JOC The Journal of Organic Chemistry
Cite This: J. Org. Chem. 2018, 83, 14969−14977
Article
pubs.acs.org/joc

A Pseudodearomatized PN^{3}P*Ni−H Complex as a Ligand and σ-Nucleophilic Catalyst

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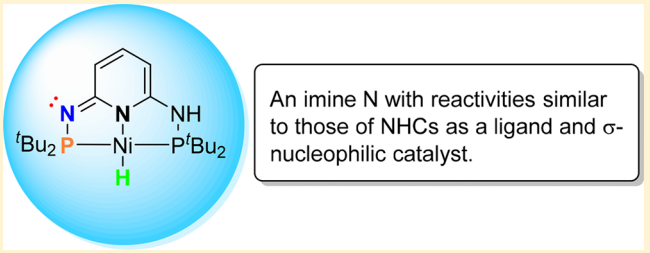
Supporting Information

ABSTRACT: In contrast to the conventional strategy of modifying the reactivities and selectivities of the transition metal and organocatalysts by varying the steric and electronic properties of organic substituent groups, we hereby demonstrate a novel approach that the sigma (σ) nucleophilicity of the imine arm can be significantly enhanced in a pseudodearomatized PN^{3}P* pincer ligand platform to reach unprecedented N-heterocyclic carbene-like reactivity. Accordingly, the imine arm of the PN^{3}P*Ni−H pincer complex efficiently catalyzes the hydrosilylation of aldehydes, cycloaddition of carbon dioxide (CO_2) to epoxides, and serves as a ligand in the Ru-catalyzed dehydrogenative acylation of amines with alcohols.



INTRODUCTION

Strong organic σ-donors such as carbenes and phosphines play an essential role in modern coordination and organic chemistry as ligands or organocatalysts.[1] While nitrogen σ-donor analogues (amines and imines) are considered more abundant and easily accessible, with many of them being utilized in various catalytic systems,[2] they are in general not applicable to the reactions where the reactivity is unique to carbenes and phosphines (Figure 1A).[3] For example, in the process of hydrosilylation of carbon dioxide, N-heterocyclic carbenes (NHCs) show superior catalytic activity,[4] but the catalysts involving the nitrogen σ-donor groups are extremely rare.[5] To the best of our knowledge, there is no strategy to modify and enhance the reactivity of the nitrogen donors to reach the same level of reactivity as those of carbenes and phosphines.

In organometallic and coordination chemistry, the reactivity of the metal center can be manipulated by modifying the steric and/or electronic properties of the surrounding ligands.[6] Likewise, the activity and selectivity of an organocatalyst or ligand can also be tuned by varying the steric and/or electronic factors of the substituent groups.[1a,2c,7] Because the coordination of a metal center could influence the property of the ligand, it is conceivable that this interaction could in principle be utilized to offer new strategies for the design and modifications of "organocatalysts" through changing the coordinated metal and its spectator ligands. Such an idea, however, has not been comprehensively examined, presumably due to the highly reactive nature of the metal atoms.

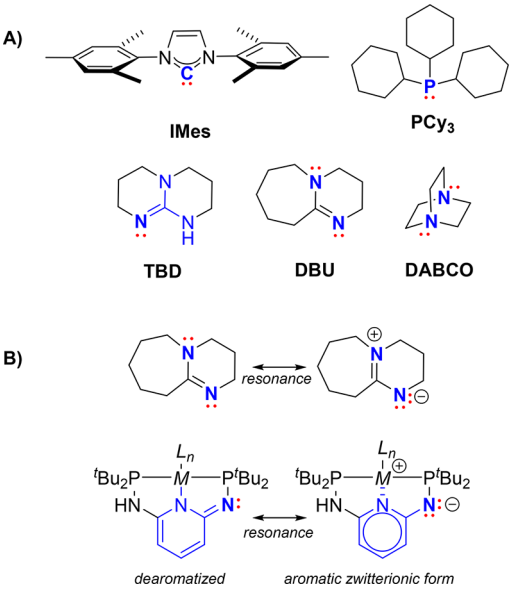


Figure 1. (A) Examples of organic σ-donors. (B) Comparison of DBU with a pseudodearomatized PN^{3}P* pincer complex.

Nevertheless, there are supporting observations showing the possibility of modifying the property or enhancing the

Received: August 26, 2018
Published: October 24, 2018

DOI: 10.1021/acs.joc.8b02205
J. Org. Chem. 2018, 83, 14969−14977

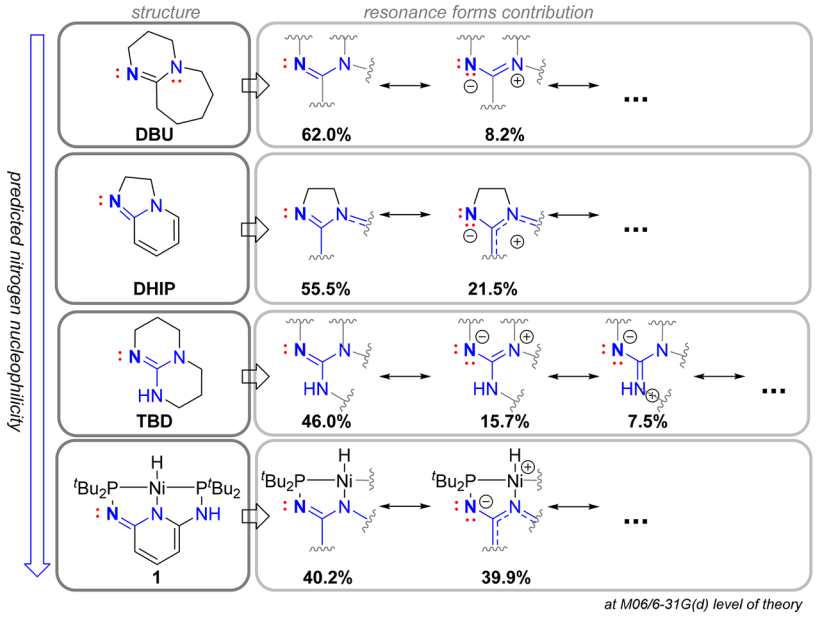
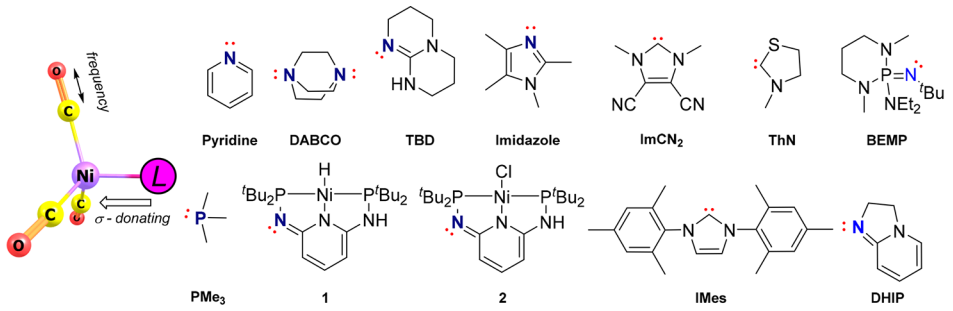


Figure 2. Contribution of resonance forms in DBU, DHIP, TBD, and **1** from NBO analysis.



Entry	Ligand (*L*)	ν (CO)[a]	ν (CO)[b]	NPA[c]
1	Pyridine	2075.0	2070.5	**-0.47**
2	DABCO	2071.6		**-0.51**
3	TBD	2067.3		**-0.62**
4	Imidazole	2066.8	2051.7	**-0.53**
5	DHIP	2066.8		**-0.56**
6	$ImCN_2$	2066.6	2066.2	
7	PMe_3	2065.9	2065.2	
8	ThN	2063.0	2061.0	
9	**2**	2063.95		**-0.99**
10	**1**	2060.7		**-1.00**
11	IMes	2051.4	2050.5	
12	BEMP	2060.7		-1.18

Figure 3. Calculated TEP and NPA for σ-donating ligands. [a]Frequencies are in cm^{-1} at M06/6-31G(d,p)/SDD scaled by 0.955. [b]Values taken from reference 14. [c]Natural Population Analysis charge on the nucleophilic nitrogen atom.

reactivity of the ligand through complexation with a metal.[8] For instance, Mayer and co-workers studied hydrogen atom transfer (HAT) organometallic reaction and found that hydrogen donor abilities of ligands were influenced by the spectator metal.[8b] Ogasawara and co-workers applied kinetic resolution of racemic (arene)chromium complexes via asymmetric ring-closure metathesis (ARCM) and observed that the constructed planar−chiral environment onto chro-

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mium atom reflects the significant change in the enantioselectivity with only a small modification of the ligand.[8d] In some even more relevant cases, "cooperating" ligands can participate directly in the bond breaking and forming steps together with the metal center to activate substrates to achieve metal−ligand cooperative catalysis.[9]

We have shown that the seemingly small change of replacing the CH_2 group with an NH spacer in the central pyridine ring and dearomatization of the PN^3P-type pincer complexes has significantly changed the thermodynamic and kinetic properties compared to their CH_2 analogues.[10] Furthermore, we have also demonstrated the importance of the aromatic mesomeric form in the pseudodearomatized pyridine-based PN^3P^* metal pincer complexes.[10g] Such a zwitterionic structure could exhibit a dual character of base and nucleophile of the nitrogen atom similar to that of DBU (1,8-diazabicyclo[5.4.0]-undec-7-ene) through the resonance effect (Figure 1B).[11] We have recently developed diverse catalytic reactivity of dearomatized PN^3P^*Ni−H complex **1** for CO_2 reduction, and formylation and methylation of amines.[12] Very intriguingly, the insertion of CO_2 into the Ni−H bond was not detected.[13] These observations prompted us to explore the nucleophilicity of the imine arm of PN^3P^*−Ni complexes and their potential applications in various organic reactions.

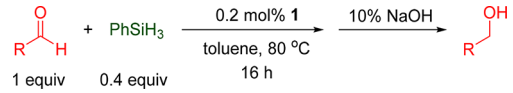
In this contribution, we demonstrate that the nucleophilicity of the imine arm of the pseudodearomatized PN^3P^* complex can be significantly enhanced such that it becomes catalytically active to reach unprecedented activities and plays a role similar to that of the N-heterocyclic carbene as a catalyst in the hydrosilylation of aldehydes to alcohols, in cyclic carbonate synthesis via cycloaddition of CO_2 to epoxides, and as a ligand in the dehydrogenative acylation of amines with alcohols.

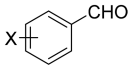
RESULTS AND DISCUSSION

Our investigation started with a close look into well-known nitrogen-based nucleophiles, such as DBU and TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene), and correlation of their nucleophilicity to the mesomeric effect. The investigation on resonance forms from Natural Bond Orbital Analysis (NBO-NRT)[15] of DBU shows that the molecule has 8.2% of the contribution from the zwitterionic forms (Figure 2). This value rises to 21.5% for DHIP (2,3-dihydroimidazo[1,2-*a*]pyridine) as a result of incorporating a dearomatized pyridine ring in the bicyclic structure.[16] As expected, the contribution from the zwitterionic structures is increased to 23.3% when the iminic moiety is conjugated with one more nitrogens in TBD, consistent with the fact the TBD is a stronger base and nucleophile than DBU.[17] Importantly and interestingly, the contribution of the zwitterionic structures of 39.9% in the pseudodearomatized PN^3P^*Ni−H complex **1** is much higher than in DBU, DHIP, and TBD Schiff bases. To reveal further the electron-donating ability of **1**, we calculated Tolman Electronic Parameter (TEP) for the range of ligand L−$Ni(CO)_3$ (Figure 3).[18,14] IMes has the lowest frequencies of CO stretching which is attributed to the strongest σ-donating character of the ligand to the metal center. The complex **1** is the second most σ-donating ligand from the present study, even stronger than some of the carbenes. In addition, the NPA charges show remarkably high negative charge on the nitrogen for the complexes **1** and **2**.[19] For further comparison, the phosphazenes, well known push−pull P=N bases, display highly electron-donating nitrogen (Figures 3, S2, and S3).[20] While BEMP has a greater NPA charge, it shows a similar TEP value compared to that of **1**, reflecting the difference between nucleophilicity and Lewis basicity presumably due to its steric bulk. Moreover, **1** is expected to unveil enhanced nucleophilicity due to the α-effect of the adjacent phosphorus atom.[21] These results suggest that **1** may act as a very strong σ-electron-donating nucleophile and encourage us to explore the nucleophilic reactivity of such complexes.

Initially, the hydrosilylation of aldehydes catalyzed by PN^3P^* complex **1** was investigated. Guan and co-workers disclosed a POCOP−NiH system which showed excellent catalytic activity for the hydrosilylation of aldehydes and moderate reactivity for ketones.[22] The insertion of the C=O double bond into Ni−H was directly observed, and this insertion reaction was revealed as one of the essential steps involved in the catalytic cycle. Under similar reaction conditions,[22] benzaldehydes **3a**−**h** bearing either electron-rich or electron-poor functional groups could all react smoothly to give the corresponding alcohols **4a**−**h** in excellent yields in the presence of **1** (Table 1, entries 1−8). All aromatic

Table 1. Hydrosilylation of Aldehyde with $PhSiH_3$ Catalyzed by PN^3P^*Ni−H Complex 1[a]



Entry	R	Yield (%)[b]
		
1	**3a**, X = H	**4a**, 99
2	**3b**, X = 4-Me	**4b**, 90
3	**3c**, X = 3-Me	**4c**, 85
4	**3d**, X = 2-MeO	**4d**, 93
5	**3e**, X = 4-Cl	**4e**, 90
6	**3f**, X = 4-Br	**4f**, 96
7	**3g**, X = 2-CF_3	**4g**, 86
8	**3h**, X = 2-OH	**4h**, 91
		
9	**3i**, R = 2-pyridyl	**4i**, 94
10	**3j**, R = Cy	**4j**, 83
11[c]	**3k**, R = PhCHCH	**4k**, 85

[a]Unless otherwise specified, all reactions were performed on a 1 mmol scale in dry toluene (1 mL) under Ar in the presence of **1** (0.2 mol %) at 80 °C. [b]Isolated yields after basic workup. [c]The reaction was performed at 60 °C for 48 h.

and aliphatic (Table 1, entries 9 and 10) aldehydes were also suitable substrates for hydrosilylation. Very surprisingly, *trans*-cinnamaldehyde was converted to cinnamyl alcohol selectively at 60 °C with no sign of the formation of 1,4-reduction product (Table 1, entry 11), in sharp contrast to the results of similar reactions catalyzed by Ni−H species[22,23] or carbene−Cu−H complexes.[24] Subsequently, hydrosilylation of a mixture of acetophenone (1.0 equiv) and benzaldehyde (1.0 equiv) catalyzed by **1** was examined to give benzyl alcohol **4a** in a quantitative yield with full recovery of acetophenone, showing a high chemoselectivity to aldehyde hydrosilylation over ketone hydrosilylation (Scheme 1). As observed in the hydrosilylation of CO_2, the reaction of complex **1** with benzaldehyde **3a** did not take place even when the mixture was heated in toluene to 80 °C for 16 h. These observations also

DOI: 10.1021/acs.joc.8b02205
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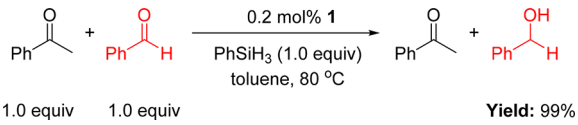
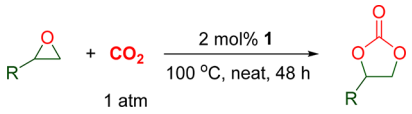
Scheme 1. Hydrosilylation of Acetophenone and Benzaldehyde Catalyzed by PN^{3}P*Ni−H Complex 1



suggest that the "active site" for the catalytic reactions may not involve the Ni−H group.

In an effort to support the assumption of nucleophilic activity of the iminic nitrogen of **1**, we continued to examine other organic transformations where carbenes serve as catalysts or ligands and the conventional reactivity of a Ni−H bond is unlikely to play any role. Under similar reaction conditions developed by Lu and co-workers for NHCs-catalyzed coupling of CO_2 with epoxides,[25] PN^{3}P*Ni−H **1** showed analogous reactivity to offer the corresponding cyclic carbonates in good yields (Table 2). On the other hand, the Hong group has

Table 2. Cycloaddition of CO_2 to Epoxide Catalyzed by PN^{3}P*Ni−H 1[a]



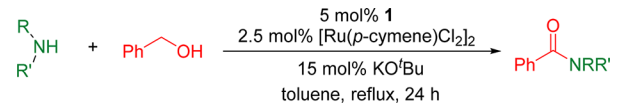
Entry	Epoxide		Product		Yield(%)[b]
1	Ph	5a	Ph	6a	73
2	*n*-Bu	5b	*n*-Bu	6b	67
3	$PhOH_2C$	5c	$PhOH_2C$	6c	74
4	Et	5d	Et	6d	65
5	ClH_2C	5e	ClH_2C	6e	81

[a]Reaction conditions: CO_2 balloon, catalyst (9 mg, 20 μmol), 1.0 mmol of epoxide, and the reaction was carried out at 100 °C for 48 h. [b]Isolated yields.

demonstrated that the dehydrogenative acylation of amines with alcohols could be catalyzed by a ruthenium catalyst precursor in the presence of an NHC ligand.[26] We demonstrated that this reaction could be achieved with the same Ru precursor and PN^{3}P*Ni−H **1** in satisfactory yields (Table 3). To the best of our knowledge, the dehydrogenative acylation of amines with alcohols has never been achieved by transition metal catalysts with imine/amine ligands. As we have previously reported that the Ru complex with the same PN^{3}P* ligand did not show any good activity in this type of dehydrogenative acylation reaction,[10c] the role of metal exchange in the observed reactivity can be ruled out. PN^{3}P*Ni−H **1** may serve as a strong σ-donating ligand similar to the NHC during this process.

The attempt to isolate the active species in the Ru-catalyzed dehydrogenative acylation of amine to support the ligand role of **1** was in vain. However, we were able to demonstrate that complex **1** can be coordinated to copper iodide to give complex **9**. The molecular structure of **9** was determined by

Table 3. Ruthenium-Catalyzed Amide Synthesis from Alcohol and Amine in the Presence of PN^{3}P*Ni−H 1[a]



Entry	Amine		Product		Yield(%)[b]
1	NH_2	7a	Ph, N, H	8a	78
2	NH_2	7b	Ph, N, H	8b	85
3	Cl, NH_2	7c	Ph, N, H, Cl	8c	83
4	MeO, NH_2	7d	Ph, N, H, OMe	8d	73
5	NH_2	7e	Ph, N, H	8e	68
6	O, NH	7f	Ph, N, O	8f	71

[a]Reaction conditions: catalyst (0.025 mmol, 12 mg), [Ru(*p*-cymene)Cl_2]$_2$ (0.013 mmol, 8 mg), KOtBu (0.075 mmol, 8.4 mg), benzyl alcohol (0.50 mmol), and amine (0.55 mmol) were refluxed in 0.6 mL of toluene for 24 h. [b]Isolated yields.

single crystal X-ray diffraction (Figure 4), analogous to the corresponding copper(I)−NHC complexes,[27] suggesting that the electron-donating ability of the imine arm of complex **1** is comparable to those of NHCs. This result indeed supports that

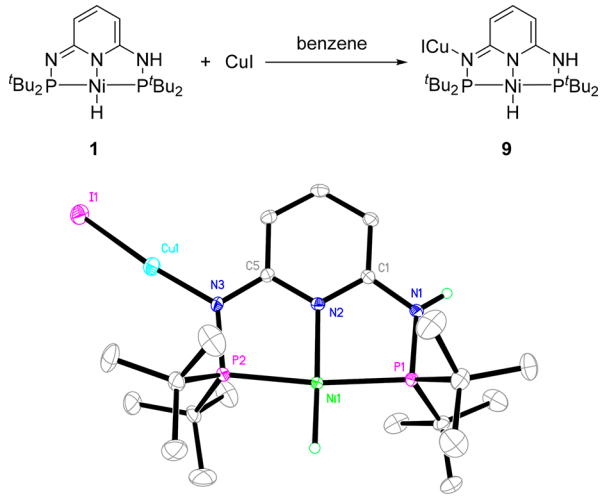


Figure 4. Synthesis of complex **9** and the ORTEP diagram of complex **9** at 30% ellipsoid probability. Hydrogen atoms (except for pincer arms and Ni−H) are omitted for clarity. Selected bond lengths (Å): Ni1−N2 1.901(5); Ni1−P1 2.1645(16); Ni1−P2 2.1649(16); N3−C5 1.364(7); N1−C1 1.388(7).

DOI: 10.1021/acs.joc.8b02205
J. Org. Chem. 2018, 83, 14969−14977

complex **1** can act as a strong σ-donating ligand and play a similar role as a carbene in transition metal catalysis.

CONCLUSION

In summary, while the conventional wisdom is to modify the reactivities and selectivities of the coordination metal catalysts and organocatalysts through changing the steric and/or electronic properties of organic substituent groups, we have demonstrated that the nucleophilicity of the imine group of the pseudodearomatized PN^3P^*Ni-H complex **1** could be significantly increased to reach unprecedented carbene-like reactivity in several organic catalytic transformations. These observations suggest a novel paradigm of strategy for the design and modifications of "organocatalysts" and ligands through coordination to metal. This study may open a new direction for the catalyst and ligand design.

EXPERIMENTAL SECTION

General Information. All manipulation of air- and/or moisture-sensitive compounds were carried out under an atmosphere of purified argon in a Vacuum Atmospheres glovebox or using standard Schlenk techniques. All solvents were distilled under Ar from appropriate drying agents. Unless otherwise stated, commercial reagents were used as received without purification. Column chromatography was performed on silica gel (200−300 mesh). NMR spectra were recorded on Bruker Advance 400, Bruker Avance-500, Bruker Avance-600, or Bruker Avance-700 NMR spectrometers in deuterated solvents. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signals of the deuterated solvents, and the ^{13}C NMR chemical shifts were referenced to the ^{13}C signals of the deuterated solvents. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, s = sextet, h = heptet, m = multiplet, br = broad), coupling constants (Hz) and integration. Gas chromatography was performed on an Agilent 5975C GC inert XL EI/CI MSD with a Triple-Axis MS detector. The X-ray diffraction data were collected using a Bruker-AXS KAPPA-APEXII CCD diffractometer (Cu Kα, λ = 1.54178 Å). Indexing was performed using APEX2 (difference vectors method). Data integration and reduction were performed using SaintPlus 6.01. Absorption correction was performed using a multiscan method implemented in SADABS. Space groups were determined using XPREP implemented in APEX2. Structures were solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full matrix least-squares on F2). Elemental analyses were conducted on a Flash 2000-Thermo Scientific CHNO analyzer.

The DFT studies were carried out with Gaussian09 program.[28] All the structures were fully optimized at M06/6-31G(d,p) level of theory, and SDD pseudopotential with corresponding basis set was used for Ni.[29,30] The A1-mode of the CO frequency was scaled by 0.955 to obtain more reliable value frequencies corresponding the Tolman electronic parameter. Postprocessing visualization was carried out with ChemCraft.[31] Natural Bond Orbital (NBO) analysis was carried with Natural Bond Orbital (NBO6) program.[32] Natural Resonance Theory (NRT) calculations were calculated at M06/6-31G(d)/SDD method level.

Procedures for Synthesis of Complex ***9***. To a solution of complex **1** (228 mg, 0.5 mmol) in dry benzene (5.0 mL) was added CuI (95.2 mg, 0.5 mmol) under an argon atmosphere, and the mixture was stirred at room temperature for 24 h. The solution was filtered, and the solid was washed with pentane (3 × 3.0 mL) and then dried under vacuum. The solid **9** was obtained as a brown solid (294 mg, 91%): mp 213−215 °C. Crystals of complex **9** suitable for X-ray diffraction were obtained by slow evaporation of its benzene solution. ^{1}H NMR (600 MHz, C_6D_6): 7.28 (t, J = 6.2 Hz, 1H), 6.76 (t, J = 8.1 Hz, 1H), 5.78 (s, 1H), 4.89 (s, 1H), 6.76 (t, J = 8.1 Hz, 1H), 1.38 (d, J = 14.2 Hz, 18H), 0.99 (d, J = 14.6 Hz, 18H), −16.50 (t, J = 58.6 Hz, 1H). ^{13}C NMR (DMF-d_7, 126 MHz): 171.2, 140.6, 125.3, 102.4 (d, J = 13.7 Hz), 93.5, 36.6, 36.5, 36.3, 36.1, 28.8, 28.7, 28.0, 27.9. ^{31}P NMR (243 MHz, C_6D_6): 135.5 (dd, J = 228.4, 44.1 Hz), 125.4 (dd, J = 229.9, 46.0 Hz). Elemental analysis (%) for $C_{21}H_{41}CuIN_3NiP_2$: Calcd C, 39.00; H, 6.39; N, 6.50. Found: C, 39.07; H, 6.44; N, 6.42.

General Procedures for Hydrosilylation of Aldehyde. To a flame-dried Schlenk flask was added a solution of nickel complex PN^3P^*Ni-H **1** (1.0 mg, 2 μmol) in toluene (1.0 mL), an aldehyde substrate (1.0 mmol), and $PhSiH_3$ (49 μL, 0.4 mmol) under an argon atmosphere. The resulting mixture was stirred at 80 °C until there was no aldehyde left (monitored by withdrawing aliquots and analyzing their ^{1}H NMR spectra). The reaction was then quenched by 10% aqueous solution of NaOH (about 1.0 mL) with vigorous stirring for more than 12 h. The solution containing the alcohol product was extracted with diethyl ether three times, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The desired alcohol was further purified by flash column chromatography using petroleum ether/EtOAc as eluent.

General Procedures for Cycloaddition of CO_2 to Epoxide. The epoxide (1.0 mmol) and complex PN^3P^*Ni-H **1** (9 mg, 20 μmol) were added to a dry flask. Then CO_2 was introduced (1 bar), and the mixture was heated at 100 °C for 48 h. The reaction mixture was then cooled to room temperature, and methylene chloride was added and concentrated under vacuum. The product was purified over a silica gel column. The desired product was further purified by flash column chromatography using petroleum ether/EtOAc as eluent.

General Procedures for the Amide Synthesis from Alcohols and Amines. In an argon-filled glovebox, a 10.0 mL oven-dried Schlenk tube was charged with complex PN^3P^*Ni-H **1** (0.025 mmol, 12 mg), KO*t*Bu (0.075 mmol, 8.4 mg), and 0.6 mL of toluene. The alcohol (0.50 mmol) and amine (0.55 mmol) were then added. The reaction mixture was heated at reflux under a flow of argon to facilitate the removal of hydrogen for 24 h before being cooled to room temperature. All the volatiles were removed under vacuum. Purification of the crude product by flash chromatography afforded the amide product.

Benzyl Alcohol ***4a***.[33] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to afford a colorless oil (107 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$,): 7.39−7.29 (m, 5H), 4.62 (s, 2H), 2.79 (br, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): 141.0, 128.6, 127.6, 127.1, 65.1.

4-Methylbenzyl Alcohol ***4b***.[34] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to afford a clear liquid (110 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.27 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 4.65 (s, 2H), 2.39 (s, 3H), 2.00 (br, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): 138.1, 137.5, 129.4, 127.3, 65.3, 21.3.

3-Methylbenzyl Alcohol ***4c***.[34] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to afford a light yellow oil (104 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.28−7.25 (m, 1H), 7.18−7.12 (m, 3H), 4.61 (s, 2H), 2.66 (br, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): 140.9, 138.2, 128.5, 128.4, 127.8, 124.1, 65.2, 21.5.

2-Methoxybenzyl Alcohol ***4d***.[35] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to afford a colorless oil (128 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.30−7.26 (m, 2H), 6.95 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 4.69 (s, 2H), 3.87 (s, 3H), 2.37 (br, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 157.4, 129.0, 128.9, 128.7, 120.6, 110.1, 62.1, 55.2.

4-Chlorobenzyl Alcohol ***4e***.[34] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to afford a white solid (128 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.33−7.31 (m, 2H), 7.28−7.26 (m, 2H), 4.64 (s, 2H), 2.02 (br, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): 139.4, 133.5, 128.8, 128.4, 64.7.

4-Bromobenzyl Alcohol ***4f***.[34] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to afford a yellow solid (180 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.47 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 4.62 (d, J = 5.7 Hz, 2H), 2.05 (t, J = 5.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): 139.9, 131.8, 128.7, 121.6, 64.7.

2-Trifluoromethylbenzyl Alcohol ***4g***.[36] This compound was purified by flash chromatography (petroleum ether/ethyl acetate =

DOI: 10.1021/acs.joc.8b02205
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10:1) to afford an orange liquid (151 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.68 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 4.85 (s, 2H), 2.37 (br, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 139.1, 132.1, 128.7, 128.4, 127.2 (q, J = 31 Hz), 125.7 (q, J = 31 Hz), 124.4 (q, J = 272.2 Hz), 61.2 (q, J = 2.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): −60.0 (3F, s).

2-Hydroxybenzyl Alcohol **4h**.[37] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to afford a yellow solid (113 mg, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.40 (bs, 1H), 7.22−7.19 (m, 1H), 7.04−7.03 (m, 1H), 6.88−6.84 (m, 2H), 4.83 (s, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz): 156.1, 129.7, 128.1, 124.9, 120.3, 116.6, 64.6.

2-Pyridinemethanol **4i**.[38] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to afford a light yellow oil (103 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): 8.37−8.36 (m, 1H), 7.58−7.55 (m, 1H), 7.29−7.27 (m, 1H), 7.07−7.05 (m, 1H), 5.27 (br, 1H), 4.66 (s, 2 H); ^{13}C NMR ($CDCl_3$, 126 MHz): 160.2, 148.3, 136.9, 122.2, 120.8, 64.4.

Cyclohexanemethanol **4j**.[34] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to afford a light yellow oil (95 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): 3.34 (bs, 1H), 3.30−3.29 (m, 2H), 1.69−1.56 (m, 5H), 1.40−1.33 (m, 1H), 1.20−1.03 (m, 3H), 0.86−0.78 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz): 68.3, 40.4, 29.7, 26.6, 25.9.

Cinnamyl Alcohol **4k**.[34] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to afford a light yellow oil (114 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.42−7.40 (m, 2H), 7.36−7.33 (m, 2H), 7.29−7.26 (m, 1H), 6.65−6.62 (m, 1H), 6.41−6.36 (m, 1H), 4.34−4.33 (m, 2H), 2.07 (br, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): 136.8, 131.2, 128.7, 128.6, 127.8, 126.6, 63.7.

4-Phenyl-1,3-dioxolan-2-one **6a**.[39] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 4:1) to afford a white solid (120 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.41−7.42 (m, 3H), 7.34−7.36 (m, 2H), 5.67 (t, J = 8.0 Hz, 1H), 4.79 (t, J = 8.0 Hz, 1H), 4.31 (t, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 155.1, 135.9, 129.7, 129.2, 126.0, 78.1, 71.2.

4-Butyl-1,3-dioxolan-2-one **6b**.[40] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 4:1) to afford a colorless oil (97 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): 4.65−4.72 (m, 1H), 4.51 (t, J = 8.0 Hz, 1H), 4.02−4.06 (m, 1H), 1.62−1.79 (m, 2H), 1.30−1.46 (m, 4H), 0.89 (t, J = 8.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 155.2, 77.1, 69.4, 33.5, 22.2, 13.7.

4-(Phenoxymethyl)-1,3-dioxolan-2-one **6c**.[41] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 4:1) to afford a light yellow solid (144 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.30−7.34 (m, 2H), 7.01−7.04 (m, 1H), 6.91−6.93 (m, 2H), 5.01−5.06 (m, 1H), 4.61 (t, J = 8.0 Hz, 1H), 4.51−4.54 (m, 1H), 4.22−4.26 (m, 1H), 4.11−4.15 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 157.8, 154.8, 129.7, 121.9, 114.6, 74.3, 66.9, 66.2.

4-Ethyl-1,3-dioxolan-2-one **6d**.[42] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 4:1) to afford a yellow oil (75 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): 4.70−4.63 (m, 1H), 4.53 (t, J = 8.3 Hz, 1H), 4.10−4.06 (m, 1H), 1.87−1.69 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 155.2, 78.1, 69.0, 26.9, 8.5.

4-(Chloromethyl)-1,3-dioxolan-2-one **6e**.[43] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 4:1) to afford a yellow oil (111 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): 5.03−4.97 (m, 1H), 4.58 (t, J = 8.7 Hz, 1H), 4.39−4.36 (m, 1H), 3.38−3.79 (m, 1H), 3.73−3.69 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): 154.5, 74.5, 67.0, 44.1.

N-Benzylbenzamide **8a**.[44] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 4:1) to afford a white solid (165 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.78−7.80 (m, 2H), 7.48−7.52 (m, 1H), 7.41−7.44 (m, 2H), 7.34−7.36 (m, 4H), 7.29−7.32 (m, 1H), 6.49 (br, 1H), 4.64 (d, J = 5.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): 167.5, 138.3, 134.5, 131.8, 129.0, 128.8, 128.1, 127.8, 127.1, 44.3.

N-Benzyl-3-methylbenzamide **8b**.[44] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 4:1) to afford a yellow solid (191 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.81 (d, J = 5.0 Hz, 2H), 7.48−7.51 (m, 1H), 7.41 (t, J = 10.0 Hz, 2H), 7.22−7.25 (m, 1H), 7.10−7.16 (m, 3H), 6.79 (br, 1H), 4.58 (d, J = 5.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): 167.5, 138.5, 138.2, 134.4, 131.6, 128.7, 128.6, 128.4, 127.1, 125.0, 44.1, 21.5.

N-Benzyl-4-chlorobenzamide **8c**.[44] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 4:1) to afford a white solid (204 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.78 (d, J = 10.0 Hz, 2H), 7.48−7.51 (m, 1H), 7.37−7.40 (m, 2H), 7.21−7.27 (m, 3H), 7.01 (br, 1H), 4.53 (d, J = 10.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): 167.7, 137.0, 134.1, 133.3, 131.8, 129.2, 128.9, 128.7, 127.1, 43.3.

N-(4-Methoxybenzyl)benzamide **8d**.[45] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 3:1) to afford a white solid (176 mg, 73%). ^{1}H NMR (600 MHz, $CDCl_3$): 7.78−7.77 (m, 2H), 7.47−7.44 (m, 1H), 7.38−7.35 (m, 2H), 7.24−7.23 (m, 2H), 6.84−6.83 (m, 3H), 4.51 (d, J = 5.7 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): 167.5, 159.1, 134.5, 131.5, 130.5, 129.3, 128.5, 127.1, 114.1, 55.3, 43.6.

N-Benzhydrylbenzamide **8e**.[46] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 4:1) to afford a pale yellow solid (195 mg, 68%). ^{1}H NMR (600 MHz, $CDCl_3$): 7.83 (d, J = 7.6 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.38−7.29 (m, 10H), 6.85 (d, J = 6.2 Hz, 1H), 6.47 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): 166.2, 141.1, 133.8, 131.3, 128.4, 128.3, 127.2, 127.1, 126.7, 57.1.

Morpholino(phenyl)methanone **8f**.[47] This compound was purified by flash chromatography (petroleum ether/ethyl acetate = 8:1) to afford a yellow oil (136 mg, 71%). ^{1}H NMR (600 MHz, $CDCl_3$): 7.36 (s, 5H), 3.70−3.39 (m, 8H); ^{13}C NMR ($CDCl_3$, 150 MHz): 170.4, 135.3, 129.8, 128.6, 127.1, 77.3, 66.9.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b02205.

NMR spectra for all products, crystallographic data, and computational details (PDF)

X-ray data for complex **9** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support and the service of Ibex, Shaheen 2 High Performance Computing Facilities were provided by King Abdullah University of Science and Technology (KAUST).

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