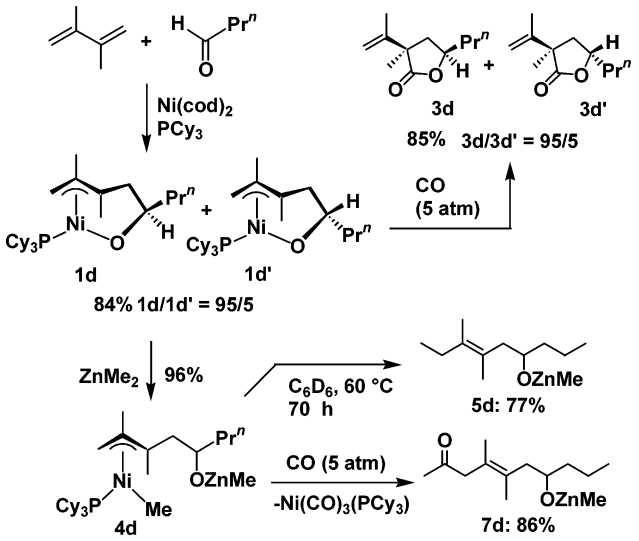
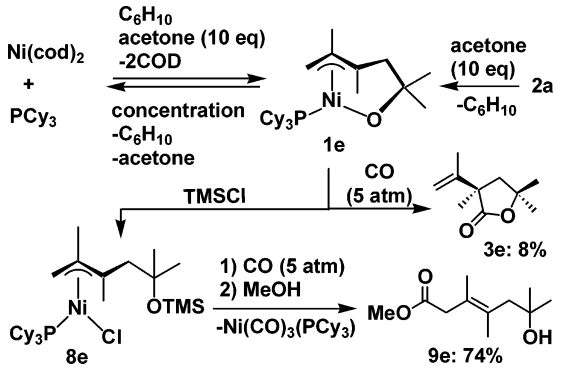
Scheme 6. Reaction of 2,3-Dimethyl-1,3-butadiene with Butanal



Scheme 7. Reaction of 2,3-Dimethyl-1,3-butadiene with Acetone

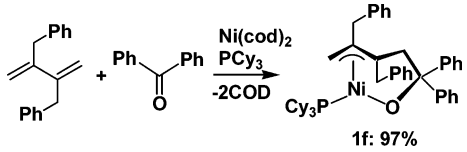


isoprene with PhCHO and Et_3B reported by Tamaru, only one regioisomer derived from an intermediate corresponding to **1c** was obtained.[4c] This isomer might be obtained by the rapid transmetalation of **1c** with an alkylzinc compound prior to the isomerization. The reaction of the mixture of **1c**, **1c′**, and **1c″** (10/76/14) with carbon monoxide gave a mixture of **3c′** and **3c″** in 51% and 13%, respectively. However, the carbonylated compound of **1c** was not observed in the reaction mixture, which might be due to the requirement of the less favorable formation of a quaternary carbon.

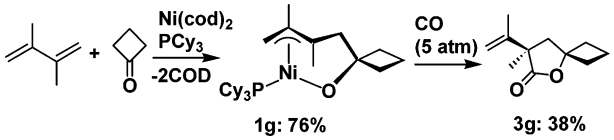
The reaction of 2,3-dimethyl-1,3-butadiene with butanal proceeded smoothly to give a mixture of two isomers in 84% isolated yield (**1d**/**1d′** = 95/5) (Scheme 6). The treatment of the mixture of **1d** and **1d′** with carbon monoxide (5 atm) led to the formation of a mixture of carbonylated compounds (**3d**/**3d′** = 95/5), although **1a**, the corresponding PhCHO analogue, gave no carbonylated compound. The reaction of **1d** with $ZnMe_2$ also gave **4d**, which could be isolated as a mixture of two isomers. The elemental analysis showed the expected composition. The reductive elimination occurred at 60 °C to give **5d** in 77% yield. The treatment with carbon monoxide (5 atm) gave **7d** in 86% yield.

Reaction of Diene with Ketone. The reaction of 2,3-dimethyl-1,3-butadiene with acetone (10 equiv) generated the corresponding η^3:η^1-allylalkoxynickel complex (**1e**) in 94% yield in C_6D_6 (Scheme 7). Unfortunately, the isolation of **1e** by the general method failed, since the quantitative regeneration

Scheme 8. Reaction of 2,3-Benzyl-1,3-butadiene with Benzophenone



Scheme 9. Reaction of 2,3-Dimethyl-1,3-butadiene with Cyclobutanone



of $Ni(cod)_2$ and PCy_3 occurred during concentration of the reaction mixture under reduced pressure. By the use of **2** as a starting material, **1e** could be isolated. However, the reaction with carbon monoxide gave the expected compound **3e** in poor yield (8%). Thus, the addition of TMSCl to the reaction mixture, as described in Scheme 4, was applied to suppress the proceeding of the reverse reaction. This method was efficient as well even for the transformation of **1e** into an ester derivative (**9e**), containing diene and ketone in its structure, by carbonylation followed by the treatment with MeOH.

The failure of the isolation of **1e** by the general method might be due to the removal of more volatile 2,3-dimethyl-1,3-butadiene and acetone generated by the reverse reaction prior to COD under reduced pressure. If a much heavier diene and ketone were employed as the coupling components, it would be easier to isolate cyclized complexes. The reaction of 2,3-dibenzyl-1,3-butadine with benzophenone proceeded cleanly to give expected η^3:η^1-allylalkoxynickel (**1f**) quantitatively, and the reverse reaction did not occur under reduced pressure to allow us to isolate **1f** (Scheme 8). The molecular structure of **1f** was determined by the X-ray diffraction analysis. The treatment of carbon monoxide (5 atm) regenerated the diene and ketone quantitatively. The η^3:η^1-allylalkoxynickel complex (**1g**) formed by the reaction of 2,3-dimethyl-1,3-butadiene with cyclobutanone could be also isolated (Scheme 9), and its molecular structure is shown in Figure 3. No occurrence of the reverse reaction under reduced pressure might be owing to the release of the steric strain energy of the cyclobutane ring by the change of hybridization of carbonyl carbon from sp^2 to sp^3. Moreover, even under carbon monoxide pressure (5 atm), **1g**

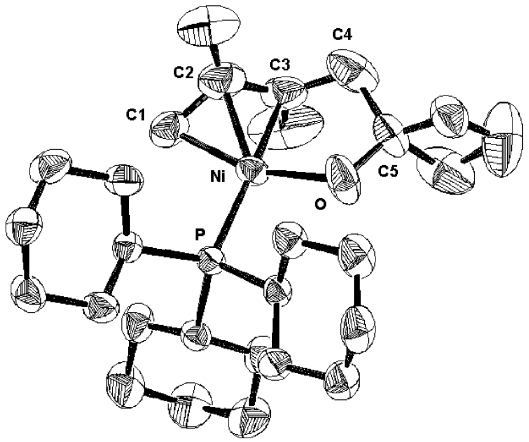
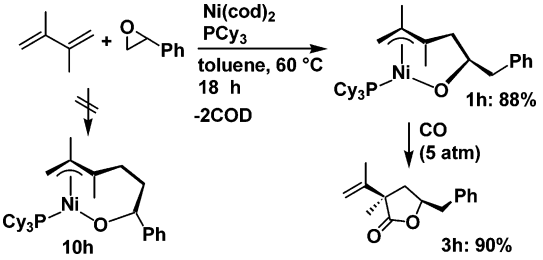
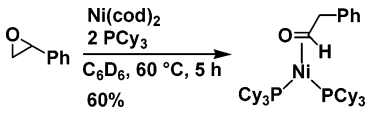


Figure 3. Molecular structure **1g**.

Scheme 10. Reaction of 2,3-Dimethyl-1,3-butadiene with Styrene Oxide



Scheme 11. Formation of (η^2-Phenylacetoaldehyde)nickel



resisted the release of the diene and ketone to some extent and underwent the carbonylation to give **3g** in 38% yield.

Reaction of Diene with Oxirane. The reaction of 2,3-dimethyl-1,3-butadiene with styrene oxide was examined to study if a ring-expanded η^3:η^1-allylalkoxynickel can be obtained or not. The reaction occurred at 60 °C in toluene to not give a ring-expanded complex (**10h**) but an unexpected complex (**1h**) derived from 2,3-dimethyl-1,3-butadiene and phenylacetoaldehyde, an isomer of styrene oxide (Scheme 10). This result indicates that styrene oxide isomerized to phenylacetoaldehyde under the reaction conditions. In fact, the isomerization occurred at 60 °C for 5 h to give (η^2-$PhCH_2CHO$)$Ni(PCy_3)_2$ in 60% yield (Scheme 11).[14] Thus, styrene oxide can be employed as a precursor of phenylacetoaldehyde.

Conclusion

The reversible oxidative cyclization of dienes and aldehydes or ketones on nickel(0) proceeded to give η^3:η^1-allylalkoxynickel complexes. The structures of some complexes were determined by the X-ray diffraction analysis. Consideration of the isomerization of the kinetic complex to the thermodynamic complexes at room temperature during the oxidative cyclization between isoprene, PhCHO, and nickel(0) and the structure of the reported three component coupling product suggests that a relatively rapid transmetalation step between the kinetic intermediate complex and alkyl metals might occur in a catalytic reaction. Moreover, the role of alkyl metals having Lewis acidic character was also revealed to be the cleavage of the nickel−oxygen bond to suppress the reverse reaction. The reaction with styrene oxide resulted in the formation of the η^3:η^1-allylalkoxynickel containing phenylacetoaldehyde as a component. This result suggests that oxiranes could be potential precursors to their isomeric aldehydes or ketones.

Experimental Section

General: All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or drybox techniques. ^{1}H, ^{31}P, and ^{13}C nuclear magnetic resonance spectra were recorded on JEOL GSX-270S and JEOL AL-400 spectrometers. The chemical shifts in ^{1}H nuclear magnetic resonance spectra were recorded relative to Me_4Si or residual protiated solvent (C_6D_5H (δ 7.16) or $CHCl_3$ (δ 7.27)). The chemical shifts in the ^{13}C spectra were recorded relative to Me_4Si. The chemical shifts in the ^{31}P spectra were recorded using 85% H_3PO_4 as external standard. Assignment of the resonances in ^{1}H and ^{13}C NMR spectra was based on ^{1}H−^{1}H COSY, HMQC, and HMBC experiments. HMQC and HMBC experiments are inverse detection heterocorrelated NMR experiments recorded at the ^{1}H frequency of the spectrometer, probing one-bond (CH) and multiple-bond (CCH and CCCH) connectivity. The relative stereochemistry about the η^3-allylnickel moiety and −ONi moiety (**1a**, **1b**, **1c**, **1c′**, **1d**, and **1h**) was determined by the NOE measurement between substituent groups bound to C3 and C5 as indicated in Figure 1. Elemental analyses were performed at the Instrumental Analysis Center, Faculty of Engineering, Osaka University. For some compounds, accurate elemental analyses were precluded by extreme air or thermal sensitivity and/or systematic problems with elemental analysis of organometallic compounds. X-ray crystal data were collected by a Rigaku RAXIS-RAPID Imaging Plate diffractometer.

Materials: The degassed and distilled solvents (THF, toluene, and hexane) used in this work were commercially available. C_6D_6 was distilled from sodium benzophenone ketyl. All commercially available reagents were distilled and degassed prior to use.

Caution: It is possible that the treatment of nickel compounds with carbon monoxide might give $Ni(CO)_4$ (extremely toxic) by short of amounts of PR_3, careless handling, or an accident. The reaction mixture must be handled in a well ventilated fume hood.

Isolation of 1a: To a solution of $Ni(cod)_2$ (220 mg, 0.80 mmol), PCy_3 (240 mg, 0.80 mmol), and 81.3 μL of PhCHO (84.9 mg, 0.80 mmol) in 5 mL of THF was added 0.45 mL of 2,3-dimethyl-1,3-butadiene (328.6 mg, 4.00 mmol) at room temperature. The solution changed from orange to yellow. The reaction mixture was stirred for 2 h followed by concentration in vacuo to give yellow solids (**1a**, 382 mg, 91%). An analytical sample and a single crystal for X-ray diffraction analysis were prepared by recrystallization from hexane at −20 °C. ^{1}H NMR (C_6D_6): δ 1.00−2.00 (m, 36H including 1H of C***H***$_2$CH(Ph)ONi at δ 1.15, 2H of NiC***H***$_2$C(CH_3) at δ 1.57 and δ 1.75), 1.46 (d, J = 2.9 Hz, $NiCH_2C(CH_3)C(CH_3)$), 2.52 (t, J = 11.0 Hz, 1H, C***H***$_2$CH(Ph)ONi), 2.19 (s, 3H, $NiCH_2C(CH_3)$), 6.28 (dd, J = 10.50 Hz, 4.00 Hz, 1H, C***H***(Ph)ONi, 7.19 (d, J = 6.90 Hz, *para* in C_6H_5), 7.37 (t, J = 7.26 Hz, 2H of *meta* in C_6H_5), 7.72 (d, J = 7.26 Hz, 2H of *ortho* in C_6H_5). ^{31}P NMR (C_6D_6): δ 42.3 (s). ^{13}C NMR (C_6D_6): δ 20.2 (d, J_{CP} = 2.3 Hz), 21.8 (s), 27.3 (s, Cy), 28.3 (d, J_{CP} = 5.3 Hz, Cy), 30.9 (s, Cy), 33.7 (d, J_{CP} = 17.5 Hz, Cy), 34.2 (d, J_{CP} = 6.1 Hz), 94.8 (d, J_{CP} = 10.7 Hz, ***C***H(Ph)(ONi)), 101.2 (d, J_{CP} = 15.2 Hz), 113.7 (s), 126.0 (s), 126.4 (s), 128.2 (s), 152.8 (s). Anal. Calcd for $C_{31}H_{49}Ni_1O_1P_1$: C, 70.60; H, 9.36. Found: C, 70.50; H, 9.69.

Reaction of (η^2-PhCHO)$Ni(PCy_3)_2$ with 2,3-Dimethyl-1,3-butadiene: To a solution of (η^2-PhCHO)$Ni(PCy_3)_2$ (14.6 mg, 0.02 mmol) in 0.5 mL of C_6D_6 were added 2.3 μL of 2,3-dimethyl-1,3-butadiene (1.6 mg, 0.02 mmol) at room temperature. The solution changed from orange to red orange immediately to give **1a** (80%, 2 h).

Reaction of 2 with PhCHO: To a solution of **2** (10.1 mg, 0.02 mmol) in 0.5 mL of C_6D_6 were added 2.0 μL of PhCHO (2.0 mg, 0.02 mmol) at room temperature. The reaction proceeded slowly to give **1a** (80%, 48 h).

Reaction of 1a with Carbon Monoxide: A pressure tight NMR tube containing 0.5 mL of C_6D_6 (0.5 mL) solution of **1a** (5.3 mg, 0.01 mmol) was treated with carbon monoxide (5 atm). The solution changed from orange to colorless immediately to give 2,3-dimethyl-1,3-butadiene, benzaldehyde, and $Ni(CO)_3(PCy_3)$ quantitatively.

Reaction of 1a with COD: To a solution of **1a** (5.3 mg, 0.01 mmol) in 0.5 mL of C_6D_6 were added 6.1 μL of COD (5.4 mg, 0.05 mmol) at room temperature. The reaction proceeded immediately to give 2,3-dimethyl-1,3-butadiene, benzaldehyde, PCy_3, and $Ni(cod)_2$ (10% each). 90% of **1a** remained intact.

(14) Palladium-catalyzed isomerization of oxirans to aldehydes was reported: Vanker, Y. D.; Chandhuri, N. C.; Singh, S. D. *Synth. Commun.* **1986**, *16*, 1621−1626.

Isolation of 1b: A solution of $Ni(cod)_2$ (275 mg, 1.0 mmol), PCy_3, (289 mg, 1.0 mmol), and 101.6 μL of PhCHO (106.1 mg, 1.0 mmol) in 5 mL of toluene was cooled to −10 °C, and 270.5 mg of 1,3-butadiene (122.5 mL (gas), 5.0 mmol) were added and the mixture was stirred for 10 min. The solution changed from red to red-purple. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 1 h followed by concentration in vacuo. The residue was washed with hexane to give orange solids (336.2 mg, 68%) as a mixture of two isomers (**1b**/**1b′** = 85/15). An analytical sample and a single crystal for X-ray diffraction analysis were prepared by recrystallization from hexane at −20 °C. **1b**: ^{1}H NMR (C_6D_6): δ 0.99 (d, J = 12.4 Hz, 1H, NiC***H***$_2$CH), 1.15−2.15 (m, 36H, including 1H of NiC***H***$_2$CH at δ 1.86 and 2H of C***H***$_2$CH(Ph)ONi), 4.14 (t, J = 12.0, 4.0 Hz, 1H, NiCH$_2$CHC***H***), 5.50 (td, J = 6.4 Hz, 12.0 Hz, 1H, NiCH$_2$C***H***), 6.17 (dd, J = 4.0 Hz, 9.8 Hz, 1H, C***H***(Ph)ONi), 7.19 (m, 1H, *para* in C_6H_5), 7.36 (t, J = 7.6 Hz, 2H of *meta* in C_6H_5), 7.69 (d, J = 7.6 Hz, 2H of *ortho* in C_6H_5). ^{31}P NMR (C_6D_6): δ 35.9 (s). ^{13}C NMR(C_6D_6): δ 27.2 (s, Cy), 28.2 (d, J_{CP} = 3.0 Hz, Cy), 28.3 (d, J_{CP} = 2.3 Hz, Cy), 30.8 (s, Cy), 31.3 (d, J_{CP} = 6.9 Hz, Ni***C***H$_2$CH), 34.0 (s, Cy), 34.2 (s, Cy), 48.5 (s, ***C***H$_2$CH(Ph)ONi), 97.1 (d, J_{CP} = 13.8 Hz, ***C***H(Ph)ONi), 97.4 (d, J_{CP} = 10.7 Hz, NiCH$_2$CH***C***H), 109.8 (s, NiCH$_2$***C***H), 126.2 (s), 126.4 (s), 128.1 (s), 152.1 (s). **1b′**: ^{1}H NMR (C_6D_6): δ 4.27 (m, 1H, NiCH$_2$CHC***H***), 5.72 (m, 1H, NiCH$_2$C***H***), 6.36 (d, J = 6.4 Hz, 1H, C***H***(Ph)ONi), 7.45 (t, J = 7.6 Hz, 2H of *meta* in C_6H_5), 7.94 (d, J = 7.6 Hz, 2H of *ortho* in C_6H_5). The other resonances are hidden by those of **1b**. ^{31}P NMR (C_6D_6): δ 34.35 (s). The resonances of the minor isomer could not be observed in a ^{13}C NMR spectrum. Anal. Calcd for $C_{29}H_{45}O_1P_1Ni_1$ (a mixture of **1b** and **1b′**): C, 69.76; H, 9.08. Found: C, 69.41; H, 9.17.

Reaction of 1b with Carbon Monoxide: A pressure tight NMR tube containing 0.5 mL of a C_6D_6 solution of a mixture of **1b** and **1b** (10.1 mg, 0.02 mmol) was treated with carbon monoxide (5 atm). The solution changed from orange to yellow immediately to give the carbonylation product[15](**3b**: 50%), 1,3-butadiene (50%), benzaldehyde (50%), and $Ni(CO)_3(PCy_3)$ (100%).

Reaction of 1a with $ZnMe_2$: To a solution of **1a** (10.5 mg, 0.02 mmol) in 0.5 mL of C_6D_6 was added $ZnMe_2$ (0.02 mmol, 20 μL, 1 M/hexane) at room temperature. The reaction proceeded immediately to give **4a** quantitatively. **4a** could not be isolated in pure form due to the decomposition during concentration under a reduced pressure. The ^{1}H NMR and ^{31}P NMR spectra indicate that **4a** is a mixture of isomers. Selected spectral data for **4a**: ^{1}H NMR (C_6D_6): δ −0.30 (brm, 3H, OZnC***H***$_3$), −0.20 (brd, J_{HP} = 3.2 Hz, 3H, NiC***H***$_3$), 3.05 (brm, 2H, C***H***$_2$CH(Ph)OZnMe), 5.79 (dd, J_{HH} = 2.7, 10.8 Hz, 1H, C***H***(Ph)-OZnMe). ^{31}P NMR (C_6D_6): δ 50.5 (m).

Reaction of 4a with TMSCH═CH_2: To a solution of **4a** generated by the reaction of **1a** (20.9 mg, 0.04 mmol) with $ZnMe_2$ (0.04 mmol, 40 μL, 1 M/hexane) in 0.5 mL of C_6D_6 was added TMSCH═CH_2 (0.08 mmol, 8.0 mg), and the mixture was heated at 60 °C for 18 h. The formation of Ni(TMSCH═CH_2)$_2$(PCy_3) (**6**) was confirmed by the comparison of the ^{31}P NMR spectrum with that of an authentic sample. **5a** was identified as an alcohol by protonation followed by separation from nickel compound by the column. ^{1}H NMR ($CDCl_3$): δ 0.94 (t, J = 7.6 Hz, 3H, −CH$_2$C***H***$_3$), 1.70 (s, 6H, −C(C***H***$_3$)═C(C***H***$_3$)−), 2.07 (m, 1H, −C***H***$_2$CH$_3$), 2.17 (q, J = 7.6 Hz, 1H, −C***H***$_2$CH$_3$), 2.28 (dd, J = 4.8, 9.4 Hz, 1H, −C***H***$_2$CH(OH)Ph), 2.68 (dd, J = 9.6, 11.6 Hz, 1H, −C*H*$_2$CH(OH)Ph), 4.79 (dd, J = 11.6, 4.8 Hz, 1H, −CH$_2$C***H***(OH)Ph), 7.25−7.41 (m, 5H, −Ph). ^{13}C NMR ($CDCl_3$): δ 13.21 (s, −CH$_2$***C***H$_3$), 18.33 (s, −C(***C***H$_3$)═C(***C***H$_3$)−), 18.78 (s, −C(CH$_3$)═C(***C***H$_3$)−), 27.41 (s, −***C***H$_2$CH$_3$), 44.81 (s, −***C***H$_2$CH-(OH)Ph), 72.44 (s, −CH$_2$***C***H(OH)Ph), 123.52 (s, −C(CH$_3$)═***C***(CH$_3$)−), 125.91 (s, Ph), 127.50 (s, Ph), 128.52 (s, Ph), 135.29 (s, −***C***(CH$_3$)═C(CH$_3$)−), 144.77 (s, Ph). HRMS Calcd for $C_{14}H_{20}O_1$ 204.3122, found *m*/*z* 204.1513.

Reaction of 4a with Carbon Monoxide: In a pressure tight NMR tube, a solution of **4a** in 0.5 mL of C_6D_6 generated by the reaction of **1a** (20.9 mg, 0.04 mmol) with $ZnMe_2$ (0.04 mmol, 40 μL, 1 M/hexane) was treated with carbon monoxide (5 atm). The solution changed from brown to colorless immediately to give **7a** and $Ni(CO)_3(PCy_3)$ (89%). **7a** was identified as the corresponding alcohol by protonation separated by a silica column.^{1}H NMR ($CDCl_3$): δ 1.68 (s, 6H, −C(C***H***$_3$)═C(C***H***$_3$)−), 2.13 (s, 3H, −COC***H***$_3$), 2.37 (dd, J = 5.1, 13.4 Hz, 1H, −C***H***$_2$CH(OH)Ph), 2.72 (dd, J = 8.9, 13.2 Hz, 1H, −C***H***$_2$CH(OH)Ph), 3.16 (d, J = 16.3 Hz, 1H, −C***H***$_2$COCH$_3$), 3.27 (d, J = 16.7 Hz, 1H, −C***H***$_2$COCH$_3$), 4.82 (dd, J = 8.9, 5.1 Hz, 1H, −CH$_2$C***H***(OH)Ph), 7.33−7.41 (m, 5H, −Ph). ^{13}C NMR ($CDCl_3$): δ 19.64 (s, −C(***C***H$_3$)═C(CH$_3$)−), 20.49 (s, −C(CH$_3$)═C(*C*H$_3$)−), 30.06 (s, −CH$_2$CO***C***H$_3$), 45.61 (s, −***C***H$_2$CH(OH)Ph), 50.77 (s, −***C***H$_2$COCH$_3$), 73.02 (s, −CH$_2$***C***H(OH)Ph), 126.44(s, Ph), 126.88 (s, −***C***(CH$_3$)═C(CH$_3$)−), 128.06 (s, Ph), 129.01 (s, Ph), 129.67 (s, −C(CH$_3$)═***C***(CH$_3$)−), 145.02 (s, Ph), 207.48 (s, −CH$_2$***C***OCH$_3$). HRMS Calcd for $C_{15}H_{18}O_1$ (−H_2O) 214.3073, Found *m*/*z* 214.1353.

Reaction of 1a with TMSCl: To a solution of **1a** (5.3 mg, 0.01 mmol) in 0.5 mL of C_6D_6 was added TMSCl (1.1 mg, 0.01 mmol, 1.3 μL) at room temperature. The reaction proceeded gradually to give an η^3-1-siloxyethylallylnickel quantitatively for 4 h as a mixture of two isomers (**8a**: 60%, **8a′**: 40%). These are diastereomers via η^1-allyl species as an intermediate. **8a**: ^{1}H NMR (C_6D_6): δ 0.07 (s, 9H, −OSi(C***H***$_3$)$_3$), 1.01−2.05 (m, 38H, including 1H of NiC***H***$_2$C(CH$_3$) at δ 1.51, 3H of NiCH$_2$C(CH$_3$)C(C***H***$_3$) at δ 1.59 and 1H of NiC***H***$_2$C-(CH$_3$) at δ 1.92), 2.21 (s, 3H, NiCH$_2$C(C***H***$_3$)), 2.62 (dd, J = 14.5, 5.8 Hz, 1H, −C***H***$_2$CH(Ph)OTMS), 2.79 (dd, J = 14.5, 7.2 Hz, 1H, −C***H***$_2$CH(Ph)OTMS), 5.08 (m, 1H, C***H***(Ph)OTMS), 7.09 (d, J = 6.9 Hz, 1H of *para* in C_6H_5), 7.16 (hidden by C_6D_6 peak, 2H of *meta* in C_6H_5), 7.33 (d, J = 6.9 Hz, 2H of *ortho* in C_6H_5). ^{31}P NMR (C_6D_6): δ 41.9 (s). ^{13}C NMR (C_6D_6): δ 0.52 (s, −OSi(***C***H$_3$)$_3$), 21.0 (s, NiCH$_2$C-(***C***H$_3$)), 23.3 (d, J_{CP} = 2.3 Hz, NiCH$_2$C(CH$_3$)C(***C***H$_3$)), 27.2 (s, Cy), 28.2 (s, Cy), 28.3 (s, Cy), 30.7 (d, J_{CP} = 3.8 Hz, Cy), 30.9 (s, Cy), 34.3 (d, J_{CP} = 18.3 Hz, Cy), 40.0 (d, J_{CP} = 6.8 Hz, Ni***C***H$_2$C(CH$_3$)), 48.8 (d, J_{CP} = 2.3 Hz, −***C***H$_2$CH(Ph)OTMS), 73.5 (d, J_{CP} = 5.3 Hz, −CH$_2$***C***H(Ph)OTMS), 98.1 (d, J_{CP} = 16.8 Hz, NiCH$_2$C(CH$_3$)***C***(CH$_3$), 114.5 (s, NiCH$_2$***C***(CH$_3$), 126.5 (s, Ph), 127.6 (s, Ph), 128.7 (s, Ph), 146.2 (s, Ph). An analytical sample was not obtained due to gradual decomposition in a solution. **8a′**: ^{1}H NMR (C_6D_6): δ 0.02 (s, 9H, −OSi(C***H***$_3$)$_3$), 1.01−2.05 (m, 38H, including 3H of NiCH$_2$C(CH$_3$)C-(C***H***$_3$) at δ 1.44, 1H of NiC***H***$_2$C(CH$_3$) at δ 1.62 and 3H of NiCH$_2$C-(C***H***$_3$)C(CH$_3$) at δ 1.72), 2.12 (1H, s, NiC***H***$_2$C(CH$_3$)), 2.48 (d, J = 14.5 Hz, 1H, −C***H***$_2$CH(Ph)OTMS), 2.70 (d, J = 10.5 Hz, 1H, −C***H***$_2$-CH(Ph)OTMS), 5.06 (m, 1H, C***H***(Ph)OTMS). The other resonances are hidden by those of **8a**. ^{31}P NMR (C_6D_6): δ 41.5 (s). ^{13}C NMR (C_6D_6): δ 0.49 (s, −OSi(***C***H$_3$)$_3$), 20.9 (d, J_{CP} = 3.0 Hz, NiCH$_2$C(CH$_3$)C-(***C***H$_3$)), 22.1 (s, NiCH$_2$C(***C***H$_3$)), 34.4 (d, J_{CP} = 18.3 Hz, Cy), 40.9 (d, J_{CP} = 6.1 Hz, Ni***C***H$_2$C(CH$_3$)), 48.5 (d, J_{CP} = 3.3 Hz, −***C***H$_2$CH(Ph)-OTMS), 72.7 (d, J_{CP} = 3.8 Hz, −CH$_2$***C***H(Ph)OTMS), 96.8 (d, J_{CP} = 16.8 Hz, NiCH$_2$C(CH$_3$)***C***(CH$_3$)), 115.3 (s, NiCH$_2$***C***(CH$_3$)), 126.4 (s, Ph), 127.5 (s, Ph), 128.8 (s, Ph), 146.6 (s, Ph). The other resonances are hidden by those of **8a**. An analytical sample was not obtained due to gradual decomposition in a solution.

Reaction of a mixture of 1b and 1b′ with TMSCl: To a solution of a mixture of **1b** and **1b′** (9.9 mg, 0.02 mmol) in 0.5 mL of C_6D_6 was added TMSCl (2.2 mg, 0.02 mmol, 2.5 μL) at room temperature. The reaction proceeded immediately to give an η^3-1-siloxyethylallylnickel quantitatively as a mixture of two isomers (**8b**: 60%, **8b′**: 40%). These are diastereomers via η^1-allyl species as an intermediate. **8b**: ^{1}H NMR (C_6D_6): δ 0.12 (s, 9H, −OSi(C***H***$_3$)$_3$), 1.05−2.03 (m, 34H, including 1H of NiC***H***$_2$CH at δ 1.34), 2.17−2.21 (m, 2H, including 1H of NiC***H***$_2$CH and C***H***$_2$CH(Ph)OTMS), 2.82 (m, 1H, −C***H***$_2$CH(Ph)OTMS), 3.77 (ddd, J = 17.8, 9.1, 4.3 Hz, 1H, NiCH$_2$-CHC***H***), 4.82 (m, 1H, NiCH$_2$C***H***), 5.16 (m, 1H, C***H***(Ph)OTMS), 7.08 (m, 1H, Ph), 7.18 (hidden by C_6D_6 peak, 2H, Ph) 7.45 (t, J = 7.2 Hz,

(15) Haaima, G.; Lynch, M. J.; Routledge, A.; Weavers, R. *Tetrahedron* **1991**, *47*, 5203−5214.

2H, Ph). ^{31}P NMR (C_6D_6): δ 34.0 (s). ^{13}C NMR (C_6D_6): δ 0.68 (s, $-OSi(\boldsymbol{C}H_3)_3$), 27.1 (s, Cy), 28.2 (d, J_{CP} = 1.5 Hz, Cy), 28.3 (s, Cy), 30.7 (s, Cy), 34.6 (d, J_{CP} = 19.0 Hz, Cy), 39.7 (d, J_{CP} = 6.9 Hz, $Ni\boldsymbol{C}H_2CH$), 44.4 (d, J_{CP} = 2.3 Hz, $\boldsymbol{C}H_2CH(Ph)OTMS$), 73.9 (d, J_{CP} = 3.9 Hz, $\boldsymbol{C}H(Ph)OTMS$), 91.0 (d, J_{CP} = 17.6 Hz, $NiCH_2CH\boldsymbol{C}H$), 109.7 (s, $NiCH_2\boldsymbol{C}H$), 126.5 (s, Ph), 127.4 (s, Ph), 128.3 (Ph, hidden by C_6D_6 peak), 146.2 (s, Ph). An analytical sample was not obtained due to gradual decomposition in a solution. **8b′**: ^{1}H NMR (C_6D_6): δ 0.11 (s, 9H, $-OSi(C\boldsymbol{H}_3)_3$), 1.05−2.03 (m, 34H, including 1H of $NiC\boldsymbol{H}_2CH$ at δ 1.27), 2.30 (m, 1H, $-C\boldsymbol{H}_2CH(Ph)OTMS$), 2.92 (m, 1H, $-C\boldsymbol{H}_2CH(Ph)OTMS$), 3.62 (ddd, J = 18.1, 9.1, 4.3 Hz, 1H, $NiCH_2CHC\boldsymbol{H}$), 4.91 (m, 1H, $NiCH_2C\boldsymbol{H}$). The other resonances are hidden by those of **8b**. ^{31}P NMR (C_6D_6): δ 33.9 (s). ^{13}C NMR (C_6D_6): δ 0.65 (s, $-OSi(\boldsymbol{C}H_3)_3$), 27.1 (s, Cy), 30.7 (s, Cy), 34.6 (d, J_{CP} = 19.0 Hz, Cy), 39.9 (d, J_{CP} = 6.8 Hz, $Ni\boldsymbol{C}H_2CH$), 43.6 (d, J_{CP} = 2.3 Hz, $\boldsymbol{C}H_2CH(Ph)OTMS$), 74.4 (d, J_{CP} = 3.8 Hz, $\boldsymbol{C}H(Ph)OTMS$), 90.6 (d, J_{CP} = 17.6 Hz, $NiCH_2CH\boldsymbol{C}H$), 109.3 (s, $NiCH_2\boldsymbol{C}H$), 127.0 (s, Ph), 127.5 (s, Ph), 128.3 (Ph, hidden by C_6D_6 peak), 145.7 (s, Ph). An analytical sample was not obtained due to gradual decomposition in a solution.

Reaction of 1a with TMSCl Followed by Carbonylation: A pressure tight NMR tube containing a solution of **8a** in C_6D_6 (0.5 mL) generated by the reaction of **1a** (21.1 mg, 0.04 mmol) with TMSCl (4.3 mg, 0.04 mmol, 5.1 μL) was treated with carbon monoxide (5 atm). The solution changed from red to light blue gradually and was quenched with methanol to give a hydroxyester (**9a**: 87%). ^{1}H NMR ($CDCl_3$): δ 1.73 (s, 6H, $-C(C\boldsymbol{H}_3)=C(C\boldsymbol{H}_3)-$), 2.34 (dd, J = 4.9, 13.4 Hz, 1H, $-C\boldsymbol{H}_2COOCH_3$), 2.72 (dd, J = 9.0, 13.4 Hz, 1H, $-C\boldsymbol{H}_2COOCH_3$), 3.04 (d, J = 15.9 Hz, 1H, $-C\boldsymbol{H}_2CH(OH)Ph$), 3.20 (d, J = 15.9 Hz, 1H, $-C\boldsymbol{H}_2CH(OH)Ph$), 3.70 (s, 3H, $-OC\boldsymbol{H}_3$), 4.82 (m, 1H, $-CH_2C\boldsymbol{H}(OH)Ph$), 7.30−7.41 (m, 5H, −Ph). ^{13}C NMR ($CDCl_3$): δ 19.12 (s, $-C(\boldsymbol{C}H_3)=C(CH_3)-$), 19.73 (s, $-C(CH_3)=C(\boldsymbol{C}H_3)-$), 40.15 (s), 45.23 (s), 52.09 (s), 72.52 (s, $-CH_2\boldsymbol{C}H(OH)Ph$), 125.91 (s, Ph), 126.25 (s, $-\boldsymbol{C}(CH_3)=C(CH_3)-$), 127.54 (s, Ph), 128.50 (s, Ph), 129.26 (s, $-C(CH_3)=\boldsymbol{C}(CH_3)-$), 144.44 (s, *ipso*-Ph), 172.58 (s, $-CH_2\boldsymbol{C}OOCH_3$). HRMS (CI) Calcd for $C_{15}H_{21}O_3$ (M + H) 249.1491, Found *m*/*z* 249.1483.

Reaction of a Mixture of 1b and 1b′ with TMSCl Followed by Carbonylation: In a pressure tight NMR tube, a solution of a mixture of **8b** and **8b′** in 0.5 mL of C_6D_6 generated by the reaction of a mixture of **1b** and **1b′** (9.9 mg, 0.02 mmol) with TMSCl (2.2 mg, 0.02 mmol, 2.5 μL) was treated with carbon monoxide (5 atm). The solution changed from red brown to light blue gradually and was quenched with methanol to give the corresponding hydroxyester (**9b**: 70%). ^{1}H NMR ($CDCl_3$): δ 2.52 (m, 2H, $-C\boldsymbol{H}_2COOCH_3$), 3.07 (d, J = 6.8 Hz, 2H, $-C\boldsymbol{H}_2CH(OH)Ph$), 3.69 (s, 3H, $-OC\boldsymbol{H}_3$), 4.73 (t, J = 6.2 Hz, 1H, $-CH_2C\boldsymbol{H}(OH)Ph$), 5.60−5.78 (m, 2H, $-C\boldsymbol{H}=C\boldsymbol{H}-$), 7.28−7.37 (m, 5H, −Ph). ^{13}C NMR ($CDCl_3$): δ 38.03 (s), 42.67 (s), 52.08 (s), 73.59 (s, $-CH_2\boldsymbol{C}H(OH)Ph$), 125.86 (s), 127.00 (s), 127.76 (s), 128.63 (s), 130.55 (s), 144.04 (s, *ipso*-Ph), 172.50 (s, $-CH_2\boldsymbol{C}OOCH_3$). HRMS Calcd for $C_{13}H_{16}O_3$ 220.1099, Found *m*/*z* 220.1095.

Isolation of 1c: To a solution of $Ni(cod)_2$ (220 mg, 0.80 mmol), PCy_3 (240 mg, 0.80 mmol), and 81.3 μL of PhCHO (84.9 mg, 0.80 mmol) in 10 mL of toluene was added 0.40 mL of isoprene (273 mg, 4.00 mmol) at room temperature. The solution changed from dark red to red. The reaction mixture was concentrated under a reduced pressure. The residue was washed with pentane to give yellow solids (297 mg, 72%) as a mixture of three isomers (**1c**/**1c′**/**1c″** = 10/76/14). **1c**: ^{1}H NMR (C_6D_6): δ 1.34 (d, J_{HP} = 3.6 Hz, 3H, $NiCH_2CHC(C\boldsymbol{H}_3)$), 5.49 (dd, J = 7.2 Hz, 12.7 Hz, 1H, $NiCH_2C\boldsymbol{H}$), 6.31 (brd, J = 6.5 Hz, 1H, $C\boldsymbol{H}(Ph)ONi$), 7.46 (t, J = 7.6 Hz, 2H of *meta*-C_6H_5), 7.98 (d, J = 7.6 Hz, 2H of *ortho*-C_6H_5). The other resonances are hidden by those of **1c′**. ^{31}P NMR (C_6D_6): δ 39.9 (s). ^{13}C NMR (C_6D_6): δ 18.6 (d, J_{CP} = 1.5 Hz, $NiCH_2CHC(\boldsymbol{C}H_3)$), 34.2 (d, J_{CP} = 17.5 Hz, Cy), 35.7 (d, J_{CP} = 6.8 Hz, $Ni\boldsymbol{C}H_2CH$), 56.6 (d, J_{CP} = 2.3 Hz, $-\boldsymbol{C}H_2CH(Ph)ONi$), 97.3 (d, J_{CP} = 11.4 Hz, $\boldsymbol{C}H(Ph)ONi$), 105.3 (s, $NiCH_2\boldsymbol{C}H$), 107.6 (d, J_{CP} = 13.7 Hz, $NiCH_2CH\boldsymbol{C}(CH_3)$, 126.2 (s, Ph), 127.4 (s, Ph), 153.7 (s, Ph). **1c′**: ^{1}H NMR (C_6D_6): 1.00−2.00 (m, 36H, including 1H of $NiC\boldsymbol{H}_2CH(CH_3)$ at δ 1.08, 1H of $NiC\boldsymbol{H}_2CH(CH_3)$ at δ 1.63 and 1H of $C\boldsymbol{H}_2CH(Ph)ONi$ at δ 1.91), 2.08 (s, 3H, $NiCH_2CH(C\boldsymbol{H}_3)$), 2.20 (m, 1H, $C\boldsymbol{H}_2CH(Ph)ONi$), 4.08 (dt, J_{HH} = 4.0 Hz, J_{HP} = 11.6 Hz, 1H, $NiCH_2CH(CH_3)C\boldsymbol{H}$), 6.08 (dd, J = 3.6 Hz, 10.5 Hz, 1H, $C\boldsymbol{H}(Ph)ONi$), 7.17 (m, 1H of *para*-C_6H_5), 7.36 (t, J = 7.6 Hz, 2H of *meta*-C_6H_5), 7.71 (d, J = 7.6 Hz, 2H of *ortho*-C_6H_5). ^{31}P NMR (C_6D_6): δ 39.0 (s). ^{13}C NMR (C_6D_6): δ 20.5 (s, $NiCH_2CH(\boldsymbol{C}H_3)$), 27.5 (s, Cy), 28.5 (d, J_{CP} = 6.1 Hz, Cy), 28.6 (d, J_{CP} = 6.8 Hz, Cy), 31.1 (s, Cy), 34.1 (d, J_{CP} = 17.5 Hz, Cy), 36.3 (d, J_{CP} = 6.1 Hz, $Ni\boldsymbol{C}H_2CH(CH_3)$), 44.6 (d, J_{CP} = 2.3 Hz, $\boldsymbol{C}H_2CH(Ph)ONi$), 93.5 (d, J_{CP} = 14.5 Hz, $NiCH_2CH(CH_3)\boldsymbol{C}H$), 96.4 (d, J_{CP} = 10.7 Hz, $\boldsymbol{C}H(Ph)ONi$), 105.3 (s, $NiCH_2\boldsymbol{C}H(CH_3)$), 126.3 (s, Ph), 126.6 (s, Ph), 128.5 (s, Ph), 152.6 (s, Ph). **1c″**: ^{1}H NMR (C_6D_6): δ 4.22 (m, 1H, $NiCH_2CH(CH_3)C\boldsymbol{H}$). The other resonances are hidden by those of **1c′**. ^{31}P NMR (C_6D_6): δ 37.2 (s). Anal. Calcd for $C_{30}H_{47}O_1P_1Ni_1$ (a mixture of **1c**, **1c′,** and **1c″**): C, 70.19; H, 9.23. Found: C, 69.67; H, 9.28.

Reaction of a Mixture of 1c, 1c′, and 1c″ with Carbon Monoxide: A pressure tight NMR tube containing a solution of a mixture of **1c**, **1c′**, and **1c″** (**1c**/**1c′**/**1c″** = 10/76/14) (10.3 mg, 0.02 mmol) in C_6D_6 (0.5 mL) was treated with carbon monoxide (5 atm). The solution changed from orange to colorless immediately to give the carbonylation products (64%) as a mixture of two isomers (**3c′**: 51%, **3c″**: 13%). **3c′**: ^{1}H NMR ($CDCl_3$): δ 1.86 (s, 3H, $-C(C\boldsymbol{H}_3)=CH_2$), 2.25 (ddd, J = 2.2, 11.6, 12.7 Hz, 1H, $-C\boldsymbol{H}_2CH(Ph)O-$), 2.76 (m, 1H, $-C\boldsymbol{H}_2CH(Ph)O-$), 3.53 (dd, J = 5.8, 8.4 Hz, 1H, $-C\boldsymbol{H}(COO-)-$), 5.02 (s, 1H, $-C(CH_3)=C\boldsymbol{H}_2$), 5.06 (s, 1H, $-C(CH_3)=C\boldsymbol{H}_2$), 5.41 (dd, J = 6.5, 8.7 Hz, 1H, $-CH_2C\boldsymbol{H}(Ph)O-$), 7.33−7.43 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 20.07 (s, $-C(\boldsymbol{C}H_3)=CH_2$), 37.23 (s, $-\boldsymbol{C}H_2CH(Ph)O-$), 49.47 (s, $-\boldsymbol{C}H(COO-)-$), 79.29 (s, $-CH_2\boldsymbol{C}H(Ph)O-$), 115.85 (s, $-C(CH_3)=\boldsymbol{C}H_2$), 125.66 (s, Ph), 128.80 (s, Ph), 129.00 (s, Ph), 139.42 (s, $-C(\boldsymbol{C}H_3)=CH_2$), 176.07 (s, $-\boldsymbol{C}OO-$). **3c″**: ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 3H, $-C(C\boldsymbol{H}_3)=CH_2$), 2.43 (m, 1H, $-C\boldsymbol{H}_2CH(Ph)O-$), 2.70 (m, 1H, $-C\boldsymbol{H}_2CH(Ph)O-$), 3.50 (dd, J = 6.9, 4.7 Hz, 1H, $-C\boldsymbol{H}(COO-)-$), 4.99 (s, 1H, $-C(CH_3)=C\boldsymbol{H}_2$), 5.05 (s, 1H, $-C(CH_3)=C\boldsymbol{H}_2$), 5.58 (t, J = 6.9 Hz, 1H, $-CH_2C\boldsymbol{H}(Ph)O-$), 7.33−7.43 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 21.00 (s, $-C(\boldsymbol{C}H_3)=CH_2$), 36.25 (s, $-\boldsymbol{C}H_2CH(Ph)O-$), 47.26 (s, $-\boldsymbol{C}H(COO-)-$), 79.24 (s, $-CH_2\boldsymbol{C}H(Ph)O-$), 114.62 (s, $-C(CH_3)=\boldsymbol{C}H_2$), 125.30 (s, Ph), 128.56 (s, Ph), 128.99 (s, Ph), 139.82 (s, $-C(\boldsymbol{C}H_3)=CH_2$), 176.72 (s, $-\boldsymbol{C}OO-$). HRMS Calcd for $C_{13}H_{14}O_2$ 202.0994, Found *m*/*z* 202.0998 (**3c′**), 202.1001 (**3c″**)

Isolation of 1d: To a solution of $Ni(cod)_2$ (220 mg, 0.80 mmol), PCy_3 (240 mg, 0.80 mmol), and 72.1 μL of ^{n}PrCHO (57.7 mg, 0.80 mmol) in 5 mL of toluene was added 0.45 mL of 2,3-dimethyl-1,3-butadiene (328.6 mg, 4.00 mmol) at room temperature. The solution changed from orange to red. The reaction mixture was stirred for 1 h followed by concentration in vacuo to give yellow solids (**1d**, 414 mg, 84%) as a mixture of two isomers (**1d**/**1d′** = 95/5), which might be caused by the stereochemistry about the η^3-allylnickel moiety and alkoxy carbon. An analytical sample was prepared by recrystallization from hexane at −20 °C. The structure in a solution was determined by the NOE measurement between an Me group bound to C3 and an alkoxy proton (2%). **1d**: ^{1}H NMR (C_6D_6): δ 1.08−1.96 (m, 46H, including 1H of $NiC\boldsymbol{H}_2C(CH_3)$ at δ 1.10, 3H of $-CH_2CH_2C\boldsymbol{H}_3$ at δ 1.13, 3H of $NiCH_2C(CH_3)C(C\boldsymbol{H}_3)$ at δ 1.43 (d, J = 2.3 Hz), 1H of $C\boldsymbol{H}_2CH(^n\text{Pr})ONi$ at δ 1.49, 1H of $NiC\boldsymbol{H}_2C(CH_3)$ at δ 1.58, 2H of $-CH_2C\boldsymbol{H}_2CH_3$ at δ 1.66 and 2H of $CH(C\boldsymbol{H}_2CH_2CH_3)ONi$ at δ 1.68), 2.31 (s, 3H, $NiCH_2C(C\boldsymbol{H}_3)$), 5.20 (m, 1H, $C\boldsymbol{H}(^n\text{Pr})ONi$). ^{31}P NMR ($C_6D_6$) δ 42.07 (s). ^{13}C NMR (C_6D_6) δ 15.5 (s, $-CH_2\boldsymbol{C}H_3$), 20.6 (d, J_{CP} = 3.0 Hz, $NiCH_2C(CH_3)C(\boldsymbol{C}H_3)$), 20.7 (s, $-CH_2CH_3$), 21.9 (s, $NiCH_2C(\boldsymbol{C}H_3)$), 27.3 (s, Cy), 28.3 (d, J_{CP} = 1.5 Hz, Cy), 28.4 (d, J_{CP} = 1.5 Hz, Cy), 30.7 (d, J_{CP} = 1.5 Hz, Cy), 31.0 (d, J_{CP} = 2.3 Hz, Cy), 33.3 (d, J_{CP} = 6.8 Hz, $Ni\boldsymbol{C}H_2C(CH_3)$), 33.6 (d, J_{CP} = 16.7 Hz, Cy), 44.6 (s, $-\boldsymbol{C}H_2CH_2CH_3$), 48.1 (d, J_{CP} = 2.3 Hz, $\boldsymbol{C}H_2CH(^n\text{Pr})ONi$), 93.2 (d, J_{CP} = 10.0 Hz, $CH_2\boldsymbol{C}H(^n\text{Pr})ONi$), 103.0 (d, J_{CP} = 15.3 Hz, $NiCH_2C(CH_3)\boldsymbol{C}(CH_3)$),

113.0 (s, $NiCH_2\boldsymbol{C}(CH_3)$). **1d′**: ^{31}P NMR (C_6D_6) δ 42.08 (s). The resonances of **1d′** in ^1H and ^{13}C spectra are hidden by those of **1d**. Anal. Calcd for $C_{28}H_{51}O_1P_1Ni_1$ (a mixture of **1d** and **1d′**): C, 68.16; H, 10.42. Found: C, 67.87; H, 10.48.

Reaction of a Mixture of 1d and 1d′ with Carbon Monoxide: A pressure tight NMR tube containing a solution of **1d** (19.7 mg, 0.04 mmol) in C_6D_6 (0.5 mL) was treated with carbon monoxide (5 atm). The solution changed from orange to colorless immediately to give the carbonylation products (85%) as a mixture of two isomers (**3d**/**3d′** = 95/5). **3d**: ^1H NMR ($CDCl_3$): δ 0.97 (t, J = 6.8 Hz, 3H, $-CH_2CH_2C\boldsymbol{H}_3$), 1.43 (s, 3H, $-C(C\boldsymbol{H}_3)(COO-)-$), 1.47−1.78 (m, 4H), 1.83 (s, 3H, $-C(C\boldsymbol{H}_3)=CH_2$), 2.09 (d, J = 7.3 Hz, 2H, $-C\boldsymbol{H}_2CH(^n\mathrm{Pr})O-$), 4.47 (m, 1H, $-CH_2C\boldsymbol{H}(^n\mathrm{Pr})O-$), 5.00 (s, 1H, $-C(CH_3)=C\boldsymbol{H}_2$, 5.03 (s, 1H, $-C(CH_3)=C\boldsymbol{H}_2$). ^{13}C NMR ($CDCl_3$): δ 14.06 (s), 18.87 (s), 19.88 (s), 22.24 (s), 37.94 (s), 41.35 (s), 49.71 (s), 77.23 (hidden by $CDCl_3$ peak), 113.17 (s), 144.71 (s), 179.58 (s). **3d′**: ^1H NMR ($CDCl_3$): δ 2.44 (d, J = 5.1 Hz, 1H, $-C\boldsymbol{H}_2CH(^n\mathrm{Pr})O-$), 2.48 (d, J = 5.1 Hz, 1H, $-C\boldsymbol{H}_2CH(^n\mathrm{Pr})O-$), 4.30 (m, 1H, $-CH_2C\boldsymbol{H}(^n\mathrm{Pr})O-$), 4.89 (s, 1H, $-C(CH_3)=C\boldsymbol{H}_2$), 4.95 (s, 1H, $-C(CH_3)=C\boldsymbol{H}_2$). The other resonances in ^1H and ^{13}C spectra are hidden by those of **3d**. HRMS Calcd for $C_{11}H_{18}O_2$ 182.1307, Found *m*/*z* 182.1316.

Isolation of 4d: To a solution of a mixture of **1d** and **1d′** (394.7 mg, 0.8 mmol) in 10 mL of hexane was added $ZnMe_2$ (0.8 mmol, 800 μL, 1 M/hexane) at room temperature. The reaction mixture was concentrated under reduced pressure to give yellow solids (**4d**, 451.3 mg, 96%). ^1H NMR (C_6D_6): δ −0.34 (d, J_{HP} = 4.4 Hz, 3H × 2, $NiC\boldsymbol{H}_3$ × 2), 0.27 (s, 3H, $ZnC\boldsymbol{H}_3$), 0.28 (s, 3H, $ZnC\boldsymbol{H}_3$), 1.13−2.05 (m, 45H × 2, including 3H × 2 of $-CH_2CH_2C\boldsymbol{H}_3$ × 2 at δ 1.22 (t, J = 7.2 Hz), 3H × 2 of $NiCH_2C(CH_3)C(C\boldsymbol{H}_3)$ × 2 at δ 1.40, 1H × 2 of $NiC\boldsymbol{H}_2C(CH_3)$ × 2 at δ 1.61, 1H × 2 of $-CH_2C\boldsymbol{H}_2CH_3$ × 2 at δ 1.89, 1H × 2 of $-CH_2C\boldsymbol{H}_2CH_3$ × 2 at δ 2.01 and 3H × 2 of $NiCH_2C(C\boldsymbol{H}_3)C(CH_3)$ × 2 at δ 2.02 (s)), 2.32 (1H × 2, hidden by $NiC\boldsymbol{H}_2C(CH_3)$ peak), 2.33 (s, 1H × 2, $NiC\boldsymbol{H}_2C(CH_3)$ × 2), 2.44 (m, 1H × 2, $-C\boldsymbol{H}_2CH_2CH_3$), 2.79 (m, 2H × 2, $-C\boldsymbol{H}_2CH(^n\mathrm{Pr})O-$ × 2), 4.78 (brs, 1H × 2, $-C\boldsymbol{H}(^n\mathrm{Pr})O-$ × 2). ^{31}P NMR (C_6D_6): δ 50.70 (s), 50.72 (s). ^{13}C NMR (C_6D_6): δ −9.0 (s, $Zn\boldsymbol{C}H_3$), −8.7 (s, $Zn\boldsymbol{C}H_3$), −6.0 (d, J_{CP} = 3.0 Hz, $Ni\boldsymbol{C}H_3$), −5.9 (d, J_{CP} = 3.8 Hz, $Ni\boldsymbol{C}H_3$), 15.5 (s, $-CH_2\boldsymbol{C}H_3$), 15.6 (s, $-CH_2\boldsymbol{C}H_3$), 19.8 (s, $-C(\boldsymbol{C}H_3)CH_2CH(^n\mathrm{Pr})O-$), 19.9 (s, $-C(\boldsymbol{C}H_3)CH_2CH(^n\mathrm{Pr})O-$), 20.7 (s, $-\boldsymbol{C}H_2CH_3$), 20.8 (s, $-\boldsymbol{C}H_2CH_3$), 23.0 (s, $NiCH_2C(\boldsymbol{C}H_3)-$ × 2), 27.3 (s, Cy), 28.3 (d, J_{CP} = 4.5 Hz, Cy), 28.4 (d, J_{CP} = 4.5 Hz, Cy), 30.8 (s, Cy), 31.0 (s, Cy), 35.5 (s, Cy), 35.7 (s, Cy), 42.9 (s, $-C\boldsymbol{H}_2CH_2CH_3$), 43.1 (s, $-C\boldsymbol{H}_2CH_2CH_3$), 46.8 (s, $-\boldsymbol{C}H_2CH(^n\mathrm{Pr})O-$ × 2), 47.78 (s, $Ni\boldsymbol{C}H_2C(CH_3)-$), 47.80 (s, $Ni\boldsymbol{C}H_2C(CH_3)-$), 75.4 (s, $-\boldsymbol{C}H(^n\mathrm{Pr})O-$), 75.5 (s, $-\boldsymbol{C}H(^n\mathrm{Pr})O-$), 79.1 (d, J_{CP} = 18.3 Hz, $-C(\boldsymbol{C}H_3)CH_2CH(^n\mathrm{Pr})O-$), 79.3 (d, J_{CP} = 18.3 Hz, $-C(\boldsymbol{C}H_3)CH_2CH(^n\mathrm{Pr})O-$), 114.4 (s, $NiCH_2\boldsymbol{C}(CH_3)-$), 114.5 (s, $NiCH_2\boldsymbol{C}(CH_3)-$). Anal. Calcd for $C_{30}H_{57}O_1P_1Ni_1Zn_1$: C, 61.19; H, 9.76. Found: C, 60.64; H, 9.50.

Reductive Elimination from 4d: A solution of **4d** (11.8 mg, 0.02 mmol) in C_6D_6 (0.5 mL) was heated at 60 °C for 70 h. The solution changed from yellow to dark brown, and black solids precipitated. The decomposition of **4d** was confirmed by ^{31}P NMR spectrum. **5d** was identified as an alcohol by protonation followed by separation from nickel compound by the column. ^1H NMR ($CDCl_3$): δ 0.96 (m, 6H, $-CH_2CH_2C\boldsymbol{H}_3$ and $=C(CH_3)CH_2C\boldsymbol{H}_3$), 1.45 (m, 4H, $-C\boldsymbol{H}_2C\boldsymbol{H}_2CH_3$), 1.69 (s, 6H, $-C(C\boldsymbol{H}_3)=C(C\boldsymbol{H}_3)-$), 2.06 (m, 3H, 1H of $-C\boldsymbol{H}_2CH(OH)^n\mathrm{Pr}$ and 2H of $=C(CH_3)C\boldsymbol{H}_2CH_3$), 2.34 (dd, J = 9.3, 13.4 Hz, 1H, $-C\boldsymbol{H}_2CH(OH)^n\mathrm{Pr}$), 3.74 (m, 1H, $-CH_2C\boldsymbol{H}(OH)^n\mathrm{Pr}$). ^{13}C NMR ($CDCl_3$): δ 12.85 (s), 14.37 (s), 18.21 (s), 18.36 (s), 19.30 (s), 27.99 (s), 39.46 (s), 42.83 (s), 69.80 (s), 124.08 (s), 134.68 (s). HRMS Calcd for $C_{11}H_{22}O_1$ 170.1671, Found *m*/*z* 170.1670.

Reaction of 4d with Carbon Monoxide: A pressure tight NMR tube containing a C_6D_6 (0.5 mL) solution of **4d** (23.6 mg, 0.04 mmol) was treated with carbon monoxide (5 atm). The solution changed from orange to colorless immediately to give **7d** and $Ni(CO)_3(PCy_3)$ (86%). **7d** was identified as an alcohol by protonation followed by separation by the column. ^1H NMR ($CDCl_3$): δ 0.94 (t, J = 7.1 Hz, 3H, $-CH_2CH_2C\boldsymbol{H}_3$), 1.47 (m, 4H, $-C\boldsymbol{H}_2C\boldsymbol{H}_2CH_3$), 1.64 (s, 3H, $-C(CH_3)=C(C\boldsymbol{H}_3)-$), 1.70 (s, 3H, $-C(C\boldsymbol{H}_3)=C(CH_3)-$), 2.08 (dd, J = 3.7, 13.4 Hz, 1H, $-C\boldsymbol{H}_2CH(OH)^n\mathrm{Pr}$), 2.15 (s, 3H, $-COC\boldsymbol{H}_3$), 2.41 (dd, J = 9.6, 13.4 Hz, 1H, $-C\boldsymbol{H}_2CH(OH)^n\mathrm{Pr}$), 3.15 (d, J = 16.6 Hz, 1H, $-C\boldsymbol{H}_2COCH_3$), 3.30 (d, J = 16.6 Hz, 1H, $-C\boldsymbol{H}_2COCH_3$), 3.74 (m, 1H, $-CH_2C\boldsymbol{H}(OH)^n\mathrm{Pr}$). ^{13}C NMR ($CDCl_3$): δ 14.37 (s), 19.14 (s), 19.32 (s), 20.20 (s), 29.68 (s), 39.59 (s), 42.85 (s), 50.24 (s), 69.70 (s), 125.74 (s), 129.81 (s), 207.03 (s). HRMS (CI) Calcd for $C_{12}H_{23}O_2$ (M + H) 199.1698, found *m*/*z* 199.1685.

Formation of 1e: To a solution of $Ni(cod)_2$ (5.5 mg, 0.02 mmol), PCy_3 (5.6 mg, 0.02 mmol), and 14.6 μL of acetone (11.6 mg, 0.20 mmol) in 5 mL of C_6D_6 were added 11.3 μL of 2,3-dimethyl-1,3-butadiene (16.4 mg, 0.20 mmol) at room temperature. The reaction proceeded gradually to generate **1e** for 4 h (94%). The reaction mixture was concentrated under reduced pressure to regenerate $Ni(cod)_2$ and PCy_3 (50%).

Attempt at Isolation of 1e by the General Method: To a solution of $Ni(cod)_2$ (220 mg, 0.80 mmol), PCy_3 (240 mg, 0.80 mmol), and 0.59 mL of acetone (464 mg, 8.00 mmol) in 10 mL of toluene was added 0.91 mL of 2,3-dimethyl-1,3-butadiene (657 mg, 8.00 mmol) at room temperature. The solution changed from orange to red. The reaction mixture was stirred for 4.5 h followed by concentration in vacuo to regenerate $Ni(cod)_2$ and PCy_3 (420.5 mg, 91%).

Isolation of 1e by Reaction of 2a with Acetone: To a solution of **2a** (503.4 mg, 1.0 mmol) in 30 mL of toluene was added acetone (10 mmol, 734.3 μL) at room temperature. The reaction mixture was stirred for 4 day followed by concentration in vacuo. To a solution of the residue in 30 mL of toluene was added acetone (1 mmol, 73.4 μL) at room temperature. The reaction mixture was stirred for 4 day followed by concentration under reduced pressure. The residue was washed with hexane to give pink-yellow solids (**1e**, 326.2 mg, 65%). ^1H NMR (C_6D_6): δ 1.13−2.06 (m, 45H, including 1H of $NiC\boldsymbol{H}_2C(CH_3)$ at δ 1.18, 3H of $NiCH_2C(CH_3)C(C\boldsymbol{H}_3)$ at δ 1.48 (d, J = 3.3 Hz), 3H of $-CH_2C(C\boldsymbol{H}_3)_2ONi$ at δ 1.54, 1H of $NiC\boldsymbol{H}_2C(CH_3)$ at δ 1.59, 1H of $-C\boldsymbol{H}_2C(CH_3)_2ONi$ at δ 1.73 (dd, J_{HH} = 12.3 Hz and J_{HP} = 2.5 Hz) and 3H of $-CH_2C(C\boldsymbol{H}_3)_2ONi$ at 1.77), 2.39 (s, 3H, $NiCH_2C(C\boldsymbol{H}_3)$), 2.74 (d, J = 12.3 Hz, 1H, $-C\boldsymbol{H}_2C(CH_3)_2ONi$). ^{31}P NMR (C_6D_6): δ 41.9 (s). ^{13}C NMR (C_6D_6): δ 22.3 (s, $NiCH_2C(\boldsymbol{C}H_3)$), 25.3 (d, J_{CP} = 2.3 Hz, $NiCH_2C(CH_3)C(\boldsymbol{C}H_3)$), 27.3 (s, Cy), 28.3 (d, J_{CP} = 10.7 Hz, Cy), 30.7 (d, J_{CP} = 1.5 Hz, Cy), 30.9 (d, J_{CP} = 1.5 Hz, Cy), 33.5 (d, J_{CP} = 16.8 Hz, Cy), 33.6 (d, J_{CP} = 6.1 Hz, $Ni\boldsymbol{C}H_2C(CH_3)$), 36.2 (s, $-CH_2C(\boldsymbol{C}H_3)_2ONi$), 37.3 (s, $-CH_2C(\boldsymbol{C}H_3)_2ONi$), 52.1 (d, J_{CP} = 2.3 Hz, $-\boldsymbol{C}H_2C(CH_3)_2ONi$), 97.2 (d, J_{CP} = 10.7 Hz, $-CH_2\boldsymbol{C}(CH_3)_2ONi$), 101.6 (d, J_{CP} = 16.0 Hz, $NiCH_2C(CH_3)\boldsymbol{C}(CH_3)$), 114.2 (s, $NiCH_2\boldsymbol{C}(CH_3)$). Anal. Calcd for $C_{27}H_{49}O_1P_1Ni_1$: C, 67.65; H, 10.30. Found: C, 66.81; H, 10.23.

Reaction of 1e with Carbon Monoxide: A pressure tight NMR tube containing a solution of **1e** (9.6 mg, 0.02 mmol) in C_6D_6 (0.5 mL) was treated with carbon monoxide (5 atm). The solution changed from orange to colorless immediately to give the carbonylation products (**3e**: 8%). ^1H NMR ($CDCl_3$): δ 1.41 (s, 3H, $-C\boldsymbol{H}_3$), 1.43 (s, 3H, $-C\boldsymbol{H}_3$), 1.46 (s, 3H, $-C\boldsymbol{H}_3$), 1.82 (s, 3H, $-C(C\boldsymbol{H}_3)=CH_2$), 1.94 (d, J = 13.4 Hz, 1H, $-C\boldsymbol{H}_2C(CH_3)_2O-$), 2.40 (d, J = 13.4 Hz, 1H, $-C\boldsymbol{H}_2C(CH_3)_2O-$), 4.96 (s, 1H, $-C(CH_3)=C\boldsymbol{H}_2$), 5.01 (s, 1H, $-C(CH_3)=C\boldsymbol{H}_2$). ^{13}C NMR ($CDCl_3$): δ 19.60 (s), 25.44 (s), 28.49 (s), 30.41 (s), 47.23 (s), 51.46 (s), 81.41 (s), 112.89 (s), 145.38 (s), 179.39 (s). HRMS Calcd for $C_{10}H_{16}O_2$ 168.1150, Found *m*/*z* 168.1146.

Isolation of 8e: To a solution of $Ni(cod)_2$ (220 mg, 0.80 mmol), PCy_3 (240 mg, 0.80 mmol), 0.59 mL of acetone (465 mg, 8.00 mmol), and 0.90 mL of 2,3-dimethyl-1,3-butadiene (657 mg, 8.00 mmol) in 5 mL of toluene were added 102 μL of chlorotrimethylsilane (86.9 mg, 0.80 mmol) at room temperature. The solution changed from red to dark red. The reaction mixture was stirred for 4 h followed by concentration in vacuo to give dark red solids (**8e**, 463 mg, 98%). ^1H NMR (C_6D_6): δ 0.16 (s, 9H, $-OSi(C\boldsymbol{H}_3)_3$), 1.11−2.07 (m, 44H,

including 3H of $-C(CH_3)_2OTMS$ at δ 1.26, 3H of $-C(CH_3)_2OTMS$ at δ 1.27, 1H of $NiCH_2C(CH_3)$ at δ 1.62, 3H of $NiCH_2C(CH_3)C(CH_3)$ at δ 1.68 (d, $J = 2.4$ Hz) and 1H of $NiCH_2C(CH_3)$ at δ 2.07), 2.11 (s, 3H, $NiCH_2C(CH_3)$), 2.35 (d, $J = 14.9$ Hz, 1H, $-CH_2C(CH_3)_2OTMS$), 2.48 (dd, $J = 14.9$, 1.5 Hz, 1H, $-CH_2C(CH_3)_2OTMS$). ^{31}P NMR (C_6D_6): δ 42.6 (s). ^{13}C NMR (C_6D_6): δ 3.07 (s, $-OSi(CH_3)_3$), 22.27 (s, $NiCH_2C(CH_3)$), 23.06 (d, $J_{CP} = 3.0$ Hz, $NiCH_2C(CH_3)C(CH_3)$), 27.2 (s, Cy), 28.2 (s, Cy), 28.3 (s, Cy), 30.8 (s, Cy), 30.9 (s, Cy), 31.17 (s, $-C(CH_3)_2OTMS$), 32.41 (s, $-C(CH_3)_2OTMS$), 34.4 (d, $J_{CP} = 19.0$ Hz, Cy), 39.33 (d, $J_{CP} = 6.9$ Hz, $NiCH_2C(CH_3)$), 51.01 (d, $J_{CP} = 3.0$ Hz, $-CH_2C(CH_3)_2OTMS$), 74.51 (d, $J_{CP} = 4.6$ Hz, $-CH_2C(CH_3)_2OTMS$), 100.54 (d, $J_{CP} = 16.1$ Hz, $NiCH_2C(CH_3)C(CH_3)$), 114.22 (s, $NiCH_2C(CH_3)$). An analytical sample was not obtained due to gradual decomposition in a solution.

Reaction of 8e with Carbon Monoxide: A pressure tight NMR tube containing a solution of **8e** (23.5 mg, 0.04 mmol) in C_6D_6 (0.5 mL) was treated with carbon monoxide (5 atm). The solution changed from red to light blue gradually. The reaction mixture was quenched with methanol to give an ester. It was isolated as a hydroxyester (**9e**: 74%) by a colum (silica). ^1H NMR ($CDCl_3$): δ 1.25 (s, 6H, $-C(CH_3)_2OH$), 1.77 (s, 3H, $-C(CH_3)=C(CH_3)-$), 1.79 (s, 3H, $-C(CH_3)=C(CH_3)-$), 2.34 (s, 2H, $-CH_2COOCH_3$), 3.12 (s, 2H, $-CH_2C(CH_3)_2OH$), 3.69 (s, 3H, $-OCH_3$). ^{13}C NMR ($CDCl_3$): δ 20.63 (s, $-C(CH_3)=C(CH_3)-$), 21.69 (s, $-C(CH_3)=C(CH_3)-$), 30.32 (s, $-C(CH_3)_2OH$), 40.20 (s), 47.92 (s), 51.98 (s), 72.62 (s), 126.29 (s, vinyl), 129.12 (s, vinyl), 172.65 (s, $-CH_2COOCH_3$). HRMS (CI) Calcd for $C_{11}H_{21}O_3$ (M + H) 201.1491, found *m*/*z* 201.1492.

Isolation of 1f: To a solution of $Ni(cod)_2$ (220 mg, 0.80 mmol), PCy_3 (240 mg, 0.80 mmol), and benzophenone (146 mg, 0.80 mmol) in 6 mL of toluene and 1 mL of benzene was added 2,3-dibenzyl-1,3-butadiene (188 mg, 0.80 mmol) at room temperature. The solution changed from orange to red. The reaction mixture was stirred for 10 min followed by concentration in vacuo to give yellow solids (**1f**, 585 mg, 97%). An analytical sample and a single crystal for X-ray diffraction analysis were prepared by recrystallization from hexane at -20 °C. ^1H NMR (C_6D_6): δ 1.38 (s, 1H, $NiCH_2C(CH_2Ph)C(CH_2Ph)$), 1.10−2.10 (m, 34H, including 1H of $NiCH_2C(CH_2Ph)C(CH_2Ph)$ at δ 1.80), 2.47 (d, $J = 14.4$ Hz, 1H, $NiCH_2C(CH_2Ph)C(CH_2Ph)$), 2.85 (d, $J = 10.0$ Hz, 1H, $CH_2C(Ph)_2ONi$), 2.97 (d, $J = 12.0$ Hz, 1H, $NiCH_2C(CH_2Ph)C(CH_2Ph)$), 3.37 (d, $J = 12.8$ Hz, 1H, $CH_2C(Ph)_2ONi$), 3.57 (d, $J = 14.4$ Hz, 1H, $NiCH_2C(CH_2Ph)$), 4.43 (d, $J = 14.4$ Hz, 1H, $NiCH_2C(CH_2Ph)$), 6.75 (d, $J = 6.0$ Hz, 2H, Ph), 7.00−7.25 (m, 12H, Ph), 7.37 (t, $J = 7.6$ Hz, 2H, Ph), 7.66 (d, $J = 7.2$ Hz, 2H, Ph), 8.00 (d, $J = 7.6$ Hz, 2H, Ph). ^{31}P NMR (C_6D_6): δ 37.9 (s). ^{13}C NMR (C_6D_6): δ 27.2 (s, Cy), 28.3 (d, $J_{CP} = 3.8$ Hz, Cy), 28.4 (d, $J_{CP} = 4.6$ Hz, Cy), 30.5 (s, Cy), 31.2 (d, $J_{CP} = 1.5$ Hz, Cy), 34.1 (d, $J_{CP} = 16.7$ Hz, Cy), 36.9 (d, $J_{CP} = 24.4$ Hz, $NiCH_2C(CH_2Ph)$), 39.1 (s, $NiCH_2C(CH_2Ph)C(CH_2Ph)$), 42.5 (s, $NiCH_2C(CH_2Ph)$), 48.8 (s, $CH_2C(Ph)_2ONi$), 103.0 (d, $J_{CP} = 42.8$ Hz, $CH_2C(Ph)_2ONi$), 103.5 (d, $J_{CP} = 67.2$ Hz, $NiCH_2C(CH_2Ph)C(CH_2Ph)$), 125.4 (s, Ph), 125.7 (s, Ph), 126.0 (s, Ph), 126.4 (s, Ph), 126.8 (s, Ph), 127.5 (s, Ph), 127.8 (s, Ph), 127.9 (s, Ph), 128.5 (s, Ph), 129.0 (s, Ph), 129.80 (s, Ph), 129.83 (s, Ph), 139.2 (d, $J_{CP} = 12.0$ Hz, $NiCH_2C(CH_2Ph$-*ipso*$)$), 140.7 (s, Ph-*ipso*), 156.1 (s, Ph-*ipso*), 157.7 (s, Ph-*ipso*). Anal. Calcd for $C_{49}H_{61}O_1P_1Ni_1$: C, 77.88; H, 8.14. Found: C, 77.63; H, 8.21.

Isolation of 1g: To a solution of $Ni(cod)_2$ (275 mg, 1.0 mmol), PCy_3 (289 mg, 1.0 mmol), and 74.7 μL of cyclobutanone (70.1 mg, 1.0 mmol) in 10 mL of toluene were added 411 mg of 2,3-dimethyl-1,3-butadiene (0.57 mL, 5.0 mmol) at room temperature. The solution changed from orange to dark orange. The reaction mixture was stirred for 4 h followed by concentration in vacuo to give yellow solids (**1g**, 376 mg, 76%). A single crystal for X-ray diffraction analysis was prepared by recrystallization from hexane at -20 °C. ^1H NMR (C_6D_6): δ 1.10−2.20 (m, 41H, including 1H of $NiCH_2C(CH_3)$ at δ 1.22, 3H of $NiCH_2C(CH_3)C(CH_3)$ at δ 1.43 (d, $J = 8.4$ Hz), 1H of $NiCH_2C(CH_3)$ at δ 1.56, 1H of $-CH_2CH_2CH_2-$ at δ 1.68, 1H of $-CH_2C(^cBu)ONi$ at δ 1.91 and 1H of $-CH_2CH_2CH_2-$ at δ 2.02), 2.26 (m, 1H, $-CH_2CH_2CH_2-$), 2.32 (s, 3H, $NiCH_2C(CH_3)C(CH_3)$), 2.33 (m, 1H, $-CH_2CH_2CH_2-$), 2.38 (m, 1H, $-CH_2CH_2CH_2-$), 2.69 (d, $J = 12.4$ Hz, 1H, $-CH_2C(^cBu)ONi$), 2.77 (m, 1H, $-CH_2CH_2CH_2-$). ^{31}P NMR (C_6D_6): δ 42.2 (s). ^{13}C NMR (C_6D_6): δ 14.7 (s, $-CH_2CH_2CH_2-$), 21.9 (s, $NiCH_2C(CH_3)$), 23.2 (s, $NiCH_2C(CH_3)C(CH_3)$), 27.2 (s, Cy), 28.2 (d, $J_{CP} = 1.5$ Hz, Cy), 28.3 (d, $J_{CP} = 1.5$ Hz, Cy), 30.7 (d, $J_{CP} = 1.5$ Hz, Cy), 30.8 (d, $J_{CP} = 2.3$ Hz, Cy), 33.1 (d, $J_{CP} = 6.1$ Hz, $NiCH_2C(CH_3)$), 33.5 (d, $J_{CP} = 16.7$ Hz, Cy), 43.5 (s, $-CH_2CH_2CH_2-$), 44.0 (s, $-CH_2CH_2CH_2-$), 50.5 (d, $J_{CP} = 2.3$ Hz, $-CH_2C(^cBu)ONi$), 102.0 (d, $J_{CP} = 10.7$ Hz, $-CH_2C(^cBu)ONi$), 103.7 (d, $J_{CP} = 15.3$ Hz, $NiCH_2C(CH_3)C(CH_3)$), 114.1 (s, $NiCH_2C(CH_3)$). Anal. Calcd for $C_{28}H_{49}O_1P_1Ni_1$: C, 68.44; H, 10.05. Found: C, 67.90; H, 9.97.

Reaction of 1g with Carbon Monoxide: A pressure tight NMR tube containing a solution of **1g** (19.6 mg, 0.04 mmol) in C_6D_6 (0.5 mL) was treated with carbon monoxide (5 atm). The solution changed from orange to colorless immediately to give the carbonylation products (**3g**: 38%). ^1H NMR ($CDCl_3$): δ 1.37 (s, 3H, $-C(CH_3)(COO-)-$), 1.68 (m, 1H, $-CH_2CH_2CH_2-$), 1.81 (s, 3H, $-C(CH_3)=CH_2$), 1.87 (m, 1H, $-CH_2CH_2CH_2-$), 2.19 (d, $J = 13.4$ Hz, 1H, $-CH_2CH(Bu^c)O-$), 2.16 (m, 2H, $-CH_2CH_2CH_2-$), 2.41 (m, 1H, $-CH_2CH_2CH_2-$), 2.57 (m, 1H, $-CH_2CH_2CH_2-$), 2.59 (d, $J = 13.4$ Hz, 1H, $-CH_2CH(Bu^c)O-$), 4.93 (s, 2H, $-C(CH_3)=CH_2$). ^{13}C NMR ($CDCl_3$): δ 12.79 (s, $-CH_2CH_2CH_2-$), 19.39 (s, $-C(CH_3)=CH_2$), 23.41 (s, $-C(CH_3)(COO-)-$), 35.63 (s, $-CH_2CH_2CH_2-$), 35.85 (s, $-CH_2CH_2CH_2-$), 46.12 (s, $-CH_2CH(^cBu)O-$), 51.02 (s, $-C(CH_3)(COO-)-$), 82.82 (s, $-CH_2CH(^cBu)O-$), 112.98 (s, $-C(CH_3)=CH_2$), 144.32 (s, $-C(CH_3)=CH_2$), 179.29 (s, $-COO-$). HRMS Calcd for $C_{11}H_{16}O_2$ 180.1150, Found *m*/*z* 180.1139.

Isolation of 1h: To a solution of $Ni(cod)_2$ (220 mg, 0.80 mmol), PCy_3 (240 mg, 0.80 mmol), and 96.1 mg of styrene oxide (91.2 μL, 0.80 mmol) in 10 mL of toluene were added 328.6 mg of 2,3-dimethyl-1,3-butadiene (0.45 mL, 4.00 mmol) at 60 °C. The solution changed from orange to red. The reaction mixture was stirred for 18 h followed by concentration in vacuo. The residue was washed with hexane to give orange solids (**1h**: 312 mg, 88%). ^1H NMR (C_6D_6): δ 1.00−2.00 (m, 39H, including 1H of $NiCH_2C(CH_3)$ at δ 1.11, 3H of $NiCH_2C(CH_3)C(CH_3)$ at δ 1.32 (d, $J = 2.8$ Hz), 1H of $CH_2CH(CH_2Ph)ONi$ at δ 1.37 and 1H of $NiCH_2C(CH_3)$ at δ 1.57), 2.21 (s, 3H, $NiCH_2C(CH_3)$), 2.39 (t, $J = 10.8$ Hz, 1H, $CH_2CH(CH_2Ph)ONi$), 2.98 (m, 2H, $CH(CH_2Ph)ONi$), 5.36 (m, 1H, $CH(CH_2Ph)ONi$), 7.11 (1H of *para* in C_6H_5, hidden by C_6D_6 peak), 7.27 (t, $J = 7.6$ Hz, 2H of *meta* in C_6H_5), 7.48 (d, $J = 7.2$ Hz, 2H of *ortho* in C_6H_5). ^{31}P NMR (C_6D_6) δ 42.4 (s). ^{13}C NMR (C_6D_6) δ 20.5 (d, $J_{CP} = 3.0$ Hz, $NiCH_2C(CH_3)C(CH_3)$), 21.8 (s, $NiCH_2C(CH_3)$), 27.2 (s, Cy), 28.1 (s, Cy), 28.3 (s, Cy), 30.7 (d, $J_{CP} = 1.5$ Hz, Cy), 30.8 (d, $J_{CP} = 1.5$ Hz, Cy), 33.4 (d, $J_{CP} = 3.0$ Hz, $NiCH_2C(CH_3)$), 33.5 (d, $J_{CP} = 17.5$ Hz, Cy), 47.6 (d, $J_{CP} = 2.3$ Hz, $CH_2CH(CH_2Ph)ONi$), 49.0 (s, $-CH_2Ph$), 94.7 (d, $J_{CP} = 10.7$ Hz, $CH_2CH(CH_2Ph)ONi$), 102.6 (d, $J_{CP} = 14.5$ Hz, $NiCH_2C(CH_3)C(CH_3)$), 113.2 (s, $NiCH_2C(CH_3)$), 125.6 (s, Ph-*para*), 127.6 (Ph-*meta*), 130.5 (Ph-*ortho*), 143.4 (s, Ph-*ipso*).

Reaction of 1h with Carbon Monoxide: A pressure tight NMR tube containing C_6D_6 (0.5 mL) solution of **1h** (10.8 mg, 0.02 mmol) was treated with carbon monoxide (5 atm). The solution changed from orange to light yellow immediately to give the carbonylation product (**3h**: 90%). ^1H NMR ($CDCl_3$): δ 1.40 (s, 3H, $-C(CH_3)(COO-)-$), 1.77 (s, 3H, $-C(CH_3)=CH_2$), 2.01 (m, 1H, $-CH_2CH(CH_2Ph)O-$), 2.20 (dd, $J = 9.2$, 6.5 Hz, 1H, $-CH_2CH(CH_2Ph)O-$), 2.94 (m, 1H, $-CH_2Ph$), 3.11 (dd, $J = 7.0$, 6.5 Hz, 1H, $-CH_2Ph$), 4.70 (m, 1H, $-CH_2CH(CH_2Ph)O-$), 5.00 (d, $J = 1.0$ Hz, 1H, $-C(CH_3)=CH_2$), 5.02 (s, 1H, $-C(CH_3)=CH_2$), 7.23−7.36 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 19.70 (s), 22.22 (s), 40.33 (s), 41.44 (s), 49.70 (s), 77.54 (s), 113.30 (s), 127.18 (s), 128.83 (s), 129.72 (s), 136.18 (s), 144.57 (s), 179.34(s). HRMS Calcd for $C_{15}H_{18}O_2$ 230.1307, Found *m*/*z* 230.1289.

Isomerization of Styrene Oxide: To a solution of $Ni(cod)_2$ (5.5 mg, 0.02 mmol) and PCy_3 (11.2 mg, 0.04 mmol) in 0.5 mL of C_6D_6 were added 2.3 μL of styrene oxide (2.4 mg, 0.02 mmol) at 60 °C. The solution changed from light yellow to orange. The reaction proceeded to give Ni(η^2-$PhCH_2CHO$)(PCy_3) (60%, 5 h).

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Supporting Information Available: Crystallographic information files (CIF/PDF) for **1a**, **1b**, **1e**, **1f**, and **1g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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